TRACE ANALYSIS WITH PARTICULAR REFERENCE TO SELENIUM AND THE APPLICATION OF ATOMIC FLUORESCENCE SPECTROSCOPY

by

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ABSTRACT

Three new spectrophotometric procedures have been developed for the determination of selenium in aqueous solution: Particular attention was paid to the development of rapid, sensitive and selective methods based on the use of stable reagents that are readily and cheaply available. The determination of selenium by atomic fluorescence spectroscopy has been examined, and a solvent extraction procedure has been applied to enhance the sensitivity obtainable.

The effect of flame composition and burner type on the practical utility of atomic fluorescence spectroscopy has been discussed, and this effect has been examined for the determination of zinc with particular reference to the extent and nature of cationic interferences. Some studies have been made of the application of the atomic fluorescence excited by a continuum source to the analysis of practical samples, and attempts have been made to explain any radiation interferences encountered. A Southern Instruments A 1740 Grating Flame Photometer has been modified for A.F.S. work; a frequency-tuned and a phase-sensitive amplifier have been made, and their performances have been evaluated.

A new type of dual-element electrodeless discharge tube has been developed: Tubes were prepared for a variety of element combinations, and the applicability of the tubes to A.F.S. was investigated. Several other new types of single and multi-element electrodeless discharge tubes have also been briefly examined, primarily with a view to obtaining an indication of future research trends.

ACKNOWLEDGEMENTS

The work described in this thesis is entirely original except where due reference is made. No part of the work has been previously submitted for any other degree. The work was carried out in the Chemistry Department of the Imperial College of Science and Technology, between October 1967 and February 1970.

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CONTENTS

Chapter 1 Introduction to the Spectrophotometric Determination of Selenium

The importance of the analytical determination of selenium has recently been reviewed[1], and will not be considered further here. Although an appreciable amount of research has been directed towards finding new selective and sensitive procedures for the determination of the element because of its physiological and technological importance, the methods reported in the literature for the determination of trace amounts of the element tend to be either time-consuming, or to require elaborate and expensive equipment.

The methods available for the determination of selenium by solution spectrophotometry may be conveniently divided into three classes: The first class involves the formation of piazselenols, which are either coloured or fluorescent, and includes the well known 3,3'-diaminobenzidene methods[2,3] and the 2,3-diaminonaphthalene method[4]. o-Phenylenediamine[5,6], 1,2-diaminonaphthalene[6], 4-methylthio-1,2-phenylenediamine[7,8], 4,5-diamino-6-thiopyrimidine[9], and 4-methyl-, 4-chloro-, and 4,5-dichloro-o-phenylenediamine[10] have also been investigated as reagents. Although this type of reaction is generally both sensitive and selective, the reagents tend to be unstable in solution even at $0^{\circ}C$, and the methods are susceptible to interference even from mild oxidising agents. Moreover the development times tend to be of the order of thirty minutes or longer.

The second class, which involves the reduction of Se(IV) to the elemental form, often with the simultaneous production of a coloured oxidation product, includes the well known selenium sol and iodine methods[11], the oxidation of phenylhydrazine-p-sulphonic acid to the diazonium ion, followed by coupling with 1-naphthylamine[12], the oxidation of N,N'-diphenylhydrazine[13], a few catalytic reactions[14,15,16], and the oxidation of pyrrole[17].

The third class involves the formation of complexes in which the selenium bonds either partially or completely to sulphur ligands. The reagents which fall into this class, which includes 2-mercaptobenzoic acid, the reagent investigated in chapter 2, are compared in table I. The determination of selenium with dithizone could also be included in this group, although the exact structure of this complex is unknown[27]. Only interferences specifically mentioned in the original papers are shown in table I.

It seems probable that the selective nature of the reactions used in the spectrophotometric determination of selenium depends upon the availability of d electrons and empty d orbitals for π-bond formation, and upon steric factors. From a number of reagents selected on this basis, the following three were selected for a fuller investigation after a rapid preliminary screening:

a) 2-Mercaptobenzoic Acid.

b) Cyclohexanone.

c) 4-Chloro-4'-aminodiphenyl (CAD).

TABLE I

Reagent	Ref.	Sens.	Molar Absorp- tivity	Interferences
2-Mercaptobenzoic acid	✱	.005	15,600	Hg, Te, Cu, Ni, Co, Ag, Li, Zr.
2-Mercaptobenzothiazole	18	.008	9,480	Fe, Cu, Zn, Cd, Pb, W, Ti, Mo, Hg, As, Sb, Pd, U, Te.
2-Mercaptobenzimidazole	19,20	.007	10,500	Te, Cu, Bi, IO_3^-, BrO_3^-, Mo.
1-Phenylthiosemicarbazide	21	.014*	5,200	Fe, Cu, V.
N-Mercaptoacetyl-p-anisidine	19	.063*	1,200	Te, Cu, Bi, Mo.
N-Mercaptoacetyl-p-toluidine	19	.063*	1,200	Te, Cu, Bi, Mo.
Thioglycollic acid	22	.045*	1,660	Ag, Cr, Cu, Fe, Ge, Hg, V, As, Bi, Mo, Sb.
Diethyldithiocarbamate	23	.041*	1,800*	Ag, As, Bi, Cd, In, V, Pb, Sb, Te, Zn.
1-Amidino-2-thiourea	24	.033	2,400*	-
Bismuthiol II	25,26	.007*	10,580	Te, Cu, Fe, Bi, As, V, Hg, Pd.

Table Comparing the Sensitivity of some Methods for the Determination of Selenium with Sulphur Ligands.

✱ The reagent studied in chapter II.

* Estimated values.

The reasons for which these reagents were selected are explained in the relevant chapters.

Chapter II The Absorptiometric Determination of Selenium with 2-Mercaptobenzoic Acid

2-Mercaptobenzoic acid has been used for the spectrophotometric determination of nickel[28] and fluoroacetates[29], and as a precipitant for thorium[30]. The reagent was selected for investigation because of the possibility of π-bonding between the filled d orbitals of the selenium atom and the empty d orbitals of the sulphur atom, and because although the instability of sulphur ligands frequently limits their applicability to routine analysis, the mercapto group in 2-mercaptobenzoic acid should be stabilized by hydrogen bonding. If the bonding anticipated did occur in practice, the resulting complex should be virtually insoluble in acid aqueous solution:

Preliminary Investigation

The reagent was found to give a precipitate with selenium in acid solution; to obtain an idea of the extent of precipitation, the precipitate was separated from the aqueous phase by centrifuging for five minutes, and then dissolved in ethanol. The UV absorption was measured at 220 nm against an ethanol blank: The effect of pH on the solubility of the complex is shown in fig. 1. Fig. 2 shows the calibration curves obtained for selenium by measurement of a) the absorption of the excess reagent, and b) the absorption of the complex dissolved in ethanol, both at 220 nm. Because of the low precision obtained, it was decided to investigate the feasibility of employing a solvent extraction procedure; as expected for a complex with bonding of the suggested type, ethyl acetate proved to be a suitable solvent, and this solvent was employed in all

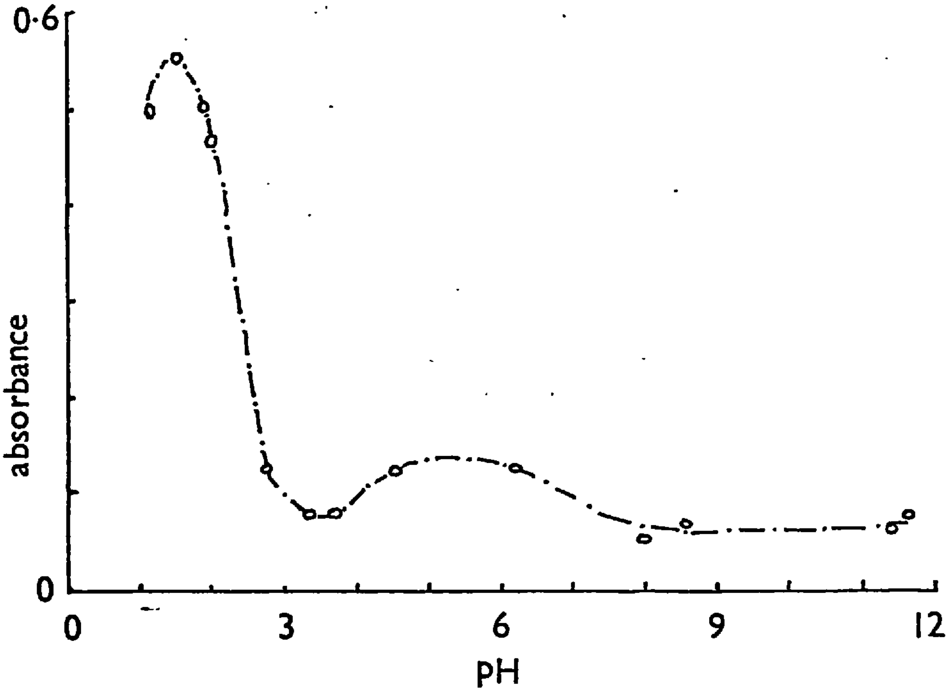

0·6
absorbance
0
0
3
6
9
12
pH

Fig. 1.

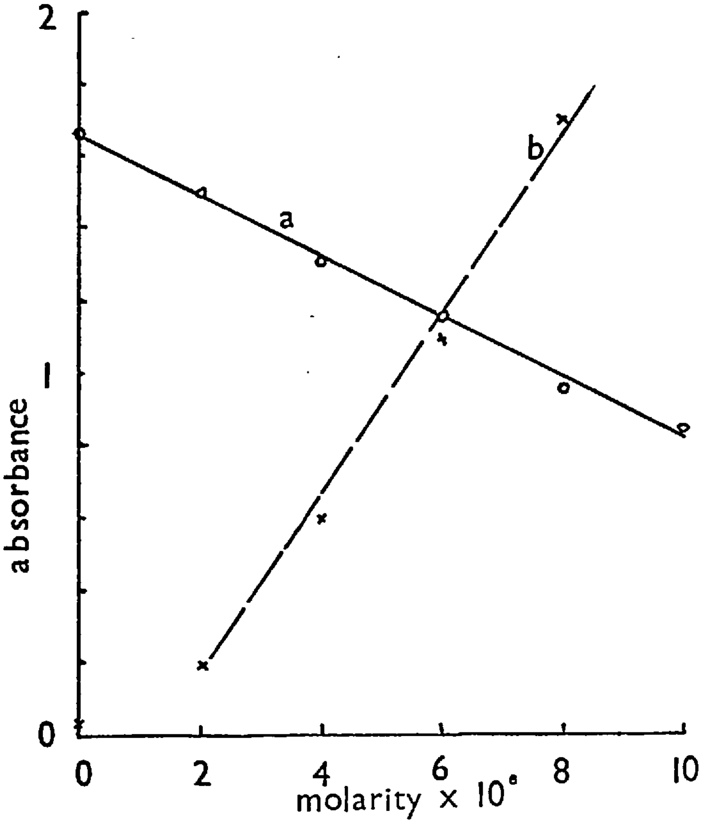

2
1
0
absorbance
a
b
0
2
4
6
8
10
molarity × 10

Fig. 2.

subsequent work.

Effect of pH

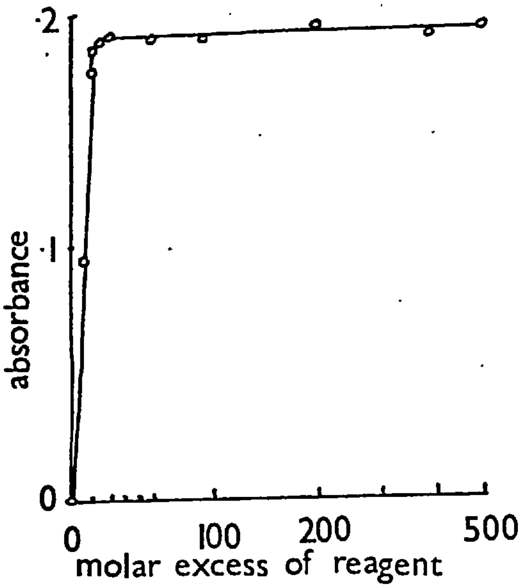
Variation of the acidity of the aqueous solution revealed that the maximum sensitivity for the extraction occurred within the pH range 0.5 to 2.5. Over this range, the extraction of the selenium (as determined by atomic fluorescence spectroscopy) was found to be virtually quantitative. At higher pH, the complex was either not formed or not extracted. Further studies were, therefore, conducted at pH 2.3. It was found in the preliminary investigation that the excess reagent is also extracted under these conditions.

Effect of Time on Complex Development

The absorption of the selenium complex reached a maximum in the aqueous solution within one minute of the addition of the reagent; both the original aqueous solution and the ethyl acetate phase showed no significant change in absorbance for at least two hours thereafter.

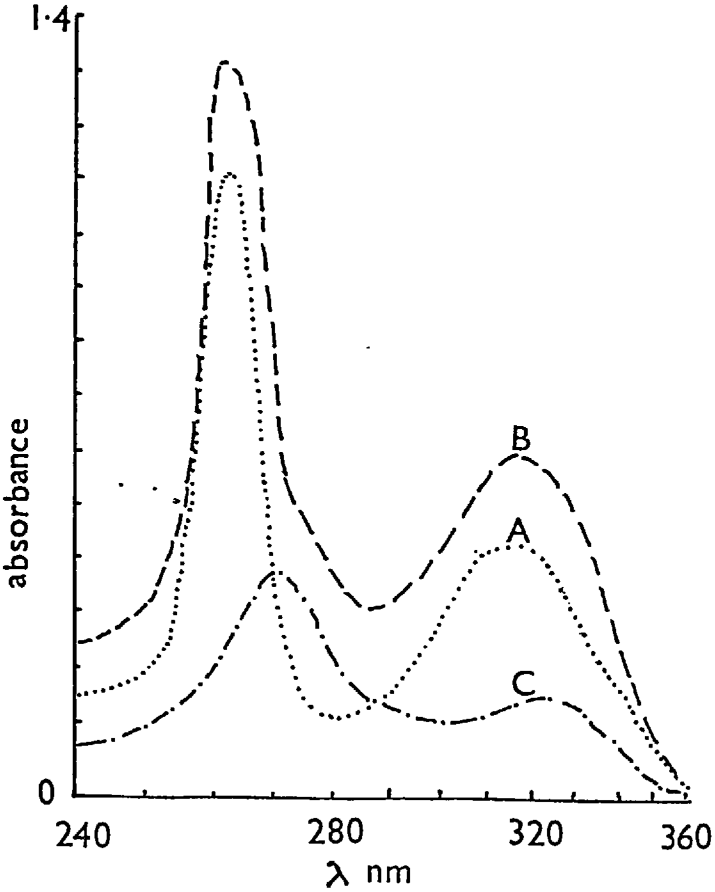
Reagent Stability and Reagent Excess

The reagent solution can be used for at least 48 hours if kept at room temperature, provided at least a twenty-fold excess of reagent is used. Only a ten-fold reagent excess is required for complete development if the reagent solution is prepared fresh daily. This shown in fig. 3, which indicates that a large excess of reagent has no deleterious effect on the system.



·2
·1
0
absorbance
0
100
200
500
molar excess of reagent

Fig. 3.



1·4
0
absorbance
B
A
C
240
280
320
360
λ nm

Fig. 4.

Development of the Complex

Fig. 4 shows the absorption spectra of (A) the extracted reagent, and (B) the extracted complex, together with the extracted excess of reagent necessary for complete colour development, plotted against an ethyl acetate blank. Both spectra show strong absorption bands at 256 and 313 nm in the approximate intensity ratio 2:1. An examination of both the organic extract and the aqueous phase by measurement of the atomic fluorescence of selenium at 196.1 nm[31] in an air-propane flame indicated quantitative extraction of selenium, whereas no selenium was extracted in the absence of the reagent. This, taken together with the precipitation of a Se(IV)-2-mercaptobenzoic acid adduct in aqueous solution and the clear 1:3 stoicheiometry of the complex, q.v., is clear evidence of the existence of a complex, despite the apparent absence of bathochromic or hypsochromic shifts upon complexation when an ethyl acetate blank is used. When (B) is plotted against (A), however, the complex is the predominant absorbing species, and the two absorption maxima occur at 268 and 315 nm, the former being considerably more sensitive, as shown in (C).

Nature of the Reaction Product

Both the molar ratio method and the method of continuous variation clearly indicated the formation of a 3:1 reagent:Se(IV) complex at pH 2.3. This result was confirmed in a preliminary investigation of the application of the reagent to the gravimetric determination of selenium. It seems probable that the three sulphur atoms form σ-bonds with the selenium atom, which are stabilised by π-bonding between the sulphur d orbitals and Selenium d electrons, and one oxygen also forms a σ-bond with the selenium atom: It is possible that all three ligand molecules are identical. The mole-ratio plot and the Job plot obtained for this system are shown in figs. 5 and 6.

Effect of Temperature

Temperatures between 0^{o} and $70^{o}C$ had no significant effect on the system provided that a hundred-fold excess of reagent was used, and the blank was prepared under identical conditions to the test solution. The solutions must, however, be cooled before extraction, because of the volatility of ethyl acetate.

Beer's Law and Sensitivity

The system was employed over the range 0.02 to 12 ppm in the organic phase, and 0.008 to 4.8 ppm in the aqueous phase. Beer's law was obeyed over the range 0.02 to 4.0 ppm (concentrations in the organic phase), and the molar absorptivity over this range was found to be $e_{268nm} = 15,600$. A calibration curve, based on ten replicates for each point, is shown in fig. 7: The variation in standard deviation taken from the calibration curve is shown in table II.

Interferences

Two hundred-fold excesses of the following ions caused less than 3% interference in the determination of a 1 ppm (concentration in the organic phase) selenium solution: Na^{+}, K^{+}, Al^{3+}, Ga^{3+}, Ca^{2+},

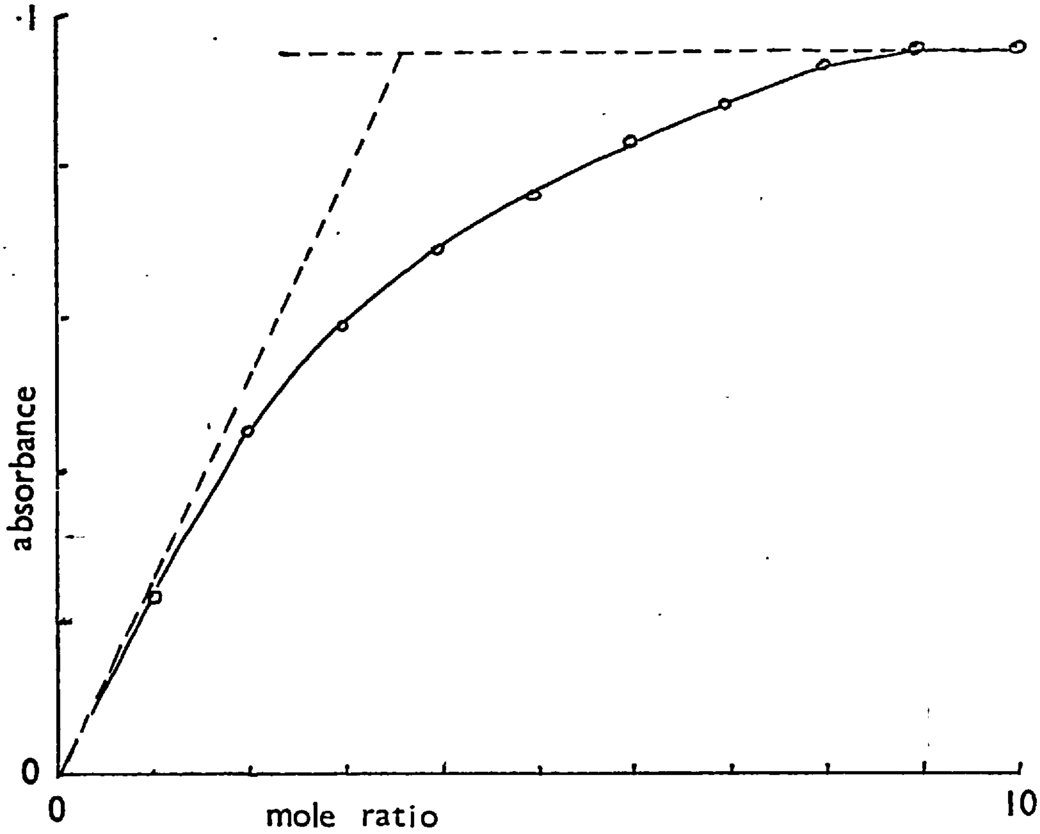


Fig. 5.

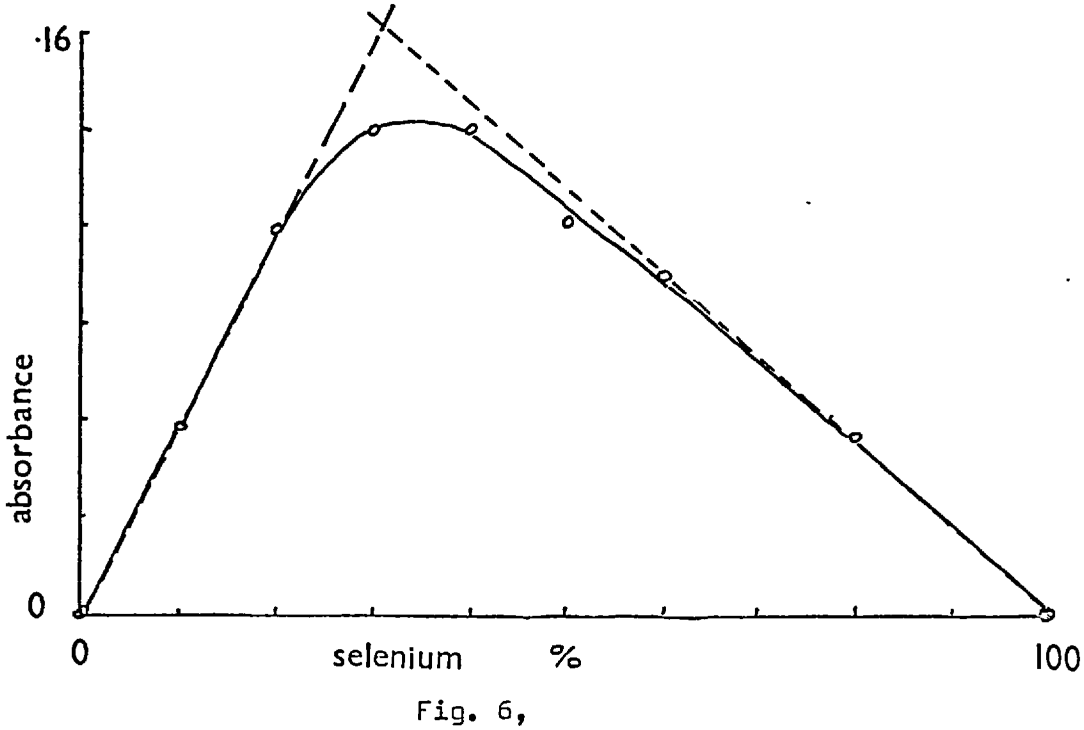


Fig. 6,

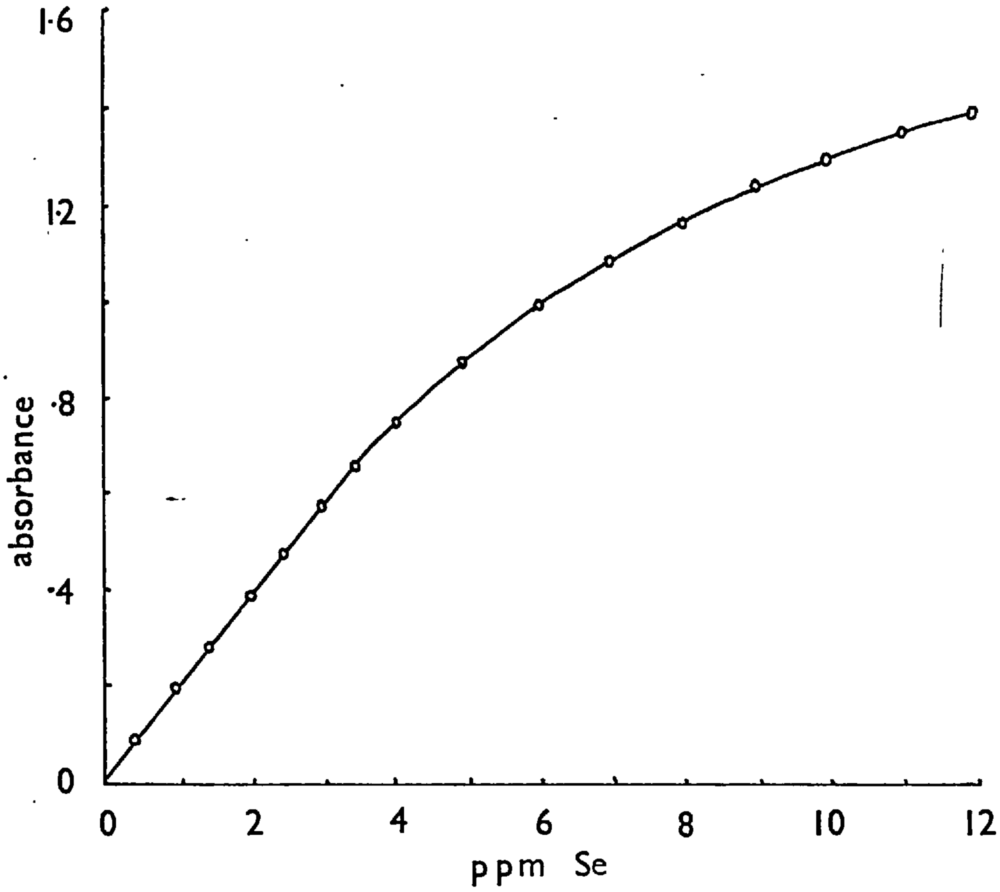


Fig. 7.

TABLE II

Conc. of Se (IV) ppm.	Absorbance Range	$\overline{A}$	St. Dev.	Rel. St. Dev. %
0.02	0.003 - 0.009	0.006	0.002	33.3
0.50	0.092 - 0.096	0.094	0.002	2.1
1.00	0.188 - 0.193	0.190	0.003	1.5
2.00	0.376 - 0.386	0.380	0.004	1.1
3.00	0.560 - 0.575	0.570	0.006	1.1
4.00	0.750 - 0.770	0.760	0.008	1.1

Precision Data for the Determination of Selenium with MBA.

Sr^{2+}, Ba^{2+}, Cd^{2+}, Mg^{2+}, Be^{2+}, Zn^{2+}, Fe^{3+}, SeO_4^{2-}, SO_4^{2-}, TeO_4^{2-}, PO_4^{2-}, NO_3^-, F^-, Cl^-, Br^-, $C_2O_4^{2-}$ and CH_3COO^-. Fe^{2+}, Sn(II), SO_3^{2-} and I^- interfere by reducing Se(IV) to the metal, and must be removed by preliminary oxidation. The tolerance limits (taken as the molar excess causing an interference of ± 3%) for the major interferences were as follows: Ni^{2+}, Co^{2+}, Ag^+, Li^+, Mn^{2+} and CN^-, ten-fold; Zr(IV), two-fold; Te(IV), one tenth. Mercury (II) must be absent, since the reagent is more sensitive for mercury than for selenium.

Li^+, Cu^{2+}, Ni^{2+} and Mn^{2+} can be removed quantitatively by total ion exchange. A suitable quantity of ZeoKarb 225 cation exchange resin in the H^+form is added to the neutral sample solution, which is then shaken or stirred for twenty minutes. In the absence of elements which form insoluble hydroxides, Cu^{2+}, Co^{2+}, Ni^{2+} and Ag^+ can be removed as their ammine complexes in the presence of an excess of 0.880 S.G. ammonia solution, by shaking as above for only two minutes. At the pH used, zirconium can be masked with E.D.T.A., and tellurium can be quantitatively removed[32] by extracting from 5F HCl solution with three aliquots of 5% tribenzylamine in chloroform. The sample solution must then be washed with three 10 ml aliquots of chloroform, and its pH adjusted to 2.3 with 4F ammonia solution. Provided that a blank is made up under identical conditions, this procedure gives results within 3% even when large excesses of Te(IV) are present. The results of the analyses of some synthetic samples containing some interfering ions are shown in table III.

TABLE III

Conc. of Se(IV) ppm	Interfering Ion	Molar Excess	Se(IV) found ppm	Error %
0.80	Te(IV)	1,000	0.81	+1.3
2.00	Te(IV)	5,000	1.98	-1.3
0.80	Ag^+	1,000	0.79	-1.3
0.80	Ni^{2+}	1,000	0.78	-2.5
0.80	Mn^{2+}	1,000	0.78	-2.5
0.80	Cu^{2+}	1,000	0.79	-1.3
0.80	Li^+	1,000	0.78	-2.5
0.80	Zr^{4+}	250	0.78	-2.5

Effect of Foreign Ions on the Determination of Se(IV) by MBA Procedure.

Although Hg(II) is partially removed by both the tribenzylamine procedure and the ion exchange procedure, the reagent forms an extractable complex with mercury which absorbs very strongly at 268 nm. CN^- and I^- cannot be used as masking agents, however, because these ions themselves interfere, and must be removed during the preliminary treatment of the sample.

Routine Experimental Procedure

Apparatus Spectrophotometer with 1 cm silica cells; pH meter.

Reagents 10^{-3}F Mercaptobenzoic Acid Solution

0.1542 g of reagent (British Drug Houses Ltd.) treated with a two-fold molar excess of 2F sodium hydroxide solution and diluted to one litre. The solution should be discarded after two days.

10^{-3}F Selenium (IV) Solution

0.0790 g of pure selenium shot (Johnson and Matthey Ltd.) dissolved in 10 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid, with sufficient warming to aid dissolution and completely expel brown fumes: Dilute to one litre.

pH 2.3 Sodium Acetate Buffer

136.1 g of sodium acetate trihydrate and 400 ml of 2F hydrochloric acid diluted to one litre.

Tribenzylamine

5% Tribenzylamine (British Drug Houses Ltd.) in chloroform.

Ethyl Acetate and Chloroform

Laboratory grade reagents.

Diverse Ions

10^{-1}F solutions of various cations, usually as nitrates or chlorides, and of various anions, usually as sodium or potassium salts: Analytical grade reagents were used whenever possible.

Preparation of Calibration Curve

Pipette 0.01 - 1.00 ml of 10^{-3}F selenium solution

(0.79 - 79 g Se) and 20 ml of reagent solution into a 50 ml graduated flask. Add 10 ml of pH 2.3 sodium acetate buffer solution and dilute to volume. Extract the contents of the flask with 20 ml of ethyl acetate by shaking for *ca*. 30 seconds in a separating funnel. Allow the layers to separate, discard the aqueous phase, and run the ethyl acetate layer into a 1 cm silica cuvette. Prepare a blank by taking all the reagents, except selenium, through the above procedure. Measure the absorbance of the test solutions against the blank solution at 268 nm. The calibration curve is linear over the above range, and passes through the origin. Extraction and colour measurements may be made immediately or within a total lapsed time of two hours.

Determination of Unknowns

Take an aliquot of the test solution containing less than 79 µg of selenium (IV) in $<$18 ml and proceed as above.

(a) If they are present in the original sample, Fe (II), Sn (II), I^- and CN^- should be oxidised with a mild oxidising agent which can itself be readily removed (e.g. bromine water), before proceeding with the method. Se (VI) which may be formed can be readily reduced to Se (IV) by refluxing for 20 minutes with the minimum volume of concentrated hydrochloric acid necessary to effect solution.

(b) If Co^{2+}, Cu^{2+}, Li^+, Ni^{2+}, or Mn^{2+} is present, add 1 g (approx.) of a strong cation exchange resin (e.g. ZeoKarb 225

(H^+)), and shake or stir mechanically for twenty minutes. Decant and wash the resin with the minimum amount of water before proceeding as in (a). The ion exchange time can be cut to two minutes for Co^{2+}, Cu^{2+}, Ni^{2+} and Ag^+ by the addition of an excess of ammonia solution before applying ion exchange.

(c) When zirconium is present, e.g. 200 - 300-fold excess, add 10 ml of 10^{-1}F E.D.T.A. solution before proceeding as in (a).

(d) If Te (IV) is present, make the test solution ca. 5F in HCl by adding concentrated hydrochloric acid. Shake with three successive 50 ml aliquots of 5% tribenzylamine in chloroform. Discard the organic phases, and shake the raffinate with three 10 ml aliquots of chloroform. Finally adjust the pH of the aqueous phase to ca. 2.3 with 4F ammonia solution and proceed as usual. This procedure is capable of dealing with 5,000 formal excesses of tellurium.

In all instances the blank solution should be treated as the test solution with all reagents, extractions, etc.

Conclusion

2-Mercaptobenzoic acid is one of the most sensitive reagents available for the absorptiometric determination of Se (IV). Interferences are few, and all those encountered except that of Hg (II) are readily overcome by simple separation or masking procedures. The stability of the reagent is as good as or better than that of other reagents which have been suggested for the determination of selenium, and the procedure developed is rapid to use.

Chapter III The Absorptiometric Determination of Selenium with Cyclohexanone

Selenium dioxide has been used for several years in organic chemistry as a reagent for the selective oxidation of aliphatic mono-ketones to α-diketones: Although Goto and Kakita[33] have reported the extraction of selenium and a range of other elements into hexone, and Jordanov and Futekov[34,35] have investigated the highly selective extraction of the complexes of selenium and a range of simple aliphatic mono-ketones into chloroform and carbon tetrachloride, the reaction has only been investigated as a solvent extraction procedure.

Nature of the Reaction

Since the reaction occurs in strong hydrochloric acid solution, but not in sulphuric acid[35], it is reasonable to suppose that the anion $SeCl_6^{2-}$ is extracted initially as a simple ion association system with two protonated ketone molecules into an excess of ketone. Jordanov and Futekov have reported[35] the formation of a 1:1 complex with a number of aliphatic ketones, which can be extracted into chloroform and carbon tetrachloride, but these reactions are only complete after several hours at room temperature. It is possible that the selenium is forming a complex with the doubly protonated di-ketone which is produced upon the oxidation of the mono-ketone. If this is in fact the case, it should be possible to develop a highly selective procedure for the quantitative determination of trace amounts of selenium, because the other elements which are extracted into hexone from hydrochloric acid solution [33] are extracted as ion association systems. Since the completion of the work in chapters three and five, Dagnall, Taylor and West have shown[36] that once selenium has been extracted into hexone, it cannot be back-extracted into an aqueous phase, which indicates that even when the anionic chloro-complex is extracted into the ketone, the system is not simply an ion association system; moreover, the reaction of SeO_2 on mono-ketones proceeds with the formation of elemental selenium, and although the system used here for the determination of Se (IV) and Se(VI) involved the simultaneous production of colloidal selenium, this was not observed by Jordanov and Futekov at room temperature. It is therefore not possible to assign the absorbance measurements made in this chapter to any particular species in solution. Under the conditions employed, Se (VI) is rapidly and quantitatively reduced to Se (IV), so that the initial oxidation state of the selenium is not important, an unusual advantage for a spectrophotometric procedure.

Experimental Procedure

Apparatus Spectrophotometer, 1 cm silica cells.

Reagents Cyclohexanone

Reagent grade cyclohexanone (British Drug Houses Ltd.), used without further dilution.

Selenium (IV) Solution

Dissolve 0.100 g of selenium powder (ANALAR, British Drug Houses Ltd.) in 5 ml of concentrated hydrochloric acid and 1 ml of concentrated nitric acid: Warm to aid dissolution, and heat gently to expel brown fumes. Because nitrate must be removed completely, it is advisable to add 1 ml of concentrated sulphuric acid, to prevent loss of selenium chloride. Cool, and dilute to one litre. 1 ml = 100 μg Se.

Selenium (VI) Solution

Dissolve 0.227 g of ammonium selenate (British Drug Houses Ltd.) in water, and dilute to one litre. 1 ml = 100 μg Se.

Diverse Ions

A range of metal solutions as chlorides, and anion solutions, as sodium or potassium salts, was made up. Analytical reagent grade salts were employed whenever possible.

Preparation of Calibration Curve

Pipette 0.02 to 1.0 ml (2 - 100 μg) of stock selenium solution (Se (IV) or Se (VI)) into a series of ten ml graduated flasks. Add cyclohexanone (0.1 ml) and concentrated hydrochloric acid (6.0 ml), and dilute to volume with distilled water. Pour the resulting solutions into dry test tubes, and warm for five minutes in a boiling water bath; cool under cold running water for one minute, and measure the absorbance of the test solution, at 345 nm, against a reagent blank prepared under identical conditions.

Determination of Unknowns

Treat <100 μg in 4.9 ml of aqueous solution as above. If metals which form chloro-complexes which absorb at 345 nm are present, measure the absorbance of a sample prepared as above, but without the addition of cyclohexanone, against a distilled water blank, and subtract this absorbance from the absorbance obtained by the normal procedure. This process can be applied in the presence of up to 100 μg Fe^{3+}, 5,000 μg Co^{2+} and 500 μg Cu^{2+} in the determination of 10 μg of selenium.

Tellurium interferes with the reaction, and must be removed, e.g., by extraction with tribenzylamine into chloroform[32,37] (cf. page 18).

Oxidising agents, such as nitrate, interfere, and must be removed (nitrate can be removed by heating to fumes in the presence of a small amount of sulphuric acid). Reducing agents such as SO_3^{2-}, I^- and Sn (II) also interfere, and must be removed, or oxidised with an easily removable oxidising agent such as bromine water.

Spectral Characteristics

The absorption spectrum obtained from 100 μg of selenium in 10 ml of solution plotted against a reagent blank in 1 cm cuvettes is plotted in fig. 8.

Effect of Acid Concentration

The dependance of the absorbance at 345 nm upon the acid concentration is shown in fig. 9: This shows that the

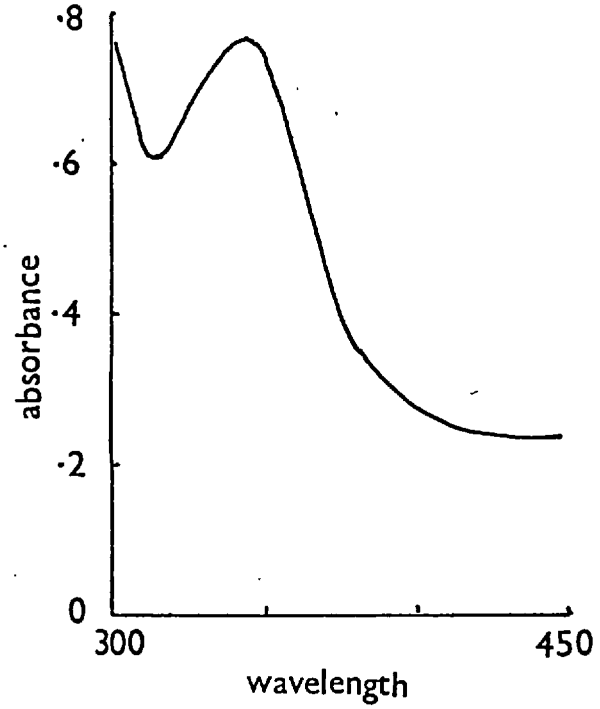

·8
·6
·4
·2
0
absorbance
300
450
wavelength

Fig. 8.

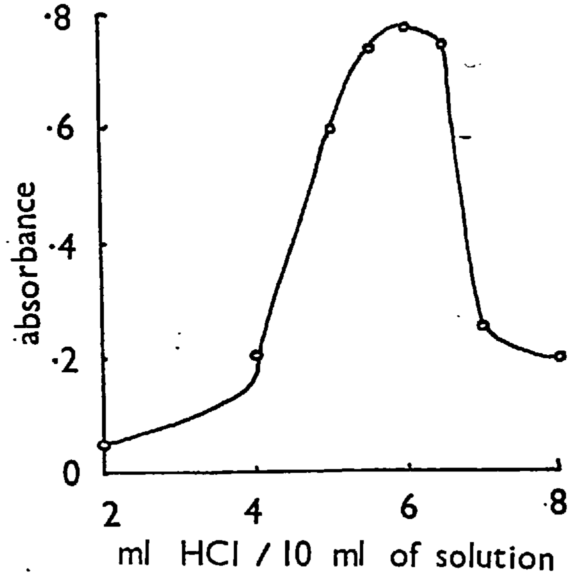

·8
·6
·4
·2
0
absorbance
2
4
6
·8
ml HCl / 10 ml of solution

Fig. 9.

hydrochloric acid concentration must be carefully controlled, and the acid was therefore added from a 50 ml burette.

Effect of Time

At room temperature the reaction is only complete after eighteen hours, and the wavelength of maximum absorbance shifts to 375 nm; this shift might be attributable to the formation of one or more different compounds. At the temperature employed here, however, the reaction is complete within five minutes. The effect of heating time is shown in fig. 10. After formation, the absorbance remains constant for at least two hours.

Effect of Reagent Concentration

The wavelength of maximum absorption increases steadily as the ketone concentration is increased, whereas the absorbance at this wavelength increases only slightly. A volume of 0.1 ml of cyclohexanone per 10 ml of solution was finally selected, because higher concentrations of ketone gave rise to turbid solutions and a much lower precision.

Beer's Law and Sensitivity

A linear calibration curve is obtained over the range 0.05 ppm to 10.0 ppm, and the extinction coefficient is e_{345} = 5,600 (see fig. 11).

Precision

The standard deviation per cent, based on ten determinations, was found to be 50%, 1.8% and 1.3% at 0.05,

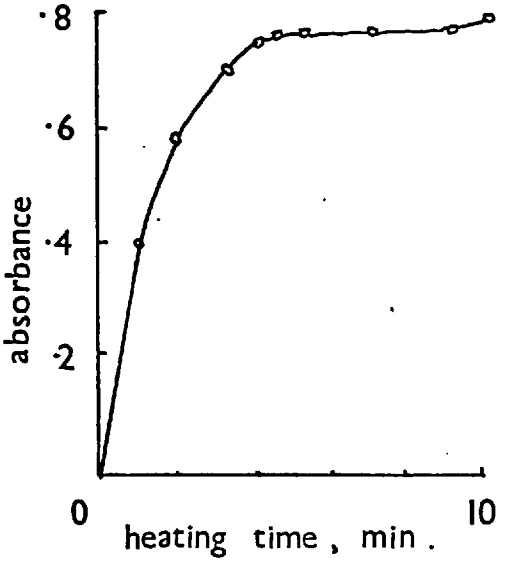

·8
·6
·4
·2
absorbance
0
10
heating time , min .

Fig. 10.

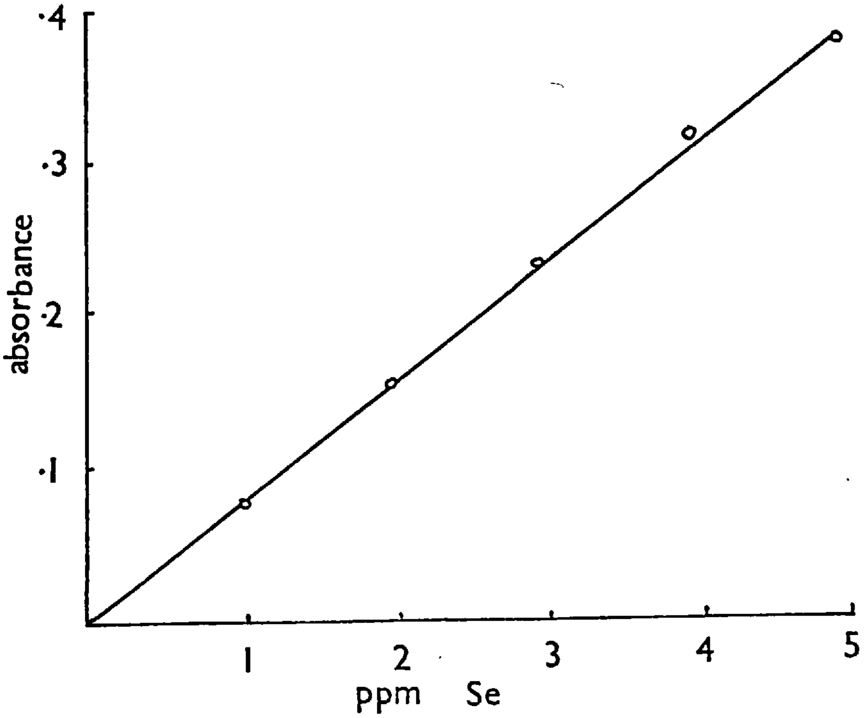

·4
·3
·2
·1
absorbance
1
2
3
4
5
ppm Se

Fig. 11.

1.0 and 5.0 ppm respectively.

Interferences

200-fold excess of the following ions caused less than 3% interference in the determination of 1 ppm of selenium: Al^{3+}, Ba^{2+}, Be^{2+}, Ca^{2+}, Cd^{2+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, NH_4^{+}, Ni^{2+}, Zn^{2+}, Br^{-}, Cl^{-}, F^{-}, SO_4^{2-}, citrate, oxalate and tartrate.
Of the ions tested, Fe^{3+}, Co^{2+} and Cu^{2+} interfere because of the absorbance of their chloro-complexes at 345 nm. Oxidising agents, reducing agents and tellurium interfere, and must be removed prior to the determination. The results obtained for the analysis of some synthetic samples are shown in table IV.

TABLE IV

Se taken μg	Interference	Se found μg	Error
10	100 g Fe^{3+}	9.8	-2%
10	100 g Cu^{2+}	10.3	+3%
10	250 g Cu^{2+}	10.4	+4%
10	1000 g Co^{2+}	9.9	-1%
10	2000 g Co^{2+}	9.8	-2%
10	500 g Te (IV)	9.8	-2%

Determination of Selenium in the Presence of Some Interfering Ions

Conclusion

Cyclohexanone is a useful reagent for the rapid determination of trace amounts of both Se (IV) and Se (VI).

Although the reagent is slightly less sensitive than some of the other reagents which have been proposed for the determination of selenium, it is unnecessary to make up a solution of the reagent, which is very stable compared with some of the reagents used for the determination of selenium. Although fairly careful control of the heating time is necessary, the method is also rapid compared to many of the other methods currently in use.

Chapter IV The Determination of Selenium with 4-Amino-4-chlorodiphenyl

During an investigation of the application of substituted benzidenes and related compounds in analytical chemistry, Belcher, Nutten and Stephen[38] reported that 4-amino-4'-chlorodiphenyl is a more sensitive reagent for the determination of trace amounts of sulphate than the widely used barium chloride. Titrimetric[38] and spectrophotometric[39] methods have been developed based on this reagent, and Belcher and Stephen have shown[40] that the reagent can detect as little as 0.1 ppm of sulphate by a precipitation reaction in a volume of 50 ml: This sensitivity is about ten times better than the basic nephelometric method with barium chloride. Martin and Stephen developed a nephelometric procedure for the determination of 2.5 to 25 ppm of sulphate[41] with this reagent (trivial name CAD), and later improved the colloidal stabiliser used in the method[42].

In their original paper[38], Belcher and his co-workers noted that selenate, tellurite, phosphate and oxalate interfered in the determination of sulphate with CAD: As selenium can be separated from these other ions by ion exchange[43], it was decided to make a brief investigation of the application of the reagent to the determination of trace amounts of selenium as selenate.

Experimental

Preparation of CAD The method used for the preparation of the reagent was identical to that used by Gray, Hartley and Jones[44] and by Belcher, Nutten and Stephen[38]. The exact quantities used were as follows:

To 6.7 g of 4-chloro-4'-nitrodiphenyl (Koch Light) add 5.8 g of electrolytic grade iron, 50 ml of ethanol, and 2.9 ml of concentrated hydrochloric acid: Reflux on a steam bath for ~12 hours, and then add 2.2 g of anhydrous sodium carbonate and stir for thirty minutes: Add a slight excess of dilute aqueous ammonia, cool rapidly in an ice-salt mixture, add 200 ml of ether, shake, and filter: Wash the precipitate with two 25 ml aliquots of ether, and reject the precipitate. The ether is boiled off from the combined filtrate and washings at reduced pressure, and the resulting slurry is stirred with 60 ml of distilled water; the amine is filtered off, washed with water, and dried in vacuuo. As the resulting colourless crystals melted sharply at 127.5°C (lit. 128°), the compound was not purified further.

Preparation of CAD Selenate

1 g of the base was dissolved in the minimum volume of 50% aqueous acetone, and an excess of ammonium selenate solution, also in aqueous acetone, was added. The precipitate was filtered off, washed with ether, and dried in vacuuo.

Determination of the Solubility of CAD Selenate

The solubility of the selenate was determined by adding an accurately weighed amount of the selenate (*ca.* 0.1 g) to one litre of distilled water and stirring for twelve hours. The excess selenate was then filtered off, dried and weighed; the amount of selenate dissolved, 17.7 ± 1.8 mg l^{-1}, is possibly slightly low, due to the inclusion of some dissolved selenate in the precipitate. It should be pointed out that this solubility is almost certainly lowered in the presence of an excess of CAD. Measurement of the UV absorbance of the excess reagent in solution obtained as above, compared with the absorbance of a suitably diluted aliquot of the stock reagent solution, indicated a solubility of 14 mg l^{-1} for CAD selenate.

Reagents CAD Solution

To 0.2035 g of CAD, add 3 ml of 2F hydrochloric acid, and dilute to *ca.* 90 ml; warm to aid dissolution, cool, and dilute to 100 ml. This solution corresponds to a 10^{-2}F solution of CAD hydrochloride in 0.05 F hydrochloric acid. Under these more acid conditions, the solubility of the selenate is probably appreciably lower than indicated above.

Selenate Solution

Dissolve 0.1889 g of sodium selenate in water, and dilute to 100 ml; the resulting solution is 10^{-2}F with respect to selenium and selenate.

Construction of Calibration Curve

To 0 to 3 ml of 10^{-2}F selenate solution, add 8 ml of 10^{-2}F reagent solution, and dilute to 12 ml. Allow to stand for twenty minutes, and filter: The selenium may then be determined either by washing the precipitate with a previously saturated solution of CAD hydrochloride, drying, and weighing (fig. 12), or by diluting the filtrate (by a factor of 10^4), and measuring the absorbance of the excess CAD hydrochloride (fig. 13).

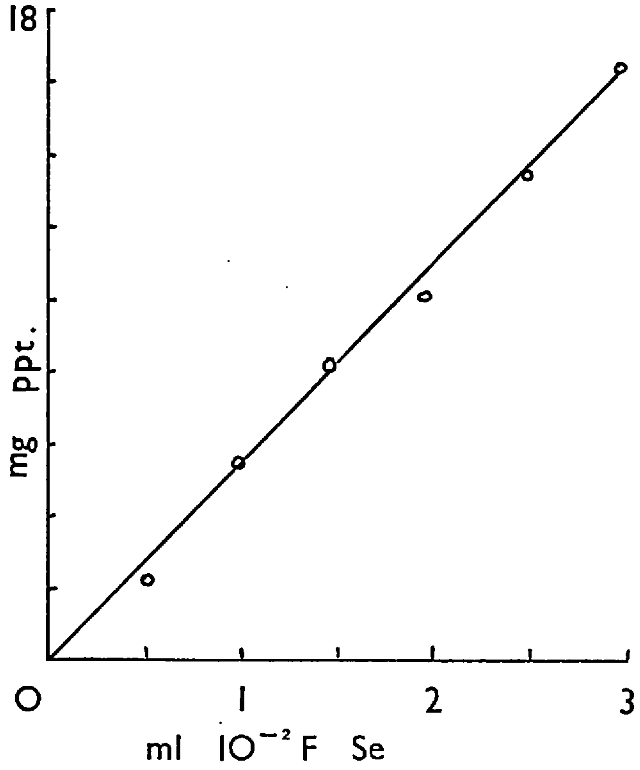


Fig. 12.

Treatment of Unknowns

Treat 4 ml of solution containing 0.0024 g of Se (VI) in neutral solution as above.

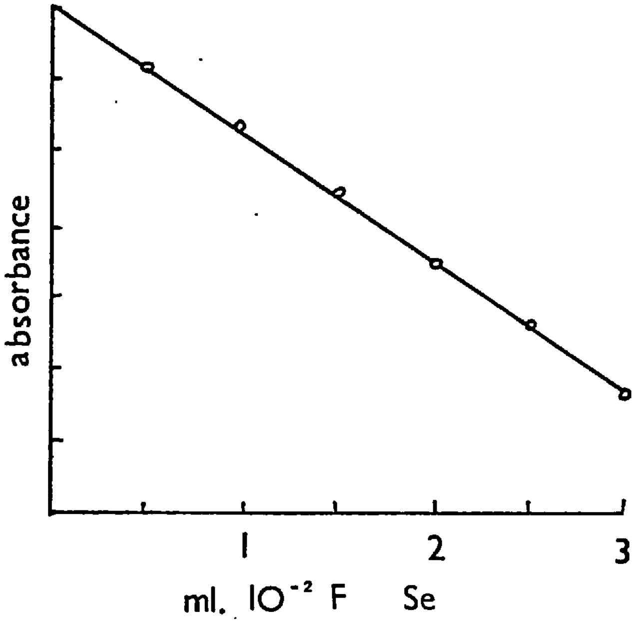


Fig. 13.

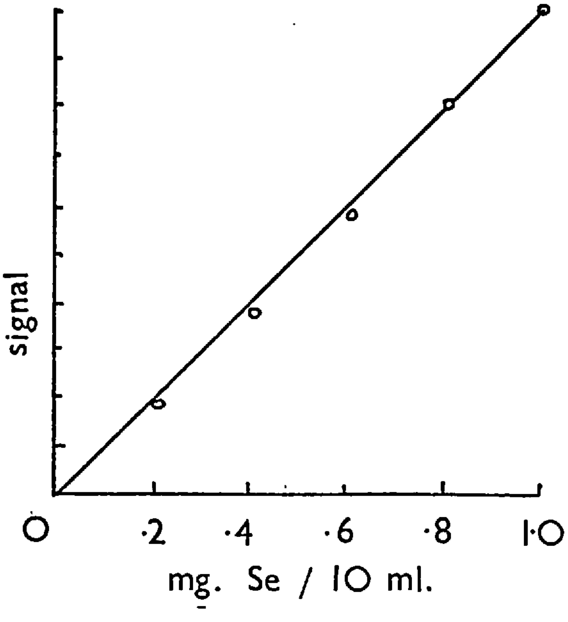


Fig. 14.

Preliminary Investigation of the Nephelometric Determination of Selenium (VI) with CAD

The results of a preliminary investigation of the application of CAD to the nephelometric determination of selenium are shown in the calibration curve in fig. 14. The procedure adopted was virtually identical to that used for the determination of sulphate[42], but the sensitivity obtained was about twenty-five times worse than that obtained for sulphate.

Procedure

12 ml of hot reagent (held at 70°C on a stirrer/heater) is added to 10 ml of hot sample solution (on a thermostatted hot-plate) containing 0 to 1 ml of Se (VI) at pH ca. 7 in a 50 ml beaker; the resulting solution is cooled to 50°C in an ice-water bath: Two minutes after the onset of crystalisation, add 0.5 ml of chilled gum-ghatti solution (prepared as in reference 42), and dilute to 45 ml; add a further 0.5 ml of gum-ghatti solution, and dilute to 50 ml. Set full scale deflection for the highest selenium concentration, and read off the other selenium solutions.

Conclusion

Although only a brief investigation has been made of the applicability of CAD to the determination of selenium, and it is possible that a more thorough investigation could lead to significant improvements in the results obtainable, it seems that the following points limit the applicability of the method:

(a) SO_4^{2-}, TeO_3^{2-}, PO_4^{3-} and oxalate must be absent or removed.

(b) The sensitivity of the method is not particularly good.

(c) For the determination of µg quantities of selenium, titrimetric procedures are probably more rapid and more precise.

Chapter V The Determination of Selenium by Atomic Fluorescence Spectroscopy

The high excitation potential of selenium (6.3 eV) prevents the determination of the element by thermal emission in conventional flame cells, although the element has been determined in the primary cone of air-acetylene and argon-oxygen-acetylene flames by chemiluminescence[45]: By this method, using burners designed to give elongated primary reaction zones, detection limits of 50 and 25 ppm were obtained for these two flames. The introduction of atomic absorption spectroscopy lead a number of workers to attempt to apply this technique to the determination of selenium: Initially, however, difficulty was experienced in preparing stable atomic line sources for the element. Rann and Hambly[46] employed RF discharge tubes containing selenium or a sulphur-selenium mixture, excited by a 15 Mc sec^{-1} RF transmitter, but found that very careful control of the filling pressure and the power supply was necessary to maintain the selenium discharge at a low selenium pressure, which is necessary to minimise self-reversal of the selenium resonance lines. The same workers have also employed hollow cathode lamps[47]: These had either hollow copper cathodes packed with copper selenide, or drilled spectrographic carbon rods in which the central hole had been soaked with molten selenium in vacuuo. Both of these were susceptible to deposition of selenium on the walls of the tube. Allen employed a continuous source[48] and a medium quartz spectrograph, and obtained a detection limit of 5 ppm for selenium. Since this early work, selenium has been determined by atomic absorption in a range of materials[49]: The sensitivities obtained (concentration giving 1% absorbance) on a number of modern instruments, taken from the instrument manufacturers data available at the end of 1969, are shown in table V below:

TABLE V

Instrument	Sensitivity, ppm.
Jarrell-Ash Atomsorb	1.0 ppm.
EEL 140	2.0 ppm.
Hilger & Watts Atomspek	0.5 ppm.
Southern Instruments A3000	0.1 ppm (Detn. limit).
Perkin Elmer 303	0.1 ppm (Detn. limit).

Some Sensitivities for Selenium by Atomic Absorption.

It should be remembered that drift in the source output is less important in atomic absorption when a double-beam instrument is used, than it is in atomic fluorescence spectroscopy, where at present no double-beam instrumentation is currently available, although it is theoretically possible to construct a double-beam atomic fluorescence spectrometer, provided that a linear relationship exists between the fluorescence signal and the integrated line intensity of the source.

Selenium has been determined by atomic fluorescence by Dagnall, Thompson and West[31,50,51], by Marshall and West[52,53], and by Winefordner and co-workers[54], and since the completion of this work, by Dagnall, Taylor and West[55]. These workers obtained detection limits of between 10 ppm and 0.18 ppm; microwave frequency electrodeless discharge tubes were used throughout as sources of irradiation.

The apparatus used in the present investigation consisted of a Southern Instruments A1740 Grating Flame Photometer, fitted with Hamamatsu UV sensitive photomultipliers and a grating blazed at 300 nm. The monochromator provided with this instrument provides facilities for automatic flame background correction, by passing the flame background immediately on either side of the line under investigation onto a second photomultiplier. D.C. background correction must be used in this instance, however, because of the proximity of other lines in the fluorescence spectrum of selenium. The monochromator has a fixed entrance and exit slit-width of only 0.1 mm, which is appreciably less than the slit-widths normally used by other workers. Using this instrument in conjunction with a selenium electrodeless discharge tube (prepared as described in reference 70) operating in a quarter wave cavity at 2450 MHz, a detection limit of 1 ppm was obtained for selenium at 196.1 nm for aqueous solutions sprayed into an air-acetylene flame, using a twenty second integration period. When the A1740 monochromator was replaced by the A1750 monochromator, which has an adjustable slit mechanism that gives six possible monochromator entrance and exit slit widths between 0.025 and 1.0 mm, and a slightly modified burner housing, both of which are described in more detail in chapter eight, a detection limit of 0.2 ppm was obtained: This limit was further improved to 0.1 ppm when a phase-sensitive pre-amplifier was used in conjunction with the above system (see chapter eight). Twenty second integration periods were used throughout, and in every case the detection limit was taken as the concentration for which the signal is twice the standard deviation.

Improvement of Detection Limit

Although detection limits can be improved considerably by using lower background hydrogen flames, these flames are far more susceptible to chemical interferences than the hotter acetylene flames, a point which is discussed more fully in chapter nine: The same can be said of the sampling-boat system, which improves the A.A.S. detection limit for selenium by a factor of ten[56]. Non-flame cells should be particularly useful for the determination of selenium, but are outside the scope of this thesis. It was, therefore, decided to investigate the possibility of increasing the intensity of the source of irradiation, and of employing a solvent extraction/

concentration step to improve the detection limit.

Some Discharge Tube Sources for A.F.S.

A large number of electrodeless discharge tubes were made at pressures between 0.1 Torr (continuous pumping on the vacuum line used) and 8 Torr, containing the following substances and argon as a filler gas: Se, Se_2Cl_2, Se/Se_2Cl_2, $SeCl_4$, $Se/SeCl_4$, Se/excess Br_2 and Br_2/excess Se. It was initially hoped that the more volatile selenium halides would give greater intensity and better stability than the elemental selenium normally used in discharge tubes. The effect of the operating power on the intensity, the noise level, and the long term drift was examined for all of the tubes made, in both the $\frac{3}{4}$ and the $\frac{1}{4}$ wave cavities. It appeared initially that tubes containing bromine with an excess of selenium, and selenium tetrachloride, both with an argon filler gas, and both operating in the $\frac{1}{4}$ wave cavity at 50 w, would be more satisfactory than tubes containing elemental selenium, as these tubes were found to be approximately ten times more intense than tubes containing the element alone, and had overall drift rates of 1.0% and 2.2% per hour respectively: Unfortunately all three tubes containing $SeCl_4$ and both of the Se/Br_2 tubes had operating lives of between six and eight hours, whereas tubes containing elemental selenium appear to have operating lives of several hundred hours. All of the fluorescence measurements were therefore made with tubes constructed and operated as described by Dagnall, Thompson and West[50,51]. Fig. 15 shows the calibration curve obtained using a tube operated under these conditions in conjunction with the fully modified system described above.

The Application of the Solvent Extraction of Selenium to A.F.S.

Possible extraction procedures that could be applied to the flame spectroscopic determination of selenium include the extraction of the selenium dithizone complex into chloroform[27], the extraction of the selenium MBA complex into ethyl acetate[57], the extraction of the selenium thioglycollic acid complex into ethyl acetate[22], the extraction of selenium keto-chloro complexes into chlorinated organic solvents[34,35], and the extraction of selenium into hexanone from strong hydrochloric acid solution[33]. Of these, the latter is probably the most useful, because no additional reagent is required, and because hexone is a suitable solvent for flame spectroscopy.

The extraction process has been investigated gravimetrically by Goto and Kakita[33], who reported a 99.12% extraction from 8.5 F HCl solution. The effect of acid concentration on the extraction was investigated here by measurement of the atomic fluorescence from both the aqueous and the organic phases: The results obtained for the organic phase for a 1:1 extraction of 100 ppm of selenium are shown in fig. 16, and substantiate that maximal extraction is

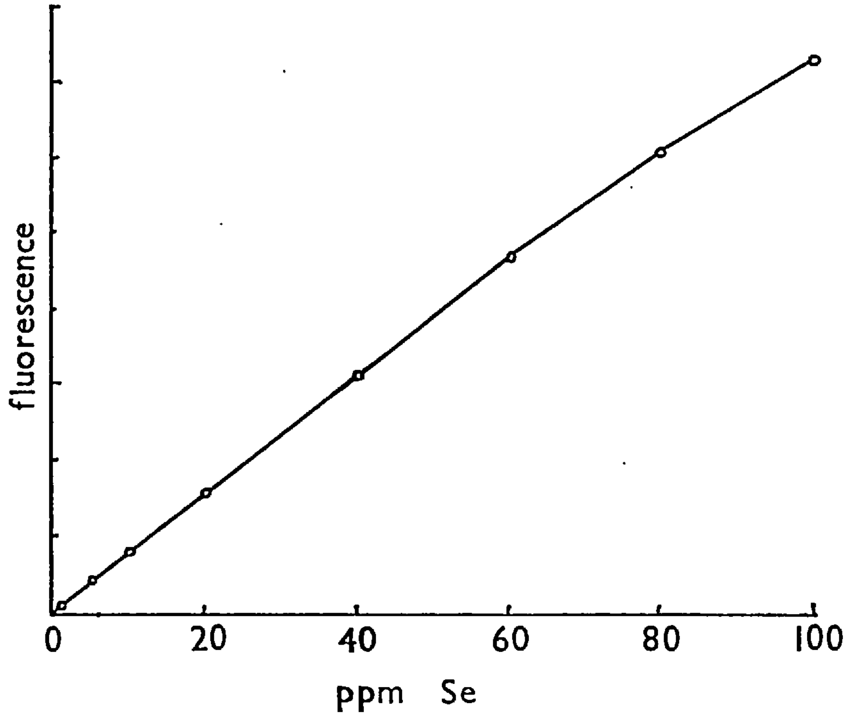

fluorescence
0
20
40
60
80
100
ppm Se

Fig. 15.

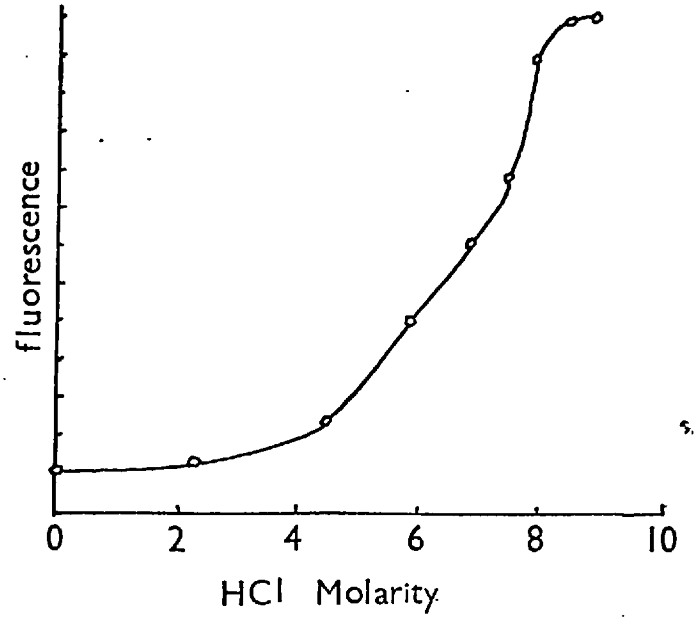

fluorescence
0
2
4
6
8
10
HCl Molarity

Fig. 16.

obtained from 8.5 F hydrochloric acid.

The fluorescence signal from a given concentration of selenium in aqueous solution was found to be only 40% of that obtained from the same concentration of selenium in hexone solution: On the basis that the extraction is virtually quantitative, the increase can be attributed almost quantitatively to the 63% increase in the take up rate when hexone is used as the solvent. With the unmodified A1740, a linear calibration curve was obtained for aqueous solutions containing between 0.4 and 100 ppm of selenium, following extraction into the organic phase. The corresponding lower limit for the fully modified instrument was 0.04 ppm, although better detection limits could have been obtained by employing a simultaneous concentration/extraction step, eg., by using a 2:1 or 3:1 extraction.

Conclusion

Although this extraction procedure does not possess the same degree of selectivity as the extraction of the ketone-chloro complexes into chlorinated organic solvents[34,35], it is very much more rapid, and is particularly suitable for atomic fluorescence, where a high degree of extractive selectivity is not normally required, provided that the system gives reproducible recovery of the desired trace element, even if it concentrates simultaneously some of the other trace elements present: Provided there is no interaction between the two extraction systems, two elements can be extracted, and determined sequentially in the same extract. This type of system could be particularly useful when the two elements in question can be used in a dual-element electrodeless discharge tube[52,53,58] (see also chapter X). The only disadvantage of the system is that the quantity of acid present must be carefully controlled.

Chapter VI Suggestions for Future Work on the Determination of Selenium

There are several potential spectrophotometric reagents still to be investigated for the determination of selenium, in all three of the classes mentioned in chapter one, and only some of the more interesting possibilities will be considered here.

It was noticed during the work on MBA that this reagent is weakly fluorescent, although the fluorescence is not sufficiently intense to be used for the determination of trace amounts of selenium. The mercapto analogue of 2-hydroxy-3-naphthoic acid, shown below, could possibly be used for the spectrophotometric and spectrofluorimetric determination of selenium.

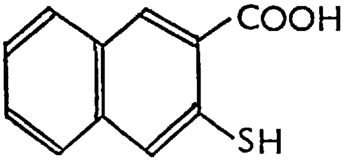


Fig. 17.

Another useful project would be to investigate the possibility of stabilisation of the ortho-diamines used in the piaz-selenol methods, either by weak compound or weak complex formation: Ideally the free diamine should be generated in solution as required by pH change or exchange reaction. Further studies of the reaction between selenium and aliphatic ketones could also lead to some interesting analytical reactions, since only one ketone was studied in detail in the present work. The selenocyanate ion, which is readily formed by reaction between selenium and sodium or potassium cyanide, might also provide the basis of a useful spectrophotometric method for the determination of selenium, by formation of a selenocyanato complex, although selenocyanates tend to be unstable in acid solution.

Kinetochromic methods were mentioned only briefly in chapter one. Most of the qualitative tests for selenium depend upon catalytic effects, however, such as the effect of Se^{o} on the reaction between S^{2-} and picric acid[59], and the catalytic effect of selenium on the reaction between S^{2-} and methylene blue[59], which has already been used for the determination of selenium. It seems likely that kinetic methods will become increasingly popular, because of their extreme sensitivity, especially if automated systems become available.

Possible developments in atomic fluorescence spectroscopy will be considered in a later chapter.

Chapter VII Introduction to Atomic Fluorescence Spectroscopy

The theoretical principals of atomic fluorescence spectroscopy have been discussed elsewhere[51,60 - 63], and will only be discussed here in so far as they effect the work in this thesis. Although thermally assisted processes were initially ignored in discussions of the excitation processes normally involved in atomic fluorescence spectroscopy (see fig. 18), several recent publications[64 - 67] have shown that mechanisms of this type can play an important role in atomic fluorescence spectroscopy. Fig. 19 shows diagramatically the types of process which can be included in this catagory. Although it has been stated[68] that the moderate intensity of continuous sources, such as the 450 w xenon arc, under absorption line profiles should excite fluorescence for only one or two lines for most elements, and in practice only a few lines are normally of sufficient intensity to be of any analytical utility, weaker resonance lines, and lines obtained by radiative excitation after preliminary thermal excitation play an important part in governing the number of interferences encountered in A.F.S. when a continuum is employed as a source of excitation, particularly if one bears in mind the facts that most workers have employed large analysing monochromator band passes when investigating the application of continuum sources, and that stepwise and direct line fluorescence from atoms in excited states reached by these paths must also be considered.

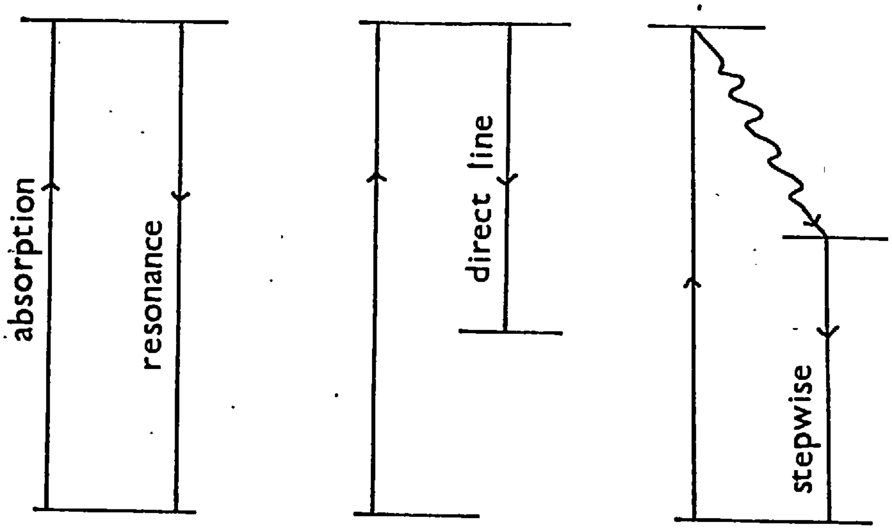

absorption
resonance
direct line
stepwise

Fig.18.

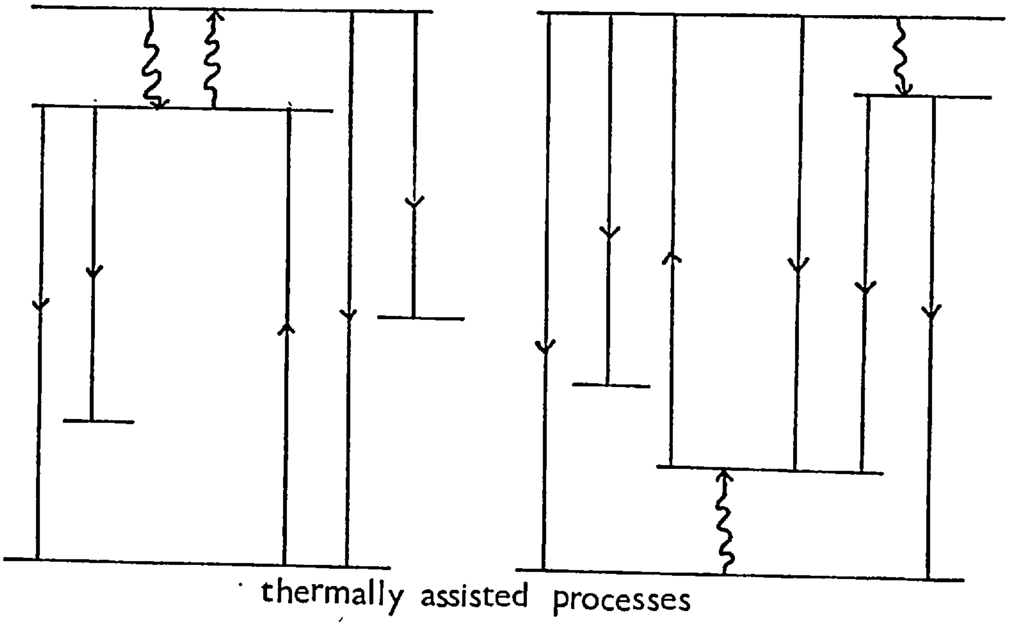

thermally assisted processes

Fig.19.

Fig. 20 shows the variation of $\frac{N^*}{N_o}$ with E, based on the equation:

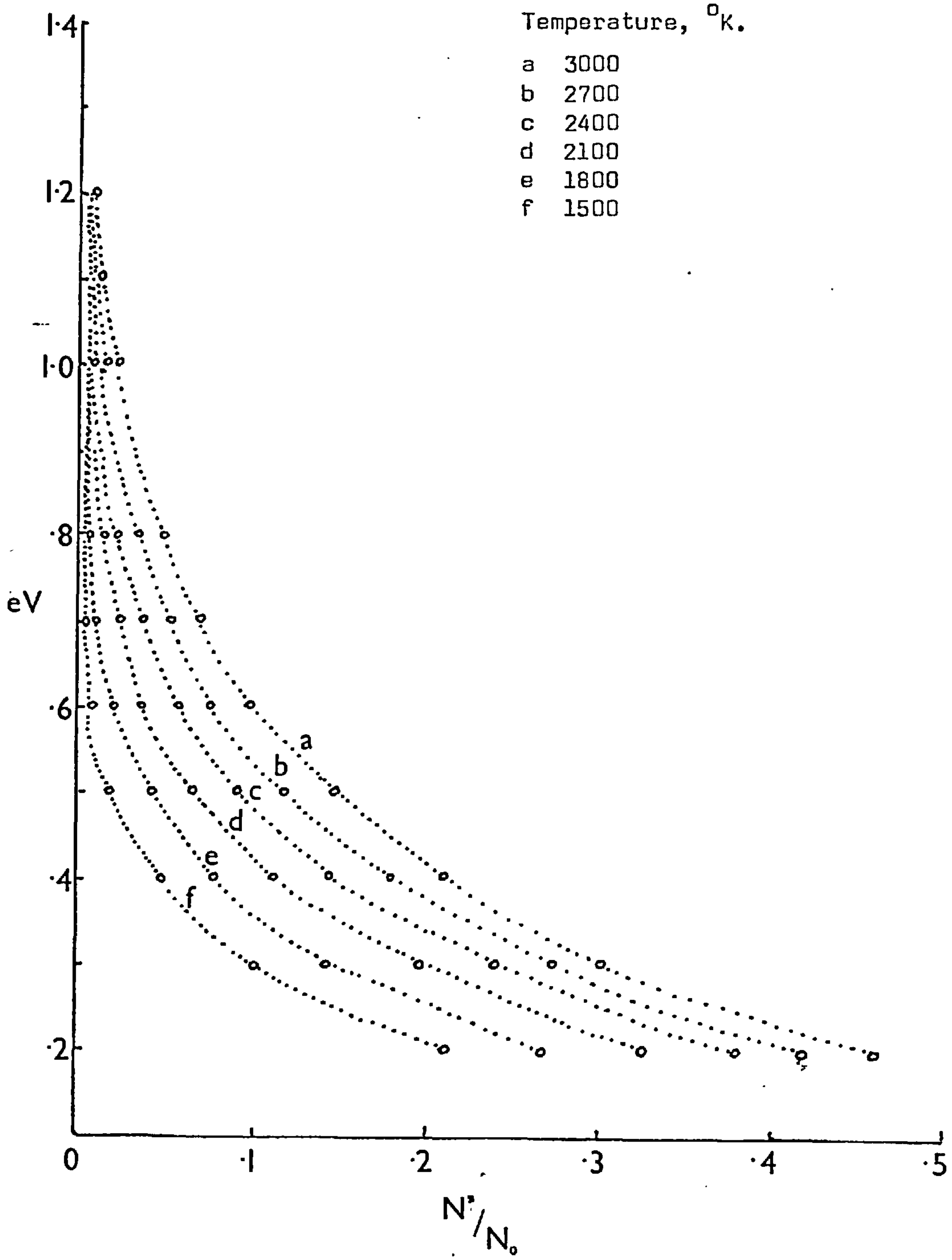
$$\frac{N^*}{N_o} = \exp - (\frac{E}{kT})$$

where N^* = number of atoms in excited state, N_o = number of atoms in ground state, k = Boltzman Constant, E = energy difference between ground state and excited state, and T = temperature in ^oK. Although this equation only applies under conditions of thermal equilibrium, and ignores possible degeneracy of energy levels, the curves in fig 20 do indicate that for elements with one or more energy levels close to the ground state, thermally assisted processes can play an important part in governing the total number and relative intensities of lines in a fluorescence spectrum over the temperature range normally employed in analytical A.F.S.

Some Instrumental Considerations in A.F.S.

Although the basic requirements of A.F.S. are always a source of irradiation, an atom cell, and a detector and read-out system, each of these substituents can assume a variety of forms. We shall concern ourselves here only with the detector and read-out system: If the fluorescence signal is passed *via* an analysing monochromator, resonance detector or filter onto a photomultiplier, a number of different amplification systems are then available. If the source of irradiation is unmodulated, a D.C. amplifier must be used: This type of system is particularly suitable if measurements are made above the region of the flame which exhibits thermal

Fig. 20.


Temperature, °K.
a 3000
b 2700
c 2400
d 2100
e 1800
f 1500
1·4
1·2
1·0
·8
·6
·4
·2
eV
0
·1
·2
·3
·4
·5
N'/N₀
a
b
c
d
e
f

emission, or if a low background, non-flame cell is used: Although readout is often simplified by smoothing the noise on the signal, this can only be done at the expense of increasing the time constant of the readout system, which limits the application of this system to fixed wavelength or slow scanning methods, where the atomic population in the cell is static for an appreciable period of time. A development of the above system is used in the Southern Instruments A1740 Grating Flame Photometer; this instrument provides facilities for integration of the photomultiplier signal with respect to time at fixed wavelength, thus providing a statistical elimination of random errors.

The second type of amplifier is used in conjunction with a mechanically or electronically modulated light source, and employs a frequency-tuned (filter) amplifier: This type of system has been used to obtain satisfactory detection limits for a number of elements by A.F.S., and will be considered further in the next chapter. The disadvantages of this type of system are that the band pass of the amplifier is not infinitely narrow, so that noise with a frequency close to that of the modulation frequency is also partially demodulated, so that the base line obtained is not linear with wavelength, and that the gain of the amplifier depends upon the stability of the modulation frequency if a narrow band filter is used.

The third type of amplifier, which is also described in more detail in the next chapter, also employs a modulated source of irradiation: In this instance, however, the amplifier is designed in such a way that only signals bearing a constant phase relationship with the modulation frequency are demodulated and amplified, so that noise with a random phase is rejected completely; amplifiers of this type are said to be "phase-sensitive". When this type of system is used in commercial atomic absorption instruments, a broad band pass filter is normally incorporated into a pre-amplification stage, to limit the frequency range that passes to the phase-sensitive amplifier. The base line obtained with systems of this type is generally much more stable than that obtained with simple frequency-tuned amplifiers, and over the frequency range normally encountered, the magnitude of the demodulated signal is virtually independant of the modulation frequency, so that minor fluctuations in the mains frequency are not important. The amplifier is controlled by a suitable gating circuit, and the gating signal can be generated in a number of ways: If mechanical modulation is used, the chopper blades can be used to generate in-phase magnetic or electric fields, or a secondary light beam passing through the same chopper can be converted to an in-phase potential by means of a suitable photo-resistor or photo-diode. The latter type of system is the one which has been used for a phase-sensitive pre-amplifier for the Southern Instruments A1740 Grating Flame Photometer, and is described in greater detail in the following chapter. If the source of irradiation is electronically modulated, the gating signal is generally derived directly from the modulated source power supply. The precision obtainable with both of the above A.C. systems can be further improved if the demodulated output from the A.C. amplifier is integrated for a suitable period, provided that the source of irradiation is not susceptible to long term drift, although the latter problem could be minimised by employing double-beam instrumentation. Perkin Elmer have developed a further improvement[56], by providing facilities for automatic averaging of a pre-set number of fixed period integrations.

The Effect of Flame Composition on A.F.S.

A.F.S. differs markedly from A.A.S. in that the signal to be measured is an absolute level that must be measured above a flame background (unless non-flame cells are used) rather than a ratio of two signals. For this reason, much of the early research done on A.F.S. involved the use of low background flames, since flames of this type tend to be less noisy, and this is especially true of the atomic fluorescence excited by a continuum source, which has been examined for a number of elements in air-propane[69], oxy-hydrogen[70,71,72], air-hydrogen[69,72], hydrogen diffusion[68,70,71] and hydrogen-oxygen-argon[73] flames. Manning and Heneage have stated[73] that a limitation of hydrogen flames in general is their inability to provide free atoms of those elements that tend to form refractory oxides, and the higher incidence of chemical and matrix effects in these flames compared to hotter acetylene flames. Matousek and Sychra have recently reported appreciable interferences[74] from one-hundred fold excesses of a number of elements that form refractory oxides in air-hydrogen in the determination of iron, nickel and cobalt, that did not occur in the air-acetylene flame. Armentrout has found[75] that 10 to 50 ppm of nickel as the sulphate gave 25% less fluorescence than the same concentrations of nickel as the nitrate in a hydrogen flame. Bratzel, Mansfield and Winefordner studied[76] the effect of acid concentration on the atomic fluorescence of cadmium in a turbulent, fuel-rich oxy-hydrogen flame, and suggested that excess acid must be removed, or that all solutions and standards must be made up to the same acid concentration. Dinnen[77], and Winefordner and co-workers[70] have reported scatter from very small quantities of metals in turbulent air-hydrogen and oxy-hydrogen flames respectively. Ellis and Demers have reported[68] extensive chemical interference in the atomic fluorescence determination of calcium and magnesium in a hydrogen diffusion flame, using a xenon arc source. Dagnall, Thompson and West found that ten fold molar excesses of Al^{3+}, Cu^{2+}, Mg^{2+}, Zn^{2+},

Na^+ and NH_4^+ all interfered in the determination of 75 ppm of arsenic in a laminar hydrogen diffusion flame, but of sixteen ions investigated, only aluminium and magnesium suppressed the fluorescence from 10^{-4}F bismuth at one hundred-fold formal excess in the same flame. Ellis and Demers[71] reported that calcium exhibited intense fluorescence in a hydrogen diffusion flame, but reported predominant scatter in the hotter oxy-hydrogen flame. Several workers have employed hotter acetylene flames [74,79 - 88], and, where direct comparison is possible, the detection limits obtained with air-acetylene are only slightly higher than those obtained with hydrogen flames[74,86], and the chemical interferences tend to be significantly less. It was, therefore, decided to investigate the effect of flame composition and burner type on the sensitivity and interferences in the determination of zinc with a line source, and to compare some detection limits for a range of elements in air-acetylene when determined by atomic fluorescence excited by a continuum source and by thermally excited atomic emission under otherwise identical conditions. The results of this investigation are reported in chapters IX and X respectively.

Chapter VIII The Modification of a Southern Instruments A 1740 Grating Flame Photometer to an Atomic Fluorescence Spectrometer

Although the Southern Instruments A 1740 Grating Flame Photometer can be used to make atomic fluorescence measurements without extensive modification[52,53,58,87], the detection limits obtainable with this instrument are limited by the use of a grating blazed at 500 nm and an E.M.I. 9663B photomultiplier. The instrument was therefore fitted with a grating blazed at 300 nm, and Hamamatsu U.V. sensitive photomultipliers.

Although these simple modifications give substantial improvements in the detection limits for those elements whose useful resonance lines are in the U.V., it is necessary to subtract any thermal emission from the total reading obtained, and the baseline obtained when a fluorescence spectrum is scanned varies irregularly with wavelength. Dagnall, Taylor and West have obtained some excellent sensitivities for the A.F.S. determination of a number of elements by using an early Hilger atomic absorption amplifier[36,55,89] in conjunction with electrodeless discharge tube sources mechanically modulated at 375 Hz. As this amplifier employs a simple parallel 'T' filter stage, it was decided to investigate the application of an amplifier of this type as a pre-amplifier for use in conjunction with the A 1740, or as an amplifier for use in conjunction with a Servoscribe chart recorder and the A 1740 monochromator and photomultiplier.

The amplifier built is shown in fig. 21, and consists of a Philbrick PF 85 AU operational amplifier powered by a Coutant -15, 0, +15 V stabilized power supply unit, which is used as a straightforward inverter amplifier with a parallel 'T' filter in the feedback loop. The input resistor was chosen to give an overall gain of fifty after demodulation. The exact gain was made adjustable by placing 1 M in parallel with the parallel 'T': An empirically selected tuning circuit was added, to ensure optimum response at the desired frequency. This amplifier was A.C. coupled to the photomultiplier. In view of the very low level of the signals to be measured, an operational amplifier based full wave rectifier circuit was employed as a demodulator[90]. This circuit, which is shown in fig. 22, inverts any applied signal, and adds to the inverted signal twice the negative half cycles, thus giving rise to full wave rectification. The 10 K variable resistance in fig. 22 is adjusted to give zero potential at the input resistance to the second operational amplifier, and in this way, an undistorted, fully rectified signal was obtained for sine and square waves applied from a signal generator, and the forward drop of the diodes has no effect on the resultant output.

The response characteristics of the combined amplifier and demodulator are shown in fig. 23: This curve was obtained

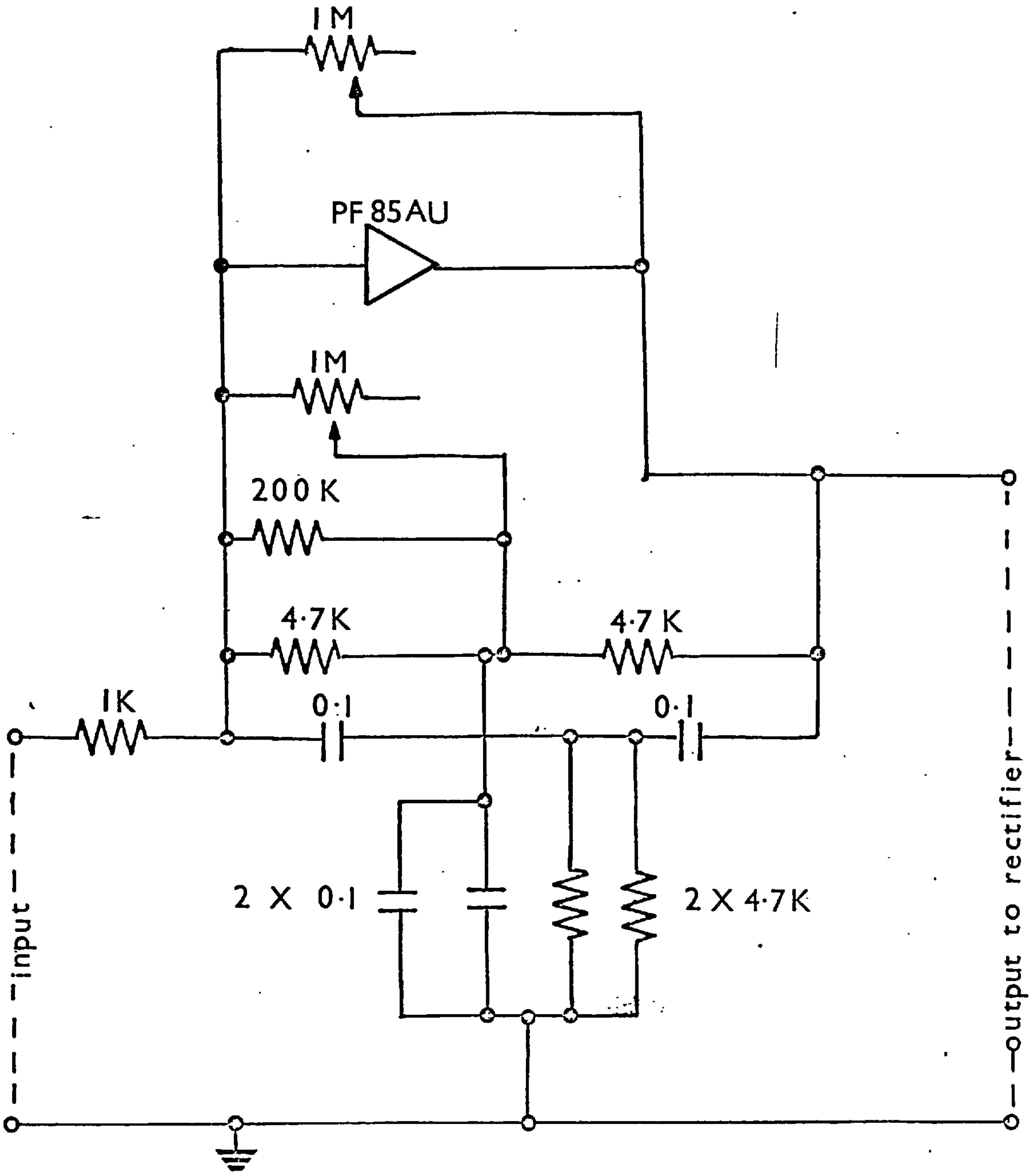
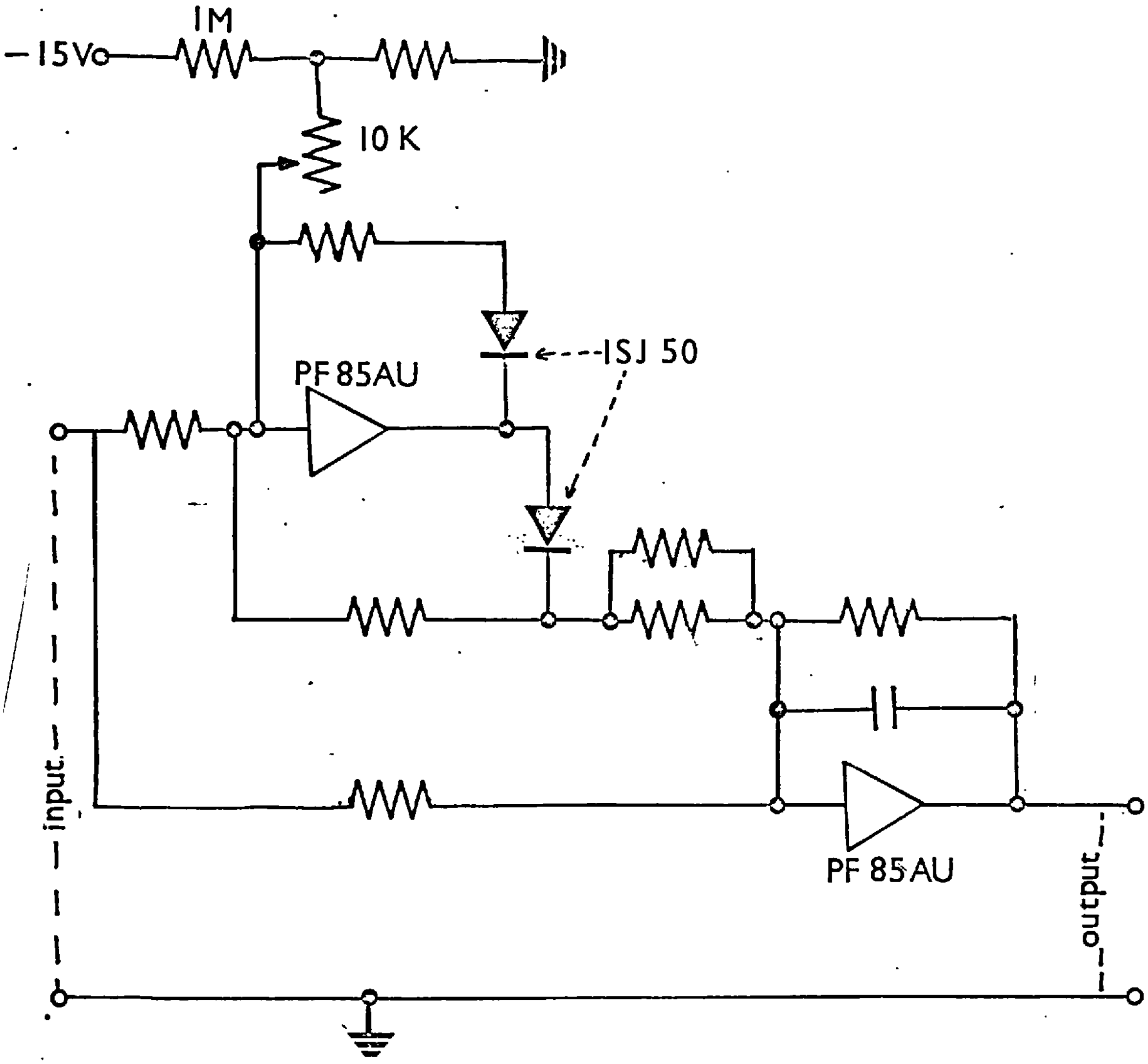

1M
PF85AU
1M
200K
4·7K
4·7K
1K
0·1
0·1
2 X 0·1
2 X 4·7K
input
output to rectifier

Fig. 21.



All resistors 1K unless marked

Fig. 22.

by feeding a 10 mV signal (sine wave) into the amplifier, and measuring both the input and the output on an oscilloscope. Fig.24 shows the output obtained for inputs between 0.01 and 10 mV at 375 Hz. Before evaluating the usefulness of this system, the amplifier was tuned to give maximum gain at the modulation frequency. The source was modulated by means of a chopper containing fifteen equally spaced holes, driven by a 1500 rpm synchronous motor: The nominal modulation frequency was thus 375 Hz.

The instrumental set up used is shown in fig. 26; both electrodeless discharge tubes (Hg and Te) and a 500 w D.C. xenon arc were employed as sources of irradiation. The light from the latter source was focused onto a point 2 cm behind the flame, by means of a silica lens of focal length 6 cm. The curves in fig. 27 show A, the spectrum obtained by aspirating 400 ppm of tellurium into an air-acetylene flame, using the above system, and B, the curve obtained with a D.C. system under otherwise identical conditions. The gain was adjusted for curve B to give identical line heights: These two curves clearly illustrate the importance of an A.C. detection system if it is necessary to scan a fluorescence spectrum. The calibration curves obtained for mercury and tellurium with line sources are shown in fig. 25: Figs. 28 and 29 show the calibration curves obtained for thallium and indium respectively with the same system, but employing the xenon arc as a source of irradiation. Although

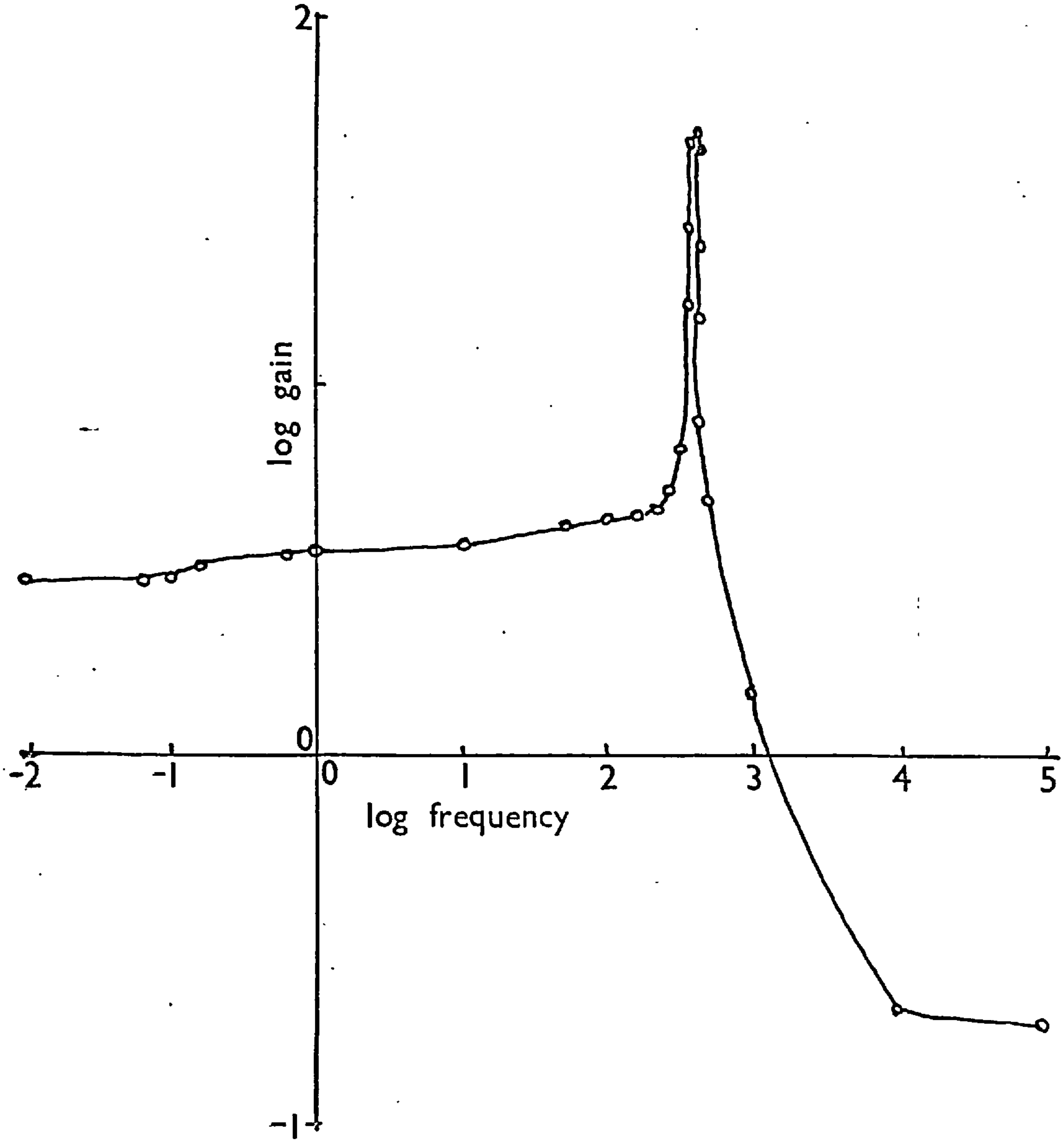


Fig. 23.

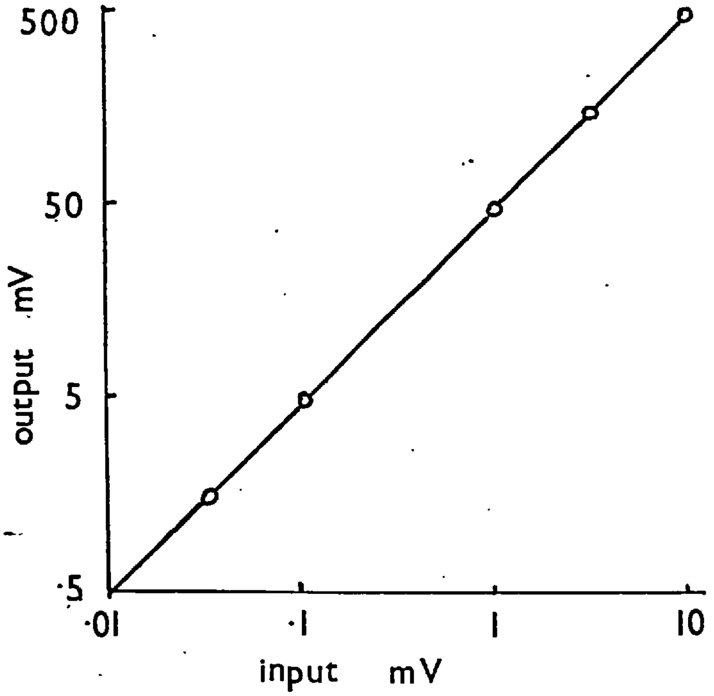

500
50
5
·5
output mV
·01
·1
1
10
input mV

Fig. 24.

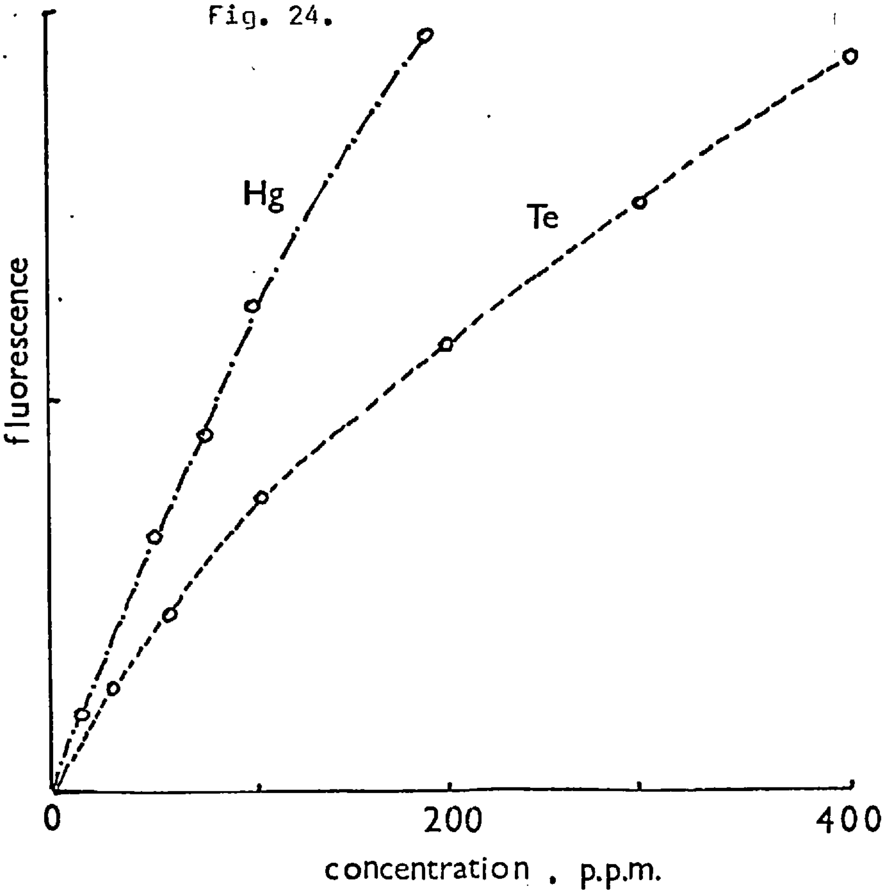
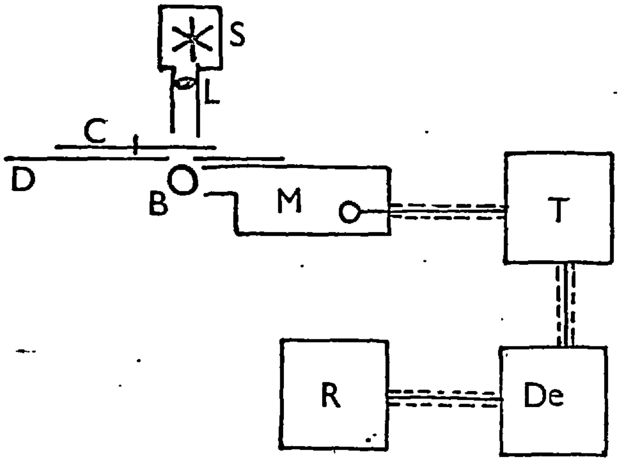

Hg
Te
fluorescence
0
200
400
concentration , p.p.m.

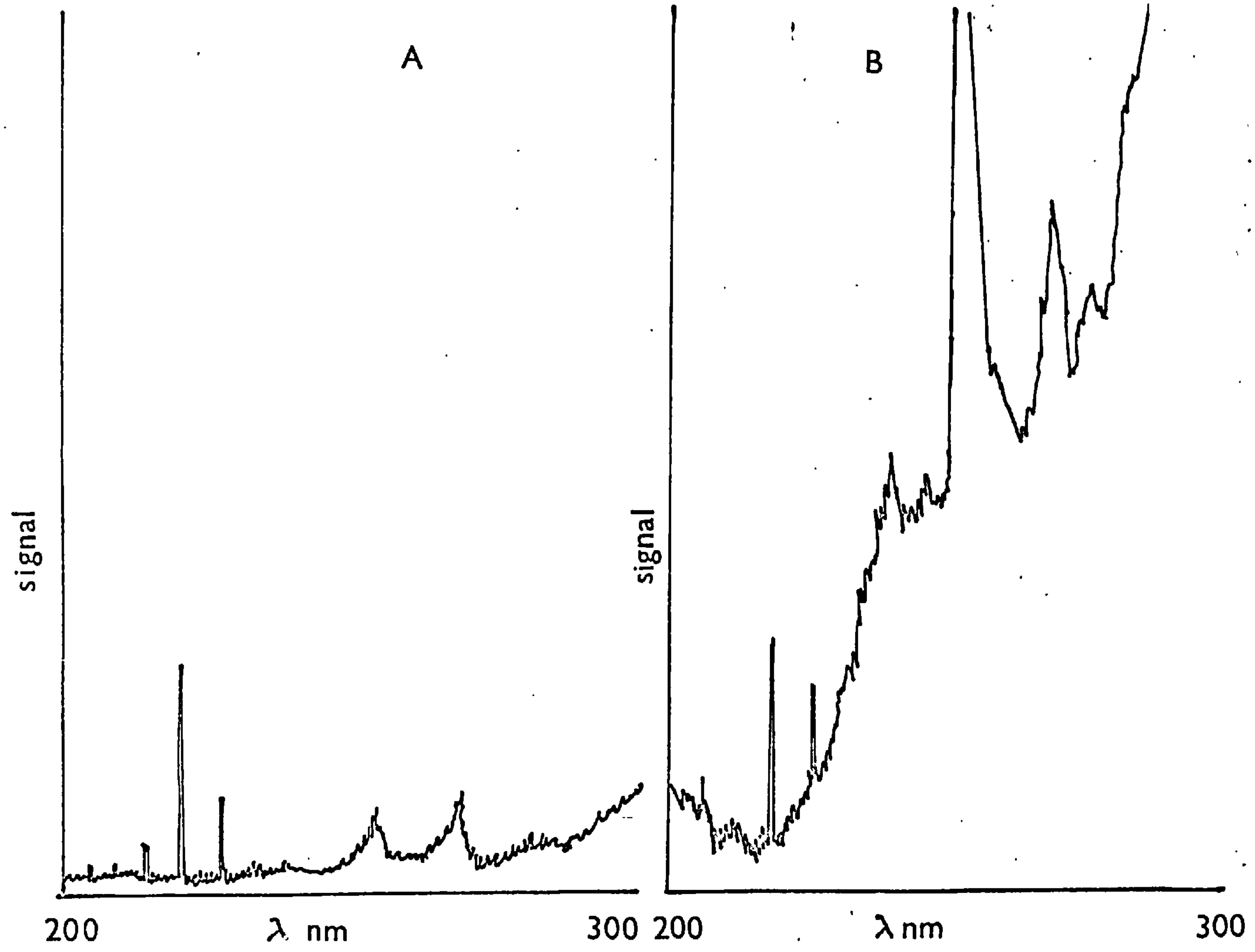
Fig. 25.



S	Xenon Arc
L	Quartz Lens
C	Chopper
D	Draught Shield
B	Burner
M	Monochromator
T	Tuned Amplifier
De	Demodulator
R	Recorder

Fig. 26.

Fig. 27.



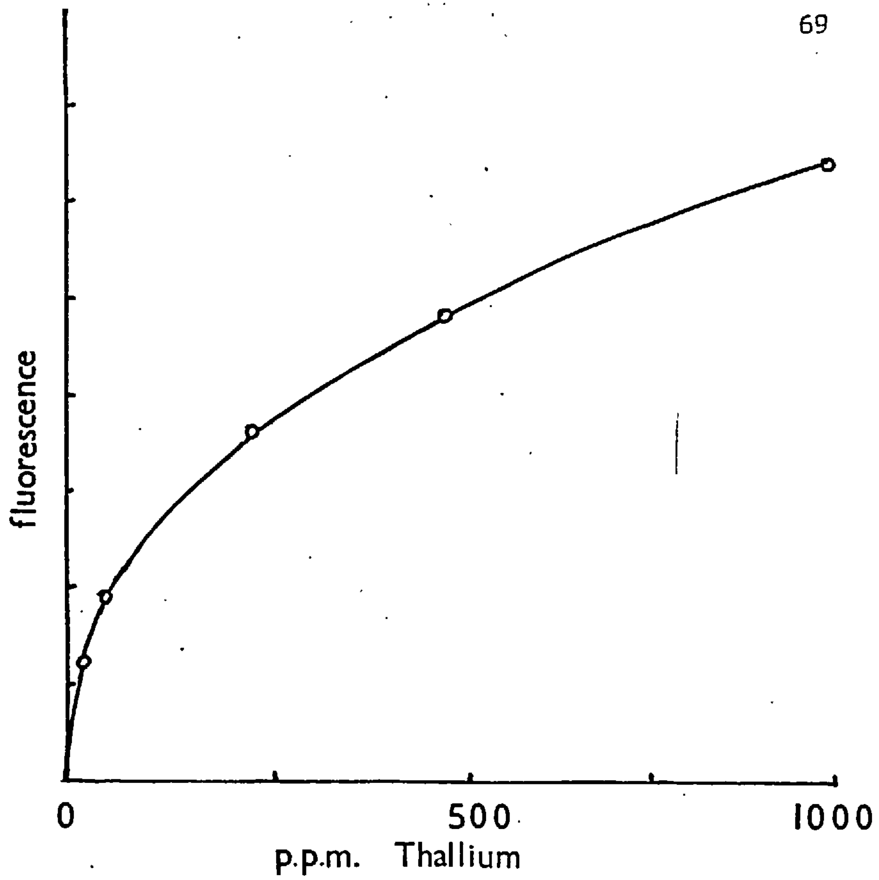

fluorescence
0
500
1000
p.p.m. Thallium

Fig. 28.

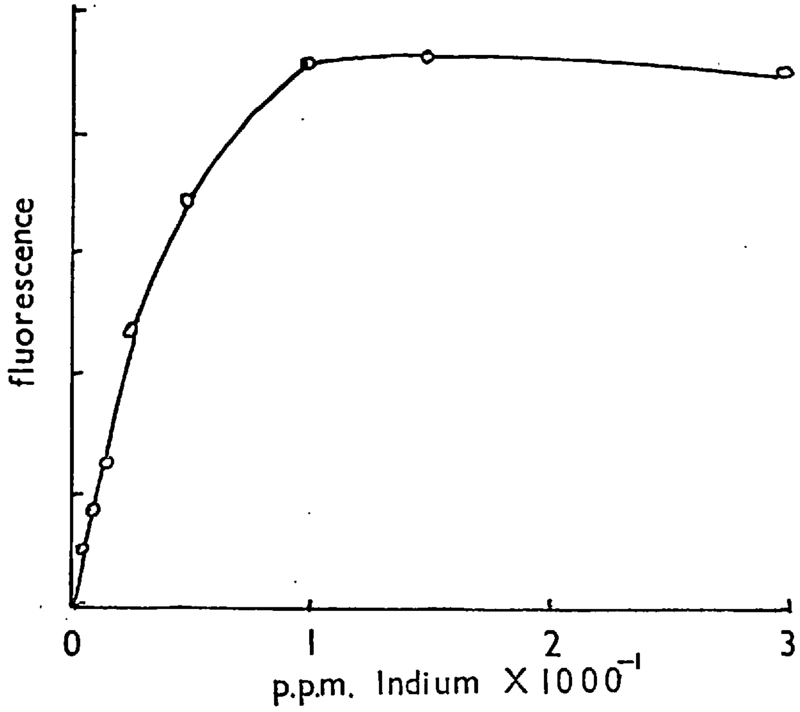
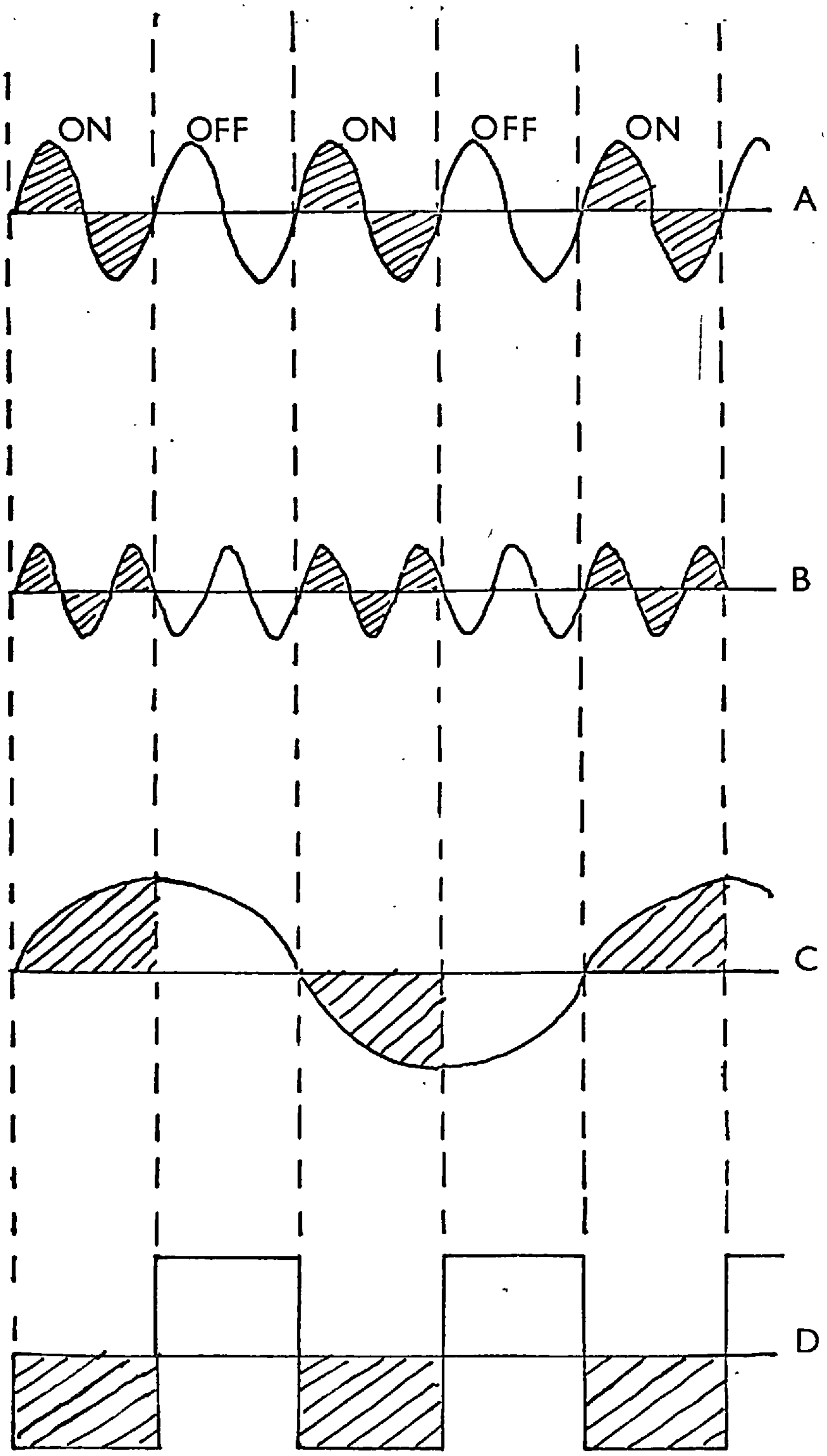

fluorescence
0
1
2
3
p.p.m. Indium X 1000⁻¹

Fig. 29.

this preliminary investigation indicates that the results obtainable with this system are superior to those that can be obtained using a D.C. amplification system (without integration), the width of the bandpass of a system of this type is such that an appreciable flame background spectrum is still obtained, due to demodulation of noise with a frequency close to the modulation frequency: This contribution is particularly significant when elements which exhibit thermal and fluorescence emission simultaneously are to be determined by measurement of the latter radiation only: It was therefore found necessary to correct the curves obtained for indium and thallium for the demodulated emission noise. Amplifiers of this type are suitable for atomic absorption, however, since when this technique is used, emission noise is generally insignificant compared to source noise. It was therefore decided to construct a phase-sensitive amplifier, rather than to investigate the application of the above amplifier as a pre-amplifier to be inserted between the photomultiplier and the A 1740 integrator.

Phase-sensitive Amplification

The concept of phase-sensitive amplification is illustrated diagramatically in fig. 30. The amplifier in this instance is effectively turned on and off in phase with the required fluorescence signal (i.e. with the same frequency and phase as the source modulation frequency); this is shown in fig. 30 D: A, B and C represent noise signals which, for the



required frequency & phase

Fig. 30.

sake of clarity, are shown as signals with a frequency which is a simple fraction or multiple of the modulation frequency: It is readily apparent that the resultant signal for curves A and C is zero: For curve B, it initially appears that the resultant is not zero, but if the waveform is displaced by $\frac{\pi}{2}$, the resultant of this wave is equal but opposite to that of the previous wave, and the sum of the two resultant signals is zero: Hence if the phase of the noise signals is random, the resultant signal after phase-sensitive demodulation is zero. A similar relationship can be seen to hold for all other frequencies, provided that the noise has random phase.

Construction of a Phase-sensitive Amplifier

It was decided to build a system similar to that which has been used by Winefordner and his co-workers for A.F.S. measurements[70]. These workers employed a cadmium selenide photoconductivity cell which received a signal from a miniature lamp which was mechanically modulated by the same chopper as the source of irradiation, and used the modulated photocell voltage as a gating signal for a commercially available phase-sensitive amplifier.

Modulation

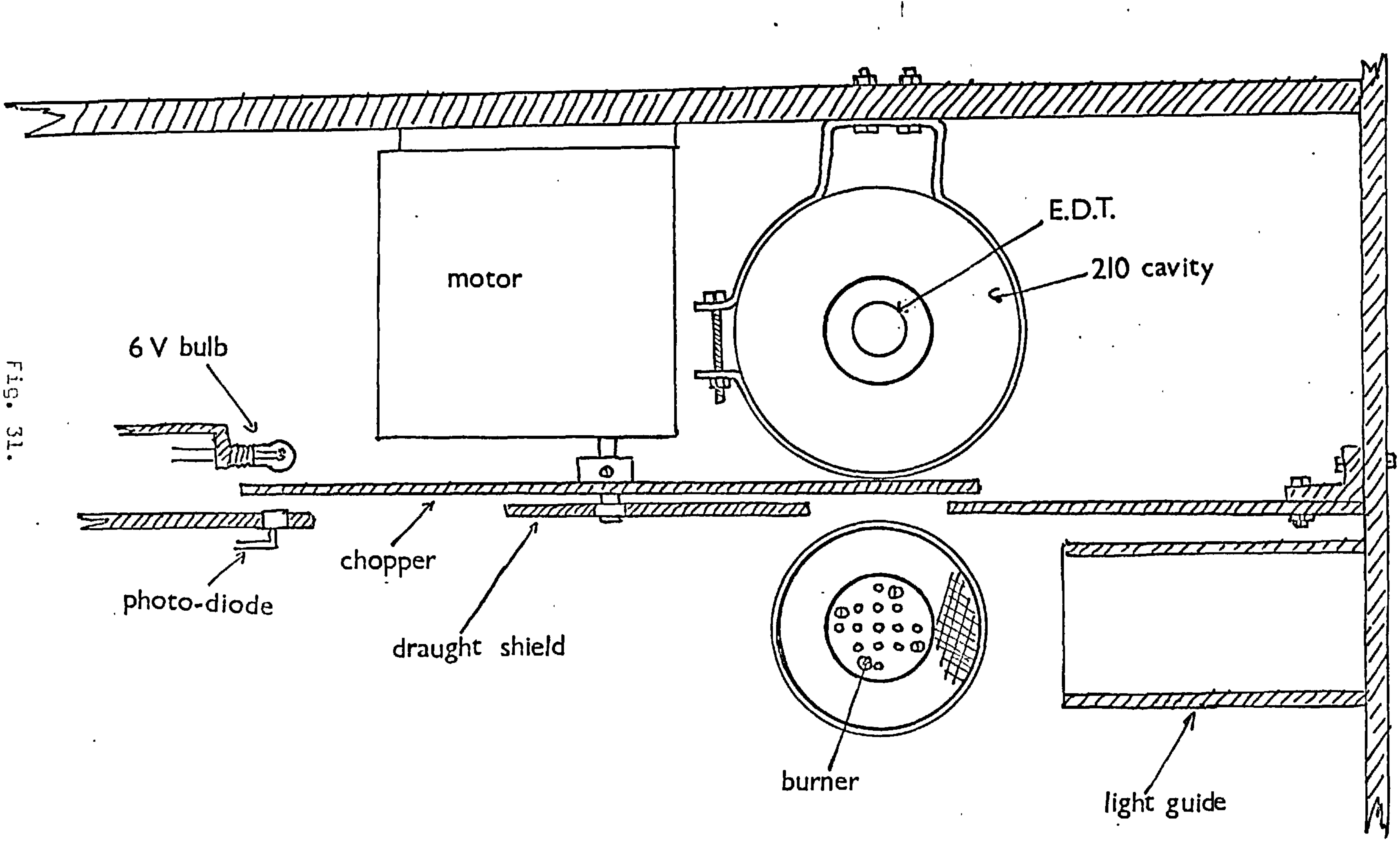
The emission from either a continuum or an electrodeless discharge tube can be readily modulated by mechanical chopping. A three bladed chopper was designed in such a way that the fluorescence signal would be a square wave for the largest possible slit that can be cut in a 210 cavity without impairing the efficient running of electrodeless tubes in the cavity. The possibility of thermal emission from the flame becoming modulated by reflection from the chopper blades was minimised by placing a sheet of blackened asbestos between the chopper and the flame: This also served to keep the cavity cool, and to protect the flame from draughts. These modifications are shown in fig. 31.

Electronic Modifications

An auto-transformer was used to supply 250 V for the chopper motor, 6.3 V for the pea-bulb used to drive the gating circuit, and -45, 0 and +45 V to the stabilised power supply, which was constructed as shown in the circuit diagram in fig. 32: Although the latter is very simple, it was found adequate for the present work. Fig. 33 shows the demodulator unit used; the 0 to +15 V square wave signal across the photo-diode was used to develop 0 to ±15 V square waves on either side of the diode bridge network shown; the two diodes connected to the signal line are thus switched alternately on and off.

The amplifier is shown in fig. 34: The photomultiplier output was A.C. coupled to the 1 M input resistance of an Amelco 809CE operational amplifier with a 10 M feedback resistance. A 30 pF capacitor was connected in parallel with the latter (this was the largest value of capacitance that could be used without significantly distorting a 75 Hz signal fed into the

Fig. 31.


E.D.T.
210 cavity
motor
6 V bulb
chopper
photo-diode
draught shield
burner
light guide

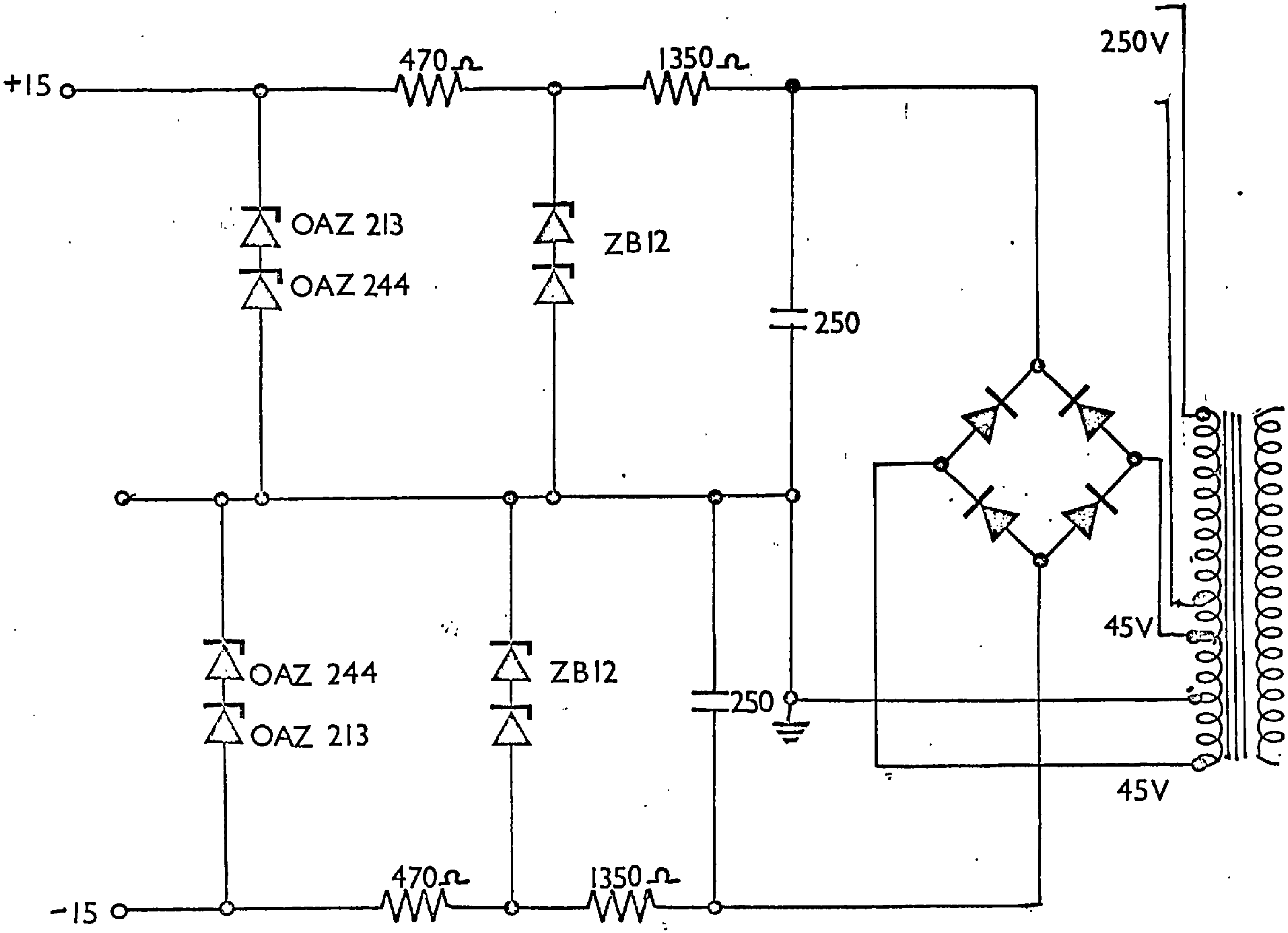

+15
470 Ω
1350 Ω
250V
OAZ 213
OAZ 244
ZB12
250
45V
OAZ 244
OAZ 213
ZB12
250
45V
-15
470 Ω
1350 Ω

Fig. 32.

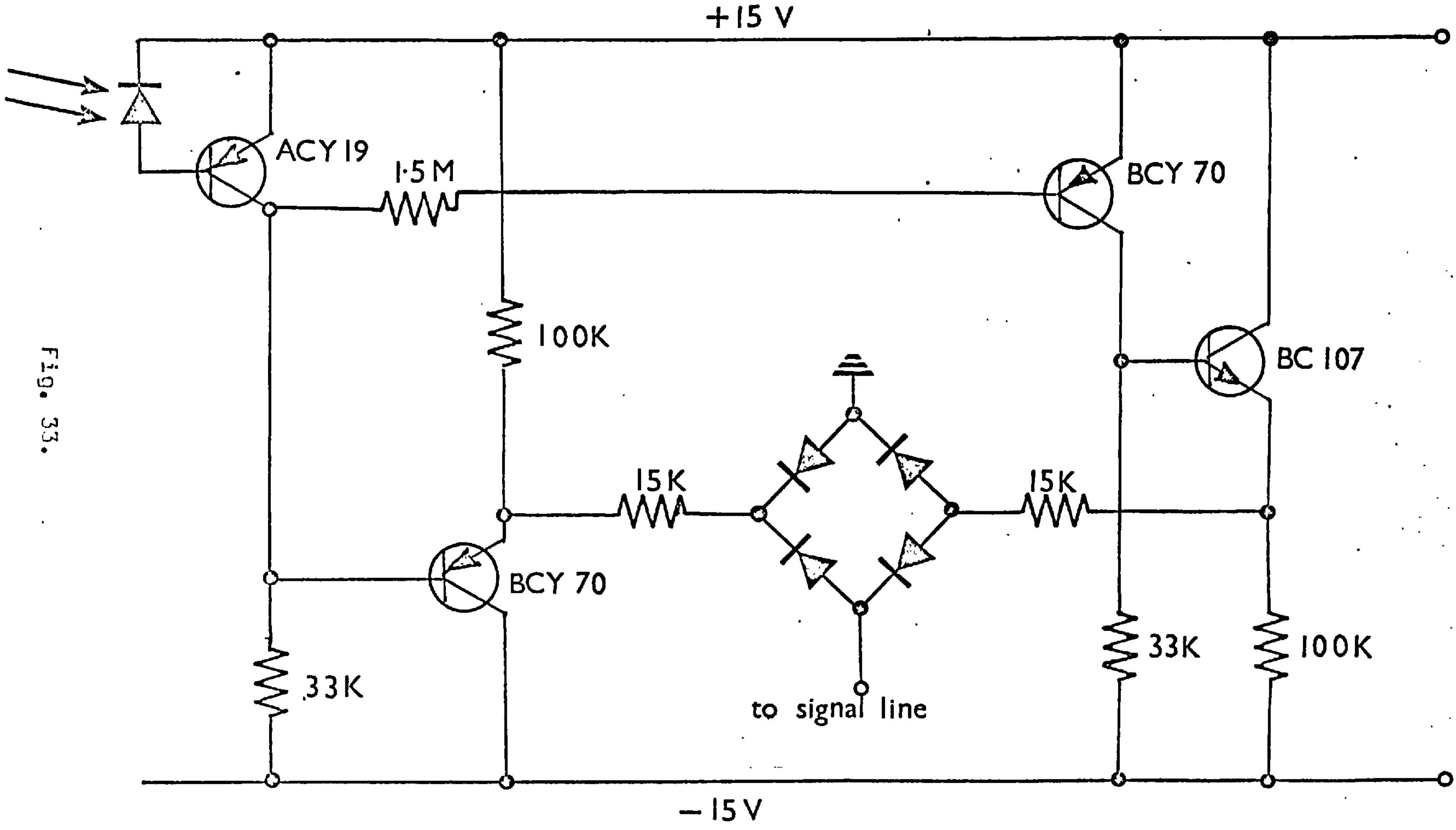

+15 V
ACY 19
1·5 M
100K
BCY 70
BC 107
15K
15K
BCY 70
33K
33K
100K
to signal line
−15 V

Fig. 33.

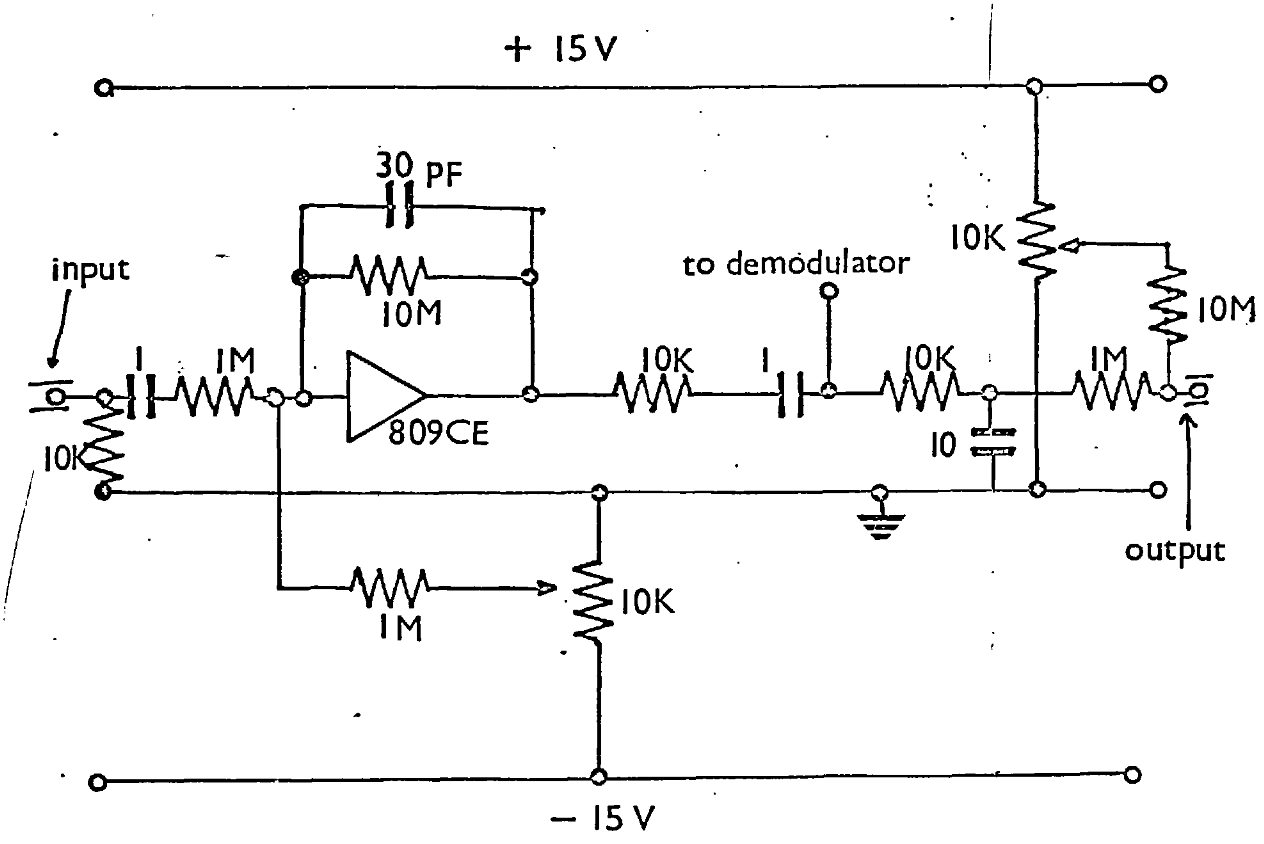
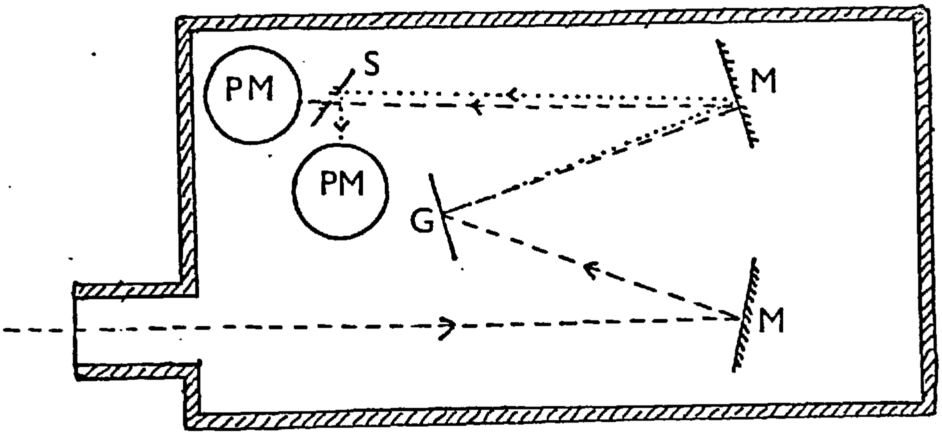

+ 15 V
30 PF
10M
input
1
1M
10K
809CE
10K
1
to demodulator
10K
10
10K
10M
1M
output
1M
10K
– 15 V

Fig. 34.

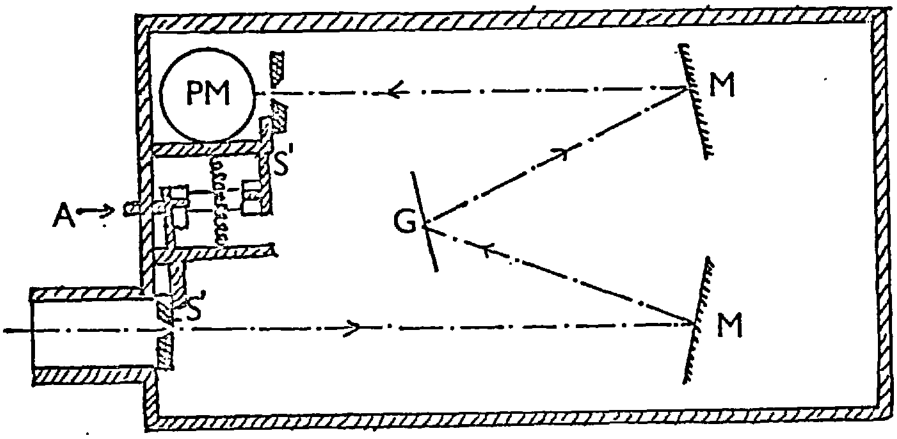
amplifier). The resulting output was A.C. coupled to the demodulator, and then via a smoothing circuit to the integrator input of the A 1740 integrator amplifier.

Modification of the Optical System

The modified burner housing is shown in fig. 31, and has already been described. The original A 1740 monochromator was designed to provide automatic background in thermal emission work, by passing a region of the flame background immediately to either side of the line under investigation onto a second photomultiplier (see fig. 35), and subtracting the suitably amplified signal on this photomultiplier from that obtained from the line photomultiplier. As this facility is superfluous when an A.C. detector is used in conjunction with a modulated source of irradiation for atomic fluorescence work, it was decided to substitute a 1750 monochromator, which has variable ganged entrance and exit slits between 0.025 and 1.0 mm, corresponding to a bandpass range of 1.5 to 60 Å, and is much more suitable for fluorescence work. The photomultiplier base was changed so that Hamamatsu photomultipliers could be used (an R213 type was used in this investigation), and the monochromator was fitted with a grating blazed at 300 nm. A flexible cable was used to drive the slit-adjust mechanism; this was passed over the top of the monochromator entrance collomator to the rear of the burner box, where it was connected



A 1740



A 1750

PM	Photomultipliers
M	Mirrors
G	Gratings
S	Slit
S'	Ganged Slits
A	Slit Adjust

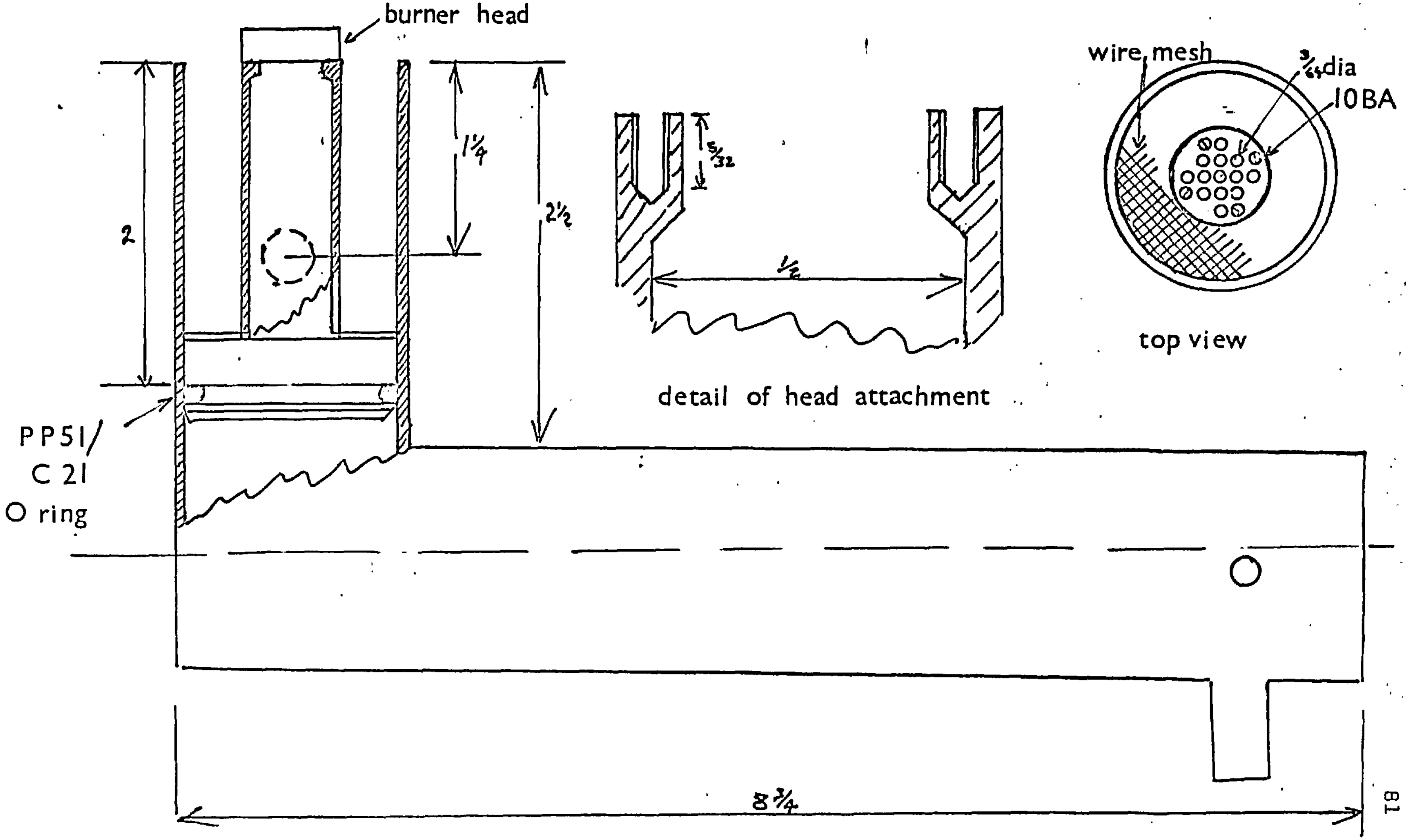
Fig. 35.

to a six-position click-stop switch of the type used on the Southern Instruments A 3000.

Burner Modification

The burner heads supplied with the A 1740 are designed for thermal emission measurements, and are not particularly suited to fluorescence work. Ideally the flame cell should be completely irradiated by the source, and this is not possible when large burner heads are used, unless large aperture lenses are employed, and even then the resulting calibration curve will exhibit greater curvature. The burner was therefore modified as shown in fig. 36. The head containing thirteen $\frac{3}{64}''$ diameter holes was found to be satisfactory for burning air-hydrogen, air-acetylene, hydrogen-nitrogen-entrained air and hydrogen-argon-entrained air flames. The air-acetylene flame obtained with this burner was found to be two to three times less noisy than the flame obtained with the original burner, and appreciably more laminar: This was attributed to the higher fuel and oxidant flow rates used with the modified burner. Although the outer sheath shown in fig. 36 was found to be adequate for surrounding the flame with filtered air, the flow was not sufficiently laminar to provide satisfactory separation when nitrogen was used as the sheath gas. The steel wool and upper wire mesh were therefore later replaced by a turned brass ring $\frac{3}{8}''$ thick, which contained three concentric rings of 32 holes of $\frac{3}{64}''$ diameter: The outer edge of the ring

Fig. 35.



detail of head attachment

top view

was turned away to a depth of $\frac{1}{16}''$, so that the top of the ring was flush with the top of the burner head: The performance of the resulting burner was similar to that of the nitrogen sheathed burners used by other workers[82,84,91].

Results

The limits of detection obtained for a number of elements in air-acetylene are shown in table VI. An unsheathed flame was used throughout, with an air pressure of 28 p.s.i. and the acetylene flow adjusted to give a flame that was just non-luminous, in conjunction with electrodeless discharge tubes as sources of irradiation: Figs. 37 and 38 show the calibration curves obtained over narrow ranges for the elements investigated, using a ten second integration period.

TABLE VI

Element	Line	Slit mm.	Detection limit ppm.
Selenium	196.1	1.0	0.1
Indium	451.1	1.0	0.03
Bismuth	302.5	0.25	1.0
Arsenic	235.0	1.0	0.2
Zinc	213.9	1.0	0.0002
Mercury	253.7	0.5	0.1
Cadmium	228.8	1.0	0.00008

Some A.F.S. Detection Limits with the Modified System.

The baseline obtained with this system when a fluorescence spectrum was scanned was about five times less

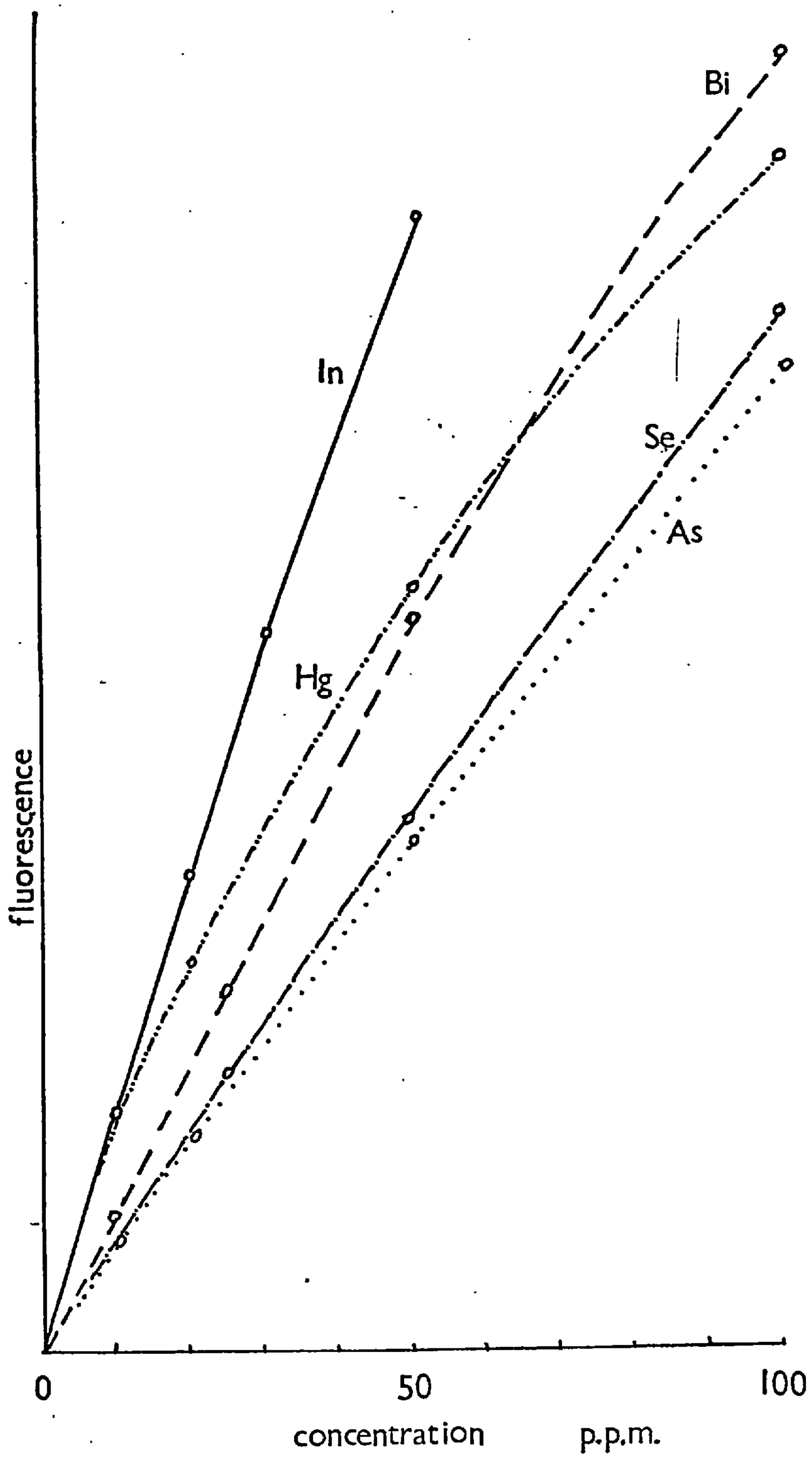


Fig. 37.

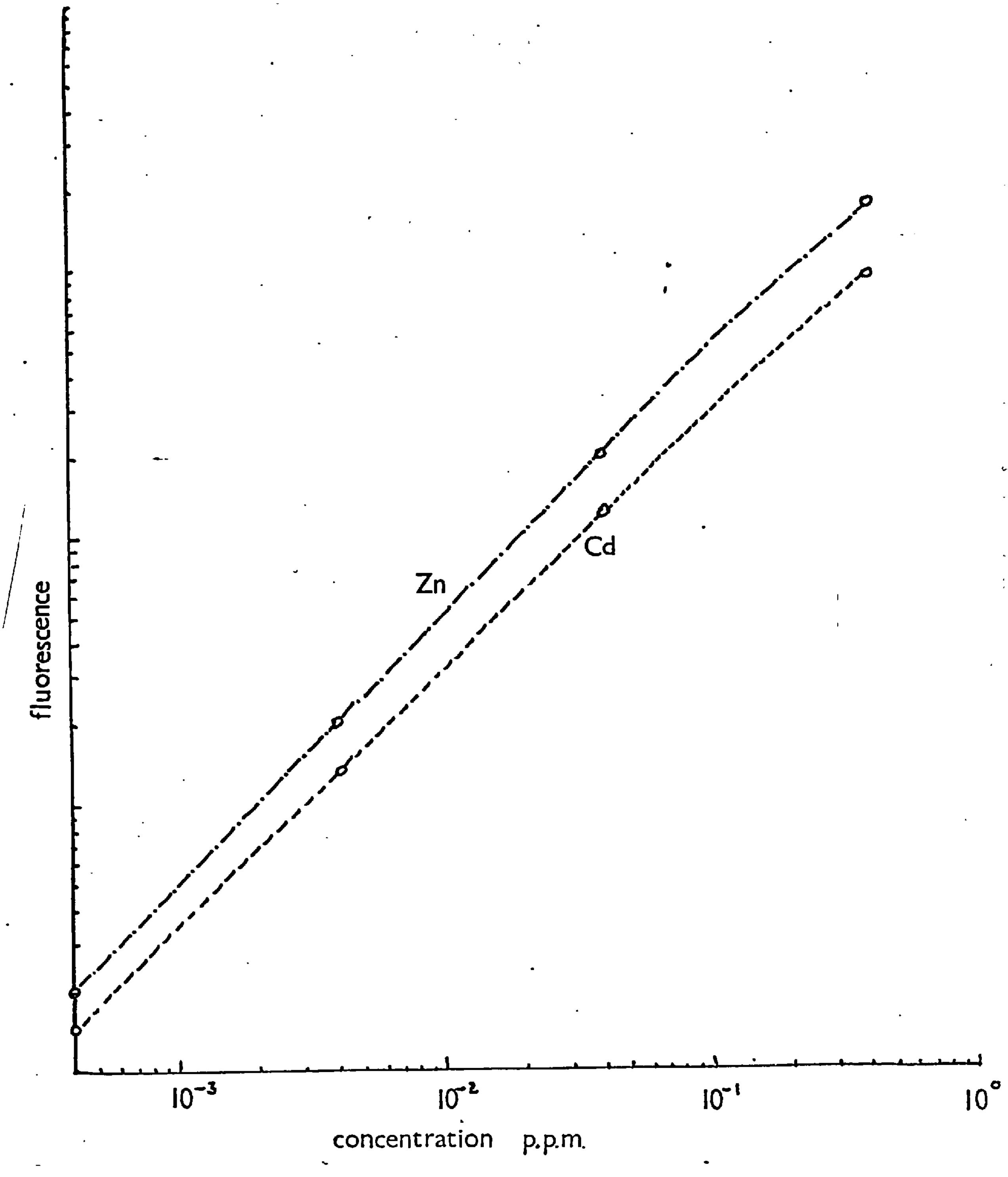


Fig. 38.

noisy than the baseline obtained at the same monochromator band pass with the frequency-tuned amplifier at the same gain and with the same damping on the chart recorder, and this clearly shows the advantage of employing a phase-sensitive demodulator. The system of demodulation employed was slightly susceptible to zero-drift, however, and although this effect was slight, it was found necessary to check the zero blank integration between each reading. The source of this drift was traced to thermal drift in the demodulator diodes: This effect could be minimised by using four pairs of temperature compensated diodes, and is unimportant if the fluorescence spectrum is to be scanned.

Table VII compares the results obtained with the modified instrument described above with those obtained by other workers using unmodified Southern Instruments Grating Flame Photometers; this table clearly illustrates the effect of improved instrumentation. As the object of the work in chapters IX to XI was to obtain some indication of the applicability of A.F.S. to analysis using commercially available instrumentation, the electronic modifications were not used in any subsequent work. This was in fact found to be necessary when the xenon arc was used as a source of irradiation, because of the large amount of 100 Hz ripple on the output of the latter source, which had a constant phase relationship with the modulation frequency.

TABLE VII

Element	Detection limit, modified instrument.	Detection limit, unmodified instrument.
Bismuth	1.0	0.5
Cadmium	0.00008	0.0003
Mercury	0.1	0.6
Indium	0.03	0.2
Selenium	0.1	10.0
Zinc	0.0002	0.002

Comparison of some detection limits obtained with the unmodified[52] and the modified Southern Instruments A 1740.

Chapter IX Some Observations on the Determination of Zinc by A.F.S. Under Conditions Favourable for Analysis

Although the relative merits of atomic emission, atomic absorption and atomic fluorescence spectroscopy have recently been the subject of controversial discussion[11,92], there seems to be general agreement that for zinc and a group of elements whose principal resonance lines lie below 320 nm, the detection limits obtainable with currently available instrumentation are superior when the fluorescence technique is used. Results reported so far for the determination of zinc by atomic fluorescence are summarised in table VIII, but most of the references quoted in the table are concerned with the optimisation of experimental parameters, rather than with the analysis of practical samples. Dagnall, Thompson and West have reported[69] that 100-fold excesses of 48 cations and 18 anions caused no interference in the determination of a 10^{-5} M zinc solution in an air-propane flame, and Klaus[93] has determined zinc in biological samples. The object of the present investigation was to examine the effect of flame composition and burner type on the interferences in and the sensitivity of the determination of zinc by A.F.S., and to establish the relative merits of the various types of flame used in fluorescence studies.

Experimental

The modified Southern Instruments A 1740 Grating Flame Photometer used in the present investigation has been described in chapter VIII and reference 87. The source of irradiation

TABLE VIII

Flame	Burner* Type	Detection Limit ppm	Source	Reference
air-propane	Ch.	0.003	Osram Vapour Lamp	69
air-propane	Ch.	0.6	150 W Xenon Arc	69
air-hydrogen	Ch.	0.6	150 W Xenon Arc	69
oxy-hydrogen	T.C.	0.1	450 W Xenon Arc	71
hydrogen-entrained air	T.C.	0.03	450 W Xenon Arc	71
oxy-hydrogen	T.C.	0.04	Osram Vapour Lamp	97
oxy-acetylene	T.C.	0.04	Osram Vapour Lamp	97
oxy-hydrogen	T.C.	0.6	150 W Xenon Arc	70
oxy-hydrogen	T.C.	0.0001	Osram Vapour Lamp	98
air-hydrogen	T.C.	0.0005	Phillips Vapour Lamp	99
air-hydrogen	Ch.	0.0002	electrodeless discharge tube	99
N_2 separated air-hydrogen	Ch.	0.005*	electrodeless discharge tube	94
air-propane	Ch.	0.002	electrodeless discharge tube	52
air-hydrogen	T.C.	0.00004	electrodeless discharge tube	54

* Ch = Chamber Type T.C. = Total Consumption

** result obtained using a solar blind photomultiplier as a detector.

employed was a microwave powered zinc electrodeless discharge tube operating at 65 W[52,55,94], placed immediately behind an asbestos screen with a 3 X 1.5 cm slit, as close as possible to the relevant burner. A Beckmann total consumption burner was used to burn turbulent oxy-hydrogen and air-hydrogen flames (both approximately stoichiometric), and the modified burner described in chapter VIII was used to burn pre-mixed air-hydrogen and air-acetylene flames (both slightly fuel rich).

Solutions

1,000 ppm solutions were made up from analytical reagent grade zinc sulphate, and zinc metal dissolved in the minimum volumes of hydrochloric acid and nitric acid.

Diverse Ions

Solutions were made up for a range of metals, from chlorides and nitrates, using analytical reagent grade salts whenever possible.

Results and Discussion

The calibration curves obtained in the four flames investigated are shown in fig. 39. Zinc chloride, nitrate and sulphate were found to give identical calibration curves within the limits of experimental error in all four flames. Measurements were made at the height in the flame which gave the optimum signal to noise ratio at low concentrations: All measurements were made using a nominal 6 nm bandpass and a ten second integration period. A 0.1 ppm zinc solution was

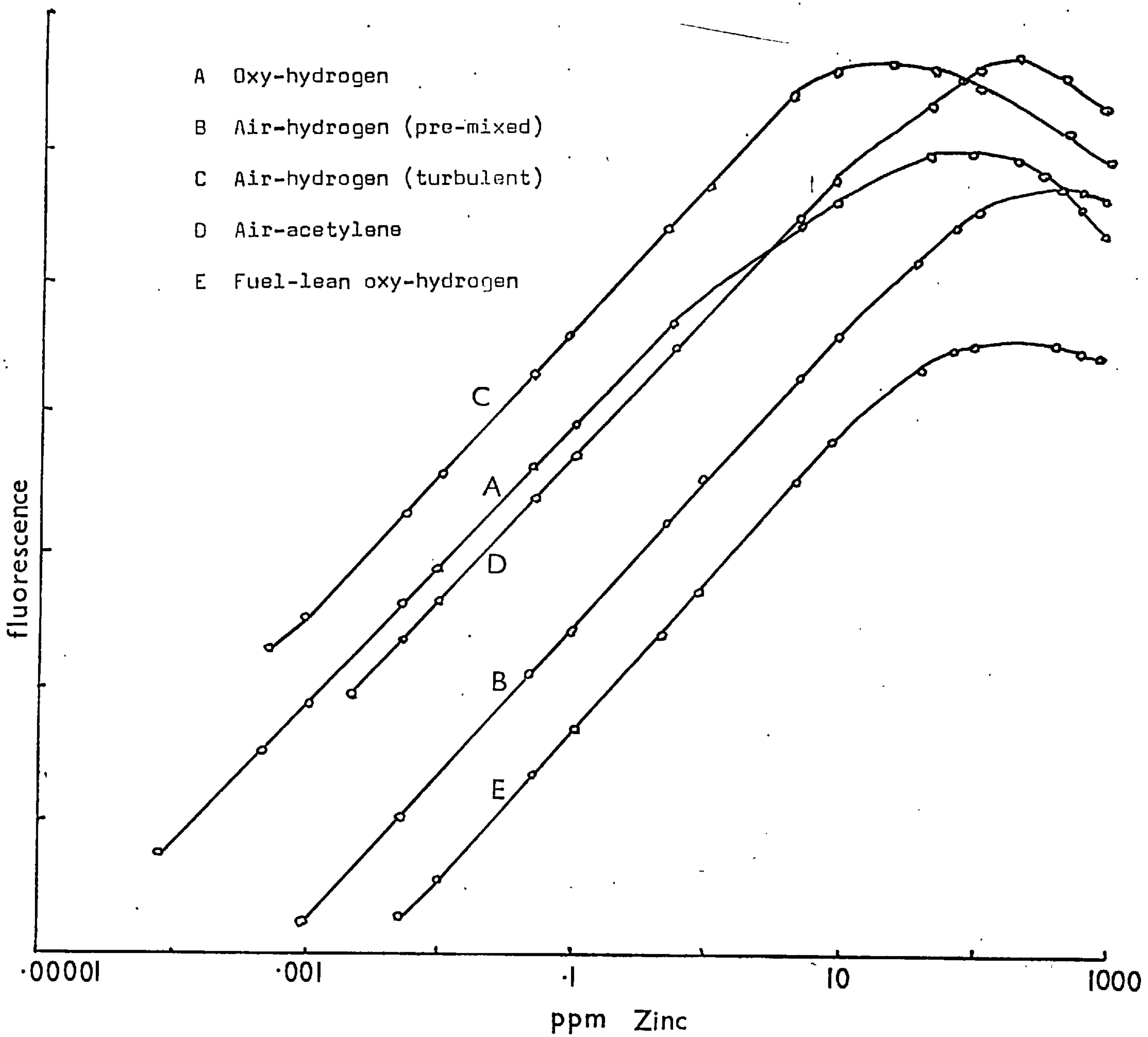

A Oxy-hydrogen
B Air-hydrogen (pre-mixed)
C Air-hydrogen (turbulent)
D Air-acetylene
E Fuel-lean oxy-hydrogen
C
A
D
B
E
fluorescence
·00001
·001
·1
10
1000
ppm Zinc

Fig. 39.

nebulised between each reading to ensure that no significant source drift had occured. The earlier incidence of curvature in the calibration curves obtained with the turbulent flames can be partially attributed to greater self-absorption. This arises because of the existance of an appreciable population of ground state atoms outside this type of flame at the heights used for measurement, ie 10 cm and 7 cm for oxy-hydrogen and air-hydrogen respectively. When a small, very fuel lean oxy-hydrogen flame was used on the total consumption burner, the incidence of curvature was reduced.

Detection Limits

The detection limits obtained in the present investigation are shown in table IX below:

TABLE IX

Flame	Burner Type	Detection Limit ppm
air-acetylene	chamber	0.002
air-hydrogen	chamber	0.001
air-hydrogen	total consumption	0.0005
oxy-hydrogen	total consumption	0.0001

Detection Limits for Zinc at 213.9 nm.

As usual when the integration system was employed, the detection limit was taken as the concentration for which the signal is twice the standard deviation. The results obtained in chapter VIII indicate that these results can be improved by up to a factor of ten by employing a suitable phase-sensitive pre-amplifier, but this effect will be most pronounced for the pre-mixed flames. All detection limits were measured under optimum signal-noise conditions with the same electrodeless discharge tube source.

Effect of Hydrochloric Acid

Bratzel, Mansfield and Winefordner have studied[76] the effect of hydrochloric acid on the fluorescence of cadmium in a turbulent, fuel rich oxy-hydrogen flame, and found that although enhancement is obtained at high concentrations (> 100 ppm of cadmium), depression occured at lower concentrations. A similar type of effect was found here for zinc in both of the turbulent flames investigated (see fig. 40), but to a lesser extent in the pre-mixed air-hydrogen flame. Gidley and Jones[95] have reported interference from hydrochloric acid in the determination of zinc by atomic absorption which they attributed to the presence of absorbing molecular species in the flame, and undoubtedly viscosity, surface tension and density effects also play an important part, but these effects should give a similar decrease in signal over the range investigated: This was found to be the case only when the pre-mixed air-acetylene flame was used, and with this flame, although the calibration curve was appreciably less sensitive, the calibration curves obtained at constant acid concentrations

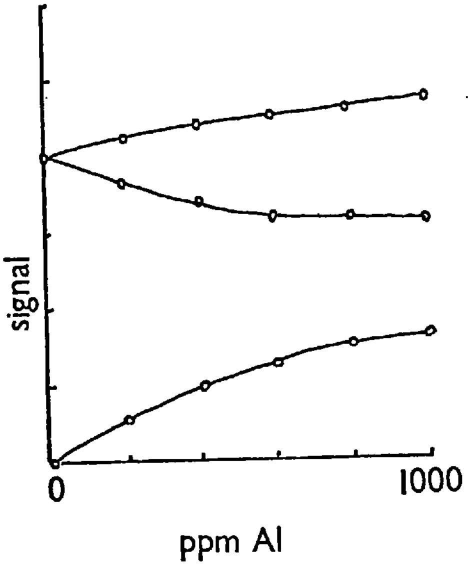

signal
0
1000
ppm Al

Fig. 41.

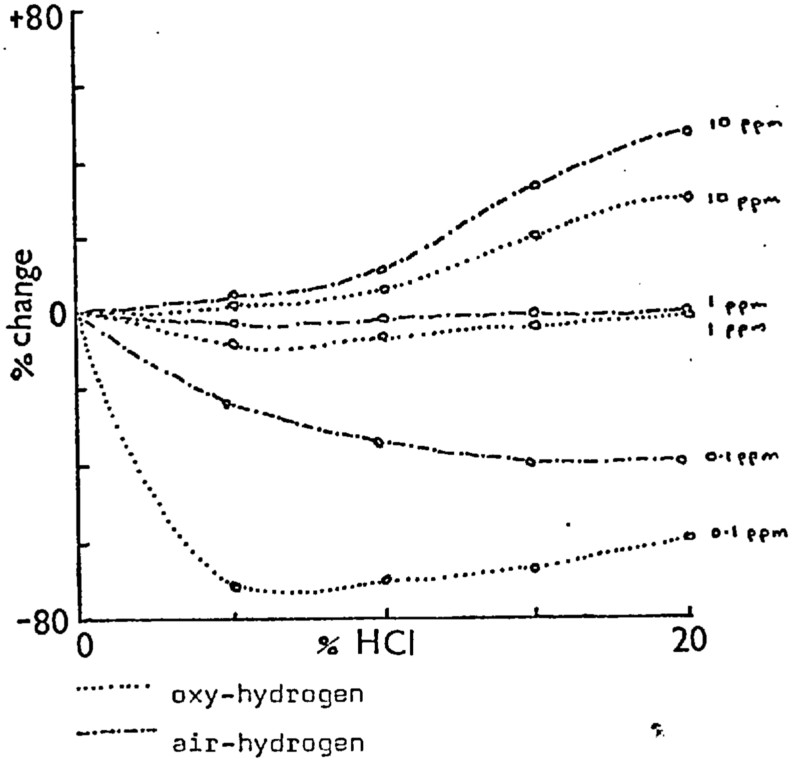

+80
0
-80
% change
0
% HCl
20
10 ppm
10 ppm
1 ppm
1 ppm
0·1 ppm
0·1 ppm
oxy-hydrogen
air-hydrogen

Fig. 40.

were not distorted. turbulent flames were used, however, the fluorescence emis rofiles were found to vary appreciably with both concentration and zinc concentration, which indicates that ompound formation plays an important part in the interferen chanism in turbulent flames, by effecting the ground atom distribution.

Cationic Interferences

The interfer effects of 24 cations were examined at 1000-fold excess (in each of the flames investigated: The results obtained own in table X. Although all of the interferences ed in the turbulent flames were enhancements, attrib to scatter of the source radiation, which is particularly ificant at the low wavelength used for the determinatio nc, some of the results appear initially to be anomalous, ct of increasing amounts of interfering ion was therefore n detail for Al^{3+}, Ca^{2+}, Cu^{2+}, Mg^{2+} and Na^{+}: The scatter from the interfering cations alone was also examined. he latter is subtracted from the total signal, a corrected c s obtained: These curves were generally of the for in fig. 41 on the previous page; this shows the effect riable amounts of aluminium on the determination of 0.1 zinc in a turbulent oxy-hydrogen flame: The corrected is similar in form to the type of curve often obtained in A. 0,000-fold excesses of aluminium gave enhancements i bulent air-hydrogen and oxy-hydrogen

TABLE X

Flame	% Interference from - to	Cations
oxy-hydrogen, turbulent.	0 - 5	Al, Bi, Ca, Cd, Cr, Hg, In, K, Mg, Mn, Na, Se.
	5 - 10	Cu, Mo.
	10 - 20	Co, Fe, Ni, Pb, Tl.
	> 20	Ba, Sn, V.
air-hydrogen, turbulent.	0 - 5	Cd, Cr, Cu, Hg, In, K, Na, Se, Tl.
	5 - 10	Al, Co, Ni, Pb, Sn.
	10 - 20	Ca, Mg, Mo, V.
	> 20	Ba, Bi, Fe, Mn.
air-hydrogen, pre-mixed.	0 - 5	Al, Cd, Co, Cr, Cu, Hg, Na, Ni, Pb, Se, Tl.
	5 - 10	Ba, Bi, Ca, Fe, In, K, Mg, Mo, Sn, V.
	10 - 20	Mn.
	> 20	None.
air-acetylene, pre-mixed.	0 - 5	Al, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, In, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sn, Tl, V.
	> 5	None.

Effect of 1000-fold Excesses of Various Cations on the Determination of 0.1 ppm Zinc by Fluorescence at 213.9 nm.

flames which could not be attributed to scatter alone, however. The effect was found to be due to changes in the fluorescence emission-height profile, <u>ie</u> the ground state atom distribution in the flame. In pre-mixed air-acetylene, the same concentration excess of aluminium gave only a 6% decrease in signal.

Conclusion

The results obtained indicate that turbulent oxy-hydrogen flames are most satisfactory for the determination of very small traces of zinc when the foreign ion content of the sample solution is very low, but that the laminar, pre-mixed air-acetylene flame is more suitable for the determination of zinc in the presence of variable amounts of diverse ions, in spite of the fact that the detection limit obtained is not as favourable in the acetylene flame. The acetylene flame also appears to be much less susceptible to interference caused by variation in ground state atom distribution than the turbulent hydrogen flames.

This study substantiates the previous observation that it is most important from the practical viewpoint that thermally efficient flames[96] such as air-acetylene, rather than cool ones, such as air-hydrogen, should be used for atomic fluorescence as for atomic absorption.

Chapter X Some Interference Studies in Atomic Fluorescence Spectroscopy with a Continuum Source

One of the principal considerations which has been responsible for the widespread interest in A.F.S. is the possible application of high intensity continuous sources to the technique. In atomic absorption spectroscopy, higher resolution monochromators are generally necessary when continuous sources are used, and generally the calibration curves show a higher degree of curvature, and the detection limits obtained are inferior to those obtainable with line sources. Although instruments have been developed that can be used for multi-element analysis[105] based on the atomic absorption technique with resonance detectors, and modern A.F.S. instruments now generally can keep up to six hollow cathode lamps running on stand-by currents, to minimise the problem of warm-up time, the fact remains that the analysis of large numbers of elements on a routine basis by A.A.S. cannot be rapidly and cheaply carried out on a single instrument.

The introduction of atomic fluorescence flame spectrometry therefore lead a number of workers to investigate the applicability of readily available, relatively inexpensive continuous sources to this technique, particularly as at that time the only suitable atomic line sources available were a few vapour discharge lamps and high intensity hollow cathodes, and a few RF electrodeless discharge tubes, which had been designed as sources for wavelength calibration rather than as high intensity atomic line sources of the type required for A.F.S. Winefordner and co-workers investigated[70] thirteen elements using a 150W xenon arc lamp as the source of excitation in conjunction with a phase sensitive amplifier, and obtained excellent detection limits for Ag, Au, Bi, Cd, Cu, Mg, Tl, Pb, and Zn in oxy-hydrogen and argon-hydrogen-entrained air (Pb, Mg, Tl only), by taking measurements 6cm above the tip of the Beckman total consumption aspirator burner used in the investigation. In the same publication these workers reported the sensitive determination of Ca, Ba, Ga, and Ni by measurement of the incident light scattering from salt particles in the oxy-hydrogen flame burning on the Beckman burner; although no interference studies were reported in this paper, it is clear that if the detection limits for these elements by scatter measurements were 1.5, 7, 20, and 13 ppm respectively, scatter will be a very serious source of interference if this type of burner is used in conjunction with a continuum. A brief investigation of the scatter interferences in the determination of silver in this flame showed that this was indeed the case, and even when the fluorescence spectrum was scanned, the increase in the noise level when attempts were made to determine 1 ppm of silver in the presence of a hundred-fold excess of calcium or magnesium made this concentration of silver indeterminable, although the detection limit obtained in otherwise pure aqueous solution was 0.1 ppm (with a 500W xenon arc source). Dagnall, Thompson and West reported[69] detection limits for Ag, Cd, Co, Cu, Fe, Mg, Mn, Pb, Tl, and Zn in air-propane and air-hydrogen burning on a chamber type burner, but did not report and interference studies. Manning and Heneage extended[73] the range to include Cr and Ni: These workers employed a 150W xenon arc and a hydrogen-oxygen-argon flame burning on a chamber type burner, The use of argon as an inert support gas rather than nitrogen, which was suggested and discussed in detail by Jenkins[106], considerably improved the detection limits obtained for most elements, and by using a chamber type burner, these workers found that solutions with a relatively low dissolved solids content ($<$ 0.01%) gave little or no scattering. Ellis and Demers employed a more powerful 450W xenon arc[68] to excite the fluorescence of calcium and magnesium in a hydrogen diffusion flame, and reported extensive interferences. Jenkins has reported[107] the use of an oxy-kerosene flame for the determination of trace metals in kerosene, and because of the absence of an additional fuel as diluent, excellent sensitivity was obtained.

Although all of these publications have mentioned the advantages of continuous sources applied to A.F.S., radiation interferences have been completely ignored. It has been stated that only one or two lines will be excited in the fluorescence spectrum of most elements, and this statement has been fully discussed in chapter VII with particular reference to the participation of thermally assisted processes in A.F.S., it should also be remembered that the intensity of the excitation source under the absorption line profile plays a vital part in the formulation of a fluorescence spectrum, and as the transition probabilities of the individual lines of interest play no part in governing this intensity when a continuum source of irradiation is employed, lines which are insignificant when an atomic line source is used may be relatively much more important when a continuous source is used.

The object of the investigation in this chapter is to examine the potential application of A.F.S., using a continuum source, to the analysis of a range of elements in the presence of elements known to interfere in their determination by thermal emission. Obviously, higher selectivity can be obtained using specific line-sources such as high intensity lamps or electrodeless discharge tubes, but this investigation is concerned with the practicability of using a single continuum source to excite atomic fluorescence.

High sensitivity is not expected with the experimental arrangement used in this study and it is probable that both the detection limits and the linear working ranges of the calibration curves obtained can be improved by at least one order of magnitude if a phase-sensitive or frequency-tuned pre-amplifier is used in conjunction with a modulated xenon arc.

Apparatus

The Southern Analytical 1740 grating flame photometer fitted with a Hamamatsu type R213 U.V.-sensitive photomultiplier, a grating blazed at 300 nm, and an A3000 adjustable slit mechanism, which gives a variable bandpass between 0.15 nm and 6.0 nm, was again used in conjunction with a d.c. high pressure 500W xenon arc, the light from which was focused on a point 2 cm behind the flame by a silica lens of focal length 6 cm. Measurements were made 2 cm above the tips of the primary cones of a non-luminous, slightly fuel-rich air-acetylene flame. The original burner was modified to take an air-acetylene burner head of similar dimensions to the normal Unicam air-acetylene head. An integration period of ten seconds was used throughout.

Results and Discussion

The detection limits obtained are shown in Table XI, together with the wavelengths g_f-values and energy levels for each transition[100].

Copper

Nickel interfered slightly by both thermal emission and fluorescence, to approximately the same extent when the 324.75 nm copper line was used. The thermal emission can be attributed to the 323.30 and 324.31 nm nickel lines, whereas the fluorescence interference is probably due to the 323.30 nm nickel resonance line which has a g_f-value of 0.17[100] and corresponds to a transition only 0.017 e.V. higher than the

TABLE XI

Element	Line (nm)	g_f	AE detn* limit (ppm)	AF detn* limit (ppm)	Energy levels	
					Lower (eV)	Upper (eV)
Cu	324.75	0.64	0.25	3	0	3.817
Cu	327.40	0.31	0.15	2	0	3.786
Ag	328.07	0.53	0.20	3	0	3.778
Ag	338.29	0.23	0.20	4	0	3.664
Ga	403.30	0.24	0.20	-	0	3.073
Ga	417.21	0.53	0.15	-	0.102	3.073
In	410.18	0.47	0.30	20	0	3.022
In	451.13	0.66	0.20	15	0.274	3.022
Tl	377.57	0.22	0.25	6	0	3.283
Tl	535.05	0.92	0.50	20	0.966	3.283
Zn	213.86	1.30	-	10	0	5.795
Cd	228.80	0.92	6	10	0	5.417
Cd	326.11	0.0014	5	-	0	3.801
Ca	422.67	0.28	0.02	0.5	0	2.932
Mg	285.21	1.10	0.30	3	0	4.346
Cr	357.87	1.60	1.5	3**	0	3.463
Cr	359.35	1.40	2.0		0	3.449
Cr	360.53	1.00	2.5		0	3.438
Cr	425.43	0.54	1.5	20**	0	2.913
Cr	427.48	0.41	0.5		0	2.899
Cr	428.97	0.26	0.4		0	2.889
Mn	279.48	0.97	0.50	2.5	0	4.433
Mn	279.83	0.78			0	4.428
Mn	280.11	0.57			0	4.423
Mn	403.08	0.33	0.05	4	0	3.075
Mn	403.31	0.23			0	3.073
Mn	403.45	0.13			0	3.072
Co	350.23	2.0	1.0	-	0.432	3.971
Co	350.26	0.066			0.174	3.713
Co	240.73	2.20	-	20	0	5.149
Co	242.49	1.90			0	5.111
Ni	232.00	0.86	-	8	0	5.342
Ni	341.48	1.00	1.0	5	0.025	3.655
Ni	352.45	0.85	0.8	5	0.025	3.542
Ni	361.94	1.50	1.5	-	0.423	3.847

* Detection limit taken as the concentration at which the signal is twice the standard deviation at that concentration.

** Although the resolution was sufficient to resolve these lines by thermal emission at minimum monochromator bandpass (0.15 nm) no resolution was possible at the maximum bandpass (6 nm) used for this and all other fluorescence measurements.

Detection Limits

readily excited copper line at 324.75 nm.

When the 327.40 nm line was used, fifty-fold excesses of silver were found completely to predominate over the signal obtained by both thermal emission and atomic fluorescence, because of the intense thermal and fluorescence emission of the 328.07 nm silver line.

Silver

As expected, the copper line at 327.40 nm interfered in the determination of silver at 328.07 nm by both techniques. At 338.29 nm, nickel was found to interfere seriously with the silver determination by both fluorescence and emission. Lines that have been observed[100] in air-acetylene for thermal emission around the silver line are shown in Table XII. Of these, only nickel line at 341.48 has already been reported[74] by atomic fluorescence in air-hydrogen, using a high intensity hollow cathode lamp as source. It seems probable, however, that other lines may also contribute to the interference when a continuum source is used, since the intensity of any line depends on the intensity of the source lines involved in the excitation mechanism. 1000 ppm of Pb^{2+}, Co^{2+}, Mn^{2+}, Bi^{3+}, K^{+}, In^{3+}, Zn^{2+}, Sn^{2+}, Te^{4+}, Na^{+}, As^{3+}, NH_4^{+}, Ca^{2+}, Cd^{2+}, and Fe^{3+} caused less than 5% interference in the determination of 20 ppm silver by either technique at both 328.07 and 338.29 nm. 250 ppm aluminium caused no interference, but 1000 ppm aluminium gave a 6% enhancement in fluorescence at both wavelengths, which was attributed to scatter.

TABLE XII

Line (nm)	g_f	Energy Levels Lower (eV)	Energy Levels Upper (eV)
336.58	0.11	0.423	4.105
336.62	0.059	0.165	3.847
336.96	0.035	0	3.678
338.06	1.0	0.423	4.089
338.09	0.055	0.275	3.941
339.11	0.16	0	3.655
339.30	0.41	0.025	3.678
341.48	1.0	0.025	3.655

Nickel emission lines near the 338.29 nm silver line.

Gallium

No atomic fluorescence could be detected for gallium in an air-acetylene flame using a continuum source. Although this result seems surprising, considering the g_f-values and energy levels involved, it agrees with previous observations in an air-hydrogen flame using a continuum source[69]. In Table XIII the g_f-values and energy level changes are compared for gallium, and for the major interferences in the thermal emission determination of gallium at 403.3 nm, potassium and manganese. Manganese and potassium were both found to exhibit fluorescence at these wavelengths, so that the failure to observe gallium fluorescence is difficult to explain, except in terms of inefficient atomisation[101].

TABLE XIII

Element	Line (nm)	g_f	Energy levels Lower (eV)	Upper (eV)
Ga	403.30	0.24	0	3.073
Ga	417.21	0.53	0.102	3.073
Mn	403.08	0.33	0	3.075
Mn	403.31	0.23	0	3.073
Mn	403.45	0.13	0	3.072
K	404.41	0.23	0	3.065
K	404.72	0.12	0	3.062

g_f-values for gallium and interfering elements

Indium

1000 ppm of tin caused a 32% enhancement in the determination of 10 ppm of indium by thermal emission at 410.18 nm because of the fairly intense SnO molecular emission, but caused no interference in the determination of 100 ppm of indium by atomic fluorescence at the same wavelength. The same concentration excesses of cobalt gave rise to a 60% enhancement by thermal emission and an 88% enhancement by atomic fluorescence; possible interfering lines are shown in Table XIV. It seems probable that the fluorescence interference is primarily from the 419.07 nm resonance line, in spite of the low g_f value, although other lines could also contribute after preliminary thermal excitation.

TABLE XIV

Line (nm)	g_f	Energy levels Lower (eV)	Energy levels Upper (eV)
409.24	0.18	0.923	3.951
411.05	0.16	1.049	4.064
411.88	0.79	1.049	4.058
412.13	0.93	0.923	3.930
419.07	0.0023	0	2.958

Cobalt lines near the indium 410.18 nm line.

Thallium

1000 ppm. of barium gave more than 100% increase in signal in the determination of 80 ppm of thallium by thermal emission because of the intense BaO emission. No interference was found for the same concentrations of Ba in the atomic fluorescence determination of thallium. Iron and nickel were found to interfere seriously in the determination of thallium at 377.57 nm by thermal emission. Iron also interfered seriously by atomic fluorescence. The fluorescence of iron, excited by a line source, at 373.49 and 373.71 nm has already been reported[74]. Nickel did not interfere at 377.56, 378.35, 380.71 and 385.83 nm. This can be attributed to the low atomic population available in the excited state 0.423 eV above the ground state, from which these lines originate.

Zinc

No zinc lines were detected by thermal emission in air-acetylene, and therefore no comparison of radiation interferences was possible.

Cadmium

The cadmium line at 228.80 nm was found to be strongly self absorbed in thermal emission at this wavelength, whereas the 326.11 nm line gave a virtually linear calibration curve between the detection limit and 1000 ppm. Although the 326.11 nm line has recently been reported[102] by fluorescence with an intense line source in a separated air-acetylene flame, it was not detected in this study using the xenon arc source. Extensive interference studies in the atomic fluorescence of cadmium with line sources have already been reported by Dagnall, West and Young[103] who found that one hundred-fold excesses of 41 cations and 18 anions caused less than 5% interference in the determination of 10^{-5} M Cd^{2+}.

Nickel was found to interfere by > 100% in the fluorescence determination of cadmium at 228.0, but only slightly in the thermal emission determination at the same wavelength, and also at 326.11 nm. The fluorescence of nickel excited by a continuum source at 232.00 nm has already been reported[73], and it seems probable that the 229.0, 231.10, 231.23, 231.40, 232.58 and 234.55 nm nickel lines also occur[74,75] to a lesser extent.

Magnesium

The magnesium 285.21 nm line is virtually free from radiation interferences. Chemical interferences in the determination of magnesium and calcium by atomic fluorescence spectroscopy with a xenon arc source in a hydrogen-entrained air flame on a total consumption burner have been reported elsewhere[68].

Calcium

The chromium line at 425.43 nm was found to interfere in the determination of calcium at 422.67 nm by atomic fluorescence, but the smaller slit-widths employed when the calcium was determined by thermal emission, provided sufficient resolution to eliminate this source of interference.

Chromium

1000 ppm of iron and cobalt interfered by +108% and +115% respectively in the determination of 20 ppm of chromium at 357.87, and 359.35 and 358.52 nm by thermal emission, but no interference was found when the chromium was radiatively excited under the same conditions. The interference by the thermal emission method may be attributed to the cobalt lines at 357.50, 357.54, 358.25, 358.72, 359.49 and 360.21 nm, and the iron line at 358.12 nm.

Manganese

The manganese lines at 279.48, 279.83 and 280.11 nm are virtually free from radiation interferences in both techniques, but the 403.08, 403.31 and 403.45 nm lines are susceptible to interference from the 404.41 nm potassium resonance line and the gallium 403.30 nm resonance line. 1000 ppm of potassium were found to give a 12% enhancement by both techniques in the determination of 20 ppm of manganese; the same concentration excess of gallium gave a 60% enhancement by thermal emission, but less than 5% in the determination of 20 ppm of manganese by atomic fluorescence.

Cobalt

The 350.23 and 350.26 nm cobalt lines are subject to extensive thermal emission interference from the strong group of nickel lines between 349.30 and 352.45 nm; no fluorescence was observed for cobalt at 350.2 nm. 1000 ppm of manganese were found to give a 40% enhancement in the determination of 10 ppm of cobalt at these wavelengths because of the 353.20 nm manganese line. The same excesses of these elements did not interfere, however, in the determination of cobalt by measurement of its resonance fluorescence at 240.73 and 242.49 nm where thermal emission for cobalt is very weak.

Nickel

The group of cobalt lines between 340.51 and 343.16 nm completely predominated over the determination of 20 ppm of nickel at 341.48 nm in the presence of 1000 ppm of cobalt only by thermal emission. For the same concentrations, when the nickel line at 352.45 nm was used, the group of cobalt lines between 350.23 and

353.34 nm gave rise to very extensive interference by both thermal and fluorescence emission although the 352.68 nm resonance line probably predominates in the fluorescence interference. At the same wavelength, 1000 ppm of manganese gave rise to a 50% enhancement in the determination of 20 ppm of nickel by thermal emission, but had no significant effect on the fluorescence emission. When the 361.94 nm nickel line was used for the determination of 20 ppm of nickel by thermal emission, 1000 ppm of iron and chromium were found to give enhancements of 500 and 450% respectively: The radiation can be attributed to the iron 360.89, 361.88 and 363.15 nm lines and the chromium 360.53 and 359.35 nm lines. No fluorescence was observed for nickel at 369.14 nm.

Conclusions

The results obtained for most of the elements investigated indicate that in air-acetylene, the detection limits obtainable by atomic fluorescence emission excited by a 500W xenon arc continuum source are, as expected, not so good as those obtained by thermal emission in the same flame. This fact has already been observed by other workers[69], using air-hydrogen and air-propane flames, for fluorescence measurements. However, for the elements to which atomic fluorescence with a continuum source has been applied, atomic radiation interferences are comparable by both atomic fluorescence and thermal emission spectroscopy, but the molecular emission interferences which are predominant in the latter technique are almost without effect in fluorescence. Moreover, Goodfellow has reported[104] that suppression effects caused by the alkali metals, which occur frequently in thermal emission, are negligible in the determination of zinc, cadmium and copper by atomic fluorescence. The relative freedom from interferences in the determination of silver by fluorescence also supports Goodfellow's findings[104] that interaction between radiatively excited atoms is negligible in flames. Although it has been suggested[68] that the moderate intensity of a 450W xenon arc under absorption line profiles should excite fluorescence only for one or two lines for most elements, radiation interferences such as those found here might limit the suggested[105] use of scanning atomic fluorescence with a continuum source to the simultaneous qualitative and semiquantitative determination of a limited number of elements, since most workers have used large monochromator entrance and exit slits when investigating atomic fluorescence with continuum sources.

It should be pointed out that when suitable line sources are used in atomic fluorescence, radiation interferences can only occur when overlap exists between a line of the source of irradiation and the absorption profile of the interfering metal, and such instances are rare, because of the narrowness of both the emission and the absorption profiles.

For elements such as zinc and cadmium, which exhibit only very weak thermal emission, the use of a nitrogen separated flame should improve the detection limits by about one order of magnitude[102]. For strongly emitting elements, however, as it is not practical to make fluorescence measurements above that region of a laminar air-acetylene flame that exhibits atomic thermal emission, the flame background noise is less important than the noise on the atomic thermal emission of the element being determined. Interference on fluorescence measurements with a continuum source can generally be eliminated[68] by scanning the fluorescence spectrum on either side of the line under investigation, provided that the particles causing the phenomenon do not significantly decrease the available atomic population of the element under investigation.

Chapter XI Some Studies in the Application and Properties of a New Type of Dual-element Electrodeless Discharge Tube

In chapters VII and X, some of the problems associated with the use of continuum sources for atomic fluorescence work were considered. Research into the use of multi-element sources for atomic spectroscopy arises because of the reduced cost per element, lower storage area, and significant time saving achieved by obviating the warm up time which is often necessary when single-beam atomic absorption or atomic fluorescence instruments are used. Several publications have recommended the application of multi-element hollow cathode lamps to A.A.S., but so far it appears that no attempts have been made to investigate the application of these sources to A.F.S..

Jones and Walsh[108] have described a calcium-magnesium lamp which contained a separate cathode for each element, but this technique was susceptible to deterioration caused by the plating-out of the metal sputtered from one cathode onto the second cathode. Early attempts to make a copper and zinc lamp using brass cathodes[109] were also unsuccessful because of the effects of preferential sputtering. Massman[110], and Butler and Strasheim[111] have described multi-element lamps constructed by pressing rings of various metals into a single cathode; by positioning the rings according to the volatilities of the metals used, stable emission was obtained for each element. Sebens, Slavin and Vollmer [112] have suggested the use of sintered cathodes made from mixed powders. Intermetallic compounds have also been used for cathodes[113,114]. Shielded cathodes, which lead to improved stability and intensity, and greater lamp life[115], have also been applied to multi-element lamps[116,117]. Although demountable hollow cathode lamps have been suggested for atomic absorption[118 - 121], and the type suggested by Goodfellow[118] with push-fit cathodes operating in a continuous flow of argon minimises the time delay due to the effects of out-gassing, this type of system is not really suited to routine sequential analysis, even for atomic absorption work with double-beam instrumentation.

Aldous, Dagnall and West[122] have noted that in aluminium electrodeless discharge tubes, there is often sufficient beryllium present to use the aluminium tube as a spectral line source for beryllium. West and co-workers have used[52,53,58] multi-element electrodeless discharge tubes containing elements of comparable vapour pressure at the working temperature of the tube for atomic absorption and atomic fluorescence measurements. Marshall and West[52,53] have reported that for systems of this type, the incorporation of two or more elements into a single discharge tube has no adverse effect on the fluorescence detection limit obtained, and did not report any interaction between simultaneously excited elementary and molecular species in discharge tubes. Attempts to prepare a zinc-mercury tube by this method were unsatisfactory because of the different volatilities of the elements involved, and either the tubes were very unstable, or, at low power, the mercury tended to completely predominate in the discharge.

In the past two years, several workers have investigated the effect of surrounding discharge tubes with low-pressure jackets[54,94,123], and have noted appreciable improvements in the stabilities of the resulting discharges, and in some cases, the occurrence of a discharge within the outer jacket[54,94]. The jacketing method employed by Aldous, Dagnall and West[94] was applied to the manufacture of dual-element electrodeless discharge tubes which contain elements of different volatility, and the stability, intensity and applicability of the resultant sources was investigated. The results obtained are reported in this chapter.

Experimental

Blank tubes were prepared as shown in fig. 42. These were degassed by strong heating of the outer tube in the normal way[124]. The internal diameters of the tubes used in the present investigation were 2 mm and 8 mm for the inner and outer tubes respectively. Normal wall, transparent vitreosil tubing supplied by Jencons Ltd., Hemel Hempstead, was used throughout. Unless the constituent to be introduced to the outer tube is extremely volatile, e.g. iodine, mercury, the elements or halides used are introduced simultaneously to the inner and outer tubes, and the elements are sublimed and the tube is sealed as usual[124]. If the element in the outer tube is highly volatile, it is advisable to seal off the outer tube before introducing the sample to the inner tube. The final appearance of a tube of this type is shown in fig. 43.

The stabilities of a number of tubes of this type are shown in table XV, p.118. The tubes were excited at 2450 Hz with a Microtron 200 high frequency generator, and operated in a $\frac{3}{4}$ wave cavity; all stability and fluorescence measurements were made on the modified Southern Instruments A 1740 described in chapter VIII, used in conjunction with a Servoscribe chart recorder.

As expected, this table shows that the element in the inner tube tends to give a more stable discharge than the element in the outer tube: Another interesting point is that for certain elements, such as tellurium, lead and thallium, stable and intense discharges can be obtained from the element in place of the halide systems normally used in this laboratory without running the tube at high power. To evaluate the usefulness of these sources as atomic spectral line sources, a series of detection limits was determined in a slightly fuel-rich oxy-hydrogen flame burning on a Beckman total consumption burner; the results obtained are shown in table XVI, p.119.

Although these results are of the expected order of magnitude, some of the results obtained for the elements in the

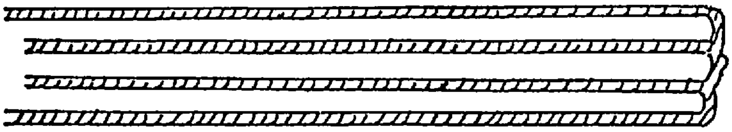


Fig. 42.

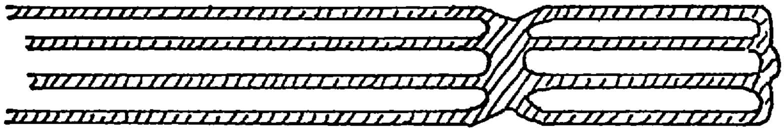


Fig. 43.

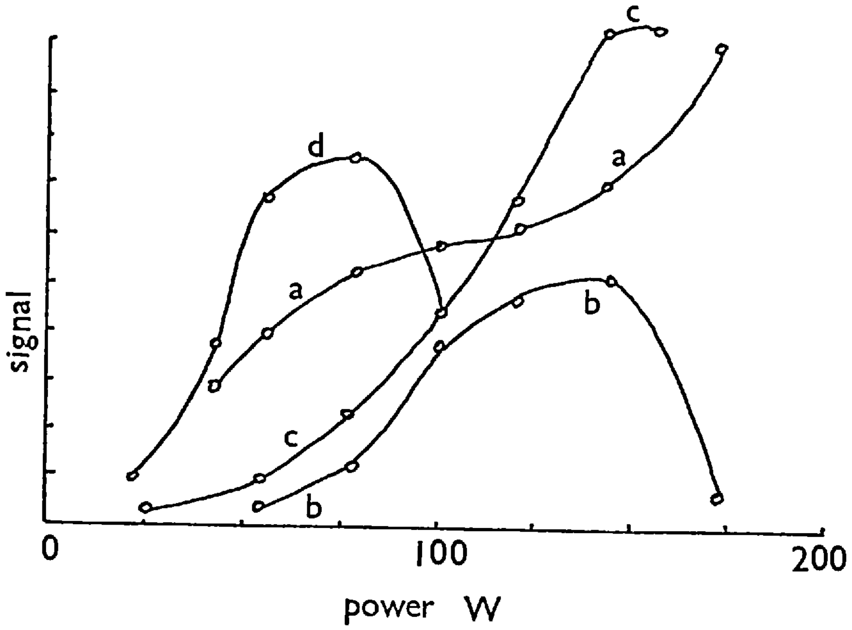


Fig. 44.

TABLE XV

Tube	Components		Stability*		Power
	Inner	Outer	Inner	Outer	W
Te/Se	Te	Se	1.7	3.8	60
As/Se	As/I_2	Se	1.9	2.5	50
Ag/Zn	Ag/AgCl	Zn	1.9	3.2	65
Ag/Cd	Ag/AgCl	Cd	1.8	1.9	65
Ag/Hg	Ag/AgCl	Hg	3.2	5.2	60
Zn/Hg	Zn	Hg	1.7	3.8	60
Pb/Cd	Pb	Cd	0.7	4.5	60
Pb/Cd	Pb/PbI_2	Cd	4.8	3.5	65
Cr/Cd	$CrCl_3$**	Cd	3.0	4.8	50
Ni/Cr	$NiCl_2$	$CrCl_3$**	3.2	4.8	60
Mn/Cr	$MnCl_2$	$CrCl_3$**	2.7	7.9	60
Sb/Bi	Sb/I_2	I_2	2.2	2.2	50

* expressed as ± % per hour after an initial running-in period of one hour.

** obtained by vacuum dehydration of the hydrated salt.

TABLE XVI

Tube	Element	Line	Detection Limit A.F.S.	Flame Height cm
Te/Se	Te	214.3	1.5	7
Te/Se	Se	196.0	0.8	7
As/Se	As	193.7	25.	7
As/Se	Se	196.0	0.6	7
Ag/Zn	Ag	328.1	0.002	10
Ag/Zn	Zn	213.9	0.0001	10
Ag/Cd	Ag	321.8	0.0008	10
Ag/Cd	Cd	228.8	0.00004	10
Ag/Hg	Hg	328.1	0.004	10
Ag/Hg	Hg	253.7	12.	10
Zn/Hg	Zn	213.9	0.001	10
Zn/Hg	Hg	253.7	16.	8
Pb/Cd	Pb	405.7	12.	10
Pb/Cd	Cd	228.8	0.00005	10
Pb/Cd*	Pb	405.7	10.	10
Pb/Cd*	Cd	228.8	0.00001	10
Cr/Cd	Cr	359.3	30.	5
Cr/Cd	Cd	228.8	0.00008	10
Ni/Cr	Ni	232.0	0.8	5
Ni/Cr	Cr	359.3	20.	5
Mn/Cr	Mn	279.4	0.1	5
Mn/Cr	Cr	359.3	20.	5
Sb/Bi	Sb	231.1	6.	6
Sb/Bi**	Bi	302.5	10.	6

* lead present as lead iodide

** detection limit obtained with strong cooling of discharge tube inner tube are slightly lower than expected, and it was therefore decided to investigate the properties of the mercury jacketed zinc tube in greater detail. Fig. 44 shows the effect of operating power on the intensity of a) a normal zinc discharge tube, b) a mercury jacketed zinc discharge tube, c) the fluorescence signal obtained for 0.1 ppm zinc with a normal zinc tube and d) the fluorescence signal obtained for 0.1 ppm zinc with a mercury jacketed zinc tube. These results indicate that self-reversal, self absorption and line-broadening are far more significant in the jacketed tube. This conclusion was supported by a brief interferometric investigation of these tubes[125], which showed that for the maximum power input in the $\frac{3}{4}$ wave cavity, even non-resonance zinc lines such as the 481.05 nm line exhibited very pronounced reversal. The temperature of the inner tube was estimated with an optical pyrometer, by taking measurements on the inner tube immediately after extinction, and the results obtained indicate that the temperature of the inner tube can be as high as 1075°C at maximum operating power. Extrapolation of the temperature-power curve obtained indicated a temperature of about 600°C at 60 W. The vapour pressure of many of the elements and compounds introduced to the centre tube is excessive at this temperature, and this preliminary investigation therefore indicates that either the compound introduced must have a relatively low vapour pressure at the working temperature of the tube, or the amount of the element introduced must be insufficient to provide a saturated vapour at the working temperature of the tube: The latter possibility is discussed in greater detail in the final chapter of this thesis.

Although these dual-element electrodeless discharge tubes have only been investigated as sources for A.F.S. in the present investigation, they should be equally applicable to A.A.S., and may well prove to be of more practical value than multi-element hollow cathode lamps, provided the conditions are chosen to minimise self-reversal and line broadening. Possible limitations of these sources due to the possibility of spectral interferences are discussed in chapter XIII.

Chapter XII Some General Observations on Multi-element Electrodeless Discharge Tubes

In the previous chapter a method was described for the preparation of dual-element electrodeless discharge tubes for elements of different volatility. A logical extension of this method is to combine two or more elements in both the inner and outer tubes, thus giving a discharge tube containing four or more elements, and this type of system is at present under investigation[126]. However a brief preliminary investigation has indicated the possibility of the occurrence of interaction between different molecular species present in the same discharge tube. Table XVII shows the ratio of three of the main thallium lines in a variety of thallium and thallium-indium discharge tubes operated in the $\frac{3}{4}$ wave cavity at 100 W. In all of the tubes other than the Tl, In, I_2 tube, the line ratios were found to vary very slightly with power, whereas in the latter tube, the line ratios varied appreciably with power.

These results could be attributed to the preferential thermal deactivation of thallium atoms by indium iodide molecules (after initial microwave excitation) to the lower level, followed by radiative deactivation. If the occurrence of this type of effect is widespread, it might limit the application of multi-element tubes of this type, unless the deactivation process yields a lower energy resonance line. The effect was much less pronounced for indium.

TABLE XVII

Present	2768	3776	5351	Type
Tl	17.0	80.0	30.0	Normal
Tl	13.3	80.0	29.0	Vacuum Jacketed
$TlCl_3$	33.0	80.0	23.7	Normal
Tl, I_2	27.0	80.0	25.0	Normal
Tl, In	11.7	80.0	27.0	Vacuum Jacketed
Tl, In, I_2	0.9	43.5	80.0	Normal

Line Ratios in some Thallium Systems

Simultaneous Operation of Groups of Discharge Tubes

Aldous, Dagnall and West have shown[94] that two small-bore discharge tubes can be operated simultaneously in a single microwave cavity. This method of producing a multi-element discharge has been applied here[126] to the production of three and four element discharges. The detection limits obtained for the indium-thallium-cadmium system are shown in table XVIII.

TABLE XVIII

Element	Line	Detection Limit
Cd	2288	0.002
In	4511	1.0
Tl	3776	0.5

Some Detection Limits in Oxy-hydrogen, (D.C. detection system).

Discharge tubes were prepared from zinc metal, cadmium metal, thallous chloride and indium metal-iodine in the normal way, but using thin-walled transparent vitreosil tubing of 2 mm internal diameter (Jencons Limited).

This system appears to be ideally suited to routine use in laboratories where small, varying groups of elements are to be determined, and is being investigated further.

Another possible type of multi-element system is shown in fig 45. The outer tube was made from 9 mm i.d. normal wall tubing, and the central and inner tubes were made from 5 and 2 mm thin-walled vitreosil tubing respectively. Tubes were made containing zinc, thallous chloride and mercury in the inner, central and outer tubes respectively. Although tubes of this type are simple to prepare, they are of limited applicability.

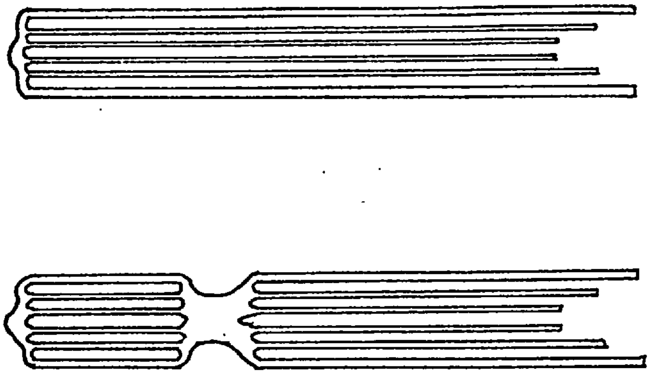


Fig. 45.

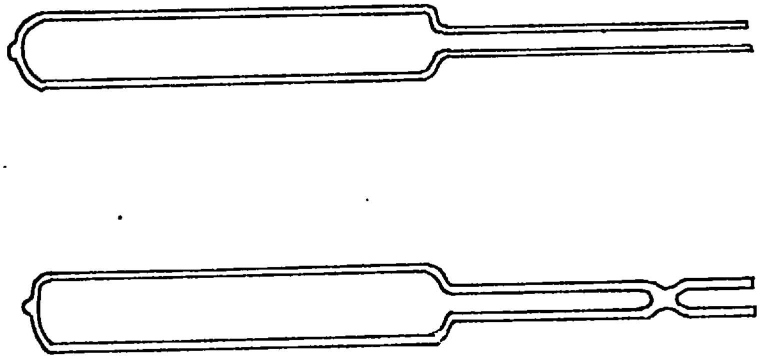


Fig. 46.

Some Observations on Mercury Tubes

The detection limits obtained in the previous chapter for mercury, using mercury jacketed tubes, were appreciably lower than those generally obtained by other workers. This was attributed to excessive line broadening and self reversal that occurs.in mercury tubes: A tube may therefore be prepared as shown in fig. 46: The tube length used was 24 cms. Figs. 47, 48 and 49 show the effect of microwave power on the integrated line intensity and fluorescence intensity (from 100 ppm mercury) in turbulent oxy-hydrogen for three electrodeless discharge tubes prepared as follows:

Fig. 47	Tube containing *ca.* 100 mg of mercury sealed at 3 torr of argon.
Fig. 48	Tube containing mercury from the vacuum gauge only, sealed under continuous pumping (nominal pressure 0.4 torr).
Fig. 49	Tube prepared as shown in Fig. 46, sealed at 3 torr of argon, containing about 0.1 g of mercury.

An interferometric investigation[125] showed that the long mercury tube exhibited Hg hyperfine structure at 75 W, whereas a tube prepared by the normal method showed no hyperfine structure at all, even at 25 W: Cooling the lower bulb in ice had little effect on the intensity-power and fluorescence-power curves (see Fig. 50). The narrow resonance line obtained by this

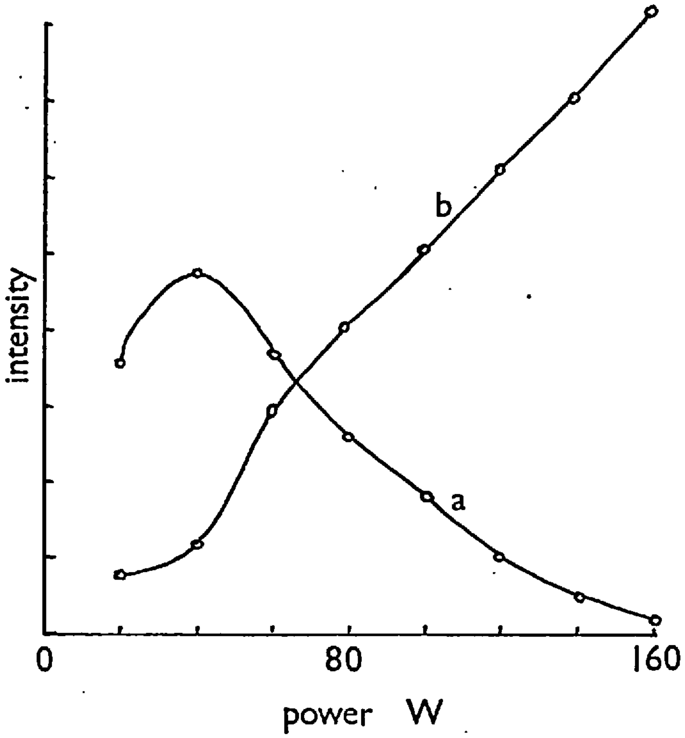


Fig. 47.

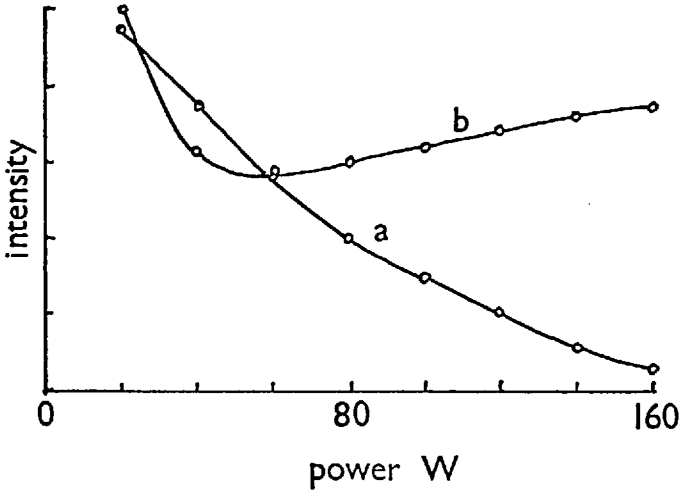


Fig. 48.

a fluorescence intensity.

b source intensity.

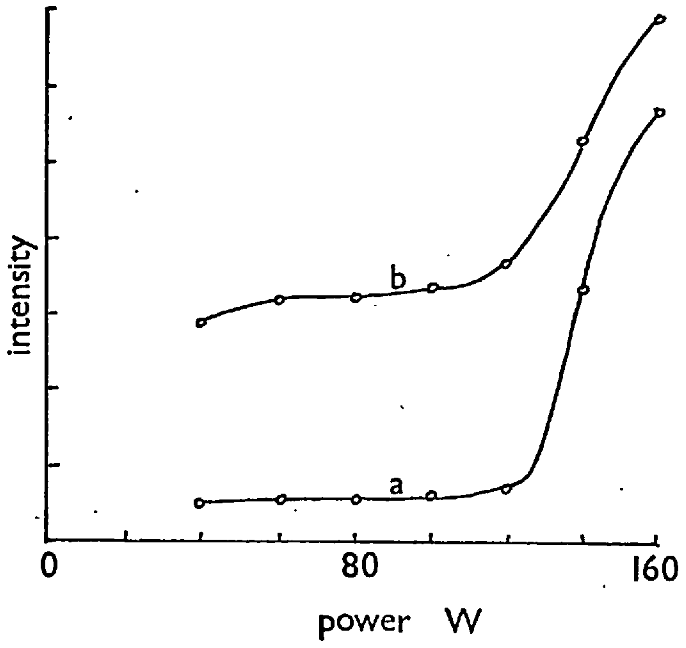


Fig. 49.

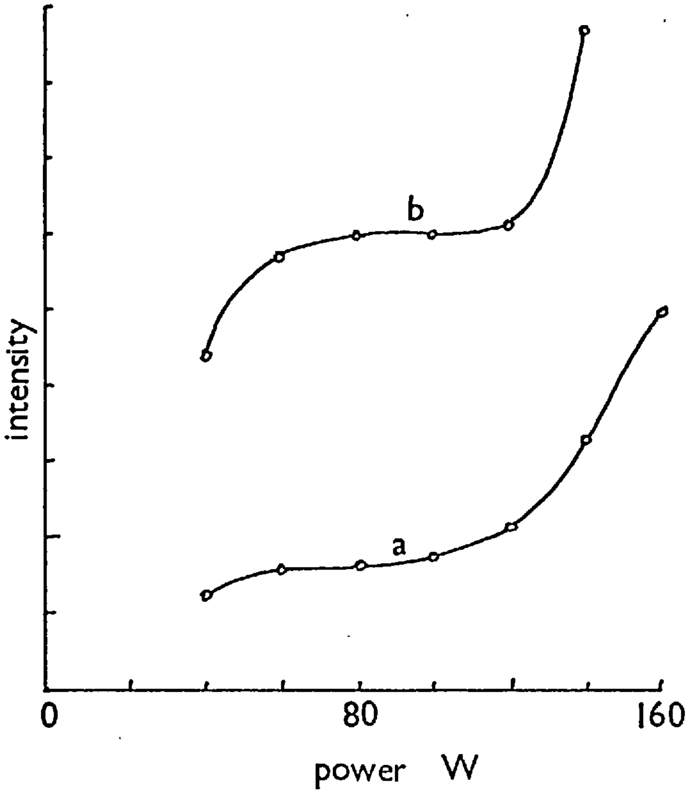


Fig. 50.

a fluorescence intensity.

b source intensity.

method should be particularly useful for atomic absorption spectroscopy.

The above results indicate that mercury jacketed tubes should be prepared as shown in Fig. 51. A suitable method for tube blank preparation is shown in Fig. 52.

Plasma-Heated Electrodeless Discharge Tubes

Several workers have suggested the operation of electrodeless discharge tubes in furnaces (see for example references 127-129). The approximate temperature measurements made in chapter XI indicate that similar temperatures are attainable in vacuum jacketed electrodeless discharge tubes. However, attempts to prepare tubes of this type for Cu and Ag as the elements were unsatisfactory because of plating out: Modified tubes, built as shown in Fig. 53, were more satisfactory, and gave fairly stable and intense discharges for several hours, but were difficult to re-light. It was therefore decided to make a brief investigation of the possible application of plasma-heated tubes. Tubes were made for Ag, Cu, Pb and Tl as shown in Fig. 54, containing the elements and sealed at 3 torr. These tubes were run under the conditions shown in table XIX. A very low flow of argon was passed through the centre of the tube, and an argon plasma was initiated: These tubes gave very intense atomic

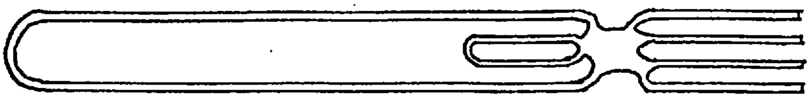


Fig. 51.

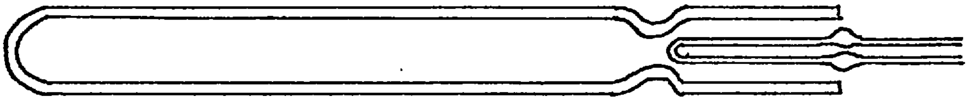


Fig. 52.

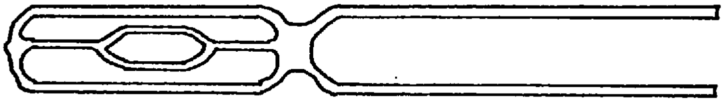


Fig. 53.

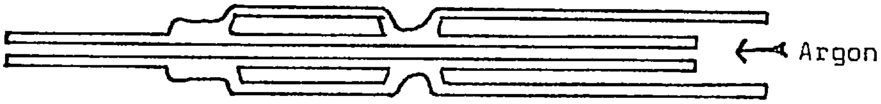


Fig. 54.

TABLE XIX

Element	Power	Reflected Power
Ag	180 W	12 W
Cu	180 W	12 W
Pb	180 W	17 W
Tl	180 W	18 W

Operating Conditions for Plasma-Heated Tubes.

line spectra with excellent line to background ratios, but were found to be of poor stability, and were not investigated further here, even though this type of system could be advantageously employed in multi-element systems.

Chapter XIII Suggestions for Future Work on Atomic Fluorescence

In the last chapter, some of the problems associated with the use of electrodeless discharge tubes as spectral line sources for analytical atomic spectroscopy were discussed. Recently Slavin and Slavin[130] have commented on the poor long term stability of some electrodeless discharge tubes at the present time. Woodward [131] has stated that certain tubes are suitable as spectral sources when a small number of analyses are to be completed for a certain element. The performance of electrodeless discharge tubes could probably be improved considerably, particularly for atomic absorption spectroscopy, if the amount of sample introduced was carefully controlled: If the quantity of element or compound introduced into the tube was sufficiently small to give a saturated vapour at temperatures below the routine operating temperature of the tube, instability due to plating out would be minimised; the quantity chosen should give the narrowest line possible for atomic absorption work, if high sensitivity is required, but care must be taken that the optimum compromise is reached between this criterion and the need for high intensity, which minimises the effects of flame noise, and a high line to background ratio. It is quite probable that the optimum conditions of preparation for tubes designed for atomic fluorescence could differ appreciably from those designed for atomic absorption, since line-broadness is less important in fluorescence work, provided there is no decrease in the source line intensity under the integrated absorption profile. If, however, the tube under preparation is to be used for the determination of a different element by the overlapping-line technique[67], it might be desirable to make the relevant line as broad as possible.

It has recently been shown[132] that intense discharges can be obtained for certain elements after the introduction of the compound required in solution form, provided the solvent is completely removed before the tube is sealed. However, this technique is only applicable to a narrow range of elements, and the introduction of organic solvents can lead to organic deposits on the walls of the discharge tube. A possible alternative method for the introduction of small amounts of sample is to introduce the element or compound to be used in the vapour phase only. This could be done by placing the relevant sample in the lower bulb shown in fig. 55: This bulb is heated to a sufficient temperature after initial out-gassing to give the required vapour pressure of the element or compound chosen, and the upper bulb is heated to a slightly higher temperature, to prevent deposition on the walls of the tube. If it is required to produce several similar tubes, it is advisable to automate the sealing system employed: If it is not practical to seal the system electrically, either a rotating tube system could be used, as shown in fig. 55, with two fixed burners, or a pair of offset ring burners could be used to provide uniform

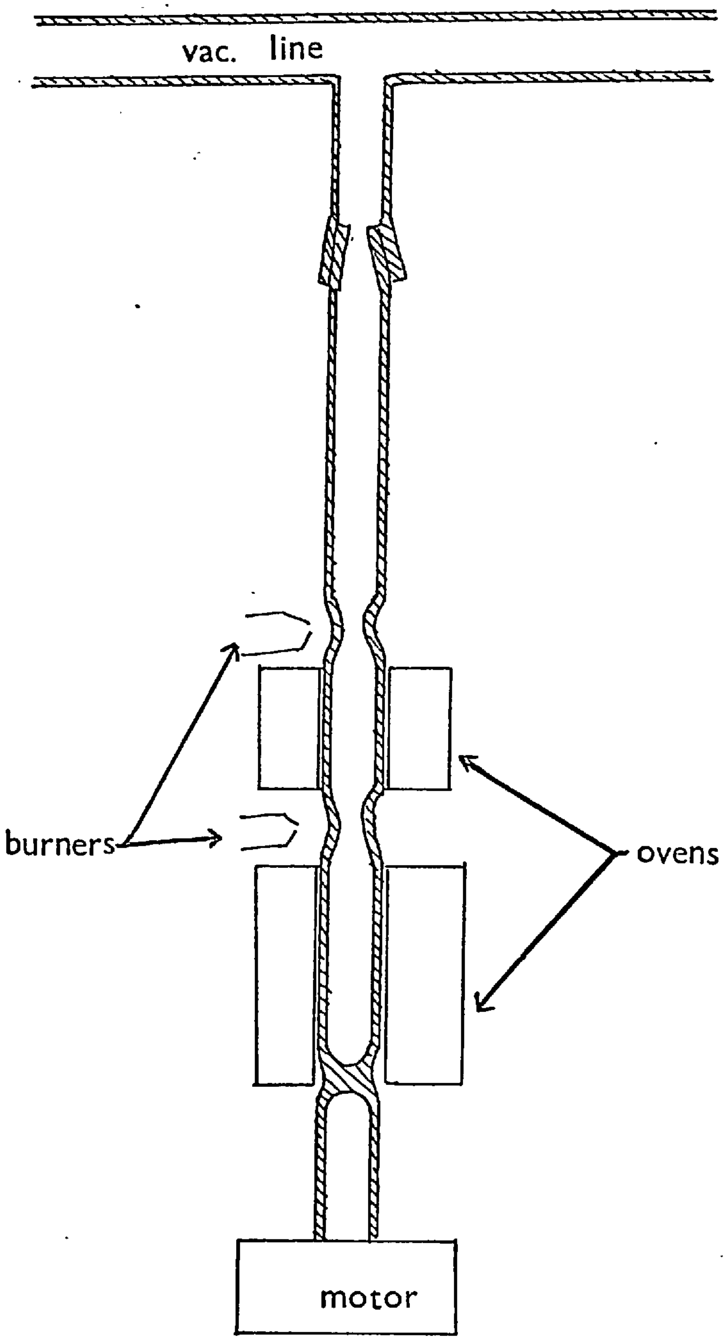


Fig. 55.

heating. Thick-walled silica tubing could be used for the tube construction, to minimise the risk of implosion. By using such a technique, it should be possible to obtain a high degree of reproducibility in tube manufacture.

In the previous chapter, the use of very long discharge tubes for mercury sources was described. It is possible that this type of source could be applied to other elements provided a compound of sufficient volatility is available: The operation of this type of source with the temperature of the lower bulb thermostatically controlled could lead to considerable improvements in the stability of the discharge obtained, which would enable greater scale expansion to be used in atomic absorption.

Most of the microwave generators used to power discharge tubes for analytical work have been designed for medical use, where high output stability is not essential, and there can be little doubt that systems designed to give a constant absorbed power would considerably improve the stability of microwave plasmas. This is particularly true when tuned cavities are used: It has recently been shown[132] that source and fluorescence signals tend to rise to a maximum value far more rapidly when a tuning stub is added to a standard $\frac{3}{4}$ wave cavity[98], but the fluorescence signal obtained tends to be far more power dependant: If an untuned cavity is used, although the detection limits obtained by atomic fluorescence are less favourable, measurements can often be made on the plateau of a fluorescence signal-power curve.

A useful development in A.F.S.[133] is the design of a system for source drift compensation, and systems of this type should find wide-spread application if atomic fluorescence is to be used on a routine basis. This type of system could be particularly useful and economical in filter instrumentation, and developments in the field of interference filters could play an important part in the development of atomic fluorescence as an analytical technique.

During the course of the work described in chapter XI, it was noted that the outer discharge in mercury jacketed tubes could be extinguished by running the tube at high power (eg. 180W) for about 30 - 40 seconds, and then rapidly reducing the power to 25W: Subsequent power increases up to 100W did not re-initiate the mercury discharge, and this method could therefore be applied to prevent decrease in the line to background ratios when low pressure jackets are used to improve the stability of discharge tubes.

Very little work has been published at the present time on multi-element sources for atomic fluorescence spectroscopy. If the interaction postulated in chapter XII is found to exist for other element combinations, the resulting tubes could be useful for investigating fluorescence mechanisms in place of the source/filter combination more generally used, although care would be necessary in the interpretation of the results, because of the possibility of changes in line widths and the extent of self-reversal.

The problems associated with the use of multi-element hollow cathode lamps have recently been discussed[117], and many of these problems also apply to electrodeless discharge tubes. Although there are less limitations in the range of elements that can be usefully combined in discharge tubes than there are in hollow cathode lamps from the point of view of obtaining stable discharges, the limitations due to the possibility of obtaining spectral interferences are similar for the two systems.

Two types of spectral interference should be considered: The first type occurs when non-absorbing atomic or ionic lines, or, for discharge tubes only, molecular emission bands, occur within the spectral bandpass used. Thus, for example, the strong chlorine molecular spectrum obtained in silver-silver chloride discharge tubes (see Fig. 56) covers a significant portion of the useful ultra-violet region of the spectrum, and limits the range of elements which could be usefully combined with silver if the tube is to be used for atomic absorption. The effect results in higher curvature in calibration plots and lower sensitivity, but no false absorption signal is obtained if the element yielding an interfering line in the source is present in the solution which is being analysed. Care must also be taken that the line is not found in the fluorescence spectrum by an indirect route.

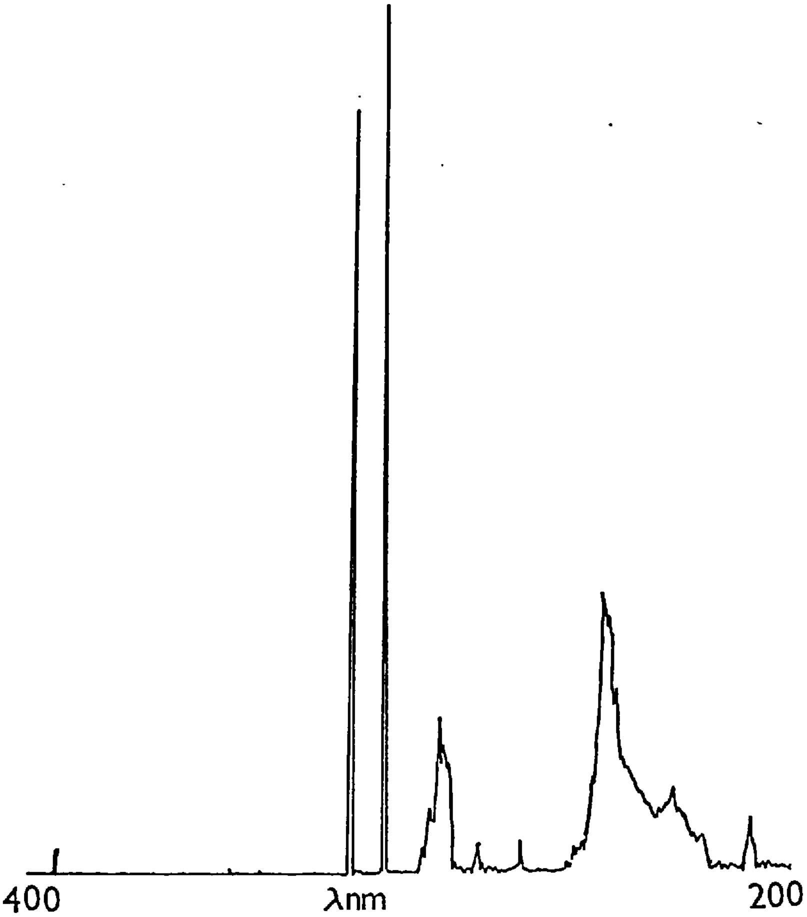


Fig. 56.

The second type of spectral interference arises when absorbing lines of one or more of the other elements present in a cathode or discharge tube are passed by the monochromator; this results in greater curvature in the working curve in atomic absorption, and also, if the element emitting the absorbing line is present in the solution an erroneous result will invariably be obtained in both atomic absorption and atomic fluorescence determinations.

Virtually any such spectral interference can be avoided by choosing a different spectral line for the determination, or by scanning through the fluorescence spectrum and making measurements at two or more wavelengths.

The possibility of line overlap at wavelengths other than that being used for a given determination giving rise to erroneous fluorescence readings are so remote that they need not be considered further if a monochromator is to be used, but if non-dispersive detection systems are used[94, 134, 135], then interference could be encountered; an example would be interference from bismuth fluorescence when tubes containing metal iodides are used.

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Addendum

On page 45, the use of the selenium-dithizone system was suggested as a possible extraction process for enhancement of the sensitivity of the determination of selenium by A.F.S.: Since this chapter was completed, it has been shown (Irving et al., Anal. Chim. Acta, 49, 9 (1970)) that selenium reacts with dithizone to yield a coloured oxidation product, and that it is this product, and not a selenium complex which is extracted.