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A thesis entitled

New Approaches to Automated

Analytical Instrumentation

presented by

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WARREN THOMAS CORNS, BSc, GRSC

In part fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

of the

COUNCIL FOR NATIONAL ACADEMIC AWARDS

November 1991

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CONTENTS

	Page No.
ABSTRACT	
ACKNOWLEDGEMENTS	
CHAPTERS 1-6 CONTENTS	i
LIST OF FIGURES	vi
LIST OF TABLES	xii
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 INSTRUMENTATION	29
CHAPTER 3 GAS-LIQUID SEPARATION PROCESSES CONTINUOUS FLOW HYDRIDE GENERAT	FOR 44 ION
CHAPTER 4 THE DETERMINATION OF MERCURY IN AQUEOUS AND GASEOUS SAMPLES	99
CHAPTER 5 DEVELOPMENT OF AN ATOMIC FLUORES SPECTROMETER FOR THE HYDRIDE FOR ELEMENTS	SCENCE 150 RMING
CHAPTER 6 CONCLUSIONS AND FUTURE WORKS	215
REFERENCES	221
LECTURES AND ASSOCIATED STUDIES	la
MEETINGS ATTENDED	1b
PRESENTATIONS Oral presentations Poster presentations	1c 1c 2c
PUBLICATIONS	1d

- -

- - ----

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ABSTRACT

WARREN THOMAS CORNS

NEW APPROACHES TO AUTOMATED ANALYTICAL INSTRUMENTATION

The development, optimisation and assessment of novel automated analytical equipment for cold vapour/hydride generation is described.

Various designs of gas-liquid separators (GLS) were investigated for continuous flow hydride generation, including a glass 'U' tube GLS, a silicone rubber membrane GLS and a microporous polytetrafluoroethylene membrane GLS. Sub parts per billion detection limits (3σ) were obtained for each type of separator using AAS and ICP-MS detection systems. Spectral overlap of ArCl⁺ causes problems in the determination of As and Se by ICP-MS when samples contain substantial amounts of chloride. Membrane gas-liquid separation produces dry gaseous streams uncontaminated with chloride, thereby eliminating ArCl⁺ formation.

Automated continuous flow and flow injection cold vapour generation coupled to AFS for mercury determination is described. The continuous flow approach was most sensitive with a detection limit (3σ) of 3 ng 1⁻¹. The effects of moisture carry-over on this technique was investigated and a novel desolvation method, utilising a Nafion hygroscopic membrane, discussed. An automated preconcentration system for the determination of mercury in gaseous samples using an absolute calibration procedure is also described.

A novel atomic fluorescence spectrometer coupled to continuous flow hydride generation is reported. This consisted of a boosted discharge hollow cathode lamp, an interference filter, a collection of lenses, a hydrogen diffusion flame and a solarblind photomultiplier tube. The atom cell design is unique since the fuel gas, hydrogen, is continuously supplied from the hydride generation reaction. Limits of detection (3σ) of 0.1 µg 1⁻¹ and 0.05 µg 1⁻¹ were obtained for arsenic and selenium respectively. Other hydride forming elements can be determined using the same apparatus by changing the lamp and interference filter.

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Figure 2.7 - Non-dispersive atomic fluorescence apparatus





- -



Page No.

CHAPTER 1 INTRODUCTION

1.1.	INTRO	DUCT	ION	1
1.	1.1.	Defir	nition of Automation	1
1.	1.2.	The I	Drive Behind Automation	2
1.	1.3.	Advar Analy	ntages and Limitations of Automated ysis	3
1.	1.4.	Appro	oaches Available for Automation	5
1.	1.5.	Futu	re of Automation	7
1.	2.1.	Vapou	ur/Hydride Generation	8
1.	2.2.	React	tions for Vapour/Hydride Generation	10
		a)	Metal-Acid Reduction	10
		b)	Sodium Tetrahydroborate - Acid Reduction	11
		C)	Tin (II) Chloride Reduction	12
1.	2.3.	Gased	ous Analyte Manipulation	12
		a)	Collection/Preconcentration Mode	12
		b)	Direct Transportation Mode	14
1.	2.4.	Deteo Gener	ction Systems for Vapour/Hydride ration	15
		a)	Atomic Absorption Spectrometry (AAS)	15
		b)	Plasma Emission Spectrometry	16
		c)	Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)	18
		d)	Atomic Fluorescence Spectrometry (AFS)	19
1.	2.5.	Inter Techi	rferences in Vapour/Hydride Generation niques	20
1.	2.6.	Spec: and 1	iation for Hydride Forming Elements Mercury	23
1.	2.7.	Atom	isation Mechanisms for Gaseous Hydrides	25
1.	2.8.	Appl	ications for Vapour/Hydride Generation	26
1.	2.9.	Futu	re of Vapour/Hydride Generation	26
1.	3.1.	Outl	ine of Thesis	27

i

-

Page No.

CHAPTER 2 INSTRUMENTATION

•

_

-

2.1. INST	RUMENTATION	29
2.1.1.	Continuous Flow Vapour/Hydride Generation	29
2.1.2.	Flow Injection Vapour/Hydride Generation	31
2.2.1.	Atomic Absorption Spectrometry (AAS)	33
2.3.1.	Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)	34
2.4.1.	Atomic Fluorescence Spectrometry (AFS)	38

<u>CHAPTER 3</u> <u>GAS-LIQUID SEPARATION PROCESSES FOR</u> <u>CONTINUOUS FLOW HYDRIDE GENERATION</u>

3.1. INTR	ODUCTION	44
3.1.1.	Experimental and Instrumentation	48
3.2.1.	Glass 'U' Tube Gas-Liquid Separator (GGLS)	50
3.2.2.	Analytical Performance of the Glass 'U' Tube Gas-Liquid Separator	57
3.2.3	Advantages and Disadvantages of the Glass 'U' Tube Gas-Liquid Separator	62
3.3.1.	Tubular Membrane Gas-Liquid Separator (TMGLS) for Atomic Absorption Spectrometry	64
3.3.2.	Analytical Performance of the Tubular Membrane Gas-Liquid Separator coupled to Atomic Absorption Spectrometry	70
3.3.3.	Advantages and Disadvantages of the Tubular Membrane Gas-Liquid Separator when coupled to Atomic Absorption Spectrometry	74
3.3.4.	Tubular Membrane Gas-Liquid Separation for Inductively Coupled Plasma - Mass Spectrometry	77
3.3.5.	Chloride Exclusion from the Plasma using the Tubular Membrane Gas-Liquid Separator	83
3.3.6.	Analytical Performance of the Tubular Membrane Gas-Liquid Separator for Inductively Coupled Plasma - Mass Spectrometry	84
3.4.1.	Microporous PTFE Membrane Gas-Liquid (MGLS) Separator for Atomic Absorption Spectrometry	87

-

-

-

		Page No.
3.4.2.	Analytical Performance of the PTFE Membrane Gas-Liquid Separator for Atomic Absorption Spectrometry	91
3.4.3.	Advantages and Disadvantages of the PTFE Membrane Gas-Liquid Separator	94
3.5.1.	Summary	95
<u>CHAPTER 4</u>	THE DETERMINATION OF MERCURY IN AQUEOUS AND GASEOUS SAMPLES	
4.1. INTRO	DDUCTION	99
4.2.1.	Continuous Flow Vapour Generation - Atomic Fluorescence Spectrometry	105
4.2.2.	Analytical Performance of the Continuous Flow Approach	112
4.2.3.	Summary	119
4.3.1.	Flow Injection - Cold Vapour - Atomic Fluorescence Spectrometry	120
4.3.2.	Summary	124
4.4.1.	The Effects of Moisture on Cold Vapour - Atomic Fluorescence Spectrometry	126
4.4.2.	Summary	137
4.5.1.	Calibration Procedures for a Computer Controlled Adsorber/Desorber System to Monitor Mercury in Gaseous Samples	137
4.5.2.	Instrumentation	138
4.5.3.	Calibration Procedure	141
4.5.4.	Summary	149

CHAPTER 5 DEVELOPMENT OF AN ATOMIC FLUORESCENCE SPECTROMETER FOR THE HYDRIDE FORMING ELEMENTS

•

5.1.	INTRO	DUCTION				150
5.	2.1	Continuous	Flow	Hydride	Generation	155

. .

		raye	NO.
5.2.2	Reagents		155
5.3.1	Instrumentation for the Monochromator System		156
5.3.2	Excitation Source for the Monochromator System		156
5.3.3	Effect of Wavelength on Atomic Fluorescence for Arsenic		163
5.3.4	Optical Configuration of the Monochromator System		166
5.3.5	Atom Reservoirs for Atomic Fluorescence		167
5.4.1	Non-Dispersive Atomic Fluorescence Spectrometer		177
5.4.2	Instrumentation for the Filter System		178
5.4.3	Boosted Discharge Hollow Cathode Lamp for the Filter System		178
5.4.4	Interference Filter		180
5.4.5	Solar-Blind Photomultiplier Tube		184
5.4.6	Optical Configuration of the Filter System		187
5.4.7	The Reduction of Flame Noise		189
5.4.8	Electronic Readout for the Atomic Fluorescence Spectrometer		192
5.4.9	Reduction of Background for the Filter System		193
5.4.10	Chemical Optimisation of Continuous Flow Hydride Generation for Arsenic		195
5.4.11	Analytical Performance of the Filter System for Arsenic		198
5.5.1	Determination of Selenium using Hydride Generation Atomic Fluorescence Spectrometry		203
5.5.2	Optimisation of the Boosted Discharge Hollow Cathode Lamp for Selenium		204
5.5.3	Chemical Optimisation of Continuous Flow Hydride Generation for Selenium		204
5.5.4	Analytical Performance of the Filter System for Selenium		206
5.6.1	Summary		212

iv

-

CHAPTER 6 CONCLUSIONS AND FUTURE WORKS

6.1	CONCI	LUSIONS	215
6.	1.1	Future Works	219

.

-

.

- -

·- ---

—

- --

LIST OF FIGURES

- -

_

Figure	2.1	Schematic diagram of the continuous flow vapour/hydride generation system, shown in the sampling position	30
Figure	2.2	Schematic diagram of the flow injection vapour/hydride generation system, shown in the blank position	32
Figure	2.3	Optical diagram of the atomic absorption spectrometer	35
Figure	2.4	Schematic diagram of a typical inductively coupled plasma-mass spectrometer	36
Figure	2.5	Types of atomic fluorescence, dashed lines represent radiationless transitions, double headed arrow represents a thermal activation process	39
Figure	2.6	Dispersive atomic fluorescence apparatus	41
Figure	2.7	Non-dispersive atomic fluorescence apparatus	41
Figure	3.1	Glass 'U' tube gas-liquid separator for continuous flow hydride generation	51
Figure	3.2	Effect of sodium tetrahydroborate concentration on peak height for As, Se and Sb using the glass 'U' tube gas-liquid separator	53
Figure	3.3	Effect of hydrochloric acid concentration on peak height for As, Se and Sb using the glass 'U' tube gas-liquid separator	53
Figure	3.4	Effect of carrier gas flow rate on peak height for As, Se and Sb using the glass 'U' tube gas-liquid separator	56
Figure	3.5	Effect of sodium tetrahydroborate concentration on plumbane generation	56
Figure	3.6	Effect of sodium hydroxide concentration on plumbane generation	58
Figure	3.7	Effect of nitric acid concentration on plumbane generation	58
Figure	3.8	Effect of hydrogen peroxide concentration on plumbane generation	59

-

. - - - -

-

-

. _ __ _ _ _ _

Page No.

Figure	3.9	Typical peak shape for a 100 µg l ⁻¹ arsenic solution using the glass 'U' tube gas-liquid separator	65
Figure	3.10	Tubular membrane gas-liquid separator	65
Figure	3.11	Effect of sodium tetrahydroborate concentration on peak height for As and Se using the tubular membrane gas-liquid separator with atomic absorption spectrometry detection	67
Figure	3.12	Effect of hydrochloric acid concentration on peak height for As and Se using the tubular membrane gas-liquid separator with atomic absorption spectrometry detection	69
Figure	3.13	Effect of carrier gas flow rate on peak height for As and Se using the tubular membrane gas-liquid separator with atomic absorption spectrometry detection	69
Figure	3.14	Effect of potassium iodide on the signal from arsenic (V) with time	73
Figure	3.15	Typical peak shape for a 100 µg l ⁻¹ arsenic solution using the tubular membrane gas-liquid separator	76
Figure	3.16	Effect of sodium tetrahydroborate concentration on peak height using the tubular membrane gas-liquid separator with inductively coupled plasma - mass spectrometry detection	80
Figure	3.17	Effect of hydrochloric acid concentration on peak height using the tubular membrane gas-liquid separator with inductively coupled plasma - mass spectrometry detection	80
Figure	3.18	Effect of forward power on peak height using the tubular membrane gas-liquid separator with inductively coupled plasma - mass spectrometry detection	81
Figure	3.19	Effect of carrier gas flow rate on peak height using the tubular membrane gas- liquid separator with inductively coupled plasma - mass spectrometry detection	81
Figure	3.20	Effect of auxiliary gas flow rate on peak height using the tubular membrane gas-liquid separator with inductively coupled plasma - mass spectrometry detection	82

٠

-

		Page	≥ No.
Figure	3.21	Mass spectrum of the blank solution showing the counts for As ⁺ and Se ⁺ in the absence of ArCl ⁺ interference	85
Figure	3.22	Schematic diagram of the polytetrafluoroethylene membrane gas-liquid separator	89
Figure	3.23	Effect of sodium tetrahydroborate concentration on peak height using the PTFE membrane gas-liquid separator with atomic absorption spectrometry detection	92
Figure	3.24	Effect of hydrochloric acid concentration on peak height using the PTFE membrane gas-liquid separator with atomic absorption spectrometry detection	92
Figure	3.25	Effect of carrier gas flow rate on peak height using the PTFE membrane gas-liquid separator with atomic absorption spectrometry detection	93
Figure	3.26	Typical peak shape for a 100 µg l ⁻¹ arsenic solution using the PTFE membrane gas-liquid separator	96
Figure	4.1	Gas-liquid separator for the tin (II) chloride reduction scheme	107
Figure	4.2	Mercury transfer system into the atomic fluorescence spectrometer	108
Figure	4.3	Block diagram of the atomic fluorescence spectrometer	109
Figure	4.4	Optical configuration for the atomic fluorescence spectrometer	110
Figure	4.5	Analytical response curves for continuous flow - atomic fluorescence spectrometry using both argon and nitrogen carrier gas	115
Figure	4.6	Standardised atomic fluorescence cell	115
Figure	4.7	Typical peak shape using the continuous flow approach for a 2000 μ g 1 ⁻¹ solution of mercury illustrating the process of self-absorption	117
Figure	4.8	Analytical response curves for flow injection - atomic fluorescence spectrometry using 75 (v), 100 (Δ) and 200 (\Box) μ l sample volumes	121

viii

. ...

____ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _

.

. . –

. . .

. . . .

Page No.

Figure	4.9	Typical peak shape for the flow injection approach for a 100,000 μ g l ⁻¹ solution of mercury, illustrating the process of self-absorption	122
Figure	4.10	Typical peak shape using the flow injection approach for a 3000 µg l ⁻¹ solution of mercury	125
Figure	4.11	Variation in peak height with run number using no drying facility	128
Figure	4.12	Schematic diagram of the physical moisture trap	130
Figure	4.13	Variation in peak height with run number using the physical moisture trap	130
Figure	4.14	Hygroscopic membrane dryer tube	132
Figure	4.15	Variation in peak height with run number using a hygroscopic membrane dryer tube before simplex optimisation	132
Figure	4.16	Variation in peak height with carrier gas flow rate using the hygroscopic membrane dryer tube	134
Figure	4.17	Variation in peak height with dryer gas flow rate using the hygroscopic membrane dryer tube	134
Figure	4.18	Variation in peak height with run number using a hygroscopic membrane dryer tube after simplex optimisation	136
Figure	4.19	Schematic arrangement of the gold sand trap and heater assembly	139
Figure	4.20	Schematic layout of the valve assembly, shown in the sampling position	142
Figure	4.21	Instrumental arrangement for mercury in air, illustrating connections between units	144
Figure	4.22	The effect of carrier gas flow rate on peak area and peak height	145
Figure	4.23	The effect of shield gas flow rate on peak area and peak height	145
Figure	4.24	A typical calibration curve for the vapour injection procedure for mercury in air	148

- -

- -

_

_

-

- -

-

_

....

Page No.

Figure	5.1	Plan of the optical arrangement for the monochromator measurement system	157
Figure	5.2	Schematic diagram of the boosted discharge hollow cathode lamp	160
Figure	5.3	Effect of boost current on arsenic lamp intensity	162
Figure	5.4	Effect of primary current on arsenic lamp intensity	162
Figure	5.5	Effect of bandpass on signal to background ratio for arsenic	165
Figure	5.6	Inverted 'Y' burner atom cell	168
Figure	5.7	Electrically heated glass tube atom cell	168
Figure	5.8	Argon sheathed electrically heated atom cell	169
Figure	5.9	Chemically generated hydrogen diffusion flame atom cell	169
Figure	5.10	Effect of carrier gas flow rate on arsenic net signal for the 3 mm i.d. tube size atom cell	175
Figure	5.11	Block diagram for the filter measurement system	179
Figure	5.12	Effect of boost current on net signal for arsenic using the filter measurement signal	181
Figure	5.13	Effect of boost current on signal to background ratio for arsenic using the filter measurement system	181
Figure	5.14	Transmission spectra of the 200 nm interference filter	182
Figure	5.15	Multiple reflected ray in an interference filter	182
Figure	5.16	Spectral response for the solar-blind photomultiplier tube (reference 163)	185
Figure	5.17	Effect of amplifier gain on the solar-blind photomultiplier tube response for various instrumental conditions	186
Figure	5.18	Effect of distance between atom cell and photomultiplier tube on net signal (configuration 1)	188

• •

-

- ·

			Page	No.
Figure	5.19	Effect of distance between atom cell and photomultiplier tube on limit of detection (configuration 1)		188
Figure	5.20	Emission spectra of the hydrogen diffusion flame between 295 and 330 nm	L	190
Figure	5.21	Effect of hydrochloric acid concentration on net signal for arsenic at various reductant concentrations		197
Figure	5.22	Effect of hydrochloric acid concentration on signal to background ratio for arsenic at various reductant concentrations		197
Figure	5.23	Effect of hydrochloric acid concentration on signal to noise ratio for arsenic at various reductant concentrations		199
Figure	5.24	Typical calibration curve for arsenic using the filter measurement system		201
Figure	5.25	Typical response for 2 μ g l ⁻¹ arsenic solution using the filter measurement system		201
Figure	5.26	Effect of boost current on net signal for selenium using the filter measurement system		205
Figure	5.27	Effect of boost current on signal to background ratio for selenium using the filter measurement system		205 `
Figure	5.28	Effect of hydrochloric acid concentration on net signal for selenium at various reductant concentrations		207
Figure	5.29	Effect of hydrochloric acid concentration on signal to background ratio for selenium at various reductant concentrations	l	207
Figure	5.30	Effect of hydrochloric acid concentration on signal to noise ratio for selenium at various reductant concentrations		208
Figure	5.31	Typical calibration curve for selenium using the filter measurement system		210
Figure	5.32	Typical response for 0.4 µg l ⁻¹ selenium solution using the filter measurement system		210

•

..

•

• • •

LIST OF TABLES

Table	3.1	Operating conditions for the Unicam SP9 atomic absorption/atomic emission spectrometer	49
Table	3.2	Hydride generation conditions for arsenic, selenium and antimony using the glass 'U' tube gas-liquid separator	52
Table	3.3	Plumbane generation conditions using the glass 'U' tube gas-liquid separator	55
Table	3.4	Limit of detection (3σ) for arsenic, selenium, antimony and lead using the glass 'U' tube gas-liquid separator	60
Table	3.5	Determination of arsenic and selenium in water reference material (IAEA/W-4) using hydride generation and the glass 'U' tube gas-liquid separator	62
Table	3.6	Hydride generation conditions for the tubular membrane gas-liquid separator with atomic absorption spectrometry detection	66
Table	3.7	Limit of detection (3σ) for arsenic and selenium using the tubular membrane gas- liquid separator coupled to atomic absorption spectrometry	70
Table	3.8	Effect of arsenic valence state on peak height at different sodium tetrahydroborate concentrations using the tubular membrane gas-liquid separator	71
Table	3.9	Determination of arsenic and selenium in water reference material (IAEA/W-4) using the tubular membrane gas-liquid separator with atomic absorption spectrometry detection	72
Table	3.10	Operating conditions for hydride generation inductively coupled plasma - mass spectrometry using the tubular membrane gas-liquid separator	78
Table	3.11	Relative signal and chloride interference using different sample introduction methods	83
Table	3.12	Detection limits for arsenic and selenium using the tubular membrane gas-liquid separator coupled to inductively coupled plasma - mass spectrometry	86

..

-- ..

· · ·

· •

Page No.

-

.

Table	3.13	Reproducibility data for arsenic and selenium using the tubular membrane gas-liquid separator coupled to inductively coupled plasma - mass spectrometry	86
Table	3.14	The determination of arsenic and selenium for certified water reference materials using the tubular membrane gas-liquid separator coupled to inductively coupled plasma - mass spectrometry	88
Table	3.15	Hydride generation conditions for the PTFE membrane gas-liquid separator with atomic absorption spectrometry	90
Table	3.16	Determination of arsenic in certified water reference material (IAEA/W-4) using the PTFE membrane gas-liquid separator with atomic absorption spectrometry detection	94
Table	3.17	Summary of advantages and disadvantages for each separator	98
Table	4.1	Vapour generation conditions using the continuous flow approach	112
Table	4.2	Determination of mercury in certified reference materials using the continuous flow approach	118
Table	4.3	Effect of sample volume on linear calibration range	123
Table	4.4	Determination of mercury in certified reference materials and battery anodes	123
Table	4.5	Relative standard deviation for the first, second, third and fourth batch of 25 runs	129
Table	4.6	The precision and output at various injection volumes at 20°C	147
Table	5.1	Spectral characteristics of the boosted discharge hollow cathode lamp emission and atomic fluorescence for arsenic	164
Table	5.2	Analytical performance using various atom cell dimensions for arsenic	174
Table	5.3	Background equivalent concentrations of the components which constitute the total background radiation for arsenic	194

		Page	NO.
Table 5.4	Background equivalent concentrations of the components which constitute the total background radiation for arsenic using a scatter device		195
Table 5.5	Precision of the filter measurement system for arsenic		202
Table 5.6	Determination of arsenic in certified water reference material (IAEA/W-4) for both measurement systems		202
Table 5.7	Background equivalent concentrations of the components which constitute the total background radiation for selenium		209
Table 5.8	Precision of the filter measurement system for selenium		211
Table 5.9	Determination of selenium in certified water reference material (IAEA/W-4)		211

b7 -

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CHAPTER 1

INTRODUCTION

1.1. INTRODUCTION

The demand for larger numbers of chemical measurements with greater speed, sensitivity and lower cost in a wide range of industrial, clinical and other applications has led, in recent years, to the design of a wide variety of automated analytical equipment. This equipment is increasingly becoming available commercially, but due to the complexity and specificity of certain applications, the equipment is often designed and built in house. With the rapid developments made in electronics, equipment is becoming increasingly microprocessor controlled and more recently robotically controlled.

1.1.1. Definition of Automation

The International Union of Pure and Applied Chemistry (IUPAC) definition of automation states "automation is the use of combinations of mechanical devices to replace, refine, extend or supplement human effort and facilities in the performance of a given process, in which at least one major operation is controlled, without human intervention, by a feedback system". This should not be confused with mechanisation which is defined as "the use of mechanical devices to replace, refine, extend or supplement human effort". Foreman and Stockwell (1) have described automation as a term which includes those developments which minimise human intervention in chemical analysis and thus releases the analyst for more demanding tasks, with an

improvement in the efficiency of the analytical process. It is this latter definition which has been adopted for this thesis on "New approaches to automated analytical instrumentation".

1.1.2. The Drive Behind Automation

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The drive behind automation began in the late 1950's when airsegmented continuous flow was introduced by Technicon (2). This approach dominated laboratory automation for many years. The main reason for automating an analytical process has always been and always will be related to economic considerations. Foreman and Stockwell (1) have expressed algebraically the basic costs of performing both manual and automated analysis. They expressed the cost of manual analysis (C_{MAH}) as:

$$C_{MAN} = F_{MAN} (T_s A_s + T_p A_p + T_m A_m + T_c A_c) ---- \{1\}$$

where T_{a} , T_{p} , T_{m} and T_{c} represent the time taken for sampling, pretreatment, measurement and calculation of the result respectively. The corresponding 'A' factors represent the proportion of the operators time for each stage of the analysis. Therefore time consuming operations such as drying or ashing would have large 'A' values. 'F' is a tariff factor which converts time into money. The cost of the same analysis using fully automated procedures (C_{AUTO}) can be expressed as:

$$C_{AUTO} = F_{AUTO} (T_{AUTO} A_{AUTO} + T_{MAINT} A_{MAINT}) ---- \{2\}$$

where T_{AUTO} and T_{MAINT} are the times for automatic analysis and maintenance of the equipment respectively. A_{AUTO} and A_{MAINT} represent the amount of activity or involvement of the operator for analysis and maintenance respectively. By consideration of the terms within equations {1} and {2} it is also possible to represent algebraically semi-automated systems. Although these expressions are only approximate they allow one to assess whether or not the introduction of automation for a particular application is cost effective.

The drive behind automation stems from two sources: the laboratory chemist and his management. Each have their own requirements, and these are often conflicting. Additional requirements are also set by government regulations, which often complicate the issue.

1.1.3. Advantages and Limitations of Automated Analysis

One of the major economic advantages offered by the introduction of totally automated systems is the capability of equipment to be operational during non-working hours. This requires a high order of reliability and safety. Most fully automated systems possess shut down procedures, for use when major deviations in instrument performance occur. Minor deviations are more difficult to detect and often go unnoticed. Automated systems not only increase sample throughput, but also offer a more effective division of labour throughout the laboratory, reducing the need for people to do routine repetitive tasks and freeing them for more interesting work (3). Rosenbrock (4) has a slightly different view in respect of the social implications of

automation and mechanisation. He believes that intelligent machines in some instances may replace skilled workers, demoting them to do unskilled work, consequently retiring those originally doing the unskilled work. He also stressed the importance of the realisation that the abilities of machines and people are different, and complementary, and that the designer of the automated system should consider these different qualities.

Apart from the economic benefits, automation also offers scientific advantages. One of these being the improved precision obtained for the analysis of large batches of samples, from the elimination of human error and fatigue. Applications which involve accurately timed reaction sequences also become more reproducible when automated. The possibility of performing automatic analysis in closed systems, especially for materials which are toxic or unstable in air is also of considerable importance for certain applications, such as those involving radioactivity.

Limitations of automation also exist, most automated analytical equipment is designed in most instances to process batches of samples of similar composition. Samples with varying concentration and matrix composition may affect the measurement device, thereby giving inaccurate results. This situation is more likely to occur in industry, where samples may have a variety of sources, compared to say clinical samples such as blood and urine which have similar compositions. This problem can be overcome by the skill of the analytical chemist by devising new methods of analysis. In designing an automated system the hardware available may cause restraints on the

materials used in construction, the engineer's role in the development of automated analytical equipment is therefore vital.

Further limitations arise when junior staff of limited experience and qualifications operate automated equipment. This arrangement is common practice and normally very successful, however, any minor deviation in instrument performance may be unnoticed by inexperienced staff. There is also a human element that one must consider when introducing new automated analytical equipment into the laboratory, in that, the new user will often try to undermine the performance of the instrument in an attempt to prove that the analyst can perform a more efficient job.

1.1.4. Approaches Available for Automation

Generally speaking, there are two approaches one can adopt for the automation of an analytical technique. These approaches may be broadly classified into: continuous flow or discrete/batch operation. Almost always these approaches have been used exclusively of each other and occasionally the two approaches have been combined. More recently centrifugal and flow injection methods have been utilised.

The discrete methodology maintains the sample as a separate entity throughout all stages of the analysis. Treated samples are presented to the detector in turn, usually via mechanical transportation or collection from a turntable. Continuous flow procedures involve introducing samples into a flowing stream, with reagent additions being made by merging sample and reagent streams. Background and sample are monitored and after passing

through the detector, the sample goes to waste.

Although discrete systems have higher sample throughput than continuous flow, they are normally more expensive and difficult to develop, since they involve a high degree of mechanisation. This means they are more suitable for large batches of straightforward analyses. Another advantage of the discrete approach is the fact that the sample is retained as a separate entity, thereby eliminating the possibility of crosscontamination or confusion of samples.

Continuous flow procedures are probably the simplest to automate and are generally applicable when sufficient sample is available. Most continuous flow analysers incorporate peristaltic pumps, as a means of sample transportation and reagent addition. With the availability of multi-channel peristaltic pumps, the number of possible applications is increased. Unlike discrete analysers, the identity of the sample in continuous flow is lost, giving rise to possible difficulties when successive samples have zero responses. However, this problem can be overcome by careful control of the time sequences between samples and standards. Continuous flow methods are often limited, due to the use of flexible pump tubing which in certain cases, may become corroded and produce erratic flow rates.

The two approaches are not mutually exclusive and combination of the two can be quite advantageous. A typical example being the use of continuous flow methods to introduce samples into a preconcentration device prior to being delivered to the detector in a discrete manner (5,6).

The coupling of discrete procedures to continuous flow methods has also been reported. The major advantage here is seen as applying the speed and convenient automated chemistry of continuous flow to handling small samples. This is the primary aim of flow injection analysis (FIA) (7). This essentially involves the introduction of small sample volumes, typically 50 to 200 µl, into a continuously flowing carrier stream. Chemical reactions or extractions which occur between the sample and the carrier can be introduced into the system. Transient signals are generated as the analyte passes through the continuous flow detection system. The advantages of using flow injection are well documented and several reviews (8,9) and books (7,10) have been written.

1.1.5. Future of Automation

Automation is a relatively new concept of analytical chemistry. By its very nature, it is a multi-disciplinary subject involving chemistry, computing, design, engineering (electrical, electronic and mechanical), and economics. The more complex an automated system becomes the greater the number of people involved. This concept of automation is becoming increasingly important and to ensure rapid developments in the field of laboratory automation, collections of specialists must work together as a multidisciplinary team.

Automated systems are becoming increasingly microprocessor and robotically controlled (11). While robotics address automation needs for relatively complex procedures with high sample throughput, they do not address many of the day-to-day needs of

bench chemists. Laboratory Workstations (12) are probably the next step in laboratory automation. They do not replace robotics, merely complement them. The ultimate automated analytical instrument has been described by Denton (13) as the "Mark I Magic Analyser". An instrument which will accept any sample, in any form, and analyse it for whatever the analyst In an ideal case the instrument would be nonrequires. destructive. Although the "Mark I Magic Analyser" is not available with today's technology there are certain concepts of this idealised instrument available in various automated systems at this present moment in time. This thesis is devoted towards novel automated analytical equipment for vapour/hydride generation. The work described in the forthcoming chapters has been carried out in conjunction with the collaborating body (P S Analytical Ltd), which comprises a team of automation specialists. This study therefore concentrates on the chemical aspects of automation.

1.2.1. Vapour/Hydride Generation

Some of the metalloid elements, in groups IVA, VA, and VIA (As, Bi, Ge, Pb, Sb, Se, Sn and Te) of the periodic table, form covalent gaseous hydrides. These hydrides are volatile and can be generated in sufficient quantities to be of analytical use in atomic spectrometry (14). The reduction of arsenic compounds with zinc producing arsine (AsH₃) is well known from the classical Gutzeit method and Marsh reaction (15). Gaseous mercury may also be generated, using similar reduction techniques (16), and this phenomenon has been extensively utilised analytically.

Holak (17) in 1969, developed a reduction procedure based on the Gutzeit method and Marsh reaction to determine arsenic by atomic absorption spectrometry (AAS). The arsine, generated by a zinc/hydrochloric acid reaction, was cryogenically trapped prior to introduction into an air-acetylene flame for AAS measurement. the analyte from the sample By separation of matrix, interferences were reduced or eliminated. In addition to this, problems associated with solution nebulisation, such as poor sample introduction efficiency and nebuliser blockage, were Since Holak's paper there have been nearly 600 eliminated. publications dealing with hydride generation coupled to atomic spectrometric techniques. Numerous reviews have been written (14,18,19,20) concerning the subject of hydride generation. Nakahara (20) has summarised the principle advantages of hydride generation atomic spectrometry. These include:

- separation of the analyte from potential matrix interferences;
- greater sample introduction efficiency compared to pneumatic nebulisation of solutions;
- 3) improved sensitivity;
- possible speciation;
- 5) usage of emission sources which have poor vaporisation characteristics;
- 6) ease of automation.

Limitations of the hydride generation technique according to Nakahara (20) include:

- interferences due to various cations and anions in solution, reducing the efficiency of hydride formation;
- 2) pH and reagent concentrations are critical in some cases;
- 3) oxidation state of the analyte may be critical;
- slow reaction kinetics, may require collection of the hydride prior to detection.

The hydride generation technique can be divided into three steps. First, the generation and volatilisation of the hydride. Second, the transportation of the hydride into an excitation source. Third, the atomisation process with subsequent spectroscopic measurement. The following sections contain a general overview of each of the hydride generation stages. Cold vapour generation techniques for mercury analysis are also included, since this element is normally generated along with the gaseous hydrides.

1.2.2. Reactions for Vapour/Hydride Generation

a) Metal-Acid Reduction

Two different reaction techniques have been utilised to generate gaseous hydrides. The first system to gain acceptance was the zinc/hydrochloric acid reduction (17). Sulphuric acid may also be used in conjunction with hydrochloric acid or by itself.

The reaction is shown by the following equation:

 $E^{m^{+}}$ Zn + 2HCl - ZnCl₂ + 2H - EH_n + H₂ (excess)

where E is the analyte and m and n may or may not be equal. This procedure was found to be impractical for routine analysis and has therefore not gained wide acceptance. Other metal-acid reactions have also been investigated, including aluminium slurry - hydrochloric acid (21) and magnesium - titanium chloride hydrochloric acid (22). The major drawback of the metal-acid reduction schemes is that it is usually only successful for arsenic, selenium and antimony. Robbins and Caruso (23) observed reaction times in excess of 20 minutes, resulting in an inability to automate the procedure.

b) Sodium Tetrahydroborate - Acid Reduction

A more effective method of generating the hydrides involves the use of sodium tetrahydroborate. The reaction is shown by the following equation:

 E^{m^+} NaBH₄ + 3H₂O + HCl \rightarrow H₃BO₃ + NaCl + 8H \rightarrow EH_n + H₂ (excess)

where E is the analyte and m and n may or may not be equal. This reaction scheme is superior in terms of reduction yield, speed of reaction, contamination of the blank and generation of all the hydride forming elements. It therefore has a greater potential for multi-element analysis and more importantly the reduction scheme is suitable for automation.

c) Tin (II) Chloride Reduction

The two reaction techniques mentioned above are also suitable for mercury (24). However, the most commonly used reduction scheme for mercury is using acidified (16) or alkaline (25) tin (II) chloride solution. This reaction is shown by the following equation:

 Sn^{2+} + Hg²⁺ \rightarrow Sn⁴⁺ + Hg⁰

1.2.3. Gaseous Analyte Manipulation

Once the reaction is complete and the gaseous analyte has been formed, the gaseous products are separated from the liquid products and then delivered to the atomic reservoir where subsequent spectrometric measurement occurs. This process is called gas-liquid separation and it is the subject of Chapter 3 and will therefore only be described briefly in this section. Once separated the gaseous analyte may be delivered to the detection system either directly or via a collection/ preconcentration device.

a) Collection/Preconcentration Mode

The majority of early publications on hydride generation included collection devices such as rubber balloons and plastic bags (26), but it was soon realised that the acidic by-products of the reaction medium quickly degraded the inner surfaces of the balloon causing leakage.

A more efficient method for trapping the hydrides was described

by Holak (17). He preconcentrated the hydrides in a glass 'U' tube submerged in liquid nitrogen. After trapping for a set time, the 'U' tube was removed from the liquid nitrogen causing the hydride species to selectively volatilise in correspondence with their boiling points. Although, very time consuming, this procedure has provided useful information on speciation of the hydrides (27).

Gaseous hydrides may also be collected in a heated graphite furnace, followed by atomic absorption spectrometry. The hydrides are normally collected at about 600°C, with subsequent atomisation at higher temperatures (2700°C). This in-situ preconcentration procedure has been adopted for all the hydride forming elements and mercury (28,29). These procedures usually involve the use of modifiers, such as palladium, which enhance collection efficiencies. An alternative to this approach is to trap the hydrides into an absorbing solution of potassium iodide and iodine (30), silver nitrate (31) or cerium (IV) and potassium iodide (32) with subsequent detection using electrothermal vaporisation-atomic absorption spectrometry.

The collection modes described above for the hydride forming elements are in some cases tedious and time consuming. Since they rely heavily on accurate timing sequences for collection, they are often associated with poor reproducibility. More importantly they are difficult to automate.

Mercury on the other hand is more suitable for automation, since it forms an amalgam with gold, platinum and silver. This chemical phenomenon has been utilised analytically by numerous

workers (6,33,34). The procedure involves generating the gaseous mercury and passing it over an amalgamation accessory. On heating the amalgamation unit, the mercury is released and delivered as a discrete plug to the spectroscopic detection system. This method will be discussed in greater detail in Chapter 4 for gaseous samples.

b) Direct Transportation Mode

The collection devices mentioned in the previous section have mostly been superseded by direct transfer modes. This is especially true for the less stable gaseous hydrides, such as plumbane (PbH₄), stibine (SbH₃), stannane (SnH₄) and tellurium hydride (TeH₂).

The sodium tetrahydroborate - acid reaction scheme has revolutionised the hydride generation technique in terms of automation, since the reaction rates are so much more rapid than that of the metal - acid techniques. Three different approaches have been adopted for automated vapour/hydride generation. These include, continuous flow, flow injection and batch techniques. Continuous flow and flow injection approaches utilise peristaltic pump manifolds to deliver sample and reagents to reaction vessels where subsequent gas-liquid separation takes place. The other approach, using pressurised reagent pumping systems, usually requires operator manipulation and is therefore only semiautomated. This approach is more commonly known as the batch technique.
1.2.4. Detection Systems for Vapour/Hydride Generation

A wide range of analytical atomic spectrometry techniques have been utilised for vapour/hydride generation. These include atomic absorption spectrometry (AAS), plasma emission spectrometry (ICP, DCP, MIP, CMP), atomic fluorescence spectrometry (AFS) and inductively coupled plasma - mass spectrometry (ICP-MS).

a) Atomic Absorption Spectrometry (AAS)

Of the techniques mentioned above AAS has been the most extensively used for vapour/hydride generation techniques. Various atomisers for hydride generation - AAS have been investigated and these include flames, flame in tubes, flame heated quartz tubes, electrically heated quartz tubes and graphite furnaces.

Early workers like Holak (17) utilised both air-acetylene and dinitrogen oxide-acetylene flame atomisers, but these have high background absorption in the low UV wavelength range. Kahn and Schallis (35) reported a 62% background absorption for an airacetylene flame at the arsenic resonance line (193.7 nm). Alternative flames such as the argon-hydrogen diffusion flame were found to reduce the background absorption to 15%. Batch approaches for hydride generation are unsuitable for flame atomisers since the sudden introduction of hydrides and hydrogen may perturb the flame.

Flame in tube atomisers have been used in combination with both

oxygen-hydrogen flames (36) and air-hydrogen flames (37). These, however are subject to background absorption and flame noise.

Externally heated quartz tube atom cells are probably the most favoured for AAS. The tube in the form of a 'T' piece is normally heated with an air-hydrogen or air-acetylene flame. To prevent excess hydrogen from igniting at the ends of the tube, a stream of nitrogen may be added transversely (38). The advantages of this system include elimination of flame noise, and therefore increased sensitivity. The quartz tube may also be heated electrically (27), the advantage here being to allow the analyst to control the temperature, which can be critical in some cases.

One of the problems associated with quartz atomisation tubes, is that the surface of the quartz deteriorates due to devitrification. This not only reduces the lifetime of the atomiser, but also causes loss in sensitivity and precision (39). Tube lifetime can be increased with the use of sulphuric acid, rather than hydrochloric acid in the reaction medium. As mentioned previously graphite furnace atomisers may also be used for hydride generation - AAS.

b) Plasma Emission Spectrometry

Plasma emission spectrometric techniques such as the direct current plasma (DCP) and inductively coupled plasma (ICP) were introduced commercially in the early 1970s and now provide a powerful alternative to AAS (40,41). More recently microwave induced plasmas (MIP) and capacitively coupled microwave plasmas

(CMP) have been introduced (42).

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As mentioned previously there are two general approaches to vapour/hydride generation, batch and continuous flow. The batch process is unsuitable for these emission techniques, since copious amounts of hydrogen and water are delivered as discrete plugs causing instability and, in severe cases, extinction of the plasma. High forward power levels have been utilised in order to keep the plasma from extinguishing (43). Although continuous flow procedures also generate large amounts of hydrogen and water vapour, they do so continuously which has a less detrimental effect on the plasma.

Thompson <u>et al.</u> (43) were the first to report the use of continuous flow hydride generation ICP-AES for the simultaneous determination of arsenic, bismuth, antimony, selenium and tellurium. They developed a continuous flow glass 'U' tube gasliquid separator which has subsequently been used by many workers (44,45,46). Nakahara (47) employed two gas-liquid separators in series to reduce excess hydrogen and water vapour being carried to the plasma.

Alternatively, continuous flow hydride generation systems have involved the use of modified nebulisers (48). The advantage here being that non hydride forming elements can also be determined.

Pyen and Browner (46) recently developed a three channel ICP-AES for simultaneous determination of arsenic, selenium and antimony. This system utilised a low resolution prism monochromator for wavelength isolation together with interference filters for

background reduction. The system was then assessed for both flow injection and continuous flow approaches and a critical comparison was made (49). The flow injection approach was found to be approximately three times less sensitive but more precise than the continuous flow approach.

Panaro and Krull (50) were the first to describe continuous flow DCP-AES, they introduced the hydride to the plasma via the spray chamber. Other workers (51,52) have developed more efficient sample introduction devices which direct the hydride to the analytical zone of the DCP.

c) Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

The combination of an inductively coupled plasma as a high temperature ion source with a quadrupole mass spectrometer as a high sensitivity detector has recently become commercially available (53). Hydride generation ICP-MS has recently attracted attention (54,55) as a way of overcoming the poor nebulisation and transport efficiency (typically 1-2%) of ICP-MS. Powell et al. (54) have described the operating conditions for the determination of arsenic, bismuth, mercury, antimony, selenium and tellurium in environmental samples. Detection limits for these elements were increased dramatically as a result of improved sample introduction efficiency. In addition, Dean et al. (55) have studied the efficiency of hydride generation for a number of organic and inorganic arsenic species. Inductively coupled plasma - mass spectrometry suffers from interferences from polyatomic ions. Such interferences are particularly troublesome for monoisotopic elements, one prime example being

arsenic. These interferences must therefore be considered when coupling hydride generation to ICP-MS, and this is discussed in greater detail in Chapter 3.

d) Atomic Fluorescence Spectrometry (AFS)

Hydride generation - AFS was first studied by Thompson (56) for the determination of arsenic, antimony, selenium and tellurium. He utilised an argon/hydrogen flame as an atom cell and achieved excitation with modulated microwave excited electrodeless discharge lamps, (EDLs). Like most of the early workers he used а modified atomic absorption/emission spectrometer as a dispersive measurement system. More recently, Ebdon et al. (57) described a similar system for arsenic and selenium using an air/hydrogen flame burning on a glass 'Y' burner. Brown et al. (58) used an argon sheathed, electrothermally heated quartz atomiser for the atomisation of hydrogen selenide. Most of the hydride forming elements can be detected using AFS in the UV region below 250 nm. This is a particularly useful spectral region, since very little background emissions are seen even from the flame atom cells. More importantly, the spectrum is not complex, since the analyte has been separated from the matrix during the hydride generation stage. It therefore follows that non-dispersive AFS is possible.

Nakahara and co-workers have published a series of papers on hydride generation non-dispersive AFS for the determination of arsenic, (59), bismuth, (60), antimony, (61), lead, (62), selenium, (63), tin, (64) and tellurium (65). They utilised an argon - hydrogen diffusion flame as an atom cell and microwave

excited EDLs as excitation sources. D'Ulivo et al. (66) developed a multielement system based on a hydrogen diffusion flame, radiated by four radio frequency excited EDLs, each being modulated at a set frequency. The emitted fluorescence radiation was detected by one photomultiplier tube, connected to four lockin amplifiers, each tuned to the frequency of the relevant EDL. The same group designed an electrothermally heated quartz tube flame atomiser, for the determination of selenium. Using the batch hydride generation approach а hydrogen miniflame spontaneously ignited at the top of the heated tube. This was sufficient to achieve atomisation indicating that atomisation was probably via a free radical mechanism within the flame (67).

Mercury, by its very nature is a good element for determination by fluorescence, since it is atomic at room temperature and also absorbs and fluoresces at the same wavelength (i.e. resonance fluorescence). Intense mercury sources are available and atomisation cells are uncomplex when the technique is coupled to vapour generation. Thompson and Godden (68) proposed the use of fluorescence for the analysis of mercury in 1975. They modified an atomic absorption/emission spectrometer to obtain a dispersive measurement system. More recently, Godden and Stockwell (69) described the development of an atomic fluorescence spectrometer specifically designed for mercury analysis. Α 254 nm interference filter was utilised to achieve wavelength isolation and reduction of background scatter.

1.2.5. Interferences in Vapour/Hydride Generation Techniques

There are basically two types of interferences which can occur,

spectral and chemical interference. The former is not usually observed for vapour/hydride generation, since the analyte is separated from its matrix. Chemical interferences are more common and may occur in both gaseous and liquid phases. A major proportion of the hydride generation literature is devoted to the severity and presence of these interference effects. Unfortunately, there is a wide divergence of opinions and most papers concentrate on the severity of the interference without any consideration to the interference mechanism, or more importantly how to overcome them. It is also difficult to compare results, since interferences are extremely dependent on the hydride generation system and conditions used.

Chemical interferences in the liquid phase cause a reduction in the formation rate of the hydride and in severe cases prevent formation, partially or completely. Competitive reactions whereby the sample matrix is preferentially reduced consuming the reducing agent (e.g. $NaBH_4$) have been suggested for both slow formation rates (70) and co-precipitation or the formation of an insoluble compound of the analyte element (71).

Welz and co-workers published a series of papers discussing interferences for hydride generation (71-74). This work suggested that interference from transition metals (e.g. Ni) could be minimised by using high acid and low sodium tetrahydroborate concentrations. The idea being that with these conditions the interferent would be reduced to a lesser extent and kept in solution with the high acid concentration. The mechanism they proposed was the preferential reduction of the interfering ion to the metal. This in turn, adsorbs and

decomposes the gaseous hydride. Further suggestions are that insoluble arsenides or similar compounds may be formed in a secondary reaction (71). Iron (III) has been found to have a releasing effect on the interference of nickel and copper for arsenic and selenium determinations respectively (73,75). The mechanism here being the preferential reduction of Iron (III) to Iron (II) by BH₄⁻ ions before reduction of the nickel ions. Bax et al. (76) developed a device to elucidate the interference mechanism of copper, nickel and cobalt for selenium determinations. They concluded that the interference is partly due to the elimination of the hydride by the reaction products from the interferent and sodium tetrahydroborate, rather than the actual interferent ions. The catalytic effect of transition metal ions on the decomposition of sodium tetrahydroborate with acid is also believed to play a major role.

Although the interference mechanism still remains a controversial issue, the primary concern of the analyst is the reduction or elimination of these interferences. Nakahara (20) has briefly summarised the various approaches workers have adopted to overcome these interferences.

(1) Use of standard additions.

(2) Varying concentration of reagent (i.e. HCl/NaBH₄).

(3) Use of masking agents (e.g. EDTA, KI, thiourea, ascorbic acid, malic acid, 1-10 phenanthroline, thiosemicarbazide and L-cystyne).

(4) Use of releasing elements such as Fe, Hg, Cu and Te.

(5) Separation techniques

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- (i) Solvent extraction.
- (ii) Co-precipitation.
- (iii) Adsorbing colloid flotation.
- (iv) Application of chelating resins.

The determination of mercury using cold vapour generation is also prone to interferences, from cations, anions and organic compounds (34). Munaf <u>et al.</u> (25) have shown that these interferences can be minimised using alkaline tin (II) chloride instead of acidified tin (II) chloride. Interferences which occur in the gaseous phases can be overcome with use of an amalgamation accessory (34)

1.2.6. Speciation for Hydride Forming Elements and Mercury

With the ever increasing legislative demands, it is becoming increasingly important for informative speciation. The hydride forming elements commonly exist in solution in two oxidation states, As (III) and As (V), Se (IV) and Se (VI), Sb (III) and Sb (V), and Te (IV) and Te (VI). These oxidation states are critical for hydride formation. Thompson and Thomerson (38) reported a less efficient reduction of As (V) compared to As (III). Se (VI) also showed a similar effect. If total inorganic concentrations are to be determined it follows that pre-reduction methods must be employed. Potassium iodide has been found to be suitable for arsenic (57) and antimony (61). Selenium (78) and tellurium (79) may be reduced by heating in 50% V/V hydrochloric

acid at 70°C for 10 mins. The reaction for selenium is shown by the following equation:

$$SeO_4^{2-} + 2HCl \rightarrow SeO_3^{2-} + Cl_2 + H_2O$$

Hydride generation must immediately follow the reduction step, since the residual chlorine may cause back oxidation of Se (IV) to Se (VI) (78). At pH < 1 it has been shown that no prereduction is required for total arsenic determination (80). By analysing samples before and after pre-reduction steps it is possible to obtain inorganic speciation (79).

Organic speciation is also becoming increasingly important. One common method of determining reducible species involves generating both organic (e.g. monomethylarsonic acid and dimethlyarsinic acid) and inorganic hydrides and then cryogenically trapping them in a 'U' tube submerged in liquid nitrogen. Each hydride species has a different boiling point, thereby allowing selective volatilisation once the cryogenic trap is removed (27).

The use of chromatographic techniques for separation followed by continuous flow hydride generation has also been investigated (81). One of the problems of hydride generation for speciation studies is that one can only speciate reducible species. However, non reproducible forms are often non-toxic e.g. arsenobetaine (82).

Magos (83) was the first to demonstrate that tin (II) chloride in an alkaline medium, in the presence of cysteine could reduce

inorganic mercury in biological samples to gaseous mercury. Under these conditions, the carbon mercury bond is not attacked and methyl mercury not determined. A displacement reaction using cadmium chloride was then used to liberate mercury from the organic forms, thereby allowing cold vapour generation. Using this procedure he was therefore able to speciate between the two forms.

1.2.7. Atomisation Mechanisms for Gaseous Hydrides

The proposed atomisation mechanism for the gaseous hydrides is not through thermal decomposition, but via free radical interactions (84). Although not fully understood, it has been shown that oxygen plays an important role in the generation of free radicals. The following equations illustrate this involvement:

 $H \bullet + O_2 \Rightarrow \bullet OH + O \bullet$ $O \bullet + H_2 \Rightarrow \bullet OH + H \bullet$ $\bullet OH + H_2 \Rightarrow H_2O + H \bullet$

The same reactions were proposed by Dědina and Ruběška (84) as being the primary reason for hydrogen radicals in hydrogen diffusion flames. This therefore suggests an atomisation mechanism via hydrogen radicals for both cuvette and flame atomic cells. For instance, the atomisation for tellurium hydride might undergo two consecutive reactions:

 $TeH_2 + H \bullet \rightarrow TeH \bullet + H_2$

 $TeH \bullet + H \bullet - Te + H_2$

and other hydride forming elements may react accordingly.

However, calculations (86) have recently shown that the amount of hydrogen radicals present is probably insufficient to sustain such a mechanism. No argument has been found to contradict the assumption that a reaction shown by the following equation should not occur:

$$4AsH_3 + 3O_2 \rightarrow 4As + 6H_2O$$

This atomisation mechanism is catalysed by hydrogen and hydroxyl radicals (87). The co-existence of AsH_3 , As and polymers of the type As_i , was also studied both theoretically using thermodynamic data and experimentally for the hydrides. These occur at lower temperatures and carrier gas flow rates (88).

1.2.8. Applications for Vapour/Hydride Generation

Hydride/Vapour generation coupled to atomic spectroscopic techniques has been extensively used in many laboratories on a routine basis for over twenty years. There are hundreds of publications which describe analytical procedures for different sample matrices. These include clinical, biological, environmental, food, geological, vegetation, metallurgical and water samples. Nakahara (20) has summarised some of these applications.

1.2.9. Future of Vapour/Hydride Generation

The advantages and disadvantages of hydride/vapour generation

coupled to atomic spectroscopy techniques have been discussed. The generation of gaseous analytes is advantageous, due to improved sample introduction efficiency and removal of the analyte from sample matrices. The technique to date has concentrated on the hydride forming elements and mercury, but recent publications (89) have suggested a trend for the generation of other volatile species.

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The capability of multi-elemental determinations for hydride forming elements and mercury using atomic emission and fluorescence spectrometry techniques is possible (simultaneously or sequentially) using compromise reaction mediums. In contrast to this, element specific detectors (69) are also available and are becoming increasingly popular for elements with demanding legislative requirements.

Most analytical techniques are subject to interferences and without a doubt, the elucidation of the interference mechanisms and their avoidance will play a role in future research in this field.

1.3.1. Outline of Thesis

This thesis is devoted toward the development of novel automated analytical equipment for vapour/hydride generation. Novel gasliquid separation devices are examined in Chapter 3 using AAS and ICP-MS detection systems. Chapter 4 focuses on mercury determination using both automated continuous flow and flow injection approaches with detection by atomic fluorescence spectrometry. The effects of moisture carry-over on mercury

determination are investigated and methods of moisture removal using desiccants, physical moisture traps and novel semipermeable hygroscopic drying tubes are discussed with reference long term stability and sensitivity. to An automated preconcentration system which utilises a gold impregnated sand trap for the determination of mercury in gaseous samples is also described. The final experimental chapter is concerned with the development of an atomic fluorescence spectrometer for the hydride forming elements. This utilises a high intensity boosted discharge hollow cathode lamp (BDHCL) as an excitation source, a chemically generated hydrogen diffusion flame as an atom cell, a solar-blind photomultiplier tube and an interference filter to achieve wavelength isolation and reduction of flame emissions. An automated system is assessed for arsenic and selenium determinations.

CHAPTER 2

INSTRUMENTATION

2.1. INSTRUMENTATION

2.1.1. Continuous Flow Vapour/Hydride Generation

An automated continuous flow vapour/hydride generation system (10.003, P S Analytical Ltd, Sevenoaks, Kent, UK) was used in this study to generate gaseous hydrides and mercury. The instrument is of a simple design which basically consists of a constant speed multi-channel peristaltic pump to deliver reagent and sample solutions, a set of electronically controlled switching valves to alternate between blank and sample solutions and a gas-liquid separator which separates and delivers the products to gaseous an atom reservoir where subsequent spectroscopic determination can take place.

The flow pattern of the system is represented schematically in Figure 2.1. When activated the unit goes through a cycle involving four stages and these are:

- (i) Delay The time required for the sample to reach the switching valve.
- (ii) Rise The time for the signal to reach steady state.
- (iii) Analysis Period in which measurements are taken.
- (iv) Decay The time for the signal to decay to the baseline.

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Figure 2.1 - Schematic diagram of the continuous flow vapour/hydride generation system, shown in the sampling position. The dotted line represents the flow of the blank solution



The time durations for each stage may be varied accordingly, depending on the application, and a facility is available to hold any stage of the cycle if desired.

2.1.2. Flow Injection Vapour/Hydride Generation

An automated flow injection vapour/hydride generation system (40.630, P S Analytical Ltd, Sevenoaks, Kent, UK) was used in this study to generate gaseous hydrides and mercury. A schematic diagram of the flow injection manifold is shown in Figure 2.2. This is almost identical to the continuous flow approach, except that the switching valve is replaced with a 6 port valve. The sample loop may be filled either manually via a syringe method or by continuously pumping the sample through the loop. - The latter method being preferred for automated systems. Once activated the valve switches pneumatically using a supply of compressed gas. Unlike the continuous flow approach, signals generated are transient. The continuous flow and flow injection vapour generation systems may be operated manually or by computer control. The latter is achieved using 5 volt transistor transistor logic (TTL).

Figure 2.2 - Schematic diagram of the flow injection vapour/hydride generation system, shown in the blank position



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2.2.1. Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry (AAS) is a well established technique and has been routinely used in many laboratories for over thirty years. Numerous reviews and books have been written (90,91).

The process of atomic absorption involves the absorption, by free atoms of an element, of light at a wavelength specific to that element. It is essentially used to determine metallic and semimetallic elements, since these elements contain valence electrons which are relatively loosely bound to the nucleus and therefore can be excited from their ground state to higher energy levels by photons of wavelengths in the range 190 to 900 nm.

For each atom of a given metal or semi-metal the energy gap for electronic transitions is nearly identical. More importantly the energy gap is characteristic to that particular element. Thus if light of a narrow wavelength is passed through an atom cloud, then it is only the atoms of one particular element which will absorb photons. Hence atomic absorption spectrometry is a highly selective technique.

The instrument requirements include a light source such as a hollow cathode lamp (HCL) or an electrodeless discharge lamp (EDL), which emits radiation characteristic of the element of interest. A flame or electrothermal cell to produce an atomic vapour which in turn absorbs the characteristic radiation from the source by various amounts, depending upon the concentration

of the free atoms, and finally a detection system, usually a photomultiplier tube. Prior to radiation entering the detector, isolation of the required wavelength is achieved using a monochromator. An Atomic Absorption/Emission Spectrometer (SP9, Unicam Ltd, Cambridge, UK) was used for this research and the optical diagram of this instrument is shown in Figure 2.3.

2.3.1. Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

The combination of an inductively coupled plasma (ICP) as a high temperature ion source with a quadrupole mass spectrometer (MS) as a high sensitivity detector has recently led to a revolutionary new method of analysis (ICP-MS), (92). The main stages of ICP-MS operation are:

(i) Sample introduction into the plasma source.

(ii) Sample dissociation, atomisation and ionization.

(iii) Ion extraction in the interface region.

(iv) Separation and measurement of ionic species in the quadrupole mass spectrometer.

A general schematic diagram of an ICP-MS instrument is shown in Figure 2.4. The argon plasma is initiated by an electrical discharge from a Tesla coil and maintained by inductive coupling of 1.2 to 1.8 kW of radiofrequency (27.12 KHz) energy from the induction coil. The plasma torch is maintained in the horizontal position in order to achieve the most efficient ion extraction.

Figure 2.3 - Optical diagram of the atomic absorption spectrometer



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Figure 2.4 - Schematic diagram of a typical inductively coupled plasma-mass spectrometer



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Ion extraction occurs at the interface between the inductively coupled plasma and the mass spectrometer, it consists of two nickel cones known as the sampler and skimmer, with apertures 1.0 and 0.7 mm respectively, which are located on the axis of the plasma torch. The extracted gas forms a beam in the first expansion stage, which operates at a pressure of about 1.0 mbar. The core of this beam passes into a second stage (8 x 10^{-3} mbar) via a.skimmer aperture behind which an ion lens focuses the ions through the final aperture into the quadrupole mass spectrometer and detector. (2 x 10^{-6} mbar).

The quadrupole mass spectrometer effectively acts as a filter, only transmitting ions with pre-selected mass : charge ratios. Transmitted ions are detected with a channeltron pulse counter electron multiplier.

In practice any sample introduction technique can be coupled to the plasma source. Sample solution introduction via pneumatic nebulisation is typically 1-2% efficient. This can be improved further by using vapour/hydride generation, thereby increasing sensitivity by 2 orders of magnitude for the hydride forming elements and mercury. This is especially true for arsenic and selenium, since they have high first ionization energies, and are therefore relatively unsensitive using nebulisation introduction systems. The determination of arsenic and selenium by ICP-MS can be problematic, particularly when samples contain substantial amounts of chloride ions. The problems result from spectral overlaps of argon chloride species on the isotopes of ⁷⁵As and ⁷⁷Se. Arsenic is monoisotopic and therefore this isobaric

interference severely limits its determination in biological and environmental samples. There are, however, a number of ways to overcome this problem, such as hydride generation (55) or the addition of nitrogen to the plasma (92) and these will be discussed in more detail in section 3.3.4. The coupling between vapour/hydride generation inductively coupled plasma - mass spectrometry is simply a short transfer line of silicone rubber tubing attached to the base of the plasma torch. The spray chamber is bypassed, to avoid sample dilution. The ICP-MS instrument used in this study was a VG Plasmaquad 2. (Fisons Instruments, Winsford, Cheshire, UK) fitted with a Fassel torch.

2.4.1. Atomic Fluorescence Spectrometry (AFS)

Atomic fluorescence is a radiational deactivation process which occurs after the excitation of free atoms by the absorption of radiation of a characteristic wavelength from an appropriate excitation source. There are two basic types of fluorescence, resonance fluorescence and non-resonance fluorescence. Resonance fluorescence is usually the most intense and has therefore been the most widely used in analytical chemistry. It occurs when the atom re-emits a spectral line of the same wavelength as that used for excitation. The most useful transitions involve the ground state however, excitation arising from non-ground state energy levels can also occur. The various types of atomic fluorescence are summarised in Figure 2.5. The energy levels are indicated by numerical subscripts used in ascending order for increasing energy. The solid lines represent radiational processes and the dashed lines non-radiational processes.

Figure 2.5 -Types of atomic fluorescence, dashed lines represent radiationless transitions, double headed arrow represents a thermal activation process



In the latter, a single-headed arrow represents non-radiational de-activation and a double-headed arrow a thermal activation process. The term anti-stokes is used when the radiation emitted is of shorter wavelength, i.e. greater energy than that absorbed.

The basic instrumentation for fluorescence consists of an excitation source with an appropriate power supply, an atomiser, a method of isolating the wavelength region of interest, a photodetector and an electronic amplifier/readout system. Illumination at right angles to the detector axis is preferred to prevent radiation from the excitation source reaching the detector.

Dispersive and non-dispersive measurement systems have been utilised and these are shown in Figures 2.6 and 2.7 respectively. Dispersive systems can be obtained with modification of atomic absorption/emission spectrometers, by placing an intense excitation source at right angles to the optical axis of the monochromator. Since atomic absorption operates according to the basic limits of the Beer-Lambert Law, one of which is that absorbance is independent of the source intensity, atomic absorption apparatus has low light gathering characteristics, especially in the far uv wavelength region. Atomic fluorescence however, requires high light gathering power to be used to the best advantage. For this reason, the entrance slits of the monochromator are fully opened in order to collect as much fluorescence as possible. In fact, no monochromator is required for atomic fluorescence because it can be arranged so that only one fluorescent species is excited by an element specific excitation source.

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Figure 2.6 - Dispersive atomic fluorescence apparatus



Figure 2.7 - Non-dispersive atomic fluorescence apparatus



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More importantly, in atomic fluorescence, it is possible to use all lines of the element if a line source is used for excitation. Summation of these fluorescence lines is possible and therefore non-dispersive systems are usually more sensitive than dispersive systems. On some occasions it may be advantageous where there is strong emissions from the flame to use a filter between the atom reservoir and the detector, see Figure 2.7. The relative advantages and disadvantages of the two approaches will be discussed in greater detail in the forthcoming chapters.

Mathematical expressions relating atomic fluorescence intensity to atom concentration can be quite complex (91), since they consider both the initial absorption process and the proportion of the absorbed energy which is re-emitted as fluorescence. They must also allow for the possibility of self-absorption of incident and emitted radiation. The other complicating factor is the number of different types of fluorescence that are possible. The expression for fluorescence intensity may be simplified by making the following assumptions:

- That the fluorescence transition considered is excited by absorption of energy at only a single frequency.
- 2) That the entire fluorescence cell is within the solid angle viewed by the detector.
- 3) That no fluorescence emission is lost by re-absorption in the cell.

In this ideal case, the integrated fluorescence intensity at right angles to the incident radiant beam is given by;

$$I_{\rm F} = I_{\rm o} W \, \frac{\Omega}{4\pi} \, A_{\rm T} \, \emptyset$$

Where I_o is the radiant flux; w is the width of the exciting beam of radiation; Ω is the solid angle (4 π is simply the total number of radians over which fluorescence is emitted from the cell); A_T is the total absorption factor at the fluorescence line; Ø is the fluorescence yield, which is the fraction of the absorbed photons which is re-emitted as fluorescence radiation.

CHAPTER 3

GAS-LIQUID SEPARATION PROCESSES FOR CONTINUOUS

FLOW HYDRIDE GENERATION

3.1. INTRODUCTION

Hydride generation essentially involves three stages. First, the generation and volatilisation of the hydride. Second, the transportation of the hydride into an excitation source and third, the atomisation process with subsequent spectroscopic measurement. This chapter will concentrate on the second stage which involves separating the gases containing the analyte from the liquid products using a gas-liquid separation device.

The majority of workers in the field (44,45,46) have used conventional glass 'U' tube separators, based on the design of Thompson <u>et al.</u> (43). Provided a suitable chemical environment exists, hydride formation will occur at the point where reductant and acidified solutions meet. Therefore in most instances a gasliquid mixture exists even before entry to the gas-liquid separator (GLS). On entry the gaseous products, either hydrogen or hydrogen and hydrides, are separated from the liquid products. The latter flows via a constant head 'U' tube to a free running drain, and the former, being purged by an inert gas such as nitrogen or argon into the atom cell.

Other designs of gas-liquid separators made from glass have been reported. Sturman (94) described a separator which achieves separation by impingement of the gas-liquid mixture on a glass surface, facilitating the release of gaseous products without the formation of large bubbles. The volume of the separator was kept

to a minimum to ensure a rapid response.

More recently, membrane gas-liquid separation has been introduced. Pacey et al. (36) were the first to describe a dual phase gas diffusion cell with a porous polytetrafluoroethylene (PTFE) membrane as a GLS for arsine generation with AAS This device had a diffusion area 70 mm long by 1 mm detection. wide and was fitted with a 0.45 μ m pore size PTFE membrane. One of the problems they encountered was that unsupported membranes stretched into the flow channel, due to the pressure differential between the two phases. Support materials such as polyethylene, wax-impregnated cellulose and perforated aluminium foil were investigated, but the most suitable support was found to be nylon This separator design was found to decrease transition mesh. metal interferences, since the fast separation process rapidly removed the gaseous hydride from the potential interferents in the liquid phase.

Yamamoto and co-workers (95) described a GLS based on microporous PTFE tubing for flow injection - hydride generation - AAS. The mixture of hydrogen, arsine, argon carrier gas and the reacted solution was passed through the inner PTFE tube. The gaseous products diffused through the membrane whilst the liquid products flowed continuously to waste. Like Pacey <u>et al.</u> (36) they also observed a reduction in transition metal interferences compared to conventional methods of separation.

It therefore follows, that there are two approaches one can adopt for membrane gas-liquid separation, either using film or tubular membranes. Wang and Barnes (96,97) studied both approaches for

the determination of arsenic using ICP-AES. The tubular membrane design consisted of two concentric tubes. Various separator dimensions were investigated. Outer glass tube dimensions were between 7-10 cm in length and 5-20 mm outer diameter, with gas inlet and exit ports located on opposite sides at each end of the tube. The inner tube consisted of microporous PTFE tubing which was firmly seated at the reduced diameter ends of the outer tube. The gas-liquid mixture passed through the inner tube and the gaseous products diffused through the membrane, subsequently being swept to the plasma discharge using an argon carrier gas which flowed through the outer tube. Using a permeation relationship (97) and a model for hydride transfer into the plasma (45), they discovered that maximum arsenic signals were obtained when the ratio of the tubing diameter to wall thickness was large. Small separator volume and tubing diameter allows for fast responses. As one would expect, rapid permeation was found with larger pore sizes.

The film membrane separator studied by Wang and Barnes (96) was constructed with two aluminium blocks. Each block had a 1 mm outer diameter groove machined into the middle of one of its surfaces. Various microporous PTFE membranes were pressed between the two blocks to cover the grooves which were aligned one above the other when the two blocks were firmly clamped together. Separation was achieved by passing a gas-liquid mixture into one side of the separator, allowing gaseous products to diffuse freely through the membrane while the liquid products flowed continuously to waste. Four types of microporous PTFE membrane were investigated, with different pore sizes, thickness, porosity and support materials. According to the permeation

theory proposed (97), the permeation rate through the membrane wall should be proportional to the membrane area and pore size and inversely proportional to the thickness of the membrane. Wang and Barnes however, found that the signal magnitude for each type of membrane was similar, and attributed this to both the accelerated linear flow rate of the generated gas and spent solution through the reduced diameter of the separator. Consequently, this increased the hydride permeation rate through the membrane thereby lessening the effects of pore size and thickness. Although similar magnitudes were obtained for each membrane, the signal to noise and signal to background ratios varied to a greater degree. The best analytical performance was obtained with a 0.2 μm pore size, 76 μm thickness, and 78% porosity PTFE membrane supported by non-woven polypropylene.

Membrane gas-liquid separator devices have not only been utilised for hydride generation, but have also been applied to other applications. These include:

- (i) carbon dioxide determinations using ion chromatography(98);
- (ii) debubblers for segmented continuous flow auto-analysers
 (99);
- (iii) simultaneous determination of cyanide and thiocyanates
 (100);
- (iv) determination of ammonia (101);
- (v) determination of chlorine (102);
- (vi) determination of mercury (103);

(vii) sulphide determinations in groundwaters (104).

Cave and Green (105) recently reported a feasibility study on the determination of iodide, tin, arsenic, selenium and bicarbonate

in groundwaters by ICP-AES using a tubular membrane gas-liquid separator. This device consisted of a 2 m PTFE outer tube (3.2 mm o.d. x 1.5 mm i.d.) and a silicone rubber inner tube (1 mm o.d. x 0.5 mm i.d.) also of 2 m in length. The two tubes were connected using variable bore 'T' connectors. Iodide was determined after oxidation to iodine using hydrogen peroxide and acidic molybdate as a catalyst, and bicarbonate was determined by displacement from solution as carbon dioxide. The hydride forming elements were determined by conventional sodium tetrahydroborate - hydrochloric acid reduction. Low parts per billion detection limits were obtained for each analyte.

This chapter is devoted towards investigating the gas-liquid separation processes involved for continuous flow hydride generation. Various separation devices have been investigated, including a conventional glass 'U' tube separator (GGLS) based on the design of Thompson et al. (43), a tubular membrane separator (TMGLS) as described by Cave and Green (104,105) and a microporous PTFE membrane mounted in a standard gas diffusion cell (MGLS), similar to that used by Pacey et al. (36). The effect of sodium tetrahydroborate and hydrochloric acid concentrations together with carrier gas flow rate on signal magnitude and response times have been investigated for each separator for one or more of the hydride forming elements. The relative advantages and disadvantages of each separator are discussed with reference to their analytical performance.

3.1.1. Experimental and Instrumentation

A commercially available continuous flow vapour/hydride generator

supplied by the collaborating body (P S Analytical Ltd, Sevenoaks, Kent) was used to investigate the various designs of gas-liquid separation devices. A schematic diagram of this instrument is shown in Figure 2.1. The system was used throughout this study, the only modification being the replacement of different types of separator. Since this instrument is a well established commercial product, major parameters such as sample flow rates were not varied. The aim of the study was therefore to assess the suitability and capability of novel gas-liquid separation devices for the existing hydride generation product.

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Table 3.1 lists the operating conditions used in these experiments for AAS using the tube in flame method (see section 1.2.4a)...These conditions were maintained for each gas-liquid separator.

<u>Table 3.1</u> Operating conditions for the Unicam SP9 atomic absorption/atomic emission spectrometer

Element	As	Se	Sb	РЪ
Wavelength/nm	193.7	196.0	206.0	283.3
Bandpass/nm	1.0	1.0	1.0	1.0
Damping/s	2.0	2.0	2.0	2.0
Mode	ABS	ABS	ABS	ABS
Background Correction	OFF	OFF	OFF	OFF
Lamp Current/mA	8.0	6.0	13.0	3.0
Burner Height/mm	10.0	10.0	10.0	10.0
Air/l min ⁻¹	5.0	5.0	5.0	5.0
Acetylene/l min ⁻¹	1.2	1.2	1.2	1.2

Before the assessment could be undertaken it was necessary to identify the criteria for an ideal gas-liquid separation for hydride generation. These criteria included:

- (i) high separation efficiency;
- (ii) fast response times;
- (iii) stable steady state signal with low noise;
- (iv) minimum carry-over of the liquid products;
- (v) low interferences;
- (vi) ease of use and robustness.

3.2.1. Glass 'U' Tube Gas-Liquid Separator (GGLS)

The construction of the GGLS (as supplied with the instrument used in this study) is shown in Figure 3.1. The main parameters found to influence the magnitude of the hydride generation signal were sodium tetrahydroborate and hydrochloric acid concentrations and carrier gas flow rate. The significance of each of these variables was investigated using univariate searches. The conditions for arsenic, selenium and antimony for the univariate searches are summarised in Table 3.2 for atomic absorption spectrometry. All parameters except the parameter being studied were held constant.
Figure 3.1 - Glass 'U' tube gas-liquid separator for continuous flow hydride generation



Table 3.2 Hydride generation conditions for arsenic, selenium and antimony using the glass 'U' tube gas-liquid separator

Element	As	Se	Sb
NaBH ₄ conc./% m/V	1-2	1	1-2
NaBH ₄ flow rate/ml min ⁻¹	3.5	3.5	3.5
HCl conc./mol l ⁻¹	5.0	5.0	3.0
HCl flow rate/ml min ⁻¹	7.5	7.5	7.5
Carrier gas flow rate/l min ⁻¹	0.25	0.25	0.25

The variations in peak height with sodium tetrahydroborate concentration is illustrated in Figure 3.2 for arsenic, selenium antimony. tetrahydroborate and Sodium solutions are intrinsically unstable, however, this can be overcome by increasing the alkalinity of the solution, typically with 0.1 mol 1^{-1} sodium hydroxide (57). The solution is then stable for two to three days. The sodium tetrahydroborate concentration giving the maximum response was about 2% m/V for arsenic and antimony. Selenium was more dependant on sodium tetrahydroborate concentration and an optimum was obtained at a concentration of These relatively high concentrations ensure excess 1% m/V. hydrogen formation allowing efficient generation of the hydride species.

The effect of hydrochloric acid concentration on peak height for arsenic, selenium and antimony is shown in Figure 3.3. The acid concentration giving maximum signal response for both arsenic and

Figure 3.2 - Effect of sodium tetrahydroborate concentration on peak height for As, Se and Sb using the glass 'U' tube gas-liquid separator



Figure 3.3 - Effect of hydrochloric acid concentration on peak height for As, Se and Sb using the glass 'U' tube gas-liquid separator



selenium is about 5 mol 1^{-1} . This is in agreement with Thompson <u>et al.</u> (43) and Ebdon <u>et al.</u> (57). A lower optimal acid concentration of 3 mol 1^{-1} was obtained for antimony. This lower concentration was also found by Nakahara (20).

Optimum carrier gas flow rates are often a compromise between peak shape and sensitivity. For instance, high carrier gas flow rates give fast response and minimal memory times, however, a reduction in sensitivity is often observed due to sample dilution. Conversely, lower carrier gas flow rates give slower signal response and memory times, but sensitivity is usually superior. One must also consider the stability of the hydride species. Unstable hydrides must be delivered rapidly to the atomisation cell to prevent decomposition. A carrier gas flow rate of 0.25 l min⁻¹ was found to be suitable for arsenic, selenium and antimony. The variations in peak height with carrier gas flow rate are shown in Figure 3.4.

In addition to the three elements mentioned above, lead hydride (plumbane) generation was also investigated. In order to achieve reasonable sensitivity, lead (II) in sample solutions must be oxidised to lead (IV). Various oxidising agents including potassium dichromate (106), malic acid - potassium dichromate and nitric acid - ammonium peroxy di-sulphate (107) have been utilised. Bonilla <u>et al.</u> (108) have found that a hydrogen peroxide-nitric acid oxidant mixture improves the reaction kinetics and sensitivity compared to other oxidants. This procedure was therefore adapted for continuous flow plumbane generation. Sodium tetrahydroborate stabilised with 0.1 mol 1^{-1}

sodium hydroxide was again used as a reductant, however, an oxidant mixture of nitric acid and hydrogen peroxide was used instead of hydrochloric acid as the sample matrix. The main parameters influencing the magnitude of the lead hydride response were sodium tetrahydroborate, sodium hydroxide and hydrochloric acid concentrations and carrier gas flow rate. The significance of each of these parameters was investigated using univariate searches. The conditions used are summarised in Table 3.3.

The effect of sodium tetrahydroborate concentration on peak height is shown in Figure 3.5. The maximum signal response was obtained at a concentration of 3% m/V, which is a higher concentration than that found for the other hydride forming elements investigated.

Table 3.3 Plumbane generation conditions using the glass 'U' tube gas-liquid separator

Element	Pb
$NaBH_4$ conc./% m/V in 0.1 mol 1 ⁻¹ NaOH	3.0
NaBH4 flow rate/ml min ⁻¹	3.5
HNO ₃ conc./% V/V	0.3
H ₂ O ₂ conc./% m/V	1.0
Blank flow rate/ml min ⁻¹	7.5
Carrier gas flow rate/l min ⁻¹	0.25

As mentioned previously sodium tetrahydroborate solutions are unstable and are therefore made alkaline with sodium or potassium hydroxide. The generation of plumbane is extremely pH dependent

Figure 3.4 - Effect of carrier gas flow rate on peak height for As, Se and Sb using the glass 'U' tube gasliquid separator



Figure 3.5 - Effect of sodium tetrahydroborate concentration on plumbane generation



Sodium Tetrahydroborate Concentration / %m/V

so the concentration of stabilising agent must be carefully controlled. Concentrations above 0.5 mol 1^{-1} sodium hydroxide resulted in a complete loss of signal, Figure 3.6. The effect of nitric acid concentration on peak height is shown in Figure 3.7. The maximum response was obtained at a concentration of 0.3% V/V. In comparison to the other hydride forming elements this concentration is extremely low. Hydrogen peroxide was utilised as an oxidant and the maximum response was found at a concentration of 1.0 m/V. Hydrogen peroxide was obtained by dilution of a stock 30% m/V solution. The variation in peak height with hydrogen peroxide concentration is shown in Figure 3.8.

3.2.2. Analytical Performance of the Glass 'U' Tube Gas-Liquid Separator

The analytical performance of hydride generation - atomic spectrometry can be characterised by figures of merit, such as the limit of detection, linear dynamic range and precision and accuracy of measurements.

The limit of detection is derived from the smallest measurement which can be accepted with confidence as genuine and is not suspected to be only an accidentally high value of the blank measure. The limits of detection obtained for arsenic, selenium, antimony and lead using the GGLS, continuous flow hydride generation atomic absorption spectrometry are given in Table 3.4.

Figure 3.6 - Effect of sodium hydroxide concentration on plumbane generation



Figure 3.7 - Effect of nitric acid concentration on plumbane generation







Hydrogen Peroxide / %m/V

<u>Table 3.4</u> Limit of detection (3σ) for arsenic, selenium, antimony and lead using the glass 'U' tube gas-liquid separator

Element	Limit of Detection (30) (µg l ⁻¹)
As	0.59
Se	0.65
Sb	0.05
Pb	1.15

The limit of detection was defined here as:

LOD (XL) = x_{BLANK} + 3 s_{BLANK}

where x_{BLANK} and S_{BLANK} are the mean and estimated standard deviation of the blank respectively. Thus, the limit of detection can be defined as the quantity of an analyte which gives rise to a reading equal to three times the standard deviation of a series of ten determinations near the blank. The detection limits shown for each element in Table 3.4 are typical of those found for continuous flow hydride generation coupled to atomic absorption spectrometry.

One of the limitations of atomic absorption spectrometry is the small linear dynamic range. Calibration curves tend to bend towards the concentration axis, principally because stray light, usually from nearby lines in the lamp, contributes to the total light falling on the detector. It therefore follows, the greater the line-width the greater the curvature and the lower the concentration at which it becomes significant. The typical linear dynamic range for hydride generation atomic absorption spectrometry is between one and two. Dynamic range is defined here as the number decades of concentration over which the calibration curve is linear.

To evaluate the GGLS on real samples, arsenic and selenium were determined in a certified water reference material (IAEA/W-4). Prior to the analysis of arsenic, potassium iodide (1% m/V) was added to the acidified sample to reduce arsenate to arsenite. The pre-reduction stage takes approximately thirty minutes at room temperature, but may be accelerated by heating. The reduction step using potassium iodide is given in the following equation:

$$AsO_4^{3-} + 2H^+ + 2I^- \rightarrow AsO_3^{3-} + I_2 + H_2O$$

Selenium (VI) was reduced to selenium (IV) prior to analysis by gently heating the sample in 5 mol 1^{-1} hydrochloric acid. The following equation shows the reduction step for selenium:

$$SeO_4^{2-} + 2HC1 \rightarrow SeO_3^{2-} + C1_7 + H_7O_7$$

Analysis must follow the pre-reduction stage as soon as possible to prevent the back oxidation from the residual chlorine. Table 3.5 gives the certified values for arsenic and selenium along with the values obtained using the GGLS.

<u>Table 3.5</u> Determination of arsenic and selenium in water reference material (IAEA/W-4) using hydride generation and the glass 'U' tube gas-liquid separator

Element	Certified Value (µg l ⁻¹)	Value Obtained (µg l ⁻¹)
As	25 ± 1.25	22.2 ± 1.2
Se	10. ± 0.5	10.5 ± 0.3

3.2.3. Advantages and Disadvantages of the Glass 'U' Tube Gas-Liquid Separator

Since the GGLS was introduced by Thompson et al. (43) in 1978, it has gained huge popularity, being used by most workers in the field. This popularity has largely been due to the high sensitivity, fast signal response, low memory times and ease of use. However there are several disadvantages, the main one being that a fine aerosol is also transported with the gaseous This aerosol essentially consists of the hydride products. generation reaction by-products, one of which is sodium chloride. This is known to cause irreversible devitrification of the quartz glass to β -cristobalite (39). Therefore regular replacement of quartz atom cells is required if one is to maintain high sensitivity and precision. The problem is even more apparent when hydride generation is coupled to inductively coupled plasma - mass spectrometry. Here, the aerosol contaminated with sodium chloride is transported to the plasma discharge. On entry to the quadrupole interface the formation of argon chloride ions may These ions have a mass : charge ration of 75 u which occur. coincides with monoisotopic arsenic, and therefore severely

limits its determination. This is particularly troublesome for samples containing high levels of chloride ions such as seawater or urine. There are numerous ways to overcome this problem and these will be discussed in detail in the next section.

The GGLS generates copious amounts of hydrogen and water vapour and these have also been found to be detrimental to plasma discharges. Nakahara (47) combined two gas-liquid separators in series in an attempt to minimise the carry-over of these byproducts to the plasma.

One further application where the transportation of a fine aerosol is disadvantageous is when the hydride species are preconcentrated on a glass 'U' tube submerged in liquid nitrogen. After a set time, the 'U' tube is removed from the liquid nitrogen and warmed, to subsequently release the hydride species. Monomethylarsenate, dimethylarsenate and inorganic arsenic may be separated in this way utilising sequential volatilisation due to their different boiling points and thus offering speciation in addition to significant pre-concentration (27). The inherent problem of the moisture carry-over from the separator can cause ice blockage in the liquid nitrogen trap. Drying traps containing chemical desiccants have been employed, but these are only temporary and may give rise to contamination and analyte losses.

The GGLS operates on the principle that sufficient backpressure from the 'U' tube drain exists to direct, when purged, the gaseous products to the atomic reservoir. However, problems may arise if any restrictions are present in the line to the atomic

reservoir, since these result in the displacement of liquid from the 'U' tube. The GGLS can therefore not operate against any substantial backpressure.

A typical peak shape for the GGLS is shown in Figure 3.9. The peak shown represents a 100 μ g l⁻¹ arsenic standard and was obtained using the conditions summarised in Table 3.2. The signal reaches steady state after 25 seconds and the memory time is about 30 seconds. Therefore total sampling time is less than 2 minutes, allowing 30 determinations per hour.

3.3.1. Tubular Membrane Gas-Liquid Separator (TMGLS) for Atomic Absorption Spectrometry

The construction of the TMGLS is shown in Figure 3.10. This separator is similar in design to that described by Cave and Green (103). It consists of a 2 m PTFE outer tube (3.2 mm o.d. x 1.5 mm i.d.) and a 2 m silicone rubber inner tube (1.0 mm o.d. x 0.5 mm i.d.), which acts as a semipermeable membrane. The two tubes are connected with variable bore 'T' piece connectors (Omnifit, Cambridge, UK).

The gas-liquid mixture which forms at the 'T' piece where the reductant and acidified flows meet, is pumped continuously through the inner silicone rubber tube. Any gaseous products (i.e. hydrogen or hydrogen and hydrides) freely diffuse through the membrane and are then subsequently swept through the outer tube to the atom reservoir. Meanwhile, the waste liquid products flow continuously to waste.





Figure 3.10 - Tubular membrane gas-liquid separator



REDUCTANT

The significance of sodium tetrahydroborate and hydrochloric acid concentration along with carrier gas flow rate were investigated using univariate searches. The conditions for arsenic and selenium using atomic absorption spectrometry are summarised in Table 3.6.

The most critical parameter for the TMGLS was found to be the sodium tetrahydroborate concentration and its effect on peak height is shown in Figure 3.11.

<u>Table 3.6</u> Hydride generation conditions for the tubular membrane gas-liquid separator with atomic absorption spectrometry detection

Element	As	Se
NaBH4 conc./% m/V	0.05	0.40
NaBH ₄ flow rate/ml min ⁻¹	3.50	3.50
HCl conc./mol l ⁻¹	4.00	4.00
HCl flow rate/ml min ⁻¹	7.50	7.50
Carrier gas flow rate/l min ⁻¹	0.10	0.10

The sodium tetrahydroborate concentration giving maximum signal response is 0.05% m/V for arsenic and 0.4% m/V for selenium. These solutions were stabilised in 0.1 mol 1^{-1} sodium hydroxide. Compared to the GGLS, these concentrations are extremely low, especially for arsenic. Cave and Green (104), using an almost identical TMGLS coupled to ICP-AES reported an optimum at 0.4% m/V NaBH₄ for both As and Se. There are several possible explanations as to why the sodium tetrahydroborate concentration should be so low. One is that at higher NaBH₄ concentrations the

Figure 3.11 - Effect of sodium tetrahydroborate concentration on peak height for As and Se using the tubular membrane gas-liquid separator with atomic absorption spectrometry detection

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Sodium Tetrahydroborate Concentration / %m/V

increase in production of hydrogen gas causes uneven flow of sample reagent mixture through the inner silicone rubber membrane, thereby giving noisy signals. Another explantation might be that excess hydrogen produced at higher concentrations preferentially diffuses through the membrane, causing a pressure differential which in turn inhibits the transfer of hydride through the membrane. One must also consider the possibility of sample dilution with the excess hydrogen, although this is unlikely since a greater volume of hydrogen is generated using the GGLS and no apparent sample dilution is observed. Whatever the reason for the low optimum concentration of sodium tetrahydroborate it is almost certainly related to the diffusion process through the membrane. Furthermore, the transfer of gaseous products through the membrane is not totally efficient since the waste products contain a considerable amount of gas and this obviously more pronounced at is higher reductant concentrations.

The variation in peak height with hydrochloric acid concentration is shown in Figure 3.12 for arsenic and selenium. Although a maximum signal response was obtained at a concentration of 6 mol 1^{-1} for both arsenic and selenium, a compromise concentration of 4 mol 1^{-1} was chosen since acid concentrations above this value cause irreversible degradation to the silicone rubber membrane tube. The effect of carrier gas flow rate (nitrogen) on peak height for arsenic and selenium is shown in Figure 3.13. The flow rate giving rise to a maximum signal response for both arsenic and selenium is about 0.1 1 min⁻¹. This might appear low, but if one considers the very small volume between the two

Figure 3.12 - Effect of hydrochloric acid concentration on peak height for As and Se using the tubular membrane gas-liquid separator with atomic absorption detection



Figure 3.13 - Effect of carrier gas flow rate on peak height for As and Se using the tubular membrane gasliquid separator with atomic absorption spectrometry detection



69

tubes (approximately 2.0 cm^3) one realises that the residence time inside the separator is short (about 1 second). It therefore follows that the distance between the atom cell and the gas exit of the separator should be kept to a minimum to avoid dispersion.

3.3.2. Analytical Performance of the Tubular Membrane Gas-Liquid Separator coupled to Atomic Absorption Spectrometry

The limits of detection for arsenic and selenium using the TMGLS are given in Table 3.7. These detection limits represent 3σ for 10 readings of a standard near the blank.

<u>Table 3.7</u> Limit of detection (3 σ) for arsenic and selenium using the tubular membrane gas-liquid separator coupled to atomic absorption spectrometry

Element	Limit of Detection, 30,	(µg l ⁻¹)
As	0.6	
Se	0.4	

The linear calibration range for both arsenic and selenium are comparable to that of the GGLS with typical linear dynamic range between one and two. The linear calibration range is dependent on the atomic absorption detection system rather than the gasliquid separation process.

As mentioned in the previous section, the valence state of the analyte is critical for hydride generation. The effect of valence state for arsenic was investigated at different sodium

tetrahydroborate concentrations using the TMGLS. Table 3.8 shows the effect of valence state on peak height at different sodium tetrahydroborate concentrations. Standard solutions (100 μ g l⁻¹) of arsenic (V) and arsenic (III) were prepared from sodium arsenate and sodium arsenite salts respectively.

<u>Table 3.8</u> Effect of arsenic valence state on peak height at different sodium tetrahydroborate concentrations using the tubular membrane gas-liquid separator

PEAK HEIGHT

NaBH ₄ conc. (% m/V)	ARSENIC (V)	ARSENIC (III)
0.05	0	223.8 ± 3.0
1.00	31.6 ± 4.0	94.5 ± 3.3
2.00	22.3 ± 1.5	49.8 ± 2.5

From Table 3.8 we see that at low sodium tetrahydroborate concentrations no response is obtained for the arsenic (V) species. Increasing the tetrahydroborate concentrations to 1.0% m/V causes a drop in signal response for arsenic (III) as expected (Figure 3.11), but the arsenic (V) response was increased. With these conditions the response for arsenic (V) was only 30% as large as that for arsenic (III). This is in agreement with Thompson and Thomerson (38). At a concentration of 2.0% m/V both arsenic (V) and arsenic (III) responses decrease further. Since the optimum tetrahydroborate concentration for arsenic using the TMGLS is about 0.05% m/V, it therefore follows that for quantitative analysis it is extremely important to ensure complete reduction of arsenic (V) to arsenic (III) prior to analysis.

To test the efficiency of the pre-reduction stage using potassium iodide, a 100 μ g l⁻¹ sodium arsenate solution in 4 mol l⁻¹ hydrochloric acid was analysed at 5 minute intervals after 1% m/V potassium iodide had been added. The results were compared to a 100 μ g l⁻¹ sodium arsenite solution. Figure 3.14 shows a plot of peak height against time for a sodium arsenate solution with added potassium iodide (1% m/V) at room temperature. It can be seen from Figure 3.14 that the reduction was complete after about 35 minutes. The reduction process could be accelerated by heating the sample.

To assess the TMGLS for the analysis of real samples, a simulated certified water reference material (IAEA/W-4) was analysed for arsenic and selenium. Prior to analysis arsenic (V) was reduced to arsenic (III) using acidified potassium iodide solution (1% m/V), and selenium (VI) was reduced to selenium (IV) using 5 mol 1^{-1} hydrochloric acid. The results along with the certified values are given in Table 3.9.

<u>Table 3.9</u> Determination of arsenic and selenium in water reference material (IAEA/W-4) using the tubular membrane gas-liquid separator with atomic absorption spectrometry detection

Element	Certified Value (µg l ⁻¹)	Value Obtained (µg l ⁻¹)
As	25 ± 1.25	22.4 ± 1.2
Se	10 ± 0.50	10.2 ± 0.4

Figure 3.14 - Effect of potassium iodide on the signal from arsenic (V) with time



The results for both arsenic and selenium show the excellent accuracy and precision of the technique.

3.3.3. Advantages and Disadvantages of the Tubular Membrane Gas-Liquid Separator when coupled to Atomic Absorption Spectrometry

The TMGLS offers several advantages over the GGLS. The most important is that the membrane acts as a physical barrier preventing any liquid products being transported to the atomic reservoir. Although no extensive study was undertaken, it is believed that the use of membrane gas-liquid separation would inhibit the devitrification process of quartz atom cells, since no sodium would be transported with the gaseous products. Furthermore, applications involving the preconcentration of hydride species using cryogenic traps would also benefit from relatively dry gaseous products. The TMGLS can also operate against substantial back pressure, unlike the GGLS where the liquid in the 'U' tube will be displaced.

The disadvantage of the TMGLS was the slow diffusion of the gaseous products through the membrane. Figure 3.15 shows a typical peak shape for a 100 μ g l⁻¹ arsenic standard. A steady state signal is not reached for over a minute and the memory time is also in the order of several minutes. This slow signal response must be related to the diffusion across the membrane rather that the second stage when the gaseous products are swept out of the separator with a flow of carrier gas. Once the hydride has passed through the membrane its residence time (t) can be calculated from the following relationship:

$$t = \frac{V}{F_c + F_1}$$

where V = volume between the inner and outer tube (cm^3) . $F_c = carrier gas flow rate (cm^3 sec^{-1})$.

> F_1 = flow rate of the generated hydrogen assuming 100% of hydrogen is transferred through the membrane (cm³ sec⁻¹).

For a carrier gas flow rate of 0.1 1 min⁻¹ and a sodium tetrahydroborate concentration of 0.05% m/V, the residence time of the gaseous hydride once passed through the membrane is 11.3 seconds. With reference to the long memory times seen in Figure 3.15, the gaseous hydrides must pass through the walls of the membrane tube very slowly. Once the sample has been removed from the inner tube the hydrogen gas must then force the remaining hydrides out of the membrane walls. One further disadvantage of the TMGLS is that the inner silicone rubber tube may be degraded by certain chemicals such as strong acids.

Several authors (36,95) have shown that fast separation processes can minimise transition metal interferences, by removing the gaseous analyte from the potential liquid interferents as quickly as possible. One would therefore expect the TMGLS to be susceptible to transition metal interferences because of the slow response.

Figure 3.15 - Typical peak shape for a 100 μ g l⁻¹ arsenic solution using the tubular membrane gas-liquid separator



3.3.4. Tubular Membrane Gas-Liquid Separation for Inductively Coupled Plasma - Mass Spectrometry

As mentioned previously, the determination of arsenic and selenium by ICP-MS can be problematic, particularly when samples contain substantial amounts of chloride. The problem results from spectral overlap of argon chloride species on the isotopes of ⁷⁵As and ⁷⁷Se. Arsenic is monoisotopic and this isobaric interference therefore severely limits its determination in biological and environmental samples. There are, however, a number of ways to overcome this problem:

- (i) by using methods such as mathematical correction (109) whereby the contribution from the interferent is calculated using natural isotope abundances;
- (ii) the use of helium plasmas (either microwave or rf),thereby eliminating argon from the spectrum (42);
- (iii) by generating the hydride in a nitric acid medium or sulphuric acid (55);
- (iv) chromatographic separation of arsenic from chloride
 (110);
- (v) the use of high resolution ICP-MS whereby the interfering species are spectrally resolved from the analyte isotope (111);
- (vi) the addition of a molecular gas (e.g. nitrogen) or an organic solvent (e.g. propanol) to the plasma (93).

All these approaches are viable for particular analyses, but in this instance work concentrated on hydride generation since the

detection limits required were extremely low.

Five parameters critically influence the magnitude of the hydride generation ICP-MS signal. These are the sodium tetrahydroborate and hydrochloric acid concentrations, forward power and carrier and auxiliary gas flow rates. Prior to each variation the ion lenses were tuned for maximum response. The significance of each variable was investigated by univariate searches using a 100 μ g l⁻¹ arsenic standard. The conditions used are summarised in Table 3.10.

<u>Table 3.10</u> Operating conditions for hydride generation inductively coupled plasma - mass spectrometry using the tubular membrane gas-liquid separator

Hydride Generation

NaBH4 conc./% m/V	0.1
NaBH ₄ flow rate/ml min ⁻¹	3.5
HCl conc./mol l ⁻¹	4.0
HCl flow rate/ml min ⁻¹	7.5
Carrier gas flow rate/l min ⁻¹	0.9

Inductively Coupled Plasma - Mass Spec	trometry
Forward power/kW	1.8
Reflected power/kW	0
Coolant gas flow/l min ⁻¹	14
Auxiliary gas flow/l min ⁻¹	0.8

Figure 3.16 shows the variation in peak height with concentration of sodium tetrahydroborate stabilised in 0.1 mol 1^{-1} sodium hydroxide. A maximum response was obtained at 0.1% m/V, and this profile is remarkably similar to that obtained using AAS detection (see Figure 3.11). Several possible explanations for the sharp optimum at low tetrahydroborate concentrations are given in the previous section.

The effect of hydrochloric acid concentration on peak height is shown in Figure 3.17. Although a maximum response was obtained at an acid concentration of 6 mol 1^{-1} , this was found to permanently damage the inner silicone rubber membrane tube. A compromise optimum of 4 mol 1^{-1} was therefore adopted.

The peak height increased with increasing forward power, Figure 3.18. A similar result was found by Powell <u>et al.</u> (54), although they reported a plateau above 1200 W, a feature not observed in this study.

Figure 3.19 shows the variation of peak height with carrier gas flow rate. This is essentially the injector gas flow and the signal rises as the plasma is punctured, reaches a maximum and then degrades due to dilution. Similarly the auxiliary gas flow produces a sharp maximum followed by rapid decay, when the argon begins to dilute the sample, Figure 3.20. The carrier and auxiliary gas flows affect the position of the plasma relative to the sampler cone. The degree of ionisation varies throughout the analytical region of the plasma and thus variations in the sampling position will result in changes in sensitivity.

Figure 3.16 - Effect of sodium tetrahydroborate concentration on peak height using the tubular membrane gasliquid separator with inductively coupled plasma - mass spectrometry detection



Sodium Tetrahydroborate Conc. / % m/V

Figure 3.17 - Effect of hydrochloric acid concentration on peak height using the tubular membrane gas-liquid separator with inductively coupled plasma - mass spectrometry detection



Figure 3.18 - Effect of forward power on peak height using the tubular membrane gas-liquid separator with inductively coupled plasma - mass spectrometry detection



Figure 3.19 - Effect of carrier gas flow rate on peak height using the tubular membrane gas-liquid separator with inductively coupled plasma - mass spectrometry detection



Carrier Gas Flow Rate / 1 min ⁻¹

Figure 3.20 - Effect of auxiliary gas flow rate on peak height using the tubular membrane gas-liquid separator with inductively coupled plasma - mass spectrometry detection



3.3.5. Chloride Exclusion from the Plasma using the Tubular Membrane Gas-Liquid Separator

Chloride interference can be monitored at 77 u, which corresponds to 40 Ar 37 Cl in the absence of 77 Se. Table 3.11 shows the magnitude of interference using various methods of sample introduction. The two atomic masses 75 u and 77 u correspond to 75 As, 40 Ar 35 Cl and 40 Ar 37 Cl.

<u>Table 3.11</u> Relative signal and chloride interference using different sample introduction methods

Sample Introduction Method	Counts from 500 μ g l ⁻¹ As 75 u	standard 77 u
Pneumatic nebulisation (As in 2% V/V HNO3)	13095	72
Pneumatic nebulisation (As in 4 mol l ⁻¹ HCl)	64725	17529
Glass Gas-Liquid Separator (As in 3 mol l ⁻¹ HCl)	84835	11785
Tubular Membrane Gas-Liquid S (As in 4 mol 1^{-1} HCl)	eparator 235127	56

Using pneumatic nebulisation in a 2% V/V nitric acid medium the number of counts at 77 u is negligible, probably arising from instrumental noise, or traces of selenium in the standard solution, we can therefore assume there is no argon chloride contribution. When the standard solution was prepared in 4 mol 1^{-1} hydrochloric acid, a large positive bias was observed at 75 u. The relative abundance of the 35 Cl : 37 Cl isotopes is 3 : 1. Given the signal at 77 u, approximately 50,000 counts at 75 u were derived from argon chloride.

As one would expect when using hydride generation the arsenic signal increased and the argon chloride decreased. However, there is still a significant argon chloride contribution when using the GGLS, this arises from the transportation of an aerosol contaminated with sodium chloride from the GGLS. This fine spray can be particularly troublesome when it condenses in transfer lines, leading to large droplets passing to the plasma, producing instability and noise. No moisture was observed in the transfer lines using the TMGLS. From Table 3.11 we not only see an increase in the number of counts for the TMGLS we also observe the elimination of argon chloride interference. Figure 3.21 is a mass spectrum of the blank solution, showing counts for ⁷⁵As and ⁷⁷Se. The residual signals are due to arsenic and selenium contamination in the reagents and this is confirmed by the arsenic and selenium isotopic patterns.

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3.3.6. Analytical Performance of the Tubular Membrane Gas-Liquid Separator for Inductively Coupled Plasma - Mass Spectrometry

The limits of detection for arsenic and selenium are shown in Table 3.12. These were derived using 3σ on ten readings near the blank.

Figure 3.21 - Mass spectrum of the blank solution showing counts for As' and Se' in the absence of ArCl' interference



<u>Table 3.12</u> Detection limits for arsenic and selenium using the tubular membrane gas-liquid separator coupled to inductively coupled plasma - mass spectrometry

Element	Limit of Detection, 3σ , (ng l ⁻¹)
⁷⁵ As	2.30
⁷⁷ Se	6.81

The limit of detection is largely dependent on the quality of the reagents used, although the ability of the TMGLS to dampen noise from the peristaltic pump is also a contributing factor. In relation to the sensitivity, reproducibility data showing counts and relative standard deviations for arsenic and selenium at different levels are shown in Table 3.13. Hence the system is capable of reproducibility of 2-3% at levels in the parts per trillion range.

<u>Table 3.13</u> Reproducibility data for arsenic and selenium using the tubular membrane gas-liquid separator coupled to inductively coupled plasma - mass spectrometry

	СОUNТ	RATE
Element .	⁷⁵ As	⁷⁷ Se
Blank (RSD%)	2725 (1.62)	234 (3.0)
100 ng l ⁻ⁱ	7928 (1.82)	549 (3.47)
10 μg l ⁻¹	412399 (2.11)	36145 (2.86)
Unlike AAS techniques, ICP-MS does not suffer from poor linearity and the hydride generation ICP-MS technique is linear over at least five orders of magnitude.

In order to evaluate the TMGLS on real samples a range of fresh (IAEA/W-4, SRM 1643B, SLRS 1), coastal (CASS 2) and seawater (NASS 1, NASS 2) certified reference materials were analysed for arsenic and selenium. These were chosen because of their low levels of analyte and varying chloride content. To ensure arsenic was in the correct oxidation state 0.1% m/V potassium iodide was added to the acidified sample prior to analysis. The final sample was prepared in 4 mol 1⁻¹ hydrochloric acid. The results are shown in Table 3.14 and clearly demonstrate the accuracy and precision of the TMGLS using hydride generation ICP-Furthermore the results show the effectiveness of the TMGLS MS. in excluding chloride from the plasma discharge, the presence of which would have led to a large positive bias in the analysis.

3.4.1. Microporous PTFE Membrane Gas-Liquid Separator (MGLS) for Atomic Absorption Spectrometry

The construction of the MGLS is shown in Figure 3.22. This type of separator is basically a modified gas diffusion cell (Technicon Instruments, Tarrytown, New York, USA). It consists of two perspex blocks (9.0 mm long, 25 mm wide and 19 mm deep). Each block has a 1 mm outer diameter groove machined onto one of its surfaces. The microporous PTFE membrane (Goodfellows, Cambridge, UK) is pressed firmly between the two blocks to cover the grooves which are aligned one above the other when firmly clamped together. The gas-liquid mixture flows through one side

<u>Table 3.14</u>	<u>le 3.14</u> The determination of arsenic and selenium for certified water reference materials using				
the tubular membrane gas-liquid separator coupled to inductively coupled plasma - mass					
spectrometry					
		ARDEN		SELENIOM	
REFERENCE M	ATERIAL	CERTIFIED (µg l ⁻¹)	FOUND (µg l ⁻¹)	CERTIFIED (µg l ⁻¹)	FOUND (µg l ⁻¹)
IAEA/W-4 (SIMULATED H	FRESH WATER)	25.0 ± 1.25	23.4 ± 0.6		
SRM 1643 B (RIVER WATER	۲)	(49)*	47.4	9.7 ± 0.5	7.9 ± 0.68
SLRS 1 (RIVER WATER	()	0.55 ± 0.08	0.40 ± 0.07		
CASS 2 (COASTAL WAT	'ER)	1.01 ± 0.07	1.40 ± 0.02		
NASS 1 (OPEN OCEAN	WATER)	1.65 ± 0.19	1.77 ± 0.01		
NASS 2 (OPEN OCEAN	WATER)	1.65 ± 0.19	2.01 ± 0.03	0.024 ± 0.004	0.03 ± 0.01

* Indicative value only

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of the separator, any gaseous products will diffuse through the membrane and will subsequently be swept to the detector. Meanwhile the liquid products flow continuously to waste. In this study a microporous PTFE membrane of thickness 0.235 mm, porosity 40% and pore size 0.02 μ m was investigated.

The significance of the carrier gas flow rate and sodium tetrahydroborate and hydrochloric acid concentrations were investigated for arsenic using univariate searches. These conditions are summarised in Table 3.15.

<u>Table 3.15</u> Hydride generation conditions for the PTFE membrane gas-liquid separator with atomic absorption spectrometry

Element	As
NaBH ₄ conc./% m/V	0.1
NaBH4 flow rate/ml min ⁻¹	3.5
HCl conc./mol l ⁻¹	6.0
HCl flow rate/ml min ⁻¹	3.5
Carrier gas flow rate/l min ⁻¹	0.1

The variations in peak height with the sodium tetrahydroborate concentration are shown in Figure 3.23. As seen with the TMGLS, a relatively sharp maximum was obtained with low tetrahydroborate concentrations. Several explanations for this observation have been discussed previously and will therefore not be repeated here.

Figure 3.24 shows the effect of hydrochloric acid on peak height. concentration of 6 mol 1-1 An optimum was obtained. Polytetrafluoroethylene has a high chemical resistance and therefore no foreseeable limitations concerning difficult sample matrices are envisaged. The variation in peak height with carrier gas flow rate is shown in Figure 3.25. A low carrier gas flow rate of 0.1 l min⁻¹ was found to give maximum response. From Table 3.15 we see that a lower sample flow rate of 3.5 ml min⁻¹ was utilised rather than the usual 7.5 ml min⁻¹. This lower sample flow rate was necessary, since the residence time of the gas-liquid mixture in the flow channel of the separator is extremely small. In the work of Wang and Barnes (96) the sample flow rates were set in the range of 0.8 - 0.9 ml min⁻¹. These workers observed a linear increase in signal with sample flow rate, however, they did not exceed flow rates of 1.12 ml min⁻¹. This suggests that a lower sample/reagent flow rate might further improve sensitivity. In this study flow rates below 3.5 ml min⁻¹ were not investigated since the aim of the investigation was to assess the potential of novel gas-liquid separation devices for an existing commercial product of which the sample flow rates were fixed. Like the TMGLS, the spent solution flowing to waste consisted of a gas-liquid mixture, therefore indicating < 100% efficiency for the transfer of hydride through the membrane.

3.4.2. Analytical Performance of the PTFE Membrane Gas-Liquid

Using the conditions summarised in Table 3.15 the limit of

Figure 3.23 - Effect of sodium tetrahydroborate concentration on peak height using the PTFE membrane gas-liquid separator with atomic absorption spectrometry detection



Figure 3.24 - Effect of hydrochloric acid concentration on peak height using the PTFE membrane gas-liquid separator with atomic absorption spectrometry detection



Figure 3.25 - Effect of carrier gas flow rate on peak height using the PTFE membrane gas-liquid separator with atomic absorption spectrometry detection



detection obtained for arsenic was $0.72 \ \mu g \ l^{-1}$. The linear dynamic range for the MGLS is similar to that of the other separators when coupled to AAS, the typical dynamic range being between one and two orders of magnitude. To assess the MGLS on real sample materials, arsenic was determined in a certified water reference material (IAEA/W-4). Sample preparation for this material has been discussed in the previous sections. The certified value for arsenic and the value obtained is given in Table 3.16, the result shows the excellent accuracy and precision obtainable using the MGLS.

<u>Table 3.16</u> Determination of arsenic in certified water reference material (IAEA/W-4) using the PTFE membrane gas-liquid separator with atomic absorption spectrometry detection

Element	Certified Value (µg l ⁻¹)	Value Obtained (µg l ⁻¹)
As	25.0 ± 1.25	26 ± 0.80

3.4.3. Advantages and Disadvantages of the PTFE Membrane Gas-Liquid Separator

Although only a brief investigation was undertaken for the MGLS, its sensitivity, accuracy and precision is comparable to the other two separators studied. Being a membrane separator, it possesses similar qualities to those of the TMGLS and therefore should be advantageous in applications where moisture carry-over is problematic. Its main advantage, however, is the extremely fast separation process and short memory times. This is illustrated in Figure 3.26 where a typical peak shape is shown for a 100 μ g 1⁻¹ arsenic standard. Several authors (36,95) have shown that fast separation processes can minimise transition metal interferences, the idea here being to remove the gaseous analyte from the potential liquid interferents as quickly as possible. Fast response times are also advantageous for flow injection analysis and the MGLS is obviously well suited to such an application.

The main disadvantage of the MGLS is that the microporous PTFE membranes are expensive and easily damaged when mounting the membrane into the separator. The liquid flow channel may also become blocked if samples are not filtered prior to analysis.

3.5.1. Summary

Three different gas-liquid phase separators have been described and assessed in detail for hydride generation coupled to atomic absorption spectrometry and in one particular case inductively coupled plasma-mass spectrometry. All the separators studied yield sub parts per billion detection limits for various hydride forming elements. To assess the separation devices and the hydride generation technique for the analysis of realistic samples, arsenic and selenium concentrations were determined in certified water reference materials (IAEA/W-4, SRM 1643B, SLRS 1, CASS 2, NASS 1, NASS 2). Accurate and precise results were obtained for one or more of the reference materials listed above. It was difficult to distinguish between the separators on the basis of their analytical performance, (i.e. limit of detection,

Figure 3.26 - Typical peak shape for a 100 μ g l⁻¹ arsenic solution using the PTFE membrane gas-liquid separator



dynamic range and accuracy and precision).

The GGLS is a well established, successful and well received device for the separation of gaseous hydrides. The main problem with this separator is that the gaseous products are accompanied by a fine aerosol which can be detrimental in certain applications. In most instances however, the problem of moisture carry-over is not too severe and can be overcome by various means. One particular application where moisture carryover from the GGLS is particularly problematic, is the determination of arsenic and selenium by ICP-MS. Here the aerosol contaminated with sodium chloride is delivered to the plasma discharge where formation of argon chloride may occur. This has a mass : charge ration of 75 u which coincides with arsenic, which is monoisotopic, and therefore severely limits its determination. It has been shown that this problem can be overcome using membrane gas-liquid separation devices, since the membrane only allows the passage of gaseous products, and therefore inhibits the transport of chloride ions to the plasma.

Although only a brief investigation was undertaken for the microporous PTFE membrane separator, it probably has greatest potential for the gas-liquid process of hydride generation since it requires less sample volume and the separation process is faster. However, further investigation is required into the type of membrane and physical geometry of the gas-diffusion cell. The relative advantages and disadvantages of each separator are summarised in Table 3.17.

<u>Table 3.17</u> Summary of advantages and disadvantages for each separator

CRITERION	Glass 'U' tube gas-liquid separator	Tubular membrane gas-liquid separator	PTFE Membrane gas-liquid separator
SENSITIVITY	GOOD	GOOD	GOOD
RESPONSE TIME	GOOD	POOR	EXCELLENT
ACCURACY & PRECISION	GOOD	GOOD	GOOD
ROBUSTNESS	MODERATE	FAIR	MODERATE
MOISTURE CARRY-OVER	POOR	GOOD	GOOD
INTERFERENCES	MODERATE	POOR	GOOD

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CHAPTER 4

THE DETERMINATION OF MERCURY IN AQUEOUS AND GASEOUS SAMPLES

4.1. INTRODUCTION

The toxicological effect of mercury compounds on environmental systems has long been recognised, but it was not until the disaster at Minamata Bay in 1953 that the subject received worldwide attention (112). Mercury in the environment occurs both naturally in the form of mineral deposits and anthropogenically from industrial and agricultural wastes. Because of its high toxicity, there has been extensive research into techniques and development to determine mercury. Furthermore these techniques have been utilised for the determination of mercury in a wide variety of sample types.

Originally spectrophotometric methods based on the formation of coloured chelates between mercury ions and dithizone were adopted (113). However these methods had poor sensitivity and entailed long and tedious manipulations which often caused contamination and loss of analyte. Today the most commonly used method for measuring mercury is cold vapour - atomic absorption spectrometry. This technique was first described in a Russian journal by Poluektov and Vitkun as early as 1963 (114) and popularised five years later by Hatch and Ott (16). In a typical determination the mercury in the sample is first oxidised to mercury (II) using a suitable oxidant and then reduced to gaseous mercury by adding an excess of reducing agent. The liberated mercury gas is purged from solution and subsequently delivered to a detection system.

Both tin (II) chloride and sodium tetrahydroborate reduction schemes have been utilised for the generation of gaseous mercury. A comparative study of these two systems was undertaken by Yamamoto and co-workers (115). Similar sensitivity was obtained for each reduction system and reasonable agreement between seawater and soil samples was obtained using the two systems. The study involved hovever, the amalgamation of mercury on gold prior to spectroscopic measurement and therefore the reaction kinetics for each system were not considered. Several authors (116,117) have reported that sodium tetrahydroborate reagent containing a small amount of copper (II) can be used to determine total mercury, without oxidative pretreatment in a variety of sample types, an observation not borne out by others (118,119). The sodium tetrahydroborate reduction scheme can be advantageous when the technique is coupled to multielement detection systems such as ICP-MS, since the hydride forming elements may also be determined (54). The majority of workers favour the use of tin (II) chloride for the reduction step. (68,69,120,121).

It is generally agreed that oxidation of mercury compounds in the sample to mercury (II) is necessary prior to the reduction process. A great variety of oxidative methods have been proposed for aqueous samples. These typically involve combination of strong acids (HCl, H_2SO_4 , HNO_3), oxidants (H_2O_2 , $K_2Cr_2O_7$, $K_2S_2O_8$, $KMnO_4$), UV irradiation and elevated temperatures (113,115,118-122). The use of high temperatures should be avoided if possible to avoid loss of mercury due to volatisation. Becknall <u>et al.</u> (123) have utilised chlorine gas to cleave both aryl and alkyl mercury bonds. Bromine can be used to the same effect, and may be generated in the sample by oxidation of bromide with acid

bromate (124). This procedure was found to be effective at room temperature and a complete breakdown of organomercury compounds was observed after several minutes. Free bromine was removed prior to analysis using hydroxylammonium chloride. Several authors have observed that the presence of excess bromine may cause interference (113,124).

The volatility of mercury compounds has been the source of many difficulties encountered during the determination of mercury in biological and geological materials. Methods of dissolution usually involve the destruction of materials using combinations of strong acids and oxidants at elevated temperatures (125,126). To prevent losses of mercury, digestion was often performed in an open system under reflux (125), or under pressure in a closed decomposition vessel (126). More recently microwave dissolution techniques have been introduced which increase the speed and convenience of the dissolution procedure (127). This approach has been utilised for the determination of mercury in biological (128) and geological samples (126).

Pyrolytic separation of mercury from solid samples has been investigated by several authors (129,130). Depending on the amount of mercury in the sample, liberated mercury can be absorbed in an oxidising solution (129,130) or trapped on a collector (e.g. Au, Pt) prior to spectroscopic measurement (131,132). Although this method is efficient and rapid, it suffers from interfering pyrolysis products. These have been avoided with the use of various filters, including silver wool (132) and alumina and silica (133). Various additives to the sample (e.g. MgO, Florisil and CaO) have also been found to

remove interference pyrolysis products and increase pyrolysis efficiency (130). However, no sufficient explanation to the role of the additives has been reported.

In order to obtain sensitivity requirements for the determination of mercury in environmental samples, several authors (6,34,115) have coupled the cold vapour technique to various preconcentration devices. These usually involve passing the mercury vapour over an amalgamating medium (e.g. Au, Pt). Once all the mercury has been generated from the sample and collected, the amalgamating medium is heated and the mercury is transported by a gas stream to a spectroscopic measurement system. Several problems associated with the coupling of vapour generation to amalgamation techniques have been reported. These include the reduced collection efficiency of mercury in the presence of moisture (34), the poisoning of the amalgamating medium surface by other gaseous reduction products (134) and the occasional necessity for cleaning (6).

The amalgamation technique is therefore more suitable for the determination of mercury in gaseous samples. Scott and Ottaway (135) determined mercury in air using a passive gold wire sampler. This device was dependent upon diffusion of mercury from the air to the adsorbing gold surface. The amount of mercury deposited in a given time is proportional to the concentration of mercury vapour in the air. Calibration of this procedure was complex, and involved exposure of the gold wire to known mercury from the wire in 50% V/V nitric acid and analysis of the resulting solutions. The method had a detection

limit of 3.6 μ g m⁻³ but had poor precision. The disadvantage of passive sampling, is that a draught free atmosphere is required, making it unsuitable for outdoor sampling. Collection of mercury by pumping air through an amalgamation device is now the preferred method of preconcentration for mercury in air (136).

Two different methods of calibration have been applied for the preconcentration technique, these are, the use of mercury standard solutions and the injection of known amounts of mercury vapour. The accuracy of the vapour injection calibration methods has been assessed by Dumarey <u>et al.</u> (33). Precision of the injection of mercury in the range 1-100 ng was found to be less than 1%, provided the syringe was preconditioned before use. The accuracy of the method was dependent on the temperature of the mercury saturated air, which must be lower than the ambient temperature. Temmerman <u>et al.</u> (136) have developed a method for the determination of mercury in air, using preconcentration by amalgamation on gold sand traps, followed by measurement using atomic fluorescence spectrometry.

A wide variety of analytical atomic spectrometry techniques have been utilised for mercury vapour detection, the most extensively used, probably because of its availability, is atomic absorption spectrometry. There are several disadvantages associated with the use of this detection system, such as limited linear calibration range, spectral interferences resulting from nonspecific background absorption of volatile organics such as acetone and benzene (137) and difficulties associated with measurements at lower levels.

Mercury, by its very nature is a good element for determination by fluorescence, since it is atomic at room temperature and also absorbs and fluoresces at the same wavelength (i.e. resonance fluorescence). Intense mercury sources are readily available and atomisation cells are uncomplex when the technique is coupled to vapour generation. West in 1974 (138) theoretically showed that cold vapour - atomic fluorescence spectrometry should be more sensitive and produce considerably less spectral interference from non-specific absorption compared to the corresponding AAS technique. This theoretical treatment was later verified practically by Thompson & Godden (68). The apparatus they described was a dispersive system based on a modified AA spectrometer and a detection limit of 0.02 ng ml^{-1} was obtained. Bertenshaw and Wagstaff (139) adopted the system as described by Thompson and Godden for the detection of mercury in drinking waters. They improved the limit of detection by using a permanganate solution to preconcentrate the liberated mercury.

Non-dispersive atomic fluorescence spectrometry has also been investigated as a technique for the determination of mercury (140). The increased light gathering power of a non-dispersive system is often offset by background scatter from the atom cell, usually a flame. However, since mercury is atomic at room temperature, no flame is required and subsequently background scatter is minimal. Godden & Stockwell (69) described the development of a filter fluorometer specifically designed for mercury analysis. Detection limits typically below 0.02 μ g 1⁻¹ were readily obtainable with this instrument. One further advantage of this system was that no atomic absorption spectrometer was required and the system was inexpensive, and

simple in both construction and operation.

This chapter reports the use of a filter fluorometer (69) for the determination of mercury in a variety of sample types. Continuous flow and flow injection approaches have been adopted for various applications and the relative advantages and disadvantages of the two approaches are discussed with reference to their analytical performance. The effect of moisture carryover on detector performance is investigated and novel methods of moisture removal have been developed. Finally, an automated preconcentration system to monitor mercury in gaseous samples is described and an absolute calibration procedure is assessed.

4.2.1. Continuous Flow Cold Vapour Generation - Atomic Fluorescence Spectrometry

A commercially available continuous flow vapour generator supplied by the collaborating body (P S Analytical Ltd, Sevenoaks, Kent, UK) was used in this study to generate gaseous mercury. A schematic diagram of this instrument is shown in Figure 2.1. This design has also been described elsewhere by Ward and Stockwell (44).

As mentioned in the previous section both tin (II) chloride (68) and sodium tetrahydroborate (116) reduction schemes have been utilised for the generation of gaseous mercury. Reductions involving the sodium tetrahydroborate reagent generate copious amounts of hydrogen. This vigorous reaction causes agitation within the reaction vessel encouraging the release of mercury vapour from solution. In contrast, the tin (II) chloride

reduction is much less vigorous and a major proportion of mercury will stay in solution. This has led to the development of a gasliquid separator which provides forced agitation of the liquid thereby releasing the mercury. The separator is illustrated in Figure 4.1. The swan neck design minimises the extent of moisture carry-over which affects the performance of the detection system. Tin (II) chloride was used in preference to sodium tetrahydroborate because it provides better precision and sensitivity.

Once generated the mercury vapour is purged out of solution and fed into the atom cell of the detector through a chimney interface and is further sheathed in a stream of argon gas. This supposedly constrains the mercury in the argon stream and provides a rapid flush out time between samples. The chimney interface is based on the design of Thompson and Godden (68). The transfer system for the mercury vapour is shown in Figure 4.2.

Mercury vapour was detected using an atomic fluorescence spectrometer (10.023 Merlin, P S Analytical Ltd, Sevenoaks, Kent, UK). A block diagram of the system is shown in Figure 4.3. It basically consists of a high intensity mercury vapour discharge lamp operated using direct current, a series of lenses and collimating devices to focus and collect light with minimisation of scatter, a 254 nm interference filter to achieve wavelength isolation and a conventional side window photomultiplier tube (IP28, Hamamatsu, Middlesex, UK). The optical configuration is shown in Figure 4.4. Essentially, light from the source is collected using a biconvex quartz lens and focused light is then

Figure 4.1 - Gas-liquid separator for the tin (II) chloride reduction scheme



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Figure 4.3 - Block diagram of the atomic fluorescence spectrometer for mercury

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Figure 4.4 - Optical configuration for the atomic fluorescence spectrometer

SIDE VIEW



PLAN VIEW



Figure 4.4 - Optical configuration for the atomic fluorescence spectrometer

SIDE VIEW



PLAN VIEW



collimated over the chimney central core. Opposite the lamp is a small photodiode reference cell. The fluorescence emission is detected after collimation and wavelength isolation. The detector may operate in either emission or ratio mode. The emission mode corresponds to the actual fluorescence emission and the ratio mode corresponds to the signal divided by the response of the reference cell. The latter mode compensates for lamp drift. The system is fully automated and controlled using commercially available TouchStone software. (P S Analytical Ltd, Sevenoaks, Kent, UK). This has been developed in association with SpinOff Technical Systems (Essex, UK). The units are connected to an IBM AT compatible computer through a DIO card, thereby allowing instrument control and data collection.

Reagents

All reagents used were of analytical reagent grade, unless otherwise stated (Aldrich Chemical Company Ltd, UK). Deionized water was used throughout (Milli-RO4, Millipore, MA, USA). Tin (II) chloride solutions were prepared by dissolving tin (II) chloride dihydrate in concentrated hydrochloric acid. Fresh solutions were prepared daily. Traces of mercury were removed from this solution by purging with argon gas for approximately 20 minutes. Standard solutions were prepared by appropriate dilution of stock 1000 mg 1^{-1} mercury (II) chloride. In all cases standard solutions were matrix matched to the samples. All glassware was soaked in 10% nitric acid for at least 24 hours prior to use, and then rinsed five times with distilled water. Table 4.1 gives the conditions for continuous flow vapour generation.

Table 4.1 Vapour generation conditions using the continuous flow approach

Delay Time /s	10
Rise Time /s	30
Analysis Time /s	30
Memory Time /s	50
Carrier gas flow rate/l min ⁻¹	0.5
Shield gas flow rate/l min ⁻¹	0.2
Tin (II) chloride concentration in 10% V/V hydrochloric acid/% m/V	2.0
Tin (II) chloride flow rate/ml min ⁻¹	3.5
Blank/Sample flow rate/ml min ⁻¹	7.5

4.2.2. Analytical performance of the continuous flow approach

The analytical performance of the cold vapour technique coupled to atomic fluorescence spectrometry can be characterised by figures of merit, such as the limit of detection, linear dynamic range and precision and accuracy of measurements.

The limit of detection as defined in section 3.2.2 for the technique using the conditions in Table 4.1 was 3 ng 1^{-1} . This is largely dependent on the purity of the reagents. Traces of mercury can be removed from tin (II) chloride by purging the solution with argon for approximately 20 minutes. The purification of acid solutions is more difficult and sub-boiling distillation methods have been employed by some authors (121). Oxidants used for digestion or as stabilising agents may be purified by heating in a muffle furnace overnight at 250°C,

provided that temperature does not exceed or equal the decomposition temperature of the oxidant. The sensitivity of the fluorescence detector can be reduced considerably with the use of alternative carrier gases. Nitrogen and air were found to reduce sensitivity by eight and thirty times respectively compared to argon. This reduction in sensitivity is due to a process known as quenching. This is basically the radiationless deactivation of excited atoms due to collisions with foreign species present in the cell. The effectiveness of this process is dependent on the rate at which collisions occur, the type of non-radioactive process involved and the effective cross-section of the quenching species. The fraction of absorbed photons actually re-emitted as fluorescence radiation is known as the fluorescence yield, Ø. This is defined as:

 $\emptyset = \frac{B_{ij}}{\text{Total probability per second of de-excitation}}$

where B_{ij} is the Einstein co-efficient for fluorescence emission. The total probability of de-excitation is the summation of B_{ij} with the rate of all non-radioactive processes contributing to quenching. The quenching process occurring with mercury in the presence of nitrogen and air are due to inelastic collisions involving transfer of energy. The process for nitrogen is thus;

 $Hg^* + N_2 \rightarrow Hg + N_2$

where the superscript * is used to indicate the excited state. The rate, r, of each collision is defined as the number of excited mercury atoms quenched per second per unit volume and can

be expressed in the form;

$$r \approx k [Hg^*] [N_2]$$

where k is the rate constant for the process. The probability of an excited mercury atom being quenched is therefore $r/[Hg^*]$. Hence the fluorescence yield factor for mercury with quenching caused by nitrogen will be;

$$\emptyset_{253.7} = \frac{B_{10}}{k[N_2] + B_{10}}$$

where B_{10} is the Einstein co-efficient for the first excited state to ground state transition. It therefore follows that the maximum value of \emptyset is unity where no quenching occurs. This, however is highly unlikely to occur.

In contrast to atomic absorption spectrometry, atomic fluorescence possesses a wide linear calibration range. Figure 4.5 shows analytical response curves for nitrogen and argon carrier gases. The linear calibration range stretches over four orders of magnitude, which is obviously beneficial in view of the wide range of mercury concentrations found in the environment. Samples with high concentrations are susceptible to selfabsorption. This causes the calibration line to curve towards the concentration axis. The process is best explained using a standardised fluorescence cell, like that shown in Figure 4.6.

Figure 4.5 - Analytical response curves for continuous flow atomic fluorescence spectrometry using both argon and nitrogen carrier gas









This theoretical model assumes that the light beams are parallel, and that we have uniform atomic concentration and temperature etc. At high concentrations, incident radiation passing through Al may be lost by absorption before excitation can occur. Useful fluorescence may also be lost by re-absorption in the region AL. In an ideal situation these regions would be infinitely small, thereby minimising self-absorption. Figure 4.7 shows a typical signal to time profile obtained using the continuous flow approach for 2000 μ g 1⁻¹ mercury solution and the self-absorption process is clearly evident. As the concentration increases we get a rapid rise in signal until the concentration has reached a level where self-absorption occurs. At this point the signal begins to fall, in severe cases to zero. When the sample is removed and the concentration begins to decline, the signal begins to rise once more. Carry-over times between samples can be up to five minutes, depending on the concentration of mercury present.

As mentioned previously the magnitude of the atomic fluorescence signal can be considerably reduced with the use of alternative carrier gases such as nitrogen or air compared to argon. In hindsight one might expect that this reduction in signal magnitude would allow the analysis of samples containing higher levels of mercury. This, however, is not the case since the self-absorption process is dependent on the atomic concentration, and the atom cell dimensions. The analytical response curve for nitrogen is shown in Figure 4.5 and the decrease in sensitivity is shown by the reduction in net signal compared to that of argon. The shape of the curves are identical.

Figure 4.7 - Typical peak shape using the continuous flow approach for a 2000 μ g l⁻¹ solution of mercury illustrating the process of self-absorption



To evaluate the continuous flow approach for cold vapour - AFS, mercury was determined in urine and water certified reference materials. As mentioned in section 4.1.1 it is necessary to oxidise mercury compounds within the sample to mercury (II) prior to analysis. This has been achieved using a variety of strong acids and oxidants. The procedure used in this study involved the generation of bromine within the sample by oxidation of bromide with acid bromate (124). Aqueous sample volumes were accurately measured and transferred into clean 100 ml volumetric flasks. To the sample 5 ml of concentrated hydrochloric acid and 4.0 ml of 0.1 N potassium bromate/potassium bromide solution was added. The generation of bromine is clearly evident from the yellow-brown colouration of the solution. Samples were allowed stand for a period of one hour to ensure complete to decomposition of organomercury compounds. Prior to analysis traces of free bromine were removed by adding several drops of 12% m/V hydroxylammonium chloride. Table 4.2 shows the results obtained along with the certified values.

<u>Table 4.2</u> Determination of mercury in certified reference materials using the continuous flow approach

CERTIFIED REFERENCE MATERIAL	CERTIFIED VALUE (µg l ⁻¹)	VALUE OBTAINED $(\mu g l^{-1})$
IAEA/W-4 - SIMULATED FRESH WATER	2.5 <u>+</u> 0.125	2.45 <u>+</u> 0.04
SERONORM URINE BATCH 108	51.0 <u>+</u> 5.0	.59.0 <u>+</u> 6.0

The results in Table 4.2 show that the technique is both accurate and precise. Furthermore, the digestion procedure involving bromination successfully decomposes organomercury species at room

4.2.3. Summary

The continuous flow approach for cold vapour - atomic fluorescence spectrometry is an extremely sensitive technique with detection limits typically in the part per trillion range (3 ng 1^{-1}). However, in order to attain this level of detection, high purity reagents are required and attention to cleanliness of glassware is vital to avoid contamination and losses. The use of alternative carrier gases, such as nitrogen and air was found to reduce the signal magnitude when compared to argon, due to quenching and this process has been discussed in detail above. In contrast to atomic absorption spectrometry, atomic fluorescence is essentially a linear technique and linearity was found to span over four orders of magnitude. Samples with concentrations exceeding the linear range are subject to self-One of the problems associated with a totally absorption. automated system, is that occasionally a sample may contain an exceptionally high level of mercury. If this situation arises, then subsequent determinations may give inaccurate results because of the excessive drift and carry-over of the previous sample. The accuracy and precision of the technique has been shown with the analysis of urine and water certified reference materials. Reasonable agreement was found in each case. The adopted digestion procedure for organomercury compounds involved bromination. This procedure has the advantages of being rapid, occurring at room temperature thereby minimising losses due to volatility, as well as allowing the decomposition of all mercury compounds.

119

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4.3.1. Flow Injection - Cold Vapour - Atomic Fluorescence Spectrometry

An automated flow injection cold vapour generation system (40.630, P S Analytical Ltd, Sevenoaks, Kent, UK) coupled to an atomic fluorescence spectrometer (69) was used to determine mercury in a variety of sample types. A schematic diagram of the system has been shown in Figure 2.2. The previous section described the analytical performance of the continuous flow approach. The limit of detection for this system is 3 ng 1^{-1} with linearity to 100 µg 1^{-1} . The linear calibration range therefore stretches over four orders of magnitude. Samples with concentrations exceeding the linear range are susceptible to self-absorption.

The flow injection approach utilises small sample volumes, typically between 50 and 200 μ l. Although not as sensitive as the continuous flow approach, it is less susceptible to selfabsorption and matrix interferences. This allows the upper limit of the calibration range to be increased. Figure 4.8 shows three analytical response curves corresponding to 75, 100 and 200 μ l loopsizes. As expected, the smaller volumes gave higher upper limit calibration ranges, with slightly less sensitivity. Table 4.3 summarises the effect of sample volume on linearity. Samples containing high levels of mercury are still susceptible to selfabsorption, and a typical profile is shown in Figure 4.9. The profile corresponds to a 10 mg 1⁻¹ solution of mercury and the self-absorption is clearly observed. However, this was not as severe as that for continuous flow (Figure 4.7), and the carry

Figure 4.8 - Analytical response curves for flow injection - atomic fluorescence spectrometry using 75 (v), 100 (Δ), and 200 (\Box) µl sample volumes


Figure 4.9 - Typical peak shape for the flow injection approach for a 100,000 μ g l⁻¹ solution of mercury, illustrating the process of self-absorption



over times between samples with high levels were negligible.

Table 4.3Effect of sample volume on linear calibration rangeSample VolumeUpper Limit of Calibration Range
(mg 1⁻¹)Slope7510.53.710010.04.42007.08.4

To assess the validity of the flow injection CV-AFS technique, a range of certified reference materials and zinc battery anodes have been analysed for mercury. The result are shown in Table 4.4.

<u>Table 4.4</u> Determination of mercury in certified reference materials and battery anodes

Certified Reference Material	Expected Certified Concentration	Concentration Found	Dilution by Weight
NIST SRM 1641b (Mercury in Water)	1.367 <u>+</u> 0.01 (µg ml ⁻¹)	1.411 ± 0.04 (µg ml ⁻¹)	0
NBS SRM 3133 (Spectrometric solution)	10.00 (µg ml ⁻¹)	9.89 <u>+</u> 0.2 (µg ml ⁻¹)	2500
ZINC ANODE A	1000 (µg g ⁻¹)	1060 <u>+</u> 30 (µg g ⁻¹)	200
ZINC ANODE B	0 (µg g ⁻¹)	4.11 <u>+</u> 0.29 (µg g ⁻¹)	200
ZINC ANODE C	1200 (μg g ⁻¹)	1150 <u>+</u> 43 (µg g ⁻¹)	200

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The results in Table 4.4 show that the technique is both accurate and precise. The advantage of this system is that minimal sample dilution is required; which considerably reduces sample preparation time and errors involved in large serial dilutions. One further advantage is that matrix interference is reduced since, firstly, the analyte is separated from the matrix by generation of gaseous mercury and, secondly, small sample volumes are utilised.

The system described has also been utilised for the direct determination of mercury in concentrated sulphuric acid. The potential difficulties with this analysis are related to the vigorous exothermic reaction between water and sulphuric acid. The flow injection approach, however, overcomes these difficulties and no problems related to heat dissipation were encountered. A typical signal to time profile within the linear range of the system is shown in Figure 4.10.

4.3.2. Summary

The flow injection approach has been utilised for the analysis of samples containing high levels of mercury. In contrast to the continuous flow approach, flow injection is less susceptible to self-absorption, carry-over and matrix interference since only small volumes are utilised. The obvious solution would be to perform dilutions, but this increases sample preparation time and may also give rise to experimental error. To assess the potential for the analysis of real samples, certified water reference materials and zinc battery anodes have been analysed and reasonable agreement was found.

Figure 4.10 - Typical peak shape using the flow injection approach for a 3,000 µg 1⁻¹ solution of mercury



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4.4.1. The Effects of Moisture on Cold Vapour - Atomic Fluorescence Spectrometry

One of the problems associated with the determination of mercury using the cold vapour technique is that moisture occasionally condenses on the transfer tube walls and eventually enters the detection system. Problems resulting from the moisture have been mentioned by numerous authors using various designs of gas-liquid separator (6,113,121,141-143). The effects of moisture are a gradual loss in sensitivity and baseline drift for AAS, AFS and ICP systems. The moisture, usually in the form of an aerosol, is a complicated mixture of reagents and sample matrix. Τn severe cases this mixture may cause fogging of optics and atom cell windows. The most commonly used method for the reduction of moisture carry-over during mercury determinations involves the use of desiccants, such as concentrated sulphuric acid (141), magnesium perchlorate (121), activated silica gel (143) and anhydrous calcium chloride (142). Although effective, these drying agents become quickly saturated and therefore need constant replacement. They may also give rise to contamination and loss of analyte at trace levels.

The problem of moisture carry-over originates from the gas-liquid separator design. Most commercial separators use a sparging procedure to liberate mercury gas from solution and therefore have associated moisture carry-over. The separator supplied with the vapour generator used in this work has a swan neck design to minimise moisture carry-over, however, this is not totally effective and moisture in the form of an aerosol may be transported along the transfer tubes to the detector.

Recently, Hoult (143) assessed the extent of moisture carry-over for this design of separator. This was achieved by placing an activated silica gel trap between the separator and detector. By weighing the silica gel trap before and after a two hour analysis period the amount of moisture carry-over was determined. With a purge gas flow rate of 1.0 l min⁻¹ approximately 0.8 g per hour of moisture was flushed through the system. Decreasing the flow rate to 0.5 l min⁻¹ reduced the moisture carry-over to 0.5 g per hour. He also noticed that the removal of moisture increased the net signal intensity by at least 60%. This increase was due to a reduction in fluorescence quenching resulting from the presence of moisture.

The severity of the moisture problem can be seen to a greater extent by performing a long term stability test. This involved repeated runs of a standard over a period of several hours without the use of a drying facility. Figure 4.11, shows the variation in peak height for a 1.0 μ g l⁻¹ mercury standard solution stabilised in 2% V/V nitric acid over a period of 3 hours, using a carrier gas flow rate of $0.8 \ lmin^{-1}$, and an average run time of 2 minutes. The relative standard deviation (RSD) for 25 runs was 1.2%, after which erratic spikes begin to These were found to be due to the formation of large appear. moisture droplets condensing in the transfer tube, and eventually entering the detector. In severe cases large droplets in the transfer tube may cause pulsation in the separator due to small back pressure fluctuations. There was also a general decrease in the net analyte signal with time and this was probably due to an increase in quenching and/or the dissolution of mercury vapour

Figure 4.11 - Variation in peak height with run number with no drying facility



in the aerosol mixture. The solubility of the mercury will be largely dependent on the aerosol composition. Table 4.5 shows the relative standard deviations for the first, second, third and fourth batch of 25 runs. The RSD for 100 runs was 7.8% obtained over a period of 3 hours.

Table 4.5 Relative standard deviations for the first, second, third and fourth batch of 25 runs

Method of Moisture	Run Number				
Removal	1–25	26-50	51-75	76-100	
No Drying Facility	1.2%	5.5%	6.0%	11.4%	
Physical Moisture Trap	2.3%	2.2%	14.8%		
Membrane Dryer Tube Before Simplex Optimisation	2.3%	4.7%	2.5%	3.3%	
Membrane Dryer Tube After Simplex Optimisation	1.8%	0.8%	1.2%	1.2%	

One arrangement which can be used to improve the stability with time involves the use of a physical moisture trap, Figure 4.12. This was constructed using a 100 ml conical flask with gas inlet and exit ports. The increase in deadspace between the separator and the detector with the inclusion of this device did not affect the sensitivity of the system. Its role was to catch or collect large droplets. A stability test was performed using this arrangement, which indicated a marked improvement at a carrier gas flow rate of 0.8 l min⁻¹, Figure 4.13. The system was stable for approximately 2 hours and the RSD's for the first two batches of 25 runs were 2.3% and 2.2% respectively, Table 4.5. After this period erratic spikes were again observed.

WET GAS FROM SEPARATOR

TO DETECTOR MOISTURE TRAPPED

Figure 4.13 - Variation in peak height with run number using the physical moisture trap



The use of chemical or physical moisture traps are effective, but only for short periods of time, typically in the order of several hours. Precision may be restored by replacing the desiccant or by cleaning out and drying the flask, this however is time consuming and is a major drawback in terms of automation. Such approaches to remove moisture may also give rise to contamination and analyte losses during trace analysis. In order to overcome moisture carry-over for longer periods of time, the moisture has to be removed continuously rather than trapped. This may be achieved using a device such as a hygroscopic membrane dryer tube (Perma Pure Products Inc., Monmouth Airport, Farmingdale NJ 07727, USA), as shown in Figure 4.14. This basically consists of two concentric tubes 24 cm in length connected with variable bore 'T' piece connectors. The outer tube is made from PTFE and has dimensions 4 mm i.d. x 6 mm o.d. The inner tube is a Nafion hygroscopic membrane with dimensions 2 mm i.d. x 3 mm o.d. As the wet gas from the separator passes through the membrane, the moisture is removed and transferred to the outer tube. Meanwhile a dryer gas flows in the opposite direction to that of the wet gas, removing the moisture on the outer surface of the membrane. The dryer can be any gas such as air, nitrogen or argon, provided it is relatively dry.

The manufacturers of this device recommend an outer dryer gas flow twice that of the inner carrier gas flow to remove moisture effectively. Based on this recommendation a carrier gas flow rate of 0.5 l min⁻¹ and a dryer gas flow rate of 1.0 l min⁻¹ was chosen and a stability test performed, Figure 4.15. This shows that after approximately 40 runs or 1.5 hours, the peak height begins to deteriorate dramatically, hence the higher RSD





Figure 4.15 - Variation in peak height with run number using a hygroscopic membrane dryer tube before simplex optimisation



in the second batch of 25 runs, Table 4.5. It is also interesting to note that there are no erratic spikes as observed previously. Although the moisture is removed, the hygroscopic membrane becomes saturated and this causes the membrane to swell. This swelling creates a back pressure which results in the displacement of liquid in the 'U' tube of the separator, and this in turn reduces the amount of agitation occurring and therefore reduces sensitivity. A variable step-size simplex optimisation procedure (144) was adopted to optimise the gas flow-rates of the system using a criteria of merit of net signal. The optimum conditions were found to be 0.32 l min⁻¹ carrier gas flow-rate and 2.6 l min⁻¹ dryer gas flow-rate. These conditions are what one would expect, since the lower carrier gas flow obviously reduced the amount of aerosol generated and the higher dryer gas flow removed the moisture more efficiently. Figures 4.16 and 4.17 show univariate searches for carrier and dryer gas flowrates, respectively, with the other parameters set at their optimal volume. The carrier flow-rate has a dramatic effect on net analyte signal, and this may be explained in terms of carrier gas dilution of the analyte and aerosol production inside the separator. The optimum carrier gas flow-rate is considerably less than the conditions normally used, but since the inner diameter of the membrane is much smaller, high gas velocities ensure rapid delivery of the analyte to the detector. Dryer gas flow-rate had little effect on net signal, since its only purpose is to remove moisture from the outer surface of the membrane. A multi-variate optimisation procedure for the gas flows was therefore not essential in this case, because the two variables are independent of each other. Using the optimum conditions found a further stability test was performed and the results

Figure 4.16 -Variation in peak height with carrier gas flow rate using the hygroscopic membrane dryer tube



Figure 4.17 -Variation in peak height with dryer gas flow rate using the hygroscopic membrane dryer tube



are shown in Figure 4.18. Over a period of 3 hours the signal remained extremely stable, with no drift or erratic spikes. An RSD of 2% was obtained for 90 analytical runs over a period of 3 hours. The Nafion membrane is chemically resistant, however, the drying capacity may be decreased if it becomes contaminated with non-volatile liquids or salts. Organic liquids can be removed with 1, 1, 1, trichloroethane. Sulphuric acid may be removed with deionized water. Inorganic salts which may be absorbed into the membrane can be removed with 10% V/V nitric acid at 50-60°C. In this study the device was used routinely for six months without observing any decrease in moisture removal efficiency, however, this will obviously depend on usage. At the end of each working day the dryer gas was left on for approximately 10 minutes to ensure that all moisture was removed from the membrane.

In order to test whether or not mercury was being lost due to diffusion through the membrane, a gold sand trap was installed at the outlet of the dryer tube (see section 4.5.2). The argon dryer gas was previously cleaned of mercury using gold sand and charcoal traps. No mercury was detected in the dryer gas flow outlet, indicating no diffusion of mercury through the membrane. Furthermore an increase in net signal of approximately 60% was observed due to a reduction of quenching from moisture molecules. Any losses through the membrane tube would therefore have been tolerable.

Figure 4.18 - Variation in peak height with run number using a hygroscopic membrane dryer tube after simplex optimisation



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The problems associated with moisture carry-over during mercury determinations using the cold vapour technique are well documented and include gradual loss in sensitivity and long term instability. Chemical and physical moisture traps are effective, but they eventually become saturated and may give rise to contamination and analyte losses. The precision may be restored by replacing the trap, but this is time consuming and is a major drawback in terms of automation. The most effective way to remove the moisture is with the use of a membrane dryer tube which continuously desolvates the wet gaseous stream. It was found that the operating conditions for this device were critical for consistent removal of moisture. Furthermore, the removal of moisture increased the net signal by approximately 60%, due to a reduction in quenching from moisture.

4.5.1. Calibration Procedures for a Computer Controlled Adsorber/Desorber System to Monitor Mercury in Gaseous Samples

In the field of occupational health, the quantitative determination of mercury concentrations in ambient air is of considerable importance. Airborne mercury concentrations in unpolluted areas are usually in the range of 1-5 ng m⁻³, making it necessary to preconcentrate the analyte. Because of its high toxicity, the adopted threshold limit (50 μ g m⁻³) for mercury (145) in workroom room air is low, and therefore there is a great need for sensitive automated systems to continuously monitor mercury in air.

This section describes a computer controlled system which utilises a gold sand impregnated trapping unit to preconcentrate airborne mercury. On completion of the collection, the mercury is revaporised and detected by atomic fluorescence spectrometry. An absolute calibration procedure based upon the injection of known volumes of mercury vapour at a fixed temperature has been developed. With the knowledge of the injected volume and temperature of the mercury vapour, the software calculates the quantity of mercury on the gold sand trap. The system is fully automated in terms of collection and quantification.

4.5.2. Instrumentation

A commercially available mercury fluorescence spectrometer (P S Analytical Ltd, Sevenoaks, Kent, UK) was used to determine mercury concentrations in ambient air. This detector is described in detail in section 4.2.1. The sensitivity of the detector is such that is possible to detect levels of mercury directly in air. However, the presence of air will tend to quench the florescence and therefore reduce sensitivity. If the levels of mercury are low, then some means of preconcentrating the mercury is required. Many trapping systems have been developed based on gold wire (135), silver (146), gold/platinum gauze (6) and gold impregnated sand (136).

A schematic diagram of the adsorber/desorber system is shown in Figure 4.19. The transport gas is swept through the trap and filters and housed in a specially designed cooling chamber. Around the trap is a nichrome coil connected to a power supply. This arrangement allows visual inspection of the coil and trap,

Figure 4.19 - Schematic arrangement of the gold sand trap and heater assembly



and allows the coolant gas to pass over the coil to reduce temperature rapidly and allow the next sample to be collected. The coolant gas flow of either nitrogen, air or argon is simply vented to waste. With careful attention to cleanliness the trap should have an extremely long lifetime. This lifetime is however significantly shortened by:

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- a) continuous high desorption temperatures which cause the gold to evaporate slowly; for this reason the maximum temperature during desorption should not exceed 800°C;
- b) contamination with solution, this causes the gold to be covered with salts upon desorption, thus reducing the area available for trapping mercury. Traps can be cleaned by flushing with sufficient quantities of distilled water and then drying completely with a gas stream without heating;
- c) contamination by aerosols during sampling of air. This causes the gold to be covered by products of the aerosols during desorption (i.e. tar like products). This may cause permanent damage to the trap. A filter placed in front of the trap during sampling is therefore recommended.

Once the mercury is amalgamated to the gold sand, the system goes through 3 cycles. The first cycle is used to stabilise conditions and to flush out any residual air or gas. On completion of this, the heating cycle takes place, thus desorbing the mercury which is then swept to the fluorescence detector. The third cycle rapidly cools the trapping unit.

A valve manifold was assembled (Neptune Research Inc., Maplewood, NJ 07040 USA) to divert the gas and argon flow over the trap. Whilst the instrument is inactivated an air or gas flow can be continuously passed over the gold sand trap. In this way, if the flow rate and time for collection are known, it is then possible to calibrate for mercury in a unit volume of air or gas. During the collection stage an argon stream is fed directly to the fluorescence detector. The flow pattern is shown in Figure 4.20, all the valves and flow paths are constructed from inert materials to ensure no sorption of mercury takes place. Once the cycle is activated the valve configuration changes so that the argon flow is directed over the trap. Air or gas is flushed out in the first stage of the cycle and conditions in the detector are stabilised. As the mercury is desorbed it is flushed into the detector and a transient signal is produced.

The system is fully automated in terms of collection and quantification when the units are connected to an IBM AT compatible computer through a U-Micro DIO (U-Micro Computers, Cheshire, UK). The software was developed by the collaborating body (P S Analytical Ltd, Sevenoaks, Kent, UK) and was written by SpinOff Technical Systems (Benfleet, Essex, UK).

4.5.3. Calibration Procedure

There are basically two methods of calibration which can be adopted, either reduction of a mercury standard solution (119) or the injection of known amounts of mercury vapour (33). The former method has several limitations. At low concentrations, the solutions become unstable. This instability is caused

Figure 4.20 - Schematic layout of the valve assembly, shown in the sampling position



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partly by volatilisation, and sorption of the mercury on the vessel walls (147). Several authors have reported an improved stability on acidification and addition of strong oxidising agents (147). However, these additions give rise to high blank contributions. The injection procedure is not subject to these limitations.

A calibration procedure based on the work described by Dumarey and co-workers (33) was adopted for this work. It involved the injection of known volumes of mercury vapour at a set temperature, into an argon carrier gas stream which directed the mercury vapour onto the gold sand trap. The mercury vapour was introduced into the argon stream via an Omnifit Septum (Omnifit Ltd, Cambridge, UK). This allowed the syringe to be inserted directly into the argon flow path to transport the mercury vapour directly over the gold sand trap. Prior to calibration the system was optimised to provide the best peak shape and to minimise tailing. Checks were run to ensure that there was no remaining mercury on the trap once it had been revaporised. Figure 4.21 shows the instrumental arrangement. The mercury vapour was injected during the flushing stage of the operation. The system was optimised univariately for carrier gas and shield gas flow-rate. The effects of carrier gas flow-rate on peak area and peak height are shown in Figure 4.22. With increasing carrier gas flow-rate both peak height and area decreased. The optimum carrier gas flow rate is 0.6 l min⁻¹. Figure 4.23 shows the effects of shielding gas on peak height and peak area. A maximum signal was obtained at 0.2 l min⁻¹. The calibration procedure was highly dependent on good house keeping and a pure argon supply. An argon clean up system was developed which

Figure 4.21 - Instrumental arrangement for mercury in air, illustrating connections between units



Figure 4.22 - The effect of carrier gas flow rate on peak area (\Box) and peak height (Δ)



Figure 4.23 - The effect of shield gas flow rate on peak area (\Box) and peak height (Δ)



145

incorporated activated charcoal and gold sand traps. This arrangement was found to remove all traces of mercury. Elemental mercury was used as the primary standard and this was contained in a closed vial which was held in a thermostatically controlled bath. The temperature of the mercury vapour was monitored using a digital thermometer. The saturation concentration of atomic mercury in air was calculated using the data of Weast (148). The saturation concentration was automatically calculated by the software using the formula (165) :

$$C = \frac{3216522.61 \times 10^{-(A+(B/T))}}{T}$$

where C = the concentration of mercury in air, in ng ml⁻¹.
A = -8.134459741
B = 3240.871534
T = absolute temperature in Kelvin

Dumarey et al. (33) found it necessary to precondition the gas micro syringe in order to obtain reproducible signals. This was done by withdrawing the maximum volume of mercury saturated air and with the syringe needle inside the vial, leaving for 10 minutes. This prevented the partial sorption of mercury onto the syringe walls. By carefully controlling the temperature of the mercury in the vial, it was possible to calibrate over different concentration ranges using the same syringe. Alternatively, one can use various sizes of micro syringe to obtain similar concentration ranges. Care must be taken when large volumes are withdrawn, since several minutes are required to allow a state of saturation to be regained.

One further disadvantage of this procedure is that the equilibrium between liquid and gaseous mercury is dependent upon the cleanliness of the surface. After some time the mercury at the surface may become oxidised by atmospheric oxygen. If this occurs then the layer must be removed and purified by distillation.

The precision of the injection procedure improved when the volumes injected where at the upper limit of the syringe range. Table 4.6 gives the precision and output (peak area) at various injection volumes at 20°C.

Table 4.6 The precision and output at various injection volumes at 20°C

INJECTION VOLUME (µl l)	CONCENTRATION (ng m ⁻³)	RELATIVE PEAK AREA	RUNS	RSD&
0	0.0	32	5	10.4
10	131.8	276	5	11.3
20	263.5	588	5	6.8
30	395.3	901	5	3.2
40	527.0	1155	5	4.4

A typical calibration curve is shown in Figure 4.24. This was found to have a linear correlation co-efficient of 0.9999. A limit of detection (3σ on 10 runs of the blank) of 4.1 ng m⁻³ was obtained. Since this development work was carried out, the system has been successfully utilised for the determination of

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147
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mercury in air, natural gas and hydrogen.

4.5.4. Summary

The procedure described above provides a simple, reliable and effective means of calibrating the system in an absolute fashion. The sensitivity of the atomic fluorescence spectrometer is such that samples containing airborne mercury need only be collected for short periods of time (10 - 30 minutes). In order to obtain good accuracy and precision it was necessary to introduce an argon clean up system to remove traces of mercury. The valve assembly provided a convenient method of controlling the gas flow over the gold sand trap and into the fluorescence detector without the introduction of air which reduces sensitivity due to quenching. The system was totally automated in terms of collection and quantification and the software performed all the necessary calculations in the range of units as desired by the user.

CHAPTER 5

DEVELOPMENT OF AN ATOMIC FLUORESCENCE SPECTROMETER FOR THE HYDRIDE FORMING ELEMENTS

5.1. INTRODUCTION

The use of the hydride generation technique coupled to atomic fluorescence spectrometry has proved to be a sensitive method for the determination of those elements which form volatile hydrides (56-67).

Thompson (56) in 1975 was the first to describe a dispersive atomic fluorescence system for the determination of arsenic, selenium, antimony and tellurium after hydride generation. He utilised an argon-hydrogen flame maintained on a pyrex tube as an atom cell and modulated microwave excited electrodeless discharge lamps (EDLs) as an excitation source for each element. Detection limits using this system ranged from 0.06 to 0.1 μ g 1⁻¹. A similar dispersive AFS system was described by Ebdon et al. (57) for the determination of arsenic and selenium using a continuous flow hydride generation approach. Atomisation was achieved using a miniature argon-hydride flame burning on a glass 'Y' burner located at the focal point of the entrance slit lens. Excitation of atomic species using EDLs was obtained with illumination at 45° in preference to the conventional 90° illumination, since this reduced background radiations and scatter thereby allowing signal amplification with minimal increase in noise. The limit of detection for arsenic and selenium was found to be 0.34 and 0.13 μ g l⁻¹ respectively. This

150

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system was later utilised for the determination of arsenic and selenium in coal (149).

Brown et al. (58) used an argon sheathed, electrothermally heated, quartz atomiser for the atomisation of hydrogen selenide. Maintaining the atomiser at 800°C, the hydride was carried to the atomiser by a stream of hydrogen evolved from the decomposition of sodium tetrahydroborate. They observed a dramatic improvement in sensitivity when the flow rate of the sheathing gas was decreased so that a small argon-hydrogen flame ignited. With the flame ignited a limit of detection of 1.4 ng of selenium was obtained from a 10 ml sample solution. The increase in sensitivity observed with flame ignition is in agreement with the research of Dědina and Rubeška (85) and Welz and Schubert-Jacobs These authors have suggested that the atomisation of (84). gaseous hydrides is caused by collisions with free hydrogen, oxygen and hydroxyl radicals within the flame. In the absence of these radicals, atoms may condense to form polyatomic species. for example, Se_2 , Se_3 and Se_4 .

Most of the hydride forming elements can be detected using atomic fluorescence spectrometry in the UV region below 250 nm. This is a particularly useful spectral region since very little background emission is seen even from the flame atom cells. More importantly, the spectrum is no longer complex, since the analyte has been separated from the matrix during the hydride generation stage. It therefore follows that non-dispersive atomic fluorescence spectrometry is feasible.

Tsujii and Kuga (150) in 1974 were the first to describe hydride

generation coupled to non-dispersive atomic fluorescence spectrometry. They reported a detection limit of 2 ng for arsenic using a zinc reduction procedure. A comparative study between dispersive and non-dispersive systems for the determination of arsenic using premixed argon-hydrogen and nitrogen-hydrogen flames was undertaken by Nakahara and coworkers (59). The best limit of detection (0.12 μ g l⁻¹) was obtained using the non-dispersive system with an argon-hydrogen flame atom cell. This system had the advantage of higher throughput (large solid angle, input and exit apertures and higher transmission) and simultaneous measurement of all fluorescence lines. Nakahara and co-workers have subsequently published a series of papers on non-dispersive atomic fluorescence spectrometry for the determination of arsenic (59), bismuth (60), lead (61), antimony (62), selenium (63), tin (64) and tellurium (65). Azad et al. determined selenium (151) and arsenic (152) in soil digests by non-dispersive AFS using a hydride generation technique. Results obtained with this system were compared to those obtained using inductively coupled plasmaemission spectrometry and good agreement was obtained.

From the pioneering work on hydride generation atomic fluorescence spectrometry it can be seen that the most suitable atom reservoir consists of an argon-hydrogen flame. The reasons for this being: (a) the flame emits very low background radiation in the region where the hydride forming elements are detected; (b) the hydrides are easily decomposed at low flame temperatures and (c) quenching is relatively low in argon supported flames. Tsujii and co-workers (153,154) have reported that lower hydrogen flow rates (i.e. smaller argon-hydrogen flames) improve the

signal to noise ratio. This led the same group to develop a new design of atom cell to accommodate the use of a miniature argonhydrogen flame. They utilised the technique to obtain depth profiles of arsenic (155) and antimony (156) in semi-conductor silicon by chemical etching. The sectioning depth was measured by determining the amount of silica dissolved in hydrofluoric with the use of acid. ICP-AES. This method permitted determination down to 10^{18} atoms of arsenic and antimony cm⁻³. The same workers (157) developed an argon sheathed, pyrolytically coated, graphite furnace atomiser used in a vertical position for the atomisation of arsenic. No atomic fluorescence was observed when the atomisation temperature was below 1100°C and therefore the furnace was maintained at a constant temperature of 1200°C. A detection limit of 0.01 ng of arsenic was obtained for a 100 µl sample solution using non-dispersive AFS detection.

D'Ulivo and co-workers used a non-dispersive AFS system coupled with hydride generation for the determination of lead (158) and dialkyl and trialkyl lead (159). The same workers (66) developed a multi-element system based on an argon-hydrogen miniature flame, irradiated by four radio frequency excited EDLs, each being modulated at a set frequency. The emitted fluorescence radiation was detected by one photomultiplier tube, connected to four lock in amplifiers tuned to the frequency of the relevant recently, the same group (67) EDL. More designed an electrothermally heated quartz tube flame atomiser, for the determination of selenium. Using the batch approach, evolved hydrides were swept into the atomiser by a stream of argon. Α small argon-hydrogen flame then self-ignited at the hot tube

outlet, due to the excess hydrogen evolved during the decomposition of sodium tetrahydroborate. This flame was sufficient to achieve atomisation indicating that atomisation is probably via a free radical mechanism within the flame. The system was used to determine selenium in a range of certified reference materials such as coal fly ash, seawater, fish muscle and fish tissues, and the results obtained agreed well with the certified values.

To date there are, surprisingly, no commercially available atomic fluorescence detectors for the volatile hydride forming elements. This is largely due to the lack of reliable high intensity excitation sources. Recently, boosted discharge hollow cathode lamps (BDHCLs) have become commercially available (160) and it would seem that these might offer a promising source for atomic fluorescence spectrometry.

This chapter is devoted to the development of an atomic fluorescence spectrometer and its suitability for coupling to continuous flow hydride generation. Preliminary work concentrated on the determination of arsenic using а monochromator AFS measurement system, utilising a BDHCL as an excitation source. The instrumentation concepts were focused on four main areas: (a) the light source, (b) the atom cell, (c) the optical configuration and (d) the readout and data processing (i.e. electronic configuration) for the instrumentation. Α detection system was later developed which utilised an interference filter for wavelength isolation and reduction of flame emission. A solar-blind photomultiplier tube was used to detect fluorescence emission. The analytical performance of both

systems is described in detail for the determination of arsenic and selenium.

Experimental

5.2.1. Continuous Flow Hydride Generation

A continuous flow hydride generation system was used in this study to generate covalent gaseous hydrides. This system was described in detail in section 2.1.1. Using the conventional glass 'U' tube gas-liquid separator, typical hydrochloric acid and sodium tetrahydroborate concentrations used were 4 mol 1^{-1} and 2.0% m/V respectively. The chemistry of the hydride generation system is discussed in sections 5.4.10 and 5.5.3.

5.2.2. Reagents

Unless specified otherwise, all reagents were of AnalaR or Aristar grade (BDH Ltd, Poole, Dorset). De-ionised water was used throughout (Milli-R04, Millipore Corp, Massachusetts, USA). Sodium tetrahydroborate solutions (SpectrosoL, BDH) in 0.1 mol 1⁻¹ sodium hydroxide solution as a stabiliser. Fresh solutions were prepared daily. Standard solutions were prepared by appropriate dilution of stock 1000 mg 1⁻¹ arsenic (III) chloride solution (SpectrosoL, BDH) using hydrochloric acid solutions. Fresh solutions were prepared daily. Potassium iodide (1% m/V in 4 mol 1⁻¹ hydrochloric acid) was used to reduce arsenate to arsenite. All glassware was soaked in 10% V/V nitric acid for 24 hours prior to use, and then rinsed five times with distilled

5.3.1. Instrumentation for the Monochromator System

A modified atomic absorption/emission spectrometer (SP9, Unicam Ltd, Cambridge, UK), coupled to a continuous flow hydride generator (P S Analytical Ltd, Sevenoaks, UK) was used in this study to develop a dispersive AFS system for the determination of arsenic. A plan of the instrumentation is shown in Figure Essentially, the conventional burner assembly of the 5.1. spectrometer was removed and replaced by a triangular optical bench, which contained a light source, lens and an atom cell. This arrangement allowed optimisation in all three planes The atom cell was illuminated at right angles to the (x,y,z). detector axis to prevent radiation from the excitation source reaching the detector. Since atomic absorption operates according to the basic limits of the Beer-Lambert law, one of which is that absorbance is independent of the source intensity, atomic absorption apparatus usually have low light gathering capabilities. For this reason, the entrance slit of the monochromator was fully opened (10 nm) in order to increase the solid angle, the gain setting was maximised and the instrument was used in the emission mode.

5.3.2. Excitation Source for the Monochromator System

As mentioned previously in section 2.4.1. fluorescence intensity is directly proportional to the intensity of the exciting

Figure 5.1 - Plan of the optical arrangement for the monochromator measurement system



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radiation. Consequently, a high radiance excitation source is required for atomic fluorescence in order to obtain good limits of detection. The basic requirements for an excitation source for atomic fluorescence are:

- 1) high radiant output over the analytical line;
- good short and long term stability with a steady uniform level of radiance;
- 3) short warm up time;
- 4) minimum maintenance and adjustment to obtain optimum performance;
- 5) long lifetime;
- low cost of source and associated power supply;
- 7) availability for a large number of elements;
- strong in construction to avoid breakage;
- 9) minimum interference to the analytical line due to the presence of spectral lines of the filler gas or impurities.

The majority of papers published on hydride generation AFS have utilised microwave excited electrodeless discharge lamps (EDLs). These consist of an evacuated quartz or glass bulb containing a small amount of pure metal or metal salt (usually a halide), in an inert gas atmosphere such as argon. When excited, these lamps are very intense (typically 200 to 2000 times more intense than a conventional hollow cathode lamp) and emit narrow lines. Unfortunately, they are often unpredictable in use and require careful temperature control to achieve good stability (161). Radiofrequency excited EDLs have also been utilised for hydride generation atomic fluorescence spectrometry (158), but these are only 5-100 times more intense than hollow cathode lamps. These are more stable than microwave excited EDLs but are usually less

stable than HCLs.

Although conventional hollow cathode lamps may be utilised for atomic fluorescence they do not provide the intensity required for adequate excitation. Increasing the intensity by increasing the current leads to broadening and later self-reversal of the resonant lines by self-absorption. In atomic fluorescence spectroscopy this phenomenon is not a problem as long as the intensity of the central wavelength can be increased. Increases in the non-absorbing intensity cause only a small increase of scattered light. The intensity of the hollow cathode lamp may be increased without self-absorption broadening by superimposing a boosted positive column discharge across the hollow cathode discharge (160). The positive column feeds additional electrons into the hollow cathode plasma without increasing sputtering, but ensuring that most of the atoms are excited. The combination of a low voltage - high current discharge in the absence of ground state atoms in the light path means that self-absorption is avoided, while high intensity may be achieved. This type of lamp is patented and is now commercially available (SuperLamp, Photron Pty Ltd, Victoria, Australia), and was thought to be a suitable high intensity source for this development work. A schematic diagram of the boosted discharge hollow cathode lamp is shown in Figure 5.2.

The BDHCL was operated from the existing SP9 instrument lamp current supply (0-20 mA), which is modulated at 150 Hz. The modulated SP9 power supply was connected to the boosted discharge supply and then to the BDHCL via male and female octal plugs respectively. Therefore, the primary discharge will be modulated





at 150 Hz and the boosted discharge will be operated using direct current. Decoding circuitry within the SP9 then detects modulated light which will be in the form of an AC signal and separates it from any flame emission which will be manifested as a DC signal.

The BDHCL was optimised for boost discharge and primary current in order to obtain the maximum radiance. This was achieved by positioning the BDHCL opposite the detector and varying one parameter whilst the other was held constant (i.e. univariant search). The effect of boost discharge on lamp intensity using primary currents of 15 and 20 mA is shown in Figure 5.3. For primary currents of 15 and 20 mA, optimum boost discharge currents were found to be 40 and 55 mA respectively. This shift in optimum boost current with increasing primary current is expected, since at higher primary currents sputtering will be increased and therefore to prevent self-absorption, more electrons from the boost discharge must pass through the cathode. Exceeding the boost current optimum will reduce the intensity of the lamp, in severe cases to zero. This is caused by electrons from the boost discharge sweeping through the cathode, preventing electrons from hitting the cathode reducing sputtering. The effect of primary current on lamp intensity with a boost discharge of 55 mA is shown in Figure 5.4. The intensity of the lamp remains constant until 10 mA after which it rises dramatically. The maximum recommended operating primary current for the arsenic BDHCL is 30 mA, unfortunately the maximum lamp current setting on the SP9 spectrometer is only 20 mA and therefore the effect of current above this value could not be investigated for the monochromator system. Using the optimum

Figure 5.3 -

Effect of boost current on arsenic lamp intensity



Figure 5.4 - Effect of primary current on arsenic lamp intensity



Primary Current / mA

conditions the BDHCL was ten times more intense than a conventional hollow cathode lamp with a lamp current of 8 mA. Watson (160) observed only a 2-3 fold increase in intensity with the BDHCL compared to conventional hollow cathode lamps, however, his BDHCL was not operated with conditions for maximum radiance.

The emission intensity ratio for 193.7:194.0 nm using a bandpass of 0.2 nm was found to be 26.3:1 and 19.2:1 for the BDHCL and the conventional HCL respectively. Therefore one would expect that the use of a BDHCL would also be advantageous for atomic absorption spectrometry. Higher radiance should give better signal to noise ratio and also lower emissions from nearby nonabsorbing lines should increase sensitivity and improve the linear calibration function.

The BDHCL has a recommended warm up time of 30 minutes. The disadvantages of the BDHCL are the high cost of the lamp (£250) and the booster power supply (£1000), the short lifetime (5000 mA/hours) and their complexity of operation and construction.

5.3.3. Effect of Wavelength on Atomic Fluorescence for Arsenic

The atomic fluorescence spectrum for arsenic is relatively complex. Some 15 spectral lines have been found to exhibit atomic fluorescence (162). Resonance lines occur at 189.04, 193.76 and 197.26 nm. The other 12 lines are due to nonresonance fluorescence. The 238.12, 243.72, 245.65, 249.29, 303.28 and 311.96 nm lines are due to direct line fluorescence, while the 228.81, 234.98, 274.50, 278.02 and 286.04 nm lines are examples of thermally assisted direct line fluorescence.

Using the dispersive measurement system with a bandpass of 10 nm, the spectral characteristics of the BDHCL emissions and fluorescence of the five most prominent lines were investigated. The results obtained are shown in Table 5.1.

<u>Table 5.1</u> Spectral characteristics of the boosted discharge hollow cathode lamp emission and atomic fluorescence for arsenic

Wavelength (nm)	Relative Emission Intensity ^(a)	Relative Atomic Fluorescence Signal ^(b)	
189.04	16.2	79.9	
193.76	32.4	100.0	
197.26	26.7	64.0	
228.81	100.0	4.0	
234.98	89.5	22.3	

(a) Relative intensity to the 228.81 nm line using a bandpass of 0.2 nm

(b) Relative fluorescence to the 193.7 nm line using a bandpass of 10.0 nm

With this system the highest sensitivity was obtained when the monochromator was tuned to a wavelength of 193.76 nm. However, using a 10 nm bandpass, it is difficult to assess whether or not the value obtained is solely due to one analytical line or includes a contribution from bordering lines. A bandpass of 10 nm is required, since the apparatus has low light gathering characteristics. Figure 5.5 shows the effect of bandpass on signal to background ratio. As expected, increasing the bandpass allowed more atomic fluorescence to be collected. The values shown in Table 5.1 were not corrected for the photomultiplier spectral response which is why there appears to be greater

164

Figure 5.5 - Effect of bandpass on signal to background ratio for arsenic



Bandpass / nm

emission intensity from the BDHCL at the 228.81 and 234.98 nm lines. Furthermore, since the spectral response of the photomultiplier is low below 200 nm, one can therefore assume that the majority of the fluorescence occurs at the three resonance lines. The values in Table 5.1 suggest that a nondispersive system with a solar-blind photomultiplier tube would be advantageous since the fluorescence obtained would be from a collection of wavelengths, thereby increasing sensitivity.

5.3.4. Optical Configuration of the Monochromator System

The basic layout of the optical configuration for the monochromator system is shown in Figure 5.1. A boosted discharge hollow cathode lamp, a biconvex quartz lens and an atom cell were mounted on a triangular optical bench at right angles to the detection axis. Emitted fluorescence was collected onto the mirror where it was reflected onto the monochromator entrance slit. The monochromator is of the Ebert type of geometry. Having passed through the entrance slit the now diverging beam arrives at one side of a collimating mirror which reflects light onto the diffraction grating. This has 1200 lines per mm over 2 cm x 2 cm area. The dispersed beam is directed back to the other side of the collimating mirror which focuses the beam onto the exit slit. Monochromatic light emerging from this slit now enters the window of the photomultiplier tube where the radiation is converted into an electrical signal.

The maximum fluorescence intensity will be obtained at the point where the highest atom density occurs in the flame. It is therefore critical to irradiate this region in the most effective

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way possible. In order to obtain this condition it was necessary to optimise both the distances between the lens and the hollow cathode discharge and the lens and the centre of the atom cell. The biconvex quartz lens used in this study had a focal length and outer diameter of 25 mm. Symmetric biconvex lenses offer the best performance obtainable from a single lens in finite conjugate imaging.

5.3.5. Atom Reservoirs for Atomic Fluorescence Spectrometry

The basic requirements of an atomic reservoir for atomic fluorescence spectrometry are an efficient and rapid production of free atoms with the minimum background (and background noise), a high degree of reproducibility with minimal memory effects, low quenching properties and minimal dilution of the atoms.

The majority of papers published on hydride generation - AFS have utilised argon-hydrogen flames. This is because: (a) the flame emits very low background radiation over the wavelength region of interest; (b) the hydride compounds are easily decomposed in such a low temperature flame and (c) the quenching effect is relatively low in argon supported flames and hydrogen.

Four atom cell designs have been investigated in this study, and these are illustrated in Figures 5.6 to 5.9. Initial studies involved the use of the atomisation cell shown in Figure 5.6. This basically consisted of a borosilicate glass tube (8.5 mm i.d. x 100 mm high) with inverted 'Y' side arms to act as gas inlets. Gases of the hydride generation process (argon, hydrogen and hydrides) were passed into one arm of the burner whilst the







Figure 5.8 - Argon sheathed electrically heated atom cell



Chemically generated hydrogen diffusion flame atom cell Figure 5.9 -



other had a low flow of hydrogen obtained from a gas cylinder. The result was an argon-hydrogen diffusion flame upon ignition. Argon-hydrogen diffusion flames are normally transparent but in this instance a characteristic orange colouration was observed due to the emission of sodium atoms. The sodium in the form of sodium chloride arises as a by-product of the hydride generation reaction (i.e. NaBH₄ + HCl) and is delivered to the flame in the form of a fine aerosol, (see section 3.2.3). The optimum gas flow rates for the atomiser shown in Figure 5.6 were found to be 0.4 and 0.3 1 min⁻¹ for hydrogen and argon respectively. At lower gas flow rates the flame was unstable, due to pulsations from the peristaltic pump of the hydride generation system. Furthermore, at low gas flow rates the base of the flame tended to sit inside the tube orifice because of insufficient gas velocities. At higher gas flow rates a decrease in fluorescence intensity was observed due to analyte dilution and shorter residence time of the atoms in the optical path. This atom cell design proved an effective means of atomising gaseous hydrides and a limit of detection (as defined in section 3.2.2) of 1.46 μ g l⁻¹ arsenic was obtained. The upper limit of the linear calibration range was found to be about 100 μ g l⁻¹ arsenic. Concentrations exceeding this value are susceptible to selfabsorption (section 4.2.3). The linear calibration range therefore only extends over 2 orders of magnitude, which is comparatively short for atomic fluorescence spectrometry.

In view of the safety regulations associated with the use of hydrogen gas cylinders, it was envisaged that a non-flame atom cell might be more suitable for a commercial instrument.

The first flameless design investigated is shown in Figure 5.7. This was basically a silica tube (8.5 mm o.d. x 150 mm long) with qas inlet for hydride generation products one (hydrogen, hydrides) and the carrier gas, argon. The silica tube was evenly wound with nichrome wire (2 m length, 6.5 Ω m⁻¹) and heated resistively via a Variac (0-240 V) transformer. With this arrangement temperatures of up to 850°C were achieved. These were measured using a thermocouple device. Using a 1% m/V sodium tetrahydroborate solution at a flow rate of 3.5 ml min⁻¹, hydrogen was generated at approximately 0.07 1 min⁻¹. At tube temperatures above 750°C the excess hydrogen ignited at the top of the burner producing a mini argon-hydrogen diffusion flame. Attempts to extinguish this flame unsuccessful. were Furthermore, once the flame had been produced, decreasing the temperature of the silica tube had no effect on the fluorescence intensity. This indicates that the atomisation process was not via thermal decomposition, but due to free radicals in the flame. Several authors have discussed this theory in detail and proposed various mechanisms (84-88). This atom cell design produced a limit of detection of 6.74 μ g l⁻¹ arsenic and the upper limit of the linear calibration range was found to be about 100 μ g 1⁻¹ arsenic.

The inability to extinguish the flame led to the design of the atom cell shown in Figure 5.8. This is similar to the previous design except that a series of capillaries were positioned around the outside of the inner electrically heated silica tube. A. .. supply of argon was then introduced as a sheath gas to prevent flame ignition. Sheath gas flow rates of at least 1.5 l min⁻¹

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were required to extinguish the flame. At an atom cell temperature of approximately 850°C in the absence of a flame, no fluorescence was observed. However, if the sheath gas was lowered sufficiently enough to allow diffusion of oxygen from the surrounding atmosphere to penetrate the sheath gas, a mini argonhydrogen diffusion flame was produced. This was found to be an effective means of atomising the gaseous hydrides. Tsujii and Kuga (157) developed an argon sheathed pyrolytically coated, graphite furnace atomiser for the atomisation of arsine. No atomic fluorescence was observed below furnace temperatures of 1100°C, and therefore the furnace was maintained at a constant temperature of 1200°C. Brown <u>et al.</u> (58) and D'Ulivo <u>et al.</u> (67) both observed an increase in sensitivity for selenium when they allowed the ignition of a mini hydrogen diffusion flame produced from the chemical reagents. As mentioned previously, this increase in sensitivity favours the suggestion that atomisation of gaseous hydrides is caused by collision with free radicals within the flame (84-88). In the absence of these radicals free atoms are thermally decomposed to polyatomic species such as Se₂, As₂ and As₄ which have no practical use in atomic fluorescence. Although the atomisation mechanisms for the gaseous hydrides is not fully understood, there are clearly distinct advantages of using argon supported flames in atomic fluorescence spectrometry.

On the basis of the above considerations, the atom cell in Figure 5.9 was investigated. This is an extremely simple design which basically consists of a 10 cm long borosilicate glass tube. Gases leaving the separator (argon, hydrogen and hydrides) are passed through the centre of the tube and upon ignition a small argon-

hydrogen diffusion flame is produced. The advantage here of using a continuous flow rather than the batch hydride generation process is that hydrogen is produced continuously thereby permitting a permanent flame. Other workers have only used this approach for the batch hydride technique (58,67). Various tube diameters were investigated, ranging from (11 mm o.d. x 9 mm i.d.) to (5 mm o.d. x 3 mm i.d.). The best optical arrangement for each tube diameter was determined and the analytical performance assessed. These findings are reported in Table 5.2.

The optimum carrier gas flow rate was 0.50 l min⁻¹ for the largest tube size and 0.28 l min⁻¹ for the other tube sizes. Larger tube diameters require higher gas flows, since at low gas flow rates the flame was found to sit inside the glass tube. However, higher gas flow rates cause a reduction in sensitivity due to atom dilution and a decrease in the residence time of the atoms in the optical path. The effect of carrier gas flow rate on peak height is shown in Figure 5.10 for a 3 mm i.d. tube size.

In terms of the analytical performance, the most striking feature with varying tube diameters was the limit of detection. The values in Table 5.2 show that an improvement in sensitivity was observed with decreasing tube diameter. This is mainly due to two factors. The first being that the flame becomes more stable with decreasing tube diameter. Large tube diameters were more susceptible to the pulsation from the peristaltic pump of the hydride generation system, an effect which was less prominent with smaller tube diameters. The second reason for the sensitivity improvement was that the smaller the flame, the higher the atom density which allowed the source to excite atoms

173

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Table 5.2 Analytical performance using various atom cell dimensions for arsenic

ATOM CELL TUBE DIMENSIONS (mm)	WIDTH OF INCIDENT BEAM (mm)	CARRIER GAS FLOW RATE (l min ⁻¹)	LIMIT OF OF DETECTION ($\mu g l^{-1}$)	UPPER LIMIT OF CALIBRATION (µg 1 ⁻¹)
11 o.d. x 9 i.d.	7	0.50	6.7	100
9 o.d. x 7 i.d.	6	0.28	0.94	70
7 o.d. x 5 i.d.	6	0.28	0.63	80
5 o.d. x 3 i.d.	6	0.28	0.28	100

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Figure 5.10 - Effect of carrier gas flow rate on arsenic net signal for the 3 mm i.d. tube size atom cell



more efficiently: Tube diameters of less than 3 mm i.d. were investigated, but in these cases the flame actually lifted off the top of the burner, because of the higher gas and burner velocities.

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The upper concentration limits of the linear calibration range for each atom cell are also given in Table 5.2. Concentrations exceeding the value shown are susceptible to self-absorption and this process has been explained in detail in section 4.2.3. With an excitation beam of 6 mm at the centre of the atom cell tube, ground state atoms in the outer portion of the flame are less likely to be excited and may reabsorb fluorescence emission. This effect will be greater with larger tube sizes and therefore one would expect self-absorption to be more prominent. The linear calibration range in each case only spans over 2-3 orders of magnitude, which is poor for atomic fluorescence spectrometry. The upper limit of the concentration range cannot be increased because of the self-absorption process, however, it is envisaged that improvements will occur at the lower concentration side of the calibration.

The major advantage of this atom cell design is that no additional supply of hydrogen is required, which is extremely important in view of the present safety regulations associated with the use of hydrogen cylinders. Because the hydrogen is generated chemically from the reagents of the hydride generation system, the concentration of the reagents is extremely important and this will therefore be discussed in section 5.4.10.

5.4.1. Non-Dispersive Atomic Fluorescence Spectrometry

There are basically two instrumental approaches for atomic spectrometry, these fluorescence may be classified into dispersive and non-dispersive measurement systems. Dispersive systems are normally based on modified atomic absorption/emission spectrometers and wavelength isolation is achieved using a monochromator. Atomic absorption apparatus usually has low light gathering characteristics, especially in the far UV wavelength region. Atomic fluorescence, however, requires high light gathering power to be used to the best advantage. In fact, no monochromation is required for atomic fluorescence because it can be arranged so that only one fluorescent species is excited by an element specific excitation source. This is quite different to the situation in atomic emission where the flame may excite all elements in the analytical solution simultaneously, in this instance a single line must be resolved. In contrast, in atomic fluorescence, it is possible to use all the lines of the element if a line source is used for excitation. Summation of these fluorescence lines is possible and therefore non-dispersive systems are usually more sensitive than dispersive systems. They are also less complex and do not require the use of an atomic absorption/emission spectrometer. A schematic diagram of a nondispersive system is shown in Figure 2.7. On some occasions it may be advantageous where there is strong emission from the flame, to use a filter between the atom reservoir and the The majority of papers on hydride generation - AFS detector. have utilised non-dispersive measurement systems because of the reasons discussed above (59-67). In this study it was found that the introduction of an interference filter was required, in order

to reduce flame background. Interference filters are basically ...miniature interferometers and therefore in the strictest sense they may be classified as a simple dispersive device.

5.4.2. Instrumentation for the Filter System

A block diagram of the filter measurement system is shown in Figure 5.11. It basically consists of a boosted discharge hollow cathode lamp with power supply, an argon-hydrogen diffusion flame maintained on a borosilicate glass tube, a collection of lenses, a solar-blind photomultiplier tube and an electronic pre-amp readout system. The individual constituent units will now be discussed in more detail.

5.4.3. Boosted Discharge Hollow Cathode Lamp for the Filter System

The boosted discharge hollow cathode lamp was described in detail in section 5.3.2. Using the monochromator system the primary discharge of the BDHCL was modulated at 150 Hz, and the boost discharge was operated using direct current. Fluorescence emission was then detected and selectively amplified using a lock-in amplifier. The filter system utilised a DC pre-amplifier (Merlin pre-amp M023P003, P S Analytical, Sevenoaks, UK) so the primary discharge was therefore operated in the DC mode. After long periods of usage running at high power settings it was noted that the booster supply began to overheat. This eventually resulted in electronic component failure. The faulty component was replaced several times, but the problem reoccurred. The manufacturers, when made aware of this problem, redesigned the



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Figure 5.11 - Block diagram for the filter measurement system

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power supply for the BDHCL (Starna Ltd, Essex, UK) and these modifications were then evaluated. Figures 5.12 and 5.13 show the effect of boost current on peak height and signal to background ratio respectively for primary currents of 25.0, 27.5 and 30.0 mA. In both cases the maximum fluorescence occurred when the primary and boost currents were set at 30 and 35 mA respectively. The new power supplies prevented any further increase in boost current and therefore higher currents were not investigated. A general improvement in the stability of the BDHCL was observed with the new power supplies.

5.4.4. Interference Filter

The interference filter (Envin Scientific Ltd, Gloucestershire, UK) investigated has a peak wavelength of 200 nm and a bandpass of + 10 nm half width. A transmission spectra of this filter is shown in Figure 5.14. This was obtained using a scanning UV-vis spectrometer (Lambda 7, Perkin Elmer, Buckinghamshire, UK) by mounting the filter in the optical beam. In section 5.3.3 the effect of wavelength on atomic fluorescence was discussed. The majority of the fluorescence was obtained at the three resonance lines, 189.04, 193.76 and 197.26 nm. The interference filter has relatively low transmission at these wavelengths and this will affect the performance of the system. The filter used is of the Fabry-Perot type and consists of an extremely thin layer of dielectric material sandwiched between semi-reflecting metallic This can be manufactured by precise deposition under films. vacuum. The process of wavelength isolation is shown in Figure 5.15. For the purpose of illustration angular incidence is shown, but normal incidence is usually used. For transmission

Figure 5.12 -

Effect of boost current on net signal for arsenic using the filter measurement system



Figure 5.13 - Effect of boost current on signal to background ratio for arsenic using the filter measurement system



Figure 5.14 - Transmission spectra of the 200 nm interference filter



WAVELENGTH / nm

Figure 5.15 - Multiple reflected ray in an interference filter



to occur there must be constructive interference, this occurs when the path difference between rays is one wavelength or a multiple thereof. The expression for the wavelength at which full reinforcement will occur is

$$2d = \frac{m\lambda}{n}$$

where d is the thickness of the dielectric layer, n is its refractive index at wavelength λ (vacuum) and m is the order (m=1,2,3...), a factor that allows for path lengths that are a multiple of the wavelength. For instance, reinforcement will occur when aa' + a'b is exactly one wavelength in the medium (λ /n), or a multiple. Partial reinforcement may occur for other path distances, and therefore the filter actually transmits a band. Wavelength that are one half 2d, one third 2d and so on will also constructively interfere and be transmitted as higher orders. Second and third order bands are narrower and most interference filters are arranged to transmit one of these. Bordering transmission bands may be blocked with additional filters or coatings.

The transmission spectra shown in Figure 5.14 is rather confusing, since several transmission bands were observed. One might assume that the 200 nm transmission band represents the third order. This would require first and second orders at wavelengths of 600 and 300 nm respectively. Ignoring the effect of wavelength on refractive index, transmission was observed in these wavelength regions. However, on closer investigation of the spectra, a transmission band was observed at 390 nm (approx.

400 nm) which would not represent an order in the above case. Alternatively, the transmission around the 400 nm region might be first order transmission, making the second order occurring at 200 nm. A first order transmission of 1200 nm would enable all transmission bands to be accounted for, the 200 nm band in this case would be the sixth order. The fifth order would occur at 240 nm and this is not observed on the transmission spectra. It was therefore impossible to predict the order at 200 nm with the data available. The transmissions occurring at higher wavelengths have obviously been blocked off and the bands observed are therefore leakages. Radiation deviating from normal incidence will cause the transmission band to be shifted toward shorter wavelengths, however, this causes a reduction in transmission.

5.4.5. Solar-Blind Photomultiplier Tube

A solar-blind photomultiplier tube (R166, Hamamatsu, Middlesex, UK) was chosen because of its high radiant sensitivity in the far UV region. A spectral response curve for the solar-blind PMT (163) is shown in Figure 5.16. It was sensitive in the range from 160 nm to 320 nm. The effect of amplifier gain on PMT response was investigated for various instrumental conditions (Figure 5.17). When the PMT was exposed to the ambient light (curve A) the readout of the detector system was offscale (2049) before a gain of 10 was reached. Clearly showing that the PMT is responsive to ambient light. In complete darkness, only a small response was obtained, even at a maximum gain of 10,000 (curve B). Curve (C) corresponds to the total background (i.e. lamp on and flame on) without the use of a filter, with the PMT

Figure 5.16 - Spectral response for the solar-blind photomultiplier tube (reference 163)



Figure 5.17 - Effect of amplifier gain on the solar-blind photomultiplier tube response for various instrumental conditions



Amplifier Gain Setting

- A Ambient light without interference filter
- B Complete Darkness
- C Flame and lamp on without interference filter
- D Ambient light with interference filter
- E Lamp on with interference filter
- F Flame and lamp on with interference filter

protected from ambient light. A gain setting of slightly less than 100 was required to make the readout offscale. The introduction of the interference filter reduced the background considerably, allowing full usage of the amplifier gain settings (curves D, E and F). In summary, the solar-blind PMT has to be maintained in dark conditions because it has a response to ambient light. The use of an interference filter considerably reduced the background thereby allowing full usage of the amplifier gain settings. These values were obtained with a photomultiplier voltage of 500 volts.

5.4.6. Optical Configuration of the Filter System

Three optical configurations have been investigated. The major differences to the system described in sections 5.3.1 to 5.3.5 were that the monochromator was replaced by an interference filter and the fluorescence was detected using a solar-blind photomultiplier tube.

The first optical configuration essentially has no collection optics, therefore the distance between the atom cell and the solar-blind PMT was critical. The effect of this distance on net signal with and without the use of an interference filter is shown in Figure 5.18. The maximum fluorescence occurred when the atom cell was positioned as close to the PMT as possible. This was expected, since the emitted fluorescence will be absorbed strongly in the ambient air and decreasing this distance increased the solid angle between the atom cell and the PMT. However, if one now considers the effect of this distance on the limit of detection, a different result is obtained, Figure 5.19.

Figure 5.18 - Effect of distance between atom cell and photomultiplier tube on net signal (configuration 1)



Figure 5.19 - Effect of distance between atom cell and photomultiplier tube on limit of detection (configuration 1)



188

Without the use of the filter, greater sensitivity was obtained when the atom cell to PMT distance was large, this is because in this situation the total signal was highly dependent on the noise and background emission of the hydrogen diffusion flame. In fact, the solar-blind PMT was sensitive up to 320 nm and therefore observed the OH emissions between 305 and 320 nm. An emission spectra of the flame in this wavelength region is shown in Figure 5.20. No other emissions were observed below this region. A sensitivity improvement was obtained by using the interference filter and the best limit of detection was obtained when the distance between the atom cell and the solar-blind PMT was minimal. All further experiments involved the use of an interference filter.

The second optical configuration introduced a biconvex lens (25 mm o.d. x 25 mm focal length) which was positioned between the atom cell and the PMT. This increased the net signal by approximately 3-4 times. The limit of detection was reduced from 1.4 μ g 1⁻¹ to 0.58 μ g 1⁻¹ arsenic. The third configuration was designed to reduce spherical abberations from the entrance optics. With this arrangement a limit of detection of 0.41 μ g 1⁻¹ arsenic was obtained. Although this new arrangement did not have a noticeable effect on sensitivity, the optical arrangement was improved considerably.

5.4.7. The Reduction of Flame Noise

Noise may be defined as any undesirable fluctuation in the readout signal of an instrumental system such as drift and random signals. The components that constitute the total noise of the

Figure 5.20 - Emission spectra of the hydrogen diffusion flame between 295 and 330 nm



readout can be divided into four main categories. These include source noise, flame noise, detector noise and amplifier readout noise. The latter two components are basically dark current short noise from the solar-blind photomultiplier tube and electronic noise from the components of the amplifier. The noise from these components was found to be negligible. Source noise from the BDHCL is dependent on the stability of the power supplies and the age of the lamp and is usually of low frequency. Provided the BDHCL had sufficient warm up time (approx. 30 mins) the source noise was also found to be negligible. The major contribution to the total noise of the system was due to the This was dependent on the type of flame and burner, the flame. spectral region observed and the position of the flame observed. The position of the flame observed was unimportant in this case since a total inverted image was focused on the PMT window. The main factor causing flame noise was the pulsation from the peristaltic pump of the hydride generation system and the delivery of the gaseous products to the atom cell. The argonhydrogen diffusion flame is relatively a low energy system and therefore no emissions occur below 300 nm. Unfortunately, the solar-blind photomultiplier tube is sensitive up to 320 nm and detects the intense OH emissions between 305 and 320 nm. Furthermore, the interference filter has a small transmission band in this wavelength region and therefore the flame noise observed was mostly due to these emissions. Carrier gas flow and liquid flows were optimised to minimise the contribution to the noise.

5.4.8. Electronic Readout for the Atomic Fluorescence Spectrometer

Two electronic readout systems have been investigated. One of which utilised the DC electronics of the mercury atomic fluorescence spectrometer M023P003, (Merlin pre-amp P S Analytical Ltd, Sevenoaks, UK) and the other utilised a lockin amplifier to selectively amplify fluorescence signals after modulation of the source using a mechanical chopper. The former approach was convenient since it is a proven, tested and reliable amplification readout system and the BDHCL could be used in the DC mode, which kept the power supply to a minimum cost. However, it is well known that DC amplification systems cannot distinguish between thermal and optically excited radiation, and therefore the measurements obtained are associated with the total noise of the system. This can be overcome using a phase sensitive amplifier which demodulates an a.c. coupled input signal via a switch that is operated in precise synchronisation with the phase and frequency of the periodic fluorescence signal. The BDHCL in this instance was modulated using a mechanical chopper (rotating sector). Although highly effective in producing an ON/OFF pulsation of the source, the chopper reduced the light intensity from the incident beam. By placing a miniature light bulb and photocell on opposite sides of the chopper blade a reference waveform was produced which was then utilised as a feedback to the amplifier. This ensured that all frequencies other than that of the reference were rejected. Thus, by using a phase sensitive lock-in amplifier it was possible to reject any components of the final signal that were not exactly in phase with the original waveform of the modulated BDHCL. As a result the signal to noise

ratio was further improved.

The effect of modulation was investigated using a rotating sector. The only available position to mount the rotating sector was about 25 mm from the flame. In this position at high frequencies the sector caused flame turbulence which in fact drew the flame towards the sector. This was detrimental to the benefits obtainable using modulation and no improvement in signal to noise ratio was observed. Furthermore, the lock-in amplifier system selectively increased the background due to lamp scatter off the top of the tube and fluorescence due to impure reagents. This resulted in an elevated background which was unfavourable in terms of analytical performance. The existing DC preamplifier and readout system was therefore adopted for future work.

5.4.9. Reduction of Background for the Filter System

One of the problems associated with the atomic fluorescence technique is that the performance is related to the background radiation. The components which constituted the total background signal were ambient light, emission from the flame, fluorescence from the reagents and lamp scatter. The components may be easily determined. Ambient light is basically the dark current and was measured when both flame and lamp are off. This contribution was usually negligible and must be subtracted from the other background components. Background radiation from the flame was due to the OH emissions between 305 and 320 nm and was measured when the lamp was off. The lamp had a relatively high background contribution since the interference filter used has a small transmission band in the emission region and the solar-blind PMT
has a spectral response at this wavelength. The background due to lamp scatter was the most prominent contribution and was obtained when the flame was extinguished. When the lamp and flame were both on the total background radiance was obtained. By subtracting the three background components (flame emission, ambient and lamp scatter) from this value the difference was due to the atomic fluorescence of the reagents. The most useful method to ascertain the various background contributions is by using background equivalent concentrations (BECs) and typical values for arsenic are given in Table 5.3.

<u>Table 5.3</u> Background equivalent concentrations of the components which constitute the total background radiation for arsenic

BACKGROUND COMPONENT	BACKGROUND EQUIVALENT CONCENTRATION ($\mu g \ l^{-1}$)
Ambient Light	0.4
Flame Emission	4.2
Lamp Scatter	20.0
Fluorescence from Reag	ents 2.0
Total Background	26.6

The ambient light contribution was negligible and would be difficult to decrease further. Background due to flame emission was dependent on flame size (section 5.4.10) and the efficiency of isolating this wavelength region with the interference filter. The fluorescence background due to the reagents can be improved using purer reagents containing smaller quantities of the analyte. These are available but the extra cost cannot always

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194
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be justified.

Of all the different background components the major contribution was due to scatter. A device was developed in conjunction with P S Analytical Ltd (Sevenoaks, UK) to minimise this scatter level. The device was found to reduce the background due to lamp scatter by approximately five times, causing a total fall in background by a factor of three. Table 5.4 shows the typical reduction in background contribution using this device.

<u>Table 5.4</u> Background equivalent concentrations of the components which constitute the total background radiation for arsenic using a scatter device

BACKGROUND COMPONENT	BACKGROUND	EQUIVALENT ($\mu g \ 1^{-1}$)	CONCENTRATION
Ambient Light		0.39	
Flame Emission		2.78	
Lamp Scatter		4.26	
Fluorescence from Reag	ents	1.93	
Total Background		9.36	

5.4.10. Chemical Optimisation of Continuous Flow Hydride Generation for Arsenic

With any hydride generation system whether it be batch or continuous flow, the concentration of the reagents and the chemical nature of the samples have a profound effect on the analytical performance of the instrument. This is especially true for this system, since the function of the reagents is two

fold. Firstly they must generate a sufficient quantity of hydrogen so that a flame can be maintained and secondly they must also generate the hydride species. The continuous flow hydride generation system used in this study was described in detail in sections 2.1.1 and 3.2.1. The hydride generator was coupled to the detector using a Nafion hygroscopic membrane dryer tube to reduce moisture carry-over reaching the atom cell (see section 4.4.1).

The effect of sodium tetrahydroborate and hydrochloric acid concentrations was investigated. Three criteria of merit were examined including net signal, signal to background and signal to noise ratios.

The effect of hydrochloric acid concentration on net signal at sodium tetrahydroborate concentrations ranging from 1 to 2.5 m/V in 0.1 mol 1^{-1} sodium hydroxide is shown in Figure 5.21. It would appear that at low reductant concentrations the variation in signal with acid concentration is negligible. The minimum net signal was obtained at a reductant concentration of 1% m/V, the flame in this instance being relatively small and rather unstable. An increase in net signal was observed with higher reductant concentrations. The maximum net signal was obtained with a sodium tetrahydroborate concentration of 2.5% m/V and a hydrochloric acid concentration of 3 mol 1⁻¹. A totally different optimum was obtained when the criteria of merit was signal to background ratio, Figure 5.22. This striking difference is explained if one considers the size of the flame. At low acid and reductant concentrations the flame is small and

196

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Figure 5.21 - Effect of hydrochloric acid concentration on net signal for arsenic at various reductant concentrations



Figure 5.22 - Effect of hydrochloric acid concentration on signal to background ratio for arsenic at various reductant concentrations



therefore the background emission from the flame will be minimal. In this instance the signal to background ratio will be large. In contrast, at high acid and reductant concentrations the flame is larger and will therefore possess a higher background. In this case the signal to background ratio will be small. It therefore follows that there is a direct correlation between the size of the flame and the signal to background ratio. Using a criteria of merit of signal to noise ratio the optimum became more clearly defined and this is shown in Figure 5.23. The results here show that the optimum signal to noise ratio occurred at a reductant concentration between 1.5 and 2.0% m/V and an acid concentration between 3 and 5 mol 1^{-1} .

If one considers the optima obtained for all three criteria of merit, then it would appear that the optimum sodium tetrahydroborate concentration is 1.5% m/V and the hydrochloric acid concentration is 3 mol 1^{-1} . Sodium tetrahydroborate concentrations below 1.0% m/V did not produce a usable hydrogen diffusion flame. The acid concentration must be above 3 mol 1^{-1} , since at lower concentrations interference from transition metals (e.g. Ni) may become prominent (71-74).

5.4.11. Analytical Performance of the Filter System for Arsenic

The analytical performance of the hydride generation atomic fluorescence spectrometer can be characterised by the limit of detection, linear dynamic range, precision and accuracy of measurements.

Figure 5.23 - Effect of hydrochloric acid concentration on signal to noise ratio for arsenic at various reductant concentrations



The limit of detection for arsenic as defined in section 3.2.2 was 100 ng 1^{-1} . This was dependent on a variety of parameters, such as reagent purity, transmission characteristics of the interference filter, intensity of the source, optical design and the chemistry of the system. The main factor presently influencing the performance in terms of sensitivity is the low transmission of the interference filter at the three resonance lines (189.04, 193.76 and 197.26 nm). A filter with a higher transmission over these wavelengths will undoubtedly improve the sensitivity because of higher signal throughput.

The upper limit of the linear calibration range was 100 μ g l⁻¹ using the continuous flow approach. Concentrations exceeding this value were susceptible to self-absorption and this process was explained in detail in section 4.2.3. Carry-over between samples with high concentrations was negligible, since the atom cell has a small volume and the analyte was rapidly removed. The linear calibration range therefore spanned over three orders of magnitude, which was not as good as one would expect for an atomic fluorescence technique, but was better than the corresponding atomic absorption method. The upper concentration limit of the calibration range may be increased with the use of flow injection analysis and this procedure was described in section 4.3.1. This approach increased the upper limit of the linear calibration range to 1000 μ g l⁻¹ using a sample volume of 100 µl. A typical calibration curve from 0 to 10 µg 1^{-1} is shown in Figure 5.24. Figure 5.25 shows a typical response for a 2 μ g 1⁻¹ arsenic solution.

Figure 5.24 - Typical calibration curve for arsenic using the filter measurement system



Figure 5.25 - Typical response for 2 μ g l⁻¹ arsenic solution using the filter measurement system



The precision of the technique has been examined and the relative standard deviations at various concentrations are shown in Table 5.5. These were obtained by taking eight consecutive readings during the analysis cycle of the hydride generation system.

Table 5.5 Precision of the filter measurement system for arsenic

Concentration (µg l ⁻¹)	Output (Peak Height)	Relative Standard Deviation % (n=8) ⁽ⁿ⁾
2	36.5	2.6
4	73.0	0.9
10	180.5	0.5

(a) where n = number of measurements

To assess the accuracy of the technique a simulated certified water reference material (IAEA/W-4) was analysed for arsenic. Prior to analysis, arsenic (V) was reduced to arsenic (III) using acidified potassium iodide solution ($1 \ m/V$). The results, along with the certified value are given in Table 5.6. The result obtained using the monochromator system is also given.

Table 5.6 Determination of arsenic in certified water reference material (IAEA/W-4) using both measurement systems

Atomic Fluorescence Measurement System	Certified Value (µg l ⁻)	Value Obtained (µg l ⁻¹)
Interference Filter	25.0 <u>+</u> 1.25	25.3 <u>+</u> 2.00
Monochromator	25.0 <u>+</u> 1.25	24.5 <u>+</u> 0.70

The data shown in Tables 5.5 and 5.6 illustrate that the technique is both accurate and precise.

5.5.1. Determination of Selenium using Hydride Generation Atomic Fluorescence Spectrometry

suitability of The non-dispersive atomic fluorescence spectrometry for simultaneous multi-element analysis has been described (66). In comparison to other multi-element techniques the apparatus required for non-dispersive atomic fluorescence spectrometry is relatively simple, requiring only a single photodetector used in conjunction with a single optical system and a bank of suitably disposed narrow line sources of high Although the system developed above was unsuitable intensity. for simultaneous multi-element determinations, the capability of the detector for the determination of the other hydride forming elements was soon realised. In fact, the only alteration that was required was the replacement of the BDHCL to the element required. The design was such that the lamp housing was easily accessible and lamps are interchangeable. In some cases the chemistry of the hydride generation system might have to be considered and in order to obtain the best sensitivity the interference filter may need to be replaced with one closer to the main fluorescence lines of a particular element. The system was therefore assessed for selenium. The optical configuration was identical to that of arsenic, the difference in the system being the operating conditions of the BDHCL and the chemistry of the hydride generation.

5.5.2. Optimisation of the Boosted Discharge Hollow Cathode Lamp for Selenium

Using the new power supplies the BDHCL was optimised for boost discharge and primary current in order to obtain maximum radiance. This should coincide with the maximum fluorescence, so therefore the atomic fluorescence was utilised as a criteria of merit rather than direct intensity measurements. The effect of boost current on peak height and signal to background ratio for primary currents of 20.0, 22.5 and 25 mA are shown in Figure 5.26 and 5.27 respectively. The maximum net signal and signal to background ratio occurs when the primary and boost currents are both set to 25 mA. These are the maximum recommended current settings for the selenium BDHCL and therefore higher current settings were not investigated.

5.5.3. Chemical Optimisation of Continuous Flow Hydride Generation for Selenium

The effect of sodium tetrahydroborate and hydrochloric acid concentrations was investigated for selenium. Three criteria of merit were examined, including net signal, signal to background and signal to noise ratio.

The effect of hydrochloric acid concentration on net signal at sodium tetrahydroborate concentrations ranging from 1.0 to 2.5 m/V in 0.1 mol 1⁻¹ sodium hydroxide solution is shown in Figure 5.28. The variation in acid concentration has little effect on the net signal and an optimum for all reductant concentrations occurred at 5 mol 1⁻¹. Lower reductant concentrations were

Figure 5.26 - Effect of boost current on net signal for selenium using the filter measurement system



Figure 5.27 - Effect of boost current on signal to background ratio for selenium using the filter measurement system



Boost Current / mA

accompanied by increasing net signal. When the criteria of merit is signal to background ratio, a different optimum is obtained, Figure 5.29. This can be explained in terms of the size of flame (see section 5.4.10), since at low reagent concentrations the flame will be small and the background emission low. At higher reagent concentrations the flame was larger and therefore the signal to noise background was less. The effect of acid concentration on signal to background ratio is minimal above 2 mol 1^{-1} . Figure 5.30 shows the effect of acid concentration on signal to noise ratio. The optimum sodium tetrahydroborate concentration is clearly 1.5% m/V and it would also seem that higher acid concentrations are preferred.

With considerations to the data obtained for all three criteria of merit examined, the optimum concentrations were 1.5% m/V sodium tetrahydroborate and 5 mol 1^{-1} hydrochloric acid concentration. However, the concentration of acid was less critical for sensitivity, but high concentrations are required in order to reduce transition metal interferences (71-74).

5.5.4. Analytical Performance of the Filter System for Selenium

The analytical performance of the detector was influenced by numerous factors and these have been outlined for arsenic in the previous sections. The two main factors which affect the sensitivity of the system for arsenic are the transmission characteristics of the filter and the relatively high background equivalent concentrations. The instrumental set up is, in fact more suitable for selenium, since the main selenium resonance lines occur at wavelengths of 196.09, 203.99 and 206.28 nm which

Figure 5.28 - Effect of hydrochloric acid concentration on net signal for selenium at various reductant concentrations



Figure 5.29 - Effect of hydrochloric acid concentration on signal to background ratio for selenium at various reductant concentrations



Figure 5.30 - Effect of hydrochloric acid concentration on signal to noise ratio for selenium at various reductant concentrations



are more favourable in terms of transmission of the filter. Furthermore, reagents can be obtained with less selenium than arsenic contamination.

The background equivalent concentrations for the various background components are given in Table 5.7 for selenium.

Table 5.7 Background equivalent concentrations of the components which constitute the total background radiation for selenium.

BACKGROUND COMPONENT	BACKGROUND	EQUIVALENT ($\mu g l^{-1}$)	CONCENTRATION
Ambient Light		0.04	
Flame Emission		0.39	
Scatter off Atom Cell		0.53	
Fluorescence from reag	ents	0.22	
Total Background		1.18	

In comparison to arsenic the total background equivalent concentration was considerably lower and this, along with the more favourable transmission characteristics of the filter resulted in a lower limit of detection for selenium (50 ng 1^{-1}). The upper limit of the linear calibration range was 100 µg 1^{-1} and therefore the linear calibration range was approximately three orders of magnitude. A typical calibration curve from 0 to 1 µg 1^{-1} is shown in Figure 5.31. Figure 5.32 shows a typical response for a 0.4 µg 1^{-1} selenium solution.

The precision of the technique for selenium has been examined and

Figure 5.31 - Typical calibration curve for selenium using the filter measurement system

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Figure 5.32 - Typical response for 0.4 μ g l⁻¹ selenium solution using the filter measurement system



the relative standard deviations at various concentrations are shown in Table 5.8. These were obtained by taking eight consecutive readings during the analysis period of the hydride generation cycle.

Table 5.8 Precision of the filter measurement system for selenium

Concentration $(\mu g l^{-1})$	Output (Peak Height)	Relative Standard Deviation % (n=8) ^(a)
0.2	19.44	5.9
0.4	43.84	0.5
1.0	104.10	2.7

(a) where n = number of measurements

To assess the accuracy of the technique a simulated certified water reference material (IAEA/W-4) was analysed for selenium at various dilutions. Prior to analysis, selenium (VI) was reduced to selenium (IV) by warming the sample in 4 mol 1^{-1} hydrochloric acid for approximately 20 minutes. The certified value and the results obtained using various dilutions are shown in Table 5.9.

<u>Table 5.9</u> Determination of selenium in certified reference water material (IAEA/W-4)

Certified Value (µg l ⁻¹)	Volume Dilution	Value Obtained (µg l ⁻¹)
10.0 <u>+</u> 0.5	10	10.0 <u>+</u> 0.4
10.0 <u>+</u> 0.5	20	10.4 <u>+</u> 0.7
10.0 <u>+</u> 0.5	50	10.3 <u>+</u> 0.7

An atomic fluorescence spectrometer has been developed for the hydride forming elements. Initial studies involved the use of а modified atomic absorption/emission spectrometer as а monochromator measurement system for the determination of Excitation was achieved using a boosted discharge arsenic. hollow cathode lamp (BDHCL). Compared to other excitation sources available (e.g. microwave excited electrodeless discharge lamps, EDLs), the BDHCL is of low intensity, however they are commercially available and possess better long and short term stability.

Flame and non-flame atom cells have been investigated. The former being preferred since no fluorescence emission was obtained using the non-flame atom cell, probably because the required temperature for atomisation was not achieved. This suggested that the atomisation mechanism probably involves collisions with free radicals (H., O. and OH.) within the flame. Furthermore, there was evidence that in the absence of these radicals, free atoms may condense to form polyatomic species such as As₂, As₄ and Se₂. The most popular atom cell for hydride generation atomic fluorescence spectrometry is the argon-hydrogen diffusion flame, and this is because it possesses low quenching, absorption and background emission characteristics. However, the use of an argon-hydrogen flame normally requires an external supply of hydrogen from a cylinder, the use of which is undesirable because of safety regulations in analytical The atom cell design for this system therefore laboratories. used chemical generation of the hydrogen continuously from the

reagents (NaBH₄ + HCl) to support a mini hydrogen diffusion flame maintained on a glass tube. This proved to be a highly effective means of atomisation and sensitivity improvements were observed for smaller tube diameters.

Dispersive measurement systems using a monochromator are generally less sensitive than non-dispersive systems because of their low light gathering capabilities and inability to detect fluorescence from more than one wavelength. They also require the use of an atomic absorption spectrometer, which just adds to the complexity and cost of the instrumentation. With these considerations in mind, an atomic fluorescence system was developed which utilised an interference filter instead of monochromator and a solar-blind photomultiplier tube because of its radiant sensitivity in the far ultra-violet wavelength region.

Various optical configurations were examined. The introduction of a collection lens between the atom cell and detector improved sensitivity by a factor of four. Optical configurations involving mirrors were not investigated, since the philosophy was to keep the instrument as simple as possible. Wavelength isolation was achieved using a 200 nm \pm 10 nm half width interference filter. This has two functions, firstly to reduce background from the flame and secondly to allow transmission at the appropriate fluorescence wavelengths. Although reasonably effective in reducing flame background emission, the filter examined had low transmission characteristics at the required fluorescence wavelengths.

The detector may be utilised for other hydride forming elements (e.g. As, Se, Te, Sb and Bi etc.) the only requirement being to replace the BDHCL. Other elements may require a different interference filter depending on their fluorescence spectrum. The chemistry of the hydride generation must also be considered.

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The sensitivity of the detector for arsenic and selenium is excellent with (3σ) limits of detection of 0.10 µg l⁻¹ and 0.05 µg l⁻¹ respectively. The accuracy and precision of the technique has been examined for certified reference water materials and good agreement was obtained with the certified values. The system was totally automated in terms of operation and data collection when the different units were connected to an IBM AT compatible computer through a DIO card. The system was controlled using commercially available software (TouchStone Software, P S Analytical Ltd, Sevenoaks, Kent, UK).

CHAPTER 6

CONCLUSIONS AND FUTURE WORKS

6.1. CONCLUSIONS

The demand for larger numbers of chemical measurements with greater speed, sensitivity and lower cost than previously, has led in recent years to the design of a wide variety of automated analytical equipment. With ever increasing legislative demands this equipment is often designed for determining elements with high toxicity, such as mercury and arsenic. Novel automated approaches are described in this thesis for the cold vapour/ hydride generation technique.

Various gas-liquid phase separation devices were investigated and critically compared for continuous flow hydride generation. These included a conventional glass 'U' tube separator (GGLS), a silicone rubber tubular membrane separator (TMGLS), and a polytetrafluoroethylene membrane separator (MGLS).

In terms of analytical performance (i.e. limit of detection, dynamic range, precision and accuracy), the separators were all similar, however, in certain applications, membrane gas-liquid separation was advantageous. The main disadvantage of the conventional separator was that the gaseous products were accompanied by a fine aerosol contaminated with hydride generation by-products and sample matrix. This is particularly problematic for the determination of arsenic and selenium using hydride generation - ICP-MS. Here the aerosol contaminated with

215

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sodium chloride is delivered to the plasma discharge where formation of argon chloride may occur. This has a mass : charge ratio of 75 u which coincides with monoisotopic arsenic and therefore severely limits its determination. Various methods to overcome this isobaric interference may been employed, such as mathematical correction (109), the use of helium plasmas (42), chromatographic separation of arsenic from chloride (110), higher resolution ICP-MS (111) and the addition of a molecular gas such as nitrogen (93) to the plasma. Although sensitive these methods do not offer the additional sensitivity and matrix isolation which is obtainable using hydride generation. The use of hydride generation however, was previously limited due to the spectral overlap of ⁷⁵As and ⁷⁷Se with ⁴⁰Ar ³⁵Cl species. Nitric acid may be used to generate the gaseous hydride (55), but interference may still occur if samples contain substantial amounts of chloride. Furthermore, moisture carry-over may cause plasma instability. Membrane gas-liquid separation effectively overcomes this problem, since the membrane only allows the passage of gaseous products and therefore inhibits the transport of chloride ions to the plasma. This approach allows the determination of arsenic and selenium in seawater samples which previously would not have been possible because of the lack of sensitivity and associated isobaric interferences.

Mercury was determined using an element specific atomic fluorescence spectrometer. Automated continuous flow and flow injection approaches were adopted for various applications, the continuous flow approach was the most sensitive with a limit of detection (3σ) of 3 ng l⁻¹ and linearity to 0.1 mg l⁻¹. Samples with concentrations above this value were subject to self-

absorption which causes the calibration to deviate towards the concentration axis. More importantly, samples with high mercury levels cause excessive carry-over between samples which inhibits the automation process. The flow injection approach was found to increase the upper concentration limit of the linear range to 10 mg 1^{-1} . Furthermore, the carry-over between samples with high levels was minimised. Although it is appreciated that there is not much call for techniques which reduce sensitivity, in certain applications it may be beneficial. For example, on-line monitoring of samples from the chlor-alkali industry. One further advantage of the flow injection approach is the reduction of matrix interferences. The technique was successfully applied to the analysis of zinc battery anodes and concentrated sulphuric acid.

The problems associated with moisture carry-over during mercury determinations using the cold vapour technique are well documented and include gradual loss in sensitivity and long term instability. Previously methods of moisture removal utilised chemical and physical moisture traps. These are effective but eventually become saturated and may give rise to contamination and losses. A novel hygroscopic Nafion membrane dryer tube was found to be an effective way to remove moisture from wet gaseous streams, allowing precise measurements for periods exceeding three hours. Furthermore, the removal of moisture increased the net signal by approximately 60% due to a reduction in quenching and/or the dissolution of mercury vapour in the moisture.

An element specific atomic fluorescence spectrometer coupled to continuous flow hydride generation was developed. Excitation was

achieved using a boosted discharge hollow cathode lamp (BDHCL). Although not as intense as other sources, such as microwave electrodeless discharge lamps, the BDHCL is commercially available and possesses better long and short term stability. Flame and non-flame atom cells were investigated, the former being preferred, since no fluorescence emission was obtained using the non-flame atom cell. This was attributed to failure to reach the required temperature for atomisation. It would appear that the atomisation mechanism in flame atom cells involves collisions with free radicals (H•, O• and OH•). Furthermore there is evidence that in the absence of these radicals, free atoms may condense to form polyatomic species such as As₂, As₄ and Se₄ (84-88). The atom cell in this system was unique, since the fuel gas, hydrogen was continuously generated by the hydride generation reaction. Other workers (58,67) have utilised a similar procedure, using the batch hydride technique, however, with this system the flame only ignites for several seconds, thereby giving erratic baseline. The advantage of the hydride diffusion flame in this work was that no external supply of hydrogen was required, which has advantages of convenience and safety.

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Dispersive and non-dispersive measurement systems were investigated and their relative advantages and disadvantages discussed. The non-dispersive system in this work was found to suffer from high background from flame emission and therefore an interference filter was introduced between the atom cell and the solar-blind photomultiplier tube. The detector may be utilised for a variety of hydride forming elements, the only requirement being to replace the BDHCL. Other elements may require a

different filter, depending on their fluorescence spectrum. The chemistry of the hydride generation must also be considered. The system developed has several advantages over the corresponding atomic absorption technique. Sensitivity was improved by a factor of five with detection limits (3 σ) of 0.10 µg l⁻¹ and 0.05 μ g 1⁻¹ for arsenic and selenium respectively. The linear calibration range was also increased by a factor of two. Most laboratories today dedicate an atomic absorption spectrometer for hydride generation. This arrangement however, does not allow the laboratory to use its resources to full potential since this instrument can be used for other applications. The element specific detector on the other hand, is more economical and efficient.

6.1.1. Future Works

Challenging future work still exists in membrane gas-liquid separation. As yet only one dimension and type of membrane has been investigated for each separator, parameters which undoubtedly affect the separation process. Future work could therefore involve the investigation of pore size, porosity, thickness and membrane material. The physical properties of other fluoropolymers such as ethylenetetrafluoroethylene (EFTE) and ethylenechlorotrifluoroethylene (ECTFE), suggest that they may be suitable for gas-liquid phase separation.

A disadvantage of the hydride generation technique is that it may suffer chemical interference from some transition metal elements, especially Ni, Co, Cu and Fe. Although the interference mechanism is not fully understood and is different for each

element, it is generally believed that the interference is caused by preferential reduction of the metal ion to a lower oxidation state or to the metal. This results in the formation of a finely dispersed precipitate which captures and decomposes the hydride formed in a secondary reaction, thereby causing a suppression in signal. Future work could examine the effects of interference using different separations. The advantage here being the fast response of the MGLS, which should remove the gaseous hydrides before capture and decomposition can take place, thereby minimising interferences (36).

An automated preconcentration system which utilises a gold impregnated sand trap for the collection of mercury in gases has been reported. Future work in this research area could concentrate on the sample collection procedures. Samples of airborne mercury can be collected on site if desired using a simple air pump linked to a gold sand trap. This can be taken back to the laboratory and analysed or alternatively the instrument can be set up on site. The technique is only as good as the sampling procedure and therefore further investigation in this area is required.

Recent reports (89,164) have described novel chemistries for vapour generation for sample introduction for sample introduction in atomic spectrometry. Sodium tetraethylborate reagent has been utilised for the alkylation of cadmium (89) and lead (164). The work so far has focused on the batch approach, which is difficult to automate. It is therefore envisaged that automated continuous flow procedures coupled to atomic fluorescence spectrometry would be advantageous.

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226

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233

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LECTURES AND ASSOCIATED STUDIES

- (i) Research visit, 18th October 1988, ICI Brixham.
- RSC lecture, 17th January 1989, Plymouth Polytechnic, Dr P Worsfold, "Flow Injection Analysis - Hands Off Analysis".
- (iv) RSC lecture, 21st November 1989, Polytechnic South West, Dr S K Scott, "Clocks, oscillations and chaos in chemistry".
- RSC lecture, 26th January 1990, Polytechnic South West,
 Dr J P Leahey, "Studies in the environmental fate of a new insecticide".
- (vi) RSC lecture, 19th October 1990, Polytechnic South West, Dr R P Wayne, "The Origin and Evolution of the Atmosphere".
- (vii) RSC lecture, 16th November 1990, Polytechnic South West, Dr D H G Grout, "Enzymes in Organic Chemistry".
- (viii) RSC lecture, 17th January 1991, Polytechnic South West, Dr R J Perriman, "Chemical Manufacturing and the Environment".
- (ix) Weekly Departmental Research Seminars 1988-1991, Plymouth Polytechnic/Polytechnic South West.

MEETINGS ATTENDED

- (i) V G Elemental User Group Meeting, 6th December 1989, Alveston Manor Hotel, Stratford-upon-Avon.
- (ii) Atomic Spectroscopy Group and Atomic Spectrometry Updates of the RSC, 30th March 1990 "Lasers in Atomic Spectrometry", Guildford.
- (iii) Analytical Division of the RSC, meeting on "Research and Development Topics in Analytical Chemistry", 16th and 17th July 1990, Runcorn.
- (iv) Atomic Spectroscopy Group of the RSC jointly with the Spectroscopy Group of the Institute of Physics, "Fifth Biennial National Atomic Spectroscopy Symposium", 18th -20th July 1990, Loughborough.
- (v) Second International conference on plasma source mass spectrometry, 24th - 28th September 1990, Durham.
- (vi) Atomic Spectroscopy Group and Atomic Spectrometry Updates of the RSC, 28th March 1991, "Alternative Plasma Sources", Plymouth.
- (vii) Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, 13th - 19th March 1991, McCormick Place-on-the-Lake, Chicago, Illinois, USA.
- (viii) P S Analytical User Group Meeting, 17th April 1991, Sheffield.

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PRESENTATIONS

Oral Presentations

- "Development, optimisation and assessment of gas-liquid phase separators for continuous flow hydride generators coupled to atomic absorption spectrometry".
 W.T. Corns, L. Ebdon, S.J. Hill and P.B. Stockwell.
 Fifth Biennial National Atomic Spectroscopy Symposium, University of Technology, Loughborough, 1990.
- "Development, optimisation and assessment of a novel gasliquid separator for continuous flow hydride inductively coupled plasma mass spectrometry".
 W.T. Corns, L. Ebdon, S.J. Hill, P.B. Stockwell, R.C. Hutton and A. Baker.
 Second International conference on plasma source mass spectrometry, University of Durham, 1990.
- (iii) "Vapour generation techniques to measure arsenic by atomic fluorescence".
 W.T. Corns, L. Ebdon, S.J. Hill and P.B. Stockwell. Pittsburgh conference and exposition on analytical chemistry and applied spectroscopy, McCormick Place-on-the-Lake, Chicago, Illinois, USA, 1991.
- (iv) "Effects of moisture on the determination of mercury".
 W.T. Corns.
 P S Analytical Ltd User Group Meeting, Yorkshire Water Laboratories, Sheffield, 1991.

Poster Presentations

- "Computer controlled adsorber/desorber system to monitor mercury in gaseous samples".
 W.T. Corns, L. Ebdon, S.J. Hill and P.B. Stockwell.
 Research and development topics in analytical chemistry, ICI Runcorn, 1990.
- (ii) "Flow injection hydride generation to measure arsenic and selenium by atomic fluorescence spectrometry".
 W.T. Corns, L. Ebdon, S.J. Hill, P.B. Stockwell and K.C. Thompson.
 Research and development topics in analytical chemistry, University of Aberdeen, 1990.

PUBLICATIONS

- "Application of a computer controlled adsorber/desorber system to monitor mercury in air or gas samples : Part 1, Calibration and system description".
 L. Ebdon, W.T. Corns, P.B. Stockwell and P.M. Stockwell. Journal of Automatic Chemistry, 1989, <u>11</u>, 247-253.
- (ii) "The determination of arsenic by hydride generation inductively coupled plasma mass spectrometry using a novel tubular membrane gas-liquid separator".
 S. Branch, W.T. Corns, L. Ebdon, S. Hill and P. O'Neill. Journal of Analytical Atomic Spectrometry, 1991, <u>6</u>, 115-119.
- (iii) "The effects of moisture on mercury determination and its removal using membrane dryer tubes".
 W.T. Corns, L. Ebdon, S. Hill and P.B. Stockwell.
 Analyst, In press.
- (iv) "Automated cold vapour flow injection analysis of mercury at high concentrations".
 W.T. Corns, L. Ebdon, S. Hill and P.B. Stockwell.
 Journal of Automatic Chemistry, In press.