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

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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 the 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.

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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:

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

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

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

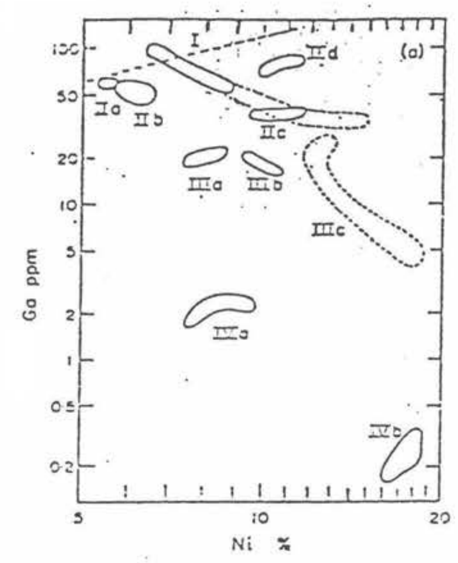

Fig. 1.1

Plot of Ga vs. Ni for Iron Meteorites

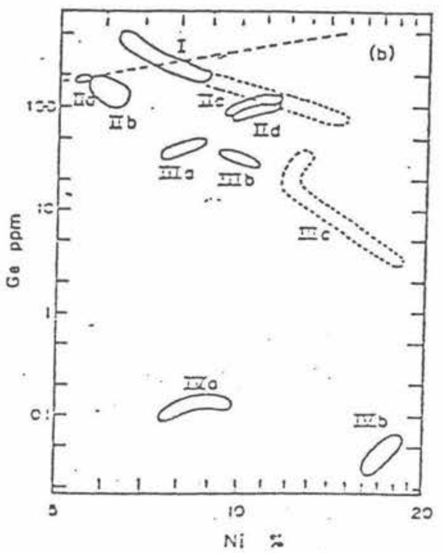

Fig. 1.2

Plot of Ge vs. Ni for Iron Meteorites

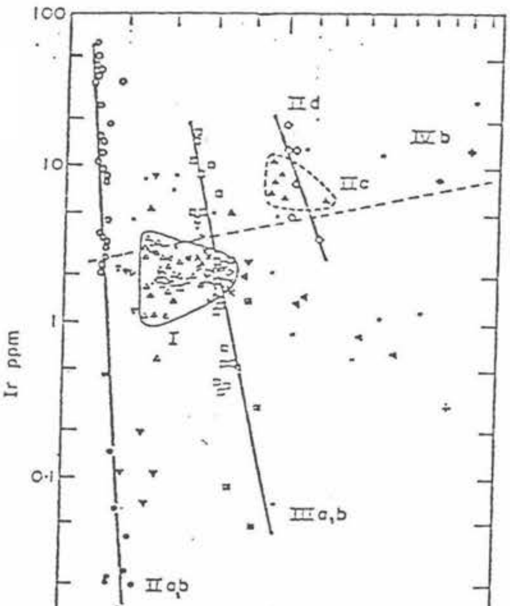

Fig. 1.3

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.