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CONSTRUCTION AND VALIDATION OF A GC-ICP-MS INSTRUMENT FOR THE ANALYSIS OF ORGANOMETALS AND OTHER TRACE ELEMENT SPECIES

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ABSTRACT

Construction and Validation of a GC-ICP-MS Instrument for the Analysis of Organometals and other Trace Element Species.

by

Alexander Walter Kim

A capillary gas chromatography - inductively coupled plasma - mass spectrometry (GC-ICP-MS) method has been successfully developed for the separation and determination for a range of environmentally important organometallic species and metal complexes. The coupled technique gave reliable quantitative and qualitative chemical speciation information, providing detection limits in the low pg s^{-1} range, Gaussian peak shapes, good linear response, high chromatographic resolution, high signal to noise ratio and few polyatomic interferences.

The study involved the construction of progressively improved transfer lines and ICP torch designs. The final transfer line design which enabled a direct interface of the GC to the ICP-MS was of simple construction, strong, inexpensive, required a relatively short installation time (2 hours) and was capable of operation over a large temperature range (ambient to 550°C). To enable ease of installation the ICP-MS was modified by removing a panel from the hood and torch box, through which the transfer line could pass. The ICP-MS was tuned using a cold mercury vapour generator.

Analysis of compounds with a relatively high retention index (RI) of up to 3422 was achieved using high temperature (HT) GC-ICP-MS. The transfer line was capable of eluting metalloporhyrins (RI>6000). However due to condensation effects within the ICP torch the analysis of metalloporphyrins using HTGC-ICP-MS was not achieved.

Following the development of the GC-ICP-MS system Figures of Merit were established for tetraethyllead, five organotin compounds, diethylmercury and metal containing complexes (ferrocene and nickel diethyldithiocarbamate).

The coupled technique was successfully applied to the determination of organometallic species in standard reference materials. These included tetraethyllead (in fuel) and organotin compounds (in two harbour sediments). Calibration techniques used were external calibration, standard additions and internal standards. The values obtained were in agreement with the certificate values within the confidence limits of the measurements.

With the eventual objective of extending this system to the determination of geologically important metalloporphyrin species, a HTGC method was developed. Retention indices for a range of authentic porphyrins standards were measured and the analysis of a porphyrin - containing shale is also described.

TO MY MOTHER, FATHER AND SISTER; FRANCES

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CHAPTER FOUR: ANALYSIS OF PORPHYRINS

CHAPTER FIVE: CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

List of Abbreviations and Symbols

A	Amps
AAS	Atomic Absorption Spectrometry
AES	Atomic Emission Spectrometry
AFID	Alkali Flame Ionisation Detector (also see NPD)
ASV	Anode Stripping Voltametry
BCR	Community Bureau of Reference
Bu	n-Butyl, $-C_4H_9$
°C	degrees Celcius
CRM	Custom-made certified Reference Material
DCM	Dichloromethane
DCP	Direct Current Plasma
DMDEL	Dimethyldiethyllead, $(CH_3)_2(C_2H_5)_2Pb$
DPEP	Deoxophylloerythroetioporphyrin
Dt	Diethyldithiocarbamate
ECD	Electron Capture Detector
EI	Electron Impact
Et	Ethyl, $-C_2H_5$
ETV	Electrothermal Vaporisation
FAAS	Flame Atomic Absorption Spectrometry
fg	femtogram (x 10^{-15} g)
FID	Flame Ionisation Detector
FTIR	Fourier Transform Infra Red Spectrometry
GC	Gas Chromatography
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
HCL	Hollow Cathode Lamp
Hex.	Hexane
HPLC	High Pressure Liquid Chromatography
hrs	hours
HTGC	High Temperature Gas Chromatography
ICP	Inductively Coupled Plasma
i.d.	internal diameter
IR	Infra Red
iso.	isothermal
°K	degrees Kelvin
k	kilo (x 10^3)
kPa	kilopascals (x 10^3 Pa)
LOD	Limit of Detection
m	metre
mA	milliamp (x 10^{-3} A)
Me	Methyl, $-CH_3$
MeOH	Methanol
mg	milligram (x 10^{-3} g)
MHz	Mega Hertz
MIP	Microwave Induced Plasma
min.	minute
ml	millilitre (x 10^{-3} l)
mm	millimetre (x 10^{-3} m)
M.p.	Melting point
$Ni(Dt)_2$	Nickel diethyldithiocarbamate, $[(C_2H_5)_2NCS_2]_2$ Ni
MS	Mass Spectrometry
m/z	mass : charge ratio

n.d.	not determined
ng	nanogram (x 10^{-9} g)
NIST	National Institute of Standards and Technology
nm	nanometre (x 10^{-9} m)
NPD	Nitrogen Phosphorous Detector (also see AFID)
o.d.	outer diameter
OEP	Octaethylporphyrin
pg	picogram (x 10^{-12} g)
Pr	Propyl, $-C_3H_7$
py.	pyrolysis
r.f.	radio frequency
RI	Retention Index
RSD	Relative Standard Deviation
s	second
SFC	Supercritical Fluid Chromatography
SRM	Standard Reference Material
TC	Thermocouple
TCD	Thermal Conductivity Detector
TEL	Tetraethyllead, $(C_2H_5)_4Pb$
THF	Tetrahydrofuran
T_i	Interface Temperature
TIC	Total Ion Current
T_{inj}	Injector Temperature
TEML	Triethylmethyllead, $(C_2H_5)_3(CH_3)Pb$
TMEL	Trimethylethyllead, $(CH_3)_3C_2H_5Pb$
TML	Tetramethyllead, $(CH_3)_4Pb$
TOE	Total Organic Extract
TPP	Tetraphenylporphyrin
µg	microgram (x 10^{-6} g)
µl	microlitre (x 10^{-6} l)
µs	microsecond (x 10^{-6} s)
UV-VIS	Ultraviolet - Visible
V	Volts
V=O	Vanadyl
W	Watts
λ	wavelength (nm)

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"Hoc opus, hic labor est."

"This is the toil,
this the labour."

—VIRGIL, *Aen.*, VI. 129

CHAPTER ONE

INTRODUCTION

1.0 INTRODUCTION

1.1 Trace Element Speciation

Many trace elements can exist in organic, as well as inorganic, forms. These inorganic forms have been loosely termed "trace element species". Notable examples of elements which exhibit "speciation" characteristics include several metals (*e.g.* Hg, Pb, Sn). Numerous definitions of the term "trace metal speciation" have been proposed [1]. In this study the term "trace element species" includes the organic form of the element, complexation with both inorganic and organic ligands and the formation of distinct organometallic compounds where the element is fixed into an organic molecule primarily by carbon - metal bonding. "Speciation" refers to the characterisation and quantification of these different physico-chemical forms of the element.

Since different trace element species may have quite different chemical (and biochemical) reactivities, chemical speciation has become particularly important in such areas such as environmental chemistry and toxicology where the physico-chemical form of an element may be a primary factor controlling bioavailability, bioaccumulation, toxicity, distribution or transport mechanisms [1,2].

Since the determination of total element concentrations is not always sufficiently specific to assess the species present, the importance of trace element speciation is now widely recognised and as a result has led a trend towards the development of elemental speciation studies. This was a particular driving force for the present research.

Some examples of trace element species dependent phenomena are illustrated in the following examples:

Tetraethyllead (one of five tetraalkyllead compounds used as an antiknock additive in fuel [3]) has been found to be more toxic to humans than tetramethyllead [4] and the toxicity decreases with the degree of alkylation in the sequence R_4Pb > R_3Pb^+ > Pb^{2+} [5,6]. However the ionic forms are more persistent in the environment [7].

Similarly, methyl mercury is more easily absorbed from the human intestine than inorganic mercury (II) chloride. Whereas Hg^0 is not absorbed at all [8]. Alkylmercury compounds are highly toxic and affect the central nervous system, inhibiting enzyme activity and cell wall transport mechanisms [8]. The toxicity of alkylmercury compounds became evident during the 1950's in Minamata, Japan [9,10], where inorganic mercury discharged into sea water from a chemical plant was methylated by sedimentary bacteria [11,12]. Once in the water column the methylmercury (produced by bacterial action) bioaccumulated in fish which was eaten by the local population resulting in a major poisoning incident. This example illustrates graphically the importance of trace element speciation in understanding environmental fate.

As a further example, arsenite (AsO_2^-) and arsenate (AsO_4^{3-}) species used in herbicides and pesticides are toxic to man whereas an organic form of arsenic, naturally occurring arsenobetaine [$(CH_3)_3\ As^+\ CH_2COO^-$], which is found in some fish, is not [13].

These three cursory examples serve to illustrate that the identification and quantification of chemical species is important for an understanding of many environmental processes. Indeed the complete environmental cycles of many elements are unlikely to be fully elucidated unless chemical speciation is taken into account. Several other species of elements have been shown to be transformed in the environment during weathering, uptake by biota, elimination from biota, fixation in sediments

and remobilisation [14]. A more detailed description is given in Chapter 3.

Total elemental analyses give insufficient information about specific reactivities and functions of the elements and the need for more sensitive and more specific analytical methods is driven by these requirements for more molecular - based information.

1.2 Methods for the Determination of Chemical Species

Several approaches to the determination of trace element species have been developed [15-17] and these can be broadly classified into two groups; experimental and theoretical **(Figure 1.1)**.

1.2.1 Theoretical Approaches to Trace Element Speciation

Theoretical approaches typically involve computer and mathematical modelling which is sometimes an attractive alternative to experimental methods. Calculation of trace element speciation using this approach is based on fundamental thermodynamic (and, in some cases, kinetic) concepts which may be used to verify analytical data or provide insight into the likely concentrations of species that cannot be quantified because of sensitivity constraints or other experimental difficulties (*e.g.* high temperature or pressure).

The application of mathematical models [18] to the elucidation of trace elements requires known thermodynamic and kinetic parameters. However the application to complex environmental systems has a number of difficulties such as the presence of ill - defined soluble and particulate organic compounds (humic substances) and inorganic colloidal materials of

uncertain mineralogy and surface properties that may influence trace metal speciation, usually in a time dependent way [19].

1.2.2 Experimental Approaches to Trace Element Speciation

The experimental methods used for the detection of trace element species can be classified into two broad categories, termed, "*in situ*" and "*in vitro*" methods. Both of these methods involve sample collection, storage and preparation that may change the environment and potentially the species originally present in the sample.

"*In situ*" methods **(Table 1.1)** avoid the need for extraction, concentration and separation procedures. However most of these techniques usually suffer from low sensitivity and are therefore seldom the most appropriate methods for environmental samples.

"*In vitro*" methods are more frequently used, but require the extraction, concentration and separation of the analyte prior to detection. This approach is the most widely investigated area of trace element speciation and has stimulated much research into electroanalytical, physicochemical and chromatographic separations **(Figure 1.1)**.

1. Electroanalytical methods include electrochemical techniques such as anode stripping voltametry (ASV) which is most commonly used to determine heavy metals (*eg*. Cd, Cu, Pb and Zn) in water. This it can do simultaneously, selectively and with high sensitivity (about 10^{-10}M) [20]. However the presence of natural organic matter and dissolved oxygen can affect ASV measurements [16].

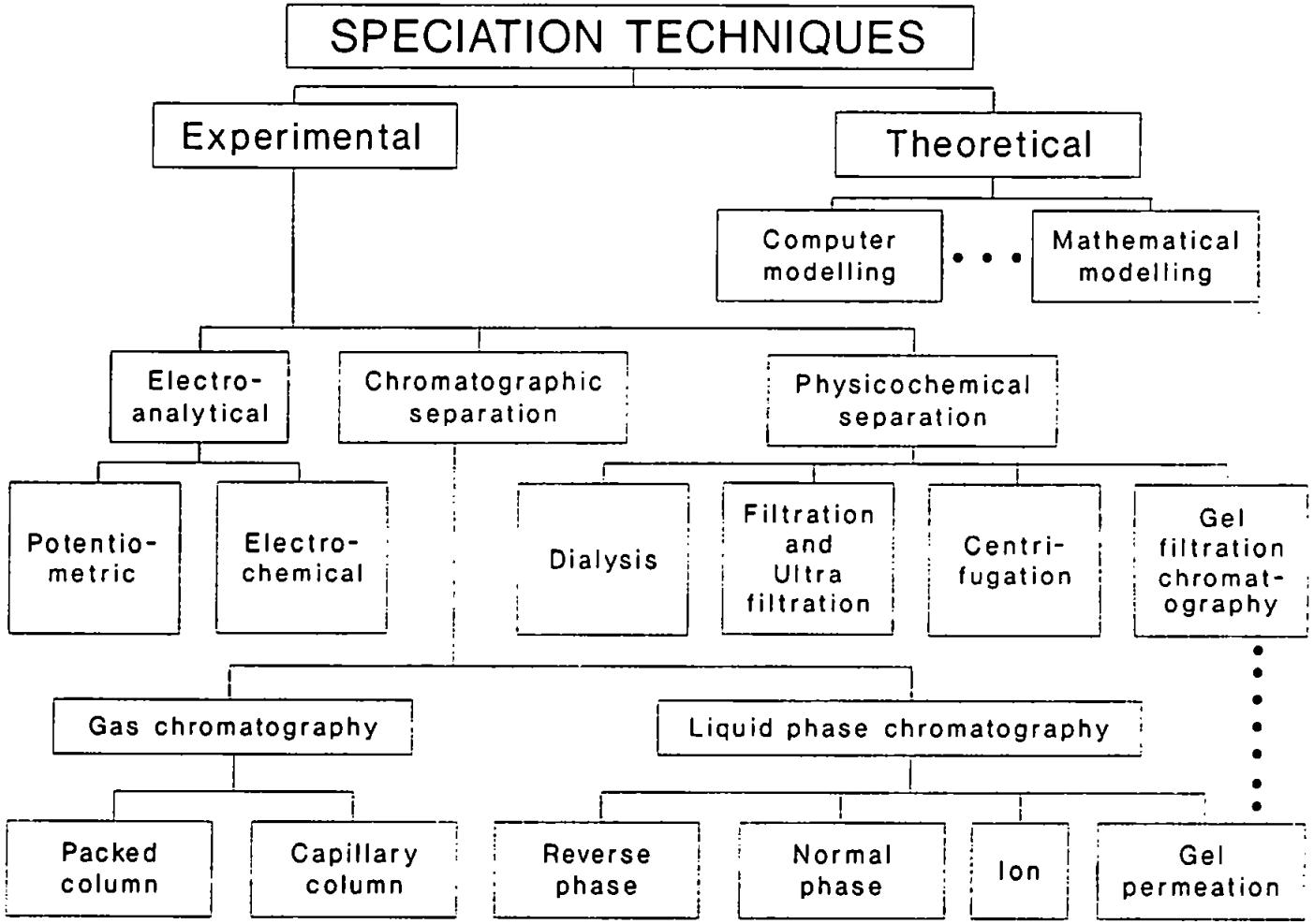


Figure 1.1 Techniques used for trace element speciation studies. Element selective detectors for gas chromatography are given in **Figure 1.2**. Detection systems for physicochemical and liquid phase chromatographic separation techniques are detailed in the references cited.

The various inorganic ionic species present in a water sample may not be in equilibrium with one another, but if they are, any procedure applied to the sample may alter the equilibria and hence the speciation. In this case a potentiometric method (*e.g.* ion selective electrode) is used without affecting the equilibria. However it is an insensitive technique (measurements less than 10^{-6}M are unreliable).

2. Physicochemical separations are based on differences in ionic charge (*e.g.* dialysis) or molecular size fractionation such as filtration, ultrafiltration, centrifugation and gel filtration chromatography (GFC). These techniques have been widely reviewed elsewhere [16,21,22].

3. The separatory powers of various chromatographic techniques have been extensively reviewed [23-27]. These use instrumental methods such as high performance liquid chromatography (HPLC) [28-30] and gas chromatography (GC) [31-33] employing element selective detection.

The chromatographic step required is governed mainly by the volatility of the analyte. Thus volatile species (*e.g.* methylselenide, methylarsines) are usually gaseous and are easily separated from the sample matrix by methods such as cold trapping or head space analysis. These compounds are also easily lost from the sample and may be difficult to collect. Once collected they can be determined by gas chromatography (GC), mass spectrometry (MS) or GC-MS without further treatment.

Species that can be converted into volatile derivatives (*e.g.* arsenite, arsenate [34], organotin chlorides] in a controlled manner, require rather more pretreatment (e.g.

separation from the matrix, derivatisation and sample clean-up) before analysis.

Nonvolatile species (*eg.* Cr^{3+}, Cr^{4+} and organo - ionic species) which are neither volatile nor convertible to volatile derivatives, in most cases must be separated from the matrix, concentrated and separated by liquid chromatography prior to element selective detection [28,29].

1.3 Conventional Gas Chromatography Detection Systems

GC is a firmly established technique which is regularly used for the separation of thermally stable yet volatile organic and inorganic compounds [35,36].

Most conventional GC detectors such as flame ionisation detectors (FID) and thermal conductivity detectors (TCD) are not element selective **(Table 1.2)**, although selectivity enhancement of a metal - sensitive FID for capillary GC has been described [37].

However some element selective detection methods are commonly used in GC. For example:

The electron capture detector (ECD) responds to electrophilic species (*eg.* halogens, polar functional groups, etc.) [38,39] **(Table 1.2)** and has been widely used in speciation studies of organometallic compounds of As [40], Se [41], Pb [42], Hg [43] and Sn [44]. The main limitations of ECD are the lack of specificity, sensitivity to contamination and changes in operating conditions. Also the response may be affected by the type and amount of solute, gas flow, concentration and temperature. Therefore the conditions used must be verified for each analytical application.

Table 1.1 Techniques useful for *in situ* speciation analyses.

Technique	Application
Electronic absorption spectrometry (ultraviolet - visible)	Determination of organic and inorganic chromophores.
Fourier transform infrared spectrometry	Determination of organic and inorganic species; identification of functional groups
Luminescence (fluorescence) spectrometry	Determination of organic and inorganic species and functional groups
Nuclear magnetic resonance spectrometry	Determination of structure, geometry, and binding conditions in organic and inorganic species
Electron spin resonance spectrometry	Characterisation of organic radicals and paramagnetic metal compounds
Resonance Raman spectrometry	Determination of organic compounds, metal complexes, certain functional groups in organic molecules
X-ray absorption spectrometry	Structure of metal complexes, electronic and chemical environment of central atom.
Electronic absorption spectrometry (circular and magnetic circular)	Characterisation of chiral chromophores

Alkali flame ionisation detection (AFID) often known as nitrogen phosphorus detection (NPD) gives selective responses for these elements. Flame photometric detection (FPD) is selective for sulphur and phosphorus.

More expensive approaches such as gas chromatography - mass spectrometry (GC-MS) may also be used [45]. GC-MS often provides unambiguous identification of the metal species separated and it is a powerful tool for trace element speciation, but the complexity of the spectra and high capital cost of the instrumentation are disadvantages. Most trace metal speciation work with GC-MS has been applied to the analysis of organotin compounds [2,46-48].

Mass spectrometric detection has also been routinely used for trace element speciation with HPLC [44,49,50] or with direct insertion probes [51].

Table 1.2 Comparison of the characteristics of conventional GC detectors.

Detector Type	Principle	Selectivity	Sensitivity (g $sec.^{-1}$)	Linear Range (ng)
Thermal conductivity detector (TCD)	Measures differences in thermal conductivity of gases	Universally responds to all compounds	10^{-10}	0.1 - $1x10^{5}$
Flame ionisation detector (FID)	Burns compounds in H_2/O_2 flame at 200°C and measures the ions created	Responds to all oxidizable carbon compounds	10^{-12}	0.01 - $1x10^{5}$
Electron capture detector (ECD)	Measures changes in electron current caused by reaction of organic compounds with electrons	Responds to all electron reacting compounds	10^{-14}	0.001 - 0.01 (in dc mode) 0.001 - 5.0 (in pulsed mode)

1.4 Coupled Chromatography - Atomic Spectrometry

1.4.1 Advantages of Coupled Chromatography - Atomic Spectrometry

Gas or liquid chromatographic techniques coupled to element selective detection systems are a useful means of determining trace element species [52], **(Figure 1.2)**.

Atomic spectrometric detectors offer both selectivity and high sensitivity for detecting a wide range of metals and non-metals but they cannot by themselves be used to identify different molecular species. However coupled to chromatographic techniques with the use of appropriate authentic organometals they can yield unequivocal identification at the levels of interest, and offer on-line analysis in real time by the use of simple interfaces between readily available instrumentation **(Figure 1.2)**.

The use of detectors responsive only to selected elements in a multi-component mixture drastically reduces the constraints placed on the chromatography step, as only those components in the mixture which contain the element of interest will be detected and enhanced analytical resolution achieved. The objectives of selective chromatographic detection are qualitative and quantitative measurement and identification of eluents based upon elemental content; simultaneous multi-element detection may also enable empirical formulae of eluents to be determined [53].

The growing interest in trace elemental speciation has provoked studies of the coupling of the separatory power of chromatographic techniques with various atomic spectrometric detectors.

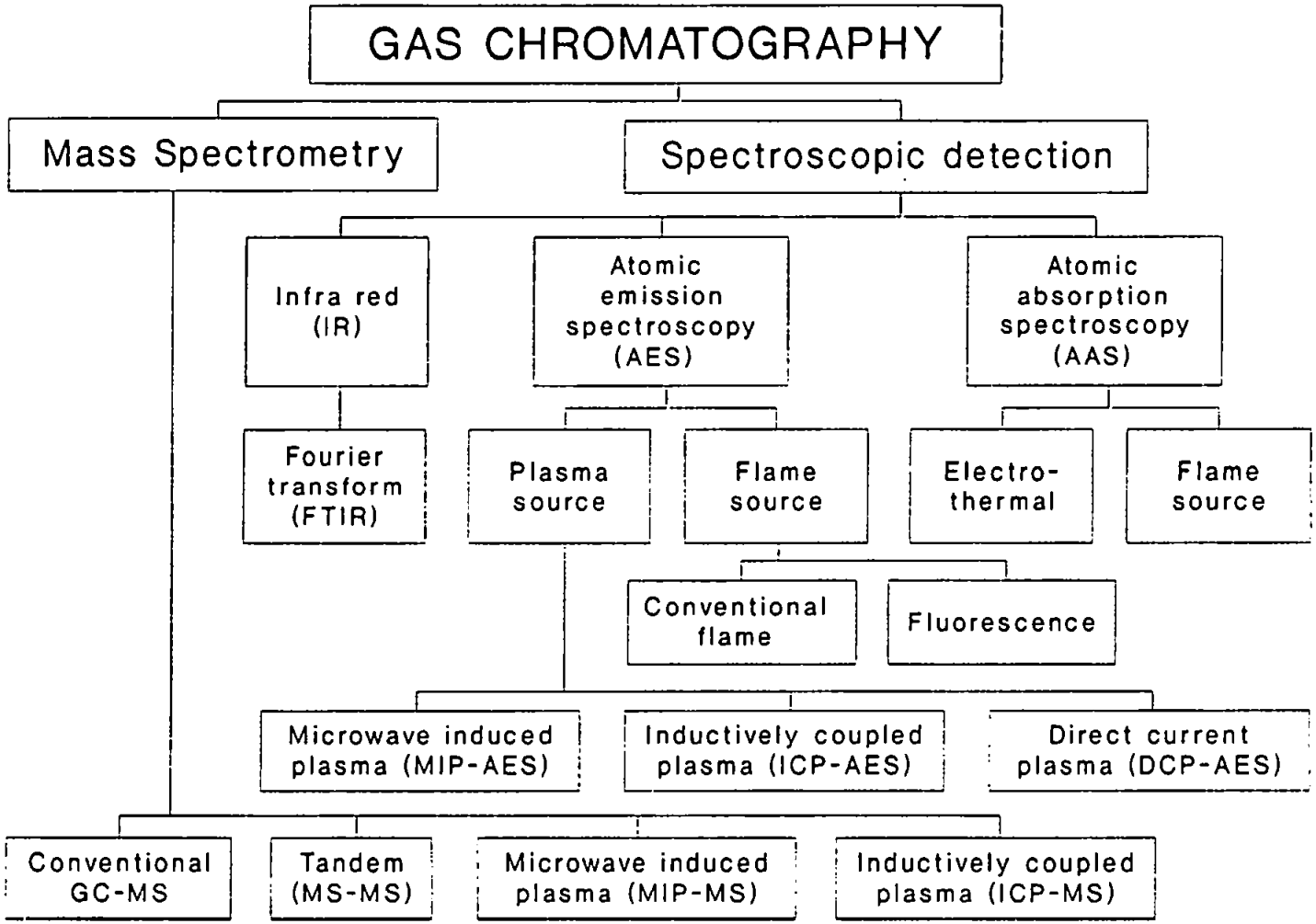


Figure 1.2 Gas chromatography - element selective detection techniques.

1.4.2 Theoretical Aspects of Gas Chromatography Interface Design.

A number of considerations must be taken into account into the design of a chromatography - element selective detection interfaced system.

1. The sample must be transferred from the chromatographic column to the detector with minimal sample loss, with minimal peak broadening (or tailing) and with no interfering chemical reactions occurring.

2. The sample must be introduced into the detector atom cell without loss.

3. The atom cell should have high sensitivity and low limits of detection for the analyte of interest.

1.5 Gas Chromatography - Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is a widely used elemental selective analytical technique which has been well documented [54,55]. The two most commonly used methods for atomization are flame (FAAS) and electrothermal (ETA) sources (e.g. graphite furnace (GFAAS)). The merits and disadvantages of graphite furnace AAS are compared with those of flame AAS in **Table 1.3.**

GC-AAS techniques have been extensively reviewed [31,33,52,56,57]. Some applications which utilise FAAS or ETA detection systems are summarised in **Table 1.4.**

Sensitivity is generally low (μg detection) with FAAS because of the dilution of analytes by the large volume of fuel gases, resulting in a relatively short residence time of the analyte

atoms in the flame. FAAS detection has the advantage of continuous operation, simplicity and inexpensive instrumentation.

The first GC-FAAS coupling was reported by Kolb *et al* [58,59] for the analysis of tetramethyllead and tetraethyllead in fuel. This coupling involved passing the column effluent via a heated tube into the nebuliser, but prolonged memory effects (due to adsorption of the analyte on the walls of the nebuliser), excessive peak broadening and sample dilution were observed.

A more efficient method of sample introduction passes the column eluent directly into the atom cell, resulting in improved detection. Three types of atom cell have been used, standard FAAS [60], a silica (or ceramic) tube heated by a flame [61,62] or electrically [48,63-68], and those using GFAAS [69-71]. Less commonly high temperature GC has been used employing a molybdenum tube [72].

Flame and electrothermally heated quartz furnaces have been found to be 15 times more sensitive than a conventional flame [73]. However a problem associated with silica atom cells is carbon deposition on the cell wall [74]. GFAAS has been found to be the most sensitive, however a disadvantage with this is graphite tube deterioration.

Table 1.3 Comparison of flame AAS (FAAS) with graphite furnace AAS (GFAAS).

Parameter	Flame AAS (FAAS)	Graphite Furnace AAS (GFAAS)
Detection limits [75]	$\mu g\ ml^{-1}$ range (poor transport efficiency, 2-5 % of the sample reaches the flame)	$ng\ ml^{-1}$ range (atoms concentrated in a smaller volume and so have a longer residence time in the optical path)
Analysis time (s)	15	120
Sample volume	5 ml	5-20 μl
Relative precision	less than 5 %	5-10 % (associated with manual pipetting)
Interferences	Relatively fewer cf. GFAAS	More susceptible cf. FAAS (memory effects, loss of volatile analytes, carbide formation, variation in sample position)
Relative cost	Low	High

Table 1.4 Gas Chromatography - Atomic Absorption Spectrometry (GC-AAS).

Chromatography	Sample	Detection	Reference
2 m x 2 mm i.d., 10% Apiezon M on Chromosorb R. N_2 = 40 ml $min.^{-1}$, T_c = 150°C	Alkyllead compounds in fuel, Me_4Pb and $EtPb_4$	First paper to describe GC-FAAS coupling for element selective detection, linear range: 50 - 700 $\mu g\ ml^{-1}$, λ = 217.0 nm	[58]
6′ x 0.25" i.d. steel column, 20% SE-30 on 30-60 mesh Chromosorb W. He = 100 ml $min.^{-1}$, T_c = 130°C (iso.), T_i = < T_c	Silylated pyridine solutions of n-alcohols C_1-C_7	Coupling as in [58], linear range = 4-20 μg, LOD = 0.11 μg, λ = 251.6 nm	[60]
1.8 m x 6 mm o.d. x 2 mm i.d., 3% OV-101 on 100-120 mesh Chromosorb WHP. Ar = 32 ml $min.^{-1}$, T_{inj} = 160°C, T_c = 130 to 245°C at 10°C $min.^{-1}$, T_i = 170°C	Organotin chloride compounds in water (pentlyated derivatives)	Quartz furnace, H_2 = 470 ml $min.^{-1}$, air = 9 ml $min.^{-1}$, acetylene/air for burner = 31/24 l $min.^{-1}$, Absolute LOD: 0.16 - 0.40 ng (as Sn), water = 4-10 ng l^{-1}, λ = 286.4 nm	[61]
Glass, 1.5 m x 4 mm i.d, 2% OV-101 on 80-100 mesh Chromosorb W-HP. N_2 = 70 ml $min.^{-1}$, T_c = 50°C (2 min. iso.) to 150°C at 15°C $min.^{-1}$	Tetraalkylead compounds (Me_4Pb, Me_3EtPb, Me_2Et_2Pb, $MeEt_3Pb$, Et_4Pb) in water, sediment and fish	Electrothermally heated silica tube (60 x 7 mm i.d., T = 1000°C). Furnace gases: air = 120 ml $min.^{-1}$; H_2 = 120 ml $min.^{-1}$. LOD: water = 0.5 ng ml^{-1}, sediment = 0.01 $\mu g\ g^{-1}$ and fish = 0.025 $\mu g\ g^{-1}$, λ = 217.0 nm	[65]

Table 1.4 (continued....)

Chromatography	Sample	Detection	Reference
Glass, 1.8 m x 6 mm i.d. 10% OV-1 on 80-100 mesh Chromosorb W. N_2 = 65 ml, T_{inj} = 150°C, min.$^{-1}$, T_c = 80°C to 200°C at 5°C min.$^{-1}$, T_i = 160°C	See ref. [65]. Alkylleads in sediment and biological samples.	See ref. [65]. Furnace temp. = 900°C, furnace gases: H_2 = 85 ml min.$^{-1}$. LOD: sediment 7.5 ng g^{-1} and biota = 15 ng g^{-1}.	[66]
1 m x 4 mm i.d. 3% OV-101 on 80-100 mesh Chromosorb W-HP. N_2 = 60 ml min.$^{-1}$, T_c = various, T_i = 180°C	Organotin chloride compounds, ethylation by sodium tetraethylborate ($NaBH_4$)	See ref. [65]. Furnace temp. = 950°C, furnace gases: H_2 = 300 ml min.$^{-1}$, air = 13 ml min.$^{-1}$ Absolute LOD: 1.2-1.8 ng, λ = 224.6 nm	[48]
Pyrex U-tube 0.3 m x 5 mm i.d. 10% OV-101 on 80-100 mesh Chromosorb GAW-HP. Cold trap in liquid N_2, He flux	Tribulyltin in marine sediment, hydride generation	See ref. [48]. Cold trap (thermal desorption GC), LOD: sediment = 1.4-8 ng g^{-1}, λ = 286.5 nm. Comparative study of methods, other methods = HPLC-GFAAS	[64]
Glass, 1.8 m x 6 mm i.d. 3% OV-1 on 80-100 mesh Chromosorb W. N_2 = 65 ml min.$^{-1}$, T_{inj} = 180°C, min.$^{-1}$, T_c = 90°C to 190°C at 20°C min.$^{-1}$, T_i = 165°C	Butylated methyltin (IV) and tin (IV) species in water, also methyltin hydrides	Electrothermally heated silica tube T = 850-900°C). Furnace gases: air = 20 ml min.$^{-1}$; H_2 = 85 ml min.$^{-1}$. Absolute LOD (as Sn) = 0.1 ng, λ = 224.6 nm	[67]

Table 1.4 (continued....)

Chromatography	Sample	Detection	Reference
Fused silica capillary column OV-101, 50 m x 0.3 mm i.d. H_2 = 5 ml $min.^{-1}$, T_c = 80°C iso., T_i = 70°C	Tetramethyllead in blood	GFAAS, atomisation temp. = 1100°C. Detection limits = 0.01 $\mu g\ ml^{-1}$ (as Me_4Pb in volume of blood), λ = 217 nm	[69]
Fused silica capillary column OV-101 (50 m x 0.32 mm i.d., Hewlett Packard). H_2 = 2.5 ml $min.^{-1}$, T_c = 30°C (1 min. iso.) to 220°C (5 min. iso.) at 16°C $min.^{-1}$, T_i = 70°C	Methyllead in fuel and blood	See ref. [69]. Absolute detection limits: Me_4Pb = 8 pg, $BuMe_3Pb$ = 16 pg and Me_3Pb^+ in blood = 3 pg ml^{-1}, λ = 217 nm	[70,71]
High temperature molybdenum column 247 mm x 1.22 mm i.d. Ar = 2.7 ml $min.^{-1}$, T_c = 2093°K	Inorganic copper, sodium, manganese, and magnesium	Electrothermally heated Mo tube, 2093 to 2473°K at 250°K $sec.^{-1}$	[72]
PTFE tubing 0.6 m x 2 mm i.d. 10% SE-30 on Chromosorb W HP 80-100 mesh. N_2 = 65 ml $min.^{-1}$, T_c = 180°C	Inorganic Cr in NBS SRM 1571 orchard leaves as $Cr(tfa)_3$	Flame, with chromatographic eluent delivered directly to the burner cavity. Linear range = 0.5 - 5 $\mu g\ ml^{-1}$, absolute LOD = 1 ng	[60]

Table 1.4 (continued....)

Chromatography	Sample	Detection	Reference
Glass column 1.5 m x 4 mm i.d., 5% Carbowax 20M on 80-100 mesh Chromosorb 750. $T_c = T_i = T_{inj}$ = 159-175°C	Tetraalkyllead compounds	Flame and flame heated ceramic tube, various atom cells developed. Absolute LOD = 17pg, λ = 283.3 nm	[62]
Glass column 1.8 m x 6 mm o.d., 10% OV-101 on 80-100 mesh Supelcoport. He = 35 ml $min.^{-1}$, T_c = 50°C (1 min. iso.) to 250°C (1 min. iso.) at 8°C $min.^{-1}$ T_{inj} = 200°C. Capillary column interface, T_i = 250°C	Alkyllead compounds	Electrothemally heated quartz furnace, temperature = 900°C, H_2 = 50 ml $min.^{-1}$. λ = 217 and 283 nm. Connection of capillary column transfer line described.	[68]
Glass column 3 m x 4 mm i.d., 3% OV-101 on 80-100 mesh Chromosorb W HP. N_2 = 100 ml $min.^{-1}$. T_c = 100°C (iso.), T_{inj} = 140°C, T_i = 180°C	Methylmercury compounds in aqueous samples. Ethylation by sodium tetraethylborate ($NaBH_4$)	Electrothermally heated silica tube T = 750-800°C). Absolute LOD (for CH_3 HgC_2H_5) = 167 pg, λ = 253.7 nm	[63]

1.6 Gas Chromatography - Plasma Emission Spectrometry

1.6.1 Capabilities of Plasma Atomic Emission - Element Selective Detection

Plasma source atomic emission spectrometry (AES) is one of the best established and widely used of all modern analytical techniques.

The use of non-combustion sources has a number of advantages over flame methods, including increased accuracy, sensitivity and precision over a wider element range. The higher temperatures and cleaner chemical environment of plasmas overcome the problems of lower temperatures and reactive chemical environments. associated with combustion flames The linear dynamic concentration range of plasma emission sources is four or more orders of magnitude (compared to flame AES) due to the narrow emission profile of the plasma which reduces self absorption. Spectra rich in atom and ion lines are also produced by non-combustion plasma flame sources.

The selectivity and sensitivity of AES makes GC-AES a valuable tool for the determination of GC volatile species in a wide variety of samples. Complex environmental samples contain many constituents which complicate the interpretation of chromatograms. Interferences from unresolved peaks, sometimes make analyte identification difficult and element selective detection can often reduce or even eliminate such interferences.

Selectivity (defined as peak area response per mole of elements divided by the peak area of the 'background' element per mole of the element [56]), of AES detection

is dependent on the emission properties of the element and the spectral resolution of the instrument. Sensitivity for a particular element is dependent on whether ICP, DCP or MIP is used and on whether He or Ar plasmas are used.

Limits of detection may be expressed as absolute values of element mass (in a resolved peak) or in mass flow rate units (eg. pg sec^{-1}). The latter is the more useful since it affords direct comparison with other mass-flow detectors (eg. FID).

The linear dynamic range of response for different elements typically extends from the upper load capacity of the fused silica columns (ca. 50 ng) down the detection limit (1-100 pg).

By employing multielement detection it is possible to determine empirical formulae of compounds eluted [53, 1071]. Multielement monitoring can be accomplished using rapid sequential wavelength-switching, a polychromator with a multichannel output or diode-array detection.

1.6.2 Gas Chromatography - Microwave Induced Plasma - Atomic Emission Spectrometry

The capabilities of microwave induced plasma (MIP) as an excitation source have been well documented [77-79]. Recently the transverse electromagnetic mode (TEM) configuration (*e.g.* TM_{010} Beenakker cavity) [80,81] has become popular because of its ability to sustain a helium plasma at atmospheric pressure. However the MIP can also operate at reduced pressures (2 kPa).

The MIP is a highly effective excitation source due to the presence of high energy electrons and metastable excited inert gas species. So where helium is used, line spectra for light elements such as Cl, F, N and O are produced. The MIP has found particular use in the determination of non-metallic elements [82].

MIP-AES has two basic characteristics that can be utilised for coupling to a gas chromatograph. The low gas temperature of the MIP allows small amounts of sample, compatible with those of GC solutes, to be introduced without extinguishing the plasma. In addition, sample introduction is easily facilitated as the carrier and plasma gases are the same. These advantages have made GC-MIP-AES a popular technique. Its use has been extensively reviewed [32,33,82-84] and many applications have been reported **(Table 1.5)**.

Use of a low-pressure argon plasma was found to lower detection limits (for phosphorous and iodine) by an order of magnitude compared to operation at atmospheric pressure [85]. The more energetic reduced pressure helium plasma has been used for the determination of halogens, phosphorus and sulphur [86,87].

Oxygen detection required the development of an analogous reduced pressure system utilising high purity plasma gases and the exclusion of air [88]. This resulted in improved detection limits (0.03 ng sec^{-1}) and linear dynamic range of three orders of magnitude.

A number of workers have also used the MIP detector to determine inter element ratios in an attempt to establish empirical formulae [53,89,90]. However it was found necessary to use a reference compound if accurate ratio formulae were to be obtained [91] since molecular

structure of the analyte influences element response [92].

Few differences in detection levels have been found with the various forms of MIP torches [93] although the Beenakker TM_{010} cavity was found to be the easiest to operate for Ar and He plasmas. However, recent developments have shown that the sensitivity and limit of detection of a water cooled capillary torch was superior to that of a tangential flow torch [94].

The reduced power of the MIP has a number of disadvantages. The passage of an organic compound through a plasma may result in the formation of carbon deposits on the walls of the quartz capillary, resulting in absorbtion of part of the radiation, increased background emission [95] and plasma instability. This can be prevented by initiating the plasma after the solvent has passed through the detector [96], solvent venting [97] or adding traces of a scavenging gas (e.g. N_2, O_2, H_2 or air) to the plasma gas [98] which results in an increased spectral background. In addition, the analyte is incompletely vaporised and small variation in easily ionisable elements (*e.g.* Na) cause large changes in emission intensity, resulting in chemical interferences.

While many systems have been described in the literature helium MIPs appear to have several advantages. Most important is that the energy of a helium plasma is sufficient to excite all elements and consume approximately 100 ml min^{-1} compared to ICPs which typically require many litres of argon or helium per minute.

Publications in the mid 1980s suggested that the use of capillary GC, atmospheric pressure He plasmas, TM_{010} cavities, computerised data acquisition and peak-area

measurements may improve the precision and accuracy attained. This led to the development of a capillary GC-MIP-AES and more recently to a commercially available instrument, described by workers at Hewlett Packard [99]. The commercial system has been applied to a wide range of samples [100-105], including metalloporphyrins in crude oils [106] and has also been adapted for pyrolysis (py-GC-MIP-AES) studies [107-108].

Table 1.5 Gas Chromatography - Microwave Induced Plasma - Atomic Emission Spectrometry (GC-MIP-AES).

Chromatography	Sample	Detection	References
0.6 m glass U column, 5 mm i.d., 5% SE 30 on 80-100 Chromasorb W., Ar = 20-115 ml min^{-1}, T_c = 160-200°C	Organophosphorus insecticide residues, diazinon in grapes	Reduced pressure Ar, 1 mm i.d. quartz discharge tube in a tapered cavity. Achieved increased sensitivity with low pressure discharge. LOD = 0.6 pg s^{-1} of P. λ = (P) 253.565 nm	[85]
Glass column, 1.8 m, 10% DC-200 on 80-100 mesh Gas-Chrom Q. T_c = 130-210°C (various isothermal settings)	Organic compounds and pesticides	Reduced pressure He plasma, tapered cavity, 5-10 mm Hg pressure LOD = 9-60 pg s^{-1}. λ (nm): Br = 478.55. Cl = 478.45, I = 533.82, P = 253.57, S = 542.38	[86]
Glass column 1.2 m x 3 mm i.d., 5% SE-30 on Gas-Chrom Q. Flow rate = 27 ml min^{-1}, T_c = 180°C, T_i = 215°C	Pesticide residues of various P, Cl and I containing compounds	Mixed Ar/He (15/85) plasma, tapered cavity and less background emission obtained. LOD = 0.07-11.5 ng. λ (nm): P = 253.57, Cl = 221.00, I = 206.2	[87]

Table 1.5 (continued....)

Chromatography	Sample	Detection	References
Fused silica capillary column 12 m x 0.25 mm i.d., SE-30. Interface = nichrome resistance wire to variable voltage supply	Chlorinated and non-chlorinated organics	Atmospheric He plasma, TM_{010} cavity. Multi-element detection and empirical formula determination. λ (nm): Se = 203.99, As = 228.81, Br = 470.49, Cl = 479.45, C = 247.86, P = 253.57, I = 516.12, S = 545.59, Pb = 283.31, Si = 288.16, H = 656.28, F = 685.60	[89]
Fused silica capillary column 30 m x 0.3 mm i.d. x 0.25 film thickness, SE-52	n-alkanes; mononuclear, polynuclear, aromatic hydrocarbons and halogenated hydrocarbons	See Ref: [89]	[53]
Fused silica capillary columns 15 m x 0.25 mm i.d., DB-5, J & W Scientific	Small molecules of unrelated structure	Reduced pressure (5-10 Torr ¼ - λ Evanson cavity, forward power = 150 W (2450 MHz). See Ref. [89].	[90]

Table 1.5 (continued....)

Chromatography	Sample	Detection	References
Gas Chromatograph: Carlo Erba, fractovap 2101	C_1-C_7 n - hydrocarbons	¼ λ Evenson low-pressure (40 Torr). TM_{010} atmospheric pressure. Ar and He plasmas, the latter viewed axially. Ratio formulae determined for known compounds (inadequate for unknowns). LOD = low ng s^{-1} range for both systems. λ (nm): C = 247.86, H = 656.28, C_2 = 576.52, CH = 431.42	[91]
Fused silica capillary column 25 m x 0.22 mm i.d. x 0.17 μm film thickness, OV-1. He = 50 kPa	n-alkanes, aromatic hydrocarbons and various oxygen and nitrogen containing compounds	Hewlett-Packard HP 5921 AED. Molecular structure influences response. Compatible internal standard must be used	[92]

Table 1.5 (continued....)

Chromatography	Sample	Detection	References
Packed column 4.7 mm i.d., Chromasorb 102	Standard solutions	Beenakker (3/4 λ), Evenson (¼ λ, and Broida (3/4 λ) cavities compared with He/Ar or Ar plasmas, forward power = 100 w. Beenakker cavity easiest to operate. LOD (3σ) = 1 ng ml^{-1}. λ (nm): As = 234.984, Ge = 303.906, Sb = 259.806, Sn = 317.502	[93]
Stainless steel packed column 2.4 m x 3 mm i.d., OV-1 on 100-200 mesh. T_{inj} = 75°C, Ar = 350 ml min^{-1}	n-pentane	Ar MIP (2.45 GHz). Two torches used: Tangential flow torch, and water cooled capillary plasma tube. LOD for carbon = low ng s^{-1} range. λ (nm): C = 388.9 and 247.8. Emission and reflected power measurements made	[94]

Table 1.5 (continued....)

Chromatography	Sample	Detection	References
Gas chromatograph: F&M Scientific Co. Model 609, He and Ar carrier gas.	Solution of simple heteroatom containing organic compounds	Tapered and co-axial cavities used, the former more sensitive, the latter accepted larger samples. 10 mm i.d. discharge tube at low pressure. He preferred carrier gas at low pressure (stable discharge). Linear dynamic range = 4 orders of magnitude. LOD = 0.2 fg s^{-1} - 0.2 μg s^{-1}. λ (nm): Co = 388.3, F = 516.6, 251.6, Cl = 278.8, Br = 298.5, I = 206.2, S = 257.5	[95]
Glass U column 0.6 m x 5 mm i.d., 5% SE 30 on 80-100 Chromasorb W., Ar = 20-115 ml min^{-1}, T_c = 160-200°C	Organophosphorus insecticide residues in pure form, agricultural and food samples	Atmospheric pressure Ar, 1 mm i.d. quartz discharge tube in a tapered cavity. LOD = 1.4-9.2 pg s^{-1}. λ = P = 253.565 nm	[96]

Table 1.5 (continued....)

Chromatography	Sample	Detection	References
Capillary column 10 m x 0.375 mm o.d. x 0.05 mm i.d., SB-50, Lee Scientific. He = 1.5 ml min^{-1}, T_c = 50°C (5 min. iso.) to 100°C at 10°C min^{-1}, T_{inj} = 250°C	Aromatic hydrocarbons	Atmospheric He MIP, TM_{010} cavity, forward power = 2070W (2450 MHz). Solvent venting described	[97]
Fused silica capillary column, 25 m x 0.32 mm i.d. x 0.17 μm methyl silicone film thickness. GC block transfer line, T_i = 250°C, T_c = 100°C iso., He = 1.1 ml min^{-1}	Various volatile compounds	Atmospheric He plasma, TM_{010} cavity. Changes to the basic MIP-AES design is described. LOD = 0.1-75 pg s^{-1}. λ (nm): N = 174.2, S= 180.7, Hg = 184.9, 253.7, C = 193.1, 247.9, 495.8, P = 177.5, Si = 251.6, Br = 478.6, Cl = 479.5, H = 486.1, 656.3, F = 685.6, O = 777.2	[99]
Three different fused silica capillary columns used, He = 2 ml min^{-1}. T_c = various programs used	Lead in petroleum, C and S in gas oil, pesticides	Commercially available GC-MIP-AES LOD = 0.1-60 pg s^{-1}. λ (nm): as ref [99], including Pb = 405.7	[109]

Table 1.5 (continued....)

Chromatography	Sample	Detection	References
Fused silica capillary column, 40 m, OV1 bonded phase, He = 0.5 ml min^{-1}, split ratio = 1:100	Alkyllead and alkylmercury compounds	Atmospheric pressure He plasma, TM_{010} cavity, optimisation described, forward power = 100W, linear dynamic range = 3 orders of magnitude. LOD = approximately 1 pg (no background correction or scavenger gases). λ (nm): Pb = 405.78, Hg = 253.6	[110]
Fused silica column, 5 m x 0.53 mm i.d. x 0.15 μm film thickness, J & W Scientific DB-1 (methyl silicone), He = 12 ml min^{-1}, T_c = 35°C (1 min. iso.) to 430°C (10 min. iso.) at 15°C min^{-1} T_i = 400°C	Metalloporphyrins in crude oil	See ref. [109], LOD = 0.05-5 pg s^{-1}, linear dynamic range = one order of magnitude, λ (nm): Ni = 301.2, 231.6, V = 292.4, 268.8, Fe = 302.1, 259.9	[106]

1.6.3 Gas Chromatography - Inductively Coupled Plasma - Atomic Emission Spectrometry

Inductively coupled plasma - atomic emission spectrometry (ICP-AES) is a well established analytical technique [54,82,111-113].

Despite its wide adoption as a spectro-analytical emission source, and in contrast to its use with HPLC [29,114,115,106,117-121], the ICP has not been routinely used as a GC detector. However it does offer several advantages over the MIP. For example the plasma is able to withstand organic solvents, owing to the higher gas temperature (i.e. ICP is a more stable plasma); oxygen or nitrogen do not have to be added to the plasma to reduce deposits; and ICP has high selectivity, high sensitivity and a wide linear dynamic range for volatile organometallics, regardless of molecular structure.

The first coupling of GC to ICP-AES was made by Windsor and Denton [122]. A packed column was interfaced to a demountable ICP torch through a T-junction, through which an argon make-up gas was introduced enabling the plasma to be punctured.

GC-ICP-AES has since been applied to analysis of a number of compounds **(Table 1.6)**. A disadvantage of this coupled system is that performance levels for non-metals are inferior to those with the MIP and this has reduced subsequent investigations of argon ICP-AES.

Table 1.6 Gas Chromatography - Inductively Coupled Plasma - Atomic Emission Spectrometry (GC-ICP-AES).

Chromatography	Sample	Detection	References
Packed column, 1.8 m x 3 mm i.d., 8% Carbonax on 80-100 mesh firebrick	Elemental analysis of various organic compounds	All Ar plasma, observations made 9 mm above load coil, single and multi channel monochromator. LOD = 0.8 ng-1 mg (depending on element). λ (nm): Br = 700.57, C = 247.86, Cl = 725.67, F = 634.67, H = 656.28, I = 206.16, Si = 251.61, Fe = 371.99, Pb = 217.00, Sn = 284.00	[122]
Packed nickel column, 1.2 m x 3 mm i.d., 20% Amine 220 on 80-100 mesh chromasorb WHP. Ar = 25 ml min^{-1}, T_c = 95°C iso, T_i = 50-70°C	Nitrogen containing compounds	See ref [122], operating frequency = 27 MHz, incident power = 1.85 kW, reflected power = <50W. Injector gas = 0.25 l min^{-1} LOD = 1 μg (as N). λ = 8216.3Å	[123]

Table 1.6 (continued....)

Chromatography	Sample	Detection	References
Fused silica capillary column, 30 m x 0.25 mm i.d., DB-5. He = 35 cm s^{-1} For coal gasification = packed glass column. 1.8 m x 2 mm i.d., 5% OV-101 on Chrom W-HP 80-100 mesh Ar = 30 ml min^{-1}	Various volatile organometallic species and coal gasification products	See ref. [122], forward power 1.5 kW, operating frequency 27.1 MHz, reflected power = <10 W, injector gas = 0.31 l min^{-1} LOD = 6-100 pg, λ (nm): Pb = 220.3, Sn = 189.9, Fe = 238.2, Se = 196.1, Si = 251.6, Cr = 267.7, C = 193.1	[124]
Fused silica capillary column, 3 m x 0.3 mm i.d. x 5 μm film thickness (methyl silicone), He = 7.5 ml min^{-1}, T_{inj} = 140°C, T_c = 50°C (0.5 min. iso.) to 150°C at 30°C min^{-1}	Methylmercury species CH_3HgX and C_2H_5HgX	Ar plasma, forward power = 0.5 kW, operating frequency = 40 MHz, injector gas = 0.31 l min^{-1}, axially viewed plasma. LOD = 3 pg (as Hg), λ = 253.7 nm	[125]
Supercritical fluid chromatography. Fused silica capillary column, 20 m x 0.2 mm i.d., 0.05 mm film thickness, dimethylsiloxane. T_c = 60°C iso., T_i = approx. 80°C, CO_2 pressure = 200 atm.	Organosilicon compounds	Ar plasma, forward power = 0.85 kW, operating frequency = 40.7 MHz, injector gas = 0.6 l min^{-1}, linear dynamic range = 7.24-145 ng of Si, LOD = 6 ng (as Si), λ = 251.6 nm	[126]

1.6.4 Gas Chromatography - Direct Coupled Plasma - Atomic Emission Spectrometry

The direct current plasma (DCP) has been described extensively [54,112,127,128]. A major limitation of DCP is that the plasma supporting electrodes are consumed by the arc and require reshaping after 2 about hours of continuous operation.

There are relatively few reported couplings of GC with direct current plasma-atomic emission spectrometry (GC-DCP-AES).

Early versions with packed GC columns used heated stainless steel transfer lines. However the use of fused silica heated interfaces with zero dead volume connections has proved the best method for capillary columns.

In comparison with GC-MIP-AES, the absolute detection limits for lead and mercury are 1-2 orders of magnitude poorer. Some further applications are given in **Table 1.7.**

1.7 Inductively Coupled Plasma - Mass Spectrometry

1.7.1 Origins and Development

By the 1970s it was noted that the analytical spectrometric techniques available suffered from the problems associated with relatively high matrix concentrations. The weak spectral lines from matrix elements interfered significantly (due to high concentrations) with the spectra of the analyte. In

Table 1.7 Gas Chromatography - Direct Current Plasma - Atomic Emission Spectrometry (GC-DCP-AES).

Chromatography	Sample	Detection	Reference
Stainless steel column 1.8 m x 0.3 mm i.d., 2% Dexsil 300 GC on 100-120 mesh Chromasorb 750. He = 25 ml min^{-1}, T_c = 130°C (iso.), T_{inj} = 160°C, T_i = 170°C	methylcyclopentadi-enylmanganesetri-carbonyl in fuel	Prototype Spectrospan III d.c. plasma echelle spectrometer. Linear range = up to 380 ng, LOD = 3ng. λ = 279.8 nm	[129]
See Ref [129], He = 60 ml min^{-1}, T_c = various (190-230°C iso.), T_i = 230°C	Various complexes of Cu, Ni, Pd, Zn, Cr and hydrocarbons	See Ref. [129]. Used sheathing gas (230°C) to prevent condensation. linear range = 2-150 ng for Cr, LOD = 0.28-320 pg s^{-1}. λ (nm) = Cu (324.7), Ni (341.7), Pd (340), C (267.7), Cr (267.7)	[130]
Glass column, 5% DEGS-PS on 100-120 mesh supelcoport. Ar = 100 ml min^{-1}, T_c = 155°C (iso.), T_{inj} = 175°C, T_i = 190°C	Methylmercury in fish NBS-RM50	See Ref. [129]. Linear range = 25-2500 μg ml^{-1}, LOD = 37.5 ng ml^{-1} (as Me Hg). λ = 253. 6 nm	[131]

emission spectrometry the intensely-line rich spectra of matrix elements (*e.g.* Ca, Al and Fe) made the choice of interference - free spectral lines for trace elements very difficult.

This resulted in the coupling of the ICP to a quadrupole mass spectrometer (ICP-MS). This offered ease of sample introduction, simultaneous multi-element analysis, simple spectra, adequate resolution and low detection limits. The detailed history and commercial realisation of ICP-MS has been described [13,132] and the current state of achievement reviewed in some detail [134-136].

1.7.2 ICP-MS Instrumentation

Commercially available ICP-MS instruments are made up of the following components:

1. ICP ion source.
2. ion sampling interface **(Figure 1.3)**
3. mass spectrometer.
4. computer instrumental control and data collection system.

Apart from the orientation and coil grounding arrangements the ICP ion source in ICP-MS instruments are essentially the same as the ICP-AES systems. Likewise the mass analysers, ion detectors and data collection systems used are similar to those used in conventional quadrupole GC-MS instruments [45].

The major advantages of ICP-MS are:

1. High sensitivity (2.25×10^7 counts s^{-1} for 1 $\mu g\ ml^{-1}$ of indium (m/z 115) with a background of 10 counts

s^{-1} giving a detection limit of about 0.4 pg ml^{-1} [137]).

2. Rapid simultaneous multi - element analysis.

3. Capability for isotope studies (isotope dilution analysis) [138,139].

4. Large linear dynamic range of 6-8 orders of magnitude, dependent on the mode of operation. When pulse counting is used 6 orders (0.01 ng ml^{-1} to 10 μg ml^{-1}) is obtained, by reducing sensitivity (operating in the analogue mode) linear calibration up to about 500 μg ml^{-1} is achieved [140].

The principal disadvantages of the ICP-MS is the high capital cost of the instrument (approximately £300,000); the difficulty in the analysis of electronegative elements (*e.g.* I, Be, O, Cl) and of course only total element concentrations are obtained when ICP-MS used without a chromatographic system (*i.e.* no speciation information is obtained).

The continuing interest in ICP-MS as an analytical tool has provided various methods of sample introduction. The most frequently used method is to introduce the analyte into the plasma as an aerosol in an aqueous or organic solvent. This employs direct pneumatic (or ultrasonic) sample nebulisation used in conjunction with a spray chamber [141-144]. Other methods employing this system include slurry atomization [145,146] and flow injection analysis [147,148]. The main disadvantage of this system is the low transport efficiency; only about 1-3 % of the actual sample reaches the plasma [149,150]. Alternatives to this are electrothermal vaporisation

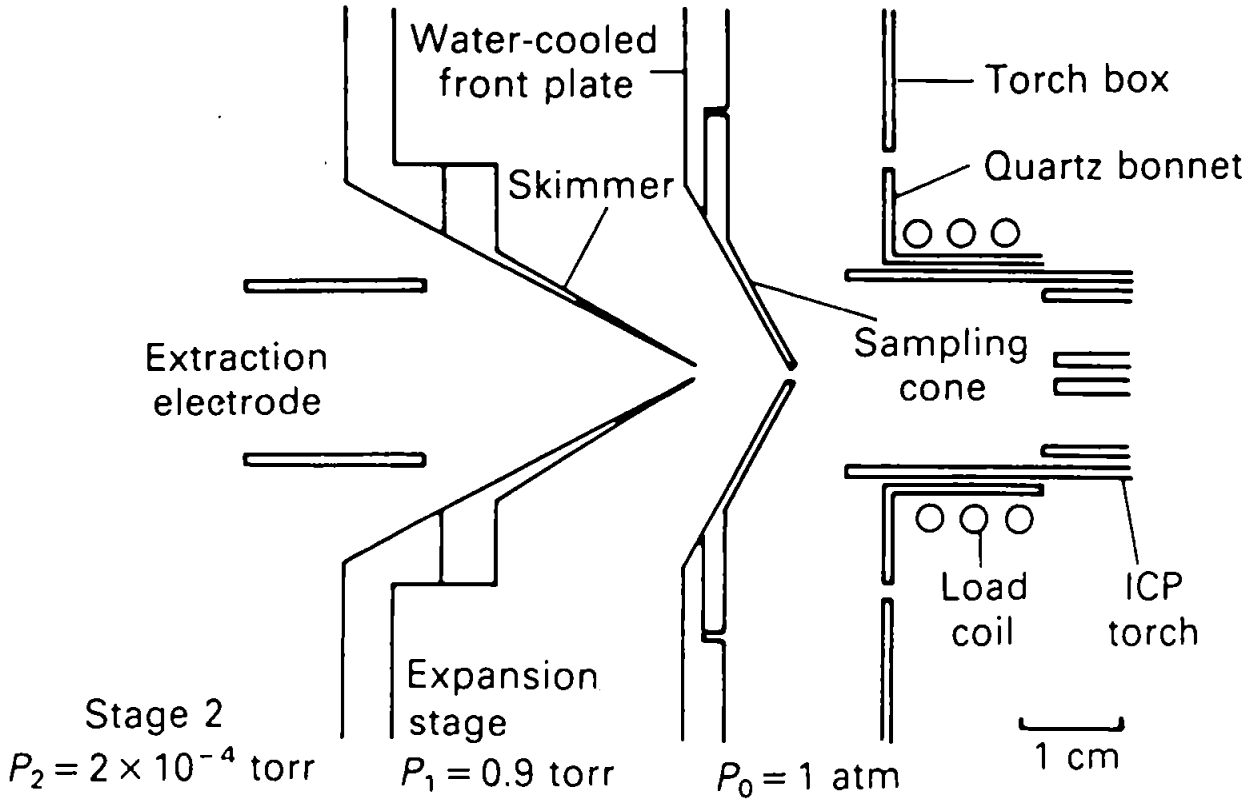


Figure 1.3 Plasma sampling interface: continuum sampling mode [151].

[152,153], laser ablation [154], hydride generation [155,156] and chemical vapour generation (Hg^0 analysis).

1.7.3 Interferences in ICP-MS

There is evidence that gas reactions occur in the zone between the cones **(Fig. 1.3)** giving rise to polyatomic and oxide species, which are thus two of the major sources of interferences in ICP-MS.

The quadrupole mass spectrometer has insufficient resolution to separate chemically different ions of the same nominal mass. Spectrometric interferences [157,158] which fall into six categories:

1. Polyatomic ions resulting from ion - molecule reactions between major species in the plasma which occur during the extraction process or in the expansion stage. The ions produced may occur at the same nominal mass in the spectrum as the trace analyte. Some examples of polyatomic interferences are shown in **Table 1.8**.

2. Analyte oxide ions resulting from incomplete dissociation in the plasma, recombination in the boundary layer or ion-molecule reactions during extraction [159].

3. Doubly charged ions of analyte (M^{2+}) appear in the spectrum at half the mass of the parent singly charged ion, because ions are filtered in the analyzer on the basis of mass-to-charge ratio (m/z) [159].

4. Isobaric overlaps between coincident isotopes of neighbouring elements (*e.g.* ^{40}Ca and ^{40}Ar).

5. Matrix suppression causes a shift in plasma equilibria by the addition of high concentrations of easily ionisable elements (*e.g.* Na, K, Ca) which are large enough to produce a significant increase in electron population from their ionisation.

6. Physical or memory effects caused by condensation of vaporised analyte on the sampler cone aperture.

The continuum background spectra in ICP-MS also produce several abundant ions derived from argon and water vapour (*e.g.* Ar^+, ArH, O^+, OH^+ and OH_2^+) [160].

1.8 Gas Chromatography - Plasma Source - Mass Spectrometry

The use of plasma source-mass spectrometry for GC detection has a number of advantages over GC-ICP-AES: detection limits are an order of magnitude better, isotope ratio measurements (isotope dilution analysis) can be made and simple mass spectra are obtained rather than complicated emission spectra prone to interferences. The mass spectra which are response independent and not influenced by the type of analyte.

1.8.1 Gas Chromatography - Microwave Induced Plasma - Mass Spectrometry

There have been relatively few studies of coupled GC-MIP-MS. Although the use of a helium plasma as an ion source for MS has been limited, it has the advantage that monopositive ions are produced from halogens and there are reduced low mass interferences (m/z <40) compared to argon plasmas.

Table 1.8 Some major polyatomic ion levels produced from 1 % solutions of three mineral acids. Polyatomic peak responses in ng ml^{-1} are the affected analyte concentrations equivalent to the interfering background when that isotope is used for determination. (Gray, 1992, [157]).

Mass	Probable ion	Acid			Analyte[1]
		HNO_3	HCl	H_2SO_4	
51	$^{35}Cl^{16}O^+$	0.12	12.0	0.84	V (99.8%)
52	$^{40}Ar^{12}C^+$ $^{36}Ar^{16}O^+$	0.53	1.2	0.71	Cr (83.8%)
53	$^{37}Cl^{16}O^+$	0.79	43.8	1.75	Cr (9.6%)
54	$^{40}Ar^{14}N^+$	90.9	108	85.9	Fe (5.8%)
55	$^{40}Ar^{14}N^1H$	0.71	0.56	0.84	Mn (100%)
56	$^{40}Ar^{16}O^+$	18.0	15.8	15.1	Fe (91.7%)
57	$^{40}Ar^{16}O^1H^+$	29.3	28.4	30.6	Fe (2.2%)
64	$^{32}S^{16}O_2^+$	1.26	1.21	480	Zn (48.6%)
66	$^{34}S^{16}O_2^+$	0.74	0.52	41.6	Zn (27.9%)
67	$^{34}S^{16}O_2{}^1H$	2.35	2.06	12.9	Zn (4.1%)
75	$^{40}Ar^{35}Cl^+$	0.19	2.1	0.46	As (100%)
80	$^{40}Ar_2^+$	1221	1257	1319	Se (49.7%)

[1]Footnote: The percentage values given in the parentheses are the natural occuring isotopic abandances of the element.

Low pressure helium MIP has certain attractive features as an ion source for plasma-MS including the isolation of the plasma from contamination due to atmospheric entrainment and lower flow-rates making gas purification much easier. These advantages minimise the isolation of plasma gas impurities and/or the formation of polyatomic ions which can interfere with the determination of certain low-mass elements.

Both atmospheric and low pressure helium GC-MIP-MS systems have been utilised for the speciation of halogenated hydrocarbons [161] and organotin compounds [162] **(Table 1.9)**. Recently an SFC-MIP-MS has been described for halogenated hydrocarbon speciation [163] **(Table 1.9)**.

1.8.2 Gas Chromatography - Inductively Coupled Plasma - Mass Spectrometry

GC has been coupled to ICP-MS less routinely. GC-ICP-MS can be used to monitor a wide range of elements simultaneously with a high degree of selectivity and sensitivity. The advantages of the system include good transport efficiency (100%), few spectral interferences, improved plasma stability and compared to HPLC-ICP-MS, reduced sampler and skimmer cone wear.

Unlike state-of-the-art GC-MIP-AES, GC-ICP-MS does not require expensive reagent gases and solvent-venting to prevent plasma instability and carbon accumulation on the discharge tube respectively (similar problems are encountered in GC-MIP-MS, where the cones of the mass spectrometer may also become blocked).

Table 1.9 Gas Chromatography - Microwave Induced Plasma - Mass Spectrometry (GC-MIP-MS).

Chromatography	Sample	Detection	References
Fused silica capillary column, 40 m x 0.33 mm i.d., SE-54 J & W Scientific	Halogenated hydrocarbons	Atmospheric pressure He MIP = TM_{010} cavity, tangential pressure He MIP = 9 x 10^{-2} mbar Mass spectrometer = Plasma Quad (VG Elemental), single ion monitoring for ^{79}Br, ^{35}Cl, ^{37}Cl. Sensitivity = pg range	[161]
Fused silica capillary column, 30 m x 0.32 mm i.d. and 0.25 μm film thickness, DB-1701, He = 10 ml min^{-1}, T_{inj} = 300°C, T_c = 78°C (2 min. iso.) to 260°C at 32°C min^{-1}, T_i = 280°C	Organotin speciation	Atmospheric pressure He MIP = TM_{010} cavity, tangential torch with tantalum injector. Forward power = <100W (2450 MHz). Mass spectrometer = see ref. [161], single ion monitoring ^{120}Sn, linear dynamic range = 3 orders of decade, LOD (3σ) = 0.09-0.35 pg (as Sn) for tantalum torch	[162]

Table 1.9 (continued....)

Chromatography	Sample	Detection	References
SFC-MIP-MS. Capillary column, 2.5 x 4m x 50 μm i.d. x 0.25 μm film thickness, SB-biphenyl-30 (Lee Scientific)	1-chloronapthalene and 1-bromo-2-methylnapthalene	Atmospheric He MIP = TM_{010}, forward power = 120 W (2450 MHz). Mass spectrometer = VG Plasma Quad, scampling orifice = 0.4 mm (Al cone). Absolute LOD = 15 pg (Cl) and 0.75 pg (Br), linear range = 50 pg - 50 ng (5% RSD).	[163]

Packed column GC-ICP-MS was first described by Van Loon *et al.*, [164] and later by Chong and Houk [165] **(Table 1.10)**. However packed column GC often does not have sufficient resolving power for adequate characterisation of the complex mixtures found in many environmental samples (eg. water, sediment, biota). SFC has also been interfaced to ICP-MS [166] **(Table 1.10)** and applied to the determination of organotin compounds but this system suffered from poor chromatographic resolution, decrease in signal with increasing CO_2 flow rate, arcing between the sampler cone and plasma (at >1.5 kW) and sampler cone became coated in carbon (10 ml min^{-1} CO_2, after 10 min.).

Recently an interface was described which allows both independent packed column GC or solution nebulisation sample introduction and was applied to volatile organochlorine [167] and organotin [168] compounds.

Table 1.10 Gas Chromatography - Inductively Coupled Plasma - Mass Spectrometry (GC-ICP-MS).

Chromatography	Sample	Detection	References
Packed column, 3% OV-1 on Chromasorb W (80-100 mesh). Ar 0_2 = 8.2 ml min^{-1}, T_{inj} = 250°C, T_c = 60°C iso. to first peak then ballistic heating to 250°C. T_i = 250°C	Organotin compounds (pentylated methyltin species)	Ar ICP, forward power = 1.25 or 1.50 kW, reflected power = approx. zero, LOD (3σ) = 6-16 ng as Sn. Problems with carbon deposition.	[164]
Packed column, 10% didecyl phthalate: 10% Carbowax 20M on Chromosorb W 80-100 mesh, T_c = didecyl phthalate (120°C iso.) and carbowax (200°C iso.), Ar = 25 ml min^{-1}, T_i = didecyl phthalate (150°C) and Carbowax (250°C),	Various organic compounds	Ar ICP, no auxiliary flow, forward power = 1.35 kW, reflected power = 15 W, sampling orifice = 0.45 mm, isotopes = $^{12}C/^{13}C$, $^{14}N/^{15}N$, $^{35}Cl/^{37}Cl$, $^{79}Br/^{81}Br$, $^{32}S/^{33}S/^{34}S$, $^{10}B/^{11}B$ and $^{28}Si/^{29}Si/^{30}Si$, LOD = 0.001 to 400 ng s^{-1}.	[165]
Supercritical fluid chromatography, column = 2.5 m x 50 μm i.d. x 0.25 μm film thickness, coated with SB Octyle-50, flow rate = 1.5 cm s^{-1}, T_c = 75°C iso., T_i = 75°C, restrictor temperature = 200°C	Tetraalkyltin compounds	VG Plasma Quad instrument, Ar ICP, forward power = 1.35 kW, reflected power = <5W, LOD = 0.035-0.043 pg	[166]

Table 1.10 (continued....)

Chromatography	Sample	Detection	References
Packed column, 2 mm i.d. x 1.75m, 6% OV-101 on Chromosorb W, 80/100 mesh, flow rate = 10 ml min^{-1} Ar, T_c = 70°C iso., T_i = 140°C (for chlorinated compounds) and 220°C (for organotin compounds)	dichloromethane, 1,1,1 - trichloroethane, trichloroethylene, tetramethyltin, tetraethyltin	Perkin Elmer SCIEX Elan 500 Ar ICP-MS, low flow torch, cooling gas = 10 l min^{-1}, auxiliary gas = 1.4 l min^{-1}. LOD = 2.5 ng (^{35}Cl) and 4.5-12 pg (^{120}Sn)	[167,168]

1.9 Aims of the Present Study

For laboratories where ICP-AES or ICP-MS are already available, use of capillary GC and construction of a simple GC-ICP interface would appear to offer an economical alternative to GC-MIP-AES for trace metal speciation analysis. Yet such a coupling has not been described previously. Since ICP-AES, ICP-MS and GC are also independent analytical methods, the construction of an easily removable interface would mean that independent ICP and GC operation would still be possible. This is an important practical consideration in many busy multi-user laboratories where expensive instrumentation may have to fulfil a number of different analytical needs.

Therefore the aim of the present work was to develop a capillary GC-ICP-MS system (**Fig. 1.4**) for use in the separation and determination of volatile organometals and other trace element species. Furthermore it was considered that development of a high temperature (HT) capillary GC-ICP-MS system for relatively involatile organometals (*e.g.* metalloporphyrins) would extend the range of analytes which could be determined. The research is described in three further chapters.

Chapter 2 describes the progressive development of a heated interface for the direct coupling of HT-GC to ICP-MS. Design aspects of the transfer line, ICP torch and modifications to the ICP-MS instrumentation are discussed.

Chapter 3 desribes the separation and determination (including Figures of Merit) of a series of environmentally important organometallic species, including tetraalkylleads in fuel, organotins in a standard reference material (harbour sediment). In

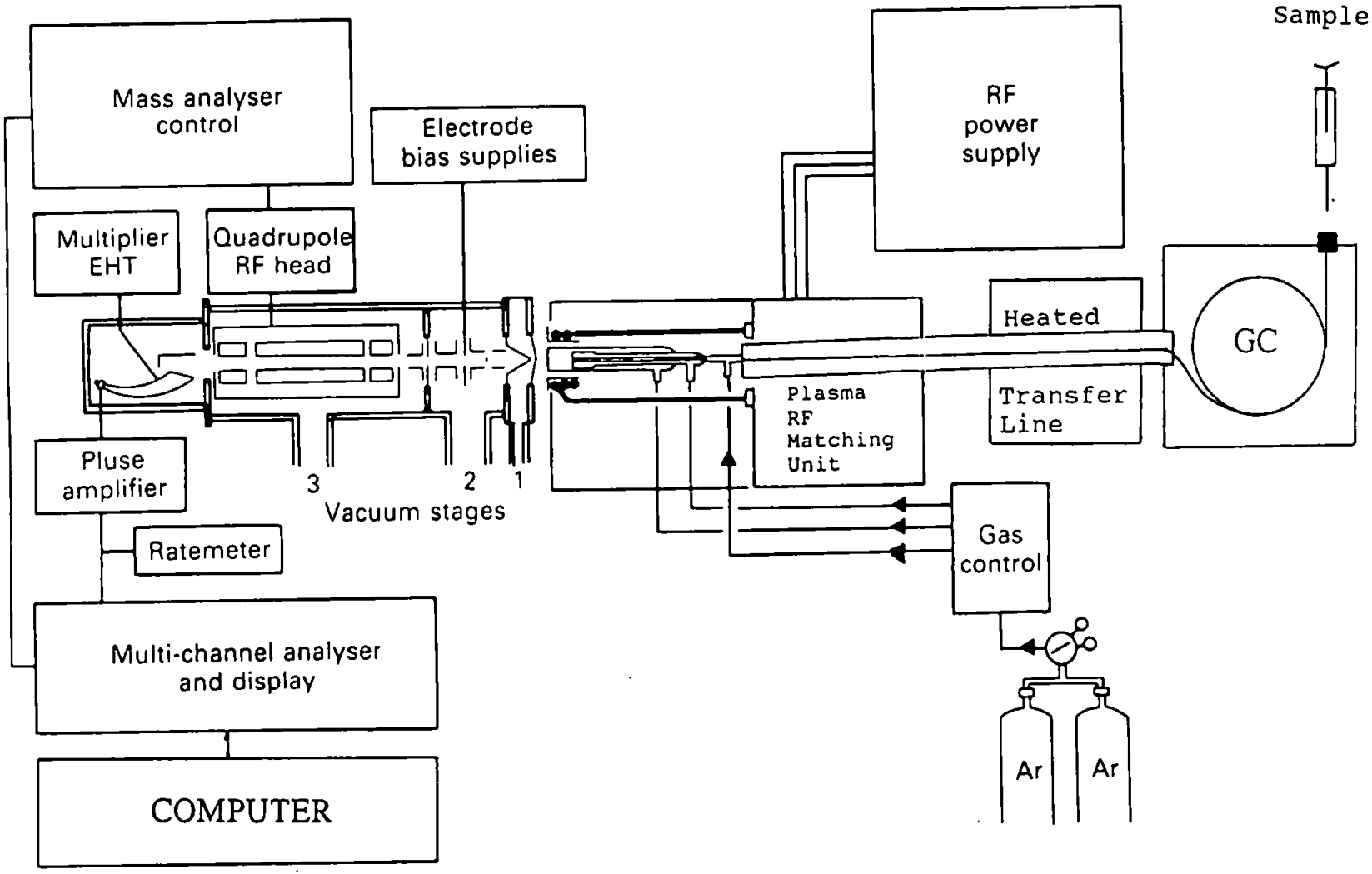


Figure 1.4 Schematic diagram of a GC-ICP-MS system. Adapted from *Date and Gray* (1983) [151].

addition, the determination of authentic organomercury compounds, ferrocene and metallo-dithiocarbamates are also described.

Chapter 4 describes the development of a HTGC technique for the separation of authentic and geological metalloporphyrins using flame ionisation detection. A method for the extraction, isolation and characterisation of metalloporphyrins in shales is also described. It is suggested that future, more efficient, coupling of the HTGC system to ICP-MS will allow determination of metalloporphyrins by this more element specific technique, thus significantly extending the volatility range of trace element species measurable by ICP-MS.

CHAPTER TWO

GC-ICP-MS INSTRUMENTAL DEVELOPMENT

2.0 GC-ICP-MS INSTRUMENTAL DEVELOPMENT

2.1 INTRODUCTION

A number of criteria may be used to define a good GC detector. First, the noise level governs the detection limit. A chromatographic peak can only be recognised if the height is at least twice the height of the noise peaks. It should be noted that unlike GC, HPLC interface techniques are prone to undesirable noise caused by air bubbles and impurities, or drift in the base line resulting from slow changes in flow rate or ambient temperature. In consideration of sensitivity distinction must be made between the absolute and the relative sensitivity of a detector. The absolute sensitivity is a function of instrument design, and measurement of and noise levels, whilst the relative sensitivity depends on the amount of analyte that is just detectable under defined conditions.

In all reported couplings of GC to spectrometric detectors a heated interface was used to prevent condensation and subsequent loss of analyte. The sample must be transferred from the chromatographic column with minimal sample loss, minimal peak broadening (or tailing) with no interfering chemical reaction occurring. Since eluates from GC columns are normally at atmospheric pressure, simplified interface configurations are possible when coupled to an atmospheric pressure plasma (ie. ICP) rather than to a reduced pressure plasma.

The factors which were considered important for interface design in the present study are given below:

1. Introduction of the total column effluent into the atom source (100% transport efficiency). Direct coupling of the GC column to the ICP torch was desirable, rather than passing the effluent into the nebuliser/spray chamber

which causes loss of analyte causing chromatographic band broadening and unnecessary dilution.

2. Simple, strong and robust construction for convenient servicing.

3. On-line for real-time analysis.

4. Relatively short installation time and readily demountable.

5. As large a temperature range as possible with current GC column technology (eg. -40°C-450°C).

6. No cold spots.

7. Stable temperature.

8. Inexpensive.

2.2 INSTRUMENTAL

2.2.1 Gas-Chromatography: The instruments used were a Carlo Erba HRGC 5300 (HT-SIMDIST) and Mega Series GC.

They were equipped with a multifunction controller (MFC 500), electrometer control module control module (EL-480) and FID (H_2 = 50 KPa, air = 100 RPa, N_2 make-up = 50 RPa, temperature = 10-20°C greater than the final oven temperature). Unless otherwise stated the GC was fitted with a high temperature aluminium-clad fused silica capillary column, 25 m x 0.32 mm i.d. x 0.1 μm film thickness siloxane - carborane copolymer HT-5 phase (Scientific Glass Engineering, Milton Keynes, UK).

The carrier gas was high purity ("Premier Grade", 99.999%) helium (Air Products, Surrey, UK), which was purified further using an oxygen and water filter. Flow rate was 2-6 ml min^{-1} (on the HRGC 5300, measured at the mid oven temperature range) or 2 ml min^{-1} (on the HT-SIMDIST, using a Carlo Erba constant pressure-constant flow module, CP-CF 516).

Injection was on-column (0.5 or 1.0 μl). FID response was acquired and stored using a Shimadzu "Chromatopac" (C-R3A) integrator.

2.2.2 ICP-MS: The instrument used was a VG Plasma Quad 2, (VG Elemental, Winsford, Cheshire, UK).

Commercially available computer software (VG Elemental, PQPROG version 3.1A) was used for instrumental control, data acquisition and processing. General operating conditions are given in **Table 2.1.**

Carrier Gas: Helium was selected as the carrier gas rather than argon since it was readily available in high purity; and gives better column efficiencies than more dense and viscous gases [169]. This is an important factor when the coupled system is to be applied to HTGC. Helium has a lower density and viscosity (0.17 g L^{-1} at 1 atm and 343.6 micropoises at 407°C) compared to argon (1.66 g L^{-1} at 1 atm. and 368.5 micropoises at 404°C) [170]. Also the addition of He to Ar produces a plasma capable of ionising elements with high ionisation potentials more efficiently than a pure Ar plasma [171].

Table 2.1 General ICP-MS operating conditions

Cooling (outer) gas	14 - 16 l min^{-1}
Auxiliary (intermediate) gas	0.5 - 0.8 l min^{-1}
Injector gas	1.0 - 1.8 l min^{-1}
Forward power	1500 W
Reflected power	<5 W
Plate current	0.6 - 0.8 A
Grid current	0.12 - 0.20 mA
Expansion pressure	2.4-3.7 Torr
Intermediate pressure	0.0 x 10^{-4} Torr
Analyser pressure	7.0 - 8.0 x 10^{-7} Torr
Sampler cone	Nickel (1.0 mm orifice)
Skimmer cone	Nickel (0.8 mm orifice)
Mode	Single ion monitoring
Dwell	163840 or 327680 μs
Number of channels	4094

2.3 Initial Coupling

The preliminary study was to confirm that the analytes eluted from a capillary GC column could be detected by ICP-MS.

2.3.1 ICP-MS Plasma Torch

The design of the ICP torch used in this study was based on that described by Chong and Houk [165]. A custom-made demountable Fassel torch **(Figure 2.1)** was supplied by H. Baumbach and Co. Ltd. (Ipswich, UK). This consisted of a T-shaped basal quartz joint at the bottom of the injector tube. The side inlet tube provided the addition of make-up argon gas which helped to puncture the axial channel through the centre of the ICP. The use of a torch with a demountable injector has two distinct advantages; firstly, it allows a range of various injector designs to be used without the need to purchase a whole new torch, and secondly, it facilitates the ease of interface assembly.

The modified demountable torch with a 3mm ICP injector **(Figure 2.1)** was used. A stainless steel tube (HPLC type, 82 mm x 1 mm i.d. x 2 mm o.d.) was passed through the injector (ending 80 mm before its tip) and held concentrically by a reducing union (¼ inch to 2 mm, SGE, Milton Keynes, UK) and graphite tape.

As a safety precaution, the large distance between the end of the tube and the tip of the injector was considered prudent because it has been reported that electrical conductivity of stainless steel tubing causes plasmas to arc if positioned too close to the load coil [172].

The capillary GC column **(Table 2.2)** protruded 2 mm from the tip of the stainless steel tube.

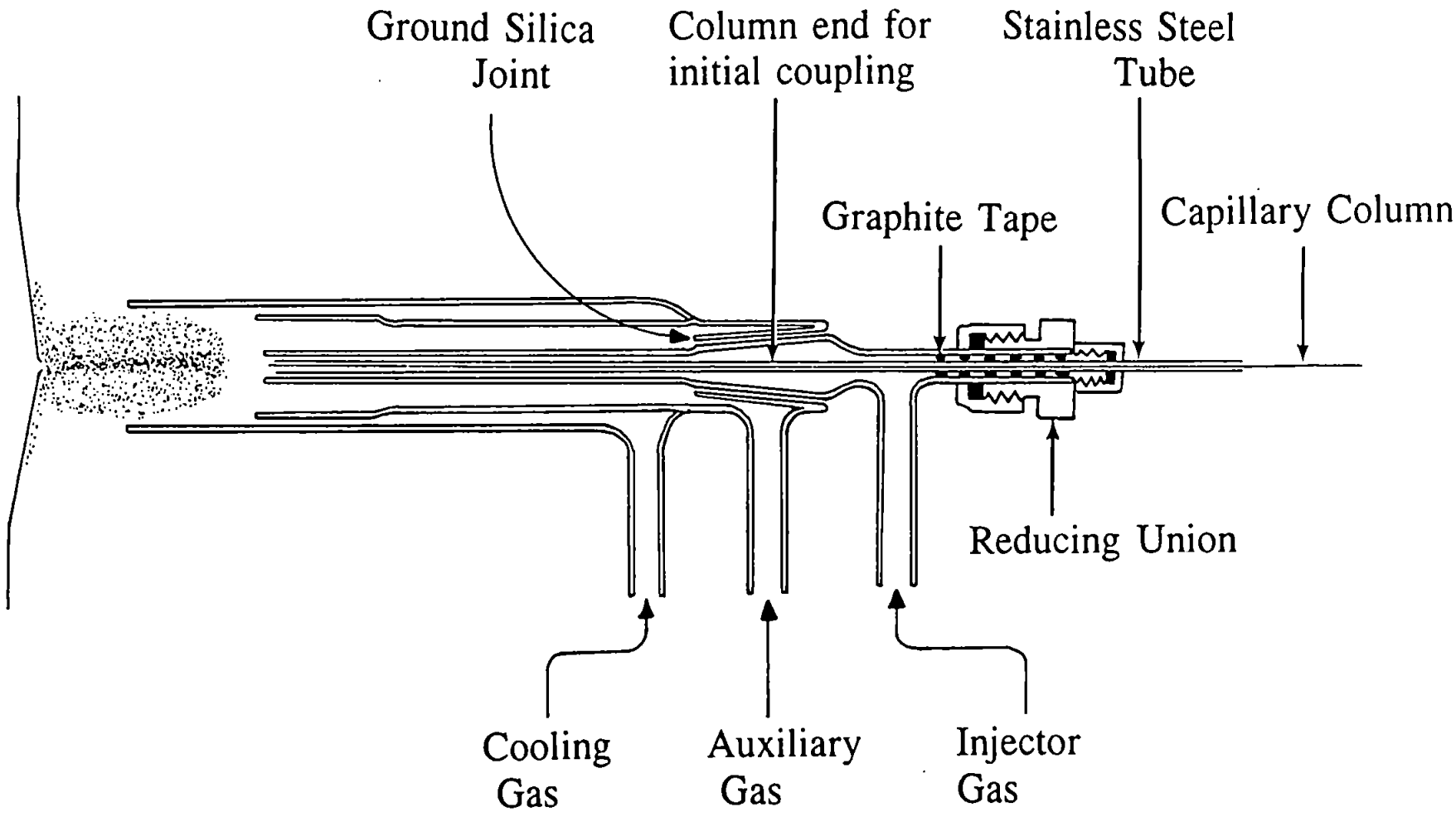


Figure 2.1 Modified demountable plasma torch used for the initial coupling (actual size).

2.3.2 Transfer Line (Mark I)

The transfer line consisted of a length of copper tubing (0.95 m x ¼" o.d. x 4.3 mm i.d.) which was wound with 2.4 m of HT9 heating tape (Electrothermal Essex, UK). The tape was wound as far as the reducing union at the base of the injector.

To prevent the possibility of the heating tape and copper tube acting as an r.f. aerial (due to their close proximity to the load coil) they were connected to the mains earth and torch box earth, respectively.

The heating tape was supplied with a variable voltage (Variac) and the temperature of the transfer line **(Table 2.2)** was monitored by a type K-thermocouple (RS Components, Northamptonshire, UK) positioned half way along its length.

The transfer line was held in position using a number of laboratory clamps secured to the torch box.

To avoid the possibility of leaks the capillary column was passed through the transfer line into the torch with no joints or dead-volume connections.

2.3.3 ICP-MS Optimisation and Tuning

A continuous signal of analyte was needed in order to optimise and tune the instrument.

So as not to obstruct the transfer line and torch, the nebuliser spray chamber assembly was removed from the torch box and positioned outside the hood of the ICP-MS. It was not possible to introduce a multi-element

solution (100 ng ml^{-1}, Be, Mg, Co, In, Pb, U in 2% HNO_3) into the plasma using the nebuliser/spray chamber assembly (connected on-line to the side arm of the torch injector using "tygon" tubing, 0.4 m x ¼" o.d.) due to the accumulation of aerosol in the injector of the torch which resulted in an absence of detectable signal.

Instead, the ICP-MS was successfully tuned using a continuous signal of cold mercury vapour (^{202}Hg, 29.8%) generated by the reduction of a solution of Hg^{2+} (100 μg l^{-1}) with tin(II) chloride dihydrate (2% m/v in 2.2% hydrochloric acid). A conventional U-tube gas-liquid separator was used and the mercury vapour introduced on-line via the injector gas inlet **(Figure 2.2)**. The optimum instrumental conditions for maximum $^{202}Hg^{o}$ response is given **(Table 2.2)**. A "survey-scan" (mass range m/z 20-240) of the background spectrum was obtained **(Figure 2.3)**, and the resolution of isotopes and isotope ratios for mercury found to be adequate. Possible identities of ions are given in **Table 2.3**.

2.3.4 Organolead Detection using the Initial Coupling

It was decided to test the coupled system with a mixture of relatively non-polar, volatile tetraalkyllead compounds which have been widely used in a number of previous speciation studies [83,101,110].

A sample containing five tetraalkylead compounds in naphtha was diluted to 45 μg ml^{-1} using hexane. The mixture was injected on-column (0.5 μl) and an ion selective chromatogram (m/z 208) obtained **(Figure 2.4a)**. Five lead species were found. No tetraalkyllead compounds were detected in the hexane blank **(Figure 2.4b)**. The naphtha sample was also examined using conventional FID using the same GC conditions **(Figure 2.4c)**, the

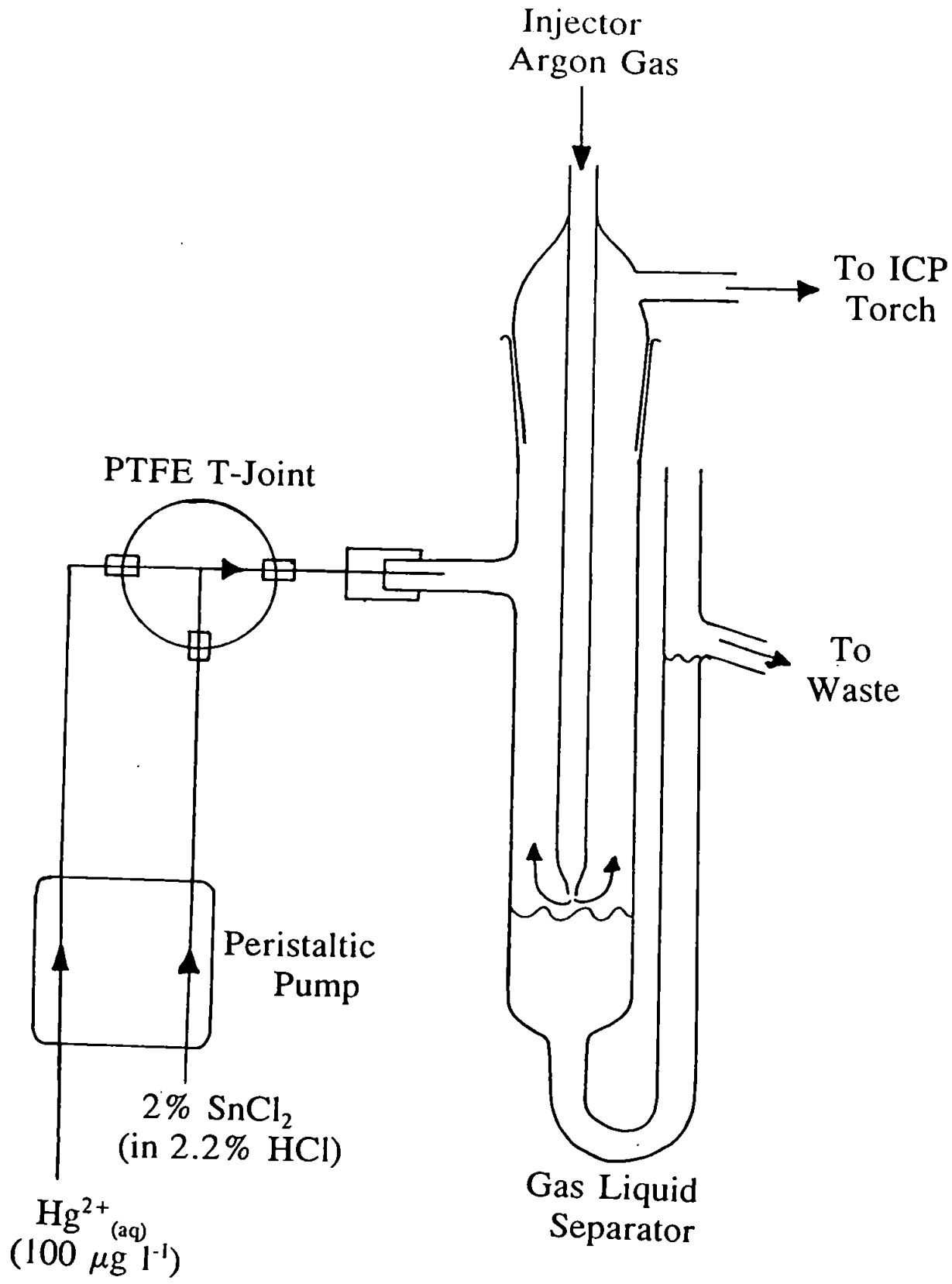


Figure 2.2 Cold mercury vapour generator gas-liquid separator used for ICP-MS tuning.

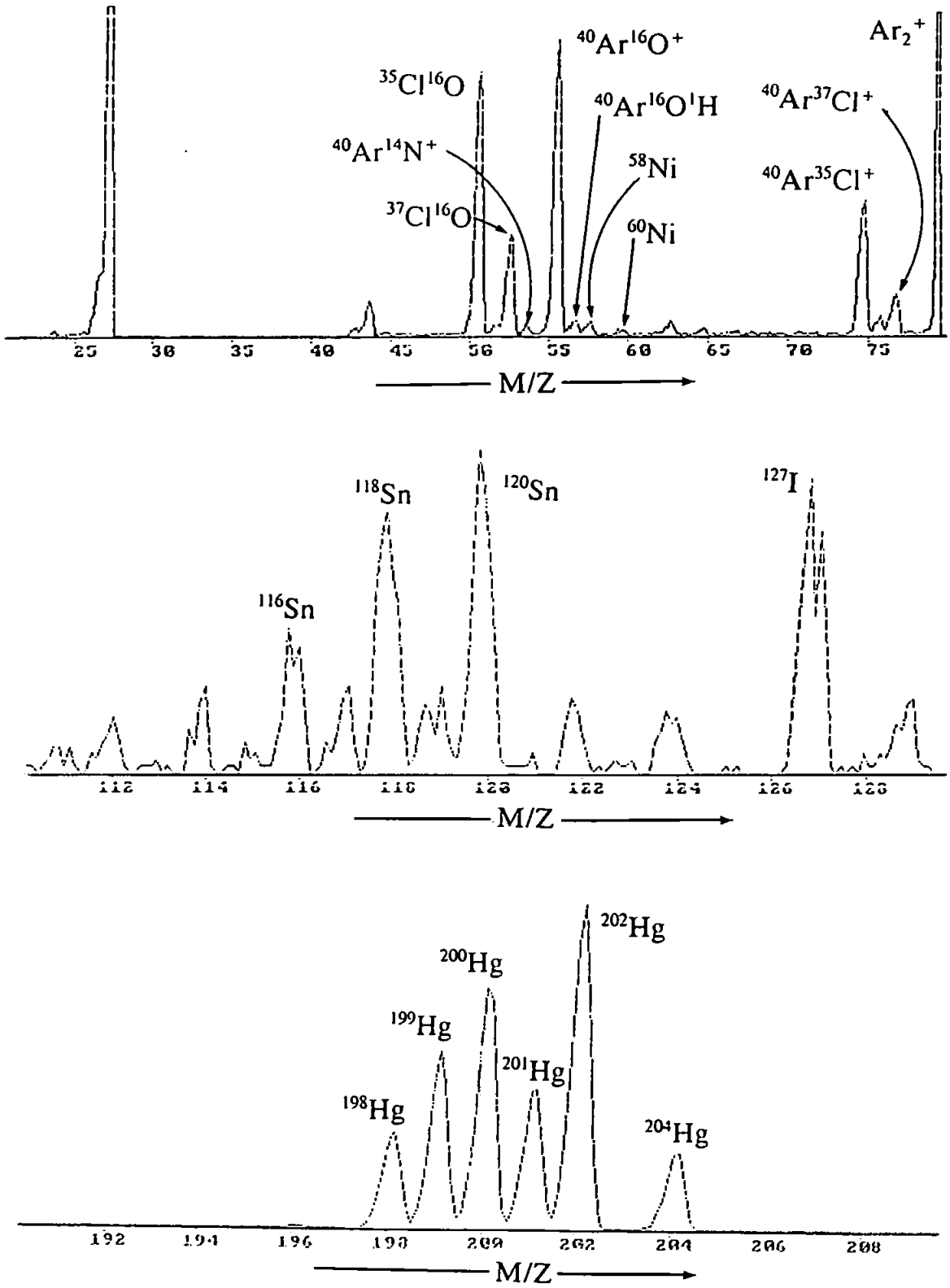


Figure 2.3 Background mass spectrum from the cold mercury vapour generator.

Table 2.3 Ions observed in the background spectrum from cold mercury vapour generation.

Nominal Mass	Ion	Origin
51	$^{35}Cl^{16}O$	chlorine from HCl or $SnCl_2$ and oxygen from water vapour
53	$^{37}Cl^{16}O$	chlorine from HCl or $SnCl_2$ and oxygen from water vapour
54	$^{40}Ar^{14}N^+$	nitrogen from air or $Hg(NO_3)_2$
56	$^{40}Ar^{16}O^+$	oxygen from water vapour
57	$^{40}Ar^{16}O^1H$	OH from water vapour
58 60	^{58}Ni ^{60}Ni	ablation from nickel sampler and skimmer cones
75 77	$^{40}Ar^{35}Cl^+$ $^{40}Ar^{37}Cl^+$	chlorine from HCl or $SnCl_2$
80	Ar_2^+	argon dimer
116 118 120	^{116}Sn ^{118}Sn ^{120}Sn	tin from $SnCl_2$
127	^{127}I	iodine memory from previous operator
198 199 200 201 202 204	^{198}Hg ^{199}Hg ^{200}Hg ^{201}Hg ^{202}Hg ^{204}Hg	mercury vapour from the generator

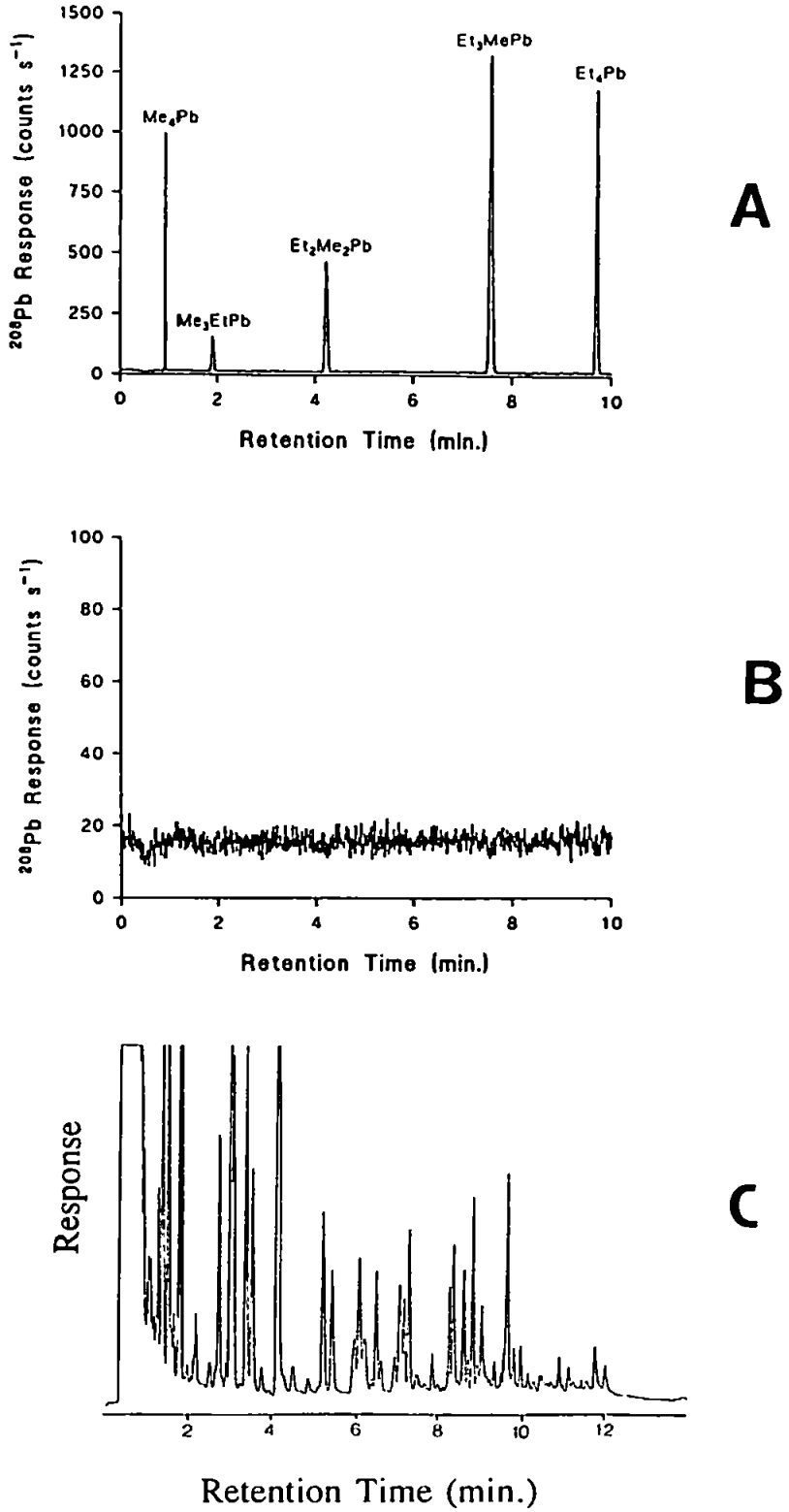


Figure 2.4 **(A)** Ion selective chromatogram (m/z 208) showing the separation of five tetraalkyllead species in naphtha. **(B)** Ion selective chromatogram (m/z 208) of a hexane blank. **(C)** Conventional FID chromatogram of the same naphtha sample.

chromatographic improvement when using GC-ICP-MS is obvious.

The first eluting component in the selective ion chromatogram was tentatively assigned as tetramethyllead and the last peak as traethyllead. Further details are presented in **Table 2.4.**

The influence of the spectrometer dwell time (data acquisition parameter) on chromatographic peak shape was investigated. At 327680 μs the tetramethyllead peak (retention time = 0.94 min.) was irregular **(Figure 2.5a)** consisting of approximately 5 data sampling points (3.1 sampling points s^{-1}). However, using a dwell time of 163840 μs the same peak was much improved **(Figure 2.5b)** and almost Gaussian, consisting of about 10 data sampling points (6.2 sampling points s^{-1}).

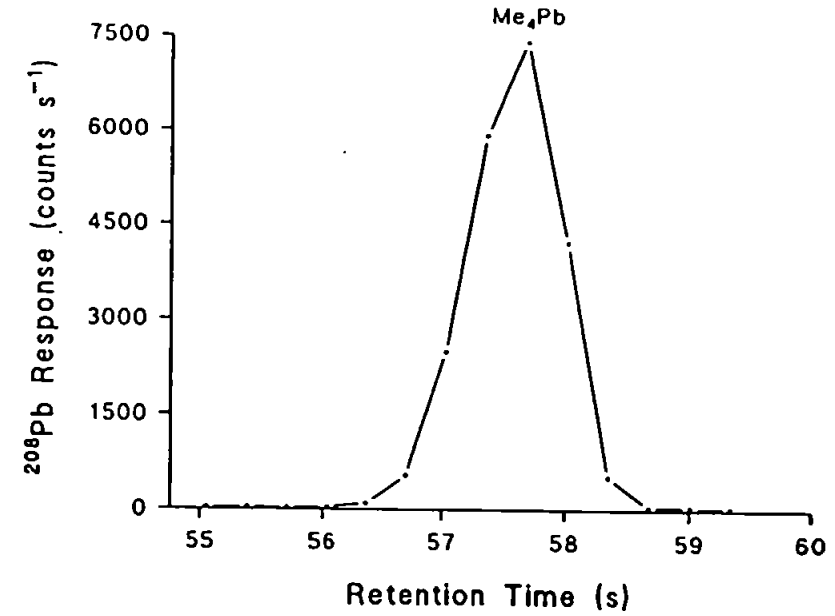
2.4 Critical Evaluation of the Initial Coupling - Considerations for Modification

Due to the inflexibility of the heating tape, difficulty was encountered whilst winding it around the narrow diameter (¼") copper tube. Manufacturers (Electrothermal, Essex, UK) recommend that the minimum diameter of heating tape curvature is 1 inch. The sharp twists caused the glass fibre braiding to fray after it had been heated, exposing the live heater wires.

Constant heating of the copper tubing caused the outer surface to become oxidised, preventing a good earth contact. It also resulted in the copper tube becoming brittle and to break when it was bent into position. Aluminium (in the form of a 1 inch diameter rod) might be a more suitable material to use because it has a high thermal conductivity (2.73 W cm^{-1} $°K^{-1}$, at 300°K), suitably high melting point (660°C), is light-weight (2.7 g cm^{-3}) and is not severely affected by oxidation.

Table 2.4 Percentage ratio of tetraalkyllead species present in a naphtha sample (using the initial capillary GC-ICP-MS coupling).

Alkyllead Species		Net peak area for Figure 2.4	Mean % peak area (duplicates)
Name	Formula		
Tetramethyllead (TML)	$(CH_3)_4Pb$	21206	9.8
Trimethylethyllead (TMEL)	$(CH_3)_3C_2H_5Pb$	9011	4.2
Dimethyldiethyllead (DMDEL)	$(CH_3)_2(C_2H_5)_2Pb$	26107	13.3
Triethylmethyllead (TEML)	$CH_3(C_2H_5)_3Pb$	81149	42.5
Tetraethyllead (TEL)	$(C_2H_5)_4Pb$	61836	30.1



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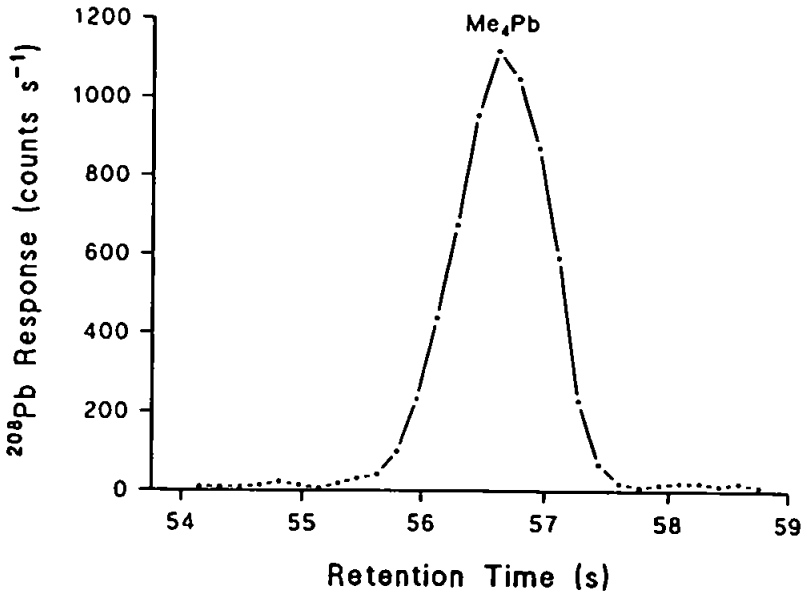


B

Figure 2.5 **(A.)** Irregular peak shape of tetramethyllead using a dwell time of 327680 μs due to an inadequate number of sampling points and **(B.)** improvement in peak shape using a dwell time of 163840 μs.

Chromatographic band (or zone) spreading should be minimised by keeping the transfer line length to a minimum, since the standard deviation is directly proportional to the length [173]. The length of the transfer line could therefore be reduced by introducing it through the side of the ICP-MS hood. This would also allow the hood to be closed properly since it previously had to be kept open as much as 50 mm which meant there was a strong possibility of the operator being exposed to harmful U.V. radiation and strong r.f.

The temperature along the length of the transfer line could not be monitored since only one thermocouple was used. Ideally three or four thermocouples should be employed to check for any cold spots. The maximum temperature obtained was 270°C which would be too low for HTGC where a minimum temperature of 430°C would be required to be compatable with the maximuim operating temperature of present HTGC stationary phases. The transfer line would probably need to be lagged with thermal insulation to achieve uniform heating and the desired temperature.

The junction between the end of the transfer line and base of the torch put physical stress on the capillary column causing it to break when minor positional adjustments to the coupling were made. This joint could be much strengthened.

2.5 Coupling and Transfer Line (Mark II)

2.5.1. Construction and ICP-MS Modifications

Another more robust transfer line was made **(Figure 2.6, 2.7)** which took into consideration the design aspects discussed above (section 2.4). The central core was made from an aluminium rod (25.4 mm diameter x 600 mm length) with a longitudinal slot (1 mm) through which the capillary column could pass. Around this heating tape was

wound (Electrothermal, Essex, UK) connected to a variable voltage supply (Variac) and sheathed with industrial pipe lagging (Encon, Cornwall, UK). The transfer line was earthed to the torch box via a steel screw to prevent the possibility of the aluminium bar acting as an r.f. aerial. The interface temperature was monitored by four "type K" high temperature thermocouples (RS Components, Northamptonshire, UK). The transfer line was potentially capable of providing a large temperature range with uniform heating in order to extend the volatility range of the organometallics that could be examined by the technique.

Modifications made to the ICP-MS instrumentation to minimise the length of the transfer line included replacing a panel from the right hand side of the hood with a detachable plate with a 80 mm diameter hole (aligned concentrically with the plasma torch) through which the transfer line could pass **(Figure 2.8a)**, thus enabling unrestricted access to the interface whilst the hood was open. The detachable plate was held in position by means of an aluminium bracket anchored to the base of the ICP-MS using two 13 mm nuts **(Figure 2.8b)**. A rectangular section (90 x 150 mm) from the right hand side of the torch box and nebuliser - spray chamber assembly was removed **(Figure 2.8b)**. Whilst the transfer line was in position, access to the vertical torch adjustment micrometer was restricted. This was overcome by the attachment of a steel collar with an Allan head nut which allowed adjustment *via* a small hole (8 mm) drilled in the top of the torch box **(Figure 2.8b)**. The GC was placed on a purpose-built trolley which incorporated a jack to allow adjustment of the GC to the correct height. The concentric alignment of the ICP

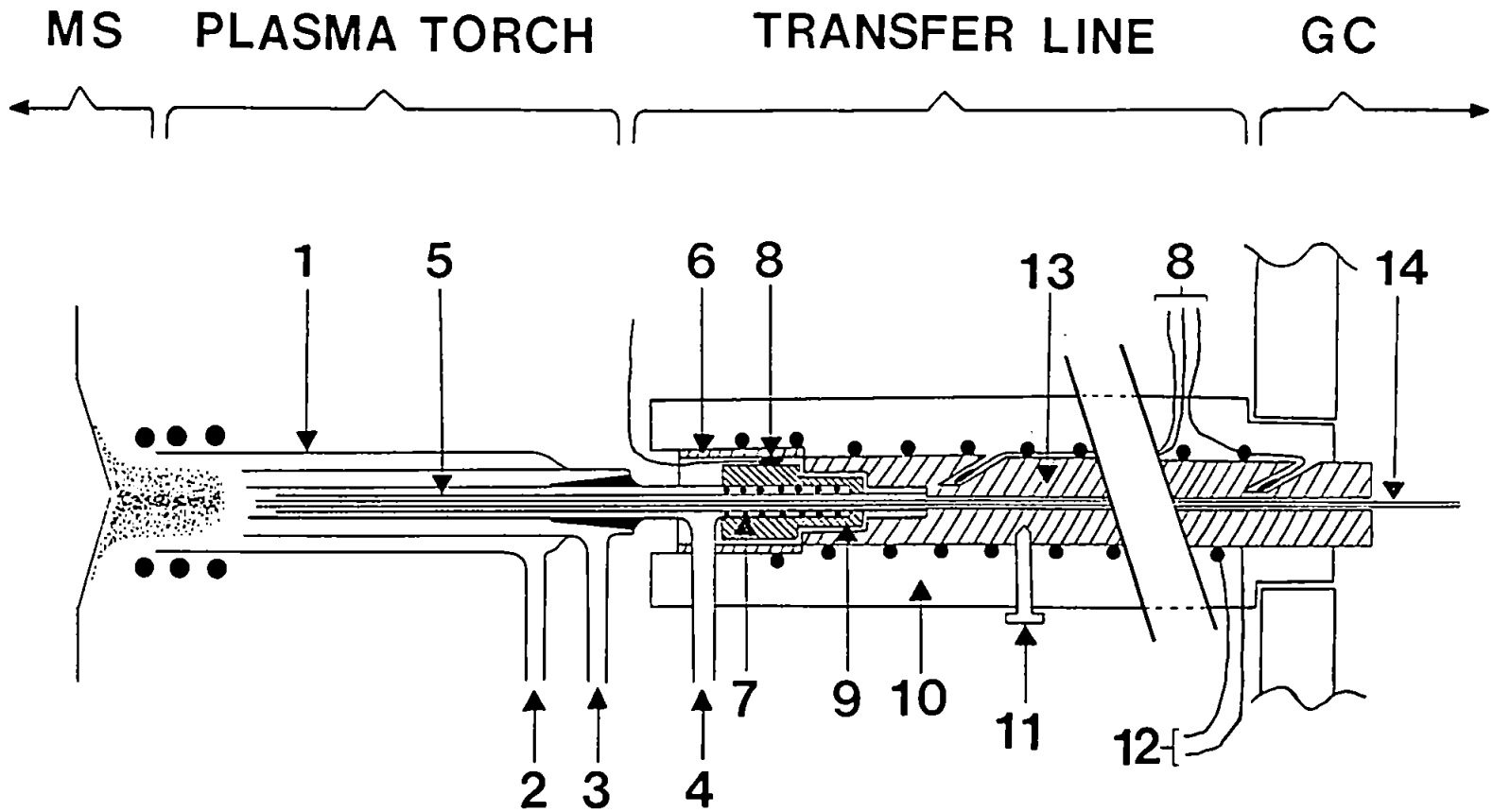


Figure 2.6 Transfer line Mark II and modified plasma torch (longitudinal section): **1**, demountable ICP torch; **2**, cooling; **3**, auxiliary gas; **4**, injector gas; **5**, stainless steel tube (1.59 mm o.d. x 0.51 mm i.d.); **6**, aluminium collar (37.9 mm o.d. x 25.4 mm i.d.); **7**, graphite tape; **8**, thermocouples; **9**, stainless steel reducing union (¼ inch to 1/16 inch); **10**, industrial pipe lagging; **11**, earthing point; **12**, heater leads to variable voltage supply; **13**, aluminium bar (1 inch x 600 mm) and **14**, capillary GC column.

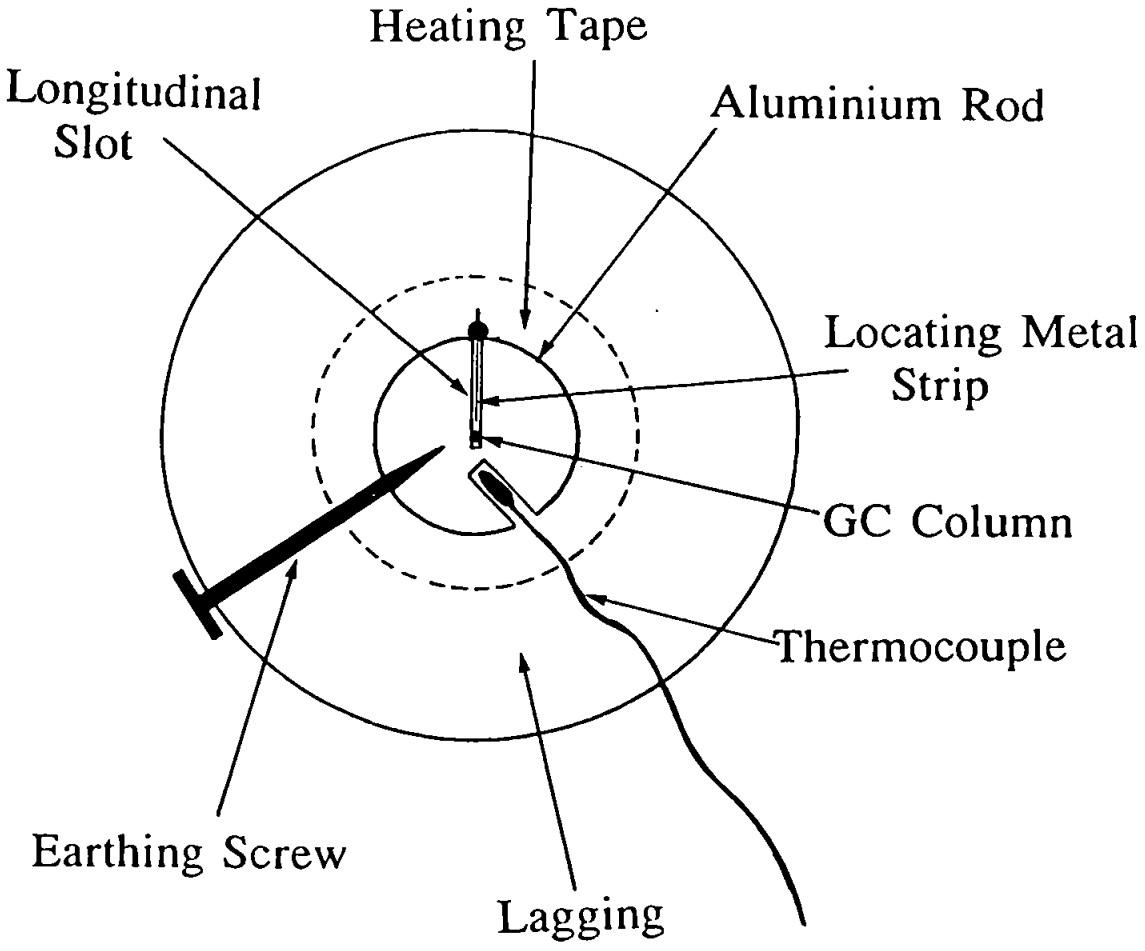
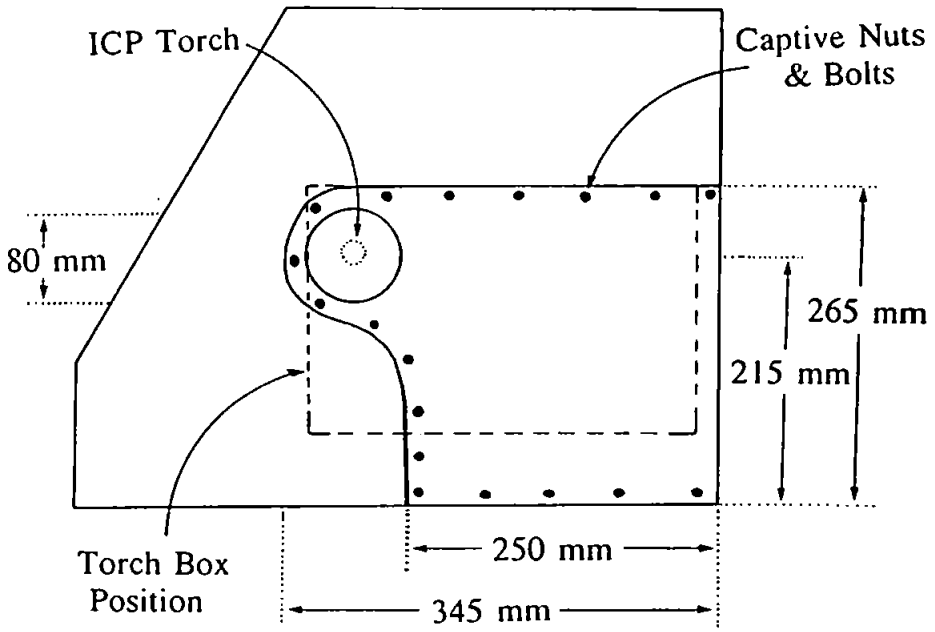


Figure 2.7 Transfer Line Mark II (transverse section)



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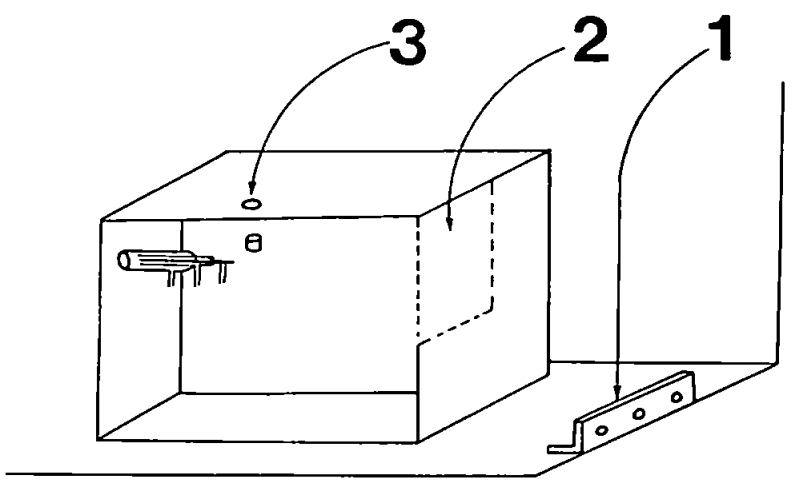


B

Figure 2.8 **(A.)** Modification to ICP-MS hood showing the detachable plate with 80 mm hole concentrically aligned with the plasma torch. **(B.)** Modification to ICP-MS instrument, showing: (1) the anchoring bracket for the detachable plate, (2) rectangular section of the torch box removed and (3) the position of the hole (8mm) for access to the vertical torch adjustment micrometer.

torch with both the sampler cone and transfer line was important; the main requirement being a lack of movement of the transfer line. A simple custom made lab-jack support for the line was found to provide sufficient stability. If the alignment was disturbed after instrumental optimisation, a significant reduction in response resulted.

2.5.2 Heating Capabilities of the Mark II Transfer Line

The transfer line was heated and the temperature systematically measured with increasing voltage **(Figure 2.9)**. Each reading was taken 3 hours after the voltage was changed to allow the temperature to equilibrate. The temperature range of transfer line was ideal for both normal and high temperature GC applications with a stability of ±2°C. The lower temperature of TC1 was due to the absence of heating tape and thinner lagging. This was necessary to allow the transfer line to fit into the GC oven through an entrance port.

In order to test this transfer line it was used without the ICP torch to couple together two gas chromatographs **(Figure 2.10a)**. Instrumental conditions are given in **Table 2.5**. A standard solution of n-C_{50} and n-C_{60} alkanes was co-injected with a solution containing a range of porphyrins. The high temperature GC capability of this transfer line is demonstrated by the elution of these relatively involatile compounds at 420°C **(Figure 2.10b)**. This experiment proved that the transfer line allowed adequate elution of the analytes from the GC. Thus any further problems of detection with GC-ICP-MS could be attributed to the ICP torch or ICP-MS rather than the transfer line.

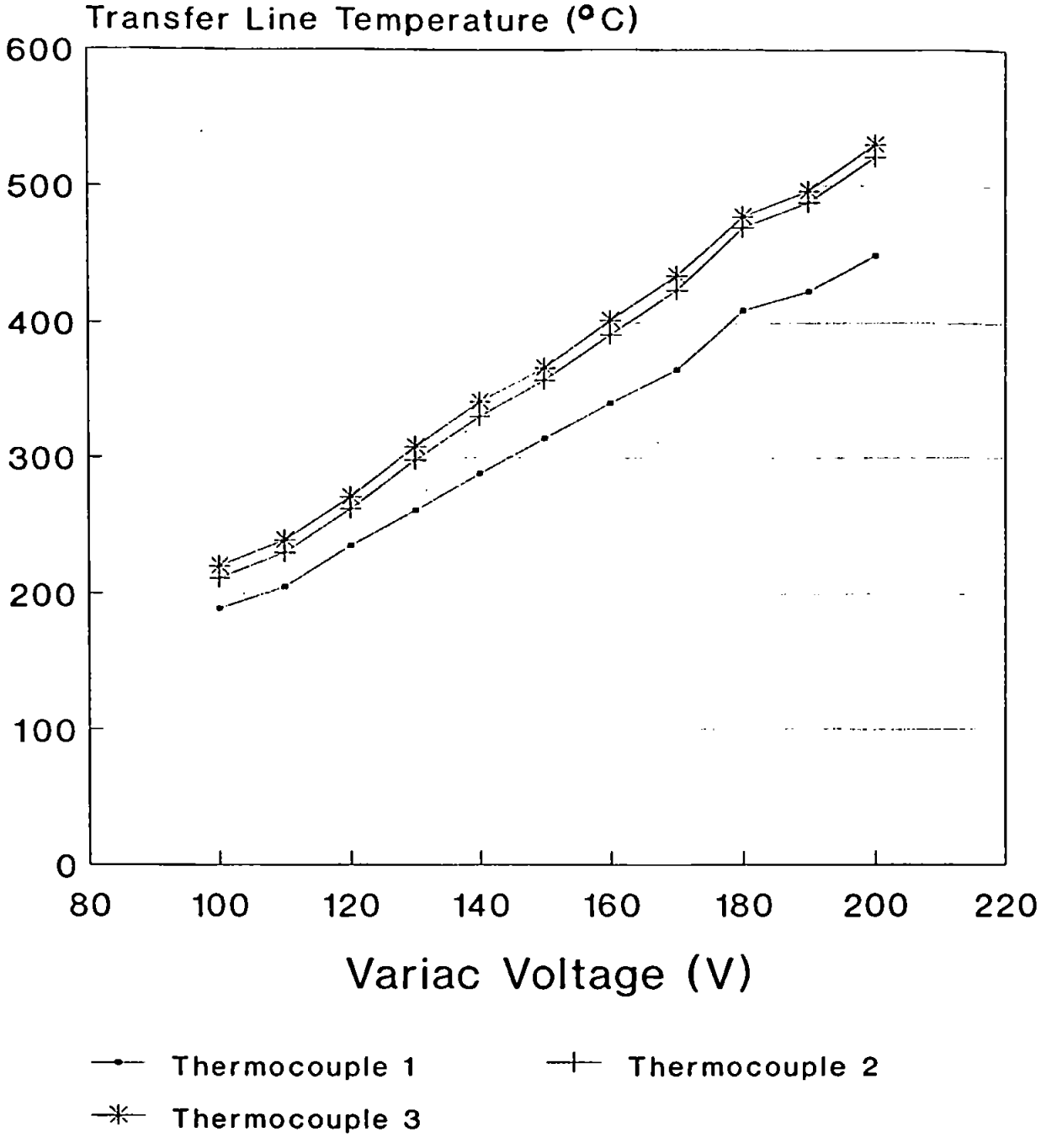


Figure 2.9 Transfer line temperature with increasing voltage; TC1, thermocouple 100 mm from the GC side; TC2 thermocouple mid point of the transfer line; TC3, thermocouple 100 mm from the base of the ICP torch.

Table 2.5 HT-GC coupled to HT-GC using the Mark II transfer line. Instrumental parameters.

Gas Chromatograph 1	
Column	SGE HT-5, 25 m x 0.32 mm i.d. x 0.1 μm film thickness
Carrier Gas	2 ml min^{-1} (85 kPa) He (measured at 300°C)
Oven Temperature Programme	60°C to 300°C (at 8°C min^{-1}) to 420°C (at 4°C min^{-1}), 10 min. iso.
Gas Chromatograph 2	
Oven Temperature Programme	420°C iso.
Detection	FID (at 437°C)
Transfer Line Temperature	
Thermocouple No.	Temperature (°C)
1	363
2	436
3	443

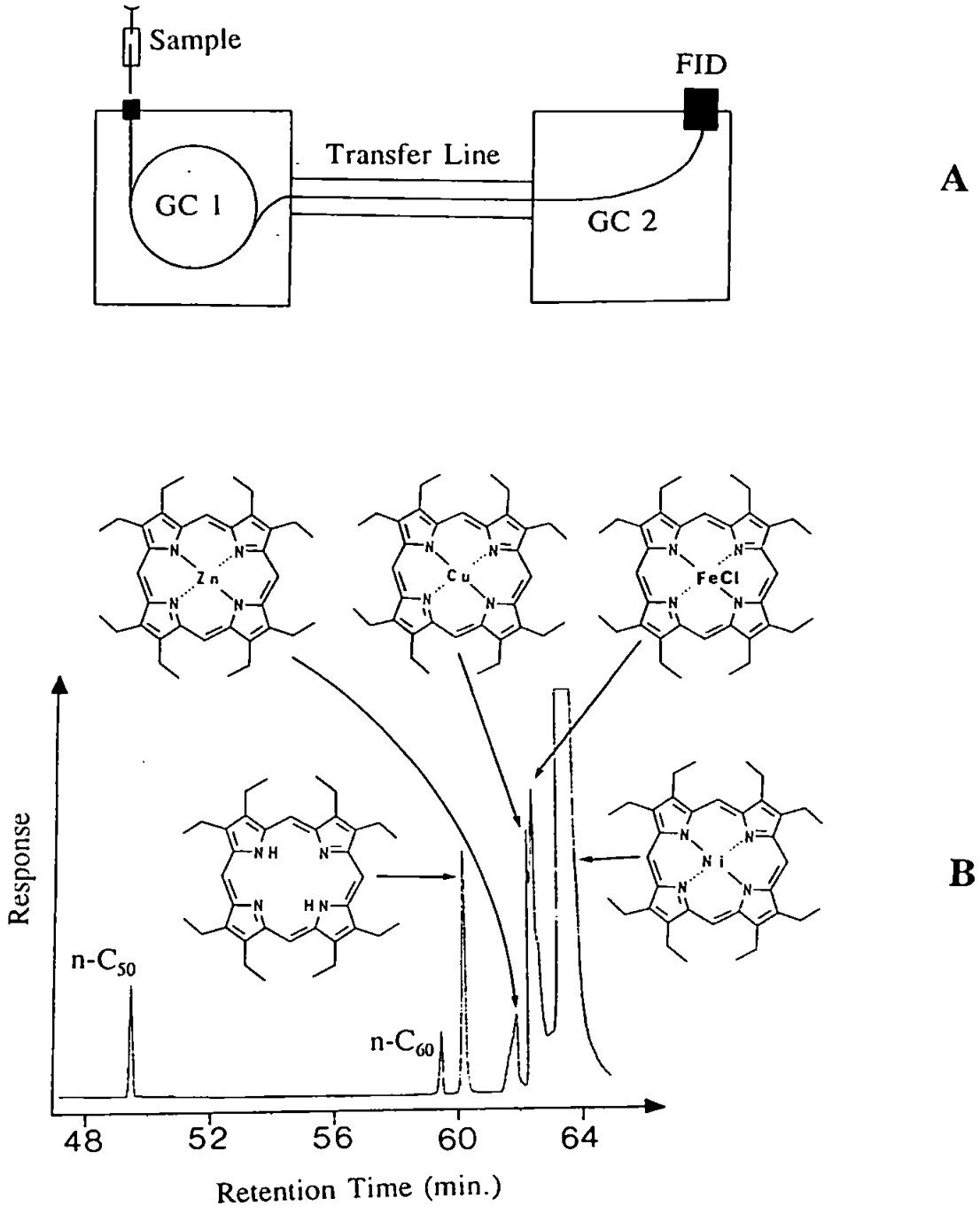


Figure 2.10 **(A.)** A schematic diagram of HTGC coupled to HTGC with FID using the Mark II transfer line. **(B.)** The chromatogram obtained shows elution of relatively involatile high molecular weight n-alkanes (n-C_{50} and n-C_{60}, 100 μg ml^{-1}, in THF, 0.5 μl) co-injected with a range of porphyrins (1 x 10^{-5} mol. ml^{-1} Ni-OEP, 1 x 10^{-6} mol. ml^{-1} other porphyrins, in CS_2, 0.5 μl).

2.5.3 Influence of the Position of the Capillary Column End

The distance of the end of the capillary GC column from the tip of the ICP torch injector was found to be important.

Instrumentation: Instrumental conditions are given in **Table 2.6.** The ICP-MS was tuned as before using the cold mercury vapour generator (section 2.3.3).

Initial precautions involved positioning of the end of the stainless steel insert and capillary column 80 mm from the tip of the injector to prevent the possibility of the plasma arcing. Analysis of a 10-fold diluted (in n-hexane) solution of SRM 1637a(II) by ion-selective monitoring for lead (m/z 208) produced a single peak chromatogram **(Figure 2.11a)**, identified as TEL. At a distance of 50 mm an identical single peak chromatogram resulted.

However at a distance of 2 mm a significant increase in the signal:noise ratio meant that a second minor component was detected **(Figure 2.11b)**. These have been identified by previous workers as TML (1.5%) and TEL (98.5%) [174]. Even though the SRM was stored as recommended, the possibility exists that the teraalkyllead was not originally added in these ratios but that the mixture may be a result from photodecomposition, volatilisation or conversion of TEL to TML.

Table 2.6 Influence of the position of the capillary column tip using the Mark II transfer line. Instrumental parameters.

Gas Chromatography		
Column	SGE HT-5 (25 m x 0.32 mm i.d. x 0.1 μm film thickness)	
Carrier Gas	2 ml min^{-1} (85 kPa) helium (at 110°C)	
Temperature Programme	40°C (1 min. iso.) to 180°C at 10°C min^{-1}	
Injection	0.5 μl on-column	
Transfer Line Temperature		
Thermocouple	**Column distance from tip of the injector**	
	80mm	2mm
1	213°C	228°C
2	271°C	285°C
3	284°C	280°C
4	248°C	245°C
ICP-MS Similar conditions to those in **Table 2.2**		
Dwell	163840 μs	
Data acquisition time	11.2 min.	

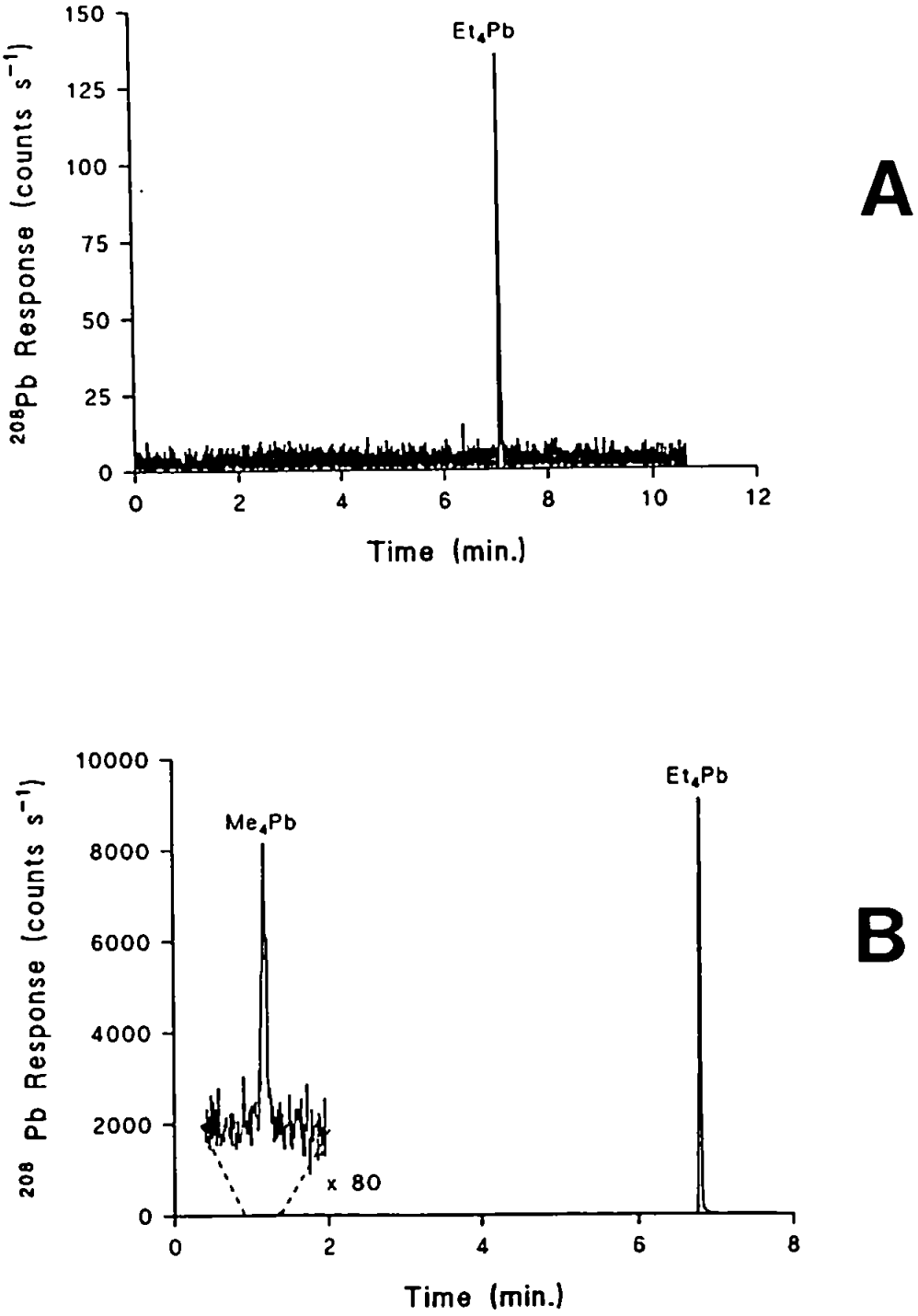


Figure 2.11 Influence of the position of the column end from the tip of the injector (mm). Ion selective chromatograms (m/z 208) of NBS-SRM 1638a. **(A.)** 80mm (0.962 ng as Pb) only showing TEL. **(B.)** 2 mm (0.745 ng as Pb) showing both TEL (98.5%) and TML (1.5%).

2.5.4 Attempted HT-GC-ICP-MS of Metallopporphyrins using the Mark II Transfer Line

The coupled system was set up as described in section 2.5.3 with the capillary column 2 mm from the tip of the torch injector. The ICP-MS was tuned for (m/z 58) using the signal arising from the constant ablation of nickel from the sample skimmer cones. GC conditions were similar to those used previously **(Table 2.5)**. Transfer line temperatures were: TC1, 415°C; TC2, 434°C; TC3, 436°C and TC4, 420°C. Data acquisition parameters were: SIM (m/z 58), dwell time (327680 μs) and data acquisition time 2 x 22.3 min. started 47 min. after the point of injection.

A solution of Ni-OEP (0.39 mg ml^{-1} as Ni, in CS_2) was injected (0.5 μl). No signal was observed over a 44.6 minute period.

The coupling was disassembled and the last 135 mm of capillary column stationary phase extracted / washed with DCM (3 ml). The UV-VIS absorption spectrum of the washings was recorded **(Figure 2.12)**. The spectum was identical to that Ni-OEP (Soret band, 390 nm; α-band, 550 nm; ß-band, 515 nm) confirming the condensation of involatile porphyrins in the length of column contained within the torch injector and not in the transfer line.

2.6 Coupling and Transfer Line-Mark III

2.6.1 ICP-Torch Design

The preceding experiments obviously demonstrate the need for adequate heating of the portion of column contained within the torch injector in order to prevent condensation of the metalloporphyrins within the column

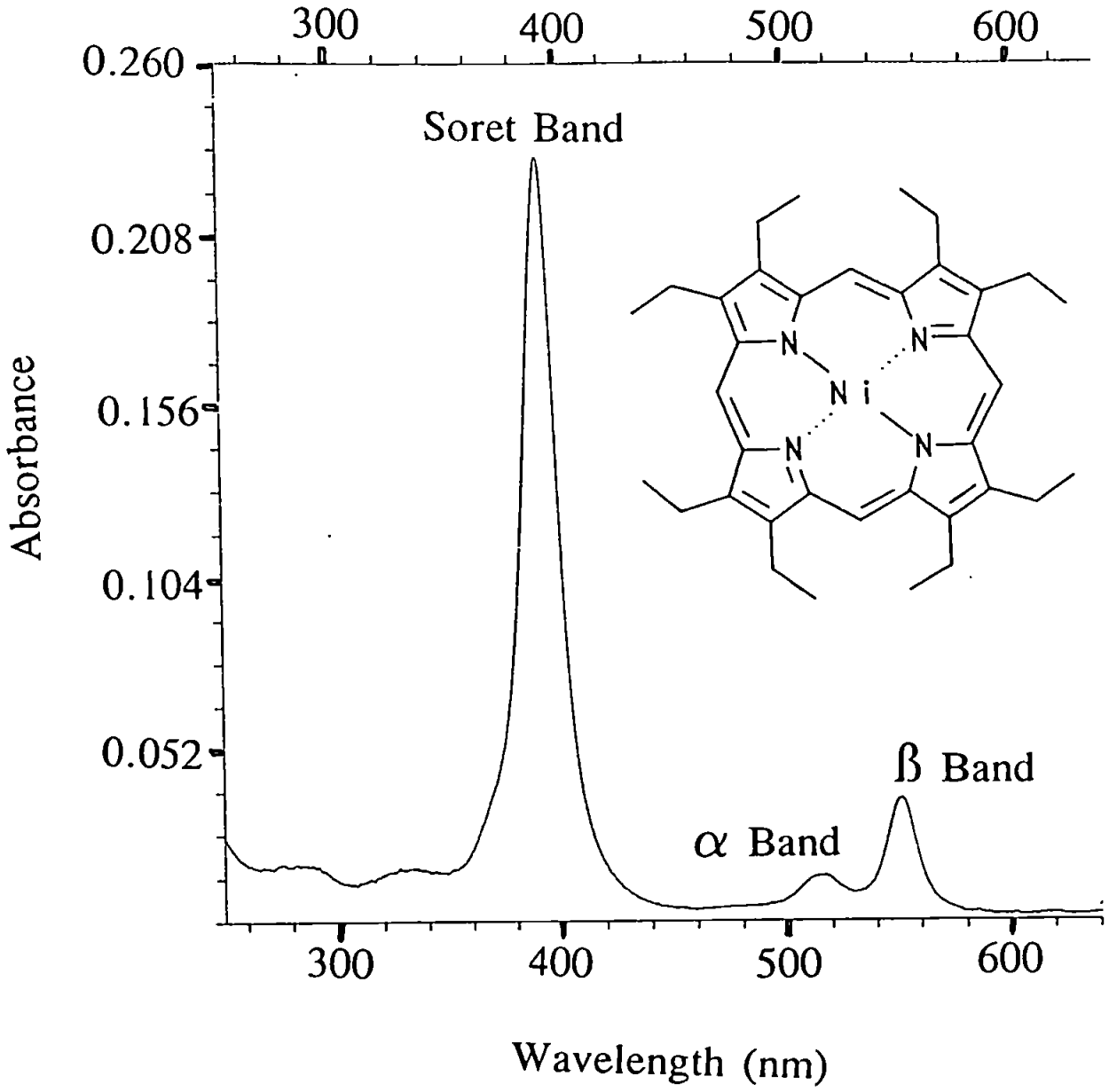


Figure 2.12 UV-VIS absorption spectrum of Ni-OEP, confirming the condensation of porphyrins in the column contained within the torch injector.

(section 2.5.4). Therefore it was decided to adopt a heating system used by Parry (1989) [175] which relies on the resistive heating of a stainless steel capillary. This system included a stable and controllable heat source and temperature monitoring during operation.

Details showing the resistively heated stainless steel tube inside a modified ICP torch injector is given **(Figure 2.13)**. To incorporate all of the electrical components inside the injector, a demountable torch was custom made (H. Baumbach and Co. Ltd., Ipswich, UK) with the same aspect ratio [176] as a conventional torch. To be able the plasma to be punctured and laminar flow achieved, the final 25 mm of the injector was narrowed to a diameter of 3 mm.

The heating source was a rewound transformer built in-house (4 V, 0-30 A maximum output), equipped with a temperature feed back loop circuit **(Figure 2.13)**. Two high temperature "type K" thermocouples (RS Components, Northamptonshire, UK) were silver - soldered onto the mid point of the stainless steel tube, the first being used to complete the feed back loop circuit (ensuring constant temperature) and the second to record the temperature (using a digital thermometer). These two thermocouples were disconnected before plasma ignition as a precaution to prevent the high voltage Tesla spark from damaging the digital thermometer and heating source.

Initially this system was tested independently from the ICP-MS. The temperature range of the stainless steel tube insert was 256-480°C (±5°C). However the feedback circuit failed when the coupled system was *in situ* (due to the close proximity of the two thermocouples to the strong r.f.) resulting in ineffectual heating.

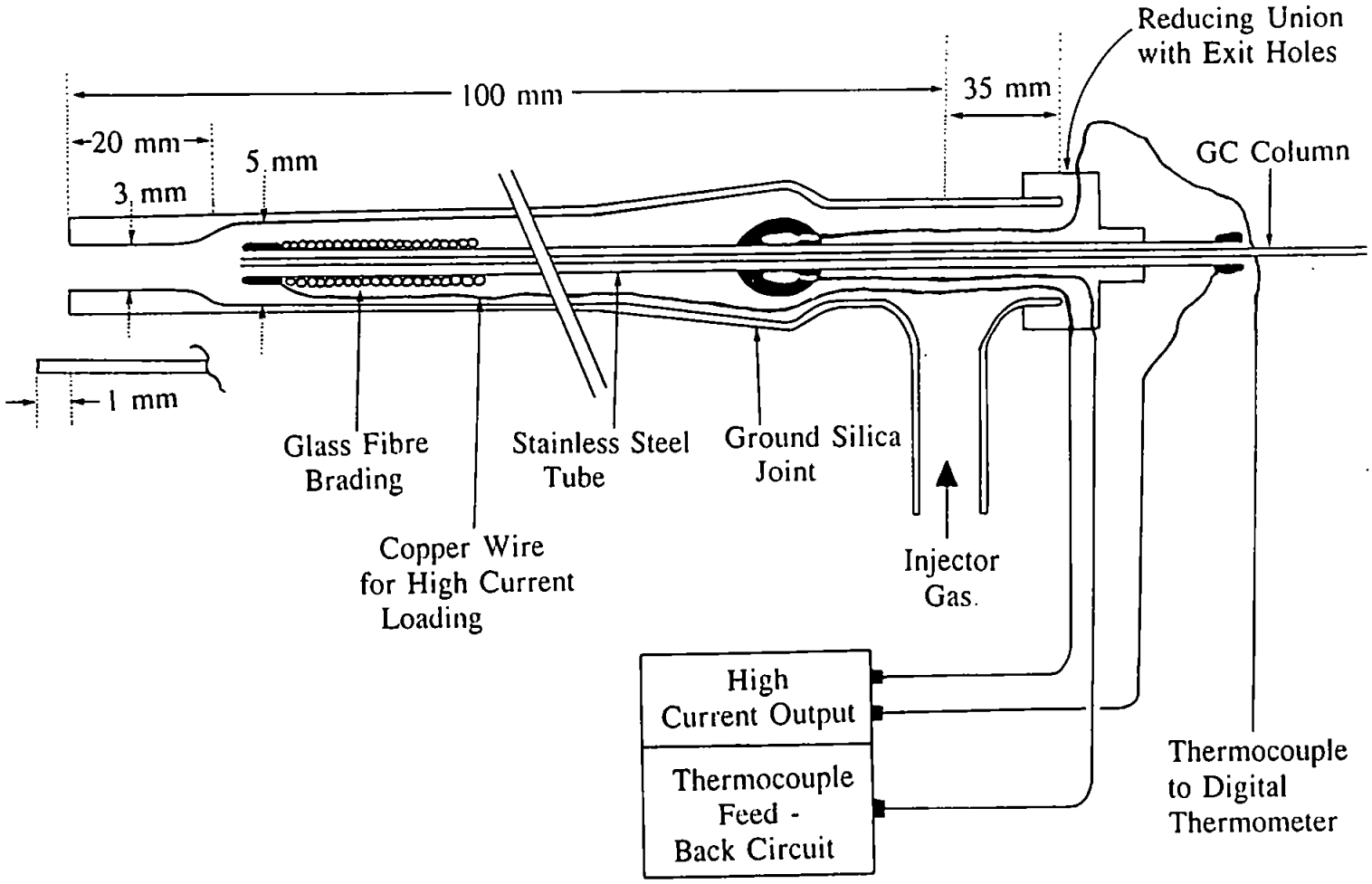


Figure 2.13 Modified plasma torch (Mark III) showing the resistively heated stainless steel tube insert.

As a result of this, the heating source was replaced with a similar, purpose-built transformer, but without temperature was controlled by manually varying the current output and monitored using only one thermocouple. The temperature range achieved was from ambient to 580°C (±40°C).

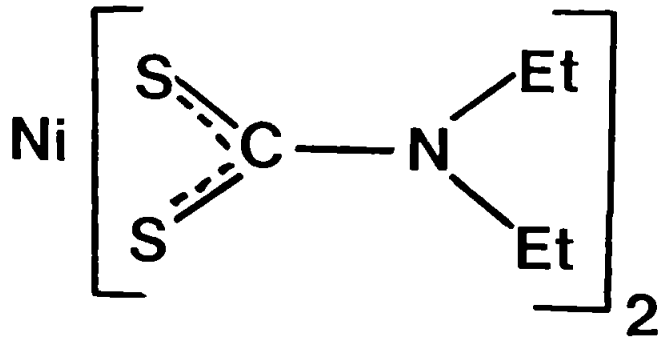
2.6.2 HTGC-ICP-MS using the Mark III Transfer Line

The coupled system was set up as described previously (section 2.5.4.). Instrumental conditions are given **(Table 2.7)**. No response to nickel (m/z 58) was observed when Ni-OEP (36 μg ml^{-1} as Ni, in CS_2) was injected, probably due to cold spots which caused condensation of the analyte.

To investigate this theory, the nickel-containing chelate nickel diethyldithiocarbamate ($Ni(Dt)_2$) with a lower retention index (RI = 3422) than Ni-OEP (RI = 6282) was synthesised and examined by HTGC-ICP-MS. The instrumental parameters used were similar to those used earlier **(Table 2.7)**. $Ni(Dt)_2$ was successfully eluted **(Figure 2.14)**, this was not possible when the insert was not heated. Analysis of few trace element species with a retention index as high as 3422 have been reported previously by GC - element selective detectors; thus even though the porphyrin analysis was not successful at this stage, the modified HTGC-ICP-MS coupling represents a significant advance in the analytical capabilities for speciation determinations.

Table 2.7 HT-GC-ICP-MS of Ni-OEP, using the Mark III transfer line. Instrumental parameters.

Gas Chromatography	
Column	SGE HT5 (12m x 0.32 mm i.d. x 0.1 μm film thickness)
Carrier Gas	2 ml min^{-1} helium (using CP-CF module)
Temperature Programme	50°C to 420°C (at 36°C min^{-1}) 20 min. iso. at 420°C
Injection	1 μl on-column
Transfer Line Temperature	
Thermocouple	**Temperature (°C)**
1 2 3 + (Stainless steel insert)	366 405 420 410
ICP-MS	
Mode	single ion monitoring (m/z 58)
Injector gas	1.37 l min^{-1}
Dwell	163840 μs
Data acquisition time	2 x 11.2 min. (started at 8 min. after injection)



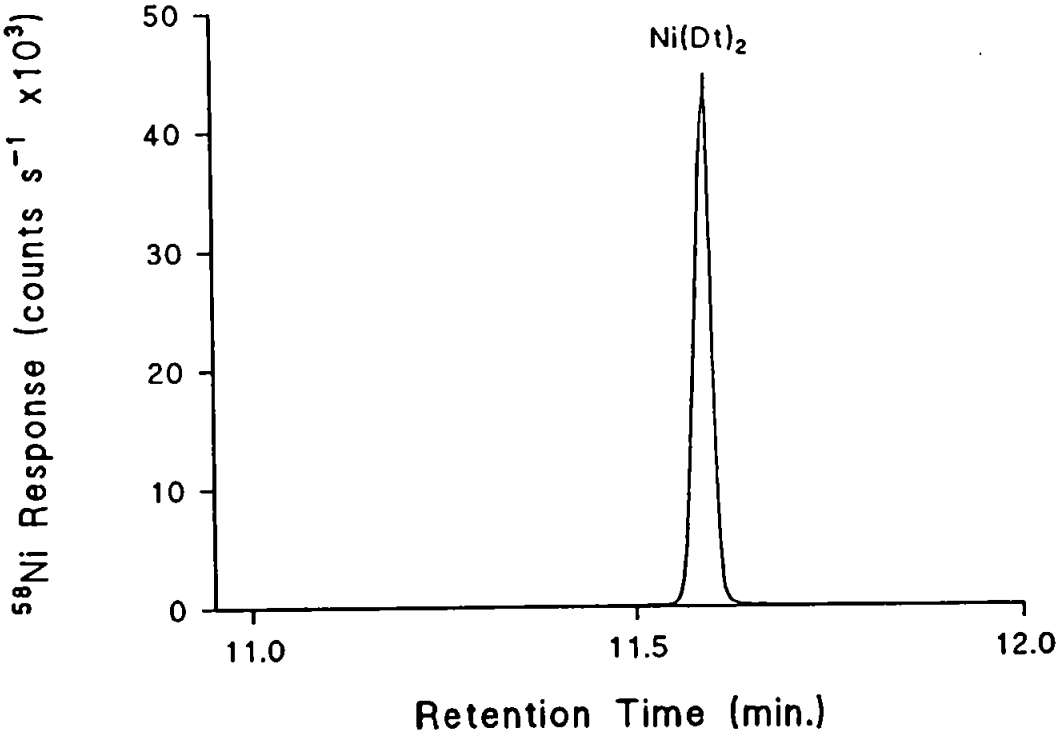


Figure 2.14 GC-ICP-MS capability of the Mark III transfer line. Ion selective chromatogram (m/z 58) showing the elution of nickel diethyl-dithiocarbamate (0.2 μg ml^{-1}). GC column 5m x 0.32 mm i.d. x 0.1 μm film thickness (SGE, HT5). GC oven temperature programme was 50°C to 300°C (10 min. iso.) at 20°C min^{-1}. Transfer line temperatures were TC1, 290°C; TC2, 325°C; TC3, 335°C; TC4, 265°C. DCM solvent, 1.0 μl injected.

2.7 Conclusions

Capillary GC has been successfully coupled to ICP-MS. A series of progressively improved transfer lines have been developed and applied to the detection of organolead and organonickel species. Many of the criteria listed in Section 2.1 have been fulfilled.

The final interface design (Mark III transfer line) is of simple construction, is robust, reliable and inexpensive. The system allows on-line direct coupling of the GC column to the ICP torch over a large temperature range (ambient - 550°C, ± 2°C for the transfer line and ambient - 580°C, ± 40°C for the resistively heated stainless steel insert in the ICP torch injector), is light-weight (approximately 800 g; dimensions 600 mm x 62 mm o.d.), requires a relatively short installation time (approximately 2 hours) and is readily demountable.

The ICP-MS was modified by removal of a panel from the hood and torch box through which the transfer line could pass over the shortest possible distance. The ICP-MS was tuned using a continuous signal of mercury (from a cold mercury vapour generator, gas/liquid separator) and the constant ablation of nickel from the sampler and skimmer-cones for Pb (m/z 208) and Ni (m/z 58) detection respectively.

It was found that the column outlet needed to be positioned at the tip of the torch injector to prevent absorption or condensation of the analyte (tetraalkyllead compounds) on the walls of the injector.

The high temperature GC capabilities of the Mark II transfer line were demonstrated by the elution of relatively involatile metalloporphyrins and high molecular weight alkanes (<u>n</u>-C_{50} and <u>n</u>-C_{60}) at 420°C, using coupled GC-GC with flame ionisation detection. However due to condensation of these compounds in the length of the column contained within the torch injector

HTGC-ICP-MS of metalloporphyrins was not achieved.

However GC-ICP-MS of relatively involatile chelates was accomplished. Using a resistively heated stainless steel insert contained within the torch injector, a nickel complex ($Ni(Dt)_2$) with a higher retention index (RI > 3400) than many organo-metals determined by previous methods was eluted.

CHAPTER THREE

DETERMINATION OF TRACE METAL SPECIES BY CAPILLARY GC-ICP-MS

3.0 DETERMINATION OF TRACE METAL SPECIES BY CAPILLARY GC-ICP-MS

3.1 Introduction

Much of the literature concerning GC-coupled techniques describes the speciation of relatively volatile and thermally stable species (e.g. tetraalkyllead, organotin and alkylmercury compounds). These compounds are well suited to GC separation and are of considerable environmental importance.

3.1.1. Organometallic compounds in the environment

Lead: Lead is added to fuel in varying proportions of five tetraaklyllead compounds as antiknocking agents. Their environmental relevance has been reviewed [177]. Such compounds are highly neuro-toxic through skin absorption, inhalation and injection [178]. They have been found to be present in air, water, sediments and biota, with higher concentrations in urban areas. There is evidence that Pb^{2+} salts can be microbially alkylated in natural aquatic sediments [179]. As a result several coupled techniques have been developed for alkyllead analysis. These have been reviewed [52,180]. However most of these procedures utilise packed column GC (with consequent low chromatographic resolution and requirement for high analyte concentrations).

Tin: Organotin compounds have been widely used in a variety of applications; as thermal stabilisers for polyvinyl chloride, as catalysts in the production of polyurethane foams, in vulcanisation of silicone rubbers, as biocides and in antifouling paints [181]. The application toxicity, environmental behaviour, bioalkylation and legislation concerning organotin

compounds have been reviewed [57,182-184]. They are toxic though inhibition of oxidative phosphorylation, and existing data indicates that toxicity increases with progressive introduction of organic groups on the tin with a maximum toxicity value for trioganotin (R_3SnX) compounds. Microbial methylation of inorganic Sn^{2+} and Sn^{4+} have been observed in waters and sediments. Also organotins have been found to degrade by the progressive removal of the organic groups from tin in the order, $R_4Sn \rightarrow R_3SnX \rightarrow R2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4$ which enables the environmental fate of these compounds to be studied. Speciation information is necessary in order to assess the effect of these compounds on the environment, and this requires sensitive analytical methods capable of species selective detection at low pg levels. Thus a variety of interfaced GC element selective techniques have been developed [52,184,185]. Recently, organotin compounds have been monitored by GC-MIP-MS [162], SFC-ICP-MS [166] and HPLC-ICP-MS [186]. However poor chromatographic resolution and/or poor peak shape were generally observed.

Mercury: Inorganic mercury is mainly used in battery manufacture, chlorine production and dentistry. Organomercury compounds have been used as biocides and catalysts for urethane and vinyl acetate production [184]. The behaviour of mercury in natural systems has been documented [8]. An example of the toxicity of organomercury compounds has been described previously (Section 1.1). The need to understand the environmental cycling of mercury has led to the search for sensitive and specific analytical methodologies. Techniques for the detection and determination of mercury-containing species have involved coupling of GC with atomic spectrometry [52,184,187], thus avoiding contamination and interferences arising from

molecular rearrangements. Hydridization trapping techniques are more sensitive because it is a total sampling (i.e. preconcentration) technique, whereas with alkylation only an aliquot of the sample is used.

3.1.2 Derivatization

Often, a derivatisation method is used prior to GC injection to increase the volatility of organometallic species. Examples includes conversion to hydrides or alkylation [31,180,188].

A range of elements (eg. As, Pb, Se, Sn) are easily converted to volatile hydrides by reaction with sodium borohydride ($NaBH_4$). The hydrides may be trapped cryogenically under liquid nitrogen for later separation and detection or they may be extracted directly into a non-aqueous solvent for GC [189]. However a major source of errors is the loss of hydrides by irreversible adsorption to the internal walls of the apparatus [190] and the reaction of $NaBH_4$ has been found to be suppressed in the presence of diesel oil and sulphides which occur at high levels in some environmental samples (eg. sediments) [191]. An alternative approach is the purge-trap procedure [47].

Two principal methods are used for the alkylation of metal species: the reaction with Grignard reagents or with sodium tetraethylborate.

Metals of Group IVA (ie. Ge, Sn, Pb and their ionic derivatives $R_nM^{(4-n)+}$), can be alkylated by Grignard reagent (equation 1) to the tetraalkyl - substituted derivatives which are more volatile and stable for GC separation.

Grignard alkylation techniques applied to the speciation of organometallic compounds include methylation [46], ethylation [2], propylation [192], butylation [67,193] and phenylation [68,194].

$$R_nM^{(4-n)+} + (4-n)'R_nMgCl \rightarrow\rightarrow\rightarrow \text{ in THF or diethylether } \rightarrow\rightarrow\rightarrow$$
$$\rightarrow\rightarrow\rightarrow R_nM'R_{n(4-n)} + (4-n)Mg^{2+} + (4-n)Cl^- \qquad \text{(eqn. 1)}$$

Alkylation using sodium tetraethylborate has been applied to organotin [48] and organomercury [63] (equation 2) compounds.

$$CH_3Hg^+ + NaB(C_2H_5)_4 \rightarrow\rightarrow\rightarrow$$
$$\rightarrow\rightarrow\rightarrow CH_3HgC_2H_5 + Na^+ + 3C_2H_5 \qquad \text{(eqn. 2)}$$

Alkylation does not require extensive sample clean-up procedures and unambiguous identification and quantification of the products can be achieved.

3.1.3 Aims

This chapter investigates the speciation and detection of organo - lead, tin and mercury species using the capillary GC-ICP-MS developed and gives Figures of Merit for the determinations. These compounds include tetraalkylleads (in fuel), organotins (in water and a standard reference material harbour sediment) and a pure organomercury compound (diethylmercury). Other organometallic compounds studied include iron containing ferrocene and metallo - diethyldithiocarbamates.

3.2 Tetraalkyllead Speciation

3.2.1 Experimental

The materials and reagents used are listed in Appendix A. The Mark II transfer line and ICP torch were used throughout. The transfer line temperature was maintained between; TC1, 190-213°C; TC2, 224-271°C, TC3, 237-284°C, TC4, 245-250°C. The ICP-MS was tuned and optimised for lead detection (m/z 208) using the signal from the cold mercury vapour generator (m/z 202) as described previously (Section 2.3.3), general ICP-MS operating conditions have been given **(Table 2.6)**. Single ion monitoring was at m/z 208.

3.2.2 Response of ^{208}Pb with Time

Injections of a series of known amounts of lead in the reference fuel (NBS SRM 1637 II) did not give reproducible results (ie. external calibration was not possible), the reason was a decrease in detector sensitivity with time **(Fig. 3.1)**.

The continuous signal from cold vapour mercury generator, was also recorded at the end of each chromatographic run **(Fig. 3.2)** which also decreased with time. Approximately 70% reduction in detector sensitivity was observed in each (ie. both Hg and Pb signal) and a stable response was attained only after 100 minutes.

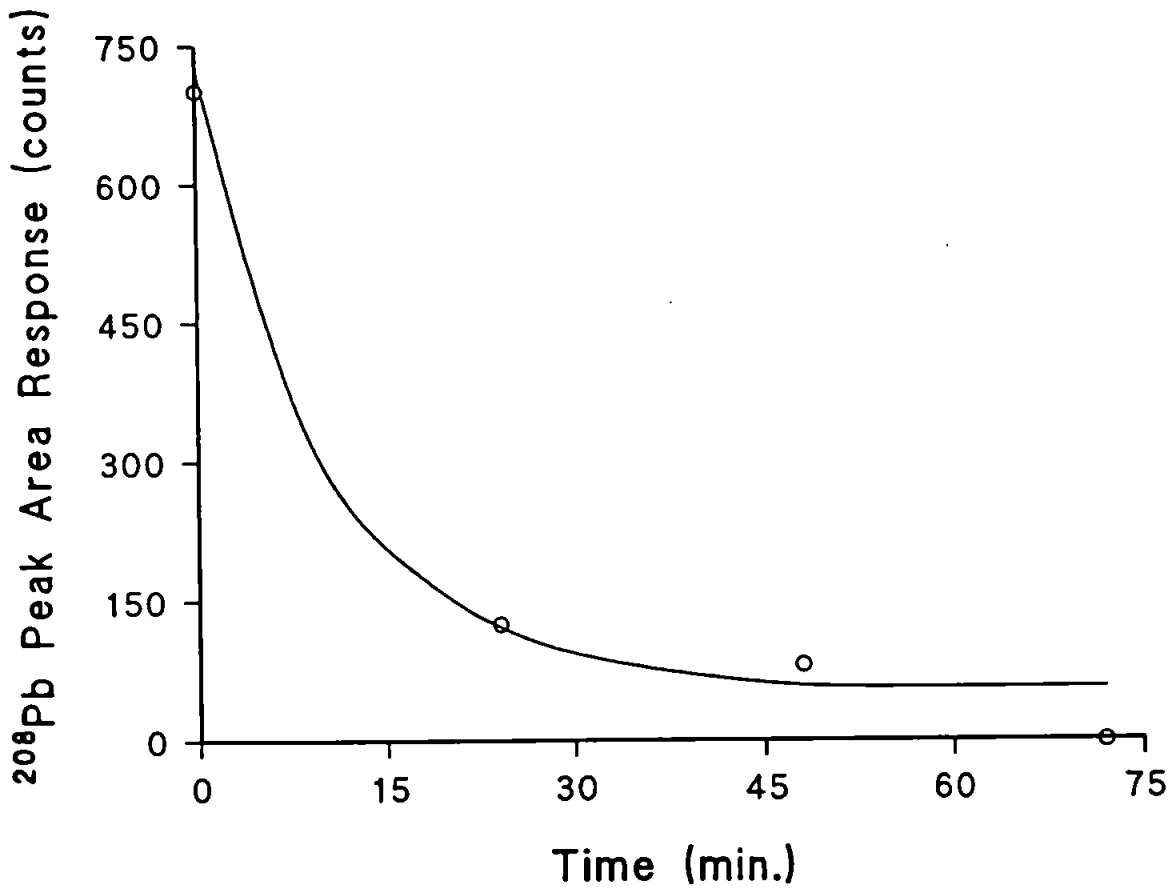


Figure 3.1 The decrease in TEL signal (1.29 μg ml^{-1}, as Pb) with time. GC oven programme = 40°C (1 min. iso.) to 180°C (5 min. iso.) at 10°C min^{-1}, hexane solvent, 0.5 μl injected

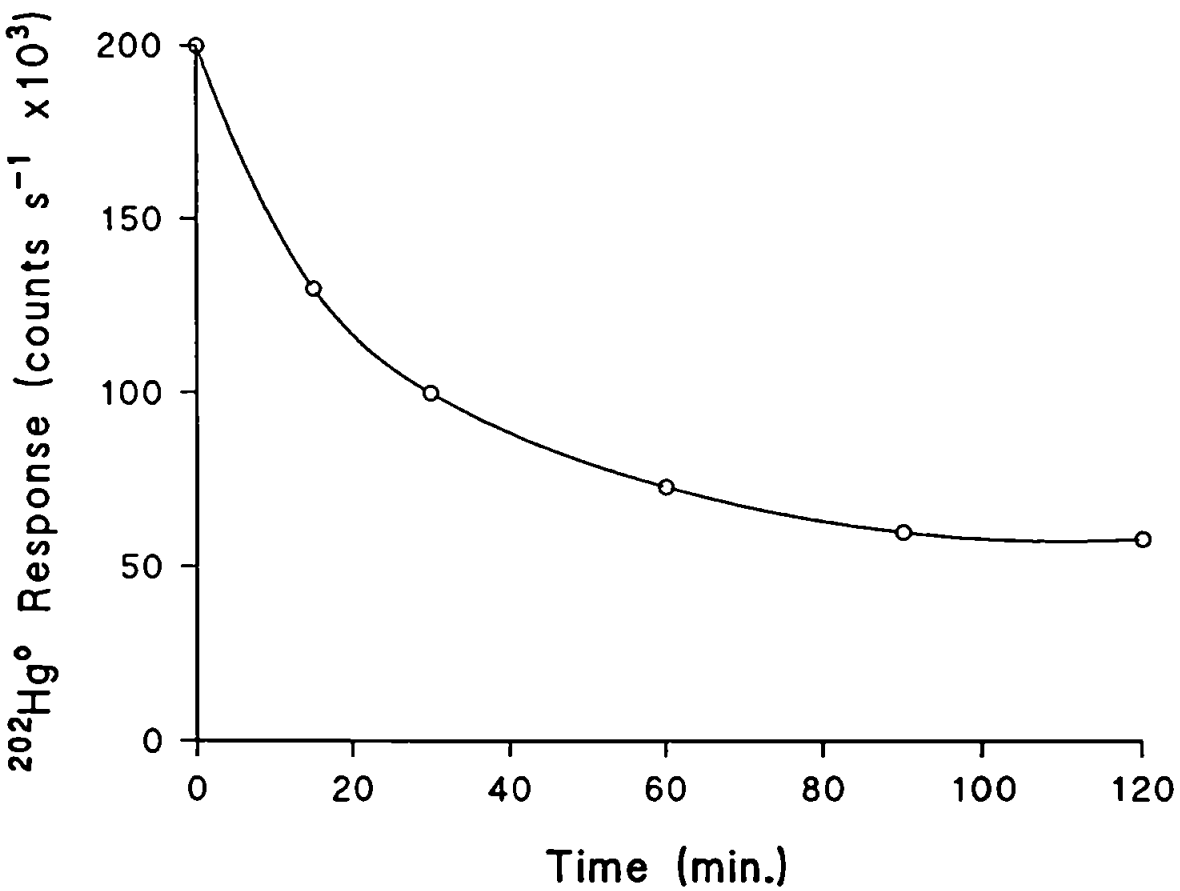


Figure 3.2 The decrease in the continuous cold mercury vapour signal with time.

The cause was thought to be carbon deposition on the sampler and skimmer cones from successive injections of hexane solvent, resulting in some of the absorption of analyte. Therefore oxygen was added to the injector gas to oxidise the carbon thus preventing any possible deposition. However excess oxygen also leads to the rapid erosion of the sampling cone. Surprisingly the same decrease in the peak area of TEL was observed **(Fig. 3.3)** and it was concluded that the decrease was not caused by carbon deposition on the cones. The ICP-MS detector simply took approximately 100 minutes to stabilise. All subsequent analyses were performed after this 100 minutes of stabilisation.

3.2.3 Figures of Merit for Tetraethyllead

Initial Figures of Merit were established for TEL **(Table 3.1)**. The limit of detection (LOD) (0.7 pg s^{-1}, 4.7% RSD) and correlation coefficient (0.9943) were calculated from ten replicate injections **(Fig. 3.4)** and a standard dilution series **(Fig. 3.5)**.

Subsequently improved Figures of Merit, including the linear dynamic range **(Table 3.1)**, were obtained using authentic TEL from commercial suppliers. It was found that doubling the volume injected to 1 μl, gave a LOD and percent RSD of approximately half the values obtained earlier **(Table 3.1)** probably because the precision of manual on-column injection is proportionally improved as larger volumes are used.

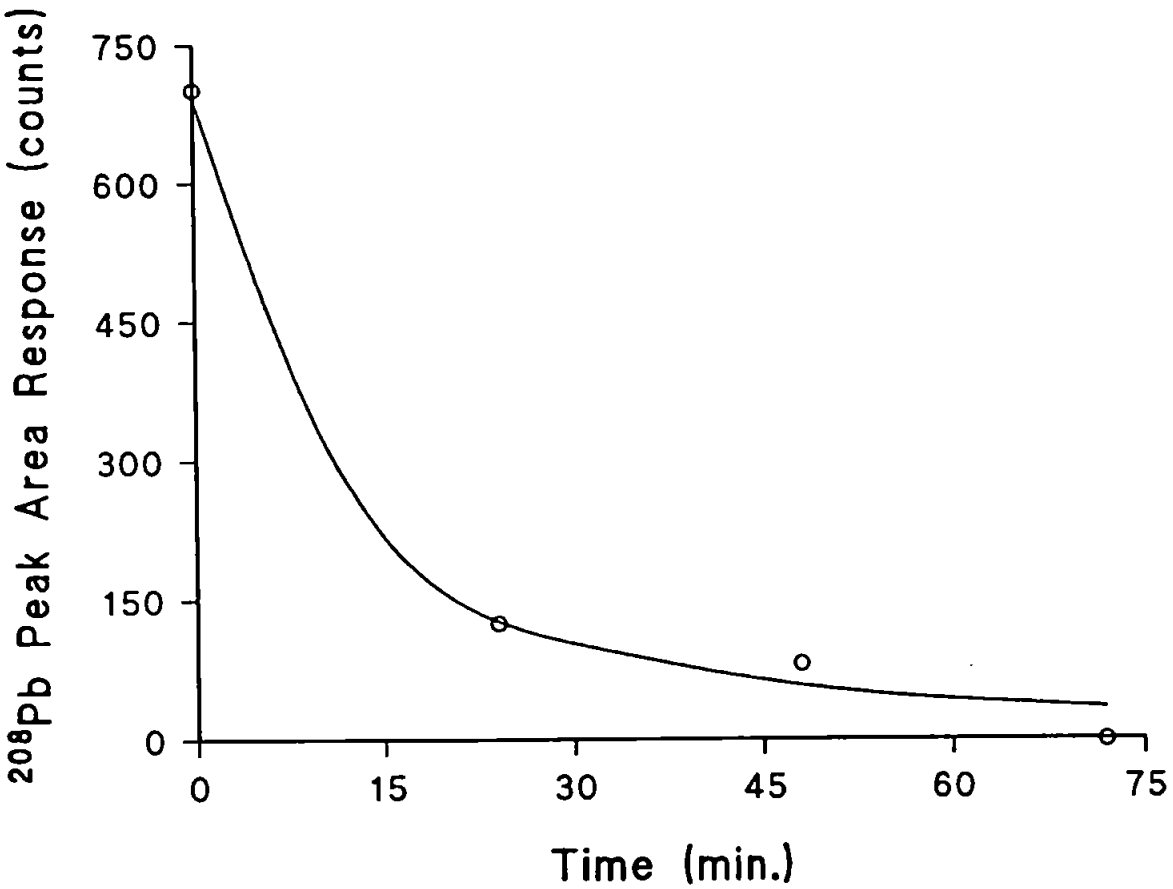


Figure 3.3 The decrease in TEL signal with time. 40 ml min^{-1} (4%) O_2 added to the injector gas. Same conditions used as in Figure 3.1, except 0.194 μg ml^{-1} (as Pb) was injected.

Table 3.1 Figures of Merit for tetraethyllead (TEL) by capillary GC-ICP-MS for 0.5 μl and 1.0 μl on-column injections (using ten replicate injections of NBS SRM 1637 and authentic TEL standard respectively). GC oven temperature programme = 60°C iso., hexane solvent, LOD is defined to be 3σ of the net peak areas of the replicate injections.

Volume Injected	**0.5 μl**	**1.0 μl**
Detection limit (3σ) (pg s^{-1})	0.7 (measured at 50 pg)	0.34 (measured at 100 pg)
Percent RSD	4.7%	2.1%
Correlation coefficient	0.9943 (measured up to 1.9 ng)	0.9999 (measured between 2-100 pg)
		0.9999 (measured between 100 pg-10 ng)
Linear dynamic range (orders of magnitude)	nd	5

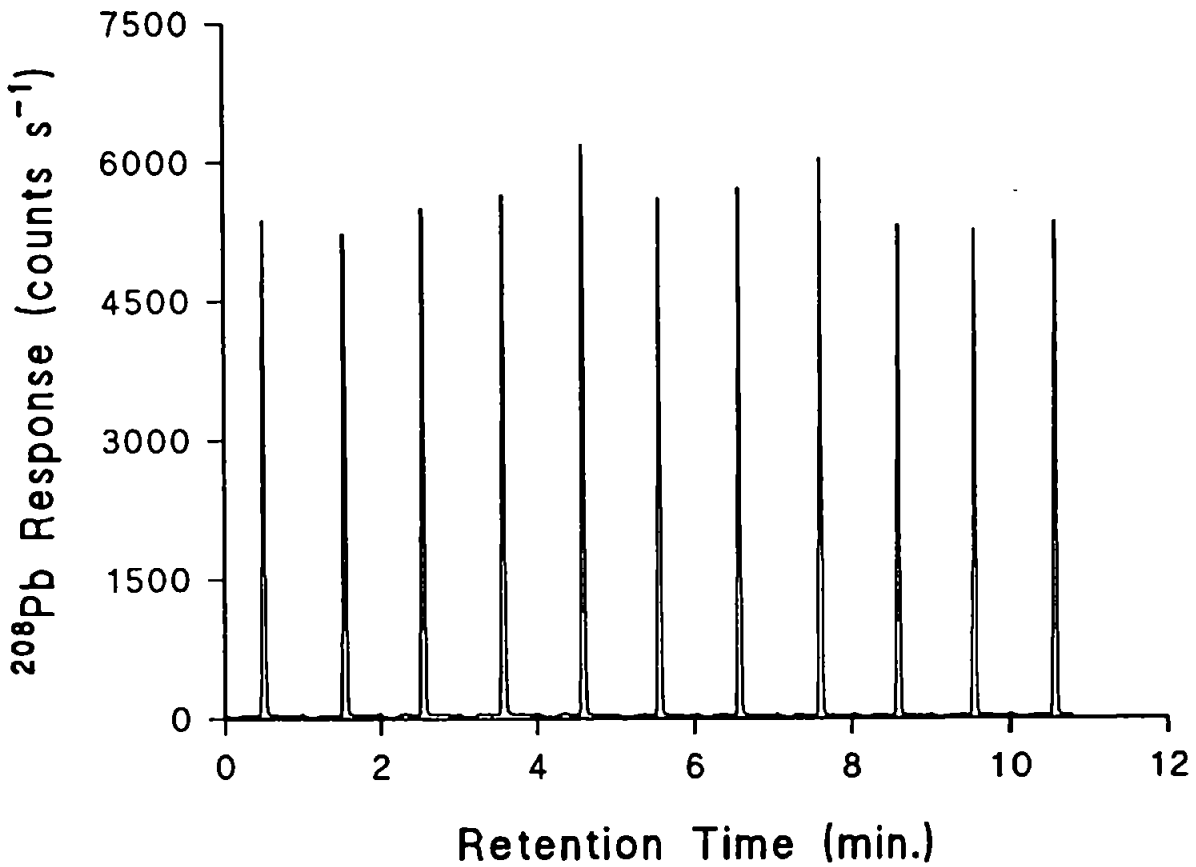


Figure 3.4 Ion chromatogram (m/z 208) of ten replicate injections of authentic tetraethyllead standard, 100 ng ml^{-1} (as Pb), 1.0 μl injected, GC oven temperature programme = 60°C iso., hexane solvent.

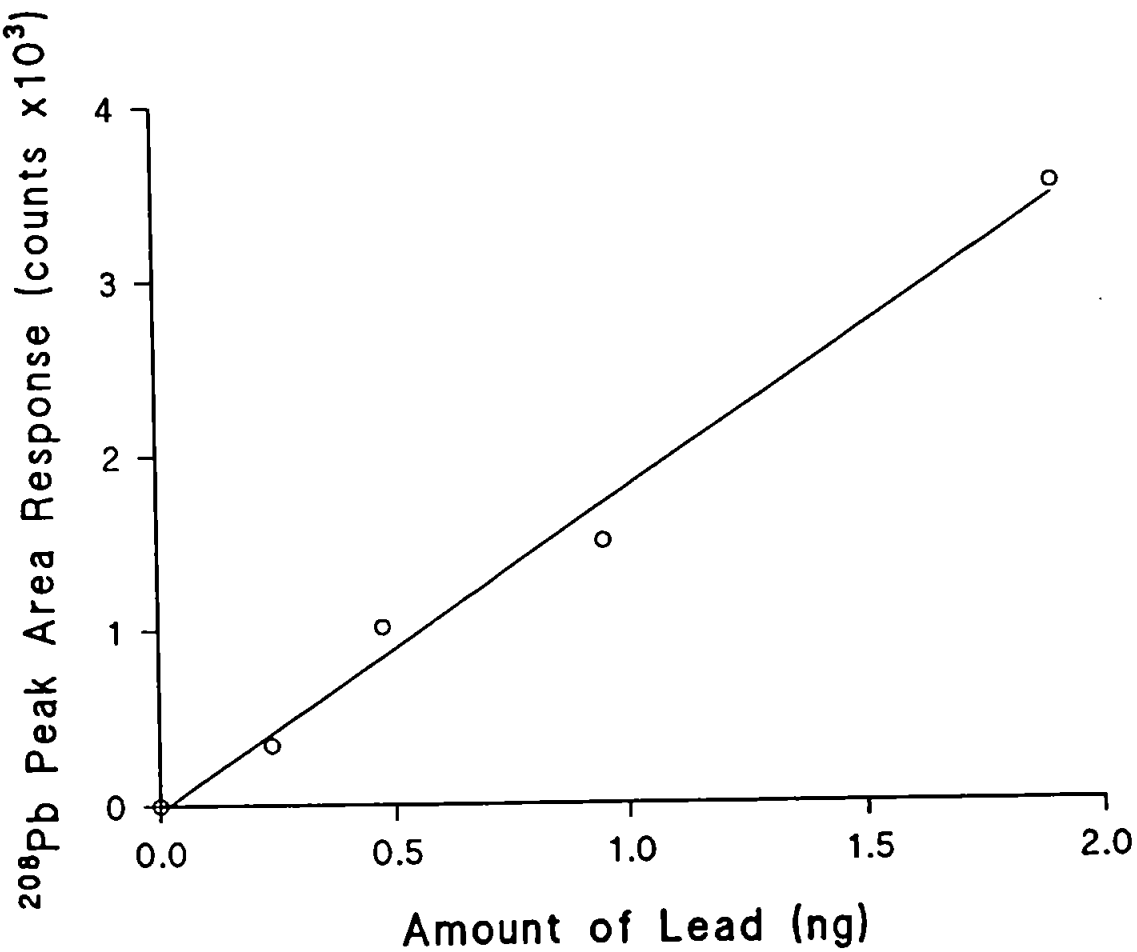


Figure 3.5 Linear external calibration of tetraethyllead using NBS SRM 1637. Same conditions used as in Fig. 3.1

The linear dynamic range was over 5 orders of magnitude (1 pg to 10 ng) **(Fig. 3.6)**. At amounts exceeding 10 ng the ICP-MS detector automatically acquired data in the "pulse counting mode". Higher concentrations may overload the column and rarely are such concentrations ($\mu g\ ml^{-1}$ range) found in the environment. The correlation coefficient was 0.999 between 2 - 100 pg and 0.9999 between 100 pg - 10 ng.

3.2.4 Tetraalkylleads Naphtha

A concentration of five tetraalkyllead species in naphtha (known value = 0.45 mg ml^{-1}, as total Pb) were determined using external calibration **(Table 3.2, Fig. 3.5)**. The experimental value obtained for total lead is 0.465 mg ml^{-1}, acceptable compared with the known value.

As expected, unleaded fuel and hexane were found to contain no detectable amounts of alkyllead.

The advantages of GC-ICP-MS over conventional GC-MS for organometal detection is demonstrated by comparing the Total Ion Current (TIC), ion selective chromatogram **(Fig. 3.7)** and mass spectra **(Fig. 3.8)** of the aklyllead compounds in the naphtha. For example, GC-ICP-MS gave better sensitivity. GC-MS gave no response for the minor components (TMEL and DMDEL) and using ion selective detection (m/z 208) only TEML and TEL were detected **(Fig. 3.8)**.

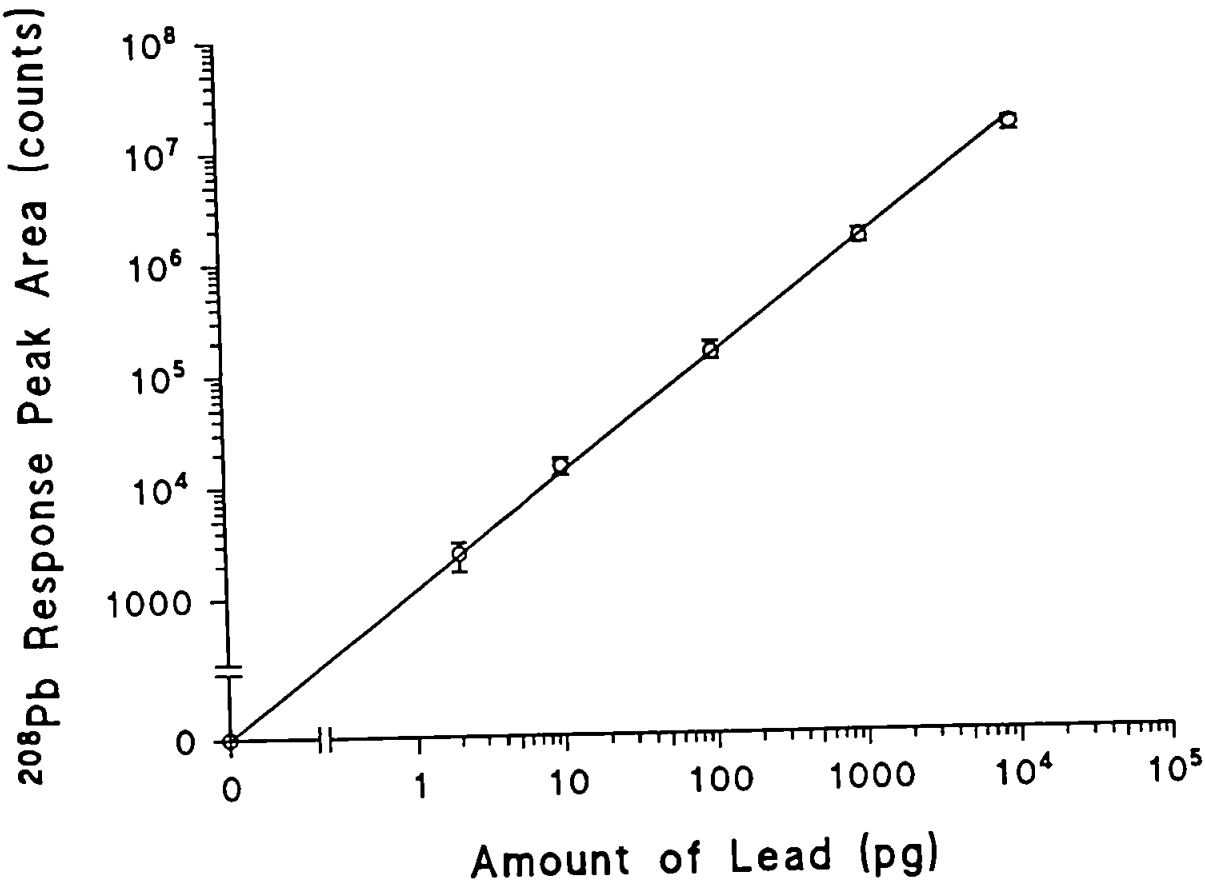


Figure 3.6 Linear dynamic range of TEL measured over 5 orders of magnitude

Table 3.2 Concentration of alkyllead species in naphtha using external calibration.

Organolead Species	Concentration (mg ml^{-1})
TML	0.095
TMEL	0.020
DMDEL	0.057
TEML	0.187
TEL	0.106
TOTAL LEAD (Experimental value)	0.465
TOTAL LEAD (Theoretical value)	0.450

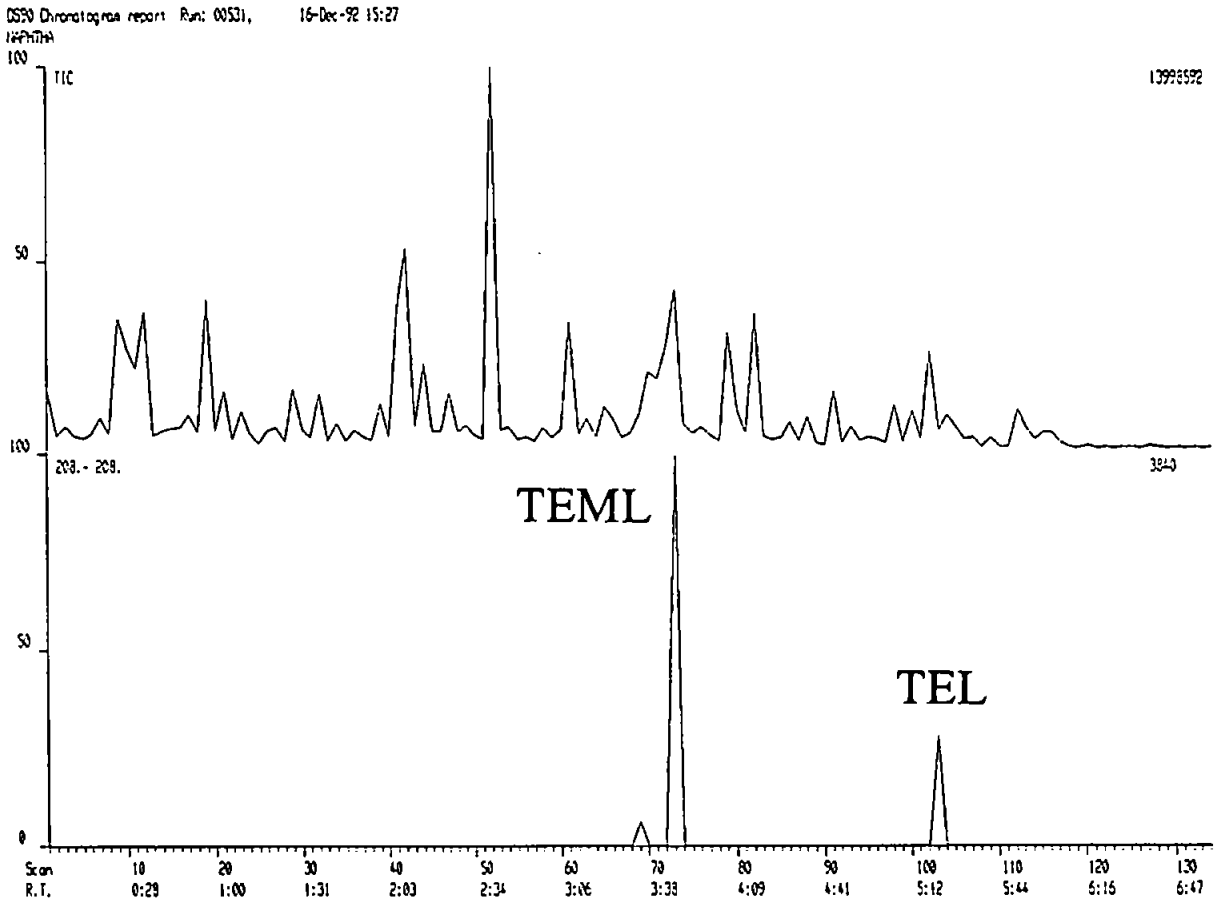


Figure 3.7 GC-MS total ion chromatogram and ion selective chromatogram (m/z 208) of the naphtha showing only TEML and TEL, the other alkyllead species were not detected

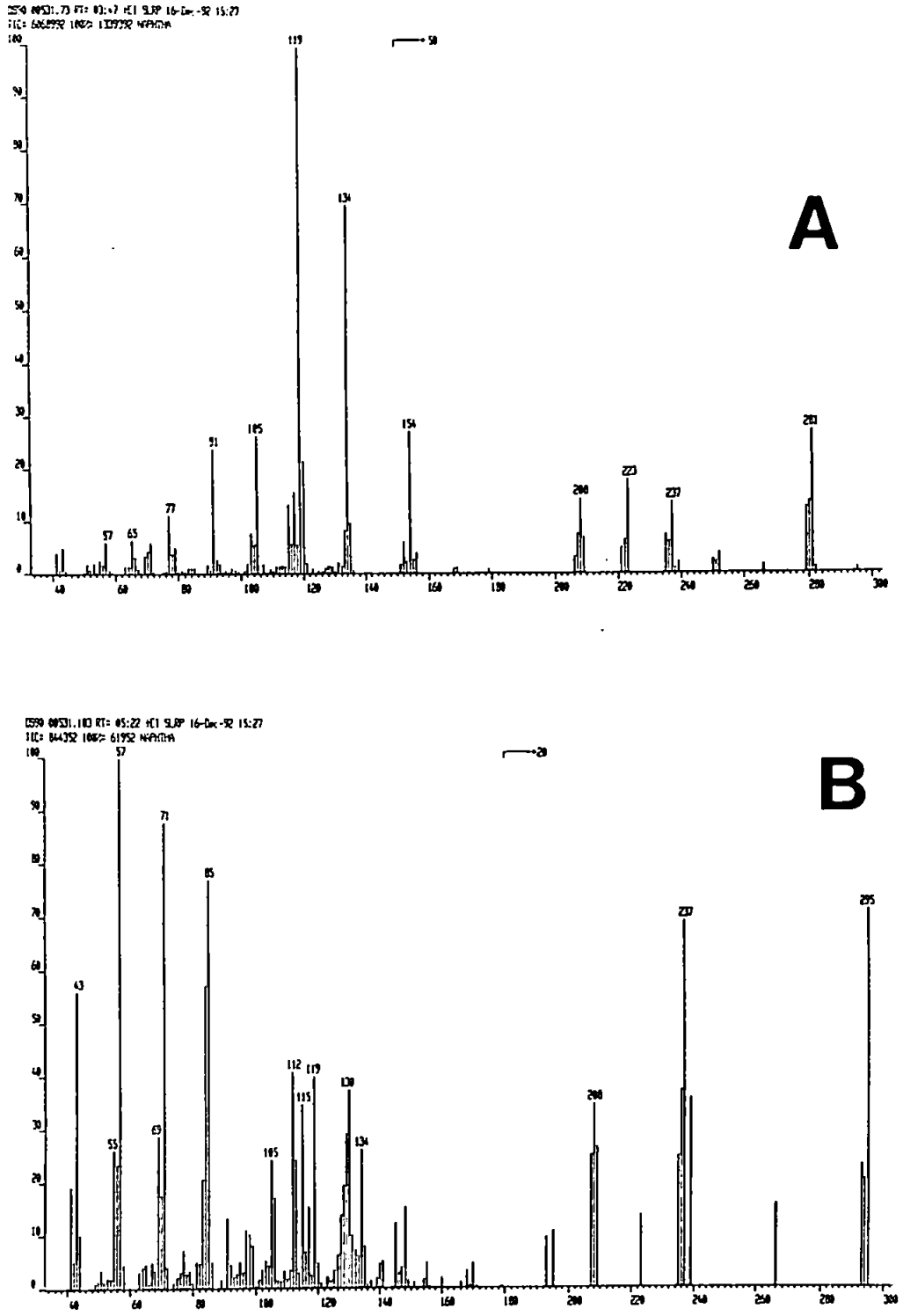


Figure 3.8 GC-MS EI mass spectra of: **(A)** triethylmethyllead: m/z 281 ($M^+-C_2H_5$), 237 ($M^+,-(C_2H_5)_2-CH_3$), 223 ($M^+-(C_2H_5)_3$), 208 (^{208}Pb); **(B)** tetraethyllead: ($M^+,-C_2H_5$) 237 ($M^+,-(C_2H_5)_3$), 208 (^{208}Pb). Low mass fragments are from co-eluting hydrocarbons present in the naphtha (eg. m/z 57 = C_4H_9, 71 = C_5H_{11}, 85 = C_6H_{13}). GC-MS conditions are given in Appendix A.

A further advantage is no solvent venting. Data acquisition for GC-MS was started 4 minutes after injection to prevent the solvent from damaging the filament, and as a result early eluting TML was not detected. A similar situation would be encountered with GC-MIP-AES where the solvent is vented to prevent the extinction of the plasma and carbon deposition in the discharge tube.

Also, mass spectra of TEML and TEL **(Fig. 3.8)** contained no molecular ions and molecular fragments (m/z > 208) gave only a weak response of 0.5% full scale deflection (FSD) for TEML and 3.5% FSD for TEL with respect to the most abundant fragment). Co-elution of other compounds (m/z < 208) made spectra interpretation complex. However, GC-MS may be used as a complementary technique, giving structural information.

3.2.5 Determination of Tetraethyllead in a Standard Reference Material

The concentration of TEL in a reference fuel (NBS SRM 1636 II) was determined by external calibration and standard addition **(Table 3.3, Fig. 3.9)**.

The experimental values obtained using both methods are in agreement with the certificate value within the confidence limits of the measurement.

3.3 Organotin Speciation

3.3.1 Experimental

The materials and reagents used are listed in Appendix A. The Mark II transfer line and ICP torch was used

Table 3.3 Determination of TEL is a standard reference fuel (NBS SRM 1637 II) by external calibration (10 replicate analyses) and standard addition (6 replicate analyses). GC oven temperature programme = 60°C iso., 1 μl injected, hexane solvent. Authentic TEL was used for preparation of standards.

Organolead Species	External Calibration Value (mg ml^{-1})	Standard addition value (mg ml^{-1})	Certificate Value (mg ml^{-1})
TML	n.d.	n.d.	12.9 (± 0.07)
TEL	13.84 (± 0.93)	13.60 (± 1.36)	

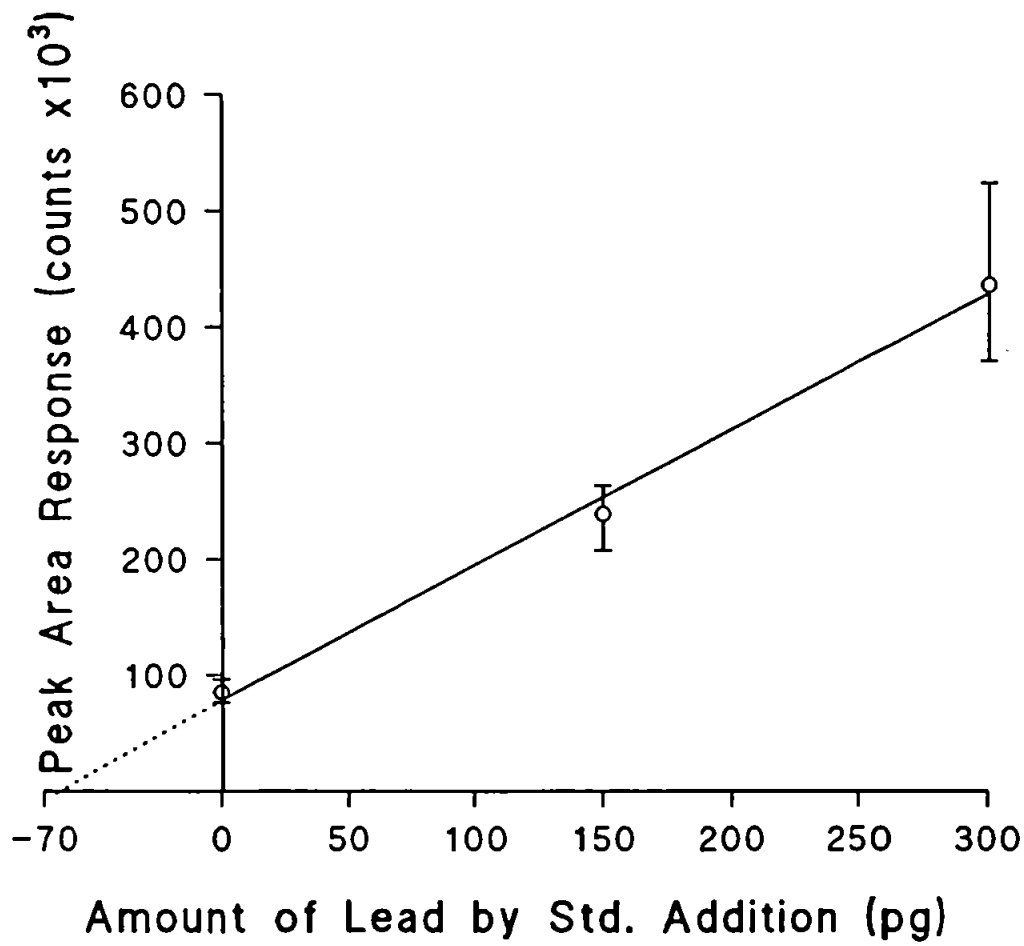


Figure 3.9 Determination of TEL (using standard addition) in a standard reference fuel NBS SRM 1637 II (diluted to 64.5 μg ml^{-1}), y intercept = -67.9 μg ml^{-1}, correlation coefficient = 0.9975, six replicate injections (1.0 μl), GC oven temperature programme = 60°C iso., hexane solvent.

throughout. The transfer line temperature was maintained between: TC1 = 230-260°C, TC2 = 260-305°C, TC3 = 280-326°C, TC4 = 265-313°C. The ICP-MS was tuned for tin detection using the signal from the cold mercury generator (m/z 120 from $SnCl_2.2H_2O$) as described previously (Section 2.3.3), this was taken off-line prior to organotin analysis. Single ion monitoring (m/z 120) was used throughout unless stated otherwise.

3.3.2 Chromatographic Elution Characteristics of Organotin Species

Tributyltin acetate (TBT Ac), Tributyltin chloride (TBT Cl) and tetrabutyltin (Bu_4Sn) were analysed separately by GC-ICP-MS **(Fig. 3.10)**. Both TBT Ac and TBT Cl gave poor gas chromatographic elution (wide peak width > 9.4 min. and jagged peak crest). Non-polar Bu_4Sn gave ideal chromatographic peak shape (peak width = 6 s and smooth peak crest).

Subsequently all organotin chlorides used in this study were converted to their non-polar derivatives by Grignard reagent (ethylmagnesium bromide) to increase their volatility making their separation more amenable to GC.

3.3.3 Preparation of Tetraalkyltin Standards

$Sn(R)_n(Et)_{4-n}$ species (where $n \geq 1$) were prepared as follows: known amounts of organotin chloride (approximately 0.12 g as Sn) were dissolved in dry diethylether (25 ml) in a 100 ml round bottom flask. Ethylmagnesium bromide (20% w/v in diethylether) was added in excess and magnetically stirred

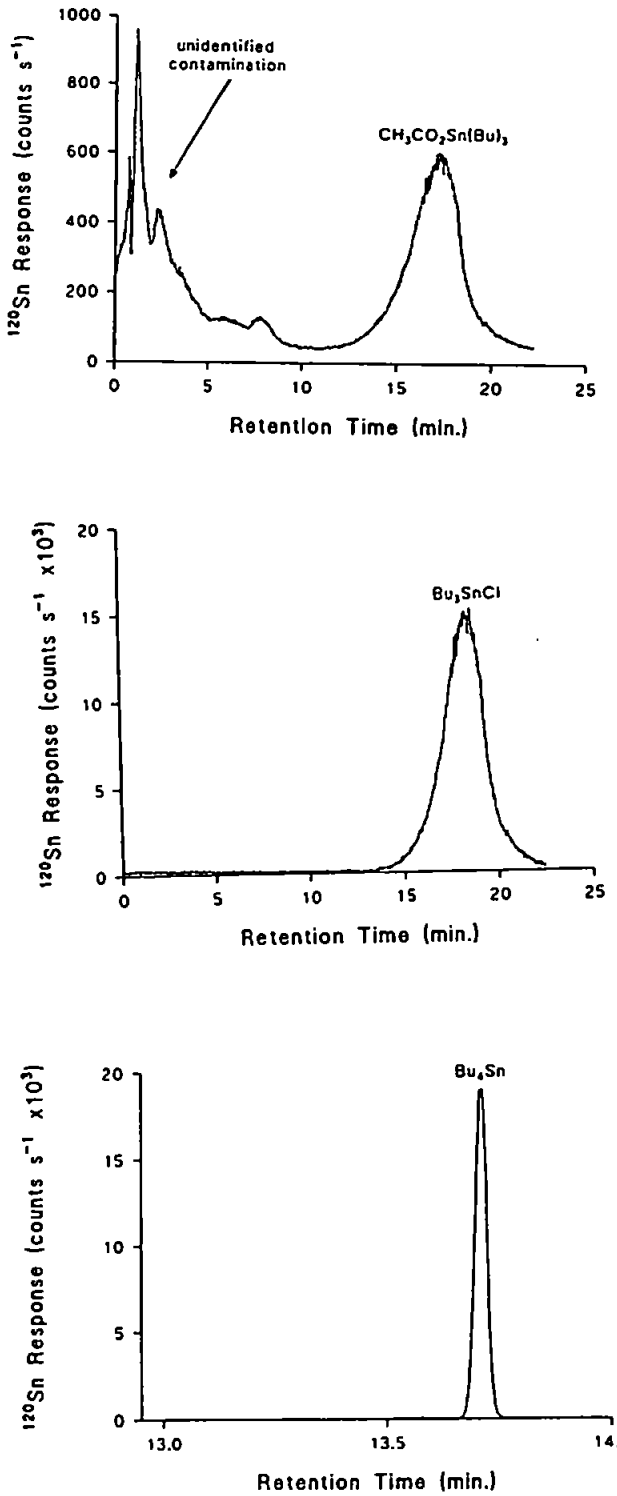


Figure 3.10 Improvement of peak shape of organotin species with decreasing polarity (A>B>C), mass selective chromatograms (m/z 120). **(A)** tributyltin acetate (10 μg ml^{-1} in methanol), **(B)** tributyltin chloride (0.1 μg ml^{-1} in methanol) and **(C)** tetrabutyltin (15.9 μg ml^{-1} in hexane). GC oven temperature programme = 40°C (1 min. iso.) to 350°C (10 min. iso.) at 10°C min.$^{-1}$, volume injected = 0.5 μl.

(30 min., 20 °C). Excess Grignard reagent was deactivated by the drop-wise addition of H_2SO_4 (0.1 M) whilst the temperature was maintained below 4°C. The products were extracted from the aqueous phase using diethylether (3 x 10 ml) and dried over anhydrous Na_2SO_4. The organic phase was reduced in volume (< 20 ml) by rotary evaporation and made up to 50 ml in a volumetric flask with diethylether. Storage conditions were < 4°C in darkness.

The concentration of these standards were determined by nitrous oxide flame AAS. The spectrometer was calibrated using a dilution series of tetrabutyltin in hexane (9.3 - 92.9 $\mu g\ ml^{-1}$ as Sn). The synthesised standards were diluted to an appropriate concentration in hexane and their concentrations determined (579 - 683 $\mu g\ ml^{-1}$ as Sn).

Purity and identity was confirmed by capillary GC and GC-MS **(Fig. 3.11 A-D)**. The mass spectra contained no molecular ions and the combination of various tin isotopes and hydrogenated fragments made the spectra complex and difficult (but not impossible) to interpret.

3.3.4 Figures of Merit for Organotins

Figures of Merit for tetraalkyltin standards were established **(Table 3.4)**. Five replicate injections (63.5 pg as tin) gave limits of detection (3σ, using peak area integrated counts) in the low $pg\ s^{-1}$ range. The response was linear to 2.5 ng tin, with correlation coefficient = 0.9995 **(Table 3.4; Fig. 3.12)**. The difference of the slope value between Et_4Sn and Bu_3EtSn is probably due to peak broadening of Bu_3EtSn whereby some of the signal is

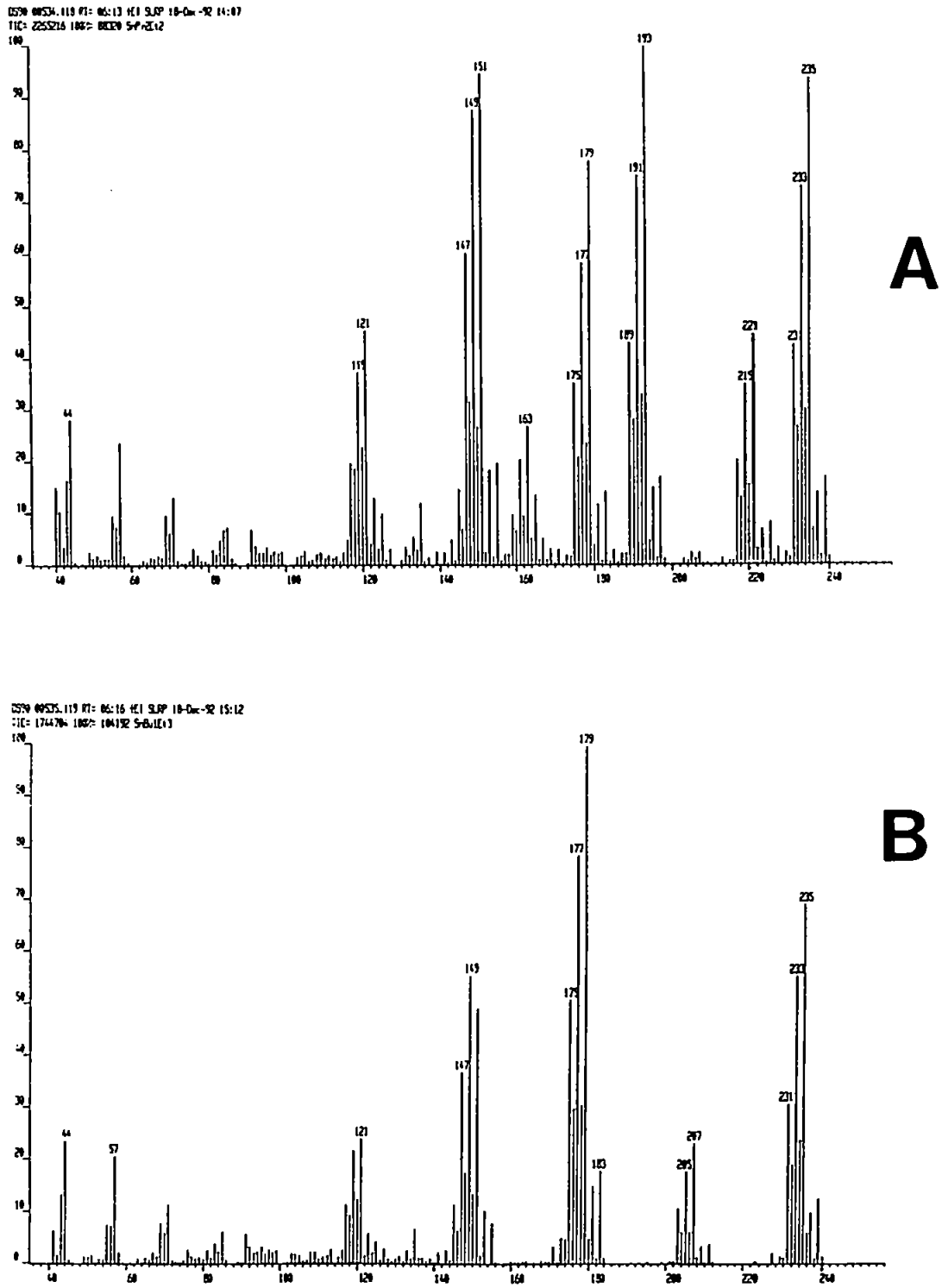


Figure 3.11 GC-MS, EI mass spectra of: **(A)** diethyldipropyltin (M^+ = 264), m/z; 235 (M^+, $-C_2H_5$), 221 (M^+, $-C_3H_7$). **(B)** butyltriethyltin (M^+ = 264), m/z; 235 (M^+, $-C_2H_5$), 207 (M^+, $-C_4H_9$). GC-MS conditions are given in Appendix A.

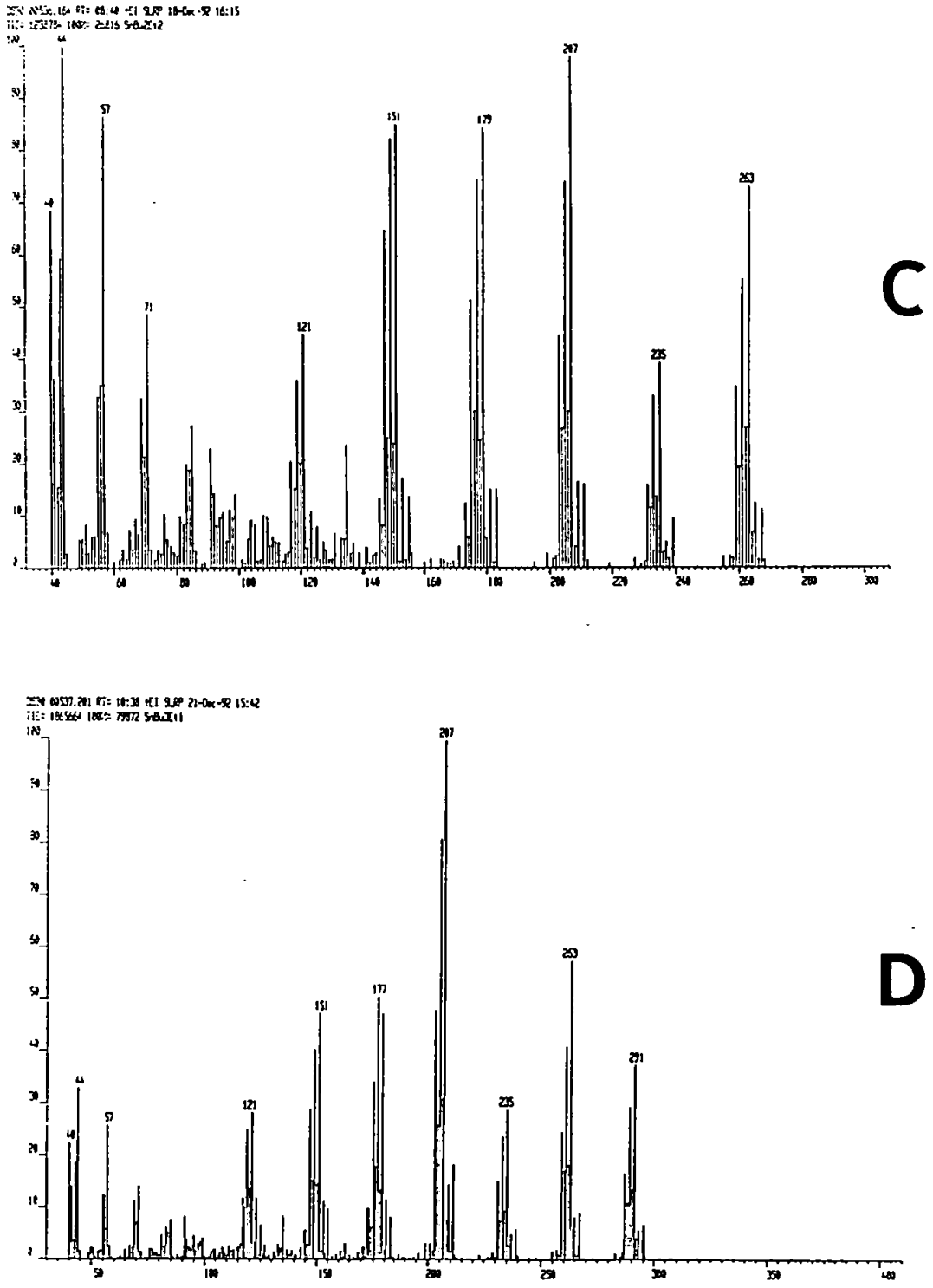


Figure 3.11 GC-MS, EI mass spectra of: **(C)** dibutyldiethyltin (M^+ = 292), m/z; 263 (M^+, $-C_2H_5$), 235 (M^+, $-C_4H_9$). **(D)** tributylethyltin (M^+ = 320), m/z; 291 (M^+, $-C_2H_5$), 263 (M^+, $-C_4H_9$). GC-MS conditions are given in Appendix A.

Table 3.4 Figures of Merit for tetraalkyltin species. GC oven temperature programme was from 40°C to 200°C (5 min. iso.) at 10°C min^{-1}, 0.5 μl injected, hexane solvent.

Species	Et_4Sn	Pr_2EtSn	$BuEt_3Sn$	Bu_2Et_2Sn	Bu_3EtSn
Detection limit (3σ) (pg s^{-1})	3.0	3.0	2.0	2.0	2.0
RSD (%)	9.6	10.6	5.4	7.4	11.3
Correlation coefficient	0.9998	0.9999	0.9999	0.9998	0.9996
Linear dynamic range measured	13 pg - 2.5 ng				
peak width (s)	6.2	6.6	6.6	7.2	9.9
Retention time (min.)	4.40	6.75	6.85	9.20	12.40
Slope (integrated counts ng^{-1} x 10^4	42.06	43.37	37.26	39.30	33.34

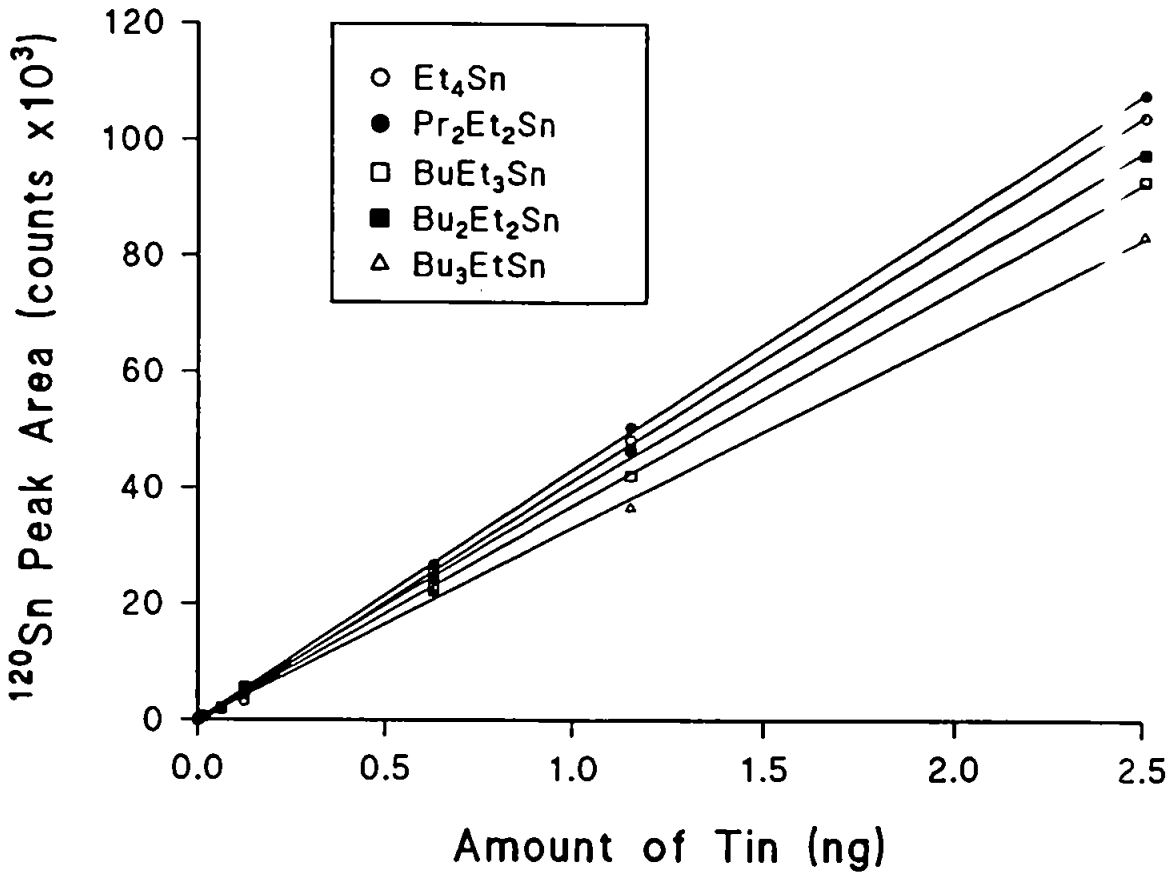


Figure 3.12 Linear response of five tetraalkyltin species. Figures of Merit are given (Table 3.4). GC oven temperature programme was from 40°C to 200°C (5 min. iso.) at 10°C min^{-1}, 0.5 μl injected, hexane solvent.

lost in the background noise.

Figure 3.13 shows a typical ion selective chromatogram (m/z 120) for the five tetraalkyltin compounds (corresponding to a 0.625 ng injection as Sn); the signal-to-background ratio is high. The high chromatographic resolution of the capillary GC-ICP-MS system is illustrated by the separation of Pr_2Et_2Sn and $BuEt_3Sn$ **(Fig. 3.14)**. It is unlikely that packed column GC-ICP-MS would achieve this. The peak shape of the organotins are Gaussian.

3.3.5 Organotin Speciation in Water

Dipropyltin dichloride is a good internal standard for organotin species determination because it is not present in the natural environment, is completely separated from other organotin compounds by GC-ICP-MS, yet elutes near the components of interest and has a similar detector response.

Known concentrations of $BuSnCl_3$, Bu_2SnCl_2, Bu_3SnCl, Pr_2SnCl_2 and Sn^{4+} **(Table 3.5)** were added to Milli-Q water (250 ml). Sn^{4+} was prepared according to Maguire and Huneault [194]. After 24 hours the water was acidified with 48% HBr (5 ml) and magnetically stirred (15 min. at ambient temperature). The acidified solutions were extracted with freshly prepared solution of 0.05% (w/v) tropolone in hexane (3 x 25 ml). The organic extract was dried over anhydrous Na_2SO_4 and derivatised with ethylmagnesium bromide (6 ml, 1.24 M is diethylether) as previously described (Section 3.2.2). The sample and procedural blank were made up to 50 ml with toluene in a volumetric flask.

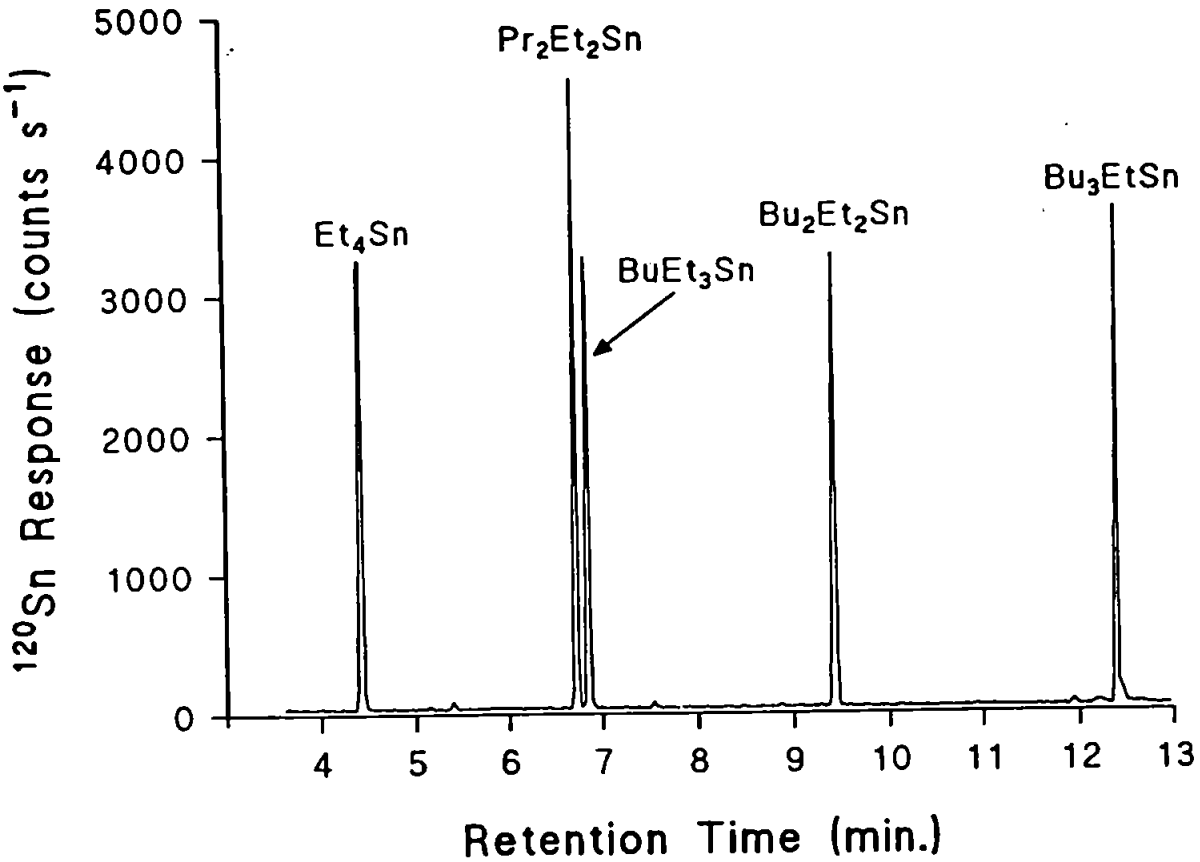


Figure 3.13 Ion selective chromatogram (m/z 120) of five tetraalkyltin standards, each corresponding to a 0.625 ng as Sn. GC conditions are given in Figure 3.12.

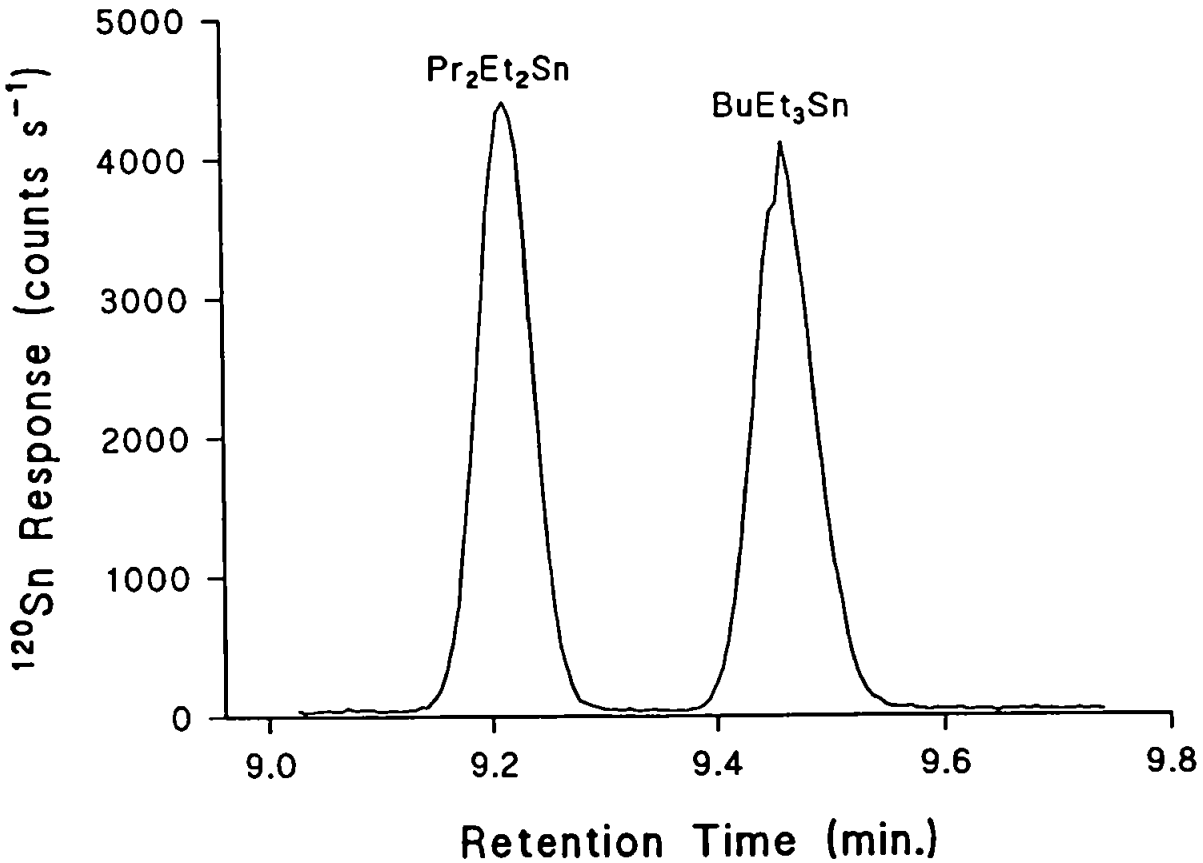


Figure 3.14 Ion selective chromatogram (m/z 120) demonstrating the high chromatographic resolving power of the capillary GC-ICP-MS system. GC conditions are given in Figure 3.12.

Table 3.5 Organotin species in a spiked water sample. Known amounts of tin were added as the organotin chloride (theoretical concentration). Experimental values are from three replicate injections. GC oven temperature programme is given (Table 3.4), toluene solvent, 0.5 μl injected.

Organotin Species	Concentration (μg ml^{-1} as total tin)		% RSD
	Theoretical	Experimental	
Pr_2Et_2Sn (internal standard)	24.2	-	-
Et_4Sn	24.20	23.51 (± 0.08)	0.34%
$BuEt_3Sn$	20.24	20.51 (± 0.33)	1.59%
Bu_2Et_2Sn	20.24	22.10 (± 0.22)	1.02%
Bu_3EtSn	20.24	18.63 (± 1.04)	5.57%

The $Bu_nEt_{4-n}Sn$ derivatives were diluted to an appropriate concentration (low $\mu g\ ml^{-1}$ range) with toluene and determined using the coupled system (Table 3.5). The experimental values obtained are in close agreement with the theoretical value within the confidence limits of the measurements; Figure 3.15 shows a typical ion selective chromatogram (m/z 120) for the spiked water sample. No organotin species were detected in the procedural blank.[1]

[1] It was noted that the toluene solvent front produced a green glow when it entered the plasma (known as "Schwann Bands", a characteristic atomic emission line for carbon) which lasted for approximately 15 seconds. This produced a small amount of carbon deposition which cleared after one minutes without oxygen entrainment. This phenomenon was not noticed with other solvents (eg. hexane, octane, DCM).

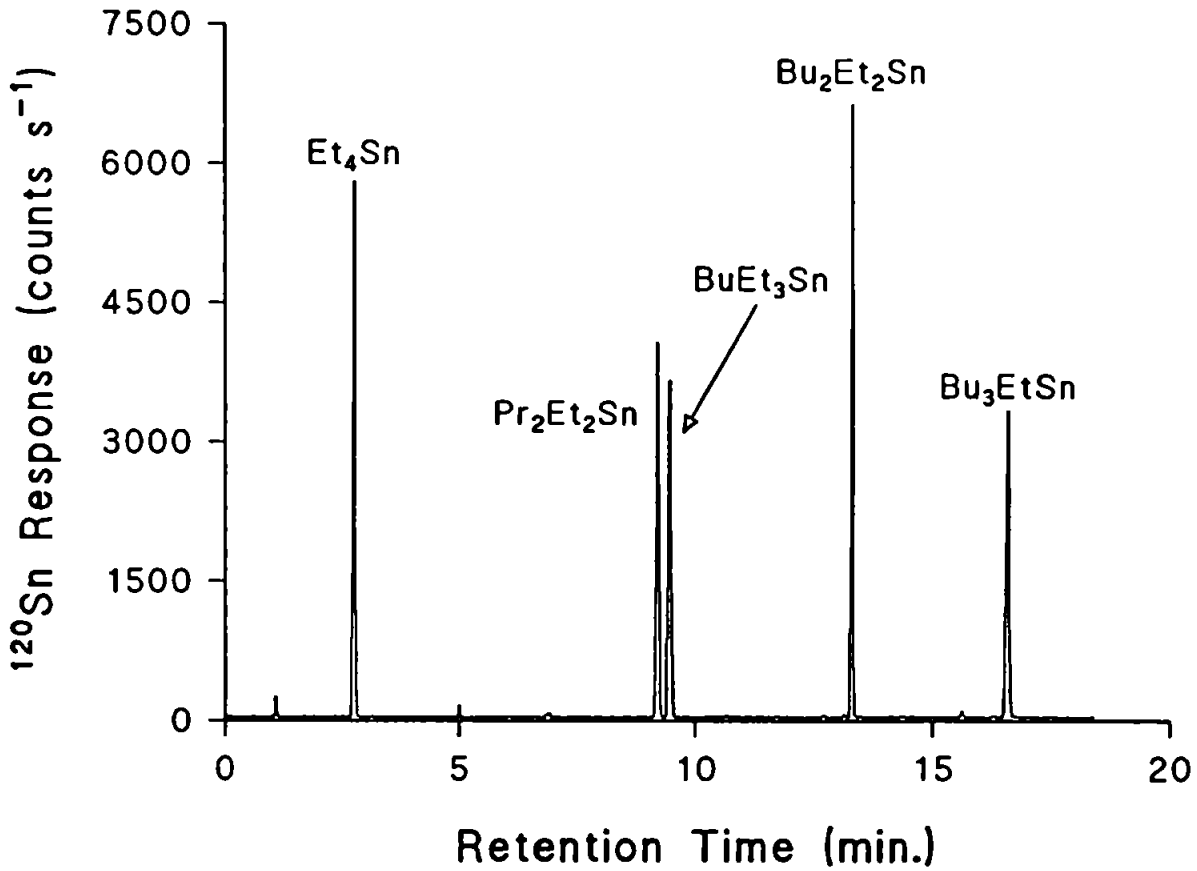


Figure 3.15 Ion selective chromatogram (m/z 120) of organotin species in a spiked water sample. GC conditions are given in Table 3.5.

3.3.6 Organotin Speciation in Sediments

Two harbour sediments containing differing concentrations of organotin chlorides ($BuSnCl_3$, Bu_2SnCl_2, Bu_3SnCl_3) were used for this study.

1. Harbour sediment (BCR-424) which was undergoing a Bureau Community Reference certification exercise was obtained from Dr W Corns (University of Plymouth, Plymouth, UK).

2. PACS-1 was obtained from the National Research Council (NCR), Canada, certified to contain (as Sn), monobutyltin (0.28 $\mu g\ g^{-1}$, ± 0.17), dibutyltin (1.16 $\mu g\ g^{-1}$, ± 0.18) and tributyltin (1.27 $\mu g\ g^{-1}$, ± 0.22).

3.3.6.1 Sediment Extraction

Initially 2 g of BCR-424 and PACS-1 (with no internal standard added) were extracted according to the method by Müller [195] with the exception that the final derivatised extract was recovered and made up to 1 ml with toluene. The extracts were injected into the coupled system. **Figure 3.16** shows an ion selective chromatogram (m/z 120) for the BCR-424 sediment, illustrating how the coupled system may be used for the analysis of a complex environmental sample. Organotin species were identified by comparing the retention times with those of known tetraalkytin compounds. The expected organotin compounds in PACS-1 were not detected most probably due to inefficient extraction. No organotin species were detected in the procedural blank.

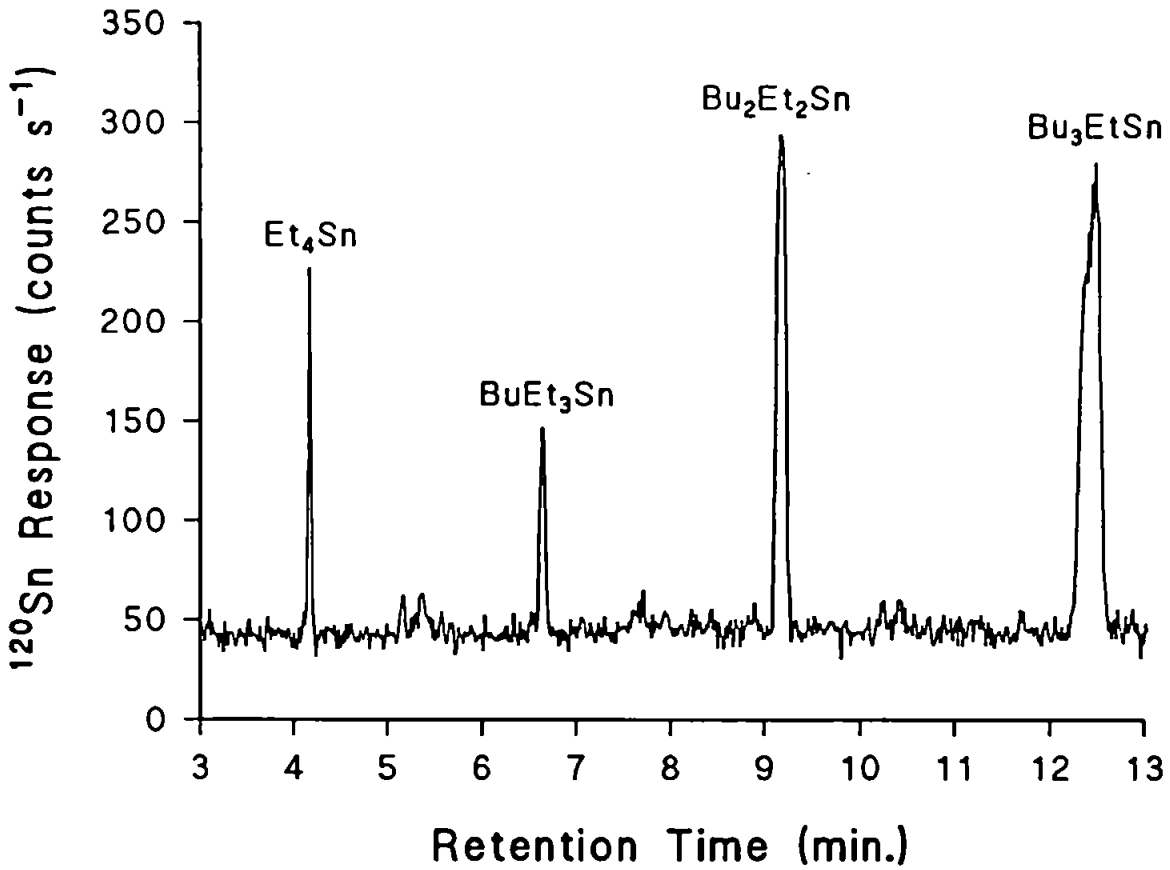


Figure 3.16 Ion selective chromatogram (m/z 120) of organotin species in a harbour sediment (BCR-424). GC conditions are given in Table 3.4.

A variety of extraction procedures were attempted as described by previous workers [44,64,189,195] with the internal standard (Pr_2SnCl_2 in DCM) added before extraction (15 $\mu g\ g^{-1}$ for PACS-1 and 30 $ng\ g^{-1}$ for BCR-424, but the low concentrations obtained did not correlate to the certified values.

3.3.6.3 Determination of Organotin Species in PACS-1 Standard Reference Sediment

Certified values for the concentrations of organotins in PACS-1 were eventually successfully determined by the following method:

Internal standard (Pr_2SnCl_2 in DCM, 3.43 $\mu g\ g^{-1}$, as Sn) was added to PACS-1 (2 g), shaken for 24 hrs in a glass stopped flask and left to stand for 72 hours to allow the internal standard to equilibrate with the sediment matrix. The sediment was extracted and derivatised (with ethylmagnesium bromide) according to the method of Lobinski *et al.*, [100], except that the final derivatised extract was made up to 5 ml in diethylether.

The organotin species were determined using the coupled system **(Table 3.6)**. The experimental values obtained were in agreement with the certificate values within the confidence limits of the measurements. **Figure 3.17** shows a typical ion selective chromatogram (m/z 120) for PACS-1. The high value obtained for monobutyltin is probably due to the contribution of signal from the partially resolved internal standard; this could probably be overcome by use of a more efficient GC column. **Figure 3.17** also shows the presence of possible methyltin species (not present in the procedural blank) and extractable inorganic tin

Table 3.6 Organotin species in SRM, NBS, PACS-1. Experimental values are from seven replicate injections. GC oven temperature programme is given in Table 3.4, diethylether solvent, 1.0 μl injected, 12m column used.

Organotin Species	Concentration ($\mu g\ g^{-1}$ as Sn)	
	Certificate Value	Experimental Value
Pr_2Et_2Sn (internal standard)	-	3.43
$BuEt_3Sn$ (monobutyltin)	0.28 (±0.17)	0.53 (± 0.06)
Bu_2Et_2Sn (dibutyltin)	1.16 (± 0.18)	1.12 (± 0.04)
Bu_3EtSn (tributyltin)	1.27 (±0.22)	1.19 (± 0.11)

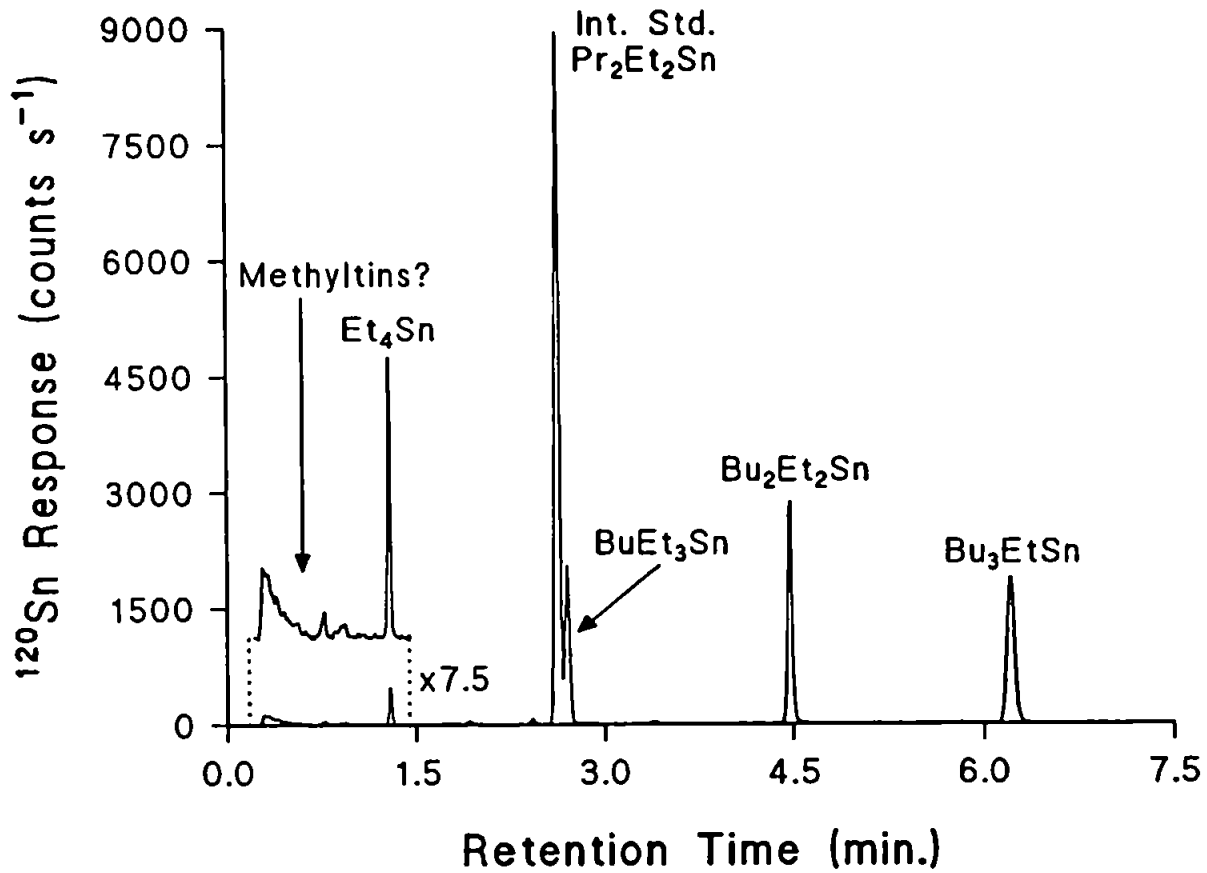


Figure 3.17 Ion selective chromatogram (m\z 120) of organotin species in a standard reference material sediment (PACS-1). GC conditions are given in Table 3.4, diethylether solvent, 1.0 μl injected, 12m column used.

Et_4Sn. The signal to noise ratio is high, peaks are sharp and Gaussian and on-line real time analysis is 7 minutes (using a 12m column). The percentage recovery was calculated to be 100.4% (calculated using the internal standard peak and a known amount of pure Pr_2Et_2Sn injected as duplicates at 1 minute intervals before the actual sample). The same sample was also examined by GC-MS but GC-MS was not sensitive enough to allow detection of the organotin species.

The multi element / ion monitoring capabilities of the ICP-MS is demonstrated in **Figure 3.18**.

3.3.5.3 Determination of Organotin Species in BCR-424 Harbour Sediment

Organotin species in BCR-424 harbour sediment was determined as previously described (Section 3.3.5.2). In the time available only duplicate determinations were made **(Table 3.7)**. As the sample was undergoing a certification exercise, there were no certified values with which to compare the experimental concentrations obtained. Discussions with personnel involved closely with the exercise disclosed that the concentration of tributyltin was estimated to be in the range of 20 - 30 ng g^{-1} (GC-ICP-MS value = 21.4 ng g^{-1}). The experiment was carried out at the same time as the analysis of PACS-1 and since the latter experiment gave certified values the concentrations obtained for BCR-424 is probably reliable.

Figure 3.19 shows an ion selective chromatogram (m/z 120) for BCR-424 with the possible presence of methyltin compounds and extractable inorganic tin.

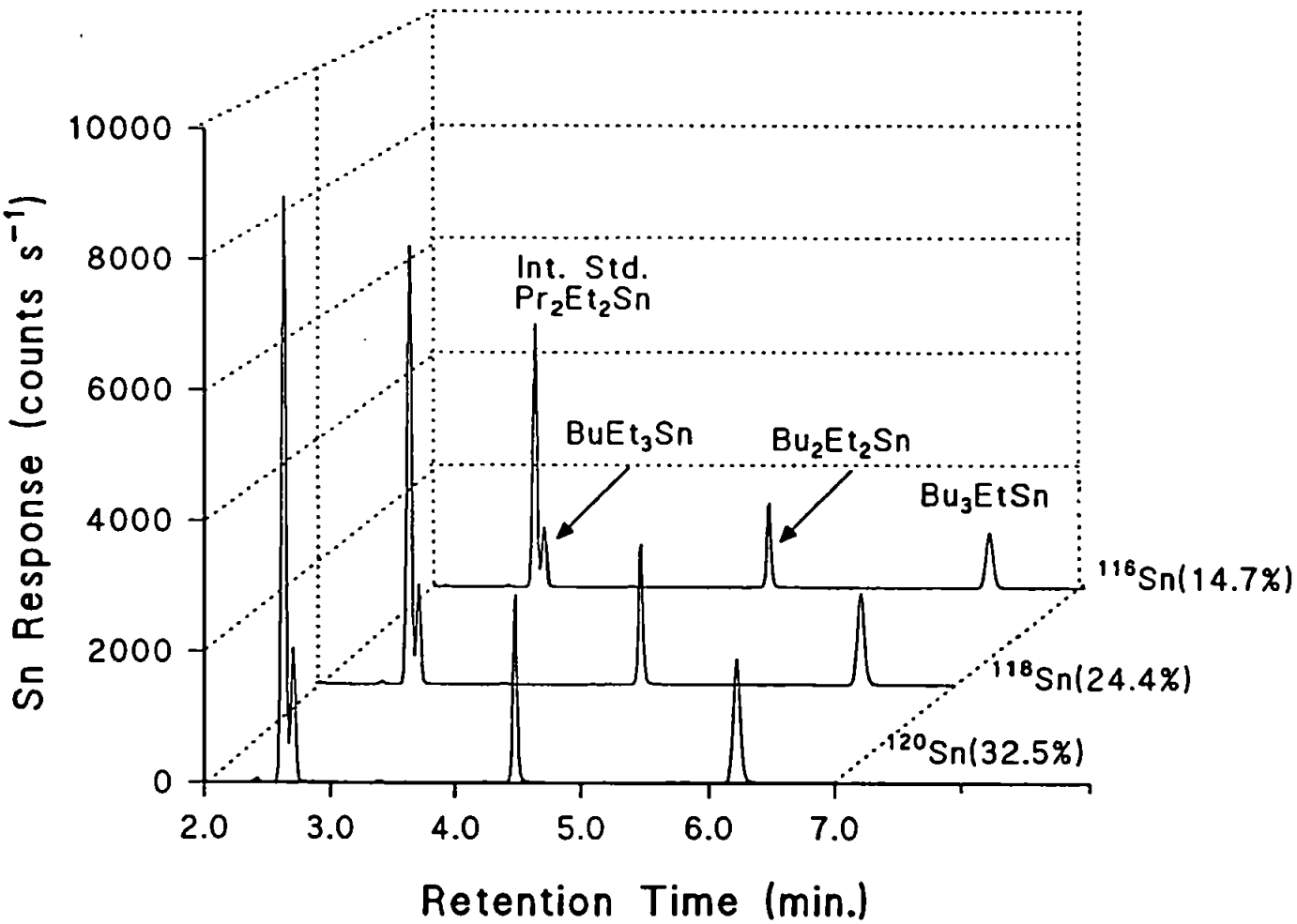


Figure 3.18 3-D ion selective chromatogram (showing the three major isotopes for tin) of organotin species in a standard reference material sediment (PACS-1). GC conditions are given in Table 3.4, 1.0 μl injected, 12m column used.

Table 3.7 Organotin species in harbour sediment (BCR-424). Only two determinations were made due to time constraint. GC oven temperature program given in Table 3.4, diethylether solvent, 1.0 μl injected, 12 m column used.

Organotin Species	Concentration (ng g^{-1} as Sn)		
	first determination	second determination	mean
Pr_2Et_2Sn (Internal standard)	12.9	12.9	-
$BuEt_3Sn$	70.8	81.5	76.1
Bu_2Et_2Sn	19.3	22.8	21.0
Bu_3EtSn	20.5	22.4	21.4

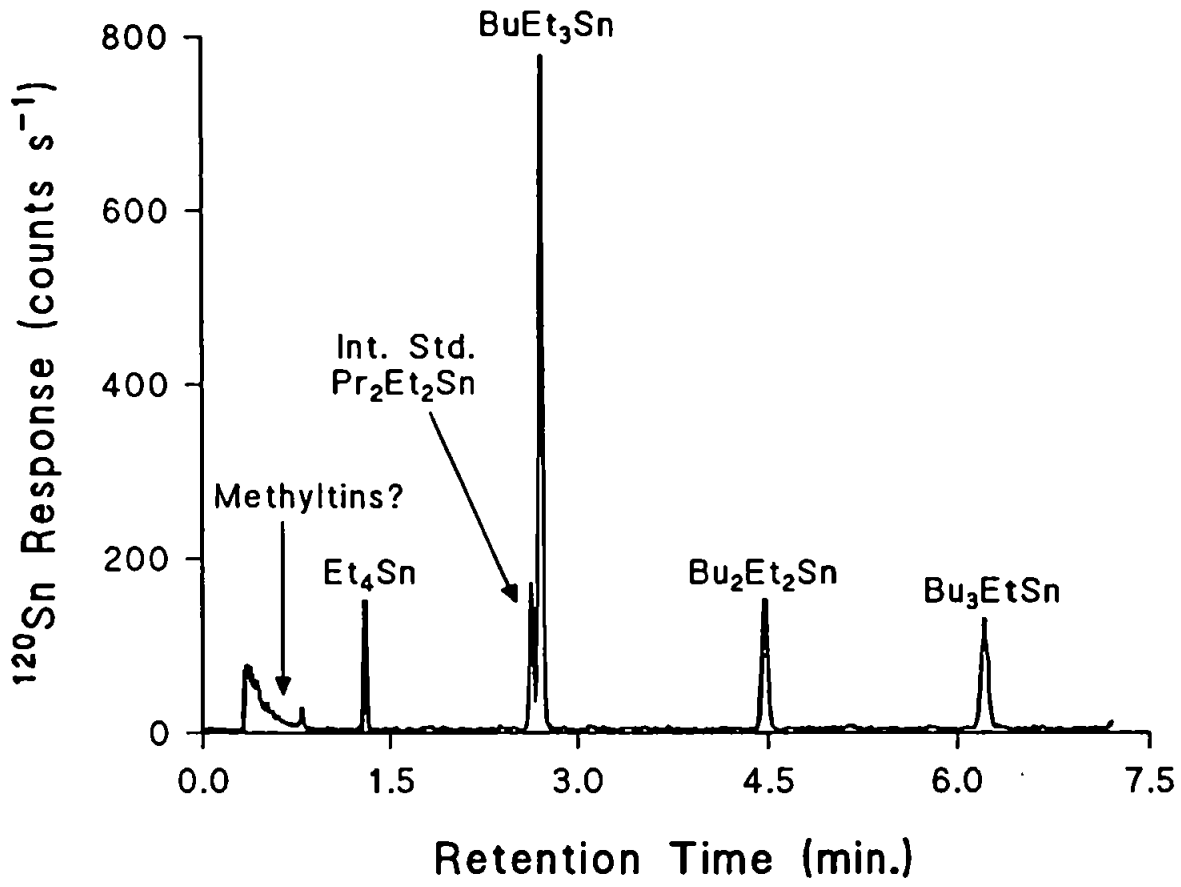


Figure 3.19 Ion selective chromatogram (m\z 120) of harbour sediment (BCR-424). GC conditions are given in Table 3.4, diethylether solvent, 1.0 μl injected, 12m column used.

3.4 Organomercury Analysis

3.4.1 Experimental

The materials and reagents used are listed in Appendix A. The Mark III transfer line and ICP torch were use throughout. The interface temperature was maintained between TC1 = 290°C, TC2 = 313°C, TC3 = 340°C and TC4 = 310°C. The ICP-MS was tuned for mercury using the signal from the cold mercury vapour generator (Section 2.3.3). The generator was not taken off-line prior to organomercury analysis, because the cold vapour mercury signal decreased to background levels approximately 10 minutes after the peristaltic pump was turned off.

3.4.2 Diethylmercury Analysis

Figures of Merit for diethylmercury standards were established **(Table 3.8)**. Four replicate injections (70 pg as Hg) gave a detection limit (3σ, using peak area integrated counts) of 1.0 pg s^{-1}. The response was linear up to 279 pg **(Fig. 3.20)**.

It was noticed that a small amount of chromatographic peak splitting was occurring **(Fig. 3.21)**. This is discussed further in the next section (Section 3.4.3).

3.4.3 Separation of Mercury Species

Methylmercury chloride (2.35 ng μl^{-1} in methanol) was examined using the coupled system under the same conditions as before (Section 3.4.2), **(Fig. 3.22)**. The broad peak width (45 s) is probably due to polar nature of the methylmercury halide and / or to peak

Table 3.8 Figures of Merit for diethylmercury detection, using four replicate injections. GC oven temperature programme was 70°C iso., helium carrier gas = 2 ml min^{-1}, octane solvent, 1.0 μl injected, column SGE HT-5 12 m x 0.32 mm i.d. x 0.1 μm film thickness.

Detection Limit (3σ), measured at 70 pg	1.0 pg s^{-1}
Percent RSD	4.9 %
Correlation coefficient	0.997
Linear range measured	34.9 - 279.2 pg
Peak width	8.0 s
Retention time	0.8 min.
Gradient	0.078 integrated counts pg^{-1} x 10^3

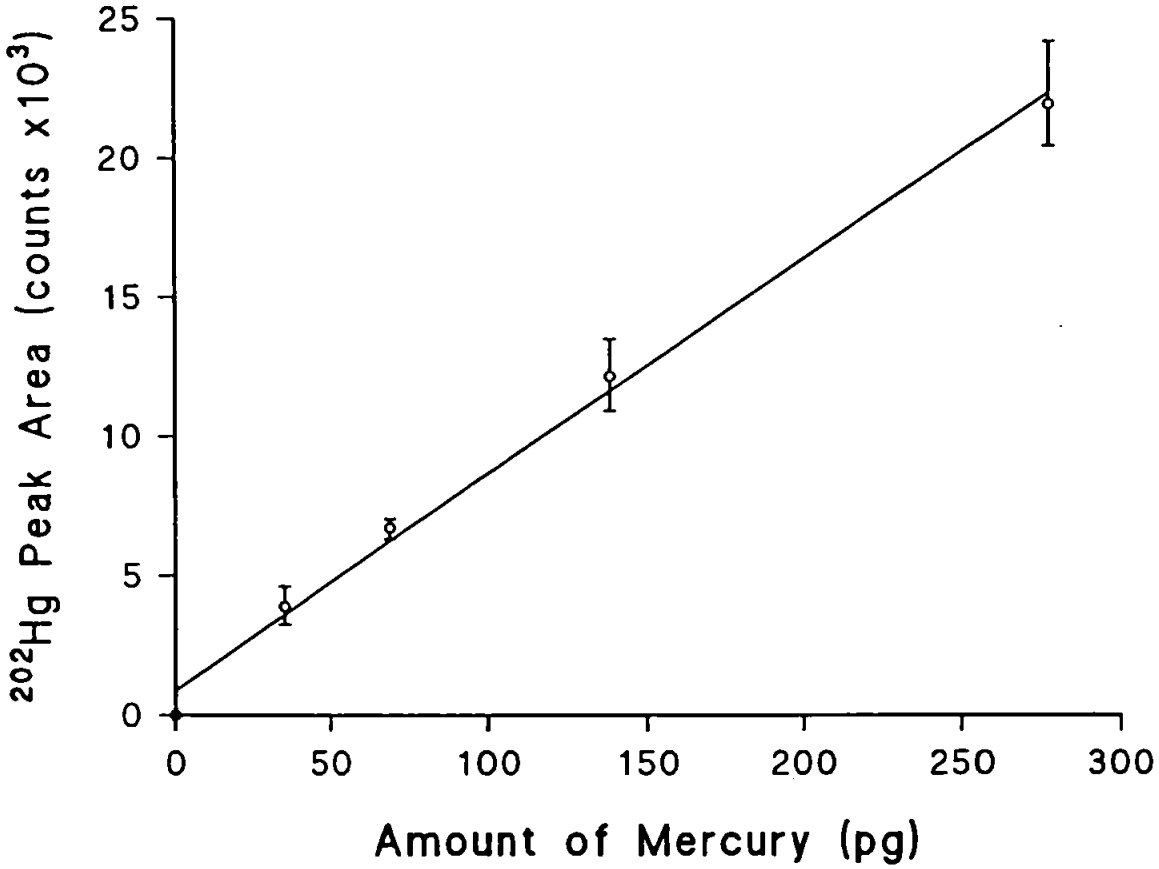


Figure 3.20 Linear response of diethylmercury. Figures of Merit and GC oven temperature programme are given (Table 3.8).

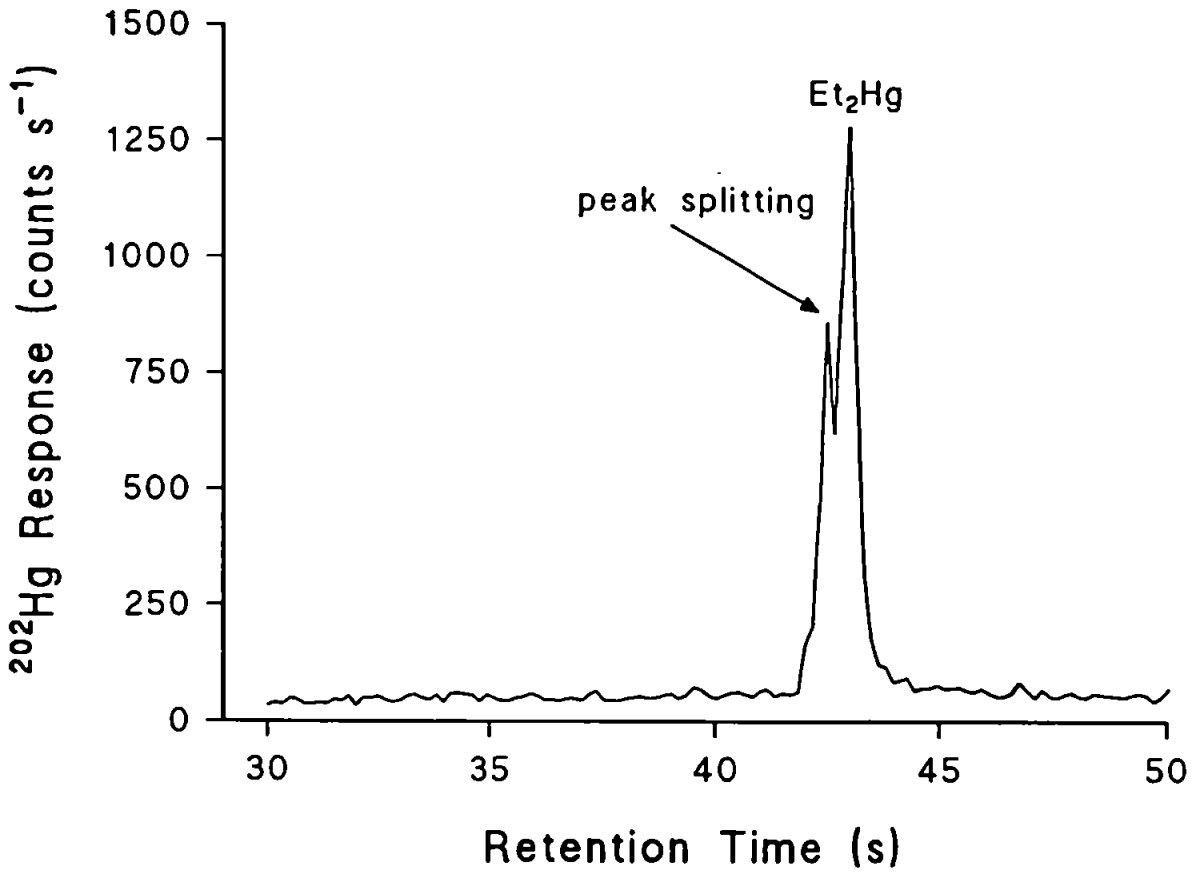


Figure 3.21 Ion selective chromatogram (m/z 202) of diethylmercury (70 pg as Hg), showing a small amount of peak splitting. GC operating conditions are given (Table 3.8)

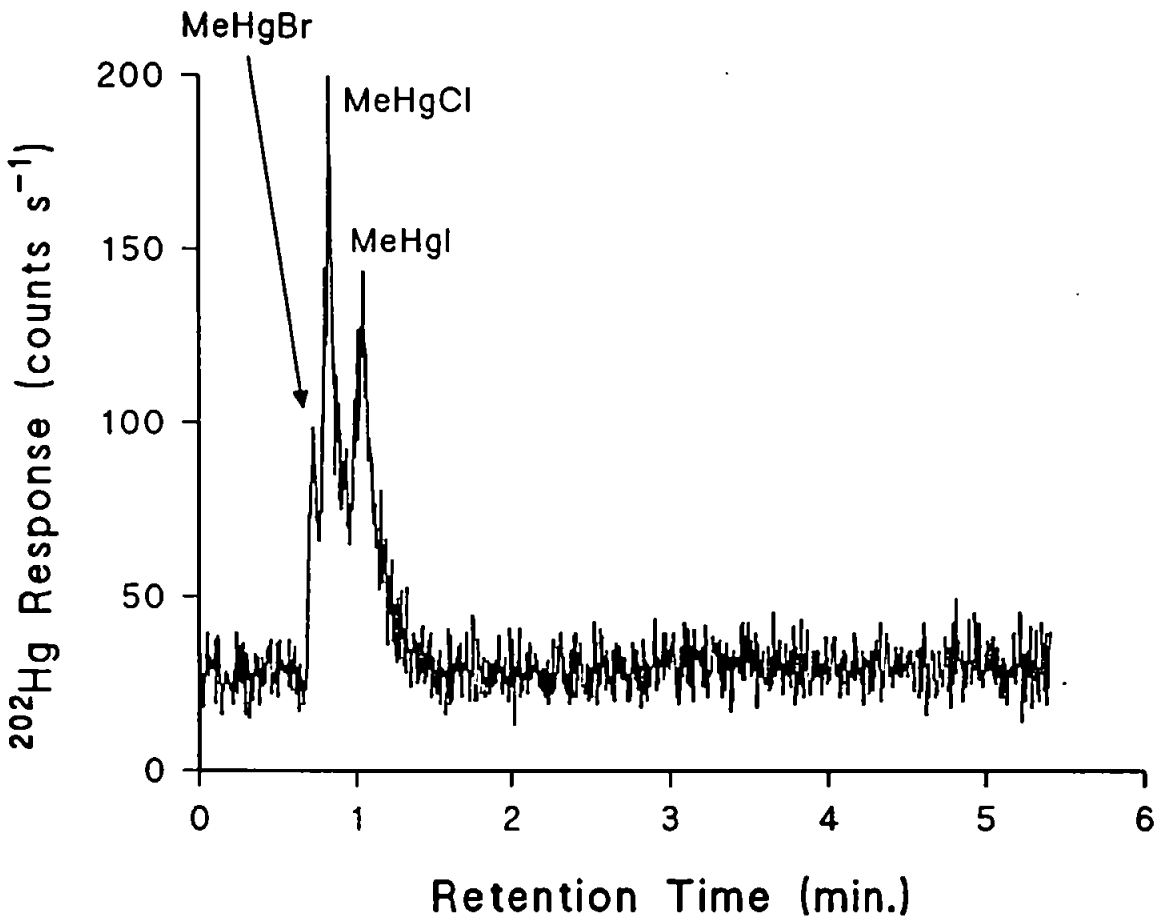


Figure 3.22 Ion selective chromatogram (m/z 202) of methylmercury chloride (2.35 ng as Hg). Peak splitting caused by conversion from the chloride to the more stable bromide and iodide. Peaks identified by Kato *et al* [125] 1, CH_3HgCl; 2, CH_3HgBr; and 3, CH_3HgI. GC operating conditions are given (Table 3.8).

splitting. Previous workers (using GC-ICP-AES) [125] attributed this to the conversion from the chloride into the more stable iodide and bromide in the injection port and column of the GC, although the source of iodide and bromide was not identified.

With the stationary phase used in the GC capillary column (SGE, HT5, 12m x 0.32mm i.d. x 0.1 μm film thickness) diethylmercury and methylmercury chloride were unresolved. Most workers have stressed the need to carry out pretreatments of the stationary phase by the injection of high concentrations of mercury II chloride at regular intervals [131] to improve chromatographic behaviour of mercury species. However this "passivation" has a number of disadvantages including rapid deterioration of chromatographic performance and progressive and irreversible contamination and a number of previous workers have investigated the use of capillary GC columns for mercury speciation without the need for this pretreatment [196]. At the time of writing no ideal solution to the chromatographic behaviour of alkylmercury compounds has been found.

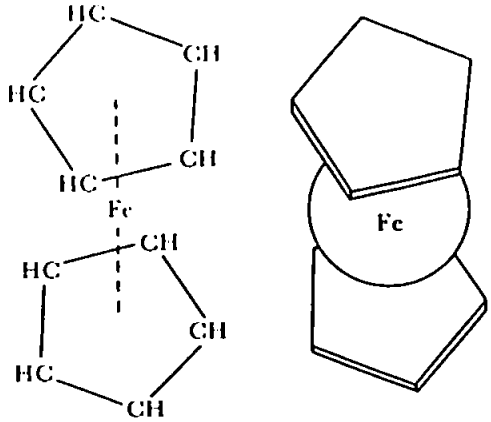
3.5 Analysis of Various Metal Complexes

3.5.1 Ferrocene

The materials and reagents are listed in Appendix A. The Mark II interface and ICP torch were used throughout. The transfer line temperature was maintained at TC1 = 190°C, TC2 = 227°C, TC3 = 241°C and TC4 = 235°C. The ICP torch position was optimised and ion less settings tuned using the constant signal of $^{40}Ar^{16}O^{+}$ produced by the cold mercury vapour generator, which was removed prior to analysis. It

was found impractical to introduce ferrocene as a vapour (using a Drechsel bottle assembly) for ^{56}Fe optimisation as this caused overloading of the detector, excessive deposition of carbon on the ICP-MS interface and prolonged memory effects. It is noted that optimum conditions for polyatomic and monoatomic ions of equivalent mass may be different; these compromise conditions were, however, both practical and effective.

Five replicate injections of ferrocene (150 pg as Fe) dissolved in hexane, gave an detection limit (3σ, using peak area integrate counts) of 3.0 pg s^{-1}. Peak width = 17.2 s, retention time = 7.75 min. and the signal to background ratio is high. **Figure 2.23** demonstrates one of the advantages of using a "dry" plasma. An alternative method is to desolvate the nebuliser gas prior to reaching the plasma [197]. Selective ion monitoring of ^{56}Fe is not usually possible using HPLC-ICP-MS owing to the polyatomic interference of $^{40}Ar^{16}O^{+}$ which results from the oxygen either present in aqueous or organic phases or often deliberately introduced into the nebuliser gas to prevent carbon deposition on the sampler and skimmer cones.



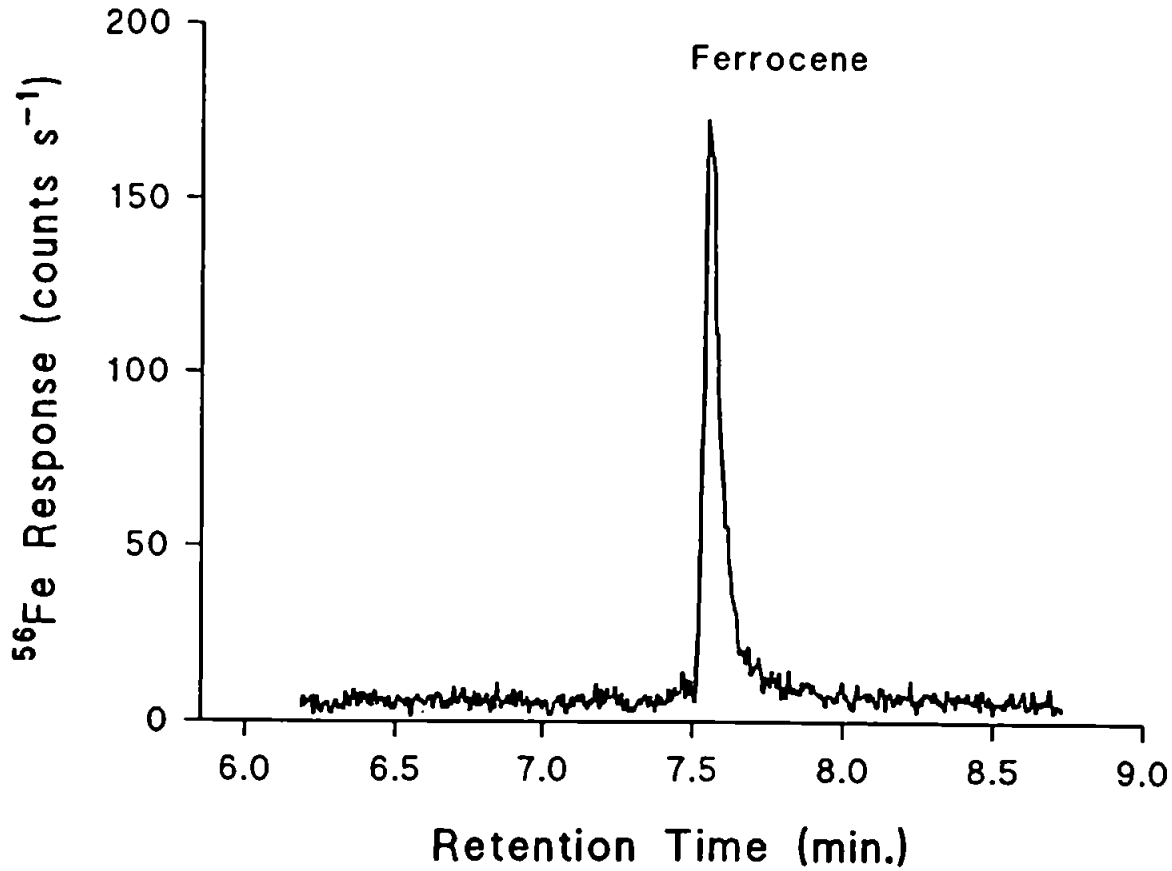


Figure 3.23 Ion selective chromatogram (m/z 56) of ferrocene (150 pg as Fe). No $^{40}Ar^{16}O^{+}$ polyatomic interference. GC operating conditions were 60°C to 180°C (5 min. iso.) at 10°C min^{-1}, He carrier gas = 2 ml min^{-1} (at 200°C), hexane solvent, 0.5 μl injected.

3.5.2 Diethyldithiocarbamate Complexes

Nickel diethyldithiocarbamate (RI = 3422) was used to investigate the limits of the retention range of organometallic compounds capable of being eluted (and subsequently analysed) using the Mk III interface (Section 2.6.2). Using the same conditions as described previously **(Fig. 2.13)**, six replicate injections (200 pg as Ni, at m/z = 58) gave a detection limit (3σ, using peak area integrated counts) of 6.5 pg s^{-1}. Peak width = 8.2 s, retention time = 10.4 min. and signal to background ratio is high.

Cobalt diethyldithiocarbamate ($Co(Dt)_3$) was injected into the coupled system (100 pg as Co) using the same conditions as for Ni $(Dt)_2$, the ICP-MS was tuned for Ni (m/z 58) and then the mass manually set to m/z = 59. An ion selective chromatogram resulted **(Fig. 3.24)** where the signal to background ratio was high. In the time available only one analysis was made. It should be noted that the peak is genuinely due to cobalt and not from the polyatomic interference $^{43}Ca^{16}O$ (m/z 59) since there was no identifiable source of calcium contamination entering the system.

3.6 Conclusions

The capillary GC-ICP-MS system developed has been proved to give reliable qualitative and quantitative analytical data for the speciation of a range of environmentally - important organometallic compounds (tetraalkylleads, organotins and diethylmercury). Other organometallic compounds studied included ferrocene and metallo-diethyldithiocarbamate complexes. The coupled technique provides valuable

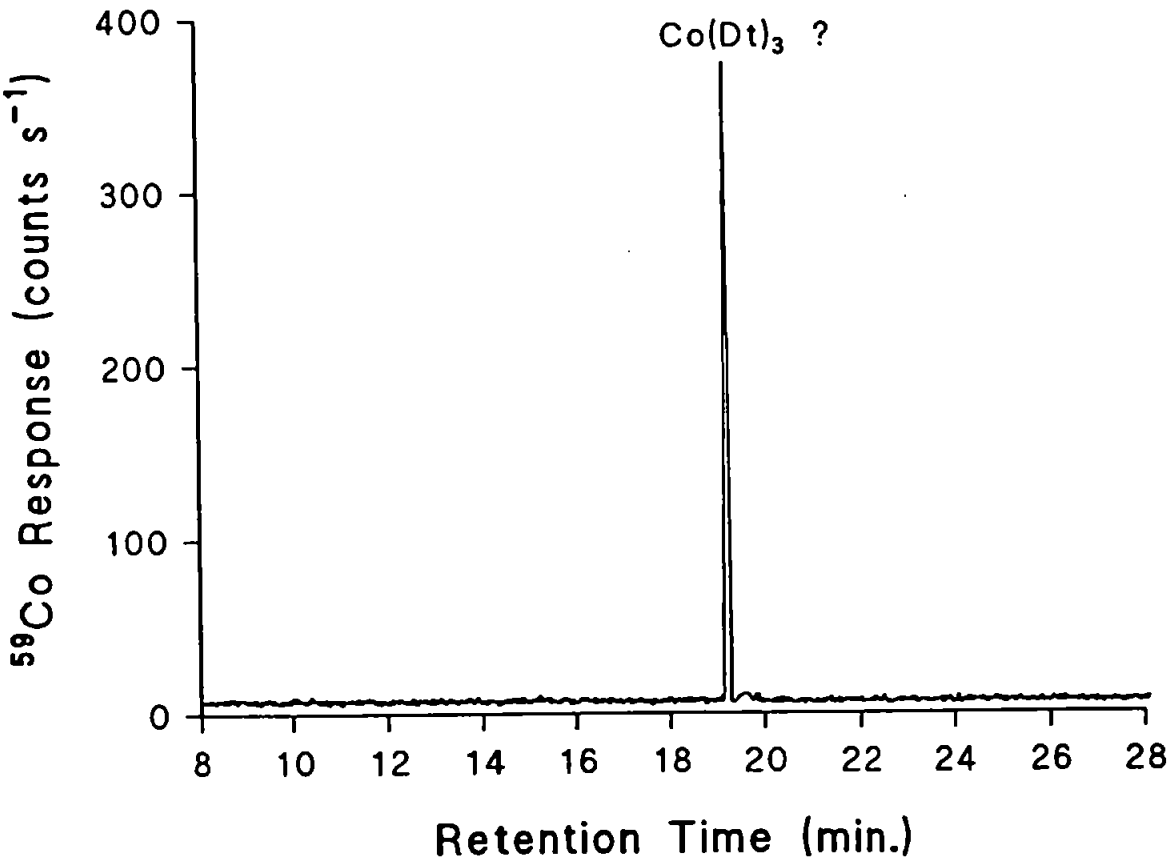


Figure 3.24 Ion selective chromatogram (m/z 59) of cobalt diethyldithiocarbamate (100 pg as Co). Instrumental conditions are given in Figure 2.13. The ICP-MS was tuned for Ni (m/z 58) and the mass setting manually set to m/z 59.

information on chemical speciation, offers limits of detection in the low pg s^{-1} range, and good linear response. In all analytical determinations the signal to background noise ratio was high.

The advantages of GC-ICP-MS over conventional GC-MS (for the analysis of tetraalkylead and organotin compounds) were demonstrated. These were better sensitivity and no requirement for delayed data acquisition (due to the effects of solvents on GC-MS filaments) to detect early eluting compounds. GC-MS spectra contained no molecular ions and spectral interpretation was usually complex.

Tetraalkylead compounds: the Figures of Merit for tetraethyllead (as Pb) were: LOD = 0.34 pg s^{-1}, RSD = 2%, r^2 = 0.9999 (measured between 2 pg - 10 ng) and linear dynamic range = 5 orders of magnitude. The concentration of tetraethyllead in a standard reference fuel was determined using external calibration and standard addition methods. The experimental values obtained using both methods were in agreement with the certificate value within the confidence limits of the measurement. The concentration of the tetralkyllead species in a naphtha sample was also determined using the external calibration method, the experimental value obtained for total lead was acceptable compared with the known (theoretical) value.

Organotin compounds: It was found necessary to derivatise organotin species using Grignard reagent (ethylmagnesium bromide) to make their separation more amenable to GC. Five organotin species were totally resolved in an analysis time of 12.4 min. (using a 25m column) and peak shape was Gaussian. Diethyldipropyltin was selected as the internal

standard. The Figures of Merit for these species were: LOD = 2 - 3 pg s^{-1} range (as Sn), RSD = 5.4 - 11.3%, r^2 = 0.999 (measured between 13 pg - 2.5 ng).

Organotin species were determined in a spiked water sample and two harbour sediments (a SRM and an unknown) using the internal standard method. The experimental values obtained were in agreement within the confidence limits of the measurement. Percentage recovery for the SRM sediment (PACS-1) was 100.4%. The utilisation of capillary GC gives good chromatographic resolution (compared with packed column GC) which is especially important for the analysis of organometallic compounds in complex environmental matrices (eg. harbour sediments).

Organomercury: Figures of Merit for diethylmercury were: LOD = 1.0 pg s^{-1} (as Hg), RSD = 5% and r^2 = 0.995 (measured between 35 - 279 pg).

The analysis of ferrocene (LOD = 3.0 pg s^{-1} as Fe) demonstrated the advantage of using a "dry" plasma (ie. no ^{56}ArO polyatomic interference).

Compounds with a relatively high retention index (RI > 3400) were eluted and analysed (nickel diethyldithiocarbamate, LOD = 6.5 pg s^{-1} as Ni).

CHAPTER FOUR

ANALYSIS OF PORPHYRINS

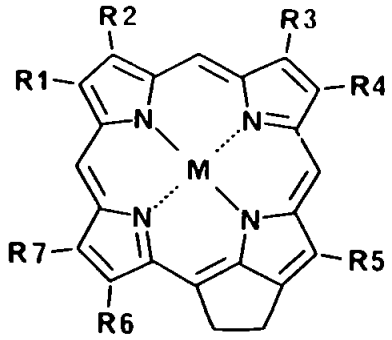
4.0 ANALYSIS OF PORPHYRINS

4.1 Introduction

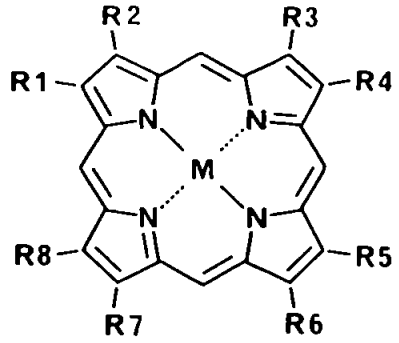
In the petroleum industry there is now considerable interest in the use of porphyrins as "biological markers" [198] and they have been used as maturity indicators for oils and sediments, and for oil-oil and oil-source rock correlations.

The existence of metal complexes in fossil fuels (known as porphyrins or petroporphyrins) was first established by Treibs in the 1930s [199-201]. The similarities in structures of porphyrins and chlorophyll-a was one of the first indications of the biogenic origin of petroleum, a subject which has been reviewed widely, [202-205].

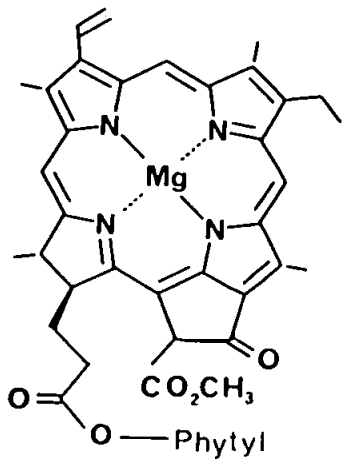
Porphyrins in geological materials such as shales, crude oils and coals have been shown to consist mainly of mixtures of nickel and vanadyl (V=O) complexes of deoxophylloerythroetioporphyrins (DPEP, **Fig. 4.1a**) and etioporphyrins (etio, **Fig. 4.1b**) [206], which are all thought to have been derived from chlorophylls (e.g. chlorophyll-a, **Fig. 4.1c**) [207-209]. Other minor porphyrin types have been observed [51,210] and proposed structural types include Di-DPEP (**Fig. 4.1d**), Rhodo-Etio (**Fig. 4.1e**) and Rhodo-DPEP (**Fig. 4.1f**). Minor metalloporphyrins of gallium [211], copper [212] and iron [213-215] have also been found in coals (Ga and Fe) and deep sea sediments (Cu). Typical concentrations range from 15 $\mu g\ g^{-1}$ in shale up to 2.5 $mg\ g^{-1}$ in crude oils [203].



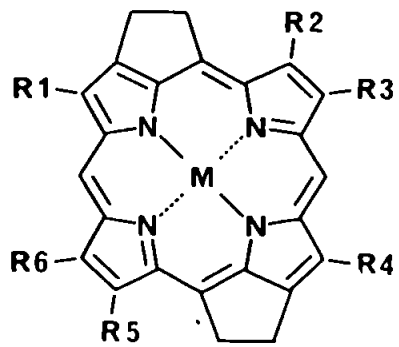
(a) DPEP - type



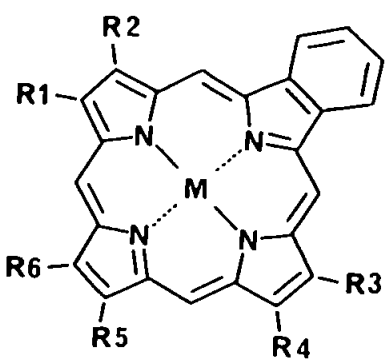
(b) ETIO - type



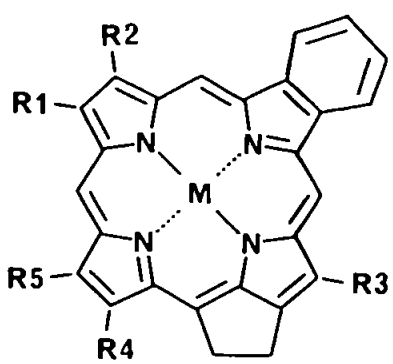
(c) CHLOROPHYLL - a



(d) Di-DPEP



(e) RHODO



(f) RHODO - DPEP

Figure 4.1 Porphyrin structures. Where M = metal atom and R = alkyl group (e.g. $-CH_3$, $-C_2H_5$).

As with other biomarker compounds the distributions of petroporphyrins have proved to be useful indicators of palaeoenvironmental conditions and petroleum generation, providing a sensitive and important measurement of the thermal maturity of sediments, oils and source rocks [216]. As thermal maturation increases there is a decrease in the proportion of DPEP to etio porphyrins [217], Ni to V=O metalloporphyrins [218,219] and average carbon number [220].

Metalloporphyrins are relatively involatile compounds (Mp approx. 400°C) making their separation by conventional GC methods difficult. As a result HPLC with ultraviolet-visible (UV-VIS) detection has been extensively for metallated [51,221] and demetallated [222-226] porphyrins. Element selective detection such as ICP-AES [114] and ICP-MS [227,228] has also been used occasionally.

Mixtures of porphyrins have been examined using conventional GC (with FID or MS detection) in a number of studies in the metallated, demetallated (free base) forms and/or followed by conversion into more volatile silicone (IV) derivatives [229-233]. However this technique suffered from excessive GC column bleed and column degradation for the separation of metalloporphyrins or loss of analytical information after demetallation or derivatisation.

During the early to mid 1980s progress in the manufacture of more thermally stable stationary phases and exterior coatings led to the development of high temperature GC (HTGC) [234-240]. This was achieved by replacing the outer polyimide coating of the fused silica capillary column with a thin layer (20 μm) of aluminium or using a column made entirely of glass or stainless steel. The stationary phase was generally bonded-cross linked methyl polysiloxane or siloxane-carborane polymethylsiloxane. These columns

can be operated isothermally at ca. 415°C or temperature programmed for brief periods to a maximum of ca. 480°C, allowing the elution of high molecular weight compounds up to about $\underline{n}$-C_{100} [235]. Subsequently both custom-made and commercially available HTGC capillary columns have been applied to the separation and characterisation of free base and metallated porphyrins using FID [241,242] and MS [243, 244].

4.1.1 Aims

This chapter describes the development of a HTGC technique for the separation of authentic porphyrin standards and geological free base and metallated porphyrins (using FID) for intended future coupling of HTGC to ICP-MS for geochemical "fingerprinting" applications. A method for the extraction, isolation and characterisation of metalloporphyrins in shales is also described.

4.2 Authentication of Porphyrin Standards

A range of porphyrins was obtained from commercial suppliers (Aldrich Chemical Co. Ltd., Gillingham, Dorset, UK) and Dr. A. Barwise (BP Exploration, Sunbury-on-Thames, UK). Metallated etio-I porphyrins were synthesised according to the methods described by Dolphin [204]. Materials and reagents used are listed in Appendix A.

4.2.1 Ultraviolet-Visible Spectrophotometry

The instrument used was a Perkin Elmer Lambda 7 UV-VIS spectrophotometer. The absorption spectra of known concentrations of porphyrins (dissolved in dichloromethane) were obtained. The porphyrin structural types were all confirmed by comparing the

absorption maxima (λ max), relative absorption intensities (A) and molar extinction coefficients (ϵ) to known literature values **(Table 4.1)**. Typical absorption spectra of metallo- and free-base porphyrins are given in **Figure 4.1.**

Etio porphyrins (types II and III) were thought to be impure due to the low ϵ values obtained compared to etio-I porphyrin which was synthesised as pure, fine, purple, crystalline needles. Due to the small quantities of etio types II and III possessed (< 0.3 mg), confirmation of purity by GC analysis was not performed.

Table 4.1 Ultraviolet-visible spectrophotometric absorption maxima (λ max), relative absorbance intensities and molar extinction coefficients of various porphyrins. Literature values are given in the parentheses [202-204]. The differences in λ max positions and absorption band intensities allow metallo- and free-base structural types to be readily distinguished.

Porphyrin	λ max (nm)	Absorbance	Molar extinction coefficient ($x10^4$) (10^{-2} m^2 mol^{-1})
V = O etio	406 (407) 532 (533) 570 (572)	1.00 (1.00) 0.05 (0.05) 0.10 (0.09)	30.79 (33.10) 1.61 (1.62) 2.99 (3.16)
Ni etio	390 (391) 515 (516) 554 (551)	1.00 (1.00) 0.05 (0.05) 0.16 (0.15)	15.43 0.87 2.31
Ni-OEP	395 (391) 515 (516) 550 (551)	1.00 (1.00) 0.05 (0.05) 0.15 (0.15)	6.53 0.35 1.01
Co-etio	390 (391) 515 (516) 550 (551)	1.00 (1.00) 0.05 (0.05) 0.10 (0.15)	n.d. n.d. n.d.
Zn-etio	388 (391) 515 (516) 550 (551)	1.00 0.07 0.08	n.d. n.d. n.d.
Pd-etio	391 (391) 511 (516) 546 (551)	1.00 (1.00) 0.09 (0.05) 0.08 (0.15)	n.d. n.d. n.d.

continued....

Table 4.1 (continued).

Porphyrin	λ max (nm)	Absorbance	Molar extinction coefficient ($x10^4$) (10^{-2} m^2 mol^{-1})
Etio I	396 (399)	1.00 (1.00)	16.66
	497 (498)	0.08 (0.08)	1.41
	530 (532)	0.06 (0.06)	1.02
	566 (568)	0.04 (0.03)	0.68
	619 (622)	0.03 (0.02)	0.50
Etio II	396 (399)	1.00 (1.00)	9.81
	497 (498)	0.08 (0.08)	0.76
	531 (532)	0.06 (0.06)	0.55
	565 (568)	0.04 (0.04)	0.40
	619 (622)	0.03 (0.02)	0.27
Etio III	396 (399)	1.00 (1.00)	5.33
	497 (498)	0.08 (0.08)	0.45
	530 (532)	0.06 (0.06)	0.32
	565 (568)	0.04 (0.04)	0.22
	619 (622)	0.03 (0.02)	0.16
OEP	398 (399)	1.00 (1.00)	16.23
	498 (498)	0.08 (0.08)	1.37
	532 (532)	0.06 (0.06)	0.99
	566 (568)	0.04 (0.04)	0.65
	618 (622)	0.03 (0.02)	0.47
C_{32} DPEP	398 (398)	1.00 (1.00)	6.79
	499 (498)	0.07 (0.07)	0.46
	534 (532)	0.02 (0.02)	0.11
	563 (564)	0.03 (0.03)	0.19
	616 (616)	0.02 (0.02)	0.17

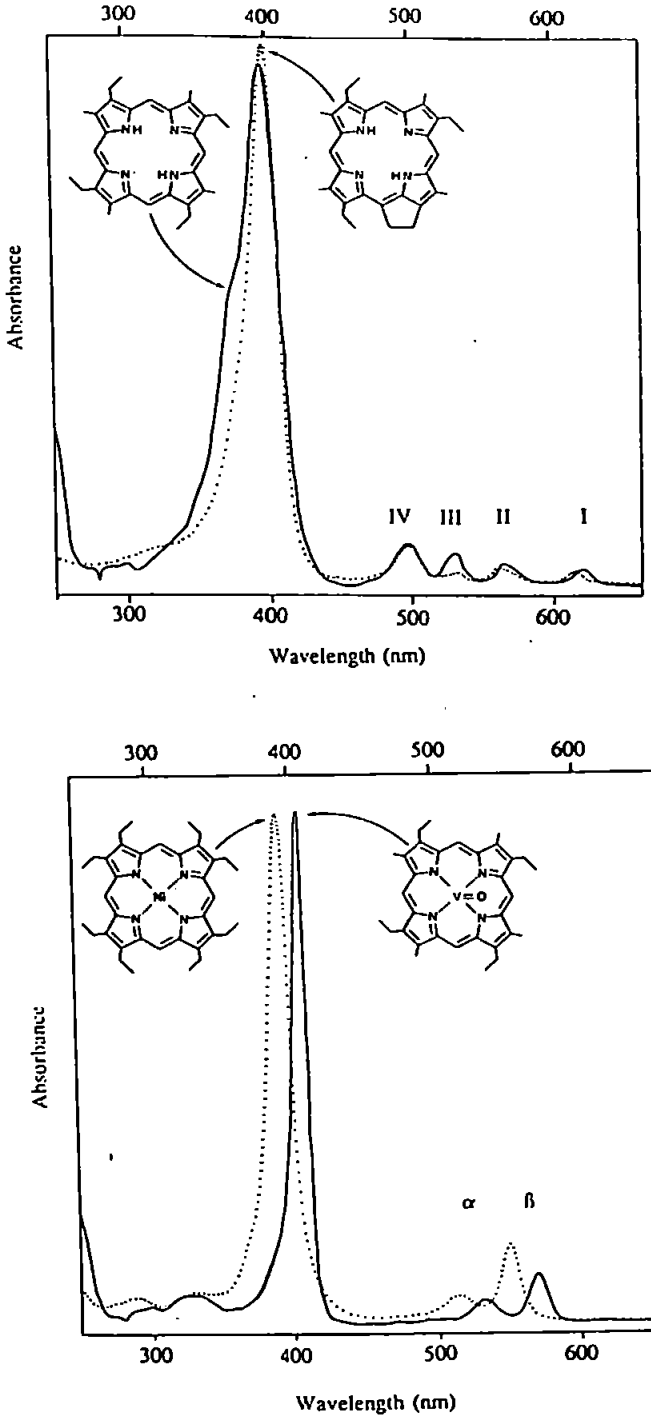


Figure 4.1 The UV-VIS absorption spectra of metallo- and free base porphyrins.
The vivid red coloration exhibited by solutions of porphyrins arises from the absorbance at approximately 400 nm, known as the Soret band. **(A.)** Free base etio-porphyrins are characterised by a IV>III>II>I order of band intensities, free base DPEP is characterised by a IV>II>I>III order. **(B.)** Metallo-porphyrins have a two banded spectrum (called α and β). The position and intensity of these absorption bands can be used to distinguish between nickel and vanadyl porphyrins and etio-porphyrins and DPEP types.

4.3 High Temperature Gas Chromatography (HTGC) of Porphyrins

4.3.1. Instrumental

The column used was an SGE 25AQ3/HT5-0.1 aluminium clad column, 25m x 0.32mm i.d. x 0.1μm film thickness (SGE Ltd., Milton Keynes, UK). The column was chosen for its thermal stability (maximum operating temperature = 460°C), low bleed, flexibility and proven separation for the analysis of metallo- and free base porphyrins [241]. Also it has the added advantage over stainless steel HTGC columns in that it can be safely brought into close proximity of high voltages (i.e. FID) or high r.f. (i.e. ICP-MS) without the possibility of conducting or arcing.

The gas chromatograph instrument used was a Carlo Erba HRGC 5300 Mega Series (Carlo Erba, Fisons, Loughborough, UK). The carrier gas (helium, 2 ml min^{-1} at 300°C) was passed through a series of oxygen and water filters to prevent column damage caused by oxidation of the stationary phase. The FID (with ceramic jet) was maintained at 430°C (10°C greater than the maximum oven temperature), supplied with air = 90 kPa, hydrogen = 50 kPa and nitrogen make up gas = 90 kPa. Injection was on-column (0.5 μl, 1.0 μl).

To prevent "electronic spiking" (caused by the FID not at ground potential) the aluminium cladding was removed from the last 5 cm from the column end according to the method used by Evershed [245]. In brief the column tip was immersed in aqueous NaOH (50% w/v) while maintaining a normal flow of carrier gas. Once the cladding was completely dissolved, it was rinsed with distilled water, dried and installed in

the FID as normal. The stripped section of column ensures complete electrical isolation as evidenced by the effective maintenance of the detector potential (*i.e.* a stable base line was produced).

4.3.2 Choice of Solvent

It was found that excessive peak tailing was associated with the elution of halogen-containing solvents (*e.g.* dichloromethane, chloroform and carbon tetrachloride). Peak tailing increased exponentially with increasing detector temperature making the chromatograms difficult to interpret. This has been observed by other workers [246] and was attributed to traces of involatile or polymeric material in the FID, which, by reacting with such solvents at high temperatures produces slightly more volatile products which bleed from the detector over time. This was partially eliminated with the use of nitrogen make-up gas.

Common non-halogenated solvents (*e.g.* hexane, toluene, tetrahydrofuran and carbon disulphide) did not produce peak tailing. Carbon disulphide (CS_2) was found to be the best solvent for both porphyrins and hydrocarbons and was subsequently used throughout this study.

4.3.3 HTGC of Porphyrin Standards

A series of metallated and free base porphyrins was analysed by HTGC. The GC retention indices (RI) were measured **(Table 4.2)** and their chromatographic behaviour observed.

The RI of any compound is the carbon number (x 100) of

a theoretical n-alkane having an identical elution time to the substrate under the conditions employed. This is defined by the following equation [247]:

$$RI = 100i \frac{t'_{R(x)} - t'_{R(n)}}{t_{R(n+i)} - t'_{R(n)}} + 100n \quad \text{..... eqn.1}$$

where: t'_R = adjusted retention time (*i.e.* retention time of the compound minus the retention time of an unretained component).

i = difference in numbers of carbon atoms of the n-alkane references.

x = compound of interest.

n = number of carbon atoms in the n-alkane.

and where: $t'_{R(n)} \leq t'_{R(x)} \leq t_{R(n+i)}$

Table 4.2 The retention indices (RI) of a series of porphyrin standards and n-alkanes calculated relative to n-C_{50} and n-C_{60} alkanes. GC oven temperature programme 60°C to 300°C (at 8°C min^{-1}) to 420°C (at 4°C min^{-1}) held isothermally at 420°C for 25 min. OEP = octaethylporphyrin, TPP = tetraphenylporphyrin.

Compound	RI	Threshold concentration ($\mu g\ ml^{-1}$)
n-C_{40} alkane	4000	n.d.
n-C_{44} alkane	4400	n.d.
n-C_{50} alkane	5000	n.d.
Etio II	5865	n.d.
Etio I	5904	239
n-C_{60} alkane	6000	n.d.
OEP	6000	268
Zn-Etio I	6056	n.d.
Cu-Etio I	6135	n.d.
Zn-OEP	6144	149
Cu-OEP	6195	n.d.
Ni-Etio I	6232	133
FeCl-OEP	6249	n.d.
Ni-OEP	6282	n.d.
V=O Etio I	6287	136
Co Etio I	6313	n.d.
C_{32} DPEP	6409	n.d.
TPP	7938	308
Cu-TPP	8618	n.d.

Equation (1) allows simple calculations of approximate RI values by linear interpolation between n-alkane standards. This approximation was used because no n-alkane standards with a retention greater than that of the porphyrins (*i.e.* > n-C_{60}) could be obtained. RI values measured by Gill (1984), [248], were found to give reliable quantification of retention behaviour, however slight variation is often observed with different chromatographic parameters (*e.g.* stationary phase, oven temperature programme and carrier gas flow rate).

Determination of the limits of detection and relative responses of the porphyrins was attempted without success. However it was noted that an approximate "threshold concentration" existed **(Table 4.2)** below which the porphyrin would not give a response. The most probable reason for this was that the GC used was not of high temperature design. According to the manufacturers advice, the FID heating unit was not sufficiently capable of maintaining the constant temperature required for routine HTGC analyses. As a result the porphyrins were probably condensing or bonding irreversibly to the stationary phase and/or silica wall of the column contained within the detector. Subsequently use of a specialised high temperature GC instrument (Carlo Erba Mega Series 5300 HT-SIM-DIST) overcame this problem [249] but this model was not available at the time of the present study.

Figures 4.2 - 4.4 are HT gas chromatograms of a series of standard porphyrins. All the porphyrins elute beyond n-C_{60} alkane (except for etio I and II) within a period of 5-6 minutes (except for TPP and Cu-TPP). The porphyrins have broad peak widths and exhibit a small degree of peak tailing compared to the n-alkanes.

The HT column used can resolve the two structural types of porphyrins (etio and C_{32} DPEP, **Fig. 4.2**) which are frequently found as a mixture in geological materials. This is an important requirement for geochemical fingerprinting and maturation studies.

Although the HT column used was incapable of resolving certain individual metal species **(Fig. 4.3 & 4.4)**, the use of coupled HTGC-ICP-MS with consequent element selective detection might overcome this problem and would then provide speciation information.

4.3.4 Column Degradation

The HT column was found to degrade rapidly with use, even though the manufacturers instructions were followed. This was apparent from the decreasing retention time observed after successive injections of porphyrins **(Fig. 4.5)** and inadequate chromatographic resolution, excessive column bleed and poor peak shape (*i.e.* jagged, tailing and fronting). A new column could be used to perform only about 30-40 porphyrin analyses.

Column degradation was attributed to the reaction of porphyrins (or their degradation products) with the siloxane-carborane stationary phase causing it to "bleed" and exposing free Si-OH binding sites on the silica wall on which the porphyrins strongly associate. This was not observed for the analyses of high molecular weight hydrocarbons (RI > 5000) using the same chromatographic conditions [250]. If the column life was extended by the analysis of non-porphyrin samples, the temperature fluctuations would cause the aluminium cladding to degrade resulting in the column to become brittle and eventually to break.

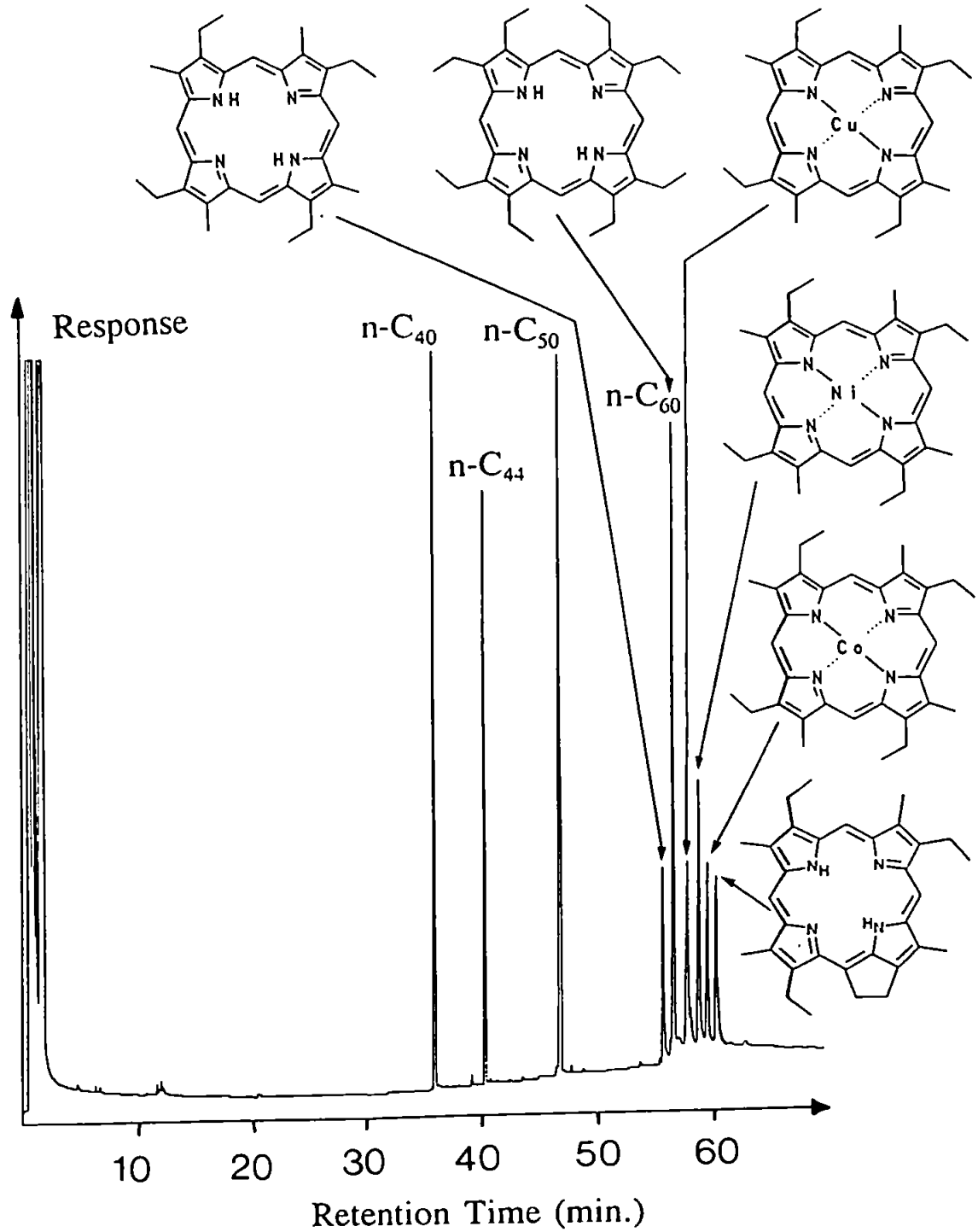


Figure 4.2 HT gas chromatogram of a series of metallo- and free base porphyrins, and n-alkanes. The HT column can adequately separate free-base etio-I porphyrins and C_{32} DPEP type, an important requirement for geochemical fingerprinting. GC oven temperature programme, 60°C to 300°C (at 8°C min^{-1}) to 420°C (at 4°C min^{-1}) held isothermally at 420°C for 10 min. Sample concentration, 1 x 10^{-3} M (in CS_2, 0.5 ul injected).

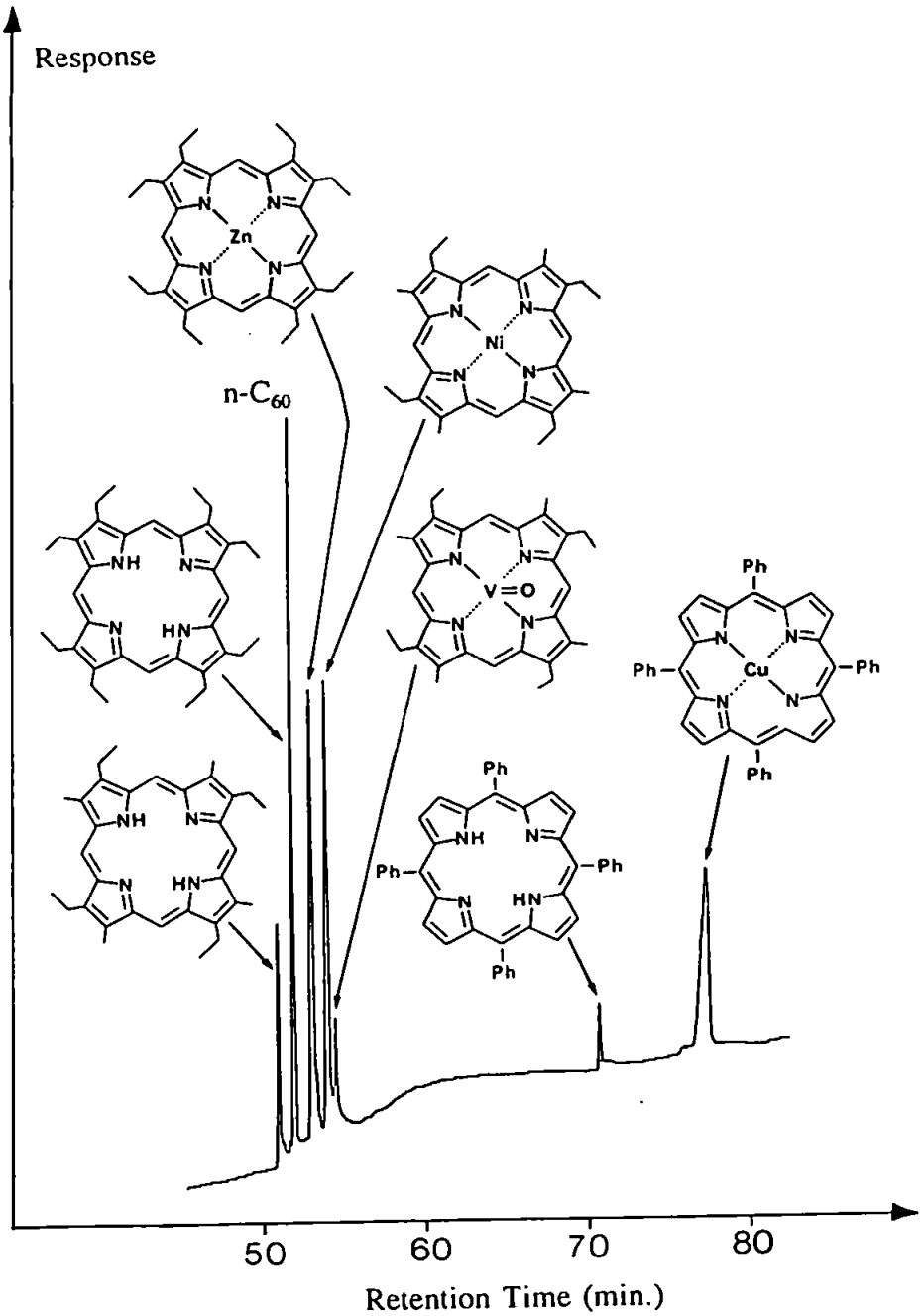


Figure 4.3 HT gas chromatogram of a series of metallo- and free base porphyrins, and n-C_{60} alkane. Vanadyl and nickel etio I porphyrins (both commonly found together in geological materials) are only partially resolved, this would not be a problem when element selective detection is used (i.e. coupled to ICP-MS). The HT column is also capable of separating high molecular porphyrins (RI > 8600) such as Cu-TPP. Oven temperature programme, 60°C to 420°C (at 10°C min^{-1}) held isothermally at 420°C for 20 min. Sample concentration, 1 x 10^{-3} M (in CS_2, 0.5 μl injected).

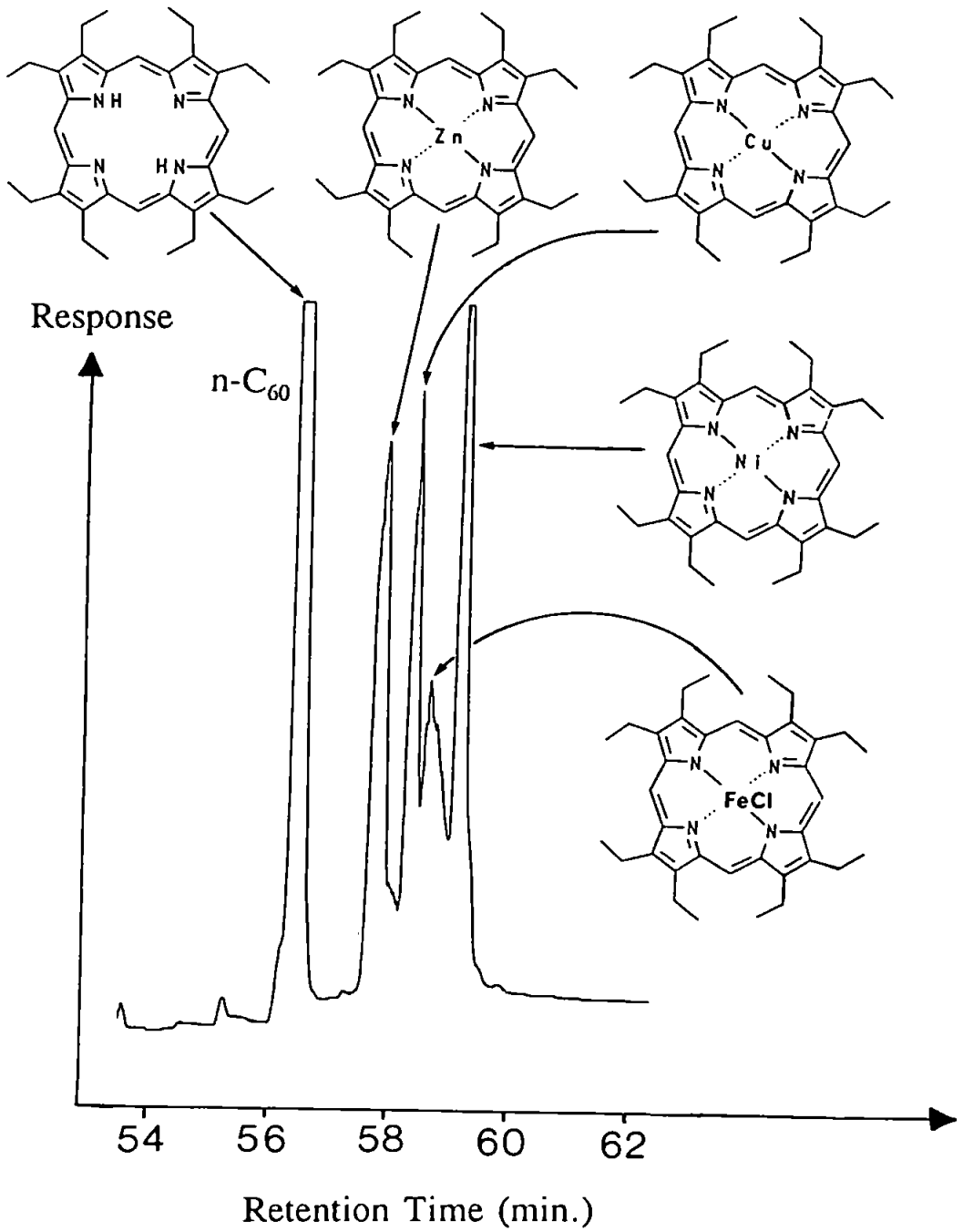


Figure 4.4 HT gas chromatogram of a series of metallo- and free base synthetic porphyrins of the same structural type (octaethylporphyrin) and n-C_{60} alkane. Peak widths are broader compared to the n-alkanes metalloporphyrins are only partially resolved and would be overcome by the use of HTGC-ICP-MS. Same conditions used as in **Fig. 4.2.**

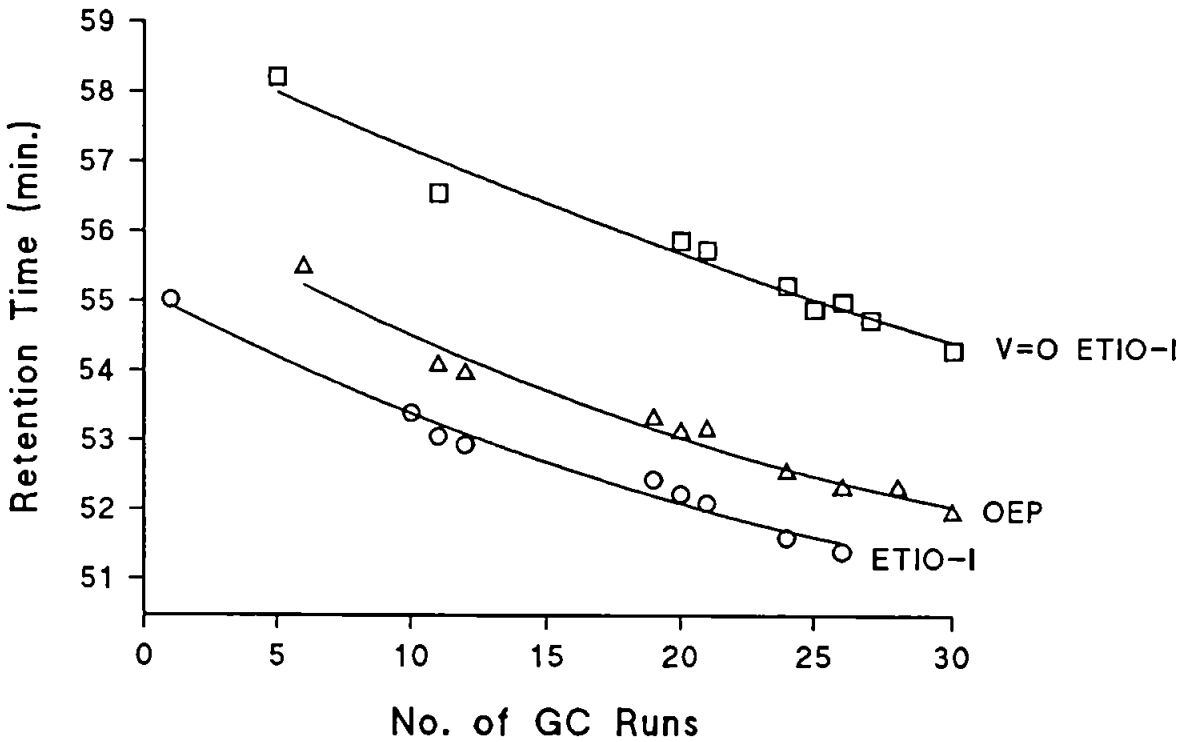


Figure 4.5 HT column stationary phase degradation as evidence by the decrease in retention time of selected porphyrins with successive analyses, with a concomitant increase in column bleed.

4.4 Analysis of Metalloporphyrins in Shales

4.4.1 Analysis of Green River Shale

Green River Shale (Eocene, USA) was obtained from Dr. G. Wolff (University of Liverpool, UK) and extracted using the method of Chicarelli *et al.*, (1990) [251] **(Fig. 4.6)**.

The presence of metalloporphyrins in the total organic extract (TOE) was confirmed by the presence of the characteristic UV-VIS absorbance at 400 nm (Soret band). The total concentration of first row transition metals in the TOE was determined by ICP-MS **(Table 4.3)**.

An aliquot of the TOE was fractionated (in order of increasing polarity) using flash chromatography **(Fig. 4.6)** and each separate fraction examined by UV-VIS spectrophotometry **(Fig. 4.7)**. The metalloporphyrins were present in fractions B1-B3 as evidenced by the presence of the Soret band (at approximately 400 nm) and the α and β bands (between 500-600 nm). The spectra obtained were compared to nickel and vanadyl porphyrin standards. Fractions B1 and B3 contained Ni and V=O porphyrins respectively and B2 a mixture of both. Using known molar extinction coefficients of standards and making the assumption that all of the metalloporphyrins were of the etio type, the approximate concentration of Ni and V=O porphyrins in the shale was calculated **(Table 4.4)**.

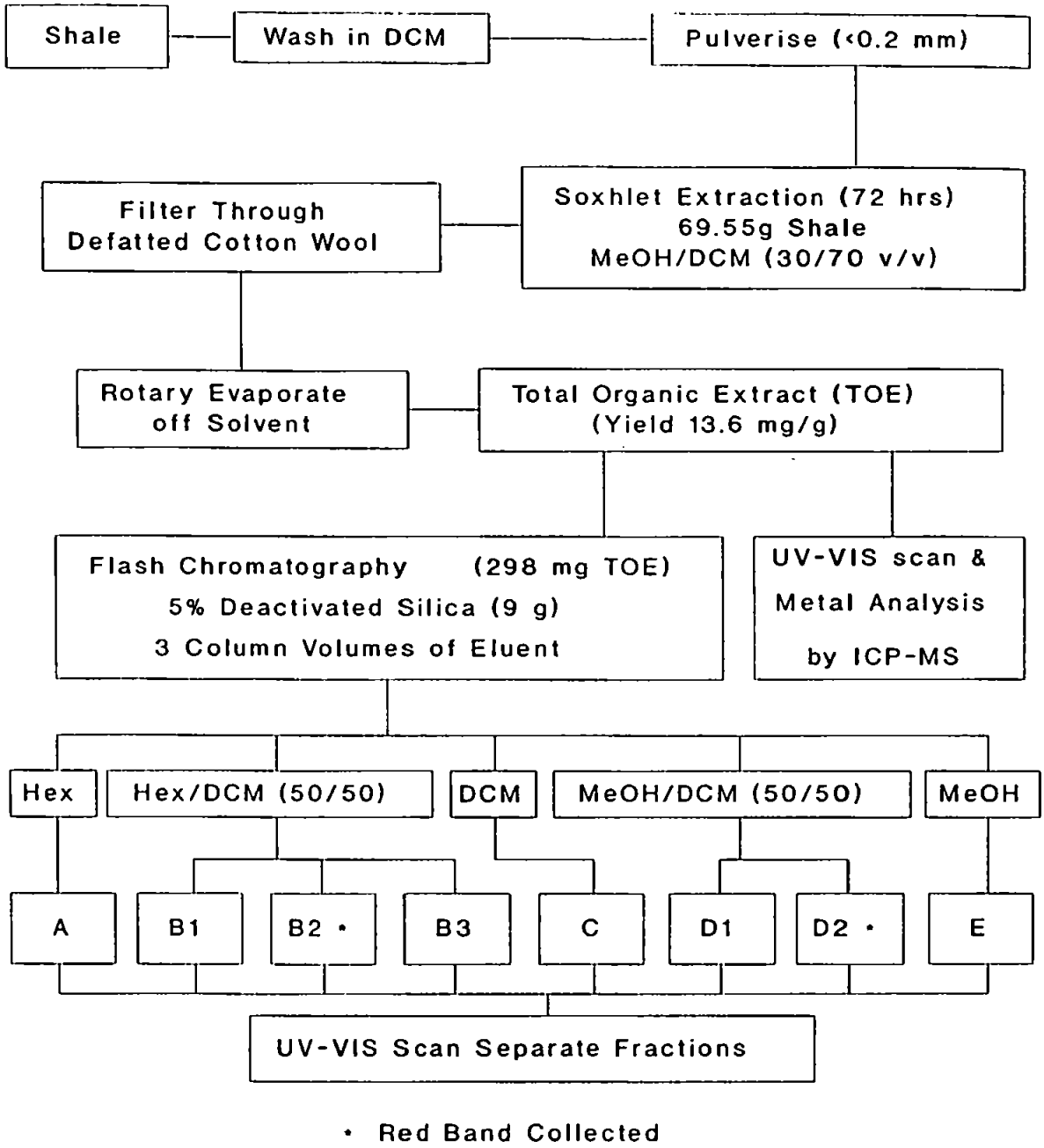


Figure 4.6 Extraction and isolation scheme of metalloporphyrins from Green River Shale. (DCM = dichloromethane, Hex = hexane and MeOH = methanol).

Table 4.3 The first row transition metal concentrations of the total organic extract of Green River Shale by ICP-MS, showing relatively high concentrations of nickel and vanadium.

Metal	Mass	Concentration ($\mu g\ g^{-1}$)
Ti	46	135
V	51	180
Cr	52	41
Fe	57	73
Ni	60	234
Cu	63	54
Zn	68	467

Footnote: An aliquot of TOE was dissolved in decalin (250 mg in 25 ml). Internal standard used = 100 ng ml^{-1} indium. ICP-MS data acquisition parameters: semi-quantitative analysis, mass range = m/z 27-214, no. of channels = 2048, no. of sweeps = 100, dwell time = 320 μs, no. of peak jump sweeps = 20. Procedural blank was clear.

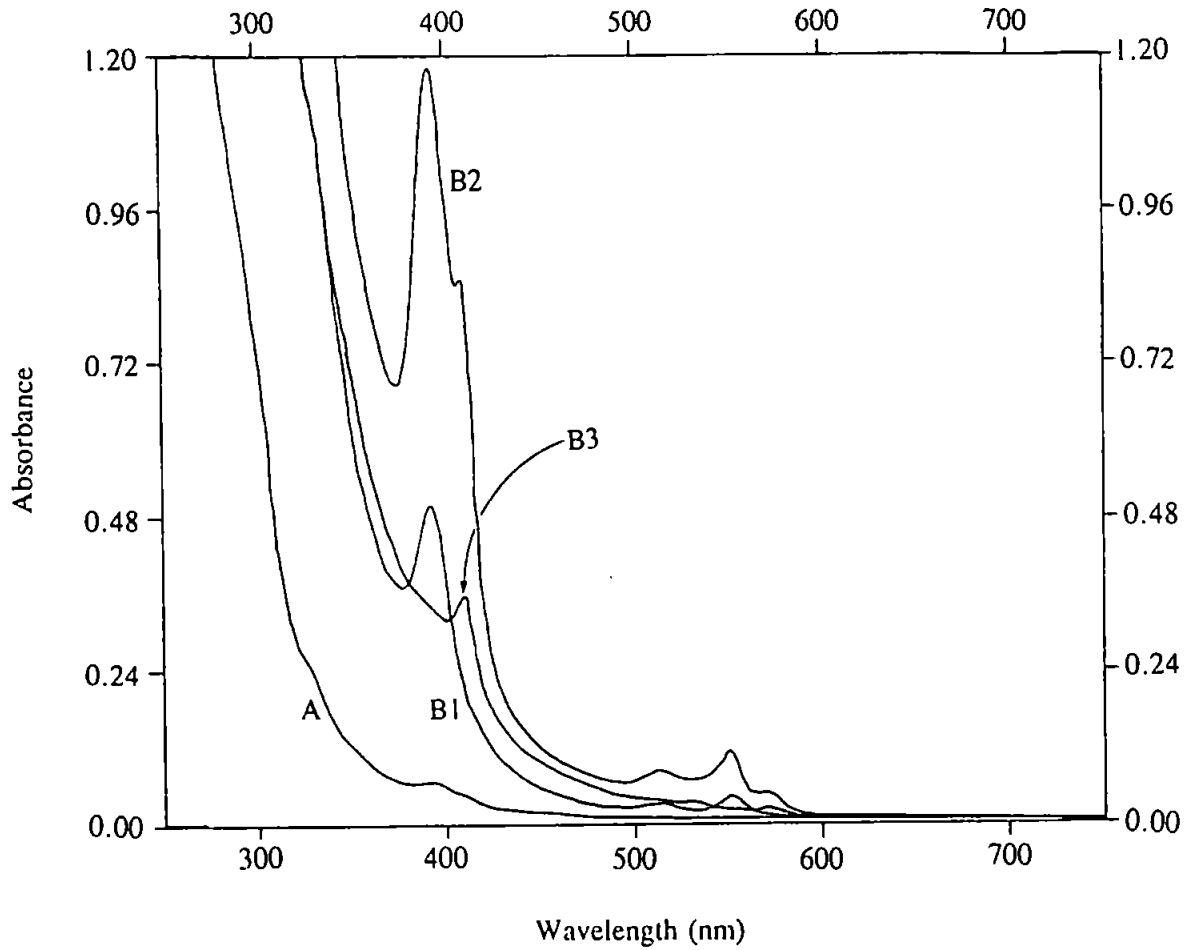


Figure 4.7 UV-VIS absorbance spectra of fractions A, B1-B3 of the Green River Shale TOE. Fractions B1 and B3 contains Ni and V=O porphyrins respectively and B2 contains a mixture of both (*i.e.* B2 has two Soret absorbances at 390 and 406 nm and a three absorbances between 500-600 nm).

Table 4.4 Concentrations (approx.) of nickel and vanadyl porphyrins in Green River Shale TOE. Concentrations were calculated using the molar extinction coefficients of standards **(Table 4.1)**, using the Soret band and α/β absorbances.

Sample	Shale concentration ($\mu g\ g^{-1}$)	
	Ni-Porphyrins	V=O Porphyrins
Fraction B1	0.5	none
Fraction B2	43.8	16.0
Fraction B3	none	1.0
TOTAL	44.3	17.0

The V=O/(V=O + Ni) porphyrin ratio was 0.28 which is in reasonable agreement with other literature values **(Table 4.5)**. The immaturity of the Green River Shale is reflected by the low V=O / (V=O + Ni) ratio obtained, compared to more mature oil shales **(Table 4.5)**.

Fraction B2 was also examined by HTGC **(Fig. 4.8)**. The HT gas chromatogram indicates the likely presence of metalloporphyrins eluting between 360-400°C. Effective coupling of HTGC to ICP-MS would make it possible to obtain a geochemical metal "fingerprint" of the Ni and V (and possibly Fe and Ti=O) porphyrins present in the shale.

4.4.2 HTGC of Nickel Porphyrins in Marl Slate

Marl Slate extract (Middle Triassic, USA) was obtained from Dr. A. G. Barwise (BP Exploration, Sunbury-on-Thames, UK).

The extract (C.4., nickel porphyrins, fractions 1-4) was examined by HTGC **(Fig. 4.9)**. The chromatogram shows the likely presence of both etio and DPEP type nickel porphyrins. The ratio of etio porphyrin to DPEP types can be used as a maturity indicator parameter [217].

Table 4.5 Comparison of V=O/(V=O + Ni) porphyrin ratios of immature and mature oil shales. Experimental ratio obtained is in agreement with the literature values, Lewan (1984) [218].

Shale Name	Basin	Period, Age	V=O/(V=O + Ni) Ratio
Green River Shale (experimental)	Piceance Peak Basin	Eocene, 42-55 Myrs.	0.28
Green River Shale (literature)	Powder River Basin	Eocene, 42-55 Myrs.	0.22
New Albany Shale (literature)	Illinois Basin	Mississippi/ Devonian, 320-400 Myrs.	0.59

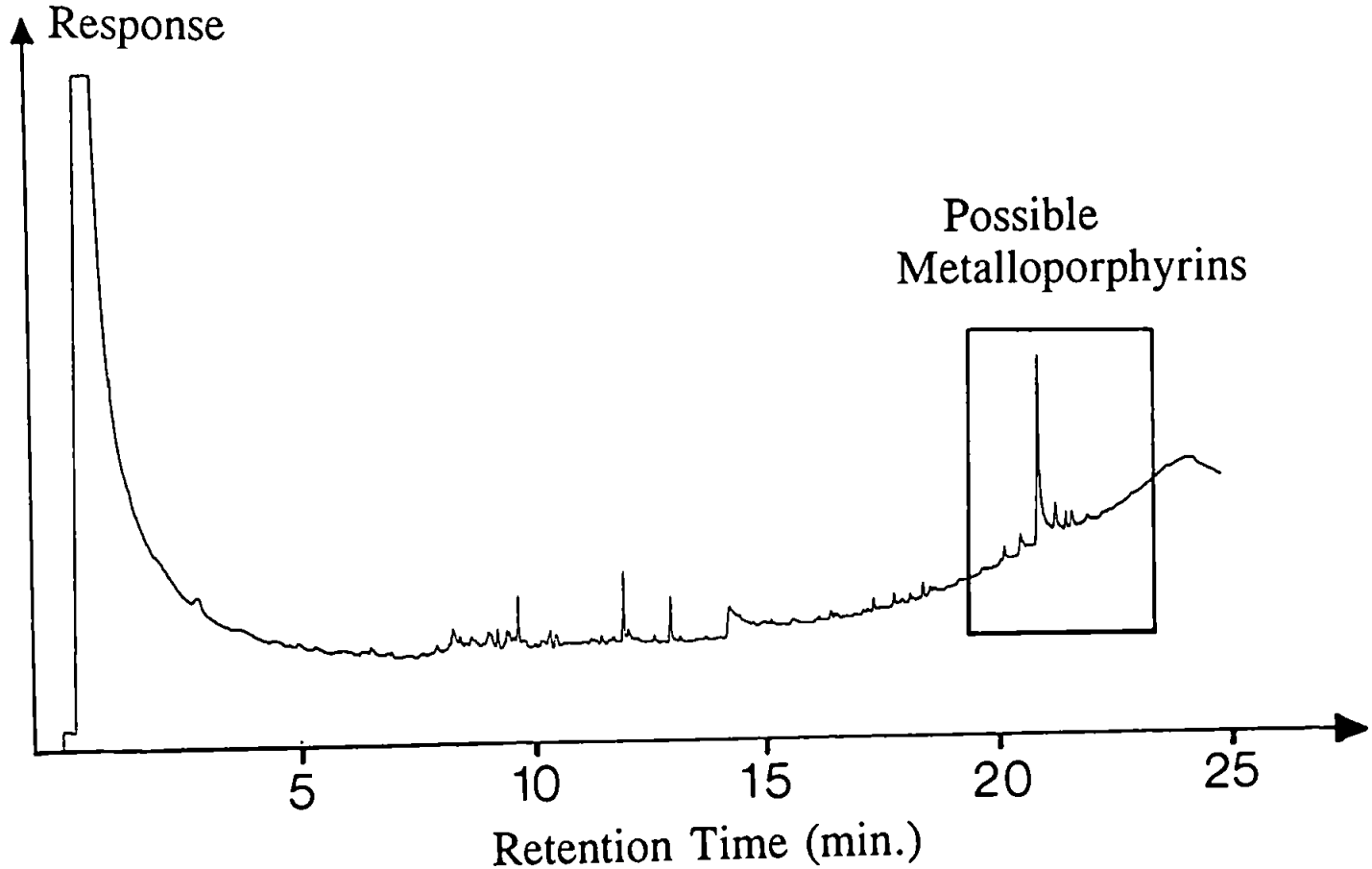


Figure 4.8 HT gas chromatogram of Green River Shale (fraction B2), showing the likely presence of metalloporphyrins. SGE HT5 aluminium clad column (12m x 0.32mm i.d. x 0.1μm film thickness), oven temperature programme 60°C to 410°C (at 15°C min^{-1}) held isothermally at 410°C for 10 min. He carrier gas (flow rate = 3 ml min^{-1}), DCM solvent, sample concentration = 54.4 mg ml^{-1}, 1.0 μl injected.

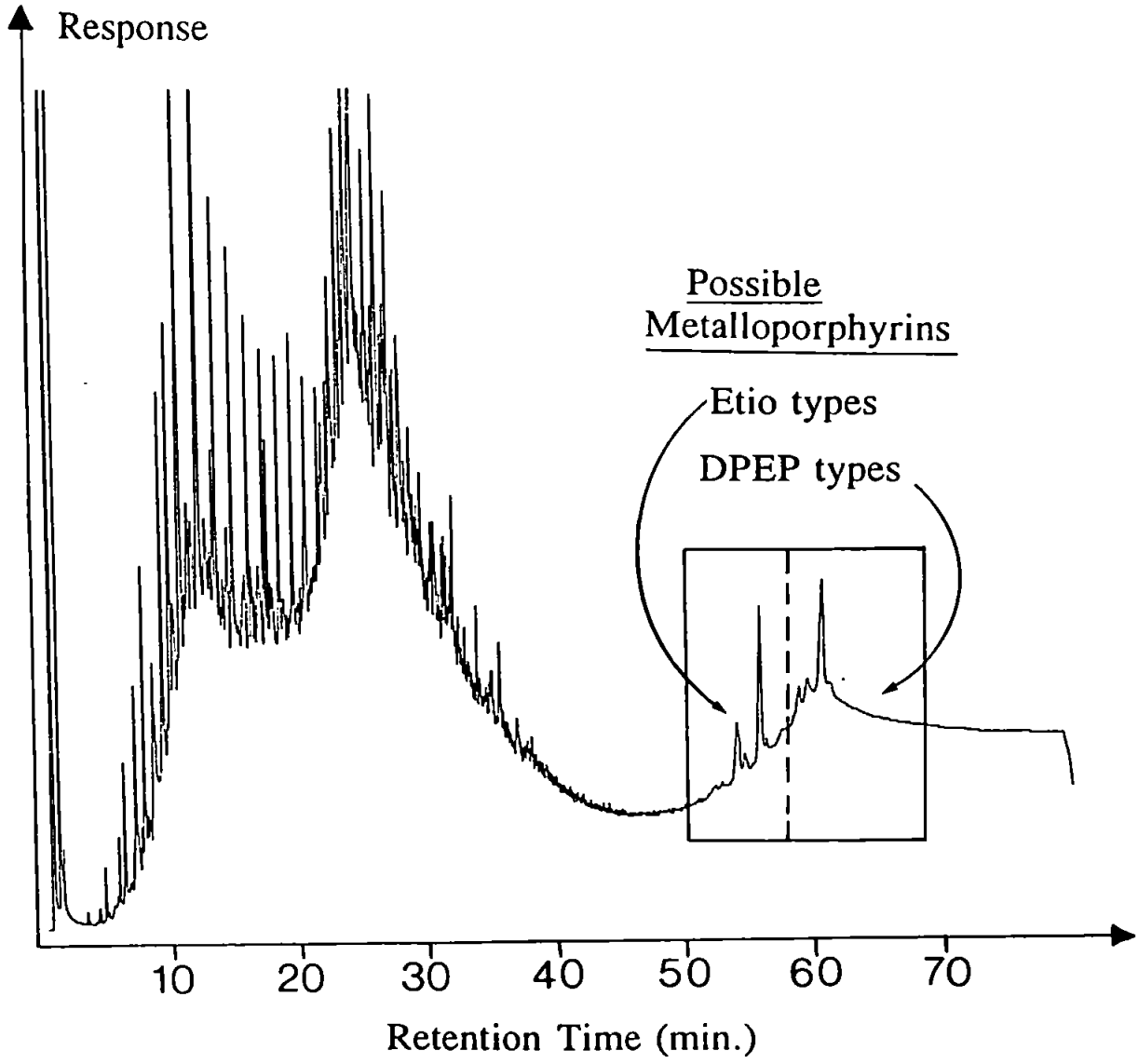


Figure 4.9 HT-gas chromatogram of nickel porphyrins in Marl Slate extract. Two distinct groups of peaks are present corresponding to etio and DPEP type porphyrins. Oven temperature programme = 60°C to 300°C (at 8°C min^{-1}) to 420°C (at 4°C min^{-1}) held isothermally at 420°C for 20 min., sample concentration = 52.6 mg ml^{-1} (CS_2 solvent, 0.5 μl injected).

4.5 Conclusions

A range of metallo- and free base porphyrin standards were authenticated using UV-VIS spectrophotometry and their molar extinction coefficients measured.

A HTGC method for the separation of porphyrins was successfully established using a commercially available aluminium clad, HT capillary column. Carbon disulphide was found to be the most compatible solvent.

HTGC retention indices (RI = 5865-8618) were calculated for the porphyrin standards. Determination of limits of detection and relative responses was unsuccessful. This was attributed to the FID not being sufficiently capable of maintaining the constant temperature required for HTGC analyses.

The HTGC technique resolved etio porphyrins from C_{32} DPEP structural types which is an important requirement for geochemical fingerprinting and maturation studies. All of the geologically significant metalloporphyrins (i.e. Ni, V=O, FeCl and Cu) eluted from the column with reasonable peak shapes.

The HT column degraded rapidly with use, resulting in a decrease in chromatographic resolution, poor peak shape and excessive column bleed. This was thought to be caused by the reactive nature of the porphyrins with the stationary phase. A maximum of approximately 40 porphyrin analyses could be performed before a replacement column was required.

Metalloporphyrins were extracted and isolated from Green River Shale and characterised using UV-VIS spectrophotometry and ICP-MS. The concentrations nickel and vanadyl (V=O) porphyrins were calculated to be

approximately 44.3 and 17.0 $\mu g\ g^{-1}$ respectively. The experimental V=O/(V=O + Ni) porphyrins ratio of 0.28 and trace metal analysis of the total organic extract (TOE) revealing high proportions of Ni to V is evidence of the geochemically immature nature of the Green River Shale.

HTGC analysis of Green River Shale and Marl Slate shows the presence of metalloporphyrins and the resolution of etio porphyrins from DPEP structural types. These ratios may be useful as another maturity parameter indicator.

Although HTGC-FID is incapable of resolving porphyrins of similar structural types (containing different metals), the use of coupled HTGC-ICP-MS with consequent element selective detection will provide speciation information necessary for the rapid fingerprinting of metalloporphyrins. The database of retention and spectral data and the collection of authenic porphyrins assembled and synthesised provides a valuable starting point for subsequent HTGC-ICP-MS studies of this interesting class of trace element species.

CHAPTER FIVE

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

5.0 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

5.1 Conclusions

Capillary GC has been successfully coupled to ICP-MS and has proved to give reliable qualitative and quantitative data for the determination of species for a range of environmetally important organometallic compounds. The coupled technique provides valuable information on chemical speciation, offers limits of detection in the low pg s^{-1} range, and good linear response. In all analytical determinations the signal to background noise ratio was high.

For laboratories where GC and ICP-MS instrumentation is already available the construction of a simple GC-ICP interface now offers an economical alternative to dedicated GC-MIP-AES instrumentation for trace metal speciation analysis. ICP-MS is also an independent analytical method and the design aspects of an easily removable interface made independent ICP-MS (and GC) operation entirely possible. This is an important factor in many busy multi-user laboratories.

The study involved the development of progressively improved transfer lines enabling direct interfacing of the GC column to the ICP-MS torch:

1. The final interface design (Mark III transfer line) ensured 100% transport efficiency (no loss of analyte), reduced chromatographic band broadening and avoiding unnecessary dilution. This transfer line was of simple construction (making service convenient),

was strong and robust, inexpensive, light-weight, operable over a large temperature range (ambient - 550°C), was on-line for real time analysis and had a relatively short installation / disassembly time (approximately 2 hrs.)

2. In order that the transfer line could as of short as possible, the ICP-MS was modified by removal of a panel from the hood and torch box through which the transfer line could pass. This also made assembly and diassembly easy.

3. The ICP-MS was tuned using a continuous signal of mercury (from a cold mercury vapour generator, gas/liquid separator) and the constant ablation of nickel from the sampler and skimmer-cones.

4. The column outlet needed to be positioned at the tip of the torch injector to prevent absorption or condensation of the analyte on the walls of the injector.

5. Using coupled GC-GC the high temperature capabilities of the Mark II transfer line was demonstrated by the elution of relatively involatile metalloporphyrins and high molecular weight alkanes ($\underline{n}$-C_{50} and $\underline{n}$-C_{60}) at 420°C. However due to condensation of these compounds in the length of the column contained within the torch injector HT-GC-ICP-MS was not achieved.

6. GC-ICP-MS of relatively involatile metal chelates was accomplished. Using a resistively heated stainless steel insert contained within the torch injector, it was possible to elute nickel diethyldithiocarbamate which has a higher retention index (RI > 3400) than many organo-metals determined by previous methods.

Following the successful development of the capillary GC-ICP-MS system Figures of Merit were established for authentic standard compounds:

1. **Tetraalkylead compounds:** the Figures of Merit for tetraethyllead (as Pb) were: LOD = 0.34 pg s^{-1}, RSD = 2%, r^2 = 0.9999 (measured between 2 pg - 10 ng) and linear dynamic range = 5 orders of magnitude.

2. **Organotin compounds:** Organotin chloride species were derivatised using Grignard reagent to make their separation amenable to GC. Five organotin species were totally resolved in an analysis time of 12.4 min. (using a 25m column) and peak shape was Gaussian. Diethyldipropyltin was selected as the internal standard. The Figures of Merit for these species were: LOD = 2 - 3 pg s^{-1} range (as Sn), RSD = 5.4 - 11.3%, r^2 = 0.999 (measured between 13 pg - 2.5 ng).

3. **Organomercury:** Figures of Merit for diethylmercury were: LOD = 1.0 pg s^{-1} (as Hg), RSD = 5% and r^2 = 0.995 (measured between 35 - 279 pg).

4. **Ferrocene** (LOD = 3.0 pg s^{-1} as Fe) and compounds with a relatively high retention index (RI > 3400) were eluted and analysed (**nickel diethyldithiocarbamate**, LOD = 6.5 pg s^{-1} as Ni).

The GC-ICP-MS system was validated using "real samples" (*e.g.* standard reference materials) and their chemical species determined:

1. The concentration of **tetraethyllead** in a standard reference fuel was determined using external calibration and standard addition methods. The experimental values obtained using both methods were

in agreement with the certificate value within the confidence limits of the measurement.

The concentration of **five tetralkyllead species** in a naphtha sample was also determined using the external calibration method. The experimental value obtained for total lead was acceptable compared with the known (theoretical) value.

2. **Three organotin species** were determined in a spiked water sample and two harbour sediments (a SRM and an unknown) using the internal standard method. The experimental values obtained were in agreement within the confidence limits of the measurement. Percentage recovery for the SRM sediment (PACS-1) was 100%.

Some advantages of capillary GC-ICP-MS were found to be:

1. Good chromatographic resolution (compared with packed column GC) which is especially important for the analysis of organometallic compounds in complex environmental matrices (*e.g.* harbour sediments and fuels).

2. Compared to conventional GC-MS, the coupled technique developed had better sensitivity and no requirement for delayed data acquisition (due to the effects of solvents on GC-MS filaments) to detect early eluting compounds. GC-MS spectra contained no molecular ions and spectral interpretation was complex for the species studied.

3. The analysis of iron-containing ferrocene, demonstrated the advantage of using a "dry" plasma (ie. no $^{40}Ar^{16}O^{+}$ polyatomic interference) making measurements of ^{56}Fe possible.

With the eventual objective of extending this coupled technique to the analyses of metalloporphyrin species, a HTGC method was developed:

1. A HTGC method for the separation of porphyrins was successfully established for range of metallo- and free base porphyrin standards (authenticated using UV-VIS spectrophotometry) using a commercially available HT capillary column. Retention indices (RI) ranged from 5865-8618. Determination of limits of detection and relative responses was unsuccessful. This was attributed to the FID not being sufficiently capable of maintaining the constant temperature required for HTGC analyses.

2. The HTGC technique resolved etio porphyrins from C_{32} DPEP structural types which is an important requirement for geochemical fingerprinting and maturation studies. All of the geologically significant metalloporphyrins (i.e. Ni, V=O, FeCl and Cu) all eluted from the column producing reasonable peak shapes.

3. The HT column degraded rapidly with use, resulting in a decrease in chromatographic resolution, poor peak shape and excessive column bleed. This was thought to be caused by the reactive nature of the porphyrins with the stationary phase.

4. Metalloporphyrins were extracted and isolated from Green River Shale and characterised using UV-VIS spectrophotometry and ICP-MS. The concentrations of nickel and vanadyl (V=O) porphyrins were approximately 44.3 and 17.0 $\mu g\ g^{-1}$ respectively. The experimental V=O/(V=O + Ni) porphyrins ratio of 0.28 and trace metal analysis of the total organic extract (TOE) revealed high proportions of Ni to V which is

consistant with the geochemical immaturity of the shale.

4. HTGC analysis of Green River Shale and Marl Slate showed the presence of metalloporphyrins and the resolution of etio porphyrins from DPEP structural types. These ratios might be useful as another maturity parameter.

5.2 Suggestions for Further Work

This work highlights several interesting areas for further research:

1. **HTGC-ICP-MS of metalloporphyrins.** To prevent the condensation of metalloporphyrins in the capillary contained within the plasma torch, the injector gas could be heated (to 400-450°C) before passing into the torch. This would require the construction of a relatively simple preheater whereby the argon gas could pass through a silica tube wound with nichrome wire and resistively heated[1].

   After obtaining Figures of Merit for metalloporphyrin standards, the method could be applied to the analysis of geological materials such as oil-source rock correlations (*i.e.* oil exploration), pollution studies of weathered / degraded oils (*e.g.* tar balls) and core maturity sequences. Using the sensitivity and selectivity of HTGC-ICP-MS it should be possible to confirm the existance of a number of other metalloporphyrins (*e.g.* titanyl porphyrins).

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[1] **Footnote:** Subsequent to completion of the experimental work described herein this modification was made by a sucessor in these laboratories and a variety of metalloporphyrins successfully determined [252].

The use of coupled HTGC-ICP-MS with consequent element selective detection will provide speciation information necessary for the rapid fingerprinting of metalloporphyrins.

To obtain quantitative information an internal standard could be used (*e.g.* Pd etio-I porphyrin, which is not naturally occuring and should exhibit similar chromatographic behaviour to that of Ni etio-I porphyrin). It is advisable that the results obtained should be compared to those from a complementary analytical technique (*e.g.* HPLC-ICP-MS, HPLC-MS-MS or HTGC-MS-MS).

At present no SRM containg certified metalloporphyrin species exists. A long term objective could be the initiation of an interlaboratory comparison of an oil or shale for this purpose.

Metalloporphyrins are also important in medicine (*e.g.* haemoglobin), so some medical applications could be found.

2. **Organomercury Speciation of SRMs.** The GC-ICP-MS technique can be used to study the environmental fate of organomercury. For instance it is well known that large quantities of organomercury are associated with natural gas deposits which when produced enter the environment [253]. An inital step might be to determine methylmercury in marine biological reference materials such as DORM-1, DOLT-1 (dogfish) and TORT-1 (lobster) available from the *National Research Council of Canada*. These are certified to contain between 0.080 - 0.731 $\mu g\ g^{-1}$ of mercury.

3. **Isotope Dilution Studies.** The intensities of the peaks that contain different isotopes of a given element in

a specific compound can be used to obtain speciation information, which avoids the need to use an internal standard.

4. **Organic Arsenic Speciation.** Organoarsenic species have been found in petroleum and natural gas in large quantities [254]. Environmental analysis using GC-ICP-MS would not suffer from the $^{40}Ar^{35}Cl$ polyatomic interference that some times make ^{75}As determinations difficult.

5. **Other Metal Containing Compounds.** Compounds to be examined by capillary GC-ICP-MS could include: methylcyclopentadienylmanganese tricarbonyl (MMT) in gasoline, organotitanium catalysts of titanium boride molecular precursors, ß-diketonates (*e.g.* metallo-trifluoroacetylacetones), nickelocene and titanocene, all of which are of industrial importance.

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APPENDICES

APPENDIX A

Reagents and Materials Used

REAGENT	SOURCE	COMMENTS
Benzene	Rathburn Chemicals Ltd., Peeblesshire, Scotland, UK	HPLC grade
Beryllium nitrate tetrahydrate, $Be(NO_3)_2.4H_2O$, standard solution	BDH Chemicals Co., Poole, Dorset, UK	*SpectrosoL* grade, 1000 mg l^{-1}
Bromoethane, C_2H_5Br	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	98% purity
Butyltin trichloride, $(C_4H_9)SnCl_3$	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	95% purity
Carbon disulphide (CS_2)	Rathburn Chemicals Ltd., Peeblesshire, Scotland, UK	Glass distilled grade, purified according to: "*Vogels's Textbook of Practical Organic Chemistry*," ed. Furniss B.S. *etal*, 5th edition, Longman Scientific & Technical, Marlow, UK, 1989, p.411
Chloroform, $CHCl_3$	Rathburn Chemicals Ltd., Peeblesshire, Scotland, UK	HPLC grade
Cobalt (II) chloride hexahydrate, $CoCl_2.6H_2O$	BDH Chemicals Co., Poole, Dorset, UK	*AnalaR* grade
Cobalt diethyldithio-carbamate, $[(C_2H_5)_2NCS_2]_3$ Co, $Co(Dt)_3$	Synthesised according to: Sandell E.B. & Onishi H., "*Photometric Determination of Trace metals: General Aspects, Part 1.*", 4th ed., John Wiley & Sons, 1978	

Cobalt etio-I porphyrin, (Co etio-I	Synthesised according to: Dolphin D., "*The Porphyrins: Volume I. Structure and Synthesis, Part A* .", Academic Press Inc., New York, USA, 1978	
Cobalt nitrate hexahydrate, $Co(NO_3)_2.6H_2O$, standard solution	BDH Chemicals Co., Poole, Dorset, UK	*SpectrosoL* grade, 1000 mg l^{-1}
Cotton wool, defatted	High Street Chemist Shop	Soxhlet extracted for 24 hrs with DCM & dried at 40 °C for 24 hrs
Decalin, decahydro-naphthalene, $C_{10}H_{18}$	BDH Chemicals Co., Poole, Dorset, UK	*AnalaR* grade
Deoxophyllo-erythroetio-porphyrin, C_{32}, DPEP	Dr. A.G. Barwise, BP Exploration Sunbury-on-Thames, UK	
Dichloromethane (CH_2Cl_2)	Rathburn Chemicals Ltd., Peeblesshire, Scotland, UK	HPLC grade
Dibutyltin dichloride, $(C_4H_9)_2SnCl_2$	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	98% purity
Diethyldithio-carbamic acid, sodium salt trihydrate, $C_2H_5CNS_2$ Na. $3H_2O$	BDH Chemicals Co., Poole, Dorset, UK	*AnalaR* grade
Diethylether, $(C_2H_5)_2O$	Rathburn Chemicals Ltd., Peeblesshire, Scotland, UK	HPLC grade
Diethylmercury, $(C_2H_5)_2Hg$	Fluka, Chemika-Bio Chemika, Bucks, Switzerland	
Dipropyltin dichloride, $(C_3H_7)_2SnCl_2$	Dr. S.J. Hill, University of Plymouth, Devon, UK	
Etio porphyrin-I	Dr. A.G. Barwise, BP Exploration Sunbury-on-Thames, UK	

Etio porphyrin-II	Dr. A.G. Barwise, BP Exploration Sunbury-on-Thames, UK	
Ferrocene	Dr. P. Jones, University of Plymouth, Plymouth, Devon, UK	
Helium	Air Products	Premier grade
Hexacontane ($C_{60}H_{122}$, n-C_{60})	Fluka, Chemika-Bio Chemika, Bucks, Switzerland	
Hexane (C_6H_{14})	Rathburn Chemicals Ltd., Peeblesshire, Scotland, UK	HPLC grade
Hydrobromic acid (HBr)	BDH Chemicals Co., Poole, Dorset, UK	48% *AnalaR* grade
Hydrochloric acid (HCl)	BDH Chemicals Co., Poole, Dorset, UK	36% *AnalaR* grade
Indium (III) nitrate, $In(NO_3)_3$, ICP/DCP standard spectrometric solution,	BDH Chemicals Co., Poole, Dorset, UK	*SpectrosoL* grade, 1000 mg l^{-1}
Lead nitrate, $Pb(NO_3)_2$, standard solution	BDH Chemicals Co., Poole, Dorset, UK	*SpectrosoL* grade, 1000 mg l^{-1}
Magnesium nitrate hexahydrate, $Mg(NO_3)_2.6H_2O$ standard solution	BDH Chemicals Co., Poole, Dorset, UK	*SpectrosoL* grade, 1000 mg l^{-1}
Magnesium ribbon	BDH Chemicals Co., Poole, Dorset, UK	For Grignard reagent: freshly scrapped & stored in dry diethylether
Mercury (II) nitrate monohydrate, $Hg(NO_3)_2.H_2O$, standard solution	BDH Chemicals Co., Poole, Dorset, UK	*SpectrosoL* grade, 1000 mg l^{-1}
Methylmercury chloride, CH_3HgCl	Dr. P. Jones, University of Plymouth, Plymouth, Devon, UK	

Nickel diethyldithio-carbamate, $[(C_2H_5)_2NCS_2]_2$ Ni, $Ni(Dt)_2$	Synthesised according to: Sandell E.B. & Onishi H., *"Photometric Determination of Trace metals: General Aspects, Part 1."*, 4th ed., John Wiley & Sons, 1978	
Nickel etio-I porphyrin, (Ni etio-I	Dr. A.G. Barwise, BP Exploration Sunbury-on-Thames, UK	
Nickel (II) nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	99.999% purity
Nickel (II) nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$, standard solution	BDH Chemicals Co., Poole, Dorset, UK	*SpectrosoL* grade, 1000 mg l^{-1}
Nitric acid, HNO_3	BDH Chemicals Co., Poole, Dorset, UK	48% *AnalaR* grade
2,3,7,8,12,13,17, 18 -Octaethyl-21H,23H-porphine (OEP)	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	97% purity
2,3,7,8,12,13,17, 18 - Octaethylporphine copper (II), (Cu-OEP)	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	λ_{max} 399 nm
2,3,7,8,12,13,17, 18 - Octaethylporphine iron (III) chloride, (FeCl-OEP)	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	λ_{max} 382 nm
2,3,7,8,12,13,17, 18 - Octaethylporphine nickel (II), (Ni-OEP)	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	97% purity, synthetic, λ_{max} 382 nm
2,3,7,8,12,13,17, 18 - Octaethylporphine zinc (II), (Zn-OEP)	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	98% purity, synthetic, λ_{max} 400 nm

n-octane, C_8H_{18}	Rathburn Chemicals Ltd., Peeblesshire, Scotland, UK	GPR grade
PACS-1 Standard Reference Material, harbour sediment	National Research Council, Canada	Certified to contain (as Sn), monobutyltin (0.28 $\mu g\ g^{-1}$, ± 0.17), dibutyltin (1.16 $\mu g\ g^{-1}$, ± 0.18) and tributyltin (1.27 $\mu g\ g^{-1}$, ± 0.22).
Palladium (II) chloride, $PdCl_2$	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	99% purity
Palladium etio-I porphyrin, (Pd etio-I)	Synthesised according to: Dolphin D., "*The Porphyrins: Volume I. Structure and Synthesis, Part A* .", Academic Press Inc., New York, USA, 1978	
Pentacontane ($C_{50}H_{102}$, n-C_{50})	Fluka, Chemika-Bio Chemika, Bucks, Switzerland	
Silica (60-100 mesh)	BDH Chemicals Co., Poole, Dorset, UK	Soxhlet extracted for 24 hrs with DCM & dried at 130 °C for 24 hrs, 5% deactivated with water
Sodium sulphate (anhydrous), Na_2SO_4	BDH Chemicals Co., Poole, Dorset, UK	*AnalaR* grade, Soxhlet extracted for 24 hrs with DCM & dried at 120 °C for 24 hrs.
Sulphuric acid, H_2SO_4	BDH Chemicals Co., Poole, Dorset, UK	*AnalaR* grade, concentrated
Tetraalkylleads in Fuel, Standard Reference Material (SRM)	National Bureau of Standards (Washing DC, USA)	No. 1637a(I, II and III), Tetraethyllead Motor Mix in Reference Fuel, certified to contain I = 7.7 $\mu g\ ml^{-1}$, II = 12.9 $\mu g\ ml^{-1}$, III = 17.3 $\mu g\ ml^{-1}$ of total lead in the form of tetramethyllead and tetraethyllead in unspecified proportions. The 91-octane number fuel is a mixture of 91% 2,2,4-trimethylpentane and 9% n-heptane by volume

Tetraalkylleads in naphtha	Dr S J Hill, University of Plymouth, Plymouth, Devon, UK	Containing 4.5 mg ml^{-1} as total Pb
Tetrabutyltin, $(C_4H_9)_4Sn$	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	93% purity
Tetraethyllead, $(C_2H_5)_4Pb$	Alpha, Johnson Matthey, Royston, UK	
Tetraethyltin, $(C_2H_5)_4Sn$	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	97% purity
Tetrahydrofuran (C_4H_8O)	Rathburn Chemicals Ltd., Peeblesshire, Scotland, UK	HPLC grade
5,10,15,20-Tetraphenyl-21H,23H-porphine, (TPP)	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	99% + purity, λ_{max} = 415 nm, contains 1-3% correspoding to chlorin
5,10,15,20-Tetraphenyl-porphine copper (II), (Cu-TPP)	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	λ_{max} = 411(536) nm
Tin(II) chloride dihydrate ($SnCl_2$. $2H_2O$)	BDH Chemicals Co., Poole, Dorset, UK	*AnalaR* grade
Toluene	Rathburn Chemicals Ltd., Peeblesshire, Scotland, UK	HPLC grade
Tributyltin acetate, $CH_3CO_2Sn(C_4H_9)_3$	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	
Tributyltin chloride, $(C_4H_9)_3SnCl$	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	96% purity
Tropolone, 2-hydroxy-2,4,6,-cycloheptatriecone	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	98% purity

Vanadyl etio-I porphyrin, (V=O etio-I)	Dr. A.G. Barwise, BP Exploration Sunbury-on-Thames, UK	
Vanadium ICP/DCP standard spectrometric solution	BDH Chemicals Co., Poole, Dorset, UK	1000 mg l^{-1}
Water	*MilliQ*	in house production
Zinc acetate dihydrate, $(CH_3CO_2)_2Zn.2H_2O$	Aldrich Chemical Company Ltd., Gillingham, Dorset, UK	98% + purity
Zinc etio-I porphyrin, (Zn etio-I)	Synthesised according to: Dolphin D., "*The Porphyrins: Volume I. Structure and Synthesis, Part A .*", Academic Press Inc., New York, USA, 1978	

GC-MS Conditions Used.

Gas Chromatography

Instrument: Carlo Erba HRGC 5300 Mega Series
Capillary Column: DB-5 (25m x 0.32mm i.d. x 0.25μm film thickness).
Temperature Programme: 40°C to 280°C (at 10°C $min.^{-1}$) (5 min. iso. at 280°C) to 300° (at 10°C $min.^{-1}$) (5 min. iso. at 300°C).
Carrier Gas: He (at 0.45 Kg/cm^2)
Injection: 0.5μl on-column (DCM solvent)

Mass Spectometry

Instrument: Kratos (Manchester, UK) MS25
Interface Temperature: 300°C
Filament Current: 5.0 mA
Emission Current: 700 μA
Electron Voltage: 40 eV
Mass Range: 40 - 568 u
Scan Rate: 1 scan s^{-1}
Source Temperature: 230°C
Data Aquisition & Processing: Kratos DS55 and DS90 software packages.

APPENDIX B

Papers Published

JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY, OCTOBER 1992, VOL. 7

COMMUNICATIONS

Material for publication as a Communication must be on an urgent matter and be of obvious scientific importance. Rapidity of publication is enhanced if diagrams are omitted, but tables and formulae can be included. Communications receive priority and are usually published within 2–3 months of receipt. They are intended for brief descriptions of work that has progressed to a stage at which it is likely to be valuable to workers faced with similar problems. A fuller paper may be offered subsequently, if justified by later work.

Manuscripts are usually examined by one referee and inclusion of a Communication is at the Editor's discretion.

Construction of a Capillary Gas Chromatography Inductively Coupled Plasma Mass Spectrometry Transfer Line and Application of the Technique to the Analysis of Alkyllead Species in Fuel

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The interfacing of a capillary gas chromatograph with an inductively coupled plasma mass spectrometer is described. The interfacing required only a simple modification to the conventional inductively coupled plasma mass spectrometry (ICP-MS) torch and the construction of a heated transfer line. Capillary gas chromatography ICP-MS has a high chromatographic resolving power, is sensitive and element specific. The technique shows great potential of becoming a very useful method for the analysis of a wide range of volatile organometallic compounds. As an example, the quantitative analysis of alkyllead compounds in a complex hydrocarbon mixture (limit of detection 0.7 pg s^{-1} and <5% RSD) is reported but the method is also applicable to the analysis of relatively involatile organometallics.

Keywords: *Capillary gas chromatography; inductively coupled plasma mass spectrometry; element selective detection; coupled gas chromatography; alkyllead determination*

It is widely recognized that the environmental fate and many other aspects of the chemistry of trace metals is significantly influenced by what has become known as metal speciation.[1] Consequently a number of analytical systems have been developed for the separation, identification and measurement of organometallic species. Most methods employ either packed column gas chromatography (GC) or high-performance liquid chromatography (HPLC) coupled to an element selective detector utilizing atomic absorption spectrometry (AAS), direct current plasma atomic emission spectrometry (DCP-AES) or inductively coupled plasma atomic emission spectrometry (ICP-AES). All of these methods have been reviewed in the literature.[2–6]

Although GC methods are useful for the analysis of volatile organometallics, packed column GC often does not have sufficient resolving power for adequate characterization of complex environmental samples. The recent availability of a commercial capillary GC microwave-induced plasma atomic emission spectrometer (GC-MIP-AES) using state-of-the-art coupling techniques has resulted in an increasing number of studies of elemental speciation in such complex samples.[7–10] However, GC–MIP-AES usually requires expensive high-purity reagent gases and solvent venting to prevent plasma instability and carbon accumulation on the discharge tube.[11] Similar problems are encountered in GC–MIP-MS where the cones of the mass spectrometer may also become blocked.[12] For laboratories where ICP-AES or ICP mass spectrometery (ICP-MS) are already available, use of capillary GC and construction of a simple GC–ICP interface offers an economical alternative to GC–MIP-AES for trace metal analysis. Unlike GC–MIP-AES, capillary GC–ICP does not require solvent venting and as ICP-AES and ICP-MS are also independent elemental analytical methods, the construction of an easily removable GC–ICP interface means that independent ICP and GC operation is still possible. This is an important factor in many busy multi-user laboratories.

In this communication a capillary GC–ICP-MS interface is described. The interface is itself simple and robust, and has been validated for the analysis of a range of organometallics. The data presented include figures of merit, for the analysis of a series of alkyllead compounds. Unlike capillary GC–ICP-AES[13] and packed column GC–ICP-MS,[14,15] capillary GC–ICP-MS does not appear to have been described previously.

Experimental

Capillary GC

The instrument used was a Carlo Erba HRGC 5300 Mega Series (Fisons, Sussex, UK), fitted with an aluminium clad high-temperature column with a siloxane carborane stationary phase (SGE, Milton Keynes, UK), HT-5, 25 m × 0.32 mm i.d. × 0.1 μm film thickness. (However, any conventional fused silica capillary column would suffice for the application described here.) The temperature programme was 40 °C (1 min isothermal) to 180 °C (10 min isothermal) at a rate of 10 °C min^{-1}. Helium was the carrier gas (Air Products, Walton-on-Thames, Surrey, UK) at a flow rate of 6 ml min^{-1}, measured at 150 °C. Helium was selected because it is a conventional GC carrier gas and addition of helium to argon during ICP-MS produces a plasma capable of ionizing elements with high ionization potentials more efficiently than pure argon.[16] Sample volumes of 0.5 μl were injected on-column.

ICP-MS

The instrument used was a VG PlasmaQuad 2, (VG Elemental, Winsford, Cheshire, UK). The operating conditions are given in Table 1. Commercially available software (VG Elemental) was used for data acquisition and processing. The ICP-MS instrument was tuned using a continuous signal of cold mercury vapour generated by the reduction of a solution of Hg^{2+} (100 μg l^{-1}) with tin(II) chloride dihydrate (2% m/v in 2.2% hydrochloric acid). A conventional gas–liquid separator was used and the mercury vapour introduced on-line *via* the injector gas inlet.

Capillary GC–MS

The instrument used was a Kratos (Manchester, UK) MS25 spectrometer and Carlo Erba HRGC 5300 Mega Series fitted with a DB-5 fused silica column (25 m × 0.32 mm i.d.). The temperature programme was that used for GC–ICP-MS. The mass spectrometer conditions were: emission current 400 μA, electron voltage 40 eV, mass range 50–500 u.

Reagents

Mercury(II) nitrate (Merck, Poole, Dorset, UK) was spectroscopic grade, tin(II) chloride dihydrate and hydrochloric acid (Merck) were both analytical-reagent grade. High-purity hexane (Rathburn Chemicals, Walkerburn, Peebleshire, UK) and doubly distilled water were used throughout. Known concentrations of tetraalkylleads were obtained as National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) Standard Reference Material (SRM) 1637, Tetraethyllead Motor Mix in Reference Fuel. The reference fuel is certified to contain 12.9 μg ml^{-1} of total lead added in the form of tetramethyllead (TML) and tetraethyllead (TEL) in unspecified proportions. The 91-octane number fuel is a mixture of 91% 2,2,4-trimethylpentane and 9% heptane by volume.

Table 1 ICP-MS operating conditions

Cooling (outer) gas	14 l min^{-1}
Auxiliary (intermediate) gas	0.75 l min^{-1}
Injector gas	1.025 l min^{-1}
Forward power	1500 W
Reflected power	<5 W
Expansion pressure	0.36 kPa
Analyser pressure	1.07×10^{-3} kPa
Sampler cone	Nickel (1.0 mm orifice)
Skimmer cone orifice	Nickel (0.8 mm orifice)
Mode	Single ion monitoring (208 u)
Dwell	163840 μs
Number of channels	4094

Results and Discussion

Several previous reports have shown the advantages of capillary and packed column GC–ICP-AES and packed column GC–ICP-MS for metal speciation analysis. However, to our knowledge none have described capillary GC–ICP-MS. The literature also gives few details of the capillary coupling transfer lines, or of the plasma torch modifications required. By reporting the latter it is hoped that existing ICP-MS users can appreciate the simplicity and convenience of the GC–ICP-MS adaptation.

Coupling and Transfer Line

The capillary GC was coupled to the ICP-MS system *via* a heated transfer line (Fig. 1) constructed to permit convenient installation and disassembly of the interface. The central core was made from aluminium rod (chosen for its high thermal conductivity and light weight) (25.4 mm diameter × 600 mm length) with a longitudinal slot (1 mm) through which the capillary column passed. Around this was wound heating tape (Electrothermal, Southend-on-Sea, Essex, UK) connected to a variable voltage supply and sheathed with industrial pipe lagging (Encon, Saltash, Cornwall, UK). The transfer line was earthed to the torch box *via* a steel screw to prevent the possibility of the aluminium bar acting as an r.f. aerial. The transfer line temperature was monitored by four thermocouples (RS Components, Corby, Northamptonshire, UK). Precautions were taken to minimize the transfer line length and to provide uniform heating in order to extend the volatility range of organometallics that could be examined by the technique.

Modifications made to the ICP-MS instrumentation to minimize the length of the transfer line included replacing a panel from the right side of the hood with a detachable plate with an 80 mm diameter hole through which the transfer line could pass, thus enabling unrestricted access to the interface whilst the hood was open. A rectangular section (90 × 150 mm) from the right side of the torch box and nebulizer–spray chamber assembly was removed. Whilst the transfer line was in position, access to the vertical torch adjustment micrometer was restricted. This was overcome by the attachment of a steel collar with an allan head nut

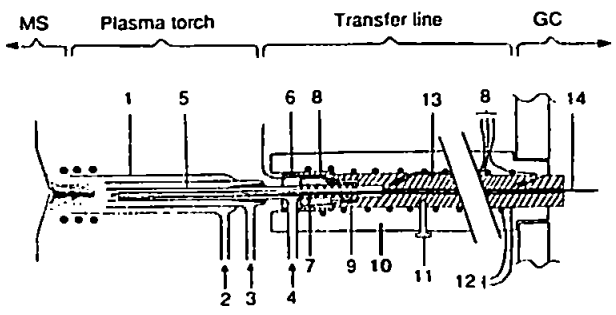

Fig. 1 Transfer line and modified plasma torch: 1, demountable ICP torch; 2, cool gas; 3, auxiliary gas; 4, injector gas; 5, stainless-steel tube (1.59 mm o.d. × 0.51 mm i.d.); 6, aluminium collar (37.9 mm o.d. × 25.4 mm i.d.); 7, graphite tape; 8, thermocouples; 9, stainless-steel reducing union (¼ in to ⅛ in); 10, industrial pipe lagging; 11, earthing point; 12, heater leads to variable voltage supply; 13, aluminium bar (25.4 × 600 mm); and 14, capillary GC column

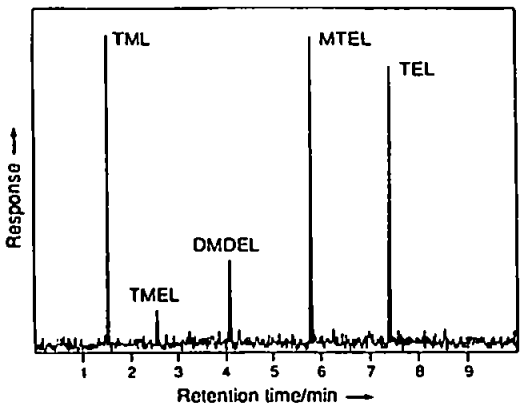

Fig. 2 GC–ICP-MS ion chromatogram (^{208}Pb) of naphtha sample containing five alkyllead components: TML, tetramethyllead; TMEL, trimethylethyllead; DMDEL, dimethyldiethyllead; MTEL, methyltriethyllead; and TEL, tetraethyllead (identities confirmed by GC–MS)

which allowed adjustment *via* a small hole drilled in the top of the torch box.

Most previous reports of GC–ICP-AES and GC–ICP-MS have been restricted to the analysis of fairly volatile metal species with typical GC retention times of only 10–15 min. Although in this paper a description and figures of merit are given only for the use of the existing system for volatile alkylleads, up to tetraethyllead (TEL), the retention index window (volatility range) for which the GC–ICP-MS method with the short transfer line has been used successfully, is in excess of 3400 (C_{34}).[17]

Plasma Torch

A modified demountable torch with a 3 mm ICP injector was used (Baumach, Ipswich, UK) (Fig. 1). A stainless-steel tube (1 mm i.d.×2 mm o.d.) was passed through the injector (ending 5 mm before its tip) and held concentrically by a reducing union and graphite tape. The column emerged 2 mm before the tip of the ICP injector and column effluent was introduced without splitting. Argon injector gas was introduced *via* a T-shaped side arm, providing a sufficient gas flow rate to puncture the plasma.

The distance of the capillary column from the tip of the ICP injector was important. At distances much greater than 40–50 mm no response to TML in the reference fuel was obtained, possibly due to analyte adsorption onto the silica inner injector wall. The alignment of the ICP torch with the transfer line was also important; the main requirement being a constant positioning (lack of movement) of the transfer line. A simple lab-jack support for the line was found to provide sufficient stability.

Alkyllead Analysis

Analysis of a 10-fold diluted (in hexane) solution of SRM 1637 by ion-selective monitoring for lead (^{208}Pb) produced a chromatogram comprising two components which were identified by capillary GC–MS as TEL (98.5%) and TML (1.4%). Injection of a standard dilution series of SRM 1637 established figures of merit for the system (Table 2). The method has comparable or better sensitivity to other coupled methods for speciation of lead and reasonable linearity of response (the correlation coefficient of 0.992 was due to the scatter of calibration points). The GC–ICP-MS method has been used to determine the concentrations of various organometallics (containing tin, iron and nickel) in a number of matrices.[17] For example, the excellent GC resolution of the capillary column coupled with the sensitivity of ICP and the coupled specificity afforded by ion-selective monitoring easily allowed measurement of five alkyllead components in a naphtha matrix at 20–200 $\mu g\ ml^{-1}$ (Fig. 2). The enhanced specificity over GC–flame ionization detection is obvious.

Table 2 Figures of merit for TEL by capillary GC–ICP-MS (using ten replicate injections)

Parameter	Value
Detection limit (3σ)	0.7 pg s^{-1} (measured at 50 pg)
Relative standard deviation	4.7%
Correlation coefficient	0.9921 (measured up to 0.75 ng)

Future monitoring of the widespread occurrence of organometallics containing mercury, lead, tin, nickel and vanadium (amongst others) in the environment and in petroleum can only benefit from the application of such sensitive, high resolution instrumental methods.

Conclusion

Capillary GC has been successfully interfaced with an ICP-MS instrument and the interface and plasma torch modification have been described. The resulting instrumentation is a new analytical tool which can provide highly specific data on trace metal speciation over a wide GC volatility range with good limits of detection and linearity of response. The instrumentation can be devised from existing GC and ICP instruments with only minor modifications and does not prevent stand-alone operation of either GC (*e.g.*, with flame ionization detection) or ICP (*e.g.*, ICP-MS).

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Determination of Organometallic Compounds by Capillary Gas Chromatography – Inductively Coupled Plasma Mass Spectrometry

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Key Words:

Capillary GC
Inductively coupled plasma MS
Element-selective detection
Organotin speciation
Organometallic compounds

Summary

The separation and detection of volatile organometallic compounds containing tin, iron, and nickel has been achieved using capillary GC – inductively coupled plasma – mass spectrometry (capillary GC-ICP-MS). Detection limits range from 3.0 to 7.0 pg/s. The presence of volatile organotin compounds in a harbor sediment has been confirmed. The retention range of the organometallic compounds analyzed by capillary GC-ICP-MS has been extended considerably beyond that possible in earlier studies (retention indices up to 3400).

1 Introduction

The form or "speciation" of trace metals is a primary factor controlling their behavior in natural systems and it is, therefore, important to develop analytical methodologies capable of differentiating and measuring individual species present in environmental matrices. Several methods have been studied.

One approach has involved the coupling of gas chromatography with various element-specific detectors [1-8]. Such systems should, ideally, be able to monitor a wide range of elements simultaneously with a high degree of selectivity and sensitivity, and with a wide linear dynamic range. Gas chromatography – inductively coupled plasma – mass spectrometry (GC-ICP-MS) has such attributes.

The advantages of GC-ICP-MS include 100 % transport efficiency, fewer isobaric interferences, good plasma stability, and reduced sampler and skimmer cone wear compared with HPLC-ICP-MS. Capillary GC-ICP-MS has a higher chromatographic resolving power than packed column GC-ICP-MS [9, 10]. This is especially important for the separation of the complex mixtures found in many environmental samples (e.g. water, sediment, biota). We have recently described the development and use of capillary GC-ICP-MS for the determination of organolead species in a complex hydrocarbon mixture. Detection limits of 0.7 pg/s were achieved [11].

This report describes the application of this methodology for the analysis of organic tin, iron, and nickel species, including the analysis of a mixture of organotin compounds (used commercially in antifouling agents and biocides) in spiked water samples and a harbor sediment.

2 Experimental

2.1 Instrumentation

2.1.1 Gas Chromatography

Gas chromatography was performed with a Carlo Erba HRGC 5300 Mega chromatograph (Fisons, Sussex, UK) fitted with 25 m (or 5 m) × 0.32 mm i.d. aluminum-clad high temperature columns coated with 0.1 μm films of HT-5 (SGE, Milton Keynes, UK). The GC operating conditions are listed in **Table 1**. Injections (0.5 μL) were performed on-column and helium was used as carrier gas (2 mL/min at 200 °C).

Table 1

GC operating conditions: T1, initial temperature [°C]; T2, final temperature [°C]; R1, ramp rate [°/min]; H1, time held at T2 [min].

Analyte:	Column length [m]	GC temperature program T1	R1	T2	H1
Organotin compounds:	25	40	10	200	5
Ferrocene:	25	60	10	180	5
$Ni(II)_2$	5	50	20	320	10

2.1.2 ICP-MS and Optimization

The instrument used was a VG Plasma Quad 2 (VG Elemental, Cheshire, UK) operated using the conditions given in **Table 2**.

The plasma torch position was optimized and ion lens settings tuned using a constant signal of ^{120}Sn and ^{56}ArO produced by a cold vapor mercury generator (the reduction of mercury(II) with tin(II) chloride dihydrate using a conventional gas-liquid separator) as described previously [11]. This was removed prior to analysis. It was found impractical to introduce ferrocene as a vapour (using a Drechsel bottle assembly) for ^{56}Fe optimization as this caused overloading of the detector, excessive deposition of carbon on the ICP-MS interface, and prolonged memory effects. It is noted that optimum conditions for polyatomic and monoatomic ions of equivalent mass may be different; these compromise conditions were, however, both easy to obtain and effective. There was no residual ^{120}Sn memory effect after the mercury generator was taken off-line. The signal arising from constant ablation of nickel from the sample and skimmer cones (used for ^{58}Ni optimization) was found to be sufficient.

Table 2

ICP-MS operating conditions.

Cooling gas	15 L/min
Auxiliary gas	0.75 L/min
Injector gas	1.12 L/min
Forward power	1500 W
Reflected power	<5 W
Mode	Single ion monitoring
Dwell time	327680 µs
No. of channels	4094
Data acquisition time	22.4 min

2.1.3 Coupling

The GC-ICP-MS is shown schematically in **Figure 1** and has been described in detail elsewhere [11]. In brief, the column was passed through a heated transfer line to prevent condensation of the analyte (**Table 3**). Slight modification of the transfer line was required for analysis of nickel diethyldithiocarbamate ($Nidt_2$); this involved resistive heating of the stainless steel tube inside the injector of the plasma torch by means of a variable high current supply. This temperature was monitored by a thermocouple (TC4).

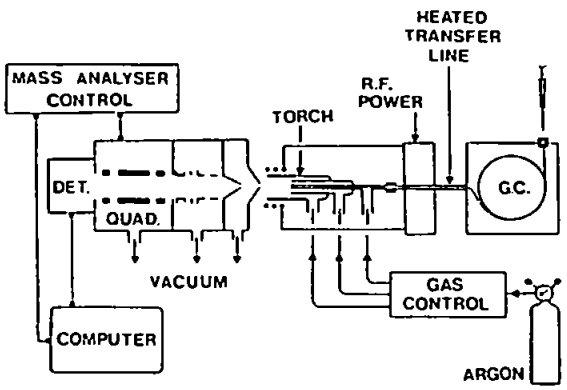

Figure 1

Schematic diagram of the coupled capillary GC-ICP-MS system.

Table 3

Transfer line temperatures (TC1–TC4 = thermocouple number).

Analyte	Transfer line temperature [°C] TC1	TC2	TC3	TC4
Organotin compounds	205	230	248	-
Ferrocene	190	227	241	-
$Nidt_2$	273	315	337	266

2.2 Reagents and Samples

Monobutyltin trichloride ($SnBuCl_3$) dibutyltin dichloride ($SnBu_2Cl_2$), and tributyltin chloride ($SnBu_3Cl$) were obtained from Aldrich (Dorset, UK). Dipropyltin dichloride ($SnPr_2Cl_2$) was supplied by *Dr S.J. Hill* (University of Plymouth, Plymouth, UK). The ferrocene and $Nidt_2$ were synthesized in-house, the latter using the method described by *Sandell* and *Onishi* [12]. Tropolone, 48 % hydrobromic acid, and bromoethane were also purchased from Aldrich. Anhydrous sodium sulfate, magnesium turnings, concentrated sulfuric acid, and tin(II) chloride dihydrate were supplied by Merck (Poole, UK). Benzene, dichloromethane (DCM), diethyl ether, hexane, tetrahydrofuran (THF), and toluene were obtained from Rathburn Chemicals (Walkerburn, Scotland). All reagents were of analytical grade. Distilled deionized water was used throughout. A harbor sediment known to contain organotin compounds was part of a certification program.

2.2.1 Preparation of Organotin Standards

$SnBuCl_3$, $SnBu_2Cl_2$, $SnBu_3Cl$, $SnPr_2Cl_2$, and tin(IV) ($SnCl_4$) were derivatized separately with ethylmagnesium bromide (2 M in THF) using the method described by *Maguire* and *Huneault* [13]. Standards containing 1 µg/mL (as tin, in hexane) were stored at <4 °C in darkness.

2.2.2 Water Sample

Distilled water (250 mL) containing $SnBuCl_3$, $SnBu_2Cl_2$, $SnBu_3Cl$, $SnPr_2Cl_2$, and $SnCl_4$ (1 mg/mL, as tin) was extracted, and the extract derivatized with ethylmagnesium bromide (2 M in THF) [13]. The organic extract was made up to 50 mL in toluene.

2.2.3 Sediment Sample

The sediment (2 g) was extracted, and the extract derivatized as described by *Müller* [14]. The organic extract was made up to 1 mL in toluene.

3 Results and Discussion

3.1 Organotin Compounds

Derivatization of the tin chlorides produced tetraethyltin ($SnEt_4$), triethylbutyltin ($SnBuEt_3$), diethyldibutyltin ($SnBu_2Et_2$), tributylethyltin ($SnBu_3Et$), and diethyldipropyltin ($SnPr_2Et_2$). This was confirmed by GC-MS. Detection limits (3 σ) and retention times for all species are presented in **Table 4**. The response was linear up to 2.5 ng tin. The detection limits (low pg/s range) and linear

Table 4

Figures of merit for capillary GC-ICP-MS analysis of organotin compounds.

Parameter	$SnEt_4$	$SnPr_2Et_2$	$SnBuEt_3$	$SnBu_2Et_2$	$SnBu_3Et$
Retention time [min]	4.40	6.75	6.85	9.20	12.40
Detection limit (3 σ) [pg/s]	5.0	6.5	5.0	3.0	4.0
Correlation coefficient	0.9994	0.9995	0.9990	0.9997	0.9980

response (correlation coefficient = 0.9990) of the coupled system appear to be acceptable for organotin analysis.

3.2 Water Sample

Figure 2 shows a typical ion chromatogram (*m/z* 120) for a number of tetraalkyltin compounds (corresponding to 125 pg injection); the signal-to-background ratio is high. The high chromatographic resolution of the capillary GC-ICP-MS system is illustrated by the separation of $SnPr_2Et_2$ and $SnBuEt_3$. It is unlikely that packed column GC-ICP-MS would achieve this.

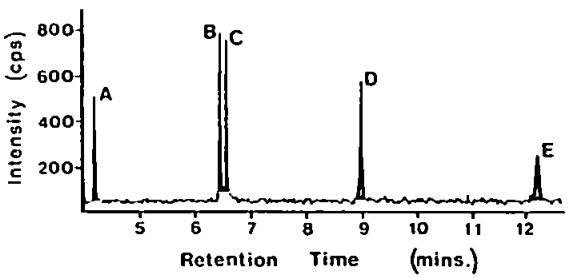

Figure 2

^{120}Sn ion selective chromatogram of tetraalkyltin compounds obtained from a spiked water sample: A, $SnEt_4$; B, $SnPr_2Et_2$; C, $SnBuEt_3$; D, $SnBu_2Et_2$; E, $SnBu_3Et$.

3.3 Sediment Sample

Figure 3 illustrates how the coupled system may be used for the analysis of a more complex environmental sample such as a harbor sediment. Because $SnPr_2Et_2$ is not present in the environment, it would be ideal as a potential internal standard for use in this application. The organotin species present in the sediment were identified by comparing the retention times with those of known tetraalkyltin compounds.

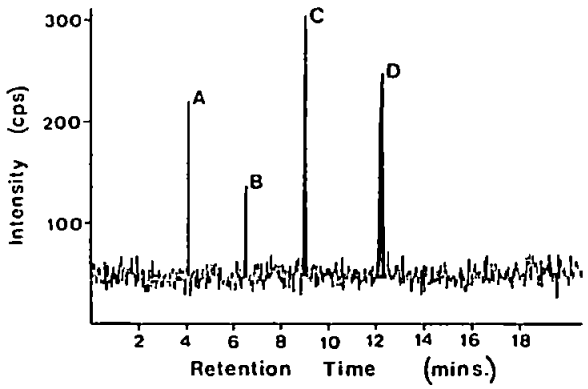

Figure 3

^{120}Sn ion selective chromatogram of tetraalkyltin compounds from a harbor sediment: A, $SnEt_4$; B, $SnBuEt_3$; C, $SnBu_2Et_2$; D, $SnBu_3Et$.

3.4 Ferrocene

The detection limit (3 σ) of ferrocene dissolved in hexane was 3.0 pg/s and the mean retention time 7.75 min. **Figure 4** demonstrates one of the advantages of using a "dry" plasma. An alternative method to obtain a "dry" plasma is to desolvate the nebulizer gas prior to reaching the plasma [15]. Selective ion monitoring of ^{56}Fe is not usually possible using HPLC-ICP-MS owing to the polyatomic interference of ^{40}ArO which results from

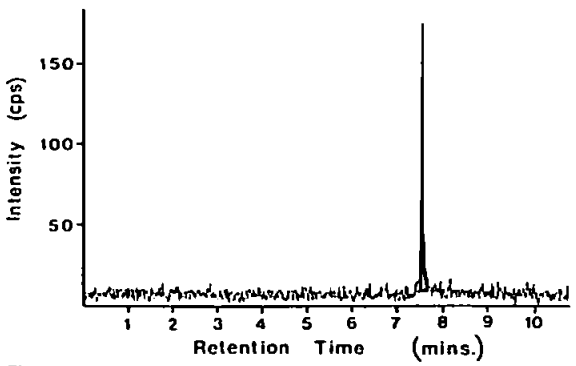

Figure 4

^{56}Fe ion selective chromatogram of ferrocene (no ^{56}ArO isobaric interference).

the oxygen either present in aqueous or organic phases or often deliberately introduced into the nebulizer gas to prevent deposition of carbon on the cones.

3.5 Nickel Diethyldithiocarbamate

Resistive heating of the stainless steel tube through which the column passed enabled capillary GC-ICP-MS to be utilized for the analysis of compounds which have a relatively large retention index (RI). **Figure 5** shows an ion chromatogram (*m/z* 58) obtained for $Nidt_2$ (RI = 3422), once again signal-to-background ratio is acceptable. $Nidt_2$ dissolved in DCM gave a detection limit (3 σ) of 6.5 pg/s and a mean retention time of 10.4 min

4 Conclusion

Capillary GC-ICP-MS, demonstrated here for tin, iron, and nickel species, provides a sensitive and selective means of detecting volatile organometallic compounds. This coupled technique pro-

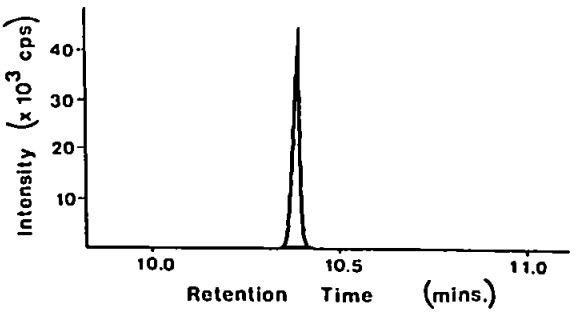

Figure 5

^{58}Ni ion selective chromatogram of nickel diethyldithiocarbamate (RI = 3422).

vides valuable information on chemical speciation, offers limits of detection in the low pg/s range, and good linear response. The utilization of capillary GC gives good chromatographic resolution (compared with packed column GC) which is especially important for the analysis of organometallic compounds in complex environmental matrices. The advantage of using a "dry" plasma (reduced polyatomic interferences) and analyses of compounds with relatively high RI values (>3400) have been demonstrated.

Acknowledgments

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Year: 1993

Journal: in draft

APPENDIX C

Oral and Poster Presentations Given

1. "*The Analysis of Organometallic Compounds by Capillary Gas Chromatography - Inductively Coupled Plasma - Mass Spectrometry (GC-ICP-MS)*", 6th Biennial National Atomic Spectroscopy Symposium, University of Plymouth, 22-24 July 1992. **Poster Presentation and Steward.**

2. "*Analysis of Organometallic Compounds by Capillary Gas Chromatography - Inductively Coupled Plasma - Mass Spectrometry (GC-ICP-MS)*", 14th International Symposium on Capillary Chromatography, Baltimore, U.S.A., 25-29 May 1992. **Poster presentation and U.S. travel award**.

3. "*The Rapid Fingerprinting of Total Metallated Petroporphyrins by High Temperature Gas Chromatography -Inductively Coupled Plasma Mass Spectrometry (GC-ICP-MS)*", BP Students CASE Event, BP Exploration, 1990-1992. **Oral presentations**.

4. "*The Rapid Fingerprinting of Total Metallated Petroporphyrins using Directly Coupled High Temperature Gas Chromatography (HTGC) with Inductively Coupled Plasma Mass Spectrometry*", European Association of Organic Geochemists, 15th International Meeting, University of Manchester, 16-20 September 1991. **Oral presentation**.

5. "*The Rapid Fingerprinting of Total Metallated Porphyrins (by HTGC-ICP-MS)*", Royal Society of Chemistry, Research and Development Topics, University of Aberdeen, 9-10 July 1991. **Poster presentation**.

6. "*Rapid Fingerprinting of Total Metallated Porphyrins by HTGC Coupled to Element Specific Detectors*", British Organic Geochemical Society, Bideford, 30 August - 1 September 1990. **Oral presentation**.

7. "*Rapid Fingerprinting of Total Metallated Petroporphyrins*", British Inorganic Mass Spectrometry Society, Royal Holloway and Bedford New College, 11 April 1990. **Oral presentation**.

APPENDIX D

Lectures Attended, Associated Study and Visits

1. "*Trace Metal Speciation using Coupled Chromatography - Atomic Absorption Spectrometry*", Dr. O. Nygren, University of Plymouth, Summer 1992.

2. Natural Environment Research Council: "*Geocolloids 1991*", Polytechnic South West, Plymouth, 9-11 September 1991

3. The Royal Society of Chemistry: "*Analytical Aspects of Water Quality*", Polytechnic South West, Plymouth, 28 August 1991.

4. British Association: "*Science '91*", Polytechnic South West, Plymouth, 25-30 August 1991.

5. Geological Chemistry Lectures: "*Biological Markers - their uses (and abuses) in Organic Geochemistry*", Dr. C.A. Lewis, Polytechnic South West, Plymouth, Spring 1991.

6. Royal Society of Chemistry: "*Alternative Plasma Sources*", Polytechnic South West, Plymouth, 28 March 1991.

7. Royal Society of Chemistry: "*Protection of the North Sea. The Analytical Challenge*", Hull, February 1991.

8. "*Analytical Scale Supercritical Fluid Extraction*", Dr. S.B. Hawthorne, Polytechnic South West, Plymouth, Winter 1991.

9. "*Fossil Natural Products*", University of Bristol, 11 May 1990.

10. Research Visit, NERC / Jöel Mass Spectrometry Facility, University of Swansea, Winter 1990.

10. Research Visit, BP Exploration, Sunbury-on-Thames, November 1989.

10. Weekly Departmental Research Seminars, 1989-1992, Polytechnic South West / University of Plymouth.

11. Plymouth Marine Laboratory, Journal Club, Weekly Seminars, 1989-1992.

W.A. MOZART

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Così fan tutte

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ATTO SECONDO — ACT II

SCENA ULTIMA — FINAL SCENE

TUTTI — ALL

Fortunato l'uom che prende
Ogni cosa pel buon verso
E tra i casi e le vicende
Da ragion guidar si fa.

Happy is the man who looks
at everything on the right side
and through trial and tribulations
makes reason his guide.