QUANTIFICATION OF GALLIUM, INDIUM AND THALLIUM IN METEORITES AND OTHER GEOLOGICAL MATERIALS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

A Thesis Presented in Partial Fulfilment of
the Requirements for the Degree of Doctor of
Philosophy at Massey University

MASSEY UNIVERSITY
NEW ZEALAND

Xun Guo

1993

ABSTRACT

Methods of solvent extraction have been developed for the determination of gallium, indium, and thallium in meteorites and other geological materials. The extraction of gallium is based on forming a chloro complex in HCl solution and extraction into MIBK. Indium was extracted into the same solvent as an iodo complex in an HBr + KI medium to which KOH had been added. Thallium was also extracted as an iodo complex from a H_2SO_4 + KI medium with addition of K_2HPO_4 as a salting out agent. Serious interference from iron(III) was eliminated by adding KI to reduce this element to its divalent state that was not extractable into the organic phase.

Graphite furnace atomic absorption spectrometric techniques were employed to determine these three elements in the MIBK phase after extraction from the aqueous phase. Very low limits of detection (l.o.d.) were obtained with these methods. It was possible to lower the l.o.d for these elements either by increasing the aqueous/organic phase ratio before extraction, or by multiple loading injections.

Using the developed methodology, gallium, indium, and thallium were quantified in iron and chondritic meteorites as well as in Cretaceous/Tertiary boundary clays, and some volcanic emissions.

The data for thallium abundances in 49 iron meteorites were the first ever recorded for this type of meteorite and allowed for taxonomic separation of the various groups of irons.

Indium abundances were only recorded in six chondrites because of the very low concentrations in iron meteorites.

My data for thallium and other elements were used to classify the previously non-studied Manitouwabing iron meteorite.

All three Group IIIA elements were determined in Cretaceous/Tertiary boundary clays and it was shown that these and other chalcophile elements have an abundance greater than that which would have been expected from either a volcanic or impact-derived source. Possible sources of this enrichment are discussed.

ACKNOWLEDGEMENTS

I would like to acknowledge the following persons:

Grateful thanks are due to my supervisors, Professor Robert R. Brooks and Associate Professor Roger D. Reeves, for accepting me as a PhD student in 1990. I appreciate their advice, assistance, and encouragement during all my studies. I shall never forget their kind help, particularly with my English that was deficient in the earlier stages of the work.

I thank Dr. T.N.M. Waters, Vice-Chancellor of Massey University, for his encouragement, assistance and his kind help since I arrived in New Zealand, particularly in providing me with a Vice-Chancellor's PhD research Scholarship to enable me to complete this project.

My thanks are also due to members of my family: my wife, Xiaohong Fan and my son, Tony F. Guo for their continual moral support in every way. I am also grateful to my parents, Linying Zhou and Zishong Guo, as well as my sister Chun Guo for their encouragement and support, particularly for initially taking care of my son when my wife and I first left China.

Finally I would like to thank all the people I have worked with for their friendship and encouragement.

LIST OF TABLES

LIST OF FIGURES

CONTENTS

PART ONE
GENERAL INTRODUCTION

PART TWO

DETERMINATION OF GROUP IIIB ELEMENTS BY HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY

PART THREE

DEVELOPMENT OF SOLVENT EXTRACTION PROCEDURES FOR ATOMIC ABSORPTION SPECTROMETRIC QUANTIFICATION OF GROUP IIIB ELEMENTS

SECTION III-1 GALLIUM

SECTION III-2 INDIUM

SECTION III-3 THALLIUM

PART FOUR
GROUP IIIB ELEMENTS IN METEORITES

PART FIVE
GROUP IIIB ELEMENTS IN CRETACEOUS-TERTIARY BOUNDARY CLAYS

PART SIX

PART ONE

GENERAL INTRODUCTION

I-1 INTRODUCTION

I-1-1 Discovery of Group IIIB Elements

The French chemist Lecoq de Boisbaudran who with Bunsen, Kirchoff and Crookes ranks as one of the founders of the science of spectroscopy discovered gallium in 1875 [1,2]. For some fifteen years he had been studying spectra and had found that the spectral lines emitted by incandescent vapours of different metals of one family were repeated with similar regular variations and a common general pattern. Anxious to identify this law for the aluminium family, and to discover one of the missing elements between aluminium and thallium, he sought the new element among the minor constituents of minerals. In the same year Mendeleev realised that gallium corresponded to his eka-aluminium and further studies of its properties revealed a remarkable correspondence between the properties predicted and found.

The first appreciable quantity (over 1 g) of gallium metal was isolated from several hundred kilograms of crude zinc blende. It involved dissolution in acid, deposition with zinc, precipitation of hydroxides, dissolution of the precipitate in hydrochloric acid, co-precipitation with ZnS using H_2S, repeated precipitation of hydroxide, dissolution in caustic potash and finally electrolysis.

Indium was discovered [1,3] in 1863 by F.Reich, a Professor of Physics at the Freiberg School of Mines, and his assistant H.T.Richter. They were examining samples of zinc blendes from Freiberg for thallium. Spectrographic examination of a crude zinc chloride liquor showed a brilliant indigo blue line which had not been observed before. After separation of this new element they named it indium from its flame coloration. Separation of the new element was achieved by cautiously heating a mixture of indium oxide and sodium carbonate on charcoal by means of a blow pipe. A pure sample was also isolated from impure zinc. Unlike aluminium which had been known to be present in the earth's crust for about a hundred years before its isolation, indium was discovered and isolated in the same year.

Thallium was first discovered in 1861 by William Crookes. From spectroscopic examination of some residues from a sulphuric acid plant he observed and described a bright-green line that flamed into view and quickly disappeared. He concluded that the material must contain a new element. The green line in the spectrum recalled the colour of spring vegetation and so he called the element thallium from the Greek *thallas*, a young twig. He announced his discovery in the journal that he founded and edited [4]. About the same time, Crookes and a French chemist C.A. Lamy isolated metallic thallium in May 1862 and independently observed the green line in the emission spectrum.

I-1-2 Chemistry of Group IIIB Elements

To develop and understand analytical methods for the group IIIB elements, some particular properties of the elements and their compounds should be first considered.

Solid gallium has a slightly bluish appearance and the liquid has a whiter colour rather like solid silver. Indium is silvery-white with a bluish tinge and has a brilliant metallic lustre. It is ductile and softer than lead. Thallium is greyish-white, heavy, soft, readily moulded - even by hand - and ductile. The melting and boiling points of gallium, indium and thallium are given in Table I-1.

Table I-1 Melting and Boiling Points of Ga, In and Tl

Element	m.p.(°C)	b.p.(°C)
Ga	29.8	2250
In	156.2	2070
Tl	302.4	1453

Chemically gallium is similar to zinc and less reactive than aluminium. It does not corrode in the air owing to an invisible surface film of oxide. At red heat in dry air or oxygen the surface tarnishes to a greyish-blue, due to a superficial coating of oxide. Complete oxidation in dry oxygen occurs at about 1000°C. Deoxygenated water has no effect at 100°C, but oxidation by water occurs at 200°C in an autoclave.

Pure gallium is slowly attacked by dilute mineral acids. It is soluble in hot nitric, concentrated hydrofluoric and hot concentrated perchloric acids. Mixtures of HCl + HNO_3 and HCl + $HClO_4$ can dissolve it rapidly. The gallate anion is formed when the metal is reacted with aqueous alkali, hydrogen and an alkali metal.

The amphoteric character of gallium is one of its principal characteristics and distinguishes it from indium and thallium. Gallium oxide is more acidic than alumina, so gallate(III) solutions are less susceptible to hydrolysis than aluminates. Advantage is taken of this difference in the commercial separation from aluminium.

Gallium salts are generally very soluble in acid solution. For example, a quantity of more than 13 g $GaCl_3$ dissolves in 100 g of a saturated aqueous solution of HCl at room temperature. Halogens, except iodine, react readily even in the cold.

Indium is stable in air or oxygen, but on heating strongly it burns with a non-luminous blue-red flame to give indium(III) oxide. On exposure to the atmosphere, a thin tenacious film forms, similar to the one appearing on aluminium but readily soluble in hydrochloric acid. The metal surface remains bright up to a little above its melting point.

At higher temperatures a surface oxide is formed. It does, however, oxidize at ordinary temperatures in moist air containing CO_2, especially if the metal is contaminated with iron.

Indium dissolves slowly in cold dilute mineral acids, more readily in hot dilute or concentrated acids, to give indium(III) salts and hydrogen. Indium dissolves in hot nitric acid with formation of oxides and nitrogen. It is also soluble in acetic acid and oxalic acid. The chemical reactivity of indium metal is less than would be expected from its electrode potential.

When heated, indium reacts with the halogens, sulphur, selenium, nitrogen and phosphorus. It reacts with atomic hydrogen and atomic nitrogen to give hydride and nitride respectively.

The toxicity of compounds of gallium and indium is low and depends upon the type of compound and the means of administration.

In moist air at normal temperatures, thallium quickly becomes covered with a grey film of thallous oxide (Tl_2O) which turns brown at 100°C. The effects of pollutants on the atmospheric corrosion of thallium have been studied. At room temperature, oxygen gives both oxides; ozone gives Tl_2O_3. Thallium is unaffected by dry oxygen or nitrogen, and by water containing no air or oxygen. Water containing dissolved air or oxygen rapidly corrodes the metal to the hydroxide, TlOH.

Aqueous hydrogen halides act weakly on thallium on account of the poor solubility of the monohalides. It dissolves readily in dilute sulphuric acid and most rapidly in 0.25 M nitric acid.

Thallium does not combine with boron, carbon, silicon or carbon dioxide. It begins to react with hydrogen at 600°C. Atomic hydrogen is absorbed by the metal to form an unstable hydride. The metal reacts with the halogens at ordinary temperatures, but reaction is slow for all except fluorine.

Thallium compounds are toxic, thallous ion solutions exceedingly so. Toxic effects have been studied in bacteria, animals and humans.

I-1-3 Geochemistry of Group IIIB Elements

The primary geochemical differentiation of elements was first suggested by Goldschmidt [5]. In his system, an element may be classified into four groups according to its geochemical affinity: siderophile, chalcophile, lithophile and atmophile. The group IIIB elements, gallium , indium and thallium, are chalcophile. The geochemical character of an element is largely governed by the electronic configuration of its atoms and hence is closely related to its systematic position in the Periodic Table. For example, the chalcophile elements are those of the boron subgroup whose ions have 18 electrons in the outer shells.

Gallium, indium and thallium have a low abundance in the Earth's crust and tend to occur at low concentrations in sulphide minerals rather than as oxides, though gallium is also found associated with aluminium in bauxite [6].

Gallium (19 μg/g) in the earth's crust is about as abundant as N, Nb, Li and Pb, and it is twice as abundant as boron (9 μg/g) but is more difficult to extract because of the absence of major gallium-containing ores. The highest concentrations of this element (0.1-1%) are in the mineral germanite (a complex sulphide of Zn, Cu, Ge and As). Concentrations in sphalerite (ZnS), bauxite, or coal, are a hundredfold less. Gallium always occurs in association with either zinc or germanium, its neighbours in the Periodic Table, or with aluminium in the same group. It was formerly recovered from flue dusts emitted during sulphide roasting or coal burning (up to 1.5% gallium) but is now obtained as a byproduct of the vast aluminium industry since bauxites contain 0.003-0.01% gallium. Comprehensive surveys of the occurrence of gallium in various ores, rocks and minerals have been presented and summarised by several workers [5,7-9]. The relatively small proportion of gallium not associated with aluminium, occurs in certain sulphide minerals. This reflects the increasingly chalcophilic character of the main group IIIB elements.

Indium as a metal does not occur naturally, and it does not form its own minerals. It occurs, however, as trace amounts in most zinc blendes and tin ores. In the combined state it is widely distributed but in minute quantities. Its abundance in the Earth's crust (10 μg/g) is about the same as silver. It has been found in many countries - Russia, Finland, Sweden, Japan, Germany, Italy, Peru, Canada and the United States. Indium (0.21 μg/g) is similar in abundance to antimony and cadmium.

Indium is found in minute amounts in many minerals, most of which contain less than 0.1%, though pegmatite dikes of western Utah are reported to contain up to 2.8% indium. In minerals, indium is distinctly chalcophilic. It is frequently, but not exclusively, concentrated in sulphide minerals. It is generally found in zinc blendes, but unlike germanium is found in blendes that are geologically old. It has been reported in cylindrite, chalcopyrite, smithsonite, tungsten minerals, franklinite, calaminite, alunite, rhodonite, phlogopite, siderite, pyrrhotite, cassiterite, wolframite, hübernite, samarskite, tin ores, lead, lead-tin bullion and in the Cottrell flue dust in the recovery of cadmium.

In common with many of the rare metals, indium becomes concentrated in various byproducts during recovery of other metals, principally lead and zinc. It is most frequently associated with zinc and so is recovered commercially from zinc residues and smelter slags.

Thallium is widely distributed, but has generally very low concentrations. Estimates [10,11] vary from 0.1-10 μg/g for its abundance in the Earth's crust, but a commonly accepted figure is 0.3 μg/g [5]. It has also been detected in volcanic rocks, meteorites and in plants [5,11,145].

The geochemistry of thallium is dominated by the fact that Tl^+ and Rb^+ have closely similar ionic radii. Both are concentrated in the later stages of magmatic crystallisation of potassium minerals such as felspars and micas. However, thallium occurs not only in oxide minerals but is also a chalcophilic element. Nearly all industrial thallium is extracted from sulphide minerals.

There are few thallium minerals and these are the rare: crookesite $(Cu,Tl,Ag)_2Se$, lorandite $TlAsS_2$, urbanite $TlAs_2SbS_5$ and hutchinsonite $(Tl,Cu,Ag)_2S.PbS.2AsS_3$. The most important ones are crookesite, occurring principally in Sweden, and lorandite, found in Greece. Minute traces of thallium are found in numerous rocks and in many cupriferous pyrites.

It is significant that the two related elements indium and thallium behave so differently when entering sulphide minerals. This is due to a difference in ionic radii. The smaller indium generally replaces zinc in sphalerite while the larger thallium will replace lead in galena [5].

The geochemistry of gallium, indium and thallium has been well summarized by Shaw [12].

I-2 REVIEW OF ANALYTICAL METHODS

Analytical methods for the determination of gallium, indium and thallium at the microlevel have been published in many papers and books which include both classical and modern instrumental techniques. A review of analytical methods for group IIIB elements is briefly summarized as follows.

I-2-1 Separation and Enrichment

No matter what type of sample is to be analyzed, interferences are always present and can seriously affect the accuracy of the results. Hence, chemical analyses almost always include two essential steps: separation and enrichment. Separation is required to remove the analyte from interferents in the original sample, and enrichment is needed to achieve better sensitivity and reproducibility.

Due to the group IIIB elements being present in natural samples at extremely low concentrations (from $\mu g/g$ to ng/g), it is necessary to separate them from their matrix in any type of analytical technique. The samples that I wished to analyze in this present work had a very complex composition. For example, in iron meteorites, the iron and nickel contents average 88% and 8% respectively. These two elements seriously affect the behaviour of the group IIIB element in flameless atomic absorption spectrometric analysis.

There was clearly a need for an efficient separation procedure, especially for iron meteorites, and this was one of the primary aims of this present work.

i. Coprecipitation

One possible separation technique for group IIIB elements may be to precipitate them as hydroxides with reagents such as ammonium hydroxide.

Gallium can be separated from other elements by precipitation with ammonium hydroxide in the presence of an excess of ammonium chloride, but an excess of ammonium hydroxide is to be avoided, for the precipitate is appreciably soluble in this reagent.

Precipitation of indium with ammonium hydroxide is very similar to the method used for gallium but must be in the absence of tartaric acid that inhibits the precipitation.

Other reagents can also be used for the precipitation of gallium and indium. For example, Moser and Brukl [13] recommended precipitation of gallium by tannin in a boiling 2% acetic acid solution in the presence of 2% of ammonium nitrate that can separate gallium from zinc, nickel, cobalt, manganese, cadmium, beryllium and thallium.

Barium carbonate can be used to precipitate indium in an ammonium acetate-acetic acid solution [14]. Precipitation by potassium cyanate [15] is also said to give quantitative separations of indium from zinc, nickel, sexivalent chromium, and, with slight modifications, from cobalt.

Thallium can be precipitated as thallous iodide where it is separated from elements such as cadmium, iron, aluminium, chromium, cobalt, nickel, zinc, manganese, alkaline earths, magnesium and the alkali metals.

ii. Ion Exchange

a. Separation by Cation Exchange

The adsorption characteristics of gallium, indium and thallium on the strongly acid cation exchange resins BioRad AG 50W and Dowex 50, X4 have been summarized in Table I-2 [16-18].

Table I-2 Distribution Coefficients of Group IIIB Elements in Mineral Acid Media on Strongly Acidic Cation Exchangers

		Metal ions			
Acid	Molarity	Ga(III)	In(III)	Tl(I)	Tl(III)
HNO_3	0.1	$>10^4$	$>10^4$	173	-
	0.2	4200	$>10^4$	91	-
	0.5	445	680	41	-
	1.0	94	118	22.3	-
	2.0	20	23	9.9	-
	3.0	9	10	5.8	-
	4.0	5.8	5.8	3.3	-
H_2SO_4	0.05	$>10^4$	$>10^4$	425	6500
	0.1	3500	3290	236	1490
	0.25	618	376	97	205
	0.5	137	87	49.7	47.4
	1.0	26.7	17.2	20.6	12
	1.5	10	6.5	11.6	7.2
	2.0	4.9	3.8	8.7	5.2
HCl	0.1	$>10^4$	10	-	<1
	0.2	3036	8	-	<1
	0.5	260	5	-	<1
	1.0	42.6	1	-	1
	2.0	7.7	<1	-	2
	3.0	3.2	<1	-	3
	4.0	0.3	<1	-	5

From the distribution coefficients in Table I-2, it can be seen that the decrease in adsorption of gallium and indium with increasing acid concentration is especially pronounced in hydrochloric acid media. This is due to the fact that these metal ions readily form anionic chloride complexes which are not retained by these resins even at relatively low acidities of hydrochloric acid. An exceptional behaviour is shown by thallium (III) in hydrochloric acid solution.

A method for separation of gallium from other elements has been described [19]. The technique employs a column of Dowex 50 equilibrated with <0.8 M hydrochloric acid solution. The gallium is eluted with 1.5 M hydrochloric acid.

Concentrated electrolyte solutions containing sodium or lithium chloride have been also used to separate gallium or indium from other elements using a column of KU-2 cation exchanger [20] in 1-2 M hydrochloric acid solution.

Thallium (I) can be absorbed on Amberlite IR-120 from a solution at pH 4 containing EDTA [21]. Elution of thallium from the resin is achieved by means of 2 M hydrochloric acid.

b. Separation by Anion Exchange

Gallium is strongly adsorbed on resins of the quaternary ammonium type, from pure aqueous solutions, with hydrochloric acid concentrations exceeding 3M [22]. Starting with this acidity, the distribution coefficient of gallium increases from 80 to 10^5 in 7 M acid, after which it decreases to become 10^4 in 12M hydrochloric acid. Under the same conditions the distribution coefficients of indium are 10, 8 and 5 respectively [22,23]. Whilst thallium (I) is only slightly adsorbed at all hydrochloric acid concentrations (0-12M), the adsorption of thallium (III) is found to decrease linearly with increasing molarity of hydrochloric acid. Thus, the distribution coefficients of thallium (III) in 2 and 12M acid are 10^5 and 500 respectively, suggesting stronger anionic complex formation at lower acidities.

Gallium and indium can also be extracted with long-chain quaternary ammonium halides dissolved in toluene, chloroform or trichlorethylene from aqueous media containing hydrochloric acid and lithium chloride [24].

The use of different acid media can successfully separate the group IIIB elements from each other and from other elements.

iii. Other Chromatographic Methods

Reversed-phase partition chromatography, on a column of cellulose acetate impregnated with dithizone-chloroform, may be used to separate indium-116 from other radionuclides [25]. Indium is retained on such a column and thereby separated from other elements. Finally the indium is eluted with 1 M hydrochloric acid.

Paper chromatography (PC) is used to separate gallium and indium by using the mobile phase of n-butanol-hydrochloric acid [26]. Under these conditions gallium travels with the solvent front and indium remains at the origin. Using a modification of the mobile phase with a 5:3:2 mixture of phenol-methanol-concentrated hydrochloric acid, gallium, indium and thallium can also separated from each other [27].

Separation of thallium from large amounts of iron (III), titanium and zirconium has been investigated [28] by use of 6 M hydrochloric acid, diluted to final volume of 2.5 litres with acetone.

Radial chromatography on paper has also been employed [29] to separate thallium (III) from comparable amounts of iron, copper, nickel etc. with a mobile phase of n-butanol saturated in 1M hydrochloric acid solution.

iv. Extraction

It is clear that extraction is a powerful separation tool in analytical chemistry. It not only can separate analytes from others, but also can enrich the analytes to increase the limit of detection. Extraction of group IIIB elements is based on an ion-association complex system in which the elements form halide complexes in a halide acid medium. Hydrochloric acid is perhaps the most commonly used medium for many of these extractive analytical procedures.

Details of the extraction procedure used in this thesis are given in Part 3 below.

I-2-2 Gravimetric Methods

In classical gravimetric methods for the determination of the group IIIB elements, they are always weighed as their oxides: Ga_2O_3, In_2O_3, and Tl_2O_3 [13]. The principle of the method is based on initial precipitation of trivalent gallium, indium and thallium by ammonium hydroxide, cupferron, or ammonium sulphite followed by ignition at 1000, 1200, and 200°C respectively.

The gravimetric method for indium can only be used for larger amounts of this element and is based on weighing indium in the form of sulphide and/or the 8-hydroxyquinolinate [30,32]. Indium also can be quantified by other precipitants such as pyridine, potassium cyanate, etc.

Gravimetric determination of thallium can be achieved by weighing as the chromate and/or iodide (Tl_2CrO_4 and TlI).

I-2-3 Titrimetric Methods

Volumetric analysis is faster and more sensitive than the gravimetric method. Compleximetric titration using EDTA can be used to quantify IIIB elements. The EDTA forms a 1:1 complex with gallium, indium and thallium. For this procedure it is necessary to remove interfering elements before carrying out the method. Both direct and back titrations can be used for these elements.

For determining gallium, a sulphate solution with 1M sodium hydroxide is added to an aqueous solution until the mixture becomes opalescent. Then are added concentrated acetic acid (to pH 2.3 or 2.5) and 1 or 2 drops of a 0.1 % aqueous solution of 4-(2-pyridylazo)-resorcinol (PAR). The solution is then titrated directly with 0.1M Na_2EDTA [30].

Indium is conveniently determined by titration with 0.1M EDTA in the presence of an acid solution (pH about 2). A more selective procedure is titration of indium by ferrocyanide [31].

There are several volumetric methods for determining thallium and they include use of iodine and/or permanganate [32]. Probably the most useful titration method is based on the reduction of thallic ion with standard iodine and back-titration of the excess iodine with thiosulphate or arsenite [32].

Most analytical procedures have to use back-titration because of slow complex formation and serious interferences from other elements.

I-2-4 Spectrophotometric Methods

Forming colour complexes of the group IIIB elements provides a relatively sensitive photometric methodology. Rhodamine B is a commonly used reagent that can be used in combination with liquid-liquid extraction, and provides sufficient sensitivity to allow determinations down to ng/g.

Onishi [33,34] was the first to used rhodamine B to determine gallium, indium and thallium as their halide complexes. The solutions are analysed at different wavelengths for each element, for example, gallium at 561 nm.

Many complexing reagents have been used for quantification of group IIIB elements. They include malachite green, 1-(2-pyridylazo-)-2-naphthol, eriochrome-hexadecylpyridinium and zephiramine-eriochrome cyanine.

They are all based on xanthene and triphenylmethane dyes, but some use has been made of azine, oxazine, thiazine and other dyes [35].

With these spectrophotometric methods, interfering elements must usually be separated in order to ensure accurate quantification of the analyte. Solvent extraction is a favoured technique for this purpose.

I-2-5 Electrochemical Methods

Sensitive and selective electrochemical techniques are sometimes employed to determine gallium, indium and thallium. Methods include conductimetry, coulometry, amperometry, polarography, oscillopolarography, square-wave polarography, and pulse anodic-stripping voltammetry.

Of the above methods polarography is a favoured method for determining these elements. Generally, forming complexes of gallium, indium and thallium provides better sensitivity than direct polarography.

Kumar *et al.* [36] using δ-valerolactam [piperidin-2-one] obtained a well defined polarographic wave for the gallium complex. He also investigated the electrochemical behaviour of a gallium (III) complex with 2,3-dihydroxypyridine [pyridine-2,3-diol] with a dropping-mercury electrode. He found well defined diffusion irreversible waves with $E_{½}$ value of -1.156 V (*vs* the SCE) [37].

Determination of indium can be carried out with a method similar to that of gallium. Zhang *et al.* [38] studied the polarographic wave of the indium-xylenol orange complex. This reagent gave a well defined single-sweep polarographic wave at a peak potential of -0.41 V (*vs*.the SCE). The limit of detection was 3.0 ng/mL.

A voltammetric technique for quantification of thallium has been used by several workers and affords the best combination of sensitivity and selectivity of all the methods so far discussed. The lower limit of detection for thallium is about 0.1 ng/g [39,40].

I-2-6 Spectrofluorimetric Methods

Because numerous inorganic compounds are photoluminescent, several fluorescent compounds can be formed with group IIIB elements. The analyte solutions are measured by spectrofluorimetry.

A very useful agent is 8-hydroxyquinaldine [41] which forms complexes of gallium, indium and thallium. The analyte is then extracted into chloroform and can be measured by a spectrofluorimeter. This method has achieved a limit of detection of 0.02 μg/g. Another reagent, lumogallion (2′,2,4-trihydroxy-5-chloro-1,1′-azobenzene-3-sulphonic acid) is one of the most sensitive fluorometric agents with a limit of detection of 1 ng/g for gallium [42].

Other reagents such as butylrhodamine B and 1-(2-pyridylazo)-2-naphthol are frequently used for spectrofluorimetric quantifications.

I-2-7 Atomic Spectrometric Methods

There are two types of spectrometric method that are based on utilisation of atomic spectra: emission and absorption.

The sensitivity of emission spectrometry depends upon excitation sources such as flames, electric arcs, spark glow discharge plasmas and even lasers. Spectral lines usually employed are 403.3, 451.1 and 535.1 nm for gallium, indium and thallium respectively. With the classical excitation techniques (like arc and spark) lower limits of detection in the range
0.02-1.0 μg/g can be achieved for the group IIIB elements.

The inductively coupled plasma (ICP) excitation source has become increasingly important during the past ten years. This technique determines many elements simultaneously and has low limits of detection which for group IIIB elements are in the range 0.0001-0.01 μg/mL. Floyd *et al.* [43] have reported some values for geochemical and environmental samples.

Another sensitive excitation source is the microwave induced plasma (MIP) that can detect ng/g level of these three elements such as 15 ng/g for thallium [44].

Atomic absorption spectrometry is a convenient and useful instrumental analytical method for determining most elements and combines both high sensitivity and accuracy. It is a reliable method for determining elements at the μg/g level and higher [45]. Using the solution injection [46,47] or noble metal loop techniques [48] the limit of detection can be increased by an order of magnitude.

For the group IIIB elements, graphite furnace AAS (GFAAS) can lower the limit of detection down to about 1 ng/g. The method, however, is subject to interferences from other elements such as iron that can considerably reduce the signal. So when applying GFAAS there should be consideration of separation of analytes prior to the instrumental determination step. Leloux *et al.* [49] have reviewed applications of the GFAAS method.

I-2-8 Neutron Activation Analysis

Neutron activation analysis (NAA) is an effective multielement technique well suited to automation and data processing operations. There are at present numerous practical applications today involving all kinds of sample types. The limit of detection for gallium is lower than that for indium and thallium. About 3 X 10^{-3} μg/g of gallium can be detected by the NAA method and the half-life of gallium is 21 minutes. The method has been used to determine a number of trace elements in meteorites. Some early work was carried out by Small *et al.* [50], Goldberg *et al.* [51], and Lovering *et al.* [52] who determined gallium in lunar, terrestrial and meteoritic basalts. Concentrations of indium and thallium in meteorites are extremely low and quantification is rendered difficult by interference from the very high concentrations of iron (*ca.* 90%). There are therefore very few values for these elements in the literature.

I-2-9 Mass Spectrometric Methods

For ultratrace analysis of samples, mass spectrometry is one of the best techniques as an alternative to other methods because of the reduced risk of contaminations. Limits of detection at the ng/g and pg/g levels can be achieved. The methodology can be combined with an inductively coupled plasma ion source (ICP-MS) [53,54]. Practical geochemical analysis by MS offers several advantages over conventional analytical methods.

Isotope dilution mass spectrometry, however, is a promising method for the ng/g range with a good precision and accuracy if used properly [55,56].

I-2-10 X-ray Fluorescence Spectrometric Methods

The years since 1948 have seen X-ray fluorescence spectrometry (XRF) become one of the standard instrumental methods for analytical chemistry. Concentrations from the percent range down to ng/g can be determined in a single measurement with good quantitative accuracy. For micro samples, such as air particulates, X-ray fluorescence spectrometry can measure down to the nanogram range. X-ray fluorescence spectrometry lends itself more to the analysis of solids rather than liquids.

The application of XRF to the group IIIB elements employs the K_α radiation lines. Gallium, indium and thallium have been determined in geological samples using this technique. However, limits of detection by XRF are not low enough to reach the ng/g level. Methods such as TXRF (total reflectance excitation XRF) or excitation with charged particles (PIXE) are not yet sufficiently developed for determination of these elements [57,58].

I-2-11 Conclusions

The determination of the group IIIB elements from most matrices at the μg/g level is nowadays a relatively simple task, for which FAAS can readily be used.

For concentrations at the ng/g level, a single universal analytical procedure for the determination of the group IIIB elements does not yet exist, although this level is common in most geological matrices.

For the determination of the group IIIB elements in the presence of others, an efficient means of separation must be developed before the instrumental step. The accuracy and precision of the developed methods can be established by use of reference materials [59].

I-3 AIMS OF THIS WORK

There were at least three major aims for this research work:

I-3-1 Classification of Meteorites

The first aim of the thesis was to assess the usefulness of group IIIB elemental abundances for the classification of iron meteorites. The current chemical classification of such meteorites presents difficulties for specimens that lie near boundaries (positions on an element vs. nickel abundance plot) between two or more classes. For example, many irons cannot be classified by usually accepted chemical methods and are placed into "anomalous" or "ungrouped" categories. Occasionally, a sufficient number of meteorites has similar abundance ratios of elements as well as similar structural characteristics to warrant the formation of a new group. For example, group IIF has recently been established by Kracher *et al.* [60].

For classification of stony meteorites (chondrites), a convenient classificatory method is to examine the relative abundances of the three isotopes of oxygen [61], as displayed in Fig.I-1. The figure shows that most processes (*e.g.* volatilisation, crystallisation, chemical reactions) are of a kind that tends to distribute samples along a line of slope close to 0.5 on a plot of one isotopic ratio against another. Type H, L, and LL ordinary chondrites cluster in similar regions of the plot, while H chondrites are clearly resolved from L chondrites and are weakly resolved from LL chondrites.

Group IIIB elements are highly volatile, especially indium and thallium. These highly volatile elements are of special interest because they may provide information on the temperature at the time of the accretion in space of the meteorite.

Of the three elements, the gallium content provides a useful classification parameter for iron meteorites when plotted against the nickel content as shown in Fig.I-2. From this plot each group of irons is readily found in separated fields.

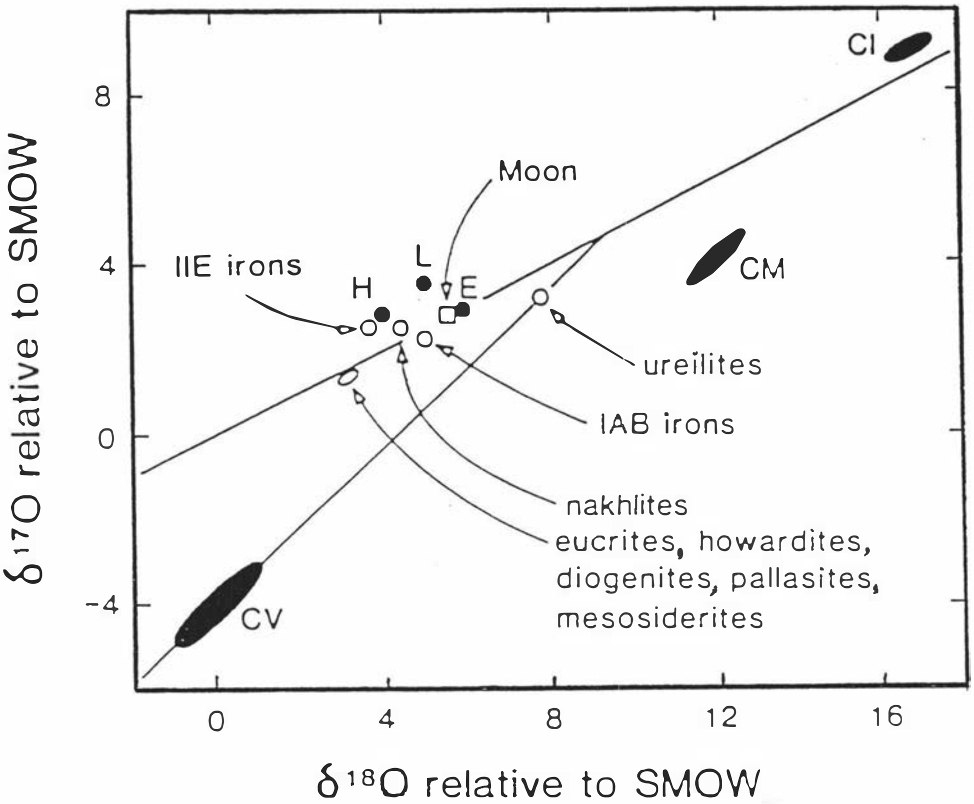


Fig.I-1 Plot showing the distribution of three isotopes of O in meteorites

The δ parameter refers to the difference in the ratio ^{17}O or ^{18}O to ^{16}O (in parts per thousand, or per mil) between the sample and standard mean ocean water (SMOW). Terrestrial and lunar samples plot along the line with slope ~ 0.5 which is referred to as the "terrestial mass-fractionation" line. The line with slope ~ 1.0 is produced by components from Allende and other meteorites and reflects mixing of an ^{16}O-enriched component and a more "normal" component, after Clayton [169].

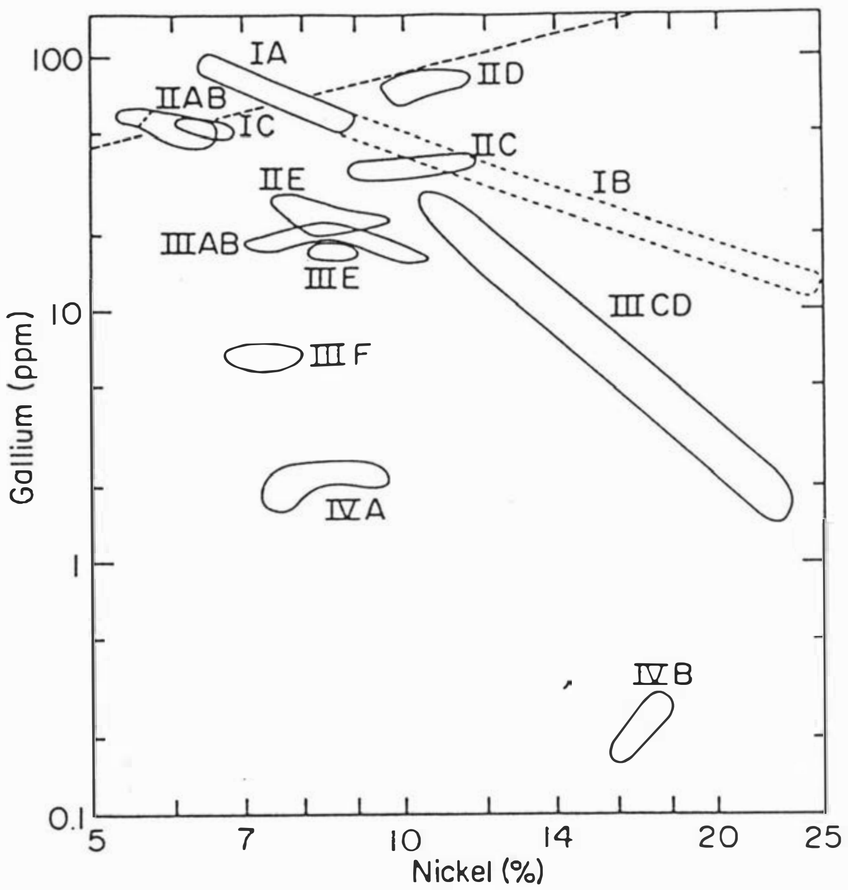


Fig.I-2 Logarithmic plot of Ni. vs. Ga in iron meteorite groups (McSween,[168]) Highly volatile elements such as indium and thallium give an enormous amount of information on thermal histories at relatively low temperatures and they are important for studies of the genesis of each meteorite group. However until this present work was concluded, the analytical difficulties were such as to preclude extensive analyses of these two elements in meteorites, particularly in irons. Part of the problem lies in the fact that many metoriticists rely very heavily on NAA as an instrumental technique. It is a well regarded method for many elements, but is not very sensitive for indium and thallium.

I-3-2 The Use of Group IIIB Elemental Abundances to Evaluate the Impact Theory of Mass Extinctions at the Terminal Cretaceous

The second aim was to investigate the group IIIB elements in Cretaceous/Tertiary (K/T) boundary samples. In their famous benchmark paper of 1980, Alvarez *et al.* [62] reported the presence of anomalous iridium concentrations in Cretaceous/Tertiary (K/T) boundary clays and deduced that this had originated from the impact of a massive bolide (rich in iridium) that had caused mass extinctions at the terminal Cretaceous.

Following this earlier work, numerous other elements have been found to be enriched at the boundary [63]. Enriched elements included siderophile and chalcophile elements [64]. Absolute concentrations of chalcophiles are much higher than would be provided directly from a mantle, crustal or meteoritic source, therefore, an enrichment process must be invoked at the boundary.

Group IIIB elements, particularly indium and thallium, are chalcophile elements that had not previously been determined at the K/T boundary due to analytical difficulties.

Because of the low concentrations of the group IIIB elements in meteorites and other geological materials such as Cretaceous-Tertiary boundary clays (pg/g to μg/g range), a sufficiently sensitive analytical method is apparently required. An excellent analytical technique for determining major, minor and trace elements in meteorites and other geological materials is neutron activation analysis (NAA). Unfortunately, sensitivities of gallium, indium and thallium are far too low to determine these elements in boundary clays by neutron activation analysis. This clearly highlights the need for the development of an alternative technique as is indeed shown in this thesis.

I-3-3 Development of an Analytical Procedure to Determine Group IIIB Elements

The third aim of this work was to develop a rapid, inexpensive, sensitive, precise and reliable analytical method for carrying out the above tasks. The developed methodology involved use of solvent extraction to separate group IIIB elements from meteorites and other geological materials and their subsequent determination by graphite furnace atomic absorption spectrometry.

PART TWO

DETERMINATION OF GROUP IIIB ELEMENTS BY HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY

II-1 INTRODUCTION

Forming volatile covalent hydrides of elements as an analytical technique has been used for the determination of trace elements in many types of sample. Originally the procedure was limited to Groups III (Al and B only), IV, V and VI of 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 only eight have been determined by hydride generation procedures. The positions of these elements in the Periodic Table are shown in Table II-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 provides a low limit of detection, such as atomic absorption spectrometry.

It appears that group IIIB elements such as gallium, indium and thallium can also form hydrides. An isotopic ERS spectrum of GaH_3 has been observed and its structure is similar to AlH_3 [65]. Indium hydride has been detected by mass spectrometry and has the formula InH_3 [66]. In the case of thallium there was spectral evidence for TlH but not TlH_3 because thallium (I) is more stable than thallium (III)[67]. The hydride of thallium (III) is very complicated and tends to decompose except under restricted conditions. A summary of physical and chemical properties of gallium, indium and thallium hydrides is listed in Table II-2.

Table II-1 The Position 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	▒ Ge	▒ As	▒ Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	▨ In	▒ Sn	▒ Sb	▒ Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	▒ Hg	▨ Tl	▒ Pb	▒ Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Ha													

▒ can form hydrides

▨ studied in this work

Table II-2 The Melting and Boiling Points of Gallium, Indium and Thallium [32]

Hydride	m.p. (°C)	Decomposition Temp.(°C)
GaH_3	-15	Room temperature
InH_3	--	20
TlH	--	140

Despite the discovery of hydrides of the group IIIB elements, it is difficult to use them for an analytical method because of their instability. There is also the problem of effecting a rapid and quantitative reduction, as well as collecting and releasing these hydrides into the atomiser.

There are, to date, only three papers that have discussed indium determination by hydride generation atomic absorption spectrometry (HGAAS). The first report dates back to 1982 when Busheina and Headridge [68] described the generation of indium hydride with atomisation in a silica tube using argon as a carrier gas. The fine black precipitate appeared in the solution after injection of the reducer. This they attributed to the formation of indium metal since the reduction of indium to InH_3 is not quantitative. However, Du Yan *et al.*[69] suggested that the precipitate was probably an indium complex that could be decomposed on addition of water. The method was modified to allow for one or two injections with water after addition of sodium borohydride to obtain two or three peaks. Total signals were summed. Castillo *et al.* [70] reported further work on the determination of indium by HGAAS in which two types of atomiser (flame and silica tube) were employed. Limits of detection of 2.6 ng/g and 0.6 ng/g were reported for flame and silica tube atomisation, respectively.

From the above experiments, it is clear that generation of hydrides of indium is chemically feasible and that adequate sensitivity can be achieved. There are however, serious problems such as unstable signals and poor reproducibility.

For the purpose of the developing HGAAS quantification of Group IIIB elements in meteorites and other geological materials, experiments were carried out to develop or improve such methods for gallium, indium and thallium.

II-2 EQUIPMENT AND REAGENTS

II-2-1 Hydride Generator

In the initial experiments, the same generator as had previously been used for HGAAS determination of germanium [96,97] was used but without the collecting unit. However, the initial studies showed nothing to confirm the findings of Du Yan *et al.*[69] that a small volume of reaction solution was adequate to generate hydrides of these elements. I therefore found it is necessary to design a new type of generator to develop the analytical technique.

An all-glass generator was designed and employed, and is shown in Fig.II-1. The reaction is carried out in a 15 mL Quickfit tube (1.5 cm *i.d.* and 15 cm length) with a number of additional inlets including one fitted with a glass stopper for introduction of samples and the reaction acidic medium, and another fitted with a rubber septum with a repeating syringe for injection of sodium borohydride solution into the reaction vessel. To the main inlet was fitted a Quickfit bubbling tube (MF 28/2) for introduction of carrier gas.

A connecting tube was used between atomic absorption spectrometer and generator with a glass tube (5 mm *i.d.*) around which was wound a heating coil for thermal control of hydrides to prevent condensation of them. The connecting tube was kept as short as possible to reduce the risk of the hydride condensing during the procedure.

A thermal water bath was used for obtaining a proper reaction temperature. The reaction vessel was dipped into

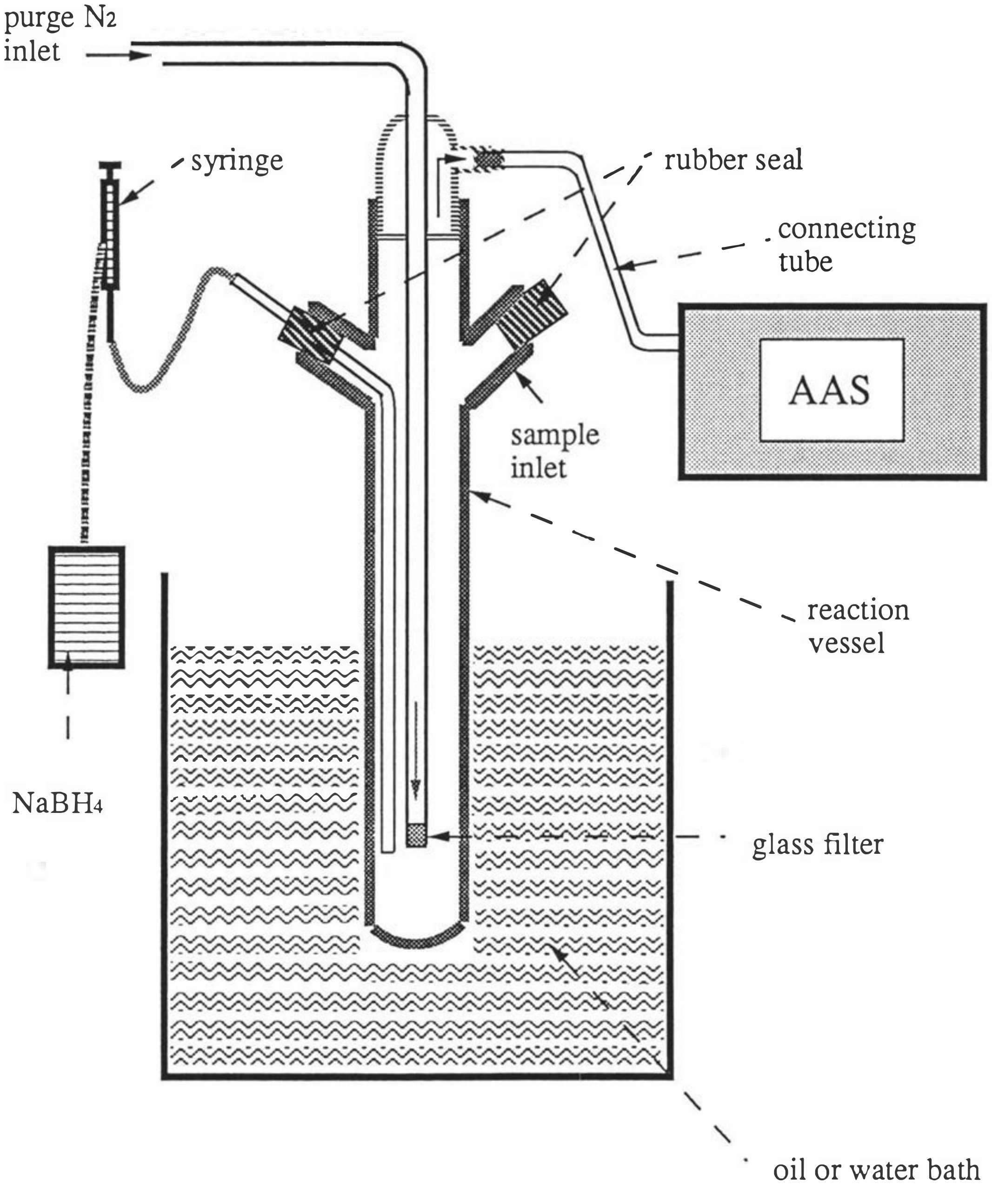


Fig.II-1 Reaction apparatus for generation of hydride the water bath for at least two thirds of its height to keep the reaction solution at the correct temperature.

To clean the vessel after each reaction, a glass syringe was used for sucking up both solutions and cleaning agents.

II-2-2 Instrumentation

All measurements were obtained by using a Varian Techtron AA-5 Atomic Absorption Spectrometer (Australia), and a SS 250 Sekonic Recorder (Japan) was used in the 10-mV range for recording signal peaks. Normally the signal peaks were symmetrical, so all calculations of the results were based on peak heights.

The radiation sources were from the hollow cathode lamps (HCL) and their operating parameters are listed in Table II-3. It is important to warm up the instrument and HCL for at least 30 minutes to ensure stable signals, particularly for indium.

Table II-3 Operating Conditions for Hollow Cathode Lamps

Element	Wavelength (nm)	Lamp Current(ma)
Ga	294.4*	5
In	303.9	8
Tl	276.8	4

* Sometimes the line at 287.4 nm was used.

II-2-3 Atomisation

After generation, the hydride is carried by an inert carrier gas such as argon or oxygen-free nitrogen through an atomiser to obtain an atomic vapour. Two types of atomiser, flame and electrothermal, are commonly used in hydride generation atomic absorption spectrometry. The analytical sensitivity is largely dependent on the choice of atomiser and its operating conditions. For HGAAS, electrothermal atomisers such as graphite furnace are not suitable because of difficult of retaining hydrides within them.

There are two kinds of atomisation method that can be used. In the first of these, the hydride is fed directly into a flame. A second procedure involves use of a heated silica tube.

(1) Direct Flame Atomisation

This method involves use of a flame into which hydrides are carried and decomposed in order to obtain an atomic vapour. Three types of flame are used for AAS: argon-hydrogen-air entrained (or oxygen-free nitrogen-hydrogen), air-acetylene and nitrous oxide-acetylene. Unlike germanium, the reducing N_2-H_2 flame was not suitable for Group IIIB elements since limits of detection were very poor. The nitrous oxide-acetylene flame provided better sensitivity but was unstable and tended to explode. An air-acetylene flame afforded the best results and was employed through the experiments.

(2) Heated Silica Tube Atomisation

There are two ways to use a heated silica tube in atomic absorption spectrometry. The first of these involves direct attachment above a burner and its flame, and the second requires use of an electrothermal heating element to obtain the atomisation temperature. An 18 cm length commercial (Perkin-Elmer MHS-10), silica tube of 15 mm *i.d.* and open at both ends, was linked to a connecting tube leading from a hydride generator. A similar tube of my own design (see Fig.II-2) was also used and proved to be more useful because the unit was more enclosed than the commercial model and retained the hydrides for a longer period.

Hydride generation is a slow process that can take from 10-120 seconds. This process is especially slow for Group IIIB elements because of the relatively high boiling points of the hydrides.

II-2-4 The Collecting Unit

A collecting trap is commonly used for hydride generation for accumulation of hydride to ensure reproducible results and higher signals. The unit consists of a U-tube trapped in liquid nitrogen or liquid air and after the reaction has been completed it can be then moved into a cold or warm water bath to ensure immediate release of the gaseous hydride. Due to higher boiling points and ready decomposition of hydrides of gallium, indium and thallium, it is very difficult to convert these hydrides to a gas from the liquid or the solid state. Use of a U-tube collector therefore gave very poor results and after initial trials was not used any further for my experiments.

II-2-5 Flame Flow Rates

An air-acetylene flame gave the most satisfactory results. To find optimum flow rates for both gases was important because of their relation to the flame temperature. For quantification of indium, varying ratios of acetylene and air were studied in conjunction with the direct flame and with a heated silica tube. The results are given in Fig.II-3. The optimum flow rates were 4 mL/min and 2.5 mL/min for air and acetylene, respectively.

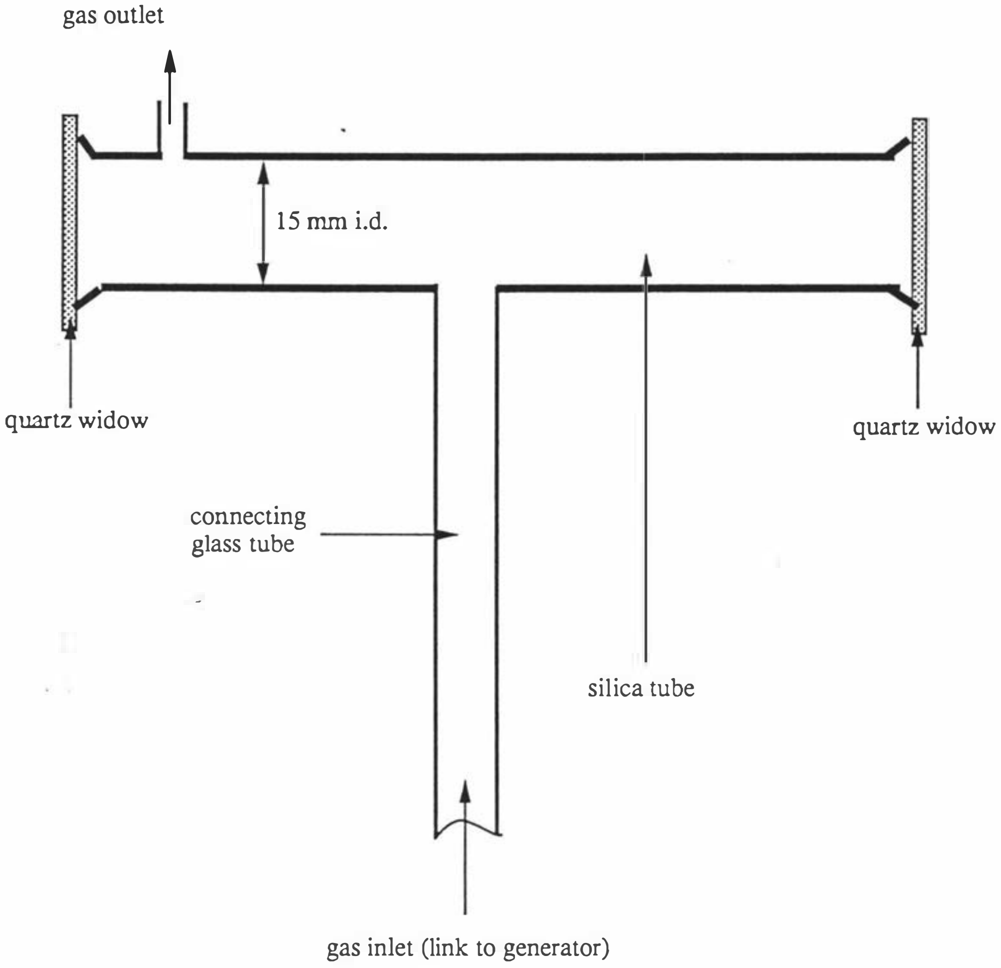


Fig.II-2 Design of silica tube for atomisation of Hydrides

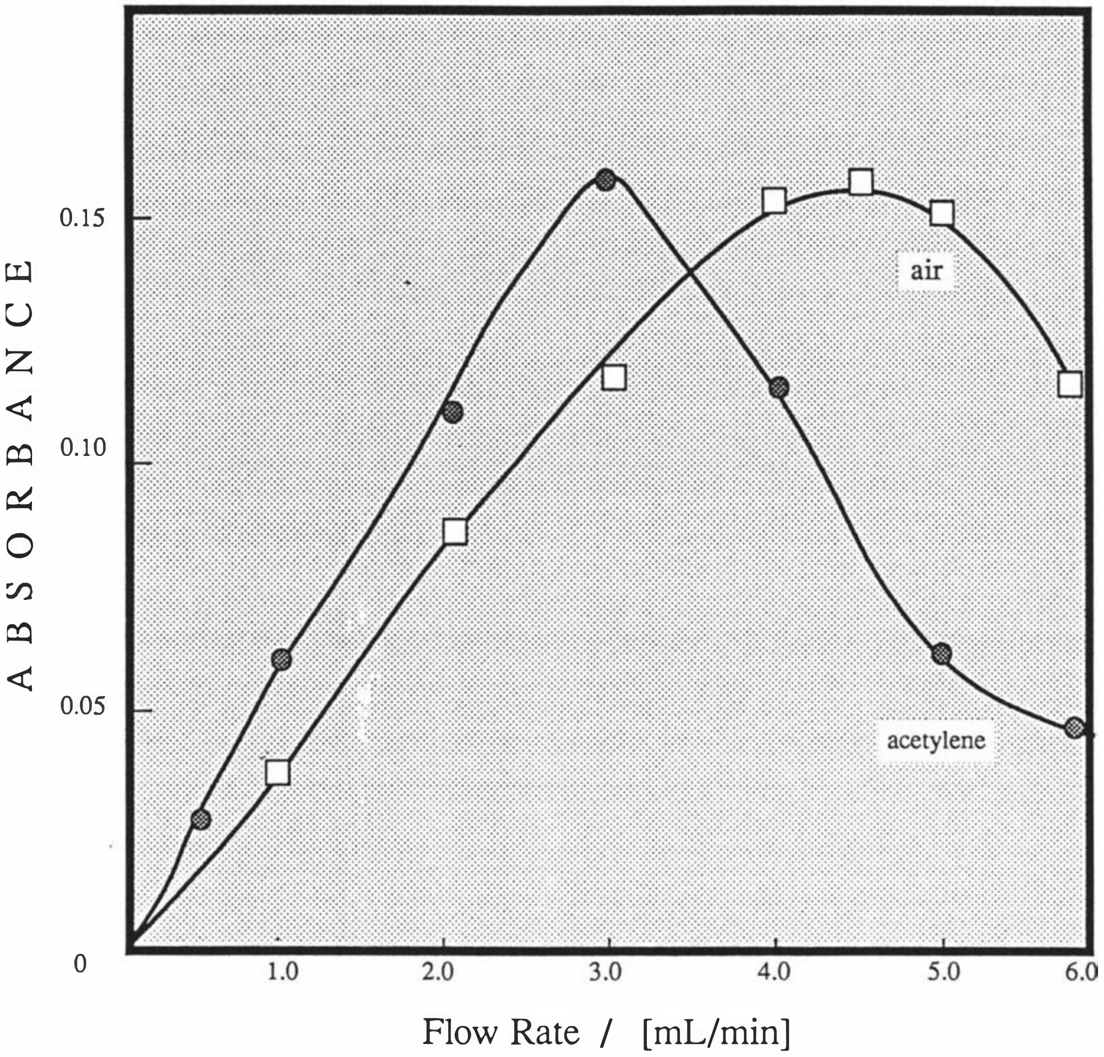


Fig. II-3 Flow rates of flame gases for quantification of indium

II-2-6 Carrier Gas Flow Rates

Both argon and oxygen-free nitrogen can be used as a carrier gas for HGAAS but argon is more expensive. The experiments showed no appreciable difference between both gases used, so oxygen-free nitrogen was preferred as a carrier gas.

Varying carrier gas flow rates were employed in obtaining signals of indium by the direct flame and the heated silica tube and the results are shown in Fig. II-4. The optimum flow rates of carrier gas were 1.25 and 1.75 mL/min respectively. Above these rates the hydride was expelled from the atomiser too quickly and at lower rates, there was appreciable diffusion of the hydride.

II-2-7 Reagents

Standard stock solutions (each of 1000 μg/mL) were prepared from Specpure reagents as follows:

gallium (III) by dissolving Ga_2O_3 in a minimum amount of alkaline solution then acidifying with 5M hydrochloric acid,

indium (III) by dissolving In_2O_3 in 4M hydrobromic acid,

thallium (I) by dissolving Tl_2CO_3 in 3M sulphuric acid,

sodium borohydride by preparing a 1.5% (w/v) solution made alkaline with 0.5% (w/v) potassium hydroxide. The reagent was prepared daily.

All acids were analytical grade unless otherwise specified.

II-3 EXPERIMENTAL

Generation of hydrides was carried out using following basic steps:

(1) The sample solution was introduced into a reaction vessel in a suitable acidic medium,

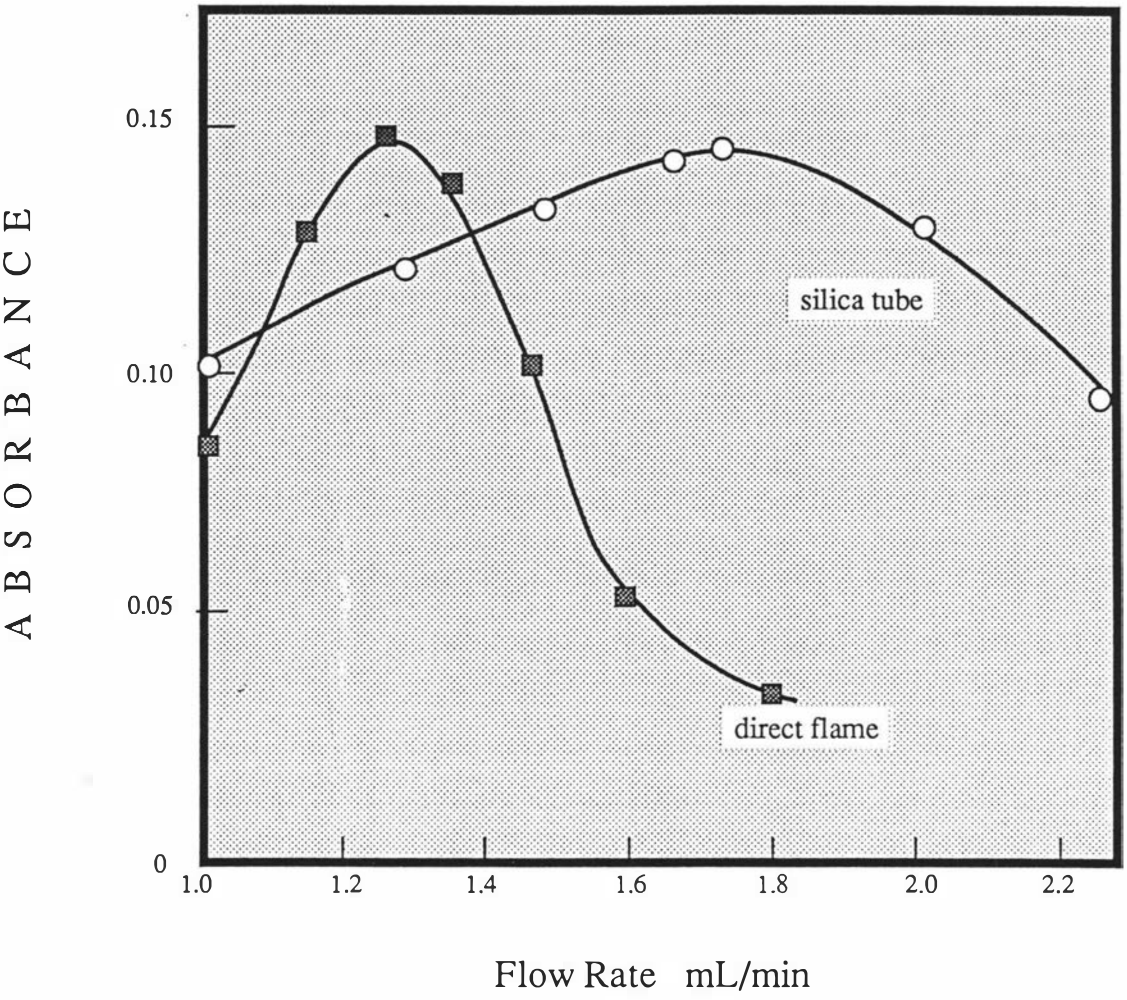


Fig.II-4 Effect of carrier gas flow rate for hydride generation quantification of indium

(2) The reducing agent was added for generating hydrides that were collected in a liquid air bath in certain cases,

(3) The hydrides were fed into an instrument by an inert carrier gas to obtain absorption signals for quantification of hydrides of the Group IIIB elements.

The optimum conditons for quantification of gallium, indium and thallium were studied and assessed.

II-3-1 Effect of Acids on Hydride Generation

An important condition for hydride generation is the presence of an acid that donates hydrogen to form the hydride of an element. The concentration of the acid directly effects the degree of hydride formation. Standard inorganic acids and some organic acids have been successfully used by many workers. In the case of indium, the literature reports only use of hydrochloric acid [66-68]. In my experiments I investigated the use of hydrochloric, nitric, sulphuric perchloric and orthophosphoric acids for hydride generation of the Group IIIB elements. The experiments using hydrochloric acid provided results that were in approximate agreement with findings of other workers. Concentrations of hydrochloric acid ranged from 0.1-7M for gallium, indium and thallium (I) and my experimental results, as well as those of other workers [68-70] are shown in Table II-4.

Table II-4 Hydrochloric Acid Molarities for Generating Hydrides of Gallium, Indium and Thallium

Reference	Ga (M)	In (M)	Tl (M)
Busheina & Headridge [68]	--	3	--
Yan et al. [69]	--	1	1
Castillo et al. [70]	--	1-2	--
This work	1.4	1.5	1.5

The best acidity of hydrochloric acid for the three elements was around 1.5M (see Fig.II-5). At other acid concentrations the HGAAS signals were severely reduced. All subsequent experiments were therefore carried out in a medium of 1.5M hydrochloric acid.

II-3-2 Effect of the Total Reaction Volume

Usually, hydride reactions can be performed without undue restriction on the volume of the analyte solution, which can range from 10-200 mL or even greater. Large volumes are however, not permissible in the case of gallium, indium and thallium. This became evident in an initial experiment where no signal was obtained from a solution of a significant volume of 50 mL. Careful selection of an optimum volume of reaction solution is therefore essential. Experiments were carried out in which differing volumes of sample, sodium borohydride and acid solutions were employed. Fig.II-6 shows the optimum volumes of each solution. The best volumes were 100-150 μL, 1-1.5 mL and 2.5-4 mL for sample, acid and sodium borohydride, respectively. The total solution volume was between 4.0-5.15 mL.

II-3-3 The Optimum Amount of Sodium Borohydride

Sodium borohydride as a reductant to form hydride is now almost universally used and it was also used throughout this work. The solution of sodium borohydride must be prepared daily to keep it fresh. The experiments for choosing optimum concentrations and volumes of sodium borohydride were performed with 1 μg of gallium, indium and thallium (I). Varying concentrations of sodium borohydride were added for generating the hydrides. The results shown in Fig.II-7 are for indium only, but similar behaviour was noted for gallium and thallium. These studies show that

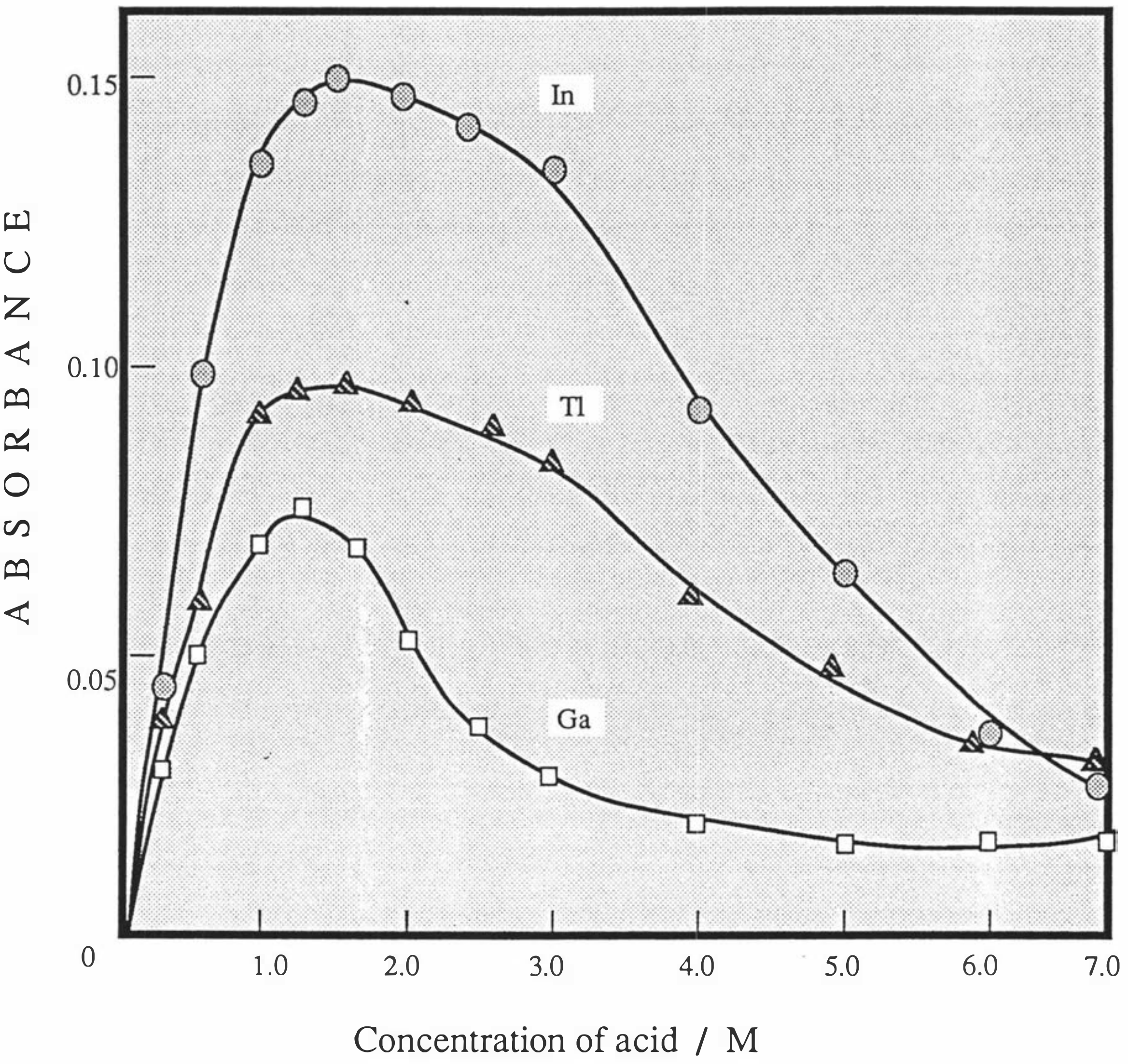


Fig. II-5 Effect of acidity for hydride generation of gallium, indium and thallium

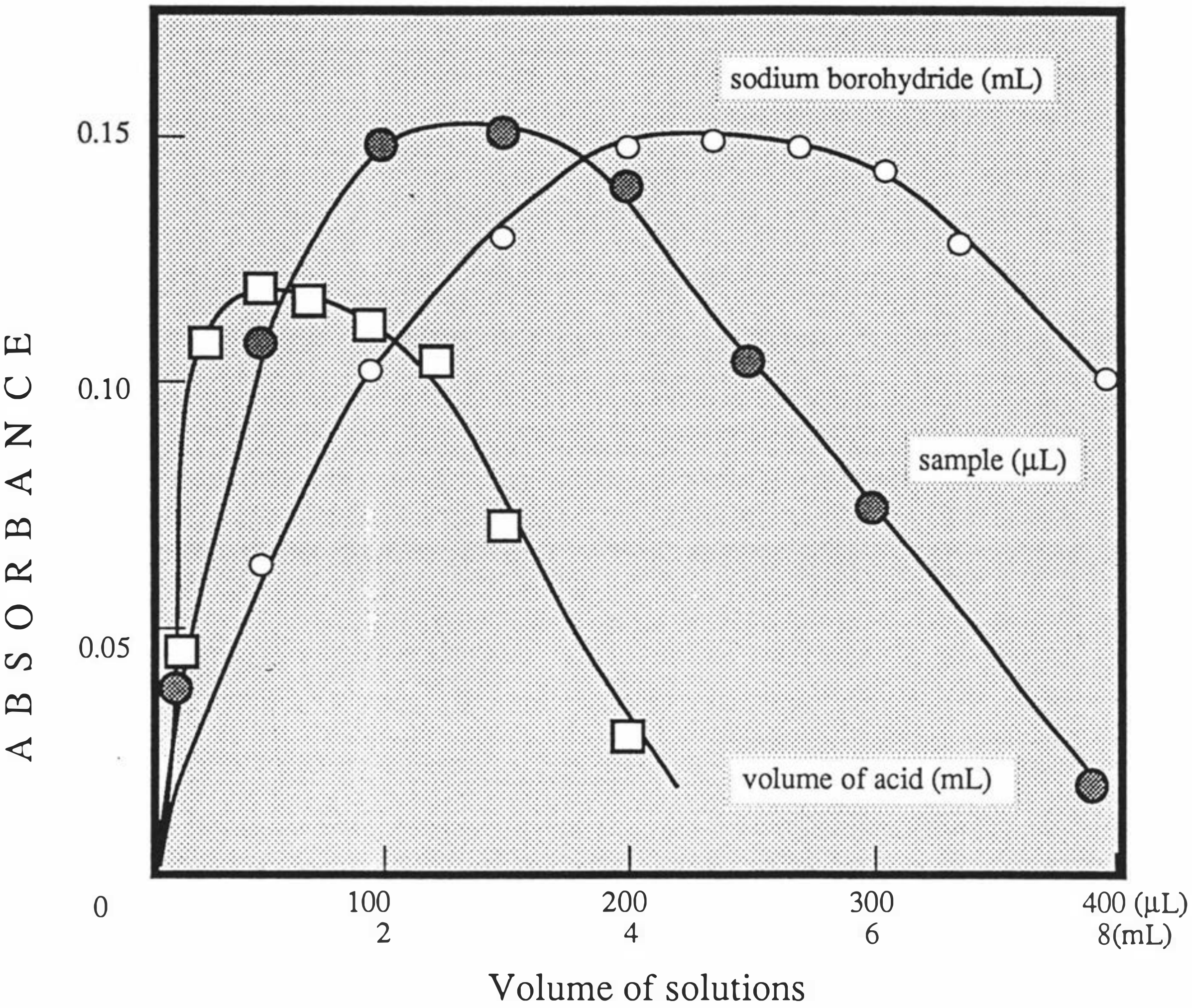


Fig.II-6 Effect of volumes of sample solution, acid, and sodium borohydride on absorbance of indium solutions

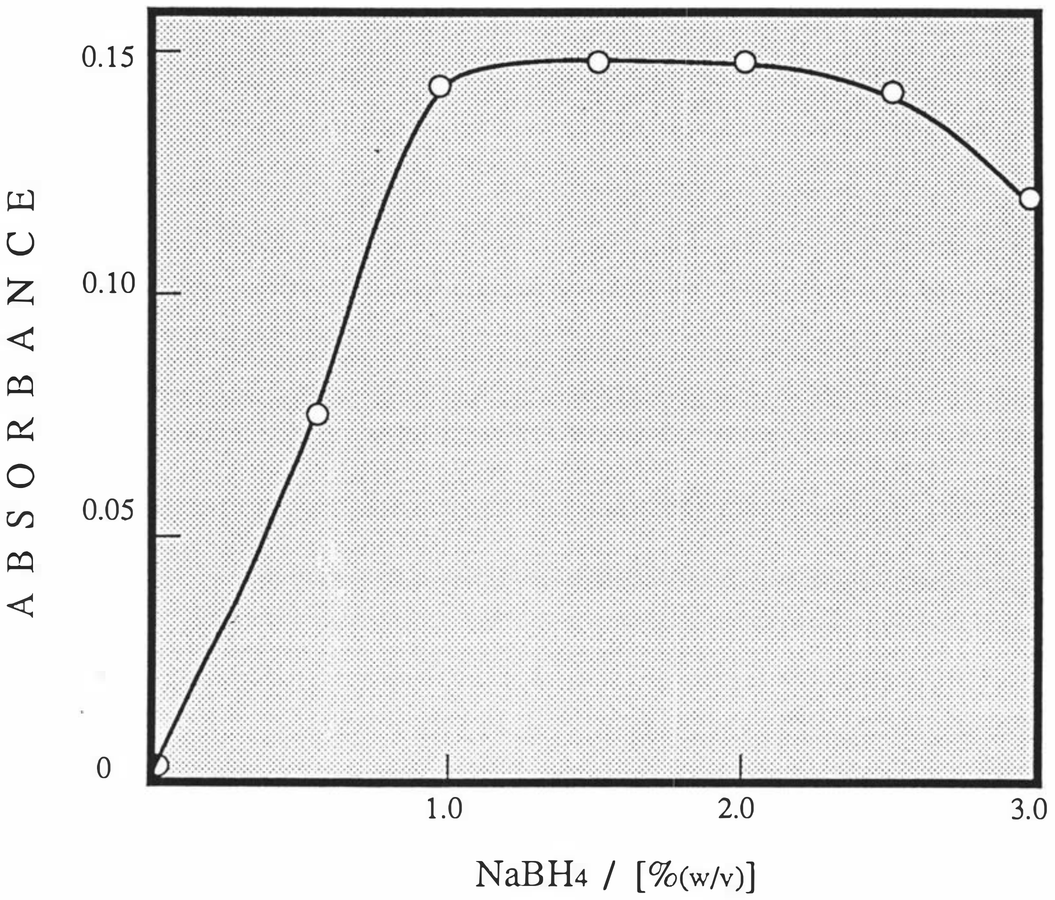


Fig. II-7 Effect of concentrations of sodium borohydride on generation of indium hydride

1.5% (w/v) sodium borohydride gave the highest signal peaks. The volumes of 1.5% sodium borohydride solution reacted with these elements to obtain the best signals were between 3.0-3.5 mL for direct flame, and 2.0-2.5 mL for silica tube (see Fig.II-8) operating modes. The minimum volumes of sodium borohydride needed to give the best conversion to hydrides were 3 mL and 2 mL, respectively.

When applied to real samples, more of the sodium borohydride solution is needed because of its initial consumption by acid and other media.

II-3-4 The Optimum Reaction Temperature

Unlike generation of many other hydrides, those of gallium, indium and thallium must be kept at a special temperature in an immersion bath containing water or some other liquid. The experiment showed very poor signals when the reaction was carried out at room temperature. The results for indium reactions at temperatures between 20-140°C (below 90°C, water was used in the bath and above that temperature, oil was used) are given in Fig.II-9. The optimum reaction temperatures were 60°, 68° and 82°C for gallium, indium and thallium, respectively. The studies also indicated that lower reaction temperatures could not release gaseous hydrides. On the other hand, higher temperature could decompose the hydrides to metal and hydrogen, so the reaction temperature is one of the key factors in generation of hydrides of these three elements.

II-3-5 Design of the Connecting Tube

The nature and design of the connecting tube which links the generator to the instrument would directly influence the effectiveness of hydride transmission because of the risk of condensation during the procedure. An electrical heating element covered with a coating of cotton wool was coiled around the connecting tube to keep a

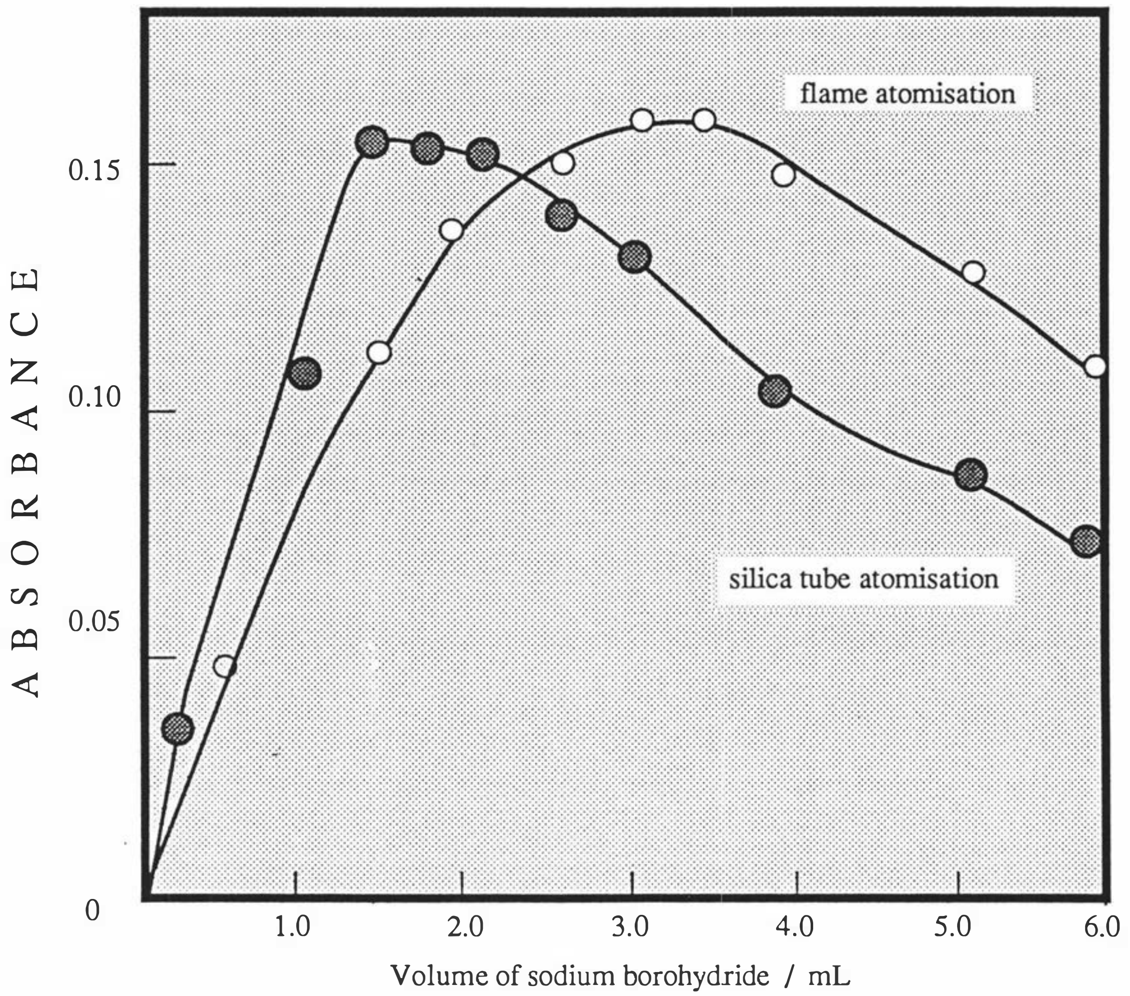


Fig.II-8 Effect of volume of sodium borohydride on formation of indium hydrides

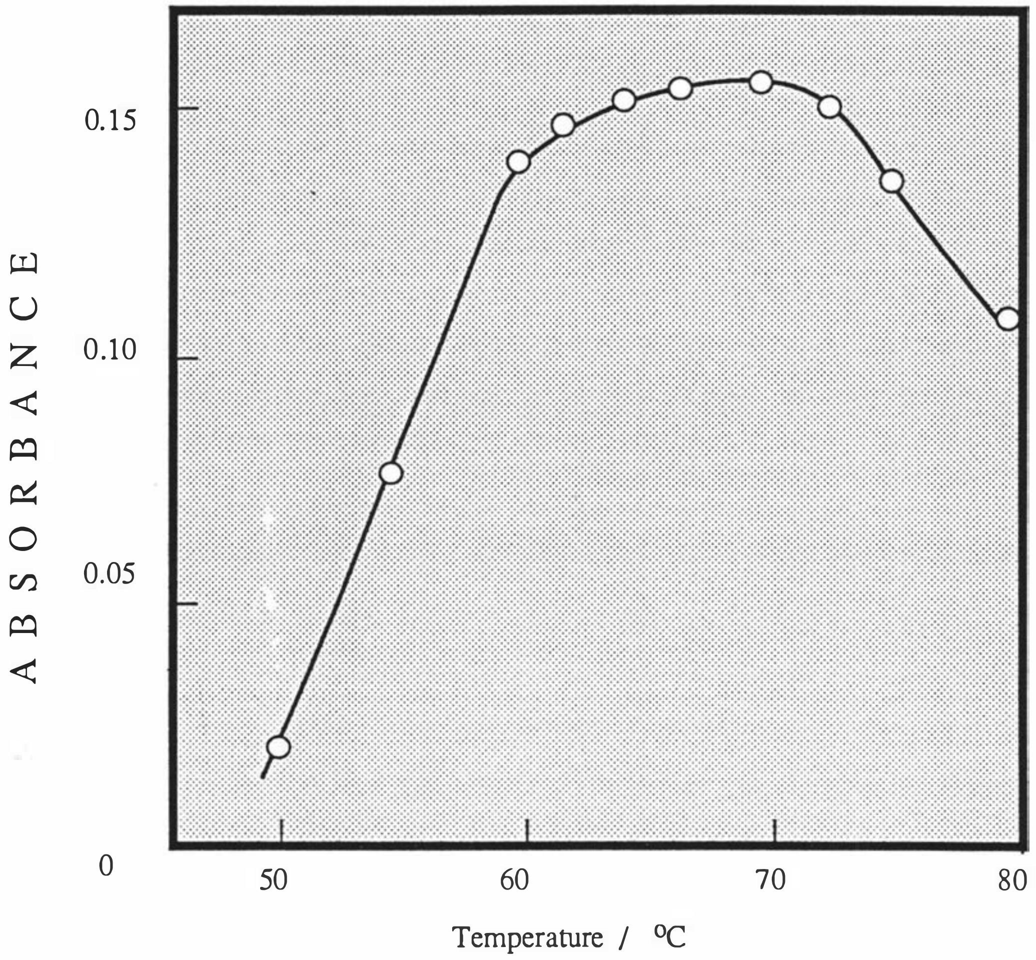


Fig.II-9 Effect of temperature on hydride generation of indium constant temperature as required for each element (see Fig.II-10). The tube was kept as short as possible, and in this work was only 10 cm long.

II-3-6 Final Analytical Procedures

For analysis of indium, place 1.5 mL of 1.5M hydrochloric acid and a 150 μL sample solution in the reaction vessel which is immersed in a hot water bath maintained at 68°C. Allow carrier gas through for at least one minute to blow out all air inside the vessel and then inject 4 mL of 1.5% sodium borohydride solution. The analyte signals are recorded as peaks.

Gallium and thallium were quantified by a method similar to that for indium except that the water bath temperatures were 60°and 82°C respectively.

II-3-7 The Form and Magnitude of Analyte Signals

The HGAAS signals for gallium, indium and thallium hydrides are shown in Fig.II-11. Indium provided the largest signals but it was not possible to improve the procedure to a degree completely satisfactory for trace element analysis. Gallium provided signals with poor symmetry and reproducibility. Thallium signals were intermediate in quality.

II-3-8 Precision and Accuracy

A standard rock - MP-1a [106] (Zn,Sn,Cu and Sb Ore) was analysed for indium and my data were compared with the certified concentration established by a different analytical procedure. The precision and accuracy of my technique are listed in Table II-5 and demonstrated that the relative standard deviation (r.s.d.) was 11.8% and the relative error was 7.9% for a standard containing several hundred μg/g indium. Unfortunately, there was still a

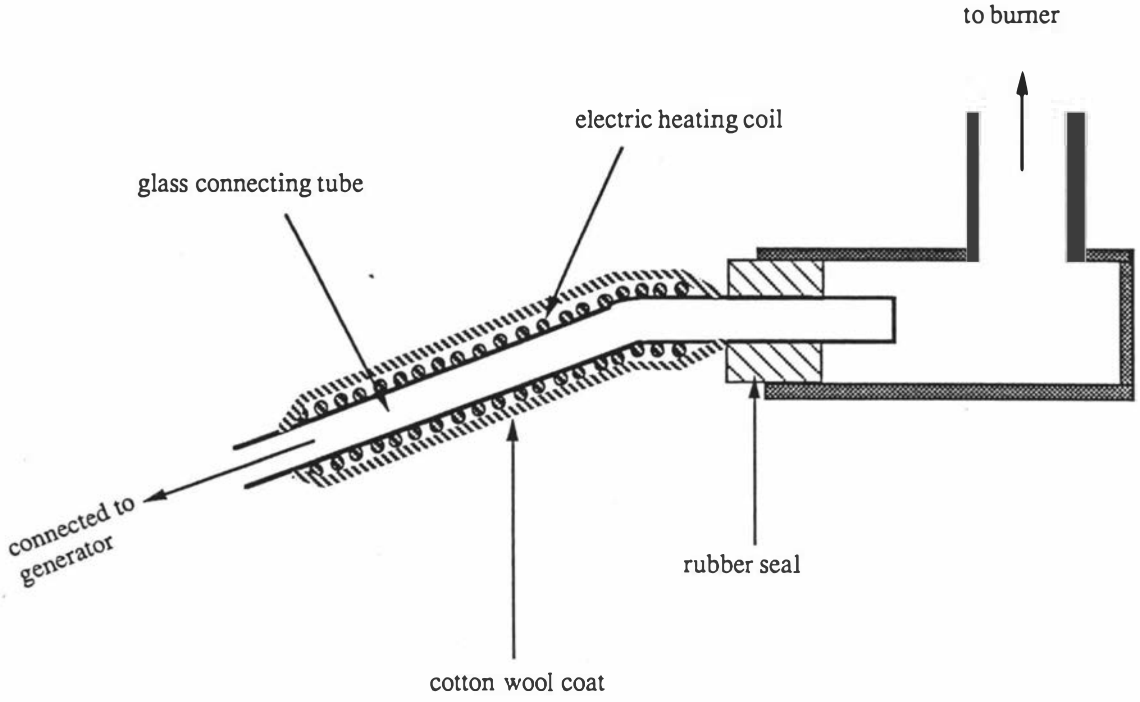


Fig.II-10 Design of connecting tube between the burner and generator for hydride generation

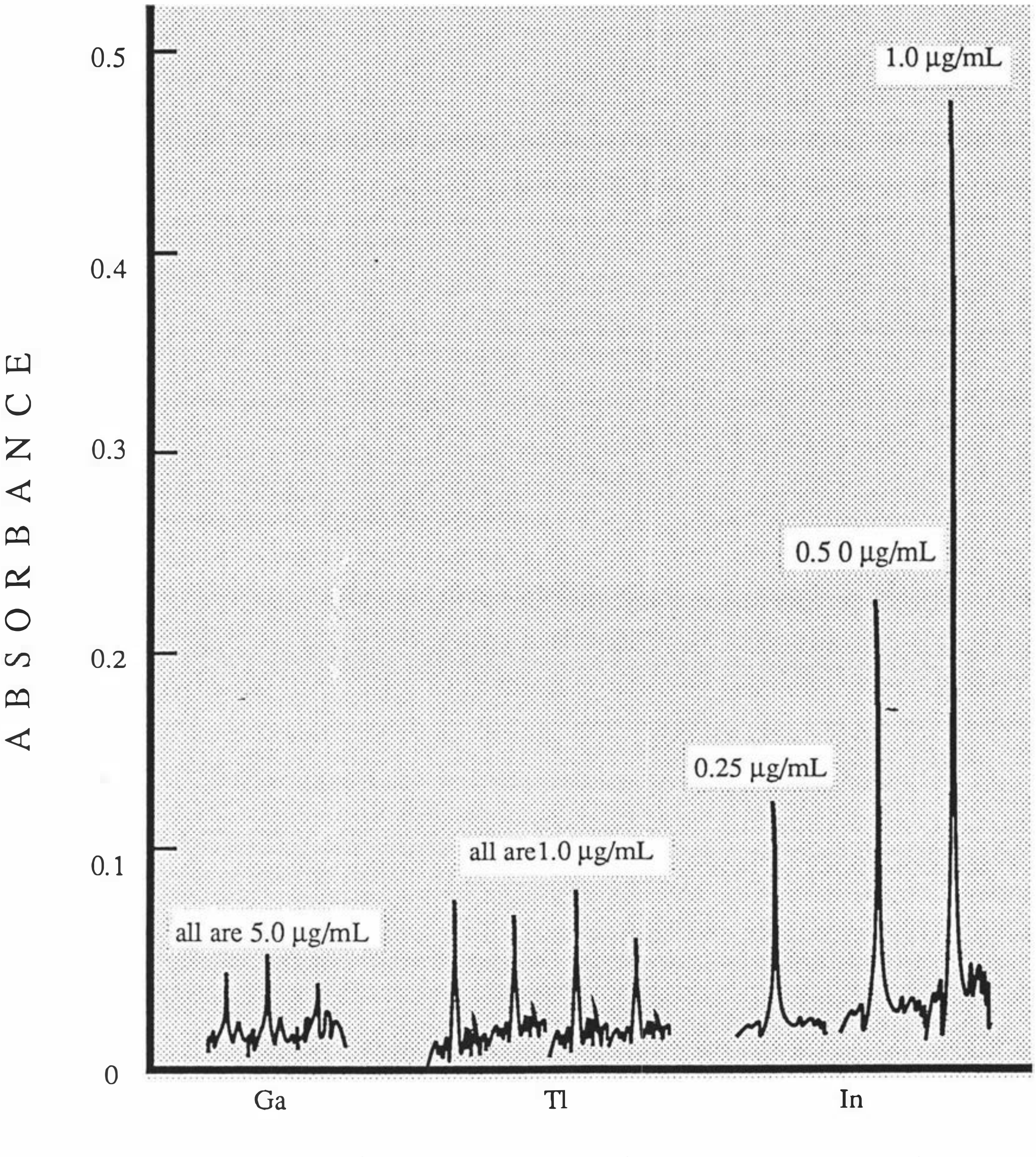


Fig.II-11 Typical absorbance signals for hydrides of gallium, indium and thallium problem of reproducibility in the case of much lower indium contents. The limit of detection (3σ) was 0.1 μg/g. Further analyses involving iron meteorites and rocks did not provide detectable signals because of the ng/g concentration levels. The procedure may however be used to determine higher contents of indium in geological samples.

Table II-5 Precision and Accuracy for Indium Determinations as Established by Analysis of a Standard Reference Rock

n	Certified (%)	Found (%)	r.s.d. (%)	r.e. (%)
12	0.033	0.0328	0.7	1.1

II-4 DISCUSSION AND CONCLUSIONS

The optimal hydride generation conditions for two types of atomiser were performed for gallium, indium and thallium. It has been shown that conditions for indium were less critical and restrictive than for the other two elements, and that it is possible for the method to be applied to real samples provided the indium concentrations are sufficiently high. Much more work will be needed before the method could be applied to the sub-μg/g level and at this stage I abandoned further experiments because of the greater promise suggested by graphite furnace atomic absorption spectrometry (GFAAS) for quantification of indium at the ng/g (ppb) level.

Despite obtaining HGAAS signals for gallium and thallium, the use of this procedure as an analytical method is very far from development and I abandoned further studies for the same reasons as for indium.

Before terminating this section, it may be appropriate to summarise my findings in the light of the studies of previous workers. In all experiments, no precipitates were observed despite reports of them in papers by Busheina and

Headridge [68] and Du Yan *et al.* [69]. This could be due to my use of higher acid concentrations or different concentrations of sodium borohydride.

In disagreement with the findings of Castillo *et al.* [70], the direct flame method could be used as an analytical method for the determination of indium because of the adequate results obtained for the determination of this element in a standard reference rock. As developed, the method was still not suitable for the low μg/g and ng/g range in rocks and minerals.

For the purpose of the determination of the Group IIIB elements in meteorites and geochemical materials, an inexpensive, and convenient analytical method was yet to be developed, and the next part of this thesis will be devoted to my work on the development of a method incorporating solvent extraction and graphite furnace atomic absorption spectrometry (GFAAS) for the quantification of these three elements in meteorites, rocks and minerals.

PART THREE

DEVELOPMENT OF SOLVENT EXTRACTION PROCEDURES FOR SPECTROMETRIC QUANTIFICATION OF GROUP IIIB ELEMENTS

III-1 INTRODUCTION

Solvent extraction is a powerful separation tool in modern analytical chemistry. The first quantitative studies of solvent extraction were carried out by Berthelot and Jungfleish [71] in 1872. Since then, particularly in the last few decades, much work has centred around the quantitative separation of metallic complexes from mineral acids into solvents. Progress in solvent extraction in recent years has been remarkable and has equalled the concomitant progress in instrumental methods of analysis.

Problems in chemical analysis almost always involve two steps: separation of the desired constituent, and measurement of the amount or concentration of this analyte. Much research has been dedicated to the development of more discriminatory methods of estimation, such as spectrographic, spectrometric and mass spectrometric methods, which need separation procedures preceding the measurement step.

Solvent extraction enjoys a favoured position among methods of separation because of its ease, simplicity, speed, inexpense and wide applicability. The equipment required for this technique is not complicated and is readily available in any analytical laboratory. In most cases, total separation often only requires a few minutes.

III-1-1 Principles of Solvent Extraction

Solvent extraction relies on the analyte being selectively extracted from an aqueous phase by an immiscible organic solvent. An element dissolved in one phase, e.*g*., in an aqueous solution, is more or less completely transferred to the second phase, which is usually an organic liquid such as benzene, chloroform, or methyl isobutyl ketone (MIBK). This is the principle of *liquid - liquid* extraction.

The *Distribution Law* [71,72] as explained by Nernst [72] in 1891, states that at equilibrium, the ratio of the concentrations of the solute in the two phases at a particular temperature will be a constant, provided the solute has the same molecular weight in each phase. For a solute X distributed between solvents 1 and 2, we have that:

$$K_D = [X]_1/[X]_2$$

where K_D is the distribution coefficient, a constant independent of total solute concentration.

The Nernst distribution law [2] states that K_D is a constant at a particular temperature, for any total concentration of solute. However, this law is not thermodynamically rigorous. It can therefore be shown that:

$$K_D = \frac{\tau_1}{\tau_2} \cdot K'$$

Where: τ_1 is the activity coefficient for phase 1
τ_2 is the activity coefficient for phase 2

Variation of the distribution coefficient will result from differences in the activity coefficients for each of the phases. When the solute concentration is very low, as is the case for the trace element extractions, the activity coefficients approach unity and K_D can be regarded as constant.

Of much greater significance because of their effect on the distribution are chemical interactions of the distributing species with the other components in each phase, since these interactions can profoundly affect the concentration of the distributing species. It becomes necessary to introduce a more practical quantity to describe the extraction, called *D*, the distribution ratio. This is a stoichiometric ratio including all species of the same component in the respective phases.

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

If conditions were ideal in that the same species were present in each phase, then *D* would be equal to K_d.

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

$$\%E = \frac{100\,D}{D + (V_a/V_o)}$$

where V_o and V_a represent the volumes of the organic and aqueous phases, respectively.

III-1-2 Classification of Extraction Systems

Since the formation of an extractable complex is a vital step in the extraction process, the nature of metal complexes and the factors governing their formation will now be discussed. Metal complexes are classified into two major types: coordination and chelate.

Coordination Complexes

Metallic ions combine with ligands in a number up to their coordination number to form coordination complex compounds, e.*g*., $Fe(CN)_6^{4-}$, $CoCl_4^{2-}(ROH)_2$ and $Cu[NH_3.(H_2O)_5]$.

Chelate complexes

Metallic ions form chelate complexes with some chelating agent such as 8-quinolinol and ethylenediaminetetraacetic acid (EDTA).

The condition for extraction of a species into an organic solvent is that there be an uncharged complex. This is achieved directly with chelate complexes but in the case of the more common co-ordination species, it is necessary to form ion association complexes. These are usually formed by the combination of a cation such as H_3O^+ with a complex anion involving the analyte and ligands such as halides, thiocyanate, or nitrate, and oxygen-containing organic compound to displace the coordinated water from metal. For example, the iron(III) complex extracted out of hydrochloric acid by ethyl ether probably has the formula $H^+,FeCl_4^-$.

Ion association complexes are commonly used for solvent extraction in analytical systems. Group IIIB elements are easily able to form such complexes in halide acid media.

In this present work, I have been concerned with the formation of ion association complexes of gallium, indium and thallium and their extraction into organic solvents under different conditions.

III-1-3 Choice of Solvent

Perhaps the most important consideration in the selection of a solvent for use in a particular extraction procedure is the extractability of the element of interest. The distribution ratio of the solute must, of course, be high if a separation is to be readily attained. By the same token the extraction of other solutes must be low if a separation is to be achieved.

In addition to a consideration of the solubility of the solute in a particular solvent, the ease of recovery of the solute from the solvent is important for subsequent analytical processing. Thus, the boiling point of the solvent or the ease of stripping by chemical reagents enters into selection of a solvent when the possibility of a choice exists. Similarly, the degree of miscibility of the two phases, the relative specific gravities, viscosities, and tendency to form emulsions should be considered.

For the point of view of safety, the toxicity and the flammability of the organic solvent obviously enter into the choice.

Usually, there are several kinds of organic solvent that can be used for the extraction procedure. These include esters, ketones, alcohols, ethers, aliphatic hydrocarbons, aromatic hydrocarbons, nitro-compounds, chlorinated solvents and others. Of these, ketones are among the most effective. For example, methyl isobutylketone (MIBK) has been widely used for extraction procedures. It is inexpensive, does not have a particularly unpleasant odour, and nor is it particularly toxic. It is only sparingly soluble in the aqueous phase, except in strong acid solutions, and has a low viscosity. Because of its many advantages, MIBK was chosen as a solvent for all my extraction procedures.

III-1-4 Solvent Extraction in Trace Element Analysis

Frequently in analysis of trace elements, the initial step is to obtain the analyte elements in solution. Acid digestion of the sample material is commonly used to achieve this. It provides an aqueous solution which will suffice as the aqueous phase in a solvent extraction system and will often, as in the case of chloro complexes, serve also as the ligand.

As metal ions in aqueous solution will not extract significantly into an organic phase, it is necessary to form a metal species which is uncharged, in order to facilitate extraction. Any water molecules coordinated to the metal must be replaced so that the metal species does not resemble the aqueous solvent. Strong extraction can be encouraged by producing a metal species which "resembles" the organic phase.

The practical applications of solvent extraction in an analytical procedure usually involve the following steps:

1. make an aqueous solution in which desired analyte elements are completely dissolved.
2. form ion association or chelate complexes with appropriate ligands.
3. extract analyte elements from aqueous solution by an appropriate organic solvent.
4. finally, analyse the extracted solution by an appropriate analytical instrumental method.

III-2 INSTRUMENTATION

After analyte elements are extracted into an organic phase from an aqueous phase, the choice of an appropriate instrumental method to quantify them can directly affect the sensitivity of the analyses. In this work, graphite furnace atomic absorption spectrometry (GFAAS) was chosen throughout all experiments.

III-2-1 Equipment

A GBC (System 1000) furnace unit, coupled to a GBC 902 Atomic Absorption Spectrometer (ICI, Sydney, Australia) was employed for all GFAAS determinations.

Sample injections were performed by a PAL 1000 automatic sampler (ICI, Sydney, Australia). All extracted sample solutions were placed into 5 mm i.d. glass tubes because of the small amount of solvent phase available.

All sample signals were printed on to an Epson LX-80 Printer and measured as peak heights or areas.

The "mini-Massman" type of graphite furnace which is 9 mm long and has an internal diameter of 3 mm was used for the System 1000 furnace unit.

Fig. III-1 shows a diagram of the System 1000 workhead. When the furnace is heated, oxygen-free nitrogen flows out of the diffuser to prevent oxidation of the graphite. The workhead is water cooled to reduce ‘down time’ between heating cycles to a minimum. The furnace is not enclosed, so it is readily accessible. Setting the furnace clamp to "load" draws the support rods apart which allows the furnace to be removed and replaced.

Two geometries of the sample injection probe are shown in Fig. III-2. Configuration B gave the best transfer of sample to the furnace.

A IKA-Labortechnik VXR Shaker and a centrifuge were employed for equilibration and phase separation during the extraction procedures.

III-2-2 Glassware

Glassware used for carrying out the solvent extractions and GFAAS determinations included test tubes, pipettes, beakers, volumetric flasks and Pasteur pipettes. The specific cleaning conditions for glassware were required for quantification of elements at the ultratrace level to avoid contamination. Generally, all glassware was soaked overnight in aqua regia before use. All traces of acid were removed by flushing with tap water followed by rinsing with deionized water or highly pure distilled water. Occasionally, potassium dichromate in concentrated sulphuric acid and/or detergent were used to clean some glassware dependent on special requirements. All glassware was of borosilicate type unless otherwise specified.

III-2-3 Reagents

All reagents used in this work were reagent grade (AR) except where otherwise specified. All acids and organic solvents were redistilled wherever possible.

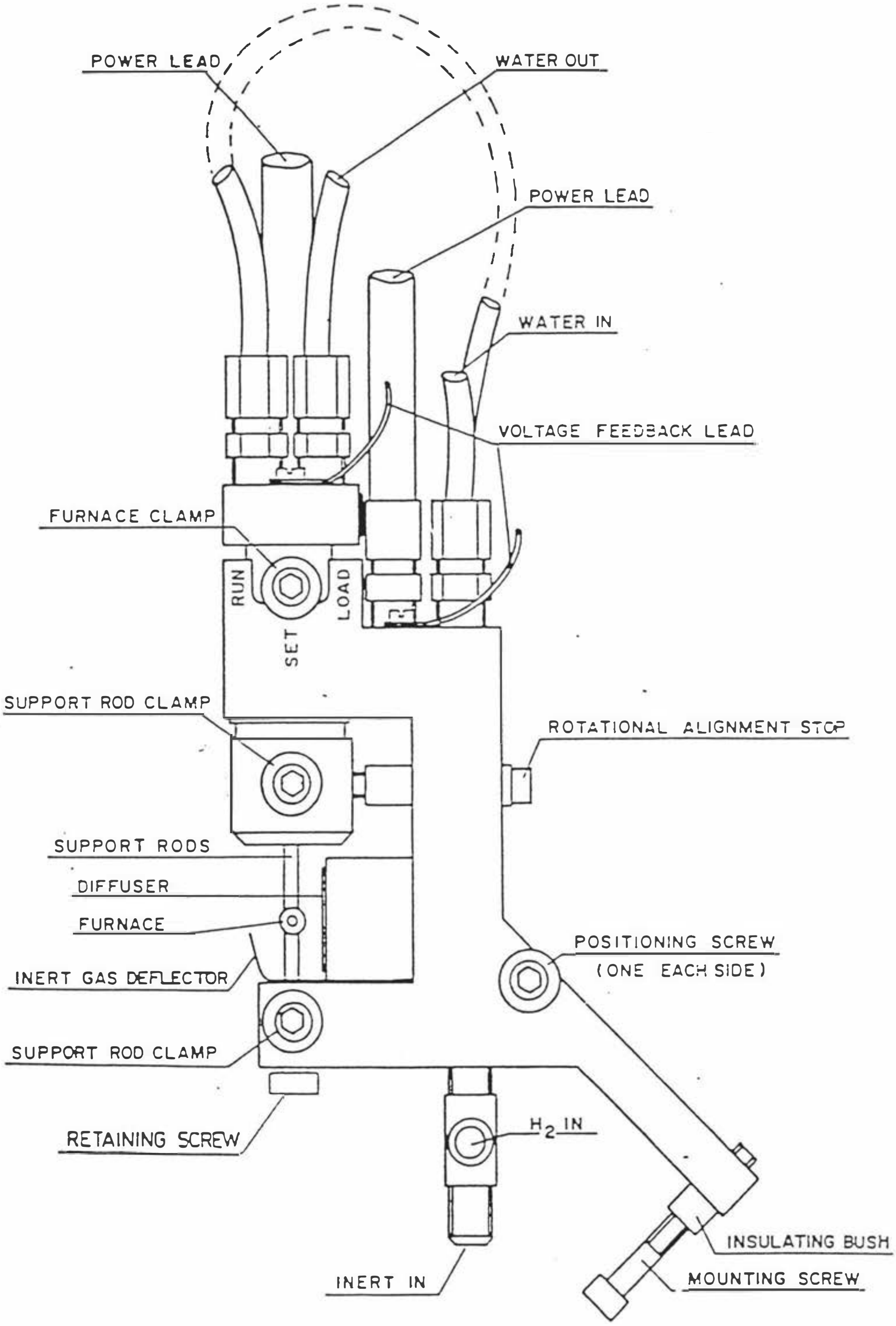


Fig.III-1 GF 1000 Workhead

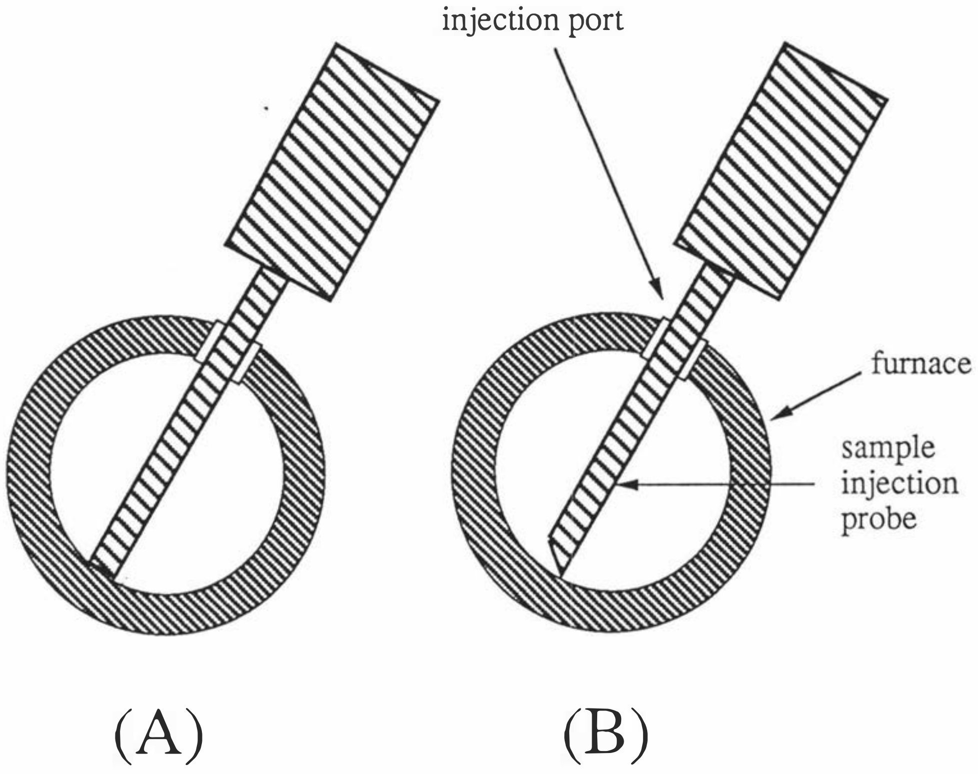


Fig.III-2 Sample injection probe geometries

Diagram of two possible geometries for the sample injection probe, at the moment of sample injection. Geometry (A) shows the probe with a flat tip that is touching the bottom of the furnace. Geometry (B) shows the probe with a 45^{o}cutting tip that is touching the bottom of the furnace

Some reagents and chemicals are listed as follows:

(1) Gallium(III), indium(III) and thallium(I) were prepared as standard stock aqueous solutions (1000 μg/mL) using the methods described in Part Two.

(2) Ascorbic acid, potassium iodide and dipotassium hydrogen phosphate (K_2HPO_4) were prepared directly by dissolving the solid in water.

(3) Acids were used in the following concentrations:

- (i) hydrochloric acid, 5M,
- (ii) hydrobromic acid, 4M,
- (iii) hydrofluoric acid, 40% (w/v),
- (iv) nitric acid, concentrated,

(4) Methyl isobutyl ketone (MIBK), was pre-equilibrated with different acids according to the nature of the aqueous phase involved in the subsequent extraction.

(5) Other reagents are discussed in the relevant sections.

III-2-4 Hollow Cathode Lamps

Hollow cathode lamps (HCL) of gallium, indium and thallium were supplied as sources for atomic absorption spectrometry. The employed analytical spectral lines were 287.4 (sometimes 296.7), 303.9, and 276.8 nm for gallium, indium and thallium, respectively. The lamp current can directly influence the baseline and sometimes causes fluctuation in the lamp signal. A large fluctuation leads to a large background absorption signal. When lamp currents of less than 5 mA are used, the background absorption signal is unacceptably large, except for thallium where a lamp current down to 3 mA is still stable. On the other hand, high currents cannot be used because of speedy shortening of lamp lives. Currents of 5-7 mA were used depending on the analyte concentration in the samples.

III-2-5 Graphite Furnace

Different inner surfaces of graphite furnaces and their installation positions were found to directly influence the analytical signals. The effect of the graphite furnace inner surface on deposition of sample solutions into the furnace was investigated on different furnaces.

In the case of thallium and gallium, the experiments showed that satisfactory deposition depended on the smoothness or coarseness of the furnace. It appeared that a rough surface was preferable to a smooth one because the solutions tended not to spread as quickly as they would on a smooth surface.

It was also observed that when smooth furnaces were used, there was greater tendency for a small amount of the analyte solution to be removed as the application tip was removed. This problem causes much trouble such as poor reproducibility and anomalous signals, particularly when multiple loading injections were used. Such signals were often reduced by as much as 20% after six injections. However, a coarse surface furnace may have a shorter working life because of its lack of the pyrolized coating. Fortunately, the atomisation temperatures used in this work were not very high (1600-2250°C). Such a furnace could be used for several dozen firings.

A rough furnace was not suitable for determination of indium because of higher background absorption signals.

Another potential problem is the positioning of the graphite furnace in the instrument. Because the optical path through the furnace is so narrow, the latter must be carefully placed in the middle of the optical axis to allow maximum passage of the emission radiation from the hollow cathode lamp.

III-2-6 Sample Injection Tip Alignment

The PAL 1000 auto-sampler uses a robot arm to manoeuvre the sample injection tip. Sample solution is drawn up into a plastic or glass tube through the tip. The robot arm then places the tip through the sample injection port, and the sample solution is injected into the furnace tube. The tip must be adjusted to the correct position, otherwise there will be incorrect sample transfer. The geometry of the teflon tube at the tip is very critical and as recommended by Wilson [73], it has been my practice to cut the tip at an angle of 45° in order not only to allow for complete sample transfer but also to ensure that solution is not removed and deposited at the injection port when the tip is withdrawn.

III-2-7 The Sampling Vial

The polythene sample vials supplied by the manufacturer of the instrument could not be used with organic solvents because the glue used to attach the base of these vials was readily solubilised in MIBK. To overcome this problem, glass test tubes that fitted into the automatic sampling carousel were cut to a height of 25 mm and initially replaced the plastic vials.

The glass test tubes had a capacity of about 1.5 mL of organic solution and could readily be reused after washing. However in my work, the volume of most extracts was only about 0.7-1 mL. Another sampling vial was therefore devised using small 1 mL Durham tubes and the manufacturer's original plastic vials and caps. A hole was punched into the cap with a cork borer and a Durham tube inserted. This cap was then placed over the plastic vial and the organic sample was placed into the tube with a Pasteur pipette. This modified tube could hold about 0.3 - 0.5 mL of solution that was enough to provide hundreds of multiple injections.

III-2-8 Multiple Loadings

The PAL 1000 auto-sampler has the capability to provide multiple loading injections whereby a much larger volume of sample solution (up to 50 μL) may be deposited into the graphite furnace tube prior to atomisation. This is a useful technique for the determination of trace level elements in samples.

A 3-5 μL aliquot of sample MIBK solution is automatically injected into the furnace tube. The temperature of the furnace tube is raised to 120°C for drying the solution and then the furnace is cooled before the next of the multiple loadings. This is repeated as often as required and then the cycle is completed by single charring and atomisation steps. Analyte elements can therefore be concentrated in the furnace in order to to increase sensitivity.

From experiments with this technique, I obtained a satisfactory agreement between the absorbance of a single loading of 0.6 μg of gallium standard and six multiple loadings each of 0.1 μg. It is necessary to emphasise that this technique cannot be used when the lamp current is not stable and where there is hence a strong background noise.

III-2-9 Furnace Heating Programmes

Usually, there are at least three steps for electrothermal atomisation procedures. Temperatures for each step should be carefully chosen for each element. The GBC System 1000 instrument allows up to ten heating stages with each heating cycle. When organic solvents are analyzed, it is common to include a pre-heating step with three principal heating steps.

Pre-heating the furnace tube before sample injection can increase sensitivity. This was observed in analysis of a standard gallium solution in MIBK. Without pre-heating, the MIBK solution had a tendency to creep along the tube and flow over both ends before the end of the drying step. With judicious choice of the pre-heating temperature, the MIBK solution can be made to dry evenly before it has a chance to move towards the furnace tube extremities. The best pre-heating temperature was 75°C for the organic solutions analysed.

The charring step temperature must be chosen after consideration of several important factors. For example, the temperature must not exceed the boiling point of the analyte element or compound otherwise this will be lost before the atomisation step is reached. Usually the charring temperature is about 400°C. According to my experiments, the optimum charring temperatures were 415°C for gallium and indium and 420°C for thallium.

Choice of the best atomisation temperature has to be made to ensure high production of atomic vapour in the furnace. The selected temperatures were based on an optimisation study. Data for gallium are plotted in Fig.III-3. This figure shows that no further increase in signal would be achieved by using an atomisation temperature exceeding 2250°C. Atomising at a higher temperature would cause unnecessary furnace wear. The optimum atomisation temperatures were established at 2250°, 2150° and 1600°C, gallium, indium, and thallium respectively.

III-2-10 Absorption Signals and Background Noise

Typical absorption signals for the three Group IIIB elements are shown in Fig.III-4. All signals observed for these elements showed an absorption maximum at just within or over one second after the atomisation step begins.

From the same figure, the noise levels were obviously different among three elements and were related to the quality of the hollow cathode lamp. Of these, the indium lamp showed the poorest stability and highest noise level compared with the others, and had the further disadvantage of signal decay after more than 2 hours.

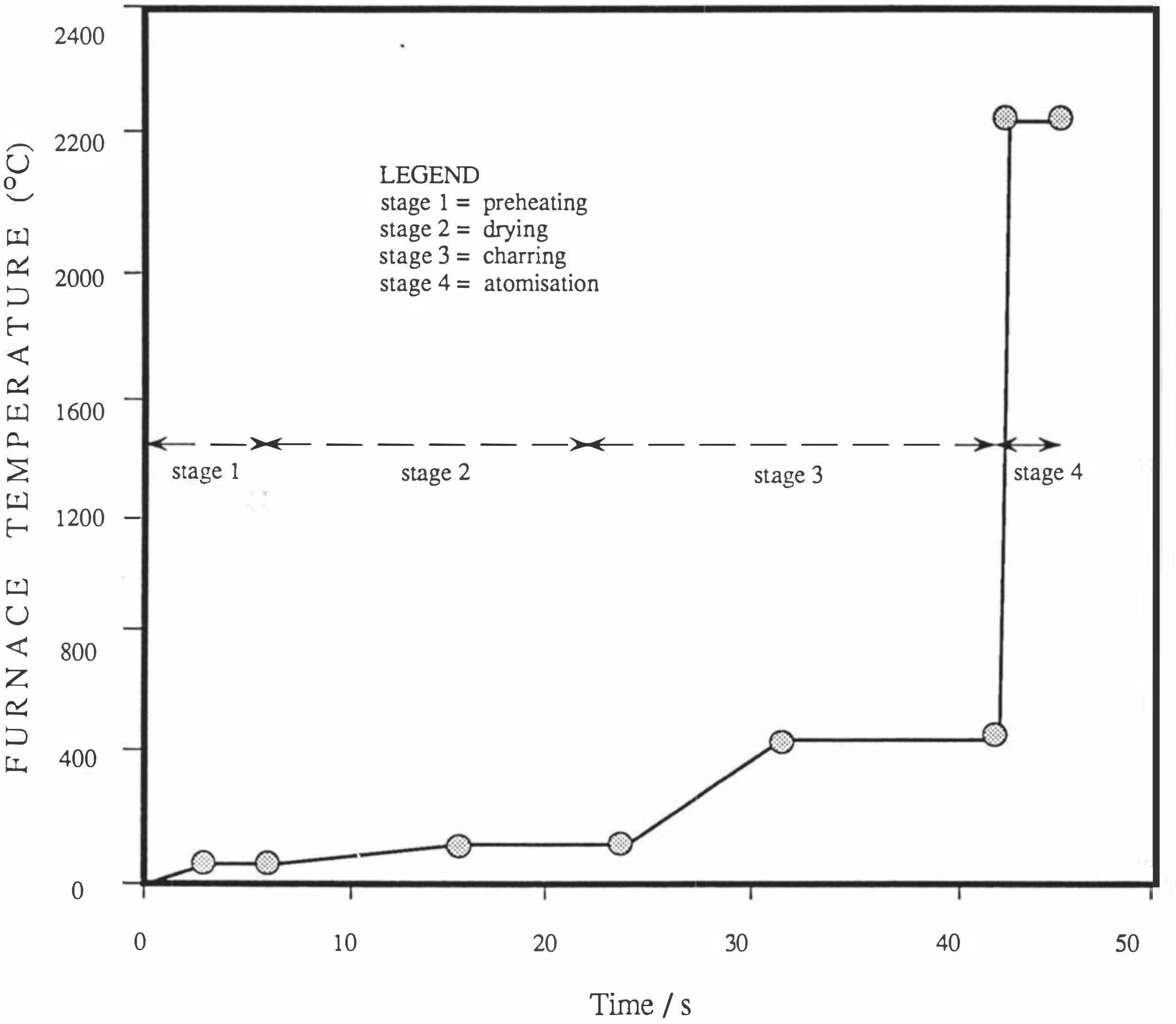
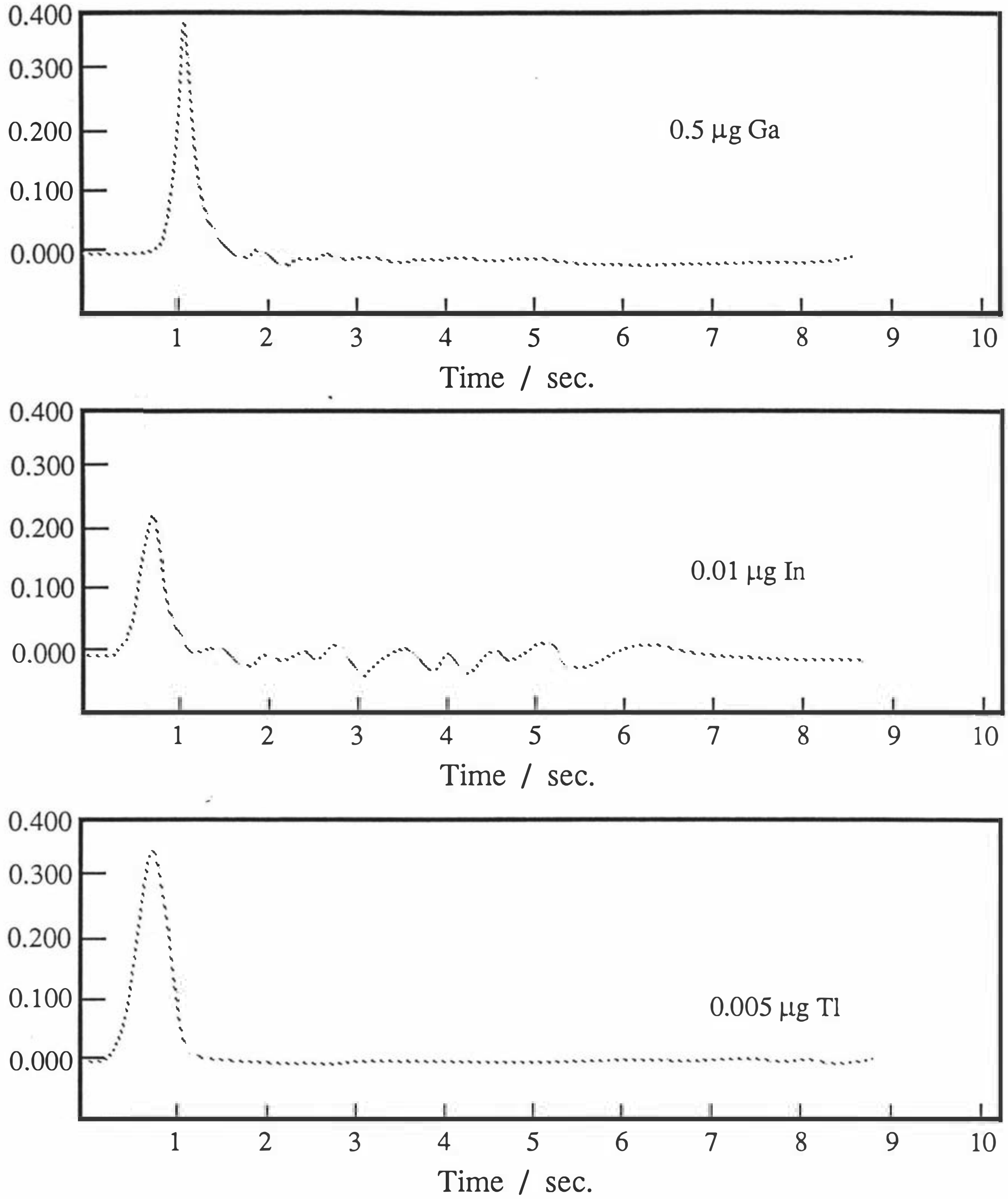


Fig.III-3 A typical furnace cycle



ig.III-4 Typical absorbance signals for gallium, indium and thallium by GFAAS

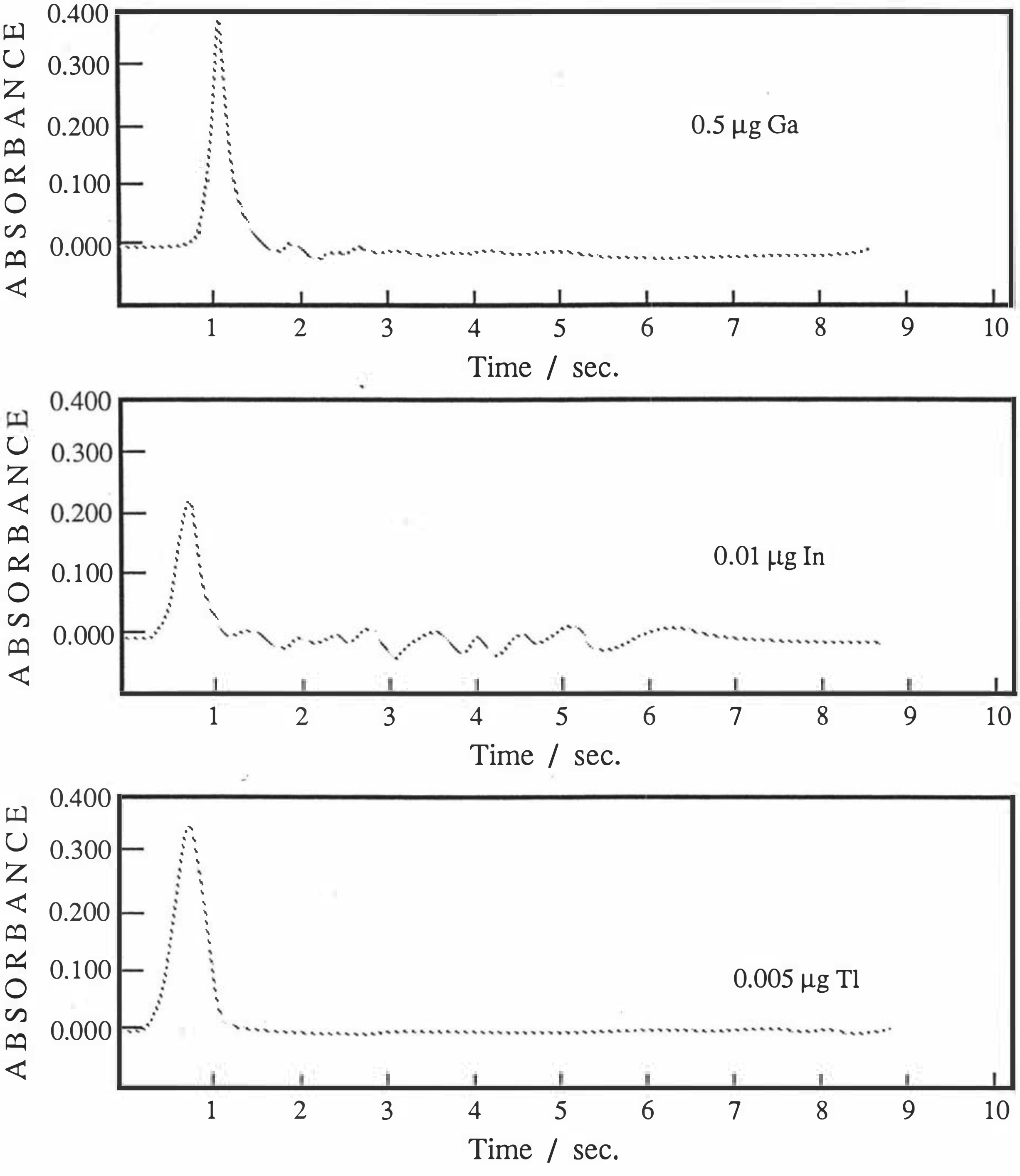


Fig.III-4 Typical absorbance signals for gallium, indium and thallium by GFAAS

SECTION III-1 GALLIUM

III-3 DEVELOPMENT OF A PROCEDURE FOR QUANTIFICATION OF GALLIUM

Gallium is an element of medium volatility and its abundance is about 20 μg/g in silicate rocks. It is an important element in geochemistry. For example, it plays a remarkable role in the chemical classification of iron meteorites (details given in Part Four).

Gallium in meteorites or silicate rocks can sometimes be determined by neutron activation analysis (NAA), but the limit of detection is not sufficient to detect this element at the ultratrace level. Another problem, as mentioned before, is that NAA is very expensive and not available in New Zealand. There was clearly a need to develop a suitable analytical procedure to quantify this element.

An obvious first step in the development of an analytical method for gallium was to pre-concentrate this element from an original solution. Solvent extraction presents a number of advantages for such a purpose. The first is that some non-extractable interfering elements can be removed. The analyte can also be extracted into a small volume of organic solvent from a much larger volume of aqueous phase and hence enrich the analyte and increase sensitivity. A second advantage is the simplicity of the apparatus and low cost of materials.

Early investigations were centred around the use of extraction as an adjunct to classical methods for the determination of gallium. Some workers [74,75] determined trace quantities of gallium in various samples using methods involving the extraction of gallium hydroxyquinolate with chloroform at a specific pH. This was a common technique to separate gallium from other elements. Steibach and Freiser [76] stated that the use of acetylacetone as an extracting agent separated gallium from an aqueous phase at pH 1.2. A gallium benzoate complex in ammonium acetate solution could be extracted into ethyl acetate [77]. A successful extraction system for gallium is to form a chloro complex that can be extracted into an organic phase. Sandell [78] and Irving [79] investigated the extraction of gallium chloro complexes and showed that the method had a good potential for separating this element from many others although iron was always co-extracted because of the similarity of the extraction curves over a wide range of hydrochloric acid concentrations.

The iron problem as mentioned above has always been the greatest hindrance to quantification of gallium in silicate rocks when a chloro-complex extraction system is used. The following work was therefore undertaken to try to circumvent this problem, particularly as it concerned geological samples such as meteorites that have a very high iron content (>90 %).

III-3-1 Experimental

As already mentioned iron and other elements are usually co-extracted together with gallium into an organic phase. Many transition elements, and iron in particular, will interfere in the determination of gallium by instrumental methods such as GFAAS. Although iron can be removed by precipitation as the hydroxide, gallium also forms an insoluble hydroxide. Some workers [80-82] used various reducing agents to reduce iron (III) to iron(II) that does not readily extract from hydrochloric acid solutions into an organic solvent such as MIBK, but none of these methods is satisfactory when the iron content of the sample is very high, as in meteorites.

i. Sample Purification and Reduction of Interferences

The aim of this experiment was to quantify gallium in meteorites and some geochemical materials. For these samples the key to the problem was to eliminate the interference from iron, nickel, copper and other elements present in high concentrations. For example, iron meteorites contain about 90% iron, 8% nickel, and various other transition elements such as chromium and cobalt. Of these elements, iron interference is the most serious since its presence prevents separation and quantification of gallium.

Fig.III-5 shows GFAAS absorbances when 1 μg of gallium was extracted into MIBK from 5M hydrochloric acid in the presence of various concentrations of iron(III). In the presence of 200 μg of iron (far below the 10 mg/mL iron to be expected if a 1 gram sample of iron meteorites were dissolved in 100 mL of acid), the signal begins to decrease. When the iron content reaches 1 mg/mL, the signal is only one sixth of its original value. This demonstrates a serious matrix effect. The presence of iron(III) interferes in the GFAAS procedure rather than in the extraction process. This is demonstrated in Fig.III-5.

The best way to remove iron is to reduce it to the divalent state because ferrous iron is not extracted into an organic phase.

The following experiments were concerned with the reduction of iron to its ferrous state and involved the use of several reductants.

a. Use of ascorbic acid

Some workers have proposed the use of ascorbic acid as a reducing agent [82,83] to eliminate interference from iron(III) at the extraction stage before instrumental quantification of gallium. However none of the samples used were high in iron, probably because of the limited reducing capability of ascorbic acid.

The effect of ascorbic acid reduction of iron(III) was investigated. Two sets of solutions were prepared, both containing 5 mL of a 0.5 μg/mL standard gallium solution in 5M hydrochloric acid. One set contained the pure standard gallium solutions with addition of various amounts (0-1.5 g) of ascorbic acid. Each of these solutions was extracted into 5 mL of pre-equilibrated MIBK. Another set of solutions was identical with the first except that each contained 1% (10

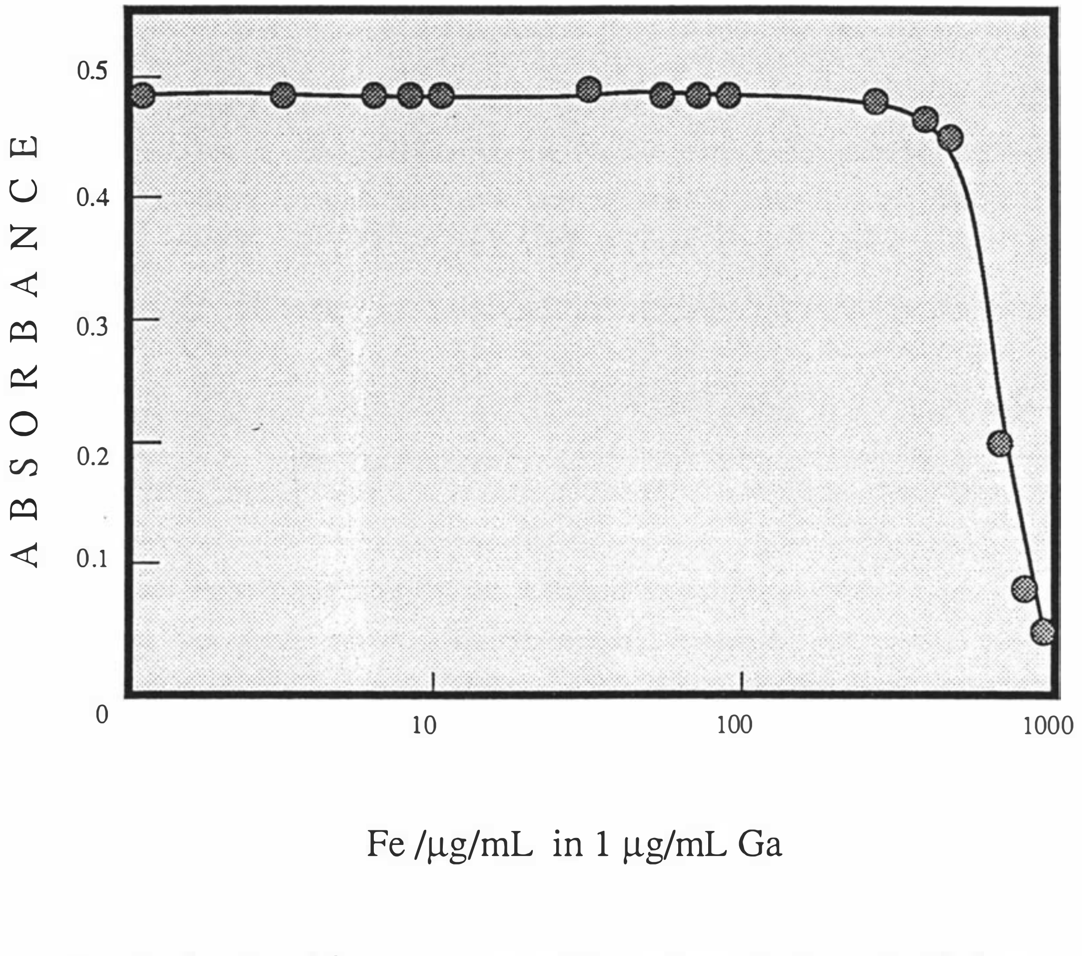


Fig. III-5 GFAAS absorbance of Ga extracted into MIBK from 5M HCl in the presence of various concentrations of iron (III) mg/mL) iron(III). The results are shown in Fig.III-6 and demonstrated that a minimum of 500 mg of ascorbic acid was needed for each 2 mg of iron to give a stable signal. However, this signal was only one third of that obtained when the same solution of gallium without added iron or ascorbic acid was measured.

From Fig.III-6 another problem exists when ascorbic acid alone was added to an iron-free gallium solution. The signal was reduced by a half for 500 mg of added ascorbic acid, and ultimately gave an absorbance even lower than when iron was also present. It is clear that both iron(III) and ascorbic acid interfere in the GFAAS determination of gallium.

b. Use of sodium borohydriode

Sodium borohydride is a very strong reductant and it has been widely used for reducing metallic ions. This reagent was used to investigate its effect on reducing iron. As was done for ascorbic acid, two sets of gallium solutions were prepared. To one set, various amounts of sodium borohydride (0.5-5.0%) were added. The results are given in Fig.III-7 and show that the signal started to increase at 0.25% sodium borohydride and reached a limiting value at 0.5%. The results were however, very disappointing due to the poor sensitivity. After even high borohydride concentrations the signal decreased to less than its initial value.

There are two possible reasons for the behaviour of borohydride as a reductant: firstly, the reagent can reduce both iron and the analyte element because some grey precipitates were observed in the reaction vessel; another reason is that gallium may have been converted into a volatile hydride by sodium borohydride and is lost from the solution. Sodium borohydride is clearly unsuitable for reduction of iron in the presence of gallium.

c. Use of other reductants

The use of other reductants such as titanium (III) sulphate or chloride and tin (II) chloride were also

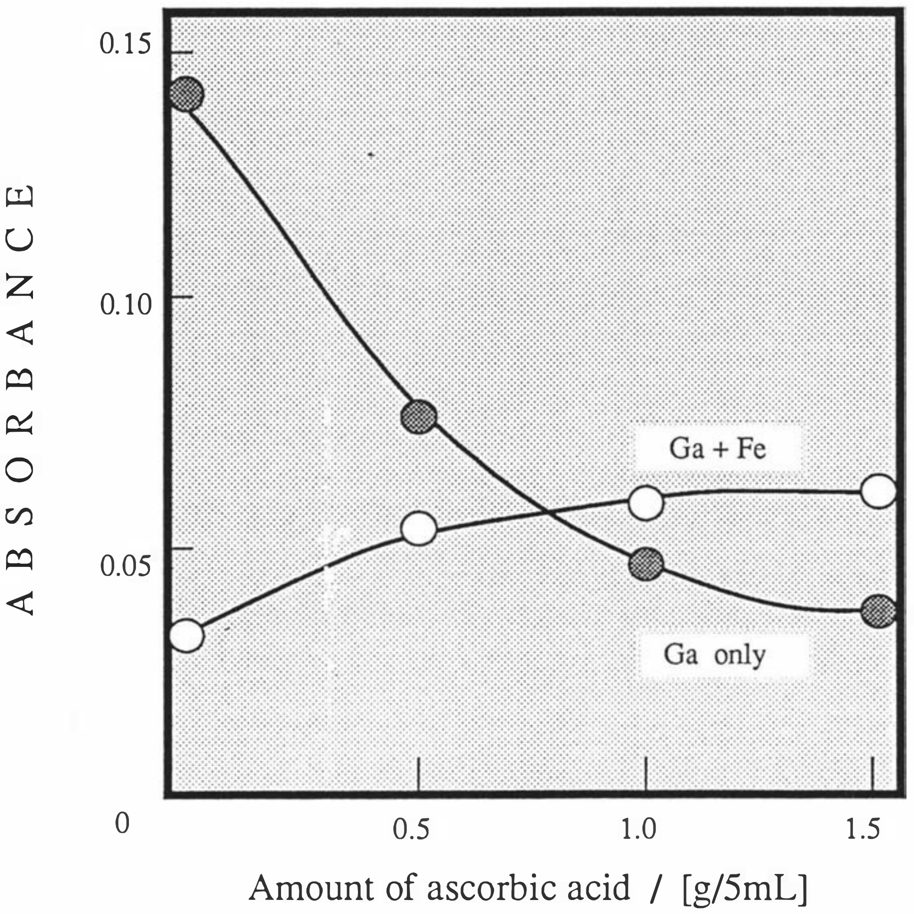


Fig.III-6 Effect of the ascorbic acid concentration on the GFAAS absorption signal for gallium with and without the presence of iron

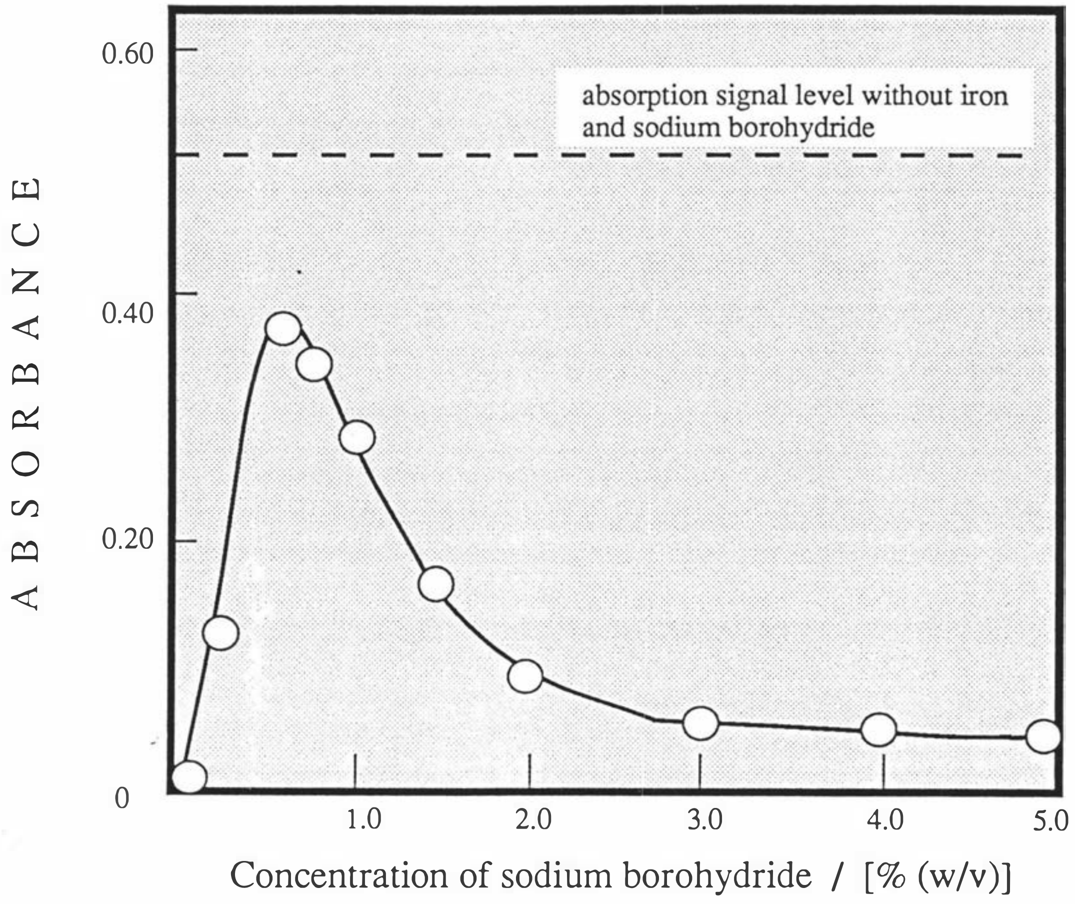


Fig.III-7 Effect of sodium borohydride on the GFAAS absorption signal for 1 μg/mL gallium in the presence of iron (2 mg/mL) investigated. Pollock [84] and Popova [85] have reported reduction to iron (II) by the addition of excess titanium (III) sulphate. Other reports mention use of tin (II) chloride to reduce iron (III) [86]. After a series of experiments, I concluded that none of these reducants was satisfactory for the purpose of the research.

d. Reduction of iron (III) with potassium iodide

The discovery of a suitable reducing agent is essential to permit trouble-free determination of gallium by GFAAS.

In the course of testing several reducing agents, I found that potassium iodide was a satisfactory reagent for the purpose of retaining iron in the ferrous state. Potassium iodide in acid solution has not previously been used in extraction systems.

Investigations on the reduction of iron with potassium iodide were carried out by determination of iron in both aqueous and organic phases after equilibration. Solutions of 10 mg/mL iron (III) in 2 mL of 5M hydrochloric acid were extracted with 1 mL of MIBK solvent after addition of various amounts of potassium iodide. The results are shown in Fig.III-8.

The extractability of gallium reached nearly 100% when 0.2 g of potassium iodide was added and remained at this level up to 0.4 g. At higher concentrations of potassium iodide the extraction started to reduce.

The extractability of iron is shown in another curve in Fig.III-8. When 0.3 g of potassium iodide was added when iron was extracted into MIBK, the iron content of the organic phase was only 200 μg/mL (2% of the total iron). When the amount of reagent was increased to 0.5 g of potassium iodide, the iron content fell well below 200 μg/mL. This threshold value is of some importance because such a concentration of iron does not affect the gallium GFAAS signal to any measurable degree.

It was clear that potassium iodide satisfactorily reduces iron (III) to iron (II) hence removing interference from this metal in the course of the extraction of gallium. Further experiments therefore made use of potassium iodide.

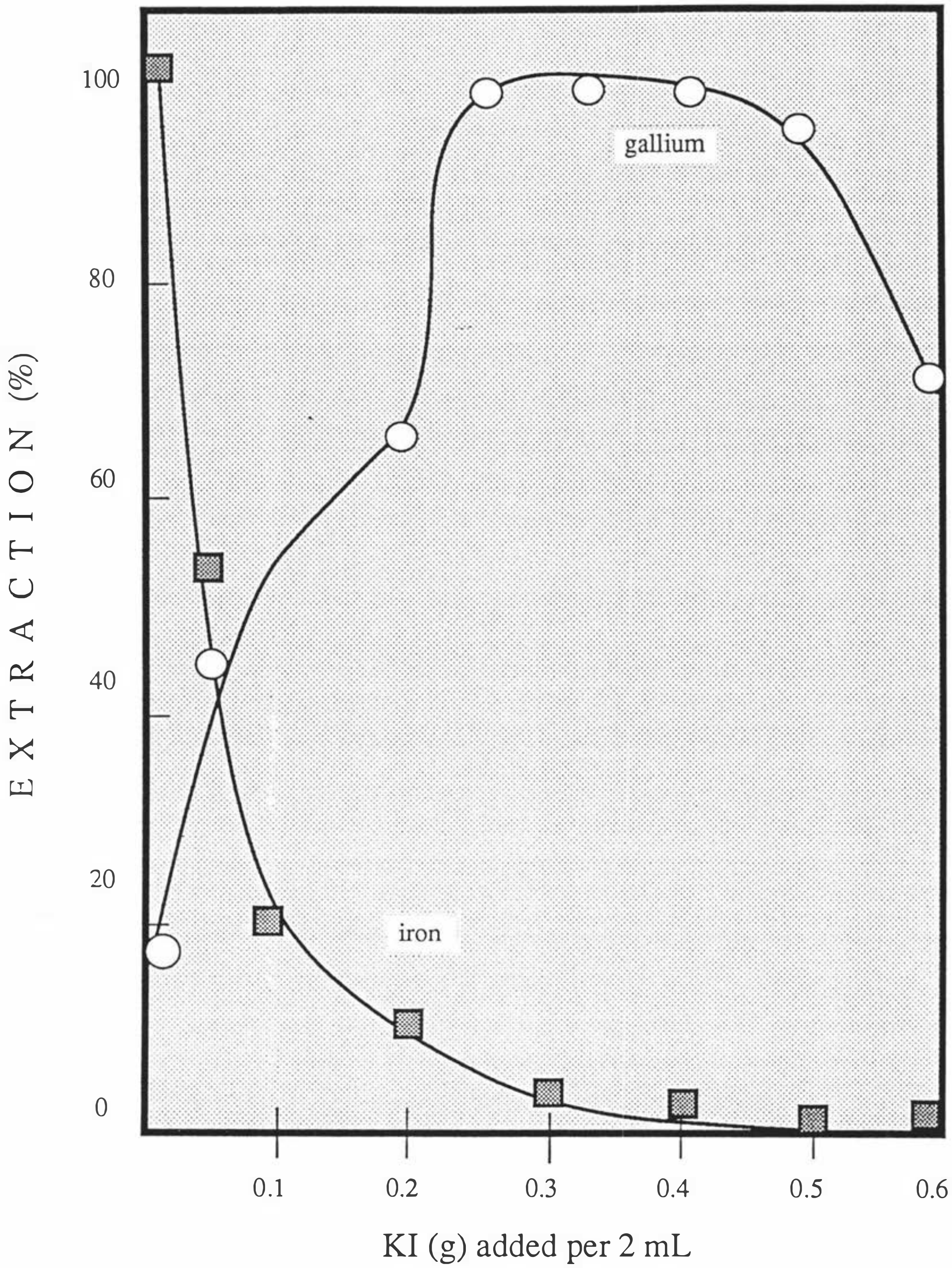


Fig.III-8 Effect of the KI concentration on the extraction of iron and gallium from 5 M HCl into MIBK

ii. Acid Type and Concentration

Gallium and iron are readily extracted into an organic phase as their ion association complexes that include an anionic halide complex in the presence of an acid to supply the proton. As early as 1892 Rothe [87] studied this extraction process for iron, and other investigators [88-90] successfully separated iron into an organic phase from many other elemental species in hydrochloric acid solution. Acidity is an important factor affecting this extraction.

The effect of various concentrations of different acids upon the extraction of gallium by MIBK was investigated. The following acids were tested: hydrochloric, hydrobromic, sulphuric, perchloric, phosphoric and acetic. One μg/mL gallium and 10 mg/mL of iron were prepared in each solution of different concentrations of each acid and equilibrated with an equal volume of MIBK. The organic layers were then analysed by GFAAS. The results are given in Fig.III-9.

Only hydrochloric acid gave a satisfactory extraction capability (almost 100% at concentrations of 4.0-6.5 M). Phosphoric and acetic acids gave poor extraction of gallium into MIBK. Hydrochloric acid was therefore selected as an acid medium and a concentration of 5M was used for this work. Higher concentrations of this acid lead to complete miscibility of the two phases.

iii. Stability of the Gallium Complex in the Organic Phase

The purpose of this experiment was to establish the stability of the gallium chloro complex in the organic phase (MIBK) after extraction from the aqueous phase. The experiment was carried out by the determination of gallium in the organic phase. A set of aqueous solutions (4 mL) containing 1 μg of standard gallium, and 0.8 g potassium iodide in 5M hydrochloric acid were shaken with MIBK and then gallium was determined in the organic phase at various times after

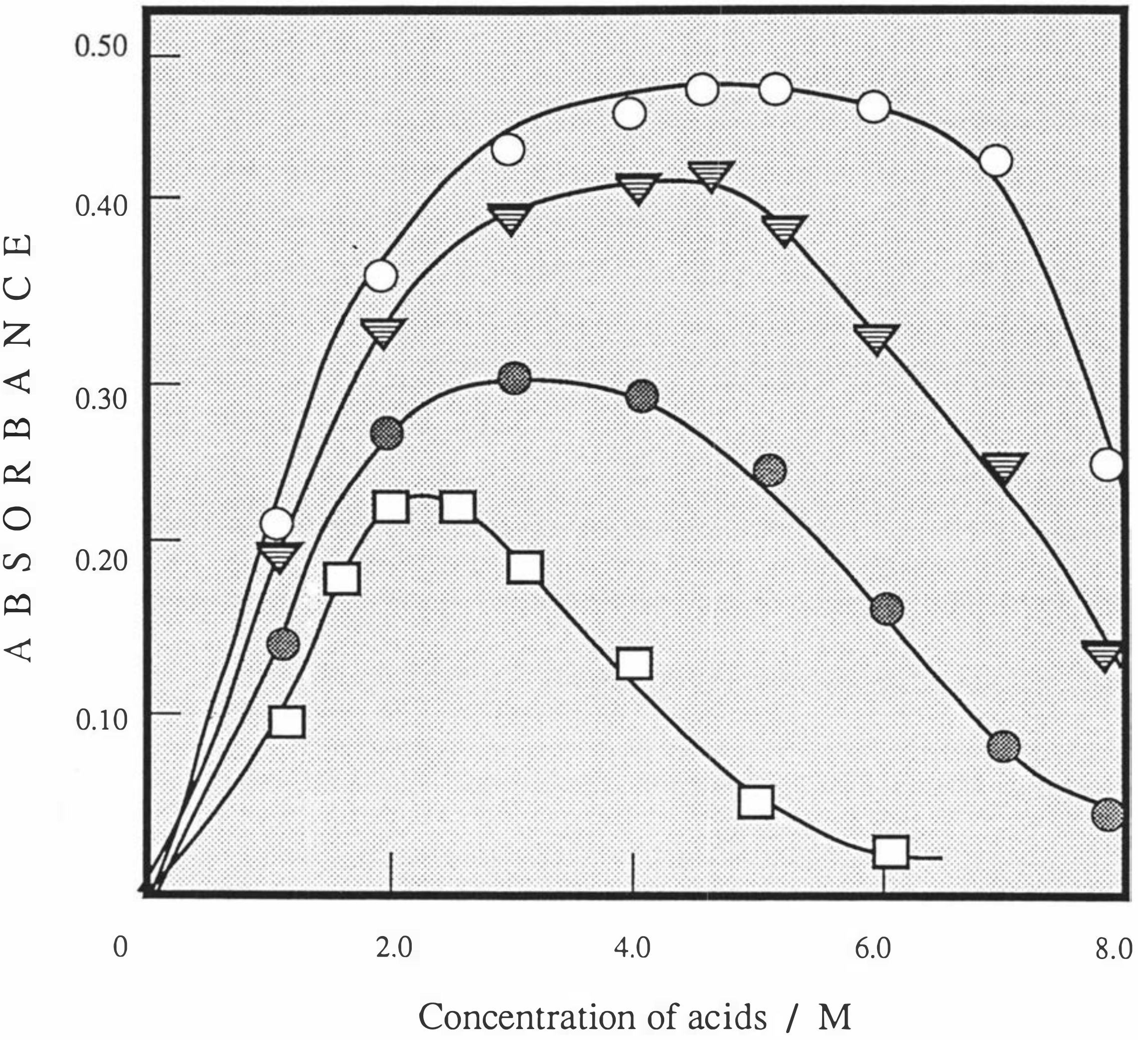


Fig. III-9 Effect of molarity of several acids on the extraction of gallium into MIBK separation. The results are given in Fig.III-10 and demonstrated that the complex was extremely stable. From 5 minutes to 6 hours after extraction the gallium absorption signal in the organic solutions remained constant. Thereafter the signal started to decrease and after standing overnight was reduced to almost zero. It was decided that it would be safer to complete all GFAAS determinations within two hours after separation, and that all organic phases and standards be quantified at the same time to reduce analytical errors.

Despite the high concentration of iodide (0.2 g of KI per mL solution) used in the extraction system, it might be expected that a small proportion of GaI_4^- be present along with the chloro complex despite the stability constant of $GaCl_4^-$ being greater than that of GaI_4^- [91] It is for this reason that the absorption signal did not reach its maximum immediately after separating the two phases. However iodide did not interfere with the extraction, as was confirmed by further experimentation.

iv. Shaking Time of Extraction

The degree and rate of extraction of gallium into MIBK was highly dependent on the shaking time. Gallium concentrations in the organic phases were measured by GFAAS after different shaking times and the data are shown in Fig.III-11. The degree of extraction increased to 100% after 1.5 minutes shaking, but started to decrease after 4 minutes. The reason may be due to slow conversion of some of the chloro complex of gallium into the poorly extractable iodo form. The optimum shaking time of three minutes was chosen for all extractions. The phases were separated by centrifuging and allowed to stand for only one minute. The upper organic layer was removed with a Pasteur pipette and transferred to a small glass tube (*i.d.* 5 mm) for the determination of gallium by GFAAS. Care was taken not to delay separation of the phases more than one minute because of the risk of back-extraction of gallium into the aqueous phase.

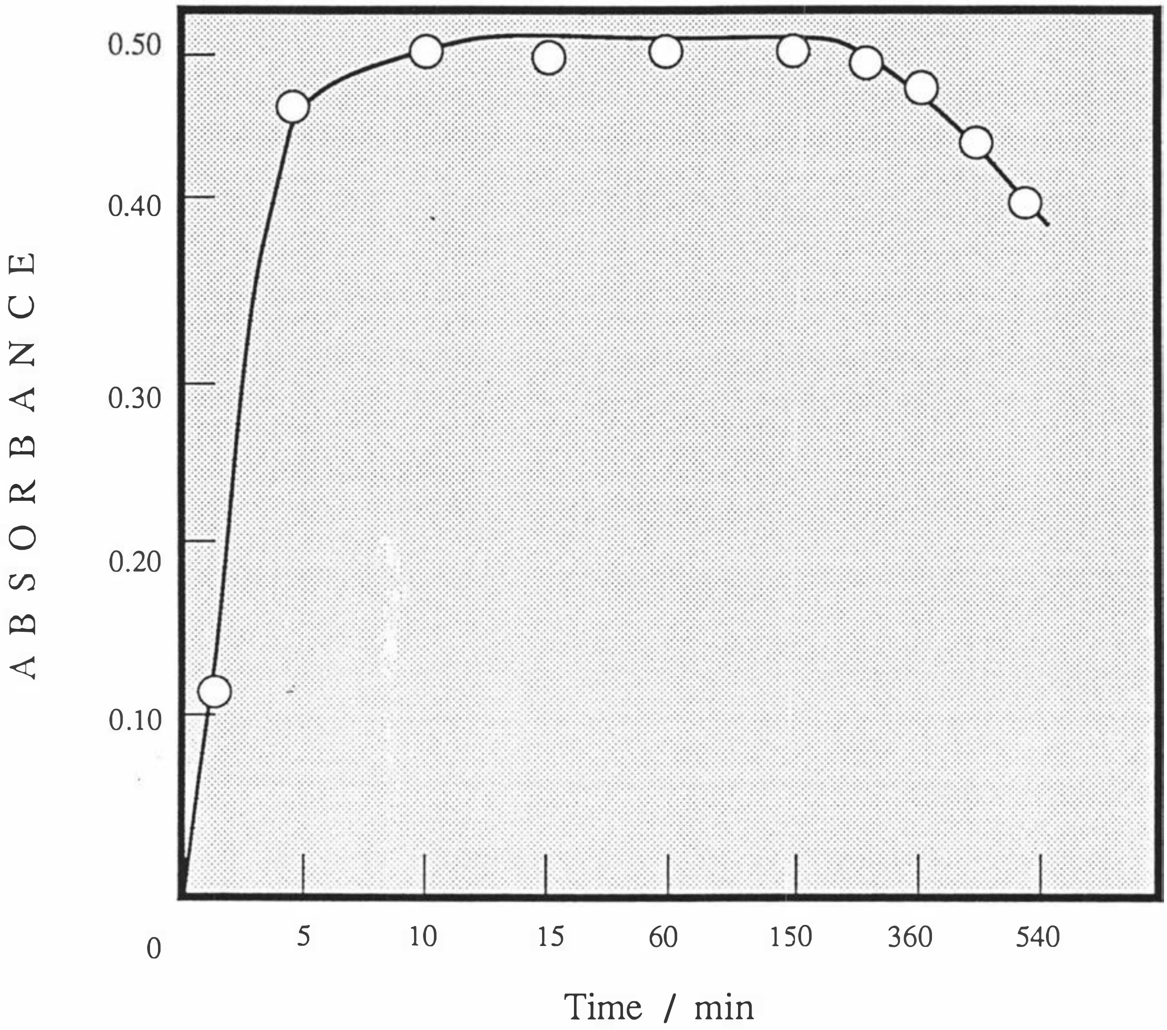


Fig.III-10 Stability of the gallium chloro complex in the organic phase after separation from the aqueous phase

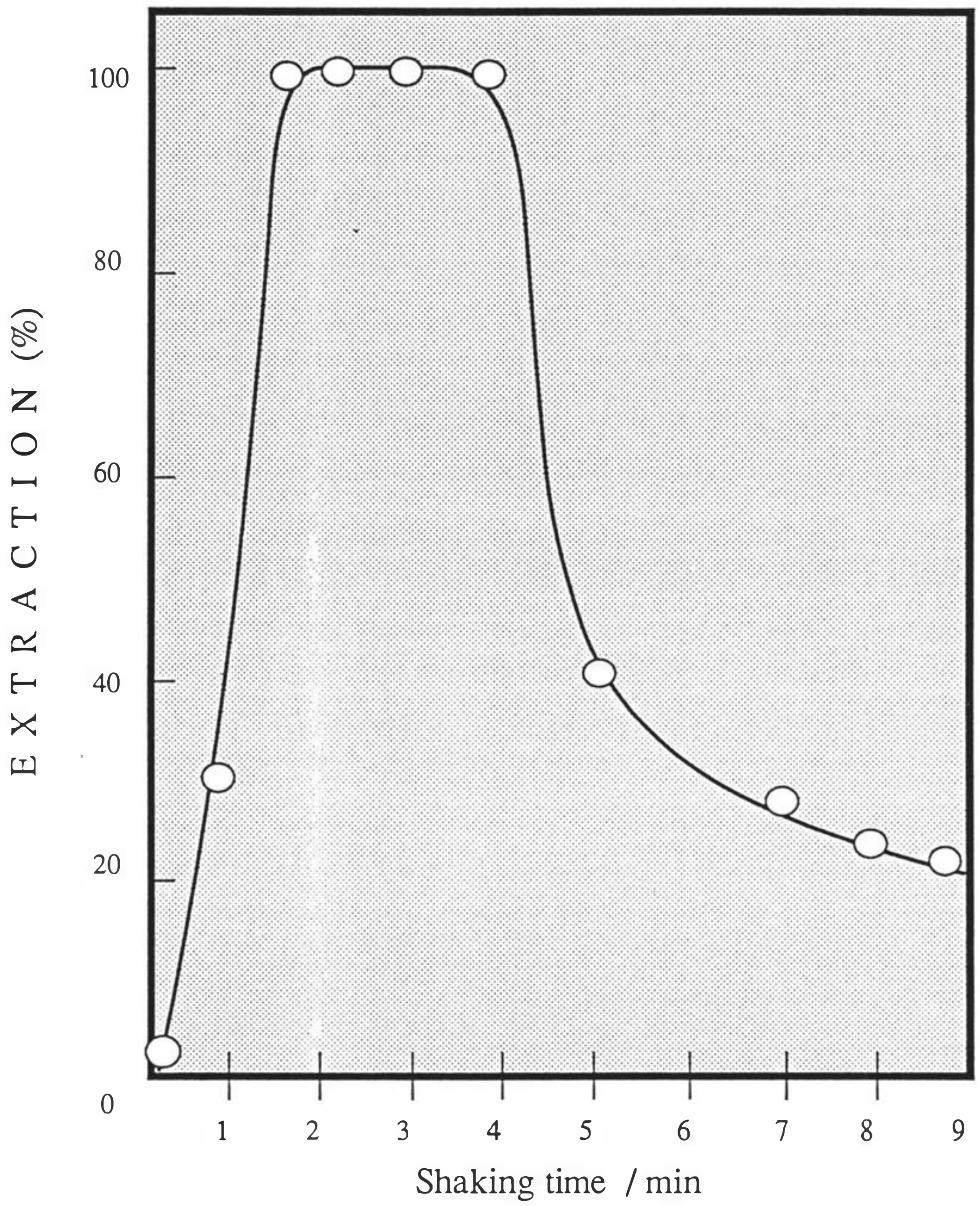


Fig.III-11 Effect of shaking time on the extraction of gallium from 5 M HCl into MIBK

v. Comparison of Manual and Mechanical Shaking

Shaking by hand or by a mechanical shaker may result in different extraction effectiveness. A study was made in which extraction of 1 μg/mL gallium into MIBK was performed with both hand and mechanical shaking for various times. The results are given in Table III-1.

Table III-1 Comparison of gallium absorbances in the MIBK phase after manual and mechanical shaking

	Shaking Time (min)					
Shaking Procedure	0.5	1.0	1.5	2.0	2.5	3.0
Manual	0.39	0.57	0.66	0.68	0.72	0.70
Mechanical	0.38	0.55	0.79	0.82	0.85	0.81

From the above results, there was no obvious difference between manual and mechanical shaking for 0.5 to 1 minutes After 1.5 minutes and above, manual shaking was clearly inferior. The reason may be the difficulty in maintaining standardised manual shaking over a longer period. Mechanical shaking was therefore used for all subsequent operations.

vi. Values of the Distribution Ratio

Morrison and Freiser [92] have summarised various extraction systems involving the chloro complexes of gallium. These are given in Table III-2

Table III-2 Extraction of Chloro Complexes of Gallium

Species	Aqueous phase	Organic phase	Extraction
Ga(III)	6M HCl	Ethyl Ether	97.0%
Ga(III)	7M HCl	Isopropyl Ether	>99.9%
Ga(III)	3M HCl	Tributyl phosp.	99.9%

To obtain the distribution ratio of the gallium chloro complex between MIBK and the aqueous phases by use of my developed procedure, a set of solutions was prepared that contained 10 μg/mL of standard gallium in various concentrations of chloride and with the acidity maintained at 5M (adjusted by HI when chloride concentrations were below 5 M). After extracting by MIBK (1 mL MIBK from 10 mL aqueous solution) gallium was determined directly in both phases by flame atomic absorption spectrometry. The distribution ratio of the gallium chloro complex $\{H_3O^+.GaCl_4^-\}$ was calculated as $D = 4640$, i.e. nearly 100 % extraction.

III-3-2 Limit of Detection

The limit of detection for the GFAAS quantification of gallium was determined by the IUPAC method [93]. Data for replicates of absorbances of a reagent blank and three standards are given in Table III-3.

Table III-3 Absorbances of Gallium Standard Solutions

Ga Concentration (μg/mL)	0.00	0.10	0.30	0.50
n = 20	0.002	0.068	0.208	0.338
	0.004	0.070	0.192	0.342
	0.003	0.064	0.188	0.333
	0.007	0.060	0.210	0.329
	0.001	0.073	0.203	0.320
	0.001	0.071	0.184	0.319
	0.000	0.064	0.179	0.339
	0.003	0.064	0.183	0.334
	0.008	0.059	0.199	0.298
	0.008	0.067	0.203	0.345
	0.003	0.069	0.213	0.332
	0.011	0.066	0.189	0.334
	0.006	0.073	0.188	0.340
	0.001	0.054	0.192	0.323
	0.007	0.059	0.198	0.342
	0.002	0.071	0.201	0.310
	0.001	0.068	0.213	0.334
	0.009	0.064	0.192	0.340
	0.004	0.075	0.178	0.384
	0.000	0.064	0.167	0.336

The limit of detection for gallium by GFAAS was calculated by the IUPAC method using the data in Table III-3 above. The limit of detection (C_l) is given by the expression:

$$C_l = \frac{3 \times sB}{m} = \frac{3 \times 0.004}{0.60} = 0.02(\mu g/mL)$$

where sB is the standard deviation of the blank, and m is the slope of the calibration curve.

The limit of detection is also dependent on the number of sample multiple loadings. If four multiples were used, the limit of detection would decrease to 0.005 μg/mL. However, above 10 multiples the background signal becomes an increasing problem.

III-3-3 Use of the Standard Addition Procedure

Unlike most other instrumental methods, GFAAS suffers from the disadvantage that the calibration graph is constantly changing its form owing to steady wear of the furnace after a number of samples have been run. One solution to this problem is use of the method of standard additions in which an initial absorbance of an extract is determined and then the operation repeated for known additions of the analyte. Because the measurements were taken almost at the same time, the conditions of the furnace are not sensibly altered. Experiments showed a lower analytical error by use of this technique albeit at the price of more expenditure of time.

III-3-4 Precision and Accuracy

The precision and accuracy of the procedure were established by analysis of two reference standard rocks and an "in house" chert standard of the Geological Survey of Canada:

(1) CAAS Sulphite Ore [94],
(2) CAAS Syenite [94], and
(3) CHRT [95]

The analyses of these standard rocks involved sample attack methods as recommended by the references and were used by me for other samples analysed (see Part Four for further details). The results are given in Table III-4 and demonstrated excellent agreement between them. The precision, as expressed by the relative standard deviation (r.s.d.) ranged from 0.8 to 1.0%. The relative error ranged from 0.92 to 7.77%. These precisions and accuracies were determined for silicate rock standards and were not exactly comparable to the iron meteorites for which the procedure had been primarily developed. There are unfortunately no meteoritic reference standards.

Further indications of accuracy of the procedure were established by analysis of some iron meteorites that had previously been analyzed by Smales *et al.* [50] using radiochemical neutron activation analysis (RNAA) which will also be discussed in Part Four.

Table III-4 Precision and Accuracy of GFAAS Gallium Determinations as Obtained by Analysis of Standard Reference Materials

Standard	n	Certified (μg/g)	Found (μg/g)	r.s.d. (%)	r.e. (%)
CAAS Sulphide Ore	10	14	13.8	1.0	0.7[a]
CAAS Syenite	10	22	20.3	1.1	7.7[a]
CHRT Chert	4	13.5	13.7	0.8	1.5

a. Relative errors are only approximate because certified values had been reported to only two significant figures [94]

III-3-5 Interferences from Other Elements

Major elements that possibly interfere with the extraction and determination of gallium were investigated before the procedure was used for real samples. Iron (III), tin (IV), antimony (V), gold (III), and thallium (III) were readily co-extracted with gallium as chloro complexes in the absence of iodide. Other elements such as nickel, copper, cobalt, germanium, and arsenic were not found to cause interference in the quantification of gallium. Of the interfering elements, iron can be reduced to iron (II) that is not extracted into the organic phase (see above) and others have concentrations in the samples that are too low to influence the determination of gallium by GFAAS.

Further experiments were based on the bulk composition of iron meteorites which were to be analysed. These studies involved finding the maximum amount of a given constituent that would not affect the analyte signal. Species tested were: tin (IV), antimony (V), gold (III) and thallium (III) added to a constant amount of 1 μg gallium. The results of these experiments are shown in Table III-5.

Table III-5 Maximum Amounts of Elements that do not Interfere with the Determination of Gallium by GFAAS

Element	Amount
Sn	15 mg
Sb	1 mg
Au	450 μg
Tl	200 μg

The geological samples that I expected to analyze in this project contain large concentrations of iron, nickel, copper, cobalt, silicon, and trace (μg/g) levels of germanium, gallium and others. There was no difficulty in determining gallium with the developed method after reduction of iron with iodide.

III-3-6 Final Analytical Procedure

About 0.5-1 g of finely ground rock is placed in a Teflon beaker with a 10-20 mL of a 1:1 HF:HNO_3 mixture. The contents are heated over a sand-bath until dry. This procedure is repeated three times. For iron meteorites, 0.5-1 g samples are placed in a Quickfit conical flask and heated under reflex with 10 mL of concentrated nitric acid until dissolution is complete (usually more than four hours). Nitric acid is used in preference to hydrochloric acid because the same solutions can then also be used for the determination of germanium [96,97]. Otherwise there is loss of germanium from hydrochloric acid solutions on heating above 40°C. The entire solution is transferred to a 40 mL Teflon beaker and the contents are evaporated to dryness over a heated sand-bath. The residue is redissolved in 10 mL of 5M hydrochloric acid by warming for up to 30 minutes. The solution is cooled to room temperature and adjusted to 25, 50, or 100 mL with 5M hydrochloric acid in a volumetric flask.

Aliquots of 1.0-4.0 mL (depending on the expected gallium content) are shaken for exactly 3 minutes with 1.0 mL of MIBK after addition of 0.15 g of potassium iodide per mL of aqueous phase, and the organic phase is removed with a Pasteur pipette after centrifuging to separate the phases that would otherwise separate slowly.

The organic phase is analyzed by GFAAS using the conditions in Table III-6 and with optional use of a standard additions procedure.

Table III-6 Instrumental Parameters for GFAAS Determination of Gallium in MIBK Extracts

Absorption line (nm)	287.4
Sample volume (μL)	3.0
Multiple injections	1-4
Sample repeats	4
Dry step for multiple injections	2
Step 1 (pre-heating):	
Final Temperature (°C)	75
Ramp time (s)	3
Hold time (s)	3
Step 2 (drying):	
Final temperature (°C)	120
Ramp time (s)	3
Hold time (s)	10
Step 3 (charring):	
Final temperature (°C)	415
Ramp time (s)	8
Hold time (s)	10
Step 4 (atomisation):	
Final temperature (°C)	2250
Ramp time (s)	1
Hold time (s)	3
Inert gas	O_2-free N_2

III-3-7 Conclusions

The developed procedure is a viable alternative to NAA for the determination of gallium in iron meteorites. Together with previous work on the determination of germanium [96,97], there is now a means of determination of the various classes of iron meteorite since both of these elements play a strong diagnostic role. It is also considered that this procedure will be equally applicable to the determination of gallium in silicate rocks, particularly those high in iron. This procedure was also used for analysis of the gallium content of K-T boundary samples that will be discussed in Part Five.

SECTION III-2 INDIUM

III-4 DEVELOPMENT OF A PROCEDURE FOR QUANTIFICATION OF INDIUM

Indium is a somewhat volatile element with an abundance of about 10 μg/g in the earth's crust, about the same as silver. Indium is present in meteorites only at the ultratrace (ng/g) level. This is probably a reflection of its volatility since almost any geochemical process can cause its loss.

Most geochemical studies have been based on radiochemical neutron activation analysis (RNAA), particularly as regards meteorites. However, RNAA is not particularly sensitive for this element and there are many analytical problems inherent in the separation and determination of small amounts of indium in the presence of other metals, especially iron. Removal of iron by its precipitation as the cupferrate coprecipitates about 4 % of the indium [98]. Other methods of removing iron have not been satisfactory when indium has had to be quantified.

There is clearly a need for an analytical procedure that would permit indium to be quantified in samples high in iron such as meteorites and other geochemical materials. I have developed an extraction-GFAAS procedure for this purpose and the results are given below.

Extraction systems have been devised to separate and enrich trace amounts of indium from other elements. For example, the use of extraction of the bromo and iodo complexes has been known for several decades. Wada and Ishii [99] extracted milligram quantities of indium into diethyl ether from a solution in 4.5M hydrobromic acid. Irving and Rossotti [100] reported complete extraction of indium over the concentration range of 0.0006-3.0 g/L from 1.5M hydriodic acid with an equal volume of ethyl ether. Other extraction systems that have been used include acetylacetone [76], benzoate [77], butylphosphoric acid [101], 8-quinolinol[102], diethyldithiocarbamate [103] and dithizone [104]. These extraction systems were originally designed to extract milligram rather than microgram quantities of indium. In later developments the quantity of indium was reduced to the microgram level as for example in the fundamental work of Hubert and Chao[105] who extracted indium as the bromo complex into MIBK. However, none of the above procedures could be used for samples inordinately rich (>90%) in iron such as iron meteorites.

III-4-1 Experimental

i. Acids and Their Concentrations

A potentially useful way of separating indium by solvent extraction may be to use the ion association complex of this element in the presence of halides with their corresponding halogen acids except chloride or hydrochloric acid. In early work by Irving and Rossotti [100] several different acids were used to extract indium into diethyl ether, MIBK, and other organic solvents. They established that for any one solvent the halides were extracted in the order iodide > bromide > chloride. In my own work I chose the iodide ion in solutions of hydrobromic acid because iodide could also be used for reducing iron(III) to iron(II) (see above).

Solutions of various concentrations of hydrobromic acid (0.5-7.0M) with 1 μg standard indium and including 10 mg/mL of ferric iron were shaken with 0.8 mL of MIBK (pre-equilibrated with 4M HBr). The organic phases were then analysed by GFAAS. The results are plotted in Fig III-12. Beginning with 2.5M hydrobromic acid, the percent extraction of indium started to increase and continued up to 5M. When this acidity was exceeded the two phases started to become mutually soluble. The concentration of hydrobromic acid was therefore maintained at 5M.

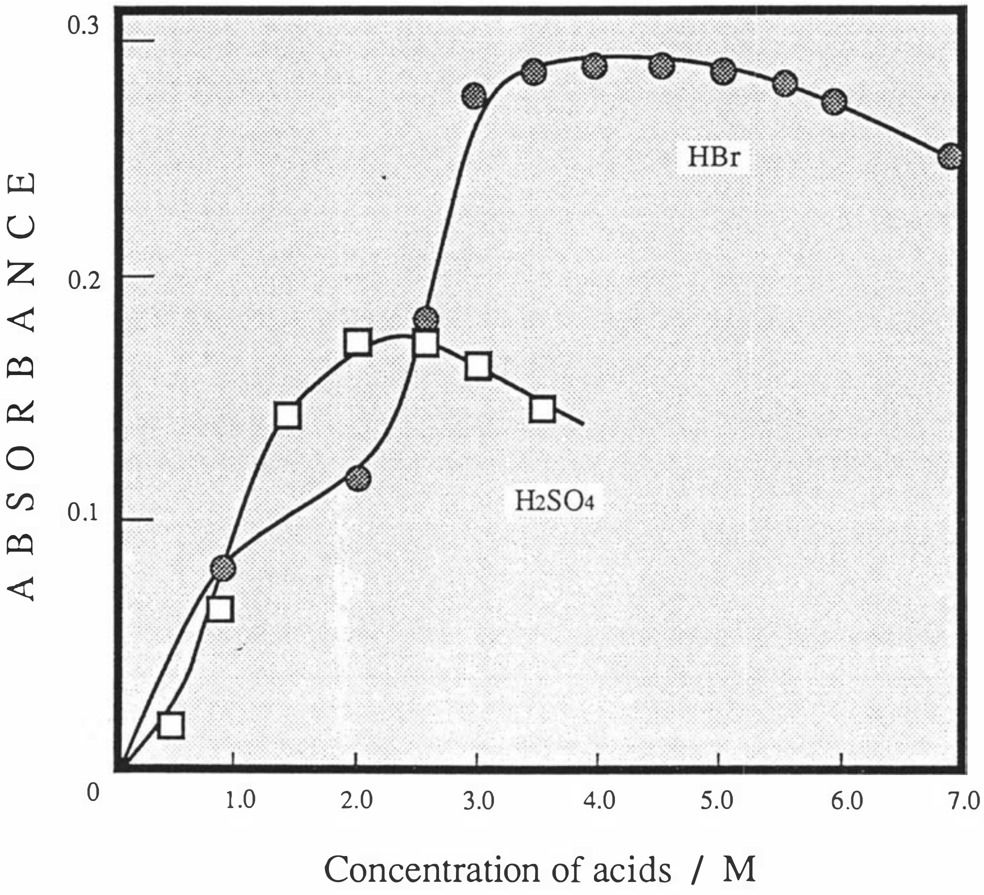


Fig.III-12 Effect of acidity on the extraction of indium into MIBK

Sulphuric acid was also tested, but it was found that the percent extraction of indium was lower than in the case of hydrobromic acid. A comparison of extractability of indium in the presence of hydrobromic or sulphuric acids is also shown in Fig.III-12.

ii. Effect of Iodide on Extraction of Indium from Hydrobromic Acid Solutions

Theoretically, the iodo complex of indium is more stable than the bromo complex [100]. Since hydriodic acid is much more expensive than hydrobromic acid, the experiments therefore used the latter as an acid solution throughout all the experiments. As mentioned before iodide plays the dual role of complexing indium and at the same time reducing iron(III) to (II). The extractability of indium into MIBK from 5M hydrobromic acid containing a constant amount of iron (2000 μg/mL) and different concentrations of potassium iodide is shown in Fig.III-13 and shows that when the concentration of iodide was 0.125 g/mL the percent extraction of indium reached nearly 100% and remained at this level up to 0.17 g/mL. Owing to the limited solubility of potassium iodide in the aqueous solution (127 g/100mL water), the lower iodide concentration was preferred. When 0.20 g/mL iodide was added, the absorbance began to decrease. Therefore 0.15 g/mL of iodide was used to extract indium throughout all subsequent work.

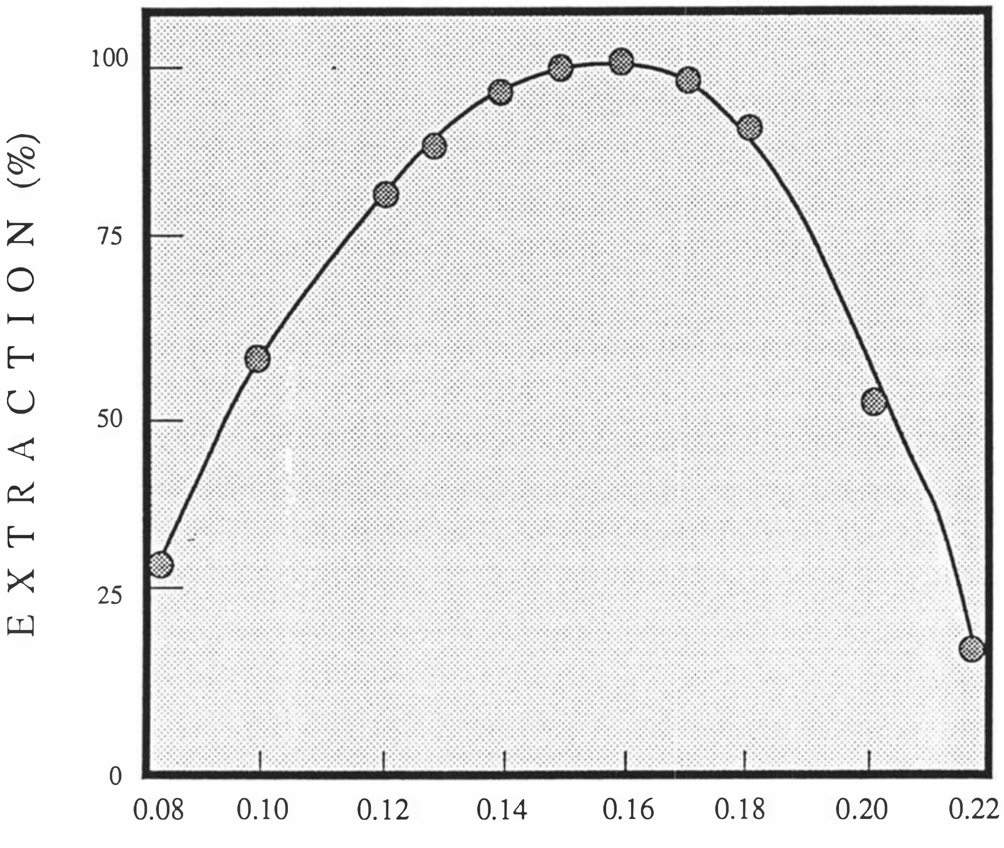


Fig.III-13 Effect of KI concentration on the extraction of indium in the presence of iron

iii. Effect of Addition of Potassium Hydroxide and the Acidity of the Solution

Despite good extraction of trace (μg/mL) levels of the iodo indium complex into MIBK, this extraction was incomplete at the ultratrace (ng/mL) level (see Fig.III-14). Salting out experiments were therefore conducted to increase the extractability of indium into the MIBK phase by raising the solubility of the complex in the organic phase.

The experiments involved the use of several salting out reagents including various electrolytes, potassium and sodium hydroxides. A surprising result was that potassium hydroxide increased the solubility of indium in the organic phase much more than did other salts. The results are given in Fig.III-14.

It appears that potassium hydroxide is a better salting out agent than the corresponding sodium compound. The optimum concentration of potassium hydroxide was determined by extracting indium from a constant iodide/bromide solution containing various amounts of potassium hydroxide. In Fig.III-15 a plot of the concentrations of potassium hydroxide against indium absorbances is given and demonstrates that maximum absorbances were achieved in the range of 0.06-0.12 g/mL of added potassium hydroxide. The mean value at 0.09 g/mL became the standard for future work.

Due to addition of potassium hydroxide to the aqueous solution the acidity is changed. To establish the degree of change, the acidity of the solution was measured before and after adding potassium hydroxide. The experiments showed that the reduction of acidity corresponded to only 0.2M hydrobromic acid.

It must of course be pointed out that the true salting out agent must be considered as potassium bromide rather than the hydroxide which is of course destroyed by reaction with the acid.

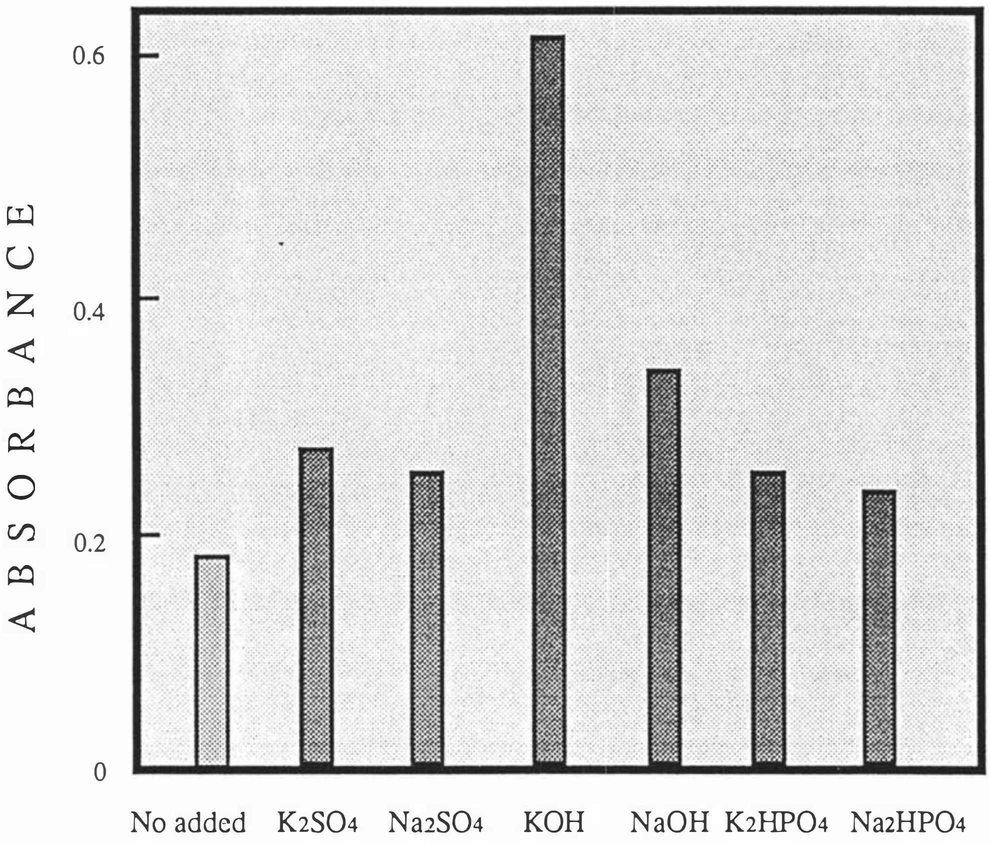


Fig.III-14 Effect of addition of salts and electrolytes for extraction of indium into MIBK

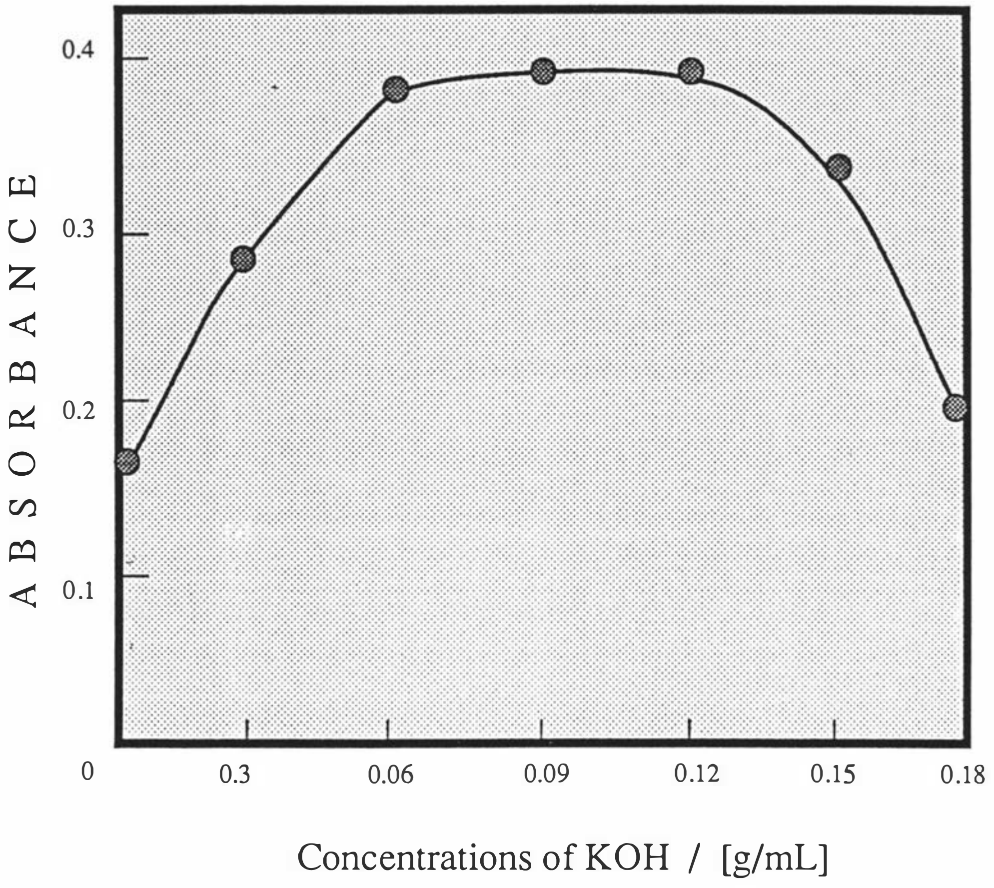


Fig.III-15 Effect of the concentration of KOH on extraction of indium into MIBK

iv. Shaking time

The effect of shaking time upon the extractability of indium was determined by analysing the organic phase by GFAAS after various shaking times. From Fig.III-16, when shaking was performed for 2.5 minutes, only about 95% of the indium was extracted into the MIBK phase. With a shaking time of 3 minutes. however, the extraction was nearly 100% but after shaking for 4 minutes the percent extraction percentage of indium began to decrease. The optimum shaking time was chosen at 3.5 minutes for all subsequent work.

v. The Distribution Ratio

The system exhibited strong extraction of indium with MIBK from hydrobromic acid in the presence of iodide as determined from measurement of the distribution ratio.

A set of solutions was prepared that contained 10 μg of indium in various concentration of iodide and a residual acidity of 4M hydrobromic acid after addition of potassium hydroxide. The solutions were shaken with an equal volume of pre-equilibrated MIBK and indium was determined by GFAAS in both phases. A maximum value of 4000 was obtained for D in solutions containing 0.12 g/mL of iodide and 0.09 g/mL of added potassium hydroxide. This value of D corresponded to 99.98% extraction.

vi. Stability of the Indium Complex in the Organic Phase

Experiments were performed in order to assess the stability of the indium complex by analysing the organic phase at different times after extraction. A plot of indium absorbances as a function of time is shown in Fig.III-17 and shows a maximum absorbance at about 3 min. The complex remained stable only for 45 minutes after which time it started to decompose. It is clear that analysis of the organic phase must be performed within 40 minutes, otherwise analytical errors may arise.

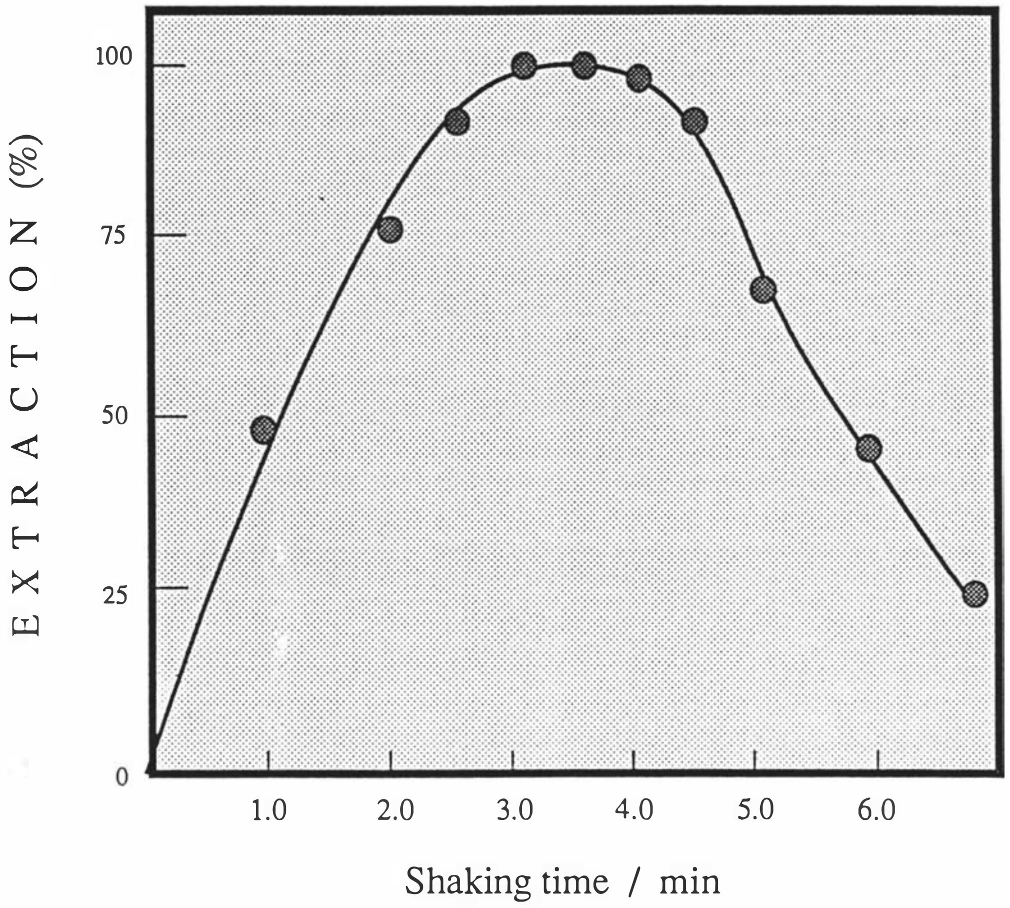


Fig.III-16 Effect of shaking time on extraction of indium into MIBK

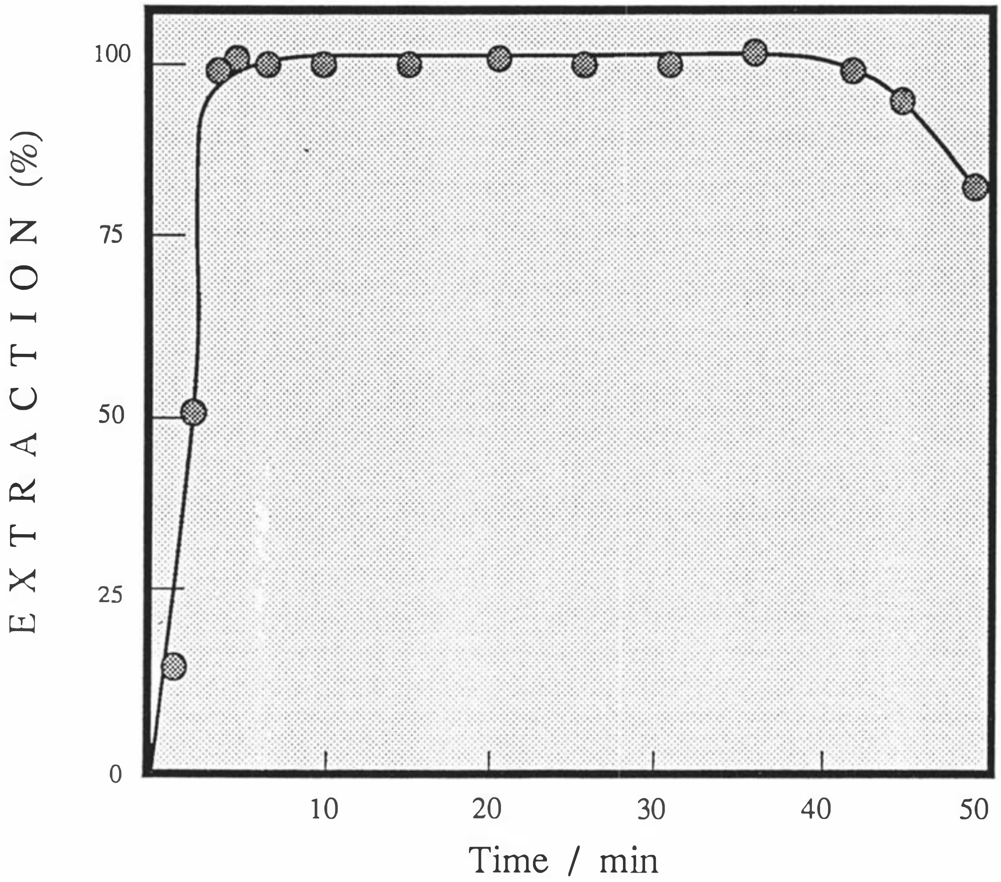


Fig.III-17 Stability of the indium iodo complex in the organic phase after separation from the aqueous phase

vii. Limit of Detection

As with gallium, the limit of detection for indium with the established method was obtained by using the IUPAC method [93]. The technique of four multiple loading injections was used in the determination. The blank consisted of all reagents used.

The limit of detection (C_l) was calculated as shown on p.63 above and was found to be 0.015 μg/mL. The limit of detection of indium is sufficiently low for quantifying this element in chondritric meteorites and geochemical materials but not for iron meteorites in which the indium contents are probably too low to detect. Part of the problem lies in the high background noise of the indium lamp that was available to us.

III-4-2 Choice of Analytical Method for Determining Indium

Indium can be determined either by the conventional calibration curve procedure or by the method of additions. Since the physical condition of the graphite furnace changes rapidly with use, calibration curves have to be run at frequent intervals to keep pace with these changes. Several such curves are shown in Fig III-18 and demonstrate the poor reproducibility that is to be expected. However, the use of the method of standard additions avoids this problem but does involve a longer operating time and more sample solutions which sometimes are not available. As the problem showed on the above, the standard additional analysis is therefore recommened for the determination of indium by GFAAS, particularly in ultratrace level analysis.

III-4-3 Precision and Accuracy

To examine the precision and accuracy of the analytical method developed for indium, a Canadian certified reference ore (MP-1a) [106] was analysed 12 times for this element. The results are given in Table III-7.

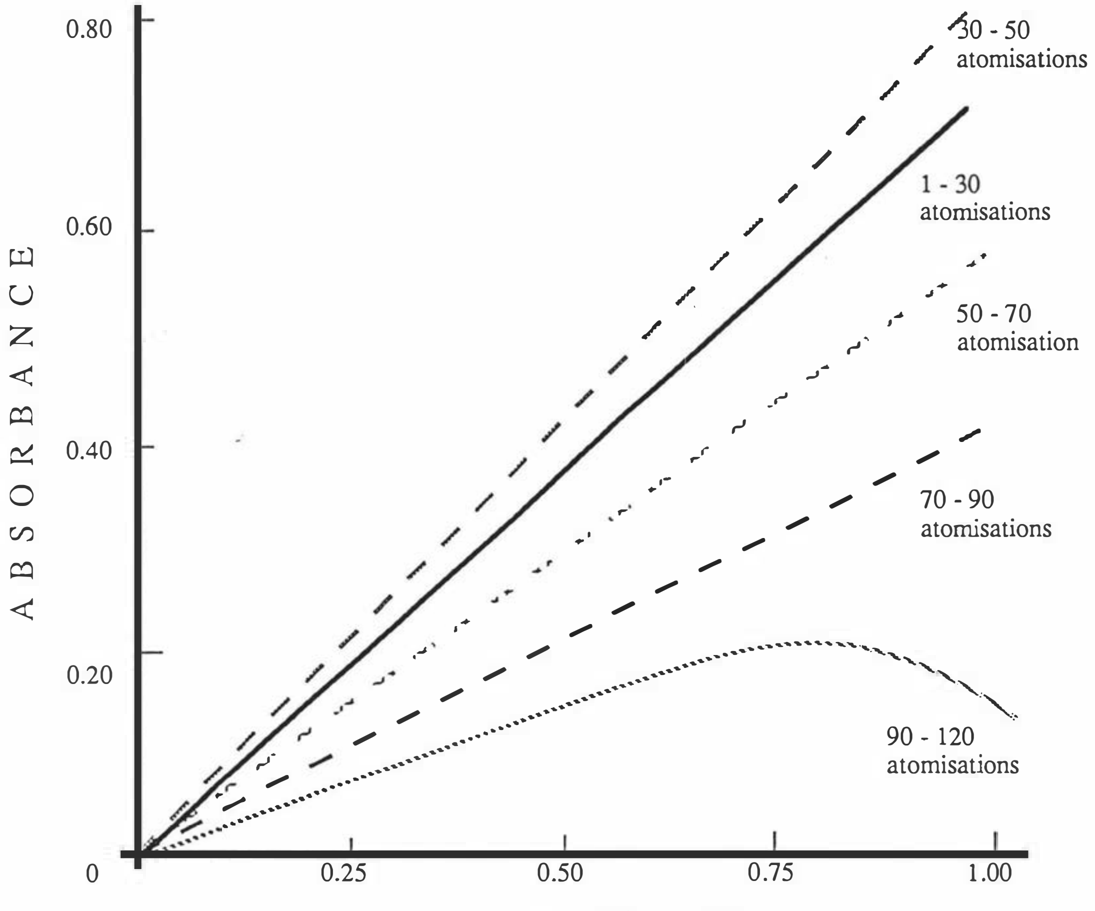


Fig.III-18 Analytical curves

Showing the effect of furnace wear upon the absorbance of indium

Table III-7 Precision and Accuracy for the Indium Method as Determined by Analysis of Standard Reference Rock (MP-1a) [106]

n	Certified (μg/g)	Found (μg/g)	R.S.D. (%)	R.E. (%)
12	330	324±4	0.3	0.9

There are no standard reference meteorites and there are few other reference standards that contain μg/g levels of indium. However, a further indication of accuracy of the procedure was established by analysis of a carbonaceous chondrite (Allende) that was of the same type as Orgeuil for which an indium content of 78 ng/g was reported by Anders and Grevesse [107]. My value was 56 ng/g.

III-4-3 Final Analytical Procedure

The treatment of all samples was the same as that described in Parts Four and Five, as well as in III-3-5.

To aliquots of 2.0-4.0 mL of sample solutions in 5M hydrobromic acid was added 0.12 g/mL of potassium iodide and 0.09 g/mL of potassium hydroxide. After the added solids had dissolved the solutions were shaken for three and a half minutes with pre-equilibrated MIBK and allowed to separate for two minutes. The organic phase was removed into a small glass tube for GFAAS analysis by either the conventional calibration procedure or by the method of additions. The GFAAS instrumental parameters are listed in Table III-8.

Table III-8 Instrumental Parameters for GFAAS Determination of Indium in MIBK Extracts

Absorption line (nm)	303.9
Sample volume (µL)	4.0
Multiple injections	4-8
Sample repeats	4
Dry step for multiple injections	2
Step 1 (pre-heating):	
Final temperature (°C)	75
Ramp time (s)	3
Hold time (s)	3
Step 2 (drying):	
Final temperature (°C)	120
Ramp time (s)	3
Hold time (s)	10
Step 3 (charring):	
Final temperature (°C)	415
Ramp time (s)	8
Hold time (s)	10
Step 4 (atomisation):	
Final temperature (°C)	2150
Ramp time (s)	0.9
Hold time (s)	2.5
Inert gas	O_2-free N_2

III-4-5 Conclusions

The developed procedure has allowed for the quantification of indium in many geological samples including some meteorites.

Although indium could be determined in several silicates such as K/T boundary clays, chondritic meteorites, lavas, and others, it could still not be used for samples with extremely low indium contents, as for example, iron meteorites which average below 1 ng/g indium. Although sensitivity can theoretically be increased by multiple loading of up to 20, the consequent increase in background signal limits the number of multiple injections to not more than eight.

The procedure is an alternative to INAA or RNAA procedures that have a limit of detection of about 0.1 µg/g.

SECTION III-3 THALLIUM

III-5 DEVELOPMENT OF A PROCEDURE FOR QUANTIFICATION OF THALLIUM

Like indium, thallium is also a highly volatile element. The quantification of thallium in geochemical materials is important for a variety of reasons. In mineral exploration, this element is an important pathfinder element for sulphide mineralization where its abundance can reach about 20 μg/g in contrast with background levels of about 0.1 and 0.7 μg/g respectively in basalts and granites. The content of thallium in meteorites is also of importance because a knowledge of this abundance can shed light on the origin of meteorites and of the earth itself.

A recent review [108] of analysis of thallium in various matrices lists a variety of analytical procedures such as UV-visible spectrophotometry, flame atomic absorption spectrometry (FAAS), graphite furnace AAS (GFAAS), inductively coupled plasma (ICP) emission spectrometry, arc emission spectrometry, and voltammetric techniques.

The solvent extraction behaviour of thallium is similar to that of indium and it can be readily extracted into an organic phase as a halide ion-association complex.

Quantification of thallium in meteorites presents even greater problems than in the case of silicate rocks. This is because the thallium content of meteorites is extremely low (ca. a few ng/g) and it is associated with iron concentrations usually exceeding 90% in iron meteorites. Attempts have been made to quantify thallium in meteorites by radiochemical neutron activation analysis (RNAA) in which the thallium is irradiated in a reactor and converted to radioactive ^{204}Tl which is mixed with a stable carrier and its activity determined after determination of the chemical yield [108,109].

III-5-1 Experimental

i. Solvent Extraction Systems

According to Irving and Rossotti [100] thallium may be extracted into several organic solvents from halide solutions. The GFAAS technique is however not suitable for these systems because thallium can be readily lost in the charring step of the GFAAS procedure.

Table III-9 lists melting and boiling point data for thallium halides and shows that this element is highly volatile both as the chloride and bromide. The iodo complex system was therefore chosen to extract thallium from samples. This system has several advantages. The first is that the iodo thallium complex is formed with thallium (I) which is far less volatile than the chloro and bromo complexes that have to be formed with thallium (III). Thallium (I) is also much more stable than thallium (III) and there is not the problem in which the chloro and bromo complexes gradually disintegrate as the central atom becomes reduced.

In view of the advantages of the iodo system, this was chosen for development of an analytical procedure to quantify thallium in rocks and meteorites.

Table III-9 The Physical Properties of Thallium Halides

Compound	m.p.(°C)	b.p.(°C)
TlCl	430	720
$TlCl_3$	25	Decomposes
TlBr	480	815
$TlBr_3$	Decomposes	Decomposes
TlI	440	825
TlI_3	Decomposes	Decomposes

ii. Effect of the Amount of Iodide Added

Iodide has a dual purpose in this extraction system. The first is to form an iodo thallium complex and the second is to reduce iron that may co-extract with the analyte. A study was made of the extraction of 1 μg/mL thallium (I) in the presence of various iodide concentrations with and without addition of 1000 μg/mL iron(III) and 0.15 μg/mL K_2HPO_4. The matrix was 3M H_2SO_4. The results are shown in Fig.III-19.

From the figure, when a 0.05 g/mL solution of potassium iodide was added the signal started to increase. It reached a maximum value with a 0.1 g/mL solution of potassium iodide and reached a constant limiting value up to 0.25 g/mL of added potassium iodide. When this concentration was exceeded at 0.3 g/mL, the signal started to decrease, perhaps due to precipitation of thallous iodide.

An optimum choice was therefore made by using 0.15 g/mL solution of potassium iodide throughout all subsequent extractions of thallium.

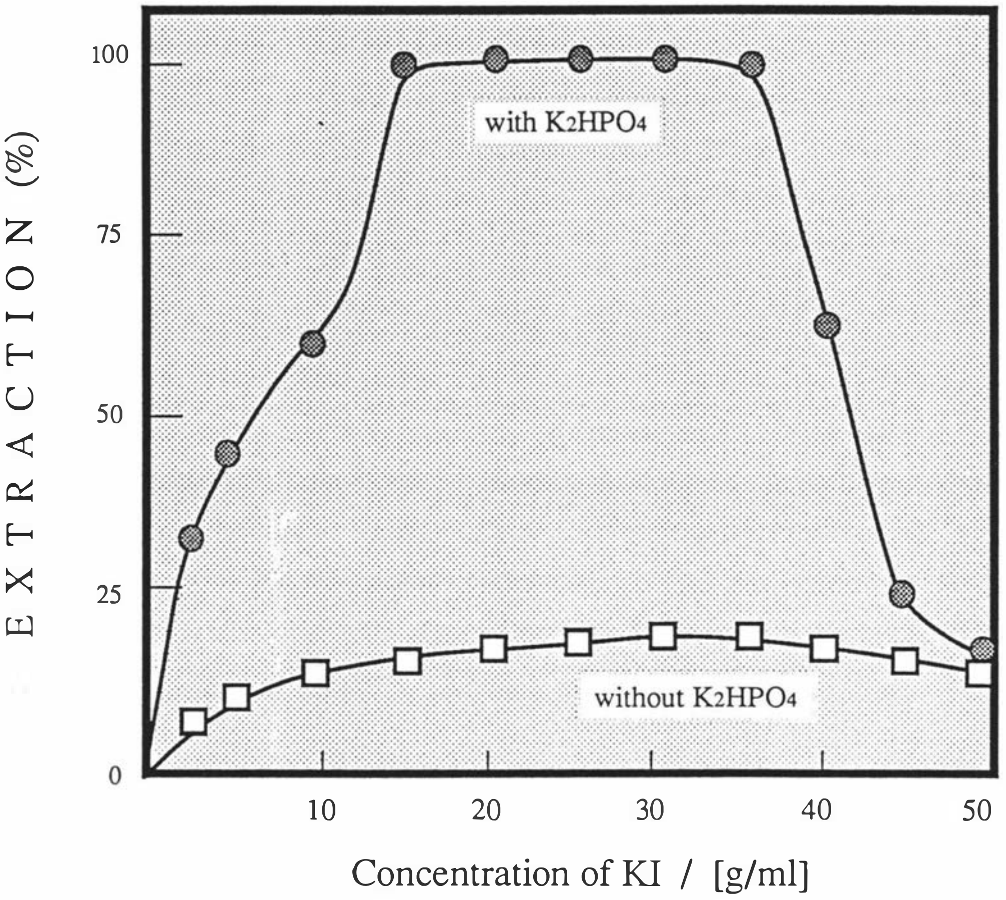


Fig.III-19 Effect of varying iodide concentration on the extraction into MIBK of thallium from a solution in 3 M H_2SO_4 and in the presence of 10 mg/mL of iron(III). The plots show addition of 0.15 g/mL of K_2HPO_4 (upper curve) and without addition of phosphate (lower curve)

iii. Effect of Acids and Their Concentrations

It is often preferable to use the corresponding halide acid when chloro, bromo, or iodo complexes are formed prior to extraction. In this case however, sulphuric acid was used to avoid co-extraction of other elements that form chloro or bromo complexes. Sulphuric acid was no more effective than hydriodic acid but the latter is expensive and unstable. When these two acids were compared, they demonstrated almost the same capability of allowing the extraction of thallium (I) into MIBK. Because of its relative cheapness and its great stability, sulphuric acid was chosen for all further experiments.

The experiments were performed by varying the concentrations of sulphuric acid in the range 0-5M (beyond this upper limit, the two phases become mutually soluble). The effect of sulphuric acid concentrations on extraction of thallium(I) is shown in Fig.III-20. The optimum acid concentration was 3M sulphuric acid.

iv. Effect of Salting Out

Despite the observations of Irving and Rossotti [100] that thallium is readily extracted into diethyl ether from iodide solutions, extraction into MIBK was not as good. In order to improve the extraction, various conditioning agents were tested as salting out agents. Reagents that were used for these tests were: KOH, K_2SO_3, K_2SO_4, K_3PO_4, K_2HPO_4 and KH_2PO_4. Of these, the most effective was K_2HPO_4, perhaps because of its greater solubility. The results are plotted in Figs.III-21 and III-22. It is obvious that addition of this reagent increased extraction fivefold.

To establish the optimum concentration of K_2HPO_4, various concentrations of this reagent were added to solutions of 1 μg/mL thallium (I) in 3M sulphuric acid. The results are given in Fig.III-22. The optimum concentration of phosphate was 0.15 g/mL of sample solution and gave nearly 100% extraction.

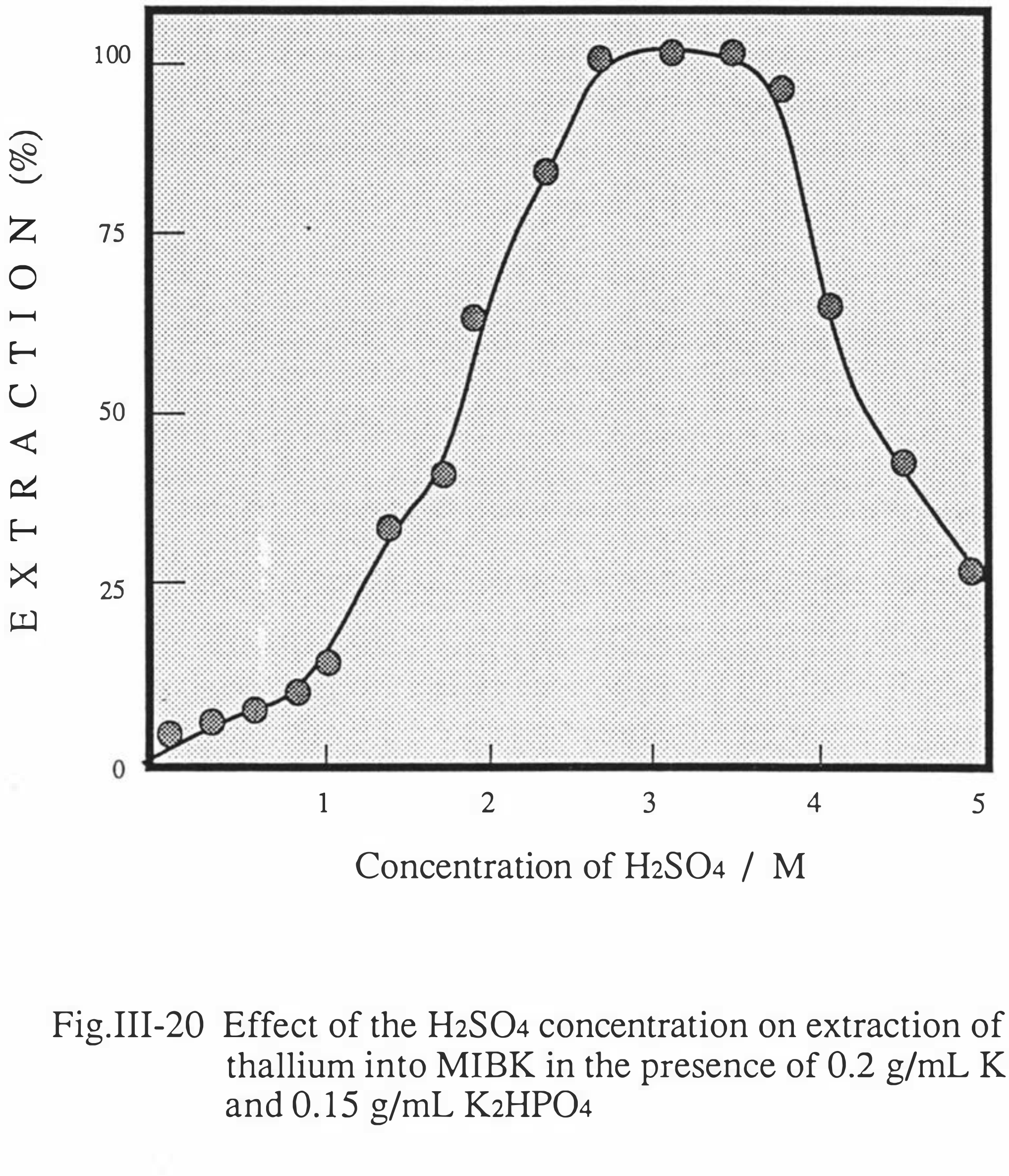


Fig.III-20 Effect of the H_2SO_4 concentration on extraction of thallium into MIBK in the presence of 0.2 g/mL KI and 0.15 g/mL K_2HPO_4

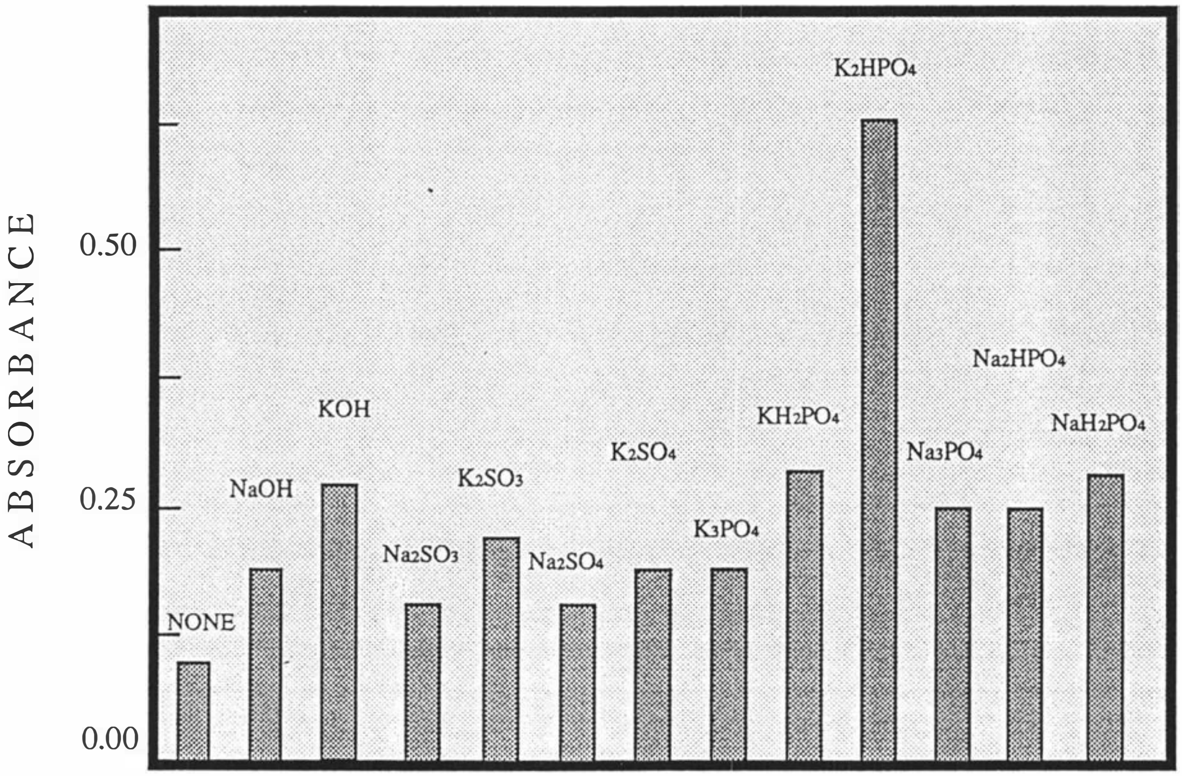


Fig.Ⅲ-21 Effects of various agents on the extraction of thallium

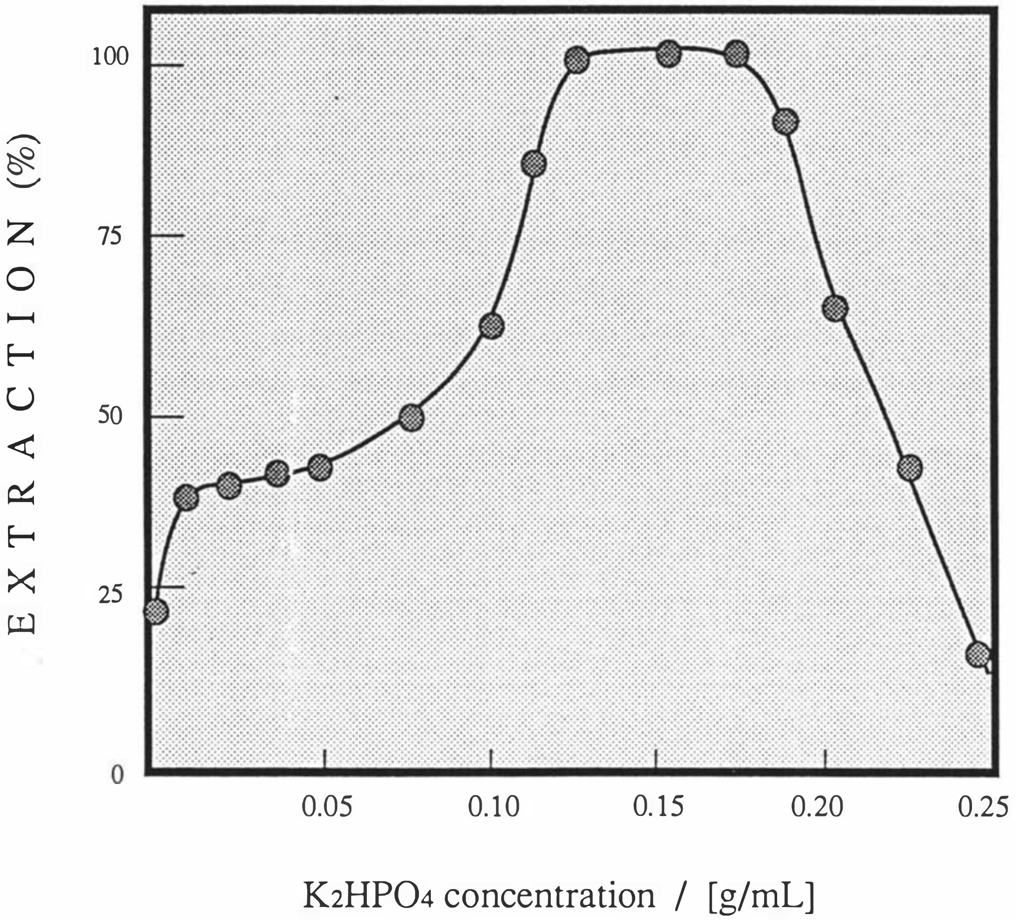


Fig.III-22 Effect of varying K_2HPO_4 concentrations on the extraction of thallium into MIBK from a solution of 0.2 g/mL KI in 3 M H_2SO_4

v. Extraction Shaking Time

Various shaking times were tested by analysing the MIBK phase after extracting from aqueous solution. The results are plotted in Fig.III-23 and demonstrated that after one minute shaking time about 95% of the thallium (I) was extracted and that after 1.5-3.0 minutes extraction was almost 100%. When the shaking time greatly exceeded 3 minutes, the percent extraction started to reduce. In all future work a shaking time of two minutes was adopted.

vi. Stability of the Iodo Thallium(I) Complex

The GFAAS absorbance of the MIBK phase separated from the aqueous solution after extraction was determined at different times after phase separation in order to investigate the stability of the iodo thallium (I) complex in the organic phase. Experiments showed the iodo thallium complex proved to be extremely stable and remained unchanged even six hours after phase separation (see Fig.III-24). For routine analysis it was appropriate to complete the GFAAS measurements within two hours of phase separation.

vii. The Distribution Ratio for Extraction of Thallium

The distribution ratio for the extraction into MIBK of the iodo-thallium (I) complex in 3M sulphuric acid solution was investigated by addition of various amounts of potassium iodide to a solution of thallium (I) in 3M sulphuric acid. The organic/aqueous phase ratio was taken at 1:10. The value of D was 6450 (99.98% extraction).

viii Effect of Other Elements

It is well known that one of the major problems in GFAAS is the presence of coextracted elements that serve to depress the signal of the analyte. However, for practical purposes the major interferent present in silicate rocks and meteorites is iron. Potassium iodide was also used for reducing iron to

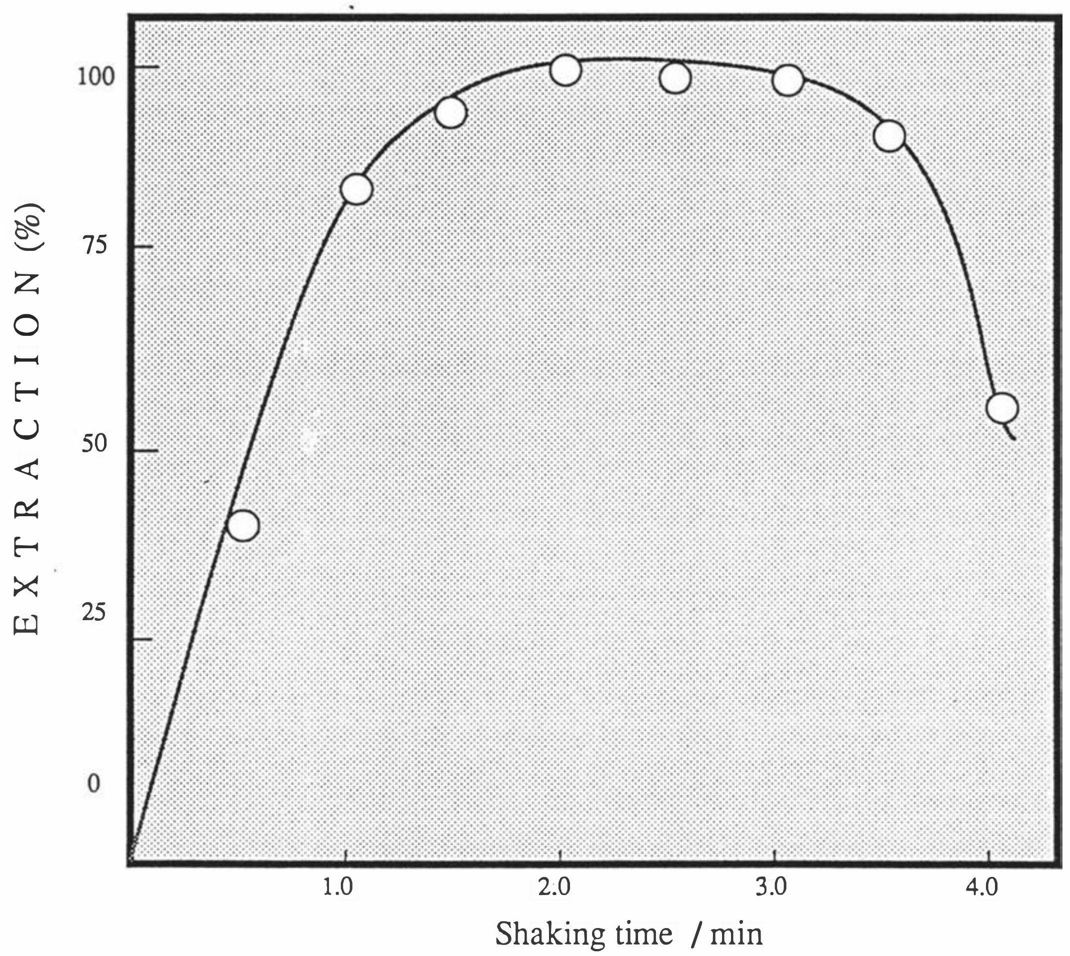


Fig.III-23 Effect of shaking time on extraction of thallium into MIBK

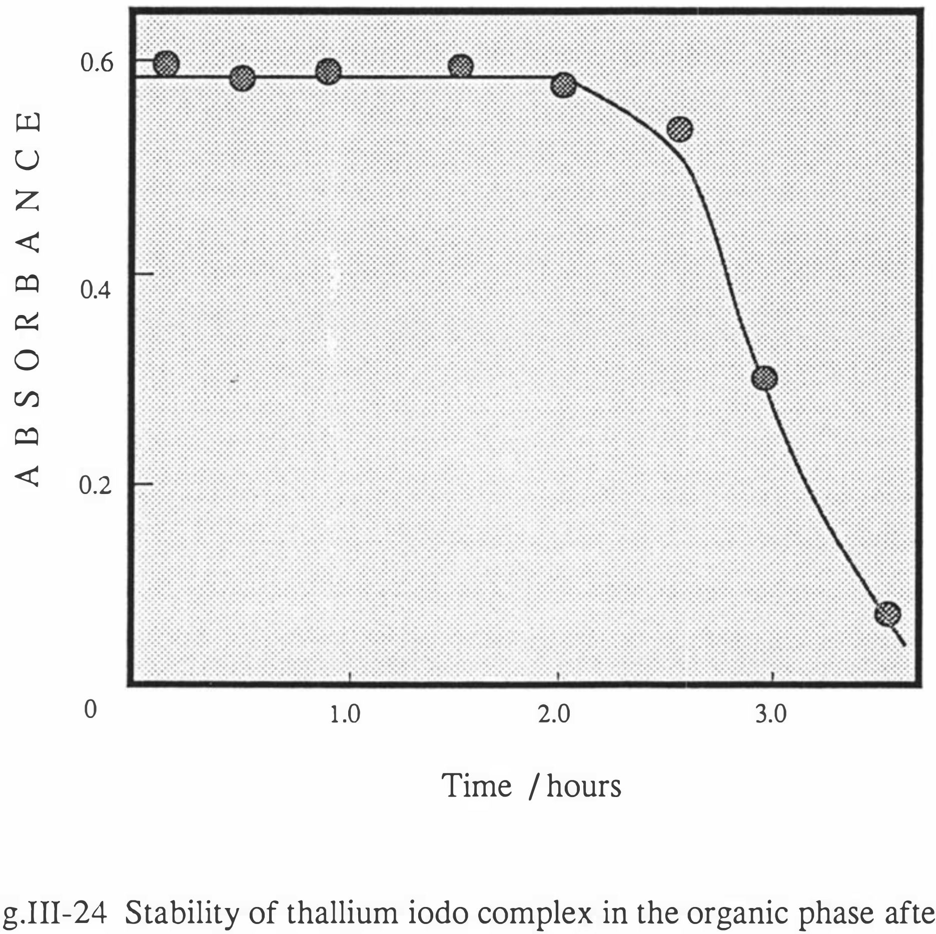


Fig.III-24 Stability of thallium iodo complex in the organic phase after extraction from the aqueous phase the ferrous state, but even then about 2% (10 mg/mL iron in original aqueous solution) of the iron still extracted into the MIBK phase that gave a positive absorbance signal to confuse with the thallium response. For overcoming the problem, a backextraction step was employed by use of 3M sulphuric acid in the presence of 0.5 g/mL of potassium iodide. After backextraction, the iron content of the organic phase was lowered to <20 μg/mL at which level there was no interference with the GFAAS thallium determination.

III-5-2 Limit of Detection

The limit of detection of the method depended on the aqueous-organic phase ratios as well as the number of multiple loadings employed during the GFAAS procedure. As with gallium and indium, four MIBK phases (one extracted reagent blank and extracts of three known concentrations of standard thallium (I)) were analysed by GFAAS after shaking and phase separations. The limit of detection (C_l) represented about 4.5 ng/g and 1.5 ng/g in the original solid sample using 6 and 10 multiple loadings respectively, according to the calculations by the IUPAC method [93].

The calibration graph is shown in Fig.III-25 and it is linear (r=0.999, n=7) between 0.5 and 10 ng in the MIBK phase, the highest concentration of 10 ng/mL giving a peak height absorbance of 0.102. This assumes a single 4 μL loading and an aqueous-organic phase ratio of 1:1.

Assuming a 100-fold dilution of the solid sample and 10 multiple loadings, the thallium content of the solid sample is 10 times that of the aqueous solution for a 1:1 phase ratio. However if a phase ratio of 4:1 is used, the thallium concentration in the original sample is only 2.5 times greater than the values used in the above calibration graph so that 2 ng/g thallium in the rock corresponds to an absorbance of about 0.008.

The limit of detection could in theory be decreased still further by increasing the aqueous-organic phase ratio and/or increasing the number of multiple loadings. However, higher phase ratios will result in a decrease of the overall

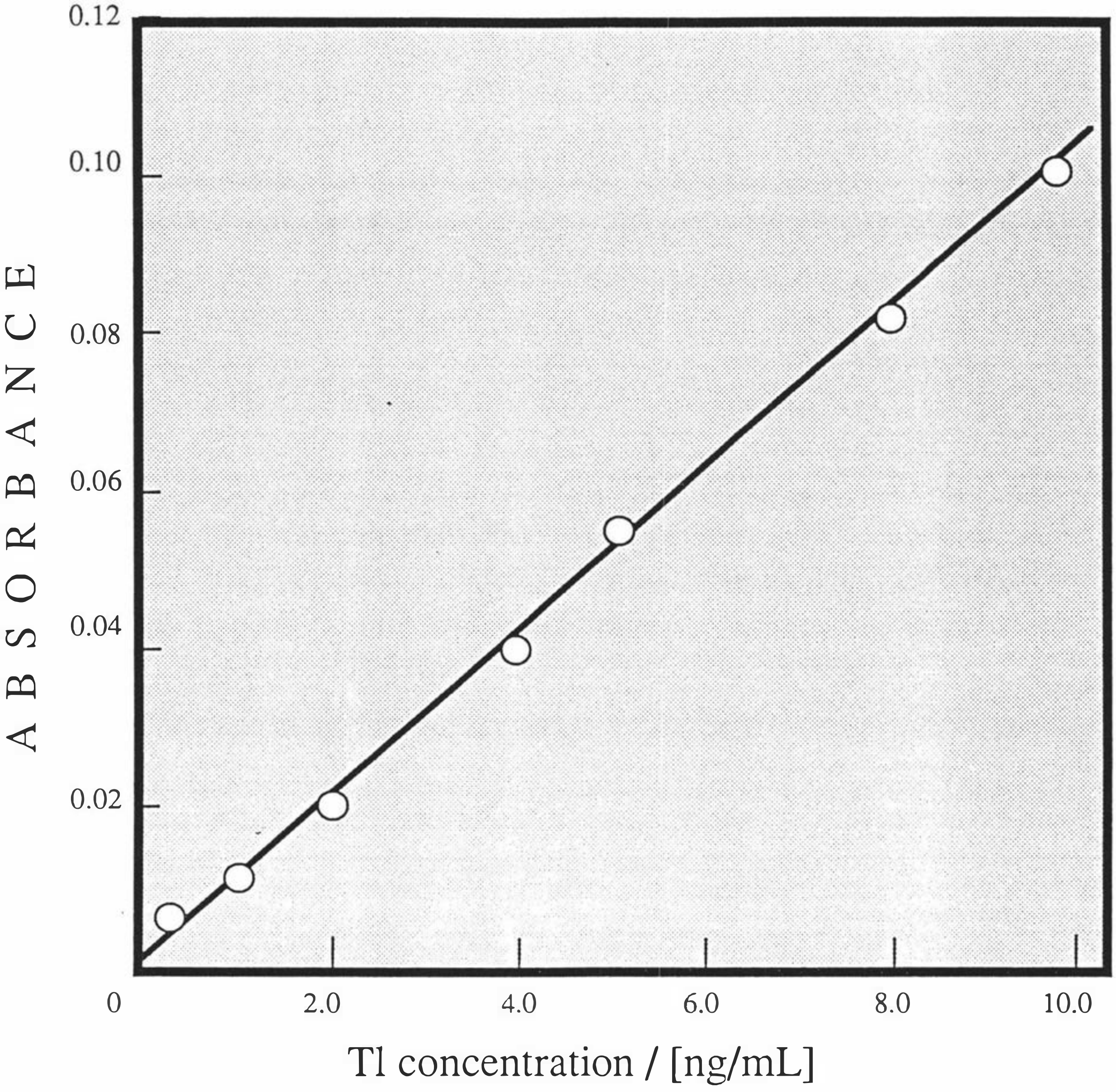


Fig.III-25 Calibration curve for GFAAS absorbance as a function of Tl concentrations in the aqueous phase prior to extraction

---

These values assume a 1:1 aqueous/organic phase ratio and refer to a single loading on the graphite furnace. Multiple loadings and increased phase ratios lower the limit of detection very considerably.

extraction and numbers of multiple loadings beyond 10 preclude speedy analysis.

III-5-3 Choice of Analytical Calibration Method

Unlike indium and gallium, the thallium hollow cathode lamp gave an exceptionally stable output and could be operated for long periods without signal decay. The stability of the signal is demonstrated from Figure III-26 which is an actual tracing of signal and background. This gave the advantage that both the conventional calibration procedure as well as the method of additions could be employed for determining thallium in geological samples. In practice there was no need to use the method of additions so that the conventional calibration method was used for all future work. A comparison of both calibration methods was undertaken by determining thallium in the iron meteorite, Toluca. There was good agreement in results obtained by both methods as are listed in Table III-10.

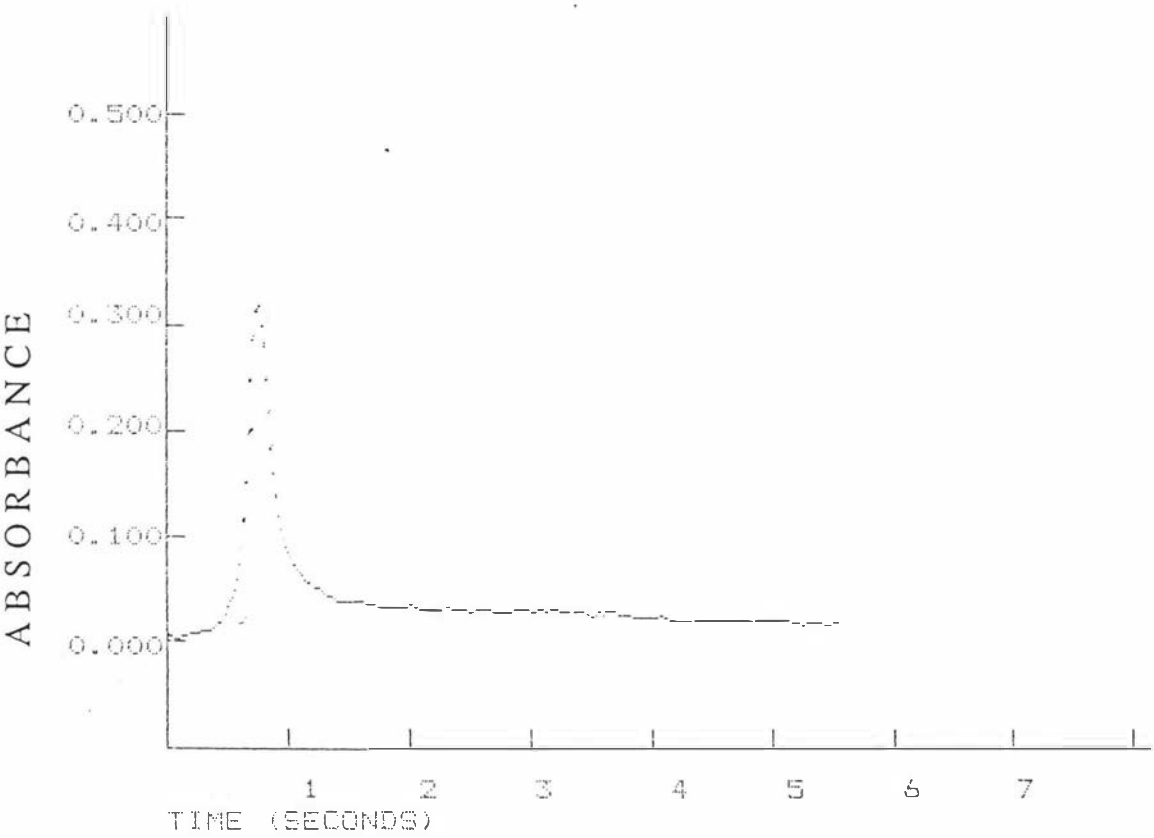


Fig.III-26 Plot showing the stable background of absorption baseline

Table 10 Comparison of Standard Addition and Conventional Calibration Methods by Quantification of Thallium in the Toluca Iron Meteorite

Sample #	Standard Addition Tl (μg/g)	Analytical Curve Tl (μg/g)
1	9.7	9.6
2	9.6	9.7
3	9.7	9.4
4	9.4	9.5
5	9.7	9.8
6	9.5	9.5

NB - Each sample was analysed six times.

Although the method of standard additions was not used after initial trials since it requires an inordinate expenditure of time and sample solution, it must be remembered that the conventional calibration method does have its problems including the need to run frequent standards because of wear of the graphite furnace and consequent changes in its porosity and geometry.

III-5-4 Precision and Accuracy

The precision and accuracy of the developed procedure were determined by replicate analyses of the standard rocks G-1 and W-1 [110], CAAS Sulphide Ore-1 [94]. The relevant data are summarized in Table III-11

Table III-11 Precision and Accuracy of Method for Quantification of Thallium in Geological Samples as Determined from Analysis of Standard Rocks

Standard	n*	Thallium (μg/g) Recommended	Thallium (μg/g) Found	r.s.d. (%)	r.e. (%)
G-1	12	1.30	1.20	3.0	6.7
W-1	12	0.110	0.105	10.5	4.1
CAAS Sulphide Ore	13	1.40	1.37	2.8	2.1

* number of complete analyses

III-5-5 Discussion

It was concluded that the above procedure will prove to be of use for the routine analysis of geological samples including rocks and meteorites.

The very low limit of detection afforded by the technique will be of particular advantage for the quantification of thallium in iron meteorites in which the metal phases do not seem to have yet been analysed by other workers because of low abundance of thallium in them. Our preliminary studies on iron meteorites indicate thallium abundances as low as 5 ng/g in these materials. It was possible to give a rough check on our new data for iron meteorites (to be shown in Part Four) by use of the semiquantitative but very sensitive technique of laser-excited ICP-mass spectrometry (ICP-MS). Analyses of the iron meteorites Bilibino and Nantan by ICP-MS (performed at the US Geological Survey, Denver) gave approximate values of 15 and 7 ng/g thallium compared with our values of 19.5 and 6.3 ng/g respectively. This can be considered as very good agreement considering the semi-quantitative nature of the ICP-MS technique.

PART FOUR

GROUP IIIB ELEMENTS IN METEORITES

IV-1 INTRODUCTION

Before interpreting properties of meteorites in terms of putative processes and conditions in the early solar system, it is necessary to understand just what sort of objects meteorites are. Therefore, such understanding begins with the classification. The purpose of the classification is to sort the meteorites into broadly similar types of object, so that their origins and relationships can be better understood. Meteorites are a unique source of information about the materials present and conditions prevailing in the solar system during the earliest phases of its history. It is quite clear that not all meteorites are the same: there are various compositional and physical differences between one meteorite and another, sometimes quantitatively minor, and sometimes major.

The scientific interest in meteorites is considerable and there is even evidence that they have played a role in the evolution of life on the Earth. The impact of large (>10km diameter) chondritic meteorite is held responsible for the extinction of 70 % of all life forms at the terminal Cretaceous [62]. A periodic pattern of extinctions throughout the history of the Earth has also been demonstrated and summarized in popular articles [111], resulting in enhanced public interest in meteorites and comets.

The simplest classification of meteorites is into three divisions: stones (chondrites and achondrites), irons (siderites), and stony-irons (pallasites).

Table IV-1 Meteorite Classes and Numbers [112]

Class	Falls	Fall frequency (%)	Finds Non-Antarctic	Finds Antarctic
Chondrites				
CI	5	0.06	0	0
CM	18	2.2	5	34
CO	5	0.06	2	6
CV	7	0.84	4	5
H	276	33.2	347	671
L	319	38.3	286	224
LL	66	7.9	21	42
EH	7	0.84	3	6
EL	6	0.72	4	1
Other	3	0.36	3	3
Achondrites				
Eucrites	25	3.0	8	13
Howardites	18	2.2	3	4
Diogenites	9	1.1	0	9
Ureilites	4	0.48	6	9
Aubrites	9	1.1	1	17
Shergottites	2	0.24	0	2
Nakhlites	1	0.12	2	0
Classignites	1	0.12	0	0
Anorthositic breccias	0	0	0	1
Stony-irons				
Mesosiderites	6	0.72	22	2
Pallasites	3	0.36	34	1
Irons				
IAB	6	0.73	97	4
IC	0	0.08	11	0
IIAB	5	0.45	60	6
IIC	0	0.05	7	0
IID	3	0.09	12	0
IIE	1	0.10	13	0
IIF	1	0.03	4	0
IIIAB	8	1.42	189	0
IIICD	2	0.14	19	0
IIIE	0	0.10	13	0
IIIF	0	0.05	6	0
IVA	3	0.39	52	1
IVB	0	0.09	12	0
Other irons	13	1.32	175	0

The meteorite classes and subclasses commonly recognised today are briefly listed in Table IV-1 above, along with some statistics of falls and finds.

IV-1-1 Chondrites

The chondritic meteorites are stony meteorites that display chondrites, spheroidal aggregations of minerals unlike any known in terrestrial rocks. Prior [170] introduced the first systematic division of stony meteorites when he replaced the superficial criteria of colour, brecciation, etc, used by Brezina, by more meaningful mineralogical and chemical criteria. He recognised that the chemical variations in the metal and silicate components are sympathetic, relating to the oxidation states: and that they seem to obey certain simple rules, which are now commonly referred to as "Prior's rules".

(1). Total nickel-iron percentage in the chondrites decreases as the nickel-iron ratio in the metal fraction increases.

(2). Total nickel-iron percentage in the chondrites decreases as the iron/magnesia ratio in the silicate fraction increases.

According to these rules, stony meteorites are divided into chondrites and achondrites. The chondrite meteorites are also subdivided so that the classification system is based on mineralogy (reflecting decrease in free iron, increase in oxidised iron) and possession of chondrules:

(1) Enstatitic chondrites,
(2) Olivine bronzite chondrites,
(3) Olivine hypersthene chondrites,
(4) Olivine pigeonite chondrites (carbonaceous chondrites type III),
(5) Carbonaceous chondrites (type I and II).

After many decades of having been considered to be almost identical in composition, small systematic differences in composition among the chondrites were discovered in the early 1950's.

On the basis of subtle differences in the proportions of major, non-volatile elements, and differences in mineralogy and mineral composition, the chondrites are divided into nine classes: the CI, CM, CO and CV chondrites, many of which are characterised by relatively high carbon contents and which are collectively termed the "carbonaceous chondrites". The siderophile elements lead to further subdivision of these classes, the ordinary chondrites into the H, L, and LL classes [113,114] and the EH and EL chondrites [115], which are collectively termed the "enstatitic chondrites" after their dominant mineral. Significantly, isotopic properties can also be used to identify most of these classes. Carbonaceous chondrites can also be subdivided to some degree on the basis of Fe/Si, but the same subdivisions are more readily made on the basis of other criteria. The details of the classification of chondrites are compiled in Table IV-2.

Table IV-2 Chondrite classes and Mean Properties[a]

Group	Mg/Si	Ca/Si	Fe/Si	Fe_{met}/ Fe_{tot}	$\delta^{18}O$ ($^{o}/_{oo}$)	$\delta^{17}O$ ($^{o}/_{oo}$)
CI	1.05	0.064	0.86	0	~16.4	~8.8
CM	1.05	0.068	0.80	0	~12.2	~4.0
CO	1.05	0.067	0.77	0-0.2	~-1.1	~-5.1
CV	1.07	0.084	0.76	0-0.3	~0	~-4.0
H	0.96	0.050	0.81	0.58	4.1	2.9
L	0.93	0.046	0.57	0.29	4.6	3.5
LL	0.94	0.049	0.52	0.11	4.9	3.9
EH	0.77	0.035	0.95	0.76	5.6	3.0
EL	0.83	0.038	0.62	0.83	5.3	2.7

a. Data from Kerridge and Matthews [112]
b. Oxygen isotope ratios are relative to standard mean ocean water (SMOW) [171]

The existence of nine distinct classes of chondrite is significant because it leads to the conclusion that those classes were established in the solar nebula. This means that the properties that distinguish one class from other, the variations in Mg/Si, Fe/Si, oxidation state and O-isotope ratios, for instance, in some way reflect nebular processes. There are four lines of evidence for nine classes:

1. They are compositionally very similar to the Sun and quite unlike other known samples of solid material in the solar system. This suggests a relatively simple origin from a

common pool of starting material.

2. They have formation ages similar to those inferred for the Earth, Moon and Sun, and presumably of the solar system as a whole, namely about 4.55 Ga.

3. Virtually all chondrites, especially some of the low type 3 ordinary chondrites (H, EL, and EH) [112], contain highly non-equilibrium assemblages that have been altered very little, if at all, since the components came together. An example is the coexistence of Si-bearing metal and silicates.

4. Chondrites contain isotopic evidence for accretion quite soon after the end of element syntheses. Also some elements are present with isotopic proportions that are not encountered in any other known solar system material. Apparently this material escaped the isotopic homogenization experienced by most solids.

The major challenge of modern meteorite studies is to study these complex, ancient samples from the earliest days of solar system history, investigate their diverse properties, and thus learn something about a unique time and place in the history of our planetary system.

IV-1-2 Iron Meteorites

For learning about the origin and evolution of the solar system and the bodies such as the oldest rocks, meteorites are probably the only suitable materials available to us at present. Meteorites formed at the same time as the Earth [116], and contribute to our understanding of this planet and its evolution.

Of the meteorites types, irons are the most readily preserved once they land on the Earth, owing to their resistance to physical and chemical weathering processes. These samples are thought by some, to be the fragments of the cores of small planets and therefore represent the product of igneous processes similar to those that produced the Earth.

To understand the nature of these samples, classification schemes are necessary to separate the different type of iron core fragments that are meteorites.

Lovering *et al.* [52] proposed one of many modern classifications, which have tended to reduce the number of classes of iron meteorite. This classification is an oversimplification, only justified as long as there is insufficient information concerning the individual meteorites. Iron meteorites may be subdivided according to their primary structure as shown in Table IV-3.

Table IV-3 Structural Classification of Iron Meteorites [117]

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

Since the 1960's, numerous analytical data of trace elements in iron meteorites have been obtained by many workers [50-52]. 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 a section under a hand lens. The other is based on accurate chemical analysis of the major elements. Both approaches support and have very good agreement with each other. The agreement of structural and chemical classes is shown in Table IV-4.

Table IV-4 Comparison between the structural and Chemical Classifications 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

The chemical classification is largely based on the gallium, germanium, iridium and nickel contents of iron meteorites [118], that are highly diagnostic of the twelve genetic classes of iron meteorite as shown in Table IV-5.

Table IV-5 Chemical Classification of Iron Meteorites [118]

Group	Ni (%)	Ga (μg/g)	Ge (μg/g)	Ir (μg/g)	Ge/Ni plot
IA	6.4-4.8	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	2-6	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	*
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
IIICD	10-23	1.5-27	1.4-70	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

NEG -- negative; POS -- positive; * too few data for estimation

Wasson and Kimberlin [119] chose gallium, germanium and iridium to plot against nickel on a log-linear scale (nickel was on the linear axis). The groups are clearly resolved. All members of the same group fall, within the limits of sampling and analytical error, on a straight line. The significance of these plots has been discussed in great detail by Scott [120].

IV-2 QUANTIFICATION OF GROUP IIIB ELEMENTS IN METEORITES

Quantification of group IIIB elements in meteorites presents a difficult analytical problem because their contents are extremely low (*ca*. a few ng/g for indium and thallium) and are associated with iron concentrations usually exceeding 90% in iron meteorites. Selection of a correct sampling method is a key to obtaining accurate results of analysis, particularly at the ultratrace level.

IV-2-1 Treatment of Samples

Sampling procedures are very important for obtaining accurate analyses and may have to be quite different for different purposes. So a successful analytical method depends on analytical subsamples having, within tolerable limits, the same concentrations of the analytes. If this requirement is not met, the most competent analyst cannot generate useful results. Since analysts are likely to be held responsible for confused data, they are well-advised to scrutinize the processes whereby the samples are generated.

Meteorite samples, particularly irons, are somewhat inhomogeneous (due in the latter case to crystals of kamacite and taenite) The following experiments were therefore concerned with choosing an optimum treatment method for these meteorites.

i. Iron Meteorites

Unlike silicate rocks, iron meteorites consist of nearly 90% iron, and have very high contents of nickel, copper, cobalt and other components. To ensure homogeneity of samples, the separation of metal, sulphide and silicate phases from iron meteorites and chondrites is usually more difficult than mineral separation from rocks or chondritic meteorites. Most attempts at separation recorded in the literature employ chemical as well as mechanical methods, and no generally applicable methods have yet been devised.

For iron meteorites, Lovering *et al.* [52] used a 3 mm drill and hoped to avoid contamination by drilling only those areas which showed negligible contamination of the samples by the drill. The separation of the finer grained aggregates is generally effected by magnetic methods, but even the initial pulverisation has usually presented a difficult problem and few investigators record the achievement of uncontaminated samples by these methods alone.

Dissolution of iron meteorite samples was carried out by direct acid attack and the method was based on experience from previous research [96,97] on the determination of germanium in iron meteorites. It involved refluxing with concentrated acid. For the determination of gallium, the meteorites could be attacked with 5M hydrochloric acid. This acid dissolved the sample at a much faster rate (15 min) than the nitric acid (8 hours) that has to be employed if chloride is to be avoided (as in the case of germanium quantification). However, there was a problem in that only very small pieces of sample were available. The procedure was therefore to make a bulk solution in nitric acid and convert aliquots of such solutions to the chloride or sulphate forms if that was required.

For determination of indium and thallium, a sulphuric acid medium was essentially required. Aliquots of the original nitric acid solution were therefore fumed to dryness and then 3M sulphuric acid was added to redissolve the residue.

A set of experiments was carried out by different attack methods. The comparison of some results of gallium contents in Cañon Diablo that were determined by NAA confirmed that all dissolution methods employed, afforded reliable analytical data. The results are listed in Table IV-6.

Since determination of thallium cannot be carried out in the presence of chloride ion, direct hydrochloric acid attack was only used for the determination of gallium.

Table IV-6 Comparison of Different Treatment Methods for Quantification of Gallium in the Cañon Diablo Iron Meteorite

Method	1	2	3	4
Ga (µg/g) found	80.9	80.3	81.4	81.5

1. Direct acid attack by HCl in open air
2. Attack by HNO_3 then converted to HCl solution in open air
3. Attack by HNO_3 under reflux then converted to HCl solution
4. Attack by HNO_3 in a Teflon bomb then HCl solution

NB - Recommended value is 81.8 µg/g[119]

From the above, it appears that there was no obvious difference between the methods. It is clear that use of nitric acid to attack samples to get original solutions then converting to different acid media is appropriate.

The final procedure for sample attack was as follows: clean the surface of an iron meteorite sample by a file or a sandpaper and cut it by a hacksaw to pieces of 0.5-2 g. Place the sample in a Quickfit conical flask with 10 mL of concentrated nitric acid in presence of boiling chips. Heat the solution under reflux for approximately 8 hours until dissolution is complete.

Cool the solution down and a portion of the original solution is then transferred into a Teflon beaker for fuming out all acids. The residue is redissolved in the appropriate acid according to the requirements of the developed analytical procedure.

Of the three analyte elements, thallium is the most likely to be lost during sample treatment, owing to the volatility of its chloride.

ii. Chondrites

The bulk composition of chondrites includes silica, aluminium, magnesium and iron. The direct acid attack with nitric or hydrochloric acids cannot be used for such samples because of the difficulty of decomposing silicates. It is therefore important to remove silica from the original samples by removing it as SiF_4 after treatment with hydrofluoric acid or else solubilising it by fusion.

Several sample decomposition methods were carried out on a sample of the carbonaceous chondrite Allende. The results are shown in Fig. IV-1.

The results of sample digestion with a 1:1 mixture of sulphuric and hydrofluoric acids for one hour were disappointing, as only one-third of the expected maximum signal was detected.

Fusion with sodium peroxide was also unsatisfactory in that the procedure was lengthy and gave poor recovery of analytes.

After two consecutive digestions with a 1:1 mixture of hydrofluoric and nitric acids, the analytical signal increased and reached a limiting value after three consecutive treatments with this acid mixture. This procedure was therefore followed for all subsequent analytical work with chondrites. Precise details of the procedure are as follows: about 1-2 g of powdered chondritic meteorite sample was accurately weighed and placed in a Teflon beaker. After addition of 20 mL of acid mixture, the contents of the beaker were heated to dryness over a hot plate. The procedure was repeated twice more. The residue was redissolved by adding a dilute acid appropriate to the quantification of a specific analyte element.

Quantification of Group IIIB Elements in Meteorites

In Part Three of this thesis, the methodology for the determination of Group IIIB elements by graphite furnace atomic absorption spectrometry (GFAAS) have been described. All analytical procedures for both iron and chondrite samples were based on these. My procedures are an alternative to classical methods such as colorimetry, and to the modern instrumental method of neutron activation analysis and are relatively sensitive and inexpensive.

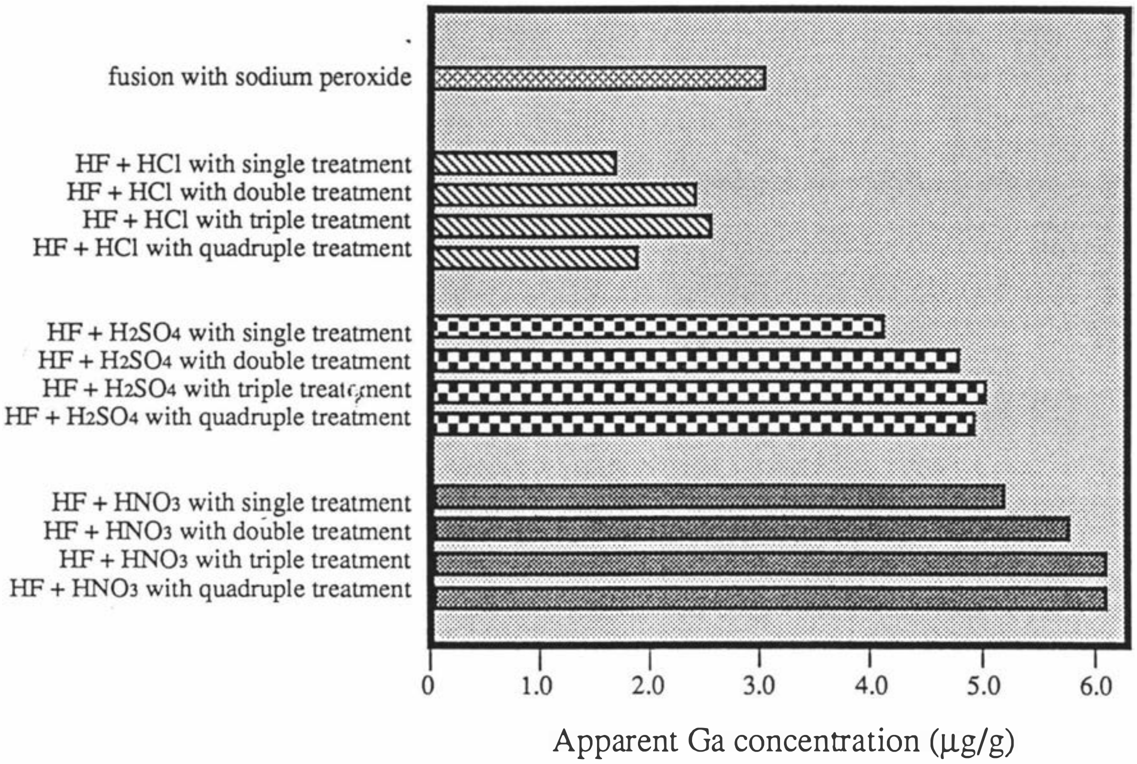


Fig IV-1 Effect of different acid mixtures and sample digestions on the dissolution of gallium from the Allende chondritic meteorite

IV-3 DISTRIBUTION OF GROUP IIIB ELEMENTS IN METEORITES

IV-3-1 Introduction

In the 1950's, Brown and co-workers [52,121,122] first determined trace elements in iron meteorites. Somewhat later, a large number of analyses of other trace elements and minor elements were made by Goldberg *et al.* [122]. This work led to the significant discovery that abundances of some trace constituents are quantised into groups that suggest division of meteorites into specific classes.

The elements gallium and germanium were selected by the above workers to establish a classification scheme for iron meteorites which differed in some respects from the structural scheme.

Accurate determinations of nickel, gallium and germanium in several hundred meteorites enabled Wasson [119,123,125] to expand and considerably improve this classification by defining a larger number of "chemical" groups with much smaller abundance ranges of specific elements such as gallium and germanium.

In the 1960's, Nichiporuk and Brown [126] showed that platinum and palladium abundances are also quantised and can be used to classify meteorites, particularly irons. Using semiquantitative emission spectrography, they determined ruthenium, rhodium, platinum and palladium in 24 iron meteorites. It is only recently that further abundance data for these elements have been obtained because of the limitations of NAA for these specific elements, though Ryan *et al.* [127] developed a successful NAA method for rhodium. Using a combination of solvent extraction and GFAAS, Hoashi *et al.* [128] were able to determine ruthenium, platinum and palladium in iron meteorites and were able to assess the use of these elemental abundances in classification. There is clearly a need to find additional elements that may have a classificatory role because many meteorites have not yet been assigned to specific groups and remain "anomalous."

IV-3-2 Gallium in Meteorites

An important concept in the study of iron meteorites was first proposed by Goldberg *et al.* [51]. In assessing their gallium abundance data obtained from 45 iron meteorites they introduced the concept of "quantized groups". According to their gallium contents they found that iron meteorites could be placed into three distinct classes, namely:
Class I, 45-100 μg/g Ga; Class II, 17-22 μg/g Ga; Class III, 1.7-2.5 μg/g Ga.

Lovering *et al.* [52] extended this concept of "quantization" in their analysis of 88 iron meteorites for gallium and some other elements. They modified the earlier three gallium groups [51], as follows:
Group I, 80-100 μg/g Ga; Group II, 40-65 μg/g Ga; Group III, 8-24 μg/g Ga; Group IV, 1-3 μg/g Ga. Of the 88 meteorites they analysed, eleven were "anomalous" in that they did not belong to any of the four groups.

My developed procedure [129] is a viable alternative to NAA for determination of gallium in iron meteorites. Thirty-five irons that included all 13 groups (reduced from the original larger groupings by amalgamation: i.e. IIIA and IIIB have become IIIAB) were determined for their gallium contents. The abundance data as compared with those obtained by NAA and other techniques are shown Fig. IV-2 and in Table IV-7.

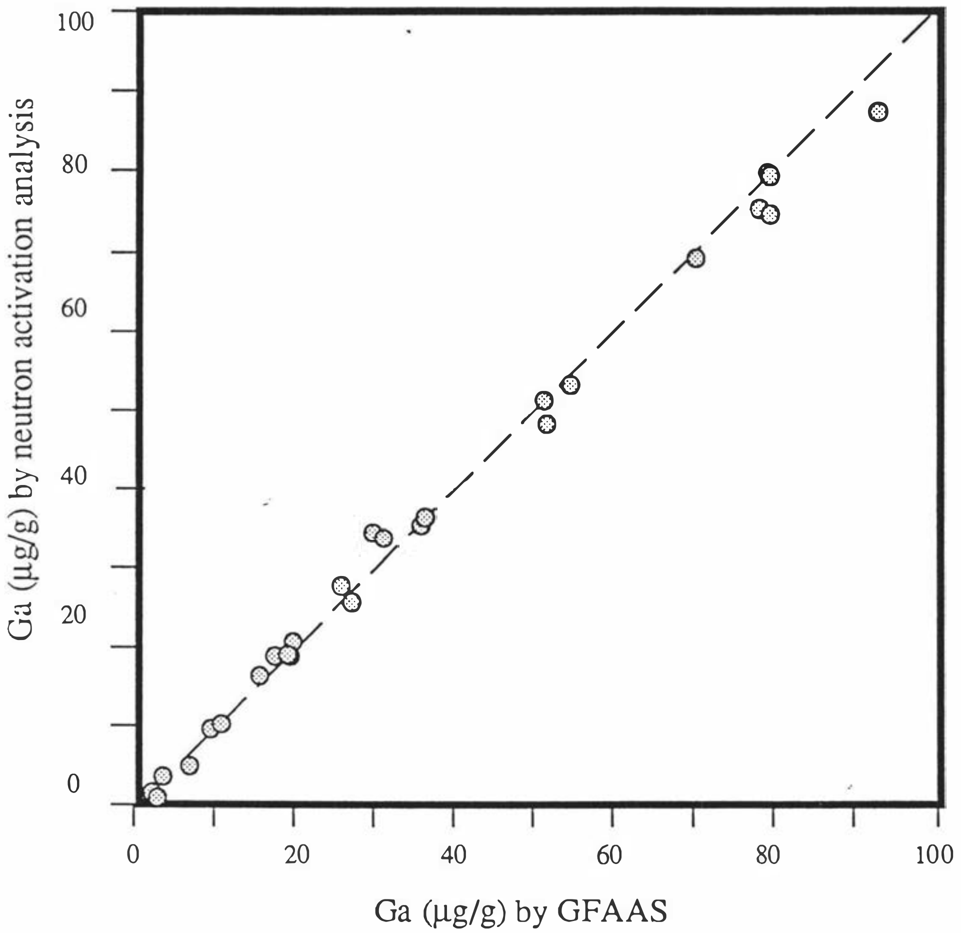


Fig.IV-2 Comparative abundance data for gallium in iron meteorites as determined by NAA and GFAAS

Table IV-7 Gallium Abundances (μg/g) in Iron Meteorites as Determined by GFAAS and other Methods

Meteorite	Ga by GFAAS	Ga by other methods
Group IA		
Annaheim	80.1	79.8
Cañon Diablo	81.4	81.8, 79.7*
Gladstone(No2)	64.5	93.7, 68*
Toluca	71.8	70.6, 18.2*
Group IB		
Bitburg	36.6	34.8
Four Corners	49.2	48.7
Woodbine	34.9	37.3
Group IC		
Chihuahua City	53.0	52.7
Santa Rosa	53.3	54.5
St. Francois	52.7	49.2
Group IIA		
Forsyth County	60.1	60.8
North Chile	61.3	58.9
Sierra Gorda	59.6	57.4
Group IIB		
Bilibino	36.5	?
Sao Juliao Moreira	33.4	37
Group IIC		
Ballinoo	29.8	--, 33*
Kumerina	34.7	36.8
Perryville	36.4	37.0
Group IID		
Carbo	71.1	70.0
Needles	75.9	77.2
Rodeo	81.3	82.1
Group IIE		
Arlington	21.8	21.8, 21.9*
Weekeroo Station	29.1	29.0, 27.4*
Group IIIA		
Cape York (Arg.)	17.5	19.2, 15*
Madoc	19.6	19.4
Manitouwabing	18.8	--
Merceditas	19.8	19.5
Waingaromia	21.5	20.9
Group IIIB		
Los Reyes	21.3	20.9
Owens Valley	20.8	21.5
Zacatecas	21.4	20.3
Group IIICD		
Carlton	11.1	11.4, 10*
Lamesa	11.1	10
Mungindi	19.9	19.4
Nandan	76.1	--, --, 77**
Group IIIE		
Cachiyuyal	16.9	16.9
Coopertown	16.9	17.0
Paneth's Iron	16.4	16.9

Group IIIF		
Clark County	6.84	6.9, 6.74*
Moobi	7.87	5.84, 7.72*
Nelson County	5.68	5.33
Group IVA		
Gibeon	2.06	1.97, 2.03*
Guanghua	1.78	--, --, 1.9**
Nelson County	4.99	5.33
Group IVB		
Hoba	0.21	--, 0.184*
Skookum	0.20	0.272
Tlacotepec	0.21	0.195
Weaver Mountains	0.24	0.233
Group Anom		
Butler	90.0	87.1
Mundrabilla	57.8	59.5
Santa Catheri	5.33	5.28, 5.4*

Unasterisked data are from Wasson [118]
* from Smales *et al.* [130]
** from Wang *et al.* [131] or Scott [120]

The gallium abundances are shown in Fig. IV-2 as plots of my data vs. those of other workers. The very close approximation to a linear relationship is further evidence of the reliability and accuracy of my procedure, one that can be carried out in many laboratories with minimum expense compared with NAA.

IV-3-3 Indium in Meteorites

Like most types of native material, the indium content of iron meteorites is extremely low probably because of its low primordial abundance and high volatility and mobility. Smales *et al.* [50] reported a range of 0.3-41 ng/g indium in chondrites as determined by NAA. This procedure could not accurately determine levels below 1 ng/g. Almost all of Smales' data showed levels below 10 ng/g.

Because of the low abundances and the limitations of the NAA method, there is as yet no clear pattern as to the distribution of indium in chondrites or iron meteorites. Smales *et al.* [50] indicated that the indium contents of coarse octahedrites are higher (about 1-2 ng/g) than in the other structural groups and gave abundances of 0.5, 0.7, and 0.8 ng/g for three hexahedrites.

With my procedure, I was able to determine indium in the following irons: Toluca, Gibeon, Carlton, Cañon Diablo and Cape York and the results are listed in Table IV-8. The values are however somewhat imprecise because of fluctuations in the hollow cathode lamp that did not allow for much scale expansion. The data must therefore be considered as semiquantitative and further analyses of iron meteorites were therefore not attempted.

Table IV-8 Indium Abundance in Some Iron Meteorites

Meteorite	Group	In (μg/g)	
		This work	Smales *et al.*[130]
Toluca	IA	0.003	<0.01
Cañon Diablo	IA	0.010	0.012
Cape York	IIIA	0.008	<0.01
Carlton	IIICD	0.008	<0.01
Gibeon	IVA	0.013	<0.01

Better results were obtained for chondrites and the data are listed in Table IV-9.

Table IV-9 Indium abundances in Chondritic Meteorites

Meteorite	Group	In (μg/g)
Allende	CV3	0.156
Mokoia	CV3	0.161
Jilin	H5	0.074
Plainview	H5	0.080
Summerfield	L5	0.083
Umbarger	L3/6	0.085

From the results shown in the Table IV-9, there were no obvious trends among the different groups of chondrite except that the carbonaceous meteorites seem to have much higher levels than do the ordinary chondrites. A similar observation has been made for thallium (see below). However, as the number of samples analysed was small (no others being available to us), the data are only presented for the sake of completeness.

To obtain reliable indium abundances in meteorites using the procedures developed by me, a more sensitive analytical method needs to be developed by use of a much larger sample weight. However, this possibility is limited because of the scarcity of meteoritic material.

IV-3-4 Thallium in Meteorites

Quantification of thallium in meteorites presents a similar problem to that of indium because of extremely low contents in the samples. Attempts have been made in the past to quantify thallium in meteorites by radiochemical neutron activation analysis (RNAA) in which thallium is irradiated to give ^{204}Tl which is mixed with a stable carrier and the chemical yield determined. This procedure is extremely complicated and open to serious error particularly as the final product has an activity typically of the order of two counts per minute [109]. Nevertheless, this method has been used for quantification of thallium in a few chondrites [109,132-135] where the thallium content is higher and the iron abundance lower, than in iron meteorites.

The quantification of thallium in iron meteorites probably represents one of the ultimate challenges to the analytical chemist. As far as I am aware, this element has never previously been determined in the metal phase of iron meteorites, though it has been determined in the more thallium-rich troilite phase of the Cañon Diablo and Toluca iron meteorites [109].

I have now been able to determine thallium in 49 iron meteorites and 6 chondrites using my analytical method described in the previous section of this thesis. The data and their geochemical significance are summarized and discussed below.

Abundance data for thallium in 49 iron meteorites and 6 chondrites are compiled in Tables IV-10 and IV-11. For irons, values range from 0.36 ng/g thallium in Sierra Gorda (IIA) to 39.2 ng/g in Gibeon (IVA). The data for iron meteorites cannot be compared with other work because no other data are available. However, my values for thallium in carbonaceous meteorites are very close to abundances reported by others [107,135-138].

My 2.8-5.3 ng/g thallium reported for four ordinary chondrites are of course not representative of the group as a whole, but in the single case where a thallium abundance for the same meteorites had been obtained by another worker, the agreement was very close. Huey and chao [105] have reported 3.79 ng/g for Plainview (H6) for which we have found 4.0 ng/g.

Certain general conclusions can be made about the abundance data. The first of these (also observed by Reed *et al.* [109], is that carbonaceous chondrites contain about 30 times more thallium than do ordinary chondrites. The second general observation is that there is some grouping of thallium values in iron meteorites with the highest values being in Group IVA (30-40 ng/g) and the lowest in some of the Group II meteorites.

i. Correlation Analysis

Thallium abundances were correlated against several variables including concentrations of nickel, arsenic, gold, iridium, osmium, palladium, platinum, rhodium, and ruthenium (data from Hoashi [139] and Hoashi *et al.* [140]). Correlation with cooling rates was also performed. Cooling rates were calculated from the expression derived by Wasson [141] based on original work by Short and Goldstein [142]. This expression can be given as follows:

$$\log CR = -2.04 \log BW - 8.94 \log[Ni] + 8.7$$

where CR is the cooling rate in °C/Ma, BW is the kamacite band width in mm, and [Ni] is the % Ni concentration.

There was a significant correlation between the thallium content of the iron meteorites and the cooling rate, for which $r = 0.40$ ($0.02>P>0.01$). There were several negative correlations between thallium and platinum group metals (PGM). This was shown for thallium vs. platinum (r

= -0.33 [0.05>P>0.02]), thallium vs. ruthenium (r = -0.39 [0.02>P>0.01]), thallium vs. iridium (r = -0.26 [0.10>P>0.05]), and thallium vs. rhodium (r = -0.28 [0.10>P>0.05]). Negative correlations with the four PGM highlight the chalcophile behaviour of thallium as has also been shown for palladium and arsenic by Hoashi *et al.* [140]. This is because chalcophile elements usually give a negative correlation with siderophile PGM.

ii. Thallium as a Taxonomic Determinant of Iron Meteorite Groups

It is well known that the abundances of germanium, gallium and certain PGM elements (especially Ir and Ru) when plotted against the nickel content of iron meteorites afford a means of classifying irons into their respective taxonomic groups. The role of the thallium content as a taxonomic parameter is shown in Fig.IV-3 which is a plot of thallium *vs.* nickel concentrations in the iron meteorites analysed by me.

There is clear separation of groups IIAB, IIC, IID, IIIAB, high-Ni IIICD, IIIF, IVA and IVB. Groups IAB, IIE, and IIIE show considerable overlap with the fields of other groups. It may be significant that two of these overlapping groups (IAB and IIE) belong to the so-called impact meteorites (supposedly formed by impacts of iron-rich material on a parent body of chondritic composition) as opposed to the remaining "magmatic" groups.

Despite the relatively good group separation achieved by a plot of nickel vs. thallium abundances in iron meteorites, there is no significant correlation between these two elemental concentrations whereby it would have been possible to determine the solid/liquid distribution coefficient of thallium by use of the Rayleigh equation. The poor correlation with nickel may be due to the relatively high volatility of thallium (b.p. 1457°C) compared with nickel (b.p. 2900°C) so that the former might suffer partial loss during the magmatic process. Indeed Reed *et al.* [109] have

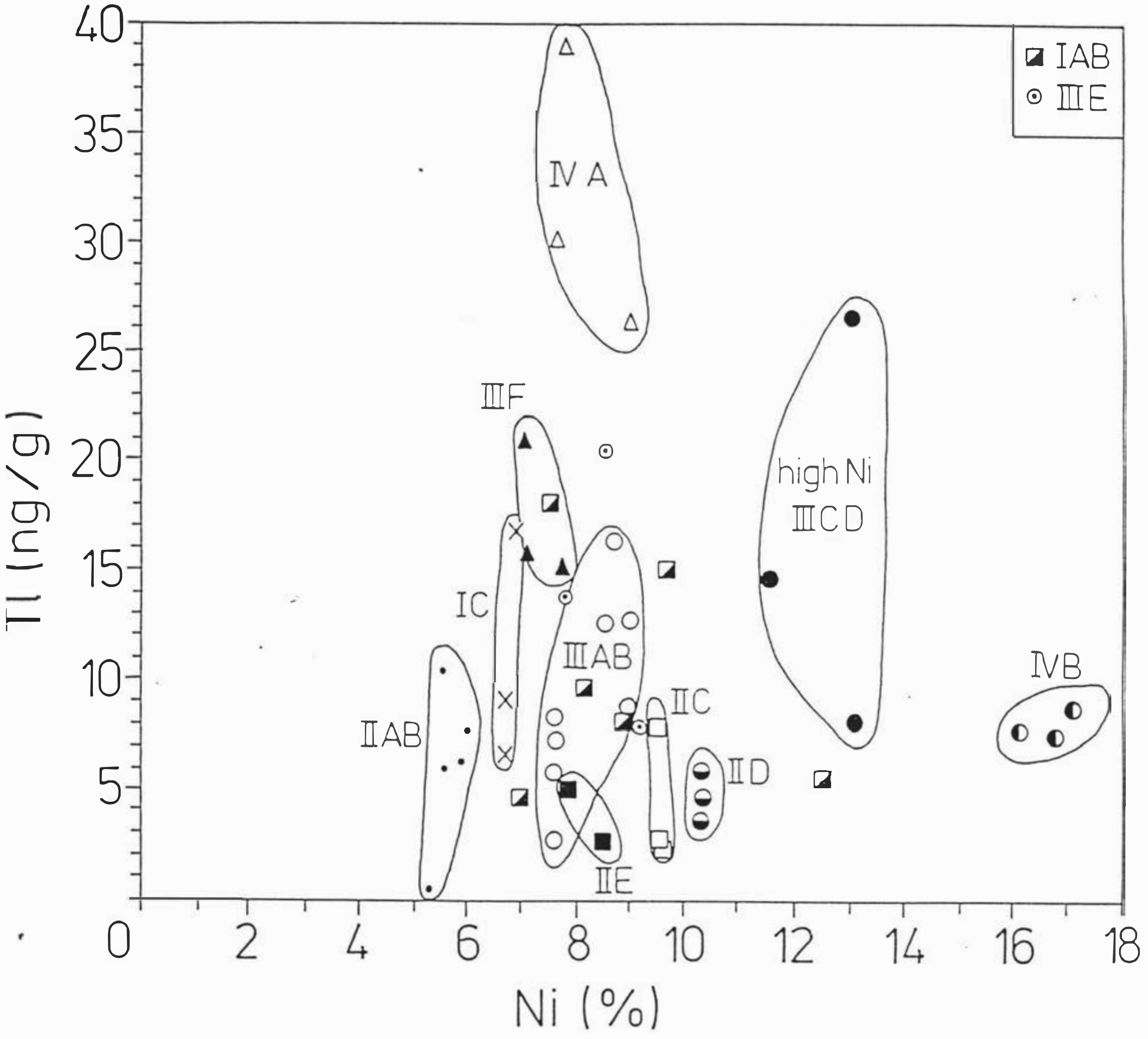


Fig.IV-3 Group separations of iron meteorites from a thallium vs. nickel abundance plot commented on the "scatter" of thallium concentrations in ordinary meteorites.

iii. Conclusion and Discussion

A relatively large pool of new data for the abundance of thallium in iron meteorites has now been established and should be used for further research on the fate of volatile elements during the evolution of the magmatic and impact groups of irons.

The data pool for thallium abundances in chondrites is too small to be able to form any definite conclusions but the initial data seem to indicate that some of the early RNAA data might have erred on the low side. The GFAAS method uses relatively available instrumentation and has the potential to provide a new large pool of data to study the largely unknown geochemistry of thallium and in particular its important role in cosmothermometry.

Table IV-10 Thallium and Nickel Abundances in Iron Meteorites

Meteorite	Group	Ni(%)	Tl (ng/g)
Annaheim	IAB	8.82	14.9
Bitburg	IAB	12.40	5.6
Cañon Diablo	IAB	6.98	4.6
Four Corners	IAB	8.90	8.1
Gladstone	IAB	7.53	18.0
Toluca	IAB	8.07	9.6
Woodbine	IAB	10.60	8.4
Chihuahua City	IC	6.68	9.1
Santa Rosa	IC	6.63	6.7
St Francois	IC	6.77	16.8
Bilibino	IIAB	5.80	6.3
Forsyth Co.	IIAB	5.50	10.1
North Chile	IIAB	5.57	6.1
Sâo Juliâo de Moreira	IIAB	6.10	7.8
Sierra Gorda	IIAB	5.27	0.36
Ballinoo	IIC	9.72	2.0
Kumerina	IIC	9.69	2.7
Perryville	IIC	9.27	8.1
Carbo	IID	10.20	4.5
Needles	IID	10.30	5.5
Rodeo	IID	10.20	3.6
Arlington	IIE	8.42	2.9
Weekeroo Station	IIE	7.51	5.7
Cape York (Woman)	IIIAB	7.58	8.1
Los Reyes	IIIAB	8.71	16.4
Madoc	IIIAB	7.52	7.3
Manitouwabing	IIIAB	7.32	5.6
Merceditas	IIIAB	7.82	2.9
Owens Valley	IIIAB	8.53	12.5
Waingaromia	IIIAB	9.14	8.6
Zacatecas	IIIAB	9.00	12.5
Carlton	IIICD	13.00	26.6
Lamesa	IIICD	13.10	8.2
Mungindi	IIICD	11.50	14.7
Nantan	IIICD	6.80	19.5

Table IV-10 Continued

Cachiyuyal	IIIE	7.88	13.6
Coopertown	IIIE	8.47	20.6
Paneth’s Iron	IIIE	8.98	7.9
Clark Co.	IIIF	6.79	21.2
Moonbi	IIIF	7.70	15.0
Nelson Co.	IIIF	7.02	16.0
Gibeon	IVA	7.68	39.2
Guanghua	IVA	7.70	30.0
Steinbach	IVA	9.08	26.3
Skookum	IVB	17.10	8.5
Tlacotepec	IVB	15.80	8.1
Weaver Mountains	IVB	16.80	7.6
Butler	ANOM	15.50	2.5
Mundrabilla	ANOM	7.72	6.9
Santa Catharina	ANOM	33.60	3.0

Table IV-11 Thallium Abundances in Chondritic Meteorites

Meteorite	Group	Tl (ng/g)
Allende	CV3	169
Mokoia	CV2	158
Jilin	H5	2.8
Plainview	H5	4.0
Summerfield	L5	5.3
Umbarger	L3/6	3.1

IV-4 THE MANITOUWABING IRON METEORITE

The Manitouwabing iron meteorite was found in Manitouwabing, Ontario, Canada (45°26’24"N, 79°52’32"S) in 1962 [117]. Initial work on the mineralogy of this meteorite was performed by Knox [143] in 1964. The main mass of about 39 kg is at present held at the University of Toronto and there is a small piece of 19 g at the National Museum, Washington DC. According to Graham *et al.* [144], Manitouwabing might be paired with Madoc.

Perhaps because of the limited distribution of Manitouwabing, surprisingly little work has been carried out on the chemical composition of this meteorite which, nevertheless, has been assigned to Group IIIAB, presumably on the basis of its medium octahedrite (Om) structure.

We have recently been fortunate enough to acquire a small piece of Manitouwabing and I have carried out a chemical analysis of its most important constituents with a view to confirming its classification and examining the thesis that it might be paired with Madoc.

IV-4-1 Analytical Methods

The following elements were quantified in Manitouwabing and Madoc: gallium [129] and thallium [145], as well as palladium, platinum and ruthenium [140] were determined by GFAAS; nickel by flame AAS; arsenic, gold, iridium osmium, and rhodium by INAA; and germanium by hydride generation AAS [96,97]. All analyses were carried out on duplicate samples.

IV-4-2 Results and Discussion

The experimental results are shown in Table IV-12. The much higher levels of iridium, osmium, arsenic, platinum, rhodium and ruthenium in Madoc compared with Manitouwabing, as well as the much lower palladium content of Madoc indicate quite clearly that these two meteorites are not paired. Agreement between my data for gallium, germanium and iridium in Madoc and those of Scott *et al*. [146] is extremely good. The thallium content of the two meteorites at 7.3 ng/g for Manitouwabing and 7.5 ng/g for Madoc is however very close, but is probably fortuitous.

Table IV-12 Elemental concentrations in Manitouwabing and Madoc [147]

Element	Manitouwabing	Madoc	
		Our Data	Other Data*
Ni (%)	7.34	7.47	
As (μg/g)	2.82	4.57	
Ga (μg/g)	18.8	19.6	19.4
Ge (μg/g)	35.0	35.5	36.4
Au (μg/g)	0.55	0.60	
Ir (μg/g)	1.52	5.76	6.8
Os (μg/g)	0.73	5.19	
Pd (μg/g)	4.40	2.87	
Pt (μg/g)	13.3	17.9	
Rh (μg/g)	1.56	2.20	
Ru (μg/g)	6.98	10.2	
Tl (ng/g)	5.6	7.3	

* From Scott *et al.* [146]

NB Data for Ni, Ga, Ge, and Tl are my own. Other elements were determined by Hoashi [140], or Ryan *et al.* [127]

VI-5 GENERAL CONCLUSIONS

It is concluded that the analytical methods developed for the quantification of gallium and thallium in meteorites have produced significant data of assistance in classification of such materials.

It is also concluded that the developed methodology (*i.e.* solvent extraction combined with GFAAS) is a viable alternative to NAA which is not available in most laboratories and certainly not in New Zealand. The methods that I have developed are sensitive, reliable, and accurate, except perhaps in the case of indium where limits of detection were too high to enable quantification of this element in iron meteorites.

The most significant achievement of this work was to provide thallium abundances in 49 iron meteorites that had never previously been analysed for this element. The acquisition of such an abundance pool has obvious applications to taxonomic classification of iron meteorites, as well as some application to the field of cosmothermometry where thallium (and indium) abundances are important.

PART FIVE

GROUP IIIB ELEMENTS IN CRETACEOUS-TERTIARY BOUNDARY CLAYS

V-1 INTRODUCTION

V-1-1 The Cretaceous-Tertiary Boundary

The science of palaeontology is governed by the existence of a number of geological periods or system boundaries at major floral and faunal breaks. Many of these boundaries seem especially well placed, for some of them represent distinct evolutionary changes or extinctions that occurred during short time intervals on a worldwide scale. Explanations of these often dramatic changes in the fossil record have not been totally satisfactory, especially since a global scale and a short, limited time must be considered.

The boundary between the Cretaceous and Tertiary geological periods can be identified in the sedimentary record by the rapid disappearance of typical Cretaceous fossils followed by the appearance of typical Tertiary forms. The precise palaeotological boundary usually corresponds to a clay layer almost devoid of fossils [147].

Ever since Alvarez *et al.* [62] proposed that mass extinctions (70%) of all life forms at the terminal Cretaceous had been caused by impact from a large (10 km) asteroid or comet, there has been lively discussion of the subject. The original Alvarez theory had been based on the discovery of an iridium-rich boundary at three different localities throughout the world, though later studies extended this to well over 100. This enrichment of iridium is significant because this element is relatively abundant in extraterrestrial materials (500-100,000 ng/g [=ppb]) and very rare in the Earth's crust

(<1 ng/g). The theory was later strengthened by the discovery of impact-derived shocked quartz at several localities [148], and by the presence of carbon particles probably originating from wild fires after the impact [149].

A countervailing argument by Officer and Drake [150] proposed that the high iridium content of the boundary clays was evidence of extensive volcanic activity at the time (possibly related to the formation of the Deccan Traps) since it has been shown by Olmez *et al.* [151] that iridium is present in volcanic emissions from Kilauea on the island of Hawaii. One of the strongest arguments proposed by the "volcanic" school of thought was that no "smoking gun" had been found. That is to say that no impact crater of the right age and size had hitherto been discovered.

The recent discovery of a 180 km impact crater in the Yucatan Peninsula, Mexico with exactly the right age [152] has shown the existence of a potential iridium source and has greatly strengthened arguments for the catastrophic impact theory of mass extinctions at the terminal Cretaceous. The original paper by Alvarez *et al.* [62] cited three localities at which the iridium-rich clay layer had been found. These included the K-T boundary at Woodside Creek first described by Strong [153]. The geochemistry of this sequence was later reported by Brooks *et al.* [63]. Several other iridium-rich K-T sites have now been reported in New Zealand at Chancet Rocks [154], Waipara River [155], Needles Point [156], and at Wharanui [157]. All of these sites except for the Mid-Canterbury Waipara River section are from Marlborough Province near the settlement of Ward (See Fig. V-1).

The Cretaceous/Tertiary (K/T) boundary rock section from the Flaxbourne River area has received considerable attention because it represents one of the most complete iridium-rich sequences yet recorded worldwide[64]. It was moreover found as a recently exposed site resulting from quarrying and was therefore completely fresh and free of weathering effects. Strong *et al.*[64] were also able to show that in this same sequence, the concentrations of nickel and chromium relative to iridium and normalized to this ratio in C1 carbonaceous chondrites, indicated a meteoritic rather than volcanic source for these elements.

Despite the now worldwide acceptance by the scientific community that a large meteoritic or cometary impact occurred at the end of the Cretaceous, there are still scientists who maintain that iridium was derived from volcanic activity. There is clearly still a need to do further work on K/T sections in order to either reinforce or disprove the impact theory.

V-1-2 Quantification of Elements in K/T Boundary clays

Following the initial work by Alvarez *et al.* [62], many elements have been quantified and investigated in the K/T boundary (Kyte *et al.* [158], Strong *et al.* [64], Brooks *et al.* [63]). Although some of the elements enriched in the K/T boundary clay (Ni, Ir, Co, Cr, Ni, etc.) are probably of cosmic origin, others are clearly terrestrial (As, Sb). The latter group of elements tends to be chalcophile (sulphur-loving). Anoxic conditions in the oceans following the K/T boundary impact would readily cause scavenging of chalcophiles from the water column since these elements are readily precipitated as sulphides under such conditions. Researchers have also noted that chalcophiles can be similarly enriched in coal ash, caused by the low oxidation potential of the medium [159]. Efficient leaching of the ejecta from the land and atmosphere would be able to concentrate most of the dissolved chalcophiles into the thin clay boundary layer.

Several chalcophiles (such as antimony, arsenic, copper, and zinc) have previously been quantified in boundary clays[64]. I have in addition determined gallium, indium, and thallium to add to this list. The technique was a modification of the procedures used above for analysis of meteorites and was applied not only to K/T boundary clays but also to volcanic lava and ash from Kilauea in Hawaii and Pinatubo in the Philippines. The boundary material was mainly from the

Woodside Creek and Flaxbourne River sequences in New Zealand but also included K/T material from outside this country. It is noteworthy that none of these elements can be determined routinely by NAA and the data on their abundances are therefore very sparse. I present perhaps the first data for these elements in the K/T boundary and have used them to interpret their significance for the volcanic vs. impact theories.

V-2 SITE LOCATIONS, GEOLOGY, GEOCHEMISTRY AND BIOSTRATIGRAPHY

Most of the work was carried out on the two important K/T boundary sites at Woodside Creek and Flaxbourne River (see Fig. V-1). Diagrams of the stratigraphic columns have already been given by Strong [153] and Strong *et al.* [64]. A brief geological description of each sequence now follows:

V-2-1 Woodside Creek

The stratigraphic interval as described by Strong [153] is well displayed in the gorge of Woodside Creek in north-eastern Marlborough (also see Fig.V-1). The section there is of particular biostratigraphic interest because the disconformable K/T contact can be accurately located in a continuously fossiliferous sequence where stratigraphic and structural relationships are straightforward. Diagnostic fossils, which can be correlated both locally and internationally, occur near the contact, both above and below.

Woodside Creek consists of two formations comprising light-coloured, hard, highly siliceous limestone. The younger Amuri Limestone, about 100 m thick is part of the Dannevirke Series. The underlying Mead Hill Formation, about 74 m thick, is of Late Cretaceous to Early Tertiary age and thus contains the Cretaceous/Tertiary boundary. Thin partings of softer limestone and silty mudstone (some only a few mm thick) are present throughout the sequence.

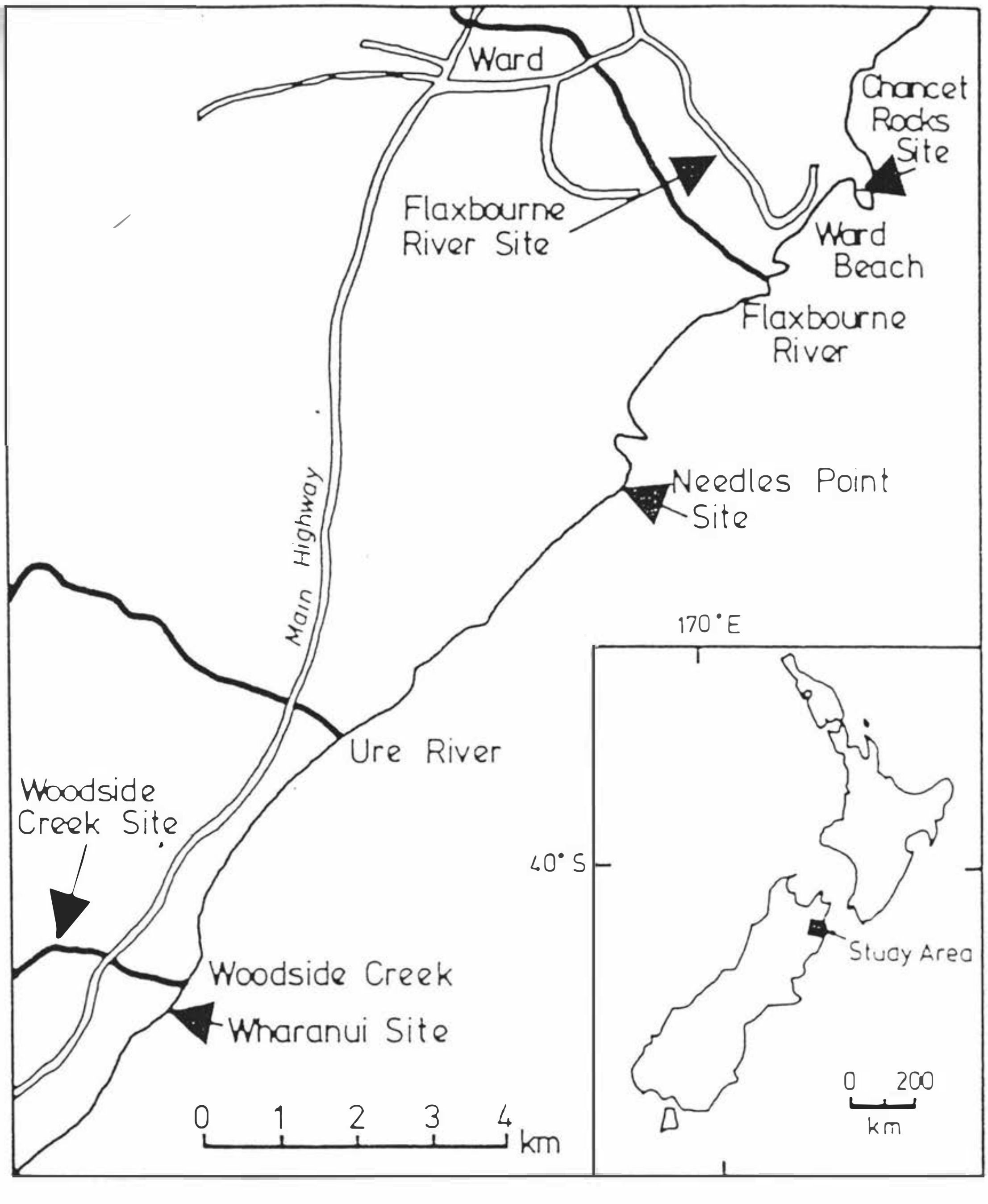


Fig.V-1 Location map showing the Flaxbourne River and Woodside Creek K/T boundary sites in relation to other similar sites in New Zealand

V-2-2 Flaxbourne River

The Flaxbourne River K/T boundary site, is in NZMS Quadrangle P29 (1:50,000), some 4 km southeast of the settlement of Ward, in the Marlborough province of New Zealand's South Island. The locality lies near the mouth of the Flaxbourne River, within the belt of moderately and completely deformed upper Cretaceous and Palaeogene limestone, which more or less parallels the coast for about 20 km, from the Ure River to Cape Campbell [160]. Other K/T boundary localities were previously described about 5 km away at Needles Point, and 2 km away at Chancet Rocks [63,154,156].

i. Lithology

Lithologically, the Flaxbourne River K/T boundary section is similar to the nearby Chancet Rocks section [63,154]. The essential difference between the two sites is that at Chancet Rocks the lowest few cm of the boundary interval, including the boundary clay, is usually missing owing to marine erosion of the relatively soft boundary unit, and infilling of the resultant cleft with sediment.

A columnar section of the Flaxbourne River sequence is shown in Fig.V-2. The $CaCO_3$ contents are shown in parentheses after the rock descriptions. Nine lithologic units were defined within, or adjacent to, the interval sampled:

(1) The interval -100 cm to -14 cm (Unit 1) consists of a thin to medium bedded, brownish grey limestone with thin marly partings.

(2) Unit 1 is overlain by 100 cm of thickly bedded massive brownish grey limestone without the marly partings (Unit 2). As the thickest single bed in the succession, it is an excellent marker for the Uppermost Cretaceous throughout the whole region, including Woodside Creek.

(3) Unit 3 is a 2-5 cm layer of soft off-white marl with a very irregular thickness. The contact with Unit 2 undulates, as Unit 3 tends to mask and fill irregularities on the surface of Unit 2. This unit is not well represented at Chancet Rocks.

(4) The boundary clay (Unit 4) is defined on the basis of the sharp lithological (and biostratigraphic) changes that occur at what is here defined as zero on the scale of the stratigraphic column. The contact with Unit 3 is planar and sharp, and is marked by an abrupt colour change from off-white to dark grey. The average thickness is 20 mm. The lower half of the clay, consisting of finely divided material, merges into the upper part of the unit which is interspersed with small limestone lenses. The basal contact shows no evidence of erosion. Instead, it appears to present continuous sedimentation during a sudden drastic change in oceanic conditions which altered accumulation rates of various sedimentary components. A major decrease in carbonate deposition was one such change.

(5) Unit 5 consists of an 8 cm layer of laminated dark-grey limestone (technically a calcareous mudstone). A similar dark limestone also occurs at Chancet Rocks where it is of comparable thickness.

(6) The dark limestone of Unit 5 is overlain by a 40 cm layer of thin-bedded greyish-green calcareous mudstone (Unit 6).

(7) Unit 6 is in turn overlain by a thickly bedded brownish weathered limestone (Unit 7).

(8) Unit 8 consists of an 8 m layer of medium-bedded yellow-green limestone that overlies Unit 7.

(9) The uppermost recorded unit consists of massive grey limestone with "sponge" fossils (Unit 9).

ii. Biostratigraphy

The preliminary foraminiferal study described by Strong *et al.* [64] confirmed the position of the K/T boundary and surveyed the general stratigraphic succession. The zero point on the scale not only indicates a position of sharp lithologic and biostratigraphic change, but also marks the lower boundary of the abrupt rise in the iridium content. This zero point lies between lithologic Units 3 and 4.

Cretaceous samples contain a typical New Zealand latest Cretaceous bathyal fauna with very abundant large planktonics and sparse benthics. Transition zone samples are characterised by a fauna of diminutive Cretaceous planktonic and benthic specimens. Except for their tiny size, practically all of them appear identical to Late Cretaceous species that have been recorded from underlying strata at Flaxbourne River or from elsewhere in New Zealand. The decrease in specimen size is the most striking feature at and above the iridium anomaly, below which many species of forams are two to three times the size of the same species found above the boundary. Only the benthic Allomorphina cretacea, rare below the anomaly but common above it, reaches about the same size.

Other contacts between the pre- and post-anomaly faunas are the appearance of new benthic taxa, an increase in the abundance of benthics from <1% to an estimated 10% and an overall decrease in foraminiferal abundance.

The question arises as to whether the post-anomaly Guembelitria cretacea zone (the boundary clay) was somehow reworked from older underlying strata. A number of factors suggests that this is not the case:

(1) appearance of taxa not recorded below the boundary clay;

(2) absence of other taxa which are abundant below the boundary;

(3) drastic decrease in size for most species;

(4) changes in relative abundance of planktonic taxa;

(5) increase in properties of benthic foraminifera;

(6) lack of sedimentological evidence for bioturbation or other reworking. The contact between the boundary clay and the underlying marl shows no signs of erosion and the sediment containing Guembelitria cretacea is finely laminated.

Reference to the existence of "Cretaceous survivors" recognizes that taxa above the boundary are not just reworked sediments [161].

iii. Previous Geochemistry

Abundances of $CaCO_3$ and more than 20 elements were obtained by Strong et al.[64] and other workers. These elements may be placed in groups as follows:

1. This group contains As, Co, Cr, Cu, Ni, Sb and Zn. These elements show an enrichment in the vicinity of the boundary (similar to that of Ir and Pd) and then return to their previous abundance levels.

2. The siderophile elements Cr, Co and Ni are depleted in crustal rocks relative to meteorites like their fellow siderophiles, Ir and Pd. Therefore some of the excess of these elements at the boundary may be derived from a meteoritic source.

3. The other four chalcophiles of the first group (As, Cu, Sb, and Zn) do not have significantly higher concentrations in meteorites than in crustal rocks. The source of their enrichment at the K/T boundary must be terrestrial.

4. In the next grouping, the elements Al, Fe, K, and Mg, are enriched at the boundary but remain at high levels in the Tertiary sediments. These elements are usually enriched in clays. It is probable that the K/T event led to a lasting change in sedimentation patterns leading to an increase in clay deposition.

5. The last four elements (Mn, P, Sr, and U) show a marked decrease in Tertiary sediments. This may be an artefact of calculating the elemental abundances on a carbonate free basis, which is only valid if the elements concerned are present in the clay fraction. It is likely that the aforementioned elements are part of the carbonate fraction.

V-3 MATERIALS AND METHODS

V-3-1 Sample Collection

Samples were obtained from the Woodside Creek and Flaxbourne River sites as well as from other well known K/T occurrences at Stevns Klint (Denmark), and Brownie Butte (continental section from New Mexico), Zumaya (Spain), and

Gubbio (Italy - site of the original work by Alvarez *et al.* [64]). Samples of volcanic lava from Kilauea and from Mt. Pinatubo were also obtained.

The materials were ground to -100 mesh and stored in sealable plastic bags. A tungsten carbide concentric ring grinder was used to grind the samples.

V-3-2 Sample Dissolution

In order to decompose limestone and silica in K/T boundary clays, a 1:1 mixture of hydrofluoric and nitric acids was used. About 0.5-2 g of powdered K/T boundary clay was weighed accurately and placed in Teflon beakers. A volume of 15 mL of the mixed acid reagent was carefully added to the sample and the samples were heated to dryness on a hot plate. Another portion of 15 mL of mixed acid was then added and the procedure repeated. The procedure was repeated once more. The residue was redissolved in an acid appropriate to the element that was to be quantified.

V-3-3 Analytical Procedures

All samples were analyzed for gallium, indium and thallium by a combination of extraction into methylisobutyl ketone (MIBK) followed by analysis of the organic phase by graphite furnace atomic absorption spectrometry (GFAAS) as detailed in Part Three of this thesis.

The abundances of gallium, indium and thallium of these K/T boundary clays and volcanic emissions are listed in Table V-1. The table also includes iridium values quantified by C.J.Orth using radiochemical neutron activation analysis (RNAA) at the Los Alamos National Laboratory, New Mexico.

V-4 RESULTS AND DISCUSSION

The analytical data include wide coverage of the New Zealand sections at Woodside Creek and Flaxbourne River as well as boundary samples from sites in Italy, Spain, Denmark and USA.

The abundance data have been expressed on a decalcified ($CaCO_3$-free) basis to avoid spurious fluctuations due to variation in carbonate deposition. The effect of this is to assume that all the trace elements were in the non-carbonate portion of each sample. The data are recorded in Table V-1.

It is clear from Table V-1 that gallium, indium and thallium are enriched at all of the six K/T boundaries analyzed. The extent of this enrichment is not immediately clear because of the background values. If however the mean of the Cretaceous and Tertiary background is subtracted from the concentrations of all three elements in the vicinity of the K/T boundary, more meaningful values for the excess abundances can be calculated. These are shown in parentheses in Table V-1 and were used in subsequent calculations.

Strong et al. [64] have shown that the abundances of siderophile elements such as cobalt, iron, chromium and nickel in boundary clays are very much higher than if their source had been volcanic emissions as suggested by Officer and Drake [150]. Based on the data of Olmez *et al.* [151] for trace elements in volcanic emissions from Kilauea, abundances of the above siderophiles in K/T boundary clays when normalized to iridium and to the Element/Ir ratio in C1 chondrites were several orders of magnitude higher than in Kilauea emissions. Strong *et al.* [64] therefore proposed that volcanic activity could not have been responsible for enrichment of iridium and siderophiles such as cobalt, iron, chromium and nickel in the K/T boundary. The same authors did however notice that chalcophile arsenic was not enriched at all in boundary clays relative to volcanic emissions and that copper, antimony and zinc were only slightly enriched, if at all.

I now have abundance data for three more chalcophiles (gallium, indium and thallium) and the element/iridium ratios normalized to C1 chondrites are shown in Fig.V-2. Data from Strong *et al.* [64] are included for comparison. It is clear from the figure that chalcophiles are not significantly enriched at the K/T boundary compared with volcanic emissions. It is also

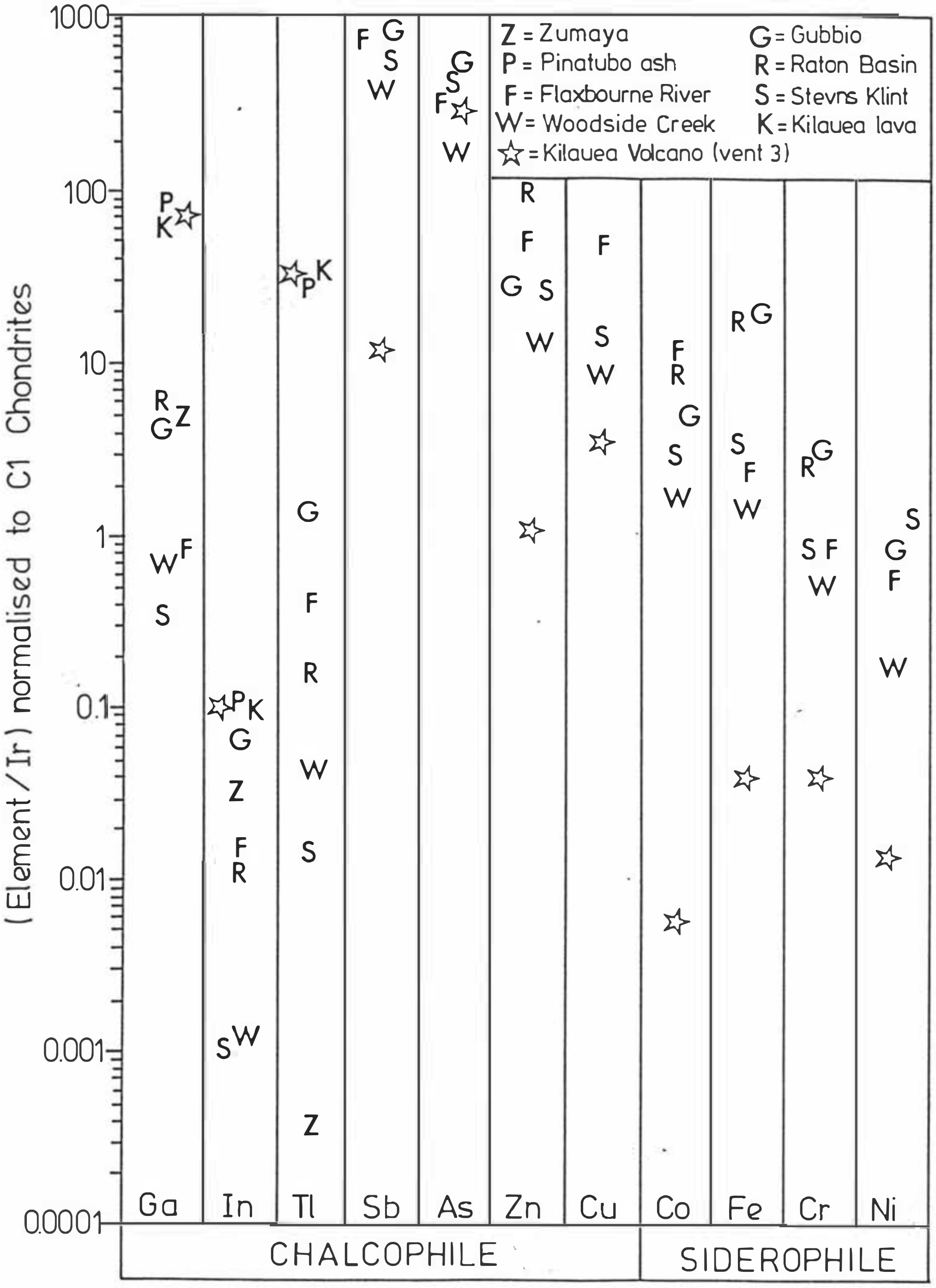


Fig.V-2 Elemental ratios in K/T boundary clays compared with those in volcanic emission (Kilauea and Pinatubo). Ratios have been normalised to Ir abundances and to metal/Ir ratios in C1 chondrites. Data for elements other than Ga, In, and Tl are from Strong *et al.* [63]

clear that these elements are not derived from volcanism since there is no concomitant reduction in the abundances of siderophiles such as nickel, chromium, and iridium that have lower abundances in volcanic emissions than in boundary clays.

Table V-1 Elemental abundances (ng/g [ppb] for In and Ir and μg/g [ppm] for Ga and Tl) in K/T boundary and other geological samples (all data expressed on $CaCO_3$-free basis)

Rock	Interval	Ga	In	Tl	Ir
WOODSIDE CREEK					
K	-3500 cm	1.5	<10	0.03	<0.05
K	-3250 cm	3.5	<10	0.03	<0.05
K	-1250 cm	2.6	<10	0.09	0.10
K	-400 cm	4.5	<10	0.22	0.11
K	-15 cm	8.5	<10	0.20	0.21
K	-6 cm	5.9	<10	0.60	4.70
K	-1 cm	14.7(9.7)	<10(1)	1.78(1.48)	6.21(5.2)
B	0	27.7(22.7)	103(93)	3.83(3.53)	118.0(117)
T	+0.2 cm	17.1(12.1)	138(128)	2.10(1.80)	42.0(41)
T	+5 cm	5.2	<10	1.50	3.07
T	+7 cm	8.1	13	0.26	2.57
T	+10 cm	5.9	<10	0.54	4.05
T	+14 cm	3.2	<10	0.22	2.43
T	+18 cm	3.4	<10	0.12	1.70
T	+250 cm	4.5	<10	0.10	<0.05
T	+500 cm	8.0	<10	0.06	<0.05
FLAXBOURNE RIVER					
K	-55 cm	12.0	<10	5.88	0.19
K	-8 cm	17.0	<10	6.21	0.64
K	-3 cm	26.0	27	7.84	1.94
B	-1.5 cm	27.7(11.7)	294(284)	10.40(6.10)	26.70(24.7)
B	-0.5 cm	26.0(12.4)	305(295)	7.70(3.30)	7.89(5.89)
B	0	31.1(10.7)	233(223)	9.85(5.55)	21.74(19.7)
T	+1.5 cm	15.3	17	4.22	2.18
T	+2.5 cm	12.0	<10	4.03	8.53
T	+4.5 cm	22.3	<10	5.39	5.10
T	+7 cm	12.6	<10	3.53	1.07
T	+11 cm	16.9	<10	2.67	1.19
T	+25 cm	11.2	<10	3.65	0.38
T	+50 cm	14.0	<10	2.19	0.20
T	+71 cm	9.2	<10	1.72	0.21
GUBBIO					
B	0	11.7	167	3.70	3.90^1
STEVNS KLINT					
B	0	21.0	86	0.96	87.00^1
ZUMAYA					
B	0	12.8	91	1.18	4.00^1
BROWNIE BUTTE					
B	0	21.9	88	0.60	5.60^2
PINATUBO ASH					
		24.7	31	9.55	0.48^3
KILAUEA LAVA					
		17.5	26	9.45	0.41^3

K - Cretaceous limestone, B - boundary clay,
T - Tertiary limestone.
1 - from Alvarez *et al.* [162], 2 - from Orth *et al.* [163],
3 - calculated from my In value and the In/Ir ratio in Kilauea volcanic emissions (Olmez *et al.* [151]).
NB - Abundances in parentheses are background corrected.

Table V-2 shows a mass balance of gallium, indium, thallium, arsenic, antimony, copper and zinc in the Flaxbourne River and Woodside Creek K/T boundary clays. The abundance data for arsenic, antimony, copper and zinc were taken from Strong *et al.* [64]. Assuming a chemical composition similar to today, if the Cretaceous ocean were a source for these trace elements, an impossibly great depth of water would be required for gallium (8300 to 17,330 m). In the case of thallium and indium, an accurate value for the corresponding ocean depth cannot be calculated because of the uncertainty as to the true elemental contents in this medium. However, a mantle or chondritic source does not seem feasible in view of the very large amounts of material (over 14 t/cm^2) needed.

Table V-2 Mass balance for chalcophiles in the Flaxbourne River and Woodside Creek K/T boundaries, New Zealand.

	Ga	In	Tl	As	Sb	Cu	Zn
Boundary clay (μg/cm^2)							
Flaxbourne River	25	0.5	13	51	9	396	1240
Woodside Creek	52	0.2	8	110	-	372	1407
Ocean mass needed (kg/cm^2)							
Flaxbourne River	833	>26	>130	17	18	132	124
Woodside Creek	1733	>10	>80	36	-	124	140
Crustal mass needed (g/cm^2)							
Flaxbourne River	1.7	5.1	26	28	45	7.2	18
Woodside Creek	3.5	2.2	16	61	-	6.8	20
Mantle mass needed (g/cm^2)							
Flaxbourne River	4.5	593	14130	22	104	4.0	22
Woodside Creek	9.5	244	8695	48	-	3.8	26

Estimates of ocean, crustal, and mantle masses are based on abundance data in Green [164].

A crustal source for some or all of the chalcophiles does not seem at all unreasonable in view of the modest quantities needed (1.7-45 g/cm^2). Such a source has also been proposed by Strong *et al.* [64] on the basis of their data for arsenic, copper, antimony and zinc.

I propose that a crustal component was derived from ejecta following the impact at the terminal Cretaceous. For gallium, indium and copper the amounts (1.7-7.2 g/cm^2) are roughly equivalent to the amount of clay (2-5 g/cm^2) deposited (assuming a density of 2.3 and clay thickness of 1-2 cm). The greater amounts of thallium, arsenic, antimony and zinc required, do however present a problem, but there is no reason to suppose that this excess could not have been contributed from the water column since only modest depths of water (up to 1400 m) would be needed to supply this excess and it is likely that the anoxic conditions following a K/T impact would have facilitated scavenging of chalcophiles from the water column. Measurement of all seven chalcophiles at continental sites would be an obvious way to assess the oceanic contribution to the abundances of these elements in K/T boundary sites. Unfortunately there are few chalcophile abundance data available except for my own values for gallium, indium and thallium. My own 0.06 μg/g thallium for the continental Raton Basin site, which is far lower than for any of the marine K/T boundary clays, would seem to derived largely from the water column.

To summarise, I propose that the major source of chalcophiles in K/T boundary clays is crustal impact ejecta and that the oceans have supplied a secondary source that is important for elements such as thallium. A firmer assessment of the relative contributions of these two sources will only follow a more detailed study of chalcophiles in continental K/T sections and it is to hoped that such work will eventuate in the non-too-distant future.

PART SIX

SUMMARY CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

VI-1 ANALYTICAL PROCEDURES

For the purpose of the quantification of the Group IIIB elements gallium, indium and thallium, in meteorites and other geological materials, it was necessary to develop a highly sensitive analytical method that could determine ng/g concentrations or even lower. Part Three of this thesis describes development of such a technique for analysis of meteorites and other geological materials.

The greatest problem inherent in extraction of Group IIIB elements into MIBK was the interference from iron that was co-extracted with the analytes thus seriously depressing the analytical signals. This was especially a problem with iron meteorites that can contain in excess of 90% iron.

The problem was solved by addition of potassium iodide to the aqueous phase that efficiently reduced iron to its divalent state so that it was not coextracted with the analytes. Although other reductants such as ascorbic acid have been used for iron(III)[105], they were not suitable for samples containing such high iron concentrations as in iron meteorites.

My developed method is speedy and sensitive, and avoids the possibility of loss of the analytes as was inherent with classical methods of iron separation involving precipitation as hydroxide.

Potassium iodide plays another important role in the solvent extraction system by forming iodo complexes with indium and thallium that are both stable and extractable into MIBK. Gallium is an exception and is better complexed as the chloro complex before extraction. The presence of chloride is however, inadvisable if thallium is to be quantified because of the volatility of the complex that can be lost during the charring stage of the GFAAS procedure. The same problem does not exist with the iodo complex.

Theoretically, thallium (I) can precipitate in the presence of iodide [32] and this might effect the extraction. However, my experiments have shown that this is not a problem if the amount of added iodide is carefully controlled. The use of 0.15 g of iodide per mL of solution was in the safe range but should not exceed 0.25 g.

A salting-out procedure by addition of appropriate reagents increased the solubility of the analyte complex in the organic phase. An example was the enhanced extraction of thallium after addition of dipotassium hydrogen phosphate. Although the iodo thallium complex is strongly extracted into diethyl ether, extraction into MIBK was only moderate. However, in the presence of 1.5 g/mL of dipotassium hydrogen phosphate, the distribution ratio for extraction of thallium increased more than three times compared with an unsalted aqueous phase. Salting out by use of potassium hydroxide was also found to be beneficial for extraction of indium. Addition of 0.1 g of potassium hydroxide per mL of indium iodide solution significantly increased the percent extraction of the complex into MIBK. Addition of such a small amount of hydroxide did not significantly affect the acidity of the 3M sulphuric acid solution.

No salting-out experiments were used for gallium because the extraction of the chloro complex into MIBK was already high enough to enable quantification of this element in meteorites and other geological materials.

In the development of a method for quantifying thallium it was observed that there still was a small amount of coextracted iron in the organic phase. This gave a small absorption peak in the GFAAS procedure. To overcome this problem, a backextraction procedure was used which involved shaking the organic phase with 4 mL of 3 M H_2SO_4 in the presence of 0.5 g of potassium iodide per mL of aqueous phase. Backextraction reduced the iron content of the organic phase to below 200 μg/mL, a concentration level that did not cause interference. There was also no detectable loss of thallium during this backextraction procedure.

Extraction of gallium was the simplest of the extraction methods and involved use of a hydrochloric acid medium which forms a strong and stable extraction system into MIBK and involves the chloro complex. Unlike indium and thallium, gallium is present in geological samples in the μg/g rather than ng/g range so that there is need of only a moderately sensitive analytical method. My developed procedure therefore had adequate sensitivity for all samples that I expected to analyse.

A useful technique for increasing analytical sensitivity in GFAAS is to utilise multiple loading injections. Sample solution is accumulated in the graphite furnace by these multiples where drying is carried out after each injection. The process is repeated until sufficient analyte has accumulated and then the usual charring and atomisation steps are performed.

A preheating step was necessary to avoid loss of sample at both ends of the graphite furnace, particularly organic solvents. A preheating temperature of 75°C produced satisfactory signals with increased magnitude and reproducibility.

Some standard reference rocks were analysed for testing the established procedures and the data obtained were close to the recommended values. These methods were also tested against samples already analysed by other workers and again gave good agreement.

Gallium, indium, and thallium were determined in geological samples by use of my developed procedures. Limits of detection were 2 ng for gallium, 15 ng for indium and 4.5 ng for thallium. These limits could, if necessary, be lowered considerably by increasing the total mass of analyte deposited in the furnace, by increasing the single injection volume or by use of multiple loading injections. Another way of lowering limits of detection was to decrease the organic/aqueous phase ratio so that the analyte became more concentrated in the small organic phase volume.

It is concluded that the developed methods are sensitive, rapid, and inexpensive to perform, as well as allowing for the routine determination of the above three elements in meteorites and other geological materials. Perhaps the most significant of the methods is the quantification of thallium that cannot otherwise be determined by neutron activation analysis (NAA) at the ultratrace level.

VI-2 ANALYSIS OF METEORITES

My developed procedures for determination of gallium, indium and thallium were successfully applied to the analysis of meteorites, Cretaceous/Tertiary boundary clays and other geological materials.

One of the aims of this work was to obtain abundance data for gallium, indium, and thallium in order to evaluate their use for classification of meteorites. New abundance data for thallium in about 50 iron meteorites were obtained by my analytical procedure. The thallium contents of these irons ranged from 0.36-39.2 ng/g. Though there are no other thallium data for iron meteorites with which my values could be compared, my levels of thallium in six chondrites were very close to abundances reported by others.

A plot of nickel vs. thallium abundances showed spatial separation of Groups IIAB, IIC, IIIAB, IIICD, IIIF, IVAB, and IVB into separate fields. There was however considerable overlap of Groups IAB, IIE, and IIIE with other fields.

Gallium abundance data in iron meteorites are usually obtained by NAA. From the results of my analyses of about 50 iron meteorites, the developed procedure appears to be a viable alternative to NAA for gallium determinations since it is far less expensive and has comparable limits of detection.

Indium concentrations in iron meteorites are apparently extremely low and were at or below the limit of detection of my methods. However, the developed procedure could be used to analyse rocks, stony meteorites and other geological materials. Six chondrites were analysed for indium with the method and satisfactory data obtained for abundances of Group IIIB elements. As no additional chondrites were available to me at the time, I was not able to obtain an overall picture for the distribution of indium among the different classes of stony meteorite.

VI-3 ANALYSIS OF CRETACEOUS/TERTIARY BOUNDARY CLAYS

The chalcophile trace elements Ga, In, and Tl were quantified in Cretaceous/Tertiary boundary clays from Woodside Creek and Flaxbourne River in New Zealand, and from Stevns Klint (Denmark), Brownie Butte (continental site from Raton Basin in USA), Zumaya (Spain), and Gubbio (Italy). Samples of volcanic ash from Kilauea (Hawaii) and Mount Pinatubo (Philippines) were also analysed for the same elements. Relative to the Ir content (normalized to C1 chondrites), there was no enrichment of Ga, In, and Tl, or of other chalcophiles such as As, Cu, Sb, or Zn, compared with volcanic emissions from Kilauea. However, because of the high degree of relative enrichment of siderophile Co, Cr, Fe, and Ni (low in volcanic emissions) at the K/T boundary, volcanic activity was clearly not a significant source of Ir accumulation in these terminal Cretaceous sediments. Mass balance calculations showed that alternative sources of chalcophiles at the boundary appeared to be impact ejecta of crustal material at least in the case of Ga, In, and Cu. Amounts of Tl, Sb, and Zn in excess of those deposited by impact ejecta could be explained by scavenging from the ocean under the anoxic conditions following a K/T impact event.

VI-4 CLASSIFICATION OF THE MANITOUWABING IRON METEORITE

A previously undescribed iron meteorite named Manitouwabing was analysed by me [165] for gallium and thallium as well as germanium. The studies showed that it belonged to Group IAB and is not paired with Madoc as had been suggested by Graham *et al.*[144]

VI-5 RECOMMENDATIONS FOR FURTHER WORK

It has been shown how my developed methods could be used to determine gallium, indium, and thallium in a wide range of geological materials. The data have served to increase our knowledge about meteorites and their origins. The methodology has however not attained its ultimate potential, so that further work along the following lines is recommended:

(1) Indium could not be determined in iron meteorites because limits of detection were not sufficiently low. There is clearly scope to improve the extraction and GFAAS procedures. This might be achieved by devising extraction systems with a higher value of the organic/aqueous phase analyte distribution ration (D). With higher values of D, a higher aqueous/organic phase ratio will be permissible and result in higher concentrations of the analyte in the organic phase and consequently lower limits of detection. Improved more stable high-intensity hollow cathode lamps will also allow for greater scale expansion of the GFAAS signal in order to lower limits of detection even further.

(2) The work has clearly shown the usefulness of thallium abundances as taxonomic parameters for classification of iron meteorites. Limitations of samples and of time have allowed for analysis of only two or three samples from each taxonomic group. It is recommended that in the future, considerably more iron meteorites be analysed for thallium, particularly in Groups IAB, IIE and IIIE, in order to fully assess the taxonomic potential of abundances of this element for classification of iron meteorites.

(3) Group IIIB elemental abundances have not been obtained to any extent in stony meteorites, again due to poor limits of detection of many classical and instrumental techniques. There is clearly a need to extend our pool of knowledge in this field in order to understand more about the evolutionary history of chondrites. The six chondrites were already analysed in this work are obviously too few to allow for any firm conclusions.

(4) My work has shown that there is some potential for the use of hydride generation AAS for determining Group IIIB elements. The main problems so far encountered were inadequate sensitivity and poor signal reproducibility.

Future work should be concentrated on producing a faster rate of hydride formation and reducing or eliminating hydride decomposition before the gaseous reaction mixture reaches the flame cell. A possible solution to this problem might be the discovery of a reductant that can accompany the hydrides in the gaseous state before decomposition in the flame.

REFERENCES

[1] **M.E.Weeks and H.M.Leicester**
Discovery of Elements
7th ed. Journal of Chemical Education, Easton, (1963)

[2] **G.H.Wagner and H.Gitzen**
Gallium
J. Chem. Education, 29, (1952), 162-167

[3] **M.T.Ludwick**
Indium
The Indium Corporation of America, N.Y.(1959)

[4] Chemical News
3, (1861), 30

[5] **V.M.Goldschmidt**
Geochemistry
Oxford University Press, London (1954)

[6] **F.W.Clarke**
The Data of Geochemistry
U.S. Geol. Survey Bull., 16, (1924), 770

[7] **V.M.Goldschmidt and C.Peters**
The Geochemistry of Gallium
Nachr, Ges. Wiss. Göttingen,
Math-physik, Klasse, (1931), 165-183

[8] **E.Einecke**
Das Gallium
Verlag Leopold Voss, Leipzig, (1937)

[9] **C.A.Hamel**
Rare Metal Handbook
2nd ed. Reinhold, London, (1961)

[10] **P.Pascal**
Nouveau Traité de Chimie Minérale
Vol.6, Masson, Paris (1961)

[11] **Gmelin**
Handbuch der Anorganischen Chemie
No.38(Thallium), Verlag Chemie, Berlin, (1940)

[12] **D.M.Shaw**
Physics and Chemistry of the Earth
Vol.II, Pergamon, London, (1957), 161 - 211

[13] **L.Moser and A.Brukl**
Determination and Separation of Rare Metals from Other Metals. XV. Quantitative Analysis of Gallium
Monatschr., 50, (1928), 181

[14] **W.F.Hillebrand and G.E.F.Lundell**
Applied Inorganic Analysis, with Special Reference to the Analysis of Metals, Minerals, and Rocks
2nd Ed.,John Wiley & Sons.Inc., New York, 1962

[15] **L.Moser and F.Siegmann**
Determination and Separation of Rare Metals from Other Metals. XVIII. Determination of Indium and Its Separation from the Monoxides and Sesquioxides
Monatschr., 55, (1930), 14-24

[16] **F.W.E.Strelow**
An Ion-exchange Selectivity Scale of Cations Based on Equilibrium Distribution Coefficients
Anal. Chem., 32, (1960), 1185-1188

[17] **F.W.E.Strelow;R.Rethemeyer;and C.J.C.Bothma**
Ion-exchange Selectivity Scales for Cations in Nitric and Sulphuric Acid Media with a Sulphonated Polystyrene Resin
Anal. Chem., 37, (1965), 106-111

[18] **F.Nelson;T.Murase;and K.A.Kraus**
Ion-exchange Procedures, I. Cation Exchange in Concentrated Hydrochloric and Perchloric Acid Solution
J. Chromatog., 13, (1964), 503-535

[19] **R.Klement and H.Z.Sandmann**
Separation of Gallium, Indium, and Germanium from Other Metals by Ion Exchange
Anal. Chem., 145, (1955), 325-334

[20] **H.M.N.H.Irving and G.T.Woods**
Adsorption of Some Anionic Complexes on a Cation-exchange Resin
J. Chem. Soc., (1963), 939-944

[21] **T.Nozaki**
Indirect Colorimetric Determination of Thallium
J.Chem. Soc. Japan, Pure Chem. Sect., 77, (1956), 493-496

[22] **K.A.Kraus and F.Nelson**
Proceedings of International Conference for Peaceful Uses of Atomic Energy
Paper 837 (USA), Geneva, (1955)

[23] **H.G.Hicks;R.S.Gilbert;R.C.Stevenson;and W.H.Hutchin**
USAEL, A Report
LRL-65, (1953)

[24] **M.L.Good;C.Srivastava and F.F.Holland**
Liquid-liquid Extraction with Long-chain Quaternary Ammonium Halides
Anal. Chim. Acta, 31, (1964), 534-544

[25] **D.Mapper and J.R.Fryer**
The Use of Dithizone-cellulose Acetate Columns of Increased Capacity in the Determination of Indium by Pierce and Peck's Neutron-activation Method
Analyst, 87, (1962), 279

[26] **T.V.Arden;F.H.Burstall;G.R.Davies;J.A.Lewis and R.P.Linstead**
New Method for the Separation, Detection, and Estimation of Inorganic Compounds
Nature, 162, (1948), 691-692

[27] **R.Fridle**
Thallium Poisoning
Deut. Z. Ges. Gericht. Med., 21, (1933), 461-462

[28] **S.Harasawa and T.Sakamoto**
Inorganic Paper Chromatography. XXIV. Separation and Determination of Thallium, Iron, Titanium, and Zirconium and Their Application to Systematic Analysis
J. Chem. Soc. Japan, Pure Chem. Sec.,
77, (1956), 165-168

[29] **G.V.Efremov and A.F.Vetoshfina**
The Separation of Thallium by Radical Paper Chromatography
Uch. Zap. Leningrad. Gos. Univ.,
279, (1960), 53

[30] **A.I.Buser**
The Analytical Chemistry of Indium
Pergamon, Oxford, (1962)

[31] **I.M.Kolthoff and P.J.Elving**
Treatise on Analytical Chemistry
Part II, Section A, Vol.2, *Interscience*,
New York, (1962)

[32] **C.L.Wilson and D.W.Wilson**
Comprehensive Analytical Chemistry
Vol.IC and Vol.IIA, *Elsevier*, Amsterdam, (1964)

[33] **H.Onishi**
Determination of Gallium with Rhodamine B
Anal. Chem., 27, (1955), 832

[34] **H.Onishi**
New Photometric Method For Determining Thallium with Rhodamine B
Bull. Soc. Chem. Japan, 29, (1956), 945

[35] **A.U.Fogg;C.Burgess; and D.T.Burns**
Use of Basic Dyes in the Determination of Anions, Particularly as a Means of Determination of Antimony, Thallium, and Gallium
Talanta, 18, (1971), 1157-1196

[36] **A.Kumar and A.Joshi**
Polarography of Gallium(III) with δ-valerolactam-[piperidin-2-one]
J. Electrochem. Soc. India, 37, (1988), 175-176

[37] **A.Kumar; R.S.Agarwal; and M.Jain**
Electrochemical Behaviour of Vanadium(V) and Gallium(III) Complexes with 2,3-dihydroxypyridine-[pyridine-2,3-diol] at Dropping-mercury Electrode
Bull. Electrochem., 5, (1989), 626-629

[38] **Q.Zhang and S.Qi**
Studies on Polarographic Adsorption Complex Wave of Indium-Xylenol Orange
Huaxue Shiji (Chinese), 9, (1987), 9-11

[39] **J.Wang**
Stripping Analysis
VCH Publ. Inc., Deerfield Beach, Florida, (1985)

[40] **M.Geßler**
Polarographische Analyse
Verlag Chemie, Weinheim, (1981)

[41] **M.Ishibashi;T.Shigematsu and Y.Nishikawa**
Fluorimetric Analysis. IV Fluorimetric Determination of Gallium with 8-hydroxyquinoline
Bull. Inst. Chem. Res., Kyoto University, 37, (1959), 191-197

[42] **M.W.Kabbani; S.Rubio-Borroso; and L.M.Polo-Diez**
Determination of Trace of Gallium in the Presence of Aluminium by Synchronous Derivative Spectrofluorimetry
Anal. Chim. Acta, 218, (1989), 167-171

[43] **M.A.Floyd; V.A.Fassel; R.K.Winge; J.M.Katzenberger and A.P.D'Silva**
Inductively Coupled Plasma-Atomic Emission Spectroscopy: A Computer Controlled, Scanning Monochrometer System for the Rapid Sequential Determination of the Elements
Anal. Chem., 52, (1980), 431-438

[44] **D.Kollotzek;P.Tschöpel; and G.Tölg**
Three-filament and Toroidal Microwave-Induced Plasmas as Radiation Sources for Emission-spectrometric Analysis of Solutions and Gaseous Samples
Spectrochim. Acta, 39B, (1984), 625-636

[45] **B.Welz**
Atomabsorptionsspectrometrie
3rd Ed., Verlag Chemie, Weinheim, (1983)

[46] **H.Berndt and W.Slavin**
Automated Traces Analysis of Small Samples Using the "Injection Method" of Flame Atomic Absorption Spectrometry: A Review
At. Abs. Newsl., 17, (1978), 109-112

[47] **C.A.Johnson**
The Determination of Some Toxic-metals in Human Liver as a Guide to Normal Levels in New Zealand. Part I. Determination of Bi, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl and Zn
Anal. Chim. Acta, 81, (1976), 69-71

[48] **H.Berndt and J. Messerschmidt**
Micro-method of Flame Atomic-absorption and Emission Spectrometry (Platinum-loop Method), II Determination of Arsenic, Bismuth, Cadmium, Mercury, Lead, Antimony, Selenium, Tellurium, Thallium, Zinc, Lithium, Sodium, Potassium, Caesium, Strontium, and Barium
Spectrochim. Acta, 36B, (1981), 809-819

[49] **M.S.Leloux; H.P.Lich; and J.R.Claude**
Flame and Graphite-furnace Atomic-absorption Spectroscopy Methods for Thallium: A Review
Atomic Spectroscopy, 8, (1987), 71-75

[50] **A.A.Smales; D.Mapper; J.W.Morgan; K.R.Webster and A.J.Wood**
Some Geochemical Determinations Using Radioactive and Stable Isotopes
Proc. 2nd Int. Conf.Peaceful Uses Atomic Energy,
United Nations, Geneva 2, (1958), 242

[51] **E.Goldberg; A.Uchiyama and H.Brown**
The Distribution of Nickel, Cobalt, Gallium, Palladium and Gold in Iron Meteorites
Geochim. Cosmochim. Acta, 2, (1958), 1

[52] **J.F.Lovering; W.Nichiporuk; A.Chodos and H.Brown**
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, 11, (1957), 263-278

[53] **H.R.Schulten; W.D.Lehmann; and R.Ziskoven**
Determination of Thallium in Brain Tissue by Stable Isotope Dilution and Field Desorption Mass Spectrometry
Z. Naturforsch., 33C, (1978), 484-487

[54] **D.J.Douglas and J.B.French**
Elemental Analysis with a Microwave-induced Plasma/ Quadrupole Mass Spectrometer System
Anal. Chem., 53, (1981), 37-41

[55] **R.J.Cotter**
Laser Mass Spectrometry: An Overview of Techniques, Instruments, and Applications
Anal. Chim. Acta, 195, (1987), 45-59

[56] **K.G.Heumann; P.Kastenmayer; and H.Zeininge**
Determination of Traces of Lead and Thallium in the ppm and ppb Range in Biological Materials by Mass-spectrometric isotopic-dilution Analysis
Fresenius Z. Anal. Chem., 306, (1981), 173-177

[57] **J.Kikkert**
Accurate Geochemical Analysis of Samples of Unknown Composition and Origin
Philip's Application Report, X-Ray and Nuclear Analysis, Ermelo, The Netherlands, (1982)

[58] **J.Kikkert**
Practical Geochemical Analysis of Samples of Variable Composition Using X-ray Fluoresence Spectrometry
Spectrochim. Acta, 38B, (1983), 809-820

[59] **B.Griepink**
Improving the Quality of Environmental Trace Analysis
Fresenius Z. Anal. Chem., 317, (1984), 210-212

[60] **A.Kracher; J.Willis and J.T.Wasson**
Chemical Classification of Iron Meteorites-IX. A New Group(IIF), Revision of IAB and IIICD, and Data on 57 Additional Irons
Geochim. Cosmochim. Acta, 44, (1980), 773-787

[61] **R.N.Clayton; N.Onuma; and T.K.Mayeda**
A Classification of Meteorites Based on Oxygen Isotopes
Earth Planet. Sci. Lett., 30, (1976), 10-18

[62] **L.W.Alvarez; W.Alvarez; F.Asaro; and H.V.Michel**
Extraterrestrial Cause for the Cretaceous-Tertiary Extinction
Science, 208, (1980), 1095-1108

[63] **R.R.Brooks; C.P.Strong; J.Lee; C.J.Orth; J.Holzbecher; J.Collen; V.E.Neall and J.Lee**
Elemental Anomalies at the Cretaceous-Tertiary Boundary, Woodside Creek, New Zealand
Science, 226, (1984), 539-542

[64] **C.P.Strong; R.R.Brooks; S.M.Wilson; R.D.Reeves; C.J.Orth; X.Y.Mao; L.R.Quintana; and E.Anders**
A New Cretaceous-Tertiary Boundary Site at Flaxbourne River, New Zealand: Biostratigraphy and Geochemistry
Geochim. Cosmochim. Acta, 51, (1987), 2769-2777

[65] **N.N.Greenwood and N.G.H.Wallbridge**
Uncoordinated Gallium Hydride
J. Chem. Soc., 7, (1963), 3912-3913

[66] **E.Wiberg and E.Amberger**
Hydrides of the Elements of Main Groups I-IV
Elsevier, Amsterdam, (1971)

[67] **E.Wiberg et al.**
Hydrides of Thallium: V.Thallium Boranate, $TlBH_4$, and Thallium Aluminum Hydride, $TlAlH_4$
Z. Naturforsch., 12B, (1957), 60-63

[68] **I.S.Busheina and J.B.Headridge**
Determination of Indium by Hydride Generation and Atomic-absorption Spectrometry
Talanta, 29, (1982), 519-520

[69] **D.Yan; Z.Yan; G.Cheng; and A.Li**
Determination of Indium and Thallium by Hydride Generation and Atomic-absorption Spectrometry
Talanta, 31, (1984), 133-134

[70] **J.R.Castillo; J.M.Mir and M.T.Gomez**
Some Observations on the Determination of Indium by Atomic-absorption Spectrophotometry Using the Volatile Covalent Hydride Technique
Mikrochim. J., 38, (1988), 387-389

[71] **M.Berthelot and J.Jungfleish**
Ann. Chim. et Phys. 26, (1872), 396

[72] **W.Nernst**
Z. Physik. Chem., 8, (1891), 110

[73] **S.M.Wilson**
The Analytical Geochemistry of Platinum Group Metals in Cretaceous/Tertiary Boundary Clays
Ph.D Thesis, Massey University, (1991)

[74] **T.Moeller and A.J.Cohen**
Analytical Applications of 8-hydroxyquinoline Derivatives of Gallium and Thallium
Anal. Chem., 22, (1950), 686-690

[75] **S.Lacroix**
Properties of the Oxinates of Aluminum, Gallium, and Indium. Separation of Gallium by Extraction with Chloroform
Anal. Chim. Acta, 1, (1947), 260-290

[76] **J.F.Steinbach and H.Freiser**
Acetylacetone as an Analytical Extraction Agent-Extraction of Aluminum, Gallium, and Indium
Anal. Chem., 26, (1954), 375-379

[77] **S.E.J.Johnson in E.B.Sandell**
Colorimetric Determination of Traces of Metals
2nd Ed.,Interscience Publishers, Inc.,
New York, (1950), p. 537

[78] Same as [77] at p. 34

[79] **H.M.N.H.Irving**
Solvent Extraction and Its Applications to Inorganic Analysis
Quart. Rev. Chem. Soc., London, Vol. V,
No.2, (1951), 200-226

[80] **E.B.Sandell**
Determination of Gallium in Silicate in Silicate Rocks
Anal. Chem., 19, (1947), 63-65

[81] **O.Kammori; H.Kawase; and I.Inamoto**
Alternating-current Polarographic Determination of Gallium in Iron and Steel
Japan Analyst, 14, (1965), 1030-1035

[82] **I.S.Balog; E.A.Yantso; P.I.Babidorich and P.P.Kish**
Extraction - Photometric Determination of Micro Amounts of Gallium in Alloyed Chalcogenide Glasses
Zavod. Lab., 56, (1990), 17-18

[83] **L.Zhou; T.T.Chao; and R.F.Sanzolone**
Removal of Iron Interferences by Solvent Extraction for Geochemical Analysis by Atomic-absorption Spectrophotometry
Talanta, 32, (1985), 475-478

[84] **E.N.Pollock**
Gallium and Germanium in Limonite by Atomic Absorption
Atomic Abs. Newsl., 10, (1971), 77

[85] **S.A.Popova; L.Bezur; L.Polos and E.Pungor**
Determination of Gallium by Extraction and Atomic-absorption Measurement
Z. Anal. Chem., 270, (1974), 180-183

[86] **S.D.Gur'ev; L.B.Ginsburg; and A.P.Shibarenkova**
Determination of Gallium and Indium in the Flue Dust of the Lead, Zinc, and Copper Industries by the Fluorescence Method
Sbor. Nauchn. Trudy, 10, (1955), 387-397

[87] **J.W.Rothe**
Chem. News., 66, (1892), 182

[88] **F.N.Speller**
Chem. News., 83, (1901), 124

[89] **A.C.Langmuir**
J. Am. Chem. Soc., 22, (1900), 102

[90] **E.F.Kern**
J. Am. Chem. Soc., 23, (1901), 685

[91] **H.M.N.H.Irving and F.J.C.Rossotti**
The Extraction of the Indium Halides into Organic Solvents
J. Chem. Soc., (1955), 1946-1966

[92] **G.H.Morrison and H.Freiser**
Solvent Extraction in Analytical Chemistry
1st Ed., John Wiley & Sons, Inc.,
New York, (1957)

[93] **G.L.Long and J.D.Winefordner**
Limit of Detection: A closer Look at the IUPAC Definition
Anal. Chem., 55, (1983), 712A

[94] **N.M.Sine; W.O.Taylor; G.R.Webber and C.L.Lewis**
Third Report of Analytical Data for CAAS [Canadian Association for Applied Spectroscopy] Sulfide Ore and Syenite Rock Standards
Geochim. Cosmochim. Acta, 33, (1969), 121-131

[95] **G.E.M.Hall; K.N.de Silva; J.C.Pelchat and J.E.Vaive**
Advances in Analytical Methods Based on Atomic Absorption Spectrometry in the Geochemistry Laboratories of the Geological Survey of Canada
Curr. Res.(Geol. Surv. Can.), Part A,
(1987), 477-484

[96] **X.Guo and R.R.Brooks**
Hydride Generation Atomic Absorption Spectrometry for the Quantification of Germanium in Iron Meteorites
Anal. Chim. Acta, 228, (1990), 139-143

[97] **X.Guo**
A Hydride Generation-Atomic Absorption Spectrometric Procedure for the Quantification of Germanium and Other Elements in Iron Meteorites
M.Sc. Thesis, Massey University, (1989)

[98] **F.C.Mathers and C.E.Pritchard**
Separation of Iron from Indium with Cupferron
Proc. Indiana Acad. Sci., 43, (1934), 125-127

[99] **I.Wada and R.Ishii**
Separation and Determination of the Elements of the Silver and Thallium Group
Sci. Papers. Inst. Phys. Chem. Reseach (Tokyo),
34, (1938), 787-818

[100] **H.M.N.H.Irving and F.J.C.Rossotti**
The Solvent Extraction of Group IIIb Metal Halids
Analyst, 77, (1952), 801-812

[101] **E.M.Scadden and N.E.Ballou**
Solvent Extraction Separation of Zirconium and Niobium
Anal. Chem., 25, (1953), 1602-1604

[102] **A.Claassen; L.Bastings and J.Visser**
Highly Selective Procedure for the Spectrophotometric Determination of Aluminum with 8-quinolinol, and Its Application to the Determination of Aluminum in Iron and Steel
Anal. Chim. Acta, 10, (1954), 373-385

[103] **H.Bode**
Systematic Studies on the Use of Diethyldithiocarbamtes in Analysis. IV. the Formation of Metal Diethyldithiocarbamates and Their Extractability with Respect to the pH of the Solution
Z. Anal. Chem., 144, (1955), 165-168

[104] **I.May and J.I.Hoffman**
Dithizone as a Reagent for Indium
J. Washington Acad. Sci., 38, (1948), 329-336

[105] **A.E.Hubert and T.T.Chao**
Determination of Gold, Indium, Tellurium and Thallium in the Same Sample Digest of Geological Materials by Atomic-absorption Spectroscopy and Two-step Solvent Extraction
Talanta, 32, (1985), 568-570

[106] MP-1a, a Standard Reference Rock, Canmet Report 81-12E
Canada Centre for Mineral and Energy Technology

[107] **E.Anders and N.Grevesse**
Abundances of the Elements: Meteoritic and Solar
Geochim. Cosmochim. Acta, 53, (1989), 197-214

[108] **B.Griepink; M.Sager and G.Tölg**
Determination of Traces of Thallium in Various Materials
Pure & Appl. Chem., 60, (1988), 1425-1436

[109] **G.W.Reed; K.Kigoshi and A.Turkevich**
Determinations of Concentrations of Heavy Elements in Meteorites by Activation Analysis
Geochim. Cosmochim. Acta, 20, (1960), 122-140

[110] **F.O.Simon; E.Y.Campbell; and P.J.Aruscavage**
Thallium Contents of 16 USGS Standard Rocks
J.Res. U.S. Geol. Surv., 5, (1977), 579-581

[111] **N.Angier; R.Buderi and C.Gorman**
Did Comets Kill the Dinoaurs? A Bold New Theory About Mass Extinction
Time, 125:18, (1985), 54-61

[112] **J.F.Kerridge and M.S.Matthews**
Meteorites and the Early Solar System
The University of Arizona Press, Tucson, (1988)

[113] **H.C.Urey and H.Craig**
The Composition of the Stone Meteorites and the Origin of the Meteorites
Geochim. Cosmochim. Acta, 4, (1953), 36-82

[114] **H.Craig**
Petrological and Compositional Relationships in Meteorites In Isotopic and Cosmic Chemistry (eds. H.Craig; S.L.Miller and G.J.Wasserburg)
Amsterdam, Holland, (1964), 401-451

[115] **D.W.Sears;G.W.Kallemeyn and J.T.Wasson**
The Compositional Classification of Chondrites: II The Enstatite Chondrite Group
Geochim. Cosmochim. Acta, 46, (1982), 597-608

[116] **R.T.Dodd**
Thunderstones and Shooting Stars: The Meaning of Meteorites
Harvard University Press, (1986)

[117] **V.F.Buchwald**
Handbook of Iron Meteorites
Vol.3, *University of California Press*, Berkeley, California, (1975)

[118] **J.T.Wasson**
Meteorites - Classification and Properties
Springer-Verlag, (1974)

[119] **J.T.Wasson and J.Kimberlin**
The Chemical Classification of Iron Meteorites-II. Irons and Pallasites with Germanium Concentrations between 8-100 ppm
Geochim. Cosmochim. Acta, 31, (1967), 2065-2093

[120] **E.R.D.Scott**
Chemical Fractionation in Iron Meteorites and Interpretation
Geochim. Cosmochim. Acta, 36, (1972), 1205-1236

[121] **H.Brown and E.D.Goldberg**
The Neutron Pile as a Tool in Quantitative Analysis; the Gallium and Palladium Content of Iron Meteorites
Science, 109, (1949), 347-353

[122] **E.Goldberg; A.Uchiyama and H.Brown**
The Distribution of Nickel, Cobalt, Gallium, Palladium and Gold in Iron Meteorites
Geochim. Cosmochim. Acta, 2, (1951), 1-25

[123] **J.T.Wasson**
The Chemical Classification of Iron Meteorites - I. A Study of Iron Meteorites with Low Concentrations of Gallium and Germanium
Geochim. Cosmochim. Acta, 31, (1967), 161-180

[124] **J.T.Wasson**
The Chemical Classification of Iron Meteorites - III. Hexahedrites and Other Irons with Germanium Concentrations between 80-200 ppm
Geochim. Cosmochim. Acta, 33, (1969), 859-876

[125] **J.T.Wasson**
The Chemical Classification of Iron Meteorites - IV. Irons with Ge Concentrations Greater than 190 ppm and Other Meteorites Associated with Group I
Icarus, 12, (1970), 407-423

[126] **W.Nichiporuk and H.Brown**
The Distribution of Platinum and Palladium Metals in Iron Meteorites and in the Metal Phase of Ordinary Chondrites
J. Geophys. Res., 70, (1965), 459-470

[127] **D.E.Ryan; J.Holzbecher and R.R.Brooks**
Rhodium and Osmium in Iron Meteorites
Chem. Geol., 85, (1990), 295-303

[128] **M.Hoashi and R.R.Brooks**
A Graphite Furnace Atomic Absorption Spectrometric Determination of Ruthenium in Iron Meteorites
Anal. Chim. Acta, 232, (1990), 317-321

[129] **X.Guo; M.Hoashi; R.R.Brooks and R.D.Reeves**
Determination of Gallium in Iron Meteorites and Other Iron-rich Materials by Graphite Furnace Atomic Absorption Spectrometry
Anal. Chim. Acta, 259, (1992), 289-294

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

[131] **D.Wang; D.J.Malvin and J.T.Wasson**
The Study of Chemical Composition of 35 Iron Meteorites and Its Application in Taxonomy
Geochemistry, 4, (1985), 210-219

[132] **W.D.Ehmann and J.R.Huizinga**
Bismuth, Thallium and Mercury in Stone Meteorites
Geochim. Cosmochim. Acta, 17, (1959), 125-135

[133] **R.R.Keays; R.Ganapathy; J.C.Laul; U.Krähenbühl and J.W.Morgan**
The Simultaneous Determination of 20 Elements in Terrestrial, Lunar and Meteoritic Materials by Radiochemical Neutron Activation Analysis
Anal. Chim. Acta, 72, (1974), 1-29

[134] **R.R.Keays; R.Ganapathy and E.Anders**
Chemical Fractionations in Meteorites IV. Abundances of Fourteen Trace Elements in L-chondrites; Implications for Cosmothermometry
Geochim. Cosmochim. Acta, 35, (1971), 337-363

[135] **S.N.Tandon and J.T.Wasson**
Gallium, Germanium, Indium, and Iridium Variations in a Suite of L-group Chondrites
Geochim. Cosmochim. Acta, 32, (1968), 1087-1109

[136] **E.Anders and M.Ebihara**
Solar-system Abundances of the Elements
Geochim. Cosmochim. Acat, 46, (1982), 2363-2380

[137] **N.Grevesse**
Abundances of the Elements in the Sun. In Frontiers of Astronomy and Astrophysics (ed.R.Pallavicini)
Ital. Astron. Soc., Florence, Italy, (1984)

[138] **N.Grevesse**
Accurate Atomic Data and Solar Photospheric Spectroscopy
Physica Scripta, T8, (1984), 49-58

[139] **M.Hoashi**
The Platinum Group Metals in Iron Meteorites
Ph.D. Thesis, Massey University, (1991)

[140] **M.Hoashi;R.R.Brooks and R.D.Reeves**
Palladium, Platinum and Ruthenium in Iron Meteorites and Their Taxonomic Significance
Chem. Geol., in press, (1993)

[141] **J.T.Wasson**
An Equation for the Determination of Iron Meteorite Cooling Rates
Meteoritics, 6, (1971), 139-147

[142] **J.M.Short and J.L.Goldstein**
Rapid Method of Determining Cooling Rates of Iron and Stony-Iron Meteorites
Science, 156, (1967), 59-61

[143] **R.Knox Jr.**
The Metallography of Manitouwabing, Parry Sound, Ontario: a New Canadian Siderite
Meteoritics, 2, (1964), 279-284

[144] **A.L.Graham; A.V.R.Bevan and R.Hutchison**
Catalogue of Metorites
British Museum (Natural History),
London, (1985), 460 pp

[145] **X.Guo; M.Hoashi; R.R.Brooks and R.D.Reeves**
Quantification of Thallium in Rocks and Meteorites by Graphite Furnace Atomic Absorption Spectrometry
Anal. Chim. Acta, 266, (1992), 127-131

[146] **E.R.D.Scott;J.T.Wasson and V.F.Buchwald**
The Chemical Classification of Iron Meteorites VII. A Reinvestigation of Irons with Germanium Concentrations between 25 and 80 ppm
Geochim. Cosmochim. Acta, 37, (1957-1983)

[147] **L.W.Alvarez**
Experimental Evidence that an Asteroid Impact Led to the Extinction of Many Species 65 Million Years Ago
Proc. Natl. Acad. Sci., 80, (1983), 627-

[148] **B.F.Bohor and G.A.Izett**
Worldwide Size Distribution of Shocked Quartz at the K/T Boundary: Evidence for a North American Impact Site
Lunar and Planetary Science Letters,
17, (1986), 68-69

[149] **W.S.Wolbach;R.S.Lewis; and E.Anders**
Cretaceous Extinctions: Evidence for Wildfires and Search for Meteoritic Materials
Science, 230, (1985), 167-171

[150] **C.B.Officer and C.L.Drake**
Terminal Cretaceous Environmental Events
Science, 227, (1985), 1161-1167

[151] **L.Olmez; D.L.Finnegan and W.H.Zoller**
Iridium Emissions from Kilauea Volcano
J. Geophys. Res., 91, (1986), 653-663

[152] **A.R.Hildebrand; G.T.Penfield; D.A.King; M.Pilkington; A.Camargo; S.B.Jacobsen and W.V.Boynton**
Chicxulub Crater: a Possible Cretaceous/Tertiary Boundary Impact Crater on the Yucatán Peninsula, Mexico
Geology, 19, (1991), 867-871

[153] **C.P.Strong**
Cretaceous-Tertiary Boundary at Woodside Creek, North-eastern Marlborough
N.Z. J. Geol. Geophys., 20, (1977), 687-696

[154] **C.P.Strong**
Cretaceous-Tertiary Boundary at Chancet Rocks Scientific Reserve, Northeast Marlorough
N.Z. J. Geol. Surv. Rec, 3, (1984), 47-51

[155] **C.P.Strong**
Cretaceous-Tertiary Boundary, Mid-Waipara River Section, North Canterbury, New Zealand
N.Z. J. Geol. Geophys., 27, (1984), 231-234

[156] **C.P.Strong**
Cretaceous-Tertiary Boundary at Needles Point, Northeast Marlborough
N.Z. J. Geol. Surv. Rec., 8, (1985), 82-87

[157] **C.P.Strong; R.R.Brooks; C.J.Orth and X-Y.Mao**
An Iridium-rich Calcareous Claystone (Cretaceous-Tertiary Boundary) from Wharanui, Marlboruogh, New Zealand
N.Z. J. Geol. Geophys., 31, (1988), 191-195

[158] **F.T.Kyte;J.Smit and J.T.Wasson**
Siderophile Interelement Variations in Cretaceous-Tertiary Boundary Sediments from Caravaca, Spain
Earth Planet Sci. Lett., 73, (1985), 183-195

[159] **B.Mason and C.B.Moore**
Principles of Geochemistry
4th Ed., *Wiley*, New York, (1982)

[160] **G.J.Lensen**
Sheet 16, Kaikoura, Geological Map of New Zealand, 1:250,000 (D.S.I.R.)
Wellington, (1962)

[161] **K.J.Hsu et al.**
Mass Mortality and Its Environmental and Evolutionary Consequences
Science, 216, (1982), 249-256

[162] **W.Alvarez; L.W.Alvarez; F.Asaro and H.V.Michel**
Current Status of the Impact Theory for the Terminal Cretaceous Extinction
Geol. Soc. Am. Spec. Pap., 190, (1982), 305-315

[163] **C.J.Orth; J.S.Gilmore; J.D.Knight; C.L.Pillmore; R.H.Tschudy; and J.E.Fassett**
Iridium Abundance Measurements Across the Cretaceous/ Tertiary Boundary in the San Juan and Raton Basins of Northern New Mexico
Geol. Soc. Am. Spec. Pap., 190, (1982), 423-433

[164] **J.Green**
Elements: Planetary Abundances and Distributions. In the Encyclopedia of Geochemistry and Environmental Science
Vol.IVA, *R.W.Fairbridge*, New York, (1972)

[165] **R.R.Brooks; X.Guo; M.Hoashi; R.D.Reeves; D.E.Ryan; J.Holzbecher and G.S.Henderson**
Elemental Abundance Data for the Manitouwabing Iron Meteorite
Meteoritics, 27, (1992), 186

[166] **S.N.Tandon and J.T.Wasson**
Neutron Activation Determination of Indium in Meteorites
Radiochim. Acta, 8, (1967), 184-188

[167] **S.N.Tandon and J.T.Wasson**
Indium Variations in Petrologic Suite of L-group Chondrites
Science, 158, (1967), 259-261

[168] **H.Y.McSween**
Meteorites and their Parent Planets
CambridgeUniv. Press, Cambridge (187)

[169] **R.N.Clayton**
Isotopic Variations in Primitive Meteorites
Phil. Trans. Roy. Soc., A303, (1981), 339-349.

[170] **G.T.Prior**
The Classification of Meteorites
Min. Mag., 19, (1920), 51-63

[171] **R.N.Clayton; N.Onuma and T.K.Mayeda**
A Classification of Meteorites Based on Oxygen Isotopes
Earth Planet. Sci. Lett., 30, (1976), 10-18