TRACE SPECTROPHOTOMETRIC ANALYSIS OF SOME METALS AND NON-METALS

by

MISS TAN LAY HAR, B.Sc., A.R.C.S.

A Thesis submitted for the Degree of Doctor of Philosophy of the University of London

September 1971

Chemistry Department,
Imperial College of Science and Technology,
London, SW7 2AY.

ABSTRACT

Part I of this thesis describes the determination of non-metals by solution spectrophotometry and Part II deals with the determination of metals by atomic absorption spectrophotometry.

In Part I, the determination of non-metals by solution spectrophotometry is generally discussed. Current methods for fluoride determination are critically reviewed and an outline is given of attempts to find new methods for the determination of fluoride ion.

The catalytic effect of fluoride on the oxidation of ferrous ion by iodine has been developed into a kinetic method for its determination. The calibration of fluoride ranges from 50 to > 1000 μg fluoride per 25 ml (i.e. 2 - 40 ppm) and the "effective" molar absorptivity at 350 nm is 5×10^4.

A fluorimetric method for fluoride has been developed based on ternary complex formation with zirconium and Calcein Blue at pH 2.5. The method is extremely sensitive and amounts of fluoride in aqueous solution down to 0.01 ppm can be determined. The increased fluorescence yield is attributed to conformational stabilisation of the excimer of the fluorophore in the ternary complex.

A similar procedure for the determination of sulphate was developed. The method can be applied to the determination of sulphate in the range 200 μg to 12 mg.

Part II describes the development of a very simple analytical method for the examination of the surface composition of steels based on the combination of electrography and ultramicro atomic absorption spectrophotometry. A short summary of how semi-quantitative analysis of Cu, Ni, Mn, V, Mo and Cr can be carried out, using the ring-oven technique

is first of all given. The sampling method is then used in conjunction with the carbon filament atomic absorption method of ultramicrotrace analysis for the quantitative determination of copper, manganese and nickel in steels.

Two papers have been published to date on the work described in the earlier part of this thesis.

ACKNOWLEDGEMENTS

The work recorded in this thesis was carried out in the Chemistry Department of the Imperial College of Science and Technology between October 1968 and August 1971.

I wish to express my sincere thanks to my supervisor, Professor T.S. West, for his invaluable assistance, guidance and encouragement during the course of this research. I would also like to thank my research colleagues, particularly Mr. R. Gee, for helpful discussions and Mrs. Janet Broom for typing this manuscript.

I am grateful to the Agricultural Research Council and the British Welding Institute for their financial support.

CONTENTS

P A R T O N E

CHAPTER I

INTRODUCTION

1.1 Preface

Solution spectrophotometry has played a predominant role in inorganic trace analysis since the introduction of instrumental techniques. In recent years developments in atomic spectroscopy has made more sensitive and selective methods available for the determination of metals. This, however, does not apply to the determination of non-metals because the wavelengths of absorption and emission for non-metals lie in the far, or vacuum, ultraviolet region of the electromagnetic spectrum, and analysis would generally require the use of vacuum monochromators. Moreover non-metallic elements tend to combine together to form polyatomic anions which are difficult to atomise. The few atomic spectroscopic methods available are generally based on indirect displacement reactions and experimental procedures have to be strictly controlled. Therefore, solution spectrophotometry is still the most widely used spectroscopic technique for trace analysis of non-metals.

The theory and apparatus of this technique are covered in most analytical text books and will not be given here. In general, the method has more modest operative requirements than other instrumental methods.

The development of such analytical methods lies in producing chemical transformations which will result in a change in the spectral characteristics or the intensity of radiation of the system, and which is proportional to the concentration of the desired constituent. Spectrophotometric methods for the determination of non-metals have been reviewed comprehensively up to 1957.[1] In the following section such methods will be briefly discussed under the nature of reaction of the

ion, drawing examples from generally accepted or recently developed procedures.

1.2 Spectrophotometric Methods for the Determination of Non-Metals

(a) Direct Absorption of Radiation

Only a few non-metals and anions, e.g. iodine, permanganate, chromate, can be determined directly by their absorption in the visible-UV region.

(b) Indirect Displacement Reactions

The most numerous though often unselective methods for non-metals depend on the ability of anions to abstract metals from a metal complex thus causing a change in the absorption of the system. Some of the earlier spectrophotometric methods for fluoride were based on the extent to which this ion bleaches some organic chelates of zirconium [2-5], thorium [6-9], aluminium [10-11], etc.

Belcher [12A] first proposed the use of the highly absorbing reagent 4-Amino-4'-chlorodiphenyl hydrochloride as a precipitant for sulphate ion in 1953. Jones and Letham [12B] subsequently applied the reaction for the submicro determination of sulphate, measuring the concentration of the excess reagent spectrophotometrically.

Several other colorimetric methods [13-16] for the determination of sulphate are based on the lower stability constants or insolubility of metal-sulphates compared to metal-organic chelates. Thus when the ion is added to solid barium chloranilate in ethanolic solution, the highly coloured acid-chloranilate ion is liberated and can be extracted into organic solvents [17].

Chloride is generally determined by the displacememt of $AgIO_3$, AgCNS [18], or $Hg(CNS)_2$ [19] followed by the spectrophotometric determination of IO_3^- *via* I_2 and CNS^- *via* $Fe(SCN)_3$.

(c) Complex Formation with Organic Reagents

These methods involve the formation of new coloured or fluorescent complexes when anions are added to organic reagents.

Spectrophotometric determinations of boron are based on the reaction of boric acid with polyhydroxyanthraquinones in strong sulphuric acid media to form highly coloured chelates. Examples include the use of quinalizarin[20] and carminic acid[21].

The unique reaction of fluoride with cerium-alizarin complexan to form a ternary complex has afforded a sensitive and selective method for its determination[22-23]. Details of the method are given in Chapter 2.

(d) Determinations Involving Solvent Extraction

Large cations and anions which form coloured or fluorescent ion-association complexes can be extracted into organic solvents and determined spectrophotometrically. Some recently developed procedures for the determination of phosphorous include the extraction of ion-pairs formed between phosphomolybdate and the cations, Crystal Violet, Iodine Green and Rhodamine B[24]. Determinations of thiocyanate, perchlorate and iodide can also be carried out by extraction of ion-pairs formed between the coloured Neutral Red cation and the anions[25]. Chlorides and bromides can be determined by oxidation of $I^- \rightarrow I^+$ and $Br^- \rightarrow Br^+$ by Chloramine B followed by reaction with a triphenylmethane dye, e.g. Brilliant Green[26].

(e) Formation of Heteropolymolybdates

The value of heteropolymolybdates in the determination of small amounts of phosphorus, silicon, arsenic and germanium, is well known. Procedures include measurement of the yellow heteropolymolybdates[27] or their reduced blue polymeric complexes[28]. Numerous reduction and

extraction methods have been investigated[29,30]. A typical highly sensitive procedure involves the extraction of the $H_3PO_4(MoO_3)_{12}$ followed by dissociation and determination of the molybdate ions with 2-amino-4-chlorobenzenethiol in chloroform thus achieving a 12-fold amplification for phosphorus[31].

(f) Reactions Involving Organic Synthesis

One of the most widely used methods for the determination of traces of nitrate ion is based on the nitration of aromatic compounds to form coloured products. Studies into the nitration of many xylenols revealed that 3-4-xylenol was best[32]. A new, highly sensitive method is based on the nitration of fluorescein in concentrated sulphuric acid[33].

(g) Diazotization Reactions

It is commonly known that nitrites react with primary aromatic amines in acidic solution with the formation of diazonium salts, which will couple with phenols to produce highly coloured dyes[34]. These reactions are extremely sensitive and selective for nitrite determinations and have also been applied to the indirect determination of nitrates[35] and selenium[36]. Various combinations of reagents have been used by different workers including sulphanilic acid and 1-aminonaphthalene[37], sulphanilamide and N-(1-naphthyl)-ethylenediamine hydrochloride[38], etc.

(h) Heterocyclic Synthesis

Selenous acid in dilute hydrochloric acid reacts with suitable diamines to form piaz-selenols. Highly sensitive and selective colorimetric and fluorimetric procedures for the determination of selenium using 3,3'diaminobenzidine[39] and 2,3-diaminonaphthalene[40] have been developed in this way.

An important colorimetric procedure for the determination of sulphur is based on the formation of methylene blue from the reaction of sulphide with p-amino-N,N-dimethylaniline in the presence of ferric chloride[41,42]. Many applications of this procedure are found in the literature including one for the determination of sulphate[43].

(i) Oxidation and Reduction Reactions

The changes in absorption of a system produced by the oxidation or reduction of anions have been extensively used for their determination. Oxidising anions such as persulphate, chromate, permanganate and hypochlorite ions oxidise benzidine to benzidine blue in neutral or weak acetic acid solutions[44]. Sulphites can be determined colorimetrically by the extent to which fushin is converted to a colourless bisulphite addition compound[45] or by reduction of iodine in the starch-iodine complex to iodide[46].

(j) Catalytic Reactions

The extent to which a reaction is catalysed by some anions has been made the basis of quantitative colorimetric measurements. An example is the kinetochromic spectrophotometric technique[47,48] which has been applied to the determination of fluorides and sulphates and is described later in Chapter 2.

Other examples include the determination of iodide by its catalytic action on the oxidation of 3,3'-Dimethylnaphthidine by hydrogen peroxide[49] and the determination of sulphide, thiosulphate and thiocyanate by their acceleration of the oxidation of ferrous ion with silver ion[50].

CHAPTER 2

Current Methods for the Determination of Trace Amounts of Fluoride

2.1 Introduction

Trace determinations of fluoride have become increasingly important owing to the growing need for its stricter control in our environment and diet. This is brought about by a greater awareness of its effects on health and an increase in the variety of materials in which it occurs. Areas which require rapid and reliable methods for fluoride determination include public water supply departments, the field of pollution studies, clinical and industrial laboratories. In the following section some of the currently used techniques and those recently reported in the literature are discussed.

2.2 Cerium-Alizarin Fluorine Blue Method [22-23]

The discovery of the unique ability of fluoride to form a blue ternary complex with cerium-alizarin complexan has led to the establishment of one of the two most widely used methods for the determination of traces of fluoride. This is the first reaction in which the fluoride ion itself produces a new coloured compound.

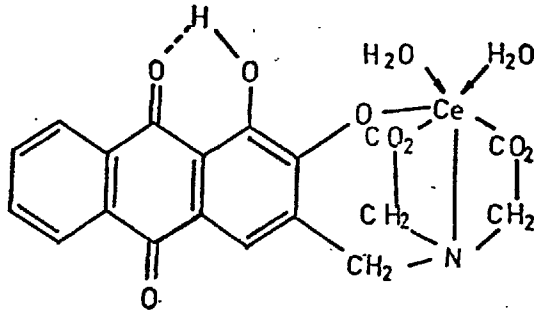
The quantitative procedure involves comparison of the red complex of cerium III-alizarin complexan with that of the lilac-blue ternary complex formed when fluoride is added in small amounts. The most suitable wavelength of measurement is 610 nm and the molar absorptivity is 3×10^4. The optimum pH conditions were found to be between pH 5.0 and pH 5.2. Maximum colour for the fluoride complex develops within 15 minutes, but the cerium III-chelate reference solution requires 60 minutes development

time in which to attain a stable colour. The method is reasonably free from anionic interference particularly that from sulphate, but suffers seriously from interference from many of the more common cations which bind fluoride, e.g., Al, Fe, CrIII, V, Ca and Be. These cations, however, can be removed by masking agents and solvent extractions. The method can be applied to a range of between 5 μg to more than 1.6 mg per 100 ml by simple variation of experimental procedure. A 200% increase in sensitivity was reported[51] by using the lanthanum instead of the cerium chelate and measuring the absorption at 281 nm. Improvements of the sensitivity and stability for the cerium and lanthanum complex have been achieved by the use of 20% acetone, acetonitrile[52] or dimethylsulphoxide media[53]. Improvements by extraction into a solvent comprising tribenzylamine in a mixture of pentyl and secondary butyl alcohols[54] or into isobutanol containing hydroxylamine hydrochloride[55] have also been reported.

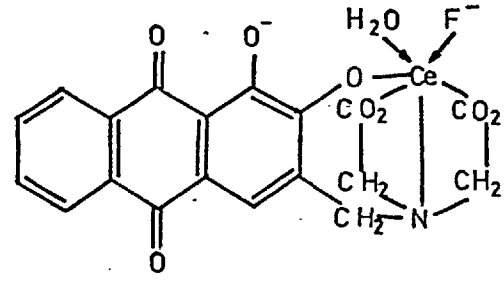
The structure of the binary and ternary complexes are shown in Fig. 2.1. Entry of the electrophilic fluoride ion into the co-ordination sphere of the cerium ion leads to a general withdrawal of electrons from the aromatic nucleus and causes deprotonation of the 1-hydroxy group and hence the blue colour which is characteristic of the fully dissociated reagent.

2.3 Lanthanum-Fluoride Ion Specific Electrode

This is the other generally used method for fluoride determination. Frant and Ross[56] first described this electrode in which the potential developed across a lanthanum fluoride crystal is dependent on the ratio of the fluoride activities on either side of the crystal. If the internal fluoride activity is kept constant the potential developed depends only on



cerium-alizarin complexan chelate



cerium-alizarin complexan-fluoride complex

FIG. 2.1

the value of the fluoride activity in the external solution. It is claimed that a Nernstian response is obtained over a range extending from saturated solutions to 10^{-7} M fluoride. In use, the electrode forms a cell with an external reference electrode, normally the calomel electrode. Hydroxide ion interferes and hence the electrode can only be used between pH 4.5 and pH 8.5. The major difficulty in extending the technique is that the activity of the fluoride ion in solution is affected by changes in the ionic strength of the solution and by the presence of complexing cations. These disadvantages may be largely overcome by the use of a Total Ionic Strength Adjustment Buffer made up from acetic acid, sodium chloride and sodium citrate[57]. However, the use of large amounts of sodium chloride introduces relatively large amounts of fluoride present as impurity. To eliminate this error, Duff and Stuart[58] recently suggested the use of a citrate-hydrochloric acid buffer.

Work has also been done on direct potentiometric measurements using the electrode for end-point detection in titrations of fluoride with thorium, lanthanum and calcium[59] and the use of a modified fluoride activity electrode for the determination of subnanogram amounts of fluoride in sample volumes of 10 µl using the technique of linear null-point potentiometry[60].

An important advantage that this method has over other methods for the trace analysis of fluoride is that it is free from interference of other anions that are normally present in the sample, hence a separation step prior to analysis is not required. However, changes in temperature will affect the electrode response and may also alter the solubility of the calomel electrode and calibrations should be done each day.

2.4 Bleaching Effect of Fluoride on Metal Chelate Complexes

A great number of combinations of metals and organic dyes have been used for the spectrophotometric determination of fluoride based on its bleaching effect. The most widely accepted method is that based on the Zr-Eriochrome cyanine R[5] complex, with a working range of 5 - 120 µg/100 ml and the most sensitive method is that of the fluorescent Thorium-Morin complex[8] capable of determining 2 - 14 µg/100 ml. These methods are inferior to that described above because Beer's law is frequently not obeyed owing to the diversity of complex fluorides which can co-exist in solution. They are also subject to interference from cations which complex with fluoride, and many anions which may be present after mineralisation of organic compounds, in particular, sulphate.

2.5 Recently Developed Techniques

Two highly sensitive methods based on kinetic reactions were reported recently.

(1) The first is called kinetochromic spectrophotometry in which fluoride is made to act as a catalyst to promote the reaction between partially polymerised solutions of zirconyl chloride and an organic chelating reagent. Investigations were first carried out between zirconium and xylenol orange and this provided a molar absorptivity of 2.0×10^5 for the fluoride ion and a calibration range of 0.5 to 5 μg/100 ml. A similar procedure using Methylthymol Blue[48a] gave a molar absorptivity of 3.2×10^5 and a calibration range of 0.25 to 4.75 μg/50 ml. Interferences include phosphate, arsenate, sulphate, citrate and oxalate and although Fe and Al interfere, the method is still freer from cationic interference than the cerium or lanthanum alizarin fluorine blue method. However, due to the substoichiometric nature of the reaction it is not possible to determine larger amounts of fluoride. Furthermore, experimental conditions, particularly the age and the acidity of the zirconium solutions have to be rigidly controlled before meaningful results can be obtained.

(2) The second kinetic method[61] involves the inhibiting action of fluoride on the catalyst in the zirconium catalysed reaction between perborate and iodide. Kinetic measurements were accomplished by an automatic potentiometric technique. The calibration range is 0.019 to 0.19 μg/50 ml. However, the method suffers serious interference from the common anions, SO_4^{2-}, PO_4^{3-}, EDTA, tartate, oxalate, citrate as well as the cations which normally complex with fluoride such as Be, Al and Th.

(3) An atomic absorption spectroscopic method[62] has also been devised for fluoride. This of course is an indirect method and makes use of the depressing effect of fluoride on the absorption of magnesium in an air-coal gas flame. The range of fluoride that could be determined was 0.2 - 20 μg/ml. Interfering ions include Al^{3+}, La^{3+}, PO_4^{3-}, $C_2O_4^{2-}$, SO_4^{2-}.

An alternative procedure, though somewhat less sensitive technique is described in the same papers. This is based on the enhancement of zirconium absorption in a nitrous oxide-acetylene flame.

CHAPTER 3

Outline of Approach Taken Towards Developing New Spectrophotometric Methods for the Determination of Fluoride

3.1 Introduction

The successful development of procedures for the determination of fluoride described in the following chapters has been accompanied by a very considerable effort spent in examining the possibilities of using new reagents and reactions for the determination of the ion. This chapter describes the general line of approach of such investigations. This work is described in outline only because it led to no positive results in the end, although considerable time was required to pursue the work.

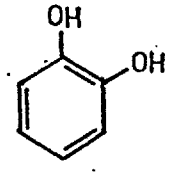
3.2 Investigation of Reagents for Ternary Complex Formation with Fluoride

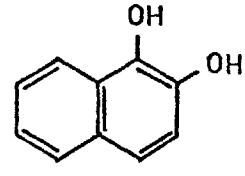
The cerium-alizarin fluorine blue method is undoubtedly one of the most useful methods for fluoride determination if overall consideration is given to simplicity of experimental procedure and apparatus, range of application, selectivity, sensitivity and precision of method. It seems logical therefore to look for new reagents which could form an absorbing or fluorescing ternary complex with fluoride. Attempts were hence made to (a) synthesis new complexing reagents, and (b) form new reactions with fluoride and various combinations of metal ions and available complexing reagents.

(1) Aminomethylation of some aromatic compounds

If the mechanism of ternary complex formation of cerium-alizarin complexan-fluoride is considered it will be noted that the important feature

of the alizarin complexan is the presence of vicinal hydroxyl groups adjacent to the dicarboxymethylaminomethyl group. The 2-hydroxyl group co-ordinates with the metal ion, (see Fig. 2.1) leaving the 1-hydroxyl group free to deprotonate when the electrophilic fluoride is introduced. At the time of consideration the two aromatic compounds with adjacent phenolic OH's were catechol and 1,2-dihydroxynaphthalene.





Catechol

1,2-dihyroxynaphthalene.

FIG. 3.1

Attempts were made to aminomethylate these compounds by a Mannich type condensation between the parent compound, formaldehyde and acetic acid.

The reaction was first carried out in an alkaline media using the procedure described by Leonard[63] in the synthesis of alizarin fluorine blue. Unfortunately, catechol was easily decomposed by alkali. When the reaction temperature was lowered sufficiently so that no decomposition

was evident no precipitation occurred. Preparations with 1,2-dihydroxynaphthalene produced a highly insoluble, crude brown precipitate which was probably a resin. Attempts at purification, characterisation and reaction of the product with metal ions failed.

Another procedure was adopted [64]. This entailed reaction in a glacial acetic acid media. With catechol as the parent compound no solid could be induced to precipitate even after endless hours of stirring. With 1,2-dihydroxynaphthalene, a colloidal solution was obtained.

Due to the discouraging results of these experiments further preparations were not carried out. It is of interest to point out, however, that Leonard has recently reported [65] a much improved method of synthesis of alizarin fluorine blue which could perhaps be applied to the preparation of these compounds.

(2) Effect of small amounts of fluoride on the absorption or fluorescence of some metal-chelates.

10^{-5} M solutions of the 1:1 metal-chelate complexes listed below were prepared. Fluoride was added so that its concentration equals half that of the metal-chelate and any changes in the absorption or fluorescence of the solutions were noted. The metal complex solutions were freshly prepared and experimental conditions such as pH and order of addition of solutions were varied as far as possible. The object of these experiments was to look for any sign of ternary complex formation or any quenching effect caused. Abstraction of the metal from the chelates was ignored as a possible analytical method. Of the complexes examined, fluoride was found to produce an increase in the fluorescence of zirconium-calcein blue and to a lesser extent that of the zirconium-morin complex. An experimental procedure for the determination of fluoride based on the

enhancement of the fluorescence of the zirconium-calcein blue complex is subsequently described in Chapter 5.

Effect of small amounts of fluoride on the absorption or fluorescence of some metal-chelates

Th + Alizarin Fluorine Blue

La + 1-Dicarboxymethylaminomethyl-2-hydroxy-3-Napthoic Acid

Zr(IV) + Calcein Blue

Zr(IV) + PAR 4-(2-pyridylazoresorcinol)

Ce(III) + PAR

Zr(IV) + Carminic acid

Zr(IV) + 8-hydroxyquinoline in chloroform

Zr(IV) + Quercetin

Zr(IV) + Pyrocatechol

Zr(IV) + Mandelic acid

Zr(IV) + Morin

Th(IV) + Morin

Ti(IV) + H_2O_2

The metal solutions used were freshly prepared and experimental conditions such as pH and order of addition of reagents were varied as far as was possible.

(3) Effect of fluoride on the emission intensity of several metals

The emission intensity of molecular or atomic species of metals in flames, depends, among other factors, on the volatility of the solutions sprayed into the flame. Since metal fluorides tend to be more volatile

than other metal species in solution it is reasonable to expect an enhancement of emission intensity with solutions containing fluoride. For this reason solutions of some common metal salts, e.g., $CuCl_2$, $PbNO_3$, $BaSO_4$, $CaCO_3$, $SrCl_2$, CsCl, $AgNO_3$, $NiCl_2$, LiCl, $ZnSO_4$, and boric acid were made up in conc. HCl, conc. H_2SO_4 and conc. HNO_3. Each of these solutions was introduced into a bunsen flame using a platinum loop. The emission produced was compared to that when fluoride was added. No significant change in the emission intensity was observed in any instance, however.

CHAPTER 4

The Determination of Fluoride by Catalysis on the Oxidation of Ferrous Ion by Iodine

4.1 Introduction

Kolthoff and Belcher report that fluoride has been used as a catalyst for the titration of ferrous ion with iodine[66]. Interest in the possibility of the use of this reaction for fluoride determinations arose from the consideration that determinations of ions based on their catalytic effects have often proved to be very sensitive and selective techniques. Catalytic methods for the determination of anions have recently been reviewed[67].

Catalytic methods are usually based on the kinetic examination of various homogenous reactions in solution. In the absence of the catalyst the reactants normally react slowly. In the presence of the catalyst, a faster reaction path becomes available and this catalysed reaction proceeds simultaneously with the uncatalysed one. The shares of these two reactions in the overall process depend on the concentration of the catalyst present. Below a certain concentration the catalyst has no marked effect on the overall reaction rate, that is, below the limit of sensitivity the presence of the catalyst cannot be detected in this way. On the other hand, if the amount of the catalyst is too high, the catalysed reaction will become predominant, and this might result in the speeding up of the reaction to such an extent that the reaction rate becomes unmeasurably high. Between these two extremes, however, there exists a concentration range within which the overall reaction rate depends strongly on the concentration of the catalyst present. This range can be used for analysis and, from kinetic measurements, the amount of the catalyst can be established.

In the fluoride catalysed oxidation of ferrous ion by iodine

$$Fe^{2+} + \tfrac{1}{2}I_2 \rightarrow Fe^{3+} + I^- \quad .... \quad .... \quad (1)$$

the rate of the overall reaction can be followed by measuring the concentration of iodine spectrophotometrically and this can be related to the concentration of fluoride. In the procedure described below fluoride is calibrated by measuring the iodine concentration after a fixed reaction time. However, before investigations of the parameters of the system could be examined, it was necessary to look into the characteristics of the absorption spectra of iodine.

4.2 Evaluation of Optimum Methods for Measuring Iodine Concentration

Iodine dissolved in water absorbs weakly across the whole of the u.v./visible region of the electromagnetic spectrum, but, in a solution of potassium iodide, it absorbs more strongly and its spectra, Fig. 4.1 , shows two distinct peaks at 289 nm and 350 nm. The presence of potassium iodide also improves the precision of measurement because it lowers the volatility of iodine. The extinction coefficient of iodine in potassium iodide solution increases with increasing potassium iodide concentration to a maximum of 0.1 M. However, according to Equation 1, one would expect the presence of potassium iodide to retard the rate of oxidation of ferrous and this was confirmed by experiment. It was then decided to carry out the reaction with iodine dissolved in water and the amount of potassium iodide required to make the final solution 0.1 M in potassium iodide was added fifteen minutes before measuring the absorbance.

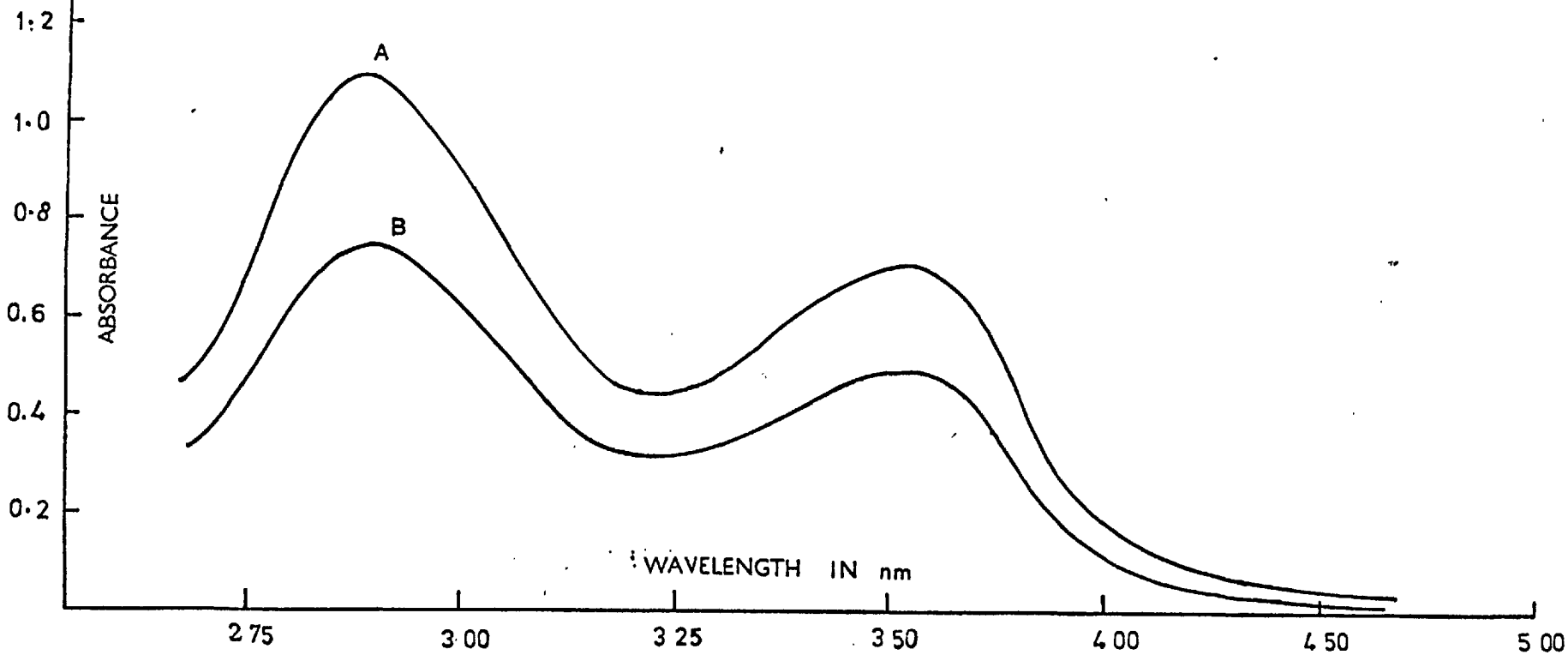
Ovenston and Rees[68] have studied the sensitivity and accuracy of measuring iodine in potassium iodide at 289 nm and 350 nm and also in starch–iodide solutions. They found that although the sensitivity at

FIG. 4.1 ABSORPTION SPECTRA OF IODINE

(A) A solution containing ferrous ion + iodine in 0.1 M KI.

(B) A similar solution but with fluoride added.

The absorbance were measured $1\frac{1}{2}$ hours after mixing of the reagents.



350 nm is only three quarters that at 289 nm and that obtained with the starch-iodide method, the precision of measurement was four times as great. We hence decided to measure the iodine in our reaction at 350 nm.

4.3 Optimum Conditions

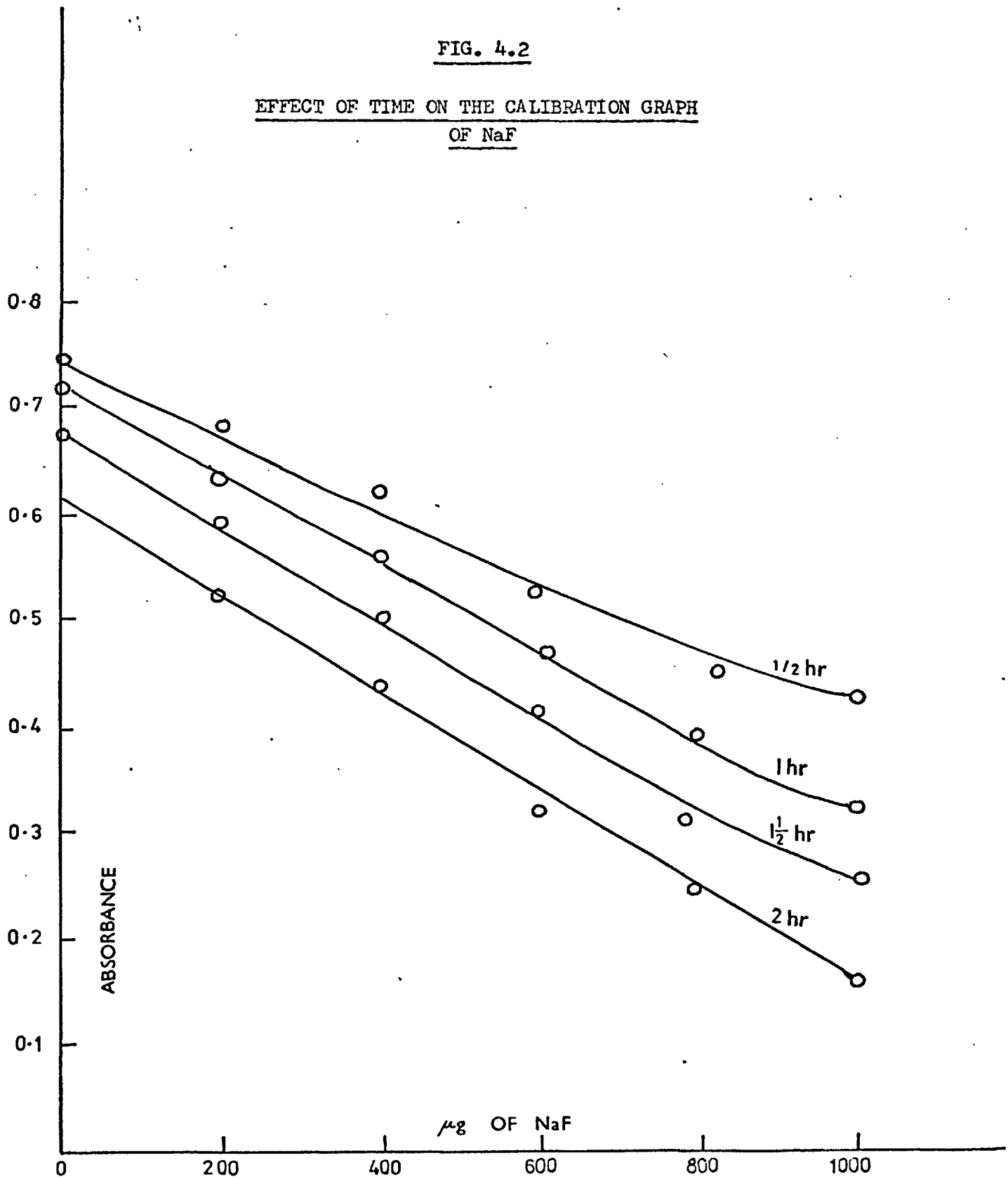
An attempt was made to optimise the conditions of pH, iodine concentration, ferrous ion concentration and time of development for the determination of fluoride. For each experiment all the variables except the one being investigated was kept constant. Throughout the investigation, unless otherwise indicated, the method of preparation of solutions was as described in the section under Calibration. The solutions were measured against water or an external standard of dilute potassium dichromate where this was advantageous.

(a) Variation of Reaction Time

In order to find the optimum development time for the fluoride catalysed oxidation of ferrous ion with iodine, the absorbance readings were taken at $\frac{1}{2}$ hour intervals without the addition of KI which would retard the reaction as explained earlier. Fig. 4.2 shows the absorbance of solutions containing 5 ml of an approximately 10^{-3} M I_2, 5 ml 2.5×10^{-2} M ammonium ferrous sulphate and 0.5 ml 2×10^{-3} M acetate buffer, pH 4.3. The solutions were measured in 1 cm cells against water. The sensitivity appears to remain constant after 1 hour. Precipitation occurred when the solutions where left for more than $2\frac{1}{2}$ hours. It was realised that varying conditions of pH, concentrations of iodine and ferrous ion would affect the optimum development time. However, in order that other experimental conditions could be investigated it was decided to measure all absorbances after $1\frac{1}{2}$ hours.

FIG. 4.2

EFFECT OF TIME ON THE CALIBRATION GRAPH OF NaF



(2) Concentration of Iodine

Fig. 4.3 shows the effect of varying the iodine concentration on (a) a solution containing 5 ml 2.5 x 10^{-2} M ferrous ammonium sulphate at pH 4.3, and (b) a similar solution containing 100 μg NaF. Because iodine is volatile and difficult to dissolve in water its concentration has to be measured by comparing its absorbance with standard potassium iodate in an acidic KI solution. The sensitivity of the fluoride reaction increases with the concentration of iodine, but it must be noted that the absorbance of the blank also increases. The optimum iodine concentration is hence the maximum concentration which would allow the blank to be measured using a particular cell path length.

(3) Effect of pH

The reaction should not be carried out above pH 4.5 because precipitation occurs. Below pH 4.5, the absorbance of the solutions, the blank as well as that containing fluoride, decreases rapidly with increasing pH. In Fig. 4.4 the solutions contain 5 ml of an approx. 10^{-3} M iodine, 5 ml of 2.5 x 10^{-2} M ammonium ferrous sulphate. Optimum sensitivity is obtained at pH = 3. Further experiments show that with higher iodine concentrations the reaction at pH 4 shows similar sensitivity. The conclusion drawn from these experiments on pH variation is that a pH range of between 3 and 4 should be used, the pH chosen according to the strength of the iodine solution used.

(4) Ferrous Ion Concentration

Fig. 4.5 shows the effect of varying the concentration of ferrous ion. The solutions contain 5 ml of an approx. 10^{-3} M iodine solution, 0.5 ml of acetate buffer at pH 3.0. The optimum concentration in this

FIG. 4.3

EFFECT OF VARYING THE IODINE CONCENTRATION

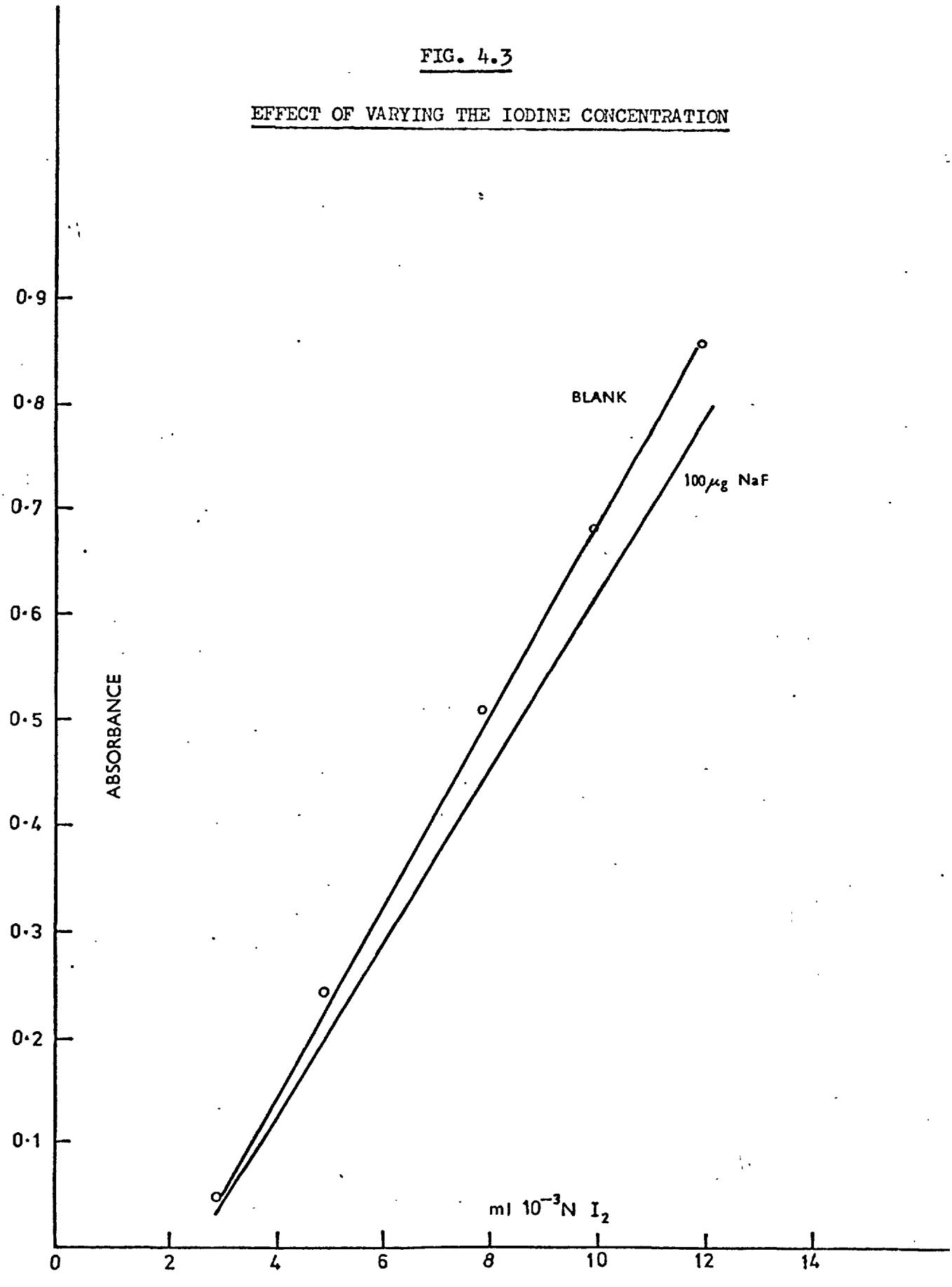


FIG. 4.4

VARIATION OF pH

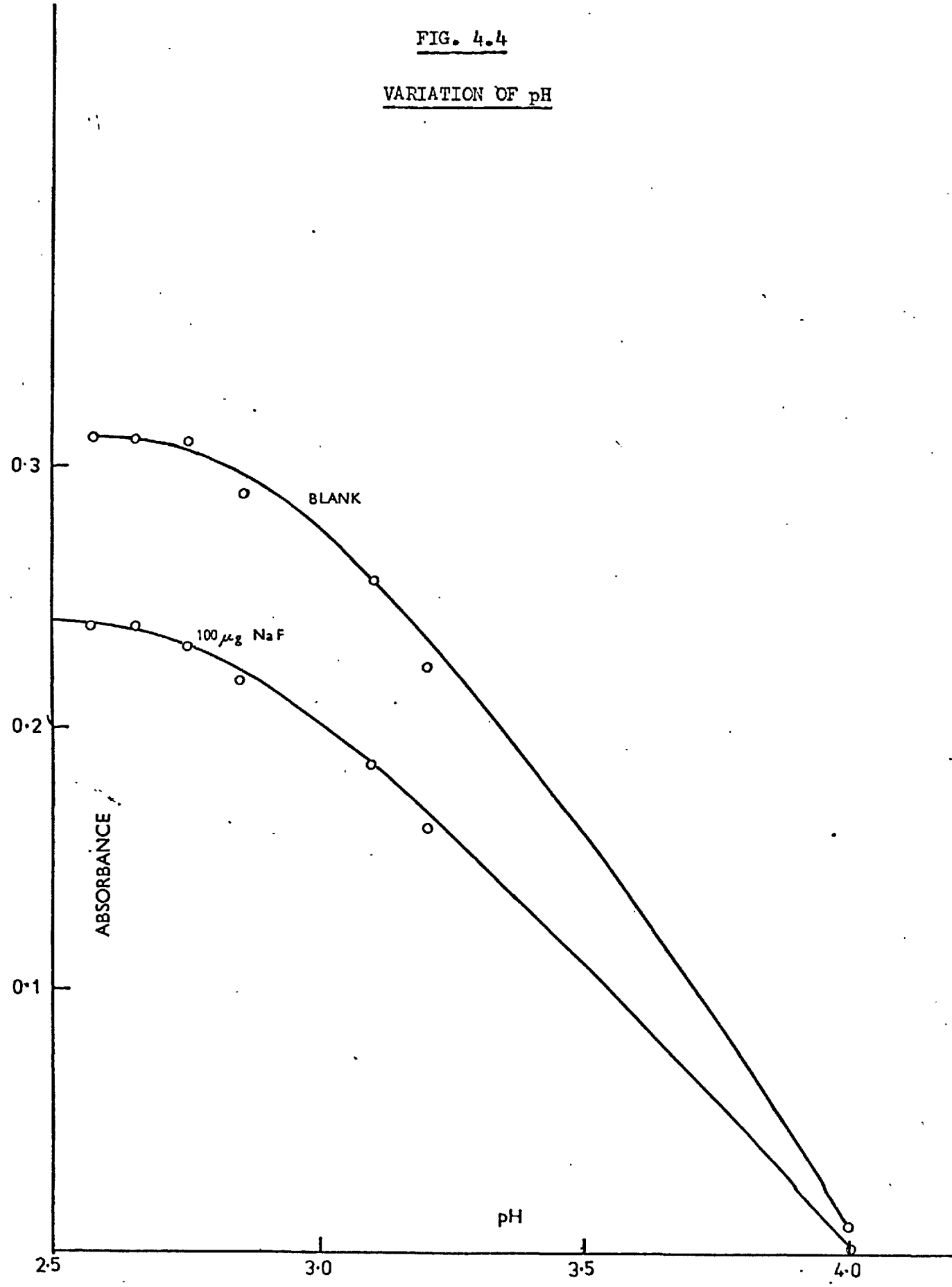
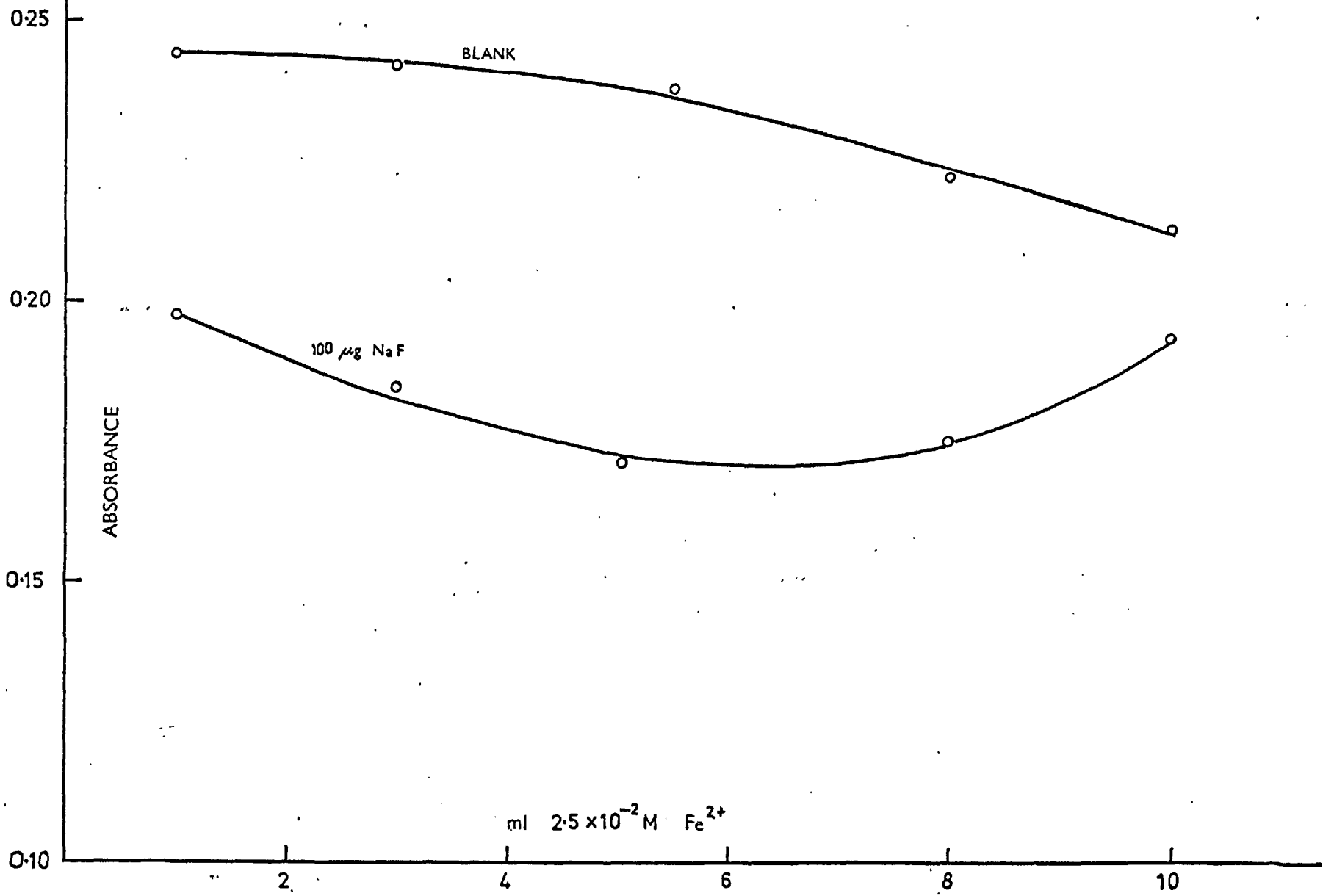


FIG. 4.5 VARIATION OF CONCENTRATION OF FERROUS ION



case is 5 ml 2.5×10^{-2} M ferrous ammonium sulphate, but the optimum would probably depend on the iodine concentration and pH used.

(5) Buffer Concentration

It was noted that the acetate buffer reduces the sensitivity of the reaction probably by complexation of the acetate ions with ferrous ions. Hence, the minimum concentration of buffer (0.5 ml) required to maintain the pH of the system at the desired value was used.

4.4 Experimental

Apparatus Beckman DB spectrophotometer.

Reagents All chemicals used were of ANALAR grade.

Iodine Solution Iodine dissolves with great difficulty in water and moreover it is volatile and cannot be accurately weighed and dissolved. The iodine solution was therefore prepared by warming excess of iodine with water and filtering the solution. Its concentration was determined by measuring its absorbance in KI at 350 nm and comparing it with standard potassium iodate in acidified KI solutions. The solutions were diluted to the desired concentration.

Ferrous Ammonium Sulphate 5×10^{-2} M. 4.902 g of ferrous ammonium sulphate were dissolved in 5 ml 2 N sulphuric acid and made up to 500 ml with water.

Buffer pH 4.3 26.25 g of sodium acetate trihydrate were dissolved in 25 ml and made up to 250 ml with water.

40% Potassium Iodide 10 g of potassium iodide were dissolved in 25 ml of water. This solution was prepared freshly before use.

FIG. 4.6

CALIBRATION GRAPH OF UP TO 1000 µg NaF

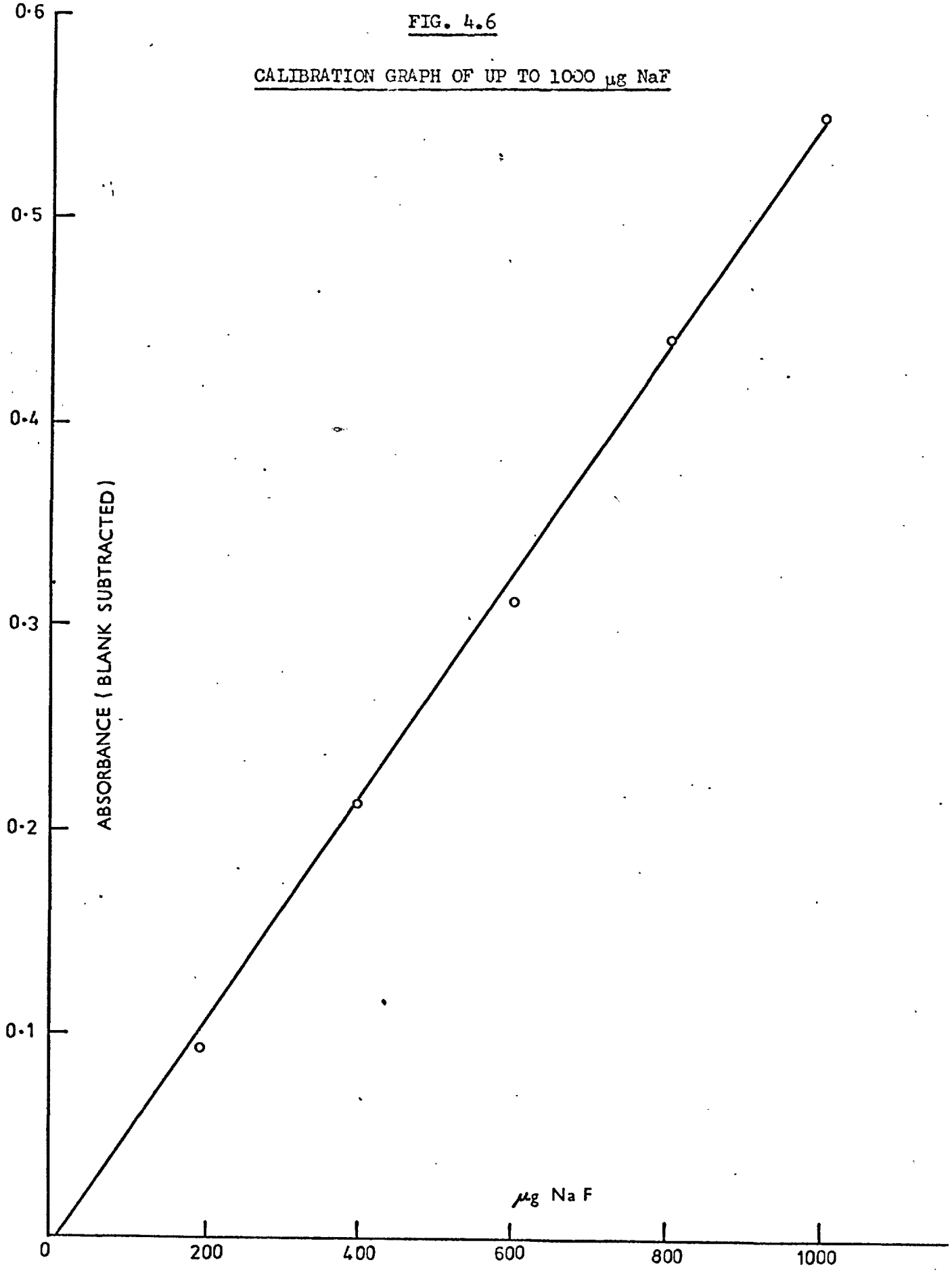
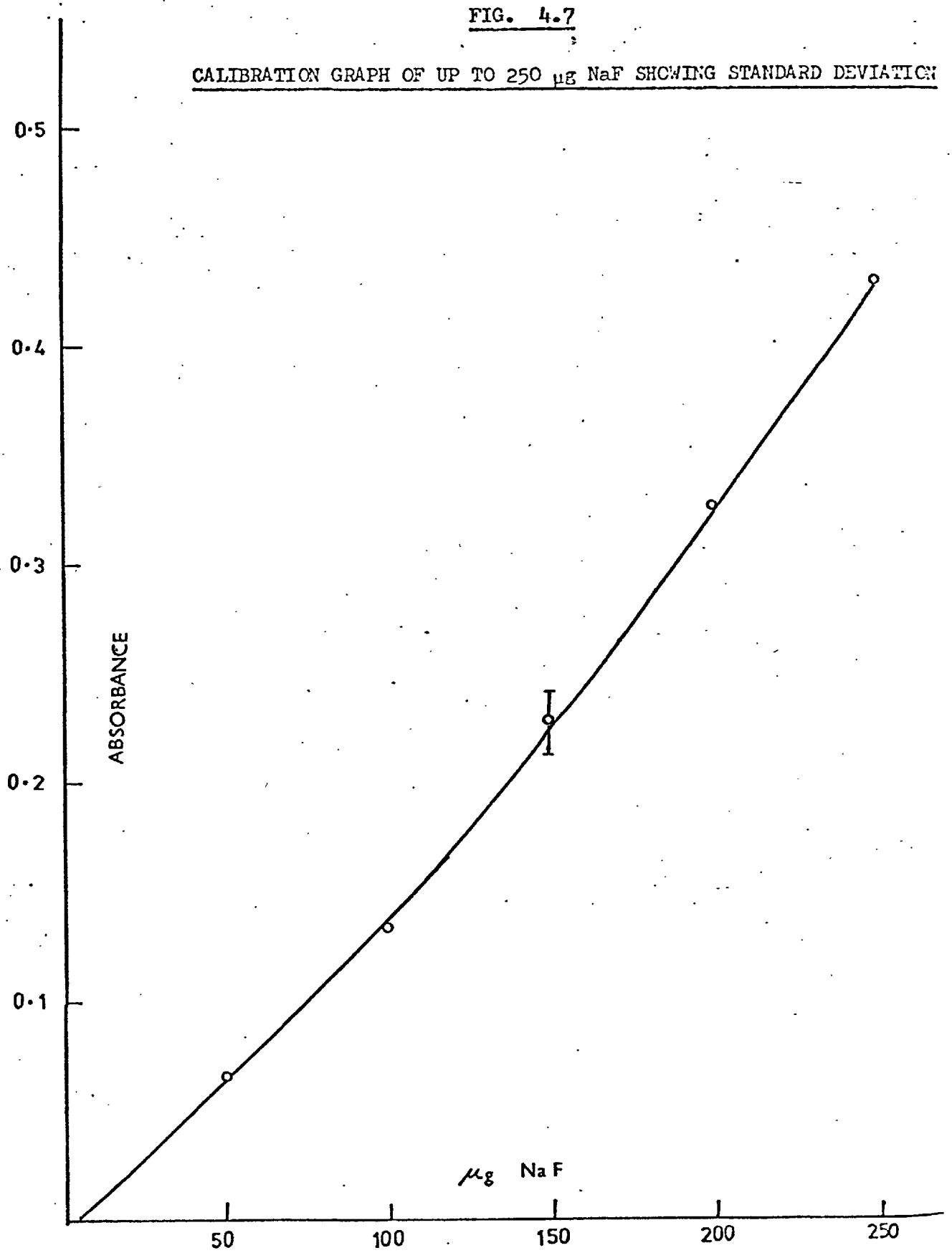


FIG. 4.7

CALIBRATION GRAPH OF UP TO 250 µg NaF SHOWING STANDARD DEVIATION



Preparation of calibration graph for 0 - 1000 μg NaF

Transfer 0.5 ml of 200 μg/ml NaF solution into a series of 25 ml flasks. To each flask add 10 ml of an approximately 1.3×10^{-3} M iodine, 0.5 ml pH 4.3 acetate buffer. At zero time add 5 ml 2.5×10^{-2} M ferrous ammonium sulphate into the first flask and dilute the solution to 25 ml. Repeat the procedure for the other flasks at 1 min. intervals. Allow the solutions to stand for 75 mins and add 1 ml 40% KI at 1 min intervals. Exactly 15 mins after the addition of KI, measure the absorbance of the solutions at 350 nm against a water blank using 2 mm cells and allowing 1 min to elapse between the measurement of each solution. The absorbance of the solutions are shown in Fig. 4.6. The effective molar absorptivity for the fluoride ion is 5×10^{4}.

Calibration of 0 - 250 μg and Reproducibility Tests

Attempts were made to increase the sensitivity of the reaction by diluting all the solutions thereby decreasing the calibration range and measuring the absorbance in 1 cm and 4 cm cells. The improvement in sensitivity was not as great as expected and it was realised that in a kinetic reaction such as this optimisation of conditions should be carried out again for these diluted solutions. Fig. 4.7 shows the calibration of 0 - 250 μg NaF using 4 cm cells. The coefficient of variation for the absorbance of 150 μg NaF was 6% when the experiment was repeated over a period of six days.

4.5 Effect of Foreign Ions

The effect of some cations and anions on the determination of fluoride by the recommended procedure was investigated and the results are presented in Table I.

TABLE I

Effect of Various Ions on the Determination of 100 μg NaF

Ion	Molar Excess	Interference %	Ion	Molar Excess	Interference %
Cl	100		Ca	10	-
NO_3	100	5	Mg	10	-
SO_4	100	-	Cd	10	-
ClO_4	100	-	Zn	10	-
PO_4	100	precipitation	Al	10	100
			Be	10	100
			Pb	10	yellow ppt.
			Ni	10	-

The cations which interfere most seriously were Al, Be and Cd. These were eliminated by stirring the solutions magnetically with Zeo-carb 225 resin, adjusting the solution to pH 4.0 using dil. NaOH and then carrying out the determination as before.

4.6 Conclusions

The method described above is less sensitive than the kinetochromic method, but it has the advantage that a wider range of fluoride can be determined. Although in the work described, the maximum concentration of fluoride used was 1000 μg in 25 ml, higher amounts can easily be determined. The method is, however, inferior to the cerium-alizarin fluorine blue method. It shares the disadvantages of other kinetic methods in that strict control of the development time of the solutions must be

applied before meaningful results can be obtained. The application of automation could render the method more useful and it should be noted that only ordinary laboratory materials are required for the reaction in contrast to all other spectrophotometric determinations of fluoride which employ more expensive organic dyes.

CHAPTER 5

Spectrofluorimetric Determination of Traces of Fluoride Ion by Ternary Complex Formation with Zirconium and Calcein Blue

5.1 Introduction

Analytical methods which are direct, generally possess greater selectivity and sensitivity than indirect methods. It was observed that there are only two direct spectrophotometric methods for fluoride determination, the cerium-alizarin-fluorine blue method[33] and kinetochromic spectrophotometry[47], both of which are colorimetric methods. It was considered that the sensitivity could be improved even further by a fluorimetric method and this led us to an investigation of the effect of fluoride on the fluorescence intensity of the zirconium-Calcein Blue complex.

Since its almost simultaneous introduction by Eggers[49] and Wilkins[70], Calcein Blue has been used extensively as a metallofluorescent indicator for the complexometric titration of several metal ions with EDTA. The indicator exhibits a brilliant blue fluorescence between pH 4 - 10, with the fluorescence decreasing outside this pH range. The addition of certain cations, e.g. Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Bi^{3+} to the fluorescent indicator at intermediate pHs, results in the quenching of the fluorescence[69]. Nickel and chromium have thus been determined[70] at between pH 4 and 10 by the addition of excess of a standard solution of EDTA, then back titrating the excess with a standard copper solution. The end-point occurs when all the EDTA has been consumed, so that the next addition of copper solution quenches the blue fluorescence of the indicator.

At pH > 12, Calcein Blue does not fluoresce, but forms fluorescent complexes with calcium, strontium and barium. These elements can thus be titrated with standard EDTA at pH 13 - 14 in the presence of Calcein Blue indicator[70]. The end-point occurs when all the metal has been preferentially complexed with the EDTA so that the metal-Calcein Blue complex is completely destroyed and the fluorescence of the solution is quenched.

The use of Calcein Blue as a direct fluorimetric reagent for the determination of zirconium was recently reported[71]. The procedure involves the addition of an aqueous solution of zirconium to a solution of Calcein Blue followed by a glacial acetic acid buffer at pH 5.5. The fluorescence intensity is then measured at 405 nm with an excitation wavelength of 350 nm. The calibration curve is linear from 20 - 100 ng of zirconium (0.0002 - 0.001 ppm). In the study of interference effects, it was found that the addition of fluoride to the zirconium-Calcein Blue complex resulted in an enhancement of the fluorescence intensity.

In this chapter, we describe an investigation of this effect, followed by the development of a method for the determination of fluoride based on this intensification of fluorescence.

5.2 Preliminary Investigations

Initial experiments to investigate the enhancement by fluoride were carried out with the experimental conditions as described in the determination of zirconium with Calcein Blue[71]. At this pH of 5.5, the fluorescence intensity of both the solutions of zirconium-Calcein Blue complex and that with fluoride, decreases rapidly with time, making measurements difficult.

In order to decide on the approach by which the investigations should be carried out, the mechanism of the enhancement by fluoride, was briefly considered. Previous direct spectrophotometric methods for fluoride have been based either on ternary complex formation or the depolymerisation of zirconium species by fluoride. In the system we are investigating, ternary complex formation was not suspected at this stage because Calcein Blue does not possess vicinal hydroxyl groups which have been involved in ternary complex formation in the cerium-alizarin fluorine blue reaction[23]. The enhancement of fluorescence of zirconium-Calcein Blue by fluoride has so far been obtained with zirconium solutions freshly diluted from 10^{-3} M Zr in 3 M HCl. 10^{-3} M Zr in 3 M HCl has been shown to be unpolymerised, but it was uncertain whether dilution could lead to any polymerisation. A kinetochromic effect was thus considered and the zirconium solutions employed were aged in the procedure as in the methods[47] based on this effect. It was found that the fluorescence of both the solutions, with and without fluoride, slowly increased with time as the zirconium depolymerises. However, the enhancement effect of the fluorescence by fluoride was not reduced even when maximum fluorescence were reached, as would have been expected in a fluoride catalysed reaction. It soon became clear, therefore, that the increased fluorescence caused by fluoride was not due to depolymerisation of zirconium solutions by the ion.

The zirconium solutions were again freshly prepared as before and a preliminary study of pH effects on the enhancement of fluorescence by fluoride was made by addition of small amounts of hydrochloric acid or ammonia. The maximum enhancement of fluorescence by fluoride was produced at a pH of between 2 and 3. Attempts to maintain the pH at this level, by addition of hexamine-perchlorate buffer to a solution

containing Calcein Blue and fluoride, before addition of zirconium resulted in a loss of the enhancement effect by fluoride. The use of sodium acetate, monochloroacetic acid was similarly investigated, but again the fluoride did not produce any significant enhancement of fluorescence. However, if the acetate buffer is added after mixing of the zirconium and Calcein Blue solutions, enhancement of fluorescence was obtained by the solution containing fluoride. This enhancement effect was, however, smaller than that obtained with solutions containing no buffer.

In order that the zirconium solutions need not be freshly diluted each day all zirconium solutions were prepared in 3 M HCl and discarded after a week.

5.3 Optimum Conditions for the Determination of Fluoride

(1) Spectral Characteristics

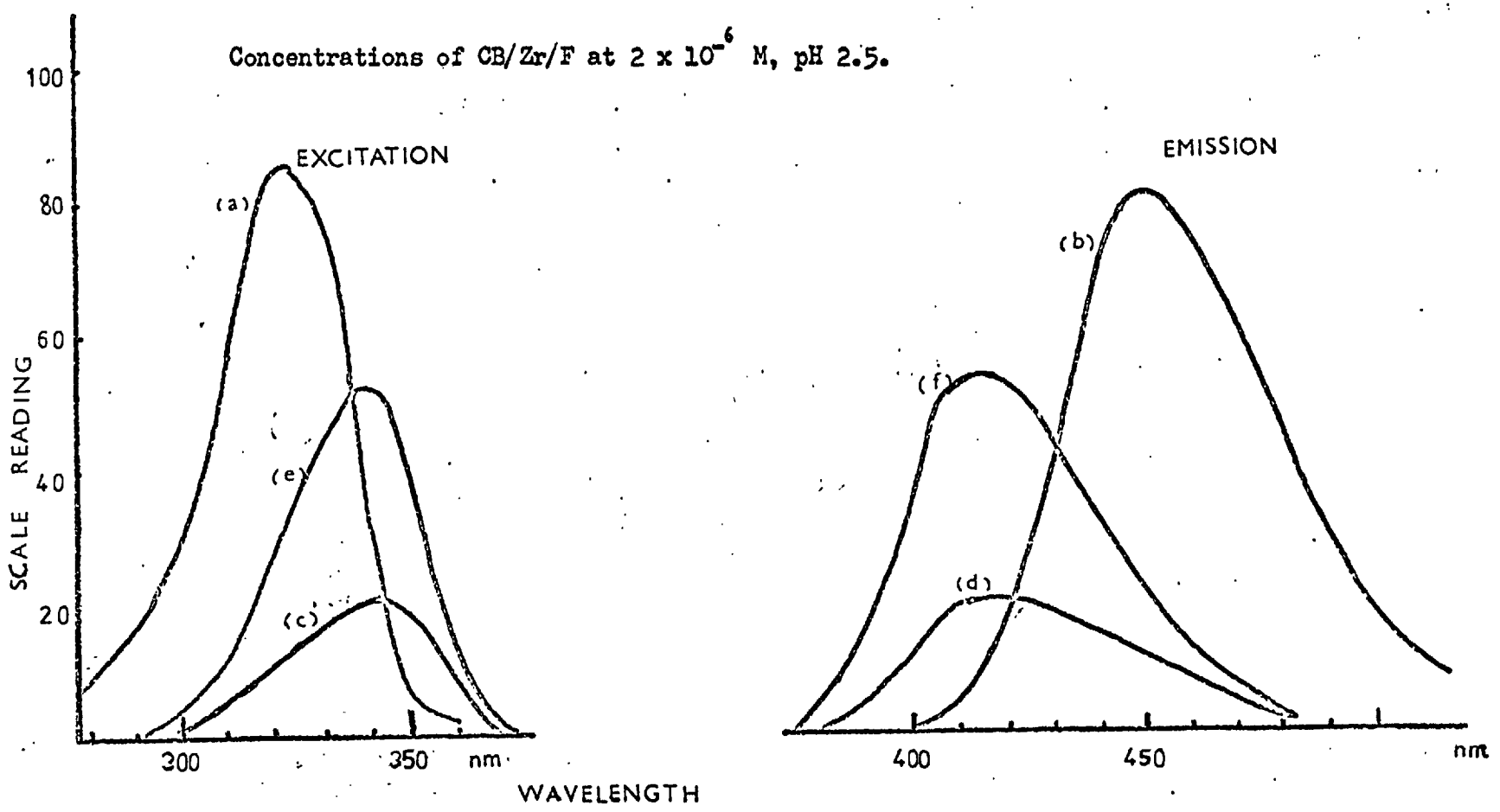
Fig. 5.1 shows the excitation and fluorescence emission spectra of a 2×10^{-6} M solution of Calcein Blue at pH 2.5, (a) and (b) respectively, a 1:1 zirconium-Calcein Blue solution, (c) and (d) respectively, and a 1:1:1 zirconium-Calcein Blue-fluoride solution, (e) and (f) respectively, at the same concentration and pH and obtained with identical instrumental settings of slit and gain, etc. These spectra are uncorrected for variations in the emission, characteristics of the 150W Xenon arc lamp and the response characteristics of the IP 28 photomultiplier and the diffraction gratings.

It will be seen that at pH 2.5 the addition of zirconium depresses the fluorescence originating from free Calcein Blue at 450 nm and produces a new emission maximum of lower intensity at 410 nm. Similarly, the excitation maxima are changed from 325 nm for Calcein Blue to 350 nm for

FIG. 5.1 FLUORESCENCE EXCITATION AND EMISSION SPECTRA FOR CALCEIN BLUE, ITS 1:1 BINARY COMPLEX WITH Zr(IV) AND ITS 1:1:1 TERNARY COMPLEX WITH FLUORIDE AND Zr(IV)

(A) CB excitation (fluorescence at 450 nm)
(B) CB fluorescence (excitation at 325 nm)
(C) CB_Zr excitation (fluorescence at 410 nm)
(D) CB_Zr fluorescence (excitation at 350 nm)
(E) CB_Zr_F excitation (fluorescence at 410 nm)
(F) CB_Zr_F fluorescence (excitation at 350 nm)

Concentrations of CB/Zr/F at 2×10^{-6} M, pH 2.5.



its zirconium complex. The addition of fluoride to the zirconium-Calcein Blue complex increases the fluorescence intensity, but the same maximum excitation and emission wavelengths are retained as for Zr:CB. This indicates that a ternary complex is formed and eliminates the possibility that the fluoride is simply abstracting zirconium from the 1:1 Zr:CB complex and releasing the more strongly fluorescent Calcein Blue. This was further confirmed by adding a 500-fold excess of fluoride to the Zr:CB complex which resulted in a decrease in fluorescence intensity at the excitation and emission maxima of the zirconium-Calcein Blue complex and an increase in fluorescence intensity at the emission and excitation maxima of the reagent itself.

(2) Influence of pH on the Stability of the Complex

Fig. 5.2 shows the fluorescence intensity of a solution 2×10^{-6} M with respect to both zirconium and Calcein Blue at various pH values plotted against time.

The dotted curves were obtained similarly, but with fluoride added in 1:1 proportion to the Zr:CB complex. The fluorescence of the solutions developed to a maximum value within ten minutes. The Zr:CB binary complex shows maximum intensity at higher pH values than the ternary Zr:CB:F complex. The drop in intensity with time at pH > 3 is probably due to progressive hydrolysis of the zirconium complexes. At pH 2.5 all solutions showed no significant change in fluorescence intensities within four hours and hence all experiments were carried out at this pH.

(3) Nature of the Complex

Job's Plot

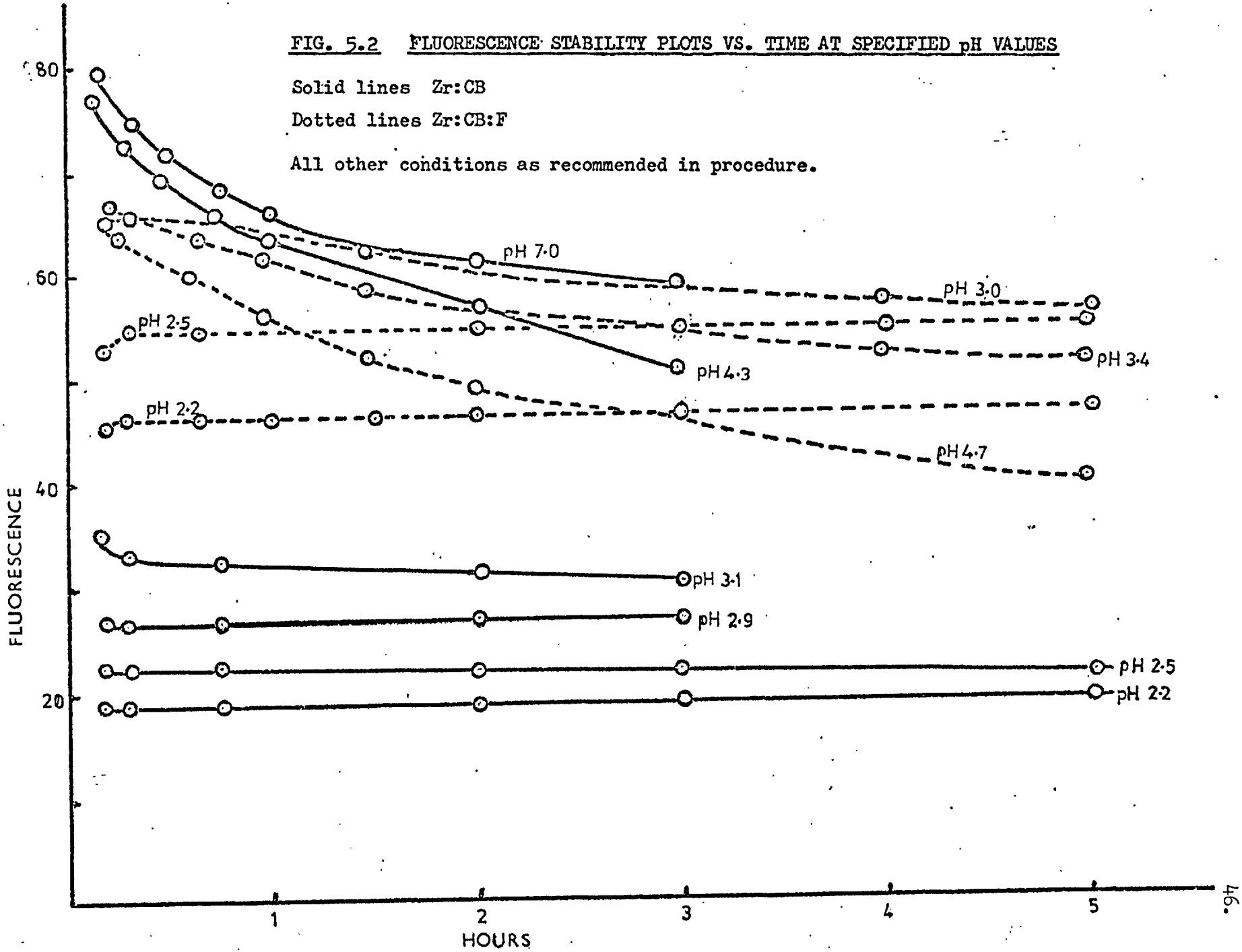
Job's method of continuous variations was applied between the 1:1 zirconium-Calcein Blue complex and the fluoride ion. (See Fig. 5.3).

FIG. 5.2 FLUORESCENCE STABILITY PLOTS VS. TIME AT SPECIFIED pH VALUES

Solid lines Zr:CB

Dotted lines Zr:CB:F

All other conditions as recommended in procedure.



This gave a binary complex to fluoride ration of 1.2:1.

Mole Ratio Plots

The effect of varying the concentration of Calcein Blue at pH 2.5 is shown in Fig. 5.4 Curve A is obtained with 2 ml of 10^{-4} zirconium, 2 ml 10^{-4} M sodium fluoride and varying amounts of 10^{-4} M Calcein Blue, diluted to 100 ml. Curve B is a similar solution, but containing no fluoride. The dotted curve represents the net effect of fluoride and is obtained by subtracting values in Curve B from that of A.

It is clear that at pH of 2.5, zirconium reacts with more than one molecule of the reagent. The decrease in fluorescence intensity of the fluoride solution in excess Calcein Blue relative to zirconium can, therefore, be explained by the breakdown of the fluoride complex in favour of a polynuclear zirconium-Calcein Blue complex. From both the continuous variation and mole ratio plots it was concluded that a 1:1:1 ternary complex was formed. The slightly high figure obtained for the Calcein Blue in the ratio was attributed to its partial decomposition when dissolved in alkali and its low assay because it is manufactured for use as a metallo-fluorescent indicator and could not be obtained 100% pure. Attempts at purification were not successful.

(4) Order of Addition of Reagents

The effect of the order of mixing of the solutions on the fluorescence intensity was investigated. It was found that the preferred order of addition of reagents to the volumetric flasks was : fluoride, Calcein Blue or ammonia (any order) and finally zirconium followed by dilution to volume with distilled water. Under these conditions maximum enhancement of fluorescence by fluoride was obtained. When the zirconium was added before Calcein Blue, no enhancement in fluorescence was obtained. Also

FIG. 5.3 CONTINUOUS VARIATIONS PLOT

F vs. Zr:CB

All other conditions as recommended in Procedure.

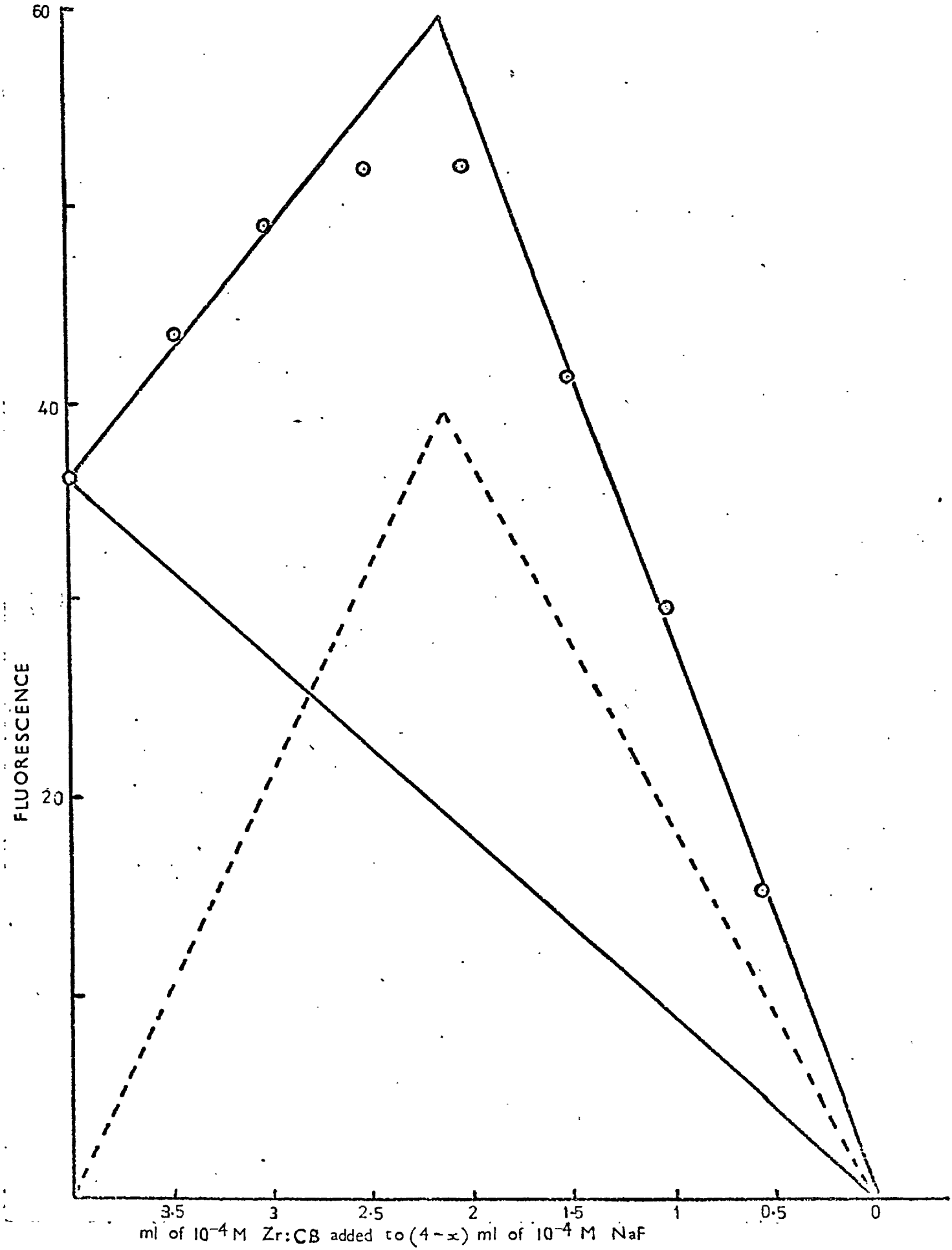
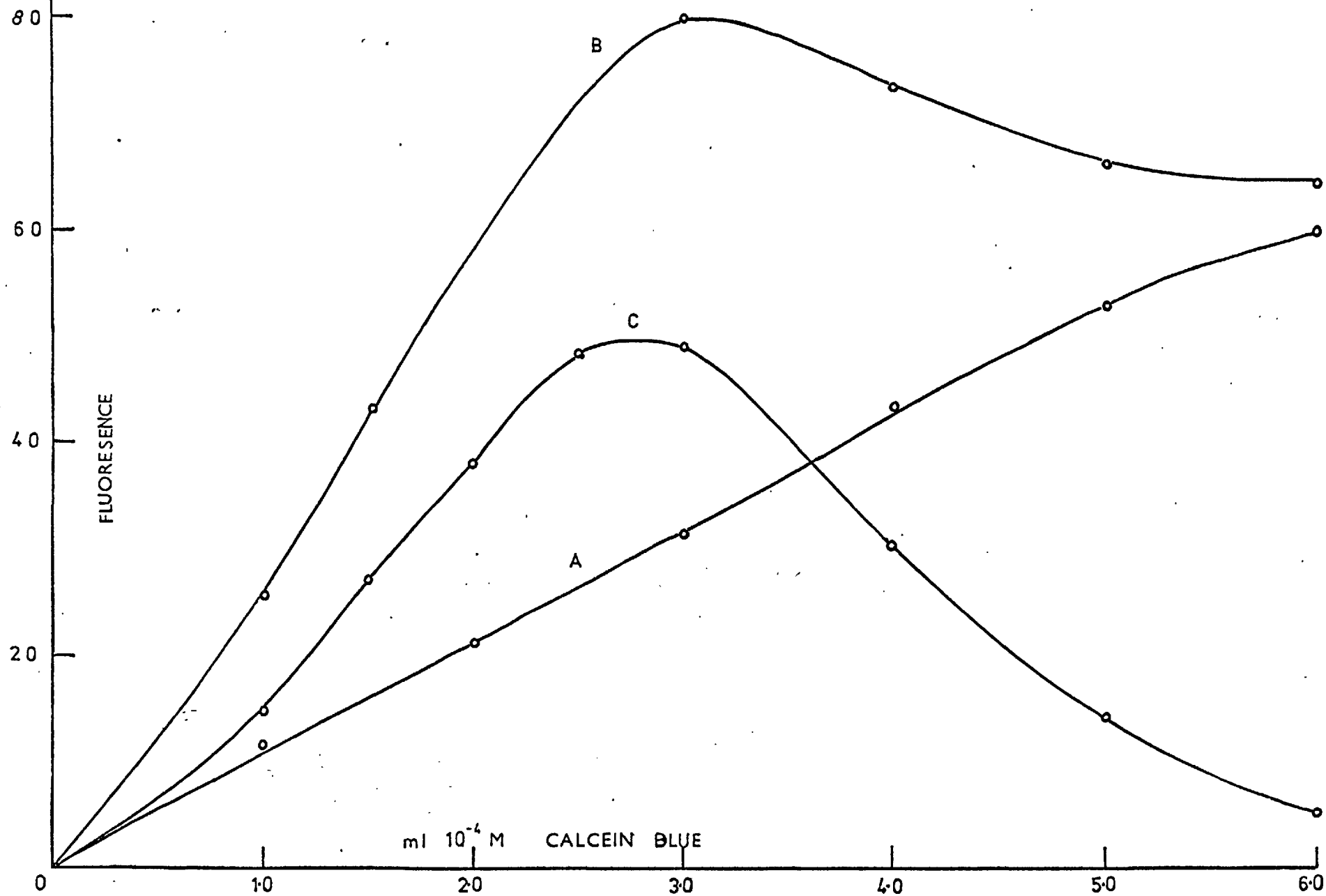


FIG. 5.4 EFFECT OF VARYING THE CONCENTRATION OF CALCEIN BLUE

(A) Zr-Calcein Blue; (B) Zr-Calcein Blue-Fluoride; (C) Effect due to Fluoride Ion



if the zirconium and Calcein Blue were mixed before addition of ammonia, the acid solution of zirconium tended to precipitate the Calcein Blue.

(5) Sensitivity of Method

The development of the method was carried out with solutions 2×10^{-6} M in fluoride. However, the maximum instrumental sensitivity was not used and it is possible to determine down to 10^{-7} M concentration in the final solution.

5.4 Experimental

(1) Apparatus

Fluorescence measurements were made with a double monochromating spectrofluorimeter (Farrand Optical Co., Cat. No. 10244) fitted with a 150W Xenon arc lamp (Hanovia Division, Cat. No. 901 c-1) and RCA IP 28 photomultiplier and equipped with a Honeywell-Brown recorder. Fused quartz cells [10 x 20 x 50 mm) were used throughout.

(2) Reagents

Sodium fluoride solution 10^{-5} M Prepare a 10^{-3} M stock solution by dissolving 41.99 mg of analytical reagent grade sodium fluoride in 1 litre of distilled water. 10 ml of the stock solution were diluted to 1 litre to obtain a 10^{-5} M solution.

1 ml of 10^{-5} M $F^- \equiv 0.1899$ µg F.

Calcein Blue 10^{-4} M Prepare a 10^{-3} M solution by dissolving 160.2 mg of Calcein Blue (Hopkin and Williams) in a few drops of 0.1 M potassium hydroxide and diluting to 500 ml with distilled water. 10 ml of this solution were diluted to 100 ml with distilled water to give a 10^{-4} M solution. After 2 - 3 days, all Calcein Blue solutions were discarded and fresh solutions were prepared.

Zirconyl chloride 10^{-4} M Prepare a 10^{-3} M solution by dissolving 32.2 mg $ZrOCl_2 . 8H_2O$ in 100 ml of 3 M HCl. It has been shown[72] that zirconium solutions 3 M in HCl do not polymerise on standing. 10^{-4} M solutions were prepared by dilution with 3 M HCl.

Ammonia Solution (approximately 1.5 M) 8 ml of concentrated ammonia (18 M) were diluted to 100 ml with distilled water.

(3) Procedure

Calibration Curve

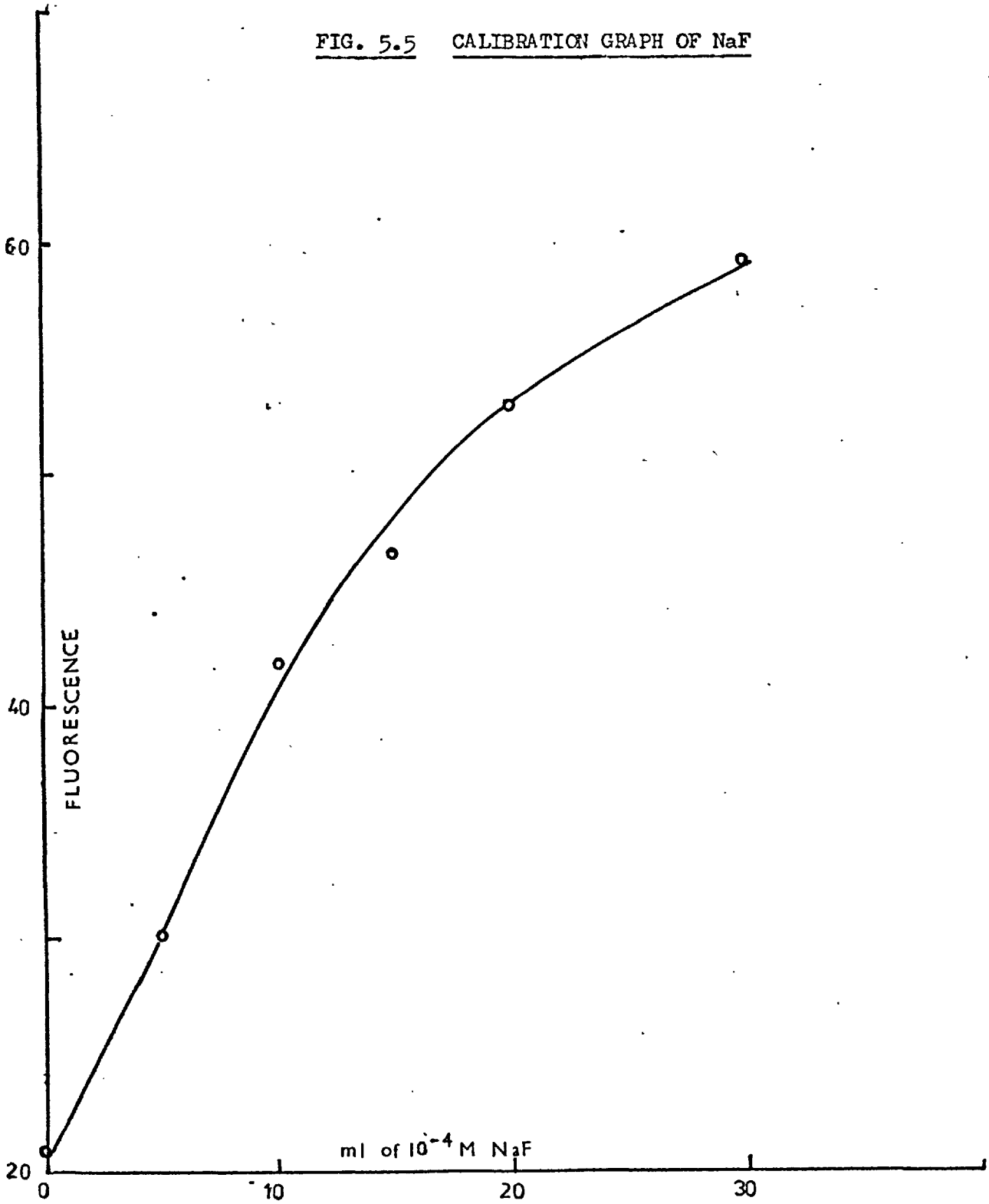
Transfer by pipette 5 - 30 ml (at suitable volume intervals) of 10^{-5} M sodium fluoride into 100 ml flasks. Add 2 ml of 10^{-4} M Calcein Blue and just sufficient NH_3 solution (ca 3 to 4 of an approximately 1.5 M NH_3 solution) to adjust the pH of the final solution to 2.5. Lastly, add 2 ml of 10^{-4} M zirconium in 3 M HCl. Mix the contents of the flask and dilute to volume.

The fluorescence of the solutions were measured after 20 - 30 mins at 410 nm with the excitation wavelength set at 350 nm. The calibration graph is shown in Fig. 5.6.

Unknown solutions containing 0.9 - 6 μg F (or $\geq$ 0.01 ppm in concentration) were analysed in a manner similar to that used to set up the calibration curves.

Because of day to day variation in lamp intensity it is necessary to run two or three standards through with each of unknowns, as in all single beam fluorimetric procedures to establish the position and slope of the calibration curve. Alternatively the fluorescence intensity can be compared with that of a solution of standard quinine bisulphate in 0.1 M sulphuric acid.

FIG. 5.5 CALIBRATION GRAPH OF NaF



5.5 Interference Studies

The influence of up to 500 fold excess of a selection of eleven other anions likely to interfere by forming complexes or precipitates with zirconium was examined as were the effects of thirteen cations likely to form preferential complexes with Calcein Blue or fluoride ion. The results of this study, which are summarised in Table 5.1 show that at a five fold excess tungstate, acetate, tartrate and phosphate cause low results whilst at 50 fold excess molybdate also yields low recoveries and sulphate high recoveries. Amongst the cations, aluminium, manganese and silver caused slight interference at five fold excess whilst at 50 fold excess, arsenic, antimony, beryllium and cobalt caused low recoveries.

TABLE 5.1

4 μg of F by Recommended Procedure

Ion added mole ratio $\frac{\text{Ion}}{\text{F}}$	% Interference	Ion added mole ratio $\frac{\text{Ion}}{\text{F}}$	% Interference
Cl^- (500)	0	Be^{2+} (50)	-33
NO_3^- (500)	0	Be^{2+} (5)	0
SO_4^{2-} (500)	+33	Ca^{2+} (500)	0
SO_4^{2-} (50)	+11	Mg^{2+} (50)	0
SO_4^{2-} (5)	0	Mn^{2+} (50)	quenched(brown solution)
PO_4^{3-} (500)	quenched	Mn^{2+} (5)	-13
PO_4^{3-} (50)	-67	Ag^+ (50)	white ppte
$B_4O_7^-$ (500)	+20	Ag^+ (5)	+10
$B_4O_7^-$ (50)	0	Al^{3+} (50)	-39
MoO_4^{2-} (500)	-42	Al^{3+} (5)	-16

Table 5.1 (continued)

Ion added mole ratio $\frac{\text{Ion}}{F}$	% Interference	Ion added mole ratio $\frac{\text{Ion}}{F}$	% Interference
MoO_4^{2-} (50)	- 9	Cd^{2+} (50)	0
MoO_4^{2-} (5)	0	Ni^{2+} (50)	0
WO_4^{2-} (500)	quenched	Zn^{2+} (50)	0
WO_4^{2-} (50)	-87	Co(III) (50)	-22
WO_4^{2-} (5)	-21	Co(III) (5)	0
VO_3^- (500)	-75	Pb^{2+} (50)	0
VO_3^- (50)	0	Sb(III) (50)	- 9
oxalate (500)	-89	(5)	0
oxalate (50)	-80	As(V) (50)	-16
oxalate (5)	-55	As(V) (5)	0
Tartrate (500)	-72		
Tartrate (50)	-66		
Tartrate (5)	-45		
Acetate	0		

5.6 Additional Experimental Investigations

(1) Absorptiometric Measurements

The enhancement of fluorescence by ternary complex formation could result from an increase in the amount of light being absorbed or an increase in the quantum efficiency of the fluorescence. If the former is true then measurement of the absorbance of solutions of zirconium and Calcein Blue with increasing concentrations of fluoride should show increasing absorbance. Table 5.2 shows the absorbance of such solutions prepared with the procedure described under the section Experimental. The readings were measured at 350 *nm* against distilled water in 4 cm cells using a Beckman DB spectrophotometer.

TABLE 5.2

Ml. NaF (10^{-4} M)	Absorbance
0.0	0.119
0.5	0.126
1.0	0.129
1.5	0.132
2.0	0.141
3.0	0.147

It can be seen that the increase in absorbance is negligible, hence enhancement of fluorescence is probably due to an increase in the quantum efficiency of fluorescence.

(2) Attempts to Determine the Purity of Calcein Blue

Theoretically, if a weighed amount of tribasic Calcein Blue is dissolved in excess standard potassium hydroxide, and the excess alkali is back titrated with standard hydrochloric acid, a plot of pH of the solutions versus volume of HCl during the back titration would show three distinct plateaus, corresponding to the pH values at which the phenolic and carboxyl oxygen groups of the indicator are protonated. The true concentration of the indicator can then be calculated and compared with the apparent concentration obtained by dissolution of the impure solid. However, the pH titration graph of the experiments carried out did not show distinct plateaus and the failure of the experiment was attributed to decomposition of the indicator by the presence of excess alkali.

(3) Formation of Hafnium-Calcein Blue-Fluoride Complex

Owing to the great similarity between the elements hafnium and zirconium, it was decided to find out if the hafnium complex would provide a more sensitive reaction with fluoride.

Unfortunately no hafnium salt was available for our investigations and solutions had to be made up from the metal. The following procedure of dissolution was adopted. 0.01785 gm hafnium metal drillings were dissolved in 1 drop concentrated hydrofluoric acid and a few mls concentrated sulphuric acid were added and the solution evaporated to dryness. The residue was dissolved in 100 ml 3M HCl in a volumetric flask to give a 10^{-3} M hafnium solution. This solution was diluted to 10^{-4} M with 3 M HCl and the experimental procedure described for the determination of fluoride with zirconium-Calcein Blue was carried out. An enhancement of fluorescence by fluoride was observed, but it was considerably smaller than that obtained with zirconium solutions. It was suspected that the

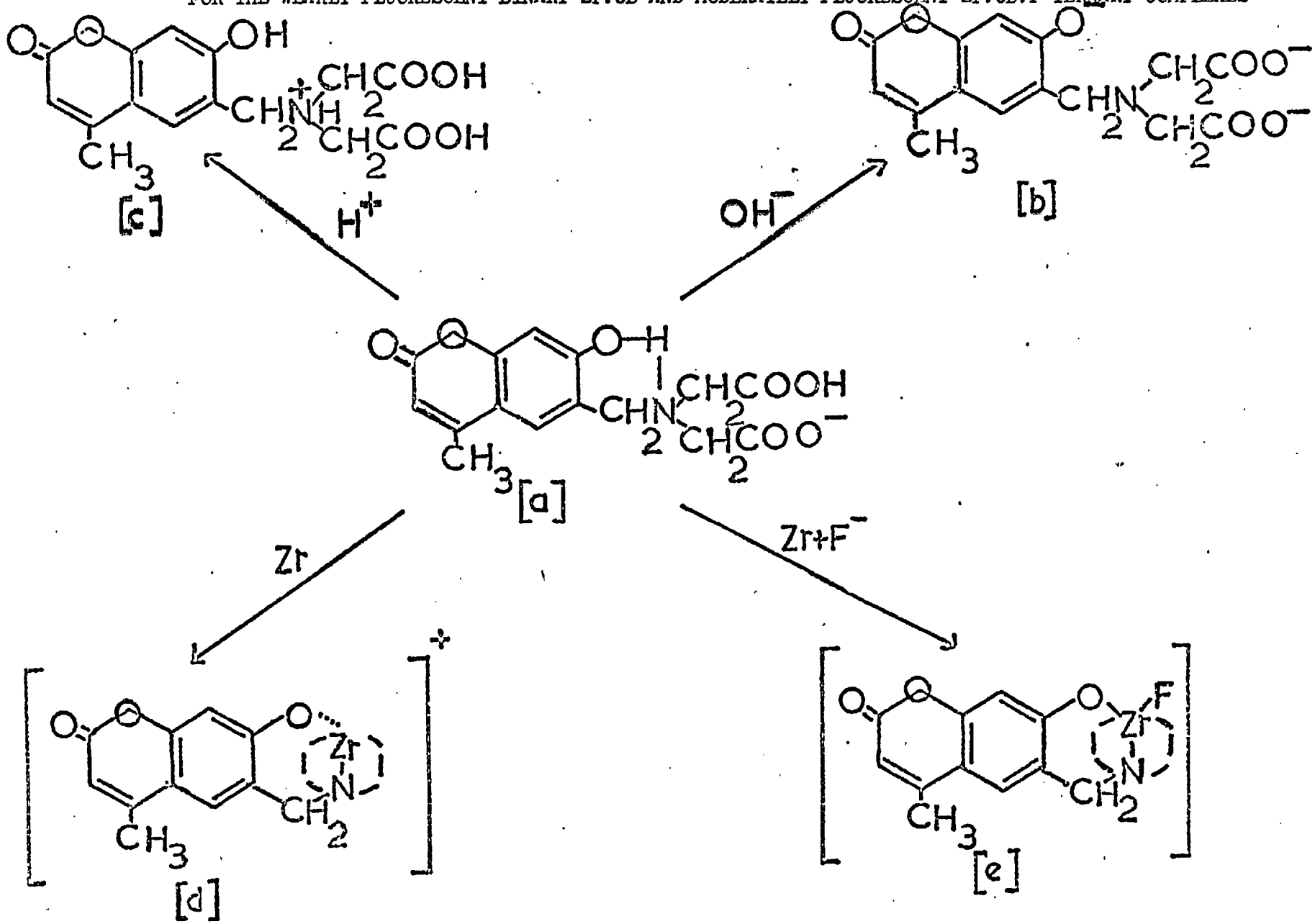
sulphate present was sufficient to interfere with the effect of fluoride. Subsequently the dissolution procedure was repeated but 5 ml concentrated perchloric acid instead of sulphuric acid was added to fume out the hydrofluoric acid. The hafnium solution obtained by this procedure of dissolution gave a considerably greater enhancement of fluorescence by fluoride, but the enhancement was still less than that obtained with a zirconium solution. Owing to the hazardous method of dissolution of hafnium and the indication that its complex will not be of greater analytical value than that of zirconium, no further experiments were carried out.

5.7 Nature of Complex Formation

The fluorescence of Calcein Blue at intermediate pHs has been attributed[69] to the formation of a H bridge between the phenolic oxygen and the nitrogen from the iminodiacetic acid group, Fig. 5.6 (a), thus preventing torsion of the group about the C-CH_2 bond and minimising non-radiative dissipation of energy. At high pH, deprotonation occurs, Fig. 5.6 (b), and at low pH the H is protonated, Fig. 5.6 (c), both resulting in breakage of the hydrogen bridge and freeing of the side chain thus weakening the fluorescence yield by rotational dissipation of energy, etc.

Little is known about the chelate chemistry of zirconium, but it will be seen from the spectra presented in Fig. 5.1 that at pH 2.5 the Zr:CB complex is less fluorescent that the reagent. This can be explained by the breakage of the H bridge on formation of a chelate complex with zirconium (see Fig. 5.6 (d)). Thus because of the largely ionic nature of the O-Zr bond the Zr:CB complex yields less fluorescence than the Calcein Blue alone at the same pH. The enhancement of fluorescence on

FIG. 5.6 STRUCTURE OF CALCEIN BLUE AT VARIOUS pH VALUES RELATED TO ITS FLUORESCENCE AND SUGGESTED STRUCTURE FOR THE WEAKLY FLUORESCENT BINARY Zr:CB AND MODERATELY FLUORESCENT Zr:CB:F TERNARY COMPLEXES



addition of fluoride, (Fig. 5.6 (e)), can be explained by the incorporation of fluoride ion in the co-ordination sphere of the zirconium, i.e. replacement of co-ordinated H_2O molecules by the small fluoride ion, which has a very high affinity for zirconium.

The electrophilic effect of fluoride may cause withdrawal of electrons resulting in the formation of a more covalent O-Zr bond. This strengthening of the degree of covalency should favour stabilisation of the excimer and hence increase the quantum efficiency of the fluorescence.

The above explanation is consistent with the observation that at higher pHs the binary zirconium-Calcein Blue complex is more fluorescent that the reagent and addition of fluoride then has little or no effect.

5.8 Conclusions

The method suggested provides a positive fluorimetric method of very high sensitivity for the determination of trace amounts of fluoride in aqueous solution down to 0.01 ppm. Of the common anions, only phosphate interferes seriously at five fold excesses. Very few cations interfere. A 1:1:1 ternary complex formation is responsible for fluorescence production. The increased fluorescence yield is attributed to conformational stabilisation of the excimer of the fluorophore in the ternary complex. The method is rapid and the procedure is reproducible.

CHAPTER 6

A Spectrofluorimetric Method for the Determination of Small Amounts of Sulphate Ion

6.1 Introduction

In Chapter 5, studies of the effect of various cations and anions on the determination of fluoride with zirconium-Calcein Blue reagent have shown that sulphate produced a positive interference effect. Subsequently, the presence of sulphate alone was shown to enhance the fluorescence of a solution of zirconium and Calcein Blue, the reaction being similar to that of fluoride. The possibility of this enhancement being of analytical value is of great interest because as can be seen from the brief review given below, present methods for the trace determination of sulphate are generally unsatisfactory. Although the reaction of zirconium and Calcein blue is much weaker than the corresponding one with fluoride it nevertheless provides us with a direct and rather sensitive method for its determination.

6.2 Analytical Methods for the Determination of Small Amounts of Sulphate

The most widely used methods for the determination of sulphate may be classified as follows :

(i) Gravimetric

(ii) Turbidimetric and Nephelometric

(iii) Titrimetric

(iv) Spectrophotometric

The first three methods will only be very briefly described because in general they are insufficiently sensitive to be applicable for trace analysis.

Gravimetric

Precipitation as barium sulphate is extensively used for the gravimetric determination of sulphate.[73] The precipitant is generally a solution of barium chloride and the precipitation is effected in the presence of small amounts of hydrochloric acid to prevent coprecipitation of other barium salts and barium hydroxide. The most common source of error is coprecipitation by other ions, though EDTA can be used to remove interference from many cations[74].

Other precipitants that have been proposed include the complex hexammino cobaltic bromide[75] and octammino-μ-amino-μ-nitro-dicobaltic nitrate[76].

Turbidimetric and Nephelometric Methods

Smaller amounts of sulphate may be determined by turbidimetric and nephelometric methods. Again precipitation as barium sulphate is widely used, generally in mixed solvent systems of water and polyhydric alcohols. The basic method was given by Denis and Reed[77]. Later, modifications by other workers improved the range of determination so that 0.01 to 100 ppm sulphate can be determined in 18% ethanol - 22% propylene glycol medium[78]. Other partial non-aqueous media that have been used include ethanol-gelatine[79], glycerol-ethanol[80] and glycine gum-arabic[81].

The discovery that 4-amino-4'-chlorodiphenyl (CAD) was an excellent precipitant for sulphate[12A] has led to its considerable application including that of turbidimetric and nephelometric methods for sulphate determination. Martin and Stephen[82] developed a nephelometric procedure by measurement of CAD sulphate suspensions stabilised by gum ghatti. The range of sulphate determined was from 1 - 25 ppm.

Titrimetric Methods

Titrimetric procedures most frequently involve titration of the sulphate ion by a soluble barium salt. With barium chloride as the titrant, indicators such as sodium or potassium rhodizonate or tetrahydroxy-quinone have been employed[83,84]. The colour change at the end-point is generally not sharp and standard colour filters can be used to overcome the problem[85]. The reproducibility and accuracy of the method can be improved appreciably with adsorption indicators such as Alizarin Red S or Thorin[86].

A major improvement in the reliability of titrimetric methods was achieved when barium perchlorate[87] was used as titrant and dimethylsulphonazo (III) as indicator[88]. Pribil and Maricova[74] showed that coprecipitation of other ions can be prevented if barium sulphate is precipitated in the presence of EDTA. Belcher and co-workers subsequently developed a satisfactory procedure that involved the dissolution of the barium sulphate precipitate in excess of a standard solution of EDTA, and then back titrating the unused EDTA with a standard magnesium chloride solution using Solochrome Black as indicator.

A radically new titrimetric procedure resulted from the work of Belcher, Nutten and Stephen[12A] who showed that 4-amino-4'-chlorodiphenyl (CAD) was an admirable precipitant for sulphate ion. The sulphate precipitate was filtered, washed and subsequently titrated with standard alkali. The method was applicable down to 2.5 - 25 mg of sulphate.

Spectrophotometric Methods

Spectrophotometric procedures allow much smaller quantities of sulphate to be determined although they are generally indirect methods.

Jones and Letham[12B] showed that CAD had a strong absorption peak at 254 nm and subsequently developed a procedure for the determination of 30 - 120 μg of sulphate. An excess of CAD (at least 100%) in 0.1 M HCl was added to the sulphate solution at pH 2 to 7, and the precipitate removed by centrifugation before the excess CAD remaining was determined spectrophotometrically at 254 nm.

The method reported by Bertolacini and Barney[17] is based on the reaction of solid barium chloranilate with sulphate ion at pH 4 in 50% ethanol solution to liberate the highly coloured acid-chloranilate ion. The absorption is measured at 530 nm and as little as 1 μg sulphate can be determined. Several modifications[90,91] of the method have improved its sensitivity.

A number of indirect spectrophotometric and fluorimetric procedures have also been described, based on the bleaching or quenching action of sulphate ion on some highly coloured or fluorescent metal-dyestuff complexes. The complexes used include Thorium-Xylenol Orange lake[14], Thorium borate-Amaranth dye[13] and Thorium-Morin[15]. The procedure based on the fluorescent Thorium-Morin complex enables the determination of up to 40 μg sulphate in 50 ml.

The reaction of sulphide with β-amino-N,N-dimethylaniline[41] in the presence of ferric chloride to form Methylene Blue has been adapted for the determination of sulphate. Of the various methods which have been used to convert the sulphate samples to aqueous solutions of sulphide, the reduction accomplished through the use of a mixture of hydriodic acid, formic acid and red phosphorus was particularly successful[43]. 5 - 50 μg of sulphate could be determined with a molar absorptivity of 34,500 at 670 nm.

Recently a kinetochromic procedure has been used to provide a direct method based on a catalytic effect of sulphate ion on the reaction between Methyl Thymol Blue[48] and a partially polymerised solution of zirconyl ions. Sulphate may be determined in the range 0.1 - 2.4 ppm with a net molar absorptivity of 2.0×10^4 at 586 nm. A similar fluorimetric procedure has been devised for sulphate ion using the fluorescent reagent Morin[48a] in place of Methyl Thymol Blue. Although these methods are very sensitive, they are kinetically controlled and require to be applied under rigidly controlled conditions.

In this chapter, we shall describe a method based on the enhancement of the fluorescence of the binary complex of zirconium with Calcein Blue at pH 1.9 to determine sulphate ion in the range 200 - 11 mg, or concentration range 2 ppm - 11,000 ppm, assuming a sample solution availability of 90 and 1 ml respectively.

6.2 Optimum Conditions for the Determination of Sulphate

The sulphate reaction with zirconium-Calcein Blue is much weaker than the fluoride reaction and it was found necessary to use a considerable (100 - 1000 mole ratio) excess of sulphate ion to set up a linear calibration curve.

(1) Spectral Characteristics

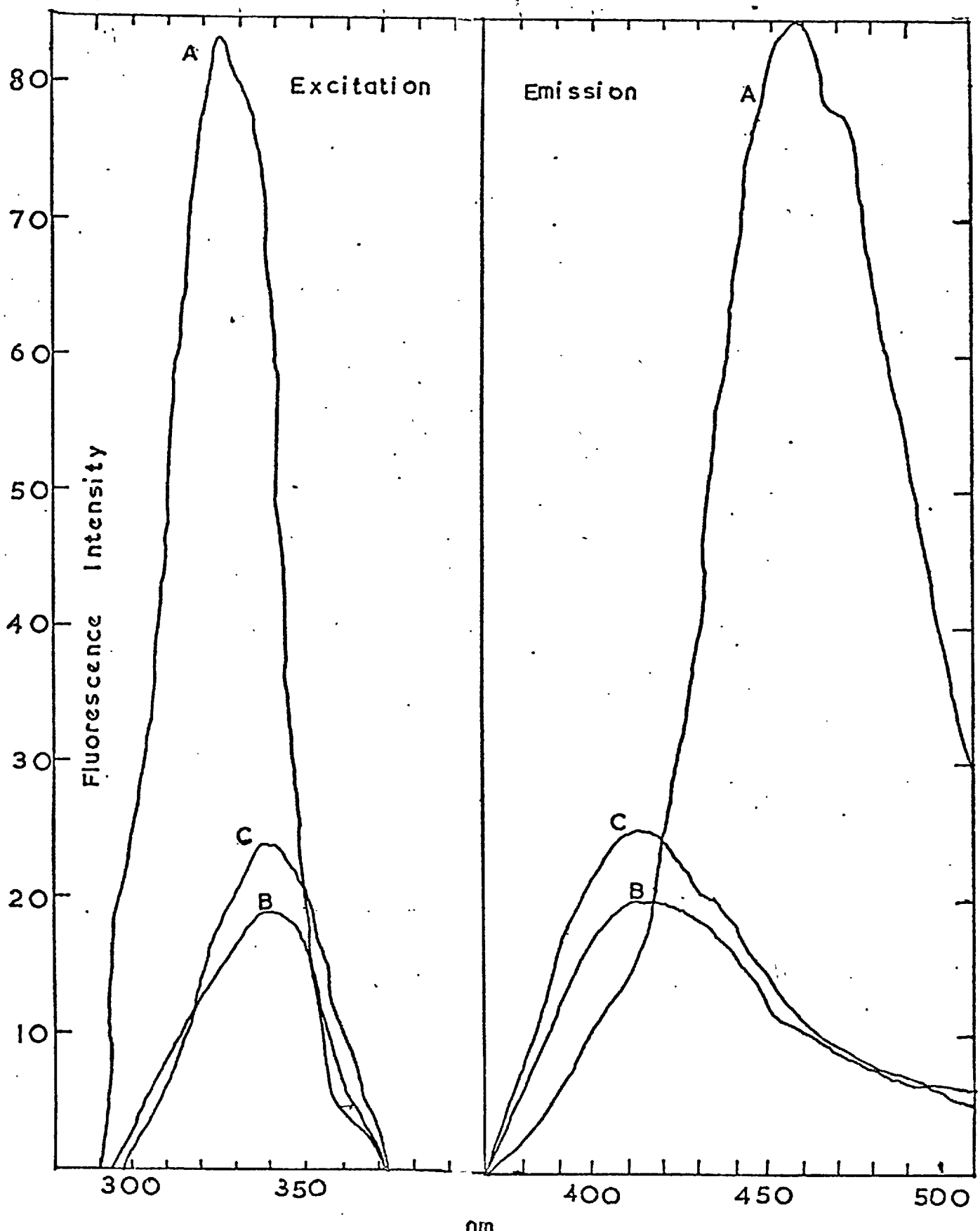
Fig. 6.1 shows the excitation and emission spectra of a 2×10^{-6} M solution of Calcein Blue, (a) and (b), an exactly formulated 2×10^{-6} M 1:1 zirconium-Calcein Blue, (c) and (d), and an exactly formulated 2×10^{-6} M 1:1 zirconium-Calcein Blue with a 200 fold molar excess of sulphate ion (e) and (f). The solutions were prepared with the procedure described under the section Experimental and are all at a pH of 1.9. For the excitation spectrum, curve (a), the fluorescence was measured at

FIG. 6.1 Excitation Emission Spectra

(A) Calcein Blue

(B) Calcein Blue _ Zr (1:1)

(C) Calcein Blue _ Zr (1:1) + excess (200) sulphate



450 nm while the emission spectrum, (b), was obtained by excitation at 325 nm. For the excitation spectra, curves (c) and (d), the fluorescence was measured at 410 nm while the emission spectra, (e) and (f), were obtained by excitation at 350 nm. These spectra were obtained with identical instrumental settings of slit and gain, etc. They are, however, uncorrected for the spectral response characteristics of the gratings of the monochromators or of the photomultiplier, nor do they account for changes in the lamp emission with wavelength.

As in the reaction with fluoride, sulphate ions enhance the fluorescence of the zirconium-Calcein Blue complex, but produce no changes in the wavelengths of excitation or fluorescence maxima.

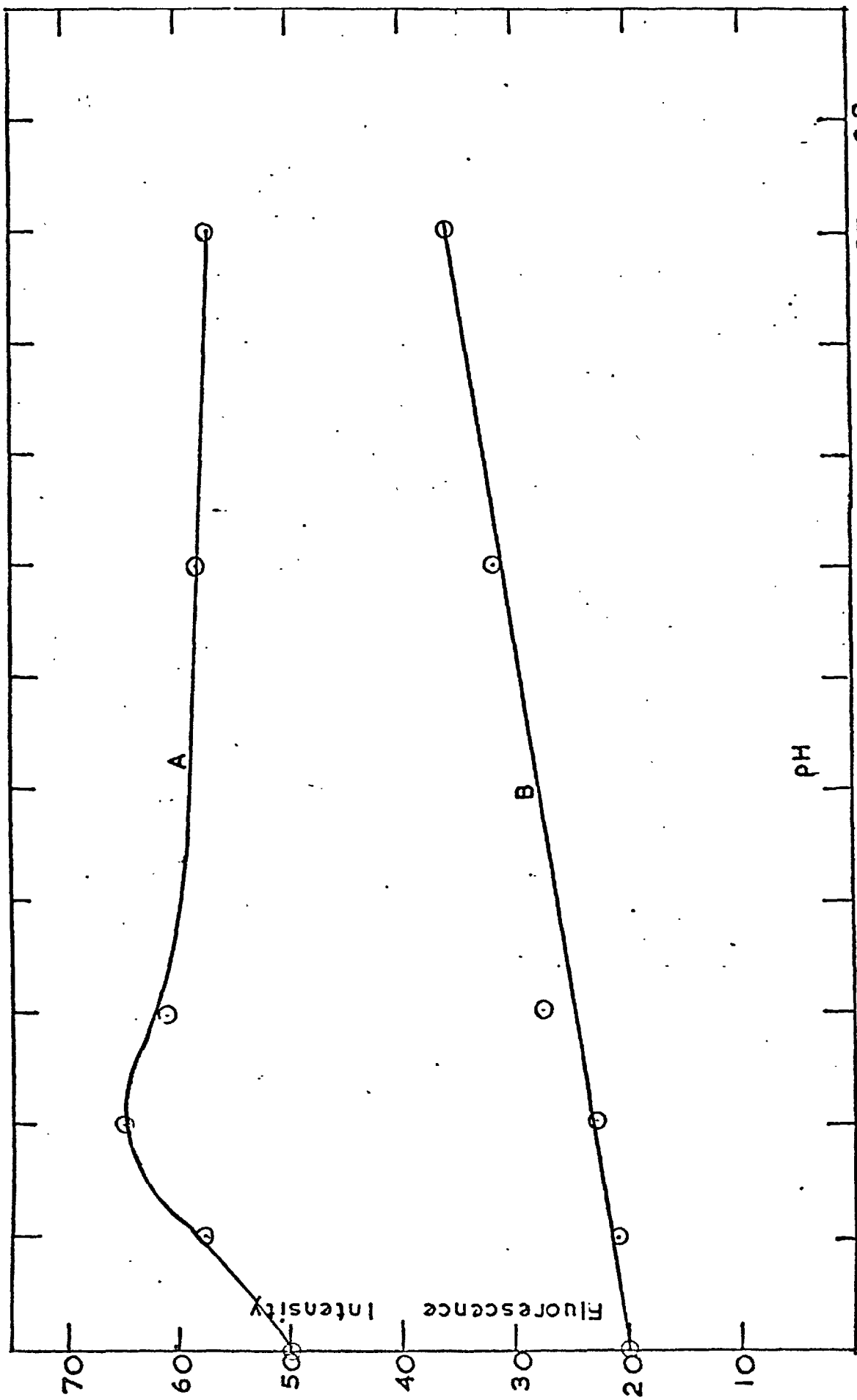
(2) pH Effects

Figure 6.2 shows the effects of varying the pH of the reaction of (A) a solution containing 2 ml of 10^{-4} M Calcein Blue, 2 ml of 10^{-4} M zirconium in 3M HCl and 4 ml of 10^{-2} M potassium sulphate in a total volume of 100 ml. Curve (B) is for an exactly similar solution but without sulphate ions. Fluorescence intensities were measured at 410 nm with the excitation set at 350 nm. The fluorescence of the sulphate enhanced system reaches a maximum at pH 1.9. The pH adjustments were made by addition of small amounts of concentrated ammonia solution. The fluorescence intensities of solutions with pH values greater than 3 are not given because their fluorescence decreases rapidly upon standing. It may, however, be relevant to observe that the fluorescence intensities of the zirconium-Calcein Blue solution and the sulphate enhanced solution increases with increasing pH above 3 when measurements are made immediately.

FIG. 6.2 Effect of pH on Sensitivity

(A) Zr - Calcein Blue - Sulphate

(B) Zr - Calcein Blue



(3) Nature of Complex

Variation of Concentration of Calcein Blue

The effect of varying the concentration of Calcein Blue is shown in Fig. 6.3. Curve (A) is for 100 ml of solution containing 2 ml of 10^{-4} M zirconium in 3 M HCl and 4 ml of 10^{-2} M potassium sulphate. Curve (B) is for a similar solution but sulphate is absent from it. Curve (C) represents the difference between the two, i.e. the net effect of the sulphate ion. It is apparent that the optimum ratio of Calcein Blue to zirconium is 1:3. This is the same ratio previously found for the reaction with fluoride and may be interpreted as evidence for a true ratio of 1:1 because of the low assay of the Calcein Blue which could not be obtained or purified to any greater extent in these studies.

Job's Plot

A continuous variation plot was made, Fig. 6.4, to investigate the probable nature of a ternary complex between sulphate, zirconium and Calcein Blue. This was done by varying a 10^{-2} M sulphate solution against an exactly formulated 10^{-2} M 1:1 zirconium-Calcein Blue solution in the usual way. Such a plot requires the use of approximately equimolar solutions of zirconium-Calcein Blue and sulphate, but as explained previously, the analytical procedure requires the presence of ca 100 fold molar excess of sulphate ion to obtain reasonable sensitivity. Consequently it was not possible to obtain a sharp maximum. The broad maximum obtained suggests the probable existence of a 1:1:1 ternary complex, but cannot be interpreted with any degree of confidence as definite evidence.

FIG. 6.3 Effect of Concentration of Calcein Blue

(A) Zr - Calcein Blue - Sulphate

(B) Zr - Calcein Blue

(C) Effect due to Sulphate Ion

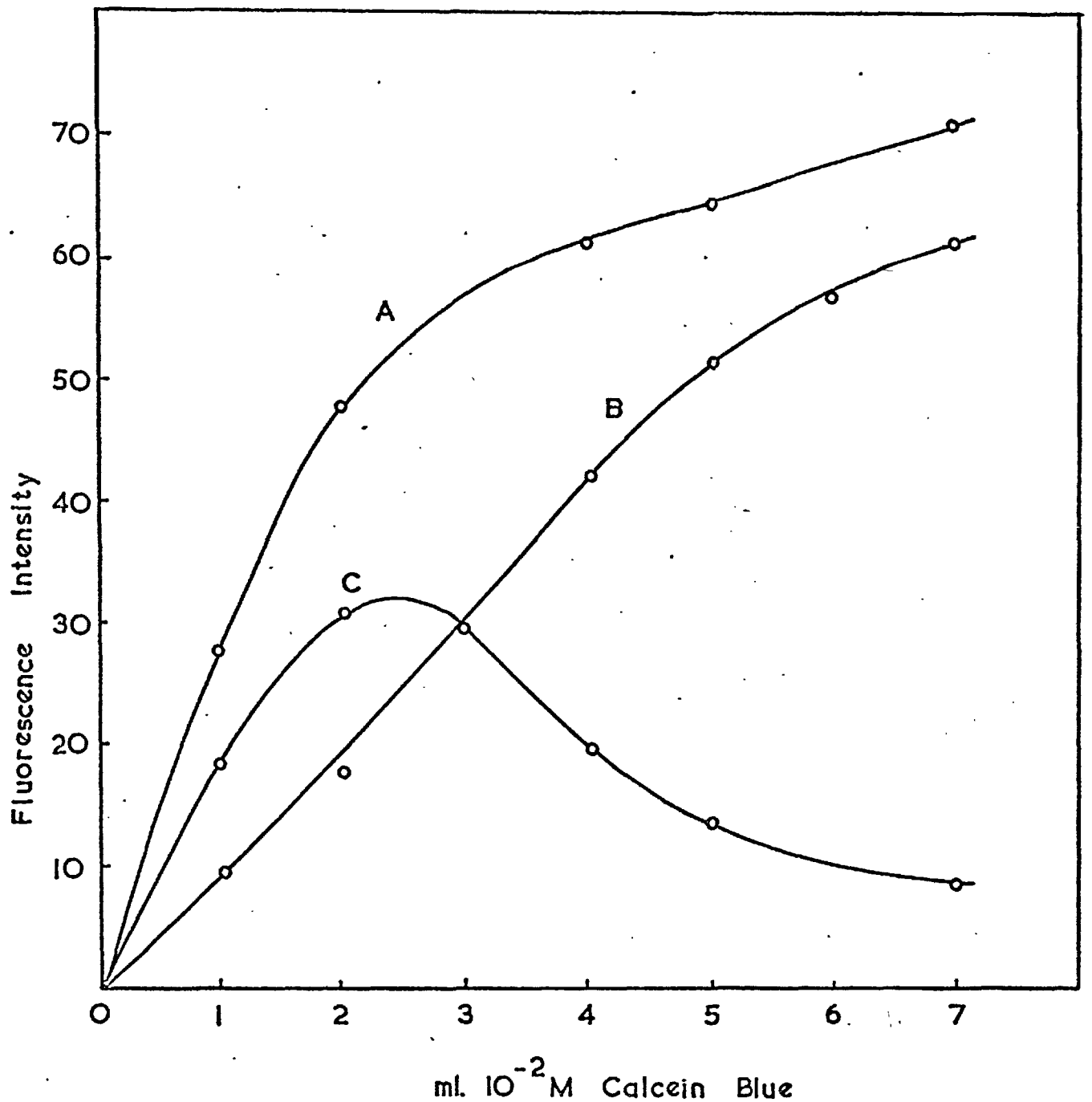
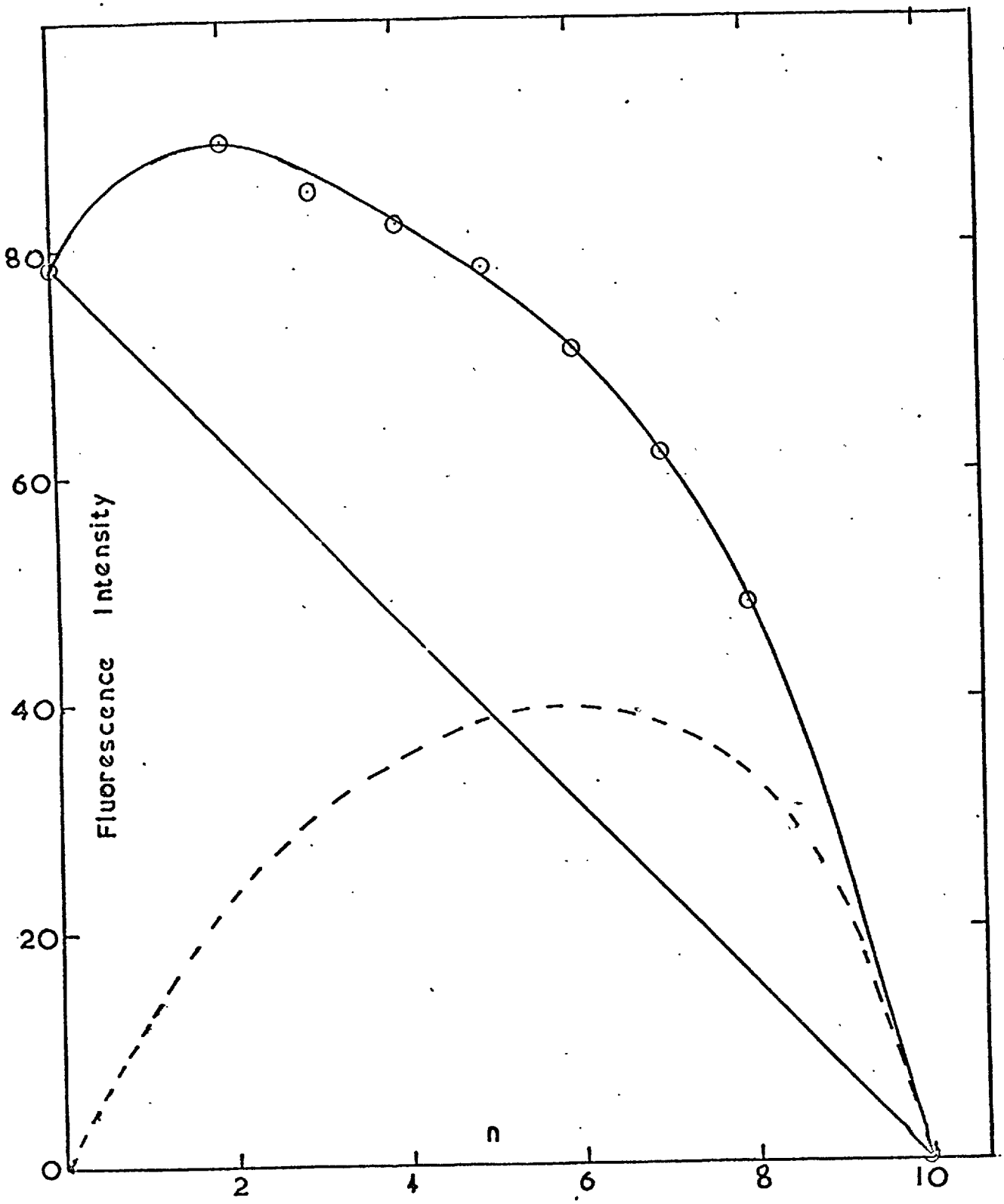


FIG. 6.4 Continuous Variations Plot

Dotted Curve - net effect, i.e. Corrected Curve
n = ml of 10^{-2} M K_2SO_4 added to (10 - n) ml of
10^{-2} M Zr - Calcein Blue.



6.4 Interference Studies

The effects of foreign ions on the determination of sulphate ion by this procedure are shown in Table 6.1. Each solution contained 4 mg of sulphate ion in a final volume of 100 ml. The solutions were prepared by the recommended procedure and the foreign ions were added in 100 fold, 10 fold or equivalent amounts to the sulphate solution before the addition of the other reagents. It will be seen that the only serious cationic interference observed in the range of metals studied is due to ferric iron. None of the common anions interfere except those which form more stable complexes than sulphate with the zirconium ion, e.g. oxalate and tartrate, or which tend to form insoluble compounds, e.g. tungstate and phosphate. These produce low results whereas fluoride exceptionally produced a positive result. The positive interference due to sulphite and to a lesser extent thiosulphate can almost certainly be attributed to oxidation to sulphate in these dilute solutions and are not regarded as reaction of these ions per se.

6.5 Experimental

(1) Reagents

Potassium Sulphate 10^{-2} M solution.

Zirconium Oxychloride, 10^{-4} M solution This was prepared by dissolving 0.0322 g of $ZrOCl_2 . 8H_2O$ in 100 ml of 3 M HCl. The 10^{-5} M solution was prepared by ten fold dilution of the 10^{-4} M solution with 3 M HCl.

Calcein Blue 10^{-4} M solution This was prepared by dissolving 0.016 g of Calcein Blue in a few drops of 0.1 M KOH and diluting to 500 ml with distilled water. The solution must be discarded after 2 - 3 days.

Ammonia Solution 8%

TABLE 6.1

(Molar Excess in Brackets)

Ion Added	% Change	Ion Added	% Change
Chloride (100)	0	Sulphite (100)	+100
Nitrate (100)	0	Sulphite (10)	+ 52
Phosphate (10)	-58	Sulphite (1)	+ 13
Phosphate (1)	-46	Fluoride (0.1)	+100
Borate (100)	0	Fluoride (0.01)	+ 14
Molybdate (100)	Quenched	Aluminium (100)	0
Molybdate (10)	-19	Beryllium (100)	0
Molybdate (1)	0	Arsenic(V) (100)	- 42
Tungstate (100)	Quenched	Arsenic(V) (10)	- 7
Tungstate (10)	-75	Arsenic(V) (1)	0
Tungstate (1)	-56	Nickel (100)	0
Vanadate (100)	-16	Copper(III) (100)	0
Vanadate (10)	0	Lead (100)	0
Acetate (100)	0	Calcium (100)	0
Oxalate (100)	-77	Cobalt (100)	- 76
Oxalate (10)	-63	Cobalt (10)	- 49
Oxalate (1)	-46	Cobalt (1)	0
Tartrate (100)	-45	Zinc (100)	0
Tartrate (10)	-37	Cadmium (100)	0
Tartrate (1)	- 8	Magnesium (100)	0
Sulphide (100)	+67	Iron(III) (100)	- 72
Sulphide (10)	0	Iron(III) (1)	- 50
Thiosulphate (100)	+33		
Thiosulphate (1)	0		

(2) Apparatus

Fluorescence measurements were made with a double monochromating spectrofluorimeter (Farrand Optical Co., Cat. No. 104244) fitted with a 150W Xenon arc lamp (Hanovia Division, Cat. No. 901 c-1) and an RCA IP 28 photomultiplier. A Honeywell Brown recorder was used in conjunction with the spectrofluorimeter. Fused quartz cells (10 x 20 x 50 mm) were used throughout. A pH meter was used to just the pH.

(3) Procedure

Calibration Graph (2 - 12 mg or 20 - 12,000 ppm)

Transfer 2 - 12 ml of 10^{-2} M potassium sulphate solution at suitable volume intervals into a series of 100 ml volumetric flasks and add, in the following order, 2 ml of 10^{-4} M Calcein Blue, 3 - 4 ml of 8% ammonia and 2 ml of 10^{-4} M zirconium oxychloride in 3 M HCl. Measure the fluorescence of the solutions at 410 nm with an excitation wavelength of 350 nm. Deduct the fluorescence of the blank solution containing all the reagents except the sulphate solution. These measurements may be made immediately or within four hours of preparation.

Since the volume of reagents added is less than 10 ml, unknown test solutions containing down to 20 ppm of sulphate may be measured if 90 ml of sample is available, or solution as concentrated as 11,000 ppm, if the test aliquot is restricted to 1 ml.

Calibration Graph (200 µg - 1000 µg or 2 - 1000 ppm)

Repeat the above procedure using 2 - 10 ml of 10^{-3} M potassium sulphate solution, 2 ml of 10^{-5} M Calcein Blue, 3 - 4 ml of 8% ammonia and 2 ml of 10^{-5} M zirconium oxychloride in 3 M HCl.

In this instance solutions as dilute as 2 ppm may be analysed if 90 ml of test solution are available.

6.6 Conclusions

A fluorimetric method has been established for the determination of sulphate ion in the range 200 μg - 11 mg, or concentration range 2 ppm - 11,000 ppm, assuming a sample solution availability of 90 and 1 ml respectively. The method is rapid and simple. Phosphate, oxalate and tartrate produce low recoveries and should be absent. Tungstate also interferes. Fluoride yields high results and must be totally absent. Sulphur species which are easily oxidised in aqueous solution interfere by sulphite formation, but the procedure shows a high tolerance towards most cations except ferric iron.

The mechanism of increased fluorescence production is not apparent from these experiments and although ternary complex formation may possibly be involved, the complex is too weak to allow unequivocal evidence to be adduced. The analytical method is moderately sensitive (2 ppm lower limit) and it has the fairly wide range which is characteristic of many fluorimetric procedures. It furnishes a potentially useful spectroscopic analytical procedure in addition to those very few which are currently available for the determination of sulphate ion.

PART TWO

CHAPTER 7

Introduction to Part 2

7.1 Introduction

The second part of this thesis is concerned with the development of a simple and rapid analytical method for determining the composition of the surface of metals using electrographic dissolution and the carbon filament atomic absorption method. The study is made with steel samples, but application to a wide variety of metals is envisaged.

In the following section some important aspects of metallurgical analysis is discussed. Chemical characterisation of metals and alloys is of the utmost importance because the composition of materials can have a significant effect on the physical and mechanical properties of materials. The obvious examples are those of semiconductor materials, laser materials, and the like, in which trace impurities produce dramatic changes in electrical conductivity and optical and other physical properties. Equally important, are the marked effects of trace impurities on mechanical properties, for example, removal of trace impurities from alloy steel results in a large and technically significant drop in the ductile-brittle impact transition temperature. Removal of trace impurities in stainless steels markedly improves their corrosion resistance.

7.2 Analytical Techniques for Metals and Alloys

A vast array of techniques is available for characterising metals and alloys. Table 7.1 obtained from Ref. 92 gives a generalised listing of the various techniques and parameters. The choice of technique naturally depends on the form and amount of sample available, the accuracy

TABLE 7.1

Some identification techniques and parameters—generalized

Technique	Determined	Simultaneously[a]	Precision[b] (percent)	Destruction	Lower limit of detection	Amount of sample consumed or examined for best detection	Useful range	Approximate costs
Emission spectrography	Metallic elements	Yes	3–10	Yes	1–10 ppm	20 mg	Lower limit to 5%	$25 to $50 3–10 elements
X-ray spectrography	Elements > atomic No. 11 (Na)	Yes	1–5	No	10–1,000 ppm	4 cm³	Lower limit to 50%	$5 per element
Spark mass spectrography	All elements	Yes		Partial	0.003–0.3 ppm	2–200 mg	Lower limit to 1%	
Photoplate readout			10–50					$75 to $200
Electronic readout			1–10					$75 to $200
Electron microprobe	Elements > atomic No. 5 (B) (plus elemental distribution)	Yes	1–5	No	100–1,000 ppm	1–200 μ^3	Lower limit to major compound	$75 to $200
X-ray diffraction	Crystal structure phases, compounds	Yes	5–10	No	1–5%	1–10 mg	Lower limit to major compound	$50 to $200
Metallography	Visual and photographic	Yes	—	No	1–1,000 × magnification	> 1 μ^2	1 μ resolution	$25 to $150
Light microscopy	Visual and photographic	Yes	—	No	1–1,000 × magnification	> 1 μ^2	1 μ resolution	$25 to $100
Electron microscopy	Visual and photographic (usually by replica)	Yes	—	Partial	1,000–100,000 × magnification	10–100,000 Å	10 Å resolution	$50 to $300
Scanning electron microscopy	Visual and photographic (replica not required)	Yes	—	No	15–50,000 × magnification	150 Å to 1 cm²	150–1,000 Å resolution	$50 to $300
Activation analysis	Most elements—some receiving chemical separation	No	1–10	Yes and No	0.001–100 ppm	grams	Lower limit to 5%	Too variable to estimate
Chemical	Most elements	No	1–5	Yes	10–100 ppm	grams	Lower limit to 50%	$5 to $35 per element
Chemical color, stain, spot test, etc.	Most elements	No	1–5	Yes	0.01–10 ppm	grams	Lower limit to 1%	$5 to $35 per element
Atomic absorption	Up to 50 elements	No	1–5	Yes	0.1–100 ppm in solution	1 ml	Lower limit to 10%	$5 to $10 per element
Flame emission	Alkali and alkaline earth elements	No	1–5	Yes	0.1–10 ppm in solution	1 ml	Lower limit to 10%	$5 to $10 per element

required and the cost that has to be met. If the sample is available at gram levels and analysis of only 1 or 2 elements are required, wet chemical techniques can provide the answer accurately and economically. Simultaneous determination of solid samples can be carried out by emission spectrography which can analyse up to 70 elements at nanogram levels. An ion-bombardment-source mass spectrometer can be used to determine the composition of monolayer surfaces and an electron microprobe used to profile compositional differences across a grain boundary with high accuracy. These methods, however, require expensive and sophisticated apparatus. In recent years the literature of analytical methods for metallurgical materials is dominated by atomic spectroscopic methods, particularly atomic absorption. The technique is popular because it is theoretically, instrumentally and procedurally simple, inexpensive and capable of analysis of major and trace constituents with a precision and accuracy frequently better than colorimetric methods. It is also relatively free from most of the troublesome interelement effects associated with spectrophtometric, polarographic or titrimetric analysis. Hence a wide variety of industrial metallurgical materials are now being analysed by atomic absorption procedures. The one great disadvantage of this technique, when applied to metallurgical samples, however, is the need to dissolve the sample prior to determination. This usually involves drilling, weighing, acid or fused-salt dissolution, cooling, dilution,and so on. Besides, being destructive, the dissolution step is tedious and time-consuming although the actual determination may be rapid and straightforward. An alternative simpler method of dissolution should be welcomed and for this reason we decided to investigate the possibility of using electrographic dissolution for quantitative analysis. However, the method can only be used if the analytical technique is capable of

handling extremely small amounts of sample and if the sample is homogeneous. The technique should also be useful if the composition of a particular area on the surface is required.

CHAPTER 8

ELECTROGRAPHY

8.1 Introduction

Electrography involves the process of electrolytic dissolution of a metal into an aqueous test medium, usually filter paper wetted with electrolyte. The basic arrangement of electrography is shown in Fig. 8.1[92].

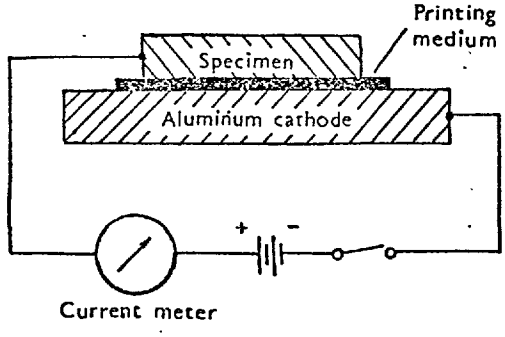


Fig. 8.1

The specimen is made the anode in a circuit with an aluminium cathode, and the filter paper is pressed in between the two electrodes. A potential difference of a few volts is applied and the electrolysis is carried out until sufficient material, as little as a few micrograms, is transferred to the paper.

This type of electrographic dissolution was first described in 1929 by Glazunov[93] who applied the technique to give metallographic prints, and Fritz[94] who worked on spot-test analysis. Since then, the technique has been used by many workers[95-100] for both purposes. The advantages of electrolytic dissolution over the usual methods of chemical attack,

include the elimination of the use of strong acids which often interfere with specific colour development, the reduction of transfer time to seconds, and the ability to control the area and amount of surface transferred.

In the printing process, the objective is to obtain a controlled transfer of metal surface into a suitable medium so that the distributive pattern of the transferred products reflects any compositional differences on the original surface, e.g. any imperfections in protecting coatings can be detected. Often, specific colorimetric reagents are added before the transfer to "develop" the print.

In spot-testing, the emphasis is on the identification of the transferred material, without any regard to the printing of distributive patterns. Electrotransfer into filter paper is a convenient means of obtaining a spot where it can be easily converted into a characteristically coloured product for identification. The simplest procedure is to add the appropriate colorimetric reagents to the electrolyte before the transfer. However, if the reagents are unstable, or if intermediate treatments are required before colour production, the dissolution and identification are carried out as separate steps. Semi-quantitative analysis can be obtained by comparison of the intensity of the ultimate colour produced with that obtained from standard specimens, if carefully controlled conditions are adopted.

Details of both electroprinting and electrospot testing procedures are given by Hermance and Wadlow[97].

The technique has frequently been used for the sorting of steels[98,99], platings[100] and corrosion resistant metals[101] by identification of the pure metal or a major constituent.

The first electrographic method for identification of a minor constituent was given by Calamari et.al.[102] who detected 0.2% molybdenum in steel. Stephen[103] and Nall and Scholey[104] combined the use of electrolytic dissolution with the ring-oven technique for the qualitative and semi-quantitative analysis of minor constituents in many ferrous and non-ferrous metals. In 1953 Monk[105] designed a very compact sampler for electrographic dissolution. We have constructed a slightly modified form of this device for our investigations and this is described in Chapter 9.

It can be seen that the electrographic work that has so far been reported is limited to qualitative and semi-quantitative estimations of components of certain favourably constructed alloys. There are many difficulties in extending the method for quantitative use, but work in this direction has been hampered mainly by limitations in equipment. A limiting factor given by Hermance and Wadlow[97] was that measurement of the total amount of material dissolved was difficult, because millicoulometers were not available. Furthermore, the advantages of a non-destructive method of dissolution have inevitably led to typical sample size of a few μg to 200 μg and techniques for the determination of the components, especially those present in trace amounts, have been complicated and unreliable. Today, these difficulties no longer exist, as advances in electronics have made integrators readily available and recent developments in atomic absorption methods have led to the establishment of a very simple ultramicrotrace technique,[106] the carbon filament atomic absorption method which is briefly described in Chapter 9.

For the method of electrographic sampling to be applicable to quantitative analysis, the sampling method must, of course, be reproducible. The second consideration then, is whether the elements in the

electrolytically dissolved sample are present in the precise proportions in which they exist in the solid sample. If the proportions differ, then a totally empirical approach to the analysis would have to be adopted, i.e. the unknown composition would have to be related to that of reference materials of known composition having similar matrix and physical form. For the study of trace elements in pure metals, e.g. steel, where the iron forms 99% of the matrix, this method of determination should be applicable.

If, however, the sample can be made to dissolve quantitatively with respect to each element, then wider applications to quantitative analysis would be possible. The procedure would simply involve fixing the total weight of material dissolved and analysing the concentration of each element by a suitable method. Glazunov[93] states that it is only when the alloy is a true solid solution, that the elements will dissolve in the precise proportions of the solid.

In the following section, some preliminary investigations into the performance of the sampler are described with a view to extending its application to quantitative analysis

8.2 Sampling Device

Description of the Sampler

A simple laboratory model of the sampling device, working on the same principle as that described by Monk[105], was constructed and is shown in Fig. 8.2. It consists of a hollow cylindrical brass casing of about 1 cm diameter and holds a carbon rod obtained from an exhausted dry battery. The rod is held by a spring and insulated from the case by a plastic cylinder which is held in place by a small screw. The brass case is connected to the positive end of a 2 x 2V Accumulator and the carbon rod to the negative end via the screw.

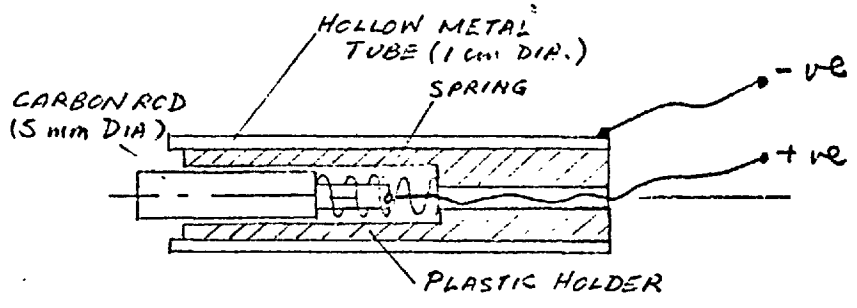


FIG. 8.2 SAMPLER

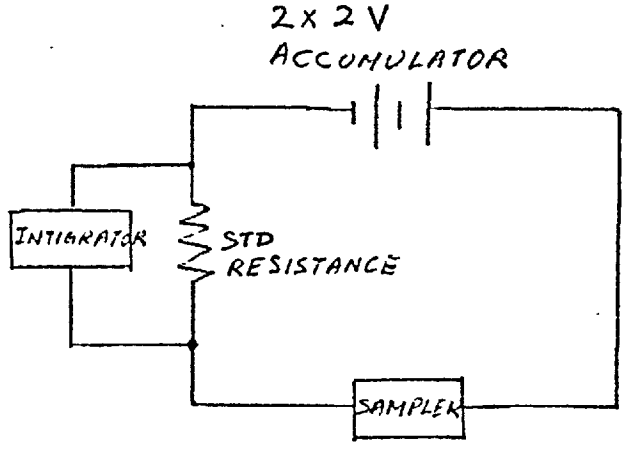


FIG. 8.3 CIRCUIT DIAGRAM

Procedure of Sampling

An area of approximately 2 cm diameter on the surface of the metal is polished with fine emery paper and excess grease removed with acetone and finally cleaned with distilled water and dried. A circular disc of filter paper 6 mm in diameter is punched out with a cork borer and placed on the clean metal surface. 1 - 3 µl of an electrolyte is placed on it using a Hammond micropipette. The spring loaded carbon rod is then placed on the filter paper and pressed firmly so that the brass cylinder touches the metal surface. The sampler is held in this position until sufficient metal has dissolved. The rate of dissolution can be varied by using different strengths of electrolyte. This method should allow metal surfaces to be analysed in areas from 0.1 mm^2 up to several sq. cm. as required. In this initial work a sampling area of $\approx$ 0.3 cm^2 was employed

8.3 Application to Semi-Quantitative Analysis

The usefulness of this sampling device for the semi-quantitative analysis of Ni, Mo, Cu, V, Mn and Cr by the ring-oven technique was investigated. The procedure employed is similar to that described in Ref. 104.

Ring-Oven - A description of the apparatus and the technique of analysis has been given by Weisz [107].

Experimental Technique

Samples were taken on discs of filter paper as described. Each disc was placed on the centre of a Whatman No.40 filter paper, 7 cm diameter, which was then placed on the ring oven. Separation of iron from the trace metals was effected by washing with ammoniacal solutions.

The trace metals washed to the outer ring were detected with the appropriate colorimetric reagents. The intensity of the colour of these rings was then compared with that prepared from standard samples of steel.

Conditions of Sampling

Choice of Electrolyte : Salt Solutions were not used because salts accumulated in the ring at the boundary of the hot zone tended to mask the colour reaction. Owing to the trace amounts of elements in steel, conditions for maximum rate of dissolution of sample were used. This corresponded to 3 µl of 40% HNO_3 or electrolyte. (2 - 3 µl of electrolyte being a convenient volume which would allow considerable wetting without causing the electrolyte to spread to the cap). The time of sampling can be adjusted according to the percentage of element in the steel sample so that its concentration falls within the sensitivity range of the analytical method. In general a sampling time of 30 secs was adopted and approximately 150 µg of iron were deposited.

Estimation of Ni, Mo, Cu and V from a Single Sample

These four elements were washed to the outer ring on the ring oven with 75% ammonium hydroxide. Repeated washing was necessary especially if Cu and V were to be effectively detected. The filter paper was dried and cut into four sectors and each element was estimated in a sector.

Estimation of Nickel

Reagents - 1% Dimethylglyoxime in ethyl alcohol.

Colour Development - The paper was sprayed with the above reagent and exposed to ammonia fumes. The red colour of nickel-dimethylglyoxime develops when the alcohol has evaporated. The colour was stable and standards prepared may be kept for reference.

Estimation of Molybdenum

Reagents - Freshly mixed solutions of equal volumes of 10% ammonium thiocyanate in ethyl alcohol and 2% stannous chloride dissolved in concentrated hydrochloric acid and ethyl alcohol.

Colour Development - After spraying with the above reagent the paper was held over concentrated hydrochloric acid. The orange-red molybdenum thiocyanate complex was stable for five mins, hence standards for comparison have to be prepared simultaneously.

Estimation of Copper

Reagent - 5% α benzoin-oxime in ethyl alcohol.

Colour Development - Spraying of the filter paper with the reagent was followed by fuming with concentrated ammonia. The green copper-benzoin oxime colour was stable.

Estimation of Vanadium

Reagent - Schiff's base formed from anthranilic acid and salicylaldehyde [108].

Colour Development - Spraying with this reagent produced a grey ring.

Estimation of Chromium

Reagents - Ammoniacal hydrogen peroxide and 5% Silver nitrate solution.

Procedure - The sample on the ring-oven was washed several times with ammoniacal hydrogen peroxide and distilled water. The paper was dried and sprayed with 5% silver nitrate solution. The yellow coloured rings were stable for 18 mins when exposed to light.

Estimation of Manganese

Reagents - 0.5% Potassium Periodate and 0.5% tetramethyldiamino-diphenylmethane in citric acid.

Procedure - The washing of manganese to the outer ring was effected with 75% ammonium hydroxide and 2% ammonium chloride. The paper was dried and sprayed with 0.5% potassium periodate and then with the tetra base. The blue coloured ring was stable for 5 mins.

Comments on the Ring Oven Technique as Used Above

In general it was found that considerable skill and care were required to ensure complete and symmetrical washing of the metals to a neat outer ring so that effective comparisons of the colour developed could be carried out. With the exception of the estimation of nickel, and to some extent copper and vanadium, the coloured complexes developed were unstable and required simultaneous preparation of standards.

8.4 Coulometric Measurements

The quantity of material transferred depends on the current passing through the sampler and the duration of sampling. For semi-quantitative work we have assumed that the current characteristics are identical for each sample taken and hence the amount of material dissolved was kept constant by fixing the duration of sampling. Differences in the pressure applied to the filter paper disc can, however, cause variations in the current. Therefore, for quantitative extension of the method, a stricter monitoring of current variations and time of sampling was necessary. For this purpose an integrator was included in the circuit of the sampler as shown in Fig. 8.3.

The integrator consists of a voltage-to-frequency converter[109] and a Harwell 2117B Scalar. When a sample is being taken the current that flows in the circuit produces a voltage drop across the resistance R. The voltage drop is fed into the voltage-to-frequency converter which produces pulses at a rate proportional to the voltage across the resistor. The pulses are counted on the scalar and the total number of counts is proportional to the number of coulombs passed.

With R = 0.95 Ω. 1 coulomb = 1292 counts. The linearity of the voltage-to-frequency converter = ± 0.07%.

8.5 Influence of the Electrolyte on Dissolution

The anodic dissolution of metals depends primarily on oxidation brought about by the potential difference at the specimen-electrolyte interface. The composition of the electrolyte, however, may have important secondary effects. It may determine whether the products of electrolysis build up on the surface of the specimen to form a partial or complete barrier to further passage of ions (polarization and passivation) or whether the ions will move, unobstructed, into the printing medium. Hermance and Wadlow[97] reported that copper, silver and lead dissolve well with a nitrate electrolyte, but poorly with chloride which coats their surface with insoluble products. Conversely, iron, aluminium, nickel and gold tend to become passive in nitrate but dissolve well in chloride electrolytes.

Calamari[99] states that passivation can influence the valence state in which the metals dissolve anodically. Polyvalent elements in their active states dissolve to form ions of lowest valence while elements which become passive enter solution as ions of a higher valence.

The electrolyte will also determine the current efficiency of the dissolution. If the potential at the anode exceeds the decomposition or deposition potential of the electrolyte, evolution of gases may take place. Not all the electrical energy is thus used for oxidation of metals hence coulometric measurements will not give a completely quantitative measure of how much sample has been dissolved.

In the following section an investigation into the effect of different electrolytes on the dissolution of pure metals is described. Comparisons of coulometric measurements and the actual concentrations of the metals electrolytically dissolved, can be used to study the current efficiency or the valence state in which the metals go into solution, if either one of the two factors is known. It was simpler to keep the valence state constant and hence the current efficiency was first studied. Nickel sheet, which will almost certainly dissolve in the divalent state, was used.

Samples were taken from pure nickel sheets using 2 µl hydrochloric acid, nitric acid and ammonium chloride on the sampling paper disc with a sampling time of 30 secs. The concentration of nickel on each disc was analysed by the spectrophotometric determination of Ni with dimethylglyoxime. See Appendix 2. The ratio of this analysed concentration of nickel to that calculated from integration of current with time gives the current efficiency of the dissolution, represented in Table 8.1. (i.e. $\frac{\text{Analysed}}{\text{Calculated}} \times 100$).

It can be seen that 100% current efficiency was obtained when ammonium chloride was used as electrolyte. The high values obtained with hydrochloric acid may be attributed to chemical attack of the metal by the acid. The low results for nitric acid may be due to the chemical formation of a passive oxide film on the nickel surface. Using 2 µl

TABLE 8.1

Sample	Electrolyte	Calculated from integrated current	Analysed	$\frac{\text{Analysed}}{\text{Calculated}} \times 100$
Nickel	30% NH_4Cl	0.3105 mg	0.327 mg	105%
	30% NH_4Cl	0.2606 mg	0.277 mg	106%
Nickel	5N HCl	0.0623 mg	0.077 mg	123%
	5N HCl	0.0724 mg	0.092 mg	127%
	5N HCl	0.0681 mg	0.087 mg	127%
Nickel	40% HNO_3	0.284 mg	0.231 mg	81.3%
	40% HNO_3	0.287 mg	0.239 mg	83.3%
Copper	30% NH_4Cl	0.0996 mg	0.100 mg	100%
	30% NH_4Cl	0.1010 mg	0.100 mg	100%

TABLE 8.2

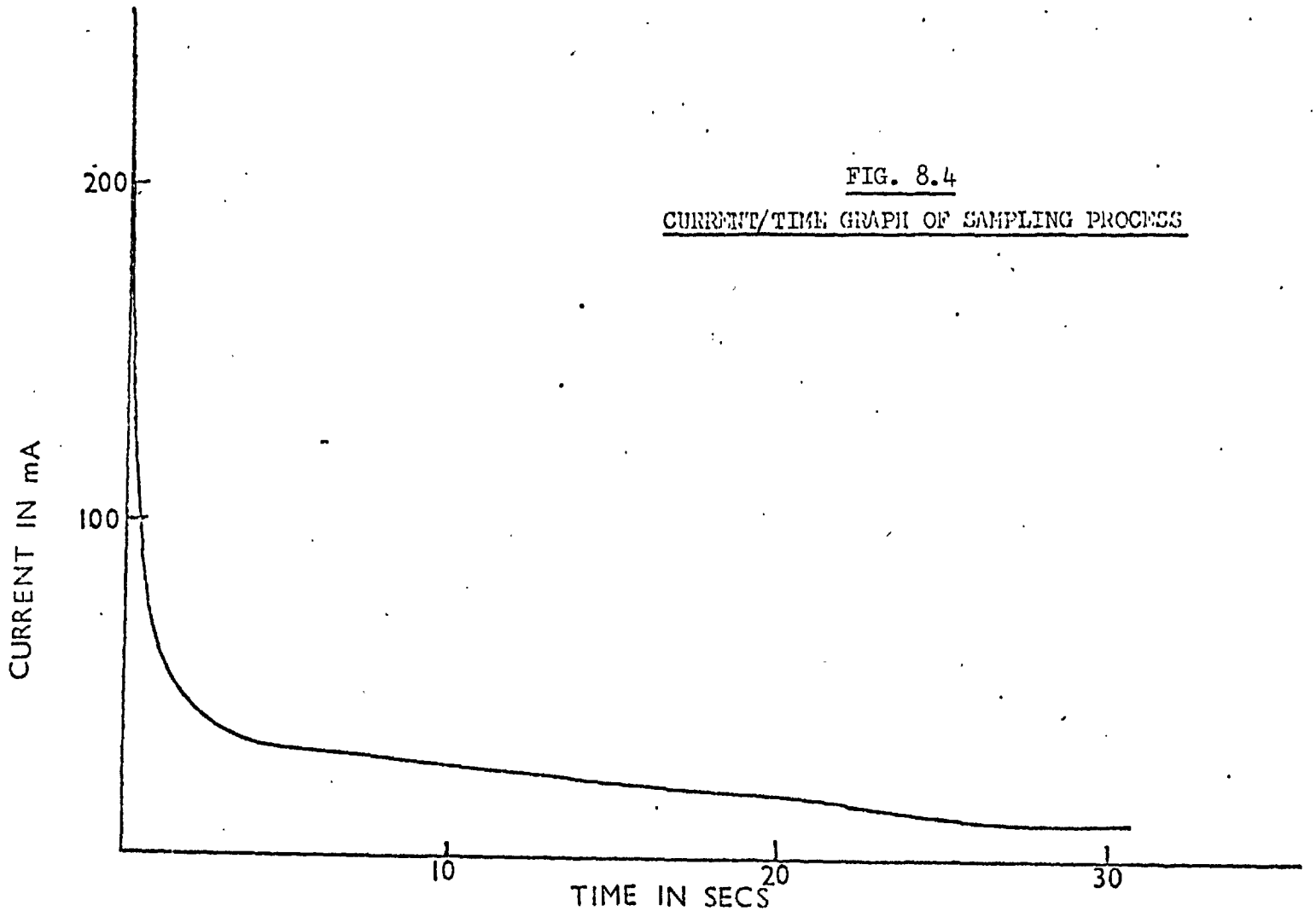
Sampling Time	Calculated wt. of Fe	Analysed wt. of Fe	$\frac{\text{Analysed}}{\text{Calculated}} \times 100$ = Current Efficiency
5 secs	66.8 µg	59 µg	88.3%
10 secs	116.8 µg	88 µg	75.2%
15 secs	154 µg	110 µg	71.4%
30 secs	221 µg	163 µg	73.7%

ammonium chloride as electrolyte the experiment was repeated with pure copper sheets. The copper on the sampling paper disc was analysed by the carbon filament atomic absorption method described in Chapter 9. Calculations from coulometric measurements were based on the dissolution of the element as CuII. Again a 100% current efficiency was obtained. It should be noted, however, that this is only an apparent value because the oxidation state of copper is not known. If coulometric measurements were based on CuI, then less than 100% current efficiency would be obtained. The efficiency would then be ca 50% only; this is rather unlikely.

The sampling of steel was subsequently investigated using 2 μl of ammonium chloride. Fig. 8.4 shows the current vs. time graph of the sampling process. The graph was obtained with a Bryans Auto Plotter 22000 XY/t recorder in place of the integrator. It can be seen that the current drops rapidly within one second. This is attributed to increased resistance of the cell due to depletion of electrolyte, precipitation of reaction products, polarisation and possibly passivation of the anode surface. To investigate the effects of this current drop, samples were taken with varying durations of sampling time. The steel used contained 99% or iron, but for this purpose was treated as pure iron. The iron was determined spectrophotometrically using a potassium thiocyanate method and measuring the absorption at 480 nm. See Appendix 3. The calculated weight of iron was obtained with the assumption that all the iron dissolved as FeII. The data if Table 8.2 shows values of $\frac{\text{Analysed}}{\text{Calculated}} \times 100$ to be less than 100% and it is not clear whether this is due to a true loss in current efficiency or the invalidity of the assumption that all the iron dissolves as FeII. A shorter sampling time, however, appears to be preferable.

FIG. 8.4

CURRENT/TIME GRAPH OF SAMPLING PROCESS



An attempt was made to determine the oxidation state of the iron as it goes into solution. Although Hermance and Wadlow[97] reported that iron dissolves without passivation in chloride media and thus according to Calamari should dissolve as FeII, it is possible that as the electrolytic reaction proceeds, passivation occurs, resulting in dissolution as FeIII. This is suggested by the current drop in Fig. 8.4, and higher $\frac{\text{Analysed}}{\text{Calculated}}$ x 100 value for shorter sampling time. Furthermore, colorimetric spot tests on the filter paper disc with o-phenanthroline for FeII and acidic potassium thiocyanate for FeIII immediately after sampling, gave positive results for both tests.

It was thus not possible to determine a true value for the current efficiency from analysis of elements like iron which could dissolve in more than one valence state. This, however, does not preclude the use of the method even for these elements, provided that good reproducibility of sampling is obtained.

CHAPTER 9

The Carbon Filament Atomic Absorption Method

9.1 Introduction

Non-Flame Atomisation Reservoirs

Numerous non-flame atomisation reservoirs have been described in the atomic absorption literature. Most of them require expensive and relatively complex apparatus though in most cases they are considerably more efficient and safer to use than flames. These include the hollow cathode sputtering chamber[110], flash-heating devices[111], variations of the King furnace, as modified by Vidale[112], the laser microprobe[113], radio frequency plasma torch[114], which are generally more suited to the analysis of solid specimens. The devices which have minute sample requirements and therefore suitable for the application of electrographic dissolution are the electronically heated carbon (graphite) tube reservoirs of L'Vov,[115,116] and Massman[117,118] and the carbon filament atom reservoir of West and Williams[106].

L'Vov Furnace[115,116]

In this technique the sample solution is dried on the top of a graphite electrode which is then introduced into a graphite tube furnace heated at up to 3000°K. The sample is volatilised by the application of a d.c. arc for about four seconds creating an atomic vapour which passes into the tube furnace. The interior of the tube is lined with tantalum or tungsten foil to prevent diffusion of the atomic vapour into the graphite walls, and thus the vapour diffuses gradually along the length of the tube. The atomic absorption is measured along the axis of the

tube and varies with time, being at a maximum immediately after the striking of the arc. The peak absorption value is the analytical parameter measured.

Massmann Tube [117,118]

Massmann's device uses a heated carbon tube for the atomic absorption and atomic fluorescence of several elements. The samples were syringed into a graphite cup with slits in opposite sides. The samples were vaporised by electrical resistance heating of the graphite cell to ca 2600°C (ca 400 A max.) in an argon atmosphere.

The Carbon Filament Atom Reservoir (CFAR)

This was first introduced by West and Williams [106]. It consists essentially of a 2 mm diameter carbon (graphite) filament in a stream of inert gas, argon or nitrogen. A measured drop of the solution to be analysed is placed on the centre of the carbon filament which may be heated up to 2600°C in a very short space of time by the passage of a high current at low voltage. A transient cloud of atoms is produced, on which spectroscopic measurements of atomic absorption or fluorescence may be made.

The devices described above have minute sample size requirements and metals down to 10^{-13} g have been determined by atomic absorption and down to 10^{-15} g by atomic fluorescence. The increased sensitivity as compared to flame methods is a result of increased atomisation efficiency and the absence of background noise associated with absorption and emission of the flame plasma. Of these devices, the CFAR is simplest in instrumental construction and operation and can be mounted on any commercial atomic absorption equipment.

9.2 Development of CFAR for the Determination of Copper, Nickel and Manganese

Papers on CFAR published to date [106, 119-121] have dealt mainly with progress in instrumentation and operation and the determination of the more volatile elements like silver and magnesium. In this section a description of the development of the technique for the determination of copper, nickel and manganese will be given

(1) Apparatus

The instrumental set-up is shown in Fig. 9.1.

CFAR Assembly

The CFAR used in this work was of the type described by Alder and West [121] as shown in Fig. 9.2. A 3 mm by 1 mm notch was made at the centre of the carbon filament so that the sample can be reproducibly placed and the hot spot, formed on application of power, largely confined to this area.

The support stem of the reservoir was mounted on the burner holder of a Hilger and Watts "Atomspek H1170". In this position it was possible to utilise the vertical and horizontal adjustments, originally intended for the burner, to position the filament so that the light beam is focussed on the notch at the centre of the filament.

The power supply to the carbon filament cell was from the mains via a step down welding transformer capable of delivering up to 100 A at 0 - 12 V The filament voltage temperature was controlled by using an 8 amp "Variac" transformer to alter the voltage across the input coils of the welding transformer. Argon was used as the sheathing gas.

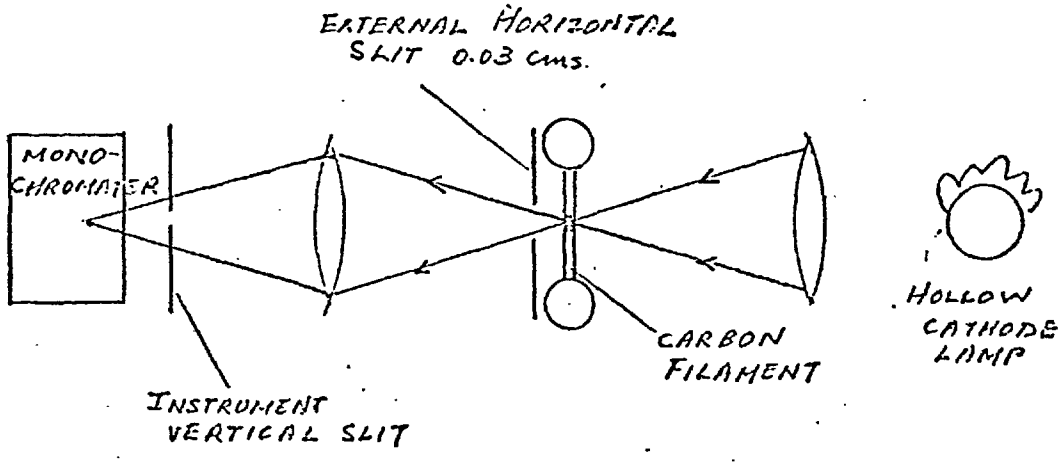


FIG. 9.1 INSTRUMENTAL SET-UP

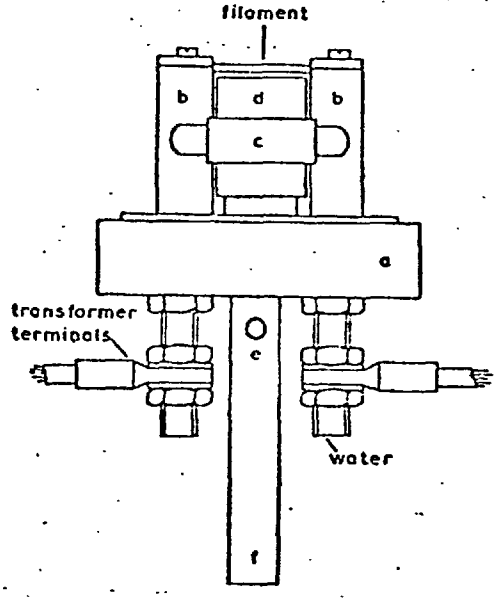


FIG. 9.2 CARBON FILAMENT ATOMIC ABSORBTION RESERVOIR

(a) base
(b) water-cooled electrodes
(c) water link between electrodes
(d) laminar flow box
(e) inlet from shield gas
(f) support stem for reservoir

Atomic Absorption Instrument

The "Atomspek H1170" modulated at 400 Hz was used without modification except that the damping on the output of the photomultiplier was removed. This was necessary because the lifetime of the signals obtained with this technique is of the order of 0.2 - 1 sec, unlike that in flames where the sample is continuously being atomised over any desired period of time. Removal of the damping caused a superimposition of a constant high fequency on the signal, but fortunately its frequency was several magnitudes greater than that of the analytical signal and was easily averaged out. It should be possible to eliminate the high frequency noise by using a low pass filter in the electronic circuit if desired.

External Optics

An external slit 0.03 cm by 0.4 cm was placed between the rod and the photomultiplier. This provided collimation of the light beam above the filament thus ensuring that maximum density of atoms can be measured before dilution or condensation of atoms has depleted the atomic population above the rod.

Recording System

A Servoscribe recorder was initially used and is adequate for the determination of pure copper, but the response time reduced considerably the shorter lifetime signal due to nickel. A Hewett-Packard 141B storage oscilloscope was hence substituted.

(2) Measurement Technique

5 µl of sample were pipetted into a Hammond micro pipette on to the small notch in the carbon filament and the solution was evaporated by operating the filament at 1.5 V for 10 secs. After a few seconds,

atomisation was effected by operating the filament at high power, between 7 - 12 V, depending on the element being determined. To prolong the lifetime of the filament the power was switched off as soon as maximum absorption has occured. The peak of the absorption vs. time trace, was the analytical parameter recorded. The whole treatment involving sample addition, dehydration, etc. takes about 1 min.

(3) Optimisation of Instrumental Settings

The optimum conditions for the determination of solutions of manganese, nickel and copper were investigated.

Hollow Cathode Lamp Current

Using an external horizontal slit of 0.03 cm and the vertical slit of the instrument at 100 millimicrons it was sufficient to operate the lamps on the low intensity mode and at the lowest current possible, i.e. 4 mA. The current can be increased up to 15 mA without any loss in sensitivity.

Vertical Span of Horizontal Slit

Initial studies on the absorption of pure copper solutions were made with varying slit widths up to 1 mm without any loss in sensitivity. However, when the effect of the presence of foreign metallic species was examined it was found that decreasing the width of the slit reduced the interference effects. A 0.03 cm slit was used subsequently throughout the investigations.

Height of Horizontal slit above the Filament

The horizontal slit was placed standing on a deck of index cards each having a thickness of 0.018 cm on the base of the CFAR. This enabled the height of the horizontal slit above the filament to be varied at

0.018 cm intervals. For pure copper and manganese solutions, maximum absorption was observed with the slit placed from zero to 0.18 cm above the surface of the notch at the centre of the filament. The determination of nickel required the slit to be placed not greater than 0.036 cm above the filament otherwise a decrease in absorption was observed. Nickel has a higher boiling point than manganese or copper and the atoms would be expected to condense at a faster rate as the distance above the rod increases.

When interference studies on these elements were made it was shown that minimum interference effects were observed with the slit placed in a position just grazing the surface of the filament. The interference effects were mainly depressions of the absorption and is attributed to the physical occlusion of the element under examination, in much the same manner as occurs in aqueous coprecipitation [121].

Instrumental Slit (Vertical)

With the horizontal slit at 0.03 cm, the vertical slit of the instrument could be opened to a maximum of 200 millimicrons without any loss in sensitivity being observed. Above this value the monochromator bandpass presumably becomes too great, causing lines which are not absorbed by the atoms to reach the detector. A constant slit width of 100 millimicrons was used for subsequent investigations.

Filament Voltage

For dehydration of the solvent, in this case, water, the filament voltage was set at ca 1.5 V. The water boils off slowly and smoothly in ca 10 secs.

The optimum voltage required for atomisation varies with the element to be determined as well as the speed of the detection and recording systems. If too low a voltage is used the filament will show memory effects, whereas too high a voltage will reduce the lifetime of the signal and hence adversely affect slower response systems, e.g. the optimum voltage for copper and manganese using the Servoscribe as the recorder was 8 - 9 V and with the oscilloscope was 10 - 11 V. Nickel, which has a higher boiling point requires a voltage of 12 V, using the oscilloscope.

Argon Flow Rate

The argon is required to provide a non-oxidising atmosphere and to sweep the atoms reproducibly through the light path. At high argon flow rates, turbulence sets in and this can adversely affect the reproducibility. It is also possible that a high argon flow rate may have a cooling effect on the atomic vapour, however minimum deterioration and hence longer lifetime of the filament is obtained. Maximum absorption signals were obtained with argon flow rate of between 1.5 to 2 litres min^{-1} for copper, and 4 litres min^{-1} for manganese and nickel.

(4) Preparations of Reagents for Analysis

All solutions were prepared from analytical grade materials. The distilled water was continually checked for contamination by the ion being studied. All volumetric flasks used were treated with silicone "Repelcote" water repellant, to minimise adsorption. The Hammond micropipettes used to introduce the sample to the filament were also treated with silicone "Repelcote" as this improved the reproducibility of sampling considerably.

Various stock solutions at 1000 ppm were prepared as follows :-

Copper - Dissolve 0.392 g of Analar $CuSO_4 .5H_2O$ in 5 ml concentrated HCl and dilute to 100 ml with distilled water.

Manganese - Dissolve 0.413 g Analar $MnSO_4 .4H_2O$ in 5 ml concentrated HCl and dilute to 100 ml with distilled water.

Nickel - Dissolve 0.404 g of Analar $NiCl_2 .6H_2O$ in 5 ml concentrated HCl and dilute to 100 ml with distilled water.

Calibration of Cu, Mn and Ni

Fig. 9.3 shows the absorbance of diluted standard solutions of copper, manganese and nickel obtained with optimum instrumental settings for each element. The reproducibility of the signals obtained with any single solution is within $\pm$ 5% of the mean.

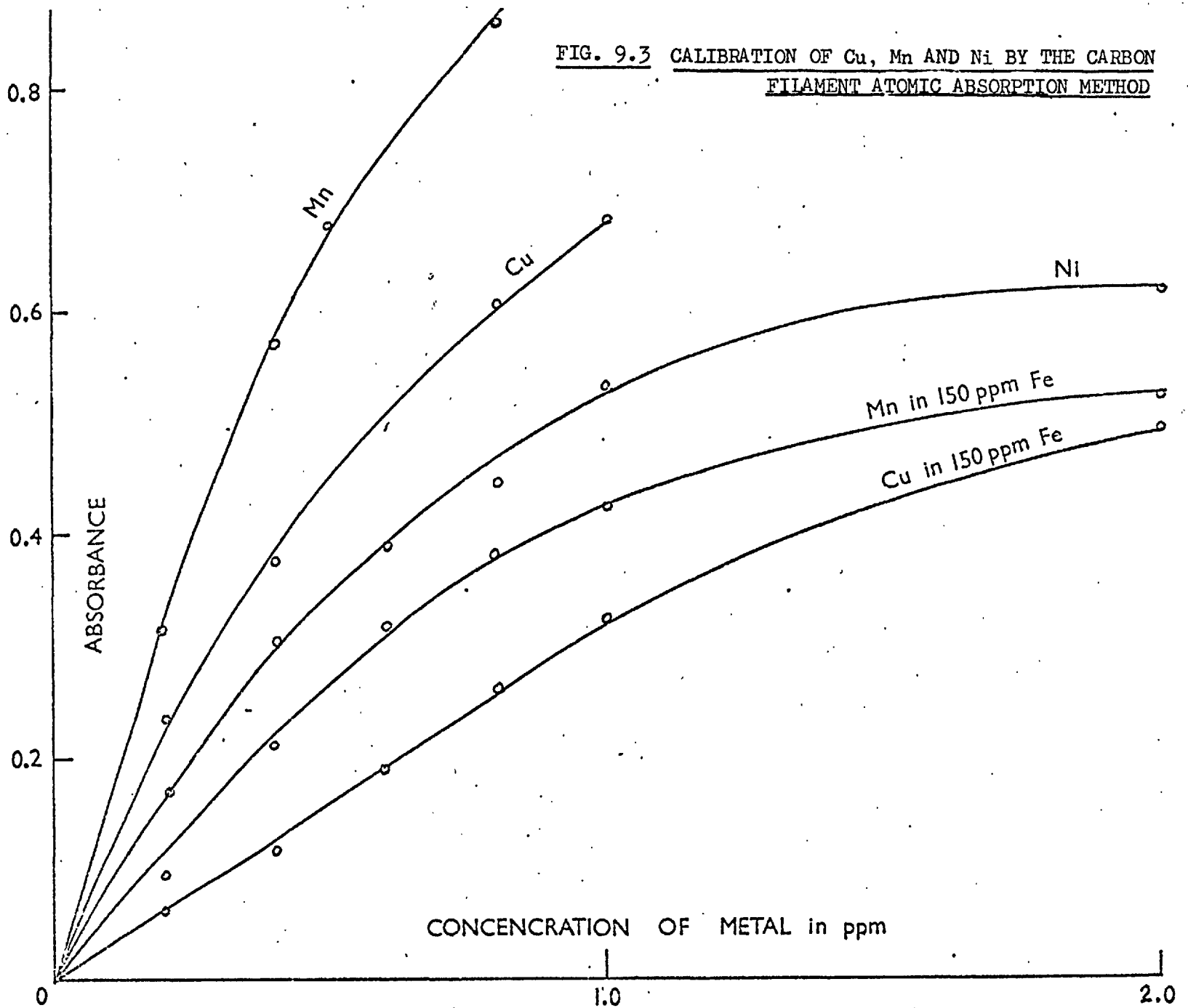
Bending of Analytical Curves

It will be noted from Fig. 9.3 that the graph is only linear up to an absorbance of 0.2 or 0.25, above this value bending occurs. The factors which cause this bending will be discussed. They can be roughly classified into two groups.

The first includes factors given by faults in the apparatus. Some of the light emitted by the lamp may not pass through the absorbing medium or may be of wavelengths other than that capable of being absorbed by the atoms. There may also be a non-linear relationship between the concentration of the atoms in the absorbing medium and the concentration in the sample. The temperature and space distribution of the absorbing atoms in the absorbing medium may be inhomogenous. The analytical parameter measured is the maximum of the time-trace signals whereas stricly speaking, the mean, or better still, the integrated signal should be measured.

The second group of factors which causes bending of analytical curves is that related to the properties of the particular spectral line itself. A discussion of these factors for atomic absorption in flames has been published in several papers [122-124]. Perhaps the most important of these for atomic absorption using the carbon filament method is that the emitted line widths from the source may not be negligibly small compared to the absorption line widths. Hence the absorption coefficient at the maximum of the absorption profile may not bear a linear relationship with concentration. The factors which suggest that the atomic absorption line widths are narrower than those in flames are (a) the temperature of the atoms in the absorbing medium is lower, hence Doppler broadening would decrease, and (b) pressure broadening would be reduced because the atoms are not surrounded by atomic and molecular species as in the flame plasma.

FIG. 9.3 CALIBRATION OF Cu, Mn AND Ni BY THE CARBON FILAMENT ATOMIC ABSORPTION METHOD



CHAPTER 10

Determination of Trace Elements in Steel with CFAR and the Electrographic Sampling Method

10.1 Introduction

In this chapter, experiments are described to investigate

(i) the optimum procedure for determination of trace elements in electrolytically dissolved steel samples with the CFAR technique.

(ii) the reproducibility of the sampling technique, and

(iii) the possibility of calibrating trace metals in standard steel samples with this technique.

10.2 Procedure

The procedure of sampling is as described in Chapter 8. The size of the samples can be controlled by discontinuing the sampling when the integrator registers the required value. Owing to the nature of the current-time graph, Fig. 8.4, it was thought that more reproducible results would be obtained with shorter sampling times, hence the size of samples was kept to the minimum necessary for determination of the trace metals. Table 10.1 shows that, with a sampling time of approximately 5 secs and 2 µl ammonium chloride as electrolyte, the integrator registers 500 counts, corresponding to a total of 4.02×10^{-6} chemical equivalents assuming that 100% of the charge is used for dissolution. The weight of each trace element is calculated on the assumption that its concentration in the sample corresponds to that in the specification of the steel.

TABLE 10.1

Weight of Trace Metals in Each Sample

Standard Steel Ref.No.	Sampling Time	Integrator Counts	Total No. of Equivalents	Weight x 10^{-6} (gm) of trace metals					
				MnII	NiII	CuII	CrIII	VV	MoVI
QT	5 secs	500	4.02×10^{-6}	0.96	0.44		0.585	0.043	0.28
B	5 secs	500	4.02×10^{-6}	0.585	0.355	0.10	0.362	0.102	0.15
F	5 secs	500	4.02×10^{-6}	0.49	0.33	0.24	3.62	0.087	0.34
	30 secs	1000	8.02×10^{-6}	twice above values					

Preparation of Sample Solution for CFAR Determination

When a specimen is electrolytically transferred to the filter paper disc, precipitation occurs in the deeper layers of the paper, as alkalinity develops, and the electrolyte evaporates. It was thus necessary to dissolve the sample on the filter paper disc with 0.05 ml concentrated hydrochloric acid, followed by dilution to 0.5 ml with distilled water. (Solutions stronger than 1 M HCl were not determined on the carbon filament instrument because loss of precision occurs owing to depletion of repelcote in the micropipette and furthermore, loss in intensity of absorption has been reported).

5 µl of the solution were then placed on the carbon filament instrument which was set up for the determination of the test element.

10.3 Elements Determined Without Prior Separation of Matrix

Analysis of elements without prior separation of matrix is normally carried out by employing standards which duplicate the matrix composition of the test element. Preparation of such standards for the determination of trace elements in steel is not difficult because the iron constitutes 99% of the matrix and, as will be seen later on, the presence of other trace elements can be ignored. In our experiment, the sample taken with an integrator count of 500, was analysed by the potassium thiocyanate spectrophotometric method given in Appendix 3 and found to contain 80 µg iron. Each sample was eventually dissolved in 0.5 ml solution hence standards used consisted of accurately prepared solutions in 150 - 160 ppm iron. The presence of this amount of iron causes ca 50% reduction of the absorption of the elements, Mn, Cu and Ni. The absorption signals are also broadened by the presence of excess iron and the reproducibility between measurements was poor for concentrations below 0.6 ppm particularly for copper.

Determination of Manganese

4 samples of 500 integrator counts were taken from each of the standard steels QT, B and F. The concentration of manganese as read off from the calibration graph, Fig. 10.2, is presented in Table 10.2. Reproducibility between the samples taken from a single standard steel is within $\pm$ 5% of the mean.

TABLE 10.2

Determination of Manganese

Sample	Counts	Final Volume	Analytical Concentration	Calculated Concentration	$\frac{\text{Anal.Conc}}{\text{Cal. Conc}} \times 100$
QT	500	0.5 ml	1.13 ppm	1.92 ppm	59%
B	500	0.5 ml	0.80 ppm	1.17 ppm	68%
F	500	0.5 ml	0.62 ppm	0.98 ppm	64%

The effect of up to 100 ppm of nickel, copper, chromium, vanadium, molybdenum on the absorption of 0.6 ppm of manganese in 150 ppm Fe was determined and no interference was found.

Determination of Copper

The determination of copper in the presence of 150 ppm iron results in the suppression and the broadening of the absorption signals. Narrower signal peaks were obtained when the Variac setting was increased to 10.5 V and the argon flow rate to 3 litres/min, but this resulted in a reduction in intensity of absorption and it was found necessary to use an oscilloscope.

Standard steel samples were analysed for copper as in the procedure for manganese. The reproducibility was poor and an analytical concentration ranging from 50% to 80% of the calculated concentration was obtained. Due to the low content of the steel samples available, it was difficult to ascertain whether the poor reproducibility arises from the sampling or the analytical method. The method, as it stands, is not satisfactory for determinations of copper in steel below 0.3%.

10.4 Elements Determined After Separation of Matrix

(1) Precipitation with Ammonia

The electrolytically dissolved samples of steel were dissolved as described previously, but concentrated ammonia was added to precipitate the iron and the solution was centrifuged. The total volume of solution was varied from 0.5 to 2 ml so that the concentration of the elements fell within the calibration range. Experiments were carried out with standard copper and nickel solutions under similar conditions and no significant coprecipitation was observed. However, this procedure resulted in the presence of large amounts of ammonium chloride which generated smoke when the sample is atomised. Sublimation of the ammonium chloride by increasing the filament voltage to 2 V after dehydration of solvent, eliminated the interference effect but the precision of analysis was reduced. The reproducibility of signals for a single steel sample was within $\pm$ 8% for nickel but was again unsatisfactory for copper. The data in Table 10.3 represents the average of readings taken with four samples of a single standard steel.

Account has not been taken of the interference of other trace metals present in the sample. Table 10.5 shows the effect of various concentrations of these elements on the absorption of 0.6 ppm of copper and nickel.

TABLE 10.3

Sample	Counts	Final Volume	Calculated Concentration	Analytical Concentration	$\frac{\text{Anal}}{\text{Calc.}}$ x 100
Determination of Nickel					
QT	500	1.5 ml	0.88 ppm	0.70 ppm	80%
B	1000	1.0 ml	0.71 ppm	0.64 ppm	91%
F	1000	1.0 ml	0.66 ppm	0.56 ppm	85%
Determination of Copper					
B	1000	1.0 ml	0.4 ppm	0.29 ppm	73%
F	1000	1.0 ml	0.2 ppm	0.16 ppm	80%

(2) Solvent Extraction

The feasibility of using solvent extractions was next investigated with standard solutions of copper containing 150 ppm iron. An attempt was made to extract the iron from 6 N hydrochloric acid medium into diethyl ether. The procedure consisted of shaking 1 ml of the standard solution in 6N HCl with three two-ml portions of diethyl ether. The upper diethyl ether was removed with a syringe. Determination of this aqueous layer on the CFAR gave low results. This is expected as strong hydrochloric acid has been reported to have adverse effects on the atomic absorption intensity. Dilution to 1 M HCl would reduce tremendously the sensitivity of the method and furthermore multiple manipulations on such small volumes are apt to introduce errors.

TABLE 10.5

Interference effect of some metals on the absorbance of 0.6 ppm			
Concentration of Interfering Metals		Copper	Nickel
FeIII	2 ppm	none	none
	10 ppm	-20%	-14%
	50 ppm	-45%	-54%
	100 ppm	-62%	-62%
	200 ppm	-62%	-62%
CrIII	1 ppm	none	none
	5 ppm	none	-20%
	50 ppm	none	-25%
	100 ppm	none	-50%
V V	10 ppm	none	none
	50 ppm	- 4%	-20%
MoVI	50 ppm	none	none
	100 ppm	none	-20%
	500 ppm	none	
NiII	1 ppm	-10%	
	5 ppm	-20%	
CuII	1 ppm		-14%
	5 ppm		-25%

10.5 Conclusion

These experiments are only exploratory in nature but nevertheless certain points have emerged which should be helpful for future work.

With regard to optimum conditions for the determination of trace elements in steel by the CFAR method, it can be said that determinations without prior separation of matrix are to be preferred. The number of operations between sampling and actual determination is hence kept to a minimum. Another less obvious, but important advantage in this procedure, is that the constant depression of the atomic absorption of the test element by the iron matrix, swamps all interference effects from other trace elements which would otherwise have been present. However, this depression of absorption by iron decreases the reproducibility and the sensitivity of the analytical method. The composition of trace elements present in less than 0.3% are hence not easily determined.

For such low concentrations of metals, separation of the matrix appears to be the only solution. Precipitation of iron by ammonia is simple and rapid, but large amounts of ammonium chloride are generated which necessitated a sublimation step before the atomic absorption of the test element could be reliably measured. This complicated the CFAR procedural sequence and reduced the precision of the method.

Removal of the iron matrix by solvent extraction has only been fleetingly investigated and further work should be done in this direction.

The reproducibility of the analytical results between samples taken from a single standard steel is within $\pm$ 5% of the mean for manganese, determined without prior separation of matrix, $\pm$ 8% of the mean for nickel, determined after precipitation of the iron matrix with ammonia. It is difficult to assess the reproducibility of sampling with respect to copper because of its low content in the samples of steel available for our work.

Having established that nickel and manganese can be reproducibily dissolved, we now consider the possibilities of determining these elements in steel of unknown composition. Comparison of the last column in Table 10.2 and 10.3 shows that the current efficiency is less than 100% and the two elements appear to dissolve in nearly, but not precisely, the same proportions as in the solid specimen. Determinations of unknown compositions would hence have to be carried out by comparison with a reference sample, i.e. calibration graphs for each element should be established with standard steel samples undergoing identical sampling and analysis treatment as the "unknown". Because of the limited number of standard steels available, we were unable to present such a calibration graph.

It should perhaps be pointed out that while attempts were made to relate the quantity of each metal dissolved to coulometric measurements, it is appreciated that dissolution of the iron which forms the bulk of the specimen could influence the dissolution of the trace metals.

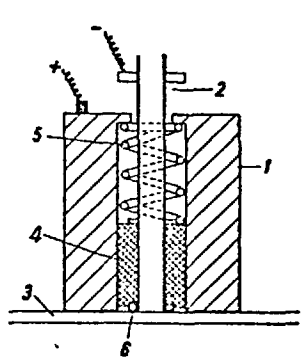
Suggestions for an Alternative Design of Sampler

In electrographic sampling, filter paper has always been employed as the transfer medium because it is appropriate for usage in conjunction with spot testing and electroprinting. However, in our investigations into the application of the CFAR it was realised that the use of filter paper as transfer medium led to many disadvantages. The electrolytically dissolved sampler tended to precipitate in the deeper layers of the filter paper and dissolution involves the use of concentrated hydrochloric acid and dilution before the sample can be analysed on the CFAR. The very simple sampling and atomic absorption method is thus complicated, and loss in precision may occur due to manipulation with such small amounts of sample.

If, however, the electrolytic transfer can take place directly into an electrolyte without being held by filter paper and precipitation can be prevented, the sampling procedure would be greatly simplified. Such an electrotransfer process would be possible with devices which have been used for coulometric measurements of the thickness of metallic film coatings. A similar sampler design would facilitate direct dissolution into an electrolyte, while maintaining electrolysis conditions constant between the samples taken. Fig. 10.1 shows an electrolysis cell [125], consisting of a heavy steel tube anode (1) held on to the sample (3) by means of a spiral spring (5) to give good electrical contact. A narrower steel tube (2) serves as cathode and holds the electrolyte solution. The cathode is isolated from the anode by means of a plastic collar (4) and a rubber gasket (6).

The volume of electrolyte can be adjusted by varying the diameter of the bore of the cathode. To ensure that precipitation does not take place, the electrolyte can be buffered to maintain a slightly acidic medium, e.g. with sodium carbonate.

The electrolytically dissolved sample could then be determined on the CFAR by direct transfer with a micropipette.



Electrolysis cell for the determination of film thickness.
1 — thick steel tube (anode),
2 — thin steel tube (cathode),
3 — sample,
4 — plastic collar,
5 — spring,
6 — rubber gasket.

FIG. 10.1

APPENDIX 1

Composition of Standard Samples of Steel

Sample Ref. No.	Quantovac Print Out												
	C	S	P	Si	Mn	Ni	Cr	Mo	V	Cu	Al	B	Sn
QT 35	0.16	0.015	0.015	0.13	0.87	1.13	0.90	0.44	0.10		< 0.005		
68/11/B	0.17	0.005	0.003	0.36	0.53	0.30	0.52	0.73	0.23	0.19	0.010	0.001	0.03
68/11/E	0.19	0.005	0.002	0.12	0.36	< 0.01	0.27	0.54	0.31	0.01	0.014	< 0.001	< 0.005
68/11/F	0.06	0.009	0.014	0.29	0.42	0.28	5.20	0.53	0.02	0.08	< 0.005	< 0.001	0.01

APPENDIX 2

Spectrophotometric Determination of Nickel with Dimethylglyoxime[126]

When dimethylglyoxime is added to an alkaline solution of a nickel salt which has been treated with an oxidising agent such as bromine, a red coloration is obtained. The red souble complex contains nickel in higher valence state. (This has been regarded as NickelIII and also as NickelIV dimethylglyoximate). The nickelic complex formed absorbs at 455 nm, provided the absorbance readings are made within 10 mins of mixing.

Procedure for the Electrolytically Dissolved Pure Nickel (pg 90)

The nickel on the filter paper disc was dissolved in ca 10 ml of distilled hydrochloric acid. Saturated bromine water, ca 1 ml was added until all the nickel has been oxidised as indicated by the persistence of the yellow colour of bromine. 1 ml of concentrated ammonia solution was added to render the solution alkaline. This was then followed by 1 ml 1% dimethylglyoxime and the solution was diluted to 100 ml with distilled H_2O. The optical density at 445 nm was measured against water in 1 cm cells after 5 mins.

The concentration of nickel was determined by comparison with calibration graphs constructed with standard nickel solutions undergoing the same procedure.

APPENDIX 3

Spectrophotometric Determination of Iron by the Thiocyanate Method[126]

Ferric iron reacts with thiocyanate to give a series of intensely red coloured compounds which remain in true solution: Ferrous iron does not react. Depending upon the thiocyanate concentration, a series of complexes can be obtained; these complexes are red and can be formulated as $[Fe(SCN)_n]^{3-n}$, where n = 1,.....6. In the colorimetric determination, a large excess of thiocyanate should be used, since this increases the intensity and also the stability of the colour. Strong acids (hydrochloric or nitric acid - concentration 0,05 - 0.5 M) should be present to suppress the hydrolysis.

Procedure for Determination of Electrolytically Dissolved Iron (pg 92)

The electrolytically transferred iron on the filter paper disc was dissolved in 2 ml concentrated hydrochloric acid followed by a few ml of distilled water. Dilute potassium permanganate solution was added drop by drop, (to oxidise any ferrous ion to ferric) until a very faint pink colour persisted in the solution. This was then followed by 5 ml 20% potassium thiocyanate solution and dilution to 100 ml with distilled water. The optical density of the solution was measured at 480 nm against distilled water in 1 cm cell.

Calibration graphs were constructed with standard ferric chloride solutions.

1. Boltz, D.F. (ed) Colorimetric Determination of Non-Metals, Interscience, New York, 1958.

2. Wharton, H.W., Anal. Chem., 1962, 34, 1296.

3. Ruzicka, J.A., Jakschova, H. and Mrklas, L., Talanta, 1966, 13, 1341.

4. Bumstead, H.E. and Wells, J.C., Anal. Chem., 1952, 24, 1595.

5. Megregian, S., ibid, 1954, 26, 1161.

6. Fluery, S., Anal. Chim. Acta, 1967, 37, 232.

7. Lambert, J.L., Anal. Chem., 1954, 26, 558.

8. Hensky, A.L. and Barney, J.E., ibid, 1960, 32, 828.

9. Taves, D.R., Talanta, 1968, 15, 1015.

10. Price, M.J. and Walker, O.J., Anal. Chem., 1952, 24, 1593.

11. Willard, H.H. and Horton, C.A., ibid, 1952, 24, 862.

12A. Belcher, R., Nutten, A.J. and Stephen, W.L., J. Chem. Soc. 1953, 1334.

12B. Jones, A.S. and Letham, D.S., Analyst, 1956, 81, 15.

13. Lambert, J.L., Yasuda, S.K. and Grotheer, M.P., Anal. Chem., 1955, 27, 800.

14. Palaty, V., Talanta, 1963, 10, 307.

15. Guyon, J.C. and Lorah, E.J., Anal. Chem., 1966, 38, 155.

16. Yamanoto Hiro, Y. and Tanaka, K., Bunseki, Kagaku, 1968, 17, 206.

17. Bertolacini, R.J. and Barney, J.E., Anal. Chem., 1957, 29, 281.

18. Lambert, J.L. and Yasuda, S.K., Anal. Chem., 1955, 27, 444.

19. Florence T.M. and Farrer, Y.J., Anal. Chim. Acta, 1971, 54, 373.

20. MacDougall, D. and Briggs, D.A., Anal. Chem., 1952, 24, 566.

21. Hatcher, J.T. and Wilcox, L.V., Anal. Chem., 1950, 22, 567.

22. Belcher, R., Leonard, M.A. and West, T.S., J. Chem. Soc. 1959. 3577.

23. Leonard, M.A. and West, T.S., J. Chem. Soc., 1960. 4477.

24. Babko, A.K., Shkaravskii, Y.F. and Kulik, V.I., Zhur. Anal. Khim., 1969, 21(2), 196.

25. Tsubouchi, M., Anal. Chim. Acta, 1971, 54, 143.

26. Bunikiene, L. and Ramanauskas, E., Zhur. Anal. Khim. 1968, 23, 1364.

27. Ringbom, A., Ahlers, P.T. and Siitonen, S., Analyt. Chim. Acta, 1959, 20, 78.

28. Woods J. T. and Mellon, M.G., Ind.Eng.Chem.Anal.Ed., 1941, 13, 760.

29. Wadelin, C. and Mellon, M.G., Anal. Chem., 1953, 25, 1668.

30. Boltz, D.F. and Mellon, M.G., Ind. Eng. Chem. (Anal. Ed.) 1947, 19, 873.

31. Djurkin, V., Kirkbright, G.F. and West, T.S., Analyst, 1966, 91, 89.

32. Holler, A.C. and Huch, R.U., Anal. Chem., 1949, 21, 1385.

33. Axelrod, H.D., Bonelli, J.F. and Lodge, J.P., Anal. Chem., 1970, 42(4), 512.

34. Rider, B.F. and Mellon, M.G., Ind. Eng. Chem., (Anal. Ed.), 1946 18, 96.

35. Sawicki, E. and Noe, J.L., Anal. Chim. Acta, 1961, 25, 166.

36. Osburn, R.L., Shendrikar A.D.and West, P.W., Anal. Chem., 1971, 43, 594.

37. Pappenhagen, J.M. and Mellon, M.G., Anal. Chem., 1953, 25, 341.

38. Barnes, H..and Folkard A.R., Analyst, 1951, 76, 599.

39. Hoste, J. and Gillis, J., Anal. Chim. Acta, 1955, 12. 158.

40. Parker, C.A. and Harvey, L.G., Analyst, 1962, 87, 558.

41. Mecklenburg, W. and Rosenkranzer, F., Z. anorg. Chem., 1914, 86, 143.

42. Sands, A.E., Grafius, M.A., Wainwright, H.W. and Wilson, M.W., U.S. Bur. Mines, Rept. Invest., No.4547, 1949.

43. Johnson, C.M. and Nishita, H., Anal. Chem., 1952, 74, 736.

44. Perrin, D.D., Organic Complexing Reagents, Interscience, 1964.

45. Atkins, S., Anal. Chem., 1950, 22, 947.

46. Katz, M., Anal. Chem., 1950, 22, 1040.

47. Cabello-Tomas, M.L. and West, T.S., Talanta, 1969, 16, 781.

48. Hems, R.V., Kirkbright, G.F. and West, T.S., Talanta, 1969, 16, 789.

48a. Hems, R.V., Ph.D. Thesis, University of London, 1969.

49. Bognar, J. and Nagy, L., Mikrochim. Acta, 1969, 108.

50. Babko, A.K. and Maksimeno, T.S., Zhur. Anal. Khim., 1967, 22, 570.

51. Belcher, R. and West, T.S., Talanta, 1961, 8, 863.

52. Yamamura, S.S., Wade, M.A. and Sikes, J.H., Anal. Chem., 1962, 34, 1309.

53. Hanoca, M. and Moller, L., Anal. Chim. Acta, 1968, 42, 349.

54. Johnson, C.A. and Leonard, M.A., J. of Pharmacy and Pharmacology, 1961, 13, 164T.

55. Hall, R.J., Analyst, 1963, 76, 88.

56. Frant, M.S. and Ross, J.W., Science, 1966, 154, 1553.

57. Frant, M.S. and Ross, J.W., Anal. Chem., 1968, 40, 7.

58. Duff, E.J. and Stuart, J.L., Anal. Chim. Acta, 1970, 52, 155.

59. Lingane, J.J., Anal. Chem., 1968, 40, 935.

60. Durst, R.A., Anal. Chem., 1968, 39, 1374.

61. Klockow, D., Ludwig, H. and Giraudo, M.A., Anal. Chem., 1970, 42, 1683.

62. Bond, A.M. and O'Donell, T.A., ibid, 1968, 40, 560.

63. Leonard, M.A., Ph.D. Thesis, University of Birmingham, 1959.

64. Budesinsky, B. and West, T.S., Anal. Chim. Acta, 1968, 42, 455.

65. Al-Ani, K. and Leonard, M.A., Analyst, 1970, 95, 1039.

66. Kolthoff, I.M. and Belcher, R., Volummetric Analysis, Vol. 3., 200, Interscience, N.Y., 1957.

67. Svehla, G., Proc. Soc. Anal. Chem., 1971, 8(4), 80.

68. Ovenston, T.C.J. and Rees, W.T., Analyst, 1950, 75, 205.

69. Eggers, J.H., Talanta, 1960, 4, 38.

70. Wilkins, D.H., ibid, 182.

71. Hems, R.V., Kirkbright, G.F. and West, T.S., Anal. Chem., 1970, 42, 784.

72. Sinha, B.C. and Das Gupta, S., Analyst, 1967, 92, 558.

73. Belcher, R. and Nutten, A.J., "Quantitative Inorganic Analysis," 2nd Ed., Butterworths, London, 1960.

74. Pribil, R. and Maricova, D., Chem. Listy., 1952, 46, 542.

75. Mahr, C. and Krauss, K., Z. Anal. Chem., 1948, 128, 477

76. Belcher, R. and Gibbons, D., J. Chem. Soc., 1952, 4216.

77. Denis, W. and Reed, L., J. Biol. Chem., 1906, 131: J. Biochem., 1926, 71, 191.

78. Toennies, G. and Bakay, B., Anal. Chem., 1953, 25, 160.

79. Takiyama, K. and Suito, E., Japan Analyst, 1954, 3, 291.

80. Omiti, S., ibid, 1963, 12, 1032.

81. Volmer, W. and Frohlich, F., Z. Anal. Chem., 1944, 126, 401.

82. Martin, J.M. and Stephen, W.I., Anal. Chim. Acta, 1967, 39, 175.

83. Alicino, J.F., Anal. Chem., 1948, 20, 85.

84. Siegfriedt, R.K., Wiberley, J.S. and Moore, R.W., Anal. Chem., 1951, 23, 1008.

85. Ogg, C.L. Willitts, C.O. and Cooper, F.J., Anal. Chem., 1948, 20, 83.

86. Fritz, J.S. and Freeland, M.Q., Anal. Chem., 1954, 26, 1593.

87. Fritz, J.S. and Yamamura, S.S., ibid, 1955, 27, 1461.

88. Budesinsky, B. and Krumlova, L., Anal. Chim. Acta, 1967, 39, 375.

89. Belcher, R., Gibbons, D. and West, T.S., Chem. and Ind. 1954, 127.

90. Carbon, R.M., Rosell, R.A. and Vallejos, W., ibid, 1967, 39, 688.

91. Schafer, H.N.S., ibid, 1967, 39, 1719.

92. Bunshaw, R.F., Modern Analytical Techniques for Metals and Alloys, Vol. 3., Part 1, Interscience, 1970.

93. Glazunov, A., Chim. et Ind., 1929, 21, 425.

94. Fritz. H., Z. Anal. Chem, 1929, 78, 418.

95. Hunter, M.S., Churchill, J.R. and Mears, R.B., Metal Progress, 1942, 42, 1070.

96. Long, M.E., Iron Age, 1949, 164, 98.

97. Hermance, H.W. and Wadlow, H.V., Standard Methods of Chemical Analysis, 6th Ed. Vol. III, Part A, Welcher, F.J., Ed., Van Nostrand, New York, 1966, Chap. 25.

98. Clark, G.C. and Hale, E.E., Analyst, 1953, 78, 145.

99. Calamari, J.A., Ind. Eng. Chem. (Anal. Ed.), 1941, 13, 19.

100. Hughes, H.D., J. Electrodep. Tech. Soc., 1944-45, 20, 17.

101. Zech, C.J., Metal Progress, 1947, 52, 824.

102. Calamari, J.A., Hubata, R. and Roth, P.B., Ind. Eng. Chem. (Anal.Ed.), 1943, 15, 71.

103. Stephen, W.I., Mikrochim. Acta (Wien), 1956, 1531.

104. Nall, W.R. and Scholey, R., Metallurgia, 1956, 97,

105. Monk, P.R., Analyst, 1953, 78, 141.

106. West, T.S. and Williams, X.K., Anal. Chem., 1968, 40, 335.

107. Weisz, H., Microanalysis by the Ring Oven Technique, Pergamon Press, 1961.

108. Jungreis, E. and West, P.W., Anal. Chim. Acta, 1969, 44, 440.

109. G.E.C., U.S.A., Transitor Manual, 7th Ed. 1964, 346.

110. Gatehouse, B.M. and Walsh, A., Spectrochim. Acta, 1960, 16, 602.

111. Nelson, L.S. and Kuebler, N.A. in E.R. Lippincott and M. Margoshes, Proc. Xth Coll. Spectroscop. Internationale, Sparton Books, 1963, 83.

112. Vidale, G.L., U.S. Dept. Com., Office Tech. Serv., P.B. Rept. 148, 206, 1960. Reported in Chemical Abstracts, 1962, 56, No.13558d.

113. Mossotti, V.G., Laqua, K. and Hagenal, W.D., Spectrochim. Acta, 1968, 23B, 197.

114. Greenfield, S., Jones, J.L. and Berry, C.T., Analyst, 1964, 89, 713.

115. L'Vov, B.V., Spectrochim. Acta, 1961, 17, 761.

116. L'Vov, B.V., I.U.P.A.C. XXth Congress, Moscow, U.S.S.R., July 9th, 1965.

117. Massmann in A.C. Menzies, XIIth Colloquium Spectroscop. Internationale, Exeter, Hilger and Watts Ltd., 1965, 275.

118. Massmann, H., Spectrochim. Acta, 1968, 23B, 215.

119. West, T.S. and Williams, X.K., Anal. Chim. Acta, 1969, 45, 27.

120. Anderson, R.G., Maines, I.S. and West, T.S., Anal. Chim. Acta, 1970, 51, 355.

121. Alder, J.F. and West, T.S., Anal. Chim. Acta, 1970, 51, 365.

122. Rebesta, I. and Svoboda, V., Anal. Chim. Acta, 1965, 32, 253.

123. Vickens, T.J., Anal. Chim. Acta, 1966, 36, 42.

124. Gelders, Z.V., Spectrochim. Acta, 1970, 25B, 669.

125. Francis, H.T., J. Electrochem. Soc. 1948, 93, 79.

126. Vogel, A.I., A textbook of Quantitative Analysis, 3rd Ed., Longmans, 1961.