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ASPECTS OF INDIRECT ATOMIC-ABSORPTION DETERMINATIONS

BASED ON MOLYBDENUM HETEROPOLY ACID CHEMISTRY

by

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*To my parents*

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## CONTENTS

		<u>Page No</u>
ABSTRACT	.....	i
CHAPTER 1:	GENERAL INTRODUCTION	1
1.1	Aim	1
1.2	Application of Indirect Methods in Analysis by Atomic Absorption Spectroscopy	2
1.3	Atom Cells in Atomic Absorption Spectroscopy	4
1.3.1	Flame Atom Cell	5
1.3.1.1	Limitations of the flame atom cell	6
1.3.1.2	Means of improving sensi- tivity	8
1.3.1.3	Discrete-volume nebuliza- tion method	8
1.3.2	Electrothermal Atom Cell	9
1.3.2.1	Advantages of electrothermal atomization	10
1.3.2.2	Disadvantages of electro- thermal atomization	11
1.3.3	Pretreatment	12
CHAPTER 2:	DETERMINATION OF ORTHOPHOSPHATE BY DIRECT AND INDIRECT SOLUTION SPECTROPHOTOMETRY	15
2.1	Introduction	15
2.2	Separation	16
2.3	Review of Methods for Orthophosphate Determination	17

	<u>Page No</u>
2.3.1 Gravimetric Methods . . . . .	17
2.3.2 Titrimetric Methods . . . . .	18
2.3.3 Electrical Methods . . . . .	19
2.3.4 Radiochemical Methods . . . . .	20
2.3.5 Kinetic Methods . . . . .	20
2.3.6 Spectroscopic Methods . . . . .	21
2.3.6.1 Spectrophotometric methods . . . . .	21
2.3.6.2 Atomic absorption spectroscopy . . . . .	24
2.3.6.3 Flame emission spectroscopy . . . . .	29
2.3.6.4 Fluorimetric methods . . . . .	29
PRACTICAL EXPERIMENTS . . . . .	30
2.4 Direct UV-Visible Spectrophotometry Methods . . . . .	30
2.4.1 Ascorbic Acid Method . . . . .	30
2.4.2 Solvent Extraction Method . . . . .	37
2.5 Indirect UV Spectrophotometry Method . . . . .	42
2.6 Indirect Determination of Orthophosphate by Atomic Absorption Spectrophotometry using Flame Atomization . . . . .	46
2.6.1 Optimization of the Instrument Parameters and Calibration for Molybdenum, Using air-C <sub>2</sub> H <sub>2</sub> and N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub> Flame . . . . .	46
2.6.2 Comparison of Sensitivities for Atomization in the Presence of Different Basic Buffer Solutions . . . . .	51
2.6.3 Extraction of 12-molybdophosphoric Acid and Subsequent Indirect Determination of Phosphorus Using Air-C <sub>2</sub> H <sub>2</sub> Flame . . . . .	53
2.6.3.1 Effect of anhydrous sodium sulphate on the recovery of heteropoly acid . . . . .	58
2.6.3.2 Effect of anhydrous sodium sulphate on blank values . . . . .	62

	<u>Page No</u>
CHAPTER 3: FLAME ATOMIZATION OF MOLYBDENUM . . . .	64
3.1 Introduction . . . . .	64
3.2 Review of Mechanism of Interferences in Flames . . . . .	65
3.3 Selective Review of Flow Injection Analysis with Flame Atomic Absorption Spectrometry	70
PRACTICAL EXPERIMENTS . . . . .	74
3.4 Approaches for Improving the Sensitivity and Detection Limit for Molybdenum Using Flame Atomization . . . . .	74
3.4.1 Modification of Flame Chemistry	74
3.4.1.1 Varying flame gases . . . .	74
3.4.1.2 Varying salts . . . .	75
3.4.2 Modification of Nebulization Process	79
3.4.2.1 Use of flow injection methodology . . . .	79
3.4.2.2 Varying solution physical properties . . . . .	82
3.4.3 Use of Drying Agent in Indirect Heteropoly Acid Procedures . . . .	89
3.5 Conclusion . . . . .	89
CHAPTER 4: CARBON ROD ELECTROTHERMAL ATOMIZATION OF MOLYBDENUM . . . . .	92
4.1 Introduction . . . . .	92
4.2 Review of Electrothermal Atomization for Molybdenum . . . . .	93
4.2.1 Mechanism of Atomization for Molyb- denum . . . . .	93
4.2.2 Atomizer Modifications . . . .	96
4.2.3 Pyrolytic Graphite Coating . . . .	105

	<u>Page No</u>
PRACTICAL EXPERIMENTS . . . . .	107
4.3 Optimization of the Instrument Parameters and Calibration for Molybdenum . . . . .	107
4.4 Extraction of 12-Molybdophosphoric Acid and Subsequent Indirect Carbon Rod Electrothermal Atomization of Phosphorus . . . . .	115
4.5 Modification of Carbon Rod Atomizer Using Sequential Gas Introduction System . . . . .	119
4.5.1 Introduction of Argon and Methane as a Flowing Sheathing Gas . . . . .	119
4.5.2 Introduction of Argon and Hydrogen as a Flowing Sheathing Gas . . . . .	123
CHAPTER 5: DETERMINATION OF GERMANIUM BY AN INDIRECT METHOD SPECTROPHOTOMETRY . . . . .	127
5.1 Introduction . . . . .	127
5.2 Separation . . . . .	128
5.3 Review of Analytical Methods for Determination of Germanium . . . . .	128
5.3.1 Gravimetric Methods . . . . .	128
5.3.2 Titrimetric Methods . . . . .	129
5.3.3 Polarographic Methods . . . . .	130
5.3.4 Spectroscopic Methods . . . . .	131
5.3.4.1 Spectrophotometric methods . . . . .	131
5.3.4.2 Atomic absorption spectroscopic methods . . . . .	135
5.3.5 Miscellaneous Methods . . . . .	143
PRACTICAL EXPERIMENTS . . . . .	144
5.4 Indirect Determination of Germanium by Atomic Absorption Spectrometry Using Carbon Rod Electrothermal Atomization . . . . .	144



	<u>Page No</u>
5.4.1 Investigation of the Formation and Extraction of the 12-Molybdo-germanic Acid . . . . .	144
5.4.2 Extraction of 12-Molybdo-germanic Acid and Subsequent Carbon Rod Elec- trothermal Atomization of Germanium	152
CHAPTER 6: DETERMINATION OF PHOSPHORUS AS 12-MOLYBDO- PHOSPHORIC ACID BY FLOW INJECTION-SOLVENT EXTRACTION WITH SUBSEQUENT INDIRECT FLAME ATOMIC ABSORPTION SPECTROMETRY . . . . .	157
6.1 Introduction . . . . .	157
6.2 Review of Solvent Extraction-Flow Injection System . . . . .	160
PRACTICAL EXPERIMENTS . . . . .	168
6.3 Indirect Spectrophotometric Determination of Phosphorus by Flow Injection-Solvent Extraction . . . . .	168
6. .1 Chemical Optimization of the Manifold and Calibration for Phosphorus	168
6.4 Extraction of 12-Molybdophosphoric Acid and Subsequent Indirect Determination of Phosphorus Using Air-C <sub>2</sub> H <sub>2</sub> Flame . . . . .	176
CONCLUSION . . . . .	180
APPENDICES . . . . .	193
REFERENCES . . . . .	204

### ABSTRACT

Molybdenum heteropoly acid chemistry with its inherent amplification factor has been used to improve the sensitivities and detection limits of methods for phosphorus and germanium determination, using both flame and electrothermal atomization atomic absorption spectrometry to determine the molybdenum.

Phosphorus extracted as 12-molybdophosphoric acid, was used as a model element for the study of certain aspects of the procedure. Solvent extraction was used for the separation of the heteropoly species from the considerable excess of molybdate (added to drive the reactions to completion), which usually produces high blank values in both flame and electrothermal atomization work. A considerable improvement in blank levels, to below the instrumental detection limits has been achieved by careful drying of the extract.

In addition to the chemistry of formation and extraction, the flame atomization (both air-C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub>) of molybdenum has been investigated with view of improving sensitivity and detection limit. Modifications to the flame gas composition by the addition e.g. possible additional reducing agents, have been investigated. Variation of the particle microenvironment in the flame by varying the salt composition of the solution was also studied. Improvement in the nebulization process by combining flow injection sample introduction with modification of the solution physical properties was investigated.

The electrothermal atomization of molybdenum was investigated as a function of the gas composition surrounding the atomizer with a view to improving the life time of the rod, sensitivity, detection limit and precision. The sensitivities and detection limits obtained were compared with existing methods.

A method was developed for determination of germanium based on the solvent extraction of the heteropoly species using carbon rod electrothermal atomization and the analytical performance compared with existing methods.

Finally, a flow injection manifold was constructed and evaluated for the formation and extraction of 12-molybdophosphoric acid.

At relevant points, the appropriate literature is surveyed. Brief reviews of (1) heteropoly acid methods, (2) mechanisms of flame and electrothermal atomization and interference effects, (3) germanium determination, (4) flow injection analysis and atomic absorption, and (5) solvent extraction by flow injection methods are included.

## CHAPTER 1

### GENERAL INTRODUCTION

#### 1.1 Aim

The project was concerned with aspects of the use of the molybdenum heteropoly acid chemistry as the basis for indirect methods.

The possibility of improving the sensitivity and detection limits for such methods using phosphorus as a model element are investigated.

One of the major problems in adapting an existing heteropoly acid method, is the need to achieve complete separation of the considerable excess of molybdenum (added to drive the reactions to completion) from the heteropoly species. Solvent extraction is the most popular method, but usually produces blank values too high for either flame or electro-thermal atomization work. The possibility of reducing blank levels is investigated.

The use of indirect methods for determination of germanium for improved sensitivity are investigated. Methods for automating the solvent extraction for formation and extraction of 12-molybdophosphoric acid are investigated for speedy analysis.



## 1.2 Application of Indirect Methods in Analysis by Atomic Absorption Spectroscopy

Atomic absorption spectrophotometry (AAS) is a well established, extremely valuable technique for the determination of trace amounts of metals. Since its introduction by Walsh (1), the method has gone through a number of development stages aimed at obtaining an increase in reliability, ease of operation and, above all, improvement in the limit of detection.

Virtually all metals in the periodic table have now been successfully determined at concentration levels varying from 1 ppm to 1 ppb. The analytical quantitative range for some elements is quite short, but for many elements, particularly the transition metals, the analytical range is very much increased by using different absorption lines with varying oscillator strengths. However some elements cannot be determined by direct methods of atomic absorption spectrometry. This is related to the fact that their resonance lines lie in the vacuum region of the spectrum such as F, Cl, Br, I, S, P, O and N. A second large group of elements for which direct atomic absorption spectrometry is difficult includes those elements for which, although their resonance lines lie in an accessible region of the spectrum, it is difficult to form and maintain a significant atomic population in the flame and the electrothermal atomizer. For example Th, Ce, U, B, W, Ta, La, Nb, Zr, Re, Lu, Hf, Gd, Ir, Pr, Nd, Sm and Tb. In addition, the attainable sensitivity for several other elements, frequently determined, may be inadequate for their determination at the trace levels commonly

encountered in the samples to be analyzed: these include As, Ge, V, Ti, Se and Te. Achievements in this field are summarized in references 2, 3 and 4.

Several distinct types of procedures may be employed in indirect determination by AAS. Most frequently, they are:

- a) Measurement of the value of the suppression or enhancement of the absorption of one element or another in the presence of the component being determined.

Phosphates (4-20 ppm of P) and sulphates (10-30 ppm of S) can be determined by the depressing effect they have on the atomic absorption of 20 ppm of Ca at the 422.7 nm line in an air-C<sub>2</sub>H<sub>2</sub> flame (5).

- b) Precipitation of an ion or compound of the element being determined by an ion of another element, whose concentration in the precipitate or the filtrate can be measured by the atomic-absorption method.

Total sulphur can be determined in biological materials by determining the barium in the barium sulphate precipitate (6).

- c) Formation of binary or ternary heteropoly acid species between the analyte ion and other ions (one of which is usually molybdate), and determination of molybdenum concentration by AAS after separation of the complex by solvent extraction.

See Chapter 2 for a more detailed explanation.

- d) Application of the oxidation-reduction properties of the component being determined to obtain an equivalent amount of the metal ion, followed by its extraction and atomic-absorption determination. Iodate oxidizes iron (II) to iron (III) in acid medium, the iron (III) may be extracted into diethyl ether from a 9M hydrochloric acid solution. The absorbance of iron in the ether phase is then proportional to the iodate concentration (7).

The above principles have been used, especially for the indirect determination of niobium, thorium and other metals as well as for determination of the ions  $F^-$ ,  $Cl^-$ ,  $ClO_4^-$ ,  $I^-$ ,  $IO_4^-$ ,  $NH_4^+$ ,  $NO_3^-$ ,  $SCN^-$ ,  $CN^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ . Extremely high sensitivities were obtained. For example, characteristic concentrations (in ppm) were: for P - 0.003; Nb - 0.015; Th - 0.063;  $ClO_4^-$  - 0.025;  $CN^-$  - 0.03.

### 1.3 Atom Cells in Atomic Absorption Spectroscopy

The two principal types of atom cells employed in AAS, to provide thermal energy for sample vaporization and atomization, are the pre-mixed flame and electrothermal devices.

The atom cell chosen for a particular determination will depend on the required sensitivity, determination limits, the occurrence of interference effects from the matrix elements, extent of sample preparation required, speed, precision and available sample mass or volume.

### 1.3.1 Flame Atom Cell

The flame and nebulizer are almost ideal as an atom cell for solution analysis by atomic absorption spectroscopy. There are five principal ways in which AAS with a flame atom cell may be used with liquid samples:

1. Direct nebulization of aqueous samples using a pneumatic nebulizer/spray chamber system;
2. Direct pneumatic nebulization of sample after preconcentration of the analyte element by solvent extraction;
3. With the boat-in-flame or Delves cup techniques;
4. With generation of the gaseous hydride of the analyte element and introduction of this into a hydrogen-based diffusion flame;
5. With flow injection analysis techniques.

The preferred technique of sample introduction will usually depend primarily upon the concentration of the analyte in the prepared sample solution (digest), the quantity of sample available, and the type of the application.

#### 1.3.1.1 Limitations of the flame atom cell

Some fundamental and possible practical disadvantages of the use of flames for analytical spectroscopy are as follows:

1. In flame atomic absorption spectrometry, 1-4 ml of sample solution is generally used for the determination of a single element. For multi-element determination, the volume of sample solution or the amount of original sample must be large. Thus for small amounts of sample, the concentration of elements to be determined may be less than the detection limit as a result of the high dilution (after sample decomposition), necessary to allow the determination of the series of elements.
2. Analytical sensitivities obtained with direct nebulization are not enough for many applications especially for solutions with high viscosity and solid content which tend to clog the nebulizer. High concentrations of salt >2% may also alter the gas flow, the nebulization rate, the flame and consequently, at a constant concentration, the absorption of the resonance light from the hollow cathode lamp. The analysis of solid samples may be more appropriate in this case.
3. The choice of appropriate solvents for direct continuous spraying into the flame is limited by several important requirements. The solvents must have good nebulization and burning characteristics, not too low a boiling point, and low solubility in water. In addition, it should be an effective solvent in solvent extraction.



Allan (8) has pointed out that  $C_6$  and  $C_7$  ketones and esters are the most suitable solvents for flame atomic absorption spectrometry. At present 4-methyl pentan-2-one (MIBK), butyl acetate, and 1,2 dimethyl benzene (xylene) are used for liquid-liquid extraction prior to flame atomic absorption spectrometry. Some common and well established organic solvents such as trichloromethane (chloroform), tetrachloromethane (carbon tetra chloride) and benzene are widely used for liquid-liquid extraction in general.

Unfortunately, the continuous nebulization of these solvents into a flame gives an unstable, noisy flame, and toxic products such as hydrogen chloride and phosgene are evolved. If these organic solvents are used, tedious and time consuming procedures are necessary before atomic absorption spectrometry e.g. evaporation of the solvent and its replacement by MIBK (9), back extraction (10) or mineralization of the extract (11).

4. Inefficiency of sample introduction. Most of the samples introduced to a flame system are sent to waste, hence the analytical signals are lower than expected.
5. The sensitivity is also limited by the flame burning velocity and the efficiency of atom production from the aerosol. Atom concentrations in flames are limited by the dilution effects of the relatively high flow rate of unburnt gas used to support the flame, and the flame gas expansion which occurs on combustion.

#### 1.3.1.2 Means of improving sensitivity

There are two possible means of increasing the sensitivity in the flame. Firstly, the efficiency of aspiration and atomization into a flame or similar cell can be improved. Secondly, the mean residence time and therefore peak atom population in the analysis light beam can be increased by using an atom cell other than a flame.

The use of ultrasonic nebulizers, as a means of increasing nebulization and atomization efficiency for flame atomizers, is found to be more efficient than normal pneumatic nebulizers and in addition, they produce a spray of more uniform size droplets, whose average dimensions are considerably smaller than those obtained by pneumatic nebulizers. An increase of as much as 30 times in sensitivity for flame atomic absorption has been observed compared to conventional nebulization (12).

#### 1.3.1.3 Discrete-volume nebulization method

It is possible however, to determine an element by flame atomic absorption spectrometry in a microlitre sample volume (less than 1 ml) to overcome some of the disadvantages, such as dilution of elements with low detection limits, high viscosity and high salt content of samples. Various workers studied this technique proving that nebulization of 100  $\mu$ l samples gives the same sensitivity as that obtained by conventional nebulization.

Flow injection analysis (FIA) (15), is a relatively new and fast technique for introducing samples into the flame, which is based on injection of a microlitre liquid sample through a sample loop into a continuously moving, non-segmented carrier stream (usually water or aqueous solutions of reagent). The injected sample forms a zone which is transported towards the nebulizer/burner. This produces a transient signal, and the analytical read out is obtained as a sharp peak on a chart recorder.

Transient signal measurements have been used with atomic absorption flame techniques before flow injection was introduced. For example, in the discrete-volume method nebulization (also variously known as the "direct injection", "aliquot" or "pulse nebulization" method) a 50-20  $\mu$ l sample is aspirated from a cone-shaped cup into the flame to give a transient signal (16). In this case the sample slug is bounded only by air as it is drawn into the nebulizer. In contrast, the flow injection analysis sample disperses into the carrier stream as it is pumped towards the nebulizer. This dispersion is highly reproducible if the flow of the carrier is constant and a consistent injection technique is used.

### 1.3.2 Electrothermal Atom Cell

Although the flame atomization is perfectly satisfactory for many sample determinations, there is an obvious challenge in achieving the extra sensitivity by using other types of atomizers which are more efficient.



For analysis of elements without a flame atomizer, sufficient energy must be introduced to thermally vaporize and dissociate compounds in the sample. This is normally achieved by depositing a discrete small volume of sample into a convenient surface immediately adjacent to the analysis light beam and heating this surface very rapidly to temperatures between 1000 and 3500°C. The thermal energy has been supplied by various means including induction coil and lasers, but is normally supplied by resistance heating of the deposition substrate itself.

#### 1.3.2.1 Advantages of electrothermal atomization

The major advantages of discrete sample electrothermal atomizers, compared to flame are as follows:

1. Dramatic increase in sensitivity due <sup>to</sup> mainly/lack of flame background, an increase in mean residence time and therefore peak atom population in the analysis light beam.
2. The absence of a nebulizer would permit viscous extracts to be analyzed. Complete removal of organic solvents from the electrothermal atomizer, by drying, would eliminate the non-specific light absorption during atomization (17).
3. The ability to analyze very small sample volumes (5-10  $\mu$ l).
4. In situ sample treatment, which allows direct analysis of solid samples.

5. The reproducibility of the analytical absorption signal in flame atomic absorption spectrometry for repetitive introduction of liquid samples can frequently be better than 1%. For electrothermal atomization, samples manually introduced repetitively into a graphite furnace give reproducibilities usually 3%, however with automatic sampling systems this becomes less than 0.5%.
6. Safety of operation. Less toxic fumes are produced.
7. Suitability for determination of non-metals, since argon is used as a sheathing gas and does not absorb in the vacuum ultraviolet region of the spectrum.

#### 1.3.2.2 Disadvantages of electrothermal atomization

The main disadvantages of discrete sample electrothermal atomizers are as follows:

1. The single biggest difficulty is concerned with occurrence of matrix effects, and their recognition, control or suppression.
2. Recently it has been suggested (18) that the nature of some organic solvents has a strong effect on the atomic absorption signal amplitude. Soaking of the extract into the graphite or its spread over the atomizer surface, and the volatility of certain extracted compounds at elevated temperature may hinder the combination of extraction with ETA-AAS.

For example, suppression and distortion of the AA-signals in the presence of halogen-containing solvents (19) are usually attributed to formation of thermally stable and volatile halides which are partially carried away from the electrothermal analyser, undissociated.

3. For non-flame devices which do not possess batch processing capabilities, the sample must undergo separate dry ash-atomize-cool down cycles. This generally increases the overall analysis time which typically requires 1 to 2 minutes for completion, even when automated sample injectors are used. Only the carbon cup (20), graphite microboat (21) and L'vov platform (22) systems are capable of batch-processing operations.

### 1.3.3 Pretreatment

Pretreatment of samples is, in most cases, necessary for one of the following reasons:

1. The discriminating power of the analytical techniques, between analyte and other sample constituents, is limited.
2. To improve detection limit.
3. To prevent deterioration of the analytical systems.

The sample can be pretreated in such a way that interferent compounds are removed and/or the analytes are concentrated. The pretreatment may either involve simple procedures, such as filtration, precipitation (e.g. of protein), or it may consist of very laborious multiple extraction,



followed by evaporation to dryness and redissolution in a solvent compatible with the selected analytical technique.

The necessary chemistry is usually tedious and may lead to considerable error due to contamination of the sample. The sample preparation, particularly for a very complex matrix, is often the time-limiting step for the determination of one or more samples. There is an increasing need for specialized instrumentation for automated sample pretreatment. Three of the more important reasons for this realization are the inherent speed, precision, and interfacing capabilities of automated procedures.

Liquid and solid extraction have proved suitable for automated sample clean up. Both techniques can be coupled on line to those analytical techniques where measurements are made in a continuous streaming fluid e.g. chromatography, flow injection analysis, atomic absorption spectroscopy with inductively coupled plasmas. Since the initial work of Karlberg (23), a great many applications of automated solvent extraction based on flow injection analysis have appeared in the literature. Recently the system has been applied for methods using electrothermal atomization (24).

Discrete methods retain the sample as an entity, and cross contamination is effectively eliminated; the fate of a sample at any time is known, and it is difficult to confuse one sample with another. As the sampling time is short, the sampling rate can be high, but the major advantages are in speed of response to an analytical change, which makes the flow

injection principle suitable for process control.

However, both liquid and solid extraction procedures have advantages and disadvantages:

Liquid extraction can be easily achieved using relatively simple equipment and very impure samples can be dealt with as the extraction solvents are continuously renewed. A weakness of the system is the phase separators which require regular control of their performance, which therefore negates the benefits of automation.

For cleaner samples, solid extraction is the most elegant method of automation, clean up and pre-concentration. The main drawback is currently, the poor reproducibility and short life times of most column packings, which quickly deteriorate, and require regular regeneration procedures to restore their retention properties.

## CHAPTER 2

### DETERMINATION OF ORTHOPHOSPHATE BY DIRECT AND INDIRECT SOLUTION SPECTROPHOTOMETRY

#### 2.1 Introduction

The literature on the determination of phosphate is vast, extending into such areas as metallurgy, pharmaceuticals, food, water, biochemistry and agriculture. Many methods for determination of phosphate are based on the ability of phosphorus to form molybdophosphate including:

- a) Gravimetric as organic base molybdophosphate or as  $\text{NH}_4^+$  salts.
- b) Mo(VI) derived from heteropoly acid reduced to Mo(V) followed by Ce(IV) titration.
- c) Alkalimetric titration.
- d) Spectrofluorimetric determination of  $\text{PO}_4^{3-}$  as e.g. Rhodamine B molybdophosphate.
- e) Atomic absorption spectroscopy determination of Mo derived from heteropoly acid.
- f) Heteropoly acid converted to Mo-oxine complex. Bromometric titration of liberated oxine.
- g) Selective extraction followed by spectrophotometric determination.
- h) Spectrophotometric determination of heteropoly acid with or without reduction.

- i) Selective suppression of some heteropoly acids followed by spectrophotometric determination of stable species.
- j) Spectrophotometric determination of Mo(VI) derived from heteropoly acids.

## 2.2 Separation

Separation is often required where phosphate is to be subsequently determined and in analysis where its presence would cause interference. The principal methods for separation are as follows:

1. Precipitation of molybdophosphoric acid. Some elements such as bismuth (III), titanium (IV) and zirconium (IV) precipitate as phosphates which then contaminate the heteropoly acids. Interferences are eliminated if precipitation is made in a higher concentration of nitric acid.
2. Solvent extraction of heteropoly acids by organic solvents.
3. Ion exchange chromatography of separating phosphate from both cations and anions.
4. Mercury cathode electrolysis as a means of separating phosphate from iron, cobalt, nickel and molybdenum, with phosphate remaining in solution.
5. Separation of phosphate from Ge(IV), Si(IV) and As(V) achieved by coprecipitation of phosphate on aluminium hydroxide.



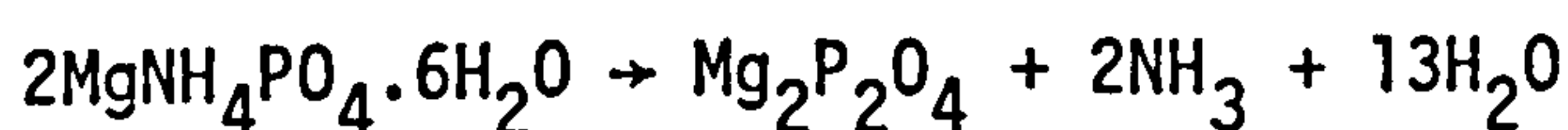
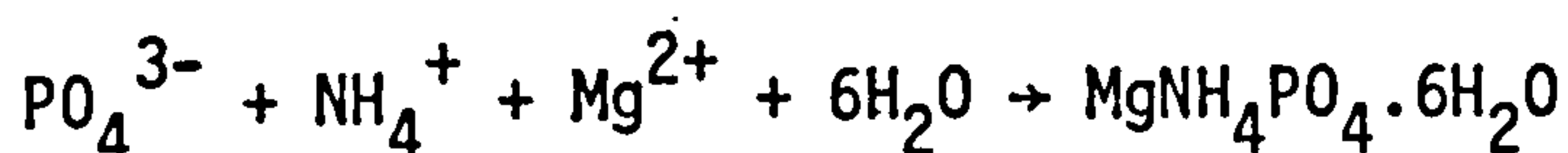
6. Selective suppression of unwanted species, such as molybdoarsenic acid and molybdosilicic acid, by addition of citric acid and perchloric acid, without affecting the formation of molybdenum and phosphorus heteropoly acids.

## 2.3 Review of Methods for Orthophosphate Determination

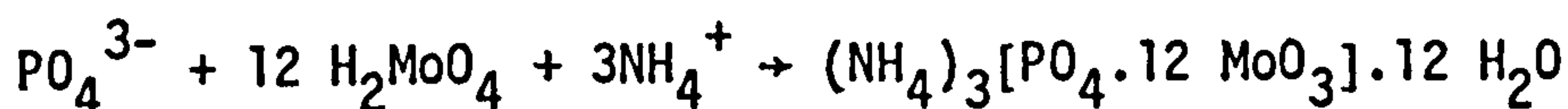
### 2.3.1 Gravimetric Methods

Phosphate can be determined gravimetrically as follows:

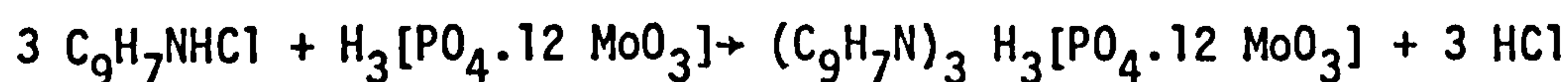
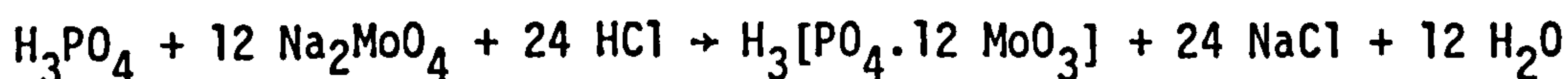
- a) Precipitation as magnesium ammonium phosphate (25).



- b) Precipitation as ammonium molybdophosphate (26).



- c) The use of organic bases such as quinoline which was first introduced by Wilson (27).





The quinoline (Benzo[b]-pyridine) molybdophosphate method is generally regarded as accurate, precise and straightforward (28). A range of organic bases has been investigated by Macdonald and Rivero (29).

- d) Precipitation as a silver phosphate, from homogeneous solution by the gradual release of silver ion resulting from the breakdown of argentous amines (30). As  $\text{NH}_3$  escapes from the heated solution, large and easily filtered crystals are precipitated, which contain 7.4%P.

### 2.3.2 Titrimetric Methods

Titrimetric methods serve as an alternate to gravimetric procedures and although perhaps not as accurate are more quickly performed, avoiding the necessity of drying a precipitate to constant weight.

Chemical procedures adopted for determination of phosphate are as follows:

- a) Alkalimetric titration of ammonium and quinoline molybdophosphates using phenolphthalein as indicator (27).

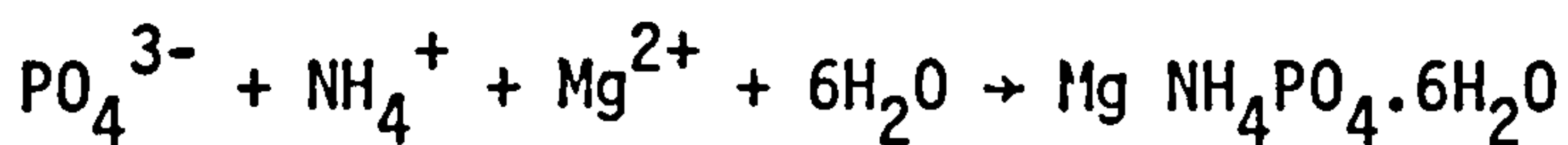


- b) Titrimetric procedures based on initial formation of molybdophosphoric acid. The phosphate is first converted to the 12-molybdophosphoric acid, the molybdenum in which is converted into the

oxine complex. This is then liberated with  $\text{KBrO}_3$  after addition of  $\text{KBr}$  (31).

- c) Indirect titrimetric determinations of phosphate with ethylenediamine tetra acetic acid (EDTA), based on the precipitation of an insoluble metal phosphate. These entail either collecting the precipitate and determining its metal content after dissolution, or adding excess of the metal ions and determining the latter in the filtrate after removing the precipitate.

Earlier work utilized  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  with compleximetric titration of  $\text{Mg}^{2+}$  in ammoniacal buffer and Eriochrome black T as indicator (32).



### 2.3.3 Electrical Methods

Several potentiometric methods have been described for the determination of phosphate. Cullum and Thomas (33) determined the total orthophosphate content of detergent powder by conversion of phosphate to the diacid form, precipitation as  $\text{Ag}_3\text{PO}_4$ , and potentiometric titration of the liberated acid.



Phosphate can also be titrated amperometrically using iron (II) (34). Orthophosphate can be determined as 12-molybdophosphate in aqueous acidic solution by linear sweep voltammetry and differential-pulse voltammetry at a glassy carbon electrode in a static system (35). The same investigators (36) also determined orthophosphate as molybdovanadophosphate at a glassy carbon electrode in a static system, and developed flow injection voltammetric determination methods for phosphate, silicate, arsenate and germanate.

#### 2.3.4 Radiochemical Methods

When tungstate is added to molybdophosphoric acid it becomes part of the molybdophosphate complex. On extraction the amount of tungsten (VI) extracted with the heteropoly acid will be proportional to the amount of heteropoly acid, and therefore to the amount of phosphate. Hahn and Schmitt (37) used  $^{185}\text{W}$  in their procedures to form 185-tungsto-molybdophosphoric acid. This was extracted and the tungsten activity determined by means of the  $\beta$  emission.

#### 2.3.5 Kinetic Methods

The catalytic effect of phosphate on the reduction of molybdenum (VI) by ascorbic acid is used in a kinetic spectrophotometric method for phosphorus (38). The kinetics of this reaction have been investigated and equations developed for the three stages each with a different reaction rate (39). In an analogous kinetic method, the catalytic effect of phosphate in the reduction of molybdenum (VI) with tin (II) is used, the rate of reaction being linear with phosphate concentration (40).



Many recent publications utilize automatic systems which enable the analysis time to be reduced to seconds. Crouch and Malmstadt (41) have developed a method based on their mechanistic study of the molybdenum blue reaction. Under controlled conditions the initial rate of formation of molybdenum blue from phosphate, molybdate and ascorbic acid is directly proportional to the phosphate concentration. Automatic instrumentation was used to provide a digital read-out proportional to the phosphate concentration. Only 20-30s of reaction time is required for each sample.

A differential kinetic method for the simultaneous determination of silicate and phosphate utilizes the faster formation of the heteropoly blue of phosphorus and is performed using an automatic reaction rate apparatus (42).

### 2.3.6 Spectroscopic Methods

#### 2.3.6.1 Spectrophotometric methods

Phosphate can be determined by three main methods: as molybdophosphoric acid, its reduction product molybdenum blue, and the yellow vanadomolybdophosphoric complex. In addition indirect methods based on chloranilates or the molybdate derived from molybdophosphoric acid may be used.

The sensitivity of spectrophotometric methods based on heteropoly acid formation is not high and depends on reaction conditions and whether extraction into an organic medium has been employed. The

heteropoly acid may be reduced to molybdenum blue and then later extracted, or it may be extracted first and subsequent reduction carried out in the organic phase. Extraction is one means of improving selectivity in phosphate determination. The other approach is based on suppression of unwanted hetero species. These methods are reviewed by several authors (43-45). The existence of two forms ( $\alpha$  and  $\beta$ ) of the heteropoly acids was postulated by Strickland (46). Studies by Pungor (47) have provided more information on the chemistry of  $\alpha$  and  $\beta$  heteropoly modifications.

Addition of ammonium molybdate solution to an acidified solution of phosphate produces a yellow colour, the maximum absorbance of which may be measured at 380-420 nm (48). The absorbance of extracted molybdophosphoric acid (or its blue reduction product) extracted with propylene carbonate in trichloromethane may be measured at 308 nm (49).

The blue polymeric species is produced when molybdophosphoric acid is reduced and forms the basis of several colorimetric procedures since its introduction by Dickman and Bray (50) in 1940. Since then the procedure has undergone several modifications aimed at increasing the precision, sensitivity and selectivity. The blue species may be extracted into oxygen containing organic solvents or extraction may be carried out on the aqueous molybdophosphoric acid solution before reduction in the organic phase (51).

The choice of reductant is important, this affecting the time required for the reduction stage as well as the molar absorptivity of the blue

products. Different reducing agents have been reported in literature such as iron (II) (48), hydroquinone (52), tin (II) chloride (53), hydrazine sulphate (48), 1-amino-2-naphthol-4-sulphonic acid (54) and ascorbic acid (55).

Determination of the yellow colour of phosphomolybdic acid without reducing it to blue product was studied by Boltz and Mellon (48).

Molybdophosphoric acid can be determined by indirect methods, which usually involve extraction of molybdophosphoric acid and re-extraction into a basic buffer solution, which has an absorbance at 230 nm or 210 nm (56).

The acidity for the formation of molybdophosphoric acid is an important factor. Over the range 0.2-1.0N sulphuric acid, the amount of the blue colour is independent of the acidity but the rate of formation decreases with increasing acid. The pH should be maintained below 0.7 to avoid the reduction of the molybdate itself (41).

A pH of 0.9 to 1.25 was recommended by Boltz and Mellon (57) as the optimum range for the formation of molybdophosphoric acid. Hurford and Boltz (58) used an optimum pH of 1.3 for the formation of both molybdophosphoric acid and molybdosilicic acid. Others recommended pH 0.9 to 1.25 (48) or 0.7 to 1.27 (59) as optimum.

Halasz and Pungor (60) used phenylfluorone (61) and the methylfluorone (62) methods to form a molybdate complex, which was extracted into a n-butyl acetate and re-extracted into water. The red complex formed by



molybdenum (VI) with either fluorone has an absorption maximum at 526 nm.

Hirai, Yoza and Ohashi (63) described flow injection methods for the determination of phosphate in environmental waters. The heteropoly blue complex formed was monitored at 830 nm. Johnson and Petty (64) used the colorimetric phosphomolybdate method to determine phosphate in sea water by flow injection analysis.

#### 2.3.6.2 Atomic absorption spectroscopy

Phosphorus is not frequently determined by atomic absorption spectrometry. The primary resonance lines of phosphorus are at 167-168 nm and 177-179 nm, which are unusable with commercial atomic absorption spectrometry instruments. At wavelengths shorter than 200 nm, nitrogen and oxygen in the atmosphere absorb as do many of the combustion products in the flame. Therefore indirect methods for determination of phosphorus have been proposed. The methods involve formation of 12-molybdophosphoric acid and extraction into an organic solvent which is then washed with citrate solution (65-67), with dilute acid (58, 68-75), or with water (76) to remove excess of molybdate transferred to the organic phase. The phosphorus content is related quantitatively to the atomic absorption measurements of Mo at 313.3 nm, by either flame or electrothermal techniques. The method shows good sensitivity because according to the heteropoly compound formed, 12 (58,65,66,68-85), 11 (86), or 10 (87) Mo atoms are associated with every P atom. A general scheme for the indirect determination of

orthophosphate by heteropoly acid compounds is shown in Figure 1.

Three different types of organic solvents have been used: alcohols (65,66), ketones (67,78,79,81) and esters (68,67,80,82-84). In general oxygenated solvents are the best extractants for heteropoly acids.

A general method for determination of inorganic phosphate, using 2-octanol as a solvent (66), has been applied to the determination of phosphate in fuel, sea water, blood, serum, bone, biological tissues and enzyme-containing reaction mixtures (65). 2-octanol was chosen as solvent after examination of n-butanol, isobutyl-alcohol, 1-hexanol, 1-heptanol, 1-octanol and 2-octanol (65). Methyl isobutyl ketone has been used as an extracting agent (67,76,78,79) mainly for high phosphate concentrations. The standard addition method has been employed to overcome matrix effects (70,78).

The most suitable methods for the indirect determination of phosphate make use of the extraction of molybdophosphoric acid into esters, such as isobutyl acetate (68,77,82) and butyl acetate (69,83,84).

Several schemes have been derived for the sequential determination of phosphorus, arsenic and silicon (82), phosphorus and arsenic (80) and phosphorus and silicon (58,68). All are based on the ability to extract 12-molybdophosphoric acid. Thus 12-molybdophosphoric acid has been selectively extracted with isobutyl acetate after formation in nitric acid medium at pH 0.7 (82). Devoto (80) used isobutyl acetate to extract 12-molybdophosphoric acid formed in an ammonium nitrate-nitric acid medium at pH 1. Isobutyl acetate has also been



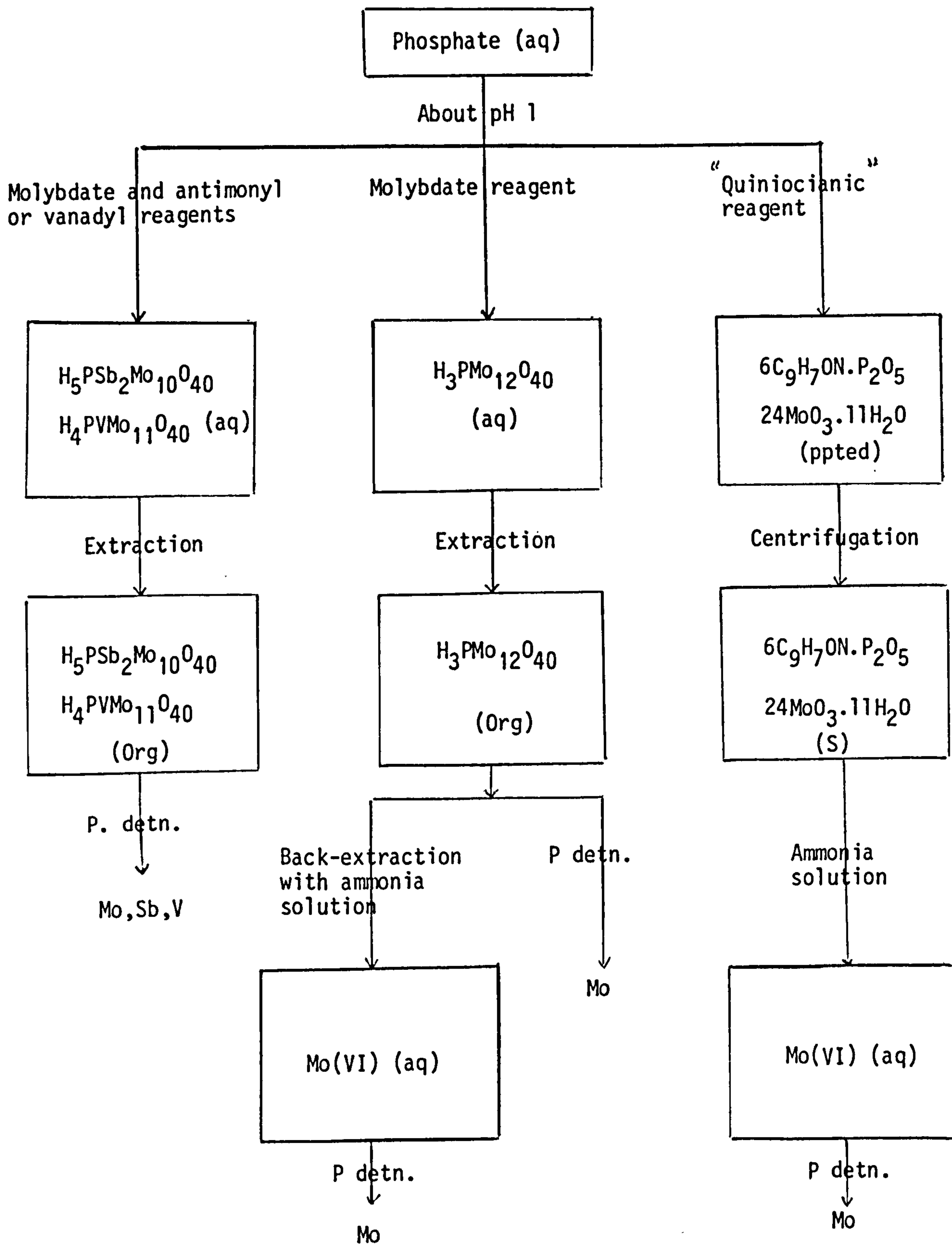


FIGURE 1: General Outline of Procedures for Indirect Determination of Orthophosphate by Heteropoly Compounds by AAS (88)

used by Kirkbright *et al.* (68) to selectively extract 12-molybdophosphoric acid formed at an acidity of 0.9M in hydrochloric acid in a single portion of solution containing phosphate and silicate, before formation of molybdosilicic acid.

The 12-molybdophosphoric acid formed at pH 1.3 has also been extracted from 1.2M hydrochloric acid medium with diethyl ether (58). After washing with dilute hydrochloric acid, the organic layer may be shaken with an ammoniacal buffer and the molybdate released measured in the aqueous phase by AAS using an air-C<sub>2</sub>H<sub>2</sub> flame.

Extraction-decomposition methods have also been applied for the determination of phosphorus, which involves the extraction of the 12-molybdophosphoric acid into esters (70,71), ethers (48), or into mixtures of ethers and alcohols (72,75), followed by its re-extraction with ammonia solution (48,70,72,75), or alternatively, by evaporation of the organic layer and dissolution of the solid residue in nitric acid (71). The molybdenum liberated into the aqueous solution is then determined by flame (48,71,72) or electrothermal (70,75) atomic absorption spectroscopy.

A very sensitive back extraction method used for the sequential indirect determination of phosphorus and arsenic in pure water has been described by Rozenblum (70). The method relies on the use of the butyl acetate as the extractant for the 12-molybdophosphoric acid and the determination of molybdenum in ammonia solution was then carried out in a graphite furnace. Other schemes have also been

devised for the sequential determination of phosphorus and silicon (48,72), and have been applied to rock analysis (72).

Phosphorus has been determined by several workers using direct chemical interference of phosphate on a metal species in a flame to produce a depression of the absorption, which is a function of the phosphorus concentration (89,90). Orthophosphate up to  $2.5 \times 10^{-4} \text{M}$  added to  $5 \times 10^{-4} \text{M}$  calcium solution produces a marked depression in the absorbance obtained for calcium at 427.7 nm with a total consumption burner (89). A modification of the quinoline molybdophosphate method has been proposed whereby the total phosphorus is determined indirectly by the AAS measurement of molybdenum (85), Melton *et al* (85) have used the gravimetric quinoline molybdophosphoric method of phosphate precipitation and dissolution in ammonia solution for determining P in fertilisers (5.5 - 48.07%  $\text{P}_2\text{O}_5$  content). The determination of Mo is carried out in an air- $\text{C}_2\text{H}_2$  flame at 320.9 nm secondary resonance line.

The formation of ternary heteropolyacids for the determination of phosphorus also has been used. The method is based on the formation of molybdovanadylphosphoric (86) or molybdoantimonyl phosphoric (85) acids followed their extraction into methyl isobutyl ketone or butyl acetate respectively. In the former, the determination of vanadium absorbance at the 318.5 nm line in a  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame is related quantitatively to the phosphorus content. In the latter, the atomic absorption of Mo at 313.3 nm or antimony at 217.6 nm is measured in a graphite furnace.



#### 2.3.6.3 Flame emission spectroscopy

For the same reason as flame atomic spectrometry, indirect emission spectroscopic methods have been suggested.

Dippel, Bricker and Furman (91) used the depression effect of phosphate on the emission of calcium and magnesium. A direct method has also been used based on an earlier gas-chromatographic method for the determination of phosphorus in organic phosphorus compounds (92). In this work a cool nitrogen-hydrogen diffusion flame is used, with several advantages being derived.

Developments in flame emission spectrometry led in 1973, to the introduction of molecular emission cavity analysis (MECA) (93). A micro-litre of sample is placed within a small cavity and introduced, after solvent evaporation into a premixed hydrogen-nitrogen-air flame. A molecular emission is <sup>t</sup>simulated within the cavity (e.g. HPO from phosphorus compounds) which is enhanced by the cool cavity wall (the so-called Salet phenomenon). The technique has already been successfully employed for the determination of nanogram amounts of organophosphorus compounds, based on their HPO emission (94), and it is adopted for detection of organophosphorus compounds in an HPLC eluent (95).

#### 2.3.6.4 Fluorimetric methods

Phosphorus has long been known to interfere in fluorimetric procedures, and this has been exploited for analytical purposes. The method used

by Kirkbright *et al* (96 ) to retain the selectivity for determination of phosphate is as follows: Phosphate is converted to the 12-molybdophosphoric acid which is reacted with the basic dyestuff Rhodamine B, to form an ion-association complex. After extraction of excess dye reagent into chloroform, the Rhodamine B molybdophosphate is extracted into chloroform-butanol (4:1 v/v) and the intensity of fluorescence in this solution measured at 545 nm with excitation at 350 nm. A similar method involving the organic base quinine was also reported by the same investigators (97 ).

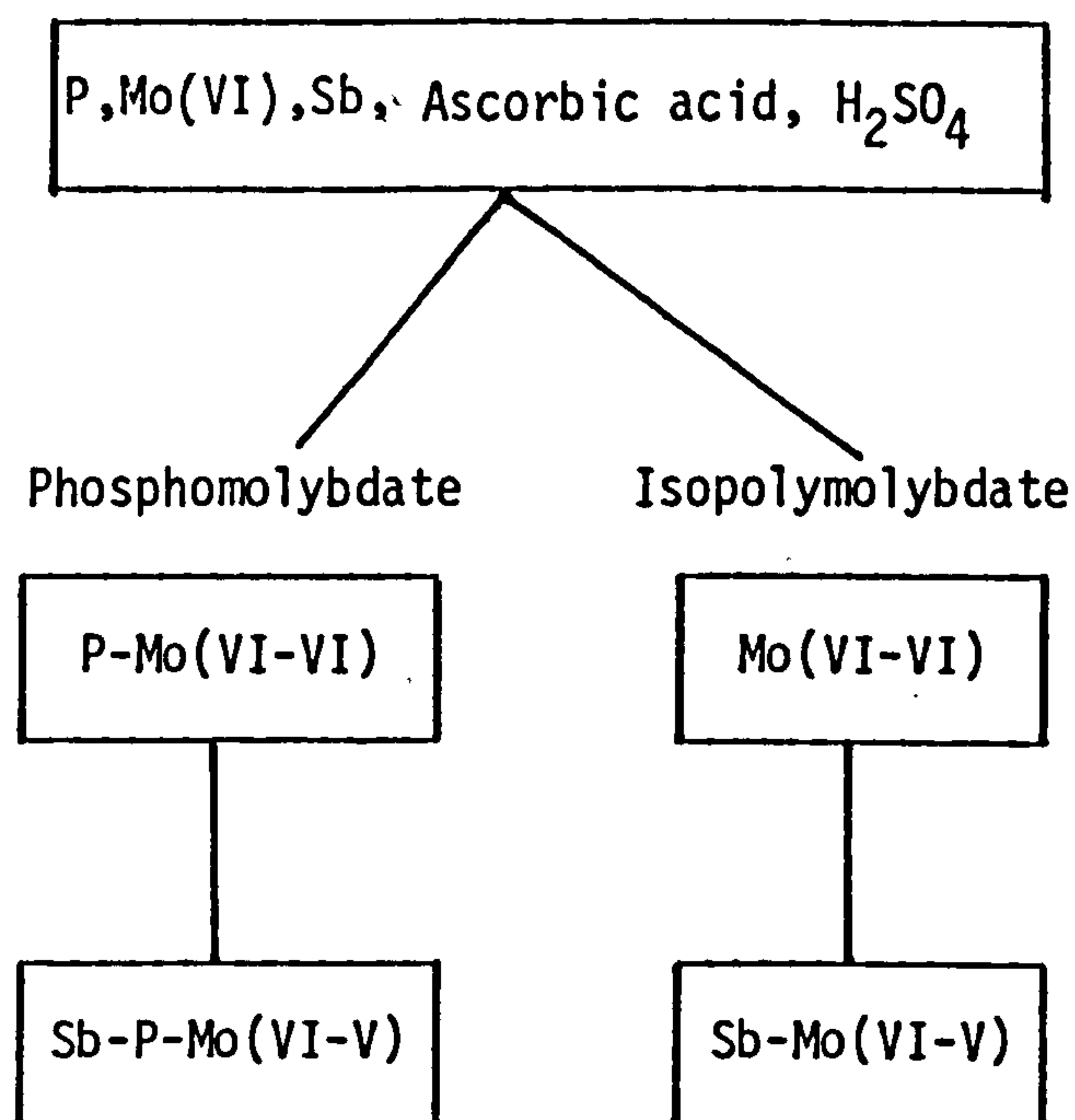
## PRACTICAL EXPERIMENTS

### 2.4 Direct UV-Visible Spectrophotometry Methods

#### 2.4.1 Ascorbic Acid Method

The method involves reaction of ammonium molybdate and potassium antimonyl tartrate with a phosphate solution in an acid medium, to form a heteropoly acid (phosphomolybdic acid) which was reduced to intensely coloured molybdenum blue by ascorbic acid. The presence of antimony enhances the formation of the bluish purple colour. The colour attained its maximum intensity in about 10 minutes (98 ).





Ratio of antimony:phosphorus is 1:1 and combination of antimony to the complex shifts the absorbance maximum for molybdenum blue or heteropoly to the higher value of 880 nm.

#### Instrument:

Visible absorption spectrophotometric measurements were made in a 1 cm glass cell using a Pye Unicam SP 600 spectrophotometer equipped with a red colour filter for use at 880 nm and 680 nm in the light beam.

#### Reagents:

##### Sulphuric acid solution, 2.5M

The acid solution was prepared by diluting 70 ml of concentrated acid to 500 ml.

Antimony tartrate solution

The solution was prepared by dissolving 2.135g of  $\text{K}(\text{SbO})\text{C}_4\text{H}_6$  in distilled water and diluting to 100 ml.

Ammonium molybdate solution

The solution was prepared by dissolving 40g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in distilled water and diluting to 1000 ml.

Ascorbic acid, 0.1M

The acid solution was prepared by dissolving 1.76g of ascorbic acid in distilled water and diluting to 100 ml.

Combined reagent

The solution was prepared by mixing 50 ml of 2.5M  $\text{H}_2\text{SO}_4$ , 5 ml of antimony potassium tartrate, 15 ml of ammonium molybdate solution and 30 ml of ascorbic acid solution in that order.

Stock phosphorus solution, 50 ppm

The solution was prepared by dissolving 219.5 mg of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) in distilled water and diluting to 1000 ml.

Standard phosphorus solution, 2 ppm

The solution was prepared by diluting 20 ml of stock phosphorus solution to 500 ml.

### Procedure:

Into a series of 50 ml volumetric flasks were transferred quantities of standard phosphorus solution covering the range 0.1 to 2.0 ppm of phosphorus. To each flask was added distilled water to make the total volume approximately 40 ml before the addition of 8 ml of combined reagent, and dilution to the mark with distilled water. The solutions were allowed to stand for 10 minutes before the absorbances at 880 nm and 680 nm were measured.

### Results:

The results show that Beer's Law was obeyed over this concentration range for 0.2 ppm to 1.5 ppm of phosphorus. A Ringbom plot was determined by measuring the relative error (as coefficient of variation) in the absorbance for each point of the calibration graph at 880 nm as shown in Figure 2.

A plot of data points for the calibration graph of the phosphorus after subtracting the blank values and the least squares linear regression analysis for a straight line was carried out using an Apple II computer as shown in Figure 3(a,b).

The method has an advantage of rapid colour development and stability of the colour for longer periods.

The limit of detection based on a determination of 0.2 ppm of phosphorus at 680 nm calculated as three standard deviations, was 30 ppb

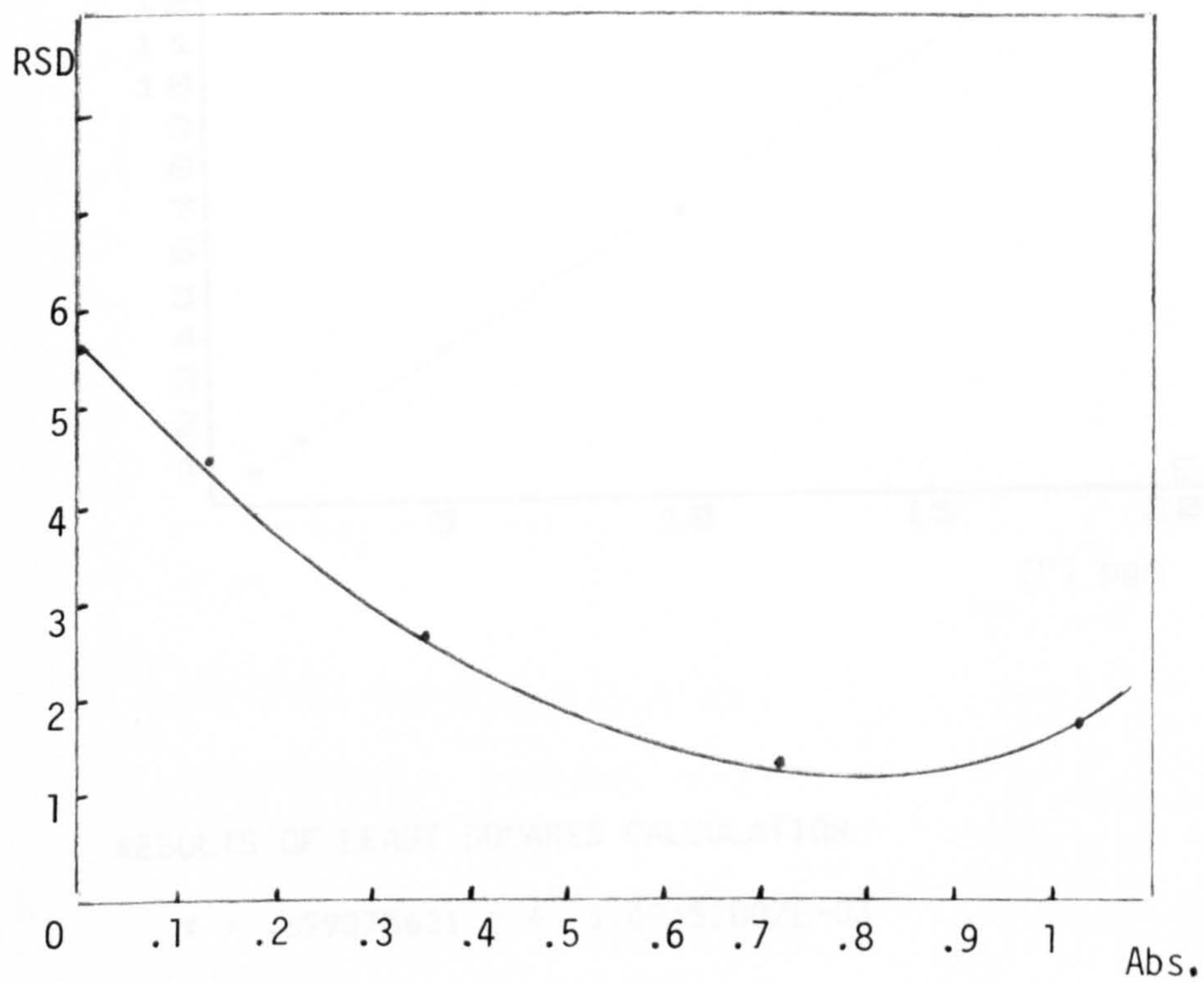
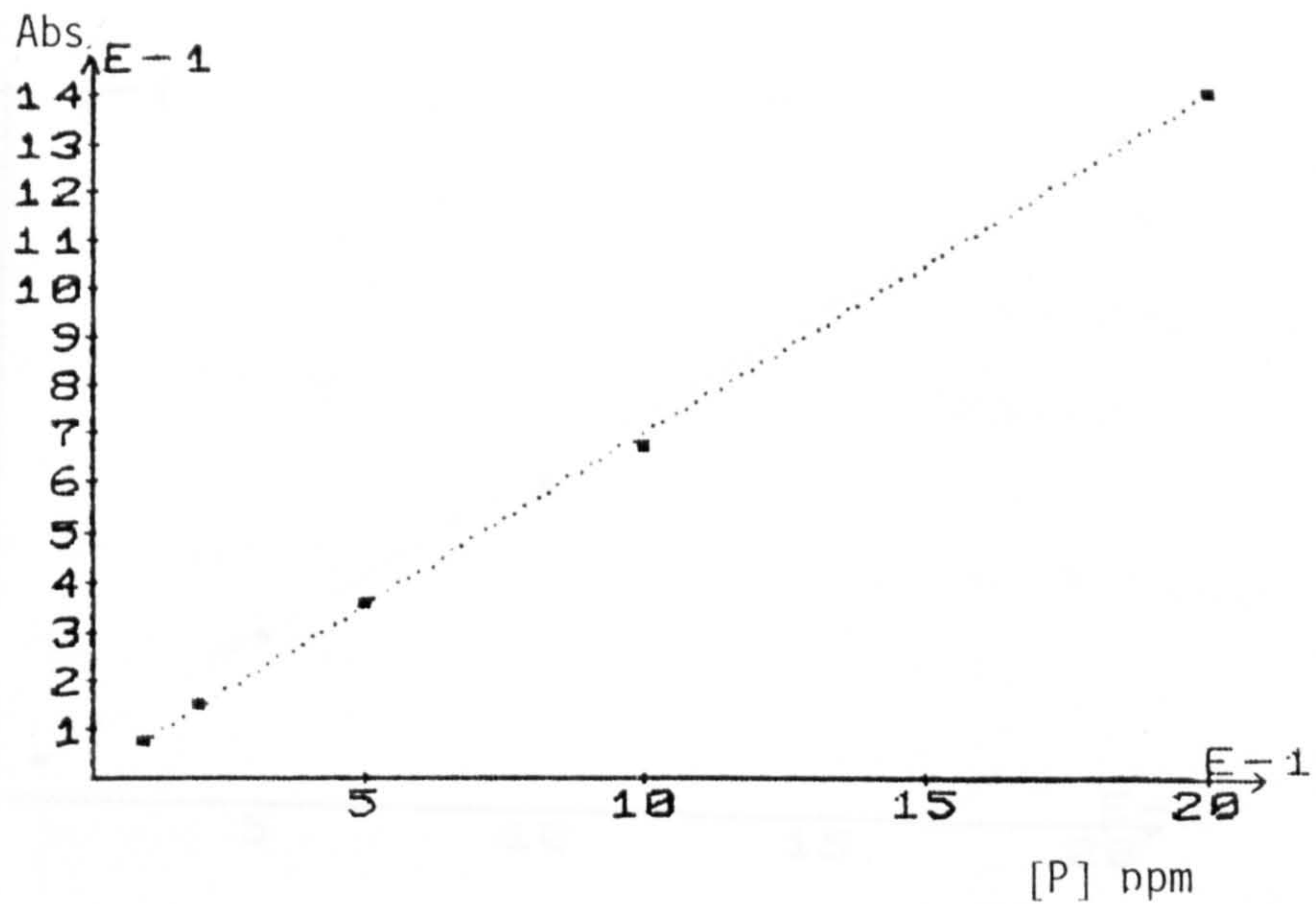


FIGURE 2: Ringbom Plot. RSD vs Absorbance





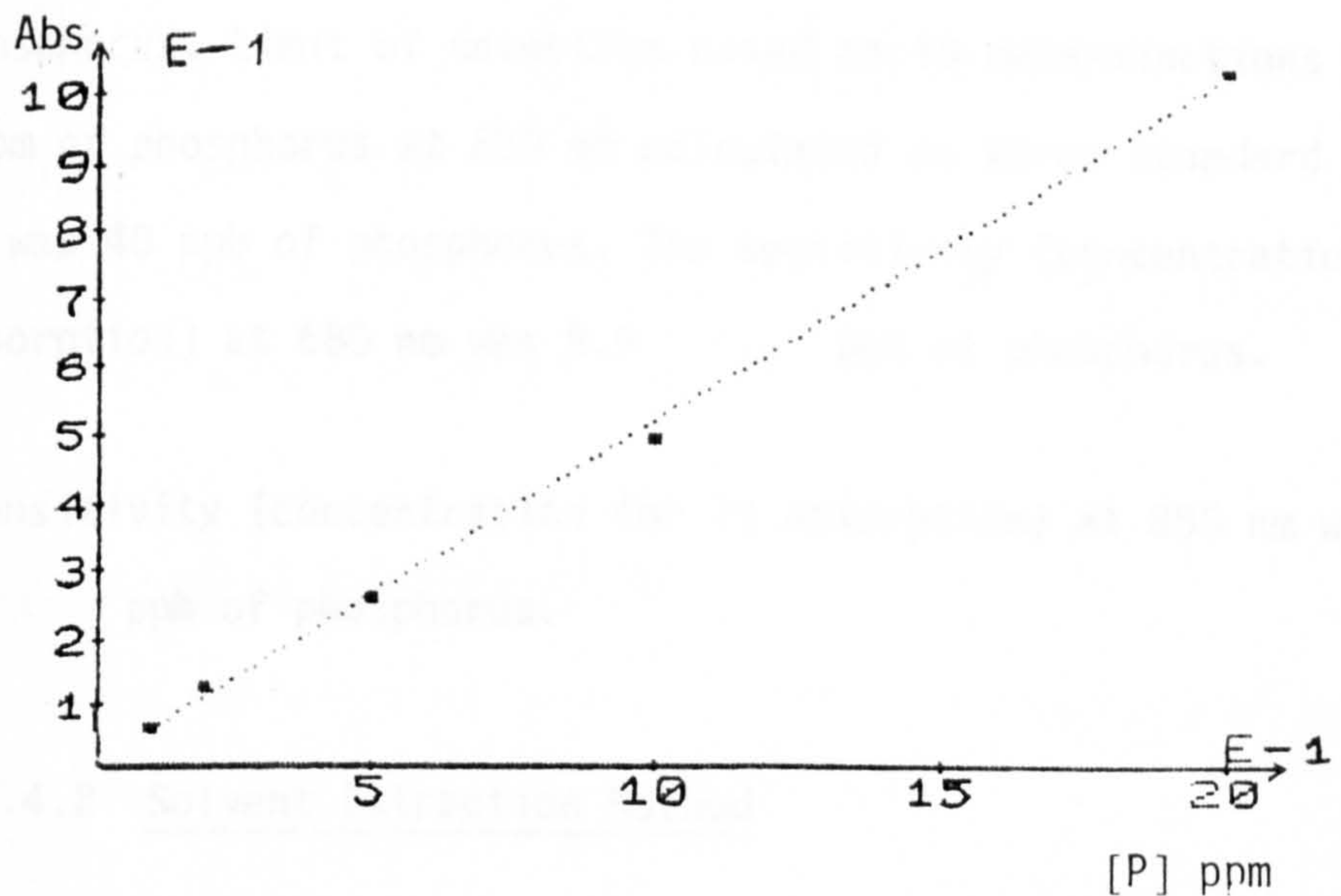
#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .699875621 X + 1.09452807E-03$$

NUMBER OF POINTS	= 5
SLOPE	= .699875621
INTERCEPT	= 1.09452807E-03
CORRELATION COEFF.	= .999727582
STANDARD DEVIATION	= .0126882099

X	Y
.1	.071
.2	.152
.5	.352
1	.68
2	1.41

FIGURE 3a: Calibration and Least Squares Linear Regression Analysis for Molybdenum Blue at 880 nm



#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .509626865 X + 9.28358234E-03$$

NUMBER OF POINTS	= 5
SLOPE	= .509626865
INTERCEPT	= 9.28358234E-03
CORRELATION COEFF.	= .999268363
STANDARD DEVIATION	= .0151464863

X	Y
.1	.063
.2	.125
.5	.26
1	.495
2	1.04

FIGURE 3b: Calibration and Least Squares Linear Regression Analysis for Molybdenum Blue at 680 nm

of phosphorus. Limit of detection based on 10 determinations of 0.2 ppm of phosphorus at 880 nm calculated as three standard deviations was 40 ppb of phosphorus. The sensitivity (concentration for 1% absorption) at 680 nm was 8.9 ppb of phosphorus.

The sensitivity (concentration for 1% absorption) at 880 nm was 6.5 ppb of phosphorus.

#### 2.4.2 Solvent Extraction Method

The procedure devised by Hurford and Boltz (58) for solvent extracting using n-butyl acetate was followed. In this procedure molybdate was added to the sample solution containing orthophosphate and the acidity was adjusted to its optimum value. The solution was mixed and allowed to stand for 5-10 minutes to ensure complete formation of 12-molybdophosphoric acid. The 12-molybdophosphoric acid was then selectively extracted into an organic solvent which was then washed with dilute acid to remove excess molybdate transferred to the organic layer. According to Wadelin and Mellon (99), n-butyl acetate is the best and most selective solvent for extraction of 12-molybdophosphoric acid, hence it was used.

#### Instrument:

Ultra violet spectrometric measurements were made in 1 cm silica cell using an SP 8-100 Pye Unicam spectrophotometer.



Reagents:Molybdate solution, 10%

The solution was prepared by dissolving 25g of  $(\text{NH}_4)_6 \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in distilled water and diluting to 250 ml.

Hydrochloric acid solution, (1+2)

The solution was prepared by mixing 1 part of concentrated hydrochloric acid with 2 parts of distilled water.

Hydrochloric acid solution, (1+10)

The solution was prepared by mixing 1 part of concentrated hydrochloric acid with 10 parts of distilled water.

Stock phosphorus solution, 50 ppm

As experiment 2.4.1.

Standard phosphorus solution, 5 ppm

The solution was prepared by diluting 10 ml of stock phosphorus solution to 100 ml.

Solvent:

n-butyl acetate.



Procedure:

Into a series of 100 ml separating funnels were transferred quantities of standard phosphorus solution covering the range 5 to 100  $\mu\text{g}$  of phosphorus. Hydrochloric acid solution (1 ml) was added and diluted to approximately 40 ml with distilled water followed by 4 ml of the 10% ammonium molybdate solution. After mixing the solutions were allowed to stand for 10 minutes. Concentrated hydrochloric acid (5 ml) was added and allowed to stand for 5 minutes. The 12-molybdo-phosphoric acid formed was extracted by shaking with 45 ml solvent for 1 minute. The organic extract was washed twice with 10 ml of a (1+10) hydrochloric acid by shaking for 30 seconds. The tip of the funnel was rinsed with stream of distilled water and dried with acetone. The organic solvent was drained into a 50 ml volumetric flask and diluted to volume with solvent.

The absorption spectrum was recorded from 350 nm to 230 nm against the blank extract as shown in Figure 4.

Results:

SP8-100 Pye Unicam <sup>spectrophotometer</sup> ↑ settings were as follows:

Wavelength speed: 0.5 mm sec<sup>-1</sup>

Chart speed: 20 sec cm<sup>-1</sup>

Bandwidth: 2

Absorbance: 2

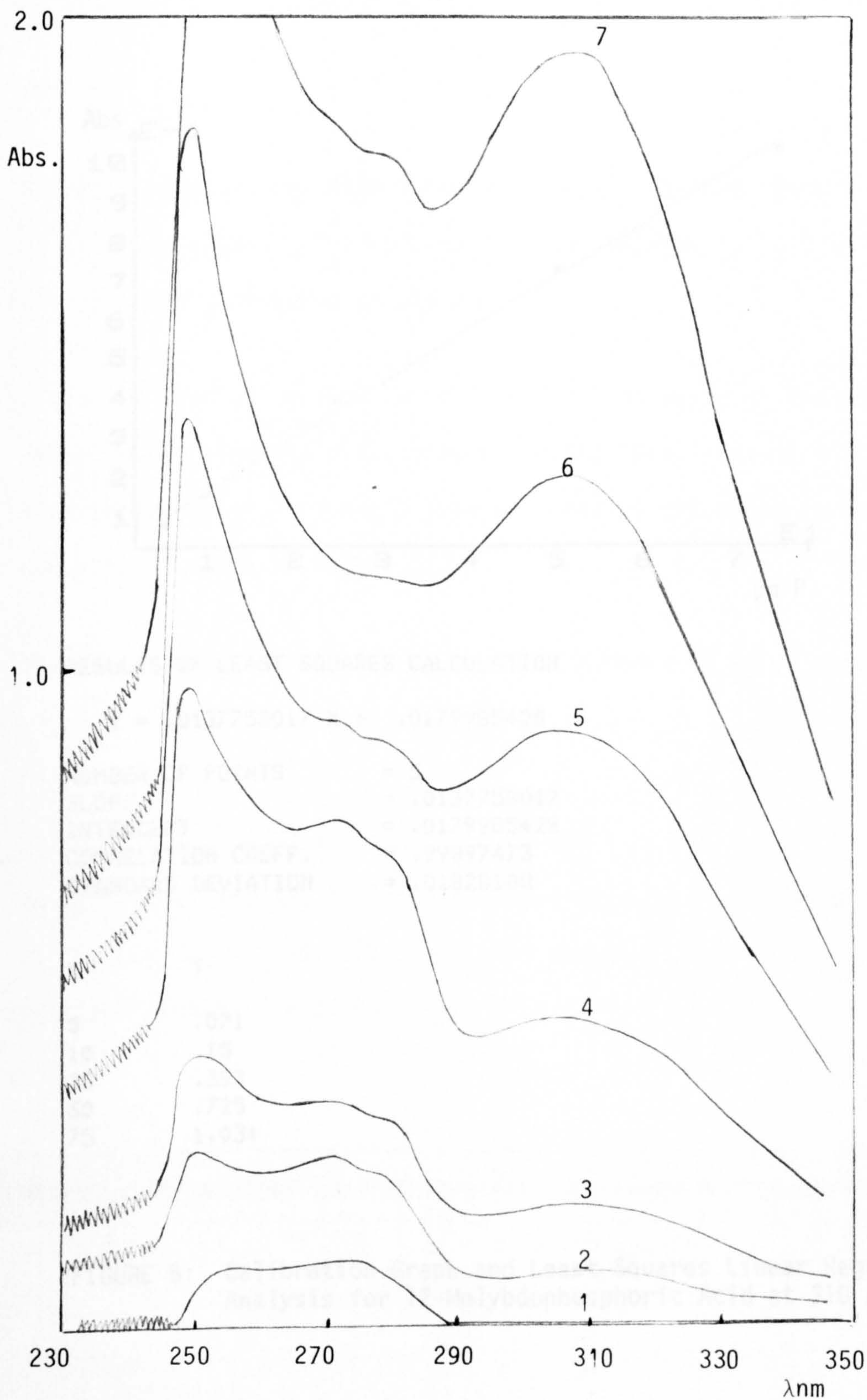
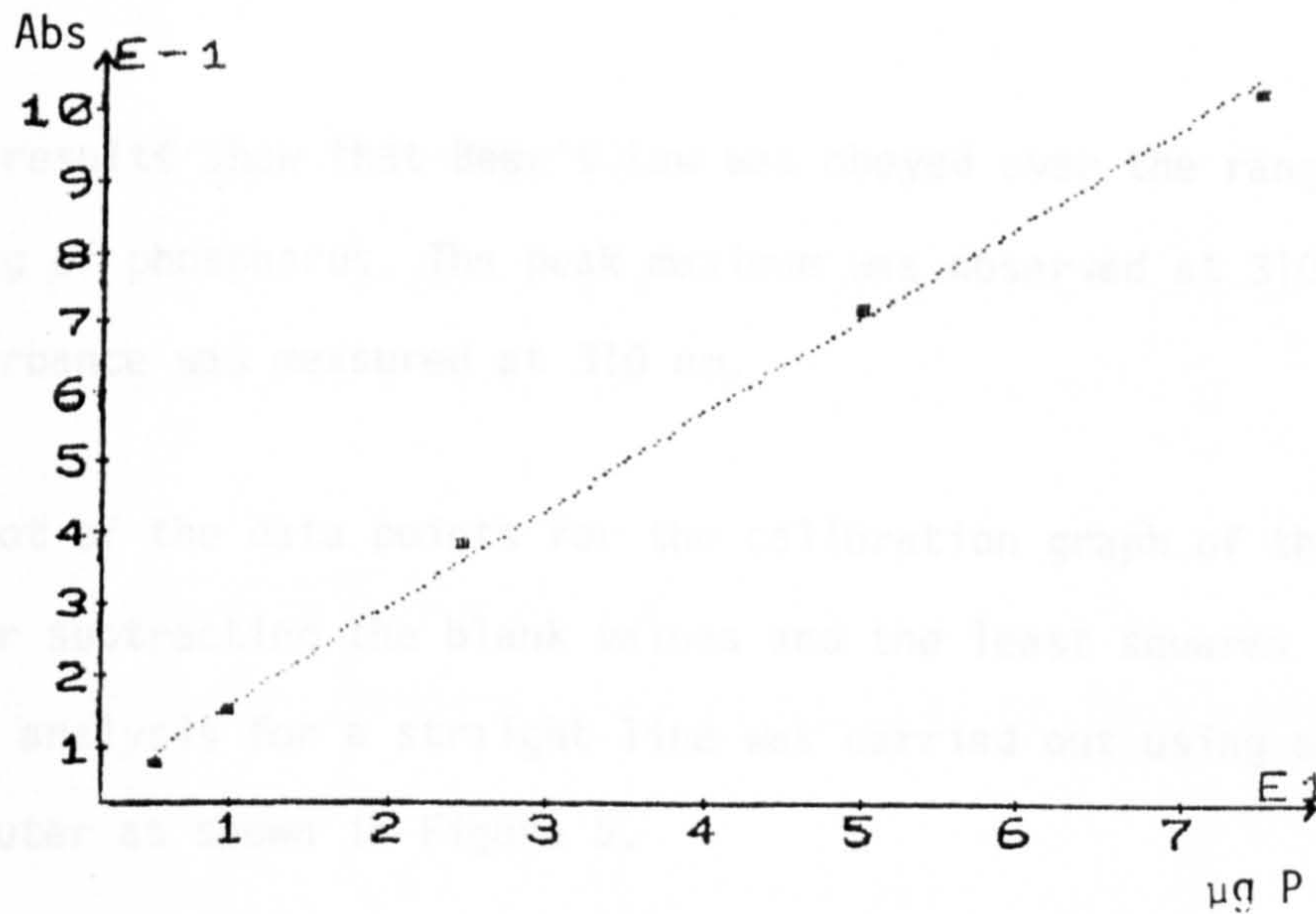


FIGURE 4: Absorption Spectrum of 12-molybdophosphoric acid from 350 nm to 230 nm.

- |                              |                 |
|------------------------------|-----------------|
| 1. Blank extract vs Solvent. | 2. 5 $\mu$ g P  |
| 3. 10 $\mu$ g P              | 4. 25 $\mu$ g P |
| 5. 50 $\mu$ g P              | 6. 75 $\mu$ g P |
| 7. 100 $\mu$ g P             |                 |





#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .0137758017 X + .0179985428$$

NUMBER OF POINTS = 5  
 SLOPE = .0137758017  
 INTERCEPT = .0179985428  
 CORRELATION COEFF. = .99897473  
 STANDARD DEVIATION = .01828108

X	Y
5	.071
10	.15
25	.383
50	.725
75	1.034

FIGURE 5: Calibration Graph and Least Squares Linear Regression Analysis for 12-Molybdophosphoric Acid at 310 nm

The results show that Beer's Law was obeyed over the range 5  $\mu\text{g}$  to 75  $\mu\text{g}$  of phosphorus. The peak maximum was observed at 310 nm and the absorbance was measured at 310 nm.

A plot of the data points for the calibration graph of the phosphorus after subtracting the blank values and the least squares linear regression analysis for a straight line was carried out using an Apple II computer as shown in Figure 5.

The sensitivity (amount for 1% absorption) was 0.28  $\mu\text{g}$  of phosphorus.

## 2.5 Indirect UV Spectrophotometry Method

In this procedure the 12-molybdophosphoric acid in the organic phase was broken down by equilibration with an alkali solution and the molybdate spectrum was recorded.

### Instrument:

Ultraviolet spectrometric measurements were made in 1 cm silica cell using a Pye Unicam SP 800 recording spectrophotometer.

### Reagents:

As experiment 2.4.2.



Ammonia-Ammonium chloride, 1M

The solution was prepared by dissolving 53.5g of ammonium chloride in 70 ml concentrated ammonia and diluting to 1000 ml.

Standard phosphorus solution, 10 ppm

The solution was prepared by diluting 20 ml of stock phosphorus solution to 100 ml.

Solvents:

n-butyl acetate and diethyl ether.

Procedure:

As experiment 2.4.2, except that into a series of 100 ml separating funnels were transferred quantities of standard phosphorus solution covering the range 10 to 100  $\mu\text{g}$  for diethyl ether and 20 to 50  $\mu\text{g}$  for n-butyl acetate. The organic extract, after acid wash, was shaken with 30 ml of buffer solution for 30 seconds. The aqueous layer was drained into a 100 ml volumetric flask and the organic extract was shaken with another 15 ml of buffer solution. The aqueous layer was drained into the same volumetric flask and diluted to volume with distilled water. The absorption spectrum was recorded from 400 nm to 200 nm against the reagent blank, Figure 6(a,b).

Results:

The molybdophosphoric acid exhibited a maximum absorption in the ultra-violet region of the spectrum at 230 nm.

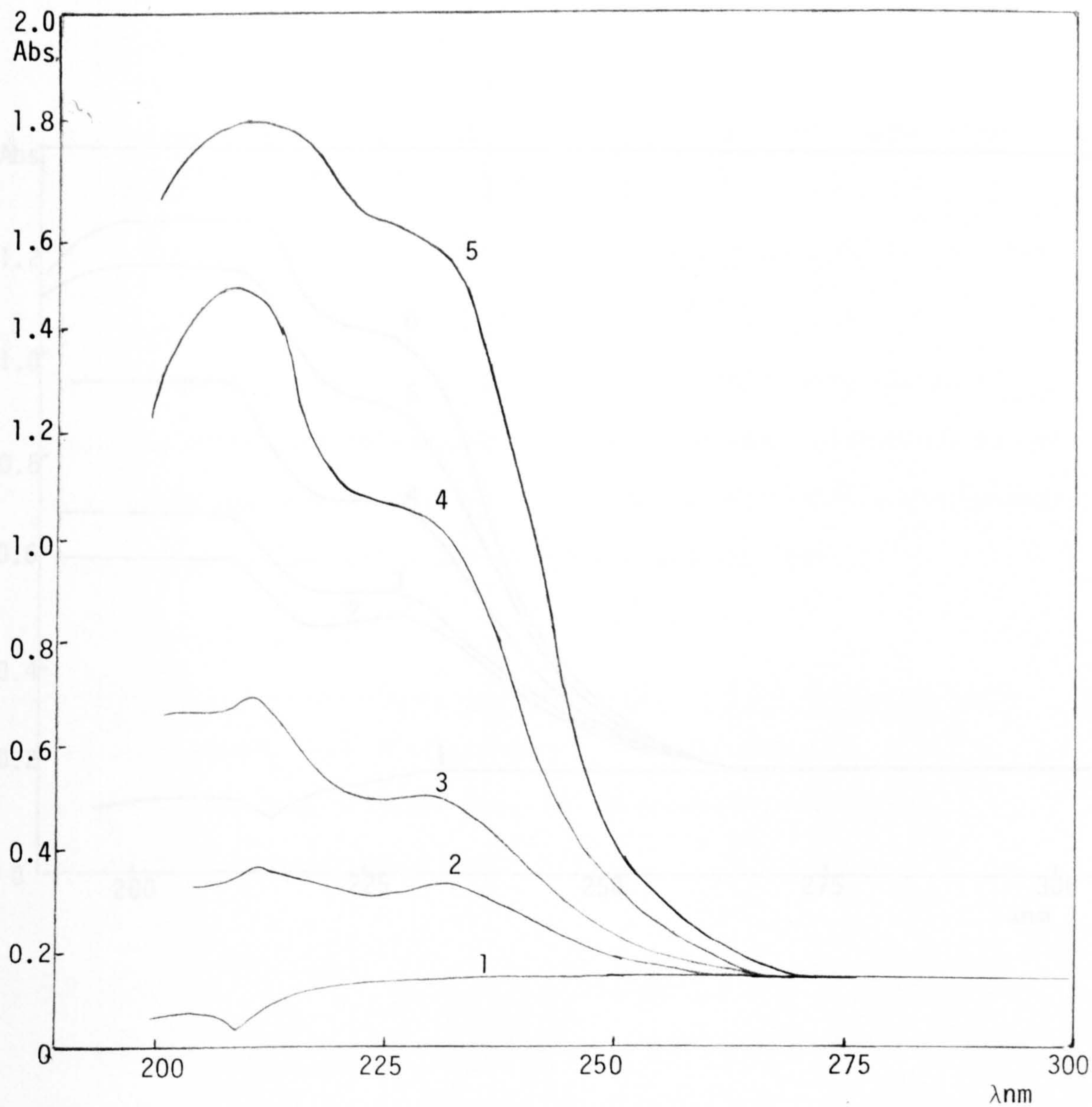


FIGURE 6a: The Absorption Spectrum of molybdate. Diethyl ether as an Extractant.

1. Blank extract vs blank extract
2. 10 μg P
3. 20 μg P
4. 50 μg P
5. 100 μg P



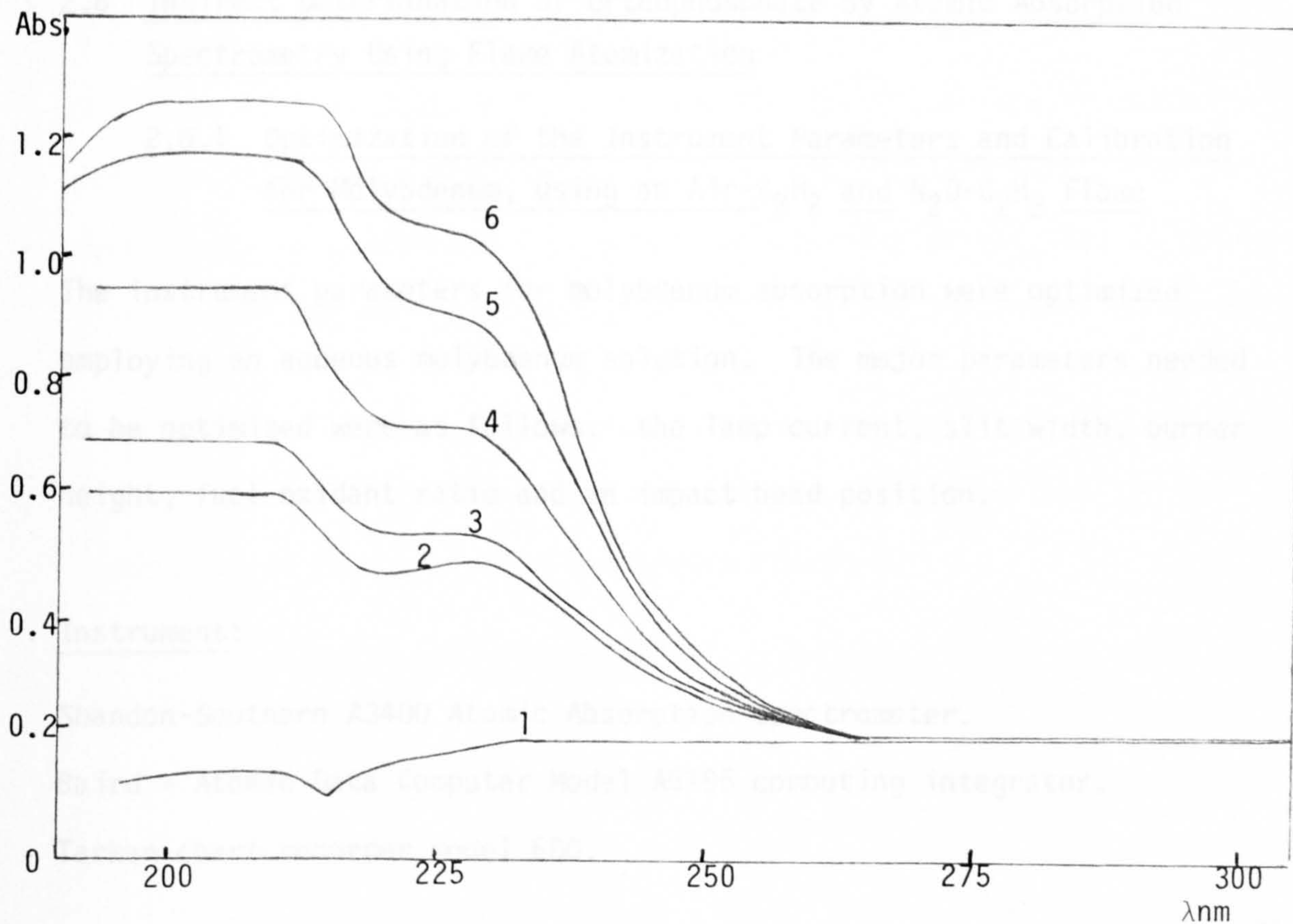


FIGURE 6b: The Absorption Spectrum of <sup>phospho</sup>molybdate, n-butyl Acetate as an Extractant.

1. Blank extract vs Blank extract
2. 20 μg P
3. 30 μg P
4. 40 μg P
5. 45 μg P
6. 50 μg P

## 2.6 Indirect Determination of Orthophosphate by Atomic Absorption Spectrometry Using Flame Atomization

### 2.6.1 Optimization of the Instrument Parameters and Calibration for Molybdenum, using an Air-C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> Flame

The instrument parameters for molybdenum absorption were optimized employing an aqueous molybdenum solution. The major parameters needed to be optimized were as follows: the lamp current, slit width, burner height, fuel-oxidant ratio and an impact bead position.

#### Instrument:

Shandon-Southern A3400 Atomic Absorption Spectrometer.

Baird - Atomic Data Computer Model A5195 computing integrator.

Tarkan chart recorder model 600.

#### Reagents:

##### Stock molybdenum solution, 1000 ppm

The solution was prepared by dissolving 1.829g ammonium molybdate (NH<sub>4</sub>)<sub>6</sub> Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and diluting to 1000 ml.

##### Standard molybdenum solution, 100 ppm

The solution was prepared daily by diluting 10 ml of stock solution to 100 ml.



### Procedure:

Solutions of 0.1, 0.25, 0.5, 1, 5, 10, 20, 25, 50, 60 and 70 ppm molybdenum solutions were prepared by diluting the standard 100 ppm molybdenum solution. Standard 25 ppm molybdenum solution was used to optimize the molybdenum signal by optimization of the instrument parameters.

The integrated signal was measured on aspirating each standard solution. The average of three integrated signals was plotted against the concentration of each aspirated molybdenum standard.

### Results:

The optimized setting for aqueous molybdenum signal for maximum sensitivity is as follows:

Parameter		Air-C <sub>2</sub> H <sub>2</sub>	N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub>
Wavelength of molybdenum absorption	nm	313.3	313.3
Slit width	nm	0.3	0.3
Lamp current	mA	5	5
Burner height	Arbitrary	2	3
Air flow rate	L.min <sup>-1</sup>	8.2	-
Acetylene flow rate	L.min <sup>-1</sup>	5.6	7.1
Nitrous oxide flow rate	L.min <sup>-1</sup>	-	6.8
Aspiration rate	ml.min <sup>-1</sup>	4.6	4.2

The setting of the other parameters were as follows:

Recorder voltage, 10 mV

Recorder chart speed, 4 cm.min<sup>-1</sup>

Integration time, 4 sec.

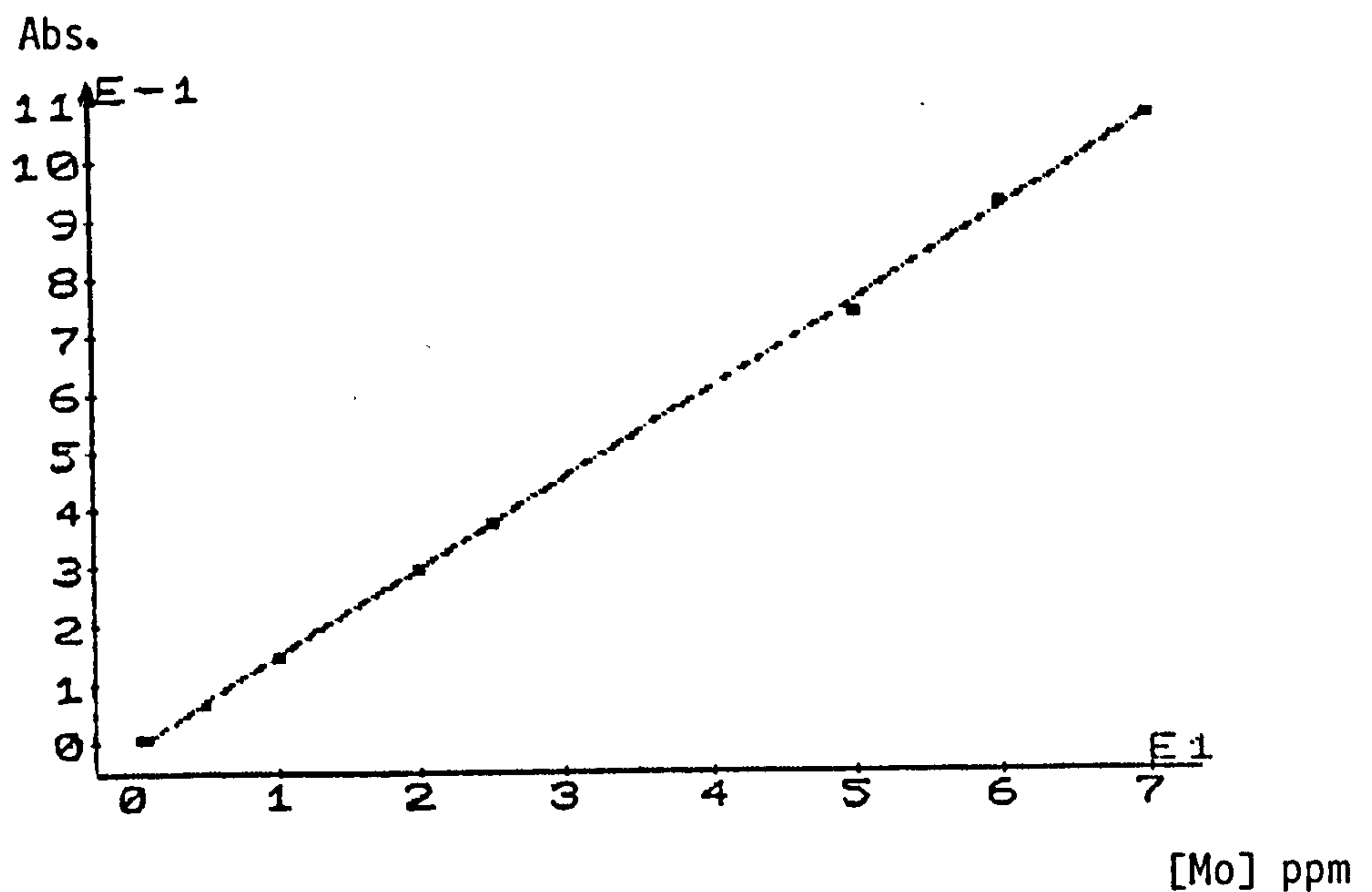
Burner type, air-C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub>.

Burner slot, 10 cm for air-C<sub>2</sub>H<sub>2</sub> and 5 cm for N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame.

Plot of data points for the calibration graph of the molybdenum and the least squares linear regression analysis for a straight line was carried out using an Apple II computer as shown in Figures 7 and 8.

The sensitivity of the instrument using air-C<sub>2</sub>H<sub>2</sub> flame is very much dependent on the flow rate of the acetylene, slight changes in acetylene flow rate will reduce the sensitivity, however the detection limit is very much dependent on the pressure of the cylinder. At low pressures less than 100 psi, acetone is drawn from the cylinder and this causes a reduction in sensitivity of the molybdenum and an increase in the detection limit. The sensitivity (concentration for 1% absorption) and the experimental detection limit for air-C<sub>2</sub>H<sub>2</sub> flame were 0.3 ppm and 0.5 ppm respectively.

The sensitivity of the instrument using N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> is less dependent on flow rate of acetylene and the detection limit for molybdenum is lower than in air-C<sub>2</sub>H<sub>2</sub> flame. The sensitivity (concentration of 1% absorption) and experimental detection limit were 0.4 ppm and 0.1 ppm respectively.



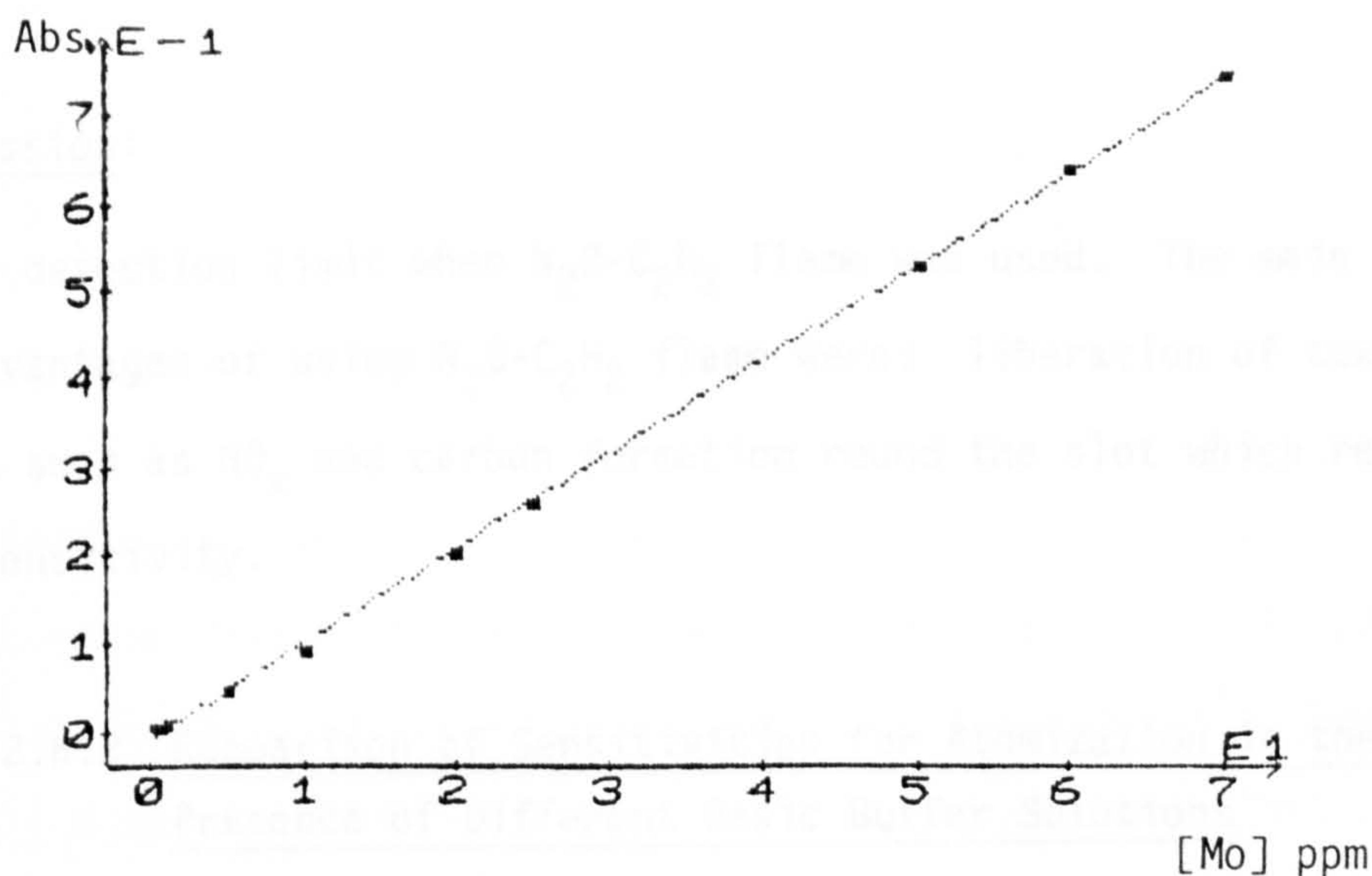
#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .0154045935 X + -9.52325952E-03$$

NUMBER OF POINTS	= 9
SLOPE	= .0154045935
INTERCEPT	= -9.52325952E-03
CORRELATION COEFF.	= .999770664
STANDARD DEVIATION	= 8.78535948E-03

X	Y
.5	2.2E-03
1	7.6E-03
5	.0678
10	.1447
20	.2947
25	.3767
50	.7404
60	.9269
70	1.0735

FIGURE 7: The Calibration Graph and Least Squares Linear Regression Analysis for Molybdenum in the air-C<sub>2</sub>H<sub>2</sub> Flame



# RESULTS OF LEAST SQUARES CALCULATION

$$Y = .0107208359 X + -5.94855916E-03$$

NUMBER OF POINTS = 11  
 SLOPE = .0107208359  
 INTERCEPT = -5.94855916E-03  
 CORRELATION COEFF. = .999787565  
 STANDARD DEVIATION = 5.7777607E-03

X	Y
.1	1E-03
.25	1.7E-03
.5	4.7E-03
1	7.8E-03
5	.0465
10	.0908
20	.2014
25	.2561
50	.5274
60	.6418
70	.7482

FIGURE 8: Calibration Graph and Least Squares Linear Regression Analysis for Molybdenum in the  $N_2O-C_2H_2$  Flame



Discussion:

Lower detection limit when  $N_2O-C_2H_2$  flame was used. The main disadvantages of using  $N_2O-C_2H_2$  flame were: liberation of toxic fumes such as  $NO_x$  and carbon formation round the slot which reduces the sensitivity.

### 2.6.2 Comparison of Sensitivities for Atomization in the Presence of Different Basic Buffer Solutions

The method involves finding the effect of the presence of basic buffer solutions such as: sodium hydroxide and ammonia-ammonium chloride on molybdenum atomization.

Instrument:

As experiment 2.6.1.

Reagents:

As experiment 2.6.1.

Ammonia-Ammonium chloride, 1M

As experiment 2.5.

Sodium hydroxide solution, 1M

The solution was prepared by dissolving 40g of sodium hydroxide in distilled water and diluting to 1000ml. Solutions of concentrations 0.5M,  $10^{-2}M$  and  $10^{-3}M$  were prepared by dilution.

### Procedure:

Into a series of 100 ml volumetric flasks were transferred 1, 5, 10, 20, 25 and 50 ml of the standard 100 ppm molybdenum solution.

Five sets of volumetric flasks were prepared, each set containing the above volumes of the molybdenum standard: to the first set, 45 ml volume of 0.5M sodium hydroxide was added and the second set, 45 ml volume of  $10^{-2}$ M sodium hydroxide was added, to the third set, 45 ml volume of  $10^{-3}$ M sodium hydroxide was added, to the fourth set, 45 ml volume of 1M ammonia-ammonium<sup>chloride</sup> was added and all five sets were made up to volume with distilled water.

### Results:

Depression of the molybdenum signal was observed using 0.5M sodium hydroxide solution. Table 1 compares the sensitivities, the slopes and correlation coefficients of each calibration graph. Both ammonia-ammonium chloride buffer and  $10^{-2}$ M sodium hydroxide were used for the back extraction of the 12-molybdophosphoric acid.

Solution	Concentration Added (M)	Sensitivity (ppm)	Slope (ppm <sup>-1</sup> )	C.C.
NaOH	0.5	1.6	0.0023	0.9995
NaOH	10 <sup>-2</sup>	0.3	0.014	0.9997
NaOH	10 <sup>-3</sup>	0.35	0.014	0.996
NH <sub>4</sub> Cl + NH <sub>4</sub> OH	1	0.27	0.0149	0.999
Aqueous	-	0.28	0.015	0.9997

TABLE 1: Comparison of the Slope, Sensitivity and the Correlation Coefficient (C.C) of Different Solutions

### 2.6.3 Extraction of 12-Molybdophosphoric Acid and Subsequent Indirect Determination of Phosphorus Using Air-C<sub>2</sub>H<sub>2</sub> Flame

The method involves the formation of 12-molybdophosphoric acid which can be separated then decomposed to give molybdate, MoO<sub>4</sub><sup>2-</sup>. Molybdate was determined at 313.3 nm resonance line of molybdenum by atomic absorption spectroscopy.

#### Instrument:

As experiment 2.6.1.

#### Reagents:

As experiments 2.5 and 2.6.1.

Molybdate solution, 10%

As experiment 2.4.2.

Hydrochloric acid solution (1+2)

As experiment 2.4.2.

Hydrochloric acid solution (1+10)

As experiment 2.4.2.

Sodium hydroxide

As experiment 2.6.2.

Solvents:

n-butyl acetate and diethyl ether.

Procedure:

Into a series of 100 ml separating funnels were transferred quantities of standard phosphorus solution covering the range 10 to 100 µg of phosphorus. The procedure was continued as in experiment 2.5.

The experiment was repeated, using a different basic buffer solution for back extraction, and a smaller volume of solvent for extraction.

The extract containing molybdate ions, and molybdenum standard solutions containing 45 ml volume of basic buffer solution, were aspirated. A calibration graph was prepared, from which the number of molybdate



ions associated with the phosphate ion in the complex was calculated.

### Results:

The procedure gives the molybdenum (VI) concentration in the extracted phase which can be determined by atomic absorption spectrometry. On the basis of knowing the total concentration of molybdenum, initially present as 12-molybdophosphoric acid in aqueous phase by calculating the theoretical chemical amplification, the percent extraction (E) was calculated. See Appendices 1 and 2, page 184.

Both diethyl ether and n-butyl acetate were tested for extraction ability. Both proved to be good extractants, however n-butyl acetate was preferred, because of its low volatility. Table 2(a,b) compares the extraction efficiency of the two solvents.

It is possible to use smaller volumes of n-butyl acetate for extraction, which was not possible with diethyl ether because of its solubility in 1.2M HCl solution from which initial extraction of 12-molybdophosphoric acid was made and in the acidic wash solution used in removing the traces of excess molybdate. Table 3 shows the percent extraction when smaller volumes of solvent were used. Table 3a shows the concentration of the molybdenum in the second acid wash which was collected, made up to volume and analysed.

The extraction efficiency using  $10^{-2}$ M sodium hydroxide is comparable with ammonia-ammonium chloride, however, 0.5M sodium hydroxide caused a depression of the molybdenum signal and a reduction in the extraction efficiency.

Abs. Y	ppm Mo Calc.X	ppm Mo 100% E	%E
0.043	3.797	3.72	102.10
0.075	6.649	7.44	89.37
0.165	14.67	14.88	98.59
0.206	18.32	18.60	98.50
0.422	37.58	37.20	101.0

TABLE 2a: Calculation of the Percent Extraction (E).45 ml of n-butyl Acetate was used as an Extractant

Abs. Y	ppm Mo Calc.X	ppm Mo 100% E	%E
0.016	4.010	3.72	107.8
0.04	8.360	7.44	112.4
0.06	11.986	11.16	107.4
0.092	17.786	18.60	95.6
0.164	30.837	37.20	82.9

TABLE 2b: Calculation of the Percent Extraction (E). 45 ml of di-ethyl ether was used as an Extractant

Abs. Y	ppm Mo Calc.X	ppm Mo 100% E	%E
0.106	3.504	3.72	94.2
0.23	8.062	7.44	107.6
0.416	14.89	14.88	100.1
0.509	18.32	18.60	98.5
0.959	34.85	37.20	93.6

TABLE 3: Calculation of the Percent Extraction (E) Using 20 ml n-butyl Acetate as an Extractant

Abs. Y	ppm Mo Calc.X
0.007	0.66
0.015	1.46
0.017	1.61
0.013	1.21
0.015	1.46
0.018	1.71

TABLE 3a: Calculation of Molybdenum (VI) Concentration in the Second Acid Wash

Table 4(a,b) compares the extraction efficiency using different concentrations of sodium hydroxide.

#### 2.6.3.1 Effect of anhydrous sodium sulphate on the recovery of heteropoly acid

The method involves drying the organic solvent after acid wash to remove molybdenum in organic phase, droplets suspended in organic phase rather than co-extracted isopolymolybdate.

##### Instrument:

As experiment 2.6.1.

##### Reagents:

As experiment 2.6.3.

##### Drying agent:

This was prepared by mixing 0.7g anti-bumping granules with 3.3g of anhydrous sodium sulphate.

##### Solvent:

n-butyl acetate.

##### Procedure:

Into a series of 100 ml separating funnels were transferred quantities of standard phosphorus solution covering the range 5 to 150  $\mu$ g of phosphorus. Experiment 2.6.3 was repeated using 45 ml volume and



Abs. Y	ppm Mo Calc.X	ppm Mo 100% E	%E
0.0125	2.938	3.72	78.99
0.021	5.955	7.44	80.04
0.041	13.05	14.88	87.72
0.042	13.23	18.60	71.12
0.067	22.10	37.20	59.41

TABLE 4a: Calculation of the Percent Extraction (E) Using 0.5M Sodium Hydroxide for Back Extraction and 45 ml of di-Ethyl Ether as an Extractant

Abs. Y	ppm Mo Calc.X	ppm Mo 100% E	%E
0.033	3.252	3.72	87.42
0.066	6.537	7.44	87.86
0.126	12.51	14.88	84.07
0.187	18.58	18.60	99.90
0.335	33.32	37.20	89.56

TABLE 4b: Calculation of the Percent Extraction (E) Using  $10^{-2}$ M NaOH for Back Extraction and 45 ml of di-Ethyl Ether as an Extractant

20 ml volume of solvent as extractants. Anhydrous sodium sulphate was used to dry the organic extract before the back extraction. A burette type column was used with a small piece of glass wool. See Figure 9.

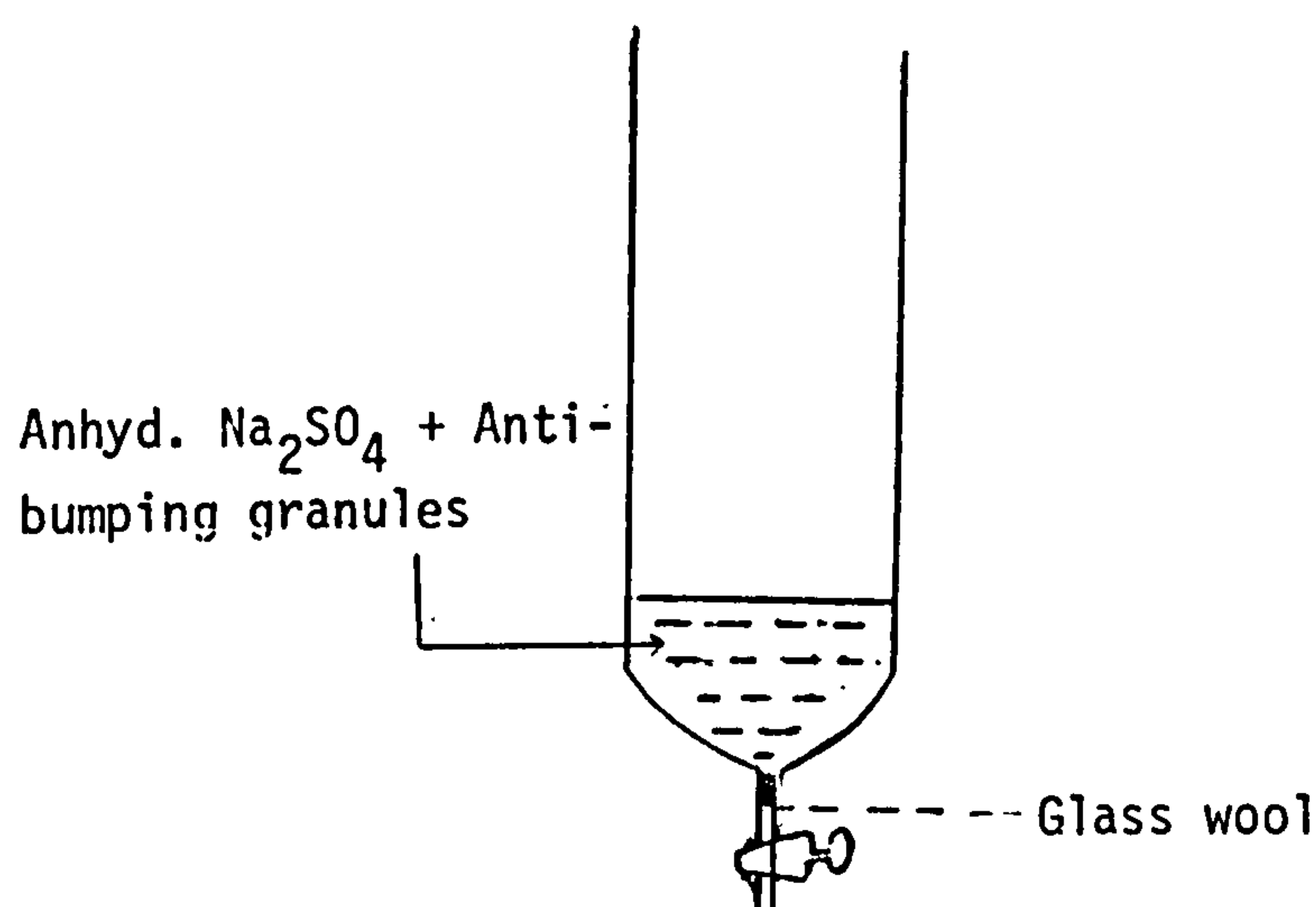


FIGURE 9: Burette type column 10 x 1.5 cm in dimension was used for drying the organic phase

### Results:

The same calculation procedure as for experiment 2.6.3 was used.

Table 5(a,b) compares the extraction efficiency of 12-molybdophosphoric acid when 20 ml and 45 ml solvent volume was used and dried after acid wash.

Abs. Y	ppm Mo. Calc.X	ppm Mo 100% E	%E
0.029	1.99	1.86	106.7
0.049	3.62	3.72	97.7
0.094	7.26	7.44	97.5
0.239	18.18	18.6	97.7
0.442	33.75	37.2	90.7
0.582	44.47	55.8	79.7

TABLE 5a: Calculation of the Percent Extraction (E) Using 20 ml n-butyl Acetate as an Extractant

Abs. Y	ppm Mo Calc.X	ppm Mo 100% E	%E
0.048	3.609	3.72	89.5
0.094	7.748	7.44	100.8
0.172	14.77	14.88	98.0
0.22	19.08	18.60	101.9
0.442	39.06	37.20	105.1

TABLE 5b: Calculation of the Percent Extraction (E) Using 45 ml n-butyl Acetate as an Extractant

Discussion:

The use of anhydrous sodium sulphate has not resulted in any loss of heteropoly acids by adsorption.

### 2.6.3.2 Effect of anhydrous sodium sulphate on blank values

Instrument:

As experiment 2.6.1.

Reagents:

As experiment 2.6.3.1.

Procedure:

As experiment 2.6.3.1. The blank in the first instance was dried then compared with undried extract.

Results:

The same calculation procedure as for experiment 2.6.3 was used.

Table 6 shows the molybdenum concentration present in the blank extract when the solvent was dried or undried after acid wash.

The molybdenum concentration in the blank which was not dried with anhydrous sodium sulphate was 1 ppm. When the drying agent was used, the blank concentration was about 0.35 ppm (see also Chapters 3 and 4).



Blank	Absolute Y	ppm Mo Calc.X
$W_{21}^D$	0.0024	0.36
$W_{22}^D$	0.0022	0.35
$W_{21}$	0.0129	1.13
$W_{22}$	0.0141	1.2
1 ppm Mo	0.013	1.0
1 ppm Mo	0.011	0.989

TABLE 6: Molybdenum (VI) Concentration in the Blank Extract.

$W_{21}^D$  and  $W_{22}^D$  = A duplicate extraction (dried)

$W_{21}$  and  $W_{22}$  = A duplicate blank extraction (undried)

### Conclusion:

The best solvent for extraction of 12-molybdophosphoric acid is n-butyl acetate. Either 20 ml or 45 ml solvent volume can be used as an extractant. For samples containing less than 10  $\mu\text{g}$  of phosphorus, 20 ml volume as an extractant was preferred. Drying the extract is important after acid wash to remove droplets of aqueous phase containing molybdenum suspended in the organic phase.

The sensitivity (amount for 1% absorption) was 1  $\mu\text{g}$  for both volumes.

### CHAPTER 3

#### FLAME ATOMIZATION OF MOLYBDENUM

##### 3.1 Introduction

Flame atomic absorption has been widely used for the determination of molybdenum in a variety of materials including the following: NaCl brines (100), niobium and tantalum alloys (101), lake and natural waters (102,103), steels and ferrous alloys (104,105,106), nickel and uranium alloys (107), soils and rocks (108-110) and in heteropoly acids for the indirect determination of metals and non-metals (2).

Molybdenum can be determined in both fuel rich, air-C<sub>2</sub>H<sub>2</sub> flame and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame. The first use of atomic absorption for the determination of molybdenum was published by David (111). He suggested, the use of a fuel rich air-C<sub>2</sub>H<sub>2</sub> flame. The wavelength most frequently monitored for molybdenum with atomic absorption measurements is 313.3 nm. Less sensitive lines can sometimes be used to avoid interferences or with high molybdenum concentrations.

The heteropoly acid chemistry of molybdenum is an attractive area for development of indirect atomic absorption procedures for the heteropoly forming elements, as these elements are often difficult to determine by direct atomic absorption methods.

Existing flame based methods are limited by (a) the rather high blank values due to the presence of some of the large excess<sup>of</sup> molybdenum added to drive the reaction to completion, in the subsequent organic extract, (b) the yield of the atom forming reactions in the flame, and (c) the noise associated with nebulization and combustion processes. All of these factors have been studied with a view to improving the sensitivity and detection limit for molybdenum, using phosphate as a model species.

### 3.2' Review of Mechanism of Interferences in Flames

Condensed phase interferences have been widely reported in the literature. Many diverse ions if present with molybdenum affect the magnitude of the absorbance values observed in determining molybdenum by AAS (112,113).

Alkaline nitrates, sulphates (108) and  $\text{HClO}_4$  (114) markedly enhance the molybdenum absorption.

Dilli, Gawni and Ocago (115), recommended dilute  $\text{HNO}_3$  or dilute  $\text{HCl}$  acid as the best choice for use with molybdenum when it is aspirated into the flame. In higher concentrations, about 2M, the molybdenum signal is depressed by the acid (112). Dilute perchloric acid about 0.1M is shown to have negligible effect upon molybdenum absorbance readings (116). Addition of large amounts of  $\text{AlCl}_3$  and  $\text{NH}_4\text{Cl}$  to both sample and standard has been found to be particularly successful in the determination of chemical interferences on molybdenum

(104,111,113). Standard addition has also been used to overcome interferences (117). Solutions containing 5% HCl, 2%  $\text{NH}_4\text{Cl}$  and 300 ppm  $\text{Na}_2\text{SO}_4$  are claimed to give optimum results for molybdenum in  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame (118). Others prefer solutions containing 500 ppm  $\text{Al}^{3+}$  and 5.8%  $\text{H}_3\text{PO}_4$  (119) or 5% (v/v) HCl + 5% (v/v)  $\text{H}_3\text{PO}_4$  +  $2.5 \text{ mg ml}^{-1} \text{ Al}^{3+}$  (120).

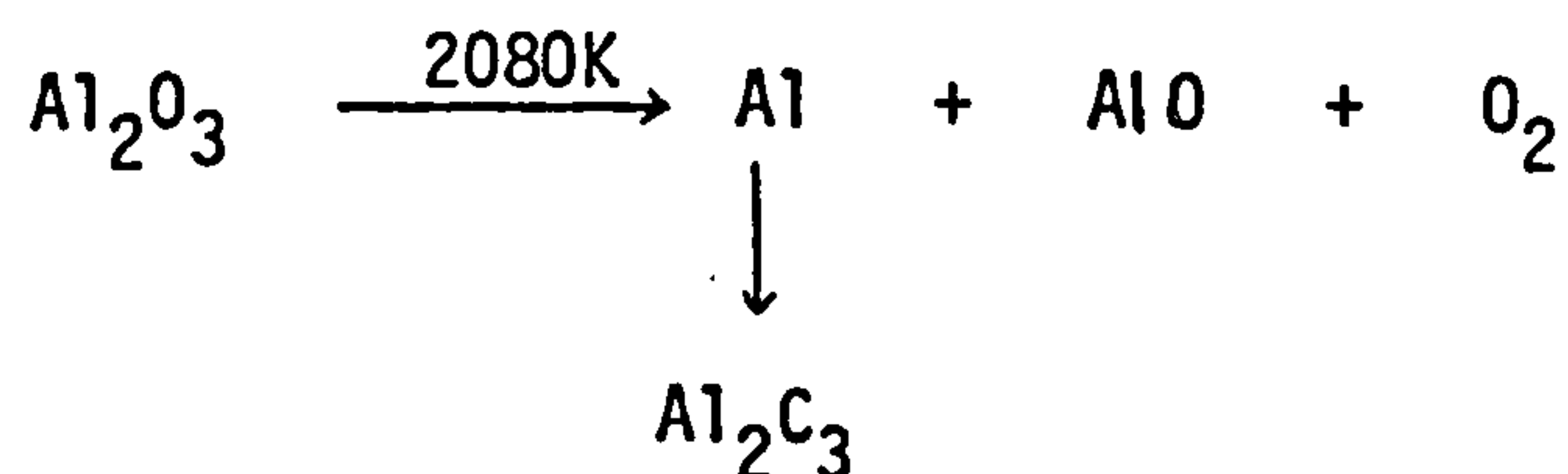
Rann and Hambly (121) have made a careful study of the distribution of atoms of several elements in a premixed air- $\text{C}_2\text{H}_2$  flame. For those elements which are difficult to atomize in the flame such as molybdenum, the maximum atomic concentration persists over only a limited flame volume and is generally greatest in the hottest part for most reducing regions of the flame. The success of the use of  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame for determination of the "refractory oxide" metal is not however due to primarily the higher temperature, it also offers an exceedingly efficient reducing environment, even in slightly fuel-rich mode via the formation of CN (and CH, NH, etc) radicals in the flame (122,123).

Factors affecting the determination of molybdenum by atomic-absorption spectrometry have been studied (124). The two to three times greater sensitivity of  $\text{Mo(CO)}_6$  as compared to less volatile organic molybdenum compounds (Mo cupfurate, Mo cyclopenta dienyl tricarbonyl dimer <sup>in</sup> all organic solvents) is due to vaporization of  $\text{Mo(CO)}_6$  in the preheated zone, thus entering the reducing flame environment as separate molecules (124).



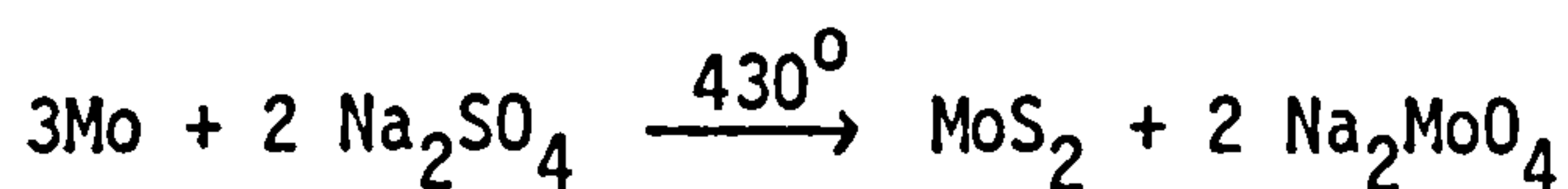
Atomization problems in atomic absorption spectrometry were studied by Willis (125). In hot fuel-rich  $N_2O-C_2H_2$  flame molybdenum oxides may be partly reduced by hydrocarbon and hydrogen to carbide and/or metal in the condensed phase (126). Since molybdenum and its carbide are less volatile than its oxides, this reduction may lead to incomplete volatilization even in hot flames. Inter-element interferences in atomic absorption analysis with  $N_2O-C_2H_2$  flame have been investigated (127). "Competition for oxygen" in condensed phase before vaporization may account for some of the enhancement effect (127). Another explanation for the enhancement was suggested by Koirttyohann and Pickett (128) later elaborated by West, Fassel and Knise<sup>e</sup>ly known as "lateral diffusion interferences" (129). These authors assume that, *"in the presence of a refractory interferent the vaporization and atomization of the analyte is delayed. Free atoms have a shorter time for lateral diffusion before entering the optical path (observation height). In consequence, they will diffuse a shorter distance and will be concentrated in the centre of the flame."* However, according to (130) the enhancement of the molybdenum by added aluminium in the  $N_2O-C_2H_2$  flame can be explained if it is assumed that the addition of salts forming alumina accelerates the heat transfer to the particle and inhibits the reduction of the oxide (130). Molybdenum oxides are known to be more easily volatilized than corresponding carbide and metal, which have high melting points around 2800K. A favourable effect of alumina on the oxidation of Mo and  $Mo_2C$  particles has been found in hot electric furnaces (see reference

cited in 131).



Oxygen liberated facilitates the vaporization of the analyte in the form of oxides. Therefore an oxidizing microclimate is maintained in the particle (131). In a more detailed investigation Ruběška (126) suggested that the effect of Al on molybdenum can be ascribed to its preventing their reduction from the oxide to the less volatile metal. Thus, the presence of aluminium in a mixture will enhance the volatilization of molybdenum by scavenging reducing species and preventing the formation of solid molybdenum.

The enhancement of the sodium sulphate (118) is believed<sup>to be</sup> due to a molybdenum oxidizing reaction (132)



Sastri, Chakrabarti and Willis (133,134) attempted to demonstrate that formation of refractory oxides in the flame preceded largely through retention of metal-oxygen bonds existing in the sample solutions.

There is evidence indicating that in acetylene flames, reduction of the solute in the condensed phase actually takes place through heterogeneous reactions with the flame gases (126,130,135,136). Reduction before vaporization is observed for quite a number of elements. If refractory compounds are formed and carbides of many elements actually are, this reduction may influence the vaporization processes and thus the analytical signal. Reduction of the analyte to a metal or a carbide may accelerate or retard vaporization depending on what form is more volatile (137). However, if an indifferent substance which does not react with analyte in any way is added, two different situations may arise. If the boiling point of the interferent is lower than the flame temperature, vaporization is heat transfer controlled (138-140). Therefore, addition of relatively volatile salt (e.g. alkaline halide) will cause delay in heating up of the particle and in the vaporization of the less volatile analyte. If a salt sublimes or decomposes to give gaseous products ( $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ), it may cause explosive disintegration (139). Aqueous solutions containing dissolved solutes ( $\text{NaCl}$  and  $\text{CaCl}_2$  mixtures) evaporate more slowly than pure droplets according to El-Golli, Arnaud, Bricard and Treiner (141) and this difference in evaporation rate can be ascribed to solute-solvent interaction. Paul (142) noted that the rate of evaporation of  $\text{Al}_2\text{O}_3$  particles increases discontinuously when the particle melts. Through detailed investigation Paul determined that the particle evaporation rate remained constant, but particle emissivity increased discontinuously upon its fusion, causing a rapid temperature jump and increased evaporation of the particle at that time.



L'vov (136) assumed that in the reaction zone the analyte is immediately reduced and the analyte starts to vaporize as the already involatile carbides, which is different from Rubeška's (143) model in which he assumed the analyte vaporizes partly in its oxide form and that the fraction vaporized after its reduction to a carbide (or a metal) is negligible.

### 3.3 Selective Review of Flow Injection Analysis with Flame Atomic Absorption Spectrometry

The simplified form of an FIA system is illustrated in Figure 10. The flow injection system consists of a carrier stream of reagent propelled by a pump; injection system; a flow-through detector; and a recorder or other data-handling device. The technique is founded on a combination of the following three principles: sample injection, controlled sample dispersion and reproducible timing.

Conventional use of atomic absorption spectrometry relies upon sample aspiration and generating of a steady state. FIA when used with atomic absorption spectrometry, differs from traditional methods in that the measurements are not taken at equilibrium. The sample having dispersed into the carrier solution is pumped into the atomic absorption nebulizer as a discrete zone, resulting in a transient signal response, which is related to the quantity of the analyte in the injected sample.



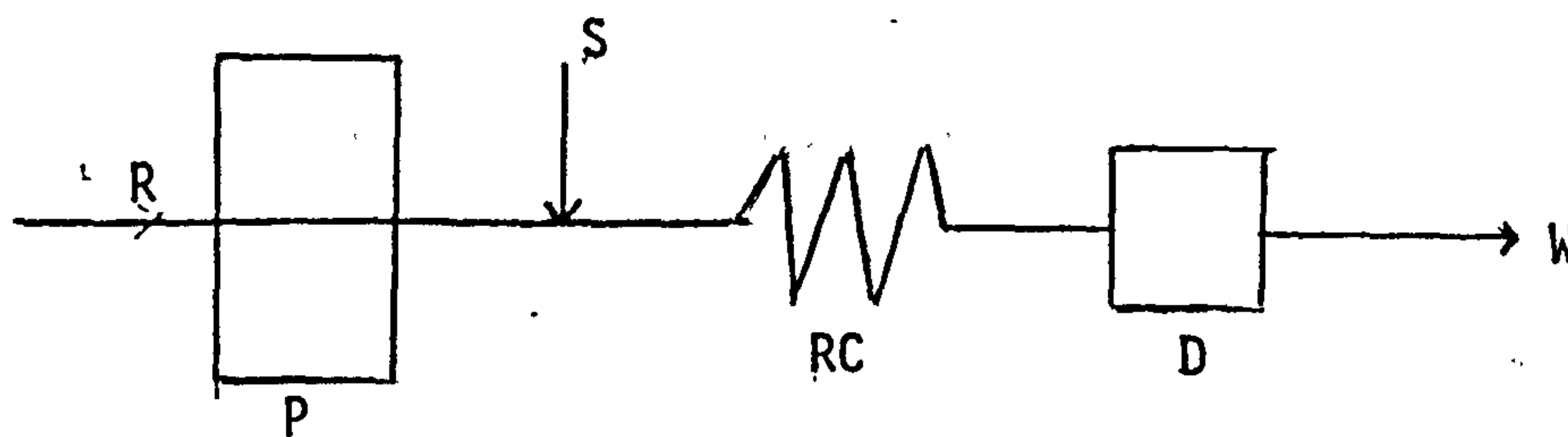


FIGURE 10: Simple FIA System

P = Pump  
 S = Sample  
 RC = Reaction coil  
 D = Detector  
 R = Reagent

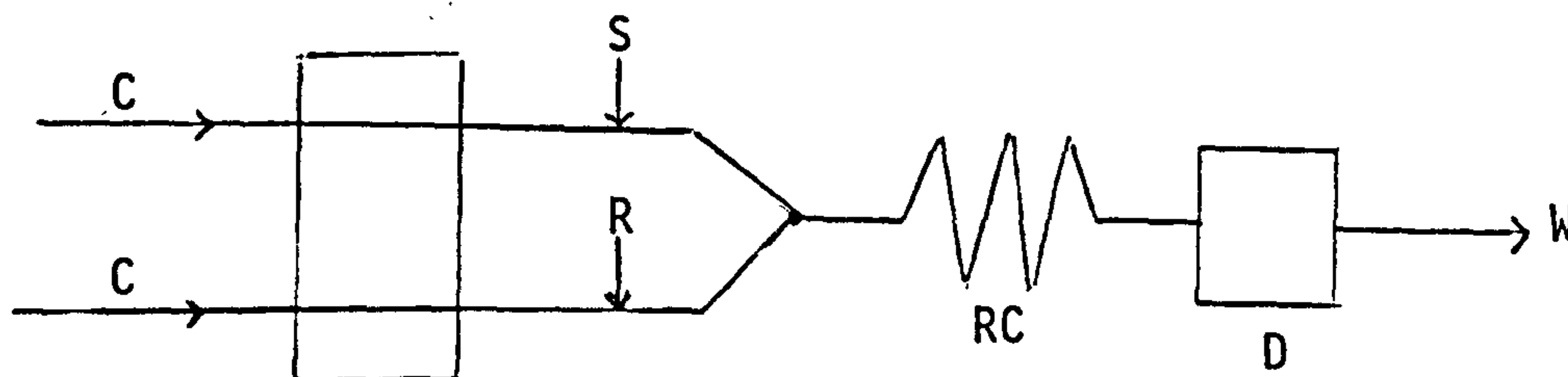


FIGURE 11: Synchronous Merging Zone FIA

C - inert carrier solution into which sample and reagent are injected

The magnitude of this dispersion is dependent on the operating parameters applied to the system, including sample volume, tubing bore size, tubing length and flow rate.

Varying the values of these parameters confers a significant degree of control over the dispersion characteristics and facilitates optimization of a flow injection system forming diverse applications. Usually, limited dispersion is applied for atomic absorption spectrometry to attain a high analytical rate. This is achieved by keeping the length of the tubing between the injector and the nebulizer short.

Reproducible timing is of the utmost importance in FIA. The time from introduction of the sample into the carrier stream until it is detected is solely dependent on the pumping speed. By adjusting the experimental variables the residence time can be adjusted to give the required sample dispersion.

FIA-AAS combination offers advantages over conventional nebulization. Viscosity effect, interference effect, clogging by high salt content can be overcome by continuous pumping of the carrier stream through the nebulizer. The other advantages are the use of small sample volume, rapid sampling, automatic dilution for higher concentrations of elements and finally the stream can contain reagents as Lanthanum.

FIA in combination with atomic absorption spectrometry was first suggested and used by Zagatto *et al* (144) as a means to dilute and add lanthanum solution prior to sample introduction into the flame. As the reagent addition was done in the zone-merging mode (see Figure 11), both reagent and time economy were improved. Only 50  $\mu$ l of reagent was required and the plant-digest samples were analysed at a rate of 300  $\text{h}^{-1}$ . Standard addition and matrix effect compensation have also been suggested to overcome interferences (145), while the unique ability of FIA-AAS to handle samples with salt contents (up to 25% magnesium chloride solution) was demonstrated (146), and direct sampling of sea water into the flame has been done using the FIA star system (147). On-line flow injection analysis pre-concentration methods were developed by Olsen (148) using a micro column of Chelex-100 resin, allowing the determination of lead at concentrations as low as 10 parts per  $10^9$  (ppb) and 1 ppb for cadmium and zinc with sampling rate of 30 to 60 per  $\text{h}^{-1}$ . Wolf and Stewart (149) replaced direct aspiration by their (automated multiple flow injection analysis) system for sample introduction, achieving 180 samples  $\text{h}^{-1}$  for determination of copper and zinc in food digest.

Enhancement in sensitivity with organic solvent carrier stream was reported for trace metals using n-butyl acetate at a rate of 300 measurements  $\text{h}^{-1}$  (150). Lower detection limits <sup>the</sup> for determination <sub>were obtained</sub> of copper at a rate of 200 measurements  $\text{h}^{-1}$  when water, methanol, ethanol or acetone were used for carrier stream, while determination

of copper samples with methyl isobutyl ketone were analysed at a rate of 300 measurements  $\text{h}^{-1}$  (151).

The technique can be applied also for the determination of copper and zinc in serum and plasma (152,153), iron in serum and total iron binding capacity TIBC (154), therapeutic levels of lithium in serum (155), trace elements in domestic water supplies (156) and plant digests (157).

## PRACTICAL EXPERIMENTS

### 3.4 Approaches for Improving the Sensitivity and Detection Limit for Molybdenum Using Flame Atomization

#### 3.4.1 Modification of Flame Chemistry

##### 3.4.1.1 Varying flame gases

Reducing conditions are beneficial for free atom production only once the analyte is vaporized. It was hoped that adding hydrogen would provide a reduction mechanism avoiding carbon containing species, since the commercial production of the metal proceeds via the process (158).

Ottaway and Coker (159), reasoned that possible candidate species responsible for the final reduction of the monoxide to the metal is CO, accordingly the effect of increasing the partial pressure of this gas was investigated.



Using atomic absorption spectrometry at its optimized setting for maximum sensitivity as in experiment 2.6.1 the addition of gases such as carbon monoxide and hydrogen were introduced via the supplementary support gas supply system.

The effect of separately adding gases to both air-C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame were investigated.

Addition of gases to both flames, produced changes in flame geometry with the formation of much larger primary reaction zone (see Figure 12), and it was not possible to lower the burner far enough to obtain a maximum on the plot of absorbance vs burner height for hydrogen (see Figure 13). Changes in fuel-oxidant rate did not overcome the depression of molybdenum signal caused by added gases.

In conclusion, the addition of neither gas produced improvement in sensitivity. It is most likely that depression caused by addition of hydrogen and carbon monoxide is due to mainly formation of more thermostable compounds.

#### 3.4.1.2 Varying salts

Interference mechanisms in flames were suggested (126) to be kinetically controlled by competing short time processes, i.e. vaporization and reduction to an involatile form. Even slight changes in the experimental conditions have a great influence on the observed interferences. Both processes depend upon the heating

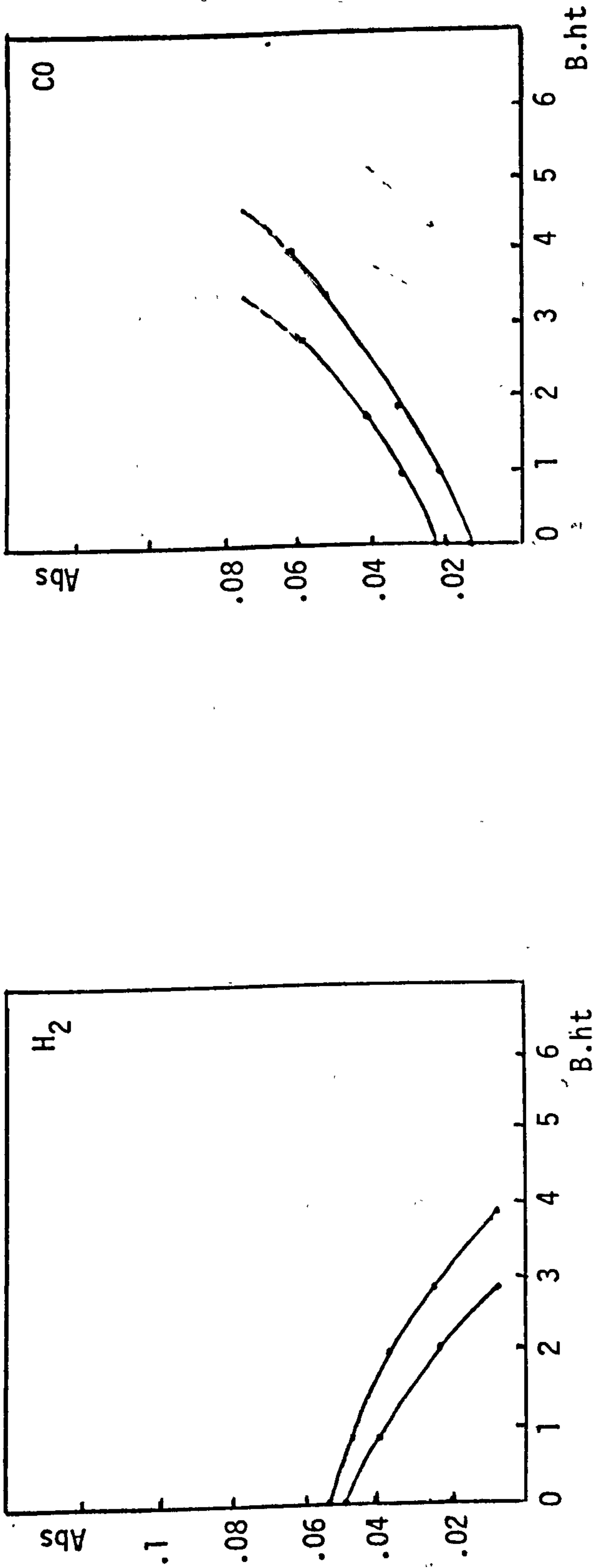


FIGURE 13: Effect of Burner Height

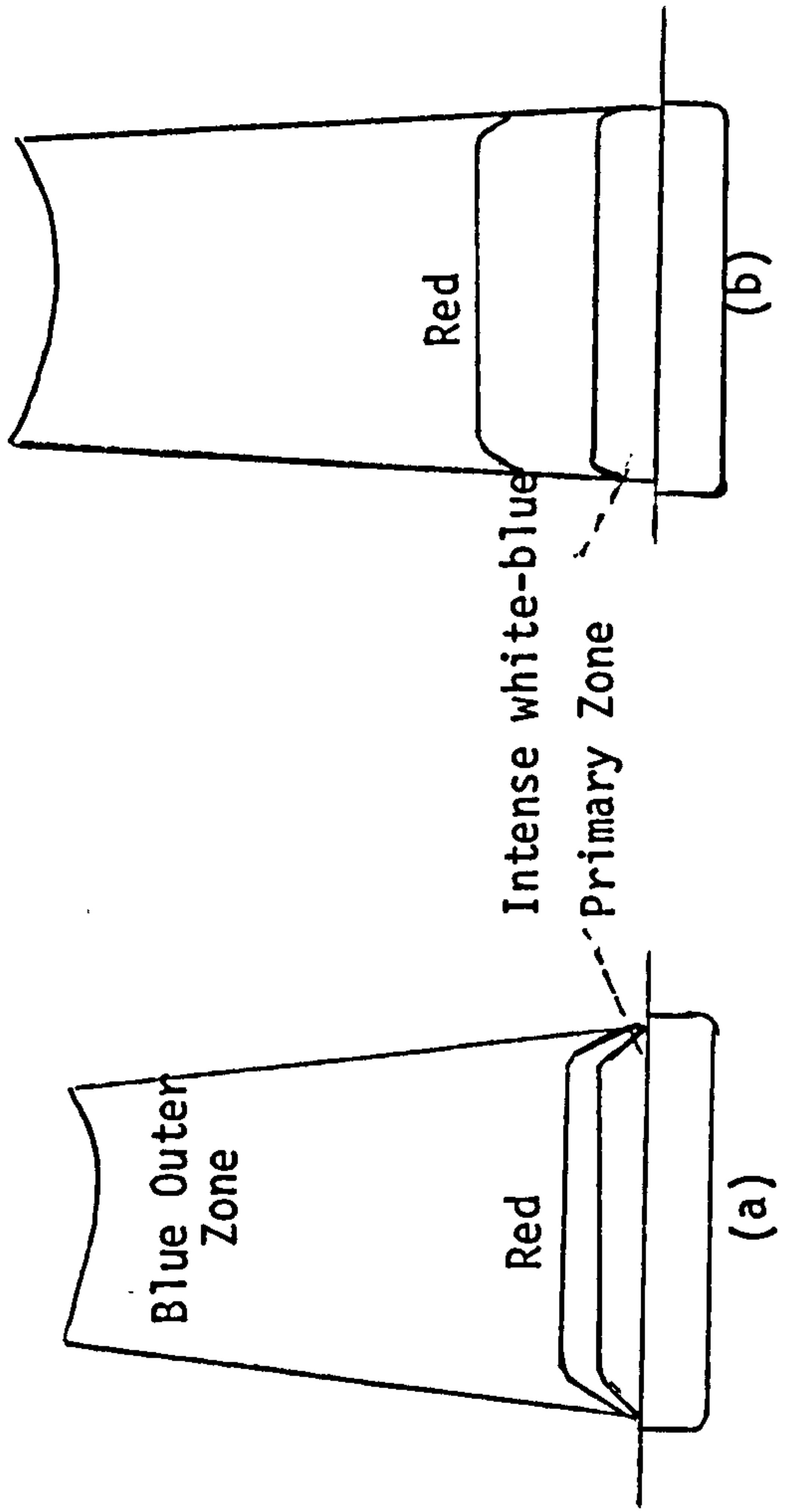


FIGURE 12: Effect of CO on the Structure of the Flame

up rate of formation, a higher heating up rate favouring vaporization and a lower, favouring reduction.

Using atomic absorption spectrometry at its optimized setting for maximum sensitivity as in experiment 2.6.1 the addition of 1000 ppm of each salt to the standard molybdenum 10 ppm solution were investigated.

In steady state measurements the addition of salts causes either enhancement or depression of molybdenum atomization.

Compounds like potassium chloride and sodium chloride have small enhancement 1-3%, in air-C<sub>2</sub>H<sub>2</sub> flame, 40-50% depression in N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame. Whereas potassium sulphate, aluminium chloride and aluminium nitrate 7-20% enhancement in air-C<sub>2</sub>H<sub>2</sub> flame and 30-50% enhancement in N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame. Depression effect on molybdenum was shown by potassium hydroxide, sodium hydroxide and calcium solution of calcium chloride, carbonate and nitrate in both flames. 98% depression by calcium solution in air-C<sub>2</sub>H<sub>2</sub> flame and 40-80% in N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame. 30-60% depression by potassium hydroxide and sodium hydroxide in air-C<sub>2</sub>H<sub>2</sub> flame and 30-50% in N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame. Figure 14 shows the enhancement by aluminium chloride and depression by potassium chloride in N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame.

Depression in both flames caused by hydroxide, can be fully removed by addition of aluminium in about equal concentrations. In conclusion, inert salts retard the vaporization if their melting points are below

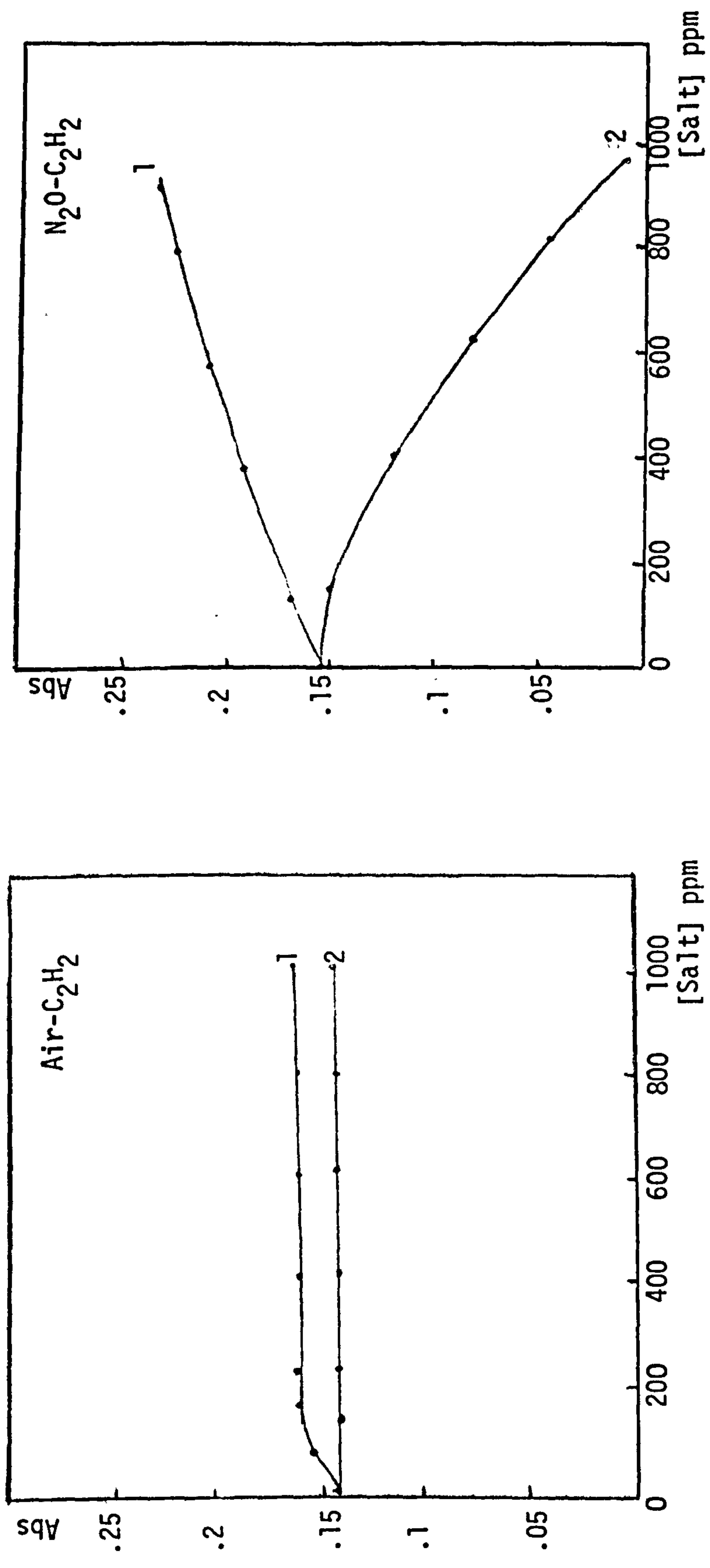


FIGURE 14: Effect of Salt on Molybdenum Absorbance  
 1. Enhancement of 25 ppm Mo on addition of AlCl<sub>3</sub>  
 2. Depression of 25 ppm Mo on addition of KCl



the flame temperature as the salt particle will maintain a temperature equal to the salt melting point until all the liquid has evaporated, by which time the particle may have travelled to a non-reducing part of the flame. In the case of the aluminium, it is thought that the salts decompose to give an alumina particle with the molybdenum species dispersed in it. The alumina then decomposes liberating oxygen and reacts with carbon containing species to form a stable aluminium carbide, both of these helping to vaporize the molybdenum as the oxide by providing an oxidizing microclimate and scavenging carbide forming species.

The effect of calcium on molybdenum is a chemical interference due to the formation of a refractory compound molecule, calcium molybdate.

The depression results because the aerosol particles formed from calcium and molybdenum are less volatile than those formed from molybdenum solution alone.

### 3.4.2 Modification of Nebulization Process

#### 3.4.2.1 Use of flow injection methodology

Pneumatic nebulization is the most frequently used method for introducing solutions into flame atomic absorption spectrometry, because of its ease of operation and general reliability. It can suffer, however, from the fact that the sample uptake rate is dependent on nebulizer gas-flow rate and sample viscosity (160).

It has been reported (149) that the use of a much reduced operation rate, discrete sampling and measurements of peak area can lead to improvements in detection limits over conventional nebulization due to (a) the substantial improvements in nebulization efficiency which occur at low flow rate, and (b) no loss in precision for peak area measurement compared with peak height measurements.

For the flow injection work a single line (0.58 mm bore) manifold was used in which carrier was pumped by an Ismatec pump model 840. A Rheodyne type 5020 rotary injection valve with an external loop volume of 200  $\mu$ l was used. Figure 15 shows a schematic flow injection system.

Experiment 2.4.2 using 45 ml solvent and experiment 2.6.3 using 20 ml solvent as an extractant were repeated. Both extracts were dried. Before using the AAS-FIA for the determination of molybdenum content of the organic phase or of the aqueous phase, optimization of the sample loop for best precision, integration time and pump rate were carried out using standard 25 ppm molybdenum solution. Solvent volume of 200  $\mu$ l was injected into a carrier stream of distilled water. Adjustment of acetylene flow using pure solvent was needed for best signal-to-noise ratio.

Precision studies with standard molybdenum solution gave the data in Table 7. The sensitivity changes slightly when the nebulization position was changed and increases by decreasing the pump rate of the sample (see Table 8). However, any imprecision in the residence

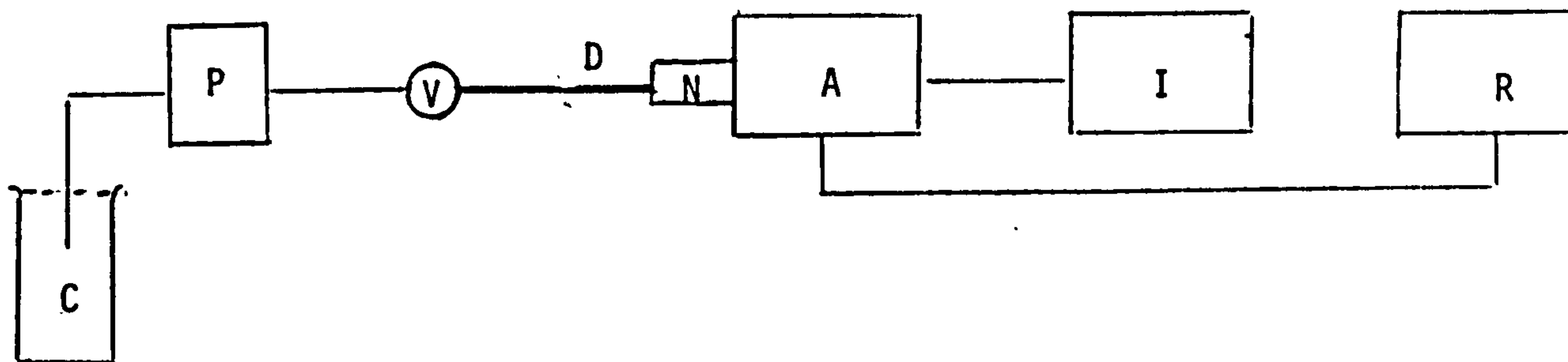


FIGURE 15: The Setting for FIA-AAS.  
Carrier reservoir (C), pump (P), valve (V),  
dispersion tube (D), nebulizer (N), integrator (I)  
and recorder (R), AAS (A)

ppm Mo	Peak Area % RSD FIA-AAS C=0.999	Peak Height % RSD FIA-AAS C=0.999	Peak Area % RSD Steady state C=0.999
0.5	16.0		13.9
1.0	11.95	13.05	8.16
5.0	1.82	3.40	1.3
10.0	2.03	3.09	0.61
20.0	0.90	1.94	0.67
25.0	1.30	2.30	0.46
50.0	1.20	2.30	0.46
100.0	1.37	2.40	
C = Correlation Coefficient			

TABLE 7: Comparison of Reproducibility by Flow Injection with  
Conventional Nebulization

time will have an effect on the read out (see Table 9). Although the peak area measurements with a detection limit of 0.24 ppm were superior to peak height measurements, both were inferior to conventional nebulization with a detection limit of 0.21 ppm (see Table 10).

Sensitivity of flow injection analysis may be improved by the addition of certain reagents to the carrier stream. Aqueous carrier stream containing 1000 ppm of aluminium chloride, potassium sulphate or ammonia-ammonium chloride were found to increase the detection limit and improve the sensitivity, Tables 11 and 12. Continuous aspiration of ammonia-ammonium chloride solution resulted in a sharp drop in acetylene flow rate (due to back pressure of ammonia gas developed in the flow meter of acetylene). Although the method did not produce any significant improvement in sensitivity, and since the level of molybdenum detection by flow injection analysis can be brought down to the level of instrumental detection limit (continuous nebulization), the combination of FIA-AAS is an attractive method for the determination of molybdenum, primarily for its small sample volume and high sampling frequency and most of all if an automated solvent extract based on flow injection is used in connection with AAS.

#### 3.4.2.2 Varying solution physical properties

Heating the solution and aspiration of the organic solvent was investigated in an attempt to increase the rate of transport of the



Asp. Rate ml min <sup>-1</sup>	Pump Rate ml min <sup>-1</sup>	Int. Sig.
3.0	3.0	30.72
3.0	2.4	35.70
3.0	2.0	38.40
2.6	2.4	31.27
2.4	2.4	34.14
4.0	2.4	36.80

TABLE 8: Effect of Uptake Rate

Aspiration rate - Rate of uptake of nebulizer in the  
absence of valve and pump with 20 cm  
of tube length

Pump rate - Flow injection introduction rate

Vol. of the Sample μl	Int. Time (sec)	Int. Signal	% RSD
160	10	29.59	0.9
200	15	39.23	1.8
240	15	40.79	2.2

TABLE 9: Effect of Sample Size

	15 sec Integ.	
	Air-C <sub>2</sub> H <sub>2</sub> FIA 200 $\mu$ l	Air-C <sub>2</sub> H <sub>2</sub> Flame 725 $\mu$ l
Sensitivity/ng ppm (Calc)	191.6 0.958	276.95 0.382
LOD/ng ppm (Calc)	48 0.24	151.166 0.21
Precision %	16	13.9

TABLE 10: Comparison of Detection Limit and Sensitivity of Flow Injection with Steady State Measurements

Asp. Rate ml min <sup>-1</sup>	Pump Rate ml min <sup>-1</sup>	Int. Signal			[Salt] ppm
		0.5 ppm Mo	1.0 ppm Mo	25 ppm Mo	
3.0	2.0	0.927	1.254	38.40	0
3.0	2.0	1.244	2.110	43.18	1000 <sup>(a)</sup>
3.0	2.0	1.320	1.834	44.50	2000 <sup>(a)</sup>
3.2	2.5	1.233	1.829	39.90	1000 <sup>(b)</sup>
3.0	2.4	1.69	2.069	40.00	Basic <sup>(c)</sup>

TABLE 11: Effect of Added Salts in Carrier Stream  
(a) AlCl<sub>3</sub>; (b) K<sub>2</sub>SO<sub>4</sub>; (c) NH<sub>4</sub>Cl+NH<sub>4</sub>OH

analyte by formation of smaller droplets and increasing the quantity of the aerosol reaching the flame.

However, a gradual depression as a function of time was observed when heated standard molybdenum solution up to  $(60-80^{\circ}\text{C})$  was aspirated into an air- $\text{C}_2\text{H}_2$  flame, 30% enhancement in  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame.

It is most likely that an increase in water vapour reaching the flame is the cause for the depression or enhancement of the molybdenum atomization (see Table 13). According to Bauer *et al* (161) aspiration of aqueous solutions reduces the flame temperature approximately  $40^{\circ}\text{C}$ . This causes a decrease in vaporization efficiency of the metal. The effects of solution temperature on atomization rates have been recently studied by Cresser *et al* (162).

Many workers (163-165) have been successful in overcoming the problem by incorporating a condenser between the heated spray chamber and the flame. The method was found to remove the great bulk of water vapour, while allowing almost all the analyte (and matrix) to pass into the flame, however, the method also has disadvantages. The presence of acetone in the acetylene cylinder makes an important parameter one must attempt to investigate. At low pressure, some of the acetone is drawn out with acetylene which may cause an enhancement or depression of the metal signal.

Acetone was found to have quenching effects on molybdenum atomization in air- $\text{C}_2\text{H}_2$  flame increases with increasing the amount of acetone,

Method	Carrier Stream	Sensitivity ppm for 1% Abs	C.C.	Std.Dev.
Steady state FIA	Distilled water	0.383	0.9998	1.23
FIA	1,000 ppm Al	0.958	0.9996	0.73
FIA	2,000 ppm Al	0.75	0.999	1.31
FIA	1,000 ppm K <sub>2</sub> SO <sub>4</sub>	0.733	0.9997	0.83
FIA		0.80	0.9993	1.98

TABLE 12: Comparison of the Sensitivities of the Added Salts in the Carrier Stream

C.C. - Correlation Coefficient

Flame	Abs. as a Function of Time	Calc. % of Mo reaching the flame	% RT
Air-C <sub>2</sub> H <sub>2</sub>	Gradual depression	20-22	20
N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub>	30% enhancement	18	17

TABLE 13: Effect of Heating Solutions (60-80°C) - Reduction in Viscosity



16% enhancement was found in fuel-rich  $N_2O-C_2H_2$  flame (see Figure 16).

Manning and Chabot (166) found reduced sensitivity in molybdenum atomic absorption spectrometry in the presence of acetone vapour from depleted acetylene cylinders. They have succeeded in increasing the absorbance of the molybdenum in air- $C_2H_2$  flame by passing the acetylene from the tank through an activated charcoal column to remove acetone prior to combustion of the flame. From Table 14 one can expect that the effect of acetone mainly due to changes of physical parameters exists. However, it has been suggested that the spray of organic liquid into the flame may result in an increase or decrease of the flame temperature, accordingly, as the gas-air mixtures are lean or rich (167). Boorn, Cresser, and Brown<sup>er</sup> (168) also presented an article on droplet size distribution effects caused by the evaporation characteristics of various organic solvent aerosols.

Acetone causes an increase in sensitivity over an aqueous solution in  $N_2O-C_2H_2$  flame, and also causes molybdenum precipitation at a concentration of 5% or greater (169). The effect can also be attributed to greater quantity of aerosol getting into the flame, because of the formation of smaller drops (170-174) or due to an increase in reducing components in the flame which aid atomization (175). An increase in temperature can sometimes be the cause (176), however several authors have shown that the temperature change of the flame is small (177,178), or the cause is due to changes in the nebulization

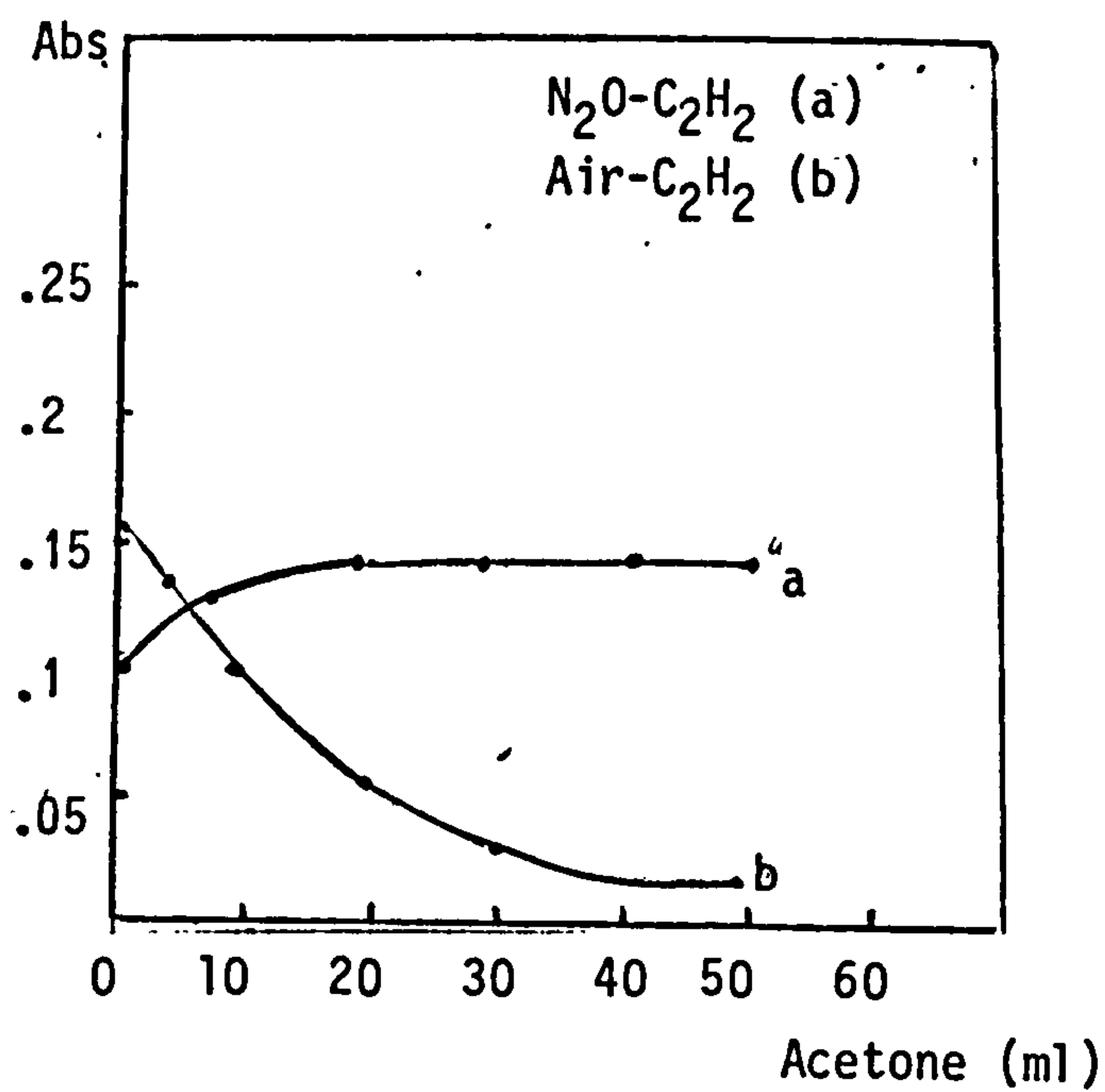


FIGURE 16: Effect of Added Acetone on Molybdenum Signal

Solvent	$\rho(\text{gcm}^{-3})$ Density	$t_b(^{\circ}\text{C})$	$\eta_o$ 1000 in P at (20°C) Coeff.of Visc.	$\sigma(\text{dyne cm}^{-1})$ Surface Tension	$d(\mu_m)$ Drop. Diam
Acetone	0.79	57	3.3	23.7	13.1
Water	1.0	100	10.0	73.0	19.0

TABLE 14: Physical Parameters of Acetone and Water

parameters, which cannot be attributed to either variation of the aspiration rate or the average drop size separately (179).

#### 3.4.3 Use of Drying Agent in Indirect Heteropoly Acid Procedures

Experiment 2.4.2 using 45 ml of solvent and experiment 2.6.3 using 20 ml of solvent as an extractant were repeated. Both extracts were dried as in experiment 2.6.3.1.

Reduction of molybdenum concentration in the blank extracts led to a decrease in detection limits to about 0.2 ppm close to the instrumental detection limit. This suggests that the high blank values are mainly due to molybdenum in aqueous phase droplets, suspended in the organic solvent (n-butyl acetate), rather than co-extracted isopolymolybdic acid. Table 15 compares the blank values and sensitivities of the extracted phosphomolybdic acid using different methods of measurement.

### 3.5 Conclusion

The blank levels are reduced if the organic extract is dried. Modification of the flame chemistry by the addition of relatively high concentrations of metal salts suggests that improvement in sensitivity may be possible.

	Spectrophotometric at 310 nm (a)	FIA-AAS (b)	FIA-AAS (c)	Steady-State (d)
Int.Time (sec)	-	20	15	15
Blank Mo ppm	0.00	0.00	0.339	0.285(D) 1.13(ND)
Sensitivity ( $\mu$ g)	0.28	8.2	2.7	1.0
Corr.Coeff.	0.9989	0.9989	0.9989	0.999

D = Use of drying agent, ND = Without the use of drying agent,  
S = Sensitivity

TABLE 15: Compares the sensitivities and blank values of the extracted molybdophosphoric acid using different methods for measurements

- (a) Solvent extraction of molybdophosphoric acid using spectrophotometer
- (b) Injection of 200  $\mu$ l of solvent extraction of molybdophosphoric acid using flow injection analysis combined with atomic absorption
- (c) Injection of 200  $\mu$ l of aqueous solution containing decomposition products of molybdophosphoric acid
- (d) Direct aspiration of aqueous solution containing decomposition products of molybdophosphoric acid



The sample introduction method of flow injection analysis offers advantages over the conventional nebulization. It reduces the viscosity effect and variation of the flame temperature by continuous pumping of carrier stream through the nebulizer. Peristaltic pumps can be used for simultaneous delivery of buffering, releasing agent and or diluent to the nebulizer thus reducing sample preparation time.

## CHAPTER 4

### CARBON ROD ELECTROTHERMAL ATOMIZATION OF MOLYBDENUM

#### 4.1 Introduction

Although the principle of electrothermal atomization and several of its advantages were known as early as 1908 (180), development of these atomizers as practical atomizers for atomic absorption spectrophotometry did not take place until the 1960's and the first commercially produced atomizers of this type did not appear until 1970. Two types of electrothermal atomizers have been used; the furnace and the filament. Furnace atomizers employing resistance heating are modifications of the design used by King (180). Pioneering work on this type of furnace was carried out by L'vov (181-183) and by Massman (184). The basic features of these furnaces have been briefly described in reviews by Kirkbright (185) and by Fuller (186). However, L'vov and Polzik (187) classified atomizers for atomic absorption spectrophotometry as "Open" and "Semiclosed", the former group including flames and the latter group graphite cells and furnaces.

Molybdenum has been atomized from a carbon rod (188-191), graphite tube (192-195) and the "tantalum" surface of a graphite tube (194,195).

Determination of trace amounts of molybdenum in biological materials (193,196,197), sea water (198-200), rocks (188), steels (190), and brines (188), by electrothermal atomization spectroscopy has gained considerable attention.

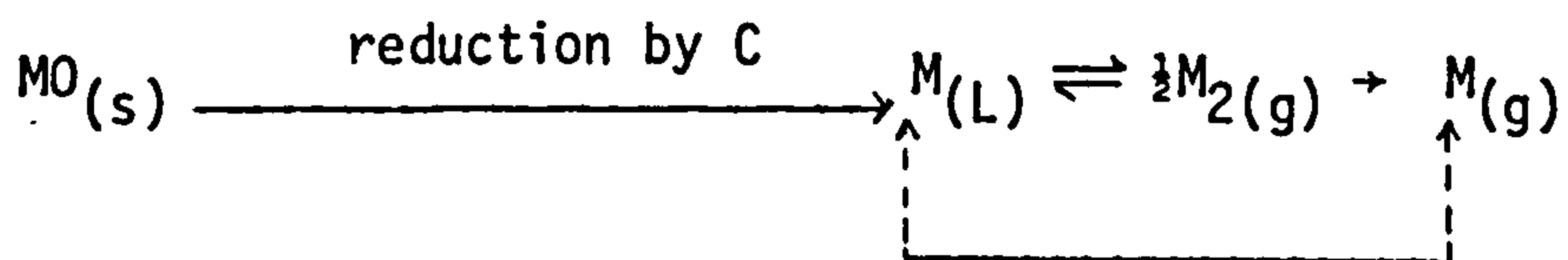
## 4.2 Review of Electrothermal Atomization for Molybdenum

### 4.2.1 Mechanism of Atomization for Molybdenum

The continuing problems of matrix interferences in electrothermal atomization have lead to several investigations of the rate and mechanism of atom formation.

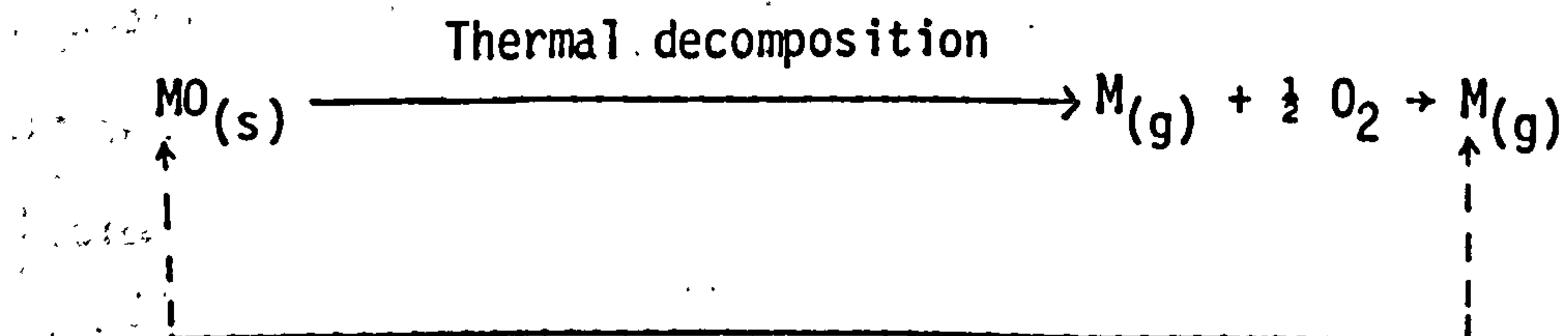
Chakrabarti *et al* (201) proposed the following four mechanisms for atomization of elements in graphite furnace atomic absorption spectrometry.

#### Mechanism 1: Reduction of solid oxide by graphite surface



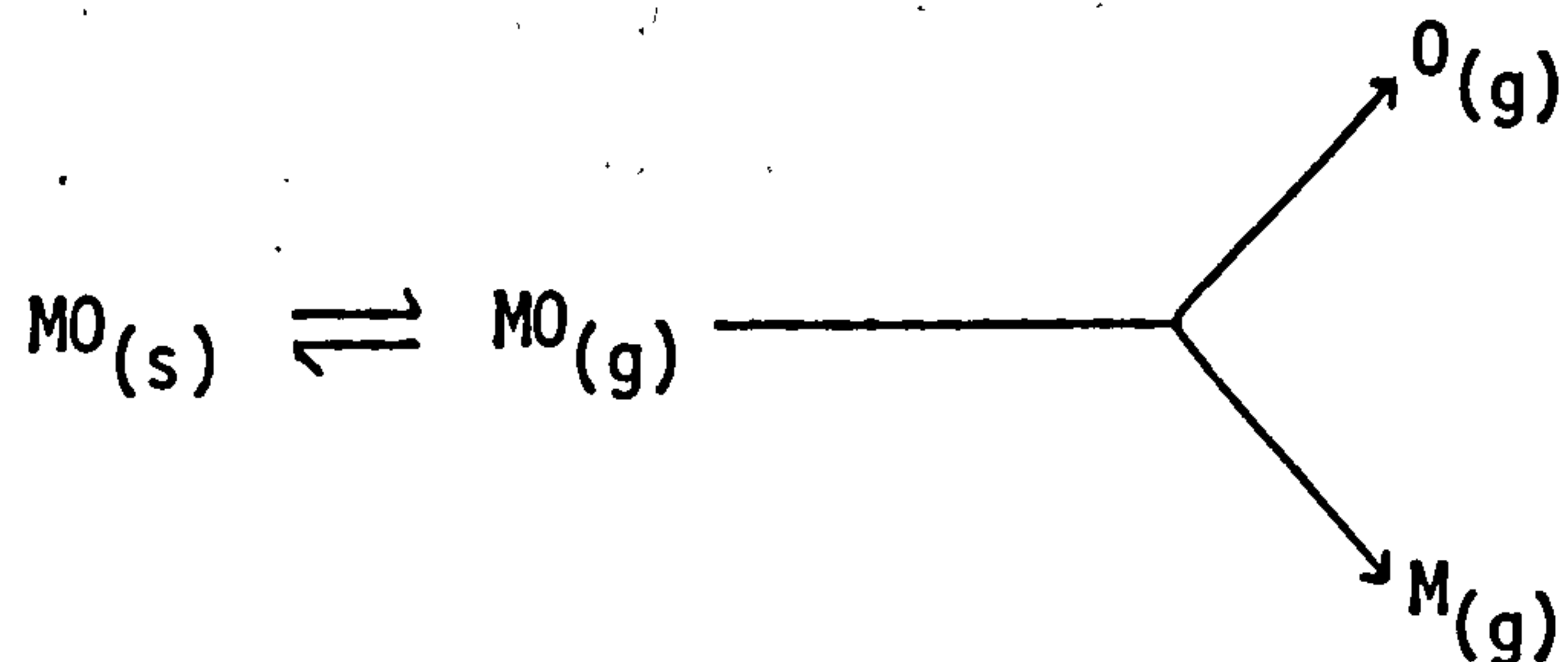
where: M = Pb, Cu, Co, Sn, Ni, Mo, V, Cr, Fe.

#### Mechanism 2: Thermal decomposition of solid oxide



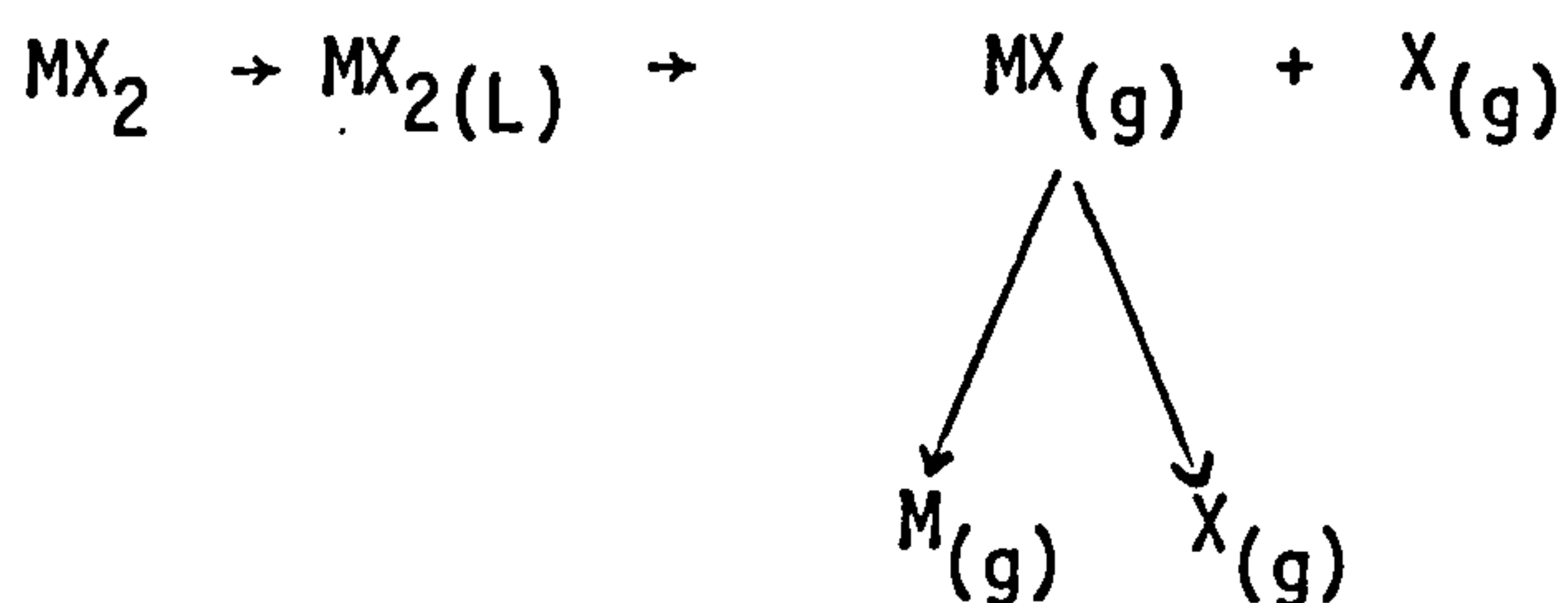
where M = Al, Cd, Zn

Mechanism 3: Dissociation of oxide vapour



where: M = Mg, Mn, Cd, Zn.

Mechanism 4: Dissociation of halide vapour



where: M = Cd, Zn, Fe; X = Cl

Mechanisms 1 and 2 involve the condensed phase reduction by carbon or thermal decomposition of the analyte compound when it is in intimate physical contact with the graphite surface, whereas mechanisms 3 and 4 involve the vapour phase dissociation of the analyte oxide or halide vapour.



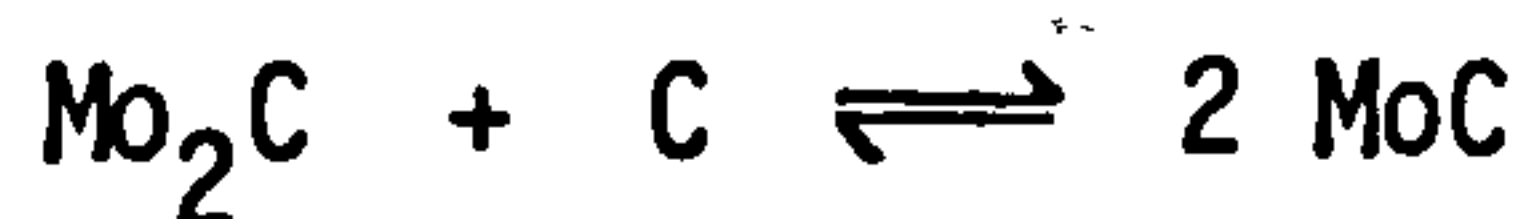
Fuller (202-204) has used the kinetic theory of atomization to examine the effect of variations in the rate of atomization, the rate of loss, and the efficiency of atomization of the analyte in relation to absorbance-time profiles in a graphite furnace. The effects were used as a basis to establish causes of interference in atomic absorption spectrometry.

Ottaway and Campbell (205,206) supported a model attributing atomic formation to reduction by carbon at the furnace wall



Musil and Rubeška (207) presented a mathematical model for electro-thermal atomization signal based on formation of free analyte atoms, interaction of free atoms with the cuvette wall, and removal of the free atoms from the cuvette to give a better correspondence between the theoretical and experimental peak shapes in atomic absorption spectrometric analysis.

Sneddon and Ottaway (208) studied the mechanism of atomization of molybdenum in carbon furnace atomic absorption spectrometry by X-ray diffraction. Measurements on the powder residues, from carbon furnaces treated with aqueous molybdenum solution and then heated, showed the presence of  $\text{MoO}_3$  and  $\text{Mo}_2\text{C}$  or  $\text{MoC}$ . Experiments with furnaces at  $900^\circ\text{K}$  showed the presence of  $\text{MoO}_3$  but  $\text{Mo}_2\text{C}$  appeared at  $1500^\circ\text{K}$  and  $\text{MoC}$  at  $2000^\circ\text{K}$ .



Molybdenum was also observed at temperatures greater than 2160°K.

The mechanisms of the reactions occurring in the furnace were elucidated by activation energy measurements.

Müller<sup>Vogt</sup>*et al* (209) applied X-ray diffraction and electron microscopy to study the chemical reaction occurring during the determination of Mo by electrothermal atomic absorption spectroscopy.

Molybdenum forms two carbide phases in the graphite tube according to the phase diagram Mo-C. At temperatures below 1900°K, only Mo<sub>2</sub>C is found, which transforms, at higher temperature with slow kinetics, to MoC



During atomization cycle, Mo<sub>2</sub>C decomposes into MoC and Mo, whereas, MoC decomposes only partly into the elements.

#### 4.2.2. Atomizer Modifications

The key component of an electrothermal atomizer is the atomizer itself. Considerable research effort is being spent in the study and development of new structures, forms and compositions for atomizers. Considerable work has focused on pretreatment of the graphite furnace with pyrolytic and metal treatments.

Many interferences reported, some recently, stem from the constant use of ordinary graphite tubes. Pyrolytically coated tubes are becoming increasingly important and have been recommended (181), since it has some effect on reducing vapour phase interferences and on improving sensitivity. Totally pyrolytic cuvettes (TPCs) are now commercially available from Pye Unicam Ltd (210).

Graphite is a porous material which soaks up aqueous solutions. Atomic vapours pass quite freely through a 1 mm thick wall of hot anisotropic graphite. Pyrolytic coatings provide a dense impervious barrier against the sample as well as against the vapour phase atoms. Problems that are associated with the depth to which solutions penetrate the graphite and adsorb or react within the porous structure, will be reduced by these coatings. Resulting intercalation compounds formed by the trapping of atoms within the carbon lattice, will be limited to a thin layer near the surface. Also, the loss of vapour due to adsorption and chemical bonding within the graphite, will be limited to the surface.

In modern furnace design, the fast heating and the use of strong impervious barrier separating the sample vapour from the graphite have greatly improved the furnace performance, and if there is a large non-specific absorption of the source radiation, the availability of Zeeman-background correctors becomes important (211,212).

Many workers have observed differences in analytical sensitivity or the extent of interferences when ordinary and pyrolytic graphite tubes

are compared. Manning and Ediger (213) found that a pyrolytic graphite coating increased the signal for several important metals by factors of as much as 4. Volland *et al* (214) observed the differences in the extent of halide interferences on Fe, Ni, Mn and Mo.

Fernandez and Iannarone (192) similarly found improvement, when the tube was heated very rapidly, especially for the more refractory metals.

The most serious interferences encountered in electrothermal atomization are halogens from the matrix which reacts with some portion of the vapour phase analyte. If a cation whose vapour phase chloride has a particularly high dissociation energy, is added to the sample, it will reduce the amount of free chlorine in the vapour. L'vov (215) chose lithium to reduce thallium interferences from sodium chloride, since lithium chloride has the relatively high dissociation energy of  $473 \text{ kJ mol}^{-1}$ . L'vov (215) also showed that 0.1% sodium chloride suppressed the absorbance of a solution containing  $1 \mu\text{g ml}^{-1}$  Al. Addition of increasing amounts of lithium (as the nitrate) greatly reduced the interference.

However, many workers were able to overcome the problem of interferences by selective volatilization and using high ashing temperature.

Nakahara and Chakrabarti (198) reported that a salt matrix can be removed completely by selective volatilization at 1700 to 1850°C. The original presence of NaCl,  $\text{Na}_2\text{SO}_4$  and KCl causes a considerable



decrease in molybdenum absorbance and  $\text{MgCl}_2$  and  $\text{CaCl}_2$  a pronounced enhancement. The presence of  $\text{MgCl}_2$  prevents the depressive effects. The direct measurements were carried out on traces of molybdenum (0.1-0.4) ng in synthetic sea water..

Barbooti and Jasim (188) reported determination of molybdenum in brines directly, in less than 8% sodium chloride solution, without chemical pretreatment or background correction, by using high ashing temperatures at which sodium chloride was totally removed. Studnicki (193) reported the effects of various acids, salts, cations, anions and pH on the determination of molybdenum in plants. Acids ( $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$ ), affected the molybdenum signal strongly, with 0.01 to 1%  $\text{H}_3\text{PO}_4$  increasing the signal most. The ammonium salts of these acids were also reported to affect the molybdenum signal.  $\text{CaCl}_2$  strongly decreased the signal and the presence of  $\text{Na}_2$  EDTA and  $\text{NH}_4\text{H}_2\text{PO}_4$  reduced this effect. The molybdenum signal was reported also to be independent of pH in the range of 4 to 5.5 in the presence of  $\text{CaCl}_2$ ,  $\text{Na}_2$  EDTA and  $\text{NH}_4\text{H}_2\text{PO}_4$ .

The different interferences of Ca, La, Ti, Zr, V, Nb, Cr and W are explained by the influence of their carbides on the decomposition reaction of the molybdenum carbide phases (209). The melting points of the carbide of Zr, Nb and W are remarkably high (3300-3900K), much higher than that of  $\text{MoC}$ . At temperatures higher than about 1300-1500K, the Mo-carbide is incorporated into the crystal lattice of these carbides, which are present in great excess. The formation of highly stable solid solutions results in the thermal stabilization of the Mo-carbide.

Amos *et al* (216) showed that by replacing the nitrogen or argon inert-gas around a carbon filament atomizer, with an argon-hydrogen mixture, improved sensitivity was obtained for many elements together with a reduction in interference effects. The improvement was attributed to the highly reducing environment created and subsequent maintenance of the atomic population at a much greater distance above the carbon rod. The reduced background signal has been attributed to a reduction in the presence of volatilized carbon, due to hydrocarbon formation (217). Steiner *et al* (196) reported a method for preventing loss of sensitivity and elimination of matrix effects for molybdenum determination in plant material without any pretreatment of samples. The method uses different gases ( $O_2$ ,  $H_2$ ,  $CH_4$  and  $N_2$ ) for in situ pretreatment of digested plant samples in the atomizer. Methane and hydrogen function as reducing agents during atomization of the sample, while methane also provides carbon for pyrolytic re-coating of the atomizer. Nitrogen was used as a sheathing gas. The presence of these gases in the atomizer is believed to facilitate a uniform injection-drying stage and improve the evaporation-combustion rate of various components during ashing of the sample.

Many workers have reported improved performance when the graphite is treated with a compound that forms a refractory carbide: La (218), Mo (219), Ta (220), Zr (221), or by W (222) have been reported to be useful. It is probable that these materials provide a less penetrable surface, since pyrolytic surfaces are damaged after repeated firings.

Baird and Gabrielian (223) explored the advantages of lining a graphite tube with tantalum foil. The foil lining increased graphite life time, preventing atoms from diffusing through walls of the tube.

L'vov and Pelieva (224) have also reported the use of a tantalum-foil lining in the graphite atomizer. Their results showed that for 32 of the 40 elements studied, a significant increase in sensitivity was achieved when a tantalum foil lining was used, except Mo, Co, Ni, Ir, Pd, Pt, Ru, Rh, where the use of lined tubes did not result in any improvement.

Gregoire and Chakrabarti (194) have also reported reduction in peak absorbances of Mo, V and Ni, when atomized from pyrolytic graphite and tantalum surfaces.

Formation of involatile intermetallic compounds between molybdenum and tantalum, or alloys between tantalum and molybdenum have been reported (225-227).

The present commercial atomizers which are based on non-isothermal conditions have always been more susceptible to vapour phase interference effects. However, much of the work at present, is concentrated on establishing conditions of constant temperature atomization, with modern commercial atomizers. L'vov (215,228) suggested that sample vaporization into a hot furnace vapour could be achieved with modern atomizers in three ways; platform atomization, rapid furnace heating e.g. capacitive discharge, and probe or separate atomization.

Slavin and Manning (22) discussed the use of a so-called L'vov platform (215) in a graphite furnace. The L'vov platform is a thin pyrolytic graphite plate placed inside the graphite furnace. Volatilization takes place from the surface into a gas that is better than the surface and, in general, this system has better analytical characteristics than volatilization of the sample from the surface. The sample was deposited on a graphite platform mounted within the electrically heated tube. Since the platform and the sample were heated by radiation from the wall of the tube, there was time for the tube to approach a stable final temperature before the sample was volatilized. The L'vov platform and the stabilized temperature platform furnace (22, 229-231) have proven to be attractive modifications of commercial furnaces that were based on the Massman design (184).

Gregoire *et al* (232,233) studied the atomization of Mo, V, Cu, Zn and Cd from a rectangular pyrolytic graphite platform, inserted into pyrolytically coated graphite tube and observed 1.8 fold enhancement in the sensitivity for Mo and V.

The concept of rapid heating by capacitive discharge, where the furnace curvette is instantaneously heated at rates of  $50 \text{ K ms}^{-1}$ , has been investigated by Chakrabarti *et al* (234). At high rates of heating by capacitive discharge, the vapour phase temperature lags behind the surface temperature - the higher the heating rate, the greater the lag in the vapour phase temperature. Therefore an increase in sensitivity for relatively low volatile elements,



especially those which follow atomization mechanisms 1 and 2 would be explained..

Cresser and Mullins (235) have also suggested the use of a large electrolytic capacitor for rapidly heated metal filament atomizers. Both platform and capacitive heating attempt to approach conditions of constant temperature atomization, without separating the process and to heat the vapour and volatilize the sample. Gregoire *et al* (236) measured the effect of heating rate, in graphite furnace atomic absorption spectrometry. Mo, V, Al, Ni, Cu, Zn, and Cd were studied and the increase in peak absorbance with heating rate was correlated with the activation energy of the rate determining step in the atomization process. Integrated absorbances of relatively volatile elements decreased exponentially with increasing heating rate, whereas those of relatively non-volatile, such as Mo and V increased exponentially with increasing heating rates.

Recent work is concentrated on probe atomization which is believed to have advantages over currently available graphite furnaces, particularly with respect to vapour phase interference effects. The approach relies on separate heating of the furnace environment, and the atomization surface. Initial experiments were performed by Manning *et al* (237), who mounted a tungsten wire coil on the arm of an autosampler for convenient introduction of a sample into an already heated furnace. Although the wire probe had limited use, especially at high temperature and could accommodate only a few microlitres of solution, considerable reductions in vapour phase interferences were achieved for volatile analyte element.

Slavin and Manning (238) modified a Perkin-Elmer HGA-500 atomizer to allow separate operation with a specially designed tee-tube furnace cuvette (see Figure 17). A 5  $\mu\text{l}$  volume was deposited towards the end of a small graphite strip, 0.1 mm thick, and the sample dried and ashed outside the atomizer. The cuvette was then heated at a high and constant temperature, prior to introduction of the probe via the side-arm of the tee-tube. The sensitivity was better than wall atomization, although some problems were encountered due to involatile elements, memory effects and the spreading of the sample droplets.

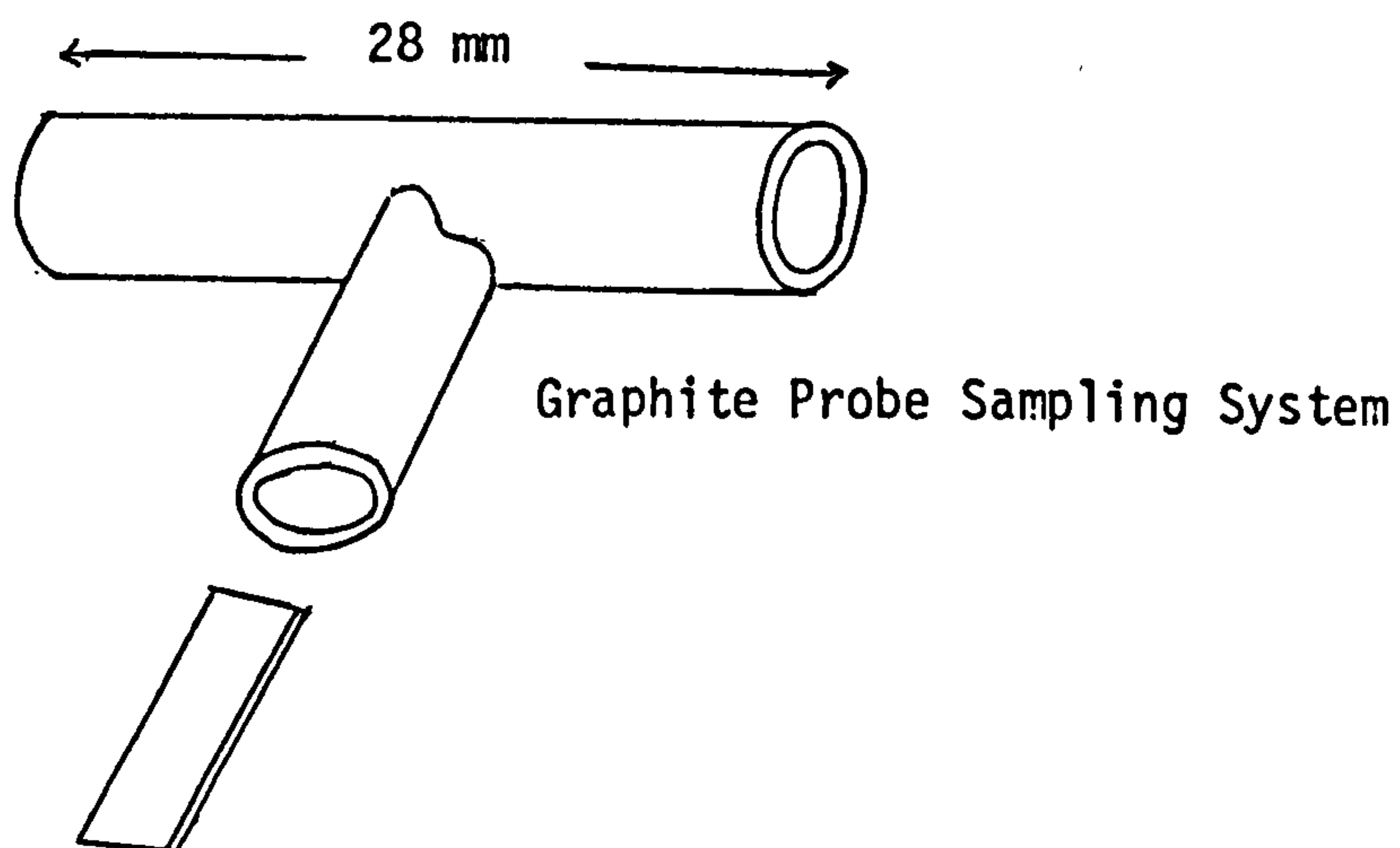


FIGURE 17: The Graphite Probe and Tee-Tube Furnace

Ottaway *et al* (239,240) modified Perkin-Elmer HGA-70 and HGA-72 atomizers for manual probe atomization with a cuvette and a probe made of totally pyrolytic graphite. Sampling volumes used were 50  $\mu$ l.

Freedom of interferences from  $\text{MgCl}_2$ ,  $\text{CaCl}_2$  and  $\text{NaCl}$  concentrations greater than 1% w/v (240) were reported for lead in atomic absorption.

They have recently described a fully automated probe attachment for use with modern commercial atomizer-spectrometer systems (241).

#### 4.2.3 Pyrolytic Graphite Coating (see also Section 4.2.2)

The use of pyrolytic coatings of carbon rods and tubes, is becoming increasingly important since it has some effect on reducing vapour phase interferences, improving sensitivity and increasing life times of the tubes and rods.

The commercial procedure for deposition of a pyrolytic coating utilizes an oven at approximately constant temperature, through which flows a mixture of a hydrocarbon in an inert gas.

A means of restoring decrepit graphite atomizers or maintaining new ones, was developed by Clyburn, Kantor and Veillon (242). Their technique consisted of incorporating methane into the purge gas surrounding the atomizer during its operation. Thermal decomposition of the methane continuously applies a new pyrolytic surface and greatly



extends the atomizer life time. However care must be taken to properly regulate the methane flow to prevent excessive build up of pyrolytic carbon.

In a similar procedure, Siemer, Woodriff and Watne (243) introduced items to be coated with pyrolytic carbon into a tube furnace through which methane is passed. In this way, layers of carbon can be deposited on the items at rates between 0.01 to 0.1 mmh<sup>-1</sup>. Inexpensive carbon frits could also be made in the furnace by sintering 20 to 150 mesh graphite powders which had been packed into a quartz tube.

Thompson, Godden and Thomerson (244) observed that propane, ethylene and acetylene deposit pyrolytic carbon, just as well as methane.

In recent reports (245,246), pyrolytic graphite coatings on carbon rods were produced by pyrolysis of acetylene in nitrogen gas.

Szydlowski *et al* (247) studied the surface of pyrolytically coated tubes with a scanning electron microscope using tubes from the Perkin-Elmer HGA 200. They found that the temperature of deposition had to be greater than 2300°C to achieve a pyrolytic coating. Smith and Leeds (248) reported that the substrate temperature must be between 1750 and 2250°C to achieve a pyrolytic coating, with pyrolytic properties improving steadily at higher temperature. They also pointed out that a *"pyrolytic coating is not a single invariant material but has a structure and related properties that are completely dependent upon the manufacturers process"*.



Some compounds are particularly destructive of the pyrolytic graphite coating by mechanisms that are not well understood. Montgomery and Paterson (249) claim that  $\text{NaNO}_3$  is destructive and Julshamn (250) found  $\text{HClO}_4$  particularly destructive.. This acid has been recommended to digest graphite and pyrolytic carbon prior to a chemical analysis of these materials (251).

Chromic acid is reported to exfoliate pyrolytic graphite (248) and  $\text{AlCl}_3$ ,  $\text{H}_2\text{SO}_4$ , and heat are the commercial processes for exfoliating pyrolytic graphite.

## PRACTICAL EXPERIMENTS

### 4.3 Optimization of the Instrument Parameters and Calibration for Molybdenum

The twelve molybdenum atoms associated with each phosphorus atom in the 12-molybdophosphoric acid in the organic extract can be determined by carbon rod electrothermal atomization at 313.3 nm.

Before the molybdenum content in the 12-molybdophosphoric acid can be determined, the instrument parameters for molybdenum absorption have to be optimized by employing aqueous molybdate solution.

Generally, the sample is placed in the graphite rod cavity and the unit goes through a fully automated sequence consisting of an evaporation stage, two dry-ashing procedures, atomization and finally signal processing.

The evaporation stage, normally consists of a low temperature heating cycle to evaporate any solution. Normally a temperature just below the boiling point of the solvent is ideal, as this prevents sputtering of the sample. The dry-ashing stage is normally set to the highest temperature possible to heat the sample without significant loss of the element being determined. In this way the sample matrix can be broken down or vaporized prior to the atomization stage, thereby reducing problems caused by interelement interferences and background light scattering or absorption. The atomization stage is a very high temperature heating cycle so atoms are formed. The atomization temperature varies from one element to another. Normally the analytical signal for each element is determined as a function of atomization temperature. The lowest temperature which gives the maximum signal is used, to increase the life time of the carbon rod.

A variety of stationary and flowing sheathing-gases can be used to minimize the rate at which the physical properties of the atomizer deteriorate. Oxygen-free nitrogen and argon are the most common inert gases used for electrothermal atomizers.

Pyrolytic coating of the graphite during a determination or between determinations is important for refractory metals (Mo, Bi, Ti and V). This is usually done by introducing a hydrocarbon gas to the inert gas flowing round the graphite rod at high temperature.

A high temperature rod cleaning stage was also applied to remove any remaining sample.

### Instrument:

A Shandon Southern A3470 electrothermal atomizer and an A3400 atomic absorption spectrophotometer were used.

The A3470 electrothermal atomizer (see Figure 18), is based on a simplified version of the carbon rod of West and Williams (252).

It consists of a carbon rod 75 mm long by 3.1 mm diameter, clamped between two metal support pillars which are water cooled. Power is fed to the atomizer through the cables connected to the graphite rod head terminals. The atomizer is positioned in the optical path of the atomic absorption spectrophotometer so that the light from the hollow cathode lamp passes over the surface of the graphite rod and through external apertures. Liquid samples can be injected into the cavity at the centre of the graphite rod. The graphite rod can then be heated, in a stream of inert gas, to a temperature in excess of  $3000^{\circ}\text{C}$  within 2 seconds.

The output from the spectrophotometer was recorded by a Tarkan model 600 recorder. Graphite rods with a nominal capacity of 1  $\mu\text{l}$  were used. Solutions were transferred with an Oxford microlitre pipette.

### Reagents:

#### Standard molybdenum solution, 10 ppm

The solution was prepared daily by diluting 5 ml of stock solution (experiment 2.6) to 500 ml.



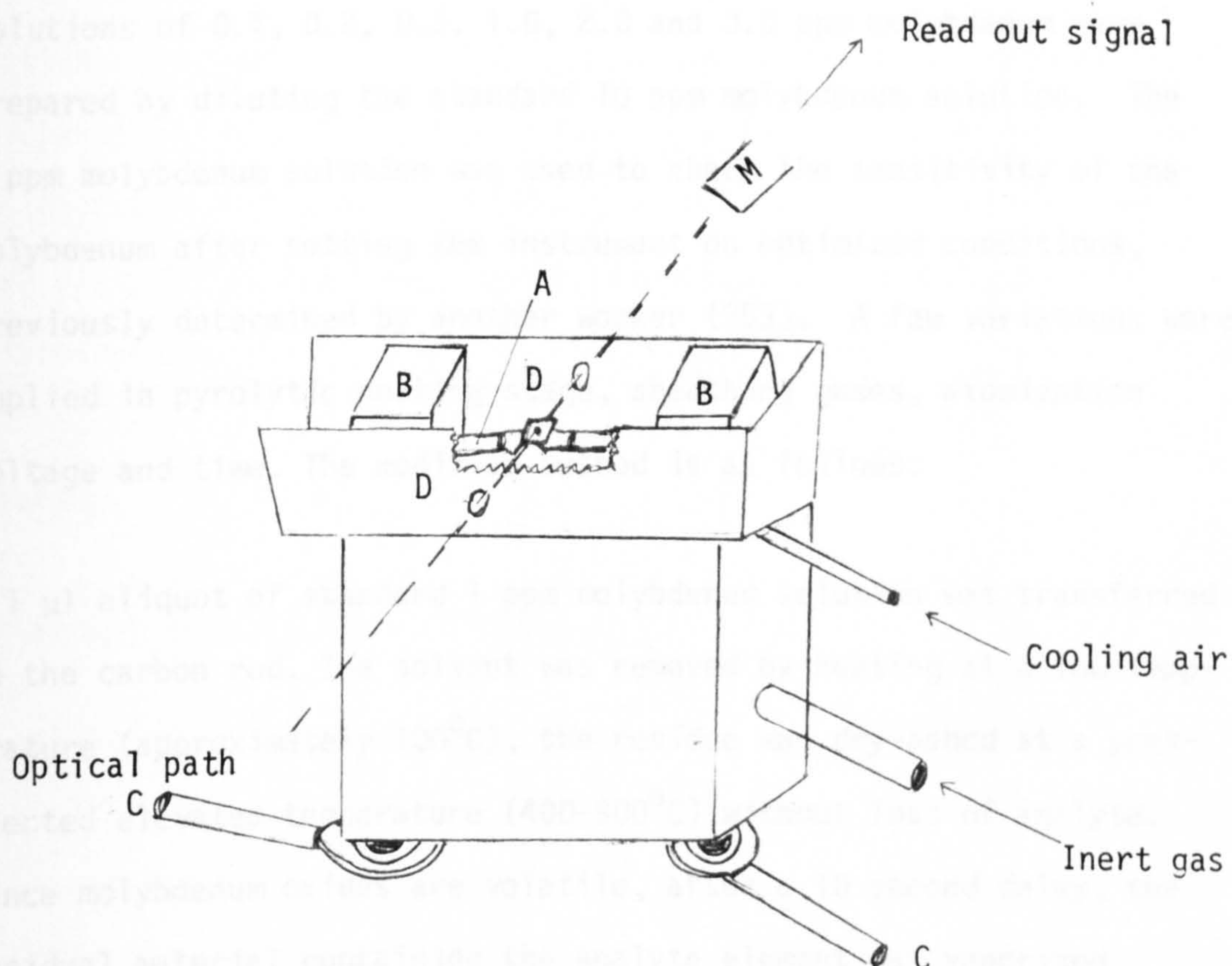


FIGURE 18: Schematic Diagram of the Shandon Southern A3470

A = Carbon rod

B = Metal support pillars

C = Cables

D = External Aperture

M = Monochromator



### Procedure:

Solutions of 0.1, 0.2, 0.5, 1.0, 2.0 and 3.0 ppm molybdenum were prepared by diluting the standard 10 ppm molybdenum solution. The 1 ppm molybdenum solution was used to check the sensitivity of the molybdenum after setting the instrument on optimized conditions, previously determined by another worker (253). A few variations were applied in pyrolytic coating stage, sheathing gases, atomization voltage and time. The modified method is as follows:

A 1  $\mu$ l aliquot of standard 1 ppm molybdenum solution was transferred to the carbon rod. The solvent was removed by heating at a low temperature (approximately 100°C), the residue was dry-ashed at a preselected elevated temperature (400-900°C) without loss of analyte. Since molybdenum oxides are volatile, after a 10 second delay, the residual material containing the analyte element was vaporized (atomized) at a high temperature (up to 3000°C) for 2 seconds with a hold time of 1.5 seconds. The absorbance<sup>was</sup> measured at the molybdenum wavelength 313.3 nm.

A cleaning stage, which is a high atomization temperature, was applied before the rod was ashed for transfer of the next sample. A thermistor probe was inserted into the hole in the top of the rear metal support pillar of the graphite rod head, to monitor the temperature of the pillar. Sample was added when the temperature was within the recommended sample addition temperature range (40-60°C). Oxygen-free nitrogen was used as the sheathing gas. This procedure, although satisfactory

with new rods, resulted in rod life times of only a few firings and a rapid deterioration due to increased porosity. To overcome this problem, the rods were coated with pyrolytic graphite produced by the pyrolysis of 95% Argon + 5% Methane bled (at  $150 \text{ ml min}^{-1}$ ) into the nitrogen sheathing gas (flowing at  $0.2 \text{ lmin}^{-1}$ ). Two coatings were produced at the normal atomization temperature between each determination.

### Results:

Instrument settings were as follows:

Wavelength of molybdenum absorption	: 313 nm
Slit width	: position 1 (0.18 nm)
Lamp current	: 7.5 mA
Damping control	: position 1
Read out mode	: direct
Recorder voltage	: 10 mV
Recorder chart speed	: $4 \text{ cm.min}^{-1}$
Scale expansion	: X1
Nitrogen gas flow rate	: $3.2 \text{ l.min}^{-1}$
95% Argon + 5% Methane	: $150 \text{ ml.min}^{-1}$
Graphite rod	: Type 1

The electrothermal atomizer unit was set at the following conditions:

## 1. Evaporation, drying and atomization:

	Voltage (V)	Time (sec)
Channel 1, Evaporation	6	25
Channel 2, Dry-ash 1	4	10
Channel 3, Dry-ash 2	6	10
Channel 4, Atomization	9	2

Nitrogen flow rate:  $3.2 \text{ l.min}^{-1}$ .

## 2. Rod cleaning stage:

	Voltage (V)	Time (sec)
Channel 1, Evaporation	6	0
Channel 2, Dry-ash 1	4	0
Channel 3, Dry-ash 2	6	0
Channel 4, Atomization	9	2

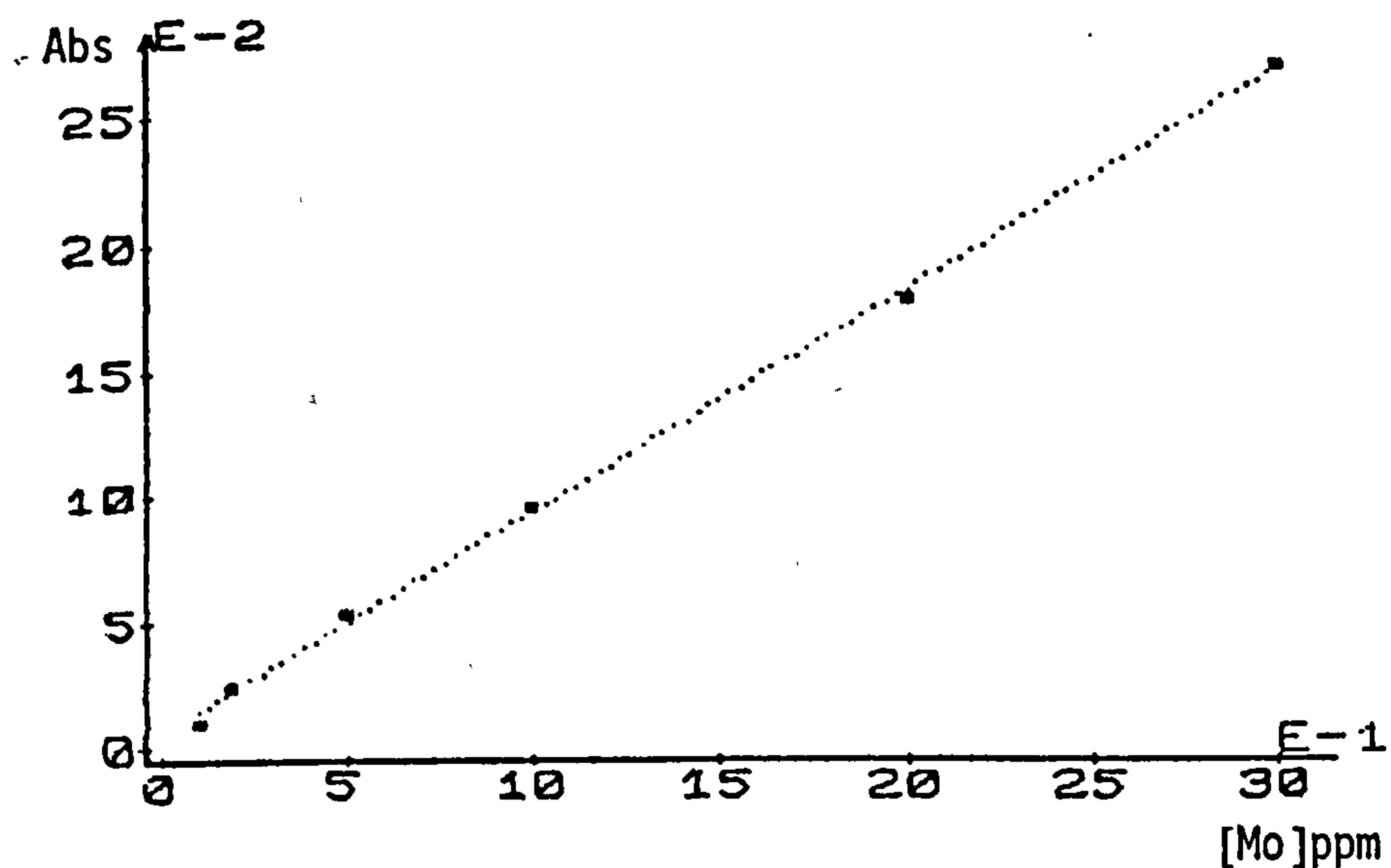
Nitrogen flow rate:  $3.2 \text{ l.min}^{-1}$

## 3. Pyrolytic coating stage:

	Voltage (V)	Time (sec)
Channel 1, Evaporation	6	0
Channel 2, Dry-ash 1	4	0
Channel 3, Dry-ash 2	6	0
Channel 4, Atomization	9	2

Nitrogen flow rate:  $0.2 \text{ l.min}^{-1}$

95% Argon + 5% methane flow rate:  $150 \text{ ml.min}^{-1}$ .



## RESULTS OF LEAST SQUARES CALCULATION

$$Y = .0884368048 X + 5.30495456E-03$$

NUMBER OF POINTS	= 6
SLOPE	= .0884368048
INTERCEPT	= 5.30495456E-03
CORRELATION COEFF.	= .999321747
STANDARD DEVIATION	= 3.74224538E-03

X	Y
.1	9.2E-03
.2	.024
.5	.054
1	.096
2	.178
3	.272

FIGURE 19: Calibration graph of molybdenum and the least squares linear regression analysis of six points



A plot of the data points for the calibration graph of the molybdenum and the least squares linear regression analysis for a straight line was carried out using an Apple II computer (see Figure 19).

The graph was linear up to 3.0 ppm of molybdenum. The limit of detection based on 10 determinations of 0.125 ppm Mo calculated as twice standard deviation was  $2.5 \times 10^{-2}$  ppm and sensitivity (concentration for 1% absorption) was  $3.7 \times 10^{-2}$  ppm. The precision was 8% at an absorbance of 0.016 (0.125 ppm).

Memory effects, porosity of the graphite rod surface, short life time of operation and carbide formation are limiting factors for molybdenum determination. Coated graphite rods show significant improvement in analytical performance.

#### 4.4 Extraction of 12-Molybdophosphoric Acid and Subsequent Carbon Rod Electrothermal Atomization of Phosphorus

The method involves the formation and extraction of the 12-molybdophosphoric acid and subsequent indirect determination of phosphorus by carbon rod atomic absorption spectrometry.

##### Instrument:

As experiment 4.2.

### Reagents:

As experiment 2.4.2.

### Standard phosphorus solution, 0.5 ppm

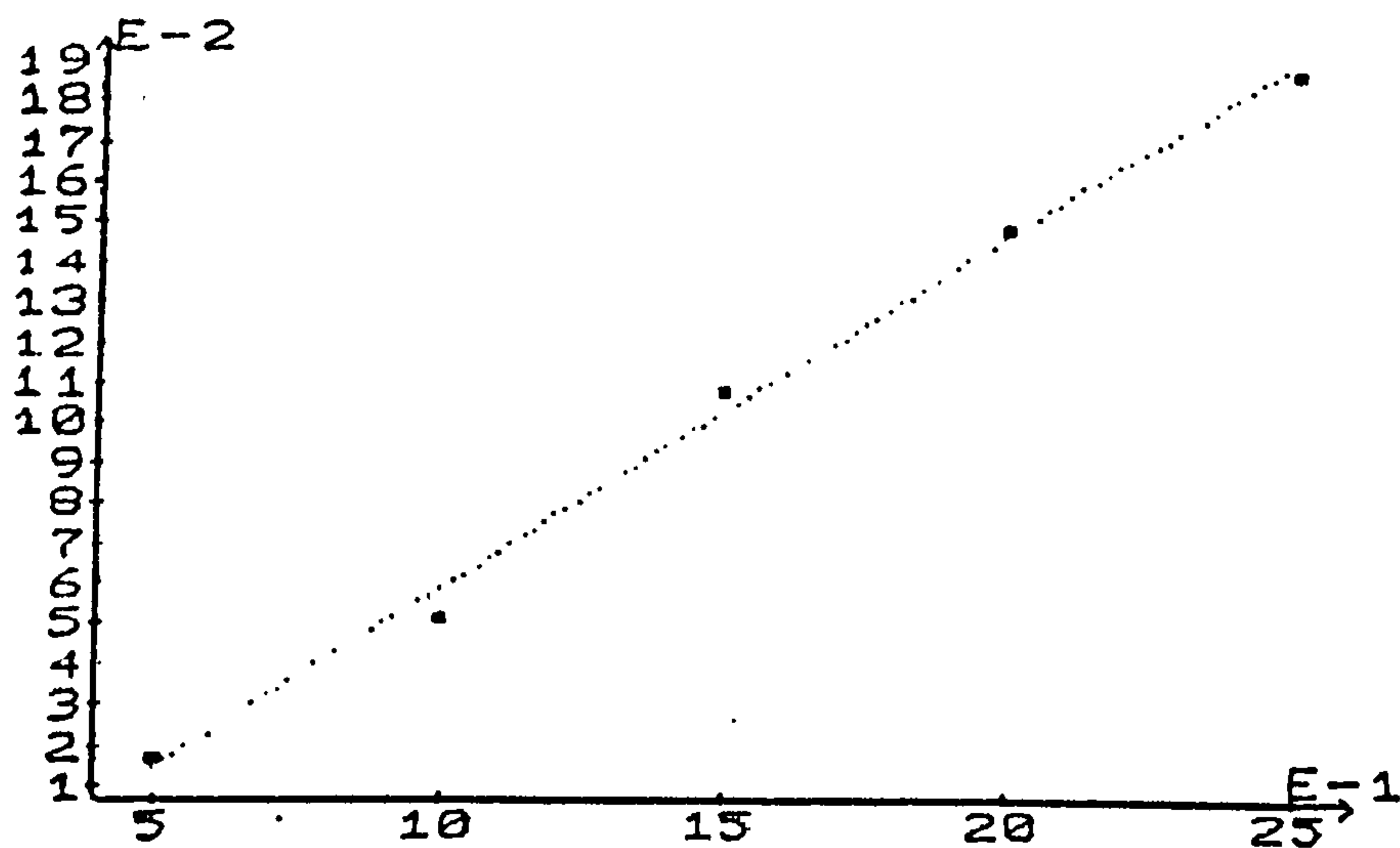
The solution was prepared daily by diluting 5 ml of stock phosphorus solution (experiment 2.4.1) to 500 ml.

### Procedure:

Solutions containing 0, 0.25, 0.5, 1.0, 1.5, 2.0 and 2.5  $\mu\text{g}$  of phosphorus solution were transferred into 100 ml separating funnels. Experiment 2.4.2 was repeated, except that the organic solvent was dried with anhydrous sodium sulphate. The separating funnel was washed with a further 2 ml of solvent, which was dried and then added to the extract. The extract was made up to volume with the pure solvent. The experiment was repeated using 20 ml extractant. The absorbances were measured by injecting 1  $\mu\text{l}$  portions of each solvent extract.

### Results:

A plot of data points for the calibration graph of the phosphorus and least squares regression analysis for a straight line was carried out using an Apple II computer as shown in Figures 20 and 21. The graph was linear up to 2.5  $\mu\text{g}$  of phosphorus. The experimental limit of detection using 45 ml and 20 ml solvent as an extractant was 0.5  $\mu\text{g}$  and 0.25  $\mu\text{g}$  of phosphorus respectively. The sensitivity (amount for 1% absorption) using 45 ml and 20 ml solvent as an extractant were



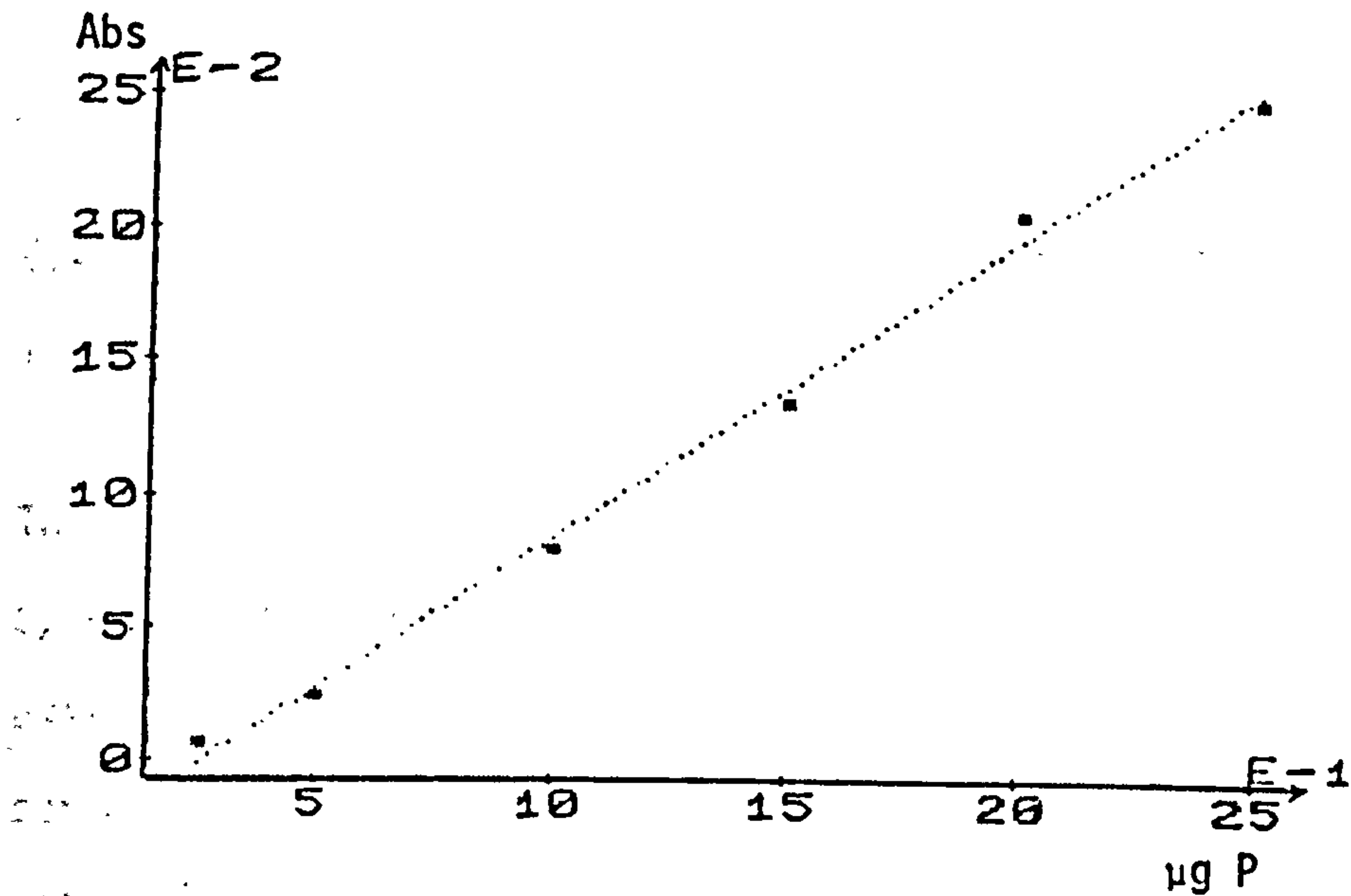
#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .088 X + -.0296$$

NUMBER OF POINTS = 5  
 SLOPE = .088  
 INTERCEPT = -.0296  
 CORRELATION COEFF. = .99785814  
 STANDARD DEVIATION = 4.5607017E-03

X	Y
.5	.016
1	.052
1.5	.108
2	.148
2.5	.188

FIGURE 20: Calibration graph of phosphorus extracted as 12-molybdophosphoric acid using 45 ml solvent as an extractant



#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .111539726 X + -.0284054794$$

NUMBER OF POINTS = 6  
 SLOPE = .111539726  
 INTERCEPT = -.0284054794  
 CORRELATION COEFF. = .99792208  
 STANDARD DEVIATION = 6.28004015E-03

X	Y
.25	6E-03
.5	.024
1	.078
1.5	.134
2	.204
2.5	.248

FIGURE 21: Calibration graph of phosphorus extracted as 12-molybdophosphoric acid using 20 ml solvent as an extractant



$8.4 \times 10^{-2} \mu\text{g}$  and  $5.6 \times 10^{-2} \mu\text{g}$  of phosphorus respectively for 1  $\mu\text{l}$  injection.

The experimental limit of detection compared with conventional flame spectrophotometer methods, using 45 ml and 20 ml solvent as an extractant were 1  $\mu\text{g}$  and 0.5  $\mu\text{g}$  of phosphorus respectively and the sensitivity (amount for 1% absorption), was 1  $\mu\text{g}$  of phosphorus for both solvent volumes.

A considerable improvement in detection, and sensitivity of phosphorus determination compared with conventional flame spectrophotometer methods, due to (a) lack of flame background, (b) preconcentration and increase in atom population by atomization of dried samples, and (c) an increase in residence time and peak atom population in the light beam. An improvement in detection limit was observed when 20 ml solvent was used, and no blank values were detected in this experiment.

#### 4.5 Modification of Carbon Rod Atomizer Using Sequential Gas Introduction System

##### 4.5.1 Introduction of Argon and Methane as a Flowing Sheathing Gas

The method involves the use of a mixture of argon and methane as a flowing sheathing gas instead of nitrogen.

### Instrument:

As experiment 4.3.

Argon flow rate:  $3.2 \text{ l.min}^{-1}$ .

Very small amounts of methane (less than  $20 \text{ ml min}^{-1}$ ) were bled into the argon flow. Pyrolysis gas metering (A3479) was used to allow continuous flow of pyrolysis gas about the graphite rod. The setting up of the pyrolysis gas metering is shown in Figure 22.

### Reagents:

As experiment 4.3.

### Procedure:

Solutions containing 0.1, 0.2, 0.5, 1.0 and 3.0 ppm molybdenum solution were prepared by diluting the standard 10 ppm molybdenum solution.

The setting up of the instrument was as in experiment 4.3, except a mixture of argon-methane was introduced (see Figure 22) replacing the nitrogen inert gas to improve the molybdenum sensitivity.

The procedure was continued as in experiment 4.3.

### Results:

A plot of data points for the calibration graph of the molybdenum and the least squares linear regression analysis for a straight line was carried out using an Apple II computer as shown in Figure 24.

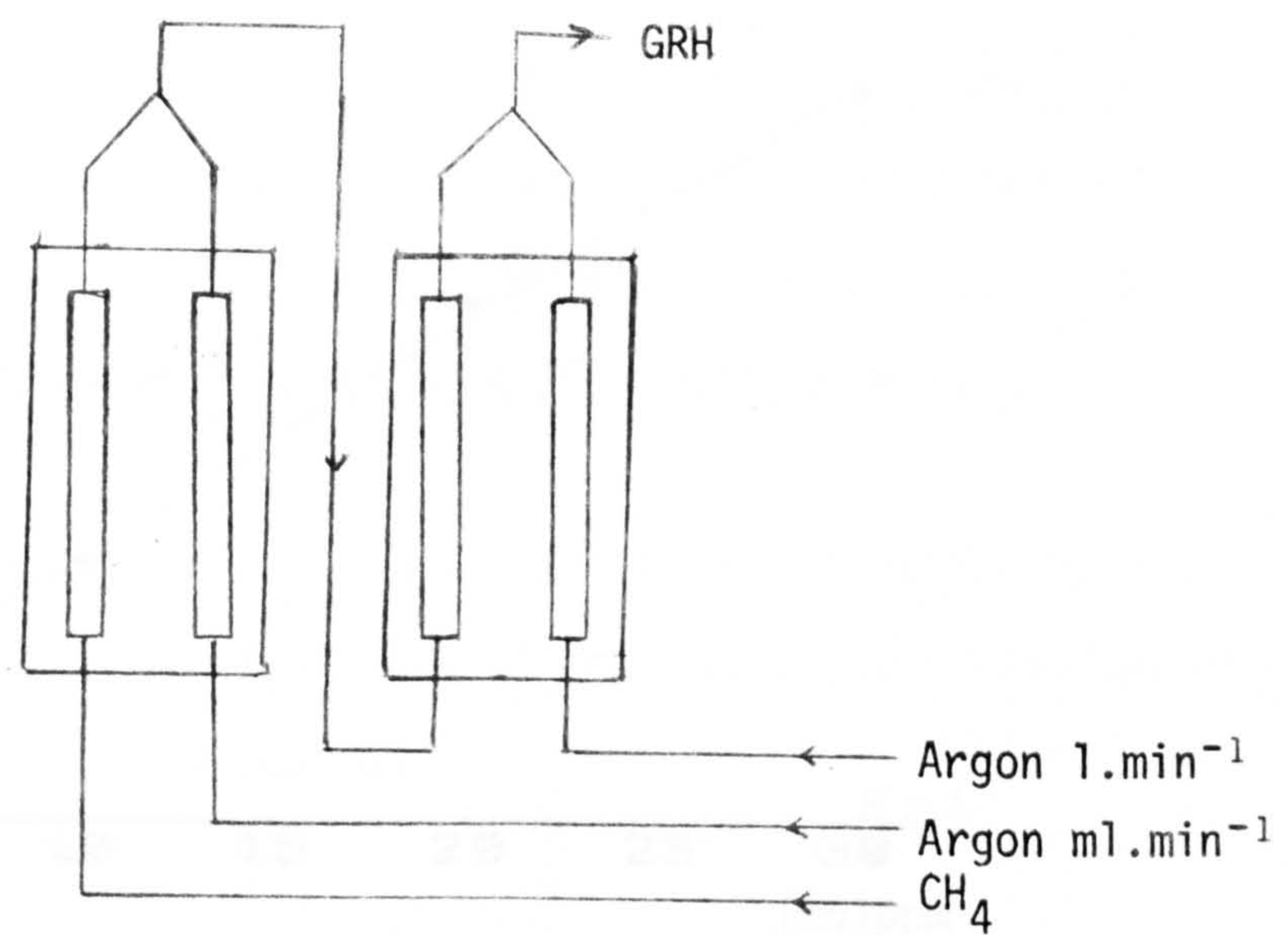


FIGURE 22: Pyrolysis gas meter setting for introduction of methane

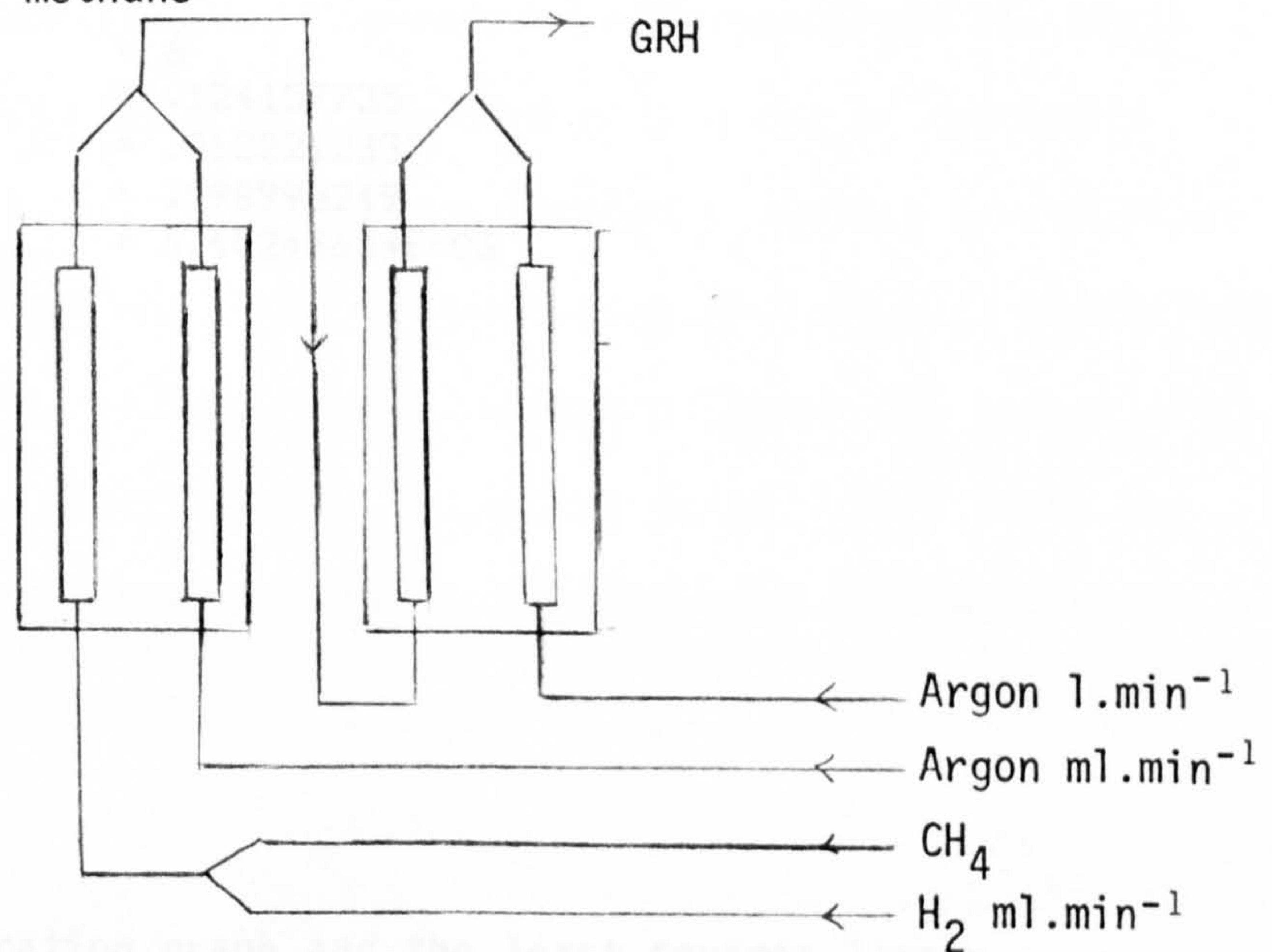
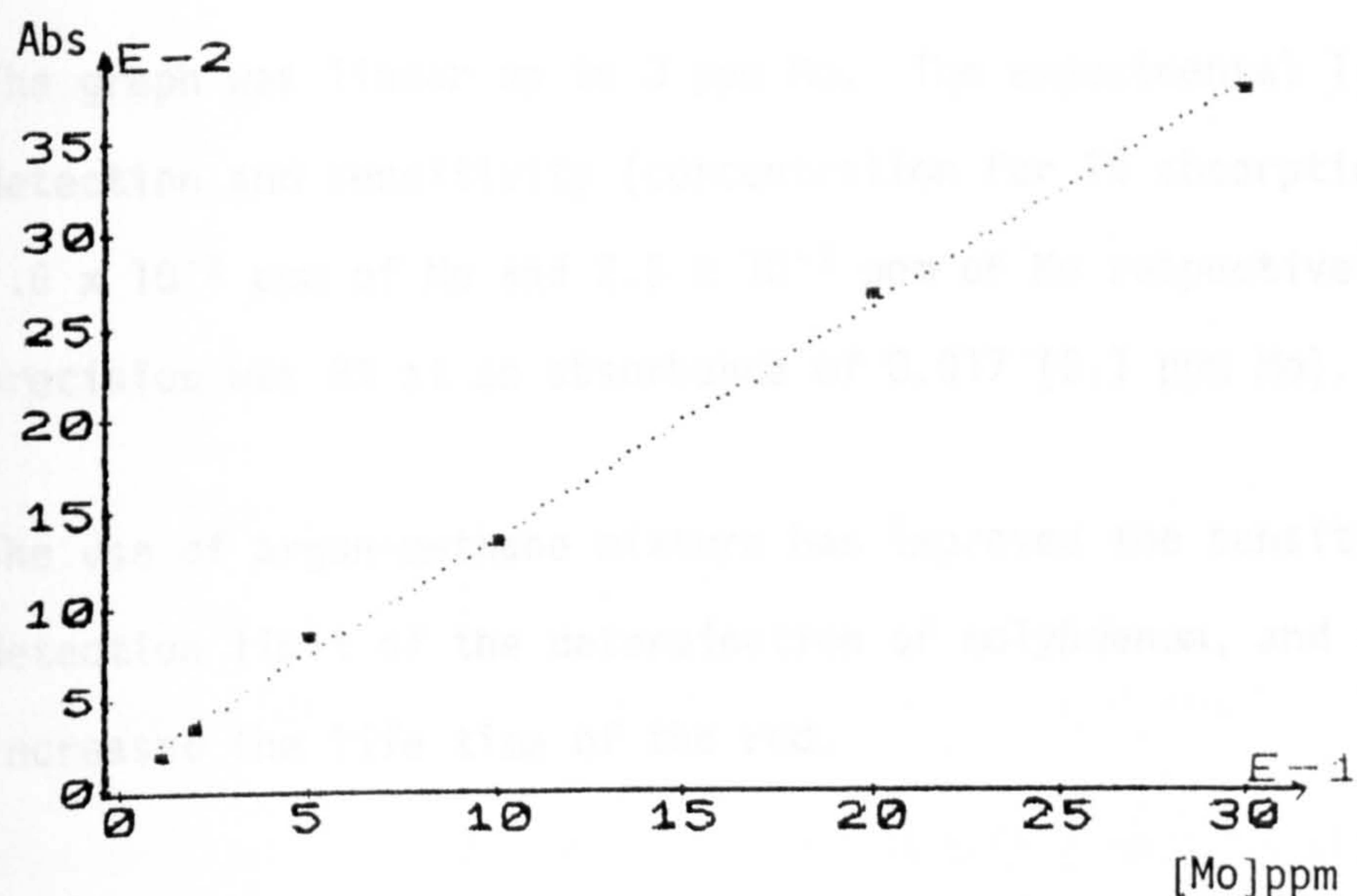


FIGURE 23: Pyrolysis meter setting for introduction of H<sub>2</sub>





#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .124157735 X + .0122212337$$

NUMBER OF POINTS	= 6
SLOPE	= .124157735
INTERCEPT	= .0122212337
CORRELATION COEFF.	= .998993249
STANDARD DEVIATION	= 6.40243634E-03

X	Y
.1	.0176
.2	.034
.5	.084
1	.136
2	.266
3	.38

FIGURE 24: Calibration graph and the least squares linear regression analysis for molybdenum using a mixture of argon-methane as a flowing sheath gas



The graph was linear up to 3 ppm Mo. The experimental limit of detection and sensitivity (concentration for 1% absorption) were  $1.6 \times 10^{-2}$  ppm of Mo and  $2.5 \times 10^{-2}$  ppm of Mo respectively. The precision was 8% at an absorbance of 0.017 (0.1 ppm Mo).

The use of argon-methane mixture has improved the sensitivity and detection limit of the determination of molybdenum, and also greatly increased the life time of the rod.

#### Discussion:

A possible explanation for the improvement in sensitivity is mainly due to thermal decomposition of methane at high temperatures, which forms free carbon and hydrogen. The free carbon can be deposited on the graphite rod, giving continuous pyrolytic coating and improved sensitivity. Hydrogen will provide a reducing environment, maintaining the atomic population at much greater distances above the carbon rod, and also reduce the interferences in the gas phase. This leads to an improvement in the detection limit compared with nitrogen inert gas used as sheathing gas.

#### 4.5.2 Introduction of Argon and Hydrogen as a Flowing Sheathing Gas

The method involves use of a mixture of argon-hydrogen as a flowing sheathing gas, instead of nitrogen and methane, for pyrolytic coating of carbon rod.



Hydrogen was used to improve the sensitivity and detection limit of molybdenum atomization.

#### Instrument:

As experiment 4.3.

Argon flow rate:  $3.2 \text{ l.min}^{-1}$ .

Hydrogen flow rate:  $30\text{--}40 \text{ ml min}^{-1}$ , bled into argon gas.

The setting up of the pyrolysis gas metering unit is shown in Figure 23.

#### Reagents:

As experiment 4.3.

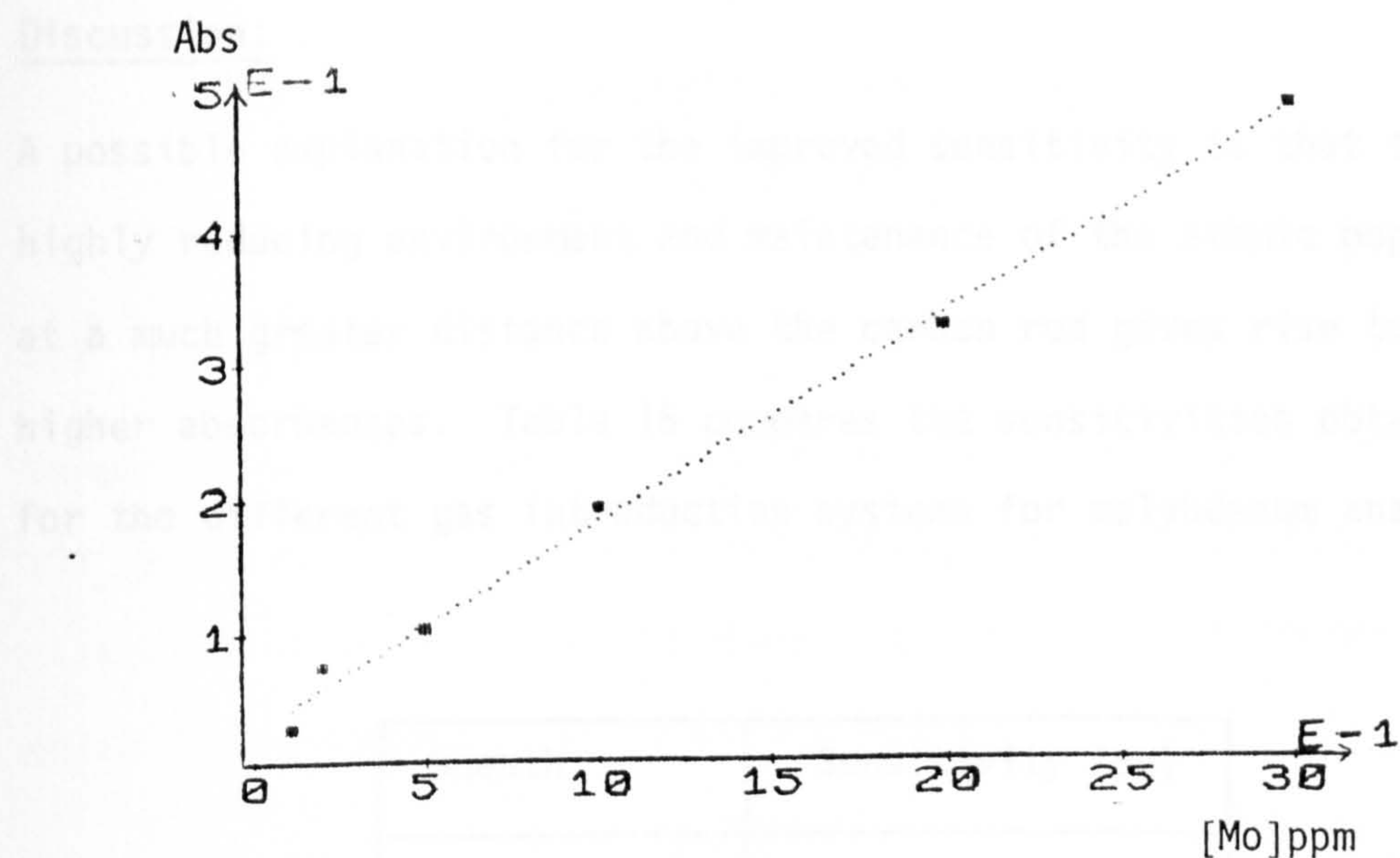
#### Procedure:

As experiment 4.3, except a mixture of argon-hydrogen was used as a sheathing gas and methane for pyrolytic coating

#### Results:

A plot of data points for the calibration graph of the molybdenum and the least squares linear regression analysis for a straight line was carried out using an Apple II computer as shown in Figure 25.

The graph was linear up to 3 ppm Mo. The sensitivity (concentration for 1% absorption) was  $1.02 \times 10^{-2}$  ppm of Mo.



#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .152244691 X + .0284560164$$

NUMBER OF POINTS	= 6
SLOPE	= .152244691
INTERCEPT	= .0284560164
CORRELATION COEFF.	= .997864584
STANDARD DEVIATION	= .0114435883

X	Y
.1	.028
.2	.074
.5	.102
1	.19
2	.324
3	.488

FIGURE 25: Calibration graph and the least squares linear regression analysis for molybdenum using a mixture of argon-hydrogen as a flowing sheath gas



### Discussion:

A possible explanation for the improved sensitivity is that the highly reducing environment and maintenance of the atomic population at a much greater distance above the carbon rod gives rise to higher absorbances. Table 16 compares the sensitivities obtained for the different gas introduction systems for molybdenum analysis.

Sheath	Sensitivity (pg)
N <sub>2</sub>	37
Ar + CH <sub>4</sub>	25.8
Ar + H <sub>2</sub>	10.21

TABLE 16: Comparison of Sensitivities of Gases Introduction for Molybdenum



## CHAPTER 5

### DETERMINATION OF GERMANIUM BY AN INDIRECT METHOD

#### SPECTROPHOTOMETRY

##### 5.1 Introduction

Germanium was discovered by Winkler in 1886 (254). Winkler obtained his germanium from the mineral argyrodite, which is  $\text{Ag}_8\text{GeS}_6$ . The element also occurs in canfieldite,  $[\text{Ag}_8(\text{SnGe})\text{S}_6]$  and in germanite, which is approximately  $\text{Cu}_5(\text{Cu,Fe})_6\text{AsGeS}_{12}$ .

Many other minerals (especially those of zinc, arsenic, tin, lead, copper, and antimony) contain some germanium.

Coal ash from brown coal frequently contains germanium in the range 0.005% to 0.1%; the ash of some anthracites may run as high as 4% or even 7.5% germanium, thereby providing a possible source of the element (255).

The abundance of germanium in the igneous rocks of the earth is usually given as 7g per metric ton, or  $7 \times 10^{-4}\%$  (256), so it is somewhat more rare than Ga and Pb (15 and 16 ppm, respectively) but more abundant than As, Be, B and Br.

Germanium is a rare element, and is one of a class of materials known as semiconductors. Such materials have found wide application in

electronic devices in the past two decades. Germanium has been used as semiconductor in rectifiers, amplifiers, oscillators and in other specialized devices.

## 5.2 Separation

The classic method for separation of germanium from most of the interfering elements is to distil germanium tetrachloride from 6N hydrochloric acid, leaving most of the other compounds in the distillation flask.

Where feasible, liquid-liquid extraction has replaced distillation. Germanium tetrachloride in hydrochloric acid solution from 7.3 to 12N is readily extracted by esters, benzene, trichloromethane, tetrachloromethane, and tris (n-butyl) phosphate. The most commonly used extractant is tetrachloromethane. Electrochemical methods are also used for separation from cations (Cu, Bi, Pb) before the photometric determination of germanium by phenylfluorone.

## 5.3 Review of Analytical Methods for Determination of Germanium

### 5.3.1 Gravimetric Methods

Germanium may be precipitated as a  $\text{Ge}(\text{OH})_4$  from 6N sulphuric acid solution; hydrochloric acid can be used but is not the preferred medium. Germanium  $\text{Ge}(\text{OH})_4$  is rarely weighed as such, but is oxidized to  $\text{GeO}_2$  (257).

Precipitation with tannin in an acid solution has been widely used. Precipitation from oxalic acid solution is said to be the most satisfactory (258). Tannin is an organic group precipitating agent; upon heating it will char and provide reducing conditions unless the ignition is carefully controlled. The final ignition to  $\text{GeO}_2$  must be at  $900^\circ\text{C}$ . Magnesium germanate may be precipitated from ammonical solution, in the presence of ammonium sulphate (259).

Germanium also forms complexes with molybdate and tungstates, which can be precipitated with organic bases. The resultant precipitates can be ignited to constant weight but do not give stoichiometric factors (260).

### 5.3.2 Titrimetric Methods

Germanium in solution forms a complex acid with polyhydric alcohols. This reaction forms the basis of a titrimetric analysis for germanium (261). The germanium solution is freed of  $\text{CO}_2$  and the pH is adjusted to 6.2, and measured using either bromocresol purple indicator or a pH meter. Mannitol is added, which combines with the germanium to give a monoprotic acid. The solution is treated with dilute,  $\text{CO}_2$ -free sodium hydroxide solution to pH 6.2.

The recommended procedure is precipitation of the germanium as  $\text{Ge}(\text{OH})_4$  from 6N sulphuric acid solution, dissolving the  $\text{Ge}(\text{OH})_4$  in ammonia, and oxidizing the  $\text{Ge}(\text{OH})_4$  with hydrogen peroxide.

The solution is freed of excess ammonia and hydrogen peroxide by boiling, first in alkaline and then in acid solution. Sulfur dioxide is passed through the acid solution to reduce arsenic, the excess sulfur dioxide is boiled off, and the solution is titrated.

Germanium (IV) can be reduced to germanium (II) with sodium hypophosphite, and the germanium (II) can be reoxidized with potassium iodate (262).

Germanium can be converted into molybdo-germanic acid, precipitated with 2% quinoline-8-ol, and treated with known excess of aqueous  $\text{KBrO}_3$ -KBr. The unconsumed bromide is determined by conventional iodometric titration. The method has been applied for determination of 1-30% of germanium in alloys and intermetallic compounds with niobium (263).

### 5.3.3 Polarographic Methods

Germanium is determined as germanium (II) in polarography and can be formed by reduction of germanium (IV) with sodium hypophosphites. Reduction of germanium (II) to the metal in 6N hydrochloric acid is reported to give a wave at a half wave potential of -0.45V (264).

Karpinski *et al* (265) used voltammetric and chronoamperometric techniques for determination of germanium. The deposition of germanium into and onto hanging mercury drop electrodes was investigated within a pH range of 6-8.5 at a  $\text{Ge(IV)}$  concentration, ranging



from  $2 \times 10^{-5}$  to  $5 \times 10^{-3} \text{ mol l}^{-1}$  at scan rates from 0.002 to  $20 \text{ Vs}^{-1}$ .

Adsorption accumulation in stripping voltammetry for Ge at 10 mM concentration was determined by Kalvoda (266), via adsorption of germanium catechol. The addition of catechol to the test solution in  $\text{ClO}_4^-$  media increases the polarographic wave height using a static mercury drop electrode (267). Detection limit of 82 ppb was reported.

#### 5.3.4 Spectroscopic Methods

##### 5.3.4.1 Spectrophotometric methods

Germanium is generally found in the +4 oxidation state as oxide or in solution as germanic acid. Germanium forms divalent and tetravalent compounds of which only the latter are stable under environmental conditions.

Germanium in low concentrations has been largely determined by spectrophotometric methods. While useful for the determination of these elements in the submicrogram range, such methods are sometimes complicated by the need for extraction or distillation procedures to avoid interferences from other trace metals (268,269).

Germanium (270-272) at trace levels can be determined spectrophotometrically using a variety of reagents such as quinalizarin (273), oxine (274), N-benzoyl-N-phenyl hydroxylamine (275,276),

sodium lauryl sulphate (277), bromopyrogallol red (278, 279), phenyl fluorone (280-282), alizarin (283), catechol violet (284), dimethyl amino phenyl fluorone (285) and molybdate (286).

The most widely used method is based on the sensitive but slow reaction of germanium with phenyl fluorone (2,6,7-trihydroxy-9-phenyl-3H-xanthene-3-one) (281), using gelatine or gum arabic as the dispersing agent. The stoichiometric ratio of the complex in solution is  $\text{Ge:PF} = 1:2$  and the complex in the solid phase is  $(\text{PF})_2\text{Ge} \cdot 4\text{H}_2\text{O}$ .

At pH 4.7 a 1:2:2 complex is formed by germanium, diphenylguanine and alizarin, which is 1,2-dihydroxyanthraquinone (283). When extracted with 1:4 chloroform-acetone it has a maximum absorption at 470 nm. Beer's law is followed for 0.1-5  $\mu\text{g}$  of germanium in 8 ml of solution.

Bromopyrogallol red forms a 3:1 complex with germanium and conforms to Beer's Law for 0.2-15 ppm of Ge (278). In aqueous solution at pH 4.8, germanium forms a complex with catechol violet that is purple in the absence of gelatin and has a maximum absorption at 555 nm (284). In the presence of gelatin at pH 3.4-3.6, the complex is green and has a maximum absorption at 650 nm. Beer's Law is applicable at 0.15-0.5 ppm in the absence of gelatin but only at 0.3-0.5 ppm in its presence.

Dimethylamine phenyl fluorone (2,6,7-trihydroxy-9-dimethyl amino phenyl fluorone) forms a 3:1 complex with germanium in N-hydrochloric acid (285). The maximum absorption of the reagent and of the complex are at 460-470 and 500 nm, respectively.

The acidic solution of germanium (IV) reacts with molybdenum (VI) to form 12-molybdogermanic acid. The complex acid can be measured directly in the ultra violet region, extracted for ultra violet measurements or decomposed and measured as the molybdate (286). To avoid instability, a large excess of molybdate must be present at the time the yellow acid is formed. The complex is 12:1 molybdenum-germanium. For the maximum absorption, the ratio of molybdenum to germanium in the solution must be at least 36:1, to provide the essential excess of molybdate. Colour is fully developed at a pH of 1.5 in 30 mins.

The familiar molybdenum blue reaction is applicable to germanium but requires standardization of detail (287). Variability in results by different laboratories is attributed to differences in the time interval between the addition of the molybdate and addition of the reducing agent (288). As, P, Si, and W interfere seriously.

Although the heteropoly blue is sensitive, it lacks precision because of its instability (289).

The determination of germanium as germanomolybdate or its reduced form was regarded by Boltz and Mellon (57) as unsatisfactory because of the stringent reaction conditions required; and the main source of error was the rapid conversion of the  $\beta$  and  $\alpha$  form.

The existence of  $\alpha$  and  $\beta$  forms of molybdo-germanic acid was suggested by Chalmers and Sinclair (44). Addition of acetone stabilizes the  $\beta$ -form of the heteropoly acid which would otherwise change with time to the less intensely coloured  $\alpha$ -form, it also increases the rate of formation of the heteropoly acid (44).

Kitson and Mellon (290) achieved a considerable degree of stabilization by forming germanomolybdate in 6N acetic acid solution. A detailed study of properties and analytical application of the molybdo-germanic acid was reported by Halasz and Pungor (47).

Tobia *et al* (291) studied the reaction between germanium and phenyl fluorone and a method was developed. The absorbance was measured at 525 nm after 20 minutes. The sensitivity of  $2.55 \times 10^{-3}$  mg ml<sup>-1</sup> of Ge was reported.

Kuwabura *et al* (292) compared the sensitivity of phenyl fluorone with the effect of 16 quaternary ammonium salts on the spectrophotometric determination of germanium and suggested the use of benzalkonium (II) for better sensitivity. The calibration curve is linear up to 0.16 ppm of Ge and measured at 508 nm.



#### 5.3.4.2 Atomic absorption spectroscopic methods

The most satisfactory region of the spectrum for the determination of germanium by atomic absorption, flame emission, or atomic fluorescence (293) is the doublet at 265.12 nm and 265.16 nm.

The second most sensitive line for determination by atomic fluorescence or flame emission in a  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame is at 275.46 nm, while 259.25 nm is the second best line for the absorbance measurements.

A fuel-rich hot flame is required. Early work has been reported in atomic absorption spectroscopy using oxy- $\text{C}_2\text{H}_2$  (194,195) and air- $\text{C}_2\text{H}_2$  flame (194).

In  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame, workers (294,296) reported sensitivities of 1.5  $\mu\text{g}$  and 2.5 ppm of Ge respectively. Popham and Schrenk (297) found a limit of detection of 0.5 ppm of Ge with the same flame system, using a (1+1) acetone-water solvent system. Hydrochloric acid, sulphuric acid and phosphoric acid in concentrations of 0.1 and 1N depresses germanium absorbance by up to 19% in a  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame in aqueous solution. This depression is halved in a 50% acetone-water solution. Kirkbright *et al* (298) reported that the low background of the argon-separated  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame enabled the limit of detection to be lowered to 0.2 ppm of Ge. The emission characteristics of germanium in the premixed  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame was studied by Pickett *et al* (299) and the detection limit of 0.5 ppm of Ge was reported.

$\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame is often used in combination with solvent extraction. Yanagisawa *et al* (300) determined germanium in synthetic fibres at concentrations of 0.1 to 0.02% after extracting into methyl isobutyl ketone from 7.5M HCl, which provided a 10 fold absorption enhancement over that obtained by spraying aqueous solutions. Fe, Sb, As, Sr and Au were reported not to interfere. Pollock (301) determined germanium in limonite by atomic absorption spectrometry after extraction with methyl isobutyl ketone. Chloroform extraction of germanium from 0.1 to 10M HCl solution containing potassium ethyl xanthates was studied (302) for separation of metallic ferrous materials, germanium partly extracted from 6 to 10M media as the chlorocomplex.

Extraction of  $\text{GeCl}_4$  into n-hexane was reported to have an increase in sensitivity and selectivity over methyl isobutyl ketone in the  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame (303). A 5 fold enhancement in sensitivity was obtained when germanium was extracted into n-butyl acetate from 8M HCl (304). This enhancement was ascribed to a nebulizer effect and was probably due to the different chemical form of germanium extracted from various concentrations of HCl. The sensitivity of 0.13 ppm (for 1% absorption) was reported.

The indirect determination of germanium by atomic absorption spectrometry, based on the formation of molybdo-germanic acid in which the molybdenum:germanium combining ratio is 12:1 has been described by Jakubiec and Boltz (286). A sensitivity of 0.05 ppm was reported with linear calibration up to 1.6 ppm. No interference

was found for 500 ppm of Ca, Co, K, Mg, Mn, Na, Ni, Zn, acetate, chloride, perchlorate, nitrate or sulphate ions in the determination of 1.5 ppm Ge. The maximum permissible concentration of foreign ions for non-interference in the determination of 1.5 ppm of Ge were established as: Al, Cd, Cr (III), Cu, Mo (VI), 500 ppm; Pb 50 ppm; Fe(II), Fe (III), Ti (IV), Cr (VI), W (VI) 10 ppm; As (III), As (V), P (V) and Si interfered at any concentration.

The extraction conditions for 12-molybdo germanic acid have been carefully studied (305) using diethyl ether, n-butyl acetate, methyl isobutyl ketone, 4:1 chloroform-n-butanol and 5:1 diethyl ether:1 pentanol. Methyl isobutyl ketone was reported to be the best extractant for molybdo germanic acid at pH 1.5.

Volatile hydride generation techniques have also been applied to the determination of germanium by atomic absorption spectrometry (306-312) but the sensitivity and reproducibility are inferior to those elements such as As, Se and Sb (306). The reduction of Ge in solution to the volatile halide ( $\text{GeH}_4$  bp -  $88.5^\circ\text{C}$ ) by sodium borohydride and subsequent detection of the gaseous germane by atomic absorption was first used by Pollock and West (307), who achieved a relatively high limit of detection (about  $0.5\ \mu\text{g}$  of Ge) by injecting the gas into a standard atomic absorption flame. Similar limits of detection were achieved with an externally heated silica tube atomizing furnace (309). Braman and Tompkins (310) combined the borohydride technique with dc discharge atomic

emission detection and achieved a detection limit of 0.4 ng of Ge, in environmental samples. Compounds are first converted to their respective hydrides at pH 1.5 with sodium borohydride.

Jin *et al* (306) compared three types of hydride generators and atomizer systems; (a) collection type hydride generator connected to nitrogen-hydrogen flame (b) direct transfer type generator connected to heated silica tube, (c) direct transfer type generator connected to nitrogen-hydrogen flame. Of these three types, direct transfer of the generated hydride into nitrogen-hydrogen flame for atomization was reported to be the most suitable. Interferences of Ni(II), Au(III), and Co(II) in HCl medium was reduced by adding ethylene diamine tetra acetate as a masking reagent or replacing the acid medium by mallic acid. Detection limit of 7 ng was reported for the determination of germanium in standard rocks. Direct introduction of  $\text{GeH}_4$  into an  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame was determined by Castillo *et al* (311). The sensitivity of 0.012 ppm and detection limit of 0.0038 ppm was reported. Possible interferences from Pb, As(III), As(V), Fe(II), Fe(III), Te(V), Se(IV), Sb(III), Sn(II), tartrate, oxalate and fluoride were studied.

The major contribution to the information on interferences has been made by Smith (312), who undertook a general study of the effect of 48 elements at concentration of  $1 \text{ mg ml}^{-1}$  on the determination of 2 ppm Ge. The work was carried out using sodium tetrahydroborate (III) pellets and an argon-hydrogen flame, and gave a germanium atomic absorption suppression of greater than 50% in the



presence of As, Au, Cd, Co, Fe, Ni, Pd, Pt, Rh, Sn, Sb, Se and between 10-50% in the presence of Bi, Cu, Ir and Te.

Although flame methods have often been used for determining germanium, the detection limit and sensitivity have not always been satisfactory. This is mainly due to: (a) the atomization of germanium is inhibited by the formation of a volatile and very stable oxide (313), (b) the germanium hollow cathode lamps are inefficient (314).

Johnson *et al* (313) who first studied the determination of germanium by electrothermal atomization, using both carbon rod and carbon tube atomizers, suggested that difficulties in the determination of germanium were due to GeO formation, and recommended a rapid increase in temperature to prevent loss of sample as germanium monoxide. A graphite<sup>tube</sup> was preferred because the residence time of material in the high temperature environment was greater than when using a rod. Germanium dioxide is first reduced by carbon to the volatile monoxide, which can sublime without further reduction. Ohta and Suzucki (315) reported improved sensitivity at a lower temperature, using a tungsten microtube atomizer with argon-hydrogen as the purge gas.

Solvent extraction in combination with carbon rod has also been used for the determination of germanium in Ginseng rodox (316). Thor burn Burns and Dadgar (317) compared tantalum carbide coated

tubes with pyrolytically coated tubes in determination of Ge in organogermanium compounds, and reported that pyrolytically coated tubes gave the most reproducible results. Extraction from aqueous solutions into benzene followed by atomic absorption spectrometry determination using Zr-coated tube with 1M aqueous ammonia as matrix modifier gave a 20 fold increase in sensitivities (318).  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  suppress the absorption signal.

Germanium samples should be evaporated from a flat graphite platform without a pyrolytic coating, within a graphite-tube furnace, and the atomization temperature should be 2980 K. An excess of acid in the solution, affects the absorption, and the effect being greatest with  $\text{HNO}_3$  and least with  $\text{H}_3\text{PO}_4$ . A detection limit of 0.02 ng was reported (319).

Indirect determination of picogram amounts of germanium by electrothermal atomic spectroscopy have been reported (314,320). The method involves the conversion of the germanium into yellow 12-molybdo-germanic acid into 2-ethyl-hexanol (320) or 1-pentanol-diethyl ether (314), the decomposition of the compound with aqueous ammonia and then back extraction of the liberated molybdenum into aqueous solution for electrothermal atomic absorption spectrometry determination.

There is very little information available about matrix effects on germanium in electrothermal atomizers.

The enhancement effect of various acids such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  on the germanium response was noted earlier by Ediger (321). Matrix interference effects of acids and salts on Ge, V and Ti analysis have been studied (322) using carbon furnace atomic absorption spectrometry. Acid like perchloric, phosphoric and nitric in the range 0.1-1% v/v increases the signal of Ge, whereas sulphuric and hydrochloric at 1% v/v decrease the signal. A non-specific absorption line at 265.1 nm caused by the presence of the chloride of Na, K, Ca and Mg can be removed with 0.6M acids.

The mechanism of the interferences of acids, alkalis, and salts were also investigated by Mino *et al* (323), using standard graphite tubes coated with tantalum. The positive interferences are due to inhibition of the reaction of  $\text{GeO}_2$  with carbon to form volatile  $\text{GeO}$ , and that suppression interferences due to physical occlusion effects. The addition of NaOH to the sample improves sensitivity (0.004 ppm for 1% absorption) for germanium and removes matrix interferences. This is probably due to the formation of stable  $\text{Na}_2\text{GeO}_3$  during the ashing step in the presence of NaOH. It has been reported (324) that the reaction  $\text{GeO}_2 + \text{C} \rightarrow \text{GeO} + \text{CO}$  predominates when  $\text{GeO}_2$  is heated in the presence of carbon.

$\text{H}_2$  was found to lower the atomization temperature of germanium and improve the sensitivity for germanium significantly when the optimum flow rates are applied (315) in a tungsten micro-tube atomizer. A procedure which involves  $\text{CCl}_4$  extraction of  $\text{GeCl}_4$  and back extraction of Ge into water was reported to decrease many interferences.



Wendl *et al* (325) studied the chemical reactions of germanium in the graphite furnace and indicated that after the drying cycle  $\text{Na}_2\text{GeO}_3$  is formed. At temperatures above 900K,  $\text{Na}_2\text{GeO}_3$  is reduced to metallic germanium. At temperatures higher than 1100K, the metal is oxidized to volatile  $\text{GeO}$ .

Andreae and Froelich (326) used a combination of hydride generation, graphite furnace atomization, and atomic absorption detection to determine germanium in natural water at the parts per trillion level. Precision is 4% by peak integration in the nanogram range, with an absolute detection limit of 140 pg Ge. The germanium is reduced by sodium borohydride to germane ( $\text{GeH}_4$ ), stripped from solution by a helium gas stream, and collected in a liquid-nitrogen cooled trap. Germane is released by rapid heating of the trap and enters a modified graphite furnace which is synchronized to reach the analysis temperature at 2600°C before arrival of the germane.

Application of a wire filament electrothermal vaporization technique for introducing sample into the inductively coupled plasma was described by Kitazume (327). The technique involves vaporization of a microlitre sample solution on a platinum filament wire, 0.25 to 0.3 mm in diameter, placed in a small quartz evaporation chamber (about 4.5 ml in volume) and heated by momentary condenser discharge. Detection limit of 60 pg was reported for germanium (327).

The determination of Ge by atomic absorption spectrometry in limonite (307), fibres (300), lignite ash (303), semiconductor



materials (328,329), gold-germanium alloys (330), rocks (303, 306, 315, 331), CdS (319) and in environmental samples (310, 320, 326, 332) has been described.

#### 5.3.5 Miscellaneous Methods

The determination of germanium in high purity aluminium by neutron activation analysis has been described by May and Samadi (333).

The experimental sensitivity is of the order of  $10^{-3}$  micrograms.

The sample was irradiated, then isolated by chemical processes such as precipitation, ion exchange, and solvent extraction.

Germanium was determined as chloride and counted using a liquid scintillation counter.

Neutron activation followed by high resolution,  $\gamma$ -ray spectrometry was also applied to the determination of Ge in the presence of tin in different ratios (334). The method is based on isotopes and is fast, selective, highly sensitive, and non-destructive. Analytical time is 2 minutes per sample. Fiorini *et al* (335) investigated the uses of X-ray fluorescence for the determination of germanium in aluminium-germanium alloys. This method of analysis, which involves the precipitation from aqueous solution, is applicable within a large germanium concentration range and particularly useful for the analysis of less than 1% germanium.

## PRACTICAL EXPERIMENTS

### 5.4 Indirect Determination of Germanium by Atomic Absorption Spectrometry using Carbon Rod Electrothermal Atomization

#### 5.4.1 Investigation of the Formation and Extraction of the 12-Molybdo germanic Acid

Initially Simon *et al* (305) method was followed. The procedure involves formation of 12-molybdo germanic acid in hydrochloric acid media, extraction into organic phase and finally acid wash to remove any excess molybdate transferred into the organic phase. The effect of acidity on formation of 12-molybdo germanic acid, the solvent volume needed for extraction and methods of reducing blank values were investigated in view of improving extractability of the 12-molybdo germanic acid.

#### Instrument,:

As experiment 4.3.

#### Reagents:

##### Stock germanium solution, 250 ppm

0.1803g of germanium dioxide  $\text{GeO}_2$  reagent grade was mixed with 1g of  $\text{Na}_2\text{CO}_3$  and fused in a platinum crucible until a clear melt was obtained. After cooling, the solution was dissolved in 10 ml of distilled water, adjusted to pH 2 to 3 with (1+1) sulphuric acid solution and made up to 500 ml.

Standard germanium solution, 0.5 ppm

The standard was prepared by diluting 50 ml of the stock germanium solution to 500 ml. The pH of the solution should be 3 to 4, from which 1 ml was diluted to 50 ml.

Hydrochloric acid, 4M

The solution was prepared by diluting 16.7 ml of concentrated hydrochloric acid to 50 ml.

Hydrochloric acid solution (1+10)

As experiment 2.4.2, except that the acid was shaken vigorously for 5 minutes with sufficient solvent (about 100 ml) to saturate 1 litre made up acid wash solution in a glass stoppered bottle.

Drying agent

Molecular sieve type 3A.

Anhydrous sodium sulphate prepared as in experiment 2.6.3.1.

Concentrated hydrochloric acid (Aristar 35%)Solvent:

Diethyl ether-pentan-1-ol (1+5)

Methyl iso butyl ketone.

### Procedure:

Optimization of the instrument parameters and calibration for molybdenum was as in experiment 4.3.

Into a series of 100 ml separating funnels was transferred 4 ml of 10% ammonium molybdate solution, 0.5 to 10  $\mu$ g of germanium in solution, and 0.5 ml or 1.0 ml of 4M hydrochloric acid. The final solutions were made up to 50 ml. After mixing the solutions were allowed to stand for 30 minutes. Concentrated (AnalaR) hydrochloric acid (6 ml) was added and allowed to stand for a further 5 minutes. The 12-molybdo-germanic acid formed was extracted with 25 ml or 45 ml of solvent for 2 minutes. The organic extract was washed twice with 10 ml of (1+10) hydrochloric acid by shaking for 30 seconds. The organic phases were either dried as in experiment 2.6.3.1 and then drained into 50 ml volumetric flasks and diluted to volumes with solvent, or the extractants were directly transferred into a 50 ml volumetric flask, made up to volume with solvent and then molecular sieve type 3A was added.

The average of three absorbances was plotted against the amount of germanium originally taken.

### Results:

#### A. Acidity for Formation of Molybdenum Acid

The formation of 12-molybdo-germanic acid in hydrochloric acid media was investigated. The use of 1 ml of 4M hydrochloric acid brings the



pH of the mixture to 1.55. After extraction of 12-molybdogermanic acid into methyl isobutyl ketone, the organic phase was acid washed.

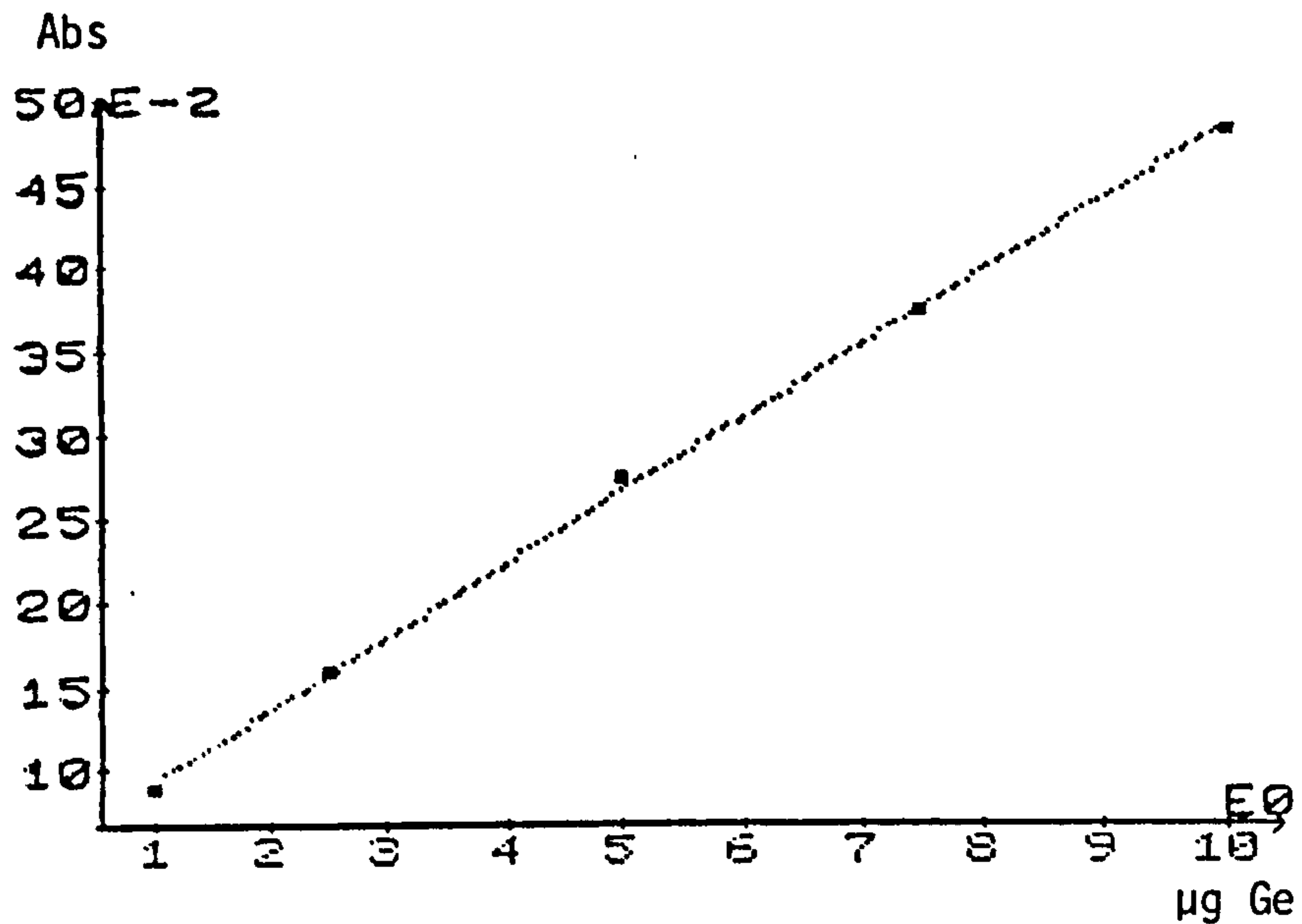
Reduction in the amount of 12-molybdogermanic acid formed after extraction into methyl isobutyl ketone was observed when 0.5 ml of 4N hydrochloric acid was used.

The plot of data points for the calibration of the germanium and the least squares linear regression analysis for a straight line was carried out using an Apple II computer. The calibration curve was linear over the range of 1 to 10  $\mu\text{g}$  of germanium when 1 ml of 4N hydrochloric acid was used (see Figure 26), and linear over the range of 0.5 to 7.5  $\mu\text{g}$  of germanium when 0.5 ml of 4N hydrochloric acid was used (see Figure 27).

#### B. Use of Drying Agent

Two types of drying agent were used: (a) anhydrous sodium sulphate and (b) molecular sieve type 3A.

Anhydrous sodium sulphate was proved to be more efficient since disintegration of molecular sieve by the solvent was observed. Drying the extract with anhydrous sodium sulphate did not reduce the blank level. This was thought to be due to formation of molybdoheteropoly acids of interferents, such as arsenic which is present in the hydrochloric acid. Therefore, AristaR 35% hydrochloric acid with low concentration of arsenic content was used to reduce the



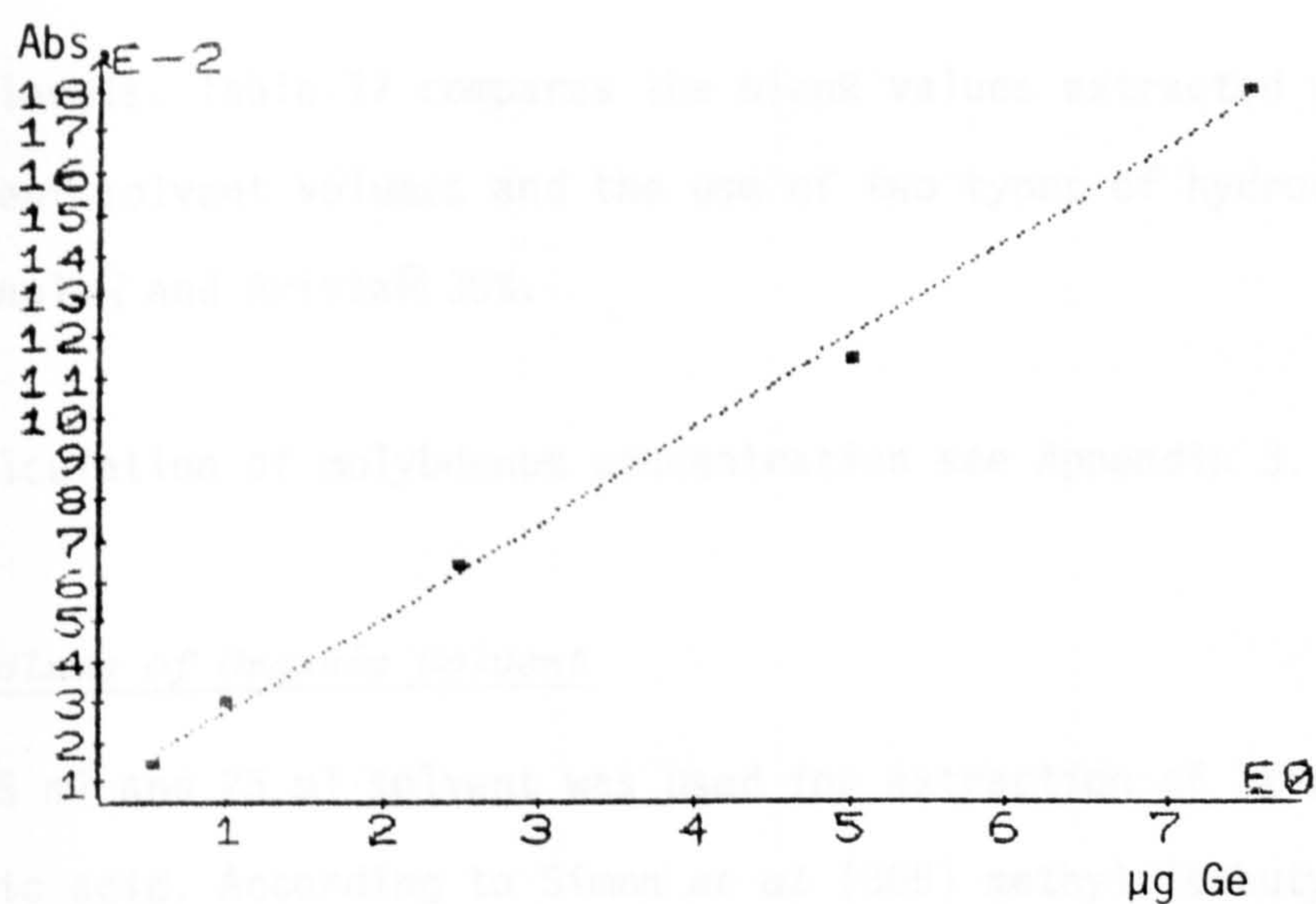
#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .043532833 X + .0488292683$$

NUMBER OF POINTS	= 5
SLOPE	= .043532833
INTERCEPT	= .0488292683
CORRELATION COEFF.	= .999655815
STANDARD DEVIATION	= 4.17035793E-03

X	Y
1	.088
2.5	.159
5	.273
7.5	.374
10	.482

FIGURE 26: Calibration curve of 12-molybdo germanic acid  
Formation of 12-molybdo germanic acid using  
1 ml of 4M HCl



#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .0230437317 X + 4.35568526E-03$$

NUMBER OF POINTS = 5  
 SLOPE = .0230437317  
 INTERCEPT = 4.35568526E-03  
 CORRELATION COEFF. = .99853635  
 STANDARD DEVIATION = 3.65494195E-03

X	Y
.5	.014
1	.03
2.5	.064
5	.114
7.5	.18

FIGURE 27: Calibration curve of 12-molybdogermanic acid.  
 Formation of 12-molybdogermanic acid using 0.5 ml  
 of 4M HCl.

blank levels. Table 17 compares the blank values extracted with different solvent volumes and the use of two types of hydrochloric acid AnalalR and AristaR 35%.

For calculation of molybdenum concentration see Appendix 3.

C. Volume of Organic Solvent

Both 45 ml and 25 ml solvent was used for extraction of 12-molybdo-germanic acid. According to Simon *et al* (305) methyl isobutyl ketone is the best extractant and di ethyl ether-pentan-1-ol (1+5) is the best alternative.

Investigating those two solvents, it was found that it was best to use methyl isobutyl ketone for graphite rod electrothermal atomization, since it was much easier to transfer the injected volume without losing solvent by evaporation during transfer. Because of the high vapour pressure of the diethyl ether-pentan-1-ol, precise volumes cannot be injected into the cavity of the graphite rod.

Table 18 compares the sensitivities of the calibration graphs for two different solvent volumes.



Solvent Vol (ml)	Drying Agent	Abs.	ppm Mo	Acid Type
25	-	0.112	~1.0	AnalaR
45	-	0.042	~0.4	"
25	Mol. Sieve	0.103	~1.0	"
25	-	0.085	0.85	AristaR 35%
25	Anh. Na <sub>2</sub> SO <sub>4</sub>	0.02	0.2	"

TABLE 17: Compares Blank Values for Different Solvent Volume, Drying Agent and Acid Types

Solvent Vol (ml)	Blank Abs.	Cal. Range (μg)	C.C.	Sensitivity (μg)	Condition
25	0.112	1 - 10	0.998	$8.8 \times 10^{-2}$	Not dried
45	0.04	2.5 - 7.5	0.999	0.132	"

TABLE 18: Compares the Sensitivities of the 12-molybdo germanic Acid Extracted with Two Different Solvent Volumes

#### 5.4.2 Extraction of 12-Molybdo germanic Acid and Subsequent Carbon Rod Electrothermal Atomization of Germanium

The method involves using conditions obtained from previous experiments for the formation and extraction of 12-molybdo germanic acid.

##### Instrument:

As experiment 4.3.

##### Reagents:

As experiment 5.4.

##### Drying agent

As experiment 2.6.3.1.

All acid solutions were prepared from concentrated (AristaR 35%) hydrochloric acid.

##### Solvent:

Methyl iso butyl ketone.

##### Procedure:

As experiment 5.4.1, except that for formation of 12-molybdo germanic acid, 1 ml of 4M hydrochloric acid was used, and for extraction and drying the solvent, 45 ml of methyl iso butyl ketone and anhydrous sodium sulphate was used respectively.

### Results:

Plots of the data points of the calibration graph of the germanium and least squares linear regression analysis for a straight line was carried out using an Apple II computer. Figures 28 and 29 are calibration curves of 12-molybdogermanic acid when it is dried and undried respectively.

The sensitivity (amount for 1% absorption) and the limit of detection based on 10 determinations of 5  $\mu\text{g}$  of germanium were 0.185  $\mu\text{g}$  and 0.3  $\mu\text{g}$  of germanium respectively.

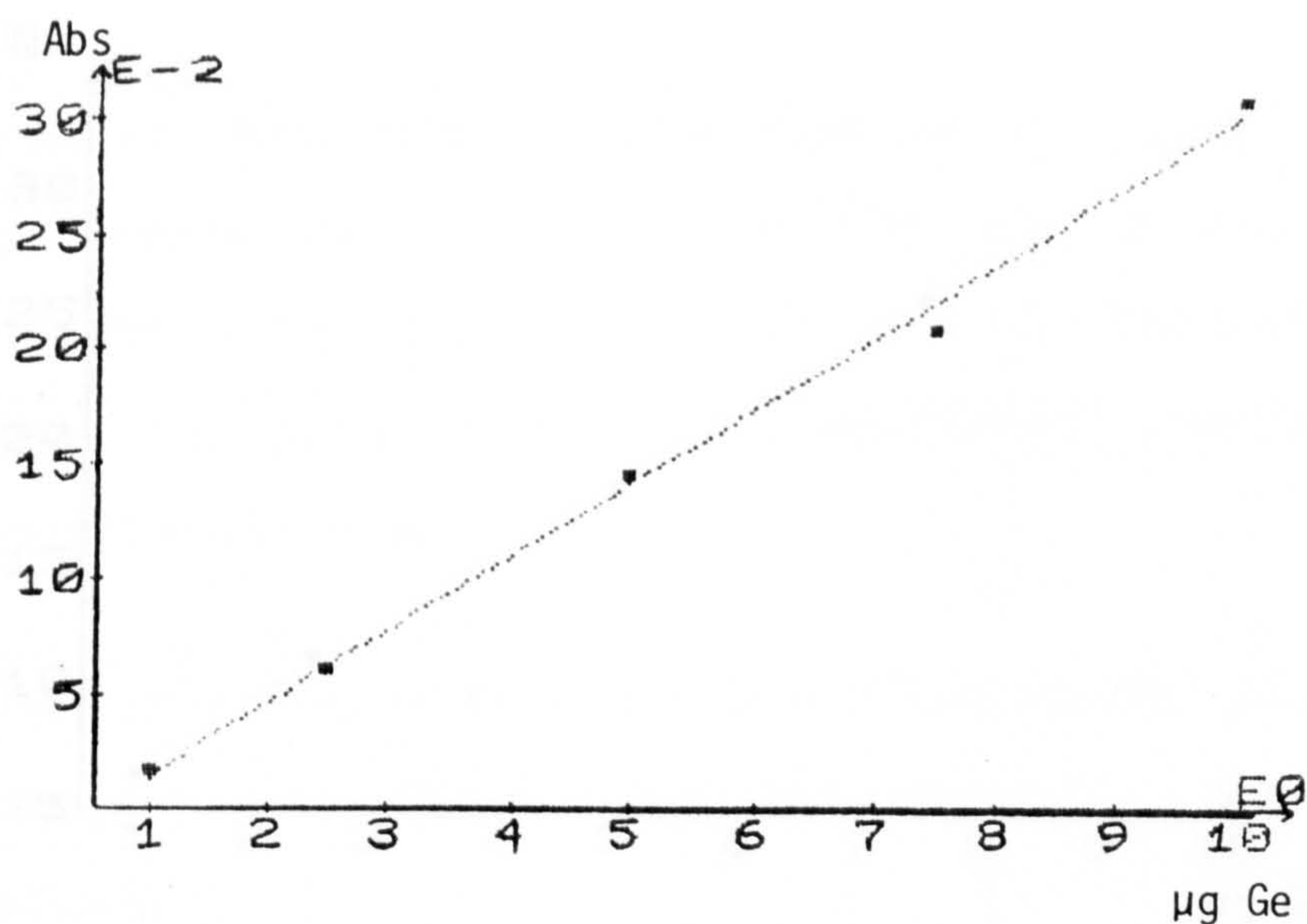
The relative standard deviation of 10 replicate atomizations of the solution corresponding to 5  $\mu\text{g}$  of germanium transferred to the rod was 7.4%.

### Discussion:

Most of the reported methods for determination of germanium are based on direct measurement using a germanium hollow cathode lamp.

Flame methods are the least sensitive method compared with hydride generation and electrothermal atomization techniques. The lowest limit of detection of Ge by the use of flame was reported as 0.2 ppm.

Volatile hydride generation techniques for direct determination of germanium are more sensitive. The limit of detection of 0.5  $\mu\text{g}$  of



#### RESULTS OF LEAST SQUARES CALCULATION

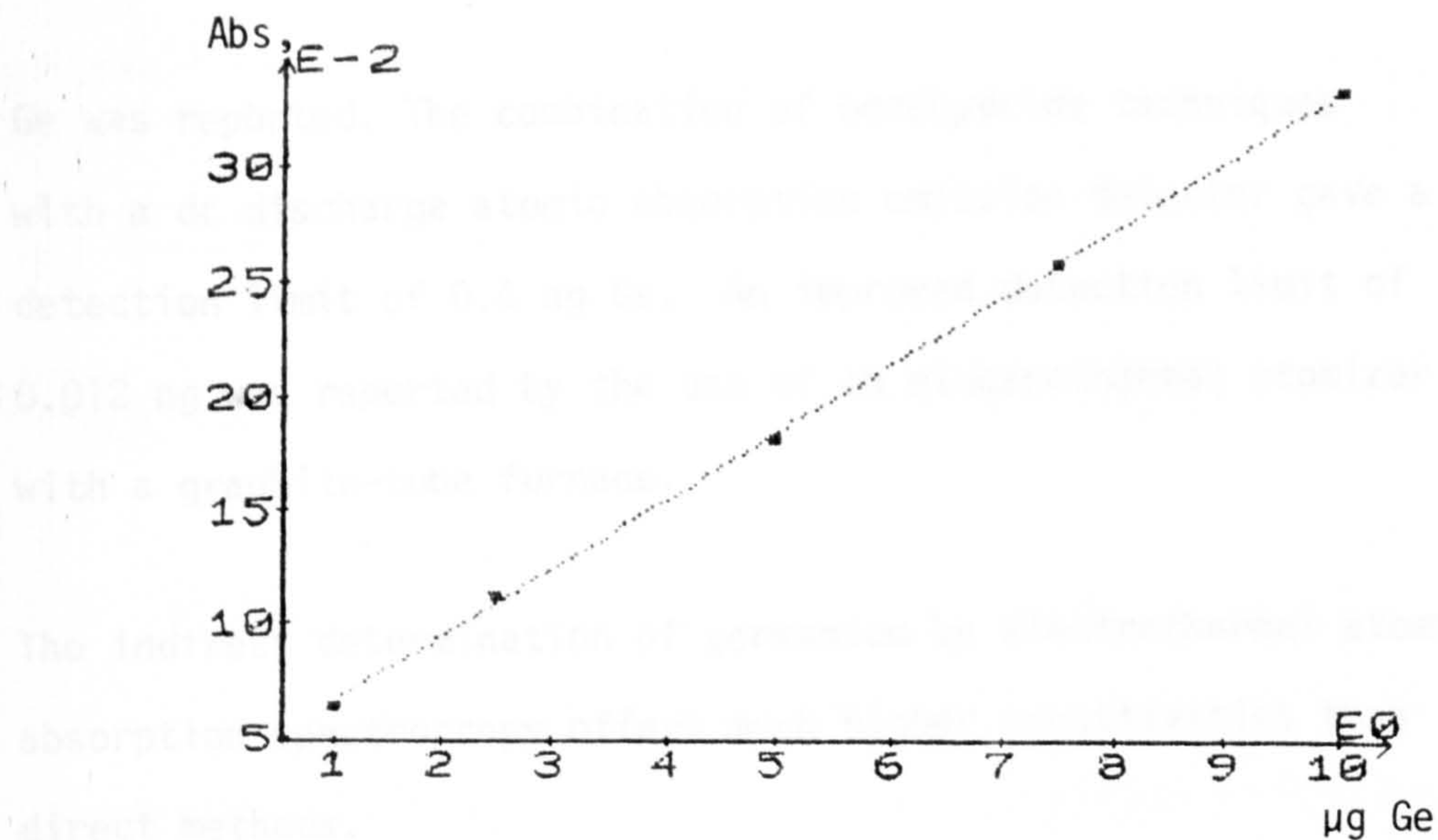
$$Y = .0318724203 X + -.0185365853$$

NUMBER OF POINTS	= 5
SLOPE	= .0318724203
INTERCEPT	= -.0185365853
CORRELATION COEFF.	= .997828379
STANDARD DEVIATION	= 7.68004649E-03

X	Y
1	.016
2.5	.06
5	.144
7.5	.208
10	.308

FIGURE 28: Calibration curve of 12-molybdogermanic acid for dried organic phase





#### RESULTS OF LEAST SQUARES CALCULATION

$$Y = .029934334 X + .0343414635$$

NUMBER OF POINTS = 5  
 SLOPE = .029934334  
 INTERCEPT = .0343414635  
 CORRELATION COEFF. = .999709401  
 STANDARD DEVIATION = 2.63487042E-03

X	Y
1	.063
2.5	.113
5	.181
7.5	.258
10	.335

FIGURE 29: Calibration curve of 12-molybdo germanic acid for undried organic phase

Ge was reported. The combination of borohydride techniques with a dc discharge atomic absorption emission detector gave a detection limit of 0.4 ng Ge. An improved detection limit of 0.012 ng was reported by the use of an electrothermal atomizer with a graphite-tube furnace.

The indirect determination of germanium by electrothermal atomic absorption spectroscopy offers much higher sensitivities than direct methods.

Determination of picogram amounts (7.5 pg) of germanium has been reported. A sensitivity of 0.185  $\mu\text{g}$  was obtained from the method which was used in this study. However it can be improved if a more selective solvent is used.

## CHAPTER 6

### DETERMINATION OF PHOSPHORUS AS 12-MOLYBDOPHOSPHORIC ACID BY FLOW INJECTION-SOLVENT EXTRACTION WITH SUBSEQUENT INDIRECT FLAME ATOMIC ABSORPTION SPECTROMETRY

#### 6.1 Introduction

Liquid-liquid extraction of metal ions from aqueous samples into an organic solvent is frequently used in connection with flame atomic absorption spectrometry (336). It is used both as a pre-concentration method and for separation of the analyte from an interfering matrix.

The other important uses of solvent extraction are as follows:

- a) The technique can be applied to the determination of non-metals by AAS (see also Chapters 1 and 2).
- b) In speciation studies where solvent extraction techniques may be applied to selectively extract an element in each of its oxidation states; e.g. tellurium (IV) may be separated from tellurium (VI) by extraction of the former into a 2:1 mixture of ethyl acetate 4-methyl pentan-2-one (337).
- c) Inorganic species which form thermally stable, volatile chelated compounds may be introduced into a flame by direct volatilization of the chelates. An electrically heated vaporization chamber has been used to introduce acetyl acetonates, trifluoroacetyl-

acetates and hexafluoromethyl acetates of Cu(II), Cr(VI) and Fe(III) into a flame (338).

However, the existing applications of solvent extract in flame spectrometry are limited to:

- a) Multielement extraction system. Sachdev and West (239) employed an <sup>ethyl</sup>  $\alpha$  -proprionate solution of diphenylthiocarbazone, 8-hydroxyquinoline and pentane-2, 4-dione for the extraction of Al, Be, Cd, Co, Cu, Fe(II), Pb(II), Ni, Ag and Zn prior to determination by AAS.
- b) Application of solvent extraction and the use of the solvent as a fuel. Hildon and Sully (365) extracted gold into 4-methyl pentan-2-one from hydrochloric acid solution and the organic solvent was burned with air as a support gas.
- c) As a preconcentration step. Several hundred examples of solvent extraction usages are summarized by Cresser (336).

One of the factors responsible for the widespread popularity of solvent extraction in analytical flame spectrometry lies in the simplicity of the additional apparatus required once a flame spectrometer is already available, particularly if manual extractions are to be carried out.

Conventional separating funnels are usually employed for solvent extraction. However the drawbacks of manual extractions are as



follows: extended or extra human effort, separation and concentration procedures are generally time consuming, the large volume of reagents required may introduce errors in the analytical results due to the reagent, container, or atmospheric contamination or due to incomplete recovery of the element in the separation. To overcome these difficulties automated solvent extraction systems may be applicable.

A separation technique in which the recovery of the desired species is frequently incomplete, can give highly reproducible automatic performance when accurately sequenced.

Automated solvent extraction is carried out in a closed system; materials which are toxic or unstable in air can be more conveniently analyzed than by a manual method of automated solvent extraction. Other advantages and disadvantages of automated solvent extraction are given in Chapter 1.

Automation of solvent extraction by the use of flow injection analysis was introduced in 1978 (23, 340). Recently, solvent extraction-flow injection analysis has been used in post column detection systems for liquid chromatography (341-345), for sample preconcentration prior to atomic absorption spectrometry (24, 346-349) and for multiple extraction (350, 351).

## 6.2 Review of Solvent Extraction - Flow Injection System

Three physical parameters are essential to automated solvent extraction-flow injection analysis systems. These are: phase segmentation (phase combination PC), extraction and phase separation PS.

Phase segmentation involves dividing the continuous aqueous and organic phase stream into a single stream of alternating segments. Modified  $A_8$  T-connectors (see Figure 31) (23, 352-355) and various configurations of glass capillary tubes (356-357) have been used for phase segmentation. The extraction process requires that the segmented phases be allowed to remain in contact while the analyte approaches a state of thermodynamic equilibrium by partitioning between two phases. This process is achieved while the segmented phases are pumped through an extraction coil. Finally, the phase separation process involves a segmentation and recombination of the segmented phases. During this process the unwanted phase is sent to waste while the other phase is pumped through the detector. Phase separation is usually accomplished by the use of a chamber type (see Figure 34) (340, 358) which relies on gravity to separate the phases, a T-piece type which employs gravity with or without some sort of phase guide made of material wetted by one phase, but not the other (23, 352-354, 359, 360), or a membrane type which depends upon the selective permeability of a porous membrane to the phase which wets the membrane material (24, 346, 349, 355-357, 361, 362).

Karlberg and Thalender described an FIA extraction manifold as shown in Figure 30 for the analysis of caffeine samples (23). The aqueous phase containing the sample zone is divided into small segments by an organic phase fed into it via a modified standard A8 T-connector (see Figure 31), so that a regular pattern of the two phases is obtained. The aqueous segments acquire an ellipsoid shape (see Figure 33) in the Teflon extraction coil. The wall drag causes turbulence within the segments, which creates conditions for fast extraction. To separate the two phases, the segmented stream is passed through another T-connector (see Figure 32), one leg of which is lined with Teflon fibres and directed downwards towards the flow cell. The organic phase preferentially follows the Teflon fibre route, with the aid of differential pumping the aqueous and excess organic phase are forced through the upper leg to waste, and no aqueous phase is taken into the flow cell. This technique has also been applied to the analysis of codeine (352) and thiamin (353) in pharmaceutical products. Typical assay times are 20 to 60s.

Bergamin *et al* (340) used a more conventional approach, sample plus reagent merge with solvent and flow together in a coil of tubing of 0.85 mm bore and phases separate in a conical 0.11 ml chamber (see Figure 34). The upper or lower phase, as required, is drawn through the colorimeter flow cell at a suitably slower rate. They achieved an assay rate of 30 samples  $h^{-1}$  for molybdenum determination by the thiocyanate method. Kawase *et al* (356,357) reported an alternative

flow injection analysis extraction system involving a phase combination which consisted of two inlets located at 45° relative to one another which generated a regular alternating pattern of organic and aqueous phases, and a phase separator provided with a stirring device based on a poly(tetrafluoroethylene) membrane, permeable to chloroform but impermeable to the aqueous phase. Anionic (356) and cationic (357) surfactants were determined as an ion-pair with methylene blue and orange 11 respectively.

Klinghoffer *et al* (363), investigated the extraction of lead solution by dithizone in tetrachloromethane at different pH values, using a T-piece separator into which was inserted a thin band of Whatman phase-separating paper facilitating the division of the stream. However, the phase separator used by Burguera (364) for the determination of copper by extraction with dithizone, makes use of the difference in density of two phases and employs phase-separating papers to complete the separation of the phases. The aqueous phase, after being forced upwards passes to waste through a hydrophilic phase-separating paper disc (Whatman, cellulose, 10 mm diameter) held between two washers. The organic phase carried to the flow cell, after passing through a hydrophobic phase-separating paper disc (silicon-treated Whatman paper, 10 mm diameter) is also held between two washers (see Figure 35). Since the key to rapid on-line solvent extraction is an efficient means of phase separation, extraction-flow injection analysis may be categorized by the type of separation employed.



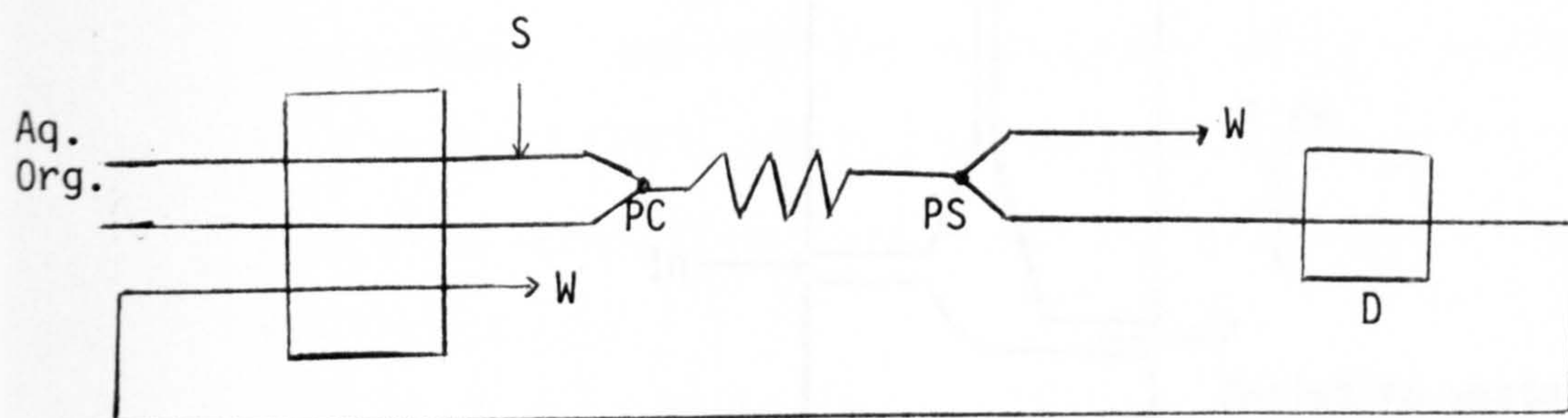


FIGURE 30: Solvent extraction manifold based on FIA. Phase combination PC, phase separation PS, Sample S, Waste W, and detector D

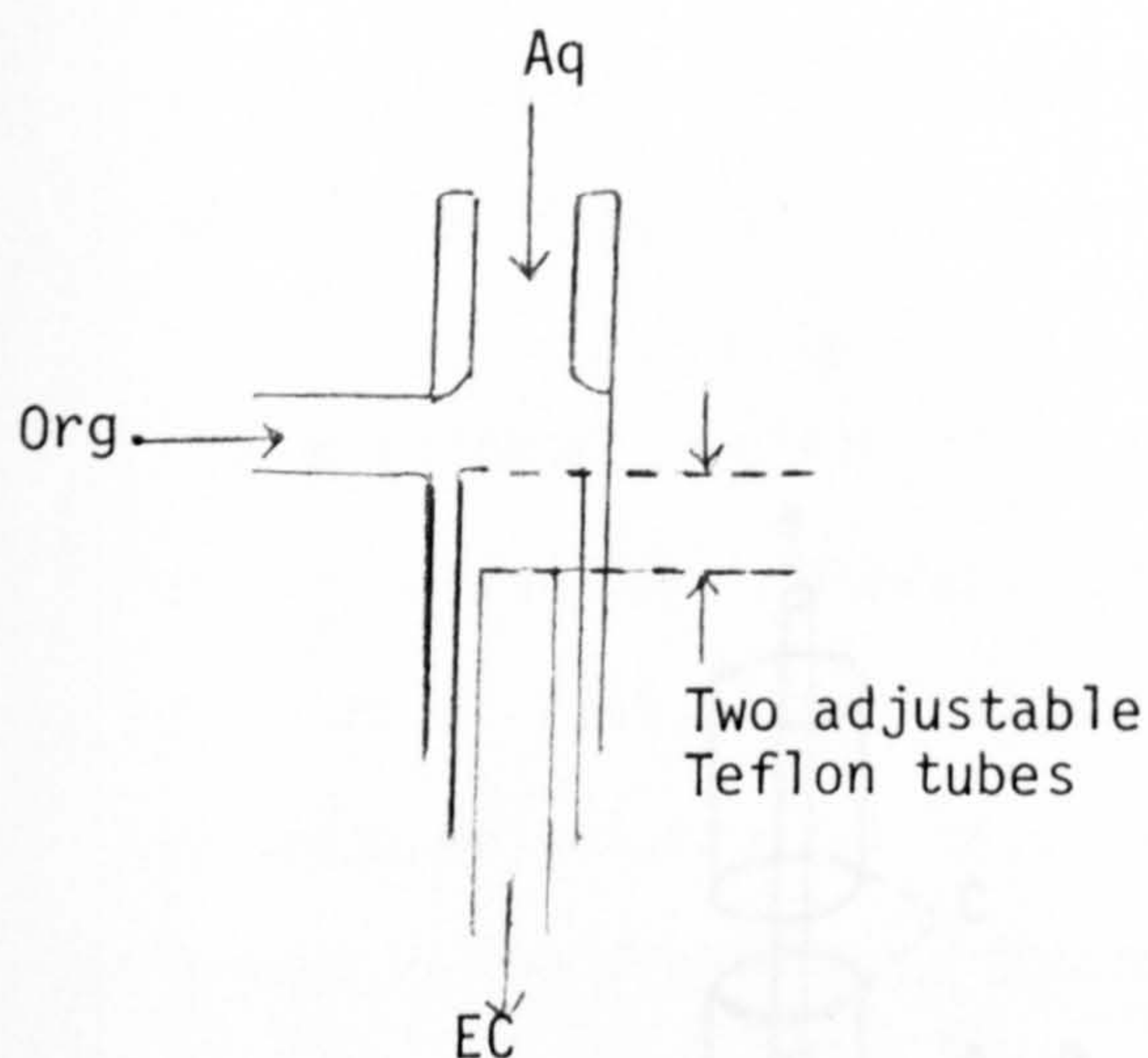


FIGURE 31: Phase segmentor design of  $A_8$  T-connector

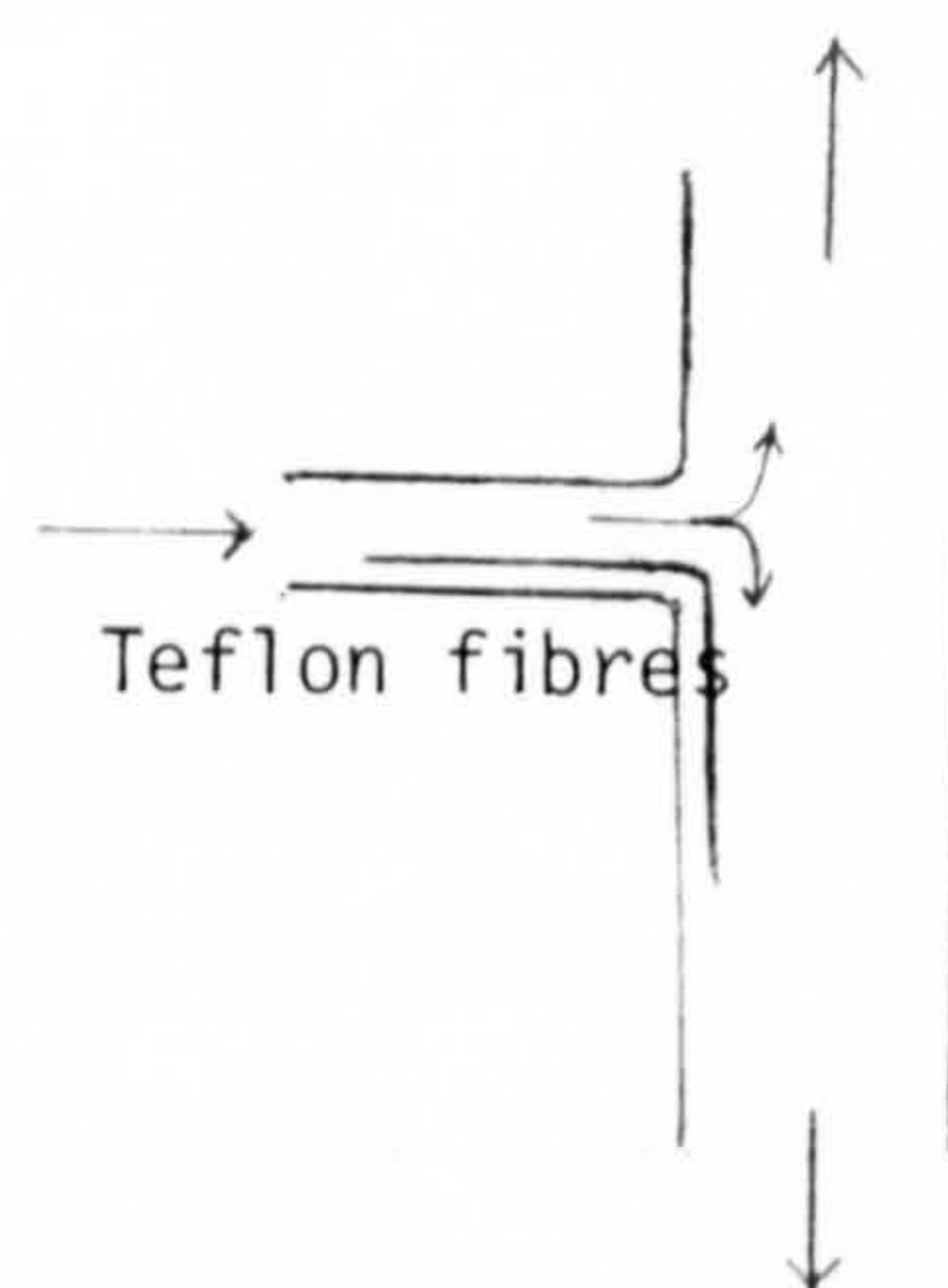


FIGURE 32: Phase separator design of T-piece type

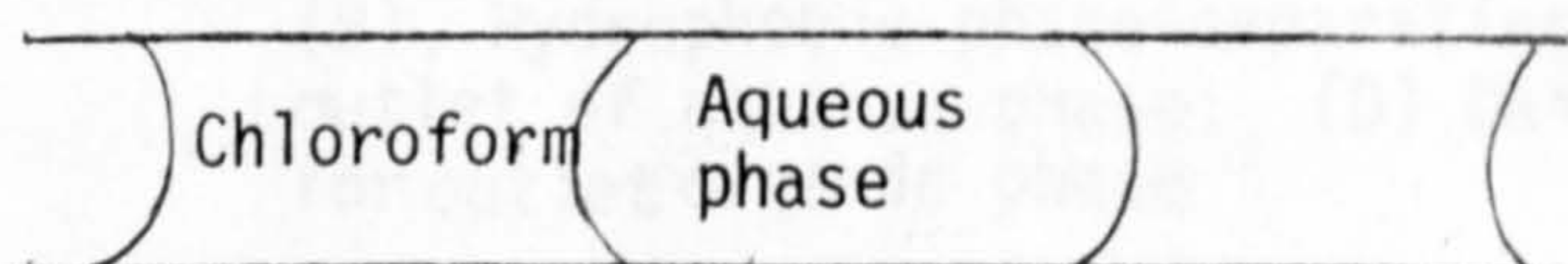


FIGURE 33: Segmented flow pattern in extraction coil (EC)

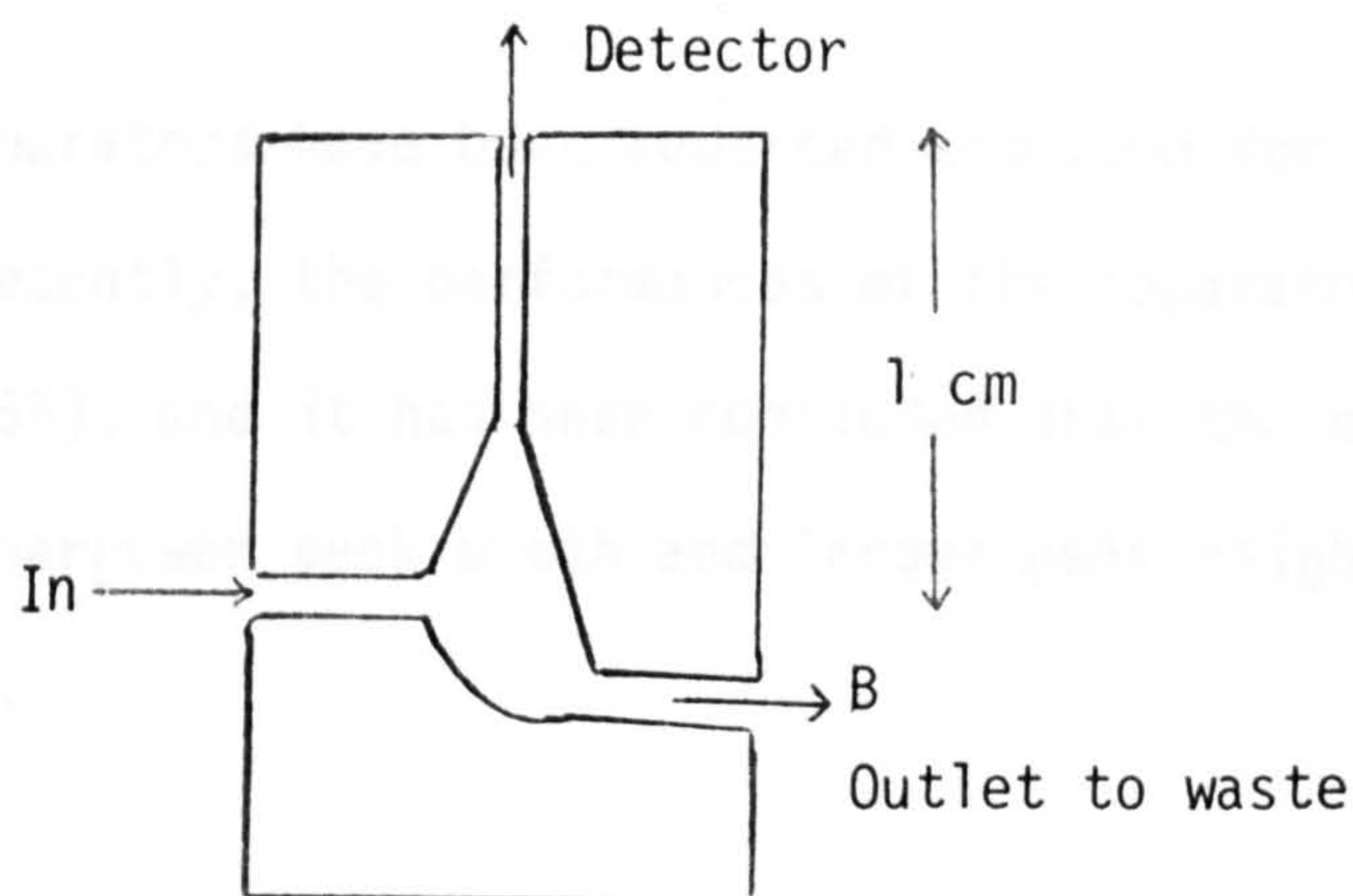


FIGURE 34: Phase separator design of chamber type

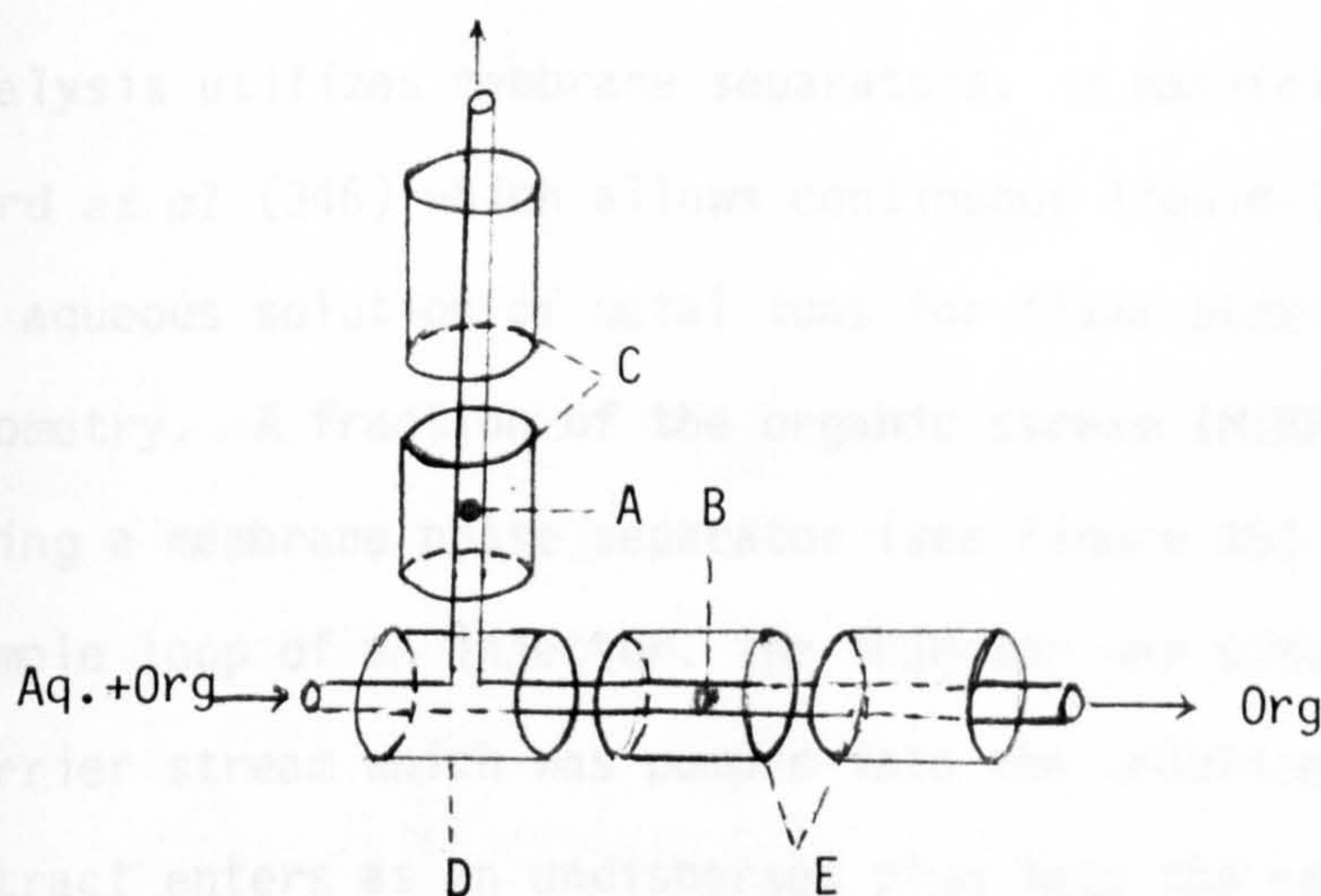


FIGURE 35: Phase separator, (A) Hydrophilic phase-separating paper; (B), Hydrophobic phase-separating paper; (C) joints for outlet of aqueous phase; (D) Daiflon body; (E) joints for outlet organic phase



Several phase separators have been reported and used for many applications. Recently, the performances of the separators have been compared (355), and it has been concluded that the membrane type gives much narrower peak width and larger peak height than the T-piece type.

The working principle of the membrane phase separator used by Nord *et al* (24, 346, 347, 355) is as follows: A PTFE membrane with polyethylene backing is sandwiched between two pieces of perspex, each of which has a groove facing the membrane. The inlet and outlet bores are 0.8 mm i.d. The separator was positioned as shown in Figure 36, when the organic solvent was less dense than water and was inverted when solvent denser than water was used.

The most recent applications for solvent extraction-flow injection analysis utilizes membrane separators. A manifold was described by Nord *et al* (346) which allows continuous liquid-liquid extraction of aqueous solution of metal ions for flame atomic absorption spectrometry. A fraction of the organic stream (MIBK) was separated using a membrane phase separator (see Figure 36) and fed into the sample loop of an injector. The injector was situated in an aqueous carrier stream which was pumped into the nebulizer. The organic extract enters as an undispersed plug into the carrier when the valve is actuated. A preconcentration factor of 5.5 resulting in a corresponding sensitivity increase was reported for aqueous samples, however extraction of metal ions in aqueous samples into 4-methyl-2-pentanone with ammonium pyrrolidine dithiocarbamate as an extracting

agent resulted in an increase in sensitivity of 15-20 times for Cu, Ni, Pb and Zn, using the same phase separator (347).

A new automated extraction system specially designed for use with the graphite furnace was reported recently (24). The chemistry of the system is based on the formation of hydrophobic complexes between metals and mixtures of dithiocarbamates. These complexes are then extracted into an organic solvent. After separation, the organic phase is segmented with an aqueous mercury solution. Mercury forming stronger complexes with dithiocarbamates, displaces the metals of interest from their complexes. The metals are subsequently transferred into the aqueous solution. Two phase separators were used. The first separator was of the design described by Nord *et al* (355), the second was a glass T-piece. Metals such as Cd, Cu, Fe, Pb, Ni and Zn could be concentrated 25-30 fold with this type of system.

Imasaka *et al* (349) used a different type of membrane phase separator (see Figure 37), and reported an improved sensitivity and selectivity of gallium with lumogallion (4-chloro-6(2,4-dihydroxy phenyl azo)-1-hydroxy benzene-2-sulphonic acid) by flow injection analysis based on solvent extraction.

A phase separator described by Fossy and Cantwell (363) incorporates both a hydrophobic Teflon membrane and a hydrophilic paper membrane, thus permitting the simultaneous monitoring of the absorbances of both the organic and the aqueous phase. Dramamine motion sickness



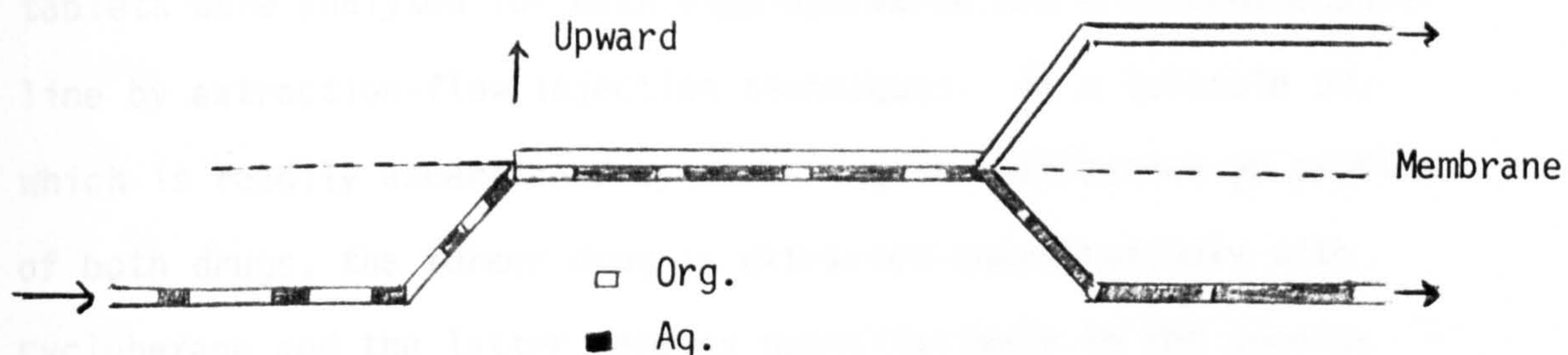


FIGURE 36: Working principle of the membrane phase separator

## PRACTICAL EXPERIMENTS

### 5.3 Indirect Spectrophotometric Determination of Phosphate

#### Flow Injection-Solvent Extraction

##### 5.3.1 Chemical Optimization of the Method and Calibration for Phosphate

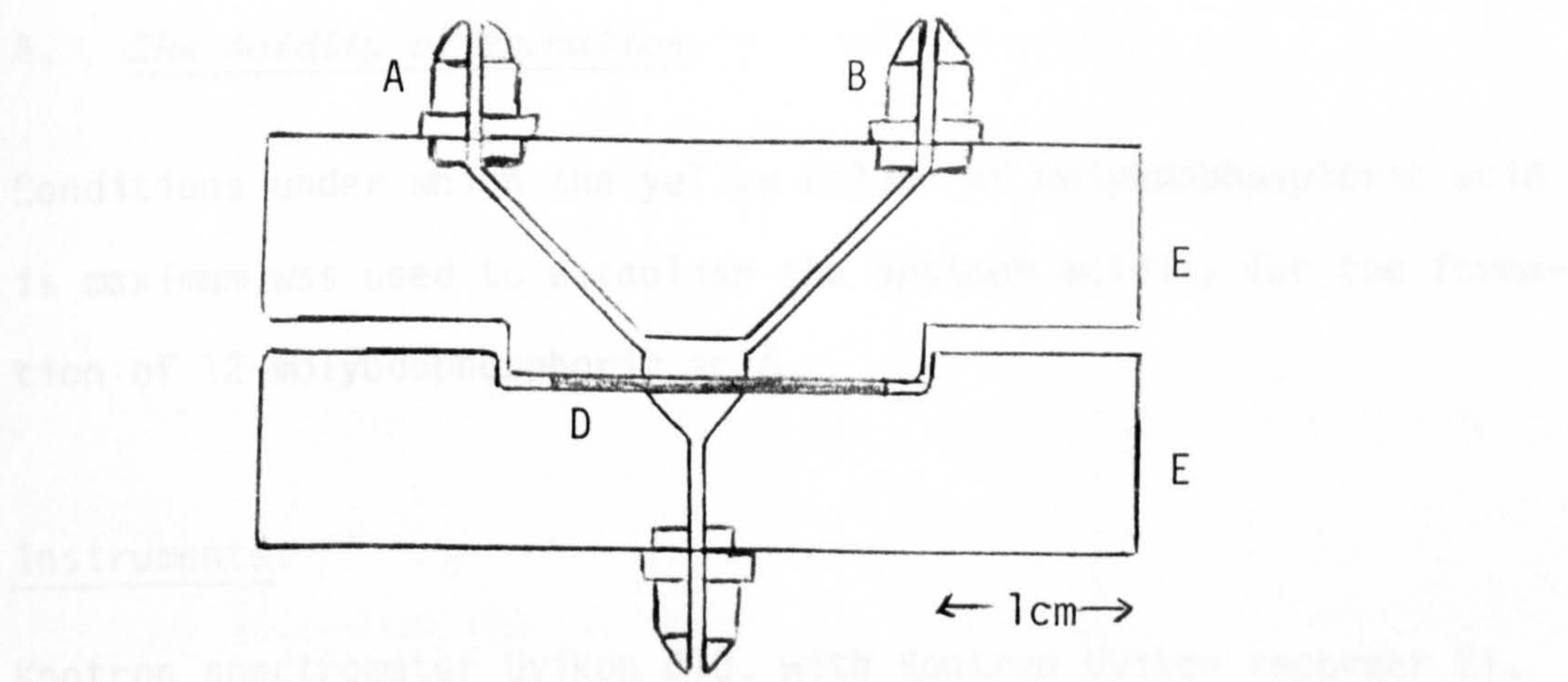


FIGURE 37: Membrane phase separator design.  
 (A) joint for inlet of segmented;  
 (B) joint for outlet of aqueous phase;  
 (C) joint for outlet of organic phase;  
 (D) PTFE membrane;  
 (E) Daiflon body.

tablets were analysed for both diphenhydramine and 8-chlorotheophylline by extraction-flow injection techniques. At a suitable pH, which is readily ascertained by measuring the extraction-pH profile of both drugs, the former drug is extracted quantitatively with cyclohexane and the latter remains quantitatively in the aqueous buffer phase.

## PRACTICAL EXPERIMENTS

### 6.3 Indirect Spectrophotometric Determination of Phosphorus by Flow Injection-Solvent Extraction

#### 6.3.1 Chemical Optimization of the Manifold and Calibration for Phosphorus

##### A. The Acidity of Formation

Conditions under which the yellow colour of molybdophosphoric acid is maximum was used to establish the optimum acidity for the formation of 12-molybdophosphoric acid.

##### Instruments:

Kontron spectrometer Uvikon 810, with Kontron Uvikon recorder 21.

A manifold for extraction and formation of 12-molybdophosphoric acid (see Figure 38), which consisted of the following parts: two peristaltic pumps (a) Gilson pump for pumping carrier stream reagent and acid solution 6N, (b) Ismatec pump model 840 for solvent displacement.

A Rheodyne type 5020 rotary injector valve with an external loop volume of 200  $\mu$ l.

PTFE tubing with (0.71 mm bore) was used for the mixing coil (5m) and for extracting coil (3m) in length.

Phase segmentor (see Figure 38c) and mixing chamber (see Figure 38b) for solvent and acid solution 6M were home-made glass.

A displacement bottle for organic solvent (n-butyl acetate).

Home-made glass column 6 x 1 cm in dimension for drying the solvent.

The membrane phase separator from Tecator consisted of PTFE tape, rolled like a sausage, and backed with PTFE membrane (controlled porosity). This is put round one of the mechanically drilled channels (2 cm long with 0.1 cm i.d) and sandwiched between two PVDF blocks (see Figure 39). The two blocks were compressed by two external metal plates and bolted together with six bolts. The mixed aqueous and organic phase enters at port 1 and the aqueous phase comes out from port 2, and the organic phase is removed at port 3 after which it is dried and collected.

#### Reagents:

Ammonium molybdate 10%

As experiment 2.4.2.

Stock phosphorus solution, 50 ppm

As experiment 2.4.2.



Drying agent

The mixture was prepared by mixing 0.2g of antibumping granules with 0.7g of anhydrous sodium sulphate.

Mixed reagent

A series of solutions with different molarities were prepared by diluting 5 ml of 10% ammonium molybdate solution and 0.85, 0.9, 0.95 and 1 ml of 6M HCl to 50 ml.

Hydrochloric acid, 6M

The solution was prepared by diluting 50 ml of concentrated hydrochloric acid to 100 ml.

Solvent:

n-butyl acetate.

Procedure:

Initial set up of the manifold was based on Nord *et al* (23) principle. The manifold was then modified to perform formation and extraction of 12-molybdophosphoric acid based on manual extraction.

200  $\mu$ l of standard phosphorus solution 40 ppm was injected into a carrier stream of mixed reagents, which reacted in the mixing coil (a) to form 12-molybdophosphoric acid. The organic solvent segmented with acid solution in the mixing chamber (b) was merged at point (c), after which both phases passed through extracting coil (d).



The organic phase was separated from the aqueous phase at point (e) and carried through the drying column (f) to be collected and measured spectrophotometrically.

The flow rate of the solvent was  $0.5 \text{ ml min}^{-1}$  and was collected over 3 minutes. For spectrophotometric measurements, replicate extraction of 200  $\mu\text{l}$  standard phosphorus solution 40 ppm was carried out, collected for 6 minutes.

Overall, formation and extraction of 12-molybdophosphoric acid was carried out within 8 minutes.

### Results:

The 12-molybdophosphoric acid exhibits absorption in the ultra-violet region of the spectrum at 310 nm. Acid solution containing 0.95 ml of HCl gave the maximum absorption (see Figure 40).

### B. Ammonium Molybdate Concentration

Optimum concentration of molybdate is required to ensure the formation of 12-molybdophosphoric acid.

### Instruments:

As experiment 6.3A.

### Reagents:

As experiment 6.3A.

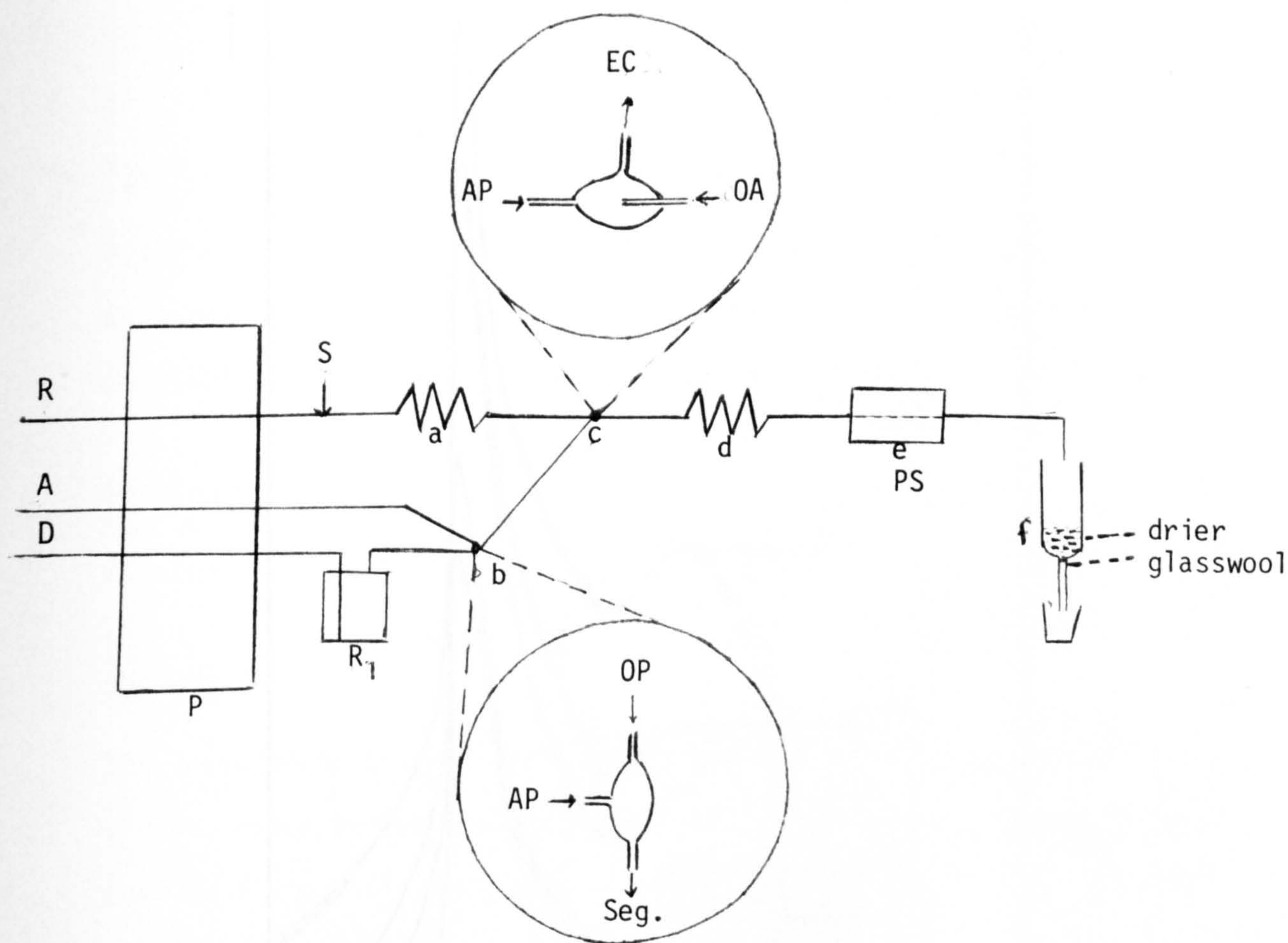


FIGURE 38: Automated solvent extraction-flow injection manifold  
 (R) reagent, (A) acid solution 6N, (D) aqueous stream,  
 (P) pump, (R<sub>1</sub>) solvent replacement bottle, (S) sample,  
 (PS) phase separator, (EC) extraction coil, (AP) aqueous  
 phase, (OA) organic and acid solution

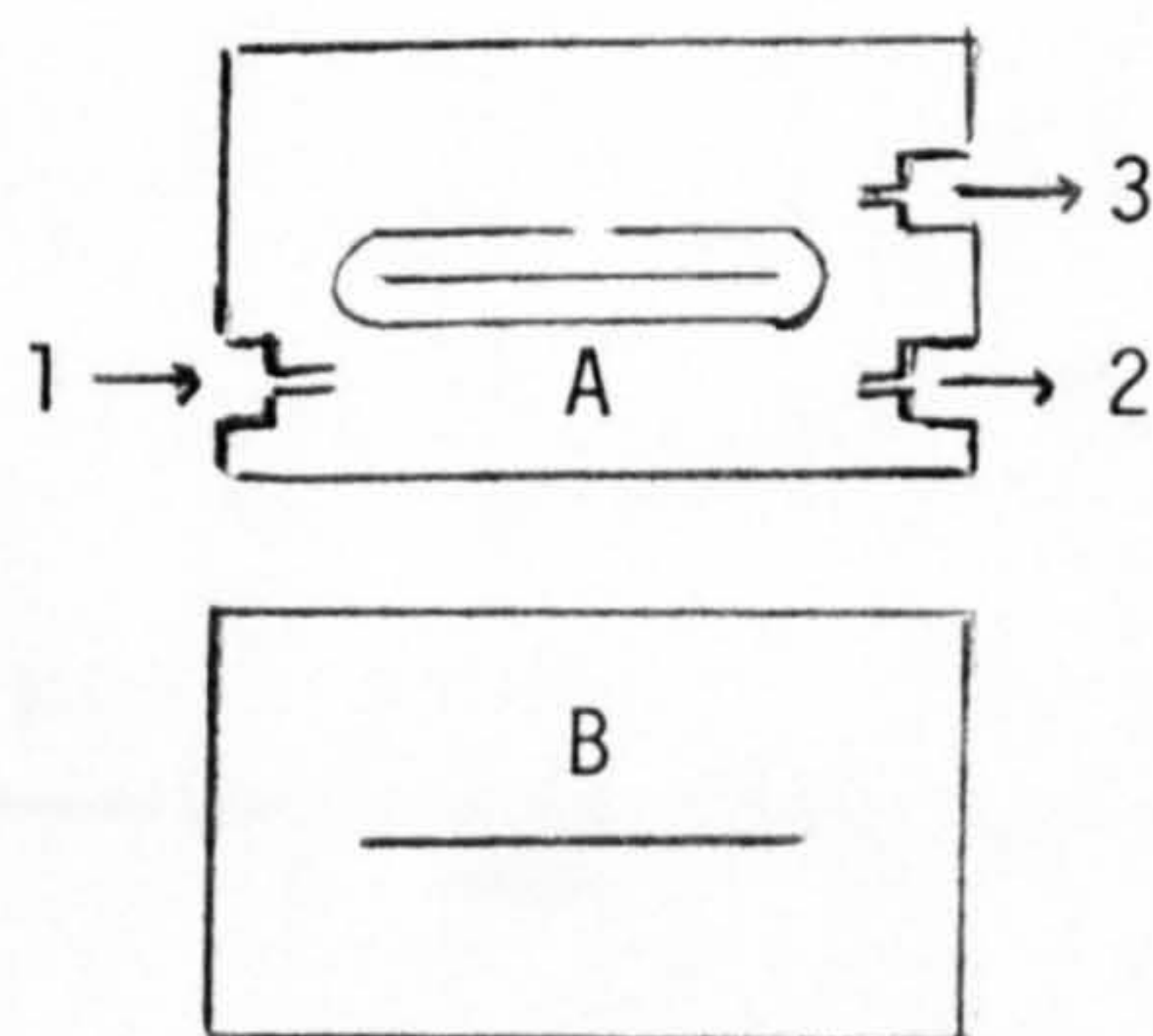


FIGURE 39: Membrane phase separator  
 (1) inlet of organic and aqueous phase  
 (2) outlet of aqueous phase  
 (3) outlet of organic phase.  
 (A) PTFE rolled tape, (B) channel at the centre of the  
 block with 0.1 x 2 cm in dimension



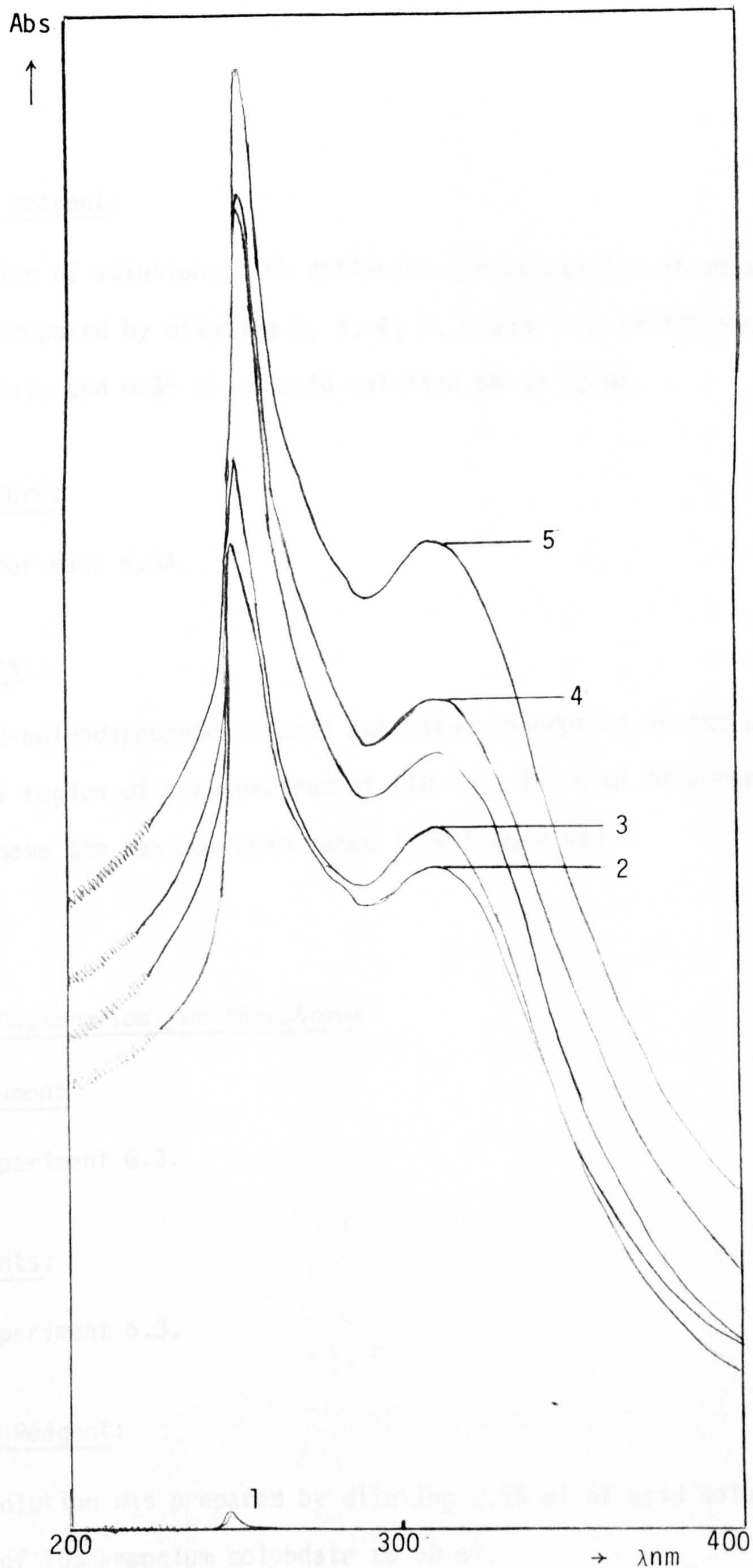


FIGURE 40: The effect of acidity on formation of 12-molybdophosphoric acid.

- |                          |                          |
|--------------------------|--------------------------|
| 1. Solvent vs solvent.   | 2. 0.102M HCl vs solvent |
| 3. 0.108M HCl vs solvent | 4. 0.12M HCl vs solvent  |
| 5. 0.114M HCl vs solvent |                          |

Mixed reagent:

A series of solutions with different concentrations of molybdate were prepared by diluting 2, 3, 4, 5, 6 and 7 ml of 10% ammonium molybdate and 0.95 ml of acid solution 6M to 50 ml.

Procedure:

As experiment 6.3A.

Results:

The 12-molybdophosphoric acid exhibited absorption in the ultra-violet region of the spectrum at 310 nm. The 6 ml of ammonium molybdate gave the maximum absorbance (see Figure 41).

C. Calibration for Phosphorus

Instrument:

As experiment 6.3.

Reagents:

As experiment 6.3.

Mixed Reagent:

The solution was prepared by diluting 0.95 ml of acid solution and 6 ml of 10% ammonium molybdate to 50 ml.



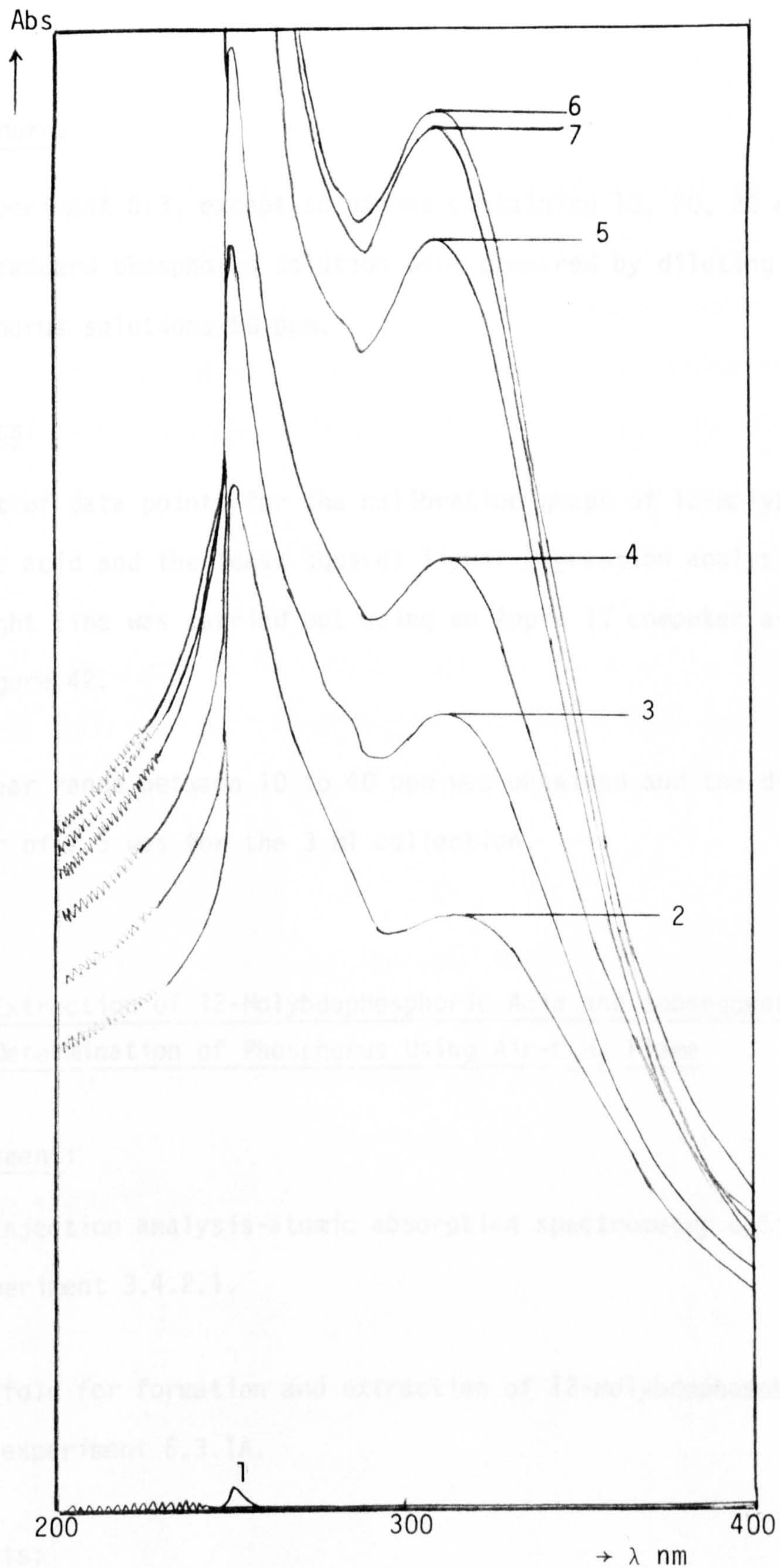


FIGURE 41: The effect of molybdenum concentration on the formation of 12-molybdophosphoric acid  
1. Solvent vs Solvent

Procedure:

As experiment 6.3, except solutions containing 10, 20, 30 and 40 ppm standard phosphorus solution were prepared by diluting stock phosphorus solutions 50 ppm.

Results:

A plot of data points for the calibration graph of 12-molybdophosphoric acid and the least squares linear regression analysis for a straight line was carried out using an Apple II computer as shown in Figure 42.

A linear range between 10 to 40 ppm was obtained and the dilution factor of 7.5 was for the 3 ml collection.

#### 6.4 Extraction of 12-Molybdophosphoric Acid and Subsequent Indirect Determination of Phosphorus Using Air-C<sub>2</sub>H<sub>2</sub> Flame

Instrument:

Flow injection analysis-atomic absorption spectrometry optimized as in experiment 3.4.2.1.

A manifold for formation and extraction of 12-molybdophosphoric acid as in experiment 6.3.1A.

Reagents:

As experiment 6.3.

### Procedure:

Formation and extraction of 12-molybdophosphoric acid using a manifold was as in experiment 6.3A. A volume (200  $\mu$ l) of the dried organic solvent was injected into the sample loop of the injector and was pumped into the nebulizer using an aqueous carrier stream. The flow injection-atomic absorption apparatus is shown in Figure 15.

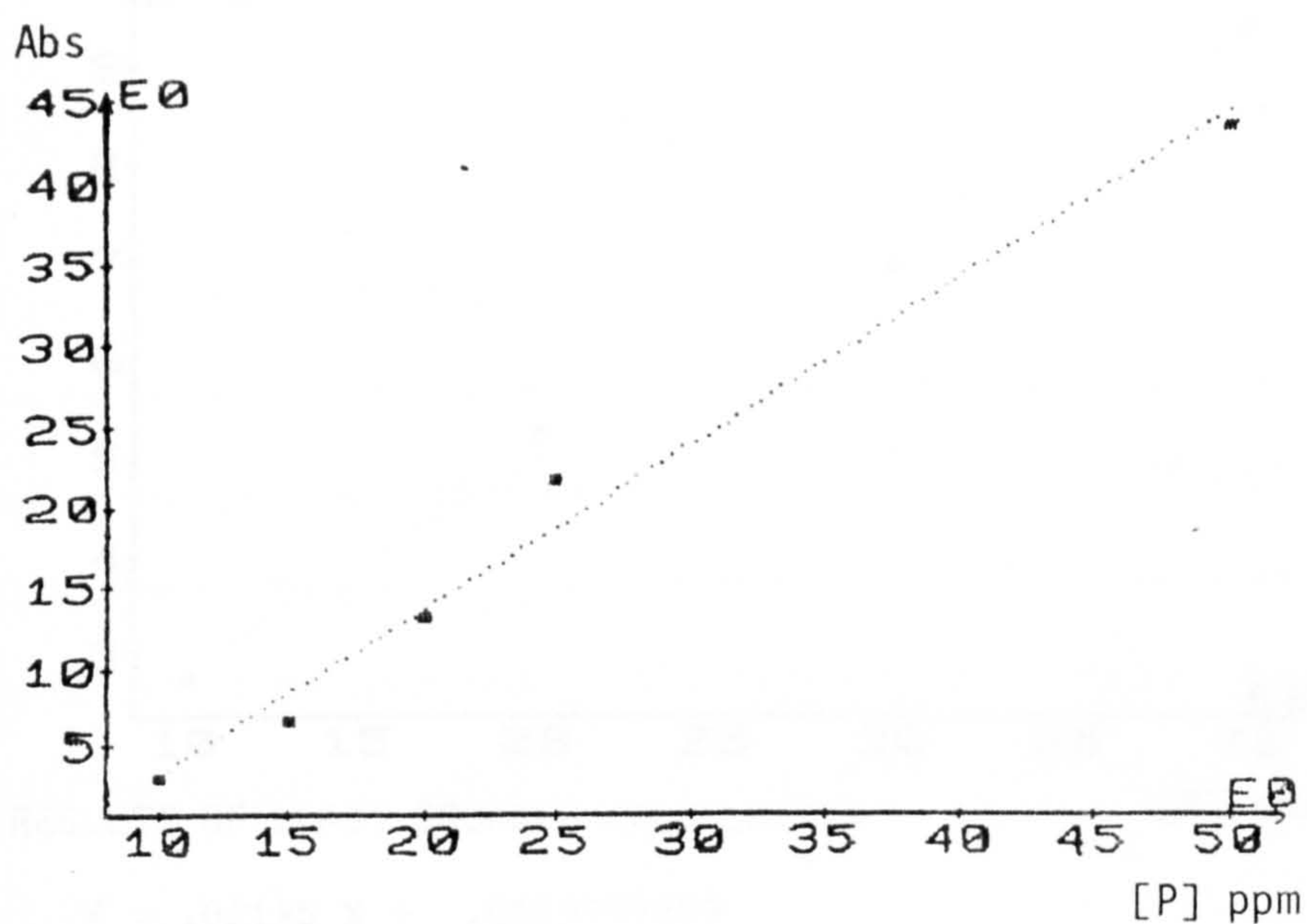
### Results:

A plot of data points for the calibration graph of the phosphorus and the least squares linear regression analysis for a straight line was carried out using an Apple II computer as shown in Figure 43.

### Discussion:

This procedure is less sensitive than manual extraction techniques. The lowest concentration measured was 10 ppm and no blank values were detected. However, the matter can be improved further, considering other optimization parameters such as physical and system variable controls.





#### RESULTS OF LEAST SQUARES CALCULATION

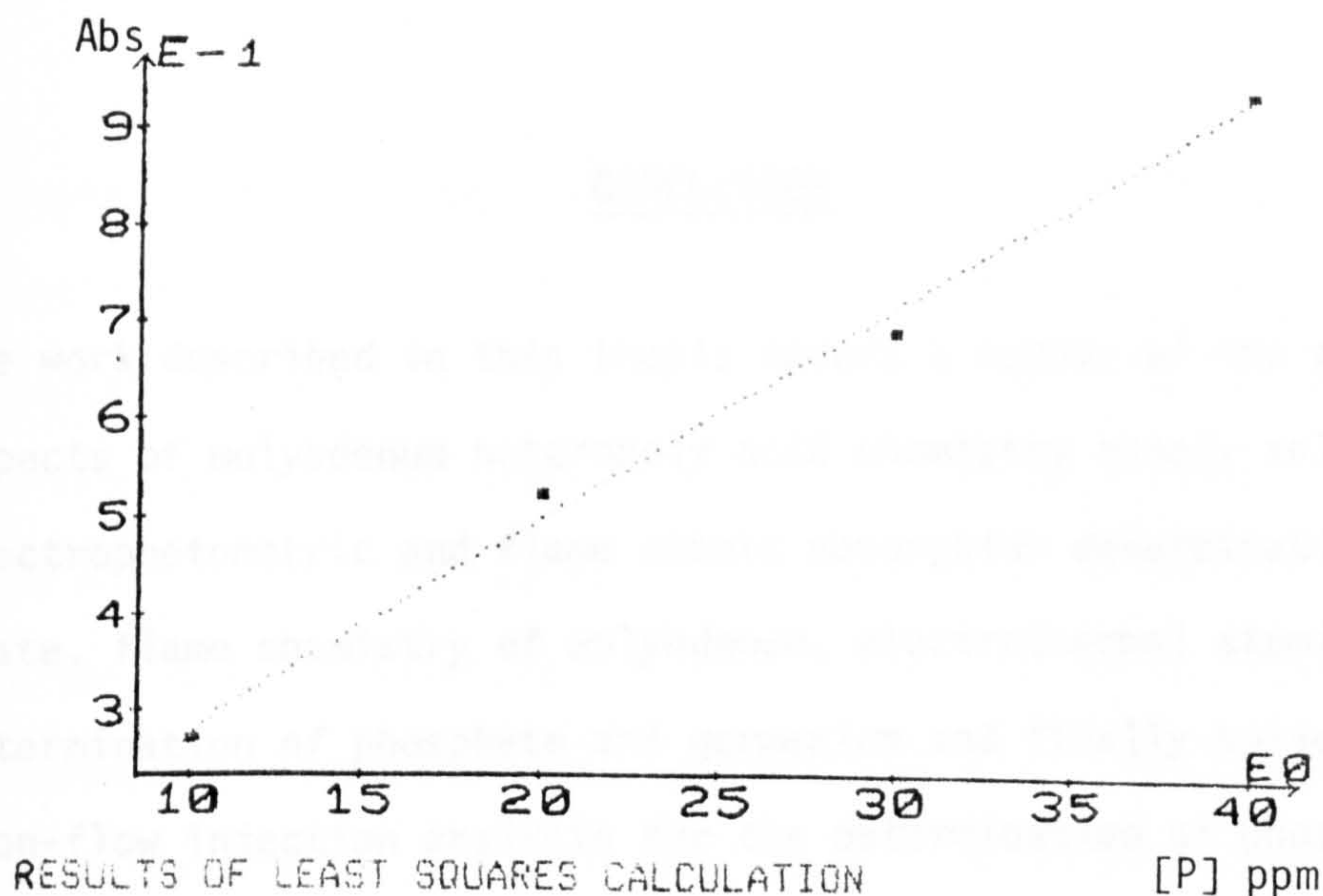
$$Y = 1.03376804 X + -7.16143298$$

NUMBER OF POINTS	= 5
SLOPE	= 1.03376804
INTERCEPT	= -7.16143298
CORRELATION COEFF.	= .993498357
STANDARD DEVIATION	= 1.84472355

X	Y
10	3
15	6.569
20	13.24
25	21.78
50	43.656

FIGURE 42: Calibration and least squares linear regression analysis for 12-molybdophosphoric acid at 310 nm





NUMBER OF POINTS = 4  
 SLOPE = .02195  
 INTERCEPT = .0579999999  
 CORRELATION COEFF. = .99645421  
 STANDARD DEVIATION = .0239269723

X	Y
10	.267
20	.526
30	.69
40	.944

FIGURE 43: The calibration graph and least squares linear regression analysis for 12-molybdophosphoric acid in the air-C<sub>2</sub>H<sub>2</sub> flame

## CONCLUSION

The work described in this thesis covers a number of the analytical aspects of molybdenum heteropoly acid chemistry namely solution spectrophotometric and flame atomic absorption determination of phosphate, flame chemistry of molybdenum, electrothermal atomization for determination of phosphate and germanium and finally solvent extraction-flow injection analysis for the determination of phosphate.

### Solution Spectrophotometry

The solution spectrometry method was based on the measurement of "phosphomolybdic acid blue" and is described here for the determination of orthophosphate. The phosphomolybdic acid blue obtained from an acidified solution of ammonium molybdate containing ascorbic acid and a small amount of antimony.

It was found that the phosphorus concentrations covered, using a 1 cm cell, were between 0.2 and 1.5 ppm, measured at 880 nm. Beer's law up to a phosphate concentration of at least 2 ppm was reported by previous workers<sup>(98)</sup>.

The sensitivity (concentration for 1% absorption) was found to be 6.5 ppb of phosphorus, which is comparable to the 1 ppb found by previous workers. They made measurements with a Unicam SP 500 spectrophotometer modified to use 7.62 and 15.24 cm cells.

The method has advantages in that the colour stability and salt error correction (as reported by the previous workers) were less than 1% for determination of soluble phosphate in a sea water sample.

Previous workers also reported that interferents such as arsenate react with molybdate reagent to produce a blue colour similar to that formed with phosphate. Concentrations as low as 1 ppm of arsenate interfere with phosphate determination. Copper and iron cause no interference and silicate causes no interference with as much as 10 ppm.

Although a number of heteropoly acids (phosphomolybdate, silicomolybdate, arsenomolybdate) absorb strongly in the UV, the absorption spectra in the ultraviolet region of the spectrum cannot be measured because of the high absorptivity of molybdate itself in the ultraviolet region. By extracting the heteropoly acids into organic solvents the acid can be separated, leaving the molybdate in the aqueous solution and overcoming the interference. In several instances selective separations are necessary to overcome interferences, such as that arising from soluble silicate leached from glass vessels.

Wedelin and Mellon<sup>(99)</sup> have shown that a selective separation of phospho - from the silico - and arsenomolybdate can be carried out by extracting with n-butyl acetate, thus this solvent was used in this work and the extraction compared with that obtained with the second best organic solvent, diethyl ether.



N-butyl acetate was found to be the better solvent for extracting 12-molybdophosphoric acid due to the ease of separation of the phases and the selectivity, thus confirming the findings of previous workers<sup>(99)</sup>. The extraction (devised by Hurford and Boltz, 58) has a similar sensitivity to the phosphomolybdenum blue method, 6 ppb measured at 310 nm in a 1 cm cell. Beer's law was obeyed from 0.1 to 1.5 ppm of phosphorus (only up to 1.0 ppm was reported by previous workers<sup>(99)</sup> using 1-butanol in chloroform as an extractant).

Further investigation could include chromatographic separations of mixtures of heteropoly acids. However the low pH needed for separation, tends to hydrolyze the stationary bonded phase. Research into the use of acid-resistant stationary phases has recently commenced at Loughborough University of Technology.

### Flame Atomic Absorption

The flame atomic absorption determination of phosphate by an amplification procedure is more selective but less sensitive than solution spectrophotometry.

In this procedure phosphate is converted to 12-molybdophosphoric acid and selectively extracted with n-butyl acetate. It is then broken down by equilibrium with alkali, and the twelve molybdenum atoms associated with each original phosphate ion are determined by measurement of the absorbance at 313.3 nm resonance line of molybdenum, in an air-C<sub>2</sub>H<sub>2</sub> flame.



The optimum concentration range reported by previous workers<sup>(58)</sup> was approximately 0.1 to 1.2 ppm of phosphorus using 45 ml of 5:1 diethyl ether:pentanol as an extractant. In contrast in this work an optimum concentration range from 0.05 to 1.5 ppm of phosphorus was found. The sensitivity (concentration for 1% absorption) was 10 ppb of phosphorus when 20 ml or 45 ml solvent was used. For samples containing less than 0.1 ppm of phosphorus, 20 ml solvent as an extractant was preferred.

The poorer sensitivity of the procedure by flame atomic absorption spectrophotometry is due to the poor sensitivity for the determination of molybdenum by atomic absorption spectrometry. Using an air-C<sub>2</sub>H<sub>2</sub> flame a value of 0.3 ppm was obtained.

Existing flame based methods for the determination of molybdenum heteropoly acids are limited by (a) the high blank values, (b) the noise associated with the atomization process, and (c) the chemistry of the atom forming reactions. All these factors were studied through modifications of the flame chemistry, nebulization process, and reducing blank values with a view to improving the sensitivity and detection limit.

### Flame Chemistry

Previous workers<sup>(159)</sup> have reported that a probable candidate species responsible for the final reduction of the monoxide to the metal is carbon monoxide. Accordingly the effect of increasing the partial pressure of this gas in both flames (air-C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub>) was investigated. No major improvement in sensitivity was obtained compared with the normal situation.

Since a reducing environment is beneficial for free atom production, it was hoped that the addition of hydrogen would provide a reduction mechanism avoiding carbon containing species, since the commercial production of the metal also proceeds via this process<sup>(158)</sup>. However, the addition of hydrogen to both flames (air-C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub>) provided no improvement in sensitivity and conflicted with the theory suggested.

Varying the salt concentration in both air-C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame was also investigated. The addition of salts such as aluminates or sulphates caused enhancements in the N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame. This confirms the findings of Rubeška<sup>(130)</sup> and Kerbyson et al<sup>(118)</sup>.

In the case of aluminium salts, it is thought that the salt decomposes to give an alumina particle with the molybdenum species dispersed in it. The alumina then decomposes liberating oxygen and reacts with carbon containing species to form a stable aluminium carbide, both of

these effects helping to vaporize the molybdenum as the oxide by providing an oxidizing microclimate and scavenging carbide forming species. The enhancement of sulphate is believed to be due to a molybdenum oxidizing reaction.

Ammonium salts also cause an enhancement. In accordance with previous workers<sup>(139)</sup>, if a salt (such as  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ) sublimes or decomposes to give gaseous products, it may cause explosive disintegration which, in turn, may provide very finely divided molybdenum species. Previous workers<sup>(137)</sup> have proposed that the reduction of the analyte to the metal or a carbide may accelerate or retard vaporization depending on which form is more volatile. A more volatile salt (e.g. alkaline halide) will cause a delay in the heating of the particle (as it remains at the melting point of the salt) and in the vaporization of the less volatile analyte.

### Nebulization Processes

Sample introduction using flow injection techniques is extremely convenient, especially for samples with high viscosity and salt contents.

Results obtained using a 200  $\mu\text{l}$  sample volume and a pumping rate of 2  $\text{ml min}^{-1}$  confirmed the results of Stewart et al<sup>(149)</sup>, showing that reproducibility and detection limit (0.24 ppm of Mo) of discrete sampling can be improved by measurement of peak areas rather than peak



heights. However, contrary to the results of previous workers, both were inferior to conventional nebulization (detection limit 0.21 ppm of Mo). In agreement with the results of previous workers, it was found that nebulization efficiency was greater at lower flow rates. In addition, the system maintains a high level of precision and facilitates increased analysis rates (at normal flow rates) with diminished sample size requirements and reduced matrix effect. A slight improvement in sensitivity at low concentration (0.5 ppm of Mo) was found when high concentration of salts were added.

Disappointing results were obtained when 200  $\mu$ l of a solvent (n-butyl acetate) extract of 12-molybdophosphoric acid was injected. The sensitivity was 81 ppb of phosphorus compared with 27 ppb of phosphorus obtained when 200  $\mu$ l of aqueous alkali solution containing decomposition product of 12-molybdophosphoric acid was injected. These results are in contrast to those of Attiyat et al<sup>(151)</sup> in which enhancements in sensitivity with organic solvent (including n-butyl acetate) were obtained for trace metals.

Heating the solution and aspirating an organic solvent were also investigated in an attempt to increase the rate of transport of the analyte.

A gradual depression in molybdenum signal when a heated solution was aspirated into an air-C<sub>2</sub>H<sub>2</sub> flame was obtained in accordance with Browner et al<sup>(366)</sup>. This supports the theory that when more aerosol is introduced into the flame, not only the mass transport rate of



analyte increases, but also the mass transport rate of the accompanying solvent. This may have a significant effect in lowering the temperature of atomic absorption flames.

Acetone caused a depressive effect in the air-C<sub>2</sub>H<sub>2</sub> flame and an enhancement effect in the N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> flame, in accordance with the results of Manning and Chabot<sup>(166)</sup> and Dean et al<sup>(169)</sup>. The effect can be attributed to changes in nebulization parameters<sup>(179)</sup>.

#### Drying the Solvent Extract

A considerable improvement in blank level was obtained when the extract was dried by passing it through a column of anhydrous sodium sulphate. The blank values were reduced to below the detection limit (about 0.2 ppm of Mo). This suggests that the high blank values were mainly due to the molybdenum in aqueous phase droplets suspended in the organic solvent (n-butyl acetate), rather than co-extracted isopolymolybdate. Without the use of the drying agent, the molybdenum concentration in the blank was approximately 1.0 ppm.

#### Electrothermal Atomic Absorption

The indirect determination of orthophosphate (based on the measurement of the absorbance of the 12-molybdophosphoric acid in organic solvent) by electrothermal atomization is recommended. The method is fast, convenient, sensitive and needs only small sample volumes. The procedure can be used for between 5 ppb and 50 ppb of phosphorus. The sensitivities

(concentration for 1% absorption) using 45 ml and 20 ml solvent volumes as an extractant were found to be 1.7 ppb and 1.2 ppb of phosphorus respectively for a 1  $\mu$ l injection. In contrast, the results obtained for the same procedure by previous workers<sup>(245)</sup>, was 2.2 ppb of phosphorus.

In general, the increase in sensitivity compared with flame atomization, is mainly due to (a) the partial pressure increase in atoms by the atomization of dried samples, and (b) an increase in residence time (may not be significant with a carbon rod atomizer) and peak atom population in the light beam. The major problems in determining molybdenum by electrothermal atomization are memory effects, carbide formation and short life time of the electrothermal device due to the increasing porosity of the surface.

Previous work<sup>(189)</sup> on electrothermal atomization of molybdenum overcame the memory effects by applying a high temperature cleaning stage following the atomization stage. Although the procedure was satisfactory with a new rod, it resulted in a rapid decrease in the rod life time due to increasing surface porosity. The addition of acetylene gas to the inert sheathing gas resulted in a considerable improvement due to the pyrolytic graphite coating formed on the surface of the atomizer.

An alternative method of producing a pyrolytic coating is the use of an argon-methane gas mixture. The use of argon-methane gas as a

sheathing gas improved the sensitivity of the molybdenum considerably over the use of nitrogen gas. The sensitivity was 25 ppb of molybdenum compared with 37 ppb of molybdenum obtained when nitrogen was used as a sheathing gas. A continuous flow of traces of methane introduced via the sheathing gas provided a pyrolytic coating of the carbon rod with every firing which, in turn, increased the life time of the rod. The procedure also eliminated the specific pyrolytic coating stage which, in turn, reduced the time of the analysis.

The use of an argon-hydrogen gas mixture as a sheathing gas also improved the sensitivity for molybdenum (10.2 ppb). A comparison of the standard deviation of the points on the calibration graphs, showed that the use of argon-methane gas mixture as a sheathing gas was preferred. The standard deviation of the points on the calibration graph using argon-hydrogen is  $6.4 \times 10^{-3}$ , whereas for argon-methane gas mixture it is  $1.1 \times 10^{-2}$ .

Each gas plays a distinct role in the operation of the instrument. Methane and hydrogen function as reducing agents during atomization of the sample while methane also provides carbon for pyrolytic re-coating of the atomizer in accordance with Steiner et al<sup>(196)</sup>.

Further investigations need to be carried out on matrix effects in electrothermal atomization, and to study possible methods of eliminating these interferences by sequential introduction of gases.

### Determination of Germanium

A method was developed for the indirect determination of germanium by carbon rod electrothermal atomic absorption spectrometry, which is based on the formation of 12-molybdogermanic acid, extraction into an organic solvent and finally measurement of the absorbance at the 313.3 nm resonance line of molybdenum. The method is suitable for the determination of between 10 ppb and 200 ppb of germanium. The sensitivity was 3.7 ppb of germanium using 25 ml solvent.

In contrast, the indirect flame atomic absorption spectrometric method is suitable for up to 1.6 ppm of germanium and the sensitivity is reported to be 50 ppb of germanium<sup>(305)</sup>.

Previous workers<sup>(314)</sup> have reported the indirect determination of germanium using carbon rod electrothermal atomization, with a sensitivity of 0.4 ppb of germanium using diethyl ether-pentanol as an extractant. These workers have used a Perkin-Elmer model 306 atomic absorption spectrometer equipped with HGA 74 graphite furnace giving a sensitivity of 6.5 ppb for molybdenum.

In the work described here, methyl isobutyl ketone was used for the extraction of 12-molybdogermanic acid. According to Simon et al<sup>(305)</sup> methyl isobutyl ketone is the best extractant and diethyl ether-pentanol (1+5) is the best alternative. Investigating these two solvents, it was found that methyl isobutyl ketone was better for graphite rod electrothermal atomization, since it was much easier



to transfer the injected volume without losing solvent by evaporation during transfer. However, the solvent is not very selective. Co-extraction of heteropoly acids of interferents arising from the acid used is believed the cause for high blank values. This was confirmed by the use of Arista<sup>R</sup> instead of Anala<sup>R</sup> hydrochloric acid which reduced the blank values slightly.

Further investigations should include a study of other solvents to produce a more selective extraction of 12-molybdogermanic acid.

#### Flow Injection-Solvent Extraction

A system was designed for automated solvent extraction based on flow injection principles, which gives a simple and rapid way of pretreating samples that need a separation by solvent extraction without performing conventional solvent extraction procedures. The system was used for formation and extraction of 12-molybdophosphoric acid and subsequent indirect determination of phosphorus.

Previous work described in the literature has been concerned with extraction-flow injection analysis coupled with flame atomic absorption based on continuous uptake of the sample solution, followed by injection of the organic phase into a separate carrier stream<sup>(347)</sup>.

These preliminary studies reported here showed that the sensitivity measured spectrophotometrically or by atomic absorption were lower than previously reported procedures. However, the extraction time was reduced considerably to 8 minutes for one sample using this manifold design. For future research, more work should be carried out on the various physical and chemical parameters controlling the separation with a view to improving the sensitivity of the procedure possibly by the use of an appropriate optimization strategy.

APPENDIX 1

Theoretical chemical amplification:

In the molybdophosphoric acid complex,  $\text{H}_3\text{PMo}_{12}\text{O}_{24}$ , one atom of phosphorus combines with 12 atoms of molybdenum.

∴ 30.95g of P combines with (12 x 95.95)g of Mo.

Chemical amplification factor for phosphorus (on weight basis)

$$= \frac{12 \times 95.95}{30.95}$$

$$= 37.2.$$

APPENDIX 2

Percentage extraction of 12-molybdophosphoric acid for

$$y \text{ } \mu\text{gP} = \frac{xv}{37.2 \times y} \times 100$$

where x is concentration of Mo found in extracted phase (ppm)

v is volume of extracted phase (ml)

y is weight of P atom ( $\mu\text{g}$ )

APPENDIX 3

Theoretical chemical amplification:

In the molybdo-germanic acid complex,  $\text{H}_3\text{GeMo}_{12}\text{O}_{24}$ , one atom of germanium combines with 12 atoms of molybdenum. Therefore, 72.59g of Ge combines with  $(12 \times 95.95)\text{g}$  of Mo. Chemical amplification factors for germanium (on weight basis)

$$= \frac{12 \times 95.95}{72.59}$$

$$= 15.86$$



APPENDIX 4  
THEORY OF PHOTOMETRY

When molecules absorb UV or visible electromagnetic radiation, an electronic transition occurs and the molecule is raised from one energy level, usually the ground state, to a higher, excited state.

A molecule will absorb energy if the conditions are such that the molecule can pass from one quantized state to another and this depends essentially on the possibility that the absorption of the energy will change the electrical centre of the molecule. An examination of the absorption spectrum resulting from this will yield much evidence about (a) the energy in the process, by measuring the appropriate wavelength, and (b) the probability that the transition will occur ("oscillator strength") by calculating the intensity of the band.

Quantitative methods based on the absorption of electromagnetic radiation involve measurement of the reduction in intensity on passage through an absorbing medium, i.e. the sample. The degree of absorption is determined by comparing the intensity of the transmitted beam when no absorbing species is present, i.e. a blank, with that transmitted by the sample.

For monochromatic, collimated radiation passing through a homogeneous liquid sample, the reduction in intensity of the incident radiation

can be related to the concentration of absorbing species and to the thickness of the absorbing medium. both relationships being embodied in the Beer-Lambert law.

The Lambert Law or the Lambert-Bouguer Law, states that ratio between the intensity of the incident light  $I_0$  and the transmitted light  $I$  is independent of the intensity of the light. This means that successive equal thicknesses of a homogeneous absorbing medium will reduce the intensity by successive equal fractions, and  $I_0$  and  $I$  are related by the logarithmic expression

$$\frac{I}{I_0} = \exp (- \mu d)$$

where  $\mu$  is a constant, the absorption coefficient, and  $d$  is the absorbing path length. The expression is now more commonly represented as

$$\frac{I}{I_0} = 10^{-kd}$$

where  $k$  is the extinction coefficient of Bunsen and Roscoe ( $= 0.4343\mu$ ). Beer's Law, which is identical in form, but replaces "absorbing path length" by "concentration of absorbing solute" since it applies specifically to solutions, i.e.

$$\frac{I}{I_0} = 10^{-bc}$$

where  $c$  is the concentration in a constant path length, and  $b$  is a constant.

The two laws may be combined, and the resulting Beer-Lambert Law expressed as

$$\frac{I}{I_0} = 10^{-\epsilon cd}$$

$$\epsilon cd = \log \frac{I_0}{I} = A$$

where  $\epsilon$  is a constant and  $A$  is known as the absorbance. If  $c$  is expressed in moles per litre and  $d$  in centimetres,  $\epsilon$  is known as the molar absorptivity, and it is in the form that the absorbing properties of organic compounds are most commonly given.

Absorbance is related to transmittance  $T$  defined as  $\frac{I}{I_0}$  (the fraction of radiation transmitted) by the equation

$$A = \log_{10} \frac{1}{T}$$

However, the absorbance measurements may give rise to errors, and these may originate in either non-spectroscopic (temperature effects, concentration effects, and turbidity) or spectroscopic sources (stray light and scattering of the light). Stray light in monochromators is unwanted energy which falls on the detector and gives rise to a false

signal. Stray light effects are most pronounced at the ends of the useful range of the light source, and are therefore found below 215 nm and at the change over point between deuterium and tungsten filament lamps. Modern instruments have been designed to keep stray light at values below 0.1%.

Spectrometry is concerned with the determination of the emission and absorption spectra of elements and compounds. Photometry is a quantitative measurement of the magnitude of the absorbed radiation. Most modern instruments are equipped for both, and are called spectrophotometers. The basic components of a spectrophotometer are the light source, a monochromator, a cell to retain the sample, and a detector to measure the intensity of the radiation. Spectrophotometers can be classified as single- or double-beam instruments.

In single-beam photometry the beam is first passed through the reference and the instrument is then adjusted to read zero absorption or 100% transmission. The reference is then removed, the sample inserted in the beam, and the reading noted.

In double-beam spectrometry the light is formed into two identical beams by prisms, rotating or vibrating mirror, or opto-mechanical devices. One beam passes through the sample and the other through a reference material or blank.



The chief advantages of the double-beam design are that it permits a large degree of inherent compensation for (1) fluctuations in the intensity of the source light which might otherwise give spurious results, (2) absorbance by atmospheric components in light path thus it allows a spectrum with a flat base line to be recorded, and that it makes possible direct, one-step comparison of a sample in one path with a standard or blank solution in the other path. Chemical analysis by atomic absorption spectrometry involves converting part of the sample into an atomic vapour and measuring the absorption, by this vapour, of a radiation which is characteristic of some particular element.

The basic components of an atomic absorption spectrophotometer are therefore a hollow cathode, a flame-atomizer unit, a monochromator, a photoelectric detector, an ac amplifier and rectifier, and an output meter.

APPENDIX 5THEORY OF SOLVENT EXTRACTION

If two immiscible liquids are placed in contact with any substance will distribute or partition itself between the two phases in a definite proportion depending on its respective solubilities and on the relative volumes in one phase, for example, relatively large, non-polar species, can be more or less completely transferred from an aqueous solution to the second phase, which is often an organic liquid such as benzene, chloroform, ether, or carbon tetrachloride. The way in which a given solute partitions between two phases will, in general, be governed by the enthalpy and entropy changes associated with the process of dissolution in each phase. Thus the transfer of a metal ion (small, and strongly polarizing and highly hydrated), from an aqueous solution to an organic solvent will be aided by complexation with a relatively large non-polar ligand. The resulting complex cannot be accommodated in the water structure because too much energy is required to make a big enough hole and the release of the water of hydration on complexation contributes to a positive entropy change on transfer of the complex to the organic phase, though this may be offset by solvation effects in some cases.

According to the Nernst partition isotherm, the distribution law states that a solute will distribute itself between two essentially immiscible solvents in such a way that the ratio of the concentrations of the solute in the two phases after equilibrium has been achieved at

a particular temperature is a constant, provided the solute has the same molecular weight in each phase. For solute X distributing between two immiscible solvents 1 and 2, we then have



$$K_D = \frac{[X]_2}{[X]_1}$$

where  $K_D$  is the distribution coefficient, a constant independent of total solute concentration, and the brackets denote concentrations.

In many practical situations solute X may dissociate, polymerize or form complexes with some other component of the sample or interact with one of the solvents. Under these circumstances the value of  $K_D$  does not reflect the overall distribution of the solute between the two phases as it refers only to the distributing species. Analytically, the total amount of solute present in each phase at equilibrium is of prime importance, and the extraction process is therefore better discussed in terms of the distribution ratio D where

$$D = \frac{\text{Total concentration in organic phase}}{\text{Total concentration in aqueous phase}}$$

If no reactions involving the species in either phase, D would be reduced to  $K_D$ .

Of ultimate practical interest in describing extractions is the use of the term percent extraction %E. This quantity is related to the distribution ratio D, by the following equation:

$$\%E = 100D/[D + (V_w/V_o)]$$

where  $V_w$  and  $V_o$  are the volumes of the aqueous and organic phases, respectively. When the volumes are equal, the denominator simplifies to D+1.

Although details of the specific nature of the interactions (side reactions) obviously must differ from one metal extraction system to another, extraction systems can be classified into two broad classes depending on whether the material extracted is formally uncharged (e.g. aluminium tris-oxinate, zine dithiozonate) or whether it partitions as an ion pair (e.g. acido complexes formed by metal halides in mineral acids; salts such as  $(C_6H_5)_4As^+ReO_4^-$ ; or material extracted by long-chain amines, e.g. tetraoctylammonium perchlorate).

The extraction of uncharged species is based on the fact that it takes less energy to produce a hole in a non-polar solvent than in a polar one, since the forces binding the solvent molecules together are much smaller. Similarly, the extraction of ion-association species is explicable on the basis of the energetics of solution process; there being a more favourable free-energy change when the species is solvated



by an organic solvent instead of by water, or the species is so bulky that it is in effect squeezed out of the aqueous phase because of the hydrogen bonded water structure.

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