A HYDRIDE GENERATION-ATOMIC ABSORPTION SPECTROMETRIC PROCEDURE FOR THE QUANTIFICATION OF GERMANIUM AND OTHER ELEMENTS IN IRON METEORITES

A thesis presented in partial fulfilment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry and Biochemistry
Massey University
NEW ZEALAND

XUN GUO
1989

ABSTRACT

Covalent hydride-forming elements were investigated to explore their potential use in chemical classification of iron meteorites. Only As, Ge and Pb were detectable in these samples.

A simple and inexpensive combined hydride generation atomic absorption spectrometric method (HGAAS) was developed and was the first to be applied to quantification of these elements in iron meteorites. Variable studies were: flame type, generation reaction conditions, interferences, and atomization. A convenient nitrogen-hydrogen-air entrained flame was used to determine germanium in meteorites.

The determination of germanium in 22 iron meteorites using the above method gave data in good agreement with those obtained by J.T Wasson et al who used radiochemical neutron activation analysis (RNAA). From practical applications of my method, it was clear that the technique afforded a reliable, inexpensive, and sensitive method for me quantification of germanium in iron meteorites.

Various methods of sample attack were tried and included acid attack in an open container, under a reflux, or with a Teflon bomb, and fusion with sodium peroxide. The optimum method was acid attack under reflux or with a Teflon bomb. Nitric acid was more suitable than other acids.

The method has applied to various samples which resulted in: identification of a bogus meteorite(HANAU), classification of a newly discovered meteorite(TASSAJARA), and confirmation that the Antarctic "ONNUM VALLEY" iron was in fact part of the previously known DERRICK PEAKS shower.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor, Professor R. R. Brooks, for his advice, instruction, and encouragement throughout the period of this work.

Thanks are also due to the Department of Chemistry and Biochemistry, the University Library and the Computer Unit for their advice and assistance.

My grateful thanks go to Dr. T. N. M. Waters, Vice-Chancellor of Massey University, for his encouragement and support throughout my studies here.

I acknowledge the receipt of a fellowship from Massey University, which enable me to study here.

I am grateful to the Department of Pharmacology, Guiyang College of Traditional Chinese Medicine, Guizhou, P. R. China for granting me leave from their employ in order to further my education.

Finally, I gratefully acknowledge my wife, Xiaohong Fan, for her encouragement, support and assistance, and also my parents and my son, who are in P. R. China, for their great support during my studies at Massey University, New Zealand.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER ONE

GENERAL INTRODUCTION

CHAPTER ONE

GENERAL INTRODUCTION

I.1 Hydride Generation

Covalent hydride generation as an analytical technique has been used ever since the last century [1], but was limited only to arsenic at that time. With the development of advanced instrumental technology, hydride generation has been used for the determination of the trace elements that form volatile hydrides, particularly antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin [2]. This technique is now being rapidly developed and widely used in many scientifical research fields.

A very common procedure is to link hydride generation with an instrument such as an atomic absorption spectrometer for quantification of these hydrides. Hydride generation can also be combined with other kinds of instrumentation, e.g., inductively coupled plasma emission spectrometry (ICPES), atomic fluorescence spectrometry (AFS), mass spectrometry (MS), etc.. .

Generation of hydrides is usually carried out in three steps:

(i) The sample solution is placed in a reaction vessel in a suitable acidic medium.

(ii) The reducing agent is added for generating hydrides that are collected in a U-tube submerged in a liquid air or a liquid nitrogen trap.

(iii) The U-tube is transferred to a water bath from the liquid air trap for releasing hydrides, which are aspirated into the flame by a carrier gas (nitrogen or argon). Sometimes, hydrides can be passed directly into a flame without use of the trap [3].

I.1.1 A Review of Hydride Generation

Arsenic is extremely toxic and is also an indicator of precious metals, even at low concentrations because of its association with gold in ores. The use of flame atomic absorption spectrometry for the determination of arsenic results in poor sensitivity so that it is difficult to determine low concentrations of this element. Ever since the hydride generation technique was first applied to the determination of arsenic, a great improvement in detection limits has been obtained so that it is a very convenient technique for quantification of this element.

With the development of an argon-hydrogen-air entrained flame (usually called the argon-hydrogen flame) in atomic absorption spectrometry, a much improved signal to noise ratio was obtained in the 1960's. This flame system has a remarkable advantage in sensitivity compared with the air-acetylene flame system, using the 197.3 nm arsenic resonance line.

Despite the above problems, several interferences arise from other organic substances, incomplete salt dissociation, and molecular absorption, particularly at lower concentration of samples. In order to overcome this problem, modifications of the Gutzeit method, utilising the generation of arsine, have been applied to atomic absorption spectrometry as follows: covalent hydrides, such as arsine were collected in a liquid nitrogen trap, which was then warmed, and the evolved arsine was swept into the flame with a stream of a carrier gas (such as argon). By removing the arsenic from the sample matrix, interferences in the flame are minimised [4].

Other improvements, include the work of Madsen [5] who collected the arsine in dilute silver nitrate solution and aspirated the resulting solution directly into an argon-hydrogen flame of the type described by Kahn and Schallis [6]. A spectrophotometric method, which involves the reaction of arsine with silver diethyldithiocarbamate to form a complex, has also been proposed for the determination of arsenic. Hundley and Underwood [7] applied this method to determine arsenic in a wide variety of food products, but spectrophotometric methods have the disadvantage of requiring large amounts of sample in order to obtain sufficient sensitivity.

At the beginning of the 1970's, Dalton and Malanoski [3] were the first to report the direct aspiration of arsenic into a flame without the collecting trap. A limit of detection of 0.1 μg of arsenic was obtained by this technique.

For increasing sensitivity, improvements to the generation apparatus were made. Fernandez and Manning [8] collected the arsine in a balloon reservoir before introducing it into a flame. This procedure can also be used for the determination of selenium as the hydride selene (SeH_2). The detection limit is down to 0.02 μg of arsenic with the balloon method. The first commercially available attachment for atomic absorption spectrometry was designed by Manning [9]. With this apparatus, a total reaction time 4 - 5 minutes is usual when using a tin (II) chloride-hydrochloric acid-potassium iodide-zinc reagent.

Manning also suggested that the technique might be applied to the generation of the gaseous hydrides of antimony and bismuth.

Pollock and West [10] successfully generated stibine (SbH_3) using titanium (III) chloride-hydrochloric acid-magnesium.

Several new methods were developed to detect arsenic with greater sensitivity. A new type of atomization apparatus involved an electrically-heated tube first reported by Chu et al [11] in 1972. In this procedure arsine was generated and swept into a heated tube with a flow of argon. A limit of detection of about 5 ng was obtained for arsenic, but needed a long reaction time. In 1974, Thompson and Thomerson [12] reported a flame-heated silica tube detection device for the determination of arsenic and lead. The method obtained a good sensitivity.

For the sake of completeness, several non-atomic absorption detectors are worth mentioning. Belcher et al [13] have described molecular emission cavity analysis (MECA), and subsequently how to eliminate interferences [14], for the determination of arsenic and antimony. Tsujii and Kuga [15] reported a non-dispersive system in atomic fluorescence spectrometry (AFS), employing a solar-blind photomultiplier, for the determination of arsenic. They also described a modification of the apparatus used for the determination of arsenic and antimony [16]. Thompson and Thomerson [12] employed a modification of the reaction cell and used sodium tetrahydroborate(III) to liberate hydrides. Kobayashi et al [17] used this technique to determine bismuth and obtained a detection of limit of 5 pg/ml or 0.1 ng. Additional work was carried out on this method by other workers such as Nakahara et al [18] who reported a method for determining antimony and lead in waste waters, Thompson [19] used this method to determine antimony, arsenic, selenium and tellurium with a little improvement. With the development of inductively coupled plasma emission spectrometry (ICPES), this was coupled with hydride generation as reported by Thompson et al [20,21]. In these studies, many of the operating parameters were very critical and many interference effects were encounted.

In the 1980's, flow injection analysis was widely applied to a variety of analytical techniques, including hydride generation. This development in automated hydride generation has resulted in the achievement of better systems with regard to precision, sample throughput, and simplicity of operation. Åström [22] used this technique to determine bismuth in a highly-automated operation that also reduced the interferences from other elements. This technique has now been incorporated into new commercial instruments which allow for automation.

I.1.2 Development of Reduction Methods for Hydride Generation

In the nineteenth century when the remarkable hydride reaction (the Marsh reaction) was developed [1], use was made of zinc metal and dilute hydrochloric or sulphuric acid to reduce the arsenic. The reaction was as follows:

$$Zn + 2H_3O^+ \dashrightarrow Zn^{2+} + 2H^\bullet + 2H_2O$$

$$AsO_3^{3-} + 6H_3O^+ + 3H^\bullet \dashrightarrow AsH_3 + 9H_2O$$

However, the method could be used for a single determination only, and the time taken for the completion of the reaction was as long as 10 minutes. It is therefore necessary to store the evolved gas in some form of reservoir.

The key to the problem was to choose an appropriate acidic reaction medium. A mixture of dilute hydrochloric acid, 40% (w/v) potassium iodide solution, 40% (w/v) tin (II) chloride solution and granular zinc metal has been reported as a means of generating arsine by Dalton [3] and Fernandez [8]. This appears to give a faster reaction time, but a collection vessel, or a carrier gas, was found to be necessary. The system could also be used for the determination of selenium. Pollock et al [10] found that the system was not suitable for more elements, and used a more satisfactory reduction system, a magnesium-hydrochloric acid-titanium(III) chloride medium, to determine successfully not only arsenic and selenium, but also antimony, bismuth and tellurium.

The discovery of a new reducing agent, sodium tetrahydroborate (III), was a landmark in the development of the hydride generation method. Schmit and Royer [23] were the first to successfully use it for the generation of the hydrides of arsenic, antimony, bismuth, germanium, selenium, tellurium and tin, and subsequently lead [24]. The reaction time was dramatically shortened down to 30 seconds for bismuth and tellurium, and 2 - 3 minutes for arsenic, antimony, germanium, selenium and tin.

Sodium tetrahydroborate(III) (sometimes called sodium borohydride) generates hydrides. For example, the reaction with arsenic yields arsine. The reaction is as follows:

$$BH_4^- + 3H_2O + H_3O^+ \text{-----}\rightarrow H_3BO_3 + 8H^\bullet + H_2O$$

$$AsO_3^{3-} + 6H_3O^+ + 3H^\bullet \dashrightarrow AsH_3 + 9H_2O$$

This reducing agent offers several advantages over both the zinc-tin (II) chloride and magnesium-titanium (III) chloride procedures. In the earlier work, sodium tetrahydroborate (III) was used only in powder form, but the use of 0.25 g pellets later became established. Later the reagent was used as a solution.

A mixture of different reducing agents was used by Goulden and Brooksbank [25]. They used a solid metal powder as one of reducing agents with others {tin (II) chloride, potassium iodide and aluminium powder}. A heated packed stripping column was used to strip the selenium hydride generated from the reduced specimen, so that atoms, and not molecules, would enter the optical path.

A further method, but one which has not gained wide usage, is the zinc column to which an acidic solution of the analyte is added [26,27]. The method is applicable only to the generation of arsine and stibine.

In recent years, no better reductant than sodium tetrahydroborate(III) has been found and it continues to play an important role in hydride generation. However, it still has some shortcomings. For example, background absorption, especially when lead and tin are determined.

I.1.3 Applications

The analytical technique of hydride generation coupled with atomic absorption spectrometry has been used in environmental studies to determine toxic elements such as arsenic and selenium. Waters and effluents have often been analysed because the samples are already in a liquid form and matrix interferences are not usually severe. Such samples, including heavily-poliuted water, drinking watere, raw sewage, etc., have been analysed for arsenic and selenium [12,23], antimony and lead [18].

Toxic metals in foodstuffs have also been determined by hydride generation procedures. Many liquid food samples can be analysed directly, as for example, wine, water-soluble sugar, coffee and some organic food colourings. For solid food samples, special digestion procedures are needed for the separation of organic meterials that interfere with the detection [19,23,28-30].

Some hydride-forming elements in steel or alloy can indicate the quality of the products. The use of a hydride generation method to determine those elements in iron and steel products has been achieved and developed for quality control [31-33].

Hydride generation methods can be used for the determination of normal or abnormal concentrations of elemental constituents of body tissues, and are very important in clinic diagnoses and studies. Most samples come from hair, blood, milk, tissue, fat and urine [34-37], which are digested by a mixture of nitric and perchloric acids for the decomposition of organic meterials to avoid interferences. The resultant solution can be analysed for arsenic, bismuth, selenium and other elements.

Trace elements in geological and mineralogical samples can aid in identification of types of rocks or minerals. These samples are complex chemically, and dissolution methods are often tedious and time-consuming. Arsenic can be used to indicate the presence of some precious metals in rocks and minerals. Several methods for the determination of arsenic have been proposed. Some methods suffer from several interferences. Hydride generation methods are favoured by most workers. Other hydride-forming elements such as antimony, bismuth, germanium, lead, tellurium and tin have been determined in rocks and minerals [38-41].

There are other applications in some fields such as analysis of agricultural products for arsenic and selenium because of the widespread occurrence of these elements in minerals and pesticides. Other materials include petroleum products, tobacc, etc..

I.2 Iron Meteorites and Their Classifications

Because of their physical composition, iron meteorites usually survive the intense heat and friction when entering the Earth's atmosphere much better than stony meteorites. Iron meteorites are also easier to find because they can more readily be distinguished from ordinary rocks and can be located using a metal detector. As a result, although they only account for 7% of all meteorite falls, they are over-represented in most museum collections, and people are more familiar with them than they are with the other types of meteorite.

Iron meteorites are identified mainly in two ways. first, they usually display a smooth, black or oxidized surface often marked by pits called " thumbprints ". These thumbprints are caused when some of the meteorite ablates during atmospheric entry.

The second way to positively identify an iron meteorite is to slice, polish and etch it with a weak solution of nitric acid. This procedure will reveal a unique criss-cross pattern called the Widmanstätten Pattern, named after its discoverer. This pattern is unique to meteorites and is not found in any terrestial rocks. It is caused by the slow cooling of metals with different nickel contents and is actually the result of the growth of crystals composed of two different iron-nickel alloys, taenite and kamacite.

Iron meteorites were originally classified by their Widmanstätten structure. The first class of iron meteorites are the octahedrites. They contain about 6-13% nickel and are the most common iron meteorites. Octahedrites are further classified into 3 main groups: coarse, medium and fine, which describe the width of the bands in the crystalline pattern. The coarser the pattern, the greater the amount of iron. The finer the pattern, the higher the nickel content.

The second class, hexahedrites, is made up of less than 6% nickel and contains kamacite but not taenite. When polished, a hexahedrite displays no surface features, but reveals "Neumann Lines" that are caused by impact shocks.

The third class, ataxites, are the finest of the iron meteorites. They have a very high nickel content and contain taenite. Their Widmanstätten pattern can only be seen under a microscope.

Sometimes iron meteorites contain silicate inclusions which give the meteorite a very different and beautiful appearance. Silicated irons are much rarer than even the stony-iron pallasites.

Numerous schemes for classification of iron meteorites have proposed since Partsch [42] and Shepard [43] presented the first serious attempts, at that time on the basis of only about 65 stones and 25 irons. Then Rose [44] improved this system, which has continued to be revised and improved by Tschermak [45], Brezina [46], Piror [47], Yavnel [48] and Mason [49]. There are, other basically different classifications which have gained wide support in some countries in Europe and Latin-America.

Many modern classifications, e.g., by Lovering et al [49], have tended to reduce the number of classes of iron meteorite. More advanced schemes of classification have proposed by Buchwald and Munck [51], Yanel [52], Wasson [53] and Goldstein [54]. Some classifications are based on structure and others on chemistry. The two approaches support and agree with each other very well, particularly if, in addition to the macrostructure, the microstructure is also considered.

I.2.1 Iron Meteorites

Meteorites are assigned to three major categories on the basis of their contents of metallic nickel-iron and silicates:

(i) Irons (siderites), consist principally of metal;

(ii) Stones (chondrites), consist of silicates with less pure metal than irons;

(iii) Stony iron (pallasites), contain abundant metal and silicates.

Iron meteorites are subdivided into hexahedrites, octahedrites, ataxites, and anomalous categories.

Most iron meteorites show a characteristic texture and are composed principally of a nickel/iron alloy. Although they comprise only 7% of all meteorites, irons are so easily distingushed from terrestrial rocks that they make up more than 40% of finds.

The mineralogy of iron meteorites is much simpler than of other meteorites. Elements other than those that form kamacite and taenite are minor in most iron meteorites, but sulfur and phosphorus are abundantly present in most irons. The former occurs locally in large nodules. The latter takes various forms according to the history of the meteorite.

Other minor minerals are distributed less regularly. The most common of these are listed in Table 1.1.

Table 1.1 Minerals commonly formed in iron meteorites

MINERAL	COMPOSITION
Kamacite	α- Fe, Ni
Taenite	γ- Fe, Ni
Troilite	FeS
Daubreelite(d)	$FeCr_2S_4$
Sphalerite(s)	ZnS
Schreibersite	$(Fe, Ni)_{23}C_4$
Cohenite(c)	Fe_3C
Haxonite(h)	$(Fe, Ni)_{23}C_6$
Chromite(ch)	$FeCr_2O_4$
Graphite(g)	C
Carlsbergite(n)	CrN
Phosphates(p)	-

I.2.2 The Method of Classification of Iron Meteorites

Lovering et al [50] proposed one of many modern classifications, which have tended to reduce the number of classes of iron meteorite. This trend is an oversimplification, only justified as long as insufficient information concerning the individual meteorites is available. The iron meteorites may be subdivided according to their primary structure as shown in Table 1.2.

Table 1.2 Structural classification of iron meteorites

STRUCTURAL CLASS	SYMBOL	BANDWIDTH OF KAMACITE CRYSTALS (mm)
Hexahedrite	H	
Octahedrite		
Coarsest	Ogg	3.3
Coarse	Og	1.3 - 3.3
Medium	Om	0.5 - 1.3
Fine	Of	0.2 - 0.5
Finest	Off	<0.2 continuous
Plessitic	Opl	<0.2 spindles
Ataxites	D	
Anomalous*	Anom	various

* After Buchwald (57), meteorites that fit one of these types and designated anomalous.

Since the 1960's, numerous analytical data of trace elements in iron meteorites have been obtained by many workers [51 - 54]. Two entirely different approaches for the classification of iron meteorites have been proposed. One has been mentioned above and is based on the examination of the macrostructure of an etched section under a hand lens. The other is based on accurate chemical analysis of the major element, nickel, plus trace elements such as gallium, germanium and iridium. Both approaches support and have very good agreement with each other.

The agreement of structural and chemical classes is shown in Table 1.3.

Table 1.3 Comparison between the structural and chemical classification of iron meteorites

STRUCTURAL	CHEMICAL	STRUCTURAL	CHEMICAL
H	IIA	Of	IVA, IIIC
Ogg	IIB	Off	IIID
Og	I, IIIE	Opl	IIC
Om	IIIA,IIIB,IID	D	IVB

Chemical classification is largely based on the contents of nickel, gallium, germanium and iridium, which are highly diagnostic of the 12 genetic classes of iron meteorites as shown in Table 1.4.

Wasson et al [55] chose gallium and germanium to plot against nickel on logarithmic scales. The groups are clear resolved. All members of the same group fall, within the limits of sampling and analytical error, on a straight line. Some of the plots are shown in Fig. 1.1 - 1.3, all of those have been discussed in great detail by Scott [56].

Table 1.4 Chemical classification of iron meteorites (99)

group	Ni (w%)	Ga (ppm)	Ge (ppm)	Ir (ppm)	Ge/Ni
IA	6.4-8.5	55-100	190-520	0.6-5.5	neg
IB	8.7-25	11-55	25-190	0.3-2.0	neg
IIA	5.3-5.7	57-62	170-185	2-60	pos?
IIB	5.7-6.4	46-59	107-183	0.01-0.5	neg
IIC	9.3-11.5	37-39	88-114	4-11	pos
IID	9.8-11.3	70-83	82-98	3.5-18	pos
IIE	7.5-9.7	21-28	60-75	1-8	abs
MES	6.1-10.1	8.9-16	37-56	2.2-6.2	abs
PAL	7.9-12.9	14-27	29-71	0.01-2	neg?
IIIA	7.1-9.3	17-23	32-47	0.17-19	pos
IIIB	8.4-10.5	16-21	27-46	0.01-0.17	neg
IIIC	10-13	11-27	8-70	0.07-0.55	abs
IIID	16-23	1.5-5.2	1.4-4.0	0.02-0.07	neg
IIIE	8.2-9.0	17-19	34-37	0.05-6	abs
IIIF	6.8-7.8	6.3-7.2	0.7-1.1	1.3-7.9	abs
IVA	7.4-9.4	1.6-2.4	0.09-0.14	0.4-4	pos
IVB	16-26	0.17-0.27	0.03-0.07	13-38	pos

I.3 Aim of Present Work

Both the structural and the chemical classification of iron meteorites have deficiencies for specimens that lie near boundaries

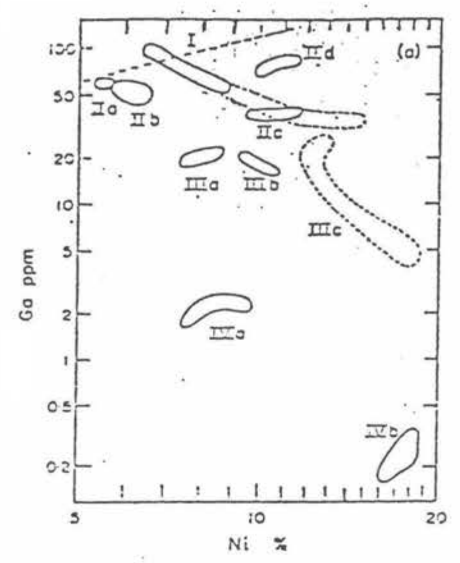


Fig. 1.1

Plot of Ga vs. Ni for Iron Meteorites

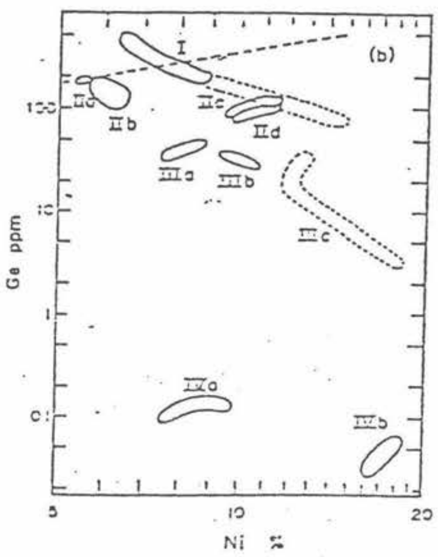


Fig. 1.2

Plot of Ge vs. Ni for Iron Meteorites

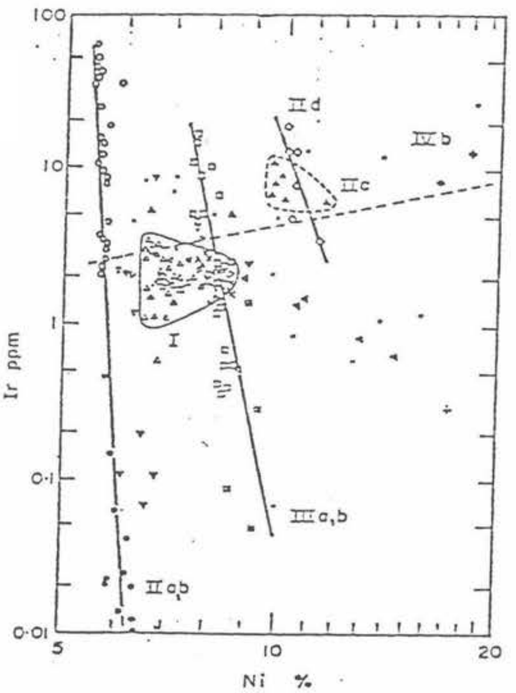


Fig. 1.3

Plot of Ir vs. Ni for Iron Meteorites

between two or more classes. Usually identification of an iron meteorite needs the determination of many elements in addition to the structural observation. No individual elemental parameter can clearly indicate each class in the chemical classification of iron meteorites. For example, Wasson and his co-workers were able to assign most of about 500 iron meteorites to 12 well-defined classes on the basis of their contents of nickel, gallium, germanium and iridium, but 73 meteorites that they analysed were anomalous using this system. It is likely that still other chemical groups, possibly more than 50 [58], exist. Therefore, finding a simpler and more accurate classification method by perfecting chemical classification is a useful project.

Some useful work has been done by workers such as Scott [56] who showed that other trace elements vary systematically among the classes, as do cooling rates and shock intensities [89]. These correlations support the chemical classification and indicate that its divisions have genetic significance. Other workers are attempting to search and establish a new chemical classification in order to supplement the 12-15 genetic classes that have been established.

Clearer definition of the smaller classes of iron meteorites and the identification of new classes will require more thorough sampling and more extensive trace-element studies, particularly in obtaining correct analytical data from iron meteorites. In our programme which seeks a new chemical classification, it was necessary to investigate other trace elements and their distributions.

This thesis has two main aims: Firstly, to investigate new elements for classification of iron meteorites, and secondly, to develop and improve analytical techniques for obtaining accurate abundance data, which do not involve expensive radiochemical neutron activation analysis (RNAA) or other methods that have hitherto been used for analysis of iron meteorites.

CHAPTER TWO

STUDIES ON HYDRIDES OF VARIOUS ELEMENTS

CHAPTER TWO

STUDIES ON HYDRIDES OF VARIOUS ELEMENTS

II.1 Introduction

The elements that form covalent hydrides are in the C, N and O groups in the periodic table, where the number of valence electrons is equal to, or greater than, the number of orbitals. These elements are arsenic, aluminium, antimony, boron, bismuth, germanium, phosphorous, lead, selenium, silicon, tellurium, tin and titanium. Of these elements, only 8 can be determined by hydride generation procedures. These are: arsenic, bismuth, germanium, lead, antimony, selenium, tin and tellurium. The positions of these thirteen elements in the Periodic Table are shown in Table 2.1.

The principle of hydride generation is to use a reduction reaction to form hydrides in the appropriate acidic medium. The modern technique is to combine hydride generation with an instrument that provide a low limit of detection, such as atomic absorption spectrometry.

Numerous studies have been carried out on hydride generation methods, but the results show that it is far from perfect. There are several shortcomings that need improving.

Table 2.1 The positions of hydride-forming elements in the Periodic Table

1a	2a	3b	4b	5b	6b	7b	8			1b	2b	3b	4a	5a	6a	7a	0
H																	He
Li	Be											B ◥	C	N	O	F	Ne
Na	Mg											Al ◥	Si ◥	P ◥	S	Cl	Ar
K	Ca	Sc	Ti ◥	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	$\overline{\text{Ge}}$ ◥	$\overline{\text{As}}$ ◥	$\overline{\text{Se}}$ ◥	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	$\overline{\text{Sn}}$ ◥	$\overline{\text{Sb}}$ ◥	$\overline{\text{Te}}$ ◥	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	$\overline{\text{Pb}}$ ◥	$\overline{\text{Bi}}$ ◥	Po	At	Rn
Fr	Ra	Ac	Rf	Ha													

Ge ◥ means can form hydrides. '-' means can be analysed.

II.2 Instrumentation

II.2.1 Apparatus

An all-glass apparatus was employed for the generation of hydrides. The basic design is shown in Fig. 2.1 and is based on the work of Liddle et al [59]. The reaction is carried out in a 250 ml pear-shaped Quickfit separating funnel with a number of additional inlets including one fitted with a glass stopper for the introduction of the sample and the reaction acidic medium, and another fitted with a rubber septum with a repeating syringe for the injection of sodium tetrahydroborate(III) solution into the reaction vessel. A main inlet was used to fit a Quickfit bubbling tube (MF 28/2) for introduction of carrier gas.

Connecting tubes (PVC internal diameter 6.5 mm) were used between the atomic absorption spectrometer and the reaction vessel in which there was a three-way tap. This tap enabled the passage of the carrier gas to be controlled in order to pass through the reaction vessel or to bypass it. All tubes were kept as short as possible to reduce hydride absorption on the surface of the tubes.

II.2.2 Collecting Unit

Usually, a device is needed to collect hydrides in a liquid air or liquid nitrogen trap to ensure reproducible results and high signals. Many types of collecting device have been designed. A U-tube constructed of pyrex glass (internal diameter 6.5 mm) was used throughout this work. Hydrides were collected in the U-tube which was immersed in the liquid air trap (-190 °C). The tube was then placed in a water bath to provide a uniform temperature for release of the hydrides.

II.2.3 Instrument

All measurements were obtained by using a Varian Techtron AA-5 Atomic Absorption Spectrophotometer, and a Type SS 250 Sekonic Recorder used in the 10-mV range for record signal peaks. Instrumental parameters for each element are reported in Table 2.2.

The signal peak is usually symmetrical, so all calculations of the results were made according to peak heights. It is important to warm up the instrument for at least 30 minutes before operation. The

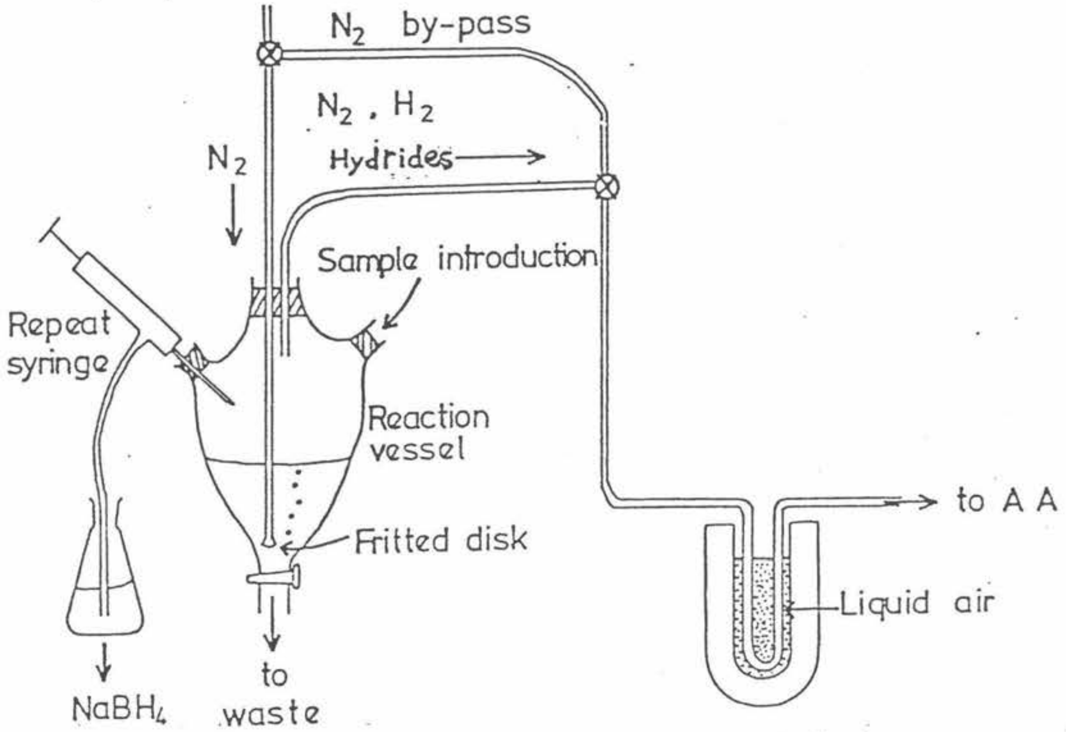


Fig. 2.1 Apparatus for Hydride Generation

tellurium hollow-cathode lamp needed to be warmed at least 2 hours in order to obtain a stable peak value.

A pH meter (Orion Research Ionanalyser) was used for the measurement of pH values in the solutions.

II.2.4 Standards and Reagents

Specpure reagents were used to make standard stock solutions containing 1000 µg/ml of the following:

arsenic (III)
arsenic (VI)
bismuth (III)
germanium (IV)
lead (III)
antimony (III)
selenium (IV)
selenium (VI)
tin (II)
tellurium (IV)
tellurium (VI)

Sodium tetrahydroborate(III) solution (3% w/v) was prepared daily and made alkaline with potassium hydroxide (1% w/v).

Trisodium citrate solution (1M) was made by dissolving the salt in distilled water.

All acids were analytical grade unless otherwise specified. Nitric acid was redistilled for eliminating impurities. The following other

Table 2.2 Instrumental parameters

element	light source	slit width (um)	wavelength (nm)	current (mA)
As	H.C.L.	120	197.3	6
Bi	H.C.L.	100	223.0	5
Ge	H.C.L.	100	265.2	6
Pb	H.C.L.	100	217.0	5
Sb	H.C.L.	100	217.6	6
Se	H.C.L.	100	196.0	8
Sn	H.C.L.	200	286.3 (224.6)*	6
Te	H.C.L.	100	214.3	5

H.C.L.: Hollow Cathode Lamp. *: It was used sometimes.

reagents were used in the course of the research:

ammonium persulphate: 1 M solution
ammonium pyrollidine dithiocarbamate (APDC)
ascorbic acid: 1 M solution
cerium(IV) sulphate: 1 M solution
hydrogen peroxide: 10% (v/v) solution
malic acid: 1 M solution
methylisobutyl ketone (MIBK): technical grade
1,10-phenanthroline: 5% (w/v) alcohol solution
2 Na-EDTA: 1 M solution
potassium dichromate: 1 M solution
potassium hydroxide: 1 M solution
potassium iodide: 1 M solution
potassium permanganate: 1 M solution
tartaric acid: 1 M solution
trisodium citrate: 1 M solution

II.3 Atomisation Conditions

II.3.1 The Type of Flame

An air-acetylene flame, a very common and useful flame in AAS, was also used for hydride generation in the early stage of the development of the technique. The poor sensitivity forced a search for a better flame. This was achieved by use of the argon-hydrogen-air entrained flame (usually called the argon-hydrogen flame) which was used for the majority of the work. Owing to the expense of argon, it was necessary to use a type of flame that was simple, economical and which provided sensitive analyses.

Three types of flame were used in the course of the experiments. The air-acetylene flame gave very poor sensitivity . The nitrous oxide-acetylene flame as recommeded by Halicz [60] and Pollock and West [10] gave adequate sensitivity but was very unstable and had a tendency to explode. However, the nitrogen-hydrogen flame gave not only the best sensitivity but also stability. This flame was used for all future work. The relative sensitivities of the three types of flame for germanium are shown in Fig. 2.2.

II.3.2 The Effects of Different Burner Heights

For atomic absorption spectrometry, the height of the burner is an important parameter to obtain a high degree of atomisation. In hydride generation procedures, this height has a great influence on sensitivity.

The effect of flame heights above the burner for eight elements was tested. Each element needed a short distance between the surface of the burner and the optical path axis, for some, the shorter the better. From curves of absorbance against burner height, the range of high sensitivities were very narrow (between 2 and 3 mm). Height adjustment when changing elements had to be done, otherwise poor sensitivity was obtained. The relations between burner height and absorbance are shown in Fig. 2.3.

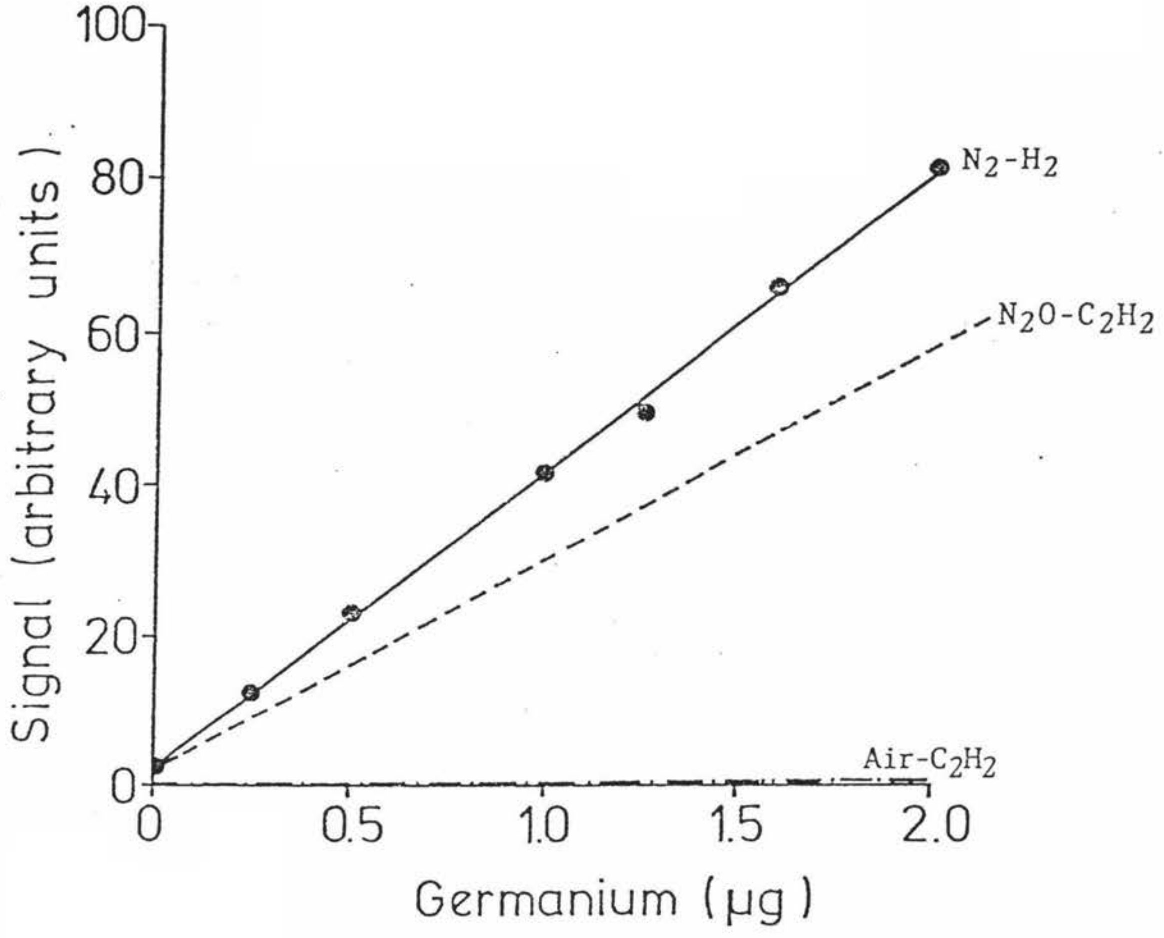


Fig. 2.2 Sensitivities for Various Types of Flame

II.3.3 The Effect of Gaseous Flow Rates in the Flame

From the above experiments, the nitrogen-hydrogen flame gave the most satisfactory results, but both of the gaseous flow rates also can directly effect sensitivity because of the relation to the flame temperature. Varying ratios of fuel and support gas were taken for each element. Hydrogen gave the peak value at a range centring on 2 - 3 L/min. Nitrogen showed strange behaviour for the majority of the elements, in which sensitivity increased with decreasing flow rate. Nitrogen flow rates had a peak value for the determination of germanium at about 4 L/min, but other optimum flow rates tended to be lower and were chosen at 2 L/min. Some curves of gaseous flow rates are shown in Fig. 2.4.

II.3.4 Carrier Gas Flow Rate

Nitrogen (dry N_2) was chosen as a carrier gas throughout this work. Flow rates for the carrier gas and for the flame mixture were critical factors in determining the sensitivity of the method. Results of varying the carrier gas rate are given in Fig. 2.5. From these cases, the optimum flow rate of carrier gas for this instrument was around 1.0 - 2.0 L/min. Beyond this range there was poor sensitivity or nothing. At higher gas flow rates, the stream of carrier gas affected the condensation of hydrides in a liquid air trap, on the other hand, at lower flow rates (as low as 0.25 L/min), the absorption peak was broadened as a result of more extensive diffusion of the hydrides

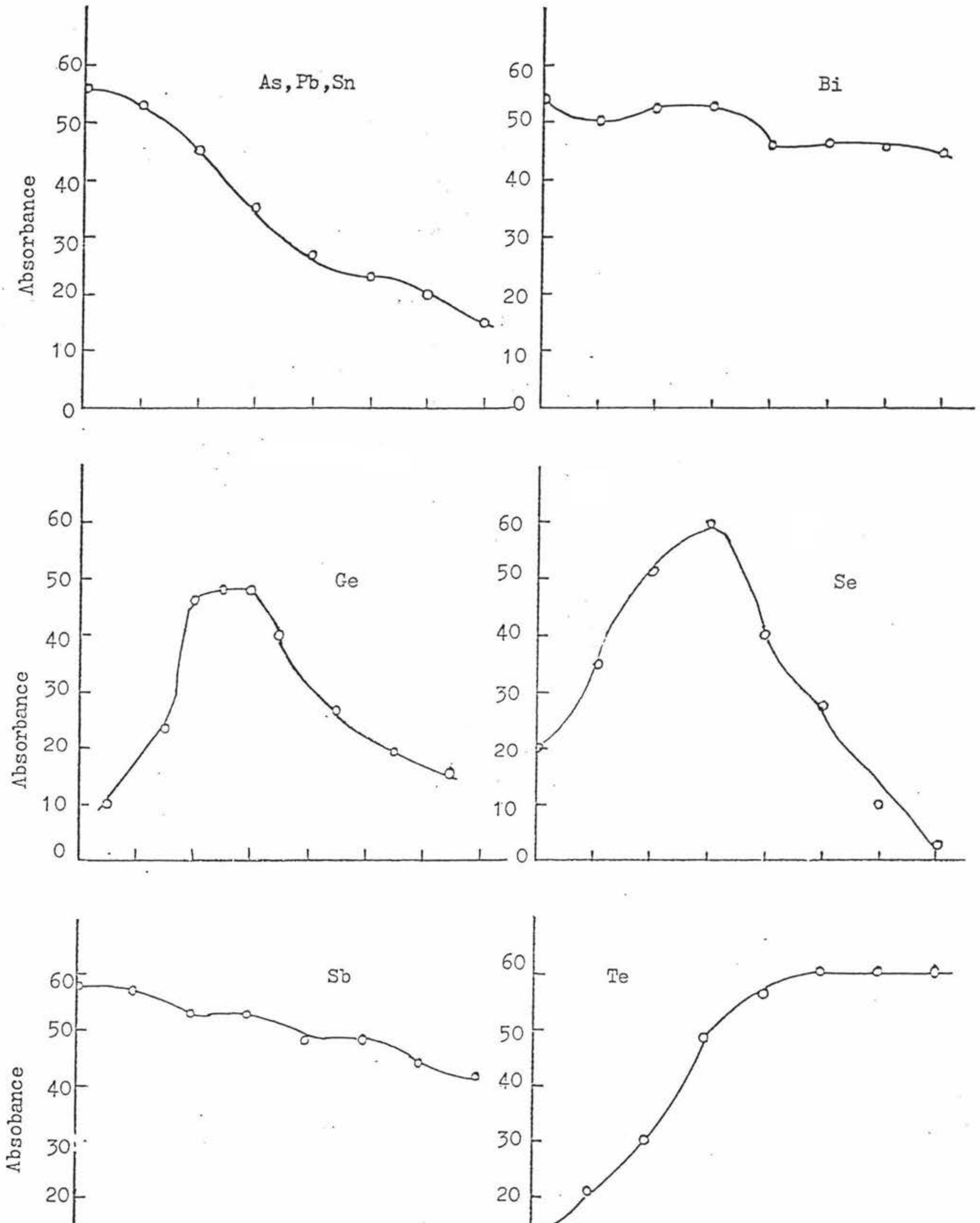


Fig. 2.3 Absorbance as a Function of Burner Height

through the gas stream.

II.4 Experimental

II.4.1 The Effect of Different Acids and Acidities

Acid as a reaction medium is essential to form hydrides with the element. The concentration of acid direct effects the sensitivity in this technique. Typical inorganic acids such as hydrochloric, sulphuric and nitric acid have been used by many workers [12,24,81,82,89,101] and even some organic acids were studied [61,62]. In the early stages, hydrochloric acid was widely used for the generation of hydrides but the results showed no regular relation to acidities and depended on instruments and apparatus. Different acids were used in various papers. Liddle [78] used sulphuric acid for the determination of arsenic, Vijan and Wood [63] used nitric acid for the determination of tin, and Jin et al. [64] performed many studies of the use of nitric acid with some oxidizing agents for the determination of tin [64-66]. It was necessary to study the optimum acids and aciditis for each element that suited my apparatus and instrument.

Standard inorganic acids were tested in my experiments, as well as some organic acids such as acetic, malic and tartaric. The organic acids gave poor sensitivities because these may have formed complexes with the analyte. The resultes of studies on these acids for eight elements are shown in Fig. 2.6.

When compared among eight elements, hydrochloric acid is still a suitable reaction medium in most cases as reported in other papers

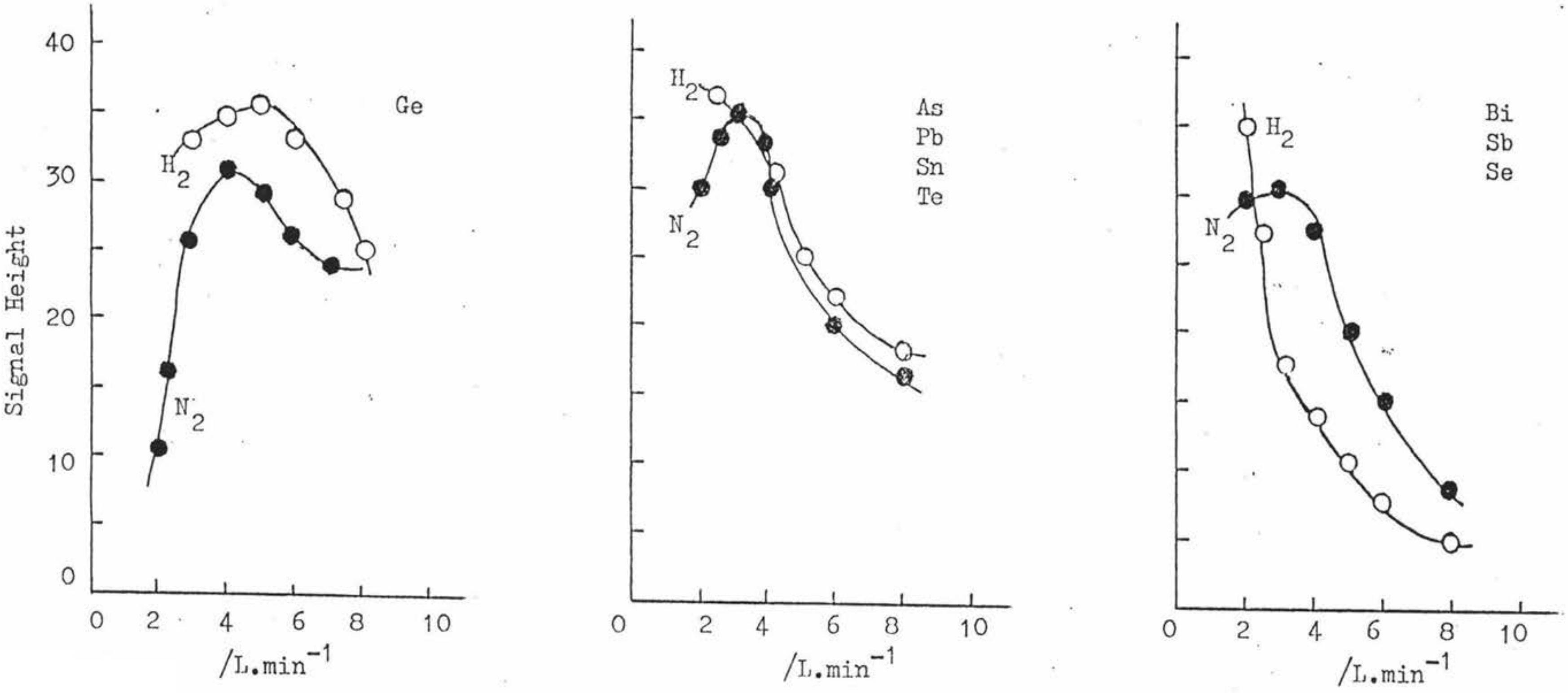


Fig. 2.4 Flame Gases Flow Rate

[12,24,67]. However, some difference appeared at least in my instrument. Sulphuric acid was suitable for antimony, hydrochloric acid was not suitable for selenium, and only nitric acid could be used for lead. These anomalies all appeared among multi-valency elements. For example, arsenic and antimony have trivalent and pentavalent states, and selenium has divalent and tetravalent states. These can form different hydrides of different valencies.

Arsenic, bismuth, germanium, antimony, selenium, lead and tin needed 0.1 - 2 M acid, but tellurium needed a strong acidity of up to 5 - 7 M. From the curves of acidities, the highest sensitivity could be obtained only over a narrow range of acidities (±0.5 M). Hydride signals decreased with increasing acidities and ultimately became zero. These results are not similar to those obtained by Thompson and Thomerson [12] who reported that there were no obvious changes in a range of hydrochloric acid concentrations of 1 - 4 M. Our results for tellurium are the same as theirs. To keep a stable acidity in the reaction vessel, a buffer solution was used for each element. It served not only to control pH, but also sometimes was able to mask several metallic interfering ions such as nickel, iron, etc.. For example, citric acid is one of those buffering agents. The final acid concentration before adding buffer solution was from 0.05 - 0.5 M before adding sodium tetrahydroborate(III). In this acidity range, sodium tetrahydroborate(III) gives its maximum reduction.

Acids used and their concentrations for each element are given in Table 2.3.

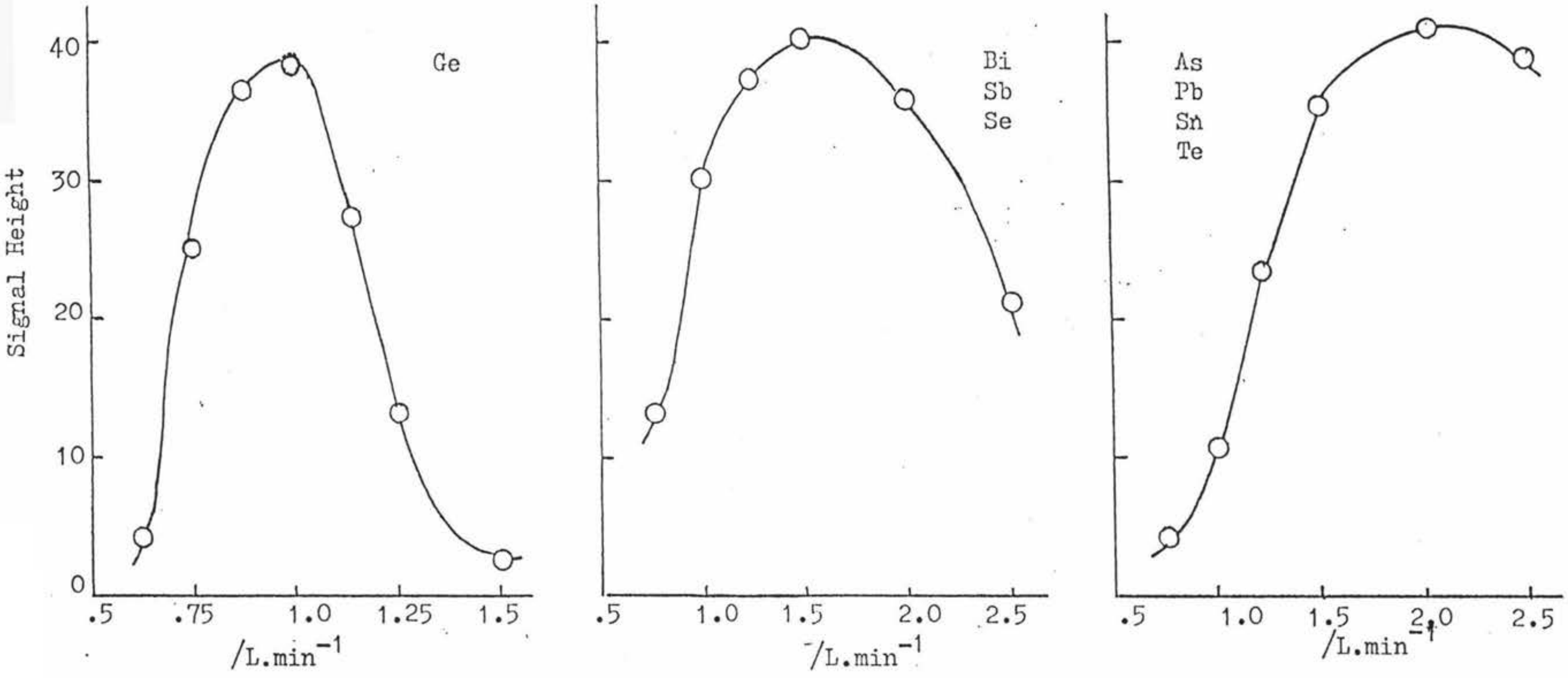


Fig. 2.5 Carrier Gas Flow Rate

II.4.2 Interference from Non-analyte Elements

One of the most widespread problems in hydride generation coupled with atomic absorption spectrometry arises from inter-elemental effects involving suppression or enhancement of the true signal. Many papers have reported several elements that interfere in the generation of arsine and stibine [68 - 71]. Braman et al [71] mentioned that copper and silver interfered with arsenic and antimony when these are generated from alkaline solution using sodium tetrahydroborate(III). They also stated that aluminium, cadmium, chromium, mercury, manganese, nickel, lead and zinc did not interfere either antimony or arsenic, and iron interfered with antimony but not arsenic. A benchmark paper by Smith [72] involved general studies of the effects of 48 elements on the determination of arsenic, bismuth, germanium, antimony, selenium, tin and tellurium. This work was carried out using sodium tetrahydroborate(III) and an argon-hydrogen flame. Certain trends in interference effects were observed. For example, there was no interference on six of the analytes from the alkai metals, alkaline earths, boron, aluminium, gallium, titanium, zirconium, hafnium, mercury, lanthanum, manganese, vanadium, and ytterbium. However, there was always some interference on six of those metals from copper, silver, gold, platinum, rhodium, ruthenium, nickel and cobalt. It was also found that nearly all of the volatile hydrides formed from the elements interfered with all the other volatile hydrides. Pierce and Brown [73,74] undertook a major contribution to a study of the interfering effects of several anions, cations and acids on arsenic and selenium using different atomization techniques. Bedard and Kerbyson

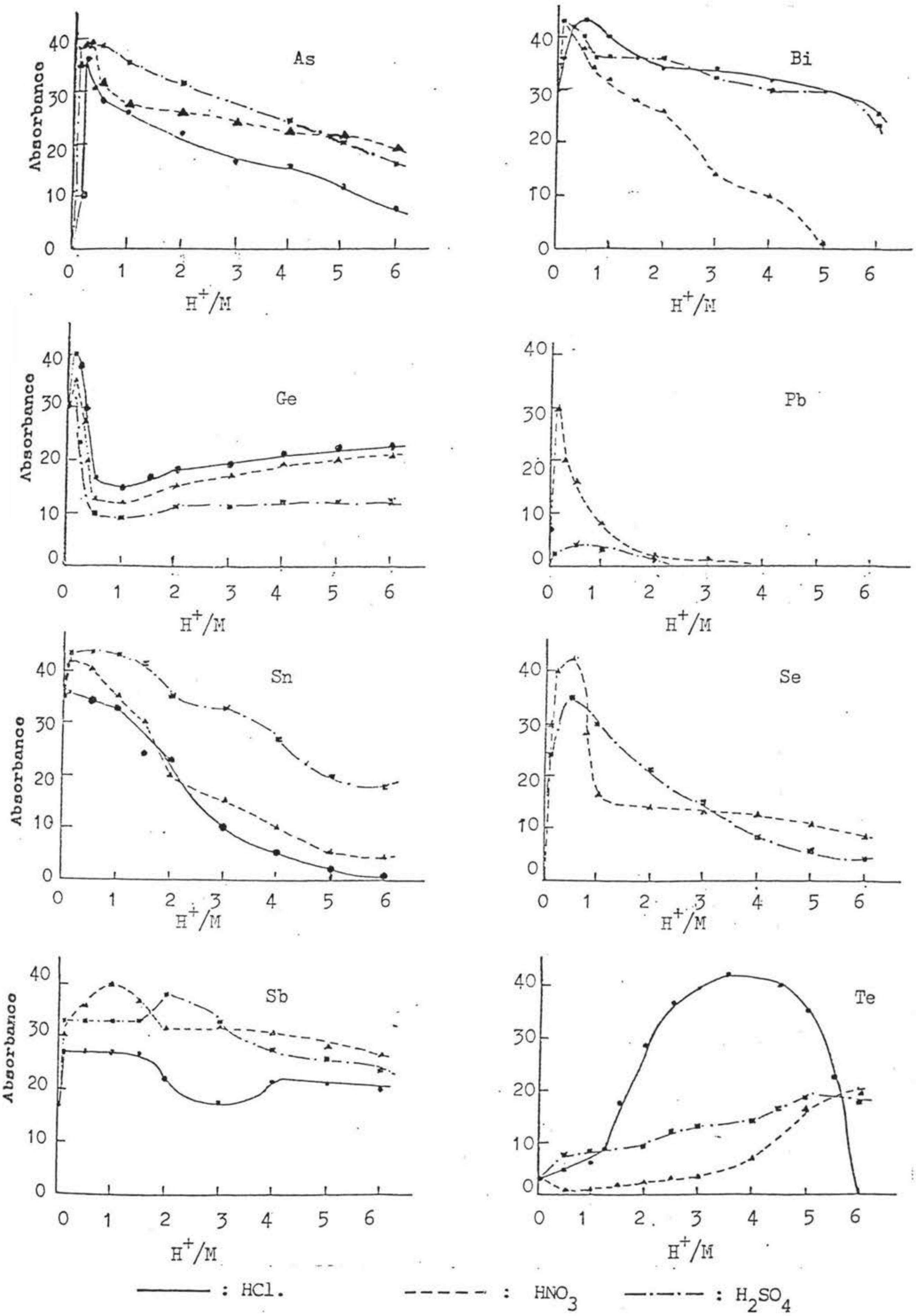


Fig. 2.6 Absorbance as a Function of Acidity

[31] reported the determination of bismuth in copper by precipitation of bismuth with lanthanum hydroxide and subsequent conversion of the bismuth into its hydride. Kirkbright and Taddia [75] described a novel method of masking the interference of large amount of copper, nickel, platinum and palladium on the determination of arsenic. some other significant papers [76,77,102] involved the studies of iron(III) as releasing agent to suppress the interference from copper in the determination of selenium.

For the determination of hydride-forming elements in iron meteorites, probable interferences needs to be investigated. Potential interferents were iron, copper, nickel, cobalt, germanium and arsenic. Their effect on the determination of eight volatile hydride elements was therefore investigated.

The results are given in Fig. 2.7. Almost all of these elements interfered with the generation of hydrides, except for iron(III) in the case of tellurium. A severe interference from copper and nickel suppressed the signals, even at low concentration down to 10-fold. Both iron(II) and iron(III) have the same degree of interference for the elements arsenic, germanium, lead, antimony, selenium and tin, but iron(II) interfered more than iron(III) for bismuth.

Of hydride-forming elements, the interference from germanium and arsenic on other elements were the only ones studied because of their high concentration in iron meteorites. From Fig. 2.7, it is obvious that the generation of hydrides for both germanium and arsenic did not interfere at low concentrations. Above a critical concentration, their effect in many cases was to increase signals of other hydride-forming elements. Some elements did not conform to this pattern, i.e.

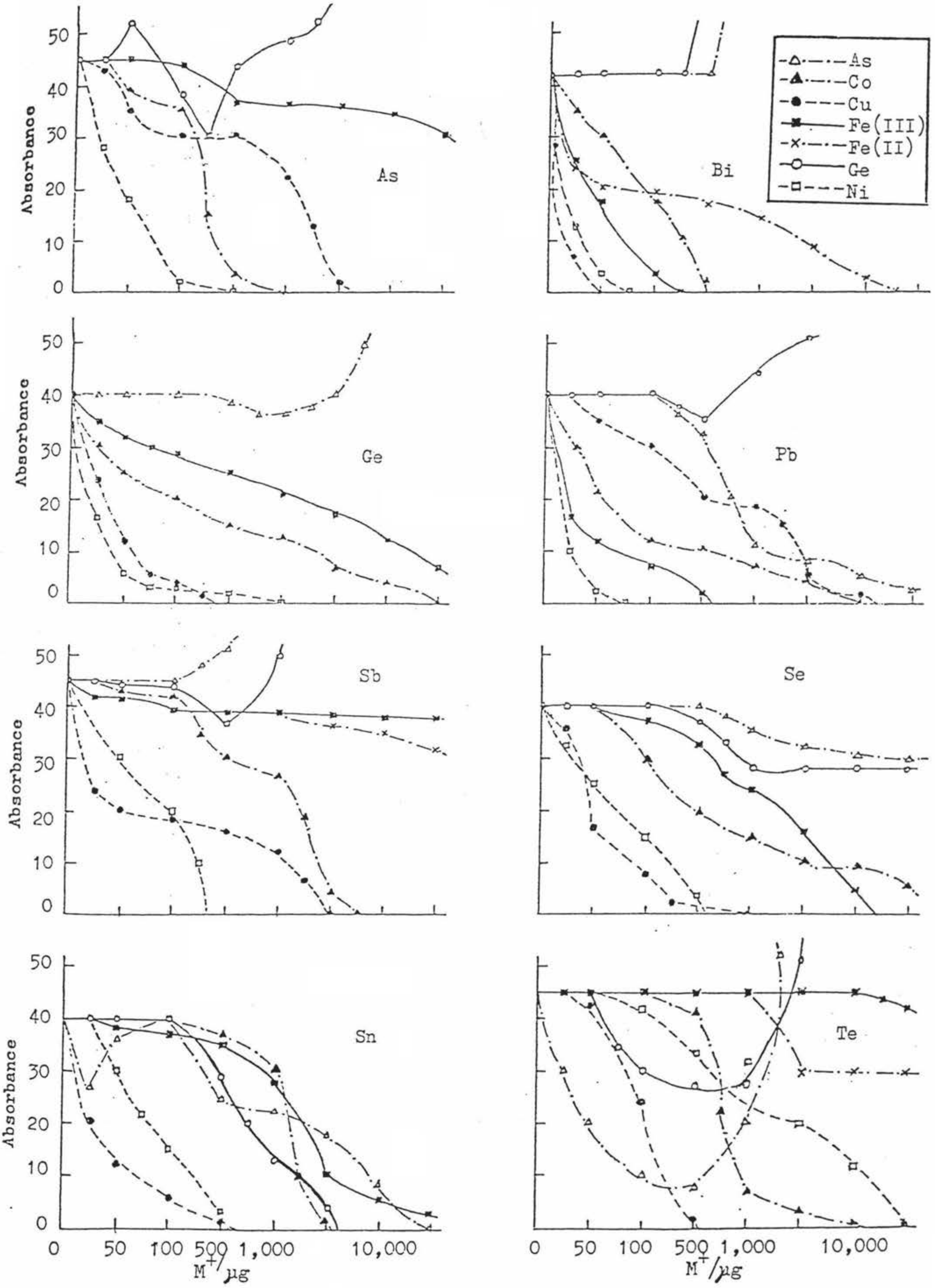


Fig. 2.7 Interferences of Several Ions

interference from germanium was quite different from that of arsenic when lead was determined, germanium gave positive interference but arsenic was negative. Compared with the majority of elements, selenium showed an opposite result in that the signal decreased with increasing amounts of germanium and arsenic.

From these experiments it appears that interferences from metallic ions are major problem for the determination of hydride-forming elements in iron meteorites.

II.4.3 The Optimun Amount of Sodium Borohydride

Sodium tetrahydroborate(III) is now almost universally used for the synthesis of hydrides. It was also used as a reducing agent throughout this work. The amount of sodium tetrahydroborate(III) used depends on each element, in which the effects are very complex and depend on oxidation states, reduction ability, acidity, etc..

A 3% (w/v) solution of sodium tetrahydroborate(III) in 1% (w/v) potassium hydroxide was prepared daily. Varying volume of the solution were added to 0.1 - 1 μg of standard of each element. The minimum amount of sodium tetrahydroborate(III) needed to give complete conversion to hydrides, and used in all future experiments, is given in Table 2.4.

Unlike most other elements, arsenic needs multiple addition of sodium tetrahydroborate(III) solution to generate arsine completely. Four 3 ml aliquots can give satisfactory results. This is similar to the findings of Liddle [78]. When applied to real samples of meteorites,

Table 2.3 Acids used and their concentrations

ELEMENT	ACID	ACIDITY(M)
As	H_2SO_4	0.5
Bi	HCl	0.3
Ge	HCl	0.1
Pb	HNO_3	0.1
Sb	HCl	0.2
Se	HNO_3 or H_2SO_4	0.5
Sn	HNO_3	0.1
Te	HCl	5

Table 2.4 The amount of sodium tetrahydroborate(III) needed to give quantitative conversion to hydrides

ELEMENT	MINIMUM AMOUNT (ml)	USED AMOUNT (ml)
As	10	12
Bi	4	6
Ge	10	15
Pb	8	10
Sb	6	8
Se	4	6
Sn	10	12
Te	6	6

more of the sodium tetrahydroborate(III) solution is needed because of its initial consumption by the citric acid buffer.

II.4.4 The Effects of the Total Reaction Volume

The response of each element is independent of the initial volume. The amount of acid added relates to the amount of sodium tetrahydroborate(III). Varying initial volumes (10 - 100 ml) were carried out with 0.1 or 1 µg of these standards . Subsequently, increasing amounts of sodium tetrahydroborate(III) were added. The results showed no obvious effect, but much lesser or greater amounts could affect the production of hydride. The optimum volume of acidic medium was in the range of 20 - 40 ml, and this volume was chosen for future work. When the reaction of the generation finished, the total volume was 30 - 50 ml.

II.4.5 Total Reaction Time

The sensitivity is a function of reaction time. By " reaction time " I mean the time between addition of sodium tetrahydroborate(III) and immersion of the condenser into the water bath. This time is obviously largely dependent on apparatus and instrument.

For obtaining the optimum time for each element, the following procedure was used:

1. The time period between the injection of sodium tetrahydroborate(III) and the release of hydrides to the flame by a carrier gas was varied.

2. The time period over which sodium tetrahydroborate(III) is added, was varied, i.e. altering the interval between two injections. This procedure was used only for arsenic because other elements did not need multiple injections.

All results are given in Table 2.5 and Fig. 2.8.

The optimum time was found from a maximum peak value for each element, i.e., from 30 seconds to 2 minutes in our apparatus and instrument. Arsenic needs the longest interval (2 minutes), but antimony and tellurium need only for 30 seconds. The elements that have multi-oxidation states need a longer reaction time (about 70 - 120

Fig. 2.5 Optimum reaction times for generation of hydrides

ELEMENT	TIME (second)
As	120
Bi	35
Ge	35
Pb	70
Sb	30
Se	70
Sn	90
Te	30

sec.) than the others. It is necessary to add more sodium tetrahydroborate(III) when a high concentration of the analyte is encountered in the sample. Overaddition can slightly reduce the sensitivity because the greater volume of liberated hydrogen probably dilutes the hydrides, and also a higher blank value appears , especially in the determination of lead, selenium and tin.

II.4.6 The Effects of Different Oxidation States

Multi-valent elements, such as arsenic(III,V), selenium(IV,VI) and tellurium(IV,VI) are always difficult to recover in hydride generation. This problem has been discussed by Smith [74], who overcame the problem

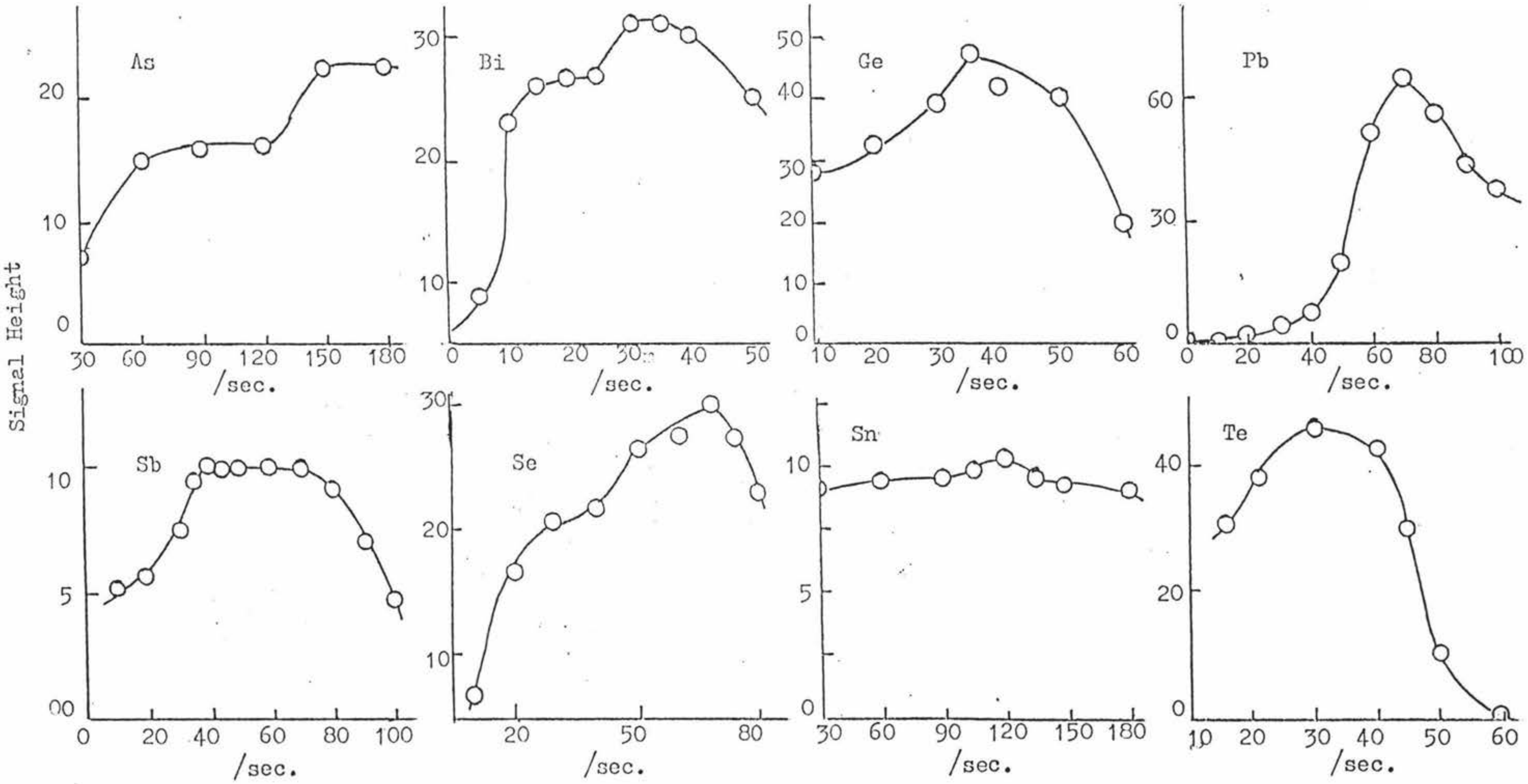


Fig 2.8 Hydride generation reaction time

by increasing the concentration of sodium tetrahydroborate(III). The main reason was that this reagent was needed to be reduced arsenic(V) to arsenic(III) in the first step:

$$4AsO_4^{3-} + BH_4^- + H_3O^+ \dashrightarrow 4AsO_3^{3-} + H_3BO_3 + 2H_2O$$

and then arsine was formed:

$$4AsO_3^{3-} + BH_4^- + 15H_3O^+ \dashrightarrow 4AsH_3 + 3H_3BO_3 + 18H_2O$$

The above problem still existed in this work when arsenic, selenium and tellurium were determined in an acidic medium. Arsenic gave good linearity at low concentrations but at a concentration of 0.5 µg/ml, a different slope of curve was encountered up to 2 µg/ml. This is shown in Fig. 2.9. Selenium showed unstable peak values and a high blank value. There was poor sensitivity for tellurium.

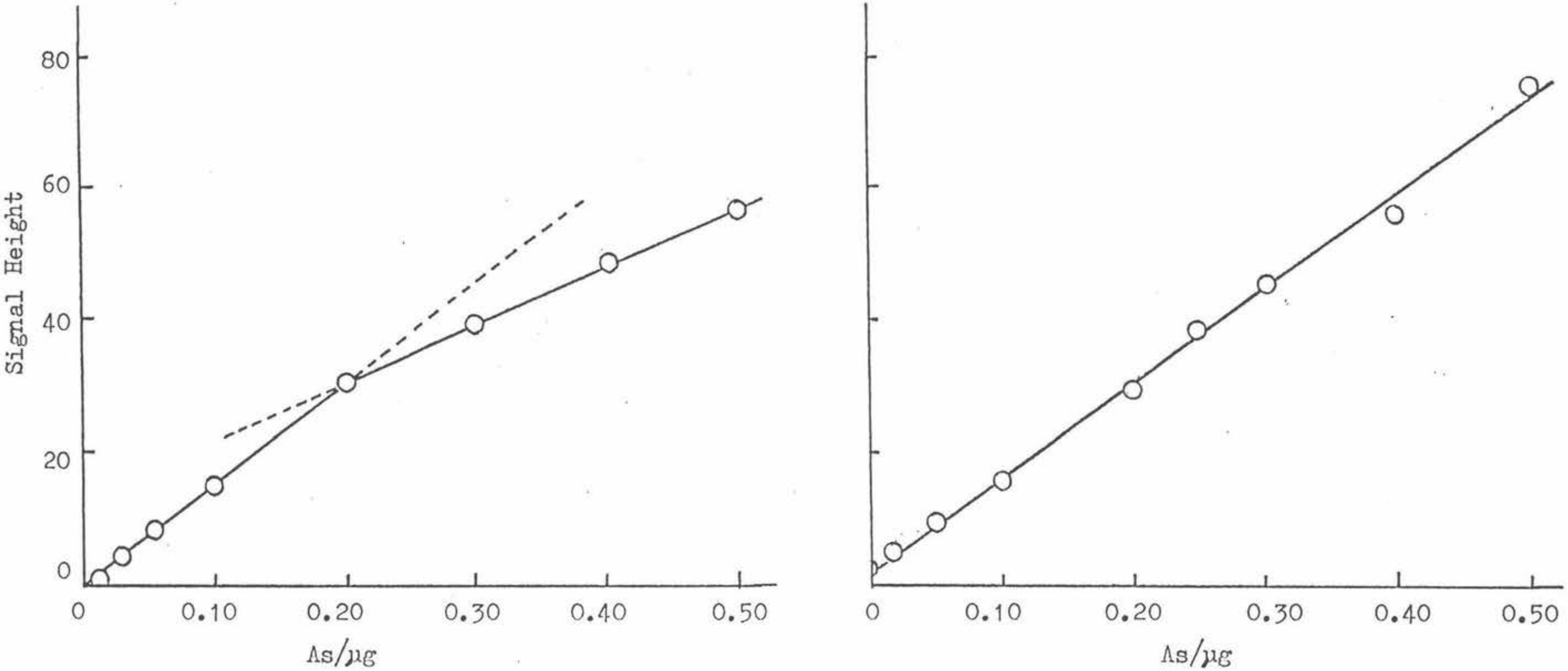
When sulphuric acid was used instead of hydrochloric acid, a good linearity was obtained for the analytical curve of arsenic and the sensitivity was improved with this change. Selenium gave a similar result with nitric acid. Tellurium remained unchanged. Arsenic(III) and arsenic(V) were respectively tested using sulphuric acid as the medium. This gave good results but the peak value of arsenic(III) was a little higher than that of arsenic(V). When the reactiom time was reduced to 30 seconds, tellurium gave satisfactory sensitivity and the blank value tended to zero.

It has been observed that titanium(III) chloride could be used for pre-reduction of tellurium. The sensitivity for this element was then doubled, but it was difficult to apply this to the determination of tellurium because of the high blank value given by this reagent. To decrease the reaction time from 70 seconds to 30 seconds gave a satisfactory result for the determination of tellurium. A very stable, signal with a ten-fold increase in sensitivity, was obtained with this procedure.

Smith [72] has recommended that all elements be in a single oxidation before generation of hydrides. He also recommended use of aqua regia for dissolution of solids, to ensure that the solution contained a single valency, such as arsenic(V), selenium(IV) and tellurium(IV). I could not use this procedure in my work because of loss of volatile elements, particularly germanium.

II.4.7 The Use of Oxidation agents before Generation of Hydrides

Sodium tetrahydroborate(III) is the most convenient reducing agent for the generation of hydrides. However, conditions for the determination of lead are somewhat different from those of other elements. The conversion efficiency of lead to plumbane is poor for direct reaction with an acidified sample solution and sodium tetrahydroborate(III) [12]. Fleming and Ide [79] and Schmidt [80] showed that the hydrochloric acid and sodium tetrahydroborate(III) concentrations are critical and that in the presence of tartaric acid and potassium dichromate, the atomic absorption signal increases considerably. Vijan and Wood [63] recommended use of nitric acid, perchloric acid, and hydrogen peroxide as the reaction medium for the reduction procedure. They used a quartz tube heated to 800 °C to increase the sensitivity to 6 ng/ml. Others such as Jin [64 - 66], Smith [80] and Castillo et al [83 - 87] studied different media, for example, malic-$K2Cr_2O_7$, KCN-$K_2Cr_2O_7$ and different oxidizing agents, such as $K_2Cr_2O_7$, $KMnO_4$, $Ce(SO_4)_2$, H_2O_2 and $(NH_4)_2S_2O_8$. Castillo et al [86]



(a). Before Improvement

(b). After Improvement

Fig. 2.9 Analytical Curves for Arsenic

studied the relationship between the redox potential of the oxidizing agent and the generation of hydrides. They stated that the effect of an oxidizing agent on the lead hydride generation had been attributed to the oxidation of lead to a metastable tetravalent state before conversion into plumbane (PbH_4).

To obtain the optimum conditions for the determination of lead in the instrument, many oxidizing agents and acidic media were used because sensitivity was poor without addition of these reagents. The experiments showed that H_2O_2, $K_2Cr_2O_7$, $KMnO_4$, I_2- KI and $Ce(SO_4)_2$ were not suitable for the procedure, but that $(NH_4)_2S_2O_8$ was useful. Study therefore focussed on $(NH_4)_2S_2O_8$. When 2 ml of 1 M $(NH_4)_2S_2O_8$ was added to the reaction vessel with an acidic medium, the plumbane signal increased nearly ten times. By increasing the volume of $(NH_4)_2S_2O_8$ the signal continuing to increase (see Fig. 2.10), but was unstable until 6 ml of solution had been added. After this experiment, 5 ml of 1 M $(NH_4)_2S_2O_8$ was chosen for future work. It was also found that the optimum reaction time was different and independent of each oxidizing agent. The optimum time for $(NH_4)_2S_2O_8$ is 70 seconds. For overcoming the blank, a mixture of oxidizing agents was studied and the result confirmed that the blank value could probably be reduced when H_2O_2 and $(NH_4)_2S_2O_8$ were coupled to use in the presence of HNO_3. The choice of acidic medium is critical when using oxidizing agents for the preoxidation of lead to the tetravalent state from the divalent state before hydride generation. Although hydrochloric, sulphuric, and organic acids gave poor sensitivities for lead, nitric acid was a suitable as an acidic medium. The optimum concentration of nitric acid was 0.1 M. The recommended mixture of 5:15:1 ($HNO_3:H_2O_2:(NH_4)_2S_2O_8$) is followed by 10 ml of 3% of sodium tetrahydroborate(III) for the determination of lead.

II.4.8 The Effects of Connecting Tubes of Different Materials

Connecting tubes of PVC were used in all parts between the apparatus and instrument. The composition of the tubes is one of the factors to affect sensitivity in hydride generation. The problem was first discussed by Parisis et al [88]. In their work, many types of tubing materials were studied and they found that silanised glass and FEP (fluorinated ethylene-propylene) tubing gave the highest sensitivity and reproducibility for the measurement of arsenic, bismuth, antimony, selenium and tin.

Some anomalous results were observed during my experiments, as follows:

(i) anomalous peak value appearing at the beginning, sometimes higher, sometimes lower,

(ii) a lower concentration of analyte in sample sometimes obtained a higher value than normal when following a sample with a higher concentration of analyte.

(iii) some elements such as selenium and tin gave unstable peak values. A study was therefore made of other types of tubing because of possible absorption of hydrides on the surface of the tubing.

Rubber tubing gave poor results. Although PVC and glass tubes gave better results, PVC tended to absorb hydrides at the beginning of the experiments. This problem disappeared after 3 - 4 samplings. Glass is not convenient for the operations. Subsequently, the use of the PVC

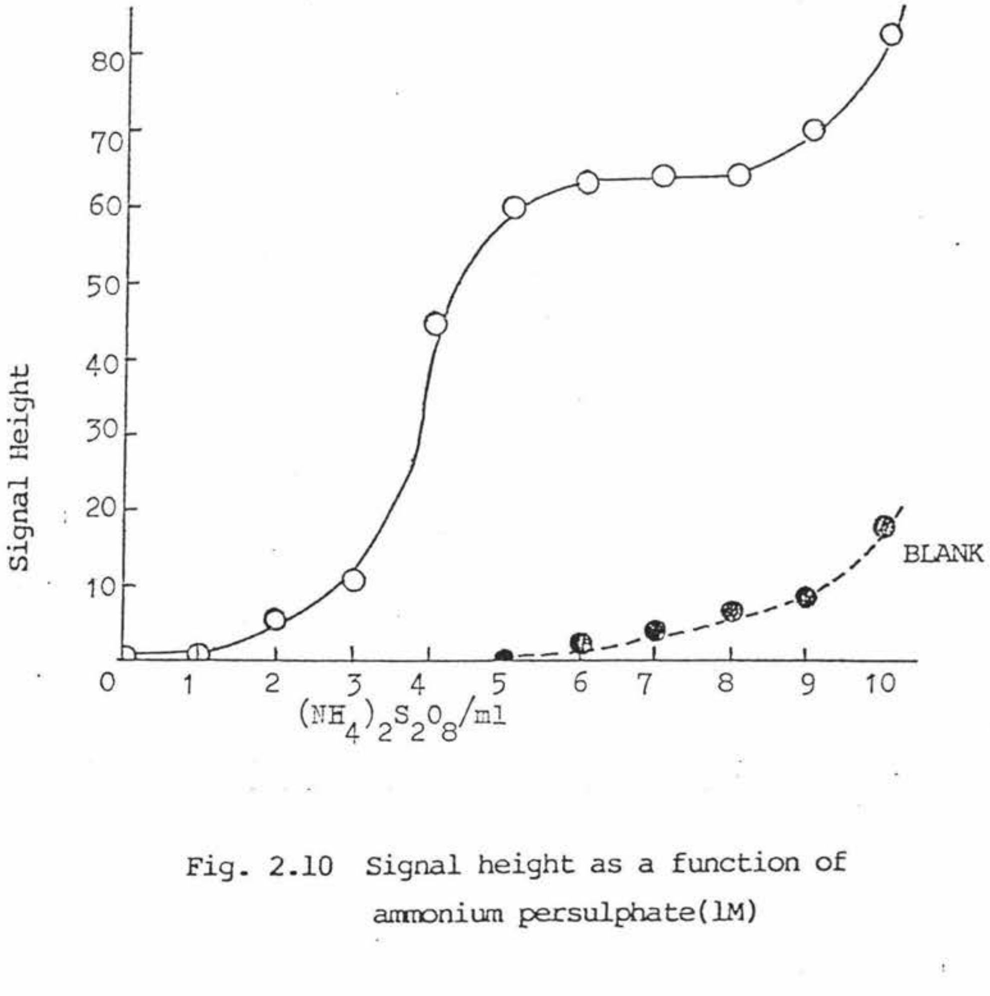


Fig. 2.10 Signal height as a function of ammonium persulphate(1M)

tubing that was as short as possible, combined with glass where appropriate, gave good sensitivity and reproducibility.

It is necessary to keep the carrier gas flowing at least 3 minutes before generating hydrides in order to remove hydrides that have absorbed on the surface and to run standards at least twice to reach saturation on the surface in order to ensure the optimum sensitivity and reproducibility.

II.4.9 Detection Limits

The high sensitivity is one of the major advantages of hydride generation. The detection limits achieved were in the ppm and ppb range. Godden and Thomerson [19] summarized typical detection limits and sensitivities for different methods for the above eight elements. This is shown in Table 2.6.

All analytical curves are shown in Fig. 2.11, indicating that they are linear in a certain range. Some deviation from linearity were evident at 2 ug of some elements.

Calculation of the detection limits is based on the principle of 2σ from the peak value against base line. The detection limits of eight elements in hydride generation in this instrument are given in Table 2.7.

Table 2.6 Sensitivities and detection limits by other workers (12)

ELEMENT	SENSITIVITY	DETECTION LIMIT
	(values are given in micrograms)	
As	0.01	0.01
Bi	0.008	0.005
Ge	0.27	0.2
Pb	-	-
Sb	0.01	0.005
Se	0.005	0.005
Sn	0.007	0.004
Te	0.014	0.005

Conditions:

REDUCING AGENT	COLECTION VESSEL	DETECTOR	SOURCE
$NaBH_4$	Balloon	$Ar-H_2$ flame	HCL

II.5 Discussion and Conclusion

For the purpose of a study of the covalent hydride-forming elements in iron meteorites, the analytical conditions of eight elements with hydride generation in atomic absorption spectrometry were studied in this work. Particular attention was paid to the reduction or elimination of interference effects and to the development of fast and

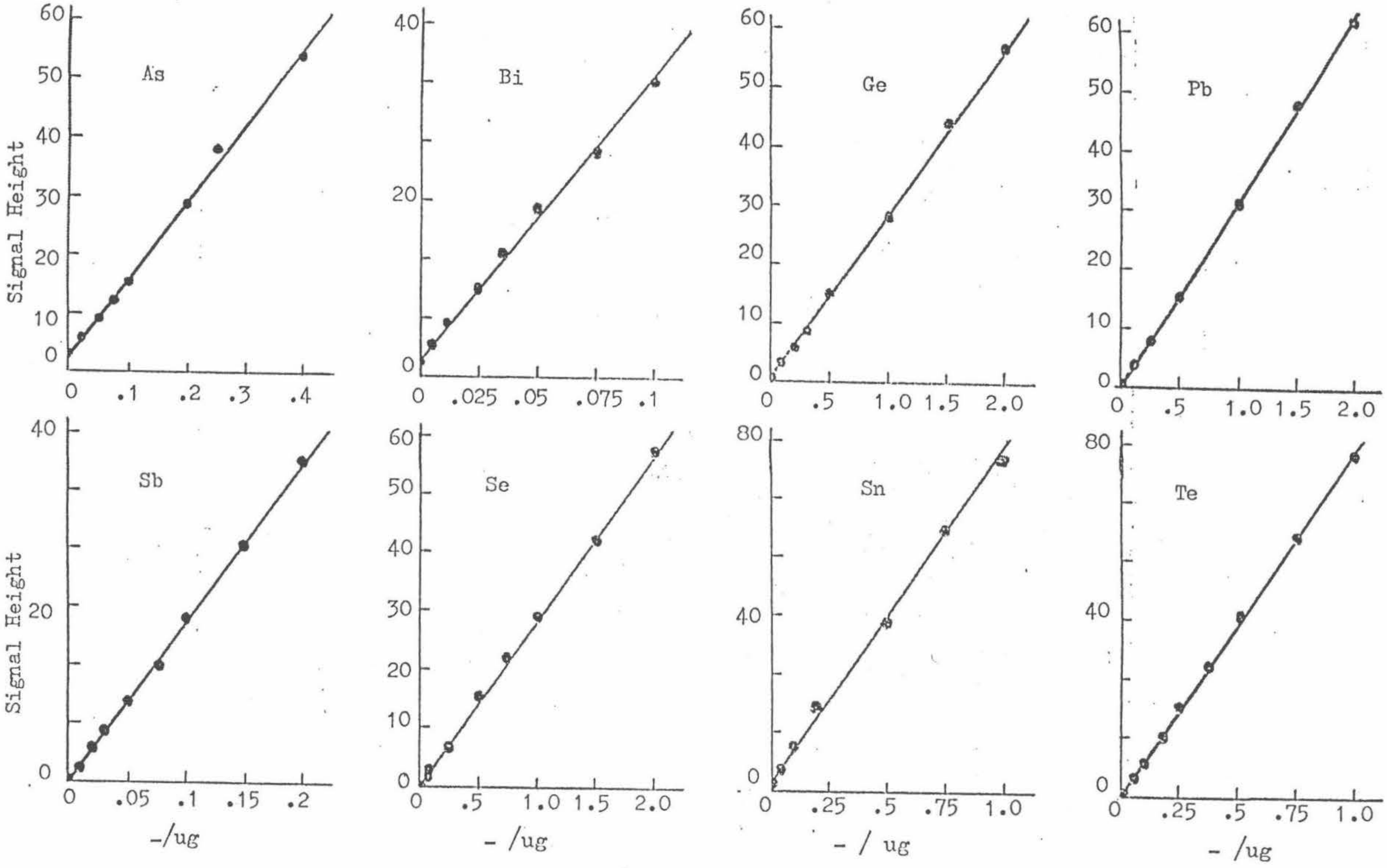


Fig. 2.11 Analytical Curves

Table 2.7 Sensitivity and detection limit

ELEMENT	SENSITIVITY (1PER CENT ABSORPTION)	DETECTION LIMIT (2σ/ug.ml^{-1})
As	0.002	0.0008
Bi	0.002	0.0008
Ge	0.03	0.01
Pb	0.02	0.008
Sb	0.001	0.0005
Se	0.05	0.01
Sn	0.02	0.009
Te	0.02	0.005

economical analytical methods of potential use for iron meteorites.

The detection limit of the technique is largely dependent on effective atomization which is a function of flame type and flame temperature. In II.3, the atomization conditions have been reported. According to these results, atomization is more effective in low temperatures than in high ones. This is because hydrides tend to be oxidized at higher temperatures. Atomization therefore is reduced so that sensitivity decrease. Commonly used flames in atomic absorption spectrometry are air-acetylene and nitrous oxide-acetylene, as well as the others. These flame temperature normally are about 1700 - 3000 °C and they are not suitable for atomization of the hydrides. Fujita et al [90] reported the effect of temperature on generation and decomposition of the group VB element hydrides. The optimum atomization temperature were between 800 °C and 920 °C for bismuth and 860 °C for arsenic and antimony. Chu et al [11] reported that the optimum temperature of their electrically heated tube appears to be in excess of 700 °C for the detection of arsenic. Dedina and Rubsks [91], as well as Welz and Melcher [92] proposed a hydrogen radical reaction for the mechanism of the atomization in the flames and in the quartz tubes. For example:

$$AsH_3 \xrightarrow{+H} AsH_2 \xrightarrow{+H} AsH + 2H_2 \xrightarrow{+H} As + 3H_2$$

The required H radicals are generated in flames by the combustion processes. They suggested that the best temperature was not in excess of 1000 °C to prevent oxidation by oxygen in the carrier gas.

Like the argon-hydrogen-air entrained flame, the less expensive cooler nitrogen-hydrogen-air entrained flame is very suitable for the method of hydride generation. I was the first to use this flame for the determination of germanium in iron meteorites, a successful example that will be discussed in Chapter 3.

Another key problem in the application of hydride generation is inter-element interferencs in the samples. The reasons for these interferences are a variety of factors as follows:

(i) interfering elements directly consuming the reducing agent without forming hydrides.

When interfering elements are present in a standard solution, the signal is only 10% or less of that without interference. In the reaction vessel, the solution becomes black after adding sodium tetrahydroborate(III), which means that the metallic ions are reduced to the elements or other states before forming hydrides. Owing to the high concentration of the interfering elements in the solution, other non-analyte hydride-forming elements are reduced together with the analyte to hydrides which then cause positive interference. For example, arsenic and germanium usually give a positive interference in my apparatus and instrument, except one or two elements.

(ii) interfering elements forming complex molecules or alloys with analyte elements during the reduction reaction.

Metallic ions, particularly the transition metals, tend to form metal hydrides, and form other types of complex molecule that would interfere with the normal generation of hydrides. In some cases, a metal alloy form during the reduction reaction and reduces sensitivity. An example of this is As*Sb.

For the above reasons, three methods were used to reduce or eliminate these interferencec. These were as follows:

(i) extraction of the analyte from the samples.

An extraction method for bismuth involved forming a bismuth ammonium pyrollidine dithiocarbamate (APDC) complex with APDC in hydrochloric acid which was then extracted into methylisobutyl ketone (MIBK).

Very low concentration of bismuth are present in the iron meteorites. To prevent the other elements interfering and to provide enough sensitivity in this instrument, bismuth should be extracted from the solution with MIBK. This method has been reported by Brooks et al [93,100]. By this method however, bismuth in the MIBK phase (organic phase) is not suitable for hydride generation because the hydride is difficult to collect in the liquid air trap. A back-extraction method was used to obtain bismuth in the aqueous phase, in which dilute nitric acid (2M) was added to the organic extraction phase. After shaking, the aqueous phase was used for hydride generation. The use of this method gave a 96.5% of recovery when 1 µg/ml of standard bismuth was tested but at low bismuth concentrations (down to 0.1 µg/ml) recovery was poor or even zero. The method can also be used for other elements such as arsenic, antimony, lead and tin, but only at higher concentration. germanium, selenium and tellurium can not be so determined because of the poor extractability of their APDC complexes.

(ii) precipitation of interfering ions with hydroxide.

Metallic ions such as those of iron, nickel, etc. can be precipitated with hydroxide. Using this separation technique, interfering ions can be removed from the samples. Standard tellurium was been tested with potassium hydroxide in the presence of interfering ions. A 2 M potassium hydroxide was used for the precipitation of metallic ions, after separating the precipitation by centrifuging, tellurium was determined and gave a 98 - 102% recovery.

(iii) use of masking agents.

A simple and effective method for eliminating interference is the use of masking agents. Many masking agents have been studied for the samples of iron meteorites. Details are given in Chapter III.

When the method was applied to iron meteorites, it was found that only germanium had a sufficiently high abundance in iron meteorites to be able to be determine in all samples. Arsenic and tin could be determined only at a few specimens that have higher contents (> 1 ppm) of these elements. The applied aspects were therefore concerned mainly with germanium as detailed in Chapter III.

CHAPTER THREE

THE DETERMINATION OF GERMANIUM IN IRON METEORITES

CHAPTER THREE

THE DETERMINATION OF GERMANIUM IN IRON METEORITES

III.1 Introduction

The determination of germanium in iron meteorites has hitherto involved the use of radiochemical neutron activation analysis (RNAA) which is a lengthy and expensive procedure. The original methodology was developed by Goldberg et al [94] and by Lovering et al [50]. Later, Smales et al [95] determined germanium in 67 different iron meteorites.

Instrumental neutron activation analysis (INAA) is a much speedier and less expensive alternative to RNAA, but it is extremely difficult to determine germanium by this method because of massive interference from elements such as cobalt whose gamma spectrum can mask those of other elements including germanium.

The dependence on RNAA for the quantification of germanium in iron meteorites has to some extent been a hindrance to classification of these meteorites, though in recent years the development of alternatives such as plasma emission (ICP) spectrometry and ICP-mass spectrometry (ICP-MS) holds out promise for progress in germanium determinations. For ICP the main problem is massive iron interference resulting from the high content of this element in the samples. This content is so high that recourse has to be made either to removal of iron prior to analysis [96], or to the use of instruments with optical systems of very low reciprocal dispersion.

A previously-neglected method of quantification of germanium involves hydride generation in atomic absorption spectrometry. The original work on determination of germanium by HGAAS was by Thompson and Thomerson [12] who reported a poor detection limit. Other modifications of the method have since been reported and have been reviewed by Godden and Thomerson [97]. Unfortunately none of these methods was specifically designed for the determination of germanium in iron meteorites. A simple and inexpensive hydride generation atomic absorption spectrometric method has been developed by me for determination of germanium in iron meteorites. This is the first time that HGAAS has been applied for the quantification of this important diagnostic element for classification of iron meteorites.

III.2 The Role of Germanium in Chemical Classification of Iron Meteorites

The chemical classification of iron meteorites is based on the concentration of the main elements which can clearly indicate genetic groups for each specimen.

The first analyses of the trace elements in a large number of iron meteorites were made by Brown and co-workers [50,94]. From the vast pool of analytical data, gallium and germanium were chosen on the basis of compositional parameters coupled with other elements together for setting up an improved method of chemical classification of iron meteorites. They found that the distributions of these elements were non-random, with pronounced clustering at certain concentrations. The germanium contents in iron meteorites, covering a range of several orders of magnitude, fell into four distinct clusters, with each meteorite essentially homogeneous. The groups are related approximately to the structure of iron meteorites and the nickel contents. In some arrangments, the analytical values for germanium reach a maximum in the coarse octahedrites and decrease slightly in the coarser structures and quite markedly in the finer structures. Subsequent work has produced more accurate data on a much larger selection of meteorites, and has confirmed that the germanium concentration is the best single classification parameter known for iron meteorites. For irons as a whole, germanium varies by a factor of 4×10^5, whereas within most of the genetic groups, the factor is <1.4 . Other elements, such as nickel, gallium, and iridium show less valuable classificatory properties than germanium.

III.3 Determination of Germanium in Iron Meteorites

III.3.1 Conditions of Analysis

i. Apparatus and Instrument

The apparatus and instrument employed are the same as described in Chapter II.

A hollow cathode lamp (HCL) was used to as a light source in this instrument. The germanium resonance line at 265.2 nm was used throughout the study, and gave a lower instrumental noise level. The lamp current was 6 mA.

ii. Acid strength

The formation of germane is strongly influenced by the molarity of the inorganic acid used, rather than its identity. Hydrochloric, sulphuric and nitric acids at the range of 0 - 6 M (0 - 3 M for H_2SO_4) were placed in the reaction vessel with 1 ug germanium were studied. The results showed no statistically-significant differences in the curves for all acids and are given in Fig. 2.6. Beyond 3 M acid, the signal remains relatively constant, but in a range of 0.05 - 3 M, the signal is strongly influenced by the acidity and not by the kind of acid. A concentration of 0.1 M of hydrochloric acid was finally chosen throughout the work.

iii. The Amount of Sodium Tetrahydroborate(III)

Unlike the case of arsenic, multiple additions of sodium tetrahydroborate(III) solution were not necessary to remove all the germanium from the sample. A 3% (w/v) solution of sodium tetrahydroborate(III), involving 1% (w/v) potassium hydroxide was used to reduce the metal to germane. Varying volumes of tetrahydroborate(III) were added to 1 µg germanium standard (standard solution in 1.5 M HNO_3). The result is shown in Fig. 3.1. It is quite clear that a minimum of 8 ml of tetrahydroborate(III) solution was needed to give a limiting value for the absorption signal. In addition, the masking agent (citric acid) was added for all determination of samples that consume sodium tetrahydroborate(III). The final chosen volume of sodium tetrahydroborate(III) was 15 ml.

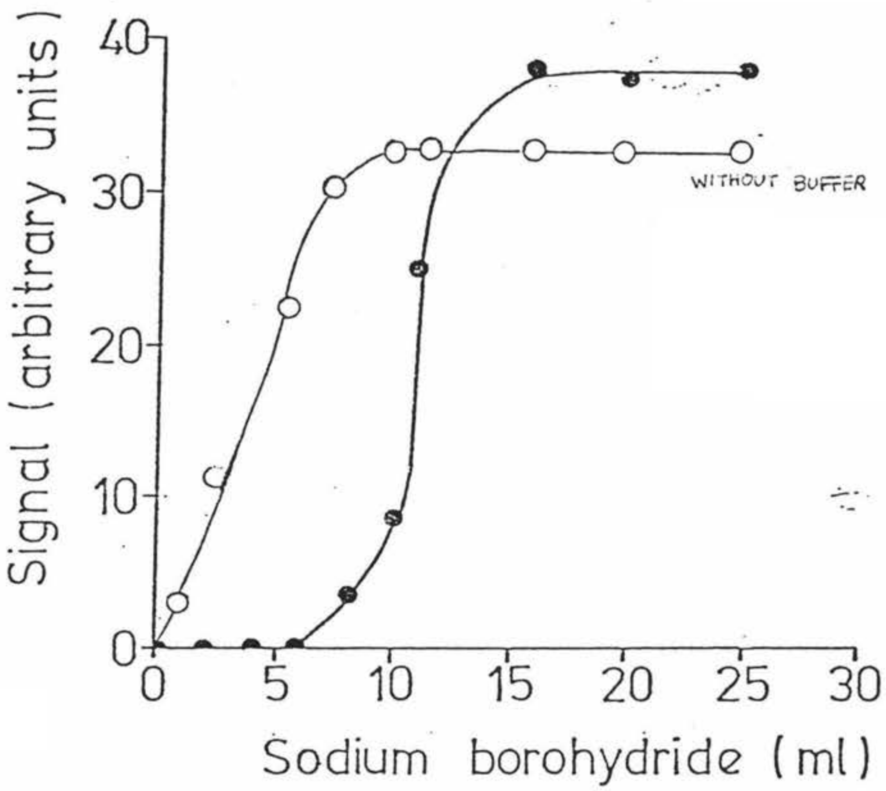


Fig. 3.1 Signal as a Function of the Amount of Sodium Tetrahydroborate(III)

iv Reaction Time for Hydride Generation

The reaction time is an essential factor influencing of the analytical sensitivity. "Reaction Time" means the time between the addition of sodium tetrahydroborate(III) and the immersion of the condenser into the water bath. It is largely dependent on the apparatus and must be determined separately for each instrument. Varying the reaction times in a range of 10 - 60 seconds was carried out with 1 µg of germanium standard. The results are given in Fig. 3.2 and demonstrate that maximum sensitivity was achieved after a period of 3 seconds. The shape of the curve, though somewhat irregular, was quite reproducible.

v. Flame Type

Several types of flames for atomization have been used for the generation of hydrides. Of these, a very successful flame was the argon-hydrogen-air entrained flame cell. This was applied for most of the work. Argon is an expensive gas, which limited widespread application. Other types of flames were used in this work. These are: air-acetylene, nitrous oxide-acetylene and nitrogen-hydrogen-air entrained. Both air-acetylene and nitrous oxid-acetylene flames gave poor sensitivity. It was found that the N_2-H_2air entrained flame gave the best sensitivity and stability and it was used for all future work. The relative sensitivities of the three types of flame are shown in Fig.2.2.

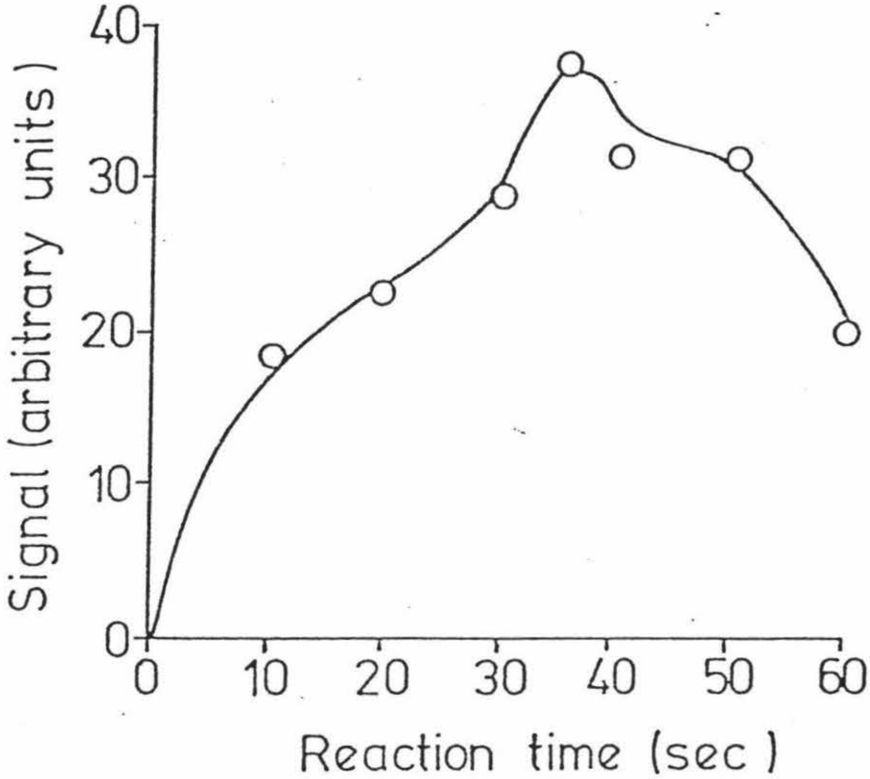


Fig. 3.2 Reaction Time for Hydride Generation

vi. Flow Rate of Gases

The sensitivity is related to both flow rate of fuel and support gas because of the influence of the temperature of the flame.

The flow rate of gases can be controlled in two ways as follows:

(i) Keeping the flow rate of fuel gas, constant and changing the flow rate of the support gas from 0.5 to 6 L/min.

(ii) Fixing the flow rate of support gas at the optimum value, and changing the flow rate of fuel gas from 0.5 to 6 L/min.

The curves were obtained by the above ways and are shown in Fig. 3.3. The optimum values are at a constant nitrogen flow rate of 3.5 L/min and a constant hydrogen flow rate of 2.3 L/min. Unlike other elements, a low flow rate of the support gas (1 - 1.5 L/min) was not suitable for germanium. Finally, optimum flow rates of 4 L/min for N_2 and 3 L/min for H_2 were established.

vii. Carrier Gas

Nitrogen and argon gave similar responses, nitrogen was chosen because it is cheaper. Different rates of carrier gas were measured for this instrument and the results are shown in Fig. 3.4. The optimum of carrier gas rate was 1 L/min. Both high and low flow rate reduced the sensitivity.

viii. General Operating Procedure

A volume of 40 ml of 0.1 M HCl was placed in the reaction vessel with 10 - 15 ml of 1 M trisodium citrate solution, and germanium solutions were introduced via an Eppendorf pipette. A stream of nitrogen was

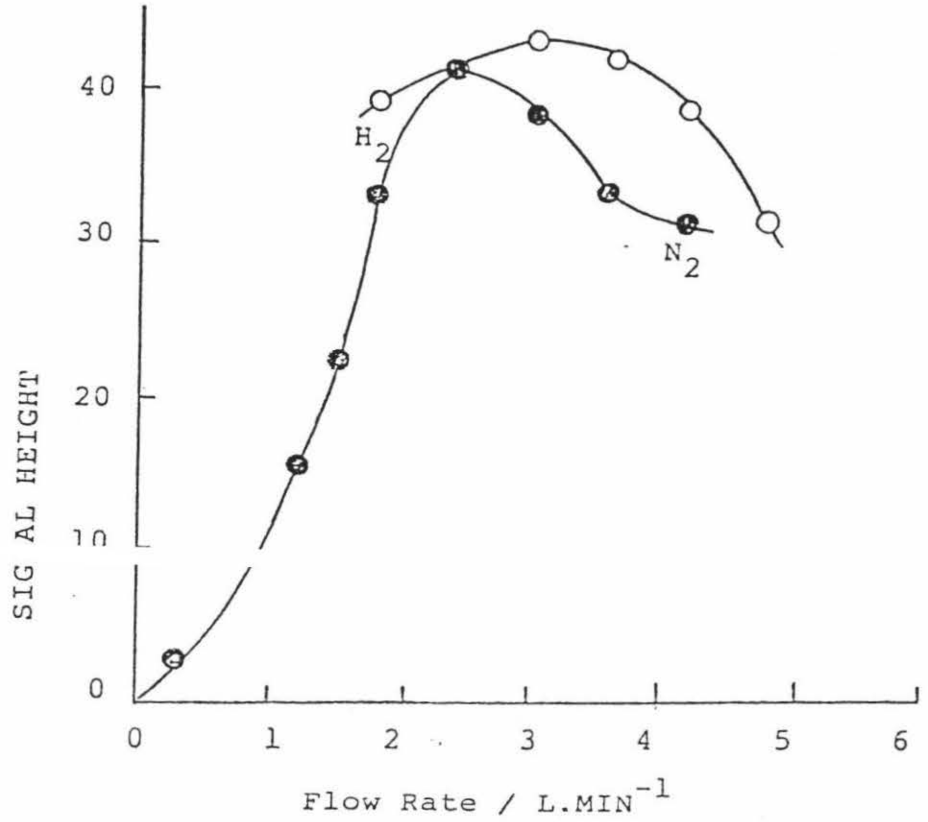


Fig. 3.3 Flow Rate of Flame Gases

passed for at least 15 seconds through the reaction solution for either stirring or blowing out air present the vessel. The U-tube condenser was placed into a liquid air trap. After the U-tube was completely cooled, sodium tetrahydroborate(III) was injected by using a repeating syringe. After finishing the reaction of the generation, the U-tube was transferred a cool water bath from the liquid air trap, and then hydrides are volatilized and carried into the flame by a nitrogen stream for the atomization.

The reaction vessel was washed with distilled water before addition of the next sample.

III.3.3 Interfering elements

In iron meteorites, the major concentrations are iron (80 - 95%), nickel (5 - 20%) and other metals, as well as non-metals. Almost all of these elements interfere in the determination of germanium when using hydride generation in atomic absorption spectrometry (HGAAS).

Tests revealed that iron, nickel, cobalt, copper and arsenic, all interfered with the determination of germanium to varying degrees. Interference from these elements was therefore a serious problem. This illustrated in Fig. 2.7 which shows the depression of the signals for 1 µg of germanium in the presence of varying amounts of iron, nickel, cobalt, copper and arsenic. At a iron/germanium ratio of 5000, a nickel/germaniu ratio of 100, a copper/germanium ratio of 500, about half of the original germanium signal has been lost. At a arsenic/germanium ratio of 10,000, the germanium signal rapidly

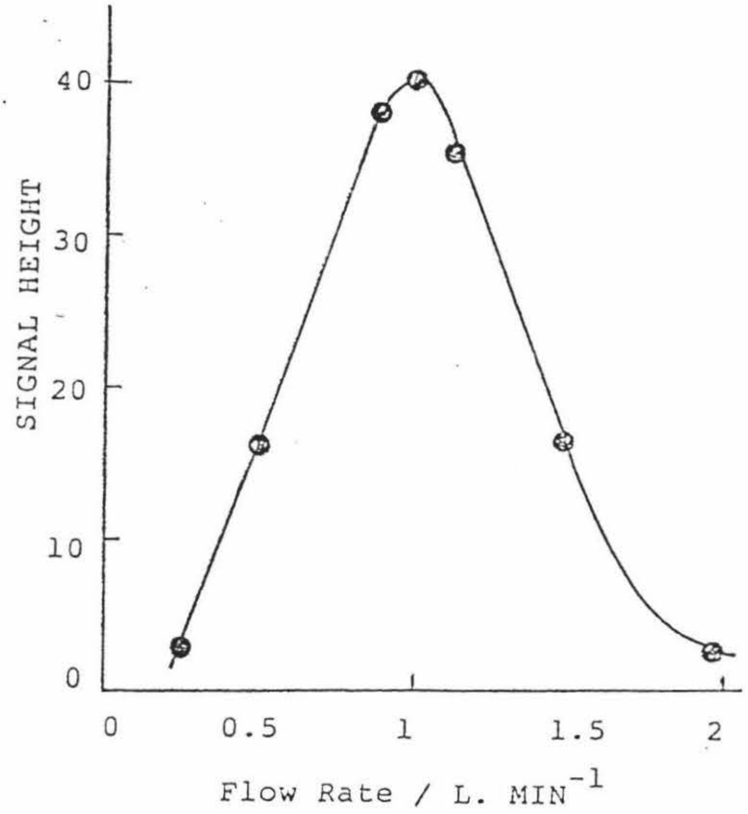


Fig. 3.4 Flow Rate of Carrier Gas

increased to cause positive interference. It is fortunate that cobalt, copper and arsenic concentrations are too low to interfere in the determination of germanium. The key to the problem is how to eliminate the interferences from iron and nickel.

III.3.4 Masking Agent

Many separating methods were carried out for the elimination of the interferences from iron, nickel, and other metals in iron meteorites. These included precipitation. extraction and redistillation. None of these methods was successful. Finally, masking agents which formed complexes with interfering elements were tested and one of them proved to be satisfactory.

Ascorbic acid, 1,10-phenanthroline, KI, 2Na-EDTA and trisodium citrate were respectively studied. Ascorbic acid is a good masking agent for iron but not for nickel and the result is given in Fig. 3.5. The reagent 1,10-phenanthroline showed a good capability of masking for nickel but not for iron and the other problem was that it caused a high blank absorption value that influenced the determination. Other unsuccessful masking agents were KI and 2Na-EDTA. Trisodium citrate had a remarkable capability for masking these interfering elements.

Anhydrous citric acid, normally is not stable, but the salts of the monohydrate, and dihydrate are very common commercial products. Usually this reagent is used as a buffer, but has another and important action in forming various complexes with different metallic ions. Bye [98] observed that it was possible to mask nickel in the determination

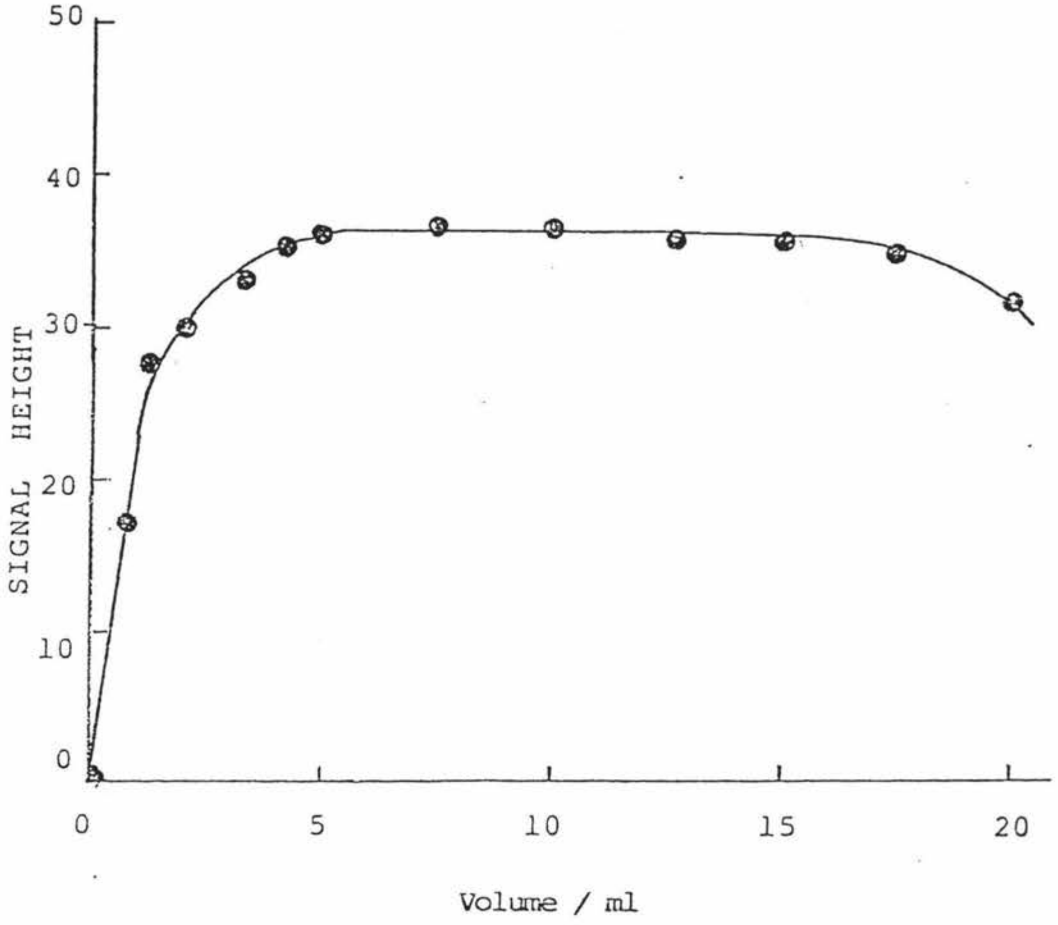


Fig. 3.5 Amount of Ascorbic Acid(1M) for Masking Fe

of selenium using hydride generation techniques in atomic absorption spectrometry. Satisfactory signals were obtained for 10 µg/L of selenium in the presence of 1600 mg/L of nickel(II).

In this work I have shown that it was possible to determine germanium using trisodium citrate to mask iron, nickel and the other metals in iron meteorites. Varying the volume of 1 M trisodium citrate solution determined the signal of 1 µg germanium standard in the presence of 10,000 µg iron and 1,000 µg nickel (typical values for class IA meteorites). The results are given in Fig. 3.6 and show a minimum usable volume of 10 ml of masking agent. To ensure that interfering elements can be masked completely, a little more trisodium citrate was usually added (up to about 15 ml) and the amount of trisodium citrate added is adjusted according to the sample volume in the reaction vessel.

Another important action of trisodium citrate is to act as a buffer to control the pH of the initial sample solution in the reaction vessel before generation. Otherwise, the sensitivity of the method would be effected. When 10 - 15 ml of 1M trisodium citrate was added, the acidity of the solution was about pH 1.5 - 1.75, a suitable range for generating germane.

III.3.5 Treatment of samples

Unlike waters and effluents, iron meteorites needs an appropriate method for the treatment of the samples in order to obtain a high recovery when they are analysed. Germanium is an extreme volatile

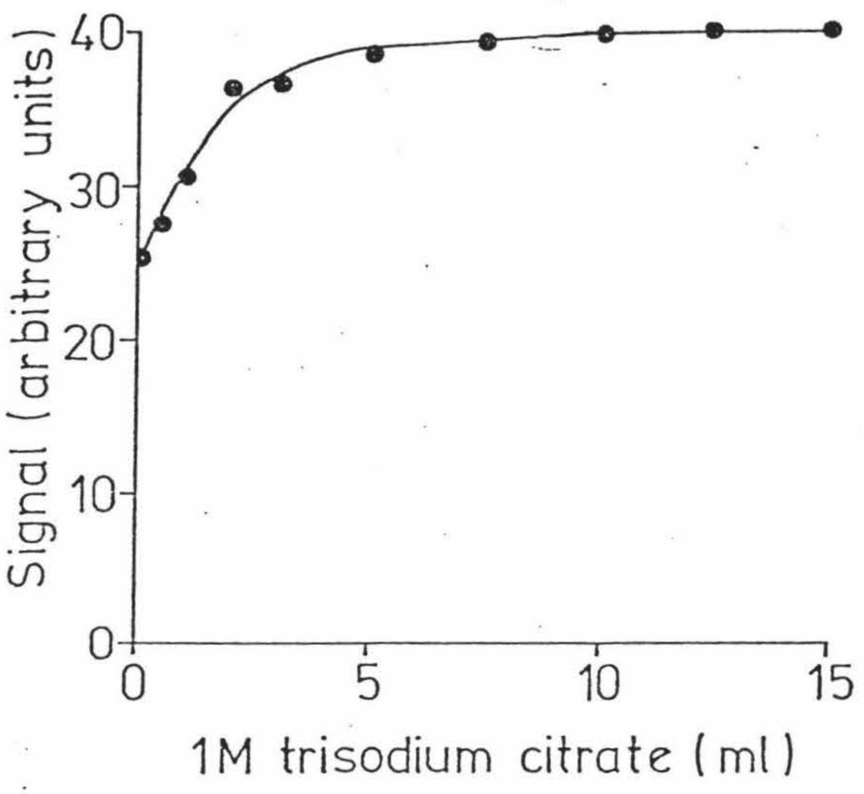


Fig. 3.6 Amount of Trisodium Citrate(1M) for Masking Interfering Elements

element, particularly as $GeCl_4$ which is easily lost even at room temperature. So the selection of an appropriate method for the digestion of the samples, is an important problem.

For metallic material samples, a very common attack technique is the use of inorganic acids. As we know, iron meteorites consist of iron, nickel, and other metals so that acid attack is sufficient to digest such samples. The kinds of acid used, of course, must be careful considered and tested. Different methods of digestion were carried out in this work and are detailed as follows:

i. Acid attack in an open container

A 0.5 - 1 g sample was accurately weighed and placed in a 50 ml glass beaker with 4 - 6 ml of concentrated HCl or HNO_3, respectively. It was heated on a hot plate until digestion was complete. After cooling, the solution was carefully transferred into a 50 or 100 ml volumetric flask (according to the weight of the samples) and diluted up to the mark with distilled water. The experimental results showed that the HCl attack took about 0.5 - 2 hours and the HNO_3 attack needed a period of about 4 - 6 hours.

ii. Acid attack under reflux

A condenser was fitted on a 50 ml Quickfit Erlenmeyer flask (see Fig. 3.7) in which was placed 0.5 - 0.8 g sample. Separate experiments were performed by addition of concentrated HCl, HNO_3 and aqua regia, respectively. Heating was continued until the sample had dissolved completely. The final volume was adjusted to 50 - 100 ml with distilled water according to the weight of the sample. This method needed a longer digestion time than that by acid attack in open containers. The results showed that HCl attack needed a short digestion time of about one hour or a little more, whereas HNO_3 attack needed a very long time about 6 - 15 hours and sometimes more than two days.

iii. Acid attack in a Teflon bomb

About 0.5 g sample which was accurately weighed, was placed in a 20 ml Teflon bomb with either concentrated HCl, HNO_3 or aqua regia, respectively. The top was screwed tightly and then the Teflon bomb was placed in a steel retaining cage. Heating was carried out in a drying oven at 105 ℃ for 24 hours for the digestion. Then the bomb was cooled to room temperature during a period of 8 hours in order to avoid losing the volatile elements when the top was opened. All the solution was carefully transferred into a volumetric flask and diluted up to the mark with distilled water.

iv. Fusion with sodium peroxide

A mixture of 0.5 g of meteorite powder (obtained by using a hacksaw) and 2 - 3 g sodium peroxide was placed in a 40 ml of platinum crucible, which was placed in a muffle furnace at 550 ℃ to fuse for a period of 1 hour. After cooling, distilled water was added drop by drop until all solid fusion had dissolved, then the solution was acidified with dilute nitric acid and transferred carefully into a volumetric flask. The final volume was adjusted with distilled water.

All the above solutions ultimately contained 1.5 - 2 M nitric acid. They were directly analysed by HGAAS without other treatment procedures.

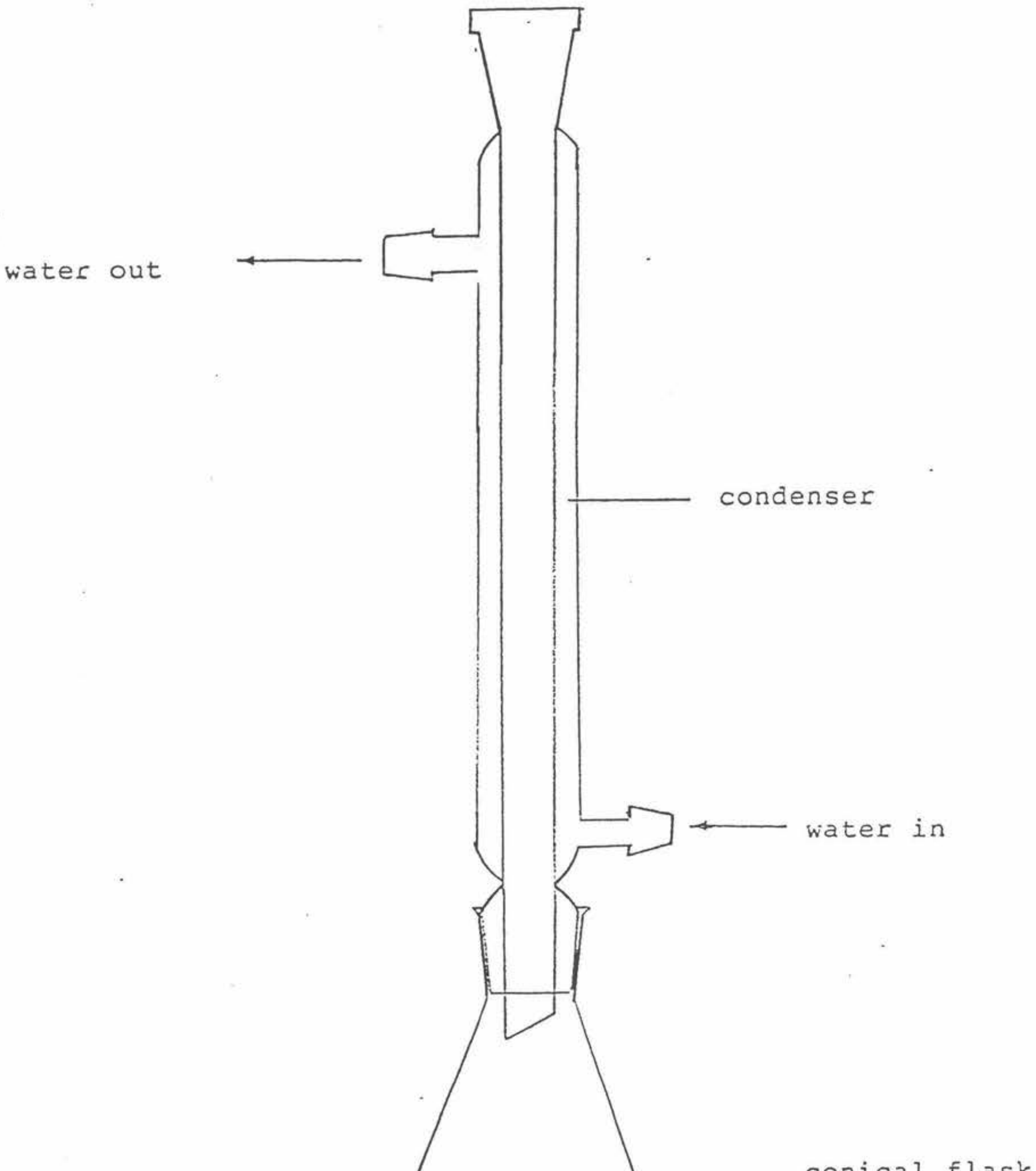


Fig.3.7 Apparatus for Digestion of Samples

Fusion of the sample with sodium peroxide gave a poor recovery. This technique seems to be on suitable for the digestion of iron meteorites. The possible reasons are that analyte elements form alloys with transition metals (like nickel, iron, cobalt, copper, etc.), and that analyte elements are oxidised at high temperature to form different oxidation states that influence hydride formation. Another possible reason is that the solution is transferred many times during the procedures and might lose analyte elements. It is fortunate that iron meteorite samples can be dissolved by other digestion methods because of their low silican content.

The use of special acid attack apparatus (with a reflux or a Teflon bomb) obtained better recovery than in the case of attack in open containers. The results are listed in Table 3.1. Acid attack in open containers was a simple and fast method but resulted in lose of volatile elements, and could not be used in this work, particularly in the case of germanium (only 10% recovery). Both acid attack with a reflux and a Teflon bomb were chosen as methods for the dissolvtion of iron meteorite samples.

Among acids which were tested for dissolving samples, hydrochloric acid gave a poor recovery because of the formation of $GeCl_4$, a very volatile compound. Aqua regia is used to attack many metals including antimony and germanium alloys because of the speed of the reaction, but according to my results, the method results in loss of 10% of the germanium. Nitric acid showed an excellent capability and gave good recovery that was nearly 100% as determined by comparison of my result for the "Toluca" meteorite, with that reported by Wasson [99].

I found that concentrated nitric acid sometimes was not able to react thoroughly with the sample because a number of metals form a protective coating of insoluble oxide, and in the experiment I saw that the resulting solution in the reaction apparatus contained black particles that would not dissovle, however long the reaction time. A mixture of a small amount of distilled water with the nitric instead of concentrated nitric acid, gave a satisfactory result. This dilute nitric acid not only was able to ensure a good recovery, but also saved digestion time. The results are listed in Table 3.1.

After the above experiments, the use of dilute nitric acid of ratio 1:3 ($H_2O:HNO_3$) was chosen for all samples. Acid attack with a Teflon bomb is suitable for a large number of samples because of the saving of time. On other hand, the reflux method is suitable when fewer samples are involved. There are no other differences between two methods.

III.4 A Comparison with the Other Methods

Analytical results for the germanium content of 22 iron meteorites were obtained by the use of the hydride generation atomic absorption method developed in this thesis. The germanium contents of 22 irons are listed in Table 3.2.

The relicates samples of the "Toluca" meteorite (class IA) gave a relative standard deviation (r.s.d.) of 3.9%. The relative error (r.e) was zero for this specimen as our value (246 µg/g) was exactly the same as that reported by Wasson [99]. Table 3.3 shows RNAA values reported by Wasson [99] and his values were used to assess the r.e. of our procedure. Since this r.e. was not based on a concentration reported for a true standard rock, it shows only the deviation of our

Table 3.1 Recovery and time consumption for different methods

METHOD	HCl		HNO_3		AQUA REGIA		Na_2O_2	
	Ge (ppm)	RECOVERY (%)	Ge (ppm)	RECOV. (%)	Ge (ppm)	RECOV. (%)	Ge (ppm)	RECOV. (%)
OPEN VESSEL	18.89	7.7	203.42	82.7	--	--	--	--
FUSION	--	--	--	--	--	--	45.70	18.6
UNDER A REFLUX	78.09	31.7	246.19	100	227.40	92.4	--	--
WITH A TEFLON BOMB	33.93	16	$\left(\begin{array}{c}HNO_3 : H_2O\\ 4 : 1\end{array}\right)$		208.08	84.6	--	--
			246.21	100				
	--	--	$\left(\begin{array}{c}HNO_3 : H_2O\\ 3 : 2\end{array}\right)$		--	--	--	--
	--	--	246.01	100	--	--	--	--

values from Wasson's data and does not take into account the inhomogeneity of the iron meteorites. Nevertheless, the agreement can be considered as highly satisfactory except perhaps in the case of the meteorites with very low germanium contents such as Class IVA and IVB. We conclude that our method can be used with confidence in the future for the determination of germanium in iron meteorites.

III.5 Summary and Conclusions

An analytical method which uses hydride generation in atomic absorption spectrometry has successfully been used for the determination of germanium in iron meteorites. This is the first time that HGAAS has been applied to study iron meteorites.

Reaction conditions were quite critical for the production of good yields of germane and the optimum conditions were studied and established for our instrument. A relatively stable hydride of germane was obtained in the presence of slight acidity (0.1 M HCl) coupled with a buffer solution (final pH 1.5 - 1.8) in the initial reaction solution. A simple and cheap flame system -- the nitrogen-hydrogen-air entrained flame was used for the determination of germanium by hydride generation. This flame provides a high degree of atomisation of germanium. Adjusting the gas flow rate can reduce the temperature of the flame and can keep the optimum atomisation temperature at about 700 ℃. The interferences from several metals and other hydride-forming elements were selectively investigated for the determination of germanium and it was found that these interfernces were so serious that

Table 3.2 Germanium contents of 22 iron meteorites

METEORITE	TYPE	RESULTS (ppm)	
		MINE	WASSON'S
CANYON DIABLO	IA	319.8	324*
TOLUCA	IA	246.19	246
WOODBINE	IB	113.13	114
ST. FRANCOIS	IC	238.81	246
COAHUILA	IIA	194.55	178
BILIBINO	IIB	156.7	---
DERRICK PEAK	IIB	160.59	135***
BALLINOO	IIC	95.90	94.4
CARBO	IID	73.09	87
ARLINGTON	IIE	65.45	64.9
CAPE YORK	IIIA	35.85	36
OWENS VALLEY	IIIB	49.60	46
CARLTON	IIIC	5.49	8.5
NANDAN	IIICD	297.56	293
PANETH'S IRON	IIIE	35.14	36**
STAUNTON	IIIE	32.86	---
NELSON COUNTY	IIIF	0.91	0.92
GIBEON	IVA	< 0.01	0.11
WEAVER MTS	IVB	< 0.01	0.085
MUNDERABILLA	ANOM	189.72	196
GLENORMISTON	ANOM	79.43	76
GAY GULCH	ANOM	9.0	10.7

* One of many values.

** From A.A.Smales et al (95).

*** From D.J.Malvin et al (103).

it was difficult to produce germane. A method of eliminating these interference involved the use of trisodium citrate to complex with interfering elements. A detection limit of 30 ng for germanium was attained by this analytical technique.

In Table 3.2 , we can see that the germanium contents which were determined by this technique are in remarkable agreetment with that obtained by other workers, except perhaps in the case of iron meteorites with very low germanium contents such as Class IV . The determination of low germanium contents in iron meteorites needs a large sample size, but this is difficult to achieve because of the scarcity of meteoritic material.

CHAPTER FOUR

SOME PRACTICAL APPLICATIONS OF GERMANIUM DETERMINATIONS IN METEORITES

CHAPTER FOUR

SOME PRACTICAL APPLICATIONS OF GERMANIUM DETERMINATIONS IN METEORITES

IV.1 Introduction

The method that I have developed for germanium determinations in meteorites has had several practical applications. These are enumerated in the following case histories.

VI.2 The Hanau Harbour "Meteorite".

A Mr Walther Zeitschel of West Germany recently offered to Prof.R.R.Brooks, a piece of meteorite alleged to have been a recent find in the River Main near the city of Hanau. The alleged circumstances of the find were as follows:

An iron meteorite weighing 86 g was alleged to have been found by Mr Zeitschel during the first half of April 1988 in a heap of river gravel on the banks of the River Main near Hanau, West Germany. The iron was said to have been detected by use of a metal detector. The heap of gravel is constantly replenished from a river dredging boat responsible for keeping open the shipping channels to the small river port of Hanau. The location of the discovery was on land owned by the Hanau Harbour Administration and not open to the general public. The site was situated close to the harbour area and has the co-ordinates of: 50 08′24"N and 8 54′23"E.

The meteorite has the typical ovaliform shape of a rounded river pebble. The original length before cutting, was 42 mm and the greatest width was 24 mm. The fusion crust had been removed and the surface was coated with a thin film of iron oxide of recent origin. The clean metal occasionally shows among the oxide coating.

A section of the meteorite was cut, polished, and etched with 5% nital (5% nitric acid in ethyl alcohol). There was no visible Widmanstatten pattern, but the surface of the iron shows dark linear markings which are typical of the well known Class IA meteorite Canyon Diablo.

Our suspicions were aroused by the strong compositional similarities between the Hanau Harbour Meteorite and Canyon Diablo. The respective values for germanium were 299 and 320 ppm and for other diagnostic elements such as cobalt were 4930 and 4830 ppm respectively. Neutron activation analysis in Canada produced respective values of 2.00 and 2.01 ppm iridium, 2.3 and 2.1 ppm osmium, 2.0 and 2.0 ppm rhodium, and 1.50 and 1.52 ppm gold. The data for the elemental contents are summarised in Table 4.1

Professor V. Buchwald of Copenhagen confirmed that the morphology and mineralogy of the meteorite was exactly the same as the highly specific Canyon Diablo iron.

The work has clearly shown that Dr Zeitschel perpetrated, or was the victim of, a fraudulent attempt to present a common meteorite as a new one.

Table 4.1 The data for the elemental contents of Canyon Diablo and Hanau Harbour

	CANYON DIABLO				HANAU	
	Wasson	Ryan	Ours	Smales	Ryan	Brooks
Ga	82	-	-	80	-	Not yet
Ge	324	-	320	322	-	299
Ir	1.90	2.10	_	-	1.90	-
Os	-	2.13	-	-	1.70	-
Au	-	1.52	-	-	1.50	-
As	-	10.1	-	-	11.6	-
Co	-	4830	-	-	4900	5700
Rh	-	2.00	-	-	1.9	-
Cu	-	-	169	125	-	163
Cr	-	-	10	9.4	-	10.3
Fe	-	-	91.0%	-	-	92.0%
Ni*	7.0-7.9%	-	8.1%	-	-	7.5%
Chemical Type	IA				IA	
Structural Type	Og				Og or Ogg	

* Very variable for different specimens of this mete

Concentrations in ppm except when otherwise stated

IV.3 The Derrick Peaks Shower

The Derrick Peaks area of Antarctica has been the source of several iron meteorites, all of which are presumed to have been part of the same meteoritic shower. Recently, two further meteorites were obtained from the same area and were provionally named Onnum Valley, and CM #66 (the catalogue number in the Canterbury Museum). My values for germanium in these and other meteorites from the same area are as follows: DP78009 - 135 ppm, DP78012 - 160 ppm, DP78014 - 161 ppm, DP78015 -162 ppm, DP78016 - 162 ppm, CM#66 - 162 ppm, Onnum Valley, 159 ppm. All of these meteorites are clearly of the same shower and should be so classified. They belong to Class IIB of iron meteorites.

IV.4 The Walker County Meteorite

We recently received a specimen of what was alleged to be the Walker County Type IIA iron meteorite. This was donated to us by the New York Museum of Natural History and is said by Wasson (1974) to contain 58 ppm germanium. I did however fail to find any trace of germanium in this specimen. It should also have had 3 ppm iridium by neutron activation work in Halifax, Canada reported <0.002 ppm of this element. The specimen in our possession is clearly not a meteorite.

IV.5 The Tassajara Meteorite

Prof. Brooks was recently given a specimen of a new iron meteorite named Tassajara (found in California). This specimen was supplied from the Meteorite Research Center at Tempe, Arizona. My germanium value of 301 ppm clearly indicated that this is a Class IA iron. The classification was confirmed by values of 8.8% for nickel, and 4438 ppm cobalt (obtained by A. Frankenberger and M. Hoashi), as well as a value of 1.53 ppm iridium obtained by neutron activation in Canada.

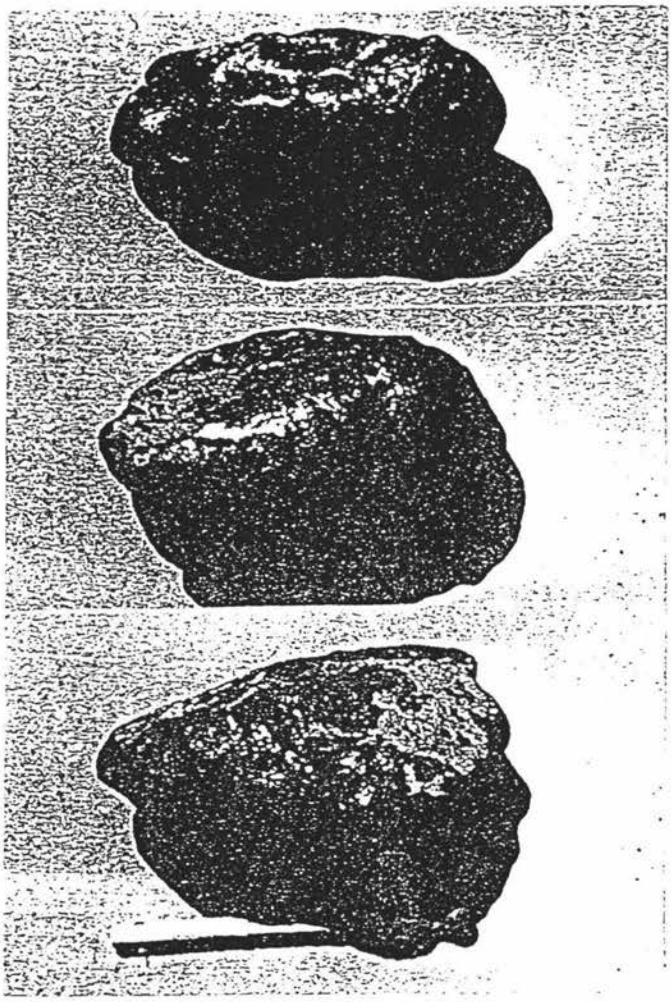


Fig. 4.1 Photographs of Hanau Harbour Iron Meteorite in Its Original State

IV.6 Conclusions

It is concluded that these brief case histories have illustrated the great usefulness of the HGAAS method for determining germanium quickly and cheaply in iron meteorites. The enormous cost of radiometric neutron activation analysis (RNAA) greatly restricts its potential use for classification of iron meteorites.

Fig 4.2 Photograph of a Cross Section of the Hanau Harbour Iron Meteorite Showing Plessite Bands

CHAPTER FIVE

SUMMARY AND GENERAL CONCLUSION

CHAPTER FIVE

SUMMARY AND GENERAL CONCLUSION

V.1 Summary of Methodology for Hydride Generation

For the purpose of the chemical classification study, a means of analysis is essentially required to obtain chemical composition parameters from iron meteorites. Numerous analytical data have been determined by radiochemical neutron activation analysis (RNAA) for iron meteorite samples, but this method is time-consuming and expensive. It is necessary to develop a simple and less expensive analytical method for determining hydride-forming elements such as germanium, that are very important for the classification of iron meteorites. Hydride generation coupled with atomic absorption spectrometry (HGAAS) was therefore chosen and developed. This technique has never been used previously in this field of research.

Eight hydride-forming elements, arsenic, bismuth, germanium, lead, antimony, selenium, tin and tellurium were studied in order to develop a programme of new classification methods for iron meteorites. The optimum conditions of generation of hydrides for these elements were studied and established to suit for this apparatus and instrument.

Table 2.7 shows that the detection limits of the above elements were in many cases better than that those obtained by others with the same method. Arsenic, germanium and lead were determined in iron meteorites using HGAAS. Values for germanium were particularly useful.

Due to inter-element interferences with above method, procedures for the reduction or elimiantion of such interferences were studied. Of these, the addition of trisodium citrate as a masking agent was successfully used for the determination of germanium in iron meteorites. After acid attack, the sample solution could be directly analysed for germanium without any separations. This first use of a nitrogen-hydrogen-air entrained flame applied for the atomisation of germanium, provided a satisfactory sensitivity.

Twenty-two iron meteorite samples were analysed by the above analytical technique and the results for the germanium contents were coincident with those obtained by Wasson [99].

To avoid losing the volatile elements during sample treatment, acid attack with dilute nitric acid in a flask, under reflux, or in a Teflon bomb was used for iron meteorite samples.

V.2 Problems in the Application of The Method to Iron Meteorites

Hydride generation in atomic absorption spectrometry is available to determine some hydride-forming elements in iron meteorites. These are all trace elements and have a wide distributions in iron meteorites. The arsenic, germanium, lead and antimony content ranges are listed in Table 5.1. Although arsenic, germanium and tin can be detected by this method, antimony has not been detected yet from 22 irons since the antimony content range is 0.003 - 2.2 ppm and is too low to be detected with this method. Class IV iron meteorites has a very low germanium content about (0.17 - 2.4 ppm) so that this element has not yet to be determined by HGAAS in this class.

The key to the problem is inter-element interferences, especially when analyte elements have a low content in samples. This is one of reasons why this technique is not able to detect antimony (or even germanium at low contents in iron meteorites).

Although citric acid as a masking agent was successfully used for the determination of germanium, this masking agent has its limitations and can only be used under critical conditions. For example, citric acid is not suitable for tellurium because of formation of a complex with this element and reduction of recovery.

Table 5.1 Some hydride-forming element ranges in iron meteorites

ELEMENT	RANGE(ppm)	MEAN(ppm)	s.r. OF MEAN
As	0.43 - 30.7	8.8	0.77
Ge	0.03 - 474	104.0	14.8
Pb	0.07 - 10.7	5.3	--
Sb	0.003 - 2.2	0.21	0.042

V.3 The Significance of the Method for Meteorite Research

Precise determination of element contents is a very important prerequisite for studies of iron meteorites. Many analytical techniques have been used for this purpose. None of these methods can universally detect all elements in samples.

However HGAAS is a viable alternative to RNAA for a number of elements, particularly germanium.

From the data from 22 iron meteorites, a satisfactory agreement was obtained with values previously obtained by RNAA. Hydride generation in atomic absorption spectrometry has many advantages: simpler operation, less expensive cost, speedier analysis, and a wider application than other methods that have been used for the study of iron meteorites.

V.4 Recommendations for Future Work

It is considered that further work is needed along the following lines:

1. Research of a suitable method for reduction and elimination of inter-element interferences in HGAAS.

2. Improvement of the apparatus for hydride generation and to lower detection limits.

3. Further research into other elements that have a clear potential for chemical classification of iron meteorites, and which have not been studied hitherto.

4. Further development of the method of hydride generation in atomic absorption spectrometry applied to other types of meteorite, including chondrites (stony meteorites) and pallasites.

REFERENCES

1 Marsh, J.

Account of a Method for Separating Small Quantities of Arsenic from Substances with which It May be Mixed

Edinburgh New Phil. J., 1836, 21, 229 - 236

2 van Loon, J.C.

Analytical Atomic Absorption Spectroscopy

____ Selected Methods

Academic Press, New York, 1980, 33, 60

3 Dalton, E.F.;and Malanoski, A.J.

Note on the Determination of Arsenic by Atomic Absorption by Arsenic Generation into an Argon-hydrogen Entrained Air Flame

At. Absorpt. Newsl., 1971, 10, 92 - 93

4 Holak, W.

Gas-sampling Technique for Arsenic Determination by Atomic-Absorption Spectrophotometry

Anal. Chem., 1969, 41, 1712 - 1713

5 Madsen, R.E.

Atomic Absorption Determination of Arsenic Subsequent to Arsenic Reaction with 0.01 M Silver Nitrate

At. Absorpt. Newsl., 1971, 10, 57 - 58

6 Kahn, H.L.;and Schallis, J.E.

Improvement of Detection Limits for As, Se and Other Elements with an Argon-hydrogen Flame

At. Absorpt. Newsl., 1968, 7, 5 -7

7 Hundley, H.K.;and Underwood, J.C.

Determination of Total Arsenic in Total Diet Samples

J. Assoc. Off. Anal. Chem., 1970, 53, 1176 - 1178

8 Fernandez, F.J.;and Manning, D.C.

The Determination of Arsenic at Sub-microgram Levels by Atomic Absorption Spectrophotometry

At. Absorpt. Newsl., 1971, 10, 86

9 Manning, D.C.

A High Sensitivity Arsenic Selenium Sampling System by Atomic Absorption Spectroscopy

At. Absorpt. Newsl., 1971, 10, 123 - 124

10 Pollock, E.N.;and West, S.J.

The Determination of Antimony at Submicrogram Levels by Atomic Absorption Spectrophotometry

At. Absorpt. Newsl., 1972, 11, 104 - 106

11 Chu, R.C.; Barron, G.P.;and Baumgarner, P.A.M.

Arsenic Determined at Sub-microgram Levels by Arsine Evolution and Flameless Atomic Absorption Spectrophotometry Technique

Anal. Chem., 1972, 44, 1476 - 1479

12 Thompson, K.C.;and Thomerson, D.R.
Atomic-absorption Studies on the Determination of Arsenic, Antimony,Bismuth,Germanium,lead,Selenium,Tellurium and Tin by Utilising the Generation of Covalent Hydrides
Analyst, 1974, 99, 595-601

13 Belcher, R.;Bogdanski, S.;Ghonaim, S.;and Townshend, A.
Molecular Emission Cavity Analysis(MECA): a New Flame-analytical Technique. IV. Determination of Arsenic and Antimony
Anal. Chim. Acta, 1974, 72, 183-187

14 Belcher, R.;Bogdanski, S;Henden, E.;and Townshend, A.
Elimination of Interferece in Determination of Arsenic and Antimony by Hydride Generation Using Molecular-Emission-cavity Analysis(MECA)
Analyst, 1975, 100, 522-523

15 Tsujii, K.;and Kuga, K.
Determination of Arsenic by Non-dispersive Atomic-Fluorescence Spectrometry with a Gas-sampling Technique
Anal. Chim. Acta, 1974, 72, 85-90

16 Tsujii, K.;and Kuga, K.
Improvemets in Non-dispersive Atomic-Fluorscence Spectrometry Determination of Arsenic and Antimony by A Hydride-generation Technique
Anal. Chim. Acta, 1978, 97, 51-57

17 Kobayashi,S.; Nakahara, T.;and Musha, s.
Non-dispersive Atomic-fluorescence Spectrometry of Trace Amount of Bismuth by Introduction of Its Gaseous Hydride into a permixed Aegon-(entrained-air)-Hydrogen Flame
Talanta, 1979, 26, 951-957

18 Nakahara, T.; Kobayashi, S.;and Musha, S.
Non-dispersive Atomic Fluorescence Spectrometry of Nanogram Amount of Antimony With a Hydride Generation Technique
Anal. Chim. Acta, 1978, 101, 275 - 384

19 Thompson, K.C.
The Atomic-fluorescence Determination of Antimony,Arsenic, Selenium and Tellurium by Using the Hydride Generation Technique
Analyst, 1975, 100, 307 -

20 Thompson, M.; Pahlavanpour, B.; Walton, S.J.;and Kirkbright, G.F.
Simultaneous Determination of Trace Concentrations of Arsenic, Antimony, Bismuth, Selenium and Tellurium in Aqueous Solution by Introduction of the Gaseous Hydrides into an Inductively Coupled Plasma Source for Emission Spectrometry.
Part I. Prehiminary Studies
Analyst, 1978, 103, 568 - 579

21 Thompson, M.; Pahlavanpour, B.; Walton, S.J.;and Kirkbright, G.F.
Simultaneous Determination of Trace Concentrations of Arsenic, Antimony, Bismuth, Selenium and Tellurium in Aqueous Solution by

Introduction of the Gaseous Hydrides into an Inductively Coupled Plasma Source for Emission Spectrometry.
Part II. Interference Studies
Analyst, 1978, 103, 705 - 713

22 Åström, O.
Flow Injection Analysis for the Determination of Bismuth by Atomic Absorption Spectrometry with Hydride Generation
Anal. Chem., 1982, 54, 190 - 193

23 Schmidt, F.J.;and Royer, J.L.
Sub-microgram Determination of As, Se, Sb and Bi by Atomic Absorption Using Sodium Borohydride Reduction
Ana. Lett., 1973, 6, 17 - 23

24 Fernandez, F.J.
Atomic Absorption Determination of Gaseous Hydride Utilising Sodium Borohydride Reduction
At. Absorpt. Newsl., 1973, 12, 93 - 97

25 Goulden, P.D.;and Brooksbank, P.
Automated Atomic-absorption Determination of Arsenic, Antimony and Selenium in Natural Water
Anal. Chem., 1974, 46, 1431 - 1436

26 Freeman, H.C.;and Uthe, J.F.
An Improved Hydride Generation Apparatus for Determination Arsenic and Selenium by Atomic-absorption Spectroscopy
At. Absorpt. Newsl., 1974, 13, 75 - 76

27 Corbin, D.R.;and Barnard, W.M.
Atomic-absorption Spectrophotometric Determination of Arsenic and Selenium in Water by Hydride Generation
At. Absorpt. Newsl., 1976, 15, 116 - 120

28 Landsford, M.; McPherson, E.N.;and Fishman, M.J.
Determination of Selenium in Water
At Absorpt. Newsl., 1974, 13, 103 - 105

29 Pierce, F.D.; Lamoreaux, T.C.; Brown, H.R.; and Frazer, R.S.
Automated Technique to Sub-microgram Determination of Selenium and Arsenic in Surface Waters by Atomic-absorption Spectroscopy
Appl. Spectrosc., 1976, 30, 38 - 42

30 Shaikh, A.U.;and Tallman, D.E.
Determination of Sub-microgram-per-litre Quantities of Arsenic in Water by Arsine Generation Followed by Graphite-furnace Atomic-absorption Spectrometry
Anal. Chem., 1977, 49, 1093 - 1096

31 Bédard, M.;and Kerbyson, J.D.
Determination of Trace Bismuth in Copper by Hydride-evolution Atomic-absorption Spectrophotometry
Anal. Chem., 1975, 47, 1441 - 1444

32 Baird Application Report
No.461, 1977, Baird-Atomic, Brantree, Essex.

33 Drinkwater, J.E.

Atomic-absorption Determination of Bismuth in Complex Nickel-base Alloys by Generation of Its Covalent Hydride

Analyst, 1976, 101, 672 - 677

34 Rooney, R.C.

Determination of Bismuth in Blood and Urine

Analyst, 1976, 101 , 749 - 752

35 Berman, E.

Biochemical Applications of Flame-emissin and Atomic-absorption Spectroscopy

Appl. Spectrosc., 1975, 29, 1 - 9

36 Orheim, R.M.;and Bovee, H.H.

Atomic-absorption Determination of Nanogram Quantities of Arsenic in Bioological Media

Anal. Chem., 1974, 46, 921 - 922

37 Clinton, O.E.

Determination of Selenium in Blood and Plant Material by Hydride Generation and Atomic-absorption Spectroscopy

Analyst, 1977, 102, 187 - 192

38 Kokot, M.L.

Modification of a Hydride-generation Apparatus for Rapid Determination of Arsenic in a large Number of Geochemical and Other Samples

Ai. Absorpt. Newsl., 1976, 15 , 105 - 106

39 Guimout, J.; Pichette, M.;and Rheaume, N.
Determination of Arsenic in Water, Rocks and Sediments by Atomic-absorption Spectrophotometry
At. Absorpt. Newsl., 1977, 16, 53 - 57

40 Rubeska, I.;and Hlavinkova, V.
Determination of Arsenic in Rocks and Soils by Atomic-absorption Spectrophotometry Using the MHS-1 Automated Hydride System
At. Absorpt. Newsl., 1979, 18, 5 - 7

41 Hermann, B.
Simple and Rapid Decomposition Technique for Atomic-Absorption Spectrophotometric Determination of Selenium in Gloss by Hydride Generation
At. Absorpt. Newsl., 1977, 16, 44 - 45

42 Partsch, P.
Die Meyeoriten Oder vom Himmel Gefallenen Steine und Eisenmassen im K.K. Hof-Mineralien-Kabinett zu Wien
1843, 162 p.

43 Shepard, C.U.
Report on Meteorites
American J. of Science, Series 2, 1846, 377 - 392

44 Rose, Gustaf
Systematisches Verzeichnis der Meteoriten in den Mineralogischen Museum der Universität zu Berlin
Annalen der Pysik, 1863, 118, 420 - 421

45 Tschermak, G.

Die Meteoriten des K. K. mineralogischen Museums am 1. October 1872

Mineralogische Mittheilungen, 1872, 165 - 172

46 Brezina, A.

Die Meteoriten sammlung des K. K. naturhistorischen Hofmuseums am 1. Maj. 1895

Annalen des Naturhictorischen Hofmuseum,
Wien., 1896, <u>10</u>, 231 - 370

47 Prior, G.T.

The Classification of Meteorites

Mineral. Mag., 1920, <u>19</u>, 51 - 63

48 Yavnel, A.A.

On the Degree of Equilibration Reflected in the Ferromagnesian Silicates in Ordinary Chondrites

Meteoritka, 1968, <u>28</u>, 19 - 29
or Translated in Meteoritica, 1968, <u>5</u>, 153 - 167

49 Mason, B.

Handbook of Elemental Abundances in Meteorities

(edited volume)

Gordon and Breach, New York, 1971, 555

51 Buchwald, V.F.;and Munck, S.

Catalogue of Meteorites in Mineralogical Museum of the University

Copenhagen Anal. Geol., 1965, <u>1</u>, 81

50 Lovering, J.F.; Nichiporuk, W.; Chodos, A;and Brown, H.
The Distribution of Gallium, Germanium, Cobalt, Chromium and Copper in Iron and Stony-iron Meteorites in Relation to Nickel Content and Structure
Geochim. Cosmochim. Acta, 1957, 11, 263 - 278

52 Yanel, A.A.
On the Classification of Iron Meteorites on the Basis of Structure
Meteoritika, 1965, 26, 140 - 145

53 Wasson, J.T.
The Chemical Classification of Iron Meteorites
I. A Study of Iron Meteorites with Low Concentrations of Gallium
Geochim. Cosmochim. Acta, 1967, 31, 161 - 181

54 Goldstein, J.I.
The Classification of Iron Meteorites in:
Millman, P. M. (Ed): Meteorite Research
Dordrecht: Reidel, 1969, 721 - 737

55 Wasson, J.T.;and Kimberlin, J.
The Chemical Classification of Iron Meteorites
II. Irons and Pallasites with Germanium Concentrations between 8 and 100 ppm
Geochim. Cosmochim. Acta, 1967, 31, 2065 - 2093

56 Scott, E.R.D.

Chemical Franctionation in Iron Meteorites and Its Interpretation

Geochim. Cosmochim. Acta, 1972, 36, 1205 - 1236

57 Buchwald, V.F.

Handbook of Iron Meteorites

Berkeley, University of California Press, 1975

58 Scott, E.R.D.

Primary Franctionation of Elements Among Iron Meteorites

Geochim. Cosmochim. Acta, 1978, 42, 1447 - 1458

59 Liddle, J.r.; Brooks, R.R.;and Reeves, R.D.

Some Parameters Affecting the Hydride Generation Method for Arsenic Determinations by Atomic Absorption Spectrophotometry

J. Ass. Off. Anal. Chemist., 1980,63, 1175 - 1180

60 Halicz, L.

Determination of Germanium in Silicate Rocks and Sulphide Ores by Hydride Generation and Flame Atomic-absorption Spectrometry

Analyst, 1985, 110, 943 - 946

61 Hinners, T.A.

Arsenic Speciation: Limitations with Direct Hydride Analysis

Analyst, 1980, 105, 751 - 755

62 Braman, R.S.; Johnson, D.L.; Foreback, C.C.; Ammons, J.M.; and Bricker, J.L.

Separation and Determination of Nanogram Amounts of Inorganic Arsenic and Methylarsenic Compounds

Anal. Chem., 1977, 49, 621 - 625

63 Vijan, P.N.;and Wood, G.R.

Semi-automated Determination of Lead by Hydride Generation and Atomic-absorption Spectrophotometry

Analyst, 1976, 101, 966 - 973

64 Jin, K.; Taja, M.; Yoshida, H.;and Hikime, S.

Determination of Trace Amounts of Lead by Atomic-absorption Spectrometry after the Hydride-evolution Process

I. Enhancement of Sensitivity by the Combined Use of Dichromate Hydrogen Peroxide, Persulphate or Permanganate with Sodium Tetrahydroborate

Bunseki Kagaku, 1978, 27, 759 - 764

65 Jin, K.;and Taga, M.

Determination of Trace Amounts of Lead by Atomic-absorption Spectrometry after the Hydride-evolution Process

II. Investigation of Same Fundamental Conditions for Determination of Lead with Hydride-evolution-atomic-absorption Spectrometry, and Application to Complex Samples

Bunseki Kagaku, 1980, 29, 522 - 526

66 Jin, K.

Determination of Lead by Continuous-flow HYDRIDE Generation and Atomic Absorption Spectrometry

Anal. Chim. Acta, 1982, 143, 229 - 236

67 Miyazaki, A.; Kimura, A.;and Umezaki, Y.

Determination of Sub-microgram Amounts of Arsenic and Antimony (in Sea-water and Waste Water) by D.C. Plasma-air Emission Spectrometry

Anal. Chim. Acta, 1977, 90, 119 - 125

68 Vogel, A.I.

A Text Book of Quantitative Inorganic Analysis

3rd Edition, Longmans, Green & Co., London

1961, 796 - 797

69 Yamamoto, Y.; Kumamaru, T.; Hayashi, Y.;and Kamada, T.

Rapid and Sensitivity Atomic-absorption Determination of Arsenic by Arsine-argon-hydrogen Flame System with Use of Zinc-powder Tablets as Reducts

Bull. Chem. Soc. Japan, 1973, 46, 2604 - 2605

70 Jolly, W.L.

The Preparation of the Volatile Hydrides of Groups IV-A and V-A by Means of Aqueous Hydroborate

American J. Chem. Soc., 1961, 83, 335 - 337

71 Braman, R.S.; Justen, L.L.;and Foreback, C.C.

Direct Volatilisation-spectral Emission-type Detection System for Nanogram Amounts of Arsenic and Antimony

Anal. Chem., 1972, 44, 2195 - 2199

72 Smith, A.E.

Interfernces in the Determination of Elements that From Volatile Hydrides with Sodium Borohydride Using Atomic-absorption Spectrophotometry and the Argong-hydrogen Flame

Analyst, 1975, 100, 300 - 306

73 Pierce, F.D.;and Brown, H.R.

Comparison of Inorganic Interferences in Atomic-absorption Spectrophotometric Determination of Arsenic and Selenium

Anal. Chem., 1977, 49, 1417 - 1422

74 Pierce, F.D.;and Brown, H.R.

Inorganic Interference Study of Automated Arsenic and Selenium Determination with Atomic-absorption Spectrometry

Anal. Chem., 1976, 48, 693 - 695

75 Kirbright, G.F.;and Taddia, M.

Application of Masking Agents in Minimising Interferences from Some Metal Ions in the Determination of Arsenic by Atomic Absorption Spectrometry with the Hydride Generation Technique

Anal. Chim. Acta, 1978, 100, 145 - 150

76 Welz, B.;and Melcher, M.

Mechanisms of Transtion Interferences in Hydride Generation Atomic-absorption Spectrometry

Analyst, 1984, 109, 569 - 572, 573 - 576, 577 - 579

77 Bye, R.

Releasing Effect of Iron(III) and Other Oxidants on the Interference from Nickel in the Determination of Selenium by Hydride Generation Atomic Absorption Spectrometry

Analyst, 1986, 111, 111 - 113

78 Liddle, J.R.

Arsenic and Other Elements of Geothermal Origin in Taupo Vocanic Zone

Ph. D Thesis, Massey University, New Zealand, 1982

79 Fleming, H.D.;and Ide, R.G.

Determination of Volatile-hydride-forming Metals in Steel by Atomic-absorption Spectrometry

Anal. Chim. Acta, 1976, 83, 67 - 82

80 Smith, R.

Use of Hydride-generation Technique for the Atomic-absorption Determination of Lead in Drinking Water

At. Spectro., 1981, 2, 155 - 158

81 Knudson, E.J.;and Christian, G.D.

A Note on the Determination of Arsenic Using Sodium Borohydride

At. Absorpt. Newsl., 1974, 13, 74

82 Knudson, E.J.;and Christian, G.D.
Flameless Atomic-absorption Determination of Volatile Hydrides Using Cold-trap Collection
Anal. Letter, 1973, 6, 1039 - 1054

83 Castillo, J.R.; Lanaja, J.;and Aznarez, J.
Determination of Germanium in Coal Ashes by Hydride Generation and Flame Atomic-absorption Spectrophotometry
Analyst, 1982, 107, 89 - 95

84 Castillo, J.R.; Lanaga, J.; Martinez, M.C.;and Aznarez, J.
Flame Atomic-absorption Spectroscopic Determination of Antimony in Atmospheric Particulates by Using Direct Atomisation of the Covalent Hydride
Analyst, 1982, 107, 1488 -

85 Martinez, M.C.;and Castillo, J.R.
Determination of Antimony in Mineral Oils and Ores by Hydride Generation Atomic Absorption with Direct Atomisation of the Covalent Hydride
Atomic. Spectro., 1983, 4, 63 - 65

86 Castillo, J.R.; Mir, J.M.; Martinez, M.C.; Val, J.;and Colón, M.P.
Influence of Oxidising Agents in Lead Determination by Hydride Generation Direct Flame Atomic Absorption Spectroscopy
Mikrochimica Acta (Wien), 1985, 1, 253 - 263

87 Castillo, J.R.; Mir, J.M.; Val, J.; Colón, M.P.;and Martinez, C.

Study of Interferences in the Determination of Lead by Hydride Generation - Direct Flame Atomic-absorption Spectrometry When Oxidising Agents are Employed to Increase the Sensitivity

Analyst, 1985, 110, 1219 - 1221

88 Parisis, N.E.;and Heyndricky, A.

Method for Improving the Sensitivity and reproducibility of Hydride-forming Elements by Atomic Absorption Spectrometry

Analyst, 1986, 111, 281 - 284

89 Jain, A.V.; Gordon, R.B.;and Lipschutz, M.E.

Hardness of Kamacite and Shock Histories of 119 Meteorites

J.Geophys. Res., 1972, 77, 6940 - 6954

90 Fujita, K.;and Takada, T.

Effect of Temperature on Generation and Decomposition of the Group Vb Element Hydride and Estimation of the Kinetic Stability of Gaseous Bismuth Hydride by Atomic-absorption Spectrometry

Talanta, 1986, 33, 203 - 207

91 Dedina, J.;and Rubeska, I.

Hydride Atomisation in a cool Hydrogen-oxygen Flame Burning in a Quartz-tube Atomiser

Spectrochim. Acta, Part B, 1980, 35, 119 - 125

92 Welz, B.;and Melcher, M.

Investigations on Aomisation Mechanisms of Volatile Hydride-forming Elements in a Heated Quartz Cell

Analyst, 1983, 108, 213 - 224

93 Brooks, R.R.; Persley, B.J.;and Kaplan, I.R.
Ammonium Tetramethylene Dithiocarbamate Isobuthyl Methyl Ketone Extraction System for the Determination of Trace Elements (cobalt copper, iron, nickel, lead and zinc) in Saline Waters by Atomi-absorption Spectrophotometry
Talanta, 1967, 14, 809 - 816

94 Goldberg, E.; Vchiyama, A.;and Brown, H.
The Distribution of Nickel, Cobalt, Gallium, Palladium and Gold in Iron Meteorites
Geochim. Cosmochim. Acta, 1967, 31, 673 - 720

95 Smales, A.A.; Mapper, D.;and Fouche, K.F.
The Distribution of Trace Elements in Iron Meteorites as Determined by Neutron Activation
Geochim. Cosmochim. Acta, 1967, 31, 673 - 720

96 Brooks, R.R.; Siriwardena, A.;and Lee, J.
A Plasma Emission Method for Determining Elemental Constituents of Geological Materials with a High Iron Content
Chem. Geol., 1985, 53, 31 - 35

97 Godden, R.G.;and Thomerson, D.R.
Generation of Covalent Hydrides in Atomic-absorption Spectroscopy
Analyst, 1980, 105, 1137 - 1156

98 Bye, R.

Citric Acid as a Masking Agent for High Concentrations of Nickel in the Determination of Selenium by Hydride Generation Atomic-absorption Spectrometry

Analyst, 1985, 110, 85 - 86

99 Wasson, J.T.

Meteorites

---Classification and Properties

Springer-Verlag, New York, 1974

100 Brooks, R.R.; Hoashi, M. Wilson, S.M.;and Zhang, R.

Extraction into Methylisobutyl Ketone of Methyl Complexes with Ammonium Pyrrolidine Dithiocarbamate Formed in Strogly Acidic Media

Anal. Chim. Acta, 1989, 217, 165 - 170

101 Aggett, J.;and Agpell, A.C.

The Determination of Arsenic(III) and Total Arsenic by Atomic-absorption Spectroscopy

Analyst, 1976, 101, 341 - 347

102 Bye, R.

Iron(III) Releasing Agent for Copper Interference in the Determination of Selenium by Hydride-generation Atomic Absorption Spectrometry

Anal. Chim. Acta, 1987, 192, 115 - 117

103 Malvin, D.J.; Wang, D.;and Wasson, J.T.

Chemical Classification of Iron Meteorites---X. Multielement Studies of 43 Irons, Resolution of Group IIIE from IIIAB, and Evaluation of Cu as a Taxonomic Parameter

Geochim. Cosmochim. Acta, 1984, 48, 785 - 804