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Microwave-assisted sequential extraction of polycyclic aromatic hydrocarbons and potentially toxic elements from urban environmental solids

by

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This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

To Jeanette, Mum, Dad & Lyn

And for Matt

Dedicated to his memory

Acknowledgements

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Contents

Abstract

A method has been developed for the sequential extraction and determination of polycyclic aromatic hydrocarbons (PAHs) and potentially toxic elements (PTEs) from urban substrates using microwave-assisted micellar extraction, the BCR sequential extraction procedure (BCR-SEP) and microwave-assisted *aqua regia* digestion. High performance liquid chromatography - ultraviolet detector was used for the determination of PAH. Flame atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry were as used for the determination of PTEs.

The method was developed using certified reference materials (CRMs) and several urban substrates. The determination of PTE by the developed sequential method was compared to a single step *aqua regia* digestion, with recoveries of 80.9-107% (without PAH extraction) and 82.3-97.1% (with PAH extraction) and statistical comparison showed no significant differences between these two procedures for most PTE. A significant difference was observed in the determination of manganese, which with extraction using the BCR-SEP was shown to be due to a large fraction of the metal being removed in the water-soluble/ extractable stage and subsequently extracted by the water based micellar extractant.

The micellar extracts required clean-up using solid phase extraction and pre-concentration by evaporation under nitrogen for determination of PAH. The analysis was applied to extracts from Glasgow urban substrates for the determination of 16 priority pollutant PAH. The co-elution of two sets of isomers meant only 14 eluates could be readily detected and poor detection for some species also affected detection. Application of the method to a CRM showed low recoveries (7 – 48 %) of PAH and subsequently the developed method could only be used to screen for these species.

The method was applied to urban sediment collected from locations around Glasgow. The highest concentration of the urban metals copper and zinc were observed from a busy city centre street, and also showed the highest relative levels of PAH.

1 Introduction

1.1 Urban pollutants and associated environmental effects

The natural environment is not suitably designed to accommodate the large population density typical of urban areas and so is modified to suit the needs of mankind. The urban environment is therefore unique in its dense population and infrastructure with which to support numerous human activities. This can include above- and below-ground structures, buildings and extensive transport networks which are implemented through physical changes to the environment (Figure 1-1), which also alter its chemical and biological characteristics in comparison to the natural environment[1].

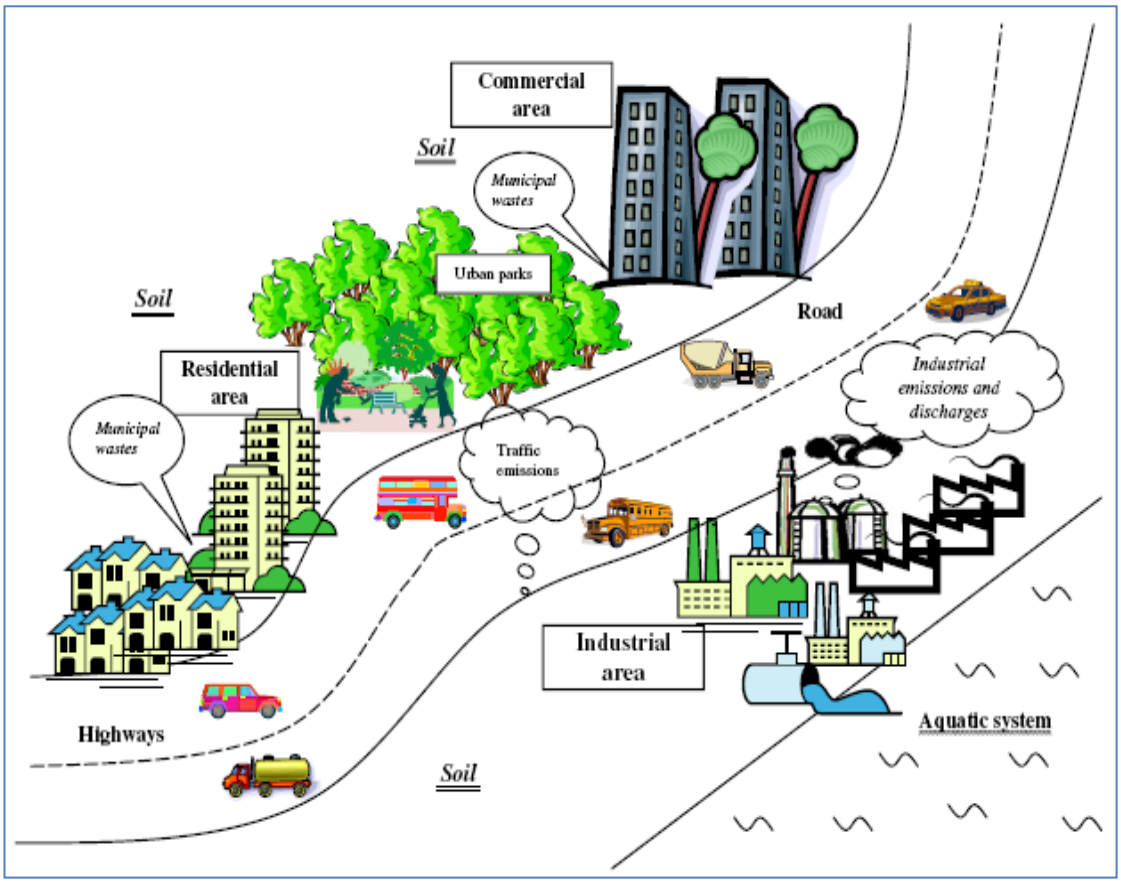


Figure 1-1 – Human impact on the urban environment[1]

In recent decades the rate of population growth has been increasing, and urban populations have also increased. It has been estimated that urban areas are occupied by more than 50 % of the world's population[1] and that future population growth will occur primarily in these areas, with a decline in the rural population[2].

The increase of population in urban areas has resulted in a subsequent increase in the level of human activities in these areas, including municipal, industrial, and commercial operations, as well as domestic concerns. In urban areas these activities can be particularly intense and release a variety of inorganic and organic compounds into the environment[3-4]. These substances can be considered to be pollutants if they are damaging to the environment or hazardous to human health[5]. These pollutants can be dispersed in air, water and soil in the environment, leading to associated ill health effects in animals and humans. This can occur either directly through dermal contact, inhalation and ingestion or indirectly through consumption of contaminated food and drink[6].

1.2 Solid substrates in the urban environment

There are many pollutants in the environment that are predominantly associated with solid material, such as soils and deposited sediment, which can be airborne, land or water based. In urban areas, pollution from residential, commercial and industrial sources often occur in the form of solid wastes, wastewater discharges and atmospheric emissions (Figure 1-2).

Atmospheric emissions are often a principle urban source of pollutants, released via vehicular exhausts and urban industrial and commercial activity. Air pollutants can be in the gaseous form, such as sulfur dioxide, or solid particles and liquid droplets can adhere to airborne particles forming fine particulates and dust[4]. Particle associated airborne pollutants can also be a source of pollution to urban infrastructure, soil and water through atmospheric deposition[7].

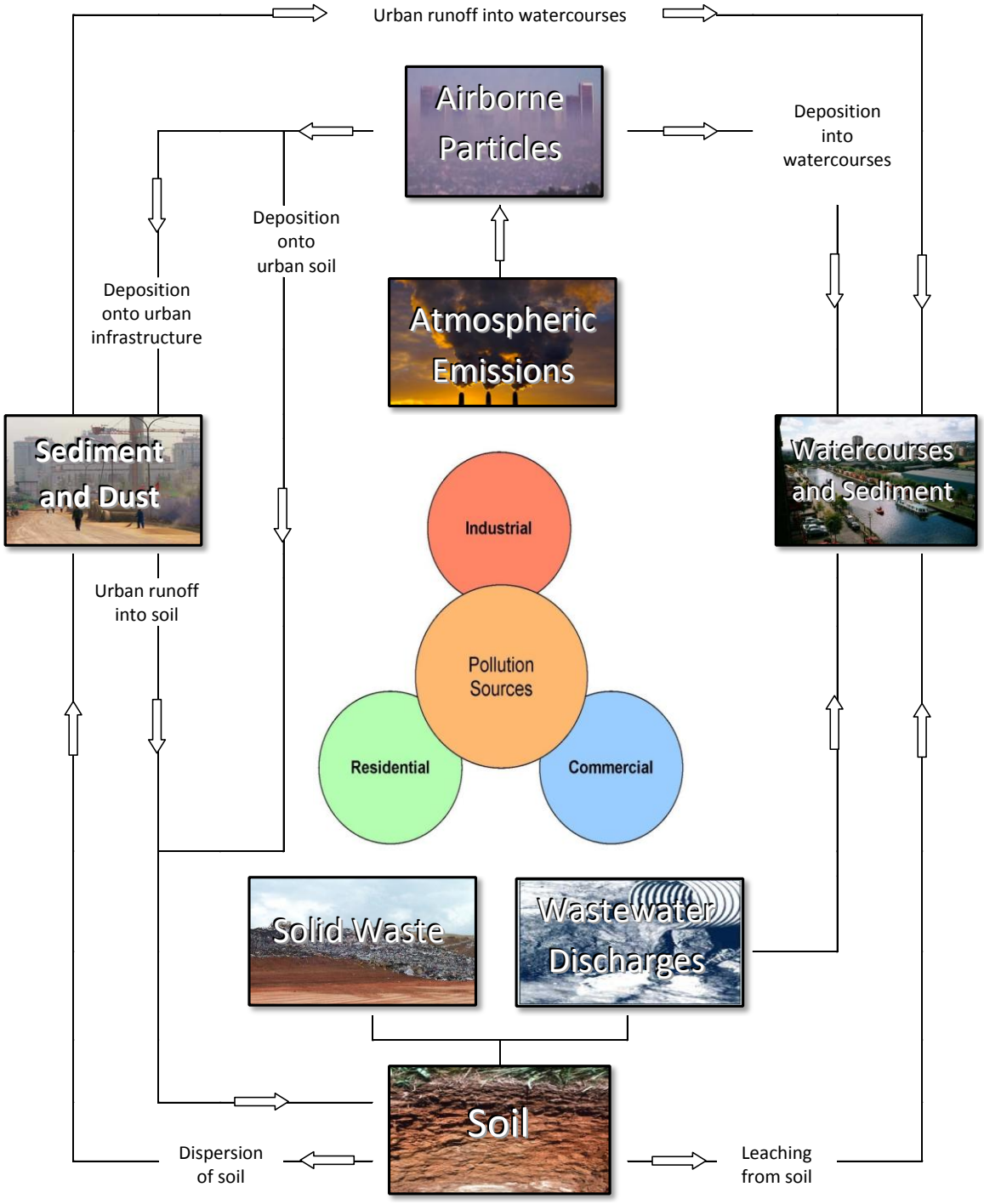


Figure 1-2 - The sources, dispersion and deposition of pollutants in the urban environment (after[1])

Depending on the location of deposition it is possible for particles and dust to become re-suspended in the atmosphere or become further dispersed by urban runoff. The disposal of solid waste in landfill sites, as well as wastewater discharge, is a common source of direct pollution of soils. Watercourses can be potentially contaminated by wastewater discharge, although they can also be polluted by dispersion from other mediums.

1.2.1 Soil in the urban environment[4,8-10]

Soil is one of the most common environmental solid materials which can be found in urban areas. Soils that are found under natural conditions can generally be defined as solid-liquid-gas systems with a variable mixture of minerals, organic matter and water in a vertical profile of distinguishable layers, known as horizons. These horizons are characterised by their specific properties, which result from physical, chemical and biological mechanisms that cause change in their composition from the parent material.

1.2.1.1 Soil mineralogy

Mineralogy strongly affects soil composition and is associated with the parent material from which the soil was formed. The composition also depends on how the parent material was formed through geological weathering, volcanic activities and/or sedimentation. Numerous classes of minerals exist including oxides, carbonates and silicates. Silicate minerals are the most prolific and, along with silica and aluminosilcate clays, constitute about 95% of the earth's crust. These minerals contain various metal ions within their structure, most commonly aluminium, calcium, iron and magnesium.

1.2.1.2 Soil organic matter

Organic matter can comprise less than 5% of soil but can still have a large effect on the properties of soil. Some organic components of soil, such as saccharides, act as the major food source of micro-organisms. The bulk of organic matter is composed

of humus and macromolecular hydrocarbons, which are the degradation resistant residues from plant decay. There are also naturally occurring organic contaminants in soil, such as polycyclic aromatic hydrocarbons (PAH) fluoranthene, pyrene, and chrysene. In natural soils these PAH compounds result, in part, from combustion sources such as forest fires and volcano emissions.

1.2.1.3 Soil classification

Soils may be classified in many ways depending upon the use of the soil. Often the classifications are based on chemical or physical properties of the soil, and the methods used. One of the most commonly used chemical classification system was devised by the US Department of Agriculture[11] and divides soils into eleven "orders" based primarily on their organic and mineralogical composition. Soils can also be classified by their particle size distribution using the British Standard method[12]. This is more relevant to construction industries, who may desire to build above or below a particular soil or indeed to use it as a building material.

In the urban environment, soils are not easily classified by such systems. High levels of human activity in the surroundings can cause soils to become highly disturbed and they may also have been transported from other locations. This means that urban soils may not show the traditional horizon profile and also may not relate directly to the parent material in the location. This also means that the mineral and organic matter content of the soil may vary significantly and can not be estimated based upon soil classification related to the parent material[1].

1.2.1.4 Soil pollution

Pollution of soil can occur when levels of inorganic and organic contaminants accumulate above the concentrations that may already naturally be present, or when substances not previously present are added to an extent that it could be harmful to organisms. There are four main routes by which soil pollution can occur: (a) wet and dry atmospheric deposition, (b) sorption of atmospheric gases, (c) sorption or deposition from flood waters and (d) direct placement (i.e. pesticide applications,

waste disposal). Depending on the composition of soil, pollutants present can undergo various adsorption processes and bind to soil components. This is the reason soil can act as a major sink for pollutants; for example trace metals are predominantly present in soil as cations in the interlayer spaces of aluminosilicate clays. The majority of organic pollutants become bound to humic material although ionic species can undergo ionic adsorption. In general the more strongly a pollutant is absorbed the less likely they are to be dispersed through soil or be available to plants.

1.2.2 Airborne particles in the urban environment[3-4,13]

Airborne particles are another major environmental solid in the urban environment that acts as an important transport medium for both organic and inorganic substances. They are a complex mixture of solid and liquid particles with diameters ranging from less than 10 nm to greater than 100 µm and come from various sources[4]. The smallest particles, known as transient nuclei, are formed by condensation of hot vapours, or gas to particle conversion. These tend to undergo coagulation with other transient nuclei or larger particles to form particles in the approximate range of 100 nm to 2 µm, called the accumulation range. The coarse particles, which are greater than 2 µm in aerodynamic diameter are composed mainly of mechanically-formed particles such as from sea-spray, wind-blown dust and volcanically emitted particles. The majority of airborne particles are in the range 0.1 to 10 µm as the finest particles are accumulated and the largest fall-out due to the influence of gravity.

In urban areas atmospheric particles have been described in terms of three main components[3].

- Combustion particles, of less than 2.5 µm, primarily arising from vehicle traffic and comprised of elemental carbon, organic carbon and trace inorganic compounds.
- Secondary particles and aerosols such as sulfuric acid and ammonium nitrate which are also usually in the fraction less than 2.5 µm.

- Coarse particles which are primarily resultant of re-suspension of soil and road dust, which principally have inorganic mineral content.

In contrast to soils, particulates in air are themselves classified as pollutants[3-4]. Reduced visibility has often been a problem associated with particulates as the particles cause scattering of light. The size of the particulates is of concern as their aerodynamic diameter directly relates to particle penetration in the human respiratory system. Particle size has therefore become a measure of particulate material in the environment. PM_{10}, the size fraction less than 10 μm, is likely to be inhaled into the thoracic region of the respiratory tract[14] and PM_2 can be deposited into the alveolar regions of the lung[15]. If these particles accumulate in the lungs, respiratory problems may arise and breathing illnesses such as bronchitis may occur.

Particulates are also of concern because chemical pollutants released into the environment can accumulate within them. Toxic elements such as trace metals and trace organic compounds can be absorbed onto the surface of particles or coagulate with other particles[7]. The fate of the chemicals then depends on the movement of particles in the environment. As shown previously the particles may become deposited through wet or dry deposition[7] and therefore come into human contact through soil and food grown therein, or water supplies. They could also remain airborne and therefore may be inhaled, the associated chemical species potentially increasing the health risks to the person breathing the polluted air.

1.2.3 Roadside deposited sediment in the urban environment[3-4,13]

Roadside deposited sediment (RDS) is not really a separate class of urban solid substrate but is rather formed from the further dispersion of airborne particles and soil in the urban environment. Airborne particles are a major source of urban sediment when larger particles (> 10 μm) undergo dry deposition onto infrastructure, such as roads and pavements. Finer particles can also be a source through wet deposition. Loose top soil can be dispersed by air flow and become deposited onto infrastructure. If these sources contain potential pollutants then subsequently the

resultant urban sediment will contain these pollutants. RDS can also undergo direct contamination from sources such as domestic litter.

1.3 Potentially toxic elements

1.3.1 Sources of potentially toxic element pollutants and their implications for health[3-4,10,14,16-18,20]

Aluminium, iron, calcium, magnesium, sodium, potassium and titanium are the metals amongst the ten most abundant elements constituting 99 % of the Earth's crust. The remaining elements, including the other metals, are known as trace elements and are general found at concentrations of less than 1000 mg kg^{-1} [18]. In the natural environment, minerals in the Earth's crust undergo weathering to form components of soils which consequently contain associated amounts of metals[10]. In an undisturbed system, the distribution of these metals will be at a steady state throughout the soil layers through mechanisms such as percolation of water and transportation by wind. Some of these metal elements are biologically essential for healthy living organisms. In large amounts, however, these essential elements, as well as non-essential elements, can become toxic[16-17].

Trace metals or potentially toxic elements (PTE) are therefore one group of inorganic pollutants which are of particular concern in the urban environment. In the urban environment, metals can be unequally distributed due to the effects of infrastructure and numerous local sources of pollution which can result in areas of high concentration. There is a wide spectrum of sources - both natural and anthropogenic - from which metals can be released into the environment. Natural sources tend to come from diverse and geographically distant sources, such as wind transportation of fine soil, forest fires and volcanic emissions, which are all part of the distribution within the global ecosystem[19]. In comparison there are numerous human activities which have urban environmental impact including, vehicular activity, the disposal of municipal waste (incineration and landfill), corrosion of infrastructure and varied industrial applications, such as metal production and coal-fired power stations (if located near urban areas)[3-4,14,20].

1.3.1.1 Aluminium

Aluminium is the third most abundant element in the Earth's crust and with a concentration of 83000 g/ tonne the most abundant metal. Aluminium is largely present in aluminosilicate rocks, which form clay minerals on weathering.

Aluminium and its alloys have many uses such as in the structure of vehicles, drinks cans, metal foil, cooking utensils, paint, electrical powers cables, heat sinks and construction materials. Aluminium has been related to acute toxicity in patients with renal failure, where the element cannot be excreted. Aluminium salts have also been found to accumulate in the brain tissue of patients suffering from Alzheimer's disease.

1.3.1.2 Barium

Barium is the 14th most abundant in the Earth's crust with a concentration of 390 g/ tonne. The concentration of barium can range from 1 – 1000 mg/ kg depending on the parent material.

The metallic form of barium is not readily used in industry, although its compounds have numerous uses. Barium sulfate can be used as a contrast agent in the x-ray imaging of the digestion system and in the production of rubber. Barium compounds are toxic and those that are soluble, such as barium carbonate which is used as a rat poison, can act as a muscle stimulant with barium ions causing ventricular fibrillation.

1.3.1.3 Cadmium

Cadmium is a highly toxic, non-essential trace metal and accumulation occurs in the bodies of mammals. The health effects of cadmium are numerous including, nausea, diarrhoea, vomiting and abdominal cramps from acute poisoning. Chronic effects have been lung damage, skeletal damage and renal dysfunction caused by

accumulation in the kidneys, which is a major effect in humans[17]. Cadmium has also been classified as a human carcinogen and linked to lung cancer.

The combustion of fuel oil for electricity generation and other industrial combustion processes are common sources of cadmium. The element has been used primarily for electroplating to prevent steel corrosion, in pigments in plastics and paints, batteries, alloying, electronics and polymer stabilization. Cadmium is 67th in the order of elemental abundance and subsequently background levels in soil are low (generally less than 1 mg kg^{-1})[10]. However natural soils with a high organic content have been reported to contain up to 22 mg kg^{-1} cadmium. The general level of cadmium in the atmosphere has been reported as <0.015 μg L^{-1}, with levels of 1 – 2 ng m^{-3} (μg L^{-1})[3] in European urban areas.

1.3.1.4 Chromium

Chromium is found in two common oxidation states, hexavalent (Cr^{VI}) and trivalent (Cr^{III}). Chromium (III) is a micronutrient and is essential for carbohydrate metabolism in mammals. However chromium (VI) is toxic and effects such as skin irritation, ulceration, and respiratory problems have been reported. Chromium, like cadmium, has been classified as a carcinogen, leading to a potential increased risk of lung cancer[3,10].

The main sources of chromium are various forms of coal combustion, metallurgical production works and the production of chromium-based chemicals. Chromium is used extensively in alloying for stainless steel and other metals. It is also used in numerous other processes including tanning, pigment production and in wood preservatives. The reported background levels of chromium in soil have varied between 34 and 62 mg kg^{-1}, with high concentrations from geochemical origins occurring in serpentine soils. In the atmosphere, background levels of 0.005 μg L^{-1} have been reported[3].

1.3.1.5 Copper

Copper is one of the biologically important trace elements and is found in several enzymes. As copper is an essential element, the adult body can contain 100-150 mg[10] and, under normal conditions, it is generally benign to humans. Toxicity

only occurs at particularly elevated levels where hemolysis, liver damage and renal damage have been observed, although recovery has been rapid on removal from exposure and treatment. In rare cases where individuals have deficiencies in Cu-binding ligands, a condition known as "Wilson's disease", toxic levels can accumulate in tissues.

The major anthropogenic sources of copper are from coal combustion, civil power generation, road transport and there are still some emissions from metal production industries. Commercially copper is used for electrical equipment, production of metal alloys such as brass, plumbing, electro-plating and in some agrichemicals. The background level of copper in soil is usually between 20 and 30 mg kg^{-1} [10].

1.3.1.6 Iron

Iron is the second most abundant metal in soil, and constitutes 5 % of the Earth's crust[18]. It is an essential micronutrient and is important in the production of haemoglobin, which is used for oxygen transport and utilization in mammals. Although iron can be potentially toxic, any effects usually occur from occupational exposure or specific ingestion as opposed to general environmental exposure.

Iron has been used for millennia in various forms of metallurgical manufacture. It is used in the production of steel and subsequent construction of buildings, ships, bridges, vehicles etc. It also finds other uses such as pigments in paints and in plastics. Although iron is used extensively, the amount of iron in the natural environment is such that emissions from anthropogenic sources have little relative impact under normal conditions.

1.3.1.7 Lead

Lead is a biologically non-essential element and has been extensively studied due to its numerous adverse health effects. There are various health effects associated with exposure to lead, including kidney damage, and anaemia. Lead is also a strong neurotoxin that may cause mental impairment[17,21].

The largest source was formerly lead from anti-knock additives in petrol. However leaded petrol was phased out in 1999 in the UK and consequently a decline in emissions from the road transport sector has been seen[14]. In the UK, in 2003, the major source was combustion in industry. Lead has found numerous uses in storage batteries, cable sheathing, pigments in paints, bullets for game shooting, water piping and alloy production, although many of these applications have been reduced or stopped. The natural level of lead in soil has been found to vary widely. General levels are between 10 and 30 mg kg^{-1}, but up to 100 mg kg^{-1} or more has been reported where accumulation occurs[10]. The background level in the atmosphere has been reported as 0.63 μg L^{-1} although higher concentrations have been found near volcanic activity. In urban areas in Europe levels of 27 – 38 ng m^{-3} (μg L^{-1}) have been reported[3].

1.3.1.8 Manganese

Manganese is an essential micronutrient for enzyme activity and growth. Like the other essential metal elements it has only been reported to be toxic at high concentrations and often primarily due to occupational exposure. Associated health effects have included pneumonia, respiratory problems, lethargy, and neurological problems.

The industrial use of manganese is primarily in steel production and for other alloys. It is also used to manufacture dry cell batteries and has been used in the electrical and construction industries. Manganese, like iron, is a major component of soil minerals, although is generally found at lower concentrations.

1.3.1.9 Zinc

Zinc is an essential component in numerous mammalian enzymes and the average healthy daily intake has been estimated as between 5 and 22 mg day^{-1}. Zinc is considered to be relatively non-toxic in comparison with the other metals and toxic effects from ingestion are uncommon. Exposure to very high levels has potentially induced nausea, vomiting, diarrhoea, lethargy, and inhalation of metallic oxide fumes can lead to metal fume fever.

The majority of zinc emissions are associated with industrial combustion and iron and steel production; although tyre wear results in the occurrence of road transport emissions. Zinc is used extensively in the galvanising of iron and steel products, production of metal alloys such as brass, dry batteries and pigments in paints. The average soil concentration of zinc is between 10 and 300 mg kg^{-1} [10] and around 0.03 μg L^{-1} in the atmosphere[3].

1.3.2 The isolation of potentially toxic elements from environmental solid substrates for analysis

Metal contamination of environmental solid substrates is of global concern due to the potentially toxic effects of many of these elements. In urban locations this can be a particular problem due to the large number of pollution sources and widespread distribution of materials in these areas. Subsequently numerous investigations have focused on the determination of metals in solid substrates from urban locations around the world and have included the employment of various isolation methods as well as different instrumental techniques. Table 1-1 and Table 1-2 highlight a number of investigations in PTE contamination from around the world using various digestion methods and analysis techniques.

The most commonly studied metals are copper, lead and zinc; although cadmium, chromium and nickel concentrations are also often reported. Guidance values for metals in soil and air are also reported. The ICRCL threshold values for contaminated parks and open spaces where used in the UK until they were withdrawn and replaced by the CLEA soil guideline values. The original CLEA model has also now been withdrawn and superseded by a new CLEA model, which assesses the risk to human health based on numerous factors for a specific site. The VROM guidelines are targeted to circumstances in the Netherlands, although they are derived generically to apply to the most sensitive land use and are non site specific.

Table 1-1 –Summary results of investigations for PTE in urban soil, road deposited sediment (RDS) and particulate matter (PM) from locations around the world employing different digestion methods and analysis techniques

City	Sample	Digestion		Analysis	Ref
		Method	Reagent		
Aveiro	Soil	BCR SEP	4 Steps	ICP-AES	[22]
Beijing	PM	As received	Direct Analysis	XRF	[23]
Buenos Aires	PM_{10}	Reflux	*AR*	ICP-AES	[24]
Delhi	RDS	"Tessier" SEP	5 Steps	FAAS	[25]
Florida	Soil	MAD	*AR*, HF	ICP-AES; GFAAS	[26]
Glasgow	Soil	BCR SEP	4 Steps	ICP-AES	[22]
Ljubljana	Soil	BCR SEP	4 Steps	FAAS	[22]
New York	$PM_{2.5}$	Hotplate	HNO_3/ HF	ICP-MS	[27]
Ontario	RDS	SEP		ICP-AES; XRF	[28]
Queensland	RDS	Hotplate	HNO_3	ICP-MS	[29]
Rio de Jeneiro	RDS	"Tessier" SEP	5 Steps	FAAS	[30]
Seoul	RDS	"Tessier" SEP	5 Steps	ICP-AES	[31]
Sevilla	Soil	BCR SEP	4 Steps	ICP-AES	[22]
Singapore	PM_{10}	MAD	HNO_3/ H_2O_2/ HF	ICP-MS	[32]
Taejon	PM	MAD	HNO_3/ $HClO_4$	ICP-MS; ICP-AES	[33]
Torino	Soil	BCR SEP	4 Steps	ICP-AES	[22]
Toronto	$PM_{2.5}$	MAD	HNO_3	ICP-MS; ICP-AES	[34]

"Tessier" SEP (Sequential Extraction Procedure, based upon the work of Tessier et al.[35]; Community Bureau of Reference Sequential Extraction Procedure (BCR SEP); Sequential Extraction Procedure (SEP); Microwave Assisted Digestion (MAD); Aqua Regia (AR); Inductively coupled plasma – atomic emission spectrometry (ICP-OES); X-ray Fluorescence Spectrometry (XRF); Flame Atomic Absorption Spectrometry(FAAS); Graphite Furnace Atomic Absorption Spectrometry(GFAAS); Inductively coupled plasma – mass spectrometry (ICP-MS).

Table 1-2 –Summary results of investigations and guidance values for PTE concentrations in urban soil, RDS (mg kg^{-1}) and PM (ng m^{-3}) from locations around the world

City	Average concentration										Ref
	Al	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
Aveiro				13	25	8040	97	8.7	77	78	[22]
Beijing	800				35	1140	97	15	304	480	[23]
Buenos Aires	893		0.27	2.8	5.4	552	21	1.7	71	37	[24]
Delhi			20	8314	1120			917	193	395	[25]
Florida	2280	13	0.07	14	3.7	1100	39	15	2.9	17	[26]
Glasgow				54	62	26400	416	39	212	185	[22]
Ljubljana				42	58		894	23	146	203	[22]
New York	39		0.34	2.7	17	160		10	7.9	29	[27]
Ontario			0.85	92	87	29700	1251	27	91	227	[28]
Queensland	7.4		0.002	0.01	0.5	11	0.19		0.03	1.3	[29]
Rio				91	324	39249	664	69	367	1205	[30]
Seoul			4.3	182	446			90	214	2665	[31]
Sevilla				36	62	14500	424	20	183	130	[22]
Singapore			1.6	59	7.3	265	10		16	41	[32]
Taejon		28	3.2	25	41	1633	50	38	243	240	[33]
Torino				227		30400	812	210	221	196	[22]
Toronto	35	3.0	0.3	1.2	2.5	55	3.8	0.8	3.4	16	[34]
ICRCL			15	1000	130			70	2000	300	[36]
CLEA			30	200				75	450		[37]
VROM (Target Value)		160	0.8	100	36			35	85	140	[38]
VROM (Intervention Value)		625	12	380	190			210	530	720	
MOEE		750	12	750	225			150	200	600	[39]
WHO			5				150		500		[40]

Inter Departmental Committee for the Redevelopment of Contaminated Land (ICRCL); Contaminated Land Exposure Assessment (CLEA);
Ministry for social building, regional planning and environmental administration [Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer] (VROM);
Minisity of Environment and Energy(MOEE); World Health Organization (WHO).
****The absence of a figure indicates the analyte was not studied***

The levels in Delhi for cadmium, chromium, copper and nickel would suggest further investigation is required as they exceed the investigation value for the VROM guidelines and also the old CLEA values for chromium and nickel. Copper and zinc VROM guidelines are also exceeded for soils in Seoul and Rio. The city of Torino exceeded levels of Chromium in accordance with the CLEA guidelines and nickel in relation to CLEA, VROM and former ICRCL guidelines. The concentration of lead in Glasgow and Torino would be highlighted by the Canadian MOEE guidelines, although they would warrant investigation under VROM or CLEA guidelines. Particulate matter guidelines are more often related to their size fraction rather than metal composition, although the WHO guideline does list values for cadmium, manganese and lead. The cities shown with concentrations for PM are all less than the guideline values.

The variation of methods used in metal investigations arises due to a number of factors such as;

- whether a non-destructive method is required,
- the information to be obtained from results,
- the speciation or metal fraction of interest,
- the sample matrix,
- the amount of sample that is available,
- the number of analytes under investigation,
- whether a single or sequential extraction is applied,
- safety and environmental impact of the method,
- the cost and time of analysis,
- the equipment that is available.

1.3.2.1 Extraction methods

Metal analytes are often isolated from solid substrates using decomposition methods, for example, dry ashing[41], fusion or the application of a metal liberating reagent. The addition of an appropriate reagent for sample digestion is a commonly applied method. However, where the sample must not be destroyed, then a non-destructive direct analysis technique, for example, X-ray fluorescence spectrometry[23] could be applied.

When digestion is applied to a sample the reagent used will depend upon the sample matrix and also the information to be obtained from the analysis. The reagent may be required to liberate all the metal analytes in the sample or information pertaining to an analytes liberation in a particular reagent may be of interest. Figure 1-3 shows a graphical comparison of some of the common methods for leaching metals using specific reagents.

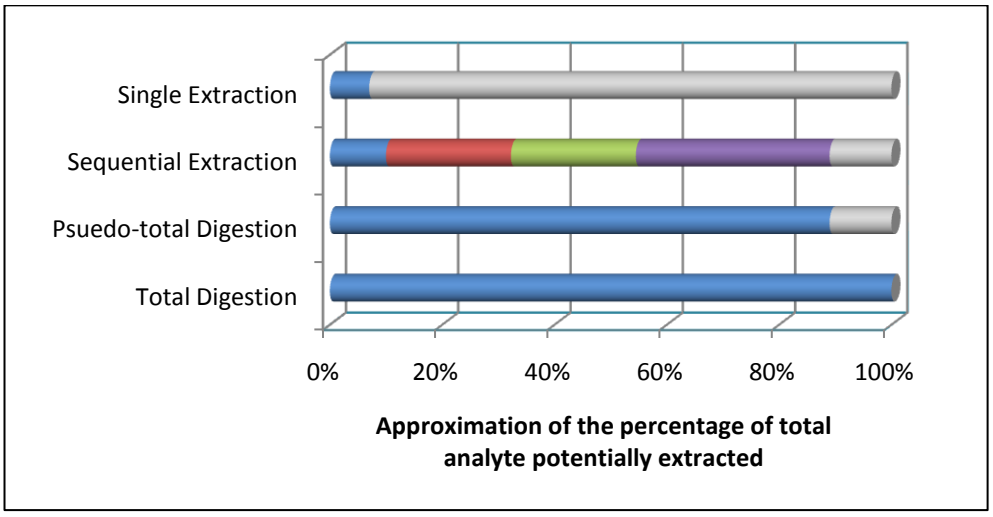


Figure 1-3 - Approaches to metal analysis (after[42])

Acid digestion is often applied in order to decompose the sample matrix; the specific acid applied depending upon the nature of the matrix. When total metal liberation is required from environmental solid substrates, hydrofluoric acid is most often applied as this is the only acid that is suitable to liberate silica-bound metals in the matrix (Figure 1-3; Total Digestion). As silica-bound metals are difficult to liberate it is

unlikely they will leach within the environment, therefore their effect on organisms are minimal. Consequently, other acids are used such as hydrochloric, nitric and perchloric acid. In environmental analysis, where the interest may be metals which are available to organisms, *aqua regia* is often applied. *Aqua regia* will liberate the metals bound in environmental solid substrates with the exception of silicates; hence it is a pseudo-total and not complete digestion (Figure 1-3; Pseudo-total Digestion).

Reagents other than acids may be applied, often so as to determine the concentration of a metal that a certain reagent will liberate, for bioaccessibility investigations. Speciation of organometallics is one such example where an appropriate organic solvent may be applied to extract species such as methyl mercury[43]. Investigations may also be concerned with the bioavailability of metal analytes to certain organisms: reagents that mimic natural processes are applied. Physiologically based extraction tests (PBETs), using reagents akin to gastro-intestinal fluids, are increasingly used as an *in vitro* alternative to *in vivo* animal testing[44-45] (Figure 1-3; Single Extraction). Plant uptake of metals from soil can also be investigated through application of a reagent, for example, EDTA which isolates a number of analytes in chemical forms which would be available to plants. This type of approach can be applied to other substrates and used with different reagents which resultantly isolate different chemical forms, such as water used to isolate water-soluble fractions or $Na_4P_2O_7$ for organically-bound material[46]. These selective extraction procedures can be used singularly or as part of a larger sequential scheme[47] which can be used to obtain multiple information on one substrate. For example, the Community Bureau of Reference (BCR) sequential extraction procedure is used to determine metal concentrations in four fractions (exchangeable, reducible, oxidizable and residual) by the sequential application and subsequent analysis of a sequence of reagents designed to simulate key changes in environmental conditions[48] (Figure 1-3; Sequential Extraction).

The application of a reagent is often performed with some method of heating or agitation, to decrease analyte liberation time. The selective and sequential schemes often involve some sort of shaking for a period of time and this is also the case for

some speciation methods, which also involve reflux and water bath incubation. In the case of PBET both heating to 37^{o}C and shaking are used as a mimic of the conditions in the human stomach. The traditional method applied to acid digestion of environmental solids is that of open vessel heating. Methods of this type are recommended as standard by both the Environmental Protection Agency (EPA)[49] and the International Organization for Standardization (ISO)[50]. Both methods involve the acid reflux of the sample material in an appropriate vessel, using nitric acid or *aqua regia* and a heating source. These standard methods offer benchmarks with which other methods can be compared. They have the advantage of being low cost and easy to implement with simple apparatus. The major limitation of these methods is the long extraction time, which can be several hours, and also the potential for non-uniform heating of the sample. As environmental analysis has become increasingly routine, with a subsequent increase in the number of samples requiring analyses, methods which allow for the accelerated extraction of solids matrices have been developed[51]. These include methods based around ultrasonic and microwave techniques.

1.3.2.2 Microwave-assisted digestion

Microwave-assisted digestion (MAD) has found application in the field of environmental analysis using both closed- and open-vessel digestion systems. It has been applied to a variety of samples for the determination of PTE including, soils[26,52], sediment[52], sewage sludge[53], plants and airborne particles[34,54]. There have been several comparisons of MAD and open decomposition methods[26,41,55]. The main advantages of MAD are decreased extraction time, less reagent consumption and more uniformed heating of samples. In some cases MAD can show improved, or at least comparable, extraction efficiency when compared to methods such as hotplate digestion[26].

1.3.2.3 Theory of microwave digestion

Microwaves are electromagnetic radiation with wavelengths of 1 mm to 1 m[56]. To prevent interferences there are microwave frequencies which are reserved for

specific domestic, industrial and scientific purposes. Microwaves like other electromagnetic waves contain both electric-field (E) and magnetic-field (B) components which are perpendicular to each other; change sinusoidally and propagate at the speed of light (c) through vacuum (Figure 1-4)[57].

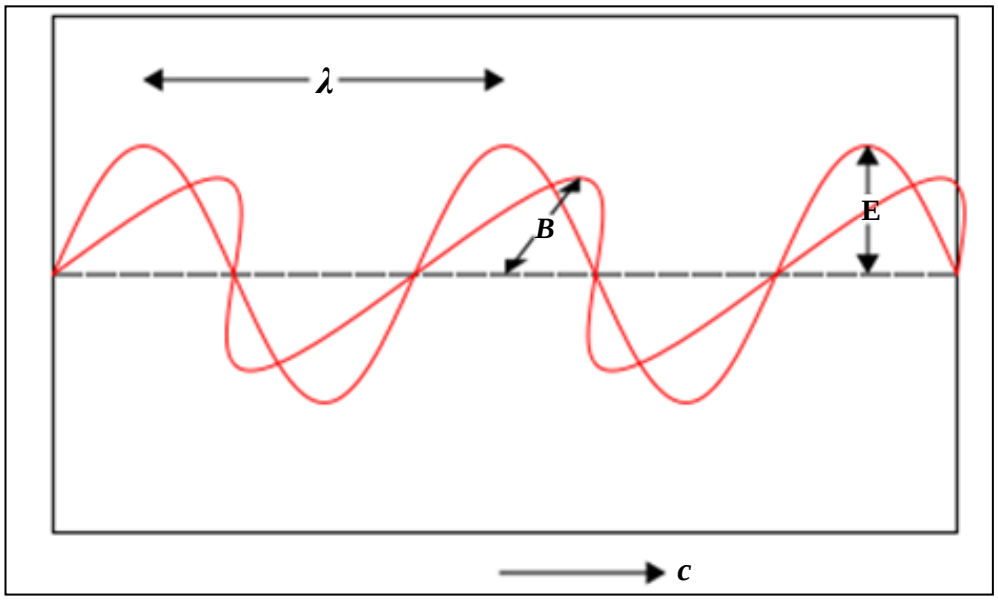


Figure 1-4 - Representation of an electromagnetic wave (after[57])

Microwave energy can be absorbed by molecules. The electric-field component affects polar molecules and there are generally two methods of interaction. Where polar molecules are free to move, ionic conductance can occur, causing the generation of a current. When the polar molecules are not mobile, they attempt to orientate themselves so they are in-phase with the electric-field, known as dialectic polarization. As the microwaves electric field is constantly polarizing and depolarizing, this causes rotation-vibration as the molecules re-orientate with the constantly changing electric field.

There are four components that summate the total dielectric polarization (α_1) and can therefore affect the dielectric heating of a given material subjected to microwave radiation (Equation 1-1).

$$\alpha_1 = \alpha_e + \alpha_a + \alpha_d + \alpha_i$$

Equation 1-1

Where α_e is the electronic polarization, α_a is the atomic polarization, α_d is the dipole polarization and α_i is the interfacial polarization. There is no heating effect from electronic and atomic polarization and depolarization as it occurs more rapidly than the change in electric field. If the polar material is suspended in a non-conducting medium then interfacial polarization can have a significant effect on dielectric heating. The main component thought to contribute to dielectric heating is permanent dipole polarization as its time period of oscillation is similar to that of the microwave electric field. This causes heating in the substance as the resultant polarization lags behind the reversal of the electric field. Therefore polar molecules and ionic solutions, which have permanent dipoles, can strongly absorb microwave radiation and pass the energy on to other molecules. The capacity of a substance to absorb microwave radiation, and therefore pass it on in the form of heat to other molecules, can be expressed in terms of its dissipation factor (δ) (Equation 1-2).

$$\varepsilon'' / \ \varepsilon' = \tan\delta$$

Equation 1-2

Where ε'' is the dielectric loss and ε' is the dielectric constant for a given substance. Materials with a low dissipation factor will have a low microwave absorbance capacity and are therefore ideal for digestion vessel material (e.g. Teflon). Conversely, polar liquids with high dissipation constants are ideal for solid sample digestion, transferring heat to a material after absorbing microwave energy.

The use of microwave heating has numerous advantages over conventional thermal convection heating in sample extraction and digestion. In conventional heating the material is heated from an external source outside of the digestion vessel (Figure 1-5A), whereas in microwave heating the digesting material absorbs the heat inside the vessel directly (Figure 1-5B). Heating from an external source requires that the vessel be heated first and a thermal gradient reached before heating of the sample

begins, thus increasing the digestion time and also increasing the energy requirement to heat both the material and the vessel. When using microwave heating the reagent will absorb the energy and heating will begin to occur almost immediately.

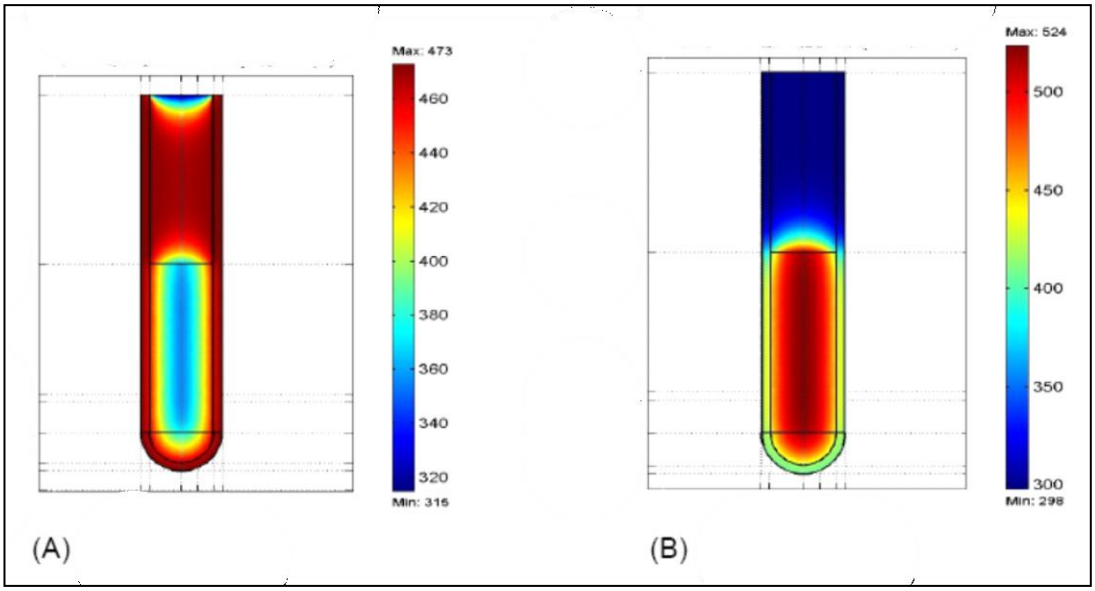


Figure 1-5 – Thermal distribution throughout a digestion vessel, (A) heated using an external source and (B) heated using microwave radiation[57]. Temperatures presented in degrees Celsius

The application of microwaves to heating was first discovered by Spencer in 1946[58], while he was testing a new vacuum tube. This vacuum tube, or magnetron, was thereafter integrated into microwave ovens and is now used as the main way of producing microwaves in decomposition instruments. The main components are highlighted in Figure 1-6.

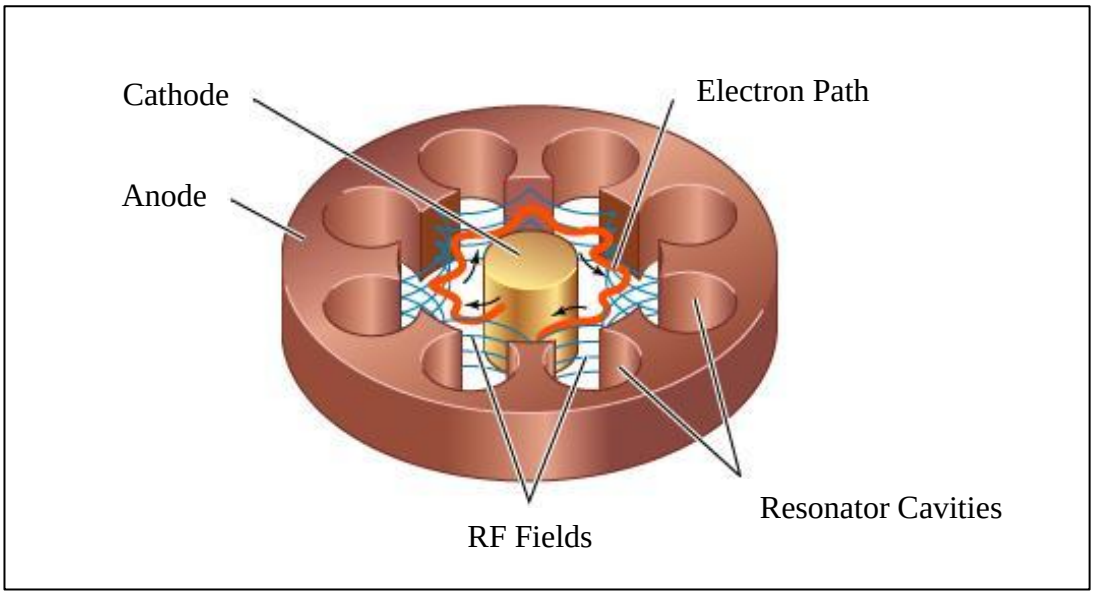


Figure 1-6 - Diagram of a magnetron (after [57])

Electrons are emitted from the cathode when high voltage is applied across it. A permanent magnetic field is applied which causes the emitted electrons to spiral out towards the anode, rather than be attracted directly towards it. At regular intervals resonator chambers are cut into the anode, in which the electric field reverses with the desired frequency and produces microwaves.

Generally microwave digestion instruments are either closed-vessel or open-vessel systems. Open-vessel systems mainly use microwave radiation which is focused on the sample (Figure 1-7).

As the digestion vessel is open the heating temperature is equivalent to the boiling point of the digestion reagents used. One potential benefit over the use of closed vessels is that any gases from any reactions evolve without build-up of pressure. However, as the vessel is open there is an increased chance of external contamination. In closed-vessel systems microwave radiation is dispersed into a cavity where samples vessels are placed (Figure 1-8).

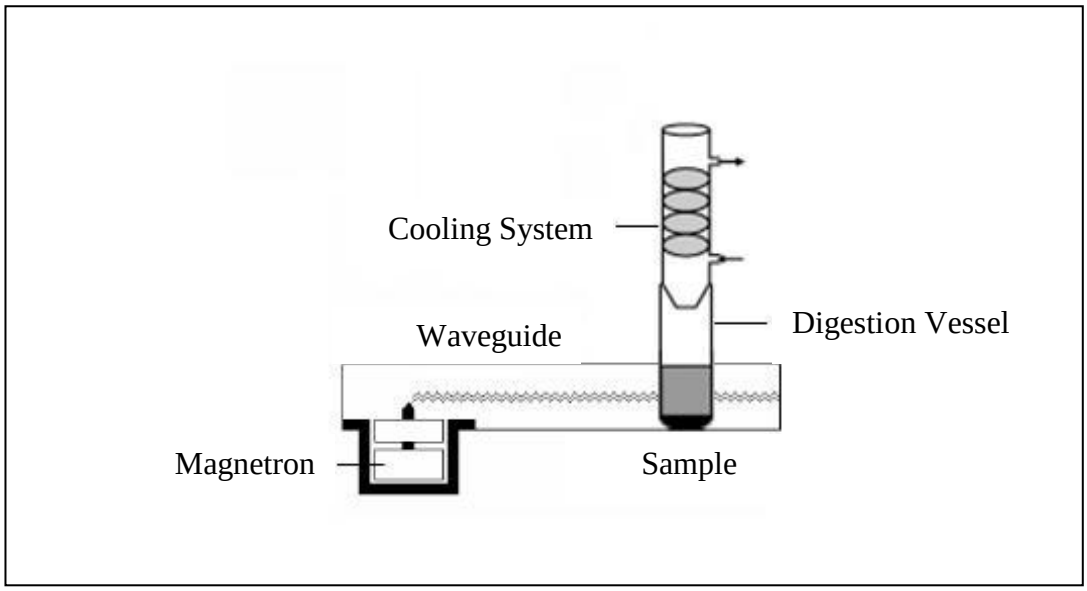


Figure 1-7 –Diagram of open-vessel microwave digestion system (after[59])

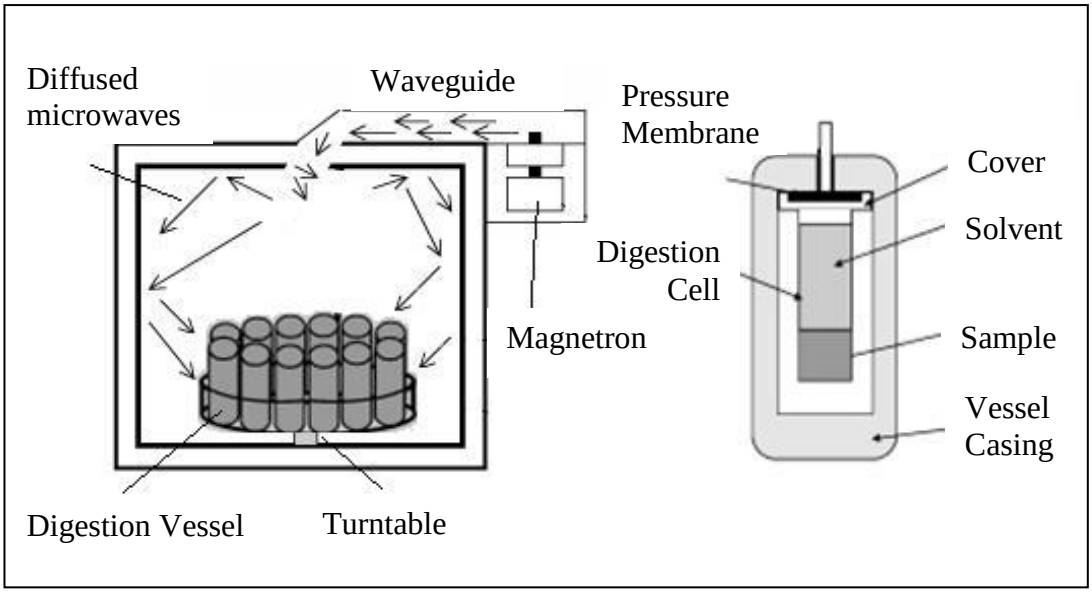


Figure 1-8 - Diagram of (A) closed-vessel microwave digestion system and (B) a closed vessel[59]

As the vessels are closed, high pressures and therefore temperatures can be obtained. The maximum temperature and pressure achieved depends upon the thermal and pressure stability of the digestion vessels and the properties of the solvent.

1.3.3 Instrumental techniques

Once the metal analytes have been isolated from the sample matrix, atomic spectrometry, either flame atomic absorption, electrothermal atomic absorption or inductively coupled plasma atomic emission, are the main instrumental techniques applied[22,26,30]. Inorganic mass spectrometry, using an inductively coupled plasma mass spectrometer, is also increasing used[29]. Direct sample analysis without the need for prior digestion is also used on occasion using techniques such as x-ray fluorescence spectrometry[23]. Where selective extraction is applied to a sample other analytical techniques may be required, such as the use of ion chromatography to determine metal ions in water extracts[60] or liquid and/ or gas chromatography for the determination of organometalic pollutants [61].

1.3.3.1 Theory of atomic spectrometry

Atomic spectrometry is concerned with the electronic transitions which result from the interaction of atoms with electromagnetic radiation. Transitions occur when a change in energy occurs which will cause an electron to move from one energy level to another. When electromagnetic radiation of a specific wavelength is applied it can be absorbed and cause excitation of an outer electron from a lower energy level (often the ground state) to a higher energy level (excited state) (Figure 1-9)[62-66].

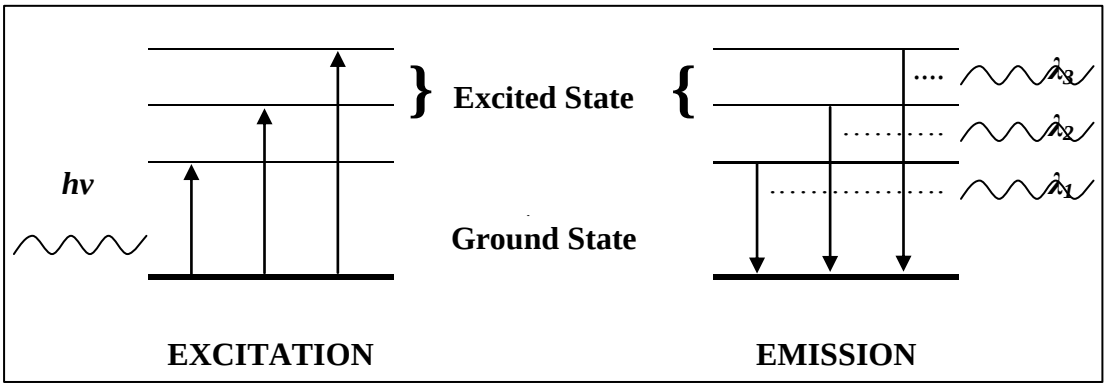


Figure 1-9 - Atomic excitation and emission processes (after[66])

The lifetime of an excited atom is brief (~10^{-8} s)[62] before collisions or photon emissions causes the loss of all or part of the excitation energy and so the electron

will return to its original state. This results in the emission of radiant energy of the wavelength characteristic of the energy difference for the transition occurring in the absorbing atom (Figure 1-9). It is possible to perform quantitative analysis by measuring the intensity of either the absorbance or emission. Each element has a characteristic set of energy levels and subsequently the difference in energy levels is unique. This means that the wavelength of a transition between two specific energy levels will also be unique and can be determined in terms of the difference in energy levels (ΔE) using Equation 1-3;

$$\Delta E = E_1 - E_0 = h\nu = \frac{hc}{\lambda}$$

Equation 1-3

Where E_1 is the energy of the higher state, E_0 is the energy of the lower state, h is the Plank constant, ν is the frequency, c is the speed of light, and λ is the wavelength. Therefore a unique spectrum is produced for each element, characteristic of the different wavelengths at which energy can be emitted.

1.3.3.1.1 Atomic absorption spectrometry

In atomic absorption spectrometry (AAS) the radiation from an external source, is absorbed by free atoms. The light absorbed increases as the number of atoms increase. The amount of analyte present can be determined quantitatively by measuring the absorbance.

Figure 1-10 shows a simplified schematic diagram of the main components found in atomic absorption instruments.

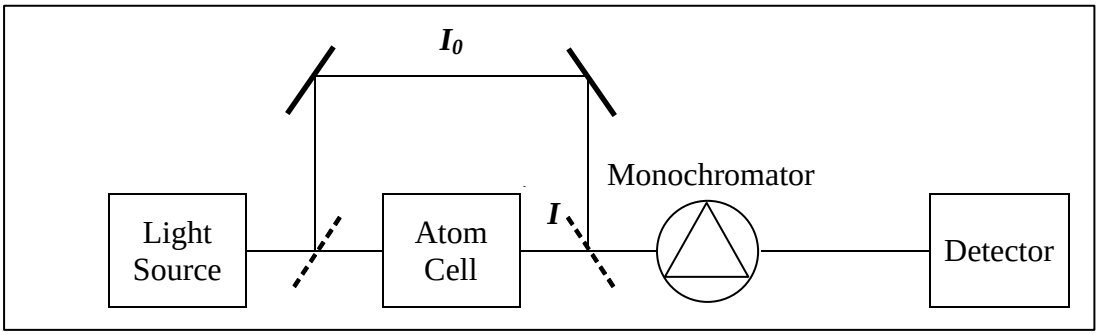


Figure 1-10 –Main components of an atomic absorption instrument (after[65-66])

Atoms, which are present in the atom cell, can absorb energy from the light source decreasing the initial intensity, I_o, by an amount which is proportional to the concentration of atoms present. The final intensity, I, of light leaving the atom cell is then measured and absorbance (A) can be determined by comparing the initial and final intensities[62-63,66-67].

$$A = \log(I_o / I)$$

Equation 1-4

Absorbance is directly proportional to the number of absorbing atoms and thus the concentration of an element in a test solution for a given set of instrumental conditions can be determined, in accordance with the relationship defined by Equation 1-5.

$$\log(I_0 / I) = kcb$$

Equation 1-5

Where, k is the relative coefficient of the absorbing species, c is the concentration proportional to the number of absorbing atoms and b is the length of the atomizer which the emitted radiation passes through. It is therefore possible to calibrate the instrument using a set of solutions of known concentration. The proportionality of concentration and number of absorbing atoms means that a linear relationship is observed between absorbance and concentration. A linear response is observed up to a point where deviation from linearity occurs, where transmission of unabsorbed

light occurs due to stray light or non-absorbing spectral lines which pass through the monochromator. It is therefore possible to determine the concentration of unknown samples from their absorbance in the linear region of the response curve[63,66]. In order to make AAS measurements an appropriate light source, atom cell and detector are required.

1.3.3.1.2 Light source

The hollow cathode lamp (HCL) is the most widely used radiation source in AAS and is shown schematically in Figure 1-11.

The cathode of the HCL is made of the element for which the spectrum is to be produced. The anode, which is a thick wire, is usually made of tungsten, nickel, tantalum or zirconium. The anode and cathode are sealed in a glass cylinder which is filled with an inert gas, usually either argon or neon, at low pressure (100-200 Pa)[62,66].

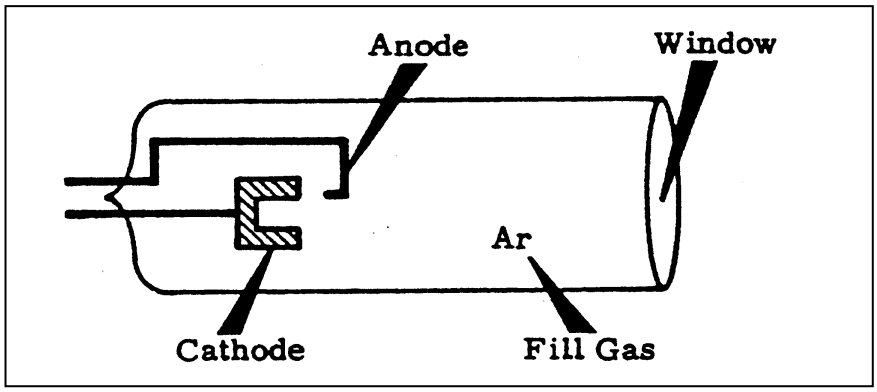


Figure 1-11 – Schematic diagram of a standard hollow cathode lamp[68]

When an electrical potential is applied the discharge causes ionisation of some of the fill gas. The cations accelerate towards the cathode which causes sputtering where surface metal atoms are dislodged. These sputtered atoms are then excited by electron collisions with the fill gas cations and subsequently when the atom spontaneous relaxes to the ground state emission of a photon occurs[63-66].

The advantage of a HCL is that it is a line source, which emits radiation over a very narrow spectral range, characteristic of the cathode element. Hence, any atoms of

this element will absorb the radiation efficiently. The emission line from a HCL will be narrower than the absorption profile, because of a number of factors which lead to spectral line broadening. The Doppler effects can cause broadening due to thermal motion of the atoms emitted or absorbed. Doppler broadening typically broadens the natural line width by 10^{-2} to 10^{-3} nm in a flame[65-66]. Collisions between emitting or absorbing atoms and other atoms can also cause broadening, known as collisional or pressure broadening, which is affected by pressure and temperature[63-66]. These collisions can occur between like atoms (Holtzmark or resonance broadening) or different atoms/ molecules (Lorentzian broadening). The combined broadening effects cause the spectral lines to be broader at higher temperature and pressure. A HCL is kept at relatively low pressure and temperature and therefore the spectral line emission of the source is narrower than that of the absorption profile of an analyte in a flame, where temperature and pressure are higher (Figure 1-12).

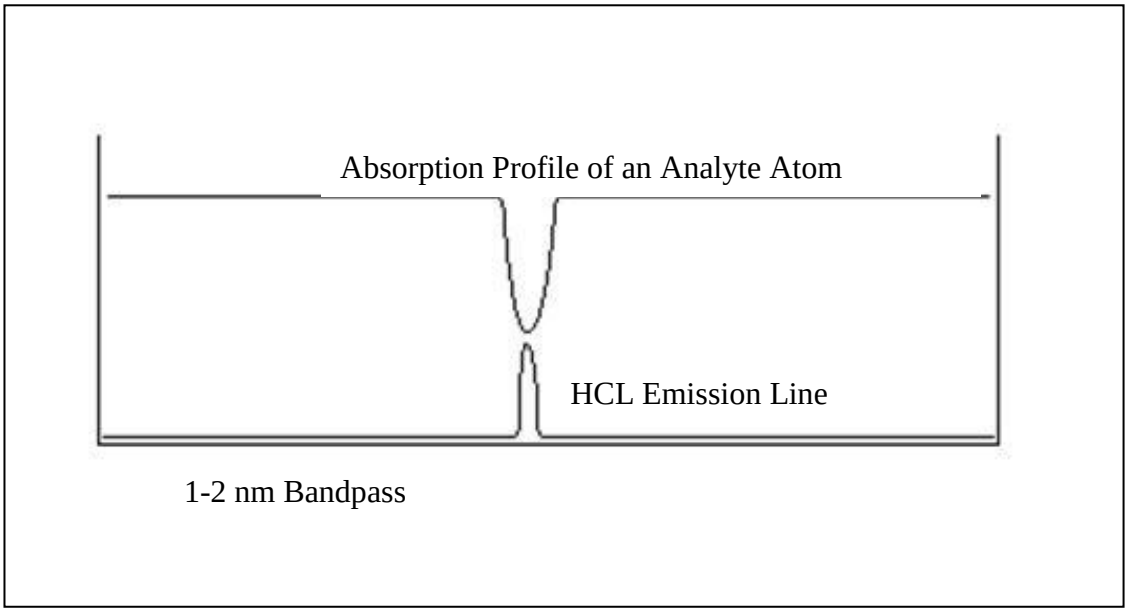


Figure 1-12 - Spectrometer band pass for an absorbing analyte with a line source (after[63,68])

1.3.3.1.3 Sample introduction and flame atomization

For analysis to be performed the sample must be introduced into the atom cell, generally in the form of an aqueous solution. In flame atomization this is achieved using a nebuliser and spray chamber. The decreased pressure of the expanding

oxidant gas draws sample solution through the nebuliser capillary into the spray chamber as small droplets. The droplets are then dispersed into a spray of finer droplets and mixed with the oxidant and fuel gases, before passing into the burner head. Residual larger droplets (85 – 90 %) of the sample are condensed and removed as waste[66].

The emission line from the light source (HCL) is passed through the atom cell so that absorption by free atoms can occur. The primary role of the atom cell is to cause atomization, generating ground state atoms of the element which was introduced into the atomizer. The most common atomization system, in atomic absorption spectrometry, is that of the combustion flame, either air – acetylene (~2300 K) or nitrous oxide – acetylene (~3200 K)[63-64,66]. The air - acetylene flame is sufficient for thermal dissociation of most analyte particles to their atomic form, for elements with low boiling points and low metal oxide bond strength. The nitrous oxide – acetylene flame can be used when a higher temperature could be required, such as for the determination of elements that form refractory oxides (e.g. aluminium, molybdenum and zirconium). However, the nitrous oxide – acetylene flame has a higher burning velocity (~ 300 cm s^{-1}), compared to that of the air-acetylene flame (~ 185 cm s^{-1}), and subsequently is not as safe.

The atoms produced in atomization absorb light energy from the light source beam which is passed through the flame. The absorbance signal is then measured by the detector and integrated to give an average absorbance for the sample.

1.3.3.1.4 Monochromator, modulation and detector

Light which is not absorbed in the atomization cell passes into a monochromator which isolates the measured line from other emissions lines. A Czerny-Turner monochromator is most often used in AAS, with a diffraction grating that disperses the incident light into different wavelengths[64,66].

A photomultiplier tube (PMT) is commonly used to detect the output from the monochromator. The PMT comprises a photocathode and collection anode, which are separated by a chain of dynodes and is shown schematically in Figure 1-13.

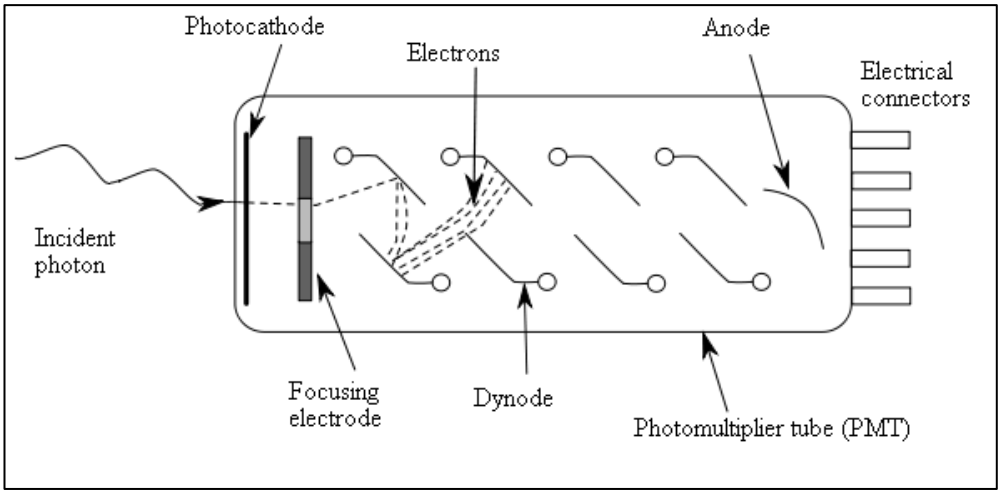


Figure 1-13 - Schematic diagram of a photomultiplier tube (after[62])

If a photon hitting the cathode is sufficiently energetic then ionization of the coating material will occur and an electron will be emitted. This electron then strikes the first dynode, releasing at least two electrons, both of which will strike the second dynode to release at least two electrons each. The signal is subsequently amplified exponentially by the process of secondary emissions from a series of dynodes. Finally the electrical current, of the electrons collected at the anode, is measured and converted into a voltage signal for a readout display. Typically one electron is amplified by 10^6 for a PMT containing nine dynodes. At increased voltages there is an increase in photon noise which is caused by statistical fluctuations of the photocurrent. This noise has a direct effect on the signal-to-noise ratio and subsequently the detection limits that can be achieved[62-66].

1.3.3.1.5 Interference effects[62-65,68]

There are various interferences which can affect the amount of light absorption in FAAS either in a suppressive or enhancing manner. They can generally be categorised into three types, spectral, physical and chemical interferences.

Spectral interferences generally occur when a species, other than the analyte, either absorb or scatter radiation from the HCL. Absorption can arise due to spectral lines overlapping with the analyte line, although this can be avoided by selecting an alternative resonance line if possible. Molecules present in the flame can lead to non-specific absorption or scattering of HCL radiation. This can be overcome using continuum-source background correction, where a D_2 lamp is applied to determine the non-specific absorption and then used to correct the HCL radiation adsorption.

The physical characteristics of the sample solution can also cause interferences during analysis. For example, if the solution viscosity is high then the aspiration rate can be lower. The surface tension of the solution also affects nebulisation. The lower the surface tension the smaller the droplets that enter the flame which is advantageous as smaller particles will generally be more easily atomized. In order to overcome this physical interference the composition of calibration standards and samples are usually matched.

Chemical interferences can be common for certain analytes which undergo reaction and subsequently affect atomization. The analyte could potentially react with another species present forming a stable compound which will not atomize, resulting in reduced absorption. This can be corrected by adding a chemical modifier, which will preferentially react with the interfering species. Analytes can also be affected by occlusion where atoms of the element are trapped by a refractory interferent particle. The addition of a reagent which the analyte and interferent will complex with separately, such as the chelating agent EDTA, can be used to overcome this problem.

1.3.3.2 Atomic emission spectrometry

Atomic emission spectrometry is concerned with the monitoring of excited atoms or ions. It involves the measurement of radiation emitted when the excited atom or ion relaxes to the ground state (see section 1.3.3.1). Figure 1-14 shows a simplified schematic diagram of the main components in an atomic emission instrument.

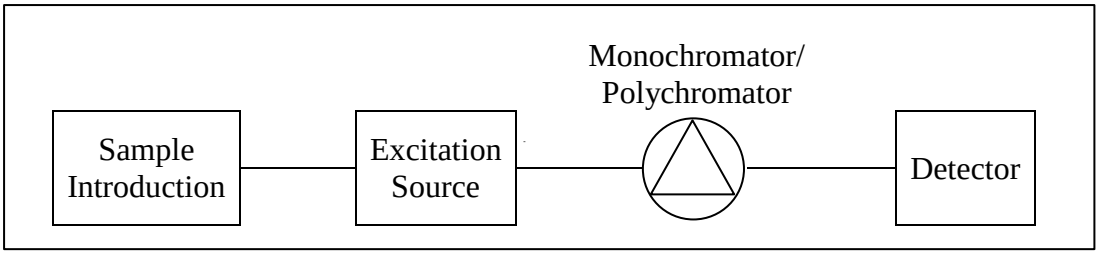


Figure 1-14 –Main components of an atomic emission instrument (after[65-66])

The sample for analysis is introduced, using an appropriate method, into the excitation source. The excitation source, now commonly a plasma, causes atomization, ionization and excitation of analyte species. When relaxation of an excited species occurs the emission line intensity is measured using the detector. If sufficient energy is present, emission may occur from any atomized or ionized species and it is therefore necessary to isolate the spectral line(s) of interest. Either a monochromator or polychromator can be used for single element or simultaneous multi element analysis, respectively.

1.3.3.2.1 Sample introduction and inductively coupled plasma excitation

Plasma is a highly ionised gas composed of ions, neutral particles and a high concentration of electrons. Inductively coupled plasma (ICP) is typically argon which is energised using a high-frequency electromagnetic field[66].

A quartz torch consisting of three concentric tubes, each with an independent gas flow input, is used to form the ICP. The plasma is generated from argon in the intermediate gas flow and an inner gas flow is used to introduce sample aerosol from the nebulizer. Coolant gas is introduced into the outer flow, tangentially to the inner flow, and is used to prevent the quartz tube from melting as well as providing argon to sustain the plasma[62,66]. A copper coil, surrounding the top of the quartz tube and connected to an RF generator, is used to create an oscillating electromagnetic field. A Tesla coil is used to generate a spark which "seeds" electrons and causes ionization of the argon. The oscillating electromagnetic field causes the electrons to accelerate and collide with the argon gas, ionising them to release more electrons[63,69]. The plasma is self sustained by the argon, argon ions and electrons contained within the torch. The outer tube of the torch is designed with an optimum diameter so that a

ring shaped plasma, with a central hole, is formed. The sample aerosol, introduced in the inner tube of the torch, passes through the central hole in the plasma where volatilization, atomization, ionization and excitation of the analytes occur. The plasma is not in thermodynamic equilibrium, and subsequently temperature in the torch cannot be simply described, and can be characterised in terms of gas, electron, excitation or ionization temperatures. The kinetic gas temperature, in the main plasma, is often quoted and is about 7000 – 10000 K, whereas a temperature of about 4000 – 6000 K is thought to occur in the inner channel[62].

The plasma which protrudes from the top of the torch can be categorised into different zones; in each of which the degree of atomization and ionization that occurs for an analyte differs (Figure 1-15).

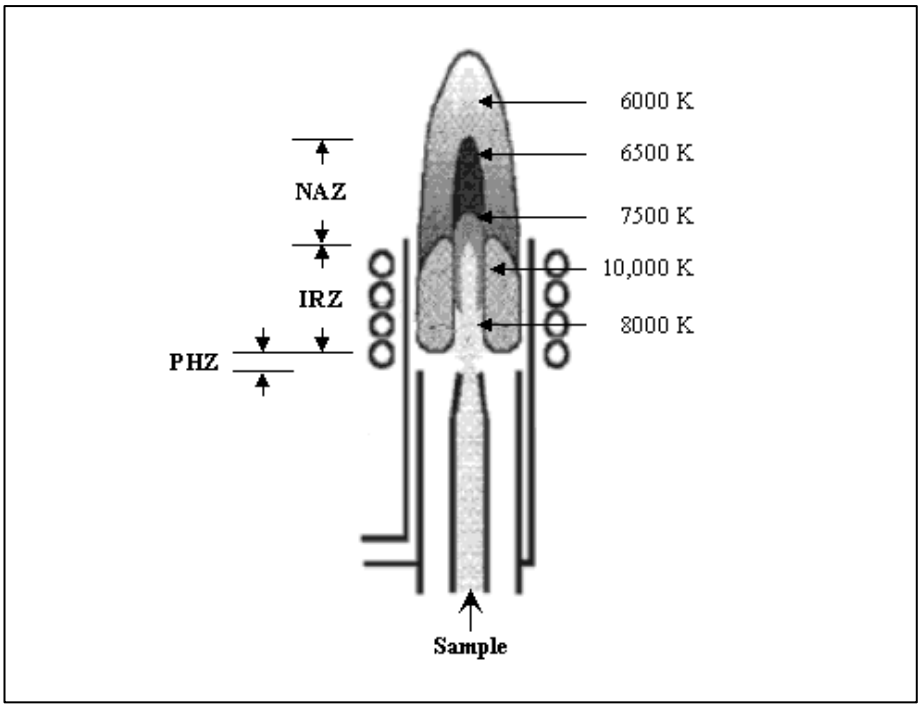


Figure 1-15 – Schematic diagram of the different zones in a plasma source (after[69])

The sample aerosol undergoes desolvation at the base of the plasma in the preheating zone (PHZ). Above this is the initial radiation zone (IRZ) were volatilization, atomization/ionization and excitation of the sample occurs. Measurements are usually made in the normal analytical zone (NAZ), a region where there are low background emissions[69]. There are a number of excitation processes that can occur

for analytes in the plasma. The most dominant are those involving collisions with electrons, molecular species and metastable species.

1.3.3.2.2 Polychromator and detector

The emission lines from species in the plasma can be monitored sequentially or simultaneously. The former will monitor a single analytical line at a time, with line isolation using a monochromator and detection using a photomultiplier tube (see 1.3.3.1.4). The latter requires the use of a polychromator which will isolate several analytical lines for simultaneous multi-element detection. The isolation of multiple lines requires a higher resolution spectrometer; the echelle-type polychromator is used in many modern instruments. Analytical lines emitted from the source are collimated and focused onto the spectrometer grating. The echelle grating uses a lower groove density with increased spectral order and blaze angle to produce high order diffraction patterns. The diffracted beam is subjected to a second dispersion, usually using a prism, to prevent overlapping of the spectral orders. The prism is mounted perpendicular to the diffraction grating, which separates the orders vertically and the wavelengths horizontally in a two-dimensional pattern. The two-dimensionally dispersed light can finally be focused onto a charge transfer device (CTD) for detection. A CTD is a two-dimensional array of pixels, each of which is capable of storing a photo-generated charge. The difference between different CTDs, including the charge-coupled device and charge-injection device, is the method by which the incident radiation is converted into a signal.

1.3.3.2.3 Interference effects[62-65,68]

Spectral interferences are the main problem observed in ICPOES measurements and non-spectral interferences are minimal compared to other atomic spectrometry techniques, although matrix effects can be potential problems. The spectral overlap of an interfering line with the analyte emission is a potential effect and can be categorised as three types.

- The direct overlap of the analyte emission line with an interfering line,
- Partial overlap of a interfering wavelength with the analyte line,

- An increase or decrease in the background level relative to the analyte.

The use of modern high-resolution spectrometers greater reduces spectral interferences, although when they still occur the most common solution is the use of a different emission line. The physical properties of the test solution can also cause matrix effects, although this can be overcome by matrix-matching the standards and samples.

1.4 Organic pollutants

1.4.1 Sources of organic pollutants and their implications for health

Modern human society relies heavily on the production of organic compounds which are used for the manufacture of a variety of products including polymers, fuels and pesticides. The production of organic materials and their use in industrial, commercial or residential activities can result in numerous contaminant species such as persistent organic pollutants (POPs) and volatile organic compounds, both of which are highlighted in the United Nation's "Convention on Long-range Transboundary Air Pollution" [70-71].

1.4.1.1 Persistent organic pollutants

POPs are toxic compounds that can accumulate in trace quantities in the environment. Many are ubiquitous causing concern due to their potential chronic toxicity and impacts on human health[8]. The term POP covers numerous compounds which include industrially-produced chemicals and by-products from reactions. Pesticides, such as organo-chlorides and organo-phosphates, are an example of industrial chemicals and are designed to deal with agricultural pests but often show non-target toxicity towards other species such as humans. The manufacture of chemicals, and controlled or accidental combustion, can lead to the formation of by-products such as polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and polycyclic aromatic hydrocarbons (PAHs). The potential health issues from many of these compounds include hepatotoxicity, immunotoxicity, neurotoxicity, reproductive effects and carcinogenicity. The PAH group of compounds are studied in this research and subsequently other species will not be discussed further.

1.4.1.2 Polycyclic aromatic hydrocarbons

PAHs are a large group of hydrocarbons which with structures of two or more benzene rings are fused in linear, angular and cluster arrangements. Formation of PAHs occurs primarily from the incomplete combustion of hydrocarbon compounds, such as fossil fuels [3]. The health concern, and subsequent environmental interest, is

due to the potential mutagenic and carcinogenic effects of these compounds. The most potent carcinogens are suspected to be benzo[a]anthracene, benzo[a]pyrene and dibenzo[ah]anthracene[4,72]. Although there are numerous PAHs, there are sixteen which are commonly investigated and were highlighted by the United States Environmental Protection Agency (USEPA) as priority pollutants[73]. The structures of these sixteen molecules are shown in Figure 1-16.

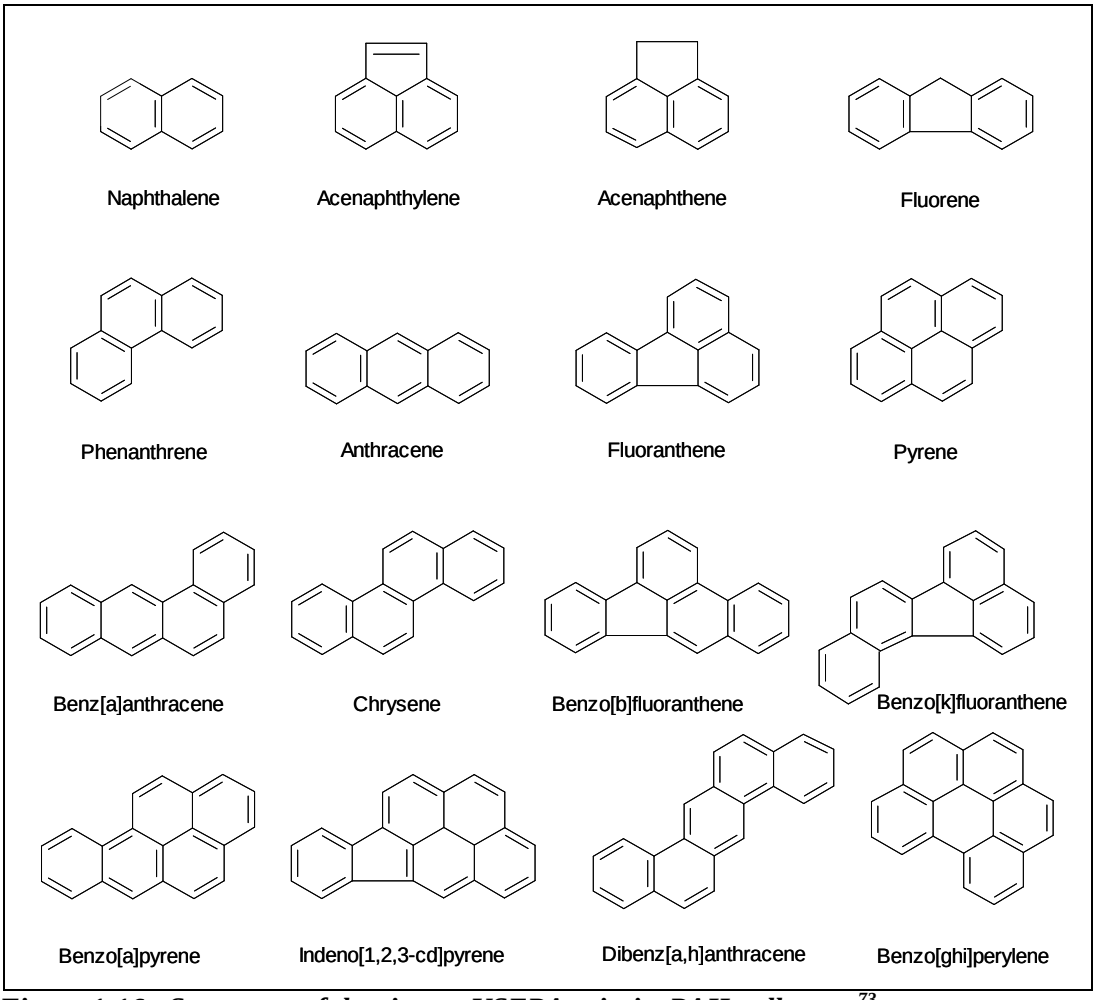


Figure 1-16 - Structures of the sixteen USEPA priority PAH pollutants[73]

1.4.1.3 Sources of polycyclic aromatic hydrocarbons

PAHs arise from both natural and anthropogenic sources. Natural combustion sources such as forest fires and volcanic eruptions both cause the formation of PAHs. They can also be formed via biologically-mediated synthesis of plant derived terpenoids. PAHs can be categorised in terms of pyrogenic and petrogenic sources[74].

Anthropogenically occurring pyrogenic emissions include residential heating, industrial production, incineration and power generation. Aluminium production and domestic coal and wood combustion are both sources highlighted in the UK in 1999[14]. There are also various PAH present in tobacco smoke[4,75]. Crude oil and refined products are the primary source of petrogenic emissions, particularly in urban areas where there are a large number of vehicles. Vehicular traffic has been identified as a major factor of PAH contamination in the urban environment[75-77]; it can show sources of both pyrogenic and petrogenic types, due to internal combustion processes and the presence of various hydrocarbon oils, respectively[74].

1.4.1.4 Atmospheric processes of polycyclic aromatic hydrocarbons

Once emitted from a source PAHs, which are semi-volatile, are initially associated with the gas phase[78]. Subsequently behaviour depends on molecular weight. The low molecular weight PAHs, those with two to three benzene rings in their structure, tend to be more volatile and persist in the gas phase[79]. The higher molecular weight PAHs, with four or more benzene rings in their structure, can undergo conversion from the gas to particle phase. This occurs via adsorption and condensation onto the surface of particulate matter and will depend upon factors such as: the amount of particulates released from the source; the surface area of the particles; the concentration of the PAHs and the vapour pressure of the PAHs[79-80].

The PAHs present in the atmosphere, either in the gas or particulate phases, can be subjected to a number of chemical and physical transitions[81]. They can

- undergo wet or dry deposition,
- be transported and dispersed throughout the environment,
- undergo atmospheric degradation or reaction with other species,
- or change equilibrium between the gas and particulate phase.

The concentration, location, and phase-association of PAHs can change greatly depending on the conditions of both the pollution source and the atmosphere. The chemical transitions of PAHs in the atmosphere can be of particular concern if

reactions lead to the formation of more harmful products. Photochemical degradation and reactions with gaseous pollutants, such as nitrogen and sulfur oxides, are the common routes of transitions. The formation of nitrogen derivatives is of interest as it can account for carcinogenicity which cannot be explained solely due to PAHs[82-83]. A more hazardous product may be formed from a polycyclic aromatic hydrocarbon which, before reaction, was not of major carcinogenic concern[84]. Figure 1-17 shows the mechanism of formation of such a compound, 2-nitrofluoranthene in the atmosphere.

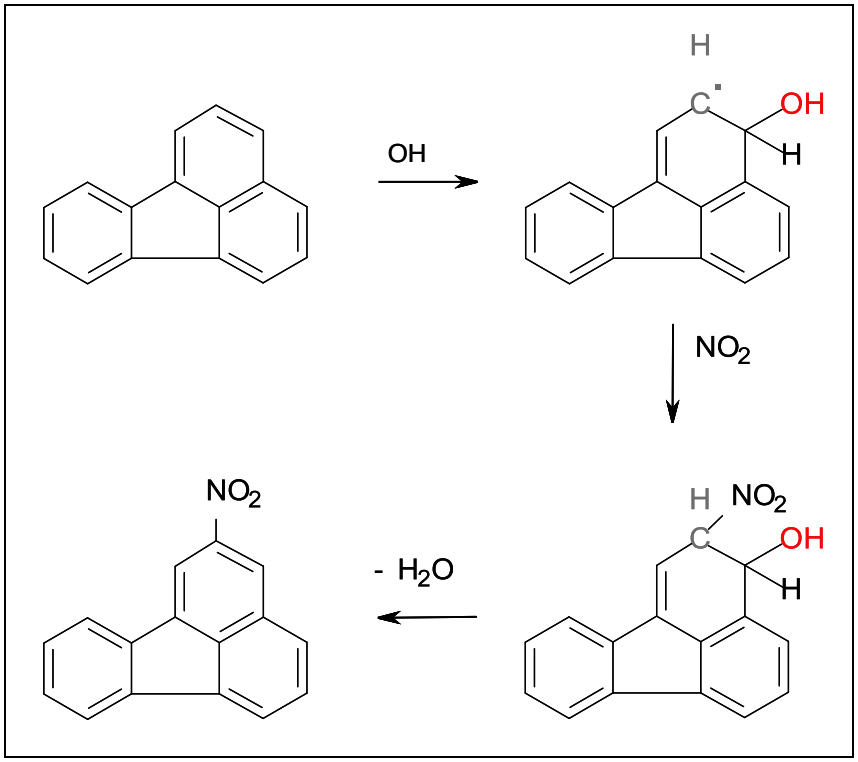


Figure 1-17 - Atmospheric formation mechanism of 2-nitrofluoranthene[69]

1.4.1.5 Carcinogenicity of polycyclic aromatic hydrocarbons

The main interest regarding human exposure to PAH is due to their potential to undergo carcinogenesis[85-86]. The International Agency for Research on Cancer has highlighted a number of PAHs as carcinogenic or potentially carcinogenic based upon laboratory testing. Benzo[a]pyrene has been the most studied PAH and has shown carcinogenicity after various routes of exposure[87]. It is not possible to accurately determine the direct effect of PAH on humans due to lack of long term

exposure investigations, although the effects on animals have been used to estimate the potential human health effects. Inhalation shows the most significant health effect with the possible associated increased risk of lung cancer, although at high levels this is thought to be a consequence of overloading the lungs with particles. The significant additional effects noted have been bone marrow toxicity, reproductive toxicity, immunosuppression and tumour induction [88-90]. The longer term effects of low dose exposure are not well documented.

PAHs are not particularly mutagenic themselves and require metabolic modification, known as initiation, in order to be able to interact with a cell's DNA. Figure 1-18 shows the initiation of carcinogenesis by benzo[a]pyrene to form the 7,8-dihydrodiol-9,10-epoxide[91].

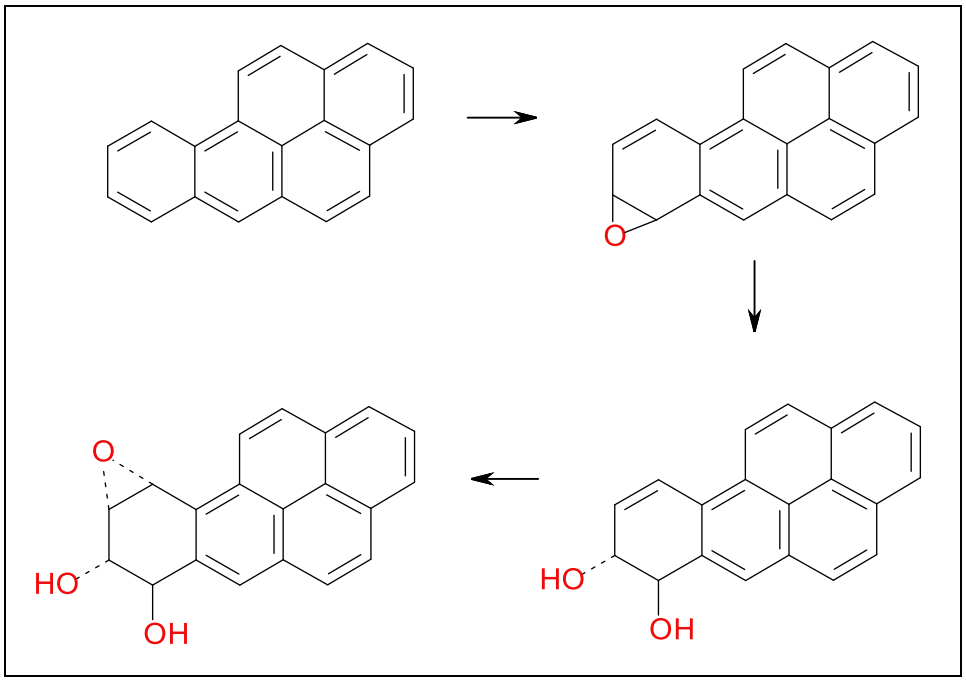


Figure 1-18 - Metabolic modification of benzo[a]pyrene[74]

The first step of initiation involves the epoxidation of benzo[a]pyrene, which is catalysed by a P450 cytrochrome enzyme, to form the 7,8-epoxide. The epoxide then undergoes hydrolysis to form a 7,8-dihydrodiol and finally a second epoxidation to the product, benzo[a]pyrene-7,8-dihydrodiol-9,10-epoxide. The epoxide group can subsequently lead to ring opening and the formation of a carbonium ion, which

can act as a alkylation agent and react with DNA[74,91]. The formation of a PAH-DNA adduct can then potentially lead to mutation and tumour formation.

1.4.2 The extraction of polycyclic aromatic hydrocarbons from environmental solid substrates

There is an extensive number of organic compounds that can be found as contaminants in environmental solid substrates. Many investigations in urban areas around the globe have focused on PAHs, as well as other organic species, and there have been a variety of methods applied to extract these analytes (Table 1-3).

Table 1-3 – Summary results of investigations for PAH in urban soil, RDS and particulate matter (PM) from locations around the world employing different extraction methods and analysis techniques

City	Sample	Extraction		Analysis	Ref
		Method	Reagent		
Beijing	Soil	Soxhlet	DCM/ ACN	GC-MS	[92]
Glasgow	Soil	UAE	DCM	HPLC	[93]
Glasgow	Soil	UAE	ACN	HPLC	[94]
Ljubljana	Soil	UAE	DCM	HPLC	[93]
London	PM	UAE	CH_3OH, C_6H_5CH3	GC-MS	[95]
London	RDS	UAE	C_6H_{14}	GC-MS	[96]
Maracay	RDS	Shaker	C_6H_{12}	GC-FID	[97]
New Orleans	Soil	ASE	DCM	GC-MS	
Torino	Soil	UAE	DCM	HPLC	[93]

Ultrasonic Assisted Extraction (UAE);
Accelerated Solvent Extraction (ASE);
Dichloromethane (DCM); Acetonitrile (ACN);
Gas Chromatography – Mass Spectrometry (GC-MS);
High Pressure Liquid Chromatography (HPLC);
Gas Chromatography – Flame Ionisation Detector.

Table 1-4- Summary results of investigations and guidance values for PAH concentrations in urban soil, RDS (μg kg^{-1}) and PM (ng m^{-3}) from locations around the world

City	NAP	ACE	ACY	FLN	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	DAN	IPY	BPE	∑PAH	Ref
Beijing																	3917	92
Glasgow	132	93		110	1951	254	1729	1763	920	1150	796	411	971	97	684	867		93
Glasgow	9650	5650		743	1640	557	776	1550	1310	1420	1910	1400	2890		2730	2600		94
Ljubljana	28	9.5		12	209	14	135	104	62	79	69	39	77	12	75	65		93
London	0.04	0.07	0.13	0.13	0.22	0.12	0.09	0.26	1.16	0.97	0.63	0.59	0.55	0.03	0.44	1.78		95
London	150	300	650	1100	3150	1467	3833	4467	3850	5983	2900	233	3433		1630	2533		96
Maracay	2.67				13	53		32										97
New Orleans	10	1	6	1	133	38	266	237	145	111	319	95	255	208	322	237		
Torino	32	14		24	227	32	272	289	162	194	155	97	229	20	86	156		93
CCME	600				5000			10000	1000	700	1000			1000	1000			[98]
VROM (Target)																	1000	38
VROM (Intervention)																	40000	38

Naphthalene (NAP); Acenaphthalene (ACE); Acenaphthylene (ACY); Fluorene (FLN); Phenanthrene (PHE); Anthracene (ANT); Fluoranthene (FLT); Pyrene (PYR); Benz[a]anthracene (BaA); Chrysene (CHR); Benzo[b]fluoranthene (BbF); Benzo[k]fluoranthene (BkF); Benzo[a]pyrene (BaP); Dibenmz[a,h]anthracene (DAN); Indeno[1,2,3-cd]pyrene (IPY); Benzo[ghi]perylene (BPE); Canadian Council of Ministers of the Environment (CCME); Ministry of housing, spatial planning and the environment [Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer] (VROM); *The absence of a figure indicates the analyte was not studied

The guideline information for PAHs in environmental substrates is limited and those that exist tend to assess the summation of several analytes, such as the Ministry of Housing, Spatial Planning and the Environment (VROM). The Soil Guideline Value report for PAH using the new CLEA model is still being developed by the Environmental Agency[99]. The results listed for the various cities do not exceed the intervention target stated under the VROM guidelines.

There are various factors which must be considered when developing or selecting a method for PAH extraction. These include

- the information to be taken from the results,
- the sample matrix and interfering species,
- the amount of sample that is available,
- the number of analytes to be analysed,
- the polarity of the analytes,
- the concentration of the analytes,
- safety and environmental impact of the method,
- the cost and time of analysis,
- the equipment that is available.

1.4.2.1 Extraction methods

The most common method for the isolation of PAHs - and other organic species - in a solid substrate is the application of an appropriate solvent, known as solvent extraction. The solvent that is used for extraction will depend upon the sample matrix, the analytes of interest and other potentially interfering species.

As the analytes are organic in nature, organic solvents are often applied. The particular organic solvent used may depend upon the sample matrix and the polarity of its component species. In general a solvent is applied that has similar polarity to the analyte or group of analytes of interest, and if possible of different polarity to other species present. For example, dichloromethane (DCM) could be used for the

liberation of non-polar compounds, e.g. PAH, but might not liberate more polar pollutants, e.g. polychlorinated biphenyls.

Other solvents and reagents may be used, to determine information such as the bioaccessibility of a particular analyte. For example, PBET may be applied using a mixture of reagents which mimic biological reagents[100]. This can be used to estimate the concentration of organic species which are bioavailable, for example, in the human gastro-intestinal system. Water could also be applied to the test substrate in order to determine the water soluble organic species[101].

The addition of solvent is usually accompanied by a method of heating, the application of pressure and/ or agitation allowing for analyte extraction at an increased rate (Figure 1-19).

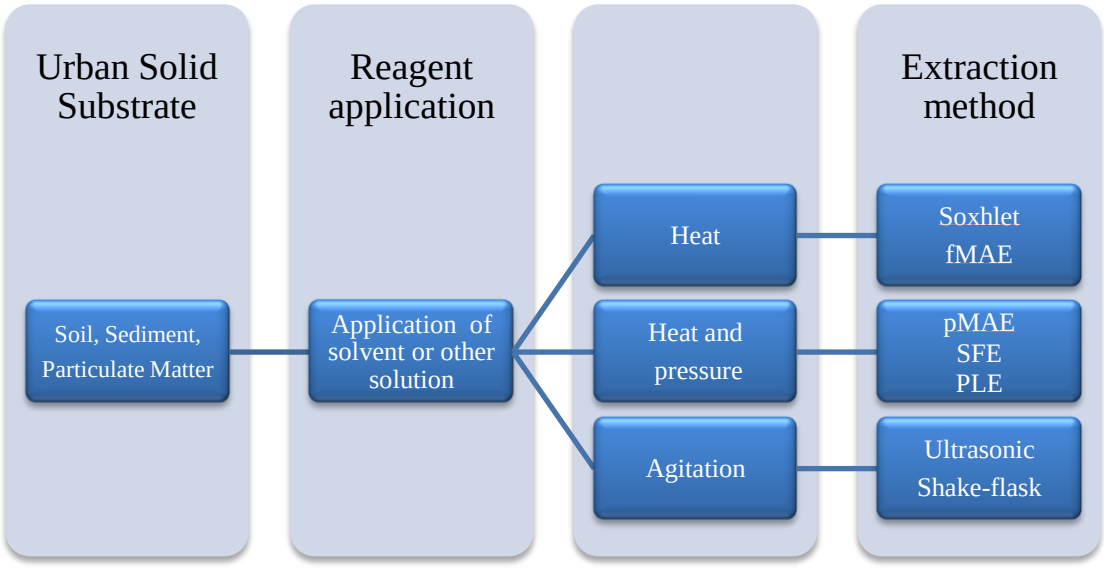


Figure 1-19 – Solid substrate extraction methods for the determination of organic species (fMAE – focused microwave-assisted extraction, pMAE – pressurised microwave-assisted extraction, SFE – supercritical fluid extraction, PLE – pressurised liquid extraction).

Soxhlet extraction is the conventional method used for the extraction of PAHs and other organic species from environmental solids. It is easily applied due to the use of low cost apparatus readily available in laboratories. It can also be used as the benchmark with which to compare other extraction methods[102]. The apparatus used for Soxhlet extraction is shown schematically in Figure 1-20.

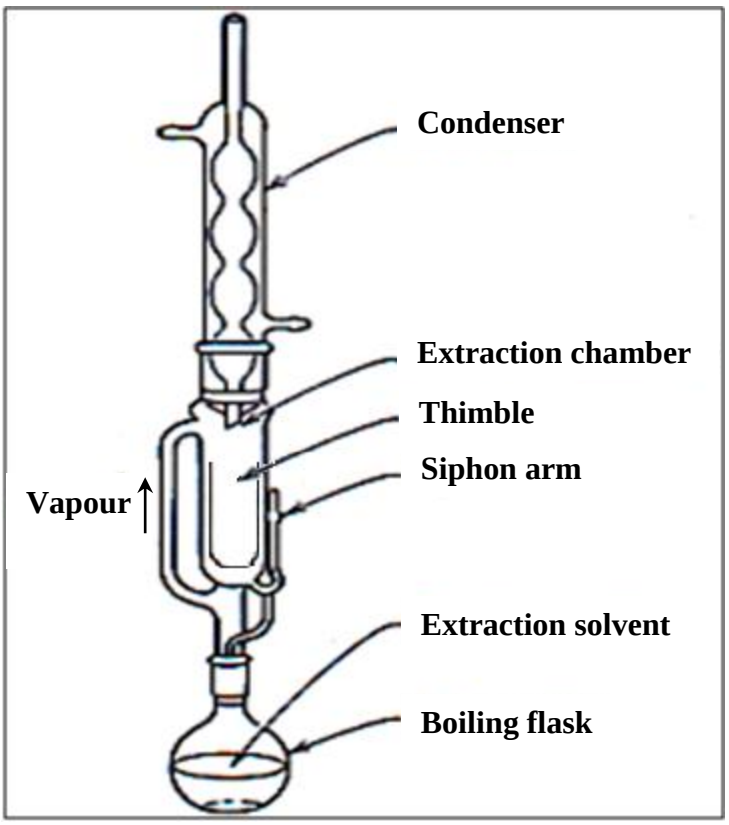


Figure 1-20 - Schematic of a Soxhlet extraction system[56]

Solvent vapour from the boiling flask is condensed into the thimble, which contains the sample. Solvent then continually passes over the sample and is siphoned, via the siphon arm, back into the boiling flask along with analytes that have partitioned into the solvent. The benefit of this method is that fresh solvent is in contact with the sample throughout the extraction. However the process is extremely time consuming and can take up to 24 hours to complete. Even considering the long extraction times, Soxhlet extraction is still commonly used in investigations concentrations of organic analytes in various solids materials including atmospheric particles[103-104], soils[105] and sediment[106]. The requirement for increased sample throughput for routine environmental analysis has, as with PTE analysis, led to increased interest in approaches for accelerating sample preparation for the measurement of organic pollutants[51], such as those mentioned in Figure 1-19.

1.4.2.2 Microwave-assisted extraction

Microwave-assisted extraction (MAE) has increasingly been applied for the extraction of organic species highlighted as a particular pollutant problem, including PAHs, as well as others such as PCBs and pesticides. These have been successfully extracted from sediment[107], soils[108] and atmospheric particulates[109]. Closed-vessel systems have been used predominantly, although open-vessel focused systems have been applied and a focused microwave system has been integrated with Soxhlet extraction with reduced extraction time[110]. MAE has also found application in environmentally friendly procedures where no, or reduced amounts of, organic solvents are used. In the case of PAHs, as well as PCBs and pesticides, water modified with a surfactant medium has been used for extraction[111-115].

1.4.2.3 Ultrasonic-assisted extraction

Ultrasonic-assisted extraction (UAE) has also been applied to PAH in soils[116] and sediments[117] and atmospheric particles[95,118] using various organic solvents, again proving to be faster than conventional methods. Comparison of UAE and MAE methods with Soxhlet extraction showed satisfactory results when extracting PAH from airborne particles[102,119-120]. UAE has also been applied for the extraction of water soluble organics in atmospheric particles[60,121].

1.4.2.4 Green extraction methods

The majority of procedures used for the extraction of PAHs, and other organic analytes, from environmental substrates involve the application of organic solvents. These methods are well investigated and implemented in the literature[95,104,117,122] and most methods discussed previously are of this type. However the problem with these methods is that organic solvent are themselves potential pollutants and therefore the analysis to determine pollutant concentrations could itself be acting as a contamination source. This has led to a number of investigations into the use of alternative methods such as water based extraction, which have the benefit of being more environmentally "friendly" and could also be cheaper[123-124].

Supercritical fluid extraction (SFE) is one available green method which uses a supercritical fluid (SF), such as CO_2, instead of an organic solvent. A SF is a substance at, or above, a critical temperature and pressure, where the densities of the liquid phase and the vapour phases become equal, resulting in the formation of a single supercritical phase that displays properties between those of a gas and a liquid, including low viscosity and high diffusion rates. The solvent strength is particularly increased and subsequently SFs are ideally suited for use in extraction.

CO_2 can be obtained at high purity, is inert and of low toxicity, and so SFE provides a good green alternative to organic solvent extraction. However, the polarity of CO_2 can be too low for the efficient extraction of some organic compounds. Water is an alternative, although the conditions required for the critical temperature and pressure can be difficult to achieve in a safe and controlled manner, and could involve more expensive equipment.

PAHs and PCBs have been extracted from soils[105,125-126], sediments and airborne particles[127] using SFE. SFE has been used for the extraction of PAH from soil[105] and compared with other methods. Although SFE, using CO_2, showed quantitative agreement with Soxhlet extraction, pressurised liquid extraction and sub-critical water extraction, it showed much better selectivity for PAH than other organic species in the soil. SFE has also been shown to give higher extraction efficiencies than Soxhlet and MAE for PAH extraction[122,128]. The main disadvantage of SFE is the relatively higher equipment cost, compared to some extraction methods.

1.4.2.5 Pure and modified water extractions

Water is often applied as an extracting reagent is often applied for the determination of water soluble species in a solid substrate, however there have been investigations into its application for the total extraction of PAHs and other organic species. Pure water extraction is often slow and so high-temperatures, high-pressures, microwave-assistance and ultrasonic-assistance can be applied to improve the method. There are many analytes which would not normally be extracted efficiently using pure water

and so modification by addition of another reagent can be used to improve efficiency.

Subcritical water extraction is one method that has been applied for the extraction of organic contaminants such as PAHs[105,129110] from soil samples. The method is simpler and less expensive than using water in SFE. The method involves the addition of the sample and water to an extraction cell which is subsequently heated. The extraction is based upon the application of high-temperature water, up to 400 ^{o}C[130], while applying sufficient pressure to maintain the liquid state. The benefit is that the solubility of organic compounds, such as benzo(e)pyrene, has been shown to increase with higher temperatures[131]. It should be noted that organic solvents are still occasionally used to modify water for the solubilisation of the least polar compounds[132].

1.4.2.6 Surfactants and micelles

The modification of water using surfactants for the extraction of organic compounds has received recent attention in the literature[114,133-135]. Surfactants are amphiphilic molecules, they have both a hydrophilic head and a hydrophobic tail. The head is a polar group, such as hydroxyl, and the tail is a non-polar hydrocarbon chain, which can be linear, branched and aromatic[136]. Polyoxyethylene 10 lauryl ether (POLE) is an example of a non-ionic surfactant used in extractions[113] (Figure 1-21), although anionic[137] and zwitterionic[138] surfactants have also been investigated.

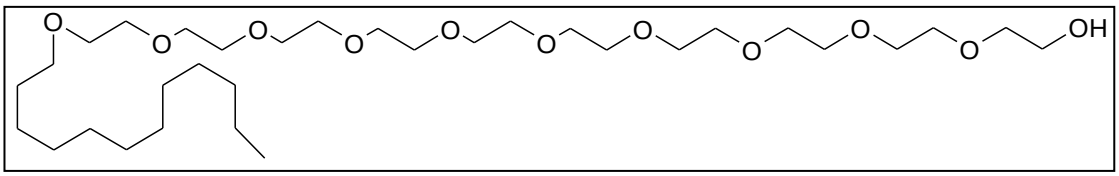


Figure 1-21 - Structure of polyoxyethylene 10 lauryl ether monomer

As a monomer the surfactant molecule may dissolve in water, due to the hydrophilic nature of the head group. The hydrophobic nature of the tail group does not interact

with water and so surfactant monomers align themselves on the surface (Figure 1-22).

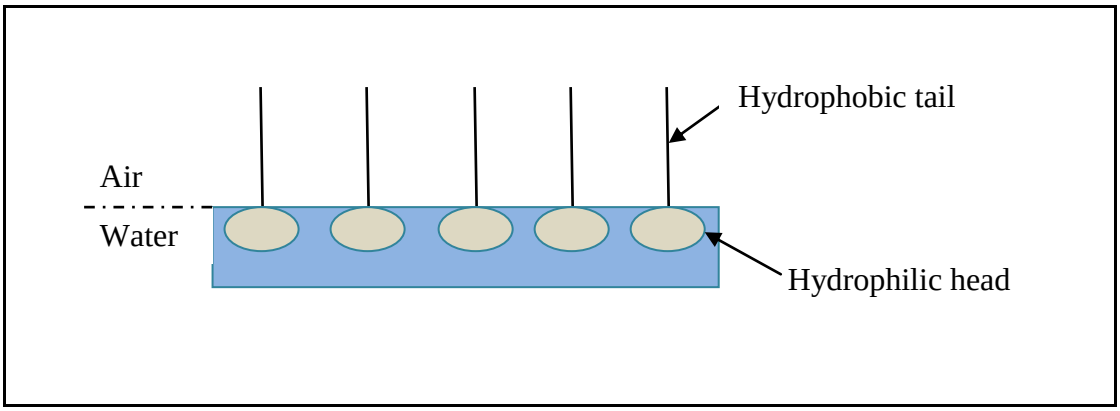


Figure 1-22 - Assembly of surfactant monomers at the air-water interface

When the surfactant concentration becomes such that the number of monomers at the surface interface reach saturation, additional surfactant is incorporated into the bulk solution. This is the critical micelle concentration and above this concentration the hydrophobic groups of the monomers associate in micellization to form organised chemical structures, or micelles (Figure 1-23).

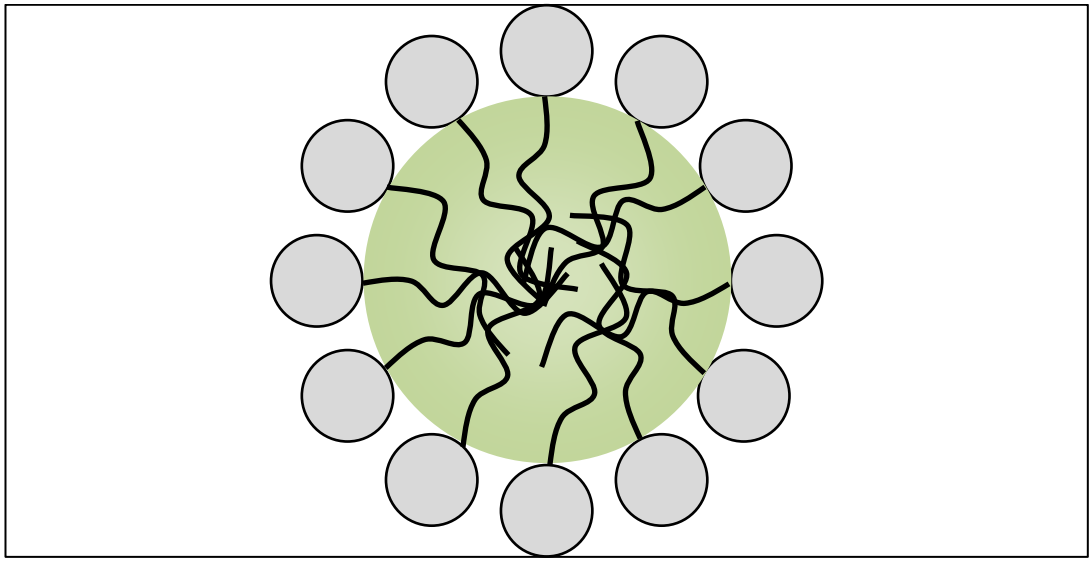


Figure 1-23 - Structure of a micelle in a polar solvent

The hydrophobic tails of the monomers forming the micelle are directed inwards and form a hydrophobic liquid core[139]. The hydrophobic core of the micelle can

accommodate non-polar compounds such as PAHs. This allows sparingly-soluble or non-water-soluble compounds to be solubilised in water and gives rise to two methodologies applied in the literature, cloud-point extraction (CPE) and microwave-assisted micellar extraction (MAME).

CPE is based upon the principle of the cloud-point, which is a temperature range over which a micelle solution forms two isotropic phases[140]. One of these phases is surfactant-rich, while the other is aqueous. Therefore, if compounds were solubilised in the micelles these would also be present in the surfactant phase. This allows for pre-concentration of compounds prior to analysis using an appropriate technique. This type of procedure has been used to extract PAHs in sewage sludge[137], water[133] and soil[141].

MAME employs the use of microwave digestion systems, as previously discussed, but micelle solutions are applied instead of organic solvents. This approach has been applied to a number of substrates using water modified with a variety of surfactants. A selection of these investigations are listed in Table 1-5.

Table 1-5 – Investigation of organic analytes applying MAME

Substrate	**Analyte**	**Surfactant**	**Recoveries/ %**	**Ref.**
Soil (CRM)	PAH	SDS	94.2 – 97.7	[114]
Marine sediment (spiked)	PCB	POLE	35.0 – 99.1	[142]
		Genapol X-080	34.7 – 82.3	
Soil (spiked)	Organo-phosphorus pesticides	POLE	25.9 - 105	[143]
		Genapol X-080	10.8 – 89.6	
Marine sediment (CRM)	PAH	POLE	57 - 102	[144]
Marine sediment (CRM)	PAH	Brij 35	71.8 - 129	[135]

SDS - sodium dodecyl sulfate
Genapol X-080 - oligoethylene glycol monoalkyl ether
Brij 35 – polyoxyethylene 23 lauryl ether

1.4.3 Instrumental techniques

Extracted PAHs, and other organic analytes, are primarily detected and quantified using chromatographic methods and these techniques are used throughout the literature[145,146]. On occasion other instrumental techniques such as nuclear magnetic resonance spectrometry have been applied to samples[101].

A variety of chromatographic techniques have previously been used for the measurement of organic analytes in environmental substrates including; gas chromatography – flame ionisation detector (GC-FID)[105], high pressure liquid chromatography with ultraviolet (HPLC-UV)[109] or fluorescence (HPLC-Fl)[118], and gas chromatography – mass spectrometry (GC-MS)[145]. The benefit of these techniques is that a number of organic species can be separated in a solution according to their affinity for the stationary phase, i.e. a number of PAHs can be determined together. However, the extracted solution may contain a number of species with similar affinities and subsequently these can elute together masking the analytes. The extraction solution therefore usually requires "clean-up" in order to remove any interfering species and allow independent elution of the analytes[147]. Solid-phase extraction is one method of "clean-up" which is applied and involves passing the sample solution over a sorbent so that the analyte is adsorbed to the surface[148].

1.4.3.1 Theory of chromatography[149-152]

The determination of organic components often requires the analysis of mixtures which may contain multiple species. Chromatography is a technique which is often used for analytical separation of mixtures for identification and/or quantification using an appropriate detection method.

The basic principle behind chromatography is the passage of a component, in a mobile phase (MP), over a stationary phase (SP) and has been defined as follows.

"Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary while the other moves in a definite direction."[150]

The SP is usually either a solid or a liquid coated onto an inert solid support. The components in a mixture, or solutes, will have some level of attraction to the stationary phase which can retard their movement through the column. The two types of SP give rise to two main mechanisms of interaction between them and the solute. Adsorption chromatography involves the adsorption of the solute directly onto the surface of a solid SP. The solid is usually unmodified silica, which in its hydrated form has polar silanol groups which can adsorb polar solutes. In partition chromatography the solutes can dissolve into a liquid stationary phase coated onto a solid support. The solid support is usually silica which is modified with alkyl chains, where the polarity of the stationary phase is decreased with increased chain length. A C18 chain is commonly used, this forms a pseudo-organic liquid into which non-polar solutes can dissolve.

There are other mechanisms by which interactions occur. Size exclusion chromatography, uses a porous SP whereby smaller molecules can penetrate the pores and are retained. In contrast larger molecules are unable to enter the pores and elute first. In ion exchange chromatography the SP is usually a resin with bonded ionic groups. Solutes ions of an opposite charge to the stationary phase are attracted and those of similar charge pass through first and elute. However, the two mechanisms mentioned in the previous paragraph are commonly applied for analysis of polar (normal phase chromatography, using the adsorption mechanism) and non-polar (reversed-phase, using the partition mechanism) solutes.

The MP, or solvent, can be either a gas or liquid which carries the solutes through the chromatographic system. Liquid MPs will also have a level of attraction for solutes and subsequently can compete with the stationary phase to effect the distribution of a solute. This is not the case for a gaseous mobile phase which will not compete with the stationary phase and as such is often referred to as the carrier gas.

The medium which holds the stationary phase can also vary and results in different forms of chromatography. It can be sheets of paper (paper chromatography), thin layers of treated silica on an inert plate (thin layer chromatography) or solid / liquid coated on an inert solid support in a column (column chromatography). Column chromatography is used for most modern analytical applications, with both gas and liquid mobile phases, i.e. gas chromatography and liquid chromatography.

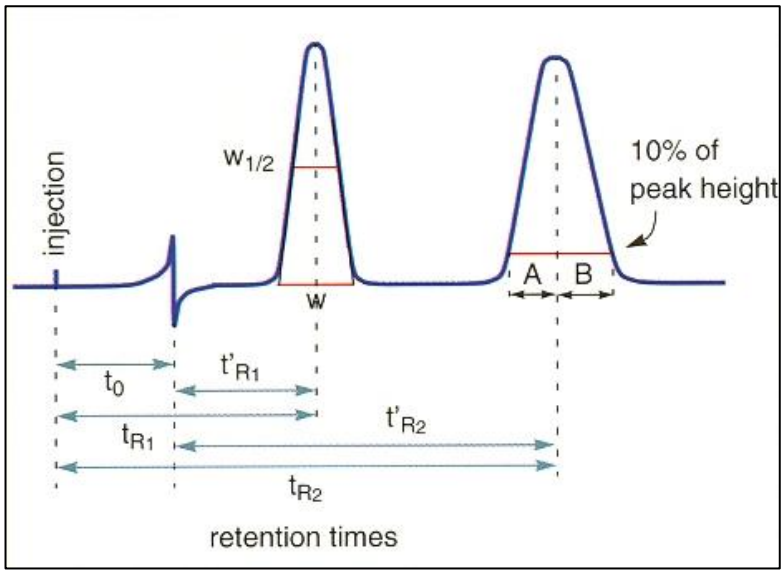
The distribution of a solute between the two phases is unique for each solute and ideally remains at equilibrium throughout migration through the chromatographic system. The distribution ratio of a solute is defined by Equation 1-6;

$$K_A = \frac{[A]_{SP}}{[A]_{MP}}$$

Equation 1-6

where, K_A is the distribution coefficient and, $[A]$ are the analyte concentrations in the stationary, *SP* and mobile phases, *MP*, respectively. The larger the value of *K* the greater the attraction of a solute for the SP. Subsequently the solute is retarded to a greater extent. As each solute will have a unique distribution coefficient their retardation will be for different times and therefore the rate of migration through the system will be different with elution occurring at different times.

The elution from a chromatographic system can be represented as a chromatogram, or elution curve. The concentration of the solute (peak area) is displayed relative to the time taken from injection to elution of a solute band, or retention time (t_R). Due to dispersion of the band, some solute will elute before the main concentration and some after, resulting in a Gaussian shaped peak (Figure 1-24).



t_0	***columns dead time***
t_R	***retention time for component 1, 2...x***
$t`_R$	***net retention time for component 1, 2...x***
$w_{1/2}$	***peak width at ½ the peak height***
w_b	***peak width at base of peak***
A	***front part of peak***
B	***rear part of peak***

Figure 1-24 - Representation of a chromatogram[152]

The t_R of a solute through a system is measured from the time of injection through to elution and subsequent detection. The time the MP takes to pass through the system can be measured using the migration of a non retained component; this is called the dead time (t_0) and is equivalent to the residence time of a solute in the MP. The dead time can then be used to obtain the corrected, or net retention time ($t`_R$), using Equation 1-7.

$$t`_R = t_R - t_0$$

Equation 1-7

Ideally it would be desirable to measure the volume of MP required to elute a solute. However, this cannot be easily measured and a constant flow rate is applied. The time a solute takes to migrate through the system can be measured and used to calculate the volume of eluting MP, the retention volume (Equation 1-8)

$$V_R = t_R F_c$$

Equation 1-8

where t_R is the retention time of a solute and, F_c is the flow rate of the MP.

The broadness of the peak (Figure 1-24) is due to dispersion of the solute band and can be used as a measure of variance (σ^2) in the elution process. In a Gaussian curve 95.5% of a sample (i.e. solute) will lie within $\pm 2\sigma$ of the mean (t_R), which is equal to a peaks base width (w_b). This relies on normal dispersion and subsequently a symmetrical peak. If a substantial amount of a solute is more strongly retained on a SP than the rest of the solute, then elution will occur after the main band and tailing could occur. The symmetry of a peak can be measured using the widths of the front (A) and rear (B) halves of a peak at 10% of the peak height (Figure 1-24). Ideally the ratio of B to A should be 1.

The number of equilibrium steps, as a solute migrates, is considered in classical chromatographic theory to effect the band broadening with more steps improving chromatography efficiency and reducing broadening (σ^2). Time also has an effect, with greater broadening occurring when a solute band has more time to disperse. The number of equilibrium steps ('theoretical plates') can be described using Equation 1-9.

$$N = \left(\frac{t_R}{\sigma}\right)^2 = \left(\frac{t_R}{w_b/4}\right)^2 = 16\left(\frac{t_R}{w_b}\right)^2$$

Equation 1-9

where *N* is the number of theoretical plates. In a column, *N*, can also be described in terms of the column length, *L*, and the height of a theoretical plate, *H*,

$$H = \frac{L}{N} = \frac{\sigma^2}{L}$$

Equation 1-10

Van Deemter *et al.*[153] highlighted that the majority of band broadening, in a column, is due to the elution process. They described, *H* in terms of three parameters that contribute to band broadening, and the velocity of the mobile phase ($\bar{u}$), using the relationship given in Equation 1-11.

$$H = A + \frac{B}{\bar{u}} + C\bar{u}$$

Equation 1-11

Where, term *A* is due to random movement of a solute through the SP, *B* is due to diffusion of a solute in the MP and, *C* represents interaction of a solute with the SP. The *A* term describes two effects which are related to the particle size of the stationary phase packing;

- as the solutes in the MP pass through the SP packing the pathways they take can vary in length,
- as the MP passes through the SP, turbulence occurs which leads to solute dispersion.

This term is independent of the mobile phase and is a function of the stationary phase particle size as described by Equation 1-12.

$$A = 2\lambda dp$$

Equation 1-12

Where, λ is a constant and *dp* is the mean diameter of the SP particles. In order to minimise the A term small uniform particles are used. The *B* term describes the effects of diffusion in random directions. Longitudinal diffusion, parallel to the mobile phase flow, causes band broadening as some solute molecules move ahead of the main band and other lag behind. The longer a solute takes to pass through the column the more diffusion can occur and therefore the *B* term is inversely proportional to the mobile phase velocity. The broadening depends upon the coefficient of diffusion for the solute in the mobile phase. The *B* term can be minimised by using higher flow rates, hence the band has less time to diffuse.

Equation 1-13 shows the relationship for the *B* term.

$$B = 2\gamma D_m$$

Equation 1-13

Where γ is a constant and, D_m is a solutes coefficient of diffusion. The *C* term describes the effects of mass transfer of the solute from the MP to the SP. At the leading edge of a solute band, in the MP, molecules will transfer into the stationary phase. The band will then move along so further solute can transfer into the SP and at this point the original solute will transfer back into the MP at the trailing edge. The time taken for the equilibrium between the two phases to be reached is therefore important and is effected by the partition coefficient. Minimisation of the *C* term can be achieved by reducing the mobile phase flow rate.

1.4.3.1.1 High performance liquid chromatography

In high performance liquid chromatography (HPLC) the MP consists of a single liquid or mixture of liquids, in which the sample solution flows through a column containing particles of the SP. The analytes migrate through the column, partitioning between the two phases, and are eluted to pass through a detector which records the peak(s) in the form of a chromatogram.

The principle components of HPLC are the mobile phase solvents, pump, injector, column and detector (Figure 1-25).

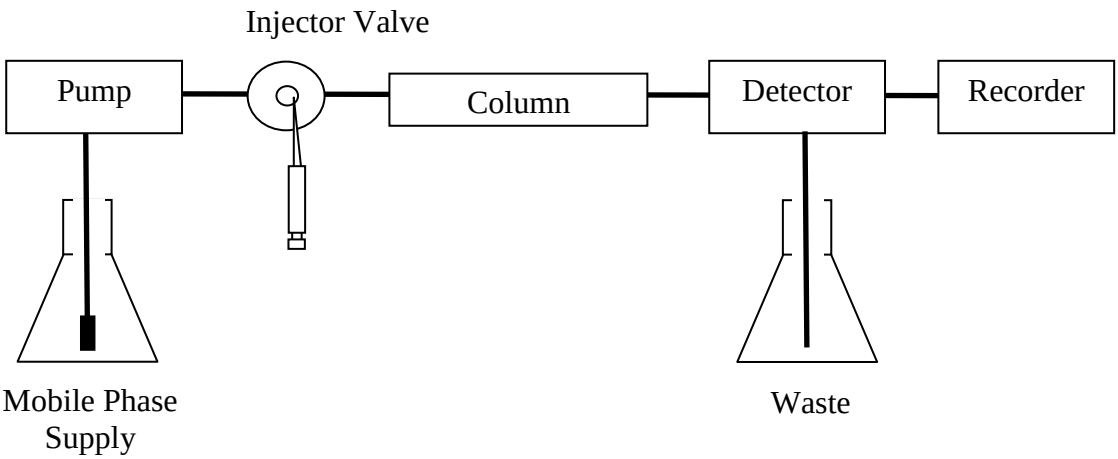


Figure 1-25 - Main components of a HPLC system

The MP is usually a high purity solvent or mixture of solvents which has been filtered and then degassed to remove any dissolved air. Commonly used solvents include hexane, acetonitrile, methanol and water.

In general, the efficiency of a column increases as the particle size of the SP decreases. The packing of small particles into the column results in high back pressures and consequently a pump must be employed to achieve the required flow rates.

A loop injector is most often applied in HPLC as it allows for sample injection while the mobile phase is at the high pressure achieved in the system. Loop injectors usually consist of a six-port valve, which has two position of operation known as the load position and inject position. In the load position the injection port is connected to a sample loop of constant volume and then to waste, and hence the sample can be injected onto the loop at atmospheric pressure. The valve is then moved to the inject position which connects the sample loop to the pump and column. The sample in the loop is forced onto the column by the MP.

Columns used in HPLC are typically 2.1 to 4.6 mm in diameter and 10 to 25 cm in length. They are usually made from steel so as to withstand the high back pressures and glass lined to prevent metal catalysis. The irreversible adsorption of sample and solvent impurities can lead the column to degrade and subsequently a short guard column is placed before the separating column to collect such impurities. The SP support is usually silica or modified silica with a particle diameter of 3 to 10 μm. When the SP is silica then adsorption can occur directly onto the silica surface. This occurs due to polar OH groups being present on the silica surface when hydrated and polar solutes, capable of hydrogen bonding, are subsequently retained. The use of a polar SP with a solvent which is less polar is known as normal phase HPLC. Various groups can be bonded onto the silica surface to produce a bonded SP which can be used to perform partition chromatography. The octadecyl, or C_{18}, group is commonly bonded to silica and used in what is termed reversed phase HPLC with a

more polar MP. Less polar components have a greater affinity for the hydrophobic surface of the SP and are therefore retained while more polar solutes elute first.

The most common detector used in HPLC is the ultraviolet detector, which is based upon the absorption of ultraviolet light (or visible) at a particular wavelength. The components must therefore contain a chromophore which is capable of absorbing, due to electronic transitions for ultraviolet and visible spectrometry, in order to be detected. The absorbance is proportional to the concentration and the Beer-Lambert law is applicable, at least at low concentrations where the absorbance versus concentration curve is linear.

A variable wavelength detector which operates at a single wavelength is often employed in HPLC. This detector uses a deuterium lamp (190 – 400 nm) with a adjustable diffraction grating monochromator, to allow selection of the required wavelength.

Alternatively a diode array detector can be used which allows for the continuous scanning of the full absorbance spectra of the eluent. This is achieved by focusing all of the light from the source onto the sample and then transmitted light is focussed onto a linear array of photodiodes using a holographic diffraction grating. All components in a solution which absorb ultraviolet light will be detected over the full range of wavelengths.

1.4.3.1.2 Solid phase extraction

An investigation of organic species in environmental solid substrates usually involves the analysis of mixtures that may contain numerous different contaminants. In general an investigation will focus on one, or maybe more, types of analyte. The species, that are not of interest, must be removed from a mixture to avoid interference in subsequent analysis. Solid phase extraction (SPE) is a separation method that can be used for the clean-up of extracts from environmental substrates[56,58,148,154-155]. SPE employs a sorbent, often in the form of a cartridge or disc (Figure 1-26), which, via different interactions with analytes and interfering components, can cause their separation.

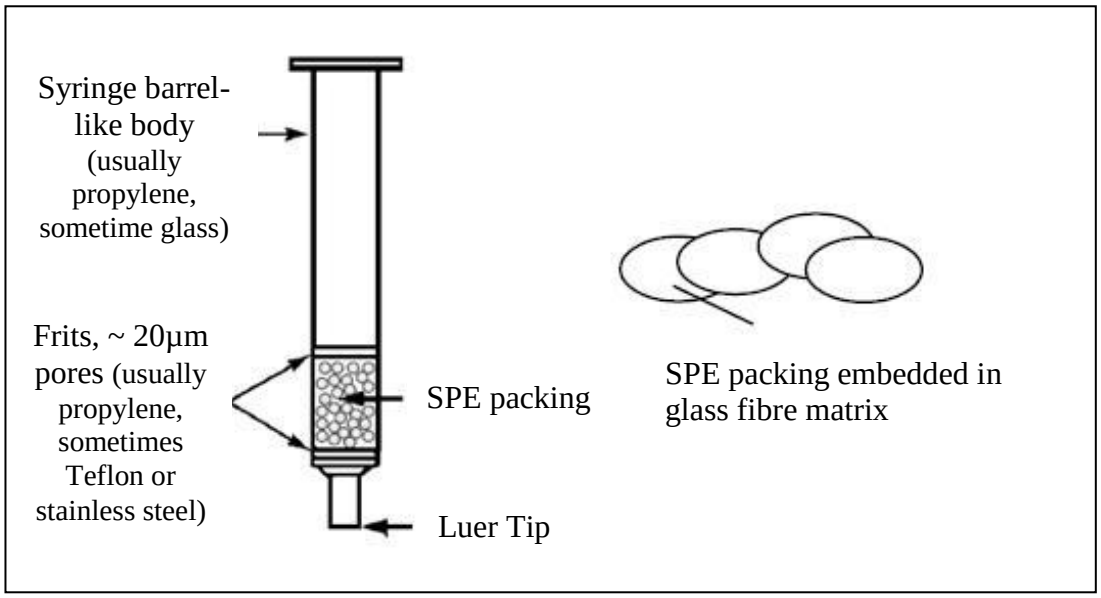


Figure 1-26 - Example of two common types of SPE media, cartridges and discs[155]

A variety of different sorbents are used in SPE to deal with organic analytes of different polarities. Reversed phase SPE involves the use of a non-polar sorbent which will interact with non-polar analytes and can allow separation from polar interfering components. Polar sorbents, which are applied in normal phase SPE, can interact with polar analytes and separate them from non-polar interferants. The application of SPE to samples usually involves four principle steps, which are shown in Figure 1-27.

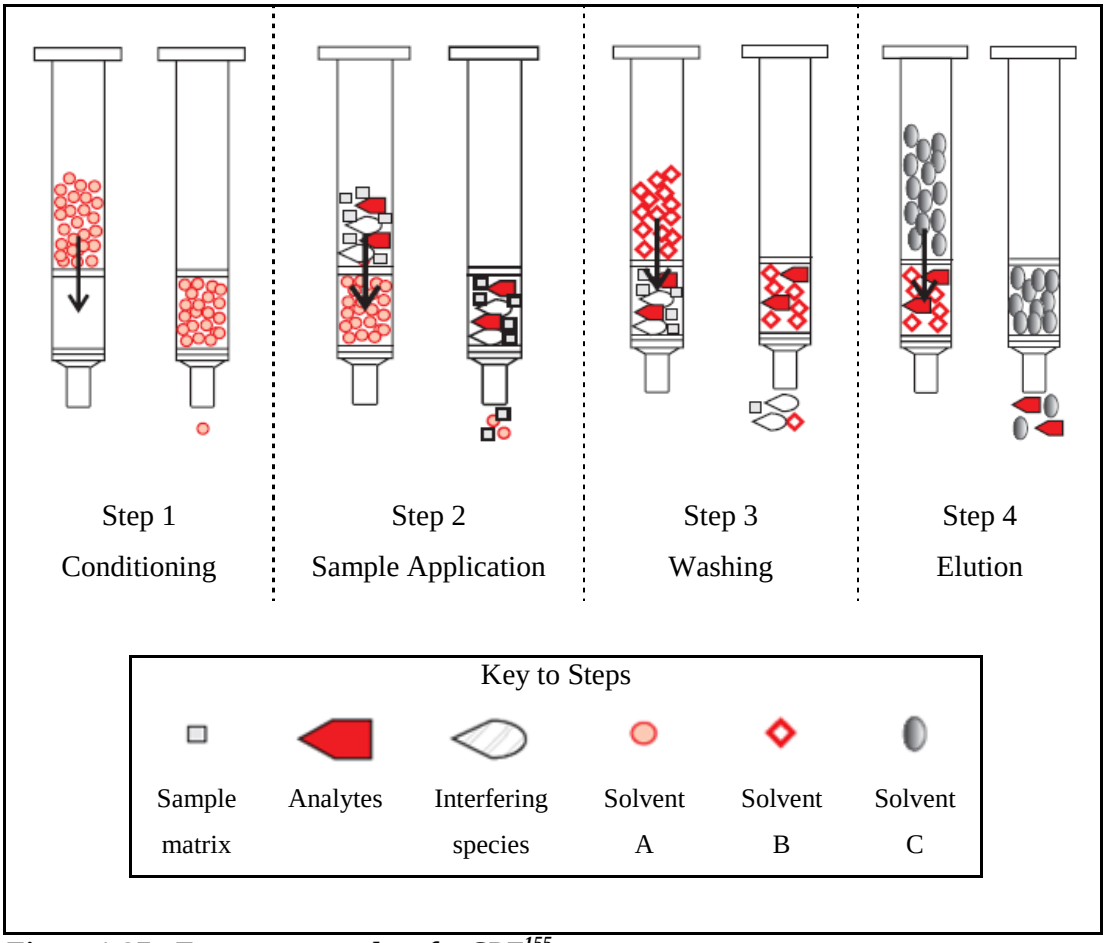


Figure 1-27 - Four step procedure for SPE[155]

The first step, conditioning, involves wetting the sorbent with an appropriate solvent and producing an environment that is suitable for interaction with the analyte. An appropriate aliquot of the sample is then applied in step 2. Analytes are retained on the sorbent. However, interfering components may also stay on the column or be weakly retained on the sorbent. The third step, washing, involves the application of a solvent which will wash out un-retained interferents. This is often the same solution in which the analytes were dissolved. However, if an interferent is weakly retained on the column, a solvent, that can remove the interfering compound but not the analyte is used. The final step is the elution of the analyte using a solvent that removes it from the sorbent. If a sorbent is used that more strongly retains the interferents than the analytes, then the third stage can be omitted and the analytes directly eluted with an appropriate solvent.

1.5 Multi-component analysis of inorganic and organic species in environmental solid substrates

The environment contains both organic and inorganic pollutants, each with their associated health effects. Most solid substrates are complex mixtures and can be contaminated with species of both types. Potentially the combined health effects could be worse than if an individual were exposed to each contaminant individually, i.e. carcinogenic and toxic effects of PAHs and metals, respectively. It is therefore important to consider both inorganic and organic species in environmental solid substrates.

The variety of pollutants that can potentially be found in environmental solids is large and so there is enormous scope for multi-component investigations. For example, there have been a number of multi-component studies that have investigated concentrations of PAH and PTE in atmospheric particles[54,156-160], soils[161-167], and sediments[96,168]. The analysis of both PAH and PTE in soil commonly involves acid digestion to leach the metals and solvent extraction to obtain the organics[161,163,165-166]. The digestion/extraction is performed on different samples or different portions of a sample (see Figure 1.28 approach A) and separate extracts are analysed using appropriate atomic spectrometry or chromatography techniques. In general, splitting a sample is not a problem for soil or sediment analyses where, in most cases, it should be possible to collect a substantial amount of material (the exception could be in a situation where sampling is difficult or the material under investigation is valuable).

The investigations of airborne particles have applied different approaches, usually involving the splitting of a sample, to determine concentrations of multiple components. The sampling of airborne particulates commonly uses an air filter, which draws air into the unit and subsequently particles become deposited onto a quartz fibre filter. The filter to be analysed may then be sub-divided into two portions for the separate analysis of PTE and PAH[158-159]. Harrison *et al.*[156] had access to additional equipment and subsequently were able to analyse PAH and PTE

on separately sampled filters. However, their investigation also involved the determination of ions and therefore one of the filters was still split to perform this analysis. Researchers have also specifically studied water-soluble inorganic and organic ionic species, although this commonly involves the extraction of the samples with water and so a single solution can be used to determine both anions and cations[60,121].

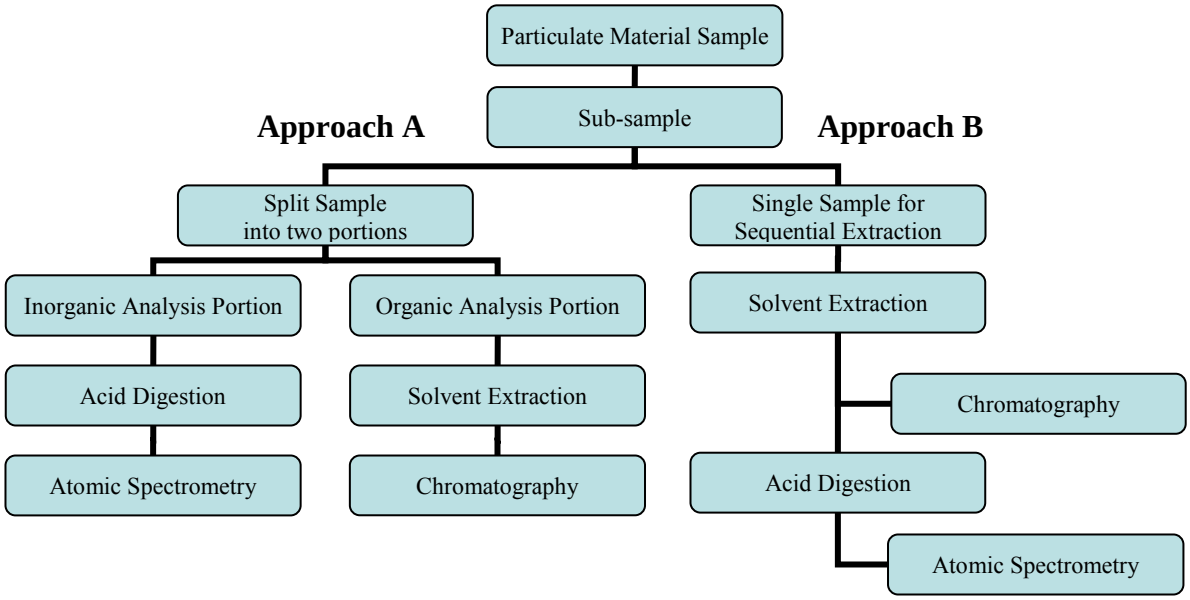


Figure 1-28 - General procedures for the sample division (A) and sequential extraction (B) approaches to the determination of multi-component species in an environmental substrate

An alternative to the splitting of air filters, is the use of a multiple channel air sampler to collect different species. Such a device was applied by Hopke *et al.*[157] to collect airborne particles for measurement of PTE, anions, cations, PAH and PM_{mass}. The research of Smith *et al.*[160] involved the subdivision of air filters sampled in Lahore, Pakistan. The air filters were sub-divided into three, with one third being kept for PTE analysis by atomic spectrometry in Lahore, while the other thirds were sent for further analysis in Birmingham (UK) and Aveiro (Portugal). In Birmingham and Aveiro, the determination of PTE, organic and elemental carbon, water-soluble metals and PAH, meant that these sub-sampled thirds were halved to perform analysis.

Whilst subdivision of the sample is generally feasible for materials such as soils, it presents difficulties where sample availability is limited. For example in the analysis of airborne urban particles of aerodynamic diameter <10 μm (the PM_{10} fraction), filters deployed for a period of a week typically collect only a few mg of material[169]. Small samples are also obtained in the study of environmental solids such as aquatic colloids. In such cases it would be desirable to maximise the amount of information obtained by measuring several types of analytes in the same sample. It is also possible that, with small samples, by further sub-dividing the material, the amount of the analytes may become too low for detection.

Determination of multiple species in the same sample can be achieved by means of sequential extraction followed by suitable instrumental analysis (see Figure 1-28 approach B). However, extraction procedures must be designed with care to ensure that each component can be isolated quantitatively without affecting the extraction of others. Pineiro-Iglesias *et al.*[54], have used a sequential extraction procedure where PAHs were extracted using a microwave-assisted method with hexane/acetone (1:1) and the solid residue was acid digested for the determination of metals. They found that there were no significant losses of metals during the PAH extractions stage. Although the PAH extraction method had previously successfully been applied, the complete procedure was not tested for determination of both analytes together. Since the work of Pineiro-Iglesias *et al.* was the only example of a multi-stage extraction of both PAH and PTE found during review of the literature, and even they did not evaluate it fully, there is therefore a need for further studies in this area. The development of numerous environmentally friendly PAH extraction methods, using aqueous-based reagents, means that the incompatibility of solvent extraction and acid digestion is no longer a major limitation in the development of these methods. Environmentally friendly extraction methods were discussed in further detail in section 1.4.2.4.

1.6 Aim

The primary aim of this research was to develop methods for the multi-component analysis of single samples of environmental solids. Specifically, the goal was to develop sequential extraction procedures for the determination of inorganic and organic priority pollutants, using PAH and PTE as test analytes. It was important to consider the extraction time and efficiency when investigating these methods and also the compatibility of the different stages in the sequential extraction.

The objectives could be split broadly into four main areas of research;

1. The development and optimization of a method for the analysis of PAH in urban solid substrates, such as soil and RDS. The extraction reagent was based on a micellar medium (MAME) as this would allow further digestion of the substrate using an acid without any potential complications.
2. The determination of PTE in soils and RDS, after prior extraction of PAH, was to be evaluated. The recovery of PTE using *aqua regia* digestion was to be compared to MAME followed by *aqua regia* digestion.
3. The application of the BCR sequential extraction to soils and RDS in sequence with MAME. The effect of MAME on the recovery of PTE in each of the BCR steps was to be investigated.
4. The investigation of PAH and PTE in RDS from Glasgow using the developed sequential procedure.

2 Experimental

2.1 Environmental solid samples

During method development, it is necessary to use samples whose availability is unrestricted and, where possible, which contain known concentrations of analytes. The majority of the development work reported here was performed using secondary urban soil reference samples and certified reference materials. Urban dust sediments were also sampled for analysis using the developed method.

2.2 Environmental solids used in method development

Two CRMs were obtained with their associated certificate of analysis. A CRM, certified for the concentrations of *aqua regia* soluble PTE present (BCR 143R, trace elements in a sewage sludge amended soil), and another, certified for PTE extractable using the BCR sequential extraction procedure (BCR 601, extractable trace metals in lake sediment (sequential extraction)). The certified target values for BCR 143R and BCR 601 are given in sections 4.3.1 and 5.3.1, respectively.

Soil samples had also been obtained from four European cities (Glasgow (GLA), Sevilla (SEV), Torino (TOR) and Ljubljana (LJB)) during the EU URBSOIL project (Contract EVK4-CT-2001-00053). The soil samples were used in that work as secondary urban soil reference materials (URMs)[170] since their *aqua regia* soluble PTE contents, hereafter referred to as 'target values', were known. Target values for sequential extraction of the GLA URM are also known. The *aqua regia* soluble PTE target values for GLA, SEV, TOR and LJB URMs are given in section 4.3.1. The BCR sequential extraction content target values for GLA-URM are given in section 5.3.1. These URM target values are not certified and therefore time in storage or different sample bottles may lead to slight differences in results. The CRMs, URMs and dust samples were used to evaluate analytical methods for the determination of, some, or all, of the PTE of interest (Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn).

2.3 Sampling

A map, along with easting and northing Cartesian coordinates, obtained from a previous investigation of soils at roadsides and parks[171], were used to locate road deposited sediment sampling sites. Details of the sampling location were recorded on a sampling sheet. A hand-held vacuum cleaner was used to collect urban sediment around the sampling location. At roadside sites a 5 m stretch of gutter was vacuumed to obtain samples. At park sites a path, or equivalent, was located near to the original sampling site and a square meter area was vacuumed to obtain samples. Sample bags, made from fabric, were produced which could be slotted into the hand-held cleaner and allow air flow for sample to be vacuumed and subsequently collected in the bags. The fabric was digested prior to use and analysed to determine potential contaminants. The results showed that none of the analytes of interest could be detected and subsequently would not affect results. Equipment that came into contact with samples was cleaned, with deionised water, and dried between sampling locations. The vacuum sample bags were placed into labelled plastic bags and transported back to the laboratory.

2.4 Sample Pre-treatment

Samples returned to the laboratory were sieved to 2 mm and the < 2 mm faction was stored in amber glass bottles for analysis. Samples were coned and quartered to obtain a representative test portion for analysis, and then weighed accurately. The CRMs were shaken to thoroughly mix the material before a test potion was taken and weighed.

The moisture content and soil organic matter (SOM) content, estimated by loss on ignition (LOI), was calculated after drying and ashing approximately 1 g of soil or road sediment. The sub-samples were accurately weighed into ceramic crucibles and then placed overnight into an oven at 105 °C. The crucibles were then left to cool, and weighed to determine the mass of dried sample. The moisture content could then be calculated using Equation 2-1 and subsequently used to convert reported results to dry weights.

$$\text{Moisture content}\,(\%) = \frac{\text{sample weight} - \text{oven dried weight}}{\text{sample weight}} \times 100$$

Equation 2-1

The residues from the moisture content determinations were then placed in a muffle furnace and ashed at 550 °C. They were then re-weighed, after cooling, and LOI determined using Equation 2-2, giving an indication of the amount of organic matter in the sample.

$$\text{LOI}\,(\%) = \frac{\text{oven dried weight} - \text{ashed weight}}{\text{oven dried weight}} \times 100$$

Equation 2-2

2.5 Extraction Procedures

All glassware and storage containers were soaked overnight in 5% (v/v) HNO_3. The HNO_3 used was of general purpose reagent grade (Merck, Poole, UK). After soaking, glassware and storage containers were washed thoroughly with distilled water. All samples and standard solutions were stored in either polyethylene bottles (for PTE analysis) or glass bottles (for PAH analysis) at 4 ^{o}C as appropriate.

2.5.1 Microwave-assisted micellar extraction

Microwave extraction (and digestion) of samples was performed using either a MDS-2000 or MARS Xpress microwave digestion system (CEM Corporation, Bucks, UK). The MDS-2000 can hold up to twelve Advanced Composite Vessels (ACV) in the cavity carousel and the microwave power, 0-630 W, was adjusted to accommodate different numbers of vessels. The system is controlled via electronic feedback from a pressure sensor connected to one of the vessels in the cavity carousel. Each ACV is assembled with a membrane, which is designed to rupture and vent if a predetermined pressure is exceeded. The MARS Xpress can hold up to forty PFA vessels and can produce 0-1600 W of microwave power which is adjusted via the instrument software. Two infrared sensors which sequentially monitor the

temperature of each vessel are used to control the system. A Teflon pressure relief device is present in each vessel and is designed to vent if a critical pressure is exceeded.

POLE, of general purpose regent grade, was supplied by Sigma-Aldrich (Gillingham, UK) was used for extraction of PAHs.

A method optimised in the work of Pino *et al.* for the extraction of PAHs was adapted[113]. A sub-sample of substrate (approximately 1.0 g) was accurately weighed into a microwave vessel. A 0.02 M solution of POLE (12.5 mL) was added and the vessel transferred to the microwave for the extraction (see Table 2-1). 380 W of the microwave systems power was applied regardless of the number of vessels in the carousel.

Table 2-1 – MDS-2000/ MARS Xpress microwave extraction program conditions for the extraction of PAH from soils using a micelle medium[113]

	MDS - 2000	MARS XPRESS
	STAGE 1	STAGE 1
Power (%)	60	60
Pressure (PSI)	29	/
Temperature (ºC)	/	120
Ramp Time (minutes)	30	10
Hold Time (minutes)	5	5

After allowing the vessels to cool, the supernatant extracts were filtered into a glass vial using a polycarbonate 0.4 μm cyclopore membrane filter (Whatman, Maidstone, UK) and stored for analysis.

2.5.2 Microwave-assisted digestion

The MDS-2000 microwave digestion system (see 2.5.1) was used to perform pseudo-total digestion. *Aqua regia*, used for digestion, was prepared fresh before use, using

a 3:1 ratio of HCl : HNO_3 (v/v). Hydrochloric (HCl) and nitric acid (HNO_3) reagents used in this research were of analytical reagent grade (Sigma-Aldrich, Gillingham, UK).

Approximately 1.0 g of sub-sample was accurately weighed into microwave vessels. *Aqua regia* (20 mL) was added and the vessels were loosely covered and left overnight (only if a single extraction for PTEs was being applied), allowing for vigorous reaction to subside, before being placed into the microwave cavity. The vessels containing the soil samples were digested using the program shown in Table 2-2. For the MDS-2000, 100 % power is used for 12 ACVs and is reduced by 5 % for each removed vessel. For the MARS Xpress, 1200 W is used for 6+ vessel, 600 W for 3-5 vessels and 300 W for 1-2 vessels.

***Table 2-2 – MDS-2000/ MARS Xpress microwave digestion program conditions for the extraction of PTE from environmental solids using* aqua regia**

	MDS-2000		MARS XPRESS
	STAGE 1	STAGE 2	STAGE 1
Power (%)	*	*	*
Pressure (PSI)	60	120	/
Temperature (ºC)	/	/	160
Ramp Time (minutes)	20	30	10
Hold Time (minutes)	5	20	20

* ***Power is dependent on the number of vessels placed into the microwave cavity***

After allowing the ACVs to cool and the internal pressure to reduce, the microwave digests were then filtered (Fisher brand QT 280) and washed several times with distilled water into 100 mL volumetric flasks and made up to the mark with distilled water. Three sub-samples of each soil were digested simultaneously, together with a procedural blank. The procedural blank was the digestion reagent subjected to the same microwave digestion program as the samples.

2.5.3 BCR sequential extraction

The procedure involves 4 steps, with sequential application of four solutions to the sample. A G.F.L. 3040 mechanical end over end shaker (G.F.L, Burgwedel, Germany) was used to perform extractions at a speed of 30 ± 10 rpm with the appropriate extractant solution. The delay between extract addition and shaking was minimal for steps 1 to 3. The extracts were separated from the sample residue using a ACL 4237 centrifuge (CAMLAB Ltd., Cambridge, UK), at 3000 g for 20 minutes.

2.5.3.1 Preparation of extraction solutions

Solution A (acetic acid; 0.11 mol L^{-1})

A 0.43 mol L^{-1} acetic acid solution was prepared by diluting 25 mL of glacial acetic acid, puriss grade (Sigma-Aldrich, Gillingham, UK), to 1 L with distilled water. This solution was then diluted by taking 250 mL and making up to 1 L to obtain the final solution.

Solution B (hydroxylammonium hydrochloride; 0.5 mol L^{-1})

34.75 g of hydroxylammonium hydrochloride, analytical reagent grade (Fisher Scientific, Loughborough, UK), was dissolved in 400 mL of distilled water. This solution was transferred to a 1 L volumetric flask and a 25 mL aliquot of 2 mol L^{-1} nitric acid was added. The flask was then made up to the mark with distilled water. The solution was always prepared on the same day that the extraction was performed.

Solution C (hydrogen peroxide; 8.8 mol L^{-1})

A 30% hydrogen peroxide solution, puriss grade (Sigma-Aldrich, Gillingham, UK), was used as supplied.

Solution D (ammonium acetate; 1.0 mol L^{-1})

77.08 g of ammonium acetate, analytical reagent grade (Fisher Scientific, Loughborough, UK), was dissolved in 900 mL of distilled water. The pH of the

solution was adjusted to 2.0 ± 0.1 with nitric acid and made up to 1 L with distilled water.

2.5.3.2 BCR sequential extraction procedure

Step 1

Approximately 1.0 g of sub-sample was accurately weighed into a 100 mL centrifuge tube with 40 mL of solution A and placed on the shaker for 16 h. The sample was then centrifuged to separate the supernatant liquid from the solid residue. The liquid was decanted into a polyethylene bottle and refrigerated at 4 °C before analysis. The residue was washed by adding 20 mL of distilled water and shaken for 15 minutes. After centrifuging the wash supernatant was decanted and discarded.

Step 2

40 mL of solution B (freshly prepared) was added to the washed residue from step 1 in the same centrifuge tube. The sample was then shaken, centrifuged and stored as in step 1.

Step 3

10 mL of solution C was added, slowly in small aliquots to avoid vigorous reaction, to the washed residue from step 2. The centrifuge tube was covered loosely with its lid and left to digest for 1 h with occasional manual shaking. The digestion was continued for a further 1 h in a water bath at 85 ± 2 °C, before removal of lids and reduction of volume to less than 3 mL. Another 10 mL of solution C was carefully added and the covered samples heated for a further 1 h at 85 ± 2 °C. After removal of the lids the volume was reduced to less than 1 mL, with care not to take to complete dryness. The resulting solution was then allowed to cool before adding 50 mL of solution D. The centrifuge tube was then shaken and centrifuged, the solution decanted and stored, and the residue washed as in step 1.

Step 4

20 mL of *aqua regia* is used to wash the residue from step 3 into an ACV and microwave-assisted digestion was performed using the procedure and conditions in section 2.5.2.

2.6 Measurement of potentially toxic elements in environmental substrates

2.6.1 Flame atomic absorption spectrometer

The concentrations of PTE were measured in extracted solutions using an Perkin Elemer AAnalyst 200 spectrometer (Perkin Elmer Instruments, Beaconsfield, Bucks, UK). Each set of sample solutions, and associated procedural blank, were analysed using an integration time of 3 seconds. The absorbance values for three repeat measurements were obtained. A capillary tube was used to provide continuous nebulisation at an average of 6 mL min^{-1}. Analysis was performed using air-acetylene and optimum conditions for the fuel flow were used to give maximum sensitivity. Each PTE of interest was analysed separately using an appropriate HCL, the currents and absorption line wavelengths applied are given in Table 2-3.

Table 2-3 – FAAS burner and HCL conditions for the PTEs of interest

PTE	Cu	Fe	Mn	Pb	Zn
HCL Current/ mA	5	15	12	10	5
HCL Wavelength/ nm	324.7	248.3	279.4	283.3	213.8

2.6.2 Inductively coupled plasma optical emission spectrometer

The Thermo Scientific iCAP 6300 Duo ICP-OES spectrometer (Thermo Fisher Corporation, Cambridge, UK) was used to obtain ICP-OES measurements. An in-built peristaltic pump was used to deliver a constant flow of sample into the system from a CETAC ASX-520 autosampler (CETAC Technologies, Nebraska, USA). The sample flows through a concentric glass nebuliser into a cyclonic spray chamber

(Figure 2-1), where larger droplets are removed to drain and fine droplets flow to the torch.

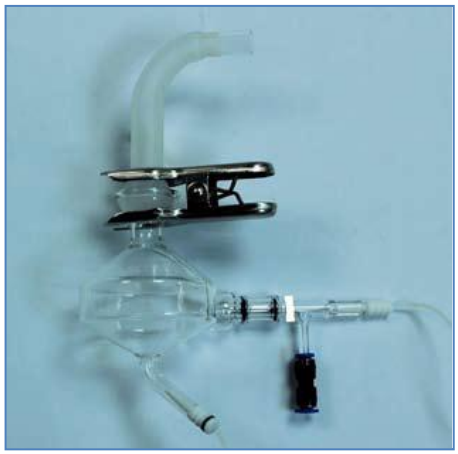


Figure 2-1: Cyclonic spray chamber from a iCAP 6300 Duo ICP-OES[172]

A demountable quartz plasma torch, with a 2 mm centre tube, was used and is fitted into a mount which incorporates the torch gas connections (Figure 2-2). These connections are for the auxiliary/ coolant gas, with respective flows of 0.5 L min^{-1} and 12 L min^{-1}. A further gas flow connects to the nebuliser, with a pressure of 0.4 MPa[172].

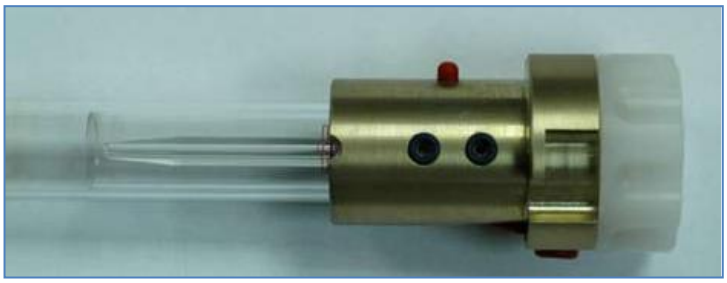


Figure 2-2 – Plasma torch from a iCAP 6300 Duo ICP-OES[172]

A solid state radio frequency generator, with a nominal frequency of 27 MHz, allows plasma coupling with power regulation from 750 – 1350 W.

The optical system of the spectrometer is shown schematically in Figure 2-3. The iCAP 6300 is a duo system and light collected either axially or radially from the plasma is focused onto the polychromator and collimator. The parallel beam from

the collimator is dispersed with a 52.91 grooves mm^{-1} grating with blaze angle of 63.5°. The beam is then cross dispersed through a 9.5° fused silica prism. Finally the beam is refocused by a final "camera" mirror onto the detector. The dispersion through the grating and prism causes a set of shorter spectra, side by side, to fall onto the detector[173].

A single charge injection device (CID) detects radiation across the UV and visible regions with a complete range from 166 – 847 nm. The CID has a sub array of 540 x 540 detector elements giving a total of 291 600 individually addressable photosensitive areas or "pixels". The entire spectrometer and optics are purged with either argon or nitrogen. The detector is housed in a self contained unit and a thermoelectric device is used to maintain a constant temperature of -45°C.

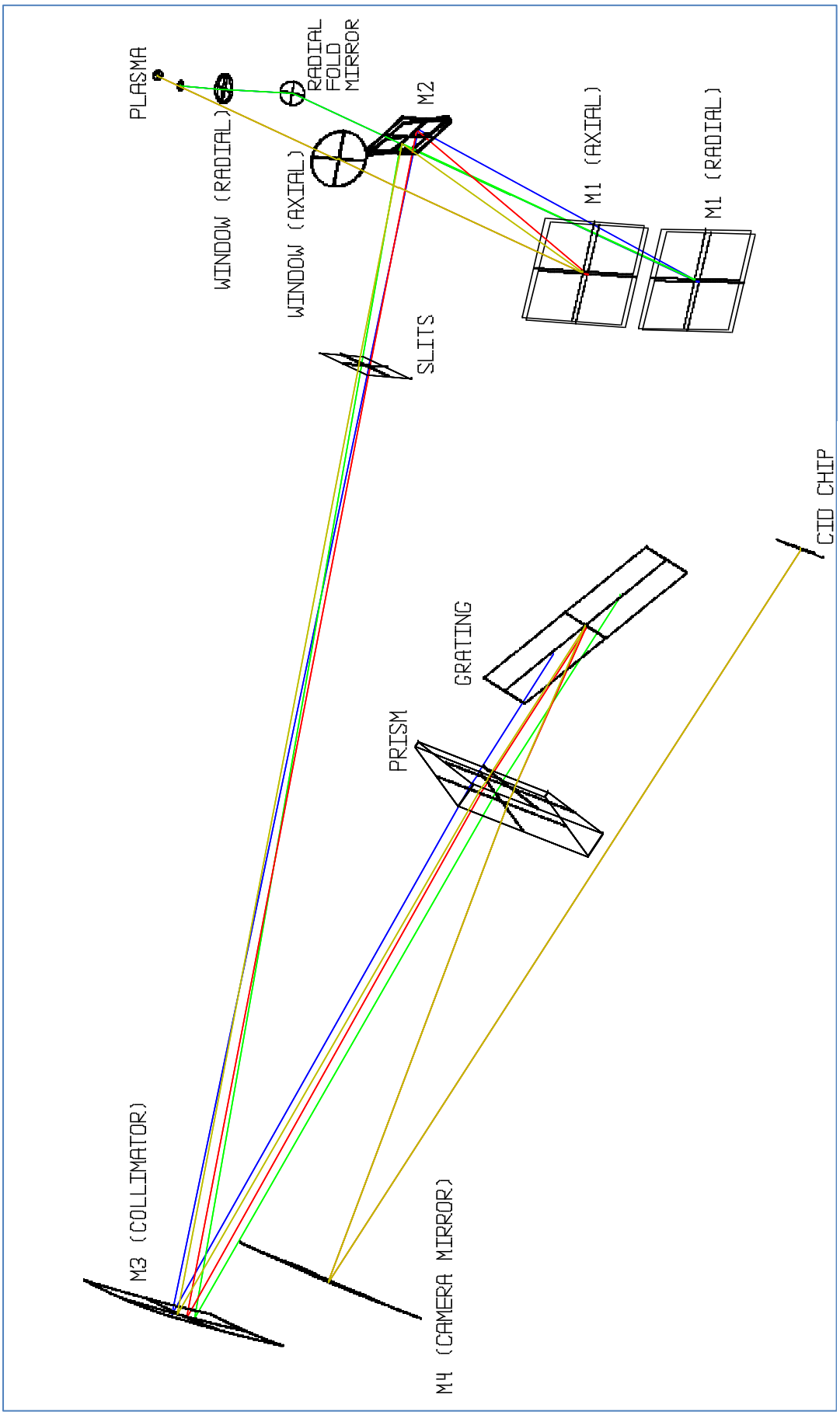


Figure 2-3 - Schematic diagram of the iCAP 6300 Duo ICP-OES optical configuration[168]

The PTE of interest were analysed simultaneously using appropriate wavelengths, the conditions are given in Table 2-4.

Table 2-4 - Instrumental characteristics and settings for ICP OES

Instrument	Thermo Scientific iCAP 6300 Duo	
Rf power	1350 W	
Frequency of rf generator	27 MHz	
Coolant gas flow rate	12 L min^{-1}	
Auxiliary gas flow rate	0.5 L min^{-1}	
Nebuliser flow rate	0.2 L min^{-1}	
Analysis pump rate	75 rpm	
Flush pump rate	50 rpm	
Automatic sampler	CETAC ASX-520	
Nebulizer	Cross-flow with cyclonic spray chamber	
Polycrhomator	Echelle grating, cross-dispersed,	
wavelength range	166 – 847 nm	
Detector	Charge injection device	
Measurement mode	Continuous nebulisation	
Wavelengths (nm)		
Aluminium	308.2	309.2
Barium	230.4	233.5
Cadmium	226.5	361.0
Chromium	267.7	284.3
Copper	219.9	224.7
Iron	238.2	240.4
Manganese	257.6	259.3
Nickel	216.5	221.6
Lead	182.2	216.9
Zinc	202.5	206.2

2.6.3 Calibration

Spectrosol stock solutions (1000 mg L^{-1}) of Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn (Merck, Poole, UK) were used to prepare PTE calibration solutions by dilution. A certified micropipette (Jencon (Scientific) Ltd, Leighton Buzzard, UK) was used to accurately measure aliquots of stock solutions to prepare required concentrations of reagent matched standard solutions. FAAS calibration was performed using single element calibration solutions; ICPOES with multi element calibration solutions.

2.7 Measurement of polycyclic aromatic hydrocarbons in environmental substrates

PAH analysis was performed using a Liquid Chromatograph 5000 system (Varian Limited, Yarnton, Oxford, UK) gradient pump HPLC and measured with a VDM-2 Variable Wavelength UV Detector (Dionex (UK) Limited, Camberley, Surrey, UK). UV spectra of analytes were obtained using a PE250 Liquid Chromatography Binary Pump system with an LC 235 Diode Array Detector (Perkin Elmer Instruments, Beaconsfield, Bucks, UK). Each solution was injected into a 10 µL injection loop and separated using a C18 column, initially using the conditions in Table 2-5.

Table 2-5 - HPLC instrumental conditions based upon previous work[113]

Mobile Phase	Acetonitrile	Distilled Water
Gradient	Composition	Time Period
	55 → 100 %	30 minutes
	100 %	10 minutes
Flow Rate	1 mL minute^{-1}	
Detector Wavelength	254 nm	

2.7.1 Calibration

A calibration standard, containing 2000 µg mL^{-1}, in dichloromethane, of the 16 EPA priority pollutant PAHs (acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[*b*]fluoranthene, benzo[*ghi*]perylene, benzo[*a*]pyrene, 2-bromonaphthalene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene and pyrene), was obtained from Sigma-Aldrich (Gillingham, UK) and diluted to prepare a working stock solution in acetonitrile. The working stock solution was then used to prepare appropriate calibration solutions. A certified micropipette (Jencon (Scientific) Ltd, Leighton Buzzard, UK) was used to accurately measure aliquots of stock solutions to prepare concentrations of reagent matched standard solutions. Acetonitrile (ACN) and dichloromethane (DCM) solvents used were of HPLC and puriss grade, respectively (Sigma-Aldrich, Gillingham, UK).

2.8 Data Handling

2.8.1 Detection limits

Detection limits (D_L), the minimum analyte signal which can be distinguished from the background within a specified statistical uncertainty, were determined for each of the analytes. The blank or low concentration standard solutions were analysed ten times and instrumental detection limits were defined using the relationship in Equation 2-3.

$$D_L inst. = \frac{(3 \times s)}{\text{gradient of the calibration slope}}$$

Equation 2-3

Where, *s*, is the standard deviation of the 10 replicate analyses and is defined according to Equation 2-4.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

Equation 2-4

Where, x_i is the individual value, *n* is the number of replicate measurements and, $\bar{x}$ is the mean defined as in Equation 2-5.

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Equation 2-5

The instrumental detection limits obtained were used to calculate procedural detection limits (D_L pro.), minimum analyte concentration that can be determined in

the environmental substrate allowing for the method of sample preparation. D_L pro. was calculated using Equation 2-6.

$$D_L\ pro. = \frac{DL \times \text{volume} \times \text{dilution factor}}{\text{mass of sample}}$$

Equation 2-6

2.8.2 Precision

Precision can be expressed as a relative standard deviation (RSD) calculated, using Equation 2-7, as a percentage for a number of replicate samples.

$$RSD = \frac{s}{\bar{x}} \times 100\ \%$$

Equation 2-7

The percentage accuracy of an analytical method can be determined by comparing the mean measured analyte concentration ($\bar{x}$) with the certified or indicative analyte concentration (μ) using Equation 2-8.

$$\text{Accuracy} = \frac{\bar{x} - \mu}{\mu} \times 100\ \%$$

Equation 2-8

2.8.3 Statistics

2.8.3.1 T-test

The t-test is used to determine if the results of two compared data sets differ significantly. It was used in this work to compare results obtained from environmental substrates extracted using different procedures. The differences are statistically tested using a null hypothesis that there are no differences between the means of the two data sets. The test is performed by first determining the variance of

each data set using an F-test and then using the appropriate t-test. The F-statistic is defined according to Equation 2-9.

$$F_{calc} = \frac{s_1^2}{s_2^2}, \qquad \text{where } s_1^2 > s_2^2$$

Equation 2-9

The result is tested against the critical value ($F_{a/2,v1,v2}$) at the degrees of freedom for both data sets and the required confidence level. If $F_{calc} < F_{a/2,v1,v2}$ the null hypothesis is accepted and variance is due to random error. If the F-test passes the t-statistic can be calculated using Equation 2-10.

$$|t_{calc}| = \frac{|\bar{x}_1 - \bar{x}_2|}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

Equation 2-10

Where *s* is the pooled sample variance defined using Equation 2-11.

$$s = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{(n_1 + n_2 - 2)}}$$

Equation 2-11

where s_1 and s_2 are the standard deviations, and n_1 and n_2 are the number of replicates, for data set 1 and 2, respectively. The result is tested against the critical value ($t_{a/2,v}$) at, $v = n_1 + n_2 - 2$, degrees of freedom and the required confidence level. If $t_{calc} < t_{a/2,v}$ the null hypothesis is accepted and any differences are due to random error.

If the F-test fails, the variance is not pooled, and the t-statistic is calculated according to Equation 2-12.

$$|t_{calc}| = \frac{|\bar{x}_1 - \bar{x}_2|}{s\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

Equation 2-12

The result is tested as with the previous t-test, however the overall degrees of freedom must be estimated using the calculation in Equation 2-13.

$$v = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{s_1^4}{n_1^2(n_1 - 1)} + \frac{s_2^4}{n_2^2(n_2 - 1)}}$$

Equation 2-13

The F-statistic and t-statistic where performed using the data Analysis ToolPak in Excel 2007 (Microsoft Corp., Washington, USA, 2006). The test results were reported as a probability of *t*, where at 95 % confidence ($\alpha = 0.05$) a value >0.05 indicates the null hypothesis is accepted.

2.9 Safety

All work involving apparatus and chemical substances were performed in a safe and controlled manner in accordance with experimental risk assessments. In this study several substances are used which are classified as hazardous to health in relation to the "Control of Substances Hazardous to Health" regulations (Table 2-6). Due to their hazardous chemical properties, substances were handled with gloves in a fume cupboard and other appropriate personal protective equipment worn. When not in use chemicals were sealed and stored in acid or solvent cupboards as appropriate. Disposal of chemicals was undertaken as highlighted in the risk assessments. Solvents were disposed of as chlorinated or non-chlorinated as appropriate.

Table 2-6 – Hazardous substance associated with experimental methods

Substance	Oxidising	Toxic	Carcinogenic	Harmful	Flammable	Corrosive	Irritant
Acetic acid						✓	✓
Acetonitrile		✓			✓		✓
Dichloromethane		✓	?	✓			✓
Hydrochloric acid		✓		✓		✓	✓
Hydrogen peroxide				✓		✓	✓
Hydroxyammonium hydrochloride				✓		✓	✓
Nitric acid	✓	✓		✓		✓	✓
PAH Standard		✓	✓	✓			✓
POLE				✓			✓
Spectrosol metal calibration solutions				✓			✓

Sample digestion was performed using a closed microwave digestion system in pressurised vessels. Vessels are designed to vent into waste should they exceed pressure and so it is important that digestion is performed in accordance with instructions. After digestion ACVs are at high temperature and pressure and so should be allowed to cool before being handled and opened in a fume cupboard.

3 Quality Control

3.1 ICPOES Line Agreement

The use of ICPOES allows for the simultaneous determination of multiple wavelengths for single and/or different analytes. Each wavelength could potentially be effected by interferences to varying degrees and subsequently the use of different spectral lines of the same analyte can generate different results. The analysis of a sample solution at multiple wavelengths allows for the comparison of determined concentrations; therefore any differences which would affect the accuracy of the results can be found. The sample solution was analysed for concentrations of aluminium, barium, chromium, copper, iron, manganese, nickel, lead and zinc at four different wavelengths for each element. The results are shown in Figure 3-1 as a multi-element control chart for the sample solution containing known concentrations (target values) for each of the analytes. Results are auto scaled by subtraction of the target mean and division by the associated precision. The target values are subsequently zero and results are plotted by the number of standard deviations from this value. The analytical procedure was considered to be within acceptable limits if the results were ±3 standard deviations of the target value.

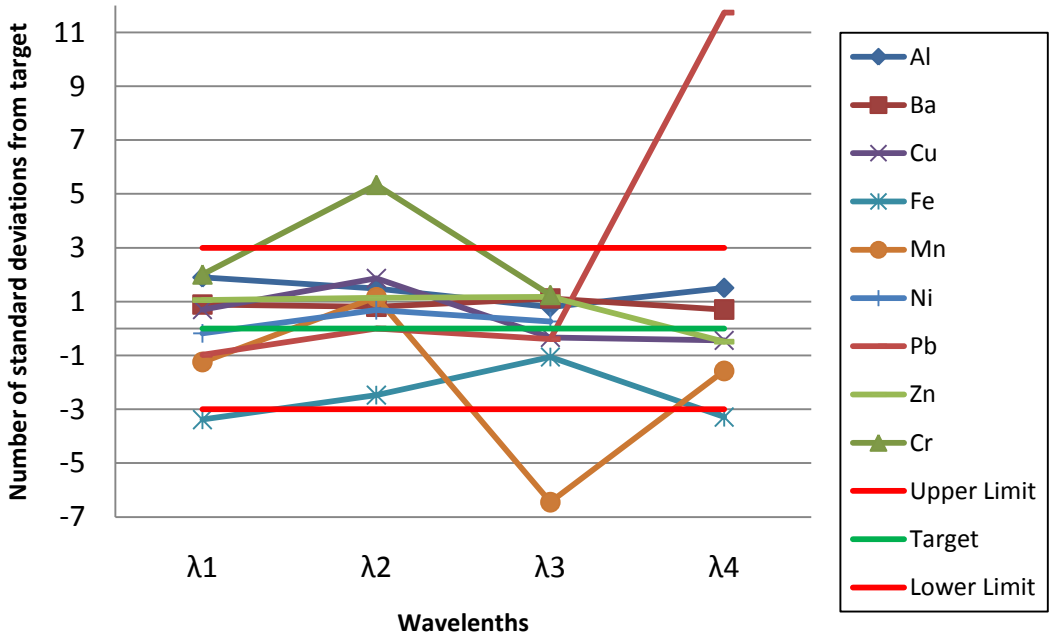


Figure 3-1 – Control chart showing the agreement of determined concentrations in a solution at four different wavelengths by ICPOES

The agreement showed there to be little difference in the result at each wavelength for most analytes. The main exceptions were chromium (283.5 nm), iron (238.2 and 259.9 nm), manganese (279.4 nm) and lead (261.4 nm) which showed either potentially enhancing or depressing interference. The spectra of the other analyte lines, obtained from the instrument, where examined for potential interference. The two lines which showed none or little interference and were most accurate in relation to the target value were selected for subsequent use and are listed in Table 2-4.

3.2 Method Quality Control

3.2.1 Method Blanks

For each batch of reference materials or samples a method blank was also digested/ extracted and analysed. These blanks were subjected to every step of the procedure for the applied method and processed simultaneously with the other samples. Where the concentration of a blank was found to be greater than the detection limits, the samples from the same batch were blank corrected.

3.2.2 Reference Materials

A reference material (RM) is a substrate matrix or pure substance which is used for quality control purposes, including method validation, determination of bias, method development and calibration. If the RM has an established homogeneity, stability and characterisation of the property values using appropriate validated methods, the information can be included as a certificate. A certified reference material (CRM) contains a certified value for one or more properties and an uncertainty based upon the different laboratories and/or different analysis methods involved in the certification process.

A CRM used in quality control is primarily selected based on matrix matching to the actual samples and the certification of the property value that is to be determined. The number of potential matrices, determinable properties and property values are vast and the time and cost required to certify a material make CRMs expensive. The

number of CRMs available is therefore limited. Also, a material more similar to the samples than available CRMs may be more appropriate for use in a particular study.

Secondary reference materials used during this work, were those produced for the URBSOIL project, a previous study focusing on urban pollutants. An urban soil reference material (URM) was characterised, for each of the partner cities, to provide a quality control sample with an urban soil matrix. The URM target values, for aqua regia soluble metals, were determined by replicate analysis in conjunction with analysis of a CRM. Although, the stability and precision of the URM is not comparable to that of a CRM, it has the advantages of being available in larger quantities.

3.2.3 Microwave Digestion

3.2.3.1 Certified Reference Material

The method described in this work, was developed using soil substrates and therefore a similar material was required. Of the certified reference materials available only BCR143R was certified for *aqua regia* soluble metals, the digestion method applied, and was therefore selected as the most suitable. When the method developed was applied to road deposited sediment, since there was no CRM available certified for *aqua regia* soluble content in this type of material, BCR143R was again used. *Aqua regia* soluble content of chromium, nickel, lead and zinc are certified for BCR143R, and also given is an indicative value for copper. The certified/ indicative target values and their associated uncertainties are shown in Table 3-1.

Table 3-1 – Certified and indicative values for aqua regia soluble content of PTE (mg kg^{-1}) in BCR-143R[174]

	Cd	Cr	Cu [c]	Mn	Ni	Pb	Zn
Certified Value [a]	72.0	426	128	858	296	174	1060
Uncertainty [b]	1.8	12	7.0	11	4	5.0	20
P	6	8	8	8	6	8	9

[a] mean value of p sets of data obtained from different laboratories
[b] half width of the 95% confidence interval of the mean
[c] indicative value

The CRM was digested in accordance with the *aqua regia* digestion procedure described in Section 3. Figure 3-2 shows the results for BCR-143R as a multi element control chart.

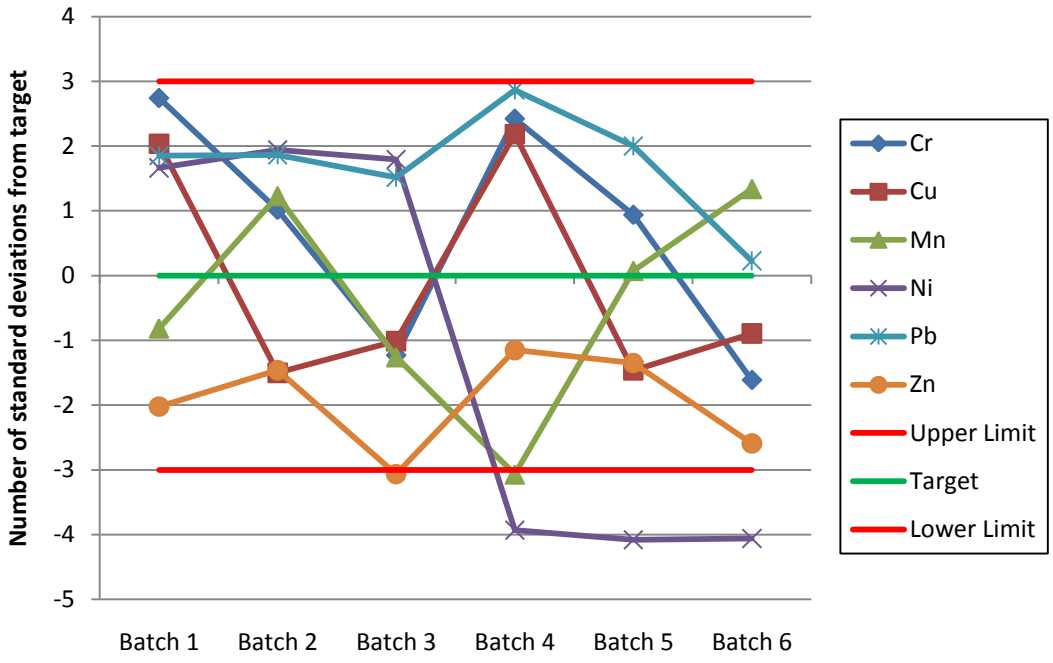


Figure 3-2 - Control chart showing the results for the analysis of aqua regia soluble PTE in BCR-143R

The results showed that the metals analysed where generally within the acceptable limits and the spread indicated no particular bias in the digestion method. Nickel extraction efficiency was found to be low for three of the batches.

3.2.3.2 Urban soil reference material

The Glasgow URM was the substrate primarily used during method development, as it was a material characteristic of urban areas. The results obtained could be used to assess that the digestion and instrumental analysis were within acceptable limits. The target values and their associated uncertainties are shown in Table 3-2.

Table 3-2 – Target values for aqua regia soluble content of PTE (mg kg^{-1}) in GLA-URM[171]

	Al	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Target Value	12300	169	43.2	111	3.06	442	48.8	389	177
SD	1460	10	3.0	5	0.12	18	7.0	25	11

During the experimental work two microwave digestion systems were used, along with both atomic absorption and atomic emission spectrometry. Figure 3-3 shows the results for the URM digested using the MDS-2000 microwave digestion system and analysed by FAAS. Figure 3-4 shows the results for the URM digested using the MARS microwave digestion system and analysed by ICPOES.

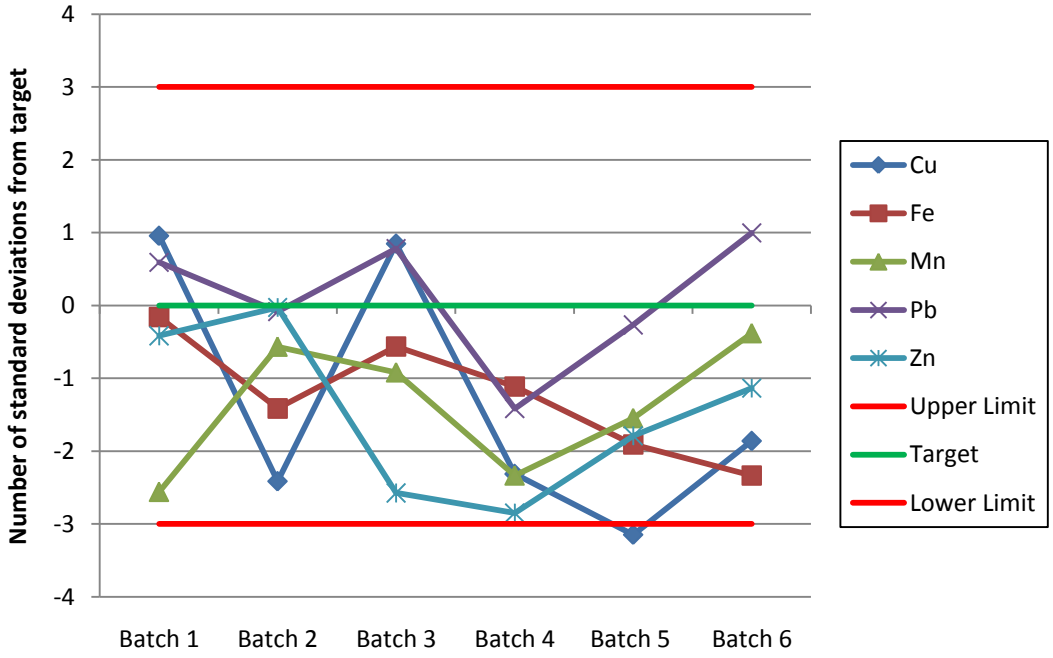


Figure 3-3 - Control chart showing the results for the analysis of aqua regia soluble PTE in GLA-URM using the MDS-2000 microwave digestion system and FAAS

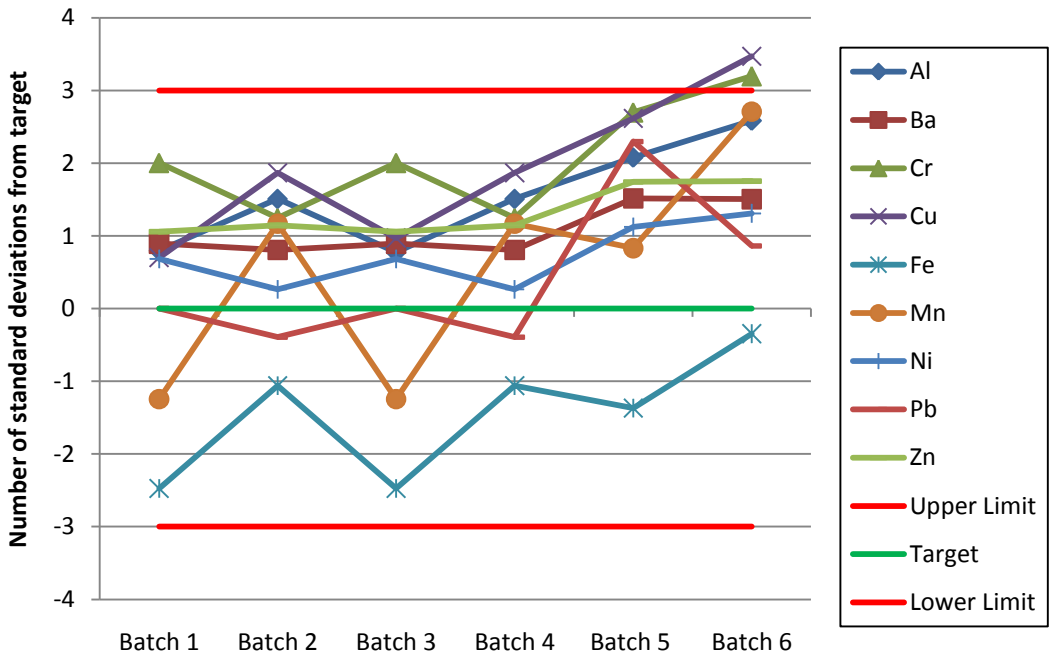


Figure 3-4 - Control chart showing the results for the analysis of aqua regia soluble PTE in GLA-URM using the MARS microwave digestion systems and ICPOES

The results showed that the recovery of each of the nine PTEs was generally within the accepted limits. This indicated that accurate digestion could be achieved using either of the microwave digestion systems. It also indicated that accurate analysis could be obtained when FAAS or ICPOES was applied. However, when the MDS-2000 and FAAS were used there was general trend of lower extraction efficiency. In comparison higher extraction efficiency was observed when the MARS system and ICPOES was used. A power test of the MDS-2000 system indicated that the maximum power output had decreased and subsequently extraction efficiency also decreased.

3.2.4 BCR Sequential Extraction

The CRM BCR601 is certified for concentrations of chromium, copper, nickel, lead and zinc extractable from the soil matrix using the BCR sequential extraction procedure. To determine that the procedure was performed within acceptable limits the CRM was analysed simultaneously with samples. The indicitive target values and their associated uncertainties are shown in Table 3-3.

Table 3-3 - Indicative values for the modified BCR sequential extraction metal content (mg kg^{-1}) in CRM-601[48]

		Cd	Cr	Cu	Ni	Pb	Zn
Step 1	Certified Value [a]	4.45	0.35	10.5	7.82	2.28	261
	Uncertainty [b]	0.67	0.08	0.8	0.84	0.44	13
	P	7	7	7	7	7	7
Step 2	Certified Value [a]	3.95	10.6	72.8	10.6	205	266
	Uncertainty [b]	0.53	0.9	4.9	1.2	11	17
	P	7	7	7	7	7	7
Step 3	Certified Value [a]	1.91	14.4	78.6	6.04	19.7	106
	Uncertainty [b]	1.43	2.6	8.9	1.27	5.8	11
	P	7	7	7	7	7	7
Step 4	Certified Value [a]	1.3	78.2	60.4	50.5	38	161
	Uncertainty [b]	2.2	6.5	4.9	4.3	8.7	14
	P	7	7	7	7	7	7

[a] mean value of p sets of data obtained from different laboratories
[b] standard deviation

The CRM was digested in accordance with the BCR sequential extraction procedure as described in Section 3. Figure 3-5 to Figure 3-8 shows the results of the four extraction steps for BCR-601 as multi element control charts.

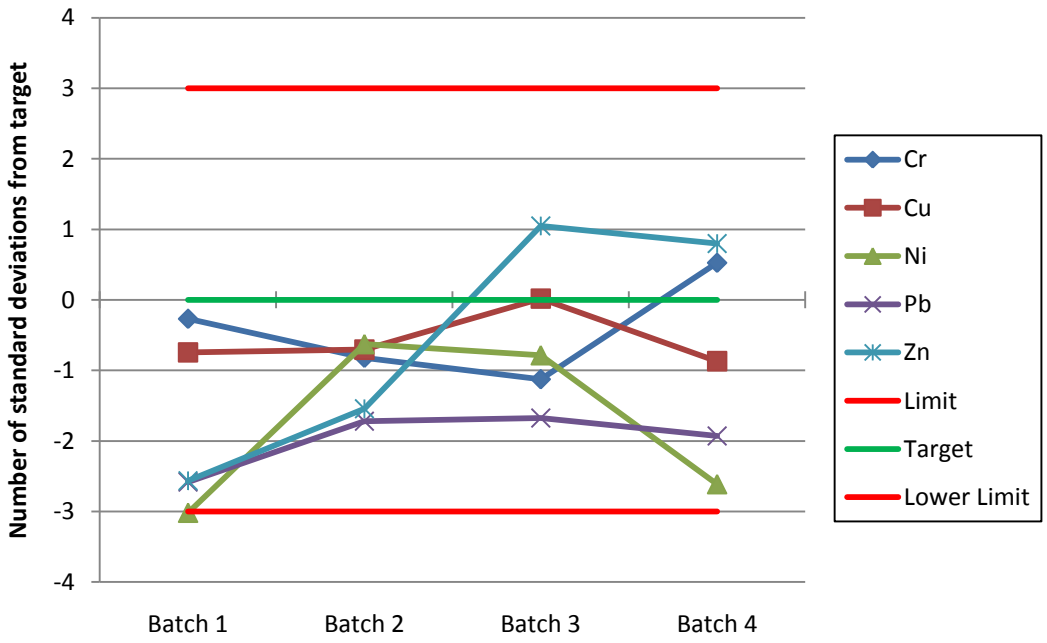


Figure 3-5 - Control chart showing the results for the analysis of PTE in Step 1 of the BCR sequential extraction procedure for BCR-601

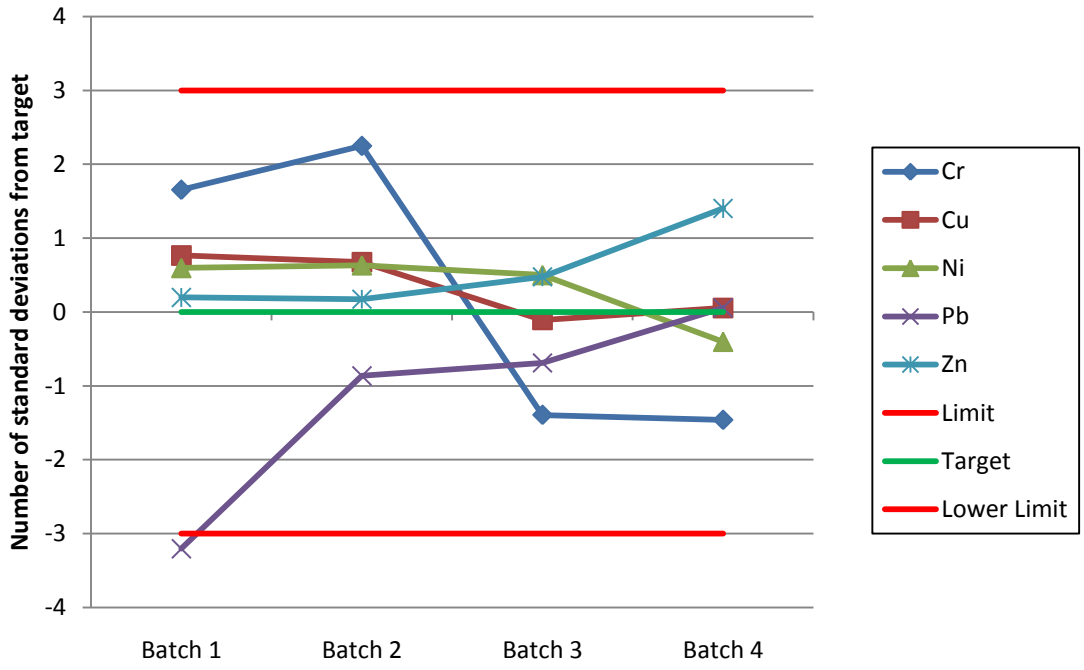


Figure 3-6 - Control chart showing the results for the analysis of PTE in Step 2 of the BCR sequential extraction procedure for BCR-601

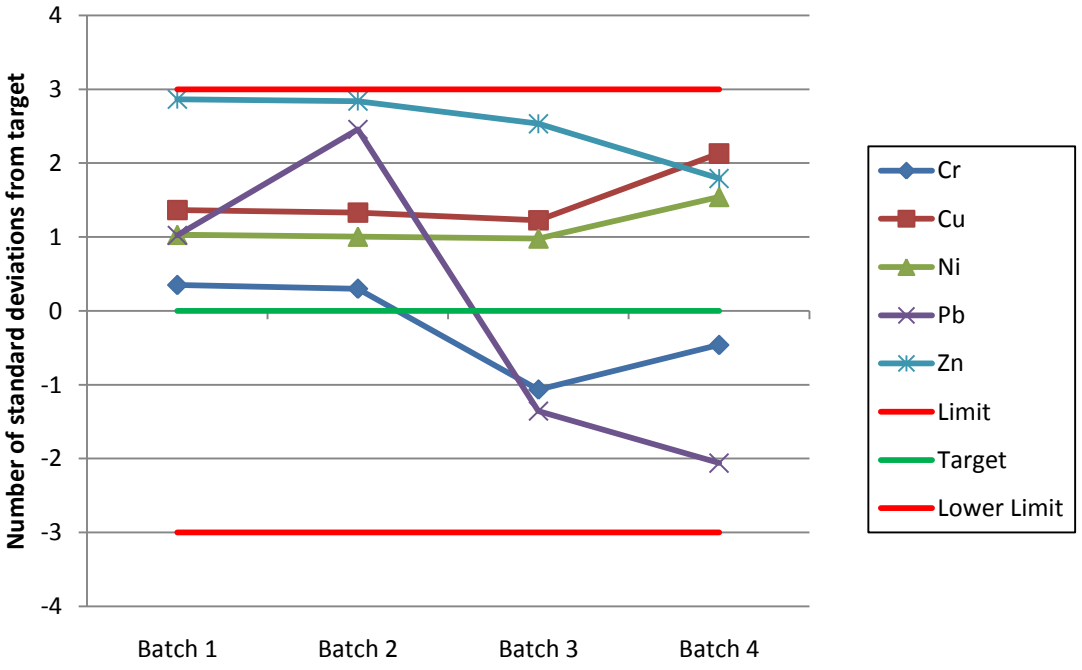


Figure 3-7 - Control chart showing the results for the analysis of PTE in Step 3 of the BCR sequential extraction procedure for BCR-601

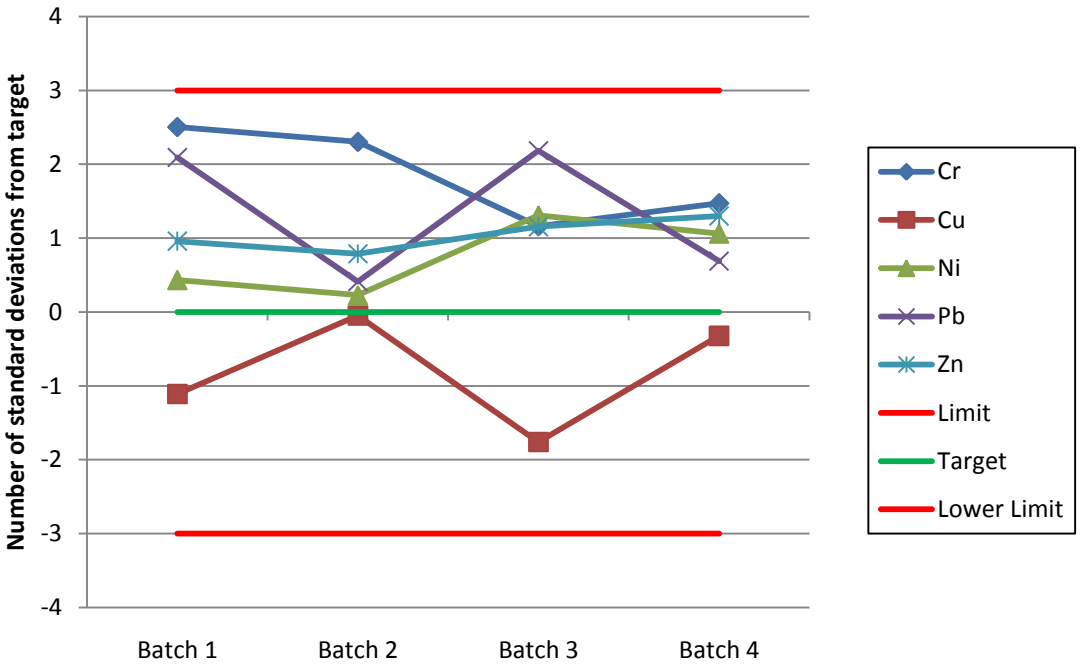


Figure 3-8 - Control chart showing the results for the analysis of PTE in Step 4 of the BCR sequential extraction procedure for BCR-601

The results were generally within acceptable limits. The notable exceptions were one batch of nickel in step 1 and one batch of lead in step 2. It was observed that extraction efficiency was generally low for step 1.

3.3 Conclusions

The use of certified and secondary reference materials, method blanks, and multiple analyte lines was used to achieve quality control in the results obtained from analysis. Samples were also digested in triplicate to give additional credence to the precision of results

4 Pseudo-total digestion of metals in combination with microwave-assisted micellar extraction

4.1 Introduction

The multi-component analysis for the determination of both PTE and PAH in a single sub-sample of a substrate requires a sequential approach (see Section 1.5). Firstly an appropriate solvent is applied to remove the PAH for determination, followed by digestion using an appropriate acid to obtain trace metal extracts. As silicate-bound metals are not usually leached under normal environmental conditions, a pseudo-total digestion is sufficient to determine the potentially toxic elements. Previous work on the analysis of trace metals in soils identified *aqua regia* MAD as a precise and accurate method with reasonable digestion times [26,171]. A sequential procedure requires that the extraction/ digestion solutions be compatible and also be target-specific so that analytes of interest can be quantified for each stage without loses of analytes during the other stage.

Review of the literature revealed potentially "environmental-friendly" PAH extraction procedures (see Section 1.4.2.4) that did not require the use of organic solvents and were thus more compatible with the use of MAD. One specific PAH extraction protocol was selected for study, which had been developed using the same commercial microwave system as used at Strathclyde[113]. The procedure involves the microwave-assisted heating of the soil samples in the presence of a micellar extractent based on POLE.

4.2 Aim

The aim of the work in this chapter was to begin the development of a two-stage extraction procedure, by assessing the effect of an initial extraction with POLE on the quantification of the PTE in the second stage of the two-stage proceedure.

4.3 Experimental

4.3.1 Samples

A number of materials with associated target values were studied in order to compare procedures with and without MAME. Certified reference material BCR 143R was studied as supplied. The certified and indicative values for *aqua regia* soluble content of Cd, Cr, Cu, Mn, Ni, Pb and Zn in BCR 143R are given in Table 4-1.

Table 4-1 – Certified and indicative values for aqua regia soluble content of PTE (mg kg^{-1}) in BCR-143R[174]

	Cd	Cr	Cu [c]	Mn	Ni	Pb	Zn
Certified Value [a]	72.0	426	128	858	296	174	1060
Uncertainty [b]	1.8	12	7.0	11	4	5.0	20
p	6	8	8	8	6	8	9

[a] mean value of p sets of data obtained from different laboratories
[b] half width of the 95% confidence interval of the mean
[c] indicative value

Four secondary reference materials, urban soil URMs from Glasgow (GLA), Sevilla (SEV), Torino (TOR) and Ljubljana (LJB) were also used. Although not as well characterised as a CRM these materials have established targets for *aqua regia* soluble metal content from a previous study[170].

The *aqua regia* soluble target values of Cu, Fe, Mn, Pb and Zn in the GLA, LJB, SEV, and TOR URMs are given in Table 4-2

Table 4-2 – Target values for* aqua regia *soluble content of PTE (mg kg^{-1}) in Glasgow (GLA), Ljubljana (LJB), Seville (SEV) and Torino (TOR) URMs[170]

	Cu	Fe (%)	Mn	Pb	Zn	n
GLA-URM	111 ± 5.0	3.06 ± 0.12	442 ± 18	389 ± 25	177 ± 11	34
SEV-URM	17.7 ± 1.0	1.11 ± 0.01	233 ± 13	36.6 ± 5.2	54.8 ± 4.6	36
LJB-URM	30.6 ± 0.4	NA	481 ± 10	74.3 ± 2.1	129 ± 6	4
TOR-URM	44.3 ± 1.9	3.70 ± 0.19	NA	55.1 ± 1.4	101 ± 8.8	10

Results presented are mean values ± 1 standard deviation for n number of samples for each soil

The four soils were chosen based upon their differing levels of soil organic matter (SOM) and PAH, established in previous studies (Table 4-3)[22,93].

Table 4-3 - Relative levels of SOM[58] and PAH[84] in four soils

PAH \ SOM		LOW (< 2%)	HIGH (> 9%)
LOW	(<1000 µg mL^{-1})	Seville	Ljubljana
HIGH	(>4000 µg mL^{-1})	Torino	Glasgow

4.3.2 Extraction and analysis

A sub-sample of analysis substrate was weighed and microwave extracted using a micellar medium as described in section 2.5.1. After filtration the POLE extract, containing organic analytes, was discarded. The membrane filter and any solid residue was replaced in the same ACV used for micellar extraction. 20 mL of *aqua regia* is added to the ACVs and microwave-assisted digestion was performed as described in section 2.5.2. This multi-stage extraction for the release of PAH and PTE is referred to henceforth in the text as 'procedure B'. A sub-sample was also extracted using only the *aqua regia* MAD without the POLE step for comparison with the multi-stage procedure mentioned (hereafter referred to as 'procedure A' in the text). Analysis was performed on triplicate test portions by FAAS for copper, iron, manganese, lead and zinc as described in section 2.6.1.

4.3.3 Detection limits

The extracts were analysed in reagent matched standards by FAAS. The detection limits found for 20 % *aqua regia* are shown in Table 4-4.

Table 4-4 – Instrumental (D_L inst./ µg mL^{-1}) and procedural (D_L pro./ mg kg^{-1}) detection limits in 20 mL aqua regia (diluted to 100 mL) matrix by FAAS analysis

Analyte		***20 % Aqua regia***		
PTE	**λ/ nm**	**Slope**	**D_L inst.**	**D_L pro.**
Cu	327.8	0.0900	0.083	8.30
Fe	248.3	0.0670	0.042	4.20
Mn	279.8	0.1138	0.060	6.00
Pb	217.0	0.0124	0.258	25.8
Zn	213.9	0.4440	0.002	0.200

The detection limits for zinc were found to be the lowest, whereas they were much poorer for lead. This is in agreement with those detection limits found in another study[175].

4.4 Results and discussion

4.4.1 Copper

The results for the five reference soils analysed for copper are given in appendix A as mean, standard deviation and relative standard deviation. The precision for the three replicates of each of the five soils was generally acceptable (< 10 % RSD) with the exception of the TOR-URM with an RSD value of 14 %. A single replicate of the TOR-URM had a greater concentration than the others and, if this is discounted then the precision is improved. However the single higher value is closer to the target value and so it could be the two lower values that are incorrect, perhaps due to inefficient digestion. Figure 4-1 shows the mean recoveries of copper using the two extraction procedures for the five soils investigated.

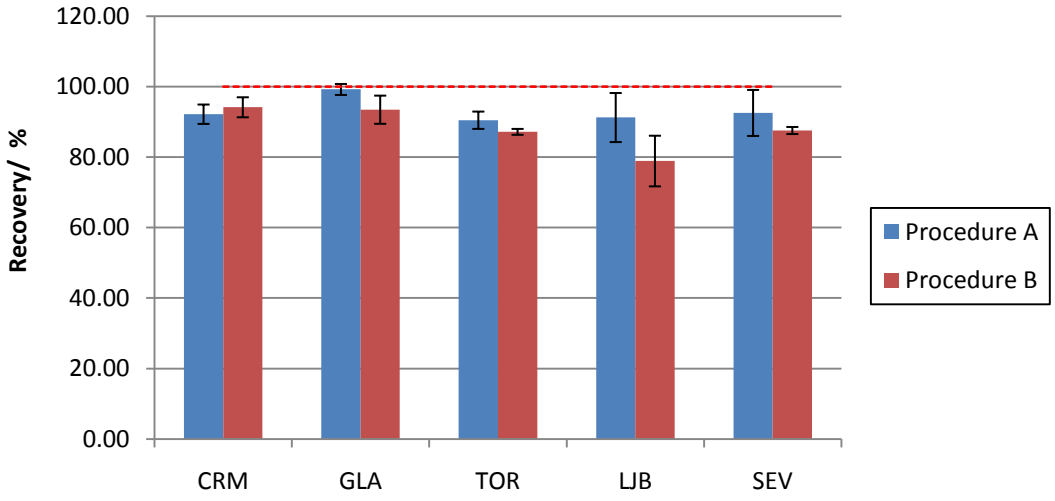


Figure 4-1 - Comparison between mean copper recoveries obtained using two extraction procedures for five reference soils (n=3).

The recoveries were all within 10 % of the target value when procedure A was applied. The application of procedure B resulted in a decrease in recovery to within

20 % of the target, with the exception of the CRM (which showed an increase of 2 %) and the LJB-URM (which showed a decrease to 79 %). The extracted analyte concentrations were statistically compared using a t-test to determine if prior extraction of organic analytes, using MAME with POLE, affected the quantification of PTEs. Table 4-5 shows the results of the t-tests.

Table 4-5 – Probability of t from student t-tests for the copper results of five reference soils when comparing extraction with and without initial microwave-assisted micellar extraction

Sample	CRM	GLA	TOR	LJB	SEV
P	0.245	0.236	0.092	0.042	0.495

The test results showed there to be no significant differences, at a 95 % confidence level, between the two procedures applied with the exception of the LJB-URM. The LJB-URM was seen to fail statistically, although analytically the results are similar in terms of the difference between recoveries using both procedures (12 %). The differences were less than 10 % for the other reference soils. This indicates that the potential sequential extraction of PAHs and PTEs does not markedly effect the quantification of copper.

4.4.2 Iron

The results for the five reference soils analysed for iron are given in appendix A. The results showed RSD values of less than 10 % which indicated acceptable precision. The mean recoveries of iron determined using the two procedures are shown in Figure 4-2. The CRM is not shown in the figure because there is no target value for iron.

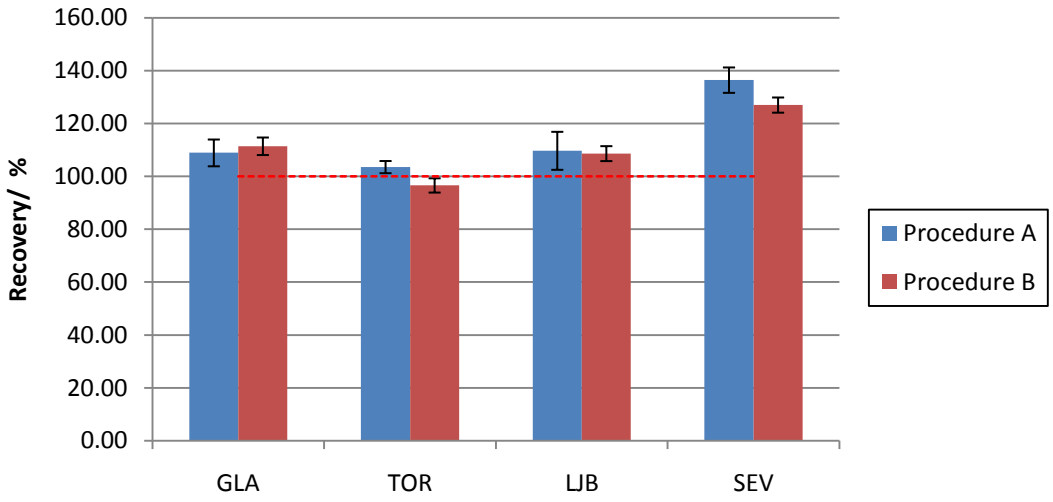


Figure 4-2 - Comparison between mean iron recoveries obtained using two extraction procedures for four reference soils (n=3).

Results for the samples, with the exception of SEV-URM, were within 10 % of the target values when either of the procedures was applied. The SEV-URM showed recoveries of more than 20 % greater than the target. The statistical results using a t-test are shown in Table 4-6.

Table 4-6 – Probability of t from student t-tests for the iron results of five reference soils when comparing extraction with and without initial microwave-assisted micellar extraction

Sample	GLA	TOR	LJB	SEV
P	0.461	0.027	0.824	0.066

The GLA, LJB and SEV-URM test results showed there to be no significant differences between procedures ($\alpha = 0.05$). The TOR-URM shows a larger difference failing the t-test at a 95 % confidence level. However, the recoveries were similar for both procedures with less than 10 % difference for TOR-URM and the other reference soils. Therefore, the results did not indicate a substantial effect on the quantification of iron.

4.4.3 Manganese

The results of the five reference soils analysed for manganese are listed in appendix A. The results generally showed acceptable precision (< 10 % RSD, n=3). Figure

4-3 shows the manganese results, for the five samples investigated, as mean recoveries.

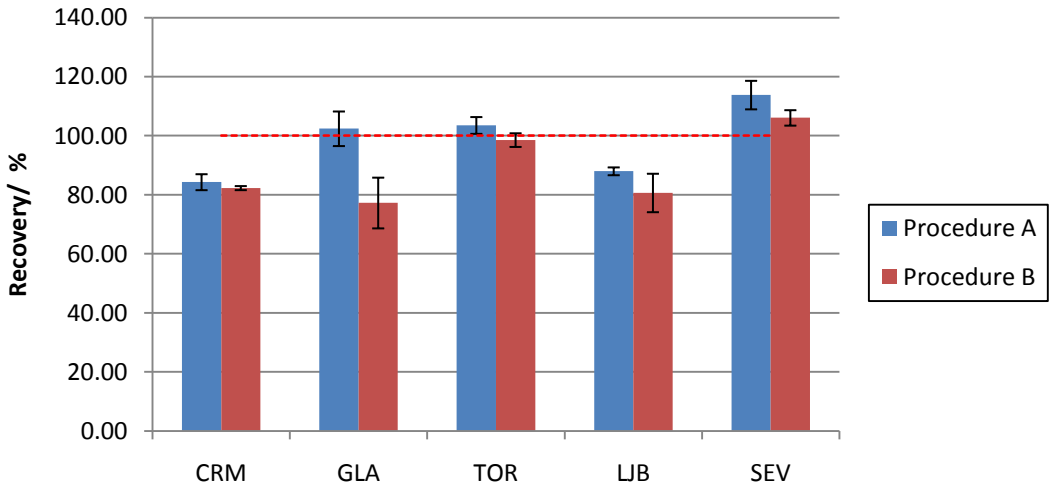


Figure 4-3 - Comparison between mean manganese recoveries obtained using two extraction procedures for five reference soils (n=3).

The recoveries for the GLA (for procedure A), TOR and SEV URMs were all within 10 % of the target value, while the other results were generally within 20 %. However, the difference in recoveries between the two procedures was less than 10 %; and therefore indicated that low recoveries were due to poor extraction efficiencies affecting both results. The major exception is the GLA-URM were determination of manganese after extraction using procedure B resulted in a 25 % lower recovery and indicated that analyte which detected in solutions after extraction using procedure A was not extracted. The results of t-tests used to compare the two procedures are shown in Table 4-7.

Table 4-7 – Probability of t from student t-tests for the manganese results of five reference soils when comparing extraction with and without initial microwave-assisted micellar extraction

Sample	CRM	GLA	TOR	LJB	SEV
P	0.533	0.0075	0.079	0.196	0.072

The test results highlight the significant difference in the GLA-URM results obtained by the two procedures, which lies well outside the 95 % confidence level. The difference indicated that a significant amount of manganese was extracted by the

initial MAME step in the sequential extraction procedure. No significant differences were found for any of the other samples investigated at a 95 % confidence level.

4.4.4 Lead

The results for the samples analysed for lead are given in appendix A. The lead results obtained for the SEV-URM were below detection limits and are not mentioned further. The other samples investigated showed acceptable precision, with RSD values < 10 %. Figure 4-4 shows the mean recoveries of lead using the two extraction procedures for the soils analysed.

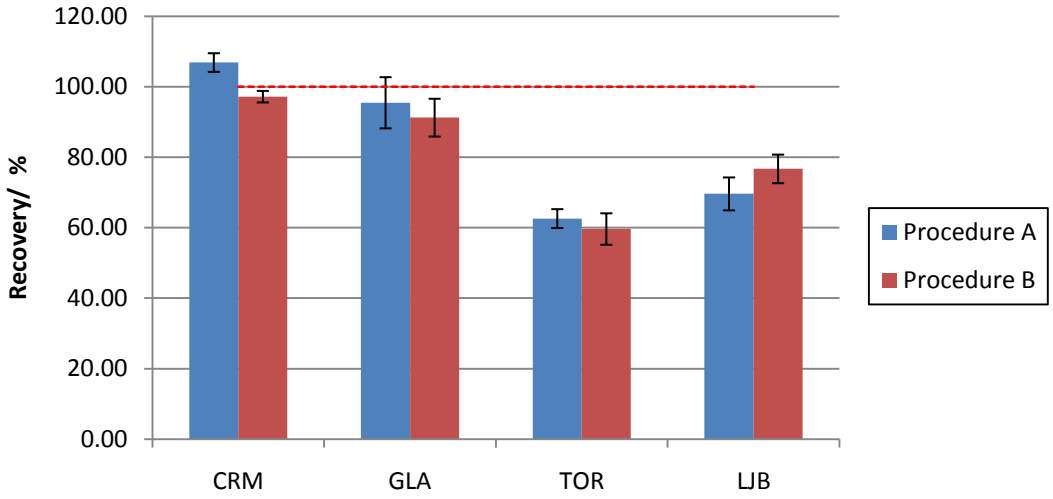


Figure 4-4 - Comparison between mean lead recoveries obtained using two extraction procedures for four reference soils (n=3).

The recoveries of the CRM and GLA-URM are both within 10 % of the target value when either procedure was applied. The TOR and LJB-URM both showed under-extraction for lead compared to the target value, although both procedures had similar recoveries. The stability of these soils is not checked and guaranteed in the same way as a certified reference material and so it is possible that their composition could have changed during storage. Table 4-8 shows the results of t-tests comparing the two applied procedures.

Table 4-8 – Probability of t from student t-tests for the lead results of four reference soils when comparing extraction with and without initial microwave-assisted micellar extraction

Sample	CRM	GLA	TOR	LJB
P	0.013	0.412	0.379	0.118

The t-test results showed there to be no significant differences between the two procedures for GLA, TOR and LJB-URM ($\alpha = 0.05$). However, the CRM failed the t-test at a 95 % confidence level. The difference in recoveries, between the two procedures, was less < 10 % for all five reference soils. These results indicated that the prior treatment of POLE does not particularly effect the quantification of lead, although statistically the CRM showed differences..

4.4.5 Zinc

The results for the determination of zinc in five reference soils are given in appendix A. The precision for the triplicates of the five soils was acceptable, with RSD values of generally < 5 %. Figure 4-5 shows the mean recoveries of zinc using the two extraction procedures for the five samples investigated.

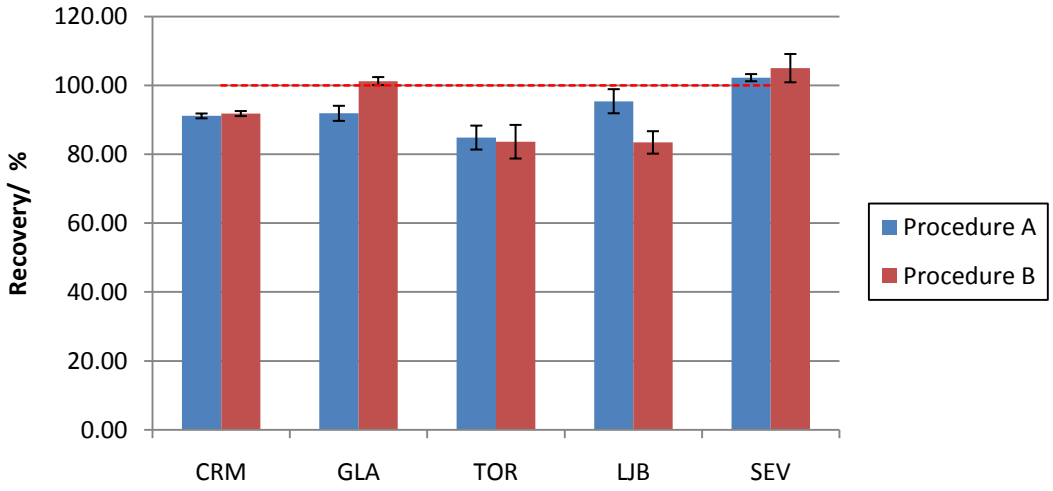


Figure 4-5 - Comparison between mean zinc recoveries obtained using two extraction procedures for five reference soils (n=3).

The recoveries were all within 10 % of the target value, with the exception of the TOR-URM and LJB-URM (for procedure B) which fell within 20 %. Table 4-9

shows the results for t-tests comparing the concentrations of zinc recovered using both procedures.

Table 4-9 – Probability of t from student t-tests for the zinc results of five reference soils when comparing extraction with and without initial microwave-assisted micellar extraction

Sample	CRM	GLA	TOR	LJB	SEV
P	0.369	0.136	0.746	0.0104	0.322

At a confidence level of 95 % all of the samples passed, with the exception of LJB-URM. Although the t-test failed, for LJB-URM, a difference of only 12 % between the recoveries using both procedures was found. The other reference soils showed < 10 % difference between the two methods. This indicates difference between the two procedures for the quantification of zinc is not substantial, although some statistical differences have been shown.

4.5 Conclusions

The results showed that metal recoveries for copper, iron, manganese and zinc were all generally within 10 – 20 % of the target value, for the five reference soils investigated. Generally the recoveries of the analytes investigated were low, perhaps due to inefficient extraction using the microwave system. A microwave power test was performed on the MDS 2000 and it was found that 84 % of the maximum rated power (650 W) was being generated. Subsequently this could lead to lower recoveries due to less power used to heat the vessels.

T-tests performed using the results from the two procedures, for the analytes investigated in the five reference soils, in general passed at a 95 % confidence level. This statistically showed there to be no significant differences between results obtained for the majority of analytes, with 78 % of the tests passing. The test result for manganese determined in the GLA-URM was the particular exception among the five failed t-test results. This was confirmed by a lower recovery that was observed following treatment with POLE and a difference in recoveries of 25 % was found between the two procedures. This perhaps indicates that POLE may cause a

significant liberation of manganese in this soil matrix. The results for the other reference soils indicated that prior treatment with POLE did not significantly affect the determination of manganese.

The results for the five reference soils potentially indicate that quantification could be possible for the analytes investigated after test portions have been treated with POLE. The differences if they exist, are not large, (except Mn), and hence the method shows potential for further development. The use of ICP-AES to investigate more analytes, or expansion of the procedure to include, for instance, the BCR sequential extraction may allow for further evaluation of the method.

5 Sequential extraction of metals in combination with microwave-assisted micellar extraction

5.1 Introduction

Sequential extraction, described briefly in section 1.3.2.1, is a chemical fractionation process, involving the treatment of a substrate with defined reagents chosen to potentially target specific phases, e.g. carbonate bound analytes in soil. These targeted fractions can include water soluble, exchangeable, organically bound, carbonate bound, manganese oxides, iron oxides and residual metal analytes, which can be extracted using various reagents.

A number of sequential extraction schemes have been applied to the analysis of soils[22], roadside dusts[25] and airborne particulates[176]. These different procedures vary in the number of steps, target phases and reagent used to target a phase. Subsequently, results are different and cannot be easily compared. An attempt to standardise the various schemes was undertaken with the development of the three stage BCR sequential extraction[177-178] and subsequent improvements[48]. The BCR procedure contains three steps and it is recommended that a fourth residual step is performed, for extraction validation in comparison to a pseudo total digestion.

The first step of the BCR procedure targets the exchangeable, water and acid soluble phases. Metals which are weakly bound to particles and those found in the soil solution are potentially released in the exchangeable and water-soluble fractions, respectively. Carbonates are also dissolved by the acetic acid applied for this step. The second step, the reducible phase, potentially targets iron and manganese oxyhydroxide mineral phases. The oxidisable phase (step 3) principally targets the organic-bound metals, via the use of an oxidising agent (hydrogen peroxide) to dissolve the organic matter, and also sulfides. Once released the metals are retained in solution by ammonium acetate. Finally *aqua regia* digestion is performed on the residue for comparison of the sum of the sequential steps with pseudo-total digestion. It should be noted that use of a different reagent for one of the steps would

potentially result in different metal partioning and therefore sequential extractions are operationally defined procedures[47]. For example, iron oxides could be more efficiently dissolved using an oxalate reagent for the reducible phase[179] (unless the analyte oxalates are in soluble[180]) and therefore recovery for step 2 would be higher than achieved using hydroxylammonium hydrochloride for the BCR procedure.

5.2 Aims

The aim of the work in this chapter was to expand on the two-stage sequential procedure for potential determination of both PTE and PAH (Section 4) by incorporating a metal fractionation method. This involved the replacement of the pseudo-total *aqua regia* digestion stage with the BCR sequential extraction procedure. The objective was to assess the effect the initial POLE extraction step had on the quantification of PTE in the four steps of the BCR procedure.

5.3 Experimental

5.3.1 Samples

Two materials with associated target values were studied to compare results obtained, with and without MAME. BCR-601, a certified reference material, is certified for BCR sequential extraction and was studied as supplied. The certified values for BCR sequential extraction content of Cd, Cr, Cu, Ni, Pb and Zn in BCR-601 are given in Table 5-1. GLA-URM, a secondary reference material, has established targets for BCR sequential extraction from a previous study[171]. The *aqua regia* and BCR extractable target values of Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in GLA-URM are given in Table 5-2. A composite road deposited sediment (RDS) material, prepared from six RDS samples, was also extracted. The RDS samples were collected using a hand-held vacuum cleaner as described in section 2.3

Table 5-1 - Certified and indicative values for BCR sequential extraction metal content (mg kg^{-1}) in CRM BCR-601[48]

		Cd	Cr	Cu	Ni	Pb	Zn
Step 1	Certified Value [a]	4.45	0.35	10.5	7.82	2.28	261
	Uncertainty [b]	0.67	0.08	0.8	0.84	0.44	13
	P	7	7	7	7	7	7
Step 2	Certified Value [a]	3.95	10.6	72.8	10.6	205	266
	Uncertainty [b]	0.53	0.9	4.9	1.2	11	17
	P	7	7	7	7	7	7
Step 3	Certified Value [a]	1.91	14.4	78.6	6.04	19.7	106
	Uncertainty [b]	1.43	2.6	8.9	1.27	5.8	11
	P	7	7	7	7	7	7
Step 4	Certified Value [a]	1.3	78.2	60.4	50.5	38	161
	Uncertainty [b]	2.2	6.5	4.9	4.3	8.7	14
	P	7	7	7	7	7	7

[a] mean value of p sets of data obtained from different laboratories
[b] standard deviation

Table 5-2 – Target values for* aqua regia *soluble content of PTE (mg kg^{-1}) BCR sequential extraction metal content (mg kg^{-1}) in Glasgow (GLA-URM) URM (n = 34).[170]

	BCR Sequential Extraction				Pseudo-total
	Step 1	Step 2	Step 3	Step 4	
Al	NA	NA	NA	NA	12300 ± 1460
Ba	NA	NA	NA	NA	169 ± 10
Cr	0.64	3.14	9.72	27.8	43.2 ± 3.0
Cu	9.19	28.3	33.2	25.8	111 ± 5.0
Fe (%)	160	6740	1190	21400	3.06 ± 0.12
Mn	123	134	25.3	147	442 ± 18
Ni	2.05	3.03	4.7	40.2	48.8 ± 7.0
Pb	25.1	235	109	73.3	389 ± 25
Zn	15.4	26.3	27.2	118	177 ± 11

Results presented are the mean value for each step and the mean value ± 1 standard deviation for the pseudo-total

5.3.2 Extraction and Analysis

A sub-sample of analysis substrate was weighed and microwave extracted using a micellar medium as described in section 2.5.1. After filtration, and storage of the filtrate prior to analysis, the membrane filter and any solid residue left in the ACV were transferred into a centrifuge tube. The sample is then subjected to the four steps of the BCR sequential extraction as described in section 2.5.3. This two-stage extraction for the release of PAH and fractionation of metals is referred to henceforth in the text as 'procedure B'. A sub-sample was also extracted using just the four steps of the BCR sequential extraction. This was as a comparison to the two-stage procedure mention above and shall henceforth be referred to as 'procedure A' in the text. Analysis was performed as described in 2.6.2 by ICPOES for aluminium, barium, cadmium, chromium, copper, iron, manganese, nickel, lead and zinc.

5.3.3 Detection Limits

The extracts were analysed in reagent-matched standards by ICPOES. The detection limits obtained for each different matrix, at two wavelengths, are shown in Table 5-3. The results showed that the lowest detection limits were achieved for barium, manganese, nickel and zinc. The result for lead was much improved compared to that for FAAS. The instrumental detection limits vary in each step for an analyte due to the different affects of the matrix on the atomization of the test solution. The procedural detections limits vary further due to the dilution factors applied based upon the treatment of 1 g of sample. The solution is made up to 40 mL for steps 1-2, 50 mL for step 3 and 100 mL for step 4 and therefore these values are used as the dilution factors. The detection limits were generally poorer for aluminium and iron, relative to the other metals and this also been seen in other research[24]. However, these geogenic metals are often present at high levels and so these limits of detection do not present a problem.

Table 5-3 – Instrumental (D_L inst./ µg mL^{-1}) and procedural (D_L pro./ mg kg^{-1}) detection limits in the four BCR sequential extraction matrices by ICPOES analysis

Analyte		Step 1		Step 2		Step 3		Step 4	
PTE	**λ/ nm**	**D_L inst.**	**D_L pro.**	**D_L inst.**	**D_L pro.**	**D_L inst.**	**D_L pro.**	**D_L inst.**	**D_L pro.**
Al	308.2	0.114	4.55	0.0170	0.542	0.0193	0.966	0.0408	4.08
	309.2	0.0675	2.70	0.0110	0.527	0.0192	0.959	0.0454	4.54
Ba	230.4	0.000373	0.0149	0.000323	0.0142	0.000642	0.0321	0.000491	0.0492
	233.5	0.000199	0.00796	0.000326	0.0164	0.000652	0.0326	0.000308	0.0308
Cd	226.5	0.000299	0.0120	0.000216	0.0112	0.000213	0.0107	0.000511	0.0511
	361.0	0.406	16.2	0.143	3.57	0.120	6.00	0.0839	8.39
Cr	267.7	0.0117	0.467	0.00182	0.0431	0.00130	0.0648	0.00118	0.118
	284.3	0.00877	0.351	0.00146	0.0463	0.00216	0.108	0.00106	0.106
Cu	219.9	0.00434	0.173	0.00576	0.173	0.00602	0.301	0.00757	0.757
	224.7	0.000856	0.0342	0.00234	0.0533	0.00127	0.064	0.00112	0.112
Fe	238.2	0.0122	0.490	0.0164	0.720	0.0198	0.991	0.0415	4.15
	240.4	0.0288	1.15	0.0155	0.714	0.02002	1.00	0.0377	3.77
Mn	257.6	0.00177	0.0710	0.000588	0.0236	0.000681	0.0340	0.000677	0.0677
	259.3	0.00212	0.0850	0.000538	0.0236	0.000727	0.0364	0.000635	0.0636
Ni	216.5	0.00114	0.0454	0.00118	0.0500	0.00127	0.0635	0.00108	0.108
	221.6	0.000434	0.0174	0.000686	0.0195	0.00101	0.0503	0.000529	0.0529
Pb	182.2	0.00437	0.175	0.00538	0.341	0.0142	0.708	0.00765	0.765
	216.9	0.0122	0.488	0.0154	0.540	0.0312	1.56	0.0205	2.05
Zn	202.5	0.000821	0.0328	0.000929	0.0530	0.00153	0.0767	0.000545	0.0545
	206.2	0.00125	0.0501	0.00116	0.0520	0.00166	0.0829	0.000638	0.0638

****Dilution Factors – Step 1 = 40; Step 2 = 40; Step 3 = 50; Step 4 =100***

5.4 Results and discussion

The results for the analytes investigated are given below, with the exception of cadmium which was below the detection limits in the samples. The CRM was only analysed, and discussed, for those analytes where target values were available. The materials were used to examine the effect of the procedure on fractionation.

5.4.1 Aluminium

The mean results and RSD values for the measurement of aluminium in each BCR sequential extraction step and pseudo total aluminium concentrations, are listed in appendix B. The level of precision was acceptable (< 10 % RSD), but were slightly worse for steps 2 (15 %) and step 3 (11 %) for the RDS sample. This could be due to poor homogeneity in dust samples, particularly as this sample is a composite from

various locations and subsequently contained different concentrations. Figure 5-1 shows the mean concentration of aluminium in each step of the BCR sequential extraction and pseudo-totals for both procedure A and B.

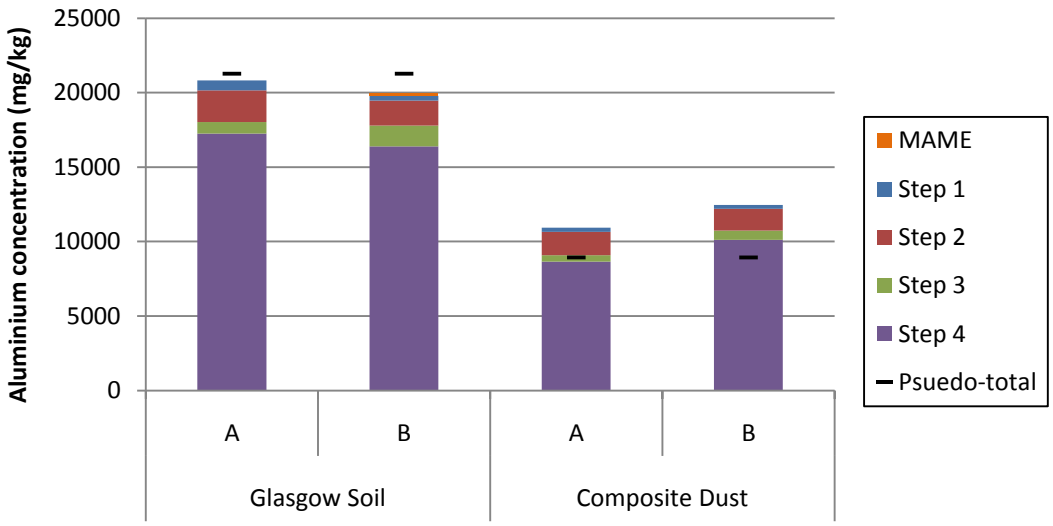


Figure 5-1 – Mean concentration obtained for aluminium in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of Glasgow soil and composite dust samples (n=3).

A mass balance of the BCR sequential extraction procedure was determined as a mean recovery, for the sum of the four steps, and compared to the pseudo-total results. The recoveries ranged from 94 – 139 %, with the sequential extraction of both the RDS samples showing over-extraction, particularly for procedure B (139 %). By visual comparison it would appear that step 1 extracted less aluminium, when procedure B was applied, for both samples. This was expected as the water in the additional MAME stage of the procedure would have extracted some of the water soluble aluminium. There was less aluminium extracted by procedure B in step 2 and more in step 3 compared to procedure A. This could indicate that some aluminium normally extracted by the step 2 regent maybe leached by surfactant not removed during the rinsing step. The analyte could potentially be trapped and precipitated (or bound) by the MAME reagent and subsequently not released in step 2, resulting in a lower recovery. The reagents used in step 3 target organic species and are therefore likely to dissolve or destroy the surfactant due to its organic "tail" and so could re-release bound analytes. This would explain the increased recovery

of aluminium found in step 3. The results of the two procedures applied were statistically tested using a student t test. Table 5-4 shows the results of the t-tests.

Table 5-4 – Probability of t from student t-tests for Glasgow soil and composite dust sample aluminium results when comparing extraction with and without initial microwave-assisted micellar extraction

	Sample	Step 1	Step 2	Step 3	Step 4	Sum of Steps
P	Glasgow Soil	2.76E-13	1.15E-03	1.05E-05	0.171	0.156
	Composite Dust	0.215	0.256	4.99E-04	0.214	0.0307

The test results for the soil samples showed that steps 1, 2 and 3 are statistically different but that there is no significant difference ($\alpha = 0.05$) between the procedures for step 4. The test of results for step 1 showed the greatest difference, suggesting that a significant amount of analyte is removed by the MAME reagent. Steps 1-2 for the composite dust sample showed no significant difference at the 95 % confidence limits, while step 3-4 both showed differences. The most significant difference was observed for step 3, which potentially highlights the possible release of analyte from surfactant still present when procedure B is applied; however there is no statistical evidence that step 2 is affected by the surfactant. The pseudo-total aluminium concentration in each sample shows no significant difference between the procedures. Figure 5-2 shows the results as a fractionation pattern, with each step as a percentage of the sum of steps.

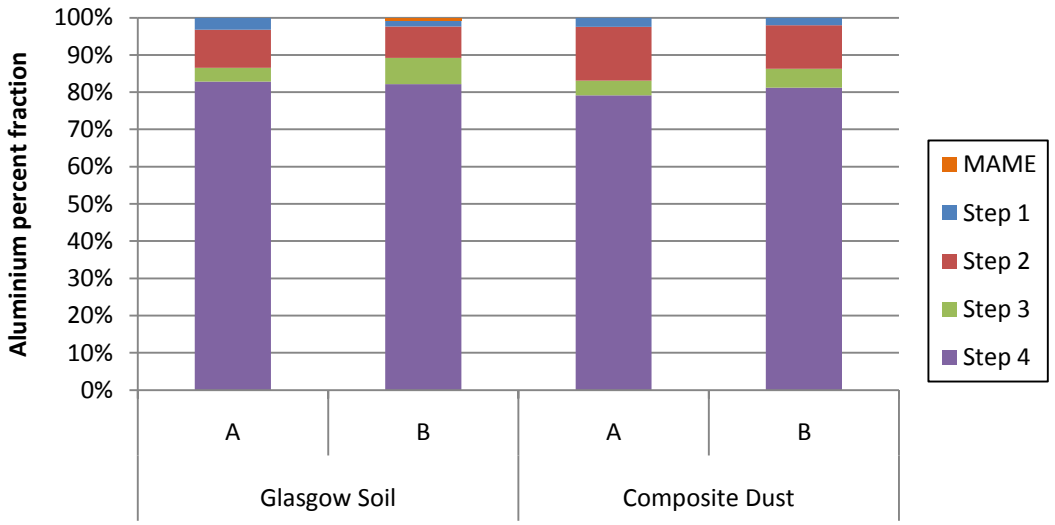


Figure 5-2 – Mean percentage fractionation of aluminium in Glasgow soil and composite dust samples after BCR sequential extraction with [B] and without [A] initial microwave-assisted micellar extraction.

The fractionation shows that, although statistical difference can be highlighted, the pattern is similar for the different samples and procedures. The difference, in percentage, of a step is less than 10 % across all samples.

The results indicate that potentially more aluminium is found in Glasgow urban soil than in RDS. The fractionation patterns are comparable, for both soil and RDS, with the majority of aluminium (approximately 80 %) found in step 4. Residual analytes are the target of step 4 and include metals more strongly bound to parent minerals, with the exception of silicates. Aluminium is known to be geogenic, as a constituent of many minerals[18], and this could indicate that dispersion of soil onto urban infrastructure is a source of RDS.

5.4.2 Barium

The mean results and RSD values for the measurement of barium in each BCR sequential extraction step and pseudo totals are listed in appendix B. The RSD values were generally < 10 %, but were slightly worse for the dust samples in steps 1 (11 %) and 4 (18 %). Figure 5-3 shows the mean concentration of barium in each step of the BCR sequential extraction and pseudo-totals for both procedure A and B.

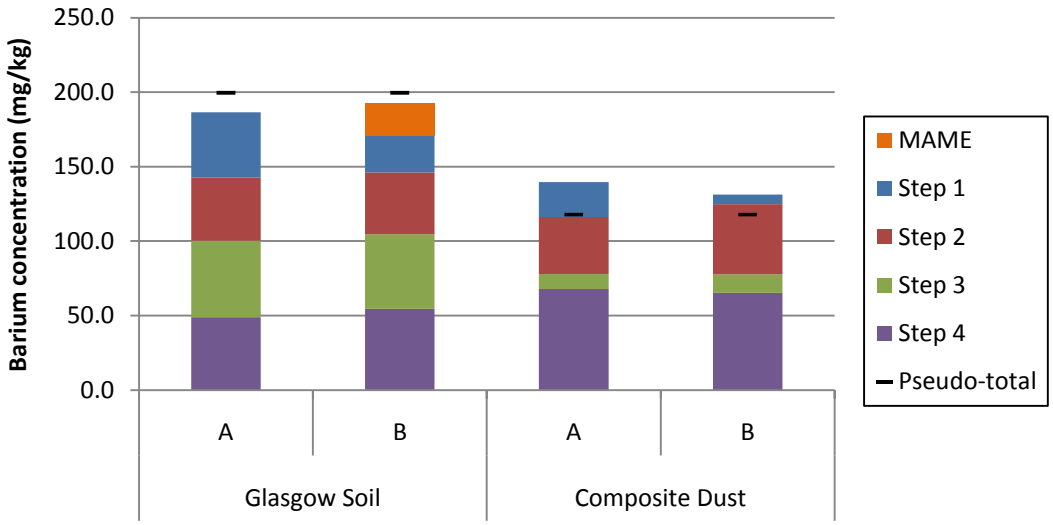


Figure 5-3 – Mean concentration obtained for barium in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of Glasgow soil and composite dust samples (n=3).

The total recoveries for the sequential extraction ranged from (93 – 119 %). The barium released in step 1 is lower when procedure B was applied, if compared visually for both samples. Steps 2-3 do not appear to show any particular difference. Table 5-5 shows the results of student t-tests comparing the two procedures.

Table 5-5 – Probability of t from student t-tests for Glasgow soil and composite dust sample barium results when comparing extraction with and without initial microwave-assisted micellar extraction

	Sample	Step 1	Step 2	Step 3	Step 4	Sum of Steps
P	Glasgow Soil	8.33E-10	0.661	0.575	0.094	0.112
	Composite Dust	7.36E-20	7.61E-04	3.22E-03	0.6676	0.2151

The results confirm that the two procedures were significantly different for the extraction in step 1, with the test failing for both samples. The t-test also failed when applied to steps 2 and 3 for the dust sample. Both step 4 and the pseudo-total barium concentration for both of the samples showed no significant difference at a 95 % confidence limit. Figure 5-4 shows the results as a fractionation pattern.

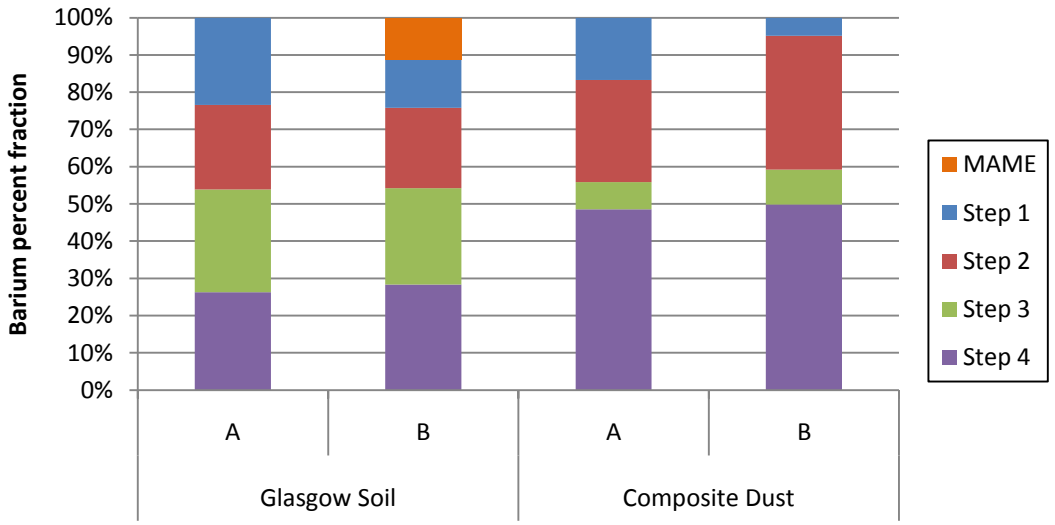


Figure 5-4 – Mean percentage fractionation of barium in Glasgow soil and composite dust samples after BCR sequential extraction with [B] and without [A] initial microwave-assisted micellar extraction.

The fractionation showed similarities between the two procedures and that barium is distributed throughout the four steps. In general the difference between fractions, extracted using different procedures, was less than 10 %, the exception being step 1 which showed the largest statistical difference.

The concentration of barium in the substrates investigated would indicate slightly higher levels in soil compared to RDS. The residual fraction of RDS contains the largest relative amount of barium, however in soil, levels are more evenly spread throughout the four fractions. This would imply that barium is potentially more environmentally mobile, with a higher fraction and concentration for the first three steps, in the soil matrix than in RDS. It would also indicate that sources of soil and RDS contamination are unrelated and possibly due to anthropogenic inputs.

5.4.3 Chromium

The mean results and RSD values for the measurement of chromium in each BCR sequential extraction step and pseudo totals are listed in appendix B. The precision of analysis was generally acceptable (< 10 %). Chromium released in step 1 from the composite dust showed poorer precision using both procedure A (19 % RSD) and B (20 % RSD), which is probably due to results being close to detection limits. The

mean concentration of chromium in each step of the BCR sequential extraction and pseudo-totals for both procedure A and B are shown in Figure 5-5.

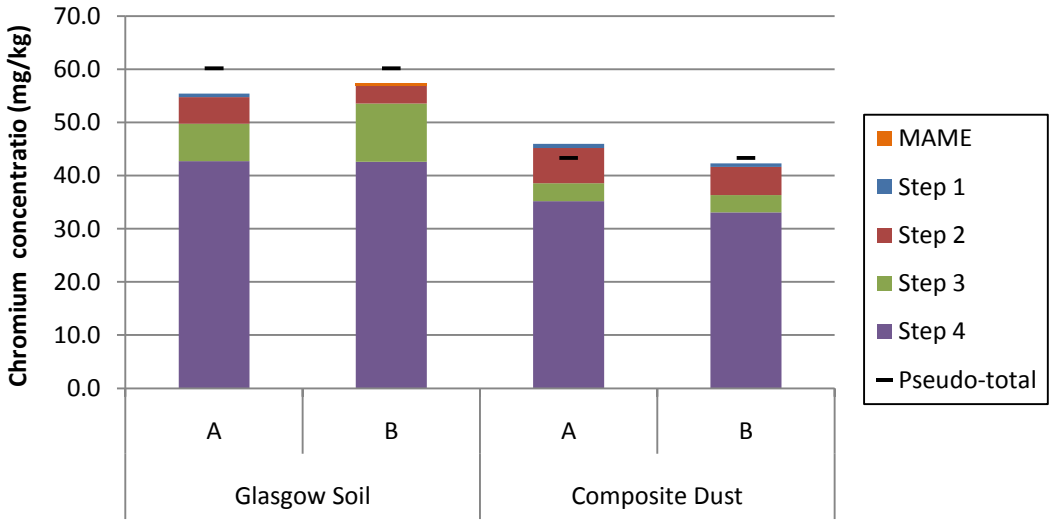


Figure 5-5 – Mean concentration obtained for chromium in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of Glasgow soil and composite dust samples (n=3).

The recoveries ranged from 92 – 106 % and showed mass balance with the pseudo-total results. The soil results, compared to the target values, showed that more chromium was released in step 2 (160 and 153 % recovery) and less in step 3 (72 % recovery). The target values were actually determined on a different sub-sample, so it is possible these different values may be correct for this sub-sample. The fractionation may also have changed over time while the sample was stored. These results were also consistent with the pseudo-total concentrations, which showed higher levels of chromium compared to the target value established on a previous sample. When procedure B was applied to the soil sample, less chromium was released from step 2 and more from step 3. The composite dust results in general are similar across the two procedures. The chromium released from step 1, for both samples, is lower on treatment with procedure B. Table 5-6 shows the results of student t-tests comparing the two procedures.

Table 5-6 – Probability of t from student t-tests for Glasgow soil and composite dust sample chromium results when comparing extraction with and without initial microwave-assisted micellar extraction

	Sample	Step 1	Step 2	Step 3	Step 4	Sum of Steps
P	Glasgow Soil	\	0.031	4.69E-04	0.966	0.602
	Composite Dust	0.314	0.891	0.211	0.364	0.414

The results showed there to be no significant difference, between the two procedures, at a 95 % confidence limit. The exceptions were steps 2 and 3, for the soil sample, which failed the t-test. There is no significant difference in the pseudo-total concentration, therefore the difference in steps 2 and 3 could again indicate that some analyte released in step 2 becomes bound to residual surfactant and is then re-released in step 3. Figure 5-6 shows the results as a fractionation pattern.

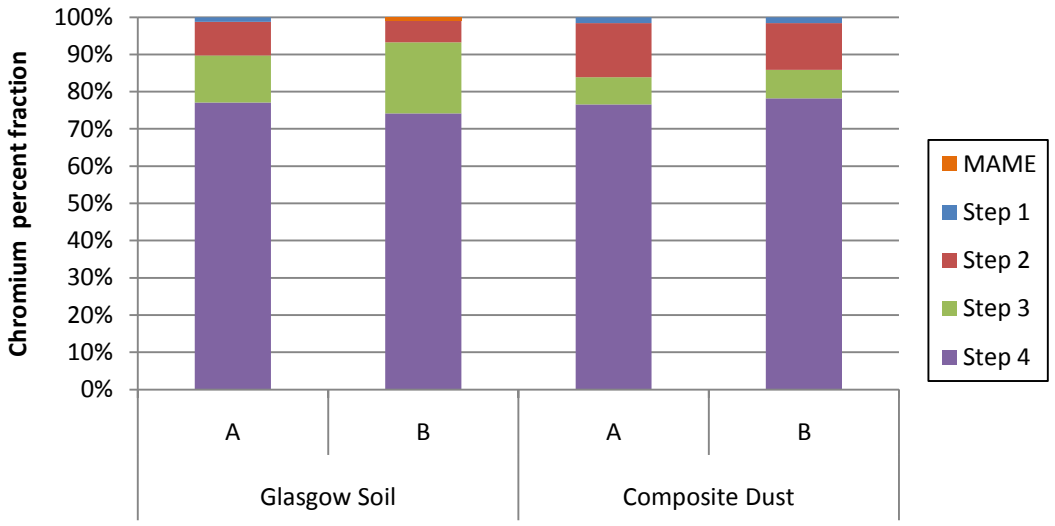


Figure 5-6 – Mean percentage fractionation of chromium in Glasgow soil and composite dust samples after BCR sequential extraction with [B] and without [A] initial microwave-assisted micellar extraction.

The figure shows that there is less than 10 % difference between the two procedures at each step and therefore similar fractionation occurs. The levels of chromium in soil and RDS, in the urban areas of Glasgow, would appear to be comparable (approximately 50 mg/kg). Around 75-80 % of chromium was found in the residual fraction for both soil and RDS. This could indicate that soil, through dispersion, is a source of chromium in RDS. However, chromium is not a common geogenic metal

in Glasgow and therefore it may be that both soil and RDS are contaminated from a common, possibly anthropogenic source.

5.4.4 Copper

The mean results and RSD values for the measurement of copper in each BCR sequential extraction step and pseudo totals are listed in appendix B. The CRM and soil sample showed acceptable precision (< 10 % RSD). The RSD values for the composite dust sample ranged from 5 – 32 %, indicating poorer precision, and were possibly due to real heterogeneity of the sample. Figure 5-7 shows the mean concentration of copper in each step of the BCR sequential extraction and pseudo-totals for both procedure A and B.

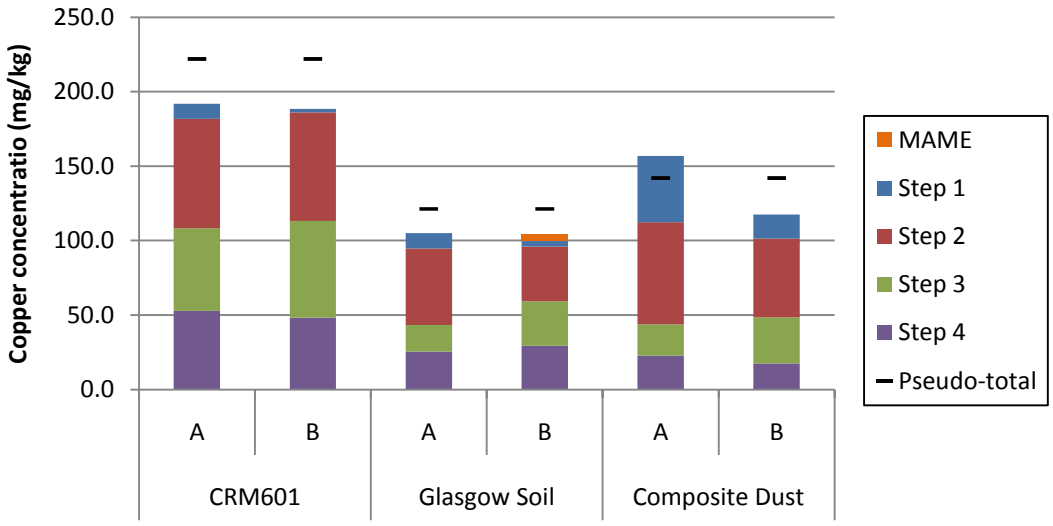


Figure 5-7 – Mean concentration obtained for copper in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of CRM BCR-601, Glasgow soil and composite dust samples (n=3).

The recovery of copper, compared to the pseudo-total concentrations were between 83 – 110 %. Visual comparison of the soil sample results to the target value showed over-extraction in step 2 and under-extraction in step 3. The CRM showed recoveries of 71 – 101 % over the four steps compared to the certified values. Step 3 was under-extracted, particular when procedure A was applied, in the CRM (71 %). Extraction using procedure B, compared to procedure A, showed less copper released in step 2 and more in step 3 for all three samples. Step 1, extracted using procedure

B for each of the sample, showed less than half the copper released by procedure A, and the CRM showed a 23 % recovery for the step. The total recovery for the CRM showed agreement of 86 and 85 %, for procedure A and B, respectively when compared to the target value. Table 5-7 shows the results of student t-tests comparing the two procedures.

Table 5-7 – Probability of t from student t-tests for CRM BCR-601, Glasgow soil and composite dust sample copper results when comparing extraction with and without initial microwave-assisted micellar extraction

	Sample	**Step 1**	**Step 2**	**Step 3**	**Step 4**	**Sum of Steps**
P	BCR-601	4.32E-05	0.750	0.041	0.225	0.310
	Glasgow Soil	4.16E-05	1.69E-05	1.76E-05	0.123	0.059
	Composite Dust	5.54E-07	0.130	8.44E-03	0.074	0.044

The t-test results confirmed the differences already highlighted for the release of copper in step 1. There were also significant difference in both steps 2 and 3, for the soil sample, where it again suggests that some analyte released in step 2 is then bound again and re-released in step 3. The t-test also failed for step 3 in both the CRM and dust sample. The t-tests passed, with no significant difference, for the release of copper in steps 2 and 4 in the CRM and dust sample. There was no significant difference for the pseudo-total copper concentration in any of the samples. Figure 5-8 shows the results as a fractionation pattern.

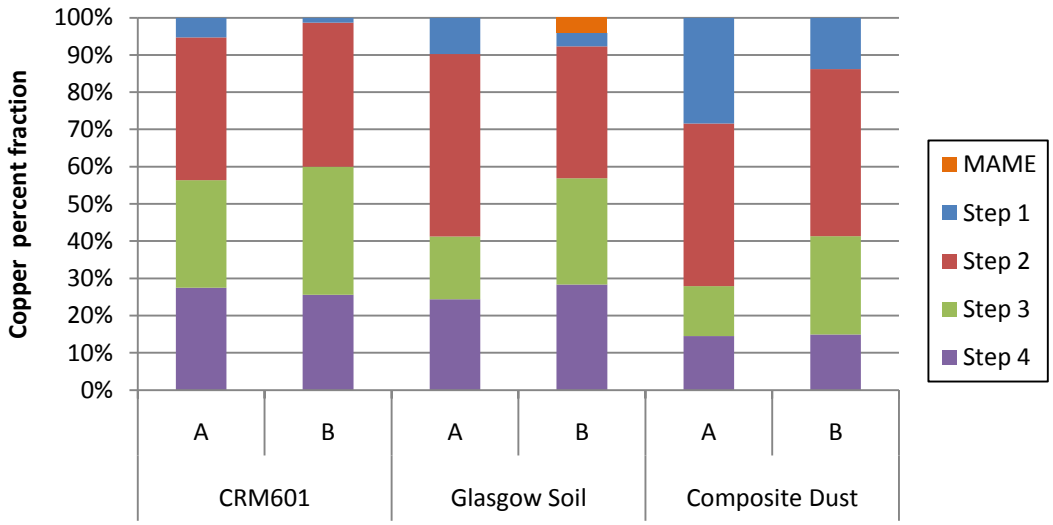


Figure 5-8 – Mean percentage fractionation of copper in CRM BCR-601, Glasgow soil and composite dust samples after BCR sequential extraction with [B] and without [A] initial microwave-assisted micellar extraction.

The patterns vary slightly between the different samples, although in general copper was released across steps 2-3, with the largest fraction being step 2 (37 – 49 %). The changes in steps 2 and 3 also slightly affect the trend when procedure B is applied, for the soil and dust samples, although step 2 remains the largest fraction. The CRM showed a more consistent trend between the two procedures, with less than 10 % between fractions. The dust, compared to the other two materials, showed a higher fraction for step 1.

The reducible fraction was found to contain the highest relative level of copper, for both soil and RDS, in substrates with comparatively similar concentrations. As 70-80 % of copper is found in the first three fractions for both soil and RDS, this could indicate greater environmental mobility in urban areas for both substrates. Copper has been identified as a "common urban metal" with anthropogenic sources leading to potential contamination. The similarities of copper would imply that either soil, via dispersion onto infrastructure, is a source of RDS or that both are potentially contaminated from a common anthropogenic source.

5.4.5 Iron

The mean results and RSD values for the measurement of iron in each BCR sequential extraction step and pseudo totals are listed in appendix B. The precision, as RSD values, was between 2 – 22 %, with slightly poorer precision when procedure B was applied. The mean concentration of iron in each step of the BCR sequential extraction and pseudo-totals for both procedure A and B, are shown in Figure 5-9.

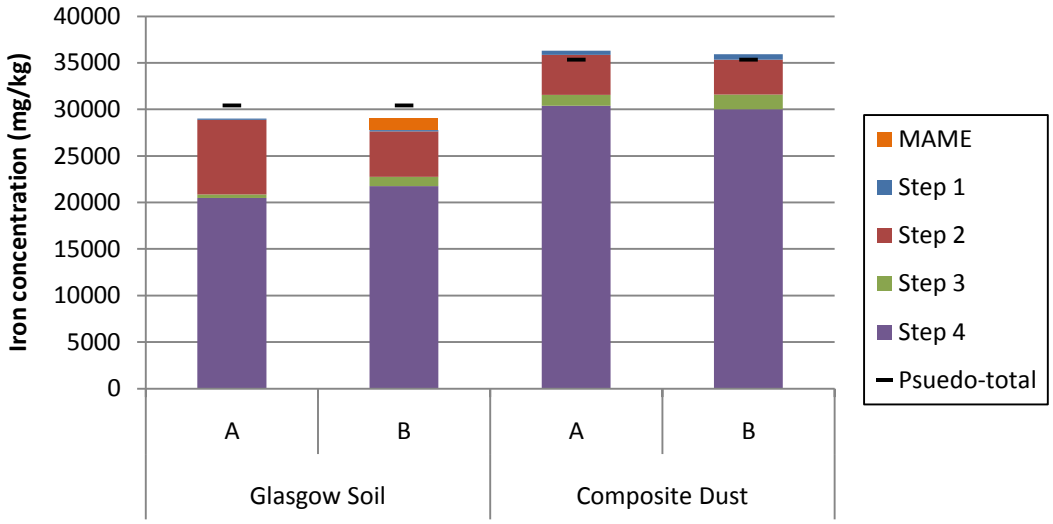


Figure 5-9 – Mean concentration obtained for iron in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of Glasgow soil and composite dust samples (n=3).

The recovery of iron, using the BCR sequential extraction, was between 95 – 103 % when either procedure was applied. The recovery for each of the steps, in the soil compared to the target values, were 72 – 119 %. There was under-extraction by the reagent in step 3 (33 %), when treated with procedure A. This could be due to inefficient extraction at that stage as release of other metals is also relatively low compared to the other steps. Table 5-8 shows the results of student t-tests comparing the release of iron using the two procedures.

Table 5-8 – Probability of t from student t-tests for Glasgow soil and composite dust sample iron results when comparing extraction with and without initial microwave-assisted micellar extraction

	Sample	Step 1	Step 2	Step 3	Step 4	Sum of Steps
P	Glasgow Soil	0.794	6.43E-04	1.65E-07	0.014	0.028
	Composite Dust	0.033	0.101	7.27E-03	0.734	0.764

The t-tests values showed that the release of iron, in steps 2 and 3 of soil analysis, was significantly different using the two procedures. This indicates the trend seen for other metals where the analyte normally expected to be extracted in step 2 is released in step 3. The dust sample also showed a significantly difference for step 3, but not for steps 2, however the respective decrease and increase of these two steps can be seen in the mean concentration values. In contrast to the other analytes, the iron released in step 1, is not significantly different for the two procedures for the soil sample. The test failed for the dust sample (step 1), however the magnitude of the result was less than observed for the other analytes. Figure 5-10 shows the results as a fractionation pattern.

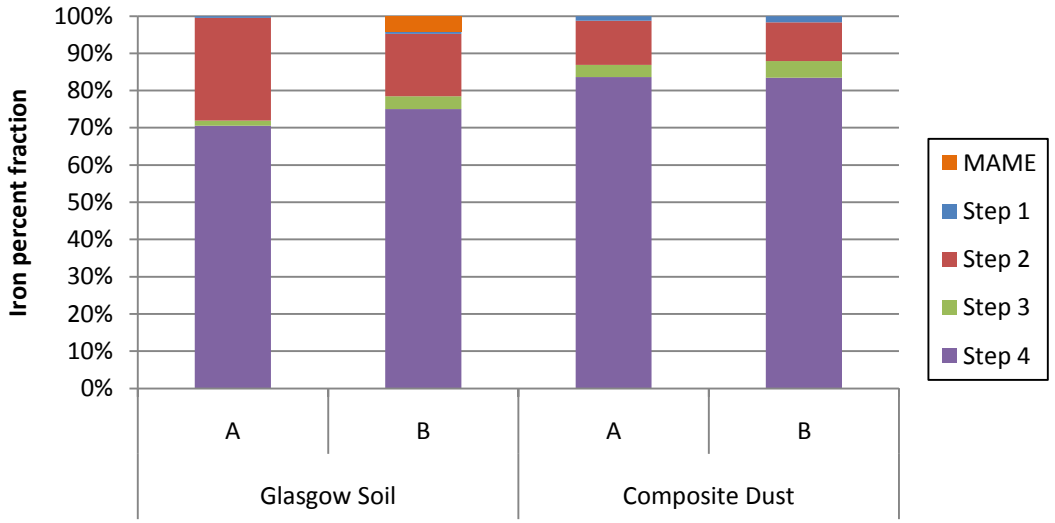


Figure 5-10 – Mean percentage fractionation of iron in Glasgow soil and composite dust samples after BCR sequential extraction with [B] and without [A] initial microwave-assisted micellar extraction.

The trends are similar across both samples and in all cases the majority of iron, 71-84 %, is released in step 4.

Soil and RDS showed similar levels of iron with approximately 3 and 3.5 %, respectively. Iron is a common constituent of mineral structures[18] and therefore these geogenic sources are more prominent than anthropogenic sources. The presence of 70-80 % of iron in the residual fraction, for both soil and RDS, would indicate that it is more strongly bound in parent minerals. This would indicate agreement that iron is due to geogenic sources and also that it is dispersed onto urban infrastructure as a component of soil, forming RDS.

5.4.6 Manganese

The mean results and RSD values for the measurement of manganese in each BCR sequential extraction step and pseudo totals are listed in appendix B. Precision of results were between 0.37 – 13 % (RSDs), however for manganese released by step 1 (procedure B) from the soil sample precision was poorer (27 %). Figure 5-11 shows the mean concentration of manganese in each step of the BCR sequential extraction and pseudo-totals for both procedure A and B.

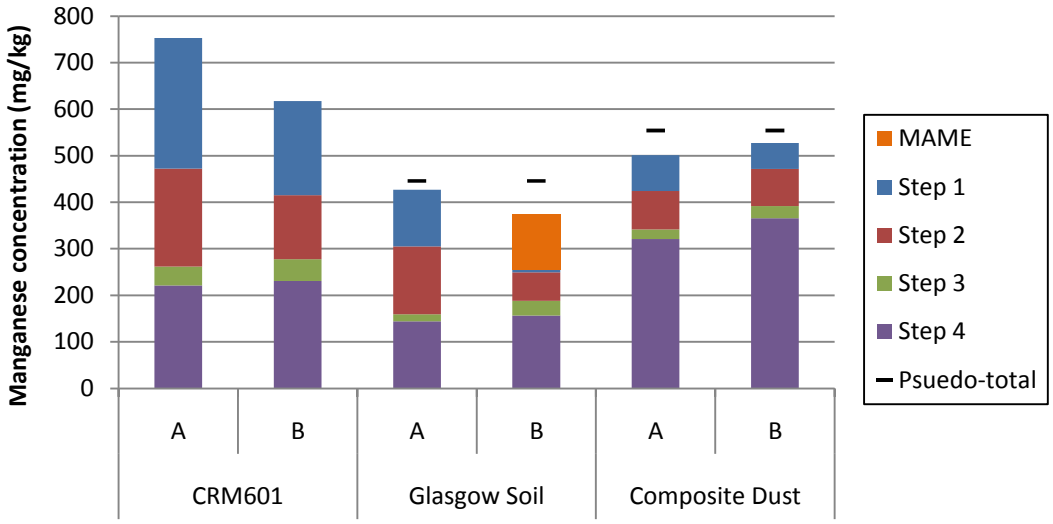


Figure 5-11 – Mean concentration obtained for manganese in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of CRM BCR-601, Glasgow soil and composite dust samples (n=3).

The soil and dust samples gave recoveries of 84 – 95 % compared to the pseudo-total values. The soil sample generally gave recoveries in the in the range 98 – 127 % for each step, however a low recovery of 46 and 59 % was obtained for step 2

(procedure B) and 3 (procedure A), respectively. On visual comparison the mean concentration of manganese in all samples released from step 2 decreases when procedure B is applied and the opposite occurs for step 3 as seen with many of the other metals. The results showed that more manganese is released in step 1 than for many of the other metals and subsequently more is potentially released by the MAME step of procedure B. This is confirmed by the concentration of manganese in the MAME step for the soil sample. Table 5-9 shows the results of student t-tests comparing the release of manganese using the two procedures.

Table 5-9 – Probability of t from student t-tests for CRM BCR-601, Glasgow soil and composite dust sample manganese results when comparing extraction with and without initial microwave-assisted micellar extraction

	Sample	Step 1	Step 2	Step 3	Step 4	Sum of BCR Steps
P	BCR-601	1.52E-04	2.16E-03	3.32E-03	0.138	0.191
	Glasgow Soil	1.00E-13	8.72E-08	9.16E-05	0.491	9.81E-08
	Composite Dust	7.99E-05	0.587	0.010	0.014	0.166

The t-test results showed there were significant differences between the two procedures for the release of manganese during step 1 from all three samples. The soil sample shows particular difference where nearly all manganese was lost from step 1 when procedure B is applied. This is due to 95 % of the manganese being released in the MAME step and subsequently this results in a significant difference in the pseudo-total manganese released from the soil. The pseudo-total manganese in the other two samples was not significantly different for the two procedures. The change in steps 2-3 between the two procedures also results in significant differences for these steps in both the reference material and the soil sample, but only step 3 in the dust sample. Step 4 showed statistically similar results whether procedure A or B was applied. Figure 5-12 shows the results as a fractionation pattern.

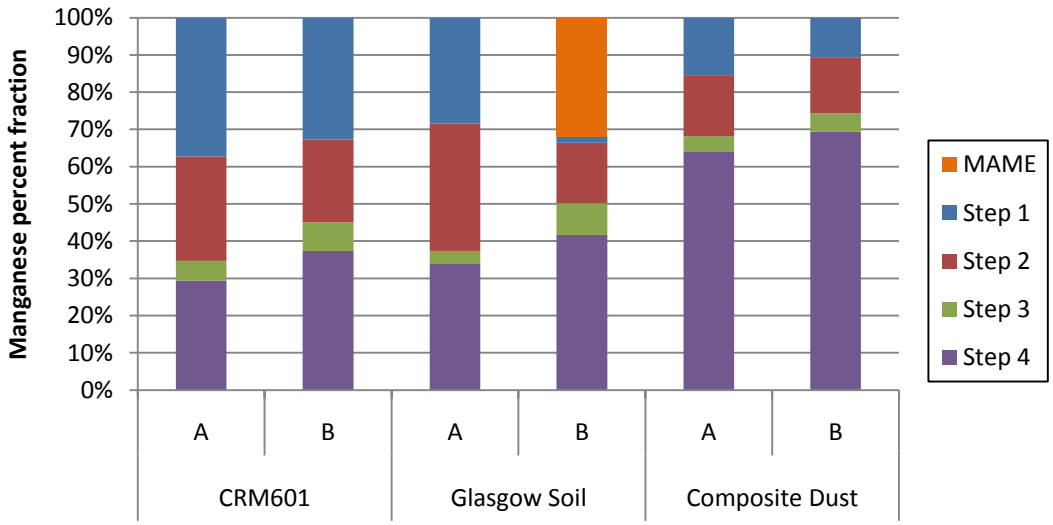


Figure 5-12 – Mean percentage fractionation of manganese in CRM BCR-601, Glasgow soil and composite dust samples after BCR sequential extraction with [B] and without [A] initial microwave-assisted micellar extraction.

The reference material and dust sample both showed similar patterns, when either procedure A or B was applied, with less than 10 % difference between the same stages in the two procedures. The soil sample showed a greater change in the pattern, with a difference of 27 % in step 1, between the two procedures. This can be accounted for by the manganese released in the MAME step. The decrease/ increase in steps 2 and 3 have already been observed, however the total of these steps also showed a change between the two procedures. The trend in the reference material and soil sample showed that manganese is distributed between step 1,2 and 4, with over 60 % in a potentially available form.

The fractionation of manganese was found to be different in soil and RDS. In soil approximately 60 % was present in the first two steps compared to RDS where around 60 % was in the residual fraction. Manganese oxyhydroxide mineral phases are one of the potential targets of the reducible fraction[180] (step 2) and this could indicate a geogenic source for the soil. The different fractionation for the RDS would imply a different source to the soil.

5.4.7 Nickel

The mean results and RSD values for the measurement of nickel in each BCR sequential extraction step and pseudo totals are listed in appendix B. The precision was generally less than 10 %, although release from step 1-2 for the dust sample showed poorer precision (9 – 22 % RSD). The reference material and soil sample also showed poorer precision when procedure B was applied with step 3 (37 %) and 2 (24 %), respectively. The mean concentration of nickel in each step of the BCR sequential extraction and pseudo-totals for both procedure A and B are shown in Figure 5-13.

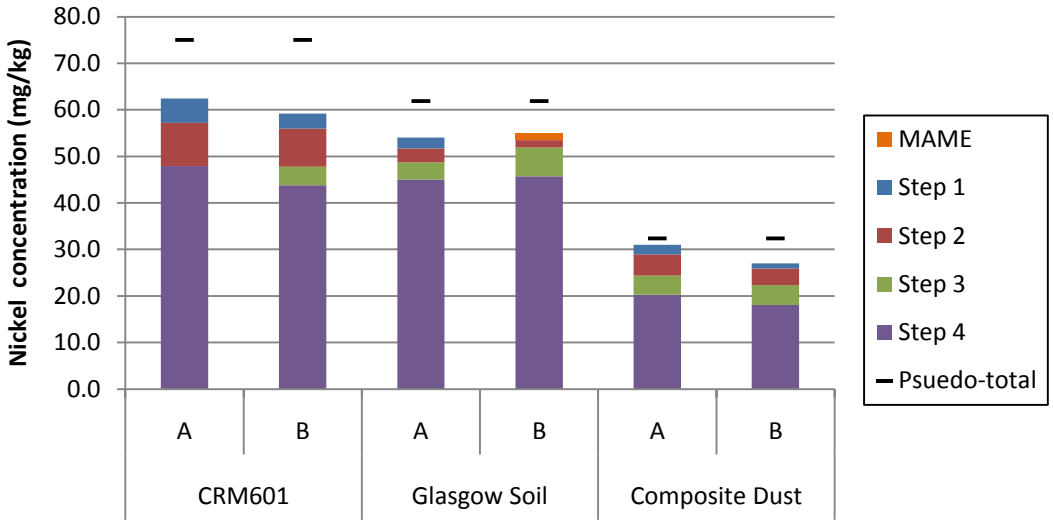


Figure 5-13 – Mean concentration obtained for nickel in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of CRM BCR-601, Glasgow soil and composite dust samples (n=3).

The mass balance of the BCR sequential extraction, compared to the pseudo-total, was acceptable with recoveries of 87 – 96 %. The CRM showed a slight low total recovery of 83 and 79 %, for procedure A and B, respectively when compared to the target value. The CRM showed acceptable recovery in step 2 and 4 (77 – 95 %), however step 1 showed under-extraction (66 % recovery) when treated with procedure A and subsequently lower with procedure B (41 % recovery). Step 3 showed poor extraction for the reference material the result being less than detection limits with procedure A, the concentration increased when procedure B was applied (66 % recovery). The soil sample, treated using procedure A, showed recoveries

between 79 – 114 % over the four steps. When procedure B was applied, there was a decrease in step 2 (51 % recovery) and a increase in step 3 (133 % recovery) for the soil sample and this was also seen for the other two samples which has been observed in other metal analytes. Step 1 also showed a low recovery when procedure B was applied, with nickel released by the MAME step. Table 5-10 shows the results of student t-tests comparing the release of nickel using the two procedures.

Table 5-10 – Probability of t from student t-tests for BCR CRM-601, Glasgow soil and composite dust sample nickel results when comparing extraction with and without initial microwave-assisted micellar extraction

	Sample	**Step 1**	**Step 2**	**Step 3**	**Step 4**	**Sum of Steps**
P	BCR-601	1.15E-03	0.070	\	0.065	0.148
	Glasgow Soil	5.03E-09	1.03E-04	8.25E-09	0.723	0.606
	Composite Dust	1.55E-04	0.012	0.064	0.059	6.13E-03

The t-tests performed on the results for step 1 showed that nickel released during the MAME step of procedure B resulted in significant differences between the two procedures. The significant differences in steps 2-3, already observed, are confirmed with failed t-tests for the soil sample. Step 4 showed no significant difference between the nickel released by application of either procedure for all three samples and only the dust sample failed the t-test for the pseudo-total nickel content. The statistical comparison of nickel in the soil sample would indicate that the changes between steps 2-3 do not affect the total content. The results for nickel are shown as a fractionation patterns in Figure 5-14.

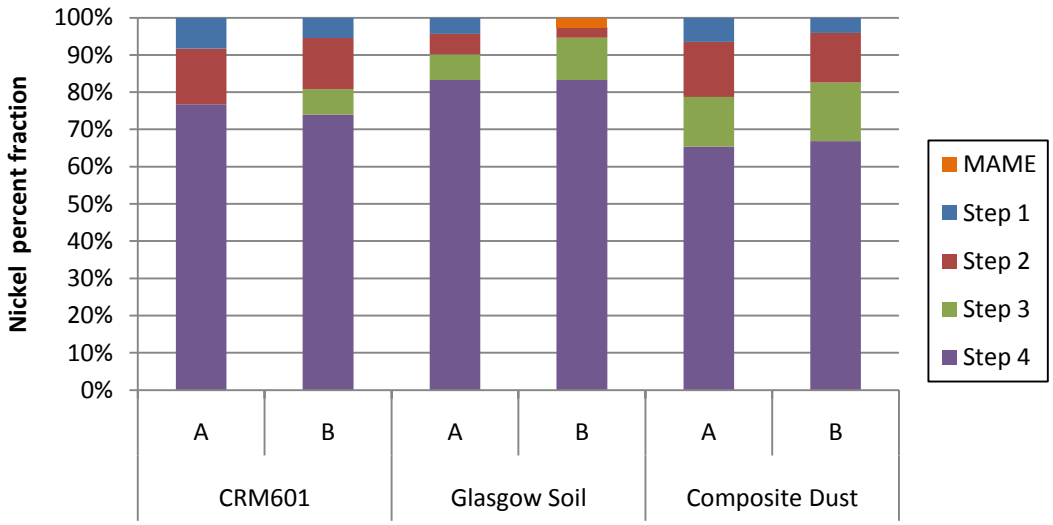


Figure 5-14 – Mean percentage fractionation of nickel in CRM BCR-601, Glasgow soil and composite dust samples after BCR sequential extraction with [B] and without [A] initial microwave-assisted micellar extraction.

The patterns were similar for all three samples, when either procedure A or B was applied, with less than 5 % difference between the same stages in the two procedures. The nickel released in step 3 (procedure A) for the reference was below detection limits and subsequently affects that fractionation between the two procedures. The step 1 result (procedure B) was also below detection limits for the soil sample; however this was detected as being released in the MAME step.

The majority of the nickel determined in both soil and RDS (~30–55 mg/kg) was present in the residual fraction (~65-80 %). This could indicate that potential contamination of both substrates with nickel, is due to common anthropogenic sources. However, as only up to 30 % of the total concentrations are present in the first three fractions, it will not be particularly mobile in the urban environment.

5.4.8 Lead

The mean results and RSD values for the measurement of lead in each BCR sequential extraction step and pseudo totals are listed in appendix B. The reference material and soil sample generally showed acceptable precision (< 10 % RSD), although poorer precision can be observed when procedure B is applied. The precision of analysis for the dust sample is also poorer (4 – 24 % RSD). Figure 5-15

shows the mean concentration of lead in each step of the BCR sequential extraction and pseudo-totals for both procedure A and B.

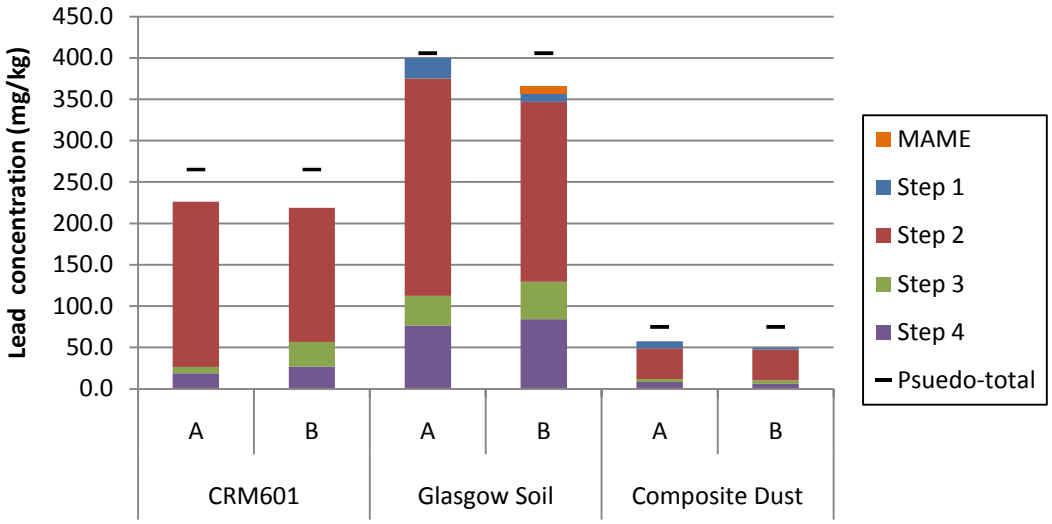


Figure 5-15 – Mean concentration obtained for lead in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of CRM BCR-601, Glasgow soil and composite dust samples (n=3).

The recovery of lead by the BCR sequential extraction, compared to the pseudo-total, was between 77 – 99 %, with under-extraction of the dust sample treated using procedure B (66 % recovery). The pseudo-total lead recovery for the CRM, compared to the target value, was 85 and 83 % for procedure A and B, respectively. The results for lead released in step 1 were below the detection limits for the CRM. Step 2 showed acceptable agreement with the target (97 % recovery) using procedure A, there was a decrease in the step with procedure B (79 % recovery). The results showed inefficient extraction for step 3 (39 %) with a large increase when procedure B was applied (151 % recovery). The recovery of lead for the soil sample was between 85 – 115 % compared to target values, with the exception of step 1 (43 % recovery in procedure B) and step 3 (68 % recovery in procedure A). Table 5-11 shows the results of student t-tests comparing the release of lead using the two procedures.

Table 5-11 – Probability of t from student t-tests for CRM BCR-601, Glasgow soil and composite dust sample lead results when comparing extraction with and without initial microwave-assisted micellar extraction

	Sample	Step 1	Step 2	Step 3	Step 4	Sum of Steps
P	BCR-601	\	7.25E-04	0.010	3.75E-04	0.140
	Glasgow Soil	1.17E-08	5.64E-04	0.015	0.240	6.31E-04
	Composite Dust	2.50E-05	0.835	0.145	0.022	0.011

The release of lead from step 1, using the two procedures, shows significant differences in both the soil and dust samples. There were significant differences in the lead extracted with step 2 and 3 by the two procedures, for the reference material and soil sample, and have been observed in the change in concentration for steps 2-3. The dust sample was not significantly affected by any changes in the concentration of step 2 or 3. The pseudo-total lead in the samples showed significant differences for the soil sample, however changes in the steps for the reference material did not affect the overall lead content. The results for lead are shown as a fractionation patterns in Figure 5-16.

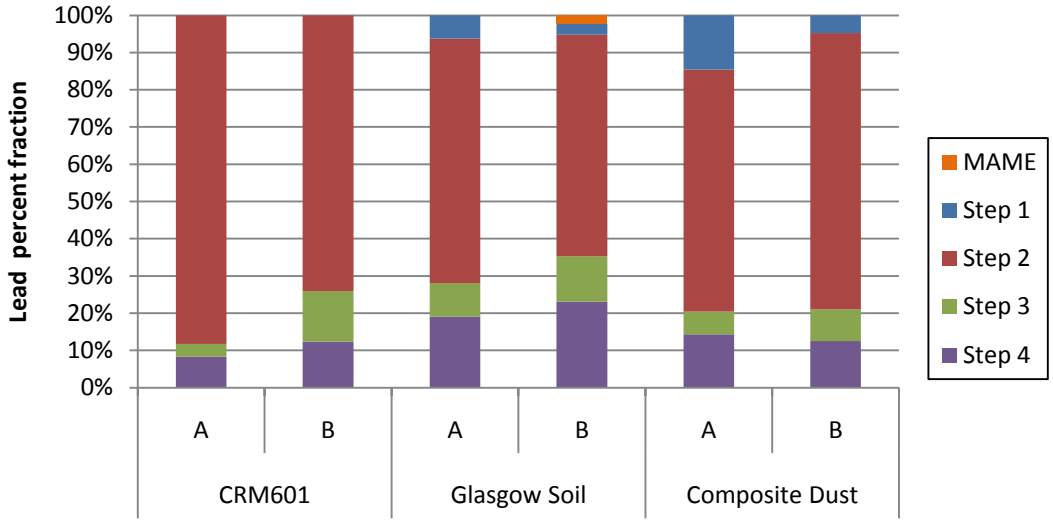


Figure 5-16 – Mean percentage fractionation of lead in CRM BCR-601, Glasgow soil and composite dust samples after BCR sequential extraction with [B] and without [A] initial microwave-assisted micellar extraction.

The difference between the same stages in the two procedures, for each of the samples, was generally less than 10 %. The exceptions were step 2-3, for the reference material, where the differences were 14 and 10 %, respectively.

The concentration of lead in soil was around eight times greater than that in RDS, although the majority was present in the reducible fraction for both substrates (~60-70 %). This would imply a greater mobility of lead in the urban environment and is consistent with the analyte being labelled a "common urban metal" along with copper and zinc. The comparable relative fractionation of the two substrates would indicate the possibility of a common anthropogenic source.

5.4.9 Zinc

The mean results and RSD values for the measurement of zinc in each BCR sequential extraction step and pseudo totals are listed in appendix B. In general the precision was acceptable for the three samples (0.8 – 12 % RSD), however poorer precision was seen when using procedure B for steps 1 (42 % RSD) and 2 (18 % RSD) for the soil sample. The dust sample also showed poorer precision for some steps (13 – 21 %). The mean concentration of zinc in each step of the BCR sequential extraction and pseudo-totals for both procedure A and B are shown in Figure 5-17.

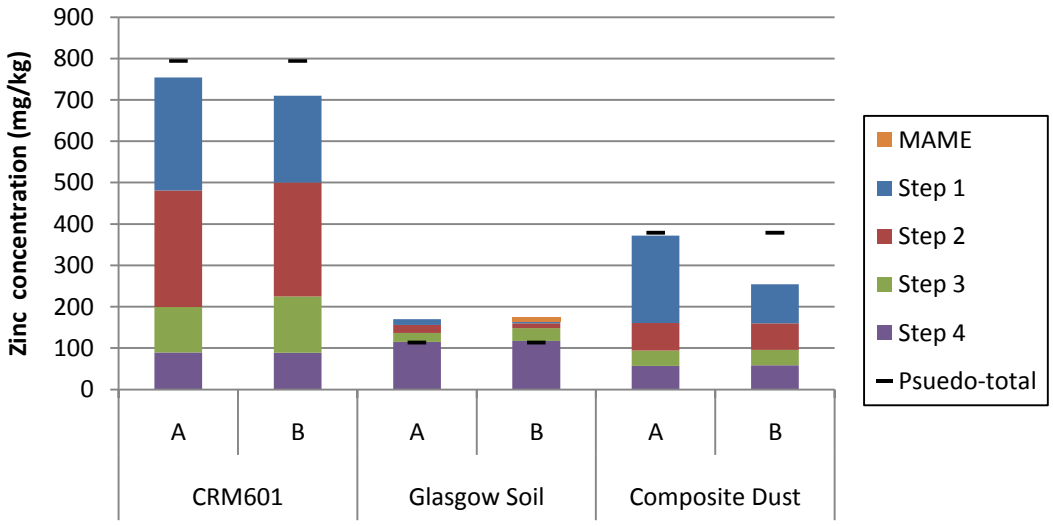


Figure 5-17 – Mean concentration obtained for zinc in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of CRM BCR-601, Glasgow soil and composite dust samples (n=3).

The recovery of zinc, compared to the pseudo-total concentrations, was between 67 – 142 %. The composite dust (procedure B) showed under-extraction with the BCR

sequential extraction (67 % recovery), mainly due to the observed loss in step 1. The poor mass balance for the Glasgow soil can be explained due to the low recovery of the pseudo-total result and when compared to the target value recoveries of 91 and 93 % are achieved for procedures A and B, respectively. The CRM, treated using procedure A, showed agreement with target values for steps 1-3 (103 – 106 % recovery), although step 4 showed under-extraction (56 %). When procedure B was applied there was a decrease in the recovery of steps 1-2 (80 and 104 %) and an increase in step 3 (129 %). However total recovery, for the CRM, compared to the target was 95 and 89 % for procedure A and B, respectively. The soil sample shows the same changes, with a decrease in recovery for steps 1-2 and an increase in step 3. Table 5-12 shows the results of student t-tests comparing the release of zinc using the two procedures.

Table 5-12 – Probability of t from student t-tests for CRM BCR-601, Glasgow soil and composite dust sample zinc results when comparing extraction with and without initial microwave-assisted micellar extraction

	Sample	**Step 1**	**Step 2**	**Step 3**	**Step 4**	**Sum of Steps**
P	BCR-601	0.020	0.357	0.098	0.639	0.258
	Glasgow Soil	5.44E-06	1.49E-04	5.96E-04	0.656	0.254
	Composite Dust	2.63E-07	0.634	0.907	0.726	3.91E-04

The t-tests performed on the results for step 1 showed that zinc released during the MAME step of procedure B resulted in significant differences between the two procedures, for all three samples. The change in steps 2-3 for the soil sample was observed for zinc, as with many other metals, and subsequently t-tests failed for both steps. The sum of the four steps for the soil sample showed no significant difference and therefore the changes in steps 2-3 did not affect the total zinc content. There was no statistical difference for steps 2, 3 or 4 in either the reference material or the dust sample. The results for zinc are shown as fractionation patterns in Figure 5-14.

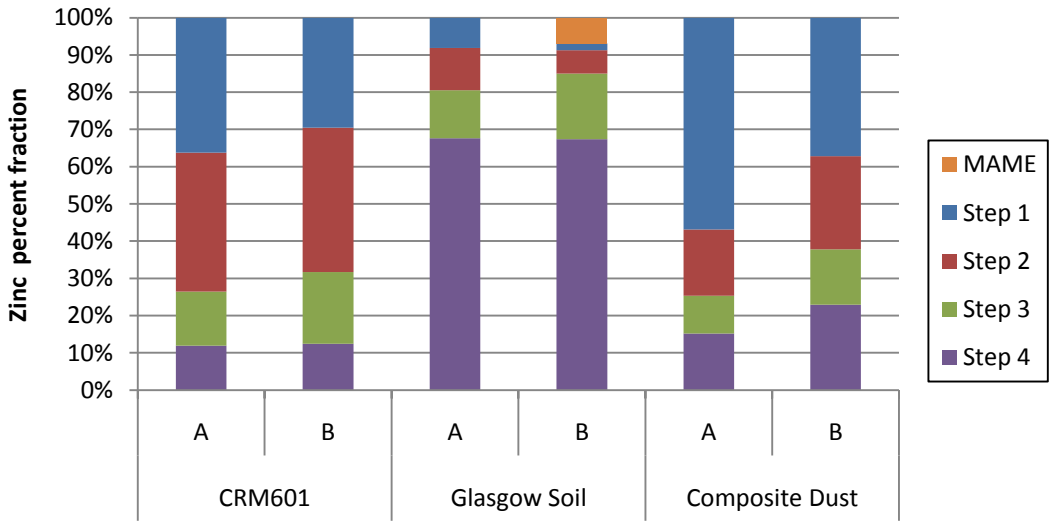


Figure 5-18 – Mean percentage fractionation of zinc in BCR CRM-601, Glasgow soil and composite dust samples after BCR sequential extraction with [B] and without [A] initial microwave-assisted micellar extraction.

The difference between the same stages in the two procedures, for each of the samples, was generally less than 10 %. The step 1 extraction of zinc for the RDS sample was the exception with a difference of 20 % between the two procedures. The loss of zinc to the MAME step in procedure B subsequently affected the rest of the fractionation, although the dominance of each fraction was the same (step 1 > step 2 > step 4 > step 3), with the majority of the zinc released in step 1.

The concentrations of zinc determined in the substrates would imply that a greater amount is present in RDS compared to soil. The extractable fraction was found to be the largest for the RDS, whereas the largest relative fraction for the soil was the residual step and subsequently there was around 50 % more potentially available zinc in RDS than soil. Zinc, like copper and lead, has been identified as a "common urban metal" and can often be found in urban substrates due to anthropogenic inputs. The differences in the fractionation patterns may imply the zinc present in the two substrates is due to different anthropogenic sources.

5.5 Conclusions

The mass balance of the BCR sequentially extracted metal concentrations with the pseudo-total digestion metal concentrations were in agreement for most analytes. The recoveries of analytes from step 1 were nearly always lower when procedure B was applied compared to procedure A. This suggested that the metal was being extracted in the MAME step and analysis of the POLE extract for the Glasgow soil sample determined concentrations which accounted for that lost from step 1.

The mass balance was generally poorer for the composite dust sample which was probably due to heterogeneity of the sample, shown by higher RSDs for most of the analytes. Therefore there was more potential variation between the sum of the BCR steps and the pseudo-total result leading to higher or lower recoveries. Poor mass balance for zinc, in the Glasgow soil, was probably due to low recovery of the metal in the pseudo-total digestion.

The release of analyte in the MAME step only affected the overall fractionation when step 1 was a dominant fraction, for example for manganese. The Glasgow soil showed 95 % (120 mg kg^{-1}) of the manganese expected in step 1 to be released in the MAME step 1 and subsequently significant differences, using a t-test, were observed for total manganese between the two procedures. It was therefore important to include the concentration determined for the MAME step to balance the total manganese and also resultantly observing no statistical differences.

Steps 2 and 3 generally showed similar changes, for each of the samples, when procedure B was applied for extraction of the analytes studied. The concentration determined in step 2 nearly always decreased, whereas there was an increase in step 3. This might suggest that the surfactant which was not washed from the extraction vessel may cause the mobility of some analytes normally associated with step 2 and subsequently they are released in step 3 where the reagent potentially targets the organic phase. This difference in steps 2 and 3 was always observed between the two procedures for the soil sample and confirmed by statistical differences. The reference material and dust sample only showed significant differences for both steps

2-3 in a single analyte each. In general the fractionation patterns were not affected by using procedure B and the same dominant fractions could still be observed.

The fractionation can be used for environmental interpretation and the larger the fraction of steps 1-3 the greater the potential mobility of the analyte. The soil sample indicated mobility decreasing in the order of Pb>Cu>Ba>Mn>Zn>Fe>Cr>Ni=Al, the dust sample in the order of Pb>Cu>Zn>Ba>Ni>Cr>Al>Fe, and the CRM Pb>Zn>Cu>Mn>Ni. The order of mobility was the same for both procedures and therefore the MAME step does not affect this environmental interpretation. The three samples showed similar trends which would indicate the sources of the analytes are similar, where elements associated with anthropogenic factors are likely to be more mobile than more naturally occurring elements which can be strongly bound to phases of the soil matrix.

It is also possible to consider variation in the fractionation pattern as an indication of anthropogenic influence. The iron fractionation patterns were similar for both the soil and dust sample and the residual fraction dominated. This suggests iron is strongly bound in the soil mineral matrix and subsequently from a natural source. In contrast copper and zinc showed high variability in their fractionation patterns and different fractions were dominant over the three samples. This would suggest anthropogenic influence with metals being released in different steps and would indicate they came from different sources.

The addition of the MAME step was shown to statistically effect the fractionation of some elements for some of the steps, in particularly step 1. However, environmental interpretation through observed trends is similar for both procedures and the sequential procedure (including MAME and BCR steps) can be used comparably to the BCR sequential extraction.

It has been shown that it is possible to first apply a reagent for the extraction of PAHs without affecting the recovery of the metals by more than 10 %, using either *aqua regia* pseudo-total digestion or the BCR sequential extraction method. It is

therefore possible to quantify the metal content in environmental substrates after the potential release of PAHs using microwave-assisted micellar extraction.

6 Development of a method for the determination of polycyclic aromatic hydrocarbons in microwave-assisted micellar extracts

6.1 Introduction

The sequential extraction procedure, under development during this research, involves the liberation of both PAH and PTE from urban environmental substrates. The previous chapters have investigated the effect, on PTE released by digestion or extraction methods, when the samples have been pre-treated for the potential extraction of PAH. Previous investigations assessing the methods of extracting organic species and the levels of PAHs in urban environmental substrates has been discussed in section 1.4.2.1. There are numerous PAHs and so representative analytes needed to be chosen for investigation. The USEPA has highlighted sixteen priority PAH pollutants and these were chosen as the analytes to be investigated.

6.2 Aim

The aim of this part of the work was the development and optimization of an analysis method for the detection of PAH analytes extracted into a micellar medium based on polyoxyethylene 10 lauryl ether (POLE).

6.3 Experimental

6.3.1 Samples

Calibration solutions and spiked solutions were initially studied in order to develop the analysis method. Spikes solutions were prepared by adding a known concentration of PAH stock standard solution to the POLE solution. Environmental substrate spikes were prepared by mixing a known concentration of PAH stock standard to 1 g of soil. The substrate were then stored in the dark and allowed to dry. LGC-6188, a certified reference material, is certified for content of 15 of the USEPA

priority PAH pollutants and was studied as supplied. The certified values for the content of PAH in LGC-6188 are given in Table 6-1.

Table 6-1 – Certified PAH concentrations (mg kg^{-1}) in LGC-6188[181]

	Certified Value [a]	**Uncertainty [b]**	**p**
Naphthalene	0.22	0.11	12
Acenaphthene	0.07	0.02	10
Fluorene	0.12	0.04	14
Phenanthrene	1.04	0.30	16
Anthracene	0.36	0.11	15
Fluoranthene	1.79	0.35	18
Pyrene	1.48	0.50	17
Chrysene	0.83	0.16	15
Benzo[a]anthracene	0.83	0.18	12
Benzo[b]fluoranthene	0.82	0.19	16
Benzo[k]fluoranthene	0.5	0.08	13
Benzo[a]pyrene	0.65	0.14	15
Dibenz[a,h]anthracene	0.13	0.05	14
Indeno[1,2,3-c,d]pyrene	0.37	0.14	14
Benzo[g,h,i]perylene	0.36	0.13	12

[a] mean value of p sets of data obtained from different laboratories
[b] half width of the 95% confidence interval of the mean

6.3.2 Extraction and Analysis

Environmental samples were extracted in a microwave using POLE as described in section 2.5.1. Spiked solutions were analysed as prepared. Analysis was performed by HPLC-UV for the sixteen PAH pollutants, initially using the conditions described in section 2.7. Procedures for pre-concentration and clean-up of samples were developed and performed using SPE columns (Chromabond® CN/ SiOH SPE columns were obtained from Thames Restek, Buckinghamshire, UK).

6.4 Results and discussion

6.4.1 Development of a high-performace liquid chromatography analysis method

The application of surfactant solutions for the extraction of various organic species has been previously researched with liquid chromatography as the technique of choice for PAH analysis[93,113-114,143]. This has been performed using reverse-phase HPLC, with a C18 column and either ultra-violet or fluorescence detection. Pino *et al.*[113] used HPLC in their work developing the extraction of PAH from sediment using POLE. They used a reverse-phase C18 column and gradient elution with an acetonitrile-water mixture (a linear gradient from 55 to 100% acetonitrile over 30 minutes and 100% acetonitrile for 10 minutes, at a flow-rate of 1 ml /min). Detection was performed using a UV/visible detector at a wavelength of 254 nm.

The conditions from the previous investigation were used as the starting point in the current work. When applied to the analysis of a multi analyte standard solution containing 16 priority pollutant PAHs the chromatogram shown in Figure 6-1 was obtained.

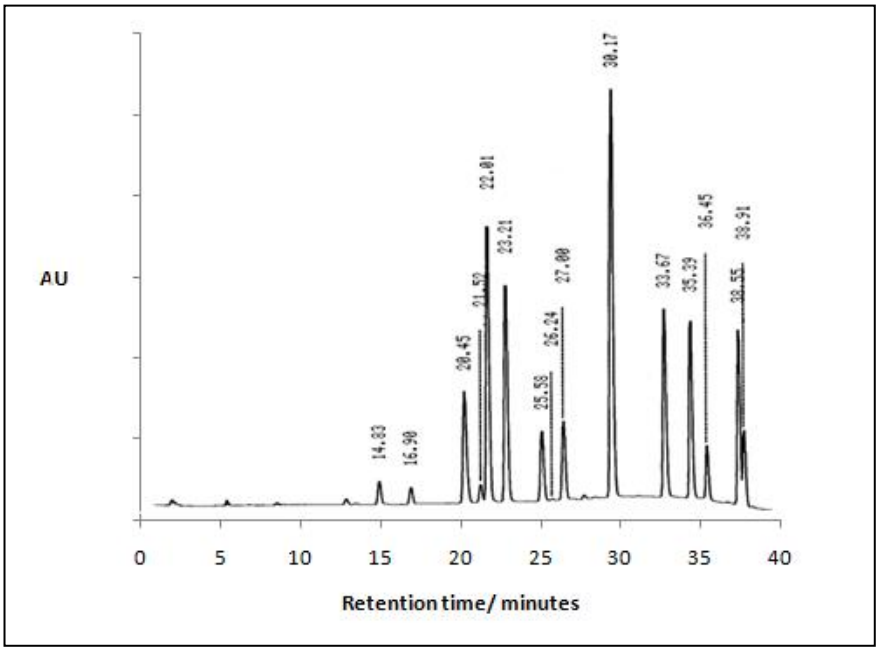


Figure 6-1 – Chromatogram of a 1.0 µg mL^{-1} standard solution of the 16 USEPA priority PAH obtained using the chromatographic conditions of Pino et al.[113]

The overall run time for the analysis was over 40 minutes and therefore optimization was performed to reduce the analysis time while maintaining or improving the quality of separation. Once the system was optimised the peaks in the chromatogram could be assigned in relation to the known content. Different flow rates and gradient programs were applied (Table 6-2) for analysis of the multi analyte standard solution. The chromatograms obtained for each of the four conditions are shown in Figure 6-2.

Table 6-2 – Gradient and flow rate conditions for optimization of HPLC

Conditions	Gradient		Flow rate/ mL min^{-1}
	Composition/ %	Duration/ minutes	
1	65% → 100% acetonitrile;	30;	1.0
2	100% acetonitrile	10	1.2
3	80% → 100% acetonitrile;	30;	1.0
4	100% acetonitrile	10	1.2

All four conditions resulted in adequately resolved chromatograms, with the exception of the final two peaks which co-eluted. The overall elution time, for the PAH standard, were 36, 33, 27 and 25 minutes for conditions 1 – 4, respectively. The minimum overall retention time was achieved using condition 4 and peak resolution was still acceptable.

The results showed that the earlier eluting PAHs (smaller molecules) elute closer together, whilst peaks due to larger ringed systems where further apart. The gradient composition was subsequently modified to change more slowly as elution started and then faster towards the end of the elution (see Table 6-3). When this set of conditions was used to analyse the PAH standard (Figure 6-3) the overall retention time improved to 24 minutes.

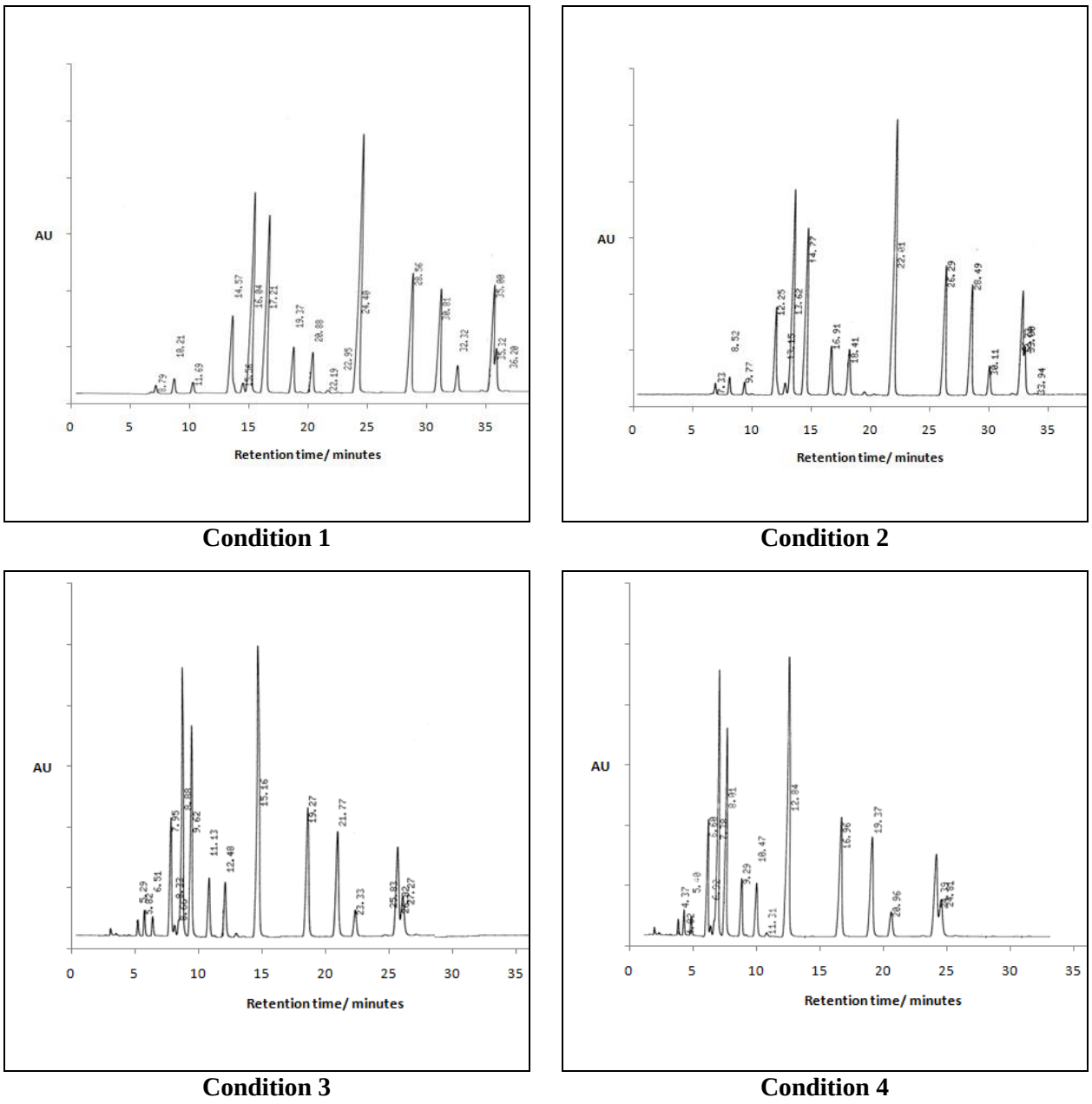


Figure 6-2 – Chromatograms of a 1.0 µg mL^{-1} standard solution of the 16 USEPA priority PAH obtained using four different chromatographic conditions (see Table 6-2)

Table 6-3 – Optimised gradient and flow rate conditions for HPLC analysis of PAH

Conditions	Gradient		Flow rate/ mL min^{-1}
	Composition/ %	Duration/ minutes	
Set 5	80% → 90% acetonitrile; 90% → 100% acetonitrile; 100% acetonitrile	15 5 5	1.2

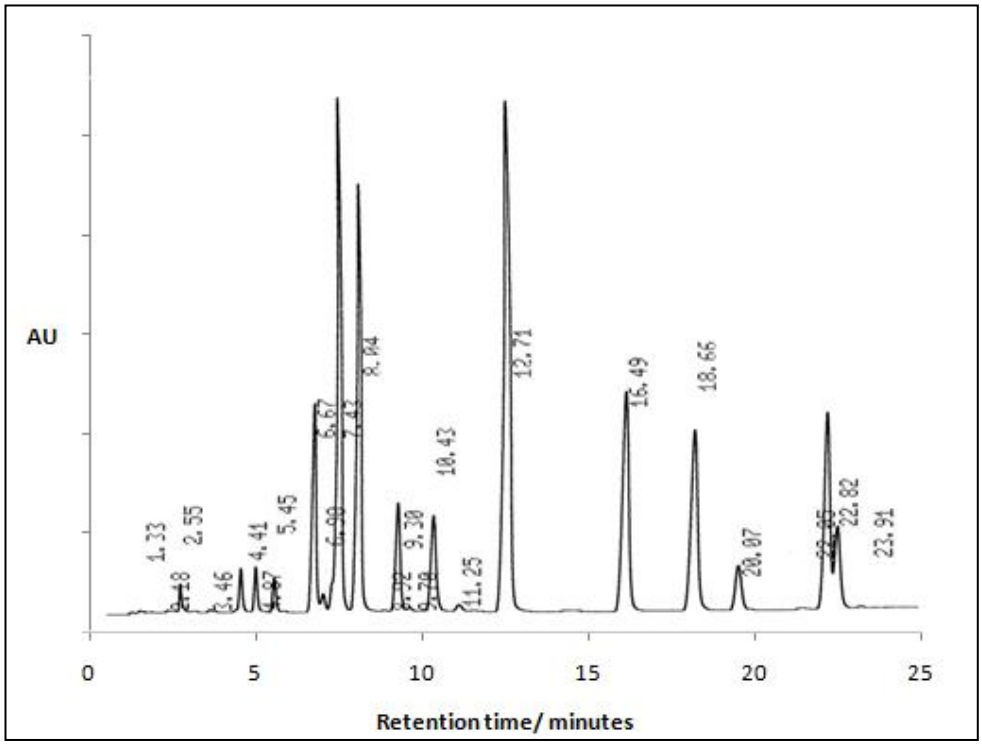


Figure 6-3 – Chromatogram of a 1.0 µg mL^{-1} standard solution of the 16 USEPA priority PAH obtained using optimised chromatographic conditions (see Table 6-3)

The optimised conditions resulted in a chromatogram with 14 peaks, for analysis of the multi analyte standard solution. In order to assign the peaks to specific PAHs single analyte standard solutions for six of the PAH analytes (naphthalene, fluorene, anthracene, pyrene, benzo[b]fluoranthene and benzo[ghi]perylene) were analysed by HPLC-UV, using the optimised conditions, and their retention times determined (Table 6-4).

Table 6-4 – Retention times obtained from the chromatograms of six single analyte standard solutions analysed using optimised chromatographic conditions

PAH	Retention time/ minutes
Naphthalene	4.91
Fluorene	6.88
Anthracene	8.44
Pyrene	10.80
Benzo[b]fluoranthene	16.42
Benzo[ghi]perylene	24.10

The retention times of the six analytes were compared to those in the chromatogram of the multi analyte standard solution (Figure 6-4).

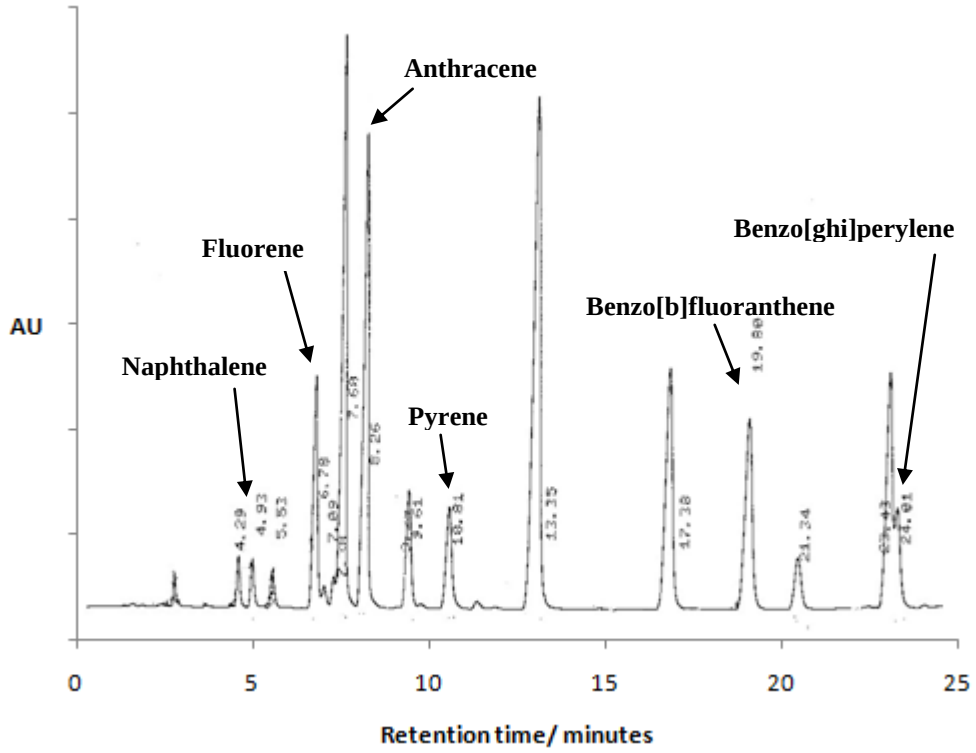


Figure 6-4 – Chromatogram of 16 PAH standard solution assigning six primary standard solutions according to retention time

There was agreement between the retention times of the single analyte standard solutions and six peaks in the mixed standard. The components identified in the multi analyte standard solution were consistent with the expected elution order due to the relative polarity of each component[152].

A second HPLC system, with a diode array detector, was used to analyse the mixed analyte standard solution and obtain ultraviolet spectra for the components in the mixture. Figure 6-5 and Figure 6-6 show the standard UV spectra for each of the 16 components.

The system was used in parallel with optimization of the fixed wavelength HPLC-UV and therefore the first set of instrumental conditions were applied (Table 6-2). The retention times in the chromatogram obtained were consistent with those in

Figure 6-2. The UV spectrum for each peak in the chromatogram of the multi analyte standard solution and the six single standards were recorded (Figure 6-7).

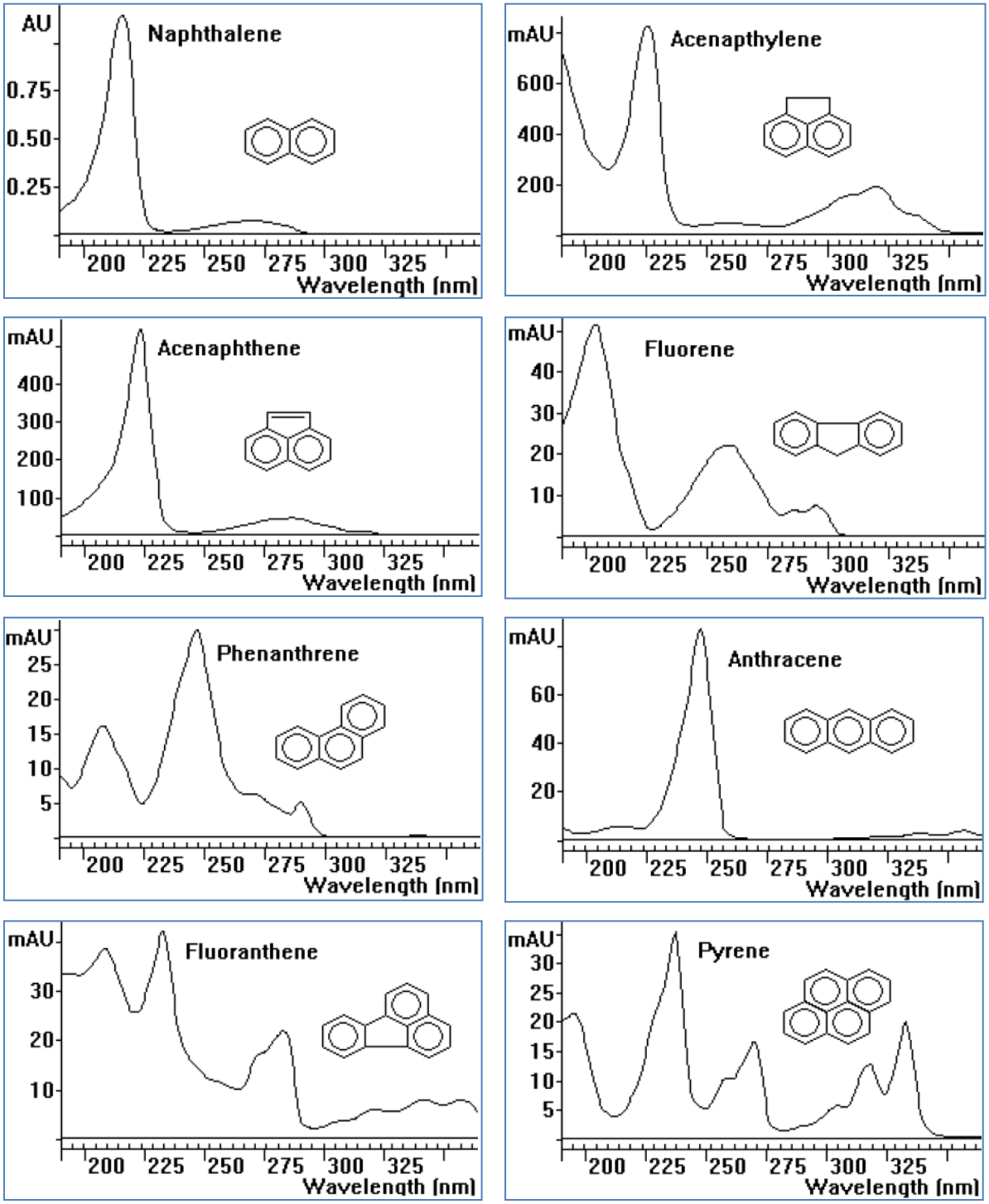


Figure 6-5 - UV spectra of the first 8 USEPA PAH priority pollutants[182]

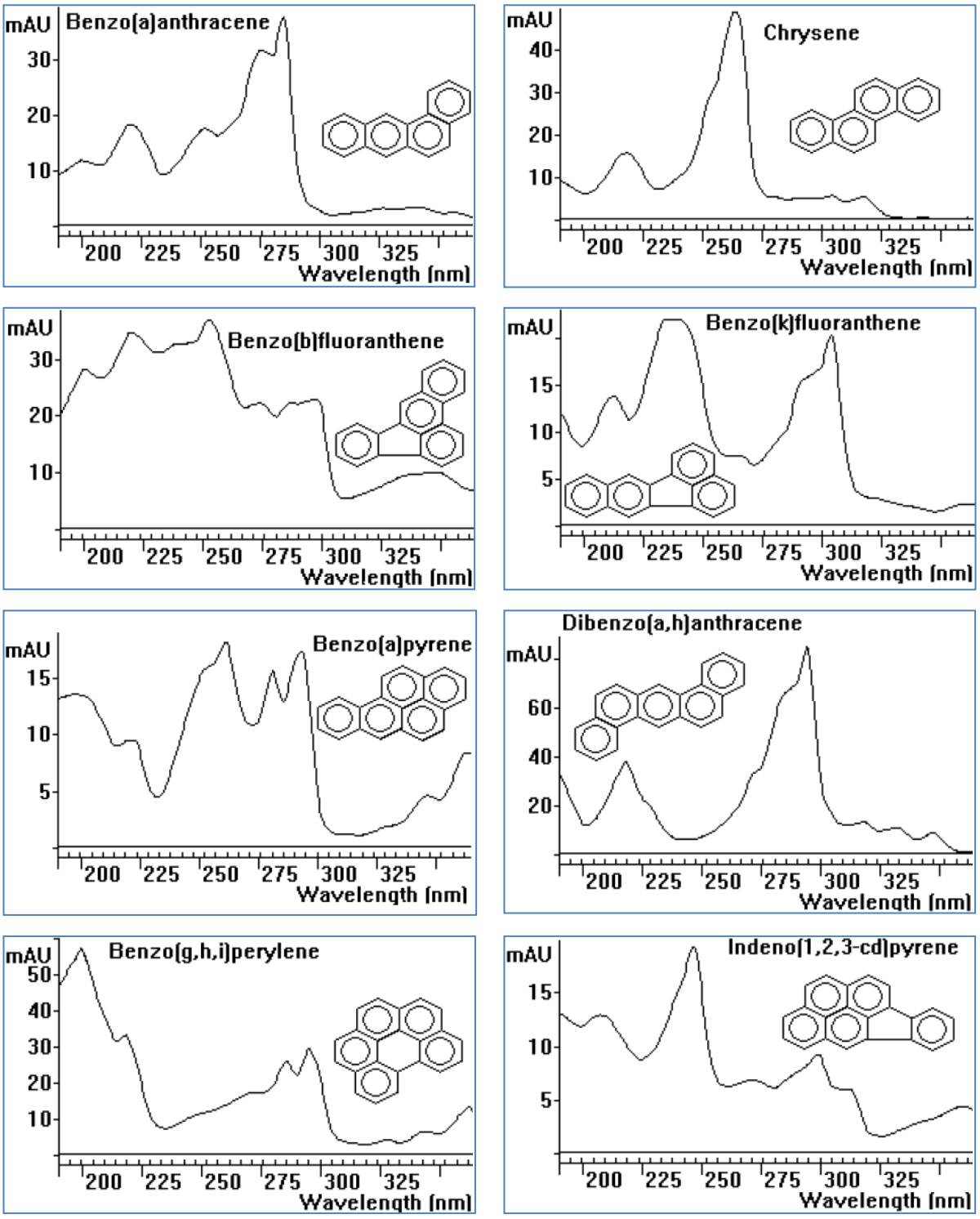


Figure 6-6 - UV spectra of the last 8 USEPA PAH priority pollutants[182]

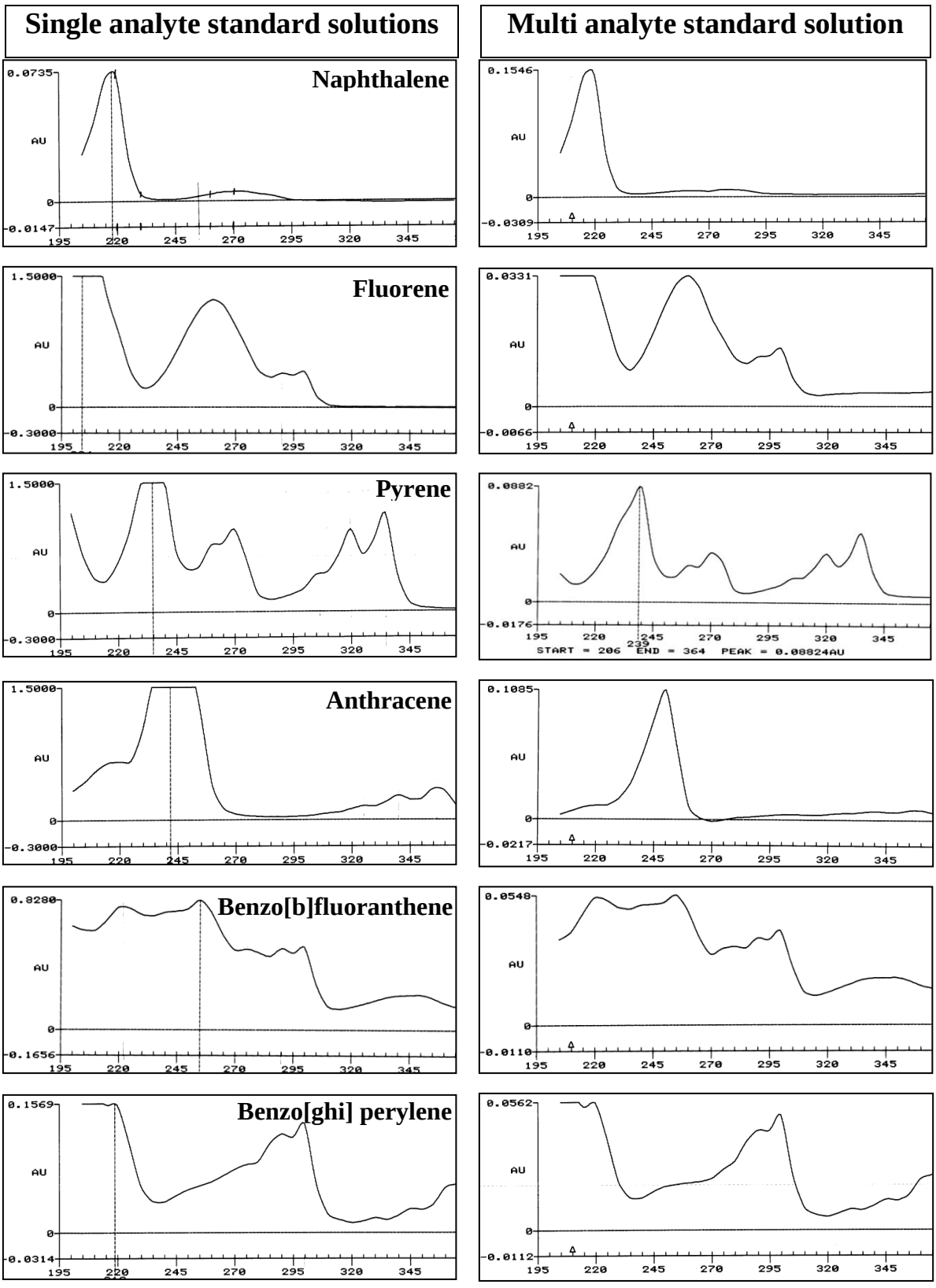


Figure 6-7 - Comparison of UV spectra obtained from the 16 PAH multi analyte standard solution and single analyte standard solutions for 6 components

These two sets of spectra were compared with each other and also with standard spectra from the literature to identify the PAH compounds.

The spectra for the six single analyte standard solutions showed agreement with the spectra for the multi analyte standard solution and confirmed previous assignment using retention times. The other components in the multi analyte standard solution showed agreement with literature spectra and were consistent with the expected elution order[152]. The remaining peaks in Figure 6-4 were assigned as acenaphthylene, phenanthrene, fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene at retention times of 5.53, 7.60, 9.61, 19.80, 21.34 and 24.01 (co-eluting with benzo[g,h,i]perylene) minutes, respectively. The peak at 13.35 minutes (Figure 6-4) produced a UV spectra with λ_{max} which can be found in the literature spectra of both benzo[a]anthracene and chrysene, and therefore these isomers appear to co-elute. There is a small peak at a retention time of 7.09 minutes eluting immediately after fluorene. When compared to the literature (Figure 6-8). The λ_{max} from the UV spectra indicated that this peak was due to acenaphthene

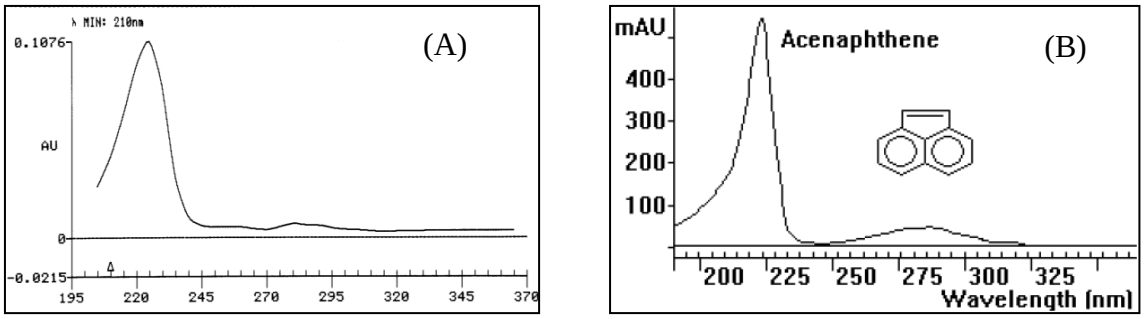


Figure 6-8 - Comparison of a UV spectra obtained for a component in the multi analyte standard solution (A) and a UV spectra for acenaphthene (B) obtained from the literature[182]

6.4.2 Detection Limits, Repeatability and Linearity

Detection limits were determined for the multi analyte standard solution at a concentrations of 0.4 µg mL^{-1}. The multi analyte standard solution was manually injected ten times and the instrumental detection limits calculated (Table 6-5).

Table 6-5 – Detection limits for 14 analytes determined in a 0.4 µg mL^{-1} multi analyte PAH standard solution

Analyte	$D_L$inst. (µg mL^{-1}) [0.4 µg mL^{-1} standard]
Naphthalene	0.0588
Acenaphthylene	0.0871
Fluorene	0.0436
Phenanthrene	0.0399
Anthracene	0.0432
Fluoranthene	0.0271
Pyrene	0.0643
Benzo[a]anthracene/ Chrysene	0.0405
Benzo[b]fluoranthene	0.0587
Benzo[a]pyrene	0.0523
Dibenz[a.h]anthracene	0.0335
Indeno[1,2,3-cd]pyrene	0.0483
Benzo[ghi]perylene	0.0677

The results showed that poorer detection limits were found for the smallest PAH molecules and also for the two largest analytes which co-eluted.

To assess the repeatability of the analysis, the precision of repeat injections of the multi analyte standard solution at concentrations of 0.04, 0.1, 0.4 and 1.0 µg mL^{-1} was determined. The analysis was performed using the fixed wavelength Varian HPLC system previously optimised. The mean and relative standard deviations are reported, for peak areas, in Table 6-7.

The data for each of the components showed that the variability decreased as concentration increased. This is expected as the signal increases above the background and moves further from the detection limits. The smallest and two largest PAHs generally showed the poorest precision. The variation in the results for the 0.04 µg mL^{-1} standard (RSD values >30 %) showed that reliable and repeatable results could not be achieved at this concentration.

Table 6-6 – Mean peak areas and RSD values (%) for replicate injections of the multi analyte standard solution in acetonitrile at concentrations of 0.04, 0.1, 0.4 and 1.0 µg mL^{-1} (n = 10)

	Standard Concentration/ µg mL^{-1}							
	0.04		**0.10**		**0.40**		**1.00**	
	Peak Areas							
Analyte	**$\bar{x}$**	**RSD**	**$\bar{x}$**	**RSD**	**$\bar{x}$**	**RSD**	**$\bar{x}$**	**RSD**
Naphthalene	2787126	117	10022640	13	1284947	8.1	854633	4.1
Acenaphthylene	1798175		9498080	15	901087	13	720544	3.8
Acenaphthene							439228	2.7
Fluorene	7508472	67	16920701	4.9	6315930	3.5	5094883	1.0
Phenanthrene	13071097	39	32220811	4.1	16359847	3.4	13704824	1.0
Anthracene	22155993	30	47422446	5.9	25231250	3.7	11321241	1.0
Fluoranthene	6934008	79	16028249	7.1	4421908	9.3	3077810	2.0
Pyrene	5869658	70	16274849	11	3954297	5.2	3005102	1.2
Benzo[a] anthracene/ Chrysene	19310140	46	46052272	2.9	23690624	3.5	18094255	1.0
Benzo[b] fluoranthene	14827851	45	31979341	5.6	11347707	5.1	8272201	0.9
Benzo[a]pyrene	15659804	53	26481416	4.4	10958178	4.2	7243754	1.6
Dibenz[a.h] anthracene	4986150	120	16495172	8.8	3846265	6.4	1737637	1.0
Indeno[1,2,3-cd] pyrene	15372487	54	25021344	26	10614416	9.7	7390507	3.8
Benzo[ghi] perylene	4106980	166	20453460	16	6039557	14	2902232	7.9

Signals may be detectable, above the background, at 0.04 µg mL^{-1}, but accurate quantification could not be achieved. The precision for the 0.10 and 0.40 µg mL^{-1} standard solutions were reasonable, excluding the first and last two analytes, with RSD values of 2.9 – 11 % (average 6.1 %) and 3.4 – 9.2 % (average 5.5 %), respectively. More acceptable precision, with an RSD range of 0.9 to 2.0% excluding the first and last two analytes (average 1.3 %), was achieved for the 1.0 µg mL^{-1} standard solution. The detection limit results obtained with the 0.4 µg mL^{-1} standard (Table 6-5) suggested that analytes of interest can be detected at concentrations as low as 0.03 – 0.09 µg mL^{-1}. However, the repeatability study showed that there would be a high level of uncertainty in results at these levels. The RSD values for the 0.10 to 1.0 µg mL^{-1} standard solution showed an increasing level of precision. The mean and relative standard deviations are reported for the retention times in Table 6-7.

Table 6-7 – Mean retention time and RSD values (%) for replicate injections of the multi analyte standard solution in acetonitrile at concentrations of 0.04, 0.1, 0.4 and 1.0 µg mL^{-1} (n = 10)

	Standard Concentration/ µg mL^{-1}							
	0.04		**0.10**		**0.40**		**1.00**	
	Retention Time/ minutes							
Analyte	**$\bar{x}$**	**RSD**	**$\bar{x}$**	**RSD**	**$\bar{x}$**	**RSD**	**$\bar{x}$**	**RSD**
Naphthalene	4.83	0.8	4.86	2.0	5.06	1.7	4.79	0.19
Acenaphthylene	5.38	1.3	5.39	2.0	5.64	1.7	5.33	0.28
Acenaphthene							6.82	0.35
Fluorene	6.49	1.1	6.48	2.2	6.86	1.6	6.50	0.33
Phenanthrene	7.21	1.2	7.19	2.1	7.64	1.6	7.24	0.41
Anthracene	7.78	1.5	7.75	2.1	8.26	1.6	7.82	0.39
Fluoranthene	8.95	1.7	8.92	2.1	9.53	1.6	9.05	0.45
Pyrene	10.0	1.8	10.00	1.8	10.7	1.5	10.15	0.50
Benzo[a] anthracene/ Crysene	12.1	2.2	12.0	1.7	12.8	1.7	12.30	0.60
Benzo[b] fluoranthene	15.6	2.5	15.4	1.4	16.5	1.6	15.93	0.68
Benzo[a]pyrene	17.8	2.8	18.0	4.5	18.8	1.7	18.05	0.72
Dibenz[a.h] anthracene	19.2	4.0	19.2	1.1	20.3	1.7	19.40	0.77
Indeno[1,2,3-cd] pyrene	22.3	2.5	22.5	0.6	23.2	1.3	22.23	0.65
Benzo[ghi] perylene	22.2	1.7	22.9	0.6	23.6	1.1	22.59	0.54

The retention times showed similar repeatability over all the standards analysed (RSD 0.19 – 4.5 %). The 1.0 µg mL^{-1} standard solution showed the highest levels of precision for retention times (RSD values ranging from 0.28 to 0.77% with an average of 0.49%). This indicated that similar results could be achieved for analysis performed on the same day, even at concentrations as low as 0.04 µg mL^{-1}.

The linearity of calibration was determined using the multi analyte standard solution for each of the analytes. Calibration standards were prepared at two concentration ranges of 0.0, 0.01, 0.02, 0.04, 0.08, 0.10 µg mL^{-1} and 0.0, 0.08, 0.16, 0.24, 0.32, 0.48 µg mL^{-1}, and analysed using the optimised HPLC conditions. Table 6-8 shows the calibration data for duplicate analysis of the 0.0 - 0.10 µg mL^{-1} multi analyte standard solutions analysed on different days.

Table 6-8 – Reproducibility of calibration linearity, for 0.0, 0.01, 0.02, 0.04, 0.08 and 0.10 µg mL^{-1} multi analyte standard solutions, on different days (t_{crit}=3.71)

Analyte	#	Slope/ $b \pm t_{(n-2)}s_b$	Intercept/ $a \pm t_{(n-2)}s_a$	R	$s_{y/x}$	t
Fluorene	1	12392901 ± 842591	-9749 ± 46787	0.999	27250	
	2	13761164 ± 729836	-16583 ± 40526	0.999	23603	3.41
Phenanthrene	1	33061123 ± 4017888	-67833 ± 223104	0.996	129942	
	2	40843412 ± 2649836	-21653 ± 147140	0.999	85698	4.50
Anthracene	1	64675230 ± 5077397	-54188 ± 281937	0.998	164207	
	2	87791197 ± 7534768	-13718 ± 418389	0.998	243680	7.07
Fluoranthene	1	7706110 ± 846017	-17798 ± 46977	0.997	27361	
	2	8816928 ± 1727974	18296 ± 95951	0.990	55884	1.61
Pyrene	1	7813577 ± 397416	-5833 ± 22068	0.999	12853	
	2	8188383 ± 2387424	54669 ± 132568	0.979	77211	0.43
Benzo[a] anthracene/ Chrysene	1	47624942 ± 2416948	1222 ± 134208	0.999	78166	
	2	49410098 ± 5011860	183906 ± 278297	0.989	162265	0.89
Benzo[b] fluoranthene	1	22462784 ± 1336478	-60509 ± 74212	0.999	43223	
	2	23871167 ± 5017345	-14726 ± 278602	0.989	162265	0.75
Benzo[a] pyrene	1	19366694 ± 949219	479 ± 52708	0.999	30698	
	2	23450419 ± 5472721	-10977 ± 303888	0.986	176992	2.04
Dibenz[a.h] anthracene	1	4941979 ± 115975	-67474 ± 8983	1.000	1802	
	2	3268354 ± 12080178	210767 ± 935727	0.601	187742	
Indeno [1,2,3-cd] pyrene	1	18422300 ± 5087036	-40404 ± 114788	0.996	74821	
	2	25429286 ± 8242554	-141464 ± 638465	0.997	82818	
Benzo[ghi] perylene	1	8473585 ± 1468217	48739 ± 151560	0.996	32868	
	2	9952564 ± 2712815	-48472 ± 210134	0.998	27257	5.59

The results showed that in general calibrations were linear with correlation coefficients > 0.99 which were confirmed by random scatter in the residual plots. The main exception was the duplicate calibration for dibenz[a,h]anthracene which did not show linearity. The comparison of calibration slopes determined at different times showed that reproducibility could be achieved. This was confirmed, for some analytes, using a t-test (t_{crit}=3.71) to compare slopes[183]. Table 6-9 shows the

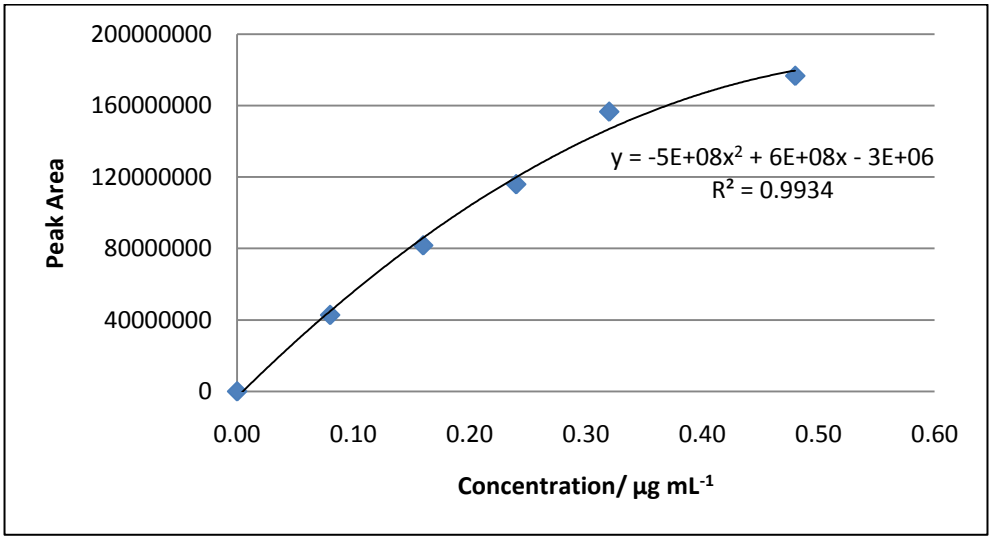
calibration data for repeat analysis of the 0.0 - 0.32 µg mL^{-1} multi analyte standard solutions, performed on two different days.

Table 6-9 – Reproducibility of calibration linearity, for 0.0, 0.08, 0.16, 0.24 and 0.32 µg mL^{-1} multi analyte standard solutions, on different days (t_{crit}=3.71)

Analyte	#	Slope/ $b \pm t_{(n-2)}s_b$	Intercept/ $a \pm t_{(n-2)}s_a$	R	$s_{y/x}$	t
Naphthalene	1	30605876 ± 17026627	544627 ± 17026627	0.984	937031	3.91
	2	14468450 ± 4971299	167888 ± 4971299	0.994	273587	
Acenaphthylene	1	17951071 ± 21507764	1378765 ± 21507764	0.930	1789500	1.22
	2	11837476 ± 301644	14785 ± 301644	1.000	16600	
Fluorene	1	101440260 ± 7598019	1828522 ± 24161700	0.992	1922164	3.68
	2	69324039 ± 4275460	998138 ± 13595963	0.994	1081615	
Phenanthrene	1	247292780 ± 24104701	1508365 ± 24104701	0.999	1917629	4.51
	2	177378430 ± 43046844	2486720 ± 43046844	0.991	3424555	
Anthracene	1	483013460 ± 31156371	2145168 ± 31156371	0.999	2478619	4.83
	2	358444755 ± 75948453	4481959 ± 75948453	0.993	6042015	
Fluoranthene	1	87407440 ± 29932848	2293096 ± 29932848	0.983	2381282	4.39
	2	42419315 ± 12810332	1275253 ± 12810332	0.987	1019115	
Pyrene	1	75806100 ± 32859460	2678835 ± 32859460	0.973	2614107	3.33
	2	38484568 ± 13794069	1311074 ± 13794069	0.981	1097376	
Benzo[a] anthracene/ Chrysene	1	346437740 ± 50871094	3974962 ± 50871094	0.997	4047007	3.45
	2	259877710 ± 61540653	4711380 ± 61540653	0.992	4895815	
Benzo[b] fluoranthene	1	200765890 ± 60985829	-526486 ± 60985829	0.987	4851676	3.91
	2	113209450 ± 36735411	3584981 ± 36735411	0.985	2922455	
Benzo[a] pyrene	1	146549070 ± 137246317	5536669 ± 137246317	0.891	10918515	0.62
	2	119526228 ± 20472015	1076944 ± 20472015	0.996	1628634	
Dibenz[a.h] anthracene	1	53305613 ± 94361230	4803342 ± 94361230	0.720	7506828	0.51
	2	37807633 ± 22051576	132897 ± 22051576	0.953	1754294	
Indeno [1,2,3-cd] pyrene	1	237559880 ± 144263168	9362387 ± 144263168	0.949	11476734	1.24
Benzo[ghi] perylene	2	176679320 ± 58877312	1533725 ± 58877312	0.984	4683935	

The 0.48 µg mL^{-1} multi analyte standard solution was omitted from the calibration data in Table 6-9 as deviation from linearity was observed at this concentration. For example Figure 6-9 shows the calibration graph for anthracene using 0.0 - 0.48 µg mL^{-1} multi analyte standard solutions (A) and also when omitting the 0.48 µg mL^{-1} multi analyte standard solution (B).

(A)



(B)

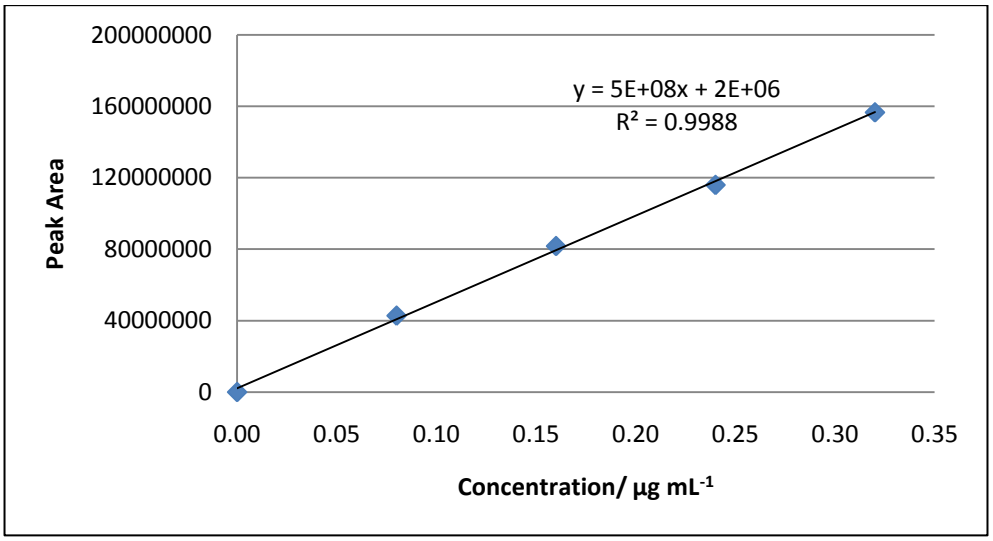


Figure 6-9 – The linearity of a calibration for anthracene using multi analyte standard solutions (A) 0.0 – 0.48 µg mL^{-1} and (B) 0.0 – 0.32 µg mL^{-1}

The results show that the linear range for analysis of PAH using the Varian HPLC-UV is from 0.0 - 0.32 µg mL^{-1}.

6.4.3 Calibration, repeatability and analysis for microwave-assisted micellar extraction solutions

The MAME procedure is applied to the substrate samples to potentially release PAH analytes into solution for subsequent analysis. The extraction is achieved by treating the sample with the non-ionic surfactant POLE (0.02 M solution in water). It is important that this solution should not adversely affect the chromatography, in order to achieve satisfactory analysis. An aliquot of the micellar solution (reagent blank) was analysed to determine if it would interfere in the chromatographic process. The micellar solution was also subjected to the microwave procedure and this procedural blank was analysed to determine if heating would affect the elution times (Figure 6-10).

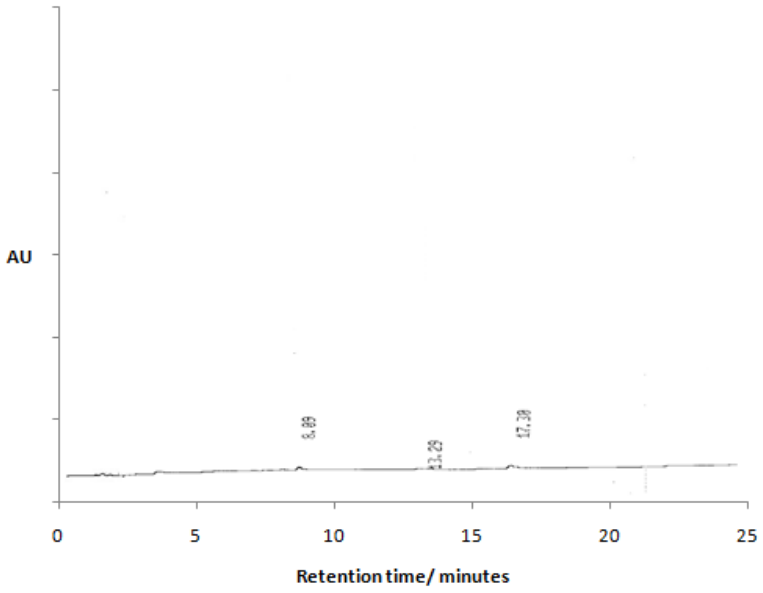


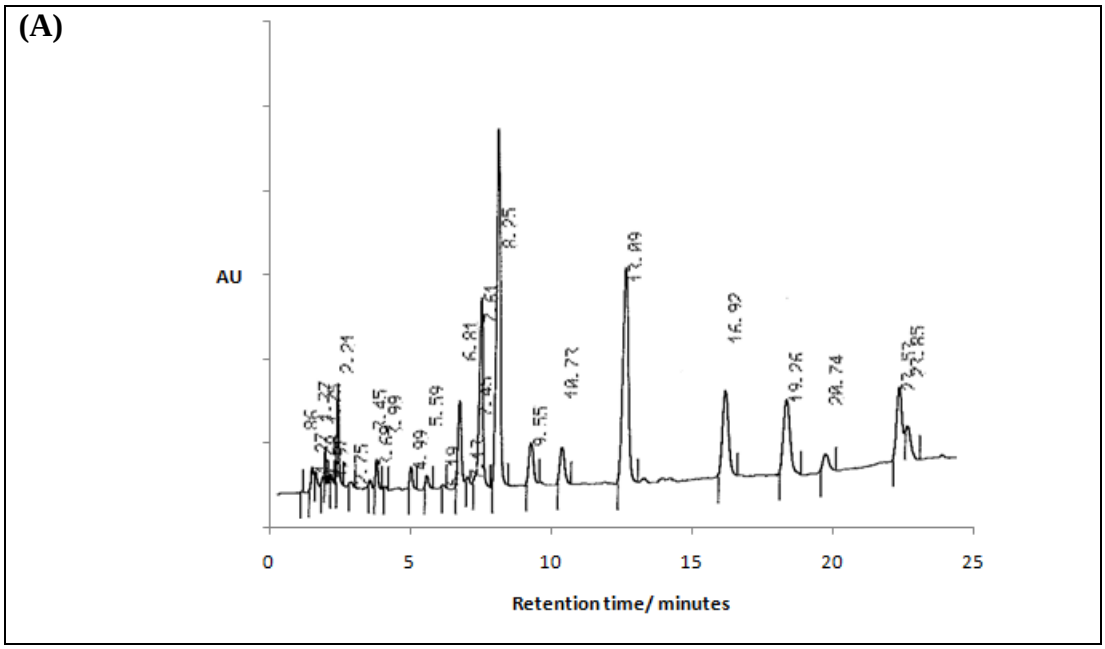
Figure 6-10 - Chromatogram of a POLE procedural blank

No peaks were found in the chromatograms of the reagent blank, analysed without treatment in the microwave, at the retentions times of the PAH analytes. The chromatogram for the procedural blank showed three small peaks. They appeared in the approximate positions of the largest peaks in the 16 PAH standard solution and may therefore have been the result of contamination during preparation. This would therefore indicate that there was no interfering effect from the POLE solution itself, whether or not microwave treatment had been applied.

Previously research using micellar solutions for organic extractions has reported that chromatography can be performed without sample clean-up or pre-concentration[113]. However, if the analytes are analysed in the micellar medium reagent matching could be required. This was investigated by comparing multi analyte calibration solutions prepared in POLE and in acetonitrile. The POLE reagent was used to prepare a 0.1 μg mL^{-1} PAH standard from the stock solution. This was then analysed and the chromatogram compared to that of a 0.1 μg mL^{-1} PAH standard prepared in acetonitrile.

Both chromatograms (Figure 6-11) showed peaks that eluted at retention times in agreement with those previously established for the PAH standard mixture. However, the component peak areas were different.

It can be seen from Table 6-10 that the peak areas in the standard prepared in POLE were, on average, a factor of 2.3 smaller than those in the standard prepared in acetonitrile. This could have been due to a fraction of each PAH molecule partitioning into the micelles in solution and therefore they were not detected. However, in acetonitrile all the PAH molecules were potentially free in solution to be detected.



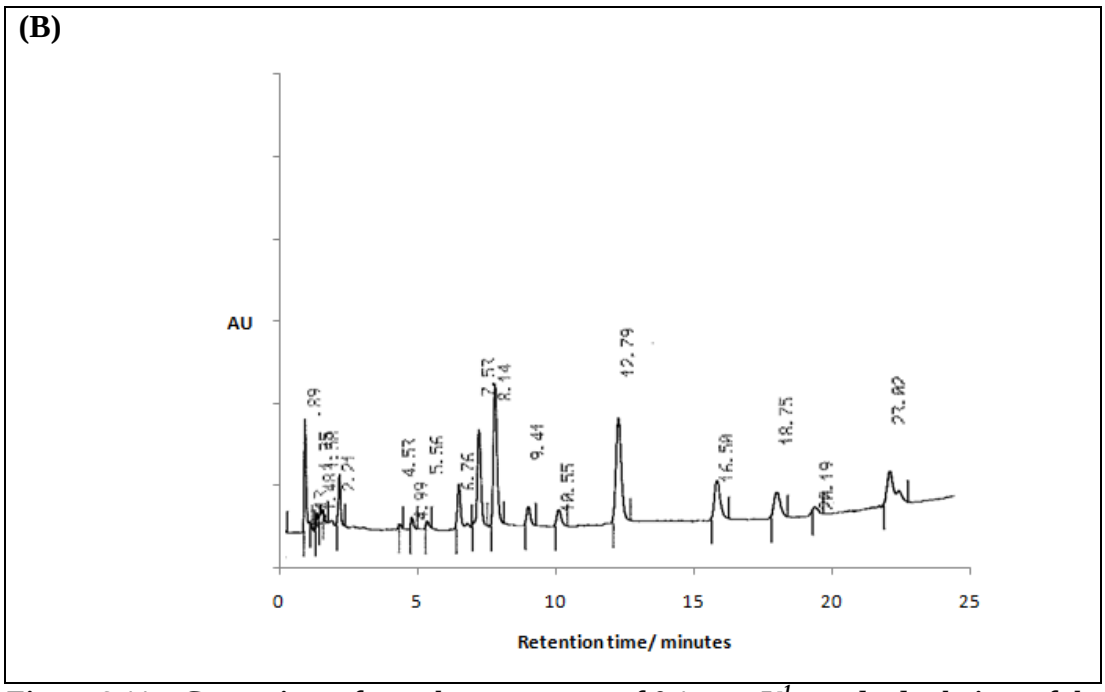


Figure 6-11 – Comparison of two chromatograms of 0.1 µg mL^{-1} standard solutions of the 16 USEPA priority PAH prepared in both (A) acetonitrile and (B) polyoxyethylene 10 lauryl ether

Table 6-10 – Comparison of peaks areas for a 0.1 µg mL^{-1} solution of the 16 component PAH standard mixture in both acetonitrile and POLE

	Peak areas		Area ratio of
PAH Component	**Acetonitrile**	**POLE**	**ACN/POLE**
Naphthalene	436885	220091	1.99
Acenapthylene	293914	145135	2.03
Fluorene	2221780	1173189	1.89
Phenanthrene	5185334	2545143	2.04
Anthracene	10044013	3843631	2.61
Fluoranthene	1217936	538487	2.26
Pyrene	1250978	551952	2.27
Benz[a]Anthracene/ Chrysene	8515408	4065118	2.09
Benzo[b]fluoranthene	3658434	1698514	2.15
Benzo[a]pyrene	3584498	1220206	2.94
Dibenzo[a,h]anthracene	702958	197699	3.56
Indeno[1,2,3-cd]pyrene	4268713	2002757	2.13
Benzo[g,h,i]perylene	436885	220091	1.99

It was therefore important to perform calibrations with solutions that were reagent matched to those of the extraction solutions.

A 0.1 μg mL^{-1} solution, in the POLE reagent, of the multi analyte standard solution was used to investigate the repeatability compared to acetonitrile (results for which were presented in Table 6-6 and Table 6-7). The mean, standard deviation and relative standard deviation are reported for both peak area and retention time (Table 6-11).

Table 6-11 - Peak areas and retention times for replicate injections of the multi analyte standard solution in POLE at a concentration of 0.1 μg mL^{-1} (n = 10)

Analyte	**Area**		**Retention time/ mins**	
	$\bar{x}$	**RSD/ %**	$\bar{x}$	**RSD/ %**
Naphthalene	291991	7.3	4.96	0.8
Acenaphthylene	166815	11	5.53	1.0
Fluorene	1761019	6.1	6.72	1.2
Phenanthrene	5037378	3.3	7.48	1.5
Anthracene	430156	6.0	8.08	1.8
Fluoranthene	1104736	3.7	9.33	2.0
Pyrene	830975	4.8	10.4	2.2
Benz[a]Anthracene/ Chrysene	7217268	2.9	12.6	2.9
Benzo[b]fluoranthene	2976282	2.7	16.3	3.1
Dibenz[a,h]anthracene	563457	12	19.9	3.6
Indeno[1,2,3-cd]pyrene	2802181	3.6	22.8	3.0
Benzo[g,h,i]perylene	1044828	2.3	23.1	2.7

The precision of repeat analysis was comparable to that achieved using a 0.1 μg mL^{-1} multi analyte standard solution in acetonitrile, with RSD values, for peak areas, of 2.3 to 12 % (mean = 5 %) and for retention times, of 0.8 to 3.6 % (mean = 2.5 %). The variability in peak area and retention times was similar in POLE and acetonitrile. However, although direct injection of a POLE extract to the HPLC was possible, the sensitivity was reduced relative to acetonitrile. This meant that standards needed to be reagent-matched and also there were poorer detection limits.

6.4.4 Microwave-assisted micellar extraction of an urban soil from Glasgow

The GLA-URM used during the work on PTE described in chapters 4 and 5, was extracted using the MAME procedure to determine if any PAHs could be identified in the chromatogram (Figure 6-12).

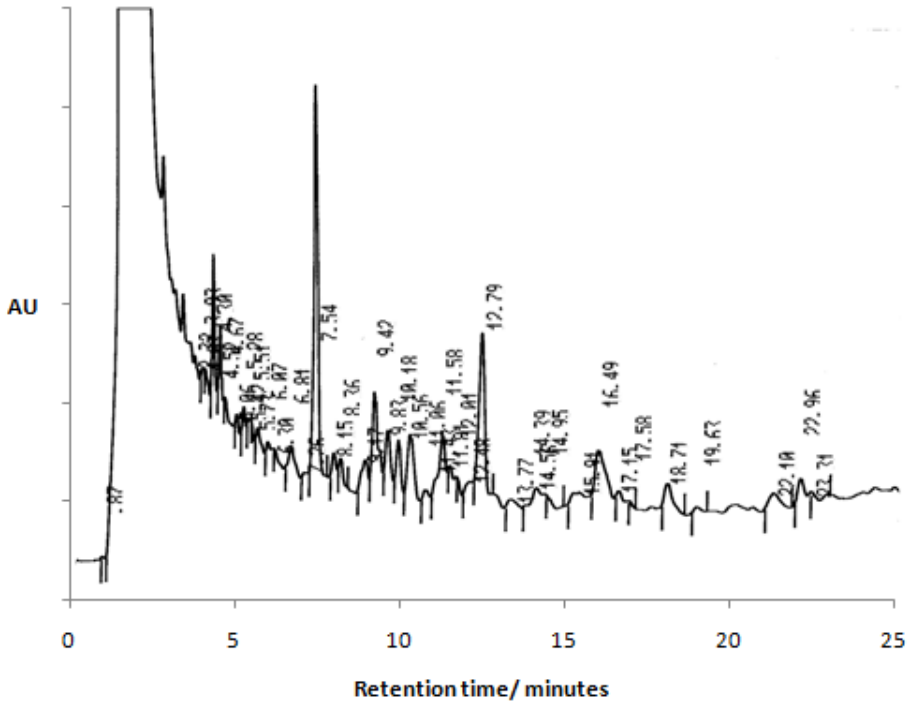


Figure 6-12 – Chromatogram of a extract obtained using the POLE extraction method with a soil substrate

The chromatogram showed peaks at several retention times which corresponded to those found for analytes of interest in the multi analyte standard solution. There were peaks at retentions times of 7.54, 9.42, 12.79, 16.49, 22.96 and 23.31 minutes, which could correspond to the standard retention times of phenanthrene, fluoranthene, benzo[a]anthracene/ chrysene, benzo[b]fluoranthene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene, respectively. However, there were also peaks at retention times that did not correspond to any of the analytes in the multi analyte standard solution. This was expected as the urban soil will contain other organic pollutants extractable by POLE. The baseline was particularly affected by the elution of a large peak at the start of the analysis, which mainly affected the lower

molecular weight analytes. The analysis suggested that phenanthrene, benzo[a]anthracene/ chrysene and benzo[b]fluoranthene were the predominant PAHs determined using the extraction applied, which was in agreement with analysis of urban soil sampled from the same location[93]. The low response obtained for the analytes of interest, and the presence of other analytes, indicated that extract solutions required pre-concentration and clean-up prior to analysis.

6.4.5 Solid phase extraction of microwave-assisted micellar extraction solutions

Solid phase extraction (SPE) is a method often used for the pre-concentration and clean-up of analytes extracted from environmental substrates prior to analysis using HPLC[93,148]. SPE was therefore investigated as a potential pre-concentration/ clean-up method following extraction of samples using the MAME procedure. A SPE stationary phase specifically designed for PAH analysis was obtained. The principle stages of conditioning, washing and elution were studied using applicable solvents.

SPE was initially performed on spiked test solutions to determine the effective pre-concentration and recovery efficiency of the cartridge investigated. The test solutions were the micellar extractant reagent spiked with the multi analyte standard, which was taken to approximate the matrix of a real extract. After SPE was completed, analysis was performed by HPLC-UV on the eluates, sample effluent after application and cartridge washing solution. The initial conditions used for SPE, adapted from the supplier's recommendations, are listed in Table 6-12.

Table 6-12 - Conditions for SPE using a CN/SiOH cartridge adapted from[154]

Column material	CN/ SiOH	
Cartridge conditioning	1. Dichloromethane 2. POLE (0.02 mol L^{-1})	4 mL 4 mL
Sample application	0.08 μg mL^{-1} PAH in POLE	5 mL
Cartridge washing	POLE (0.02 mol L^{-1})	2 mL
Analyte elution	Acetonitrile	3 x 2 mL

Analysis of the cartridge effluent, after the sample was loaded, showed no peaks for the analytes of interest in the resulting chromatogram, indicating that the analytes had been retained on the column. The POLE solution used to wash the cartridge also resulted in a chromatogram which contained no peaks for the analytes. Therefore, none of the analytes were washed from the cartridge during the washing stage. The retained analytes were eluted from the cartridge in three, 2 mL aliquots of acetonitrile, each of which were analysed individually. Acetonitrile was initially used for elution as this gave good sensitivity and well resolved peaks and it was also the mobile phase used for HPLC analysis.

The three eluate aliquots from the SPE were analysed along with a 0.08 μg mL^{-1} solution of the multi analyte standard (in acetonitrile) for comparison. The peak area (A) and concentration (c) of PAH in the multi analyte standard was used to estimate the concentration of analytes in the three solutions eluted from the cartridge using Equation 6-1.

$$c_{Elution} = \frac{c_{Std} A_{elution}}{A_{Std}}$$

Equation 6-1

The mass of analyte in each of the eluate aliquots and the subsequent total was calculated and used to determine the recovery relative to the 0.40 μg (i.e. 5 mL of a 0.08 μg mL^{-1} solution) of each analyte loaded onto the cartridge. These results are reported in Table 6-13 for two replicate SPE tests using the same conditions shown in Table 6-12.

For ideal pre-concentration to be achieved, 100% of the analyte mass loaded onto the cartridge should be transferred from a larger applied volume to a smaller eluted volume. This results in a greater analyte concentration in the eluate which can be more easily detected. The results showed there to be variation between the two replicate tests, with the majority of analyte eluting in the second 2 mL volume for test A and across all three eluate volumes for test B. This may have been due to insufficient interaction time between the eluate and the sorbent in test A. The total recoveries, of each species for both tests, were between 29 – 104%, which indicated

that some analytes were not efficiently eluted from the cartridge. This could have been due to acetonitrile being more polar than the analytes therefore the PAHs did not have a sufficiently strong affinity for the eluant to partition into solution. As the analytes are non-polar, complete elution may require a less polar solvent.

Table 6-13 – The recovery of each detectable component from two solid phase extractions of 5 mL of a 0.08 µg mL^{-1} solution of 16 PAH in POLE eluted using ACN

		Concentration/ µg mL^{-1}			**Mass of analyte/ µg**				**Recovery/ %**
		Elution (2 mL)			**Elution (2 mL)**			**Total**	
Analyte	**Test**	1st	2nd	3rd	1st	2nd	3rd		
Fluorene	A	0.000	0.098	0.007	0.000	0.195	0.013	0.208	52
	B	0.026	0.029	0.023	0.052	0.058	0.047	0.157	39
Phenanthrene	A	0.000	0.103	0.005	0.000	0.207	0.010	0.217	54
	B	0.028	0.028	0.024	0.056	0.057	0.048	0.161	40
Anthracene	A	0.000	0.096	0.007	0.000	0.192	0.014	0.206	51
	B	0.021	0.020	0.017	0.041	0.041	0.034	0.116	29
Fluoranthene	A	0.000	0.125	0.000	0.000	0.250	0.000	0.250	62
	B	0.043	0.043	0.045	0.086	0.086	0.089	0.261	65
Pyrene	A	0.000	0.110	0.000	0.000	0.221	0.000	0.221	55
	B	0.042	0.050	0.040	0.084	0.100	0.081	0.265	66
Benz[a] anthracene/ Chrysene	A	0.000	0.084	0.003	0.000	0.169	0.007	0.176	44
	B	0.038	0.034	0.020	0.075	0.067	0.040	0.182	45
Benzo[b] fluoranthene	A	0.000	0.082	0.000	0.000	0.163	0.000	0.163	41
	B	0.039	0.044	0.012	0.079	0.088	0.024	0.190	48
Benzo[a] pyrene	A	0.000	0.069	0.000	0.000	0.138	0.000	0.138	35
	B	0.039	0.044	0.012	0.100	0.071	0.042	0.213	53
Indeno[1,2,3-cd]pyrene/ Benzo[g,h,i] perylene	A	0.000	0.208	0.000	0.000	0.415	0.000	0.415	104
	B	0.056	0.041	0.008	0.112	0.083	0.015	0.210	52

DCM is less polar solvent than acetonitrile and is often used for extraction of PAHs from substrates[92-93,104,117,122]. It therefore could be a useful solvent for elution of analytes from the SPE cartridge. However, when multi analyte standard solutions in DCM, were analysed using the previously-optimised HPLC conditions, the resulting chromatograms showed broadening and tailing of eluting peaks, compared to those in acetonitrile. It was decided to investigate mixtures of ACN and DCM, to determine the effects of solvent composition on chromatographic response. Six solutions containing the multi analyte standard at a concentration of 0.2 µg mL^{-1} were prepared in varying ratios of ACN and DCM. The composition of these solutions were, 60:40, 50:50, 40:60, 30:70, 20:80 and 10:90 v/v of ACN to DCM, respectively. The associated peak areas and retention times for each analyte in all six mixtures are shown in Table 6-14.

The results showed that, as the ratio of DCM in a mixture increased, the width of the eluting peaks increased and the height decreased. The peak broadening effect was not completely linear and the area of the eluting peaks also decreased by varying amounts as the composition of DCM increased. The solutions containing >70 % DCM composition of greater than 70% showed particularly severe peak broadening. Subsequently, solvent mixtures containing up to 70% DCM were investigated for elution of the SPE cartridges.

Table 6-14 – Peak areas and retention times (t_R/ mins) for six solutions containing the 16 PAH at a concentration of 0.2 µg mL^{-1} in varying ratios of acetonitrile and dichloromethane

		Solvent ratio/ ACN: DCM (v/v)					
Analyte		**60:40**	**50:50**	**40:60**	**30:70**	**20:80**	**10:90**
Naphthalene	t_R	5.03	5.03	5	5.04	4.12	4.97
	Area	1472780	1169839	1237313	968654	474403	361675
Acenaphthylene	t_R	5.64	5.64	5.59	/	/	5.64
	Area	1010553	831729	896579	/	/	246721
Fluorene	t_R	6.91	6.91	6.85	6.9	5.93	6.92
	Area	7870682	6202311	6662317	5210890	4182864	5841164
Phenanthrene	t_R	7.74	7.74	7.67	7.72	6.8	7.75
	Area	21286299	16824116	18384761	14149654	11259229	16196966
Anthracene	t_R	8.49	8.47	8.4	8.39	7.52	8.43
	Area	34265346	29677041	35905586	30116738	24828439	29961122
Fluoranthene	t_R	9.77	9.77	9.69	9.75	8.93	9.64+9.78
	Area	4569349	3588035	4338806	3329823	2794873	3445640
Pyrene	t_R	10.98	10.99	10.89	10.96	10.23	10.81
	Area	4535315	3442015	4248829	3177015	2502091	3190937
Benz[a] Anthracene/ Chrysene	t_R	13.49	13.52	13.38	13.46	12.88	13.53
	Area	30532230	23651292	28560196	22362891	18093191	21680967
Benzo[b] fluoranthene	t_R	17.49	17.55	17.38	17.47	17.17	17.56
	Area	13292136	10386803	12295961	9681937	7719330	9626648
Benzo[a] pyrene	t_R	19.99	20.05	19.85	19.96	19.85	20.09
	Area	11998659	9380842	11313174	8913597	7154819	8587534
Dibenzo[a,h] anthracene	t_R	21.54	21.61	21.41	21.51	21.51	21.68
	Area	2726502	2031581	2457783	1909972	813937	1881258
Indeno[1,2,3-cd] pyrene	t_R	24.26	24.34	24.18	24.26	24.33	24.4
	Area	12756656	9613001	15894659	12413578	9806943	11980466
Benzo[g,h,i] perylene	t_R	24.51	24.59	/	/	/	/
	Area	3959405	3266853	/	/	/	/

Another 0.08 µg mL^{-1} test solution of the multi analyte standard in the micellar reagent was subjected to the SPE procedure applied previously, except that the eluant was changed to a mixture of ACN and DCM. These revised conditions are shown in Table 6-15.

Table 6-15 – Revised conditions for SPE using a CN/SiOH column

Column material	CN/ SiOH	
Column conditioning	1. Dichloromethane 2. POLE	4 mL 4 mL
Sample application	0.08 μg mL^{-1} PAH in POLE	5 mL
Column washing	POLE	2 mL
Analyte elution	ACN:DCM	3 x 2 mL

A solution, with a composition of 50 % acetonitrile to 50 % dichloromethane was initially tested for elution of the SPE cartridge. The three eluant volumes from the SPE cartridge were analysed by HPLC, along with a 0.08 μg mL^{-1} solution of the multi analyte standard solution for calculation of the elution concentration and the overall analyte recovery (Table 6-16). The effluent from the sample loading and the washing solution were also analysed and no eluting peaks corresponding to the analytes were found. This again indicated that analytes were retained on the SPE cartridge and were not eluted in the washing solution.

Table 6-16 - The recovery of each detectable component from the solid phase extraction of 5 mL of a 0.08 μg mL^{-1} solution of 16 PAH in POLE eluted using a 50:50 v/v mixture of ACN and DCM

Analyte	**Concentration/ μg mL^{-1}**			**Mass of analyte/ μg**				**Recovery/ %**
	Elution (2 mL)			**Elution (2 mL)**			**Total**	
	1st	2nd	3rd	1st	2nd	3rd		
Flourene	0.091	0.031	0.028	0.182	0.063	0.056	0.301	75
Phenanthrene	0.084	0.024	0.016	0.168	0.049	0.032	0.249	62
Anthracene	0.035	0.008	0.009	0.069	0.016	0.017	0.102	26
Fluoranthene	0.178	0.036	0.000	0.356	0.071	0.000	0.427	107
Pyrene	0.206	0.011	0.000	0.413	0.022	0.000	0.435	109
Benz[a] anthracene/ Chrysene	0.064	0.025	0.022	0.129	0.049	0.043	0.221	55
Benzo[b] fluoranthene	0.082	0.039	0.038	0.164	0.079	0.076	0.319	80
Benzo[a] pyrene	0.030	0.012	0.000	0.060	0.023	0.000	0.083	21
Indeno[1,2,3-cd] pyrene/ Benzo[g,h,i] perylene	0.148	0.033	0.000	0.296	0.066	0.000	0.362	91

The majority of analytes were found in the first 2 mL aliquot of eluate, which suggested that pre-concentration of PAHs was possible. The further elution of analytes in the other 2 mL aliquots indicated that not all of the PAHs were eluted. The approximate recovery of the analytes of interest also indicated that not all of the analytes had been eluted from the SPE column with a recovery range of 26 - 109%. This was an improvement to elution using only ACN; however a higher proportion of DCM would probably be required to improve the recovery values of all analytes.

The composition of the eluant mixture was changed to a ratio of 30:70 ACN:DCM to determine if this would yield complete elution of the analytes. The test sample was again a solution spiked with the multi analyte standard solution at a concentration of 0.08 μg mL^{-1}. The eluate from sample loading and the cartridge washing reagent were analysed and again found to contain none of the PAH analytes. The results determined for the cartridge elutions are reported in Table 6-17.

Table 6-17 - The recovery of each detectable component from the solid phase extraction of 5 mL of a 0.08 μg mL^{-1} solution of 16 PAH in POLE eluted using a 30:70 v/v mixture of ACN and DCM

PAH Component	Concentration/ μg mL^{-1}			Mass of analyte/ μg				Recovery / %
	Elution (2 mL)			Elution (2 mL)			Total	
	1st	2nd	3rd	1st	2nd	3rd		
Flourene	0.209	0.008	0.000	0.417	0.016	0.000	0.434	108
Phenanthrene	0.209	0.009	0.000	0.417	0.017	0.000	0.435	109
Anthracene	0.048	0.000	0.000	0.095	0.000	0.000	0.095	24
Fluoranthene	0.256	0.000	0.000	0.512	0.000	0.000	0.512	128
Pyrene	0.249	0.000	0.000	0.498	0.000	0.000	0.498	125
Benz[a] anthracene/ Chrysene	0.224	0.008	0.000	0.448	0.016	0.000	0.463	116
Benzo[b] fluoranthene	0.292	0.000	0.000	0.584	0.000	0.000	0.584	146
Benzo[a] pyrene	0.147	0.000	0.000	0.294	0.000	0.000	0.294	74
Indeno[1,2,3-cd]pyrene/ Benzo[g,h,i] perylene	0.208	0.008	0.000	0.416	0.016	0.000	0.432	108

The chromatograms of the three eluate aliquots showed broader peaks than obtained previously with the acetonitrile or 50:50 ACN:DCM eluant, but recoveries were

improved. The results also showed that pre-concentration had been achieved since most of the analytes had eluted in the first 2 mL aliquot of eluate, with little or no further elution in the second and third volumes. An exception to the improved recovery was anthracene, where the majority of the analyte appeared to be retained on the cartridge sorbent. However, analysis of the 0.08 μg mL^{-1} PAH in POLE solution showed that the peak area for anthracene was lower than expected and indicated a deterioration of the solution. Thus, less anthracene had been loaded onto the SPE cartridge than intended.

A new spiked solution was prepared from the multi analyte standard. The composition of the elution solvent mixture was changed to a ratio of 40:60 ACN:DCM, to decrease the broadening effect of DCM. Calibration solutions were also prepared in order to determine accurate concentrations for the analytes detected in the eluate rather than estimating recovery with respect to a single 0.08 μg mL^{-1} standard as in previous experiments. The calibration solutions were reagent-matched with the elution solvent at six concentrations, 0.0, 0.12, 0.18, 0.24, 0.30 and 0.36 μg mL^{-1}. Table 6-18 shows the results for the three eluant aliquots analysed.

Table 6-18 - The recovery of each detectable component from the solid phase extraction of 5 mL of a 0.08 μg mL^{-1} solution of 16 PAH in POLE eluted using a 40:60 v/v mixture of ACN and DCM

Analyte	Concentration/ μg mL^{-1}			Mass of analyte/ μg				Recovery/ %
	Elution (2 mL)			Elution (2 mL)			Total	
	1st	2nd	3rd	1st	2nd	3rd		
Fluorene	0.360	0.000	0.000	0.720	0.000	0.000	0.720	180
Phenanthrene	0.368	0.000	0.000	0.736	0.000	0.000	0.736	184
Anthracene	0..344	0.000	0.000	0.688	0.000	0.000	0.688	172
Fluoranthene	0.212	0.000	0.000	0.424	0.000	0.000	0.424	106
Pyrene	0.084	0.000	0.000	0.168	0.000	0.000	0.168	42
Benz[a] anthracene/ Chrysene	0.232	0.000	0.000	0.464	0.000	0.000	0.464	116
Benzo[b] fluoranthene	0.200	0.000	0.000	0.400	0.000	0.000	0.400	100
Benzo[a] pyrene	0.156	0.000	0.000	0.312	0.000	0.000	0.312	78
Indeno[1,2,3-cd]pyrene/ Benzo[g,h,i] Perylene	0.236	0.000	0.000	0.472	0.000	0.000	0.472	118

The results showed that the analytes were eluted in the first elution volume, with no further elution in the second and third volumes. This indicates that pre-concentration has occurred from the 5 mL load volume to the 2 mL elution volume. The recoveries were generally high when compared with the concentration initially loaded, particularly for fluorene, phenanthrene and anthracene.

A possible reason for these high recoveries lies in the physical nature of the eluate sample analysed. It could clearly be seen to separate into two layers, probably due to the immiscibility of DCM with the water based micellar solution (Figure 6-13).

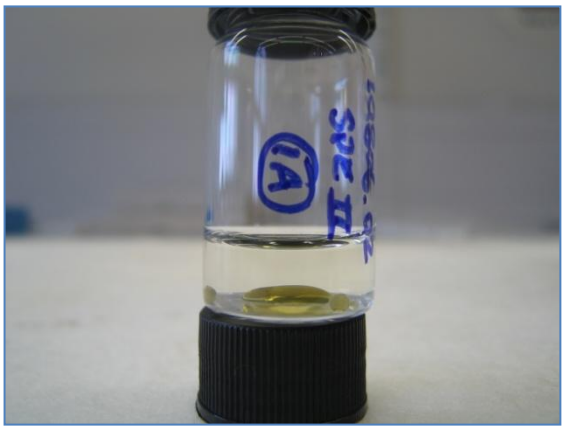


Figure 6-13 - Photograph of a solution eluted from an SPE cartridge using a mixture of acetonitrile and dichloromethane

The combination of these layers was approximately equal to the volume of eluant aliquot applied to the SPE cartridge, 2 mL. However, the DCM layer, in which the analyte was concentrated, was smaller than 2 mL. Since the concentration calculated and reported was based upon a larger volume, it had subsequently been overestimated. The volume of DCM used could also be variable which could lead to uncertainties in the results. If the results were erroneously overestimated for all the analytes it should be noted that the recoveries of some PAHs were actually low.

6.4.6 Gas 'blow down' of microwave-assisted micellar extraction solutions

The application of a purge gas over the surface of the extract is a technique also applied for the pre-concentration of analytes via the evaporation of the solvent. This technique was investigated to be used in combination with SPE, allowing for further concentration of the analytes and better control of the final extract volume.

A 0.08 μg mL^{-1} test solution of the multi analyte standard in 40:60 v/v ACN:DCM was used to determine the effect of nitrogen 'blow down' on analyte recoveries. A 2 mL aliquot of the test solution was blow down under nitrogen in duplicate, along with a blank. The concentrated solutions were then redissolved in 40:60 v/v ACN:DCM to the initial volume and analysed by HPLC along with the original test solution. The results are shown in Table 6-19.

The results show that in general an acceptable recovery was achieved, after application of a nitrogen purge gas, with an average recovery of 88 %. However, variation was observed when reproducing the experiment. The analytes with the highest sensitivity showed reasonable reproducibility, whereas greater variation occurred for the less sensitive species. The least sensitive PAH, dibenz[a,h]anthracene, showed the greatest variation, this could be due to control over the evaporation rate of the solution. The analysis of the procedural blank showed there to be no analytes present in the solution and subsequently there was no contamination from the nitrogen gas. The overall average recovery indicated that reasonable recoveries could be achieved using nitrogen 'blow down', but further investigation is required to assess the observed variability.

Table 6-19 – The recovery of each detectable component from two 0.08 µg mL^{-1} test solutions 'blown down' using a nitrogen purge gas

Analyte	Test	Peak Area		Recovery/ %
		Initial Test Solution	Re-dissolved Test Solution	
Fluorene	A	5611859	11156112	50
	B	9717139	11352088	86
Phenanthrene	A	20348368	20232720	101
	B	21260528	21217008	100
Anthracene	A	37546080	37169920	101
	B	38645600	36866464	105
Fluoranthene	A	7772688	10079312	77
	B	5402563	9913370	54
Pyrene	A	9011296	10039192	90
	B	9821178	9382490	105
Benz[a]anthracene/ Chrysene	A	27553632	34673152	79
	B	36283904	36286464	100
Benzo[b]fluoranthene	A	16322232	25901440	63
	B	26675376	24778208	108
Benzo[a]pyrene	A	14498664	24907776	58
	B	27625696	23042016	120
Dibenz[a,h]anthracene	A	6116464	20912976	29
	B	21658608	12988856	167

If a standard solution is reduced to a smaller volume, then the concentration of the solution can be predicted based upon the mass of analyte present. A solution containing 0.2 µg mL^{-1} of the multi analyte standard in 40:60 v/v ACN:DCM was blown down under nitrogen to determine if reduction to a specific volume resulted in the predicted concentration, with no loss of analytes due to volatilisation, i.e. a concentration of 0.4 µg mL^{-1} if the volume was halved. Six samples of the 0.2 µg mL^{-1} spiked solution (6 mL) were reduced under nitrogen to volumes of 6, 5, 4, 3, 2 and 1 mL, respectively. The sample vessels were graduated so that accurate volumes could be achieved and immersed in a water bath to aid the evaporation process.

The six final solutions were analysed by HPLC, along with five calibration standards (0.0, 0.2, 0.4, 0.8, 1.2 µg mL^{-1}) for quantification. The results for fluorene, phenanthrene and anthracene in the six solutions are shown in Figure 6-14.

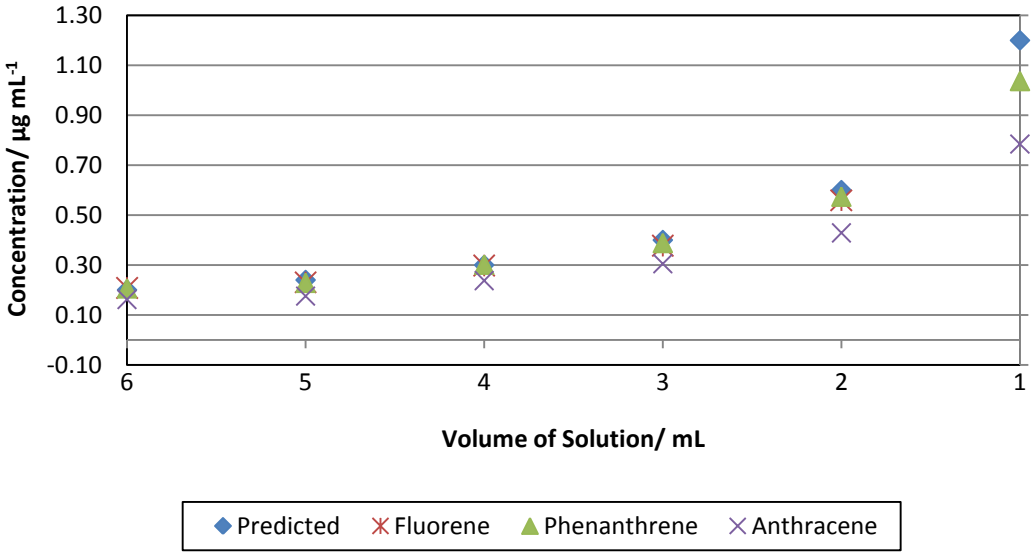


Figure 6-14 - Concentration of fluorene, phenanthrene and anthracene for six solutions obtained by evaporating a 0.2 µg mL^{-1} multi analyte standard (6 mL), using a nitrogen purge gas, and reduced to volumes of 5, 4, 3, 2 and 1 mL

The results for fluorene, phenanthrene and anthracene showed that reasonable recoveries could be achieved for a reduction in volume down to 2 mL, although anthracene showed lower recovery than the other 2 PAHs. The 'blow down' of samples to a volume of 1 mL caused losses of these analytes. The results for fluoranthene, pyrene and benzo[a]anthracene/ chrysene in the six solutions are shown in Figure 6-15.

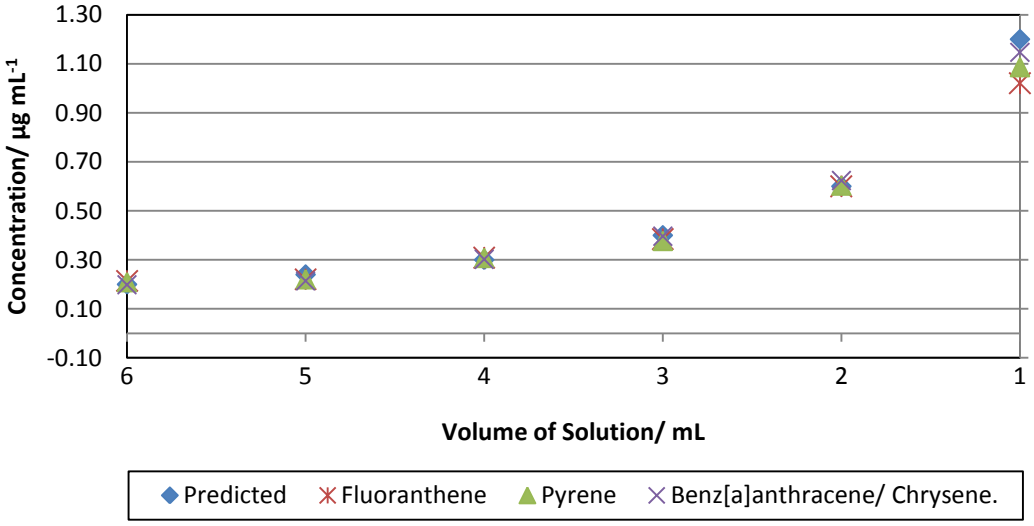


Figure 6-15 - Concentration of fluoranthene, pyrene and benzo[a]anthracene/ chrysene for six solutions obtained by evaporating a 0.2 µg mL^{-1} multi analyte standard (6 mL), using a nitrogen purge gas, and reduced to volumes of 5, 4, 3, 2 and 1 mL

The concentrations of fluoranthene, pyrene and benzo[a]anthracene/ chrysene obtained for 6, 5, 4, 3 and 2 mL volumes showed good agreement with the predicted results. When the solution was reduced to 1 mL the determined concentrations were lower than the predicted results and indicated potential loses of the three analytes. The results for benzo[b]fluoranthene, benzo[a]pyrene and dibenz[a,h]anthracene in the six solutions are shown in Figure 6-16.

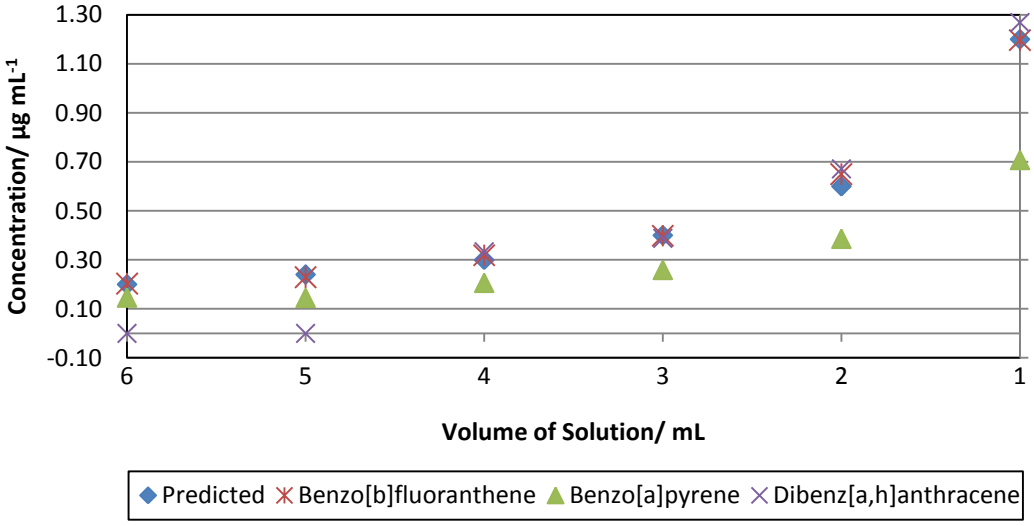


Figure 6-16 - Concentration of benzo[b]fluoranthene, benzo[a]pyrene and dibenz[a,h]anthracene for six solutions obtained by evaporating a 0.2 µg mL^{-1} multi analyte standard (6 mL), using a nitrogen purge gas, and reduced to volumes of 5, 4, 3, 2 and 1 mL

Benzo[b]fluoranthene and dibenz[a,h]anthracene both show good agreement with the expected concentrations after 'blow down' to the various volumes. The results for benzo[a]pyrene are consistent lower than the expected concentration, indicate losses of the analyte. The results for benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene in the six solutions are shown in Figure 6-17.

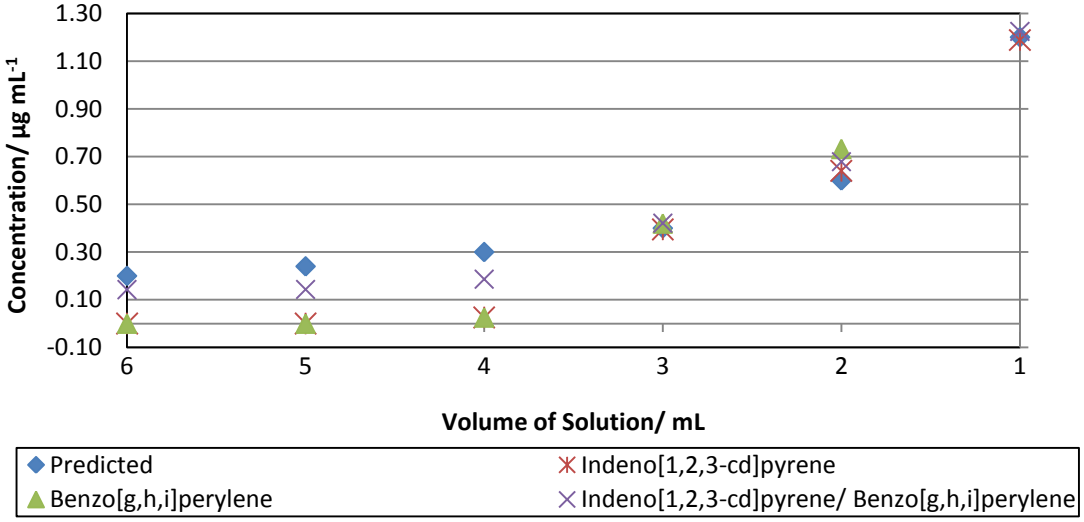


Figure 6-17 - Concentration of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene for six solutions obtained by evaporating a 0.2 µg mL^{-1} multi analyte standard (6 mL), using a nitrogen purge gas, and reduced to volumes of 5, 4, 3, 2 and 1 mL

Benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene were both below detection limits for the solutions of volumes 6, 5, and 4 mL. Indeno[1,2,3-cd]pyrene showed reasonable agreement with the expected concentrations when the volume was reduced to 3, 2 and 1 mL. Benzo[g,h,i]perylene showed agreement with the expected concentration when the volume was reduced to 3 mL. However, when reduced to 2 and 1 mL higher concentrations than expected were obtained. Due to the partial co-elution of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene a summation of the peak areas were used to determine a combined concentration. The combined concentration was detectible in all six solution volumes and showed reasonable agreement with the predicted concentration.

The results they showed that to detect all the analytes of interest the solution needed to be concentrated to at least 0.4 μg mL^{-1}. The evaporation of solution to 3 mL did not generally affect recovery of analytes but losses occurred at lower volumes.

6.4.7 Microwave-assisted micellar extraction of environmental samples

A certified reference material, with associated target values for the analytes of interest, was extracted using the MAME procedure with SPE clean-up and gas blow-down pre-concentration. The MAME extract (12.5 mL) was treated using an SPE cartridge and eluted with 6 mL 40:60 v/v ACN:DCM. The eluate was then blown down using nitrogen to a final volume of 3 mL. The extraction, clean-up and pre-concentration was performed in triplicate. Solutions were analysed by HPLC with reagent-matched calibrants. The results are reported in Table 6-20.

Table 6-20 – Mean concentration, standard deviation and recovery for PAH analytes of interest in CRM LGC-6188 extracted using the MAME procedure (n=3)

Analyte	Concentration/ µg kg^{-1}			Recovery/ %
	$\bar{x}$	s	RSD/ %	
Phenanthrene	398	41.2	10.4	38
Anthracene	269	41.1	15.3	75
Fluoranthene	1306	12.2	0.932	73
Pyrene	1769	129	7.27	120
Benz[a]anthracene/ Chrysene	245	56.2	22.9	30
Benzo[b]fluoranthene	324	79.4	24.5	40
Benzo[a]pyrene	446	6.95	1.56	69
Indeno[1,2,3-cd]pyrene	209	38.0	18.2	56
Benzo[g,h,i]perylene	608	193	31.7	169

The results showed a large variation in both recoveries and precision. In general low recoveries are achieved which indicated inefficient extraction. The fraction of analytes not recovered could have been retained in either the original POLE extract or on the SPE cartridge. The highest recoveries were achieved for anthracene, fluoranthene, pyrene and benzo[g,h,i]perylene, which correspond to some of the largest peaks in the chromatogram.

The chromatogram showed that there was a large rise in the baseline and subsequently if peak areas were integrated relative to the original baseline then the area reported may have been too large. Therefore the recoveries may well be lower than calculated and the efficiency of the extraction poorer.

The extraction of the CRM was repeated in triplicate using the MAME procedure with SPE clean-up and gas blow-down pre-concentration. The solutions were analysed by HPLC with an appropriate calibration. The concentrations of analytes were determined by linear regression of both the integrated peak areas (A) and peak areas measured manually from chromatogram printouts (B). The results are reported in Table 6-21

Table 6-21 - Mean concentration, standard deviation and recovery for PAH analytes of interest in CRM LGC-6188 extracted using the MAME procedure

Analyte	Peak Measure	Concentration/ µg mL^{-1}			Recovery/ %
		$\bar{x}$	s	RSD/ %	
Phenanthrene	A	789	74.5	9.44	76
	B	268	21.9	8.16	26
Anthracene	A	489	4.69	0.96	136
	B	112	8.94	7.96	31
Fluoranthene	A	2026	44.5	2.20	113
	B	688	40.4	5.88	38
Pyrene	A	1951	53.3	2.73	132
	B	370	36.2	9.77	25
Benz[a]anthracene/ Chrysene	A	599	49.1	8.20	72
	B	185	46.0	24.9	22
Benzo[b]fluoranthene	A	1479	14.2	0.96	180
	B	351	41.9	11.9	43
Benzo[a]pyrene	A	870	0.67	0.08	134
	B	132	8.74	6.63	20
Indeno[1,2,3-cd]pyrene	A	774	4.62	0.60	209
	B	61	4.00	6.57	16

A – Integrated peak areas from digital integrator
B – Manually measured peaks using chromatograph printouts

The results showed that peak areas calculated by the integrator were including the initial baseline and subsequently overestimating the recovery. The manually measured peak areas resulted in much lower recoveries. This indicates that, in contrast to literature[113] the extraction of PAH from environmental substrates using the MAME procedure does not result in quantitative recoveries.

It was subsequently not possible to use the method, as intended, for the quantification of PAH analytes, in environmental substrates, in series with PTE determination. However the method could be applied as a screening test to identify which analytes are present and identify samples containing the highest relative contamination.

6.5 Conclusions

A HPLC-UV method was optimised for the determination of sixteen priority pollutant PAHs in extracts from environmental solid substrates. The optimised conditions allowed for the separation of eleven components, with the co-elution of two components and partial separation of two components. The detector wavelength selected represented a compromise in sensitivity towards each of the components. The compromise meant that the lowest molecular weight PAH were not easily detectable.

Repeatable determination of 15 PAHs, for ten replicate readings, was possible for concentrations of greater than 0.10 μg mL^{-1} in solutions of ACN and POLE; and acceptable linearity was achievable on different days. The range of linearity was found to be 0.0 - 0.32 μg mL^{-1}.

The determination of PAHs in a Glasgow soil sample, extracted using the MAME procedure, indentified component peaks that could equate to PAH analytes of interest. However, these potential analytes were among other possibly interfering components and the responses were low

Solid phase extraction and volume reduction under nitrogen was applied with which to pre-concentrate the analytes in the MAME extracts and also to remove as many of the interfering components as possible. Elution of the CN/SiOH SPE sorbent was best achieved using a mixture of ACN:DCM (40:60).

Elution of an SPE cartridge, after application of a POLE based sample, causes the formation of two layers. The sample containing layer had to be separated and evaporated or made up to a set volume, to avoid overestimation of PAH concentration. Sample volume reduction under nitrogen showed that generally little or no volatilization of the analytes occurred when a 6 mL sample was reduced in volume to 3 mL.

Poor recoveries were achieved for the extraction of CRM LGC-6188, using the MAME procedure. This showed that quantification, of PAHs in environmental solid substrates, could not be achieved using the method as developed. It was, however, possible to use the method for screening of the PAH analytes of interests in environmental solid substrates.

7 Determination and fractionation of potentially toxic elements and screening of polycyclic aromatic hydrocarbons in urban roadside deposited sediment

7.1 Aims

The aim of this part of the work was to determine both the fractionation patterns of PTE and the distribution of PAH in the same Glasgow roadside deposited sediment (RDS) samples using the developed sequential extraction procedure.

7.2 Experimental

7.2.1 Samples

The sequential extraction scheme discussed in the previous chapters was applied to 10 dust samples collected from roadsides and parks around Glasgow. The details for each sample are highlighted in Table 7-1.

Table 7-1 - Details of sampling locations

Sample reference	Easting (approx.)	Northing (approx.)	Description
RS.01	258250	665750	Blythswood Square
RS.02	255250	661250	Barrhead Road
RS.03	256250	670250	Maryhill Park
RS.04	255250	668250	Great Western Road
RS.05	251750	670250	Great Western Road, close to Glasgow boundary
RS.06	258698	665198	Hope Street (Central Station)
RS.07	259828	665620	Strathclyde University (Cathedral Street)
RS.08	252250	671250	Drumchapel
RS.09	254750	665750	Elder Park
RS.10	252750	661250	Househill Park

It was decided to sample at locations where a previous study had determined the concentration and fractionation patterns of metals (chromium, copper, iron, manganese, nickel, lead and zinc) in soils[171]. There were 8 dusts sampled at these locations and 2 from sites close to previous locations. Figure 7-1 shows the location of the ten sampling sites around the city of Glasgow.

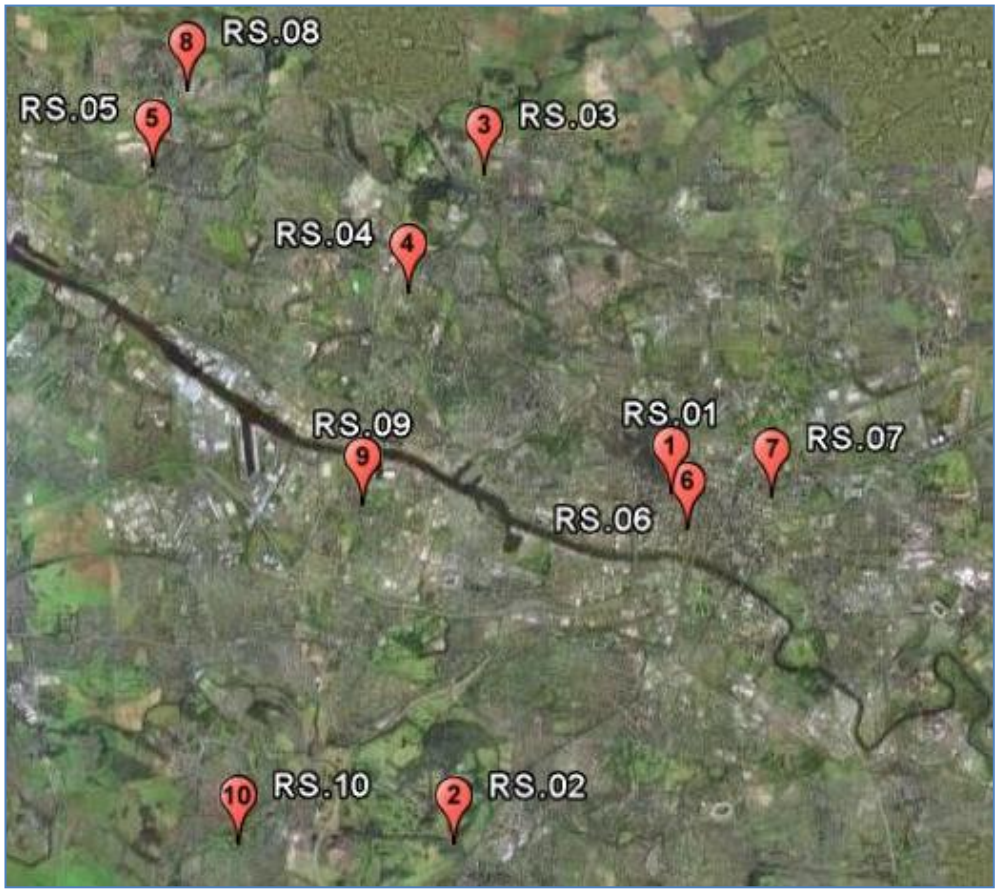


Figure 7-1- Location of Glasgow sampling sites

7.2.2 Extraction and Analysis

A sub-sample of the substrate was weighed in triplicate and microwave extracted using a micellar medium as described in section 2.5.1. After filtration, and storage of the filtrate prior to analysis, the membrane filter and any solid residue left in the ACV was transferred into a centrifuge tube. The sample was then subjected to the four steps of the BCR sequential extraction as described in section 2.5.3. A separate set of triplicate sub-samples were also digested using *aqua regia* as described in section 2.5.2. Analysis for aluminium, barium, cadmium, chromium, copper, iron,

lead, manganese, nickel and zinc was performed by ICPOES as described in section 2.6.2. Screening for the 16 priority PAHs was performed as described in section 2.7 by HPLC.

7.3 Results and discussion

7.3.1 Pseudo-total values

The pseudo-total concentrations of the nine metals investigated in each of the ten RDS samples are shown in Table 7-2.

Table 7-2 - Pseudo-total results for nine metal analytes in ten road and pavement sediment samples from the city of Glasgow (n=3).

Sample	Analyte/ mg kg^{-1}								
	Al	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn
RS.01	11200 ± 358	122 ± 12.4	69.5 ± 3.88	184 ± 73.1	26900 ± 3100	389 ± 16.2	33.4 ± 4.21	111 ± 5.21	348 ± 24.3
RS.02	12200 ± 507	118 ± 4.97	50.3 ± 1.30	76.6 ± 6.57	31000 ± 2950	500 ± 24.4	35.4 ± 2.05	70.0 ± 4.28	148 ± 9.34
RS.03	23300 ± 709	228 ± 41.0	21.5 ± 1.57	45.6 ± 4.27	35300 ± 3810	530 ± 5.78	53.0 ± 1.55	53.0 ± 1.55	113 ± 7.35
RS.04	10200 ± 745	112 ± 12.2	44.7 ± 2.51	68.6 ± 25.0	29800 ± 2730	481 ± 16.8	32.2 ± 3.61	72.1 ± 5.64	163 ± 17.8
RS.05	8440 ± 961	72.1 ± 9.62	44.9 ± 6.26	72.6 ± 22.1	26400 ± 2160	383 ± 45.9	24.9 ± 2.13	44.0 ± 3.67	185 ± 9.88
RS.06	11900 ± 939	140 ± 13.1	50.0 ± 1.73	316 ± 41.4	31700 ± 3450	464 ± 36.8	28.8 ± 1.66	117 ± 16.5	414 ± 16.8
RS.07	9930 ± 621	100 ± 3.50	38.7 ± 3.96	231 ± 22.9	31000 ± 3470	499 ± 136	24.9 ± 1.88	80.0 ± 7.20	219 ± 22.9
RS.08	15000 ± 1246	136 ± 16.7	28.4 ± 3.53	29.7 ± 2.14	26300 ± 2620	621 ± 67.2	26.3 ± 1.02	85.3 ± 3.24	156 ± 4.00
RS.09	11600 ± 2344	134 ± 27.4	47.7 ± 6.24	111 ± 6.92	23100 ± 5930	301 ± 70.8	33.9 ± 9.54	200 ± 50.9	222 ± 42.3
RS.10	15400 ± 463	156 ± 26.6	20.6 ± 2.31	50.9 ± 8.84	33000 ± 3560	434 ± 14.3	23.7 ± 1.90	89.9 ± 3.31	353 ± 41.9

The results showed that the most highly concentrated metals in the sediment samples were aluminium, iron and manganese. This was consistent with mean concentrations previously found in soil samples from the same locations of 13989, 26720 and 428 mg kg^{-1} for aluminium, iron and manganese, respectively[171]. This is expected in soil samples as these metals are found in the natural mineral phases that form soil substrates. The equally high concentration of these metals in sediment could indicate

that soil is a principle component of RDS. There was a large variation in the precision obtained for the nine metals determined with RSD values ranging from 1 – 40 %, this could reflect the intrinsic heterogeneity of road deposited sediments. Roadside sediment sampled in Honolulu showed similar findings with concentrations of 31900-78500 mg kg^{-1} for aluminium, 39900-80000 mg kg^{-1} for iron and 710-1240 mg kg^{-1} for manganese[175]. Fergusson & Ryan[184] also found that iron had the highest concentration in roadside sediments from five cities around the world (22800-58600 mg kg^{-1}). Copper, lead and zinc were the metals most often investigated in studies of roadside sediment found in the literature[25,28-30,175,184-192]. The mean concentrations of these three metals, in urban sediment, are comparable to those obtained in the previous study for soils. Concentrations in the range of 17–491 mg kg^{-1}, 19–2540 mg kg^{-1} and 48-3357 mg kg^{-1} have been reported in the literature for copper, lead and zinc, respectively. The range for copper is consistent with this work (29.7-316 mg kg^{-1}), however lead (44.0-200 mg kg^{-1}) and zinc (113-353 mg kg^{-1}) showed lower levels. The literature results for lead showed a general trend of decreasing over time. In 1981, Harisson *et al.* reported concentrations a 2540 mg kg^{-1} maximum of lead in roadside sediment in Lancaster, whereas in 2003 a maximum of 199 mg kg^{-1} was reported by Charlesworth *et al.* for the cities of Birmingham and Coventry. This is probably due to the decline in the usage of leaded petrol and its eventual banning in many countries. However, lead is persistent in the environment and therefore the lower concentrations maybe due to burial of higher contaminated material with less contaminated material. Barium was not analysed in any of the investigations found in the literature and subsequently cannot be compared with other similar substrates. An average range of 26.5-195 was found in the literature for concentrations of nickel in urban sediment and is consistent with the results of this work.

Correlation coefficients were calculated to determine the linear association of soil and dust across the ten sample sites for aluminium, iron, manganese and each of the other analytes, as shown in Table 7-3.

Table 7-3 - Correlation co-efficient between urban soil and RDS samples from ten sampling sites in Glasgow

Correlation co-efficient (R)								
Al	**Ba**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
0.137	0.072	0.566	-0.416	0.362	0.081	-0.325	0.041	0.329

Iron and - to a lesser extent - aluminium showed two of the stronger correlation between metals found in both soil and sediment. This could indicate that these two metals are from a common source and possibly naturally occurring due to similarly high concentrations observed in both substrates. There was little correlation for lead and anti-correlation for copper, possibly implicating that the source of these metals are different. Normally these three metals are anthropogenic and the correlation of copper and lead may indicate various sources. Zinc showed a much stronger correlation and could imply that its presence in urban soil and sediment is due to a common anthropogenic source. Barium showed no correlation between the soil and sediment results and nickel was anti-correlated.

The RDS and soil data sets were also statistically tested using paired t-tests to assess whether analyte concentrations in the two types of substrate could be from the same population. The results of the paired t-tests are shown in Table 7-4 as a probability values for the 95% confidence interval.

Table 7-4 - Probability values of paired t-test for statistical comparison of investigated metals in urban sediment and soil

P								
Al	**Ba**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
0.233	0.808	0.221	0.193	0.180	0.530	0.415	0.195	0.318

Statistical t-tests of the other metals showed there to be no significant difference between the average concentrations found in both urban RDS and soil obtained from sampling sites around Glasgow. This indicates that contamination levels are similar for both materials and that potential pollution probably arises from a common source, i.e. soil could be a major contribution to RDS.

7.3.2 Fractionation patterns

7.3.2.1 Aluminium

The mean concentration of aluminium and associated RSD found in each step of the BCR sequential extraction procedure, MAME extracts and pseudo-total extracts are listed in Appendix C. Figure 7-2 shows the mean results of aluminium concentration in the MAME extracts (POLE), BCR sequential extracts (steps 1-4) and pseudo-total extracts for 10 RDS from Glasgow.

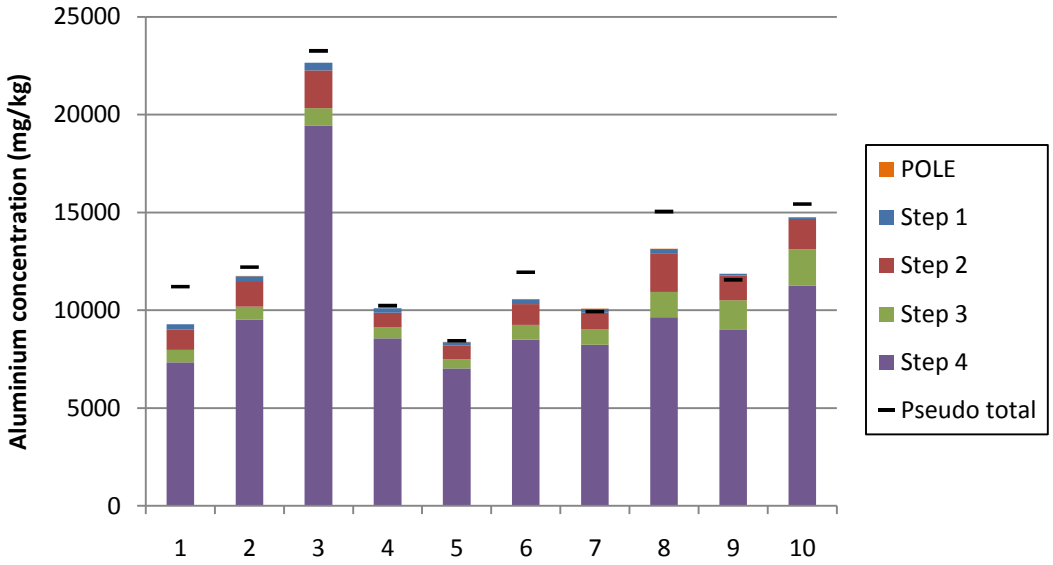


Figure 7-2 - Concentrations of aluminium in ten urban RDS samples from Glasgow for MAME extracts, the four fractions of the BCR sequential extraction procedure and pseudo-total extracts (n=3)

The sum of the four BCR steps was compared to the pseudo-total result, for each sample, to determine a mean recovery. The range of recoveries was reasonable (83 – 103 %), with an acceptable average recovery (95 %). The precision was adequate over the four BCR steps (8.7, 5.9, 12, 4.8 % average RSD's for steps 1 to 4 respectively, n=3) and pseudo totals (7.5 % average RSD, n=3).

Aluminium was primarily extracted in step 4 for the Glasgow dusts with little variation (73 – 86 %). The trend in fractionation is similar across the ten dust

samples, with less than 10 % difference between samples for each fraction. The fractionation pattern is consistent with those seen in reference materials CRM BCR-601 and GLA-URM, a sediment and urban soil substrate respectively. Aluminium was not regularly investigated in urban sediment studies found in the literature. Sutherland *et al.*, using the BCR sequential extraction procedure, found higher levels of aluminium over all four fractions compared to this study[175]. However, the relative fractionation for the two studies was in agreement, with an average of 80.4 and 79.7 % aluminium found in the residual fraction in this study and that of Sutherland *et al.*, respectively. The domination of the residual fraction is comparable to the fractionation found in soil, due to minerals such as aluminosilcates. This would indicate that soil acts a major contribution source to the formation of RDS.

7.3.2.2 Barium

Appendix C lists the mean results and RSD values for the measurement of barium, for extracts obtained at each step of the sequential extraction and pseudo-total content. Precision values for the sequential extraction were typically < 20 % RSD. The mean results of barium in each fraction and pseudo totals are shown in Figure 7-3 for the ten dust samples. An average recovery of 106 % (over a range 93 – 127 %, n=3) was obtained for the sequential extraction of barium, compared to pseudo-total digestion.

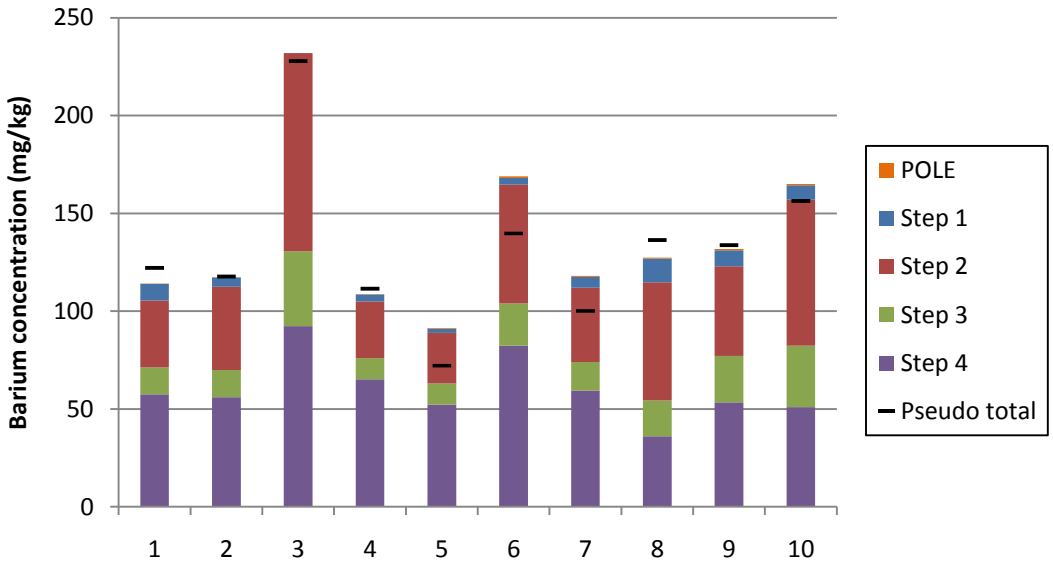


Figure 7-3 - Concentrations of barium in ten urban RDS samples from Glasgow for MAME extracts, the four fractions of the BCR sequential extraction procedure and pseudo-total extracts (n=3)

Samples 6 and 7 were over extracted by the BCR sequential extraction in comparison with pseudo totals for the same samples (127 and 121 %, respectively). The VROM soil target value for barium is 160 mg kg^{-1}, which is exceeded by samples 3, 6 and 10. However, the concentrations were not close to the intervention value of 625 mg kg^{-1}, and therefore are unlikely to pose a health hazard.

In these samples barium was primarily extracted in steps 2 and 4 with average fractions of 36 and 45 %, respectively. There was a similar trend to those seen in the reference soil and sediment although, in these materials, step 3 shows a more equal prominence overall. Barium was not investigated in any of the studies of urban sediment found in the literature, nor was it analysed in the investigation of soils in Glasgow.

7.3.2.3 Chromium

MAME extracts, BCR sequential extracts and pseudo-total extract results are reported in Appendix C as the mean and associated RSD value for the measurement of chromium, for all the samples studied. The variation in results was slightly

greater than for the other metals, although average RSD values were above 20% for steps 1-3 (22, 21 and 22 %, respectively) and < 20 % for step 4 and pseudo-totals. Figure 7-4 shows the chromium mean results, of each step and pseudo-total, plotted for the ten samples.

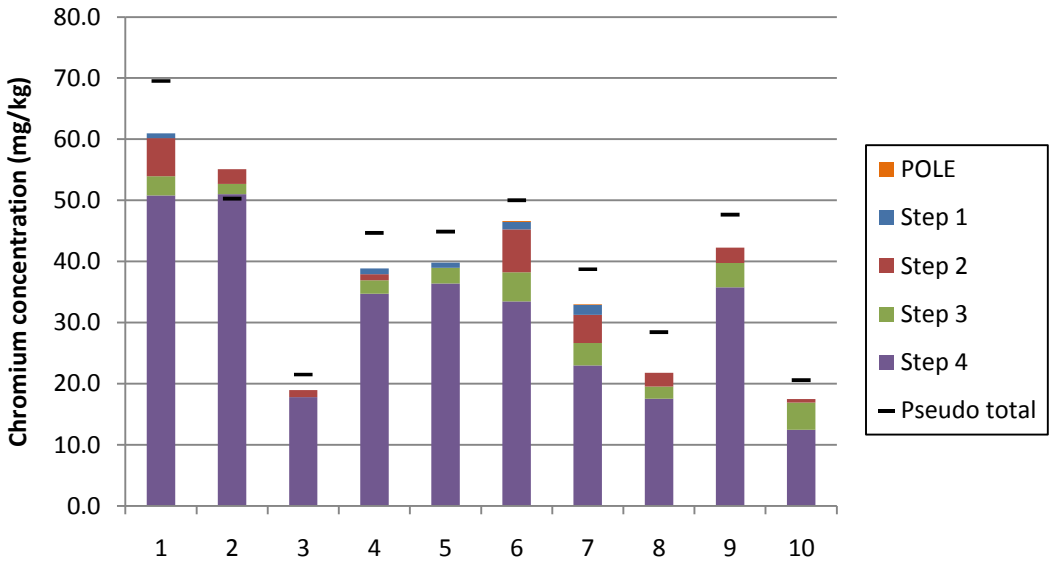


Figure 7-4 - Concentrations of chromium in ten urban RDS samples from Glasgow for MAME extracts, the four fractions of the BCR sequential extraction procedure and pseudo-total extracts (n=3)

The mean recovery over the ten samples was slightly lower than for the other analytes (89 %), for the BCR sequential extraction compared to the pseudo-total digestion. Most notably sample 8 was under extracted (77 %) and sample 2 over extracted (110 %) relative to *aqua regia* digestion. There was no indication of chromium contamination for any of the samples with all concentrations falling below the CLEA soil guideline value of 200 mg kg^{-1}.

The highest proportion of chromium was extracted in step 4, with an average of 82 % of the total, which is consistent with the trends found previously in reference materials. The dominance of chromium in step 4 is in agreement with data for soil samples (78 % average) from the same locations in a previous study[171]. The investigations of Banerjee[25] and Stone and Marsalek[28] also indentified dominant

residual fractions, in RDS from Delhi and Sault Ste Marie with 88 and 67 % of the total, respectively.

7.3.2.4 Copper

Appendix C lists the mean results and RSD values for the measurement of copper, for extracts obtained at each step of the sequential extraction and pseudo-total content. The copper extractions generally showed acceptable precision (RSD < 20 %), however poorer repeatability was found for step 3 (RSD 26 %). The mean results for each step and pseudo-totals are displayed in Figure 7-5.

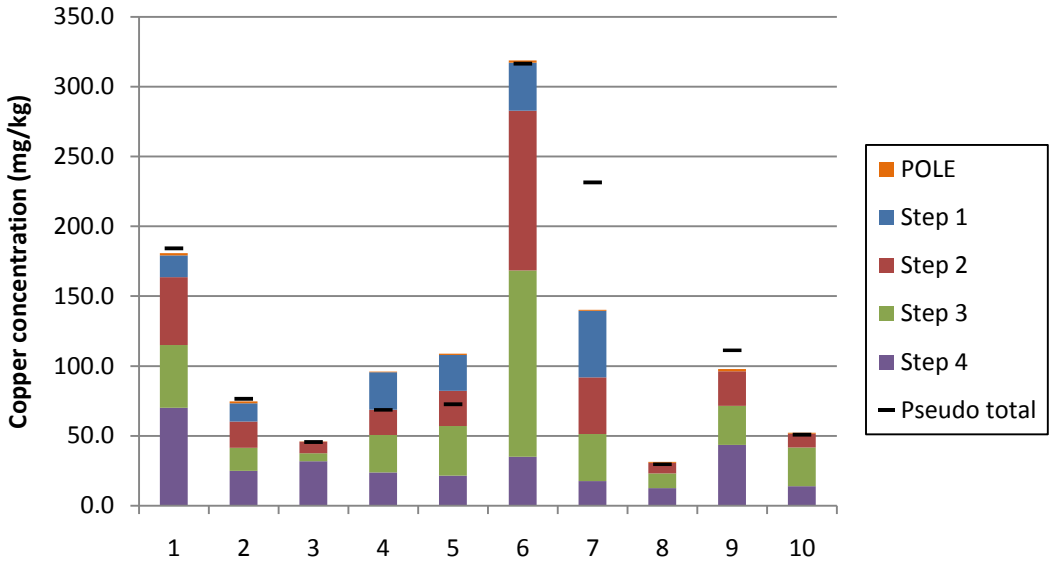


Figure 7-5 - Concentrations of copper in ten urban RDS samples from Glasgow for MAME extracts, the four fractions of the BCR sequential extraction procedure and pseudo-total extracts (n=3)

Acceptable mean recovery of 104 % was achieved for the BCR sequential extraction of copper compared to pseudo-total digestion. However, sample 7 was under extracted by the BCR procedure compared to the pseudo-total (61 %). The VROM soil target value of 36 mg kg^{-1} for copper is exceeded by nearly all of the samples, but only samples 6 and 7 (pseudo total only) are above the intervention value of 190 mg kg^{-1}. The concentration in these two samples, and sample 1, also exceed the old ICRCL guideline for copper in soil of 130 mg kg^{-1}. Samples 1 and 6 are both city

centre locations and many previous investigations have found results above 130 and 190 mg kg^{-1} in city centre RDS, therefore it is not unusual for higher concentrations to occur[30,175,189,193-194]. Although copper is not a particular concern in terms of toxicity, the high value for sample 6 could be worth further investigation.

The distribution of copper in the fractions is not consistent and there are variable amounts in each step over the ten samples. The variation in results could indicate that the copper determined is due to anthropogenic activities. The average shows it to be distributed between all the steps (16, 30, 33, and 22 % mean distribution, respectively). The copper released in step 1 is only particularly substantial for samples 4, 5, 6 and 7, and copper levels were below detection limits in samples 3, 8, 9 and 10. Previous soil data from these sampling locations has shown distribution between all the steps, with much lower average extraction in step 1 (5 %) and a greater dominance of step 3 (50 %)[171]. The range of results for the oxidizable fraction found in the literature for urban RDS were 36-70 %, indicating the potential dominance of this fraction[25,30,184-185,188-189,194-195], although the reducible/ residual fractions are also >20 % in most studies. The literature results are in general agreement with this work, and the dominance of the oxidizable fraction could indicate that organic matter is a good sink for copper in road deposited sediment.

7.3.2.5 Iron

The mean results and RSD values for the measurement of iron, for extracts obtained at each step of the sequential extraction and pseudo-total content can be found in Appendix C. The level of precision was generally acceptable (RSDs < 10 %). Figure 7-6 shows the iron mean results, of each step and pseudo-total, as a histogram for the ten samples.

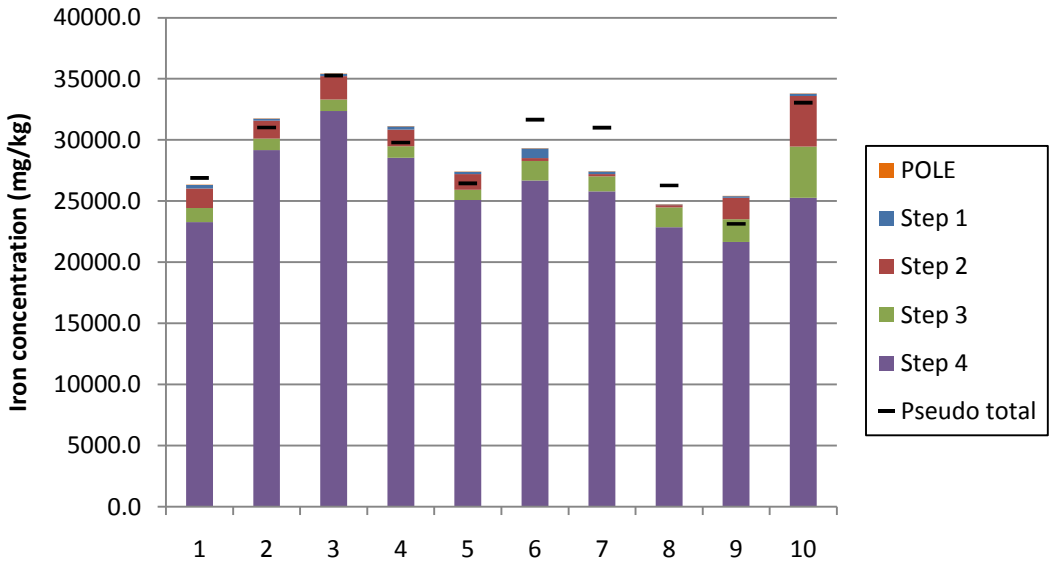


Figure 7-6 - Concentrations of iron in ten urban RDS samples from Glasgow for MAME extracts, the four fractions of the BCR sequential extraction procedure and pseudo-total extracts (n=3)

The extraction of iron following the BCR procedure gave an average recovery of 100 %. A recovery of 88 % for sample 7 showed a slight under extraction using the BCR method relative to *aqua regia*. There was little release of iron in step 1 and comparatively larger amounts were released in steps 2 and 3, however the majority of iron can be seen to be released in step 4 of the BCR procedure. This is consistent with fractionation patterns seen in soil samples from these sample locations[171].

The patterns for each sample are relatively similar with 75- 94 % released in step 4. In the case of samples 9 and 10 the fraction for step 4 is slightly lower (85 and 75 % respectively). The similarity between the ten samples is indicative that the iron is present due to a geogenic source. These results are in agreement with those obtained from the literature, where levels of iron between 76-90 % were found for urban RDS in the residual fraction[28,175,184]. McAlister *et al.* found that 51 % of the total iron was extracted from the reducible fraction[30]. However, this identifies the importance of the term "operationally defined" when using sequential extraction procedures, as his study used reagents which targeted amorphous manganese phases, amorphous manganese/ iron phases and crystalline manganese/iron phases. Subsequently more

iron is removed as it is one of the principal targets of these reagents and therefore the results cannot be compared with the BCR sequential extraction.

7.3.2.6 Manganese

Appendix C lists the mean results and RSD values for the measurement of manganese, for extracts obtained at each step of the sequential extraction and pseudo-total content. The manganese extractions showed acceptable precision (RSD < 20 %), over the different steps. Figure 7-7 shows the mean results of manganese concentration in the organic extracts (POLE), BCR sequential extracts (steps 1-4) and pseudo-total extracts for 10 dusts from Glasgow.

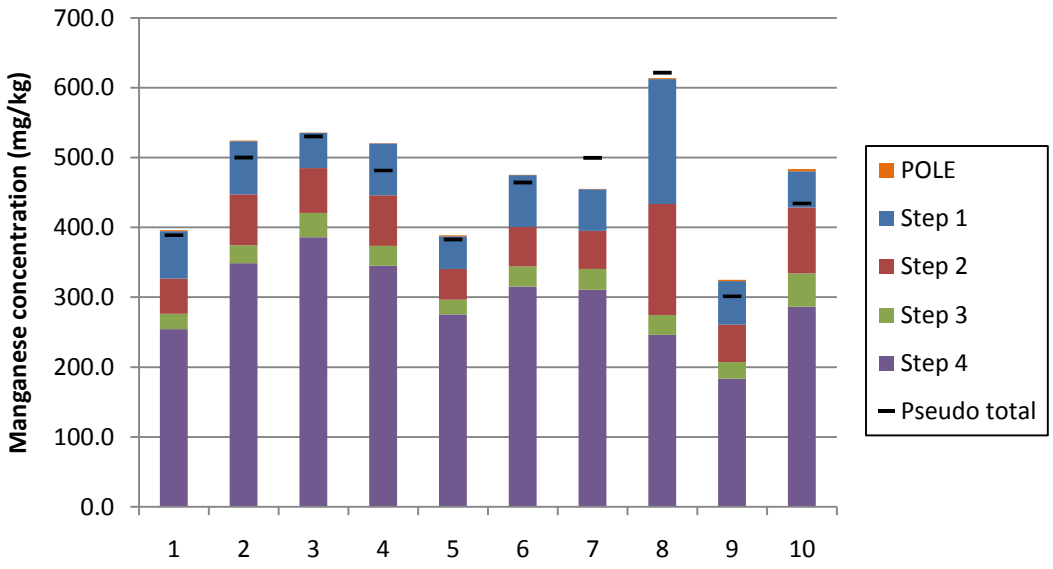


Figure 7-7 - Concentrations of manganese in ten urban RDS samples from Glasgow for MAME extracts, the four fractions of the BCR sequential extraction procedure and pseudo-total extracts (n=3)

The recovery of manganese from the samples using the BCR procedure, compared to the pseudo-total content, was acceptable (average 103 %). However, sample 8 has the highest manganese content but the lowest iron content. The majority of manganese is found in step 4.

An average of 63 % of the manganese is found in step 4, the other significant steps being 1 (average 16 %, n=3) and 2 (average 15 %, n=3). There is relatively little manganese (< 10 %) released from step 3. The pattern is similar across the ten samples, with the exception of sample 8. Previous analysis at these sites[171] and reference materials (BCR601) indicated that more manganese is released from step 2 and less from step 4 for soils. The majority of manganese being found in the residual fraction, is in agreement with the investigations of Stone and Marsalek[28] (average 46 %, n=3), Fergusson and Ryan[184] (average 51 %, n=3) and Sutherland *et al.*(average 50 %, n=3), for urban sediments.

Sample 8, which has the highest manganese content, shows a different pattern to the other samples with higher fractions of step 1 and 2. It is possible that more soil material was sampled at site 8 as the pattern is more comparative to those seen in the previous investigation for soil.

7.3.2.7 Nickel

The mean concentration of nickel and associated RSD found in each step of the BCR sequential extraction procedure, MAME extracts and pseudo-total extracts are listed in Appendix C. The average precision for the sequential extraction was acceptable (RSD value < 20 %). The mean results of nickel content in each fraction and pseudo totals are shown in Figure 7-8.

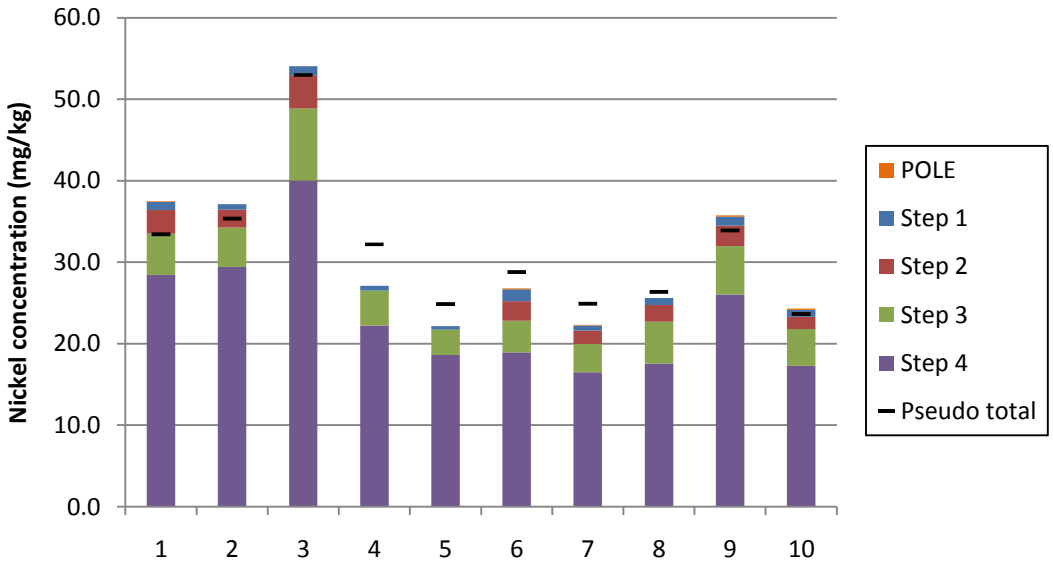


Figure 7-8 - Concentrations of nickel in ten urban RDS samples from Glasgow for MAME extracts, the four fractions of the BCR sequential extraction procedure and pseudo-total extracts (n=3)

An average recovery of 98 % was obtained for the sequential extraction of nickel, compared to pseudo-total digestion. Sample four was slightly under-extracted by the BCR procedure (84 %) relative to *aqua regia* digestion. The level of nickel found in RDS was generally lower in each fraction than for results obtained from the literature[25,28,175], however results were consistent with data for soil sampled previously at the same sites[171].

There is consistent fractionation across almost all samples, except where step 2 concentrations were below the detection limits. The release of nickel can be seen to increase sequentially through the steps 1-4, with an average of 3, 6, 16 and 75 % respectively[171]. This is in reasonable agreement with the soil data where 8, 12, 11 and 69 % was determined for steps 1-4, respectively. Nickel is also found predominantly in the residual fraction for result obtained from the literature[25,28,175] for urban RDS and, in terms of the environment impact, indicates that nickel would not be particularly mobile.

7.3.2.8 Lead

Appendix C lists the mean results and associated RSD values for the measurement of lead. The precision of lead extractions, in terms of RSDs, was generally poorer than achieved for the other metals in steps 1 (5 – 48 %), 2 (6 – 32 %), 3 (9 – 32 %), and 4 (6 – 33 %). The mean results of lead content in each fraction and pseudo totals are shown in Figure 7-9.

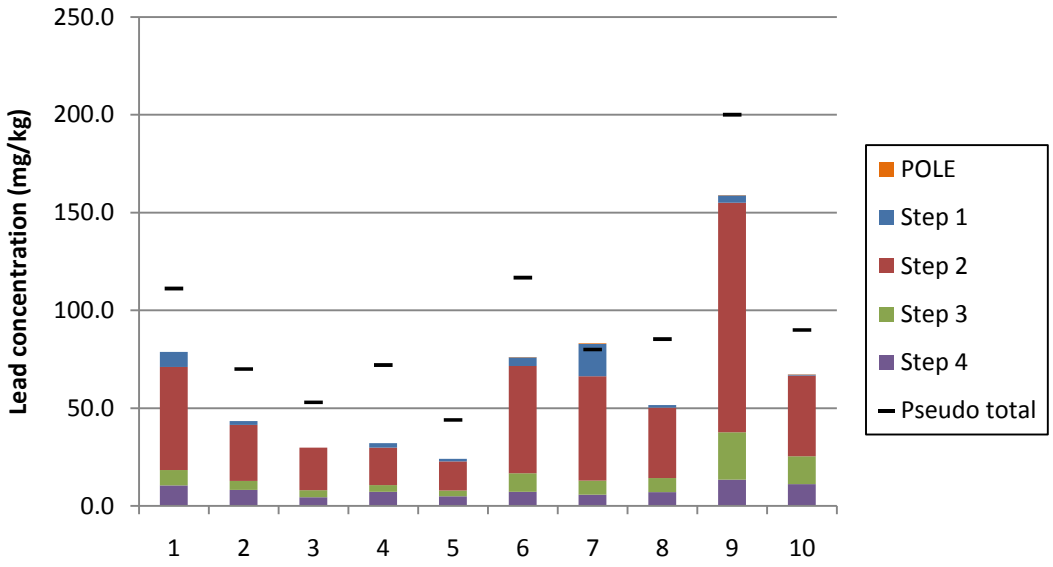


Figure 7-9 - Concentrations of lead in ten urban RDS samples from Glasgow for MAME extracts, the four fractions of the BCR sequential extraction procedure and pseudo-total extracts (n=3)

The recoveries, in comparison to pseudo-total digestion, were also poor between 44 and 79 % (average 67 %). The reference soils which were analysed with these samples showed acceptable average recoveries of 84 and 92 %, therefore the low sample recoveries appear anomalous, although the reason is probably due to the nature of the sample material. The average concentrations of lead (step 1: 4 mg kg^{-1}; step 2: 49 mg kg^{-1} ; step 3: 11 mg kg^{-1} ; step 4: 9 mg kg^{-1}) were found to be lower than the average literature result for the different fractions (step 1: 78 mg kg^{-1}; step 2: 144 mg kg^{-1} ; step 3: 37 mg kg^{-1} ; step 4: 30 mg kg^{-1}) however they were in general agreement with the results obtained previously for Glasgow soils (step 1: 3 mg kg^{-1}; step 2: 74 mg kg^{-1} ; step 3: 16 mg kg^{-1} ; step 4: 12 mg kg^{-1})[171]. It was previously

noted that generally results for more recently sampled materials were lower, possibly due to the phasing out of leaded fuels. The VROM guidelines set a target level of 85 mg kg^{-1} for lead and only sample 9 exceeds this, although it is not close to the intervention value of 530 mg kg^{-1}; or the CLEA SGV of 450 mg kg^{-1}.

The fractionation patterns show that the majority of lead is released in step 2 (average 67 %). Smaller amounts are seen to be released in steps 1 (6 %), 3 (13 %) and 4 (14 %). In the previous investigation of Glasgow soils an average of 70 % of the total lead concentration was found in the reducible step. The literature showed agreement (40-73 % average) that the reducible fraction acts as the predominant sink for lead in urban sediment[28,175,184,188,194-195]. The work of Harrison *et al.*, in 1981, found that 47 % of the total lead was in the extractable fraction. However, the total concentration was higher (1452 mg kg^{-1}) than most other studies (289 mg kg^{-1} average) and this could indicate increased levels of lead and associated with greater environmental mobility.

7.3.2.9 Zinc

Appendix C lists the mean results and RSD values for the measurement of zinc, for extracts obtained at each step of the sequential extraction and pseudo-total content. The precision was generally acceptable, with RSD valuess of < 20 %, for the ten samples. Figure 7-10 shows the mean zinc results, of each step and pseudo-total, plotted for the ten samples.

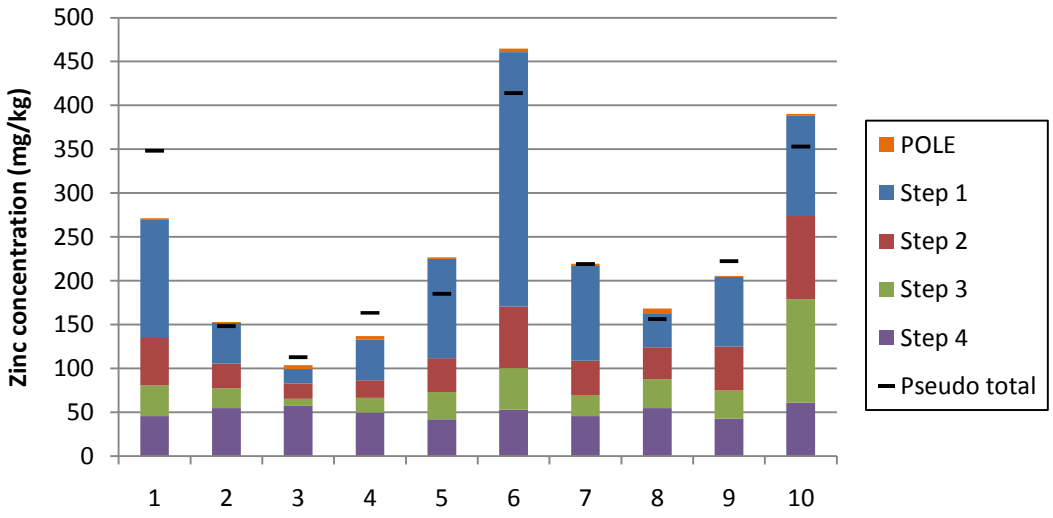


Figure 7-10 - Concentrations of zinc in ten urban RDS samples from Glasgow for MAME extracts, the four fractions of the BCR sequential extraction procedure and pseudo-total extracts (n=3)

An acceptable average recovery of 99 % was achieved for the BCR sequential extraction. Samples 1 was under-extracted (78 %) and sample 6 over-extracted (121 %) by the BCR procedure compared to the pseudo-total digestion. The concentration of zinc in each of the steps is in agreement with results obtained from the literature for urban RDS[28,175,184,188,194-195]. The VROM guideline target of 140 mg kg^{-1} for zinc in soil is exceeded by nearly all of the samples, although the highest concentration (465 mg kg^{-1}), found in sample 6, is less than the intervention value of 720 mg kg^{-1}. Sample 1 (pseudo-total), 6 and 10 all exceed the guideline value of 300 mg kg^{-1} set by the former ICRCL guidelines.

The fractionation shows that zinc is released across all the steps for the ten samples following the BCR sequential extraction. In general the fraction of zinc released in step 1 increased, and the release from step 4 decreased, as the total concentration of zinc increased. The dominant fraction overall is step 1 (average 44 %) and indicates that zinc is potentially available to the environment, although the other steps 2-4 are significant with average fractions of 19, 16 and 21 %, respectively. However there is significant variation between the ten samples and this is in agreement with the literature were different investigation have found both the exchangeable fraction[30,188-

[189,195] (41-68 %) and reducible fraction[25,175,184,194] (37-86 %) to be dominant. The variation the results of this study and those obtained from the literature is an indication that the presence of zinc is due to numerous anthropogenic sources. The results for soils at the same sampling sites[171] showed average fractions of 21, 29, 18 and 31 % for step 1-4, respectively. These are consistent with the urban sediment data, while still showing some variation.

7.3.3 Correlations between metals

The previous work on soil samples from the locations sampled in current work showed correlations between the concentrations of certain metals in the pseudo-total digestions[171]. This was used to potentially identify metals which were associated with common origins (natural and/or anthropogenic). In this and the previous work correlation was performed by plotting the concentration of one element against another and the association reported as the correlation co-efficient.

The correlation co-efficient calculated for metals digested using the pseudo-total method are shown in Table 7-5.

Table 7-5 - Correlation co-efficient between metals digested using aqua regia pseudo-total digestion

	Correlation co-efficient (R)								
	Al	**Ba**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Al		0.9599	-0.6581	-0.3832	0.5730	0.4376	0.7093	-0.1831	-0.2456
Ba			-0.5409	-0.2114	0.5616	0.2921	0.7364	0.0213	-0.0723
Cr				0.5127	-0.4878	-0.4893	-0.1036	0.3267	0.3257
Cu					0.0507	-0.1999	-0.2235	0.3117	0.6687
Fe						0.4602	0.3610	-0.5497	0.0329
Mn							0.1115	-0.5718	-0.3803
Ni								-0.0760	-0.4243
Pb									0.3963
Zn									

Aluminium concentrations were found to be strongly correlated with barium and to a lesser extent iron, manganese and nickel. Aluminium, iron and manganese are common geogenic metals and therefore correlation with barium and nickel would

also indicated similar influences for these metals. Chromium is found only to correlate with copper and is anti-correlated to both iron and manganese. This indicates that sources of chromium are predominantly anthropogenic. The reason for the relationship between chromium and copper, which was also seen for the BCR sequential extraction, is unclear. Copper is also correlated with zinc, which have previously been commonly found and related in soils (along with lead). However, lead does not show a strong correlation with either copper or zinc and the only strong relationships are those of anti-correlation with iron and manganese. Therefore anthropogenic sources are more likely for lead and sources which are probably independent of other metals. The levels of lead were generally low, which may be due to decreased use of the elements in products such as fuel and could explain the lack of a strong relationship with copper and lead that has been previously seen[171].

The same sample sites, as mentioned previously, were previously studied for soil metal concentrations and so it is also of interest to compare these with the dust concentrations. Table 7-6 shows the correlation-coefficients for metal concentrations when both the soil data and dust data for the sample locations are plotted against each other.

Table 7-6- Correlation co-efficient between soil and RDS metal concentrations from the same locations digested using ∑(BCR)

Correlation co-efficient (R)								
Al	**Ba**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
\	\	0.5371	-0.0961	0.4809	0.0978	-0.2622	0.1612	0.8851

**** Al and Ba were not studied for the soil investigation and therefore a correlation co-efficient could not be calculated***

A positive correlation between the soil and dust data was found for chromium, iron and zinc. Chromium has previous been identified as being predominantly associated with anthropogenic sources and the relationship between soil and RDS would indicate common sources. The correlation observed for iron would also indicated a common source, most probably geogenic, and would again imply that soil is a major contribution to RDS formation.

7.3.4 Precision and mass balance

Precision was generally less than 20 % (n=3), although poorer values of up to 40, 50, 90 and 100 %, were observed. This does not compare to the precision (RSD < 10 %, n=3) acheived for the soil data, although previous studies of metals in dust have shown equally high RSD values[28,184]. This would indicate real variation within the material sampled and subsequently heterogeneity of the dusts.

Average recoveries of between 89 and 104 % indicated that mass balance between the BCR sequential extraction and pseudo-total digestion was generally acceptable. The recovery of lead from samples using the BCR sequential extraction was nearly always low with an average of 67 %. This was probably due to the general low concentrations of lead found in the samples, and therefore levels close to detection limits in most of the BCR sequential extraction steps. This was also seen in the higher RSD values obtained for most of the steps.

7.3.5 General fractionation patterns

The mobility of metals, with the environment, is often interpreted using fraction patterns averaged over all the samples investigated[25,28,30]. Figure 7-11 shows the fractionation pattern averaged from all ten dust samples.

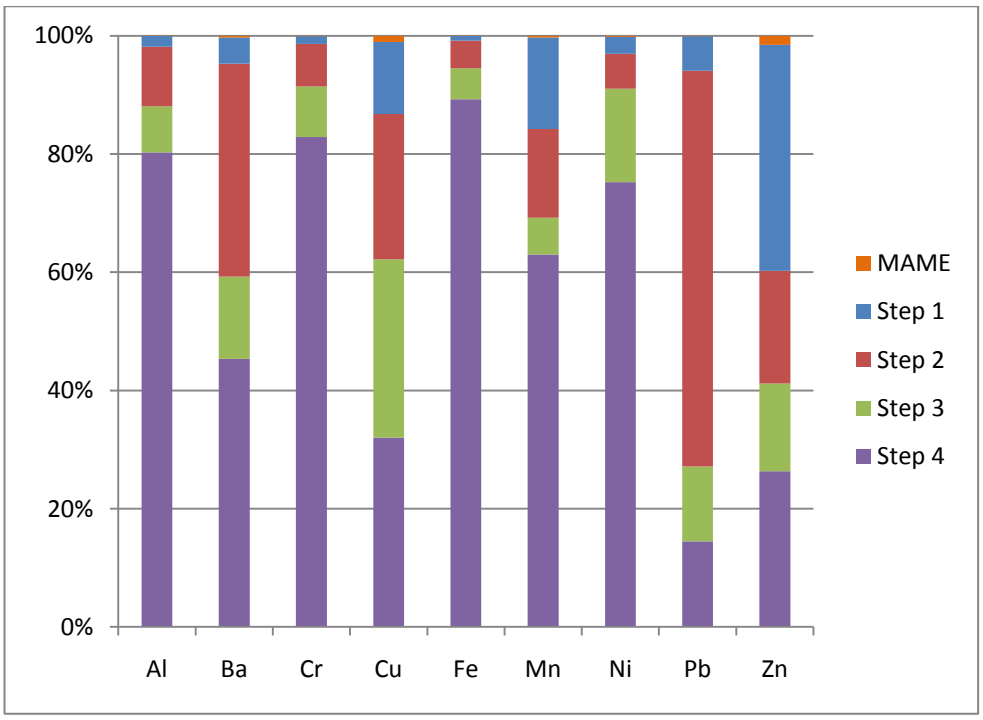


Figure 7-11 – Average fractionation patterns for nine metals determined in dust samples from Glasgow, (n=10).

The relative percentage found in the first three steps of the BCR sequential extraction are often used as an assessment of potential mobility of metals in the environment[175]. The average fractionation for the dust samples indicated a decrease of mobility in the order Pb>Zn>Cu>(Ba)>Mn>Ni>(Al)>Cr>Fe. This is in reasonable agreement with the mobility indicated for the soil samples Pb>Cu>(Ca)>Mn>Zn>Cr>Ni>Fe[171] and that elements more likely to be associated with anthropogenic influences are not as strongly bound as are geogenic metals. Investigations into the fractionation of urban RDS have also shown similar potential mobility trends, such as Zn>Cu>Pb>Mn>Fe>Ni>Cr in Rio de Janeiro[30] and Pb>Cu>Zn>Cr>Ni in Sault Ste Marie[28].

7.3.6 Potential contamination of RDS and soil at sampling sites

The results for the urban RDS samples from ten Glasgow locations were obtained at sampling sites previously investigated for metal contamination in soil[171]. This meant that comparisons could be drawn between the different sites and also the two matrices.

Aluminium was found at high concentrations in all the RDS and soil samples (6700-26000 mg kg^{-1}, average). There was no major difference between the levels found in the two substrates. A main constituent of aluminosilicates[10,18], aluminium is a common geogenic metal and the high levels would indicate weathering of parent materials as the source. The BCR fractionation was only obtained for the RDS samples, however the majority of aluminium being found in the residual fraction (around 80 % of the total) was comparable to the results for Glasgow soil and RDS during the development of the method (chapter 5). High levels in the residual fraction would also indicate that aluminium is more strongly bound within the matrix and suggests geogenic sources. It maybe that weathered parent minerals, forming a major component of soil, are dispersed onto infrastructure and form part of RDS. In general the lowest relative concentrations of aluminium in RDS were found for sampling sites at city centre roads, where possibly less soil is dispersed compared to park areas.

The levels of barium were similar regardless of the substrate or location (70-160 mg kg^{-1}). The concentrations did not exceed the VROM intervention or target SGVs at any of the ten sites. Barium is not a common geogenic element and is likely to be present due to anthropogenic sources, such as barium sulphate used in brake linings[196]. Results were only available for the fractionation of the RDS samples and these were comparable to the RDS analysed during the development of the method (chapter 5). An average of fifty percent of the total barium, in RDS, was found in the residual fraction which was different to the pattern previously obtained for soil. A smaller fraction, of similar total concentration, is potentially mobile in the urban environment for RDS compared to soil.

Chromium levels in the two substrates, for the ten Glasgow urban sampling sites, did not present a significant environmental problem in accordance with the CLEA SGV of 200 mg kg^{-1}, with the exception of soil from the first sampling site. Chromium is not a common geogenic metal in Glasgow, as opposed to cities which lay on serpentine rock[22], and therefore sources are more commonly anthropogenic. The potential sources may be common for the two substrates as similar fractionation was

observed with 80 and 70 % in the residual fraction for both RDS and soil samples, respectively. Comparable concentrations and fractionation implies either common anthropogenic sources or that soil is a major component of RDS.

Studies of RDS and soil have often identified copper to be present at significant levels in urban samples[22,25,28-30,175,197] and it has been referred to as one of the "common urban metals". Generally the concentration was higher in RDS samples (30-400 mg kg^{-1}) compared to soil samples (20-190 mg kg^{-1}) and four sites (RS. 01, 06, 07 and soil site 10) showed the highest levels (>180 mg kg^{-1}). RDS samples from Blythswood Square (RS. 01) and Hope Street (RS. 06) in particular could be highlighted as potentially contaminated using the VROM intervention SGV, with concentrations of greater than 190 mg kg^{-1}. The largest BCR fraction in soil was the oxidizable fraction, which is expected due to the binding of copper to organic species which are extracted in the associated step (2) of the BCR sequential extraction procedure. Similar fractionation was observed for the RDS samples and could indicate soil as a component of RDS. The first three fractions in combination account for around 70 % of the total and indicate that copper is potentially mobile in the urban environment. This would be of greater concern for the highly contaminated samples. The RDS samples containing high concentrations of copper are probably contaminated from specific anthropogenic sources which, due to the sites being busy city centre streets often with slow moving traffic, are likely from vehicular emissions.

Iron is a common geogenic metal forming parts of many mineral structures[10,18] and consequently the majority of Fe in soil can be found in the residual fraction. The presence of approximately 89 % of iron in the residual fraction of the RDS samples would indicate that soil is dispersed onto urban infrastructure as RDS. Similarly high concentrations (1.8 – 4.0 %), expected due to iron based minerals, were observed in both substrates and along with the fractionation would imply a geogenic source.

Manganese is also found in the structures of parent minerals[10,18]; however manganese oxyhydroxides are one of the target phases of the reducible fraction[180] and therefore can be an indication of geogenic sources. This expected pattern was observed for the soil results, whereas around 60 % of the total manganese in RDS samples was found in the residual fraction. With an average of 36 % in the residual fraction of soil, and similar total concentrations to RDS, the mobility of manganese is potentially greater from soil.

Nickel, like chromium, is not common in the parent minerals which weather to form the soil around Glasgow[22]. In general the concentration of nickel, between 20-50 mg kg^{-1}, was comparable for RDS and soil samples. These levels indicated no potential contamination, with the possible exception of soil sample 10, as the concentrations did not exceed the CLEA SGV of 75 mg kg^{-1}. The potential mobility of nickel was also low with 74 and 69 % of the total being found in the residual fraction of the RDS and soil samples, respectively.

The concentrations of lead observed in the study were generally lower than those found previously in soil. Lead, like copper and zinc, is commonly found in urban soils and is known to accumulate with soil acting as a sink for lead. The lower levels in RDS samples may be due to fewer anthropogenic sources (i.e. the banning of lead from petrol), where as soil levels are probably indicative of historical accumulation. Higher levels were observed for RDS samples from park locations (RS. 03, 08, 09) and may be due to dispersion of soil with historical lead accumulation. Lead can often be found to be potentially mobile in the urban environment to be potentially mobile in the urban environment with the majority of the total concentration found in the reducible fraction. This is the case for both RDS samples (66 %) and soil samples (73 %), however the concentrations obtained relative to the CLEA SGV of 450 mg kg^{-1} would not indicate contamination at the sampling site with the exception of soil sample 10.

The concentration of zinc (70-620 mg kg^{-1}) in the soil and RDS samples at the ten sampling sites did not indicate contamination when compared to the VROM intervention SGV, although many exceeded the target SGV. The levels were particularly high at four sites (RS. 01, 06, 07 and soil sample 10), three of which are busy city streets and also contain high copper levels. This is expected as both metals have been referred to as "common urban metals". The fractionation indicated that different anthropogenic sources may be the cause of zinc in the two substrates, with the majority of the total found in the exchangeable fraction for the RDS samples (40 %) and the residual fraction for the soil samples (50 %). The potential mobility is therefore greater for the RDS samples (approximately 75 % of the total in the first three fractions) compared to soil samples (50 %).

7.3.7 Polycyclic aromatic hydrocarbons

The MAME extracts, for the ten Glasgow dust samples, obtained from the first step of the extraction scheme were also analysed for PAH content in triplicate as previously described. The samples were analysed for all 16 priority PAH pollutants, however naphthalene, acenaphthalene, acenaphthylene, dibenz[a,h]anthracene, ideno[1,2,3-cd]pyrene, benzo[g,h,i]perylene were all below the detection limits of the method and subsequently are not reported. The results for fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[b]fluoranthene and benzo[a]pyrene are listed in Table 7-7.

Table 7-7 – Average concentration (mg/ kg) and associated relative standard deviation of eight PAH analytes in ten dust samples from Glasgow

		Sample									
Analytes		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Fluorene	$\bar{x}$	<DL	0.121	0.077	0.108	0.077	0.140	0.12	<DL	0.170	<DL
	RSD		6.7	20	14	7.4	41	37		27	
Phenanthrene	$\bar{x}$	0.116	0.150	0.157	0.241	0.080	0.385	0.119	0.089	0.235	0.089
	RSD	13	44	20	77	49	58	45	38	36	14
Anthracene	$\bar{x}$	0.050	0.047	0.061	0.097	0.053	0.142	0.026	0.024	0.072	0.022
	RSD	12	20	4.9	43	45	49	50	26	39	89
Fluoranthene	$\bar{x}$	0.259	0.267	0.357	0.432	0.223	0.949	0.391	0.091	0.360	0.152
	RSD	4.7	33	15	62	30	55	26	29	56	25
Pyrene	$\bar{x}$	0.106	0.166	0.149	0.307	0.183	0.766	0.182	0.118	0.289	0.131
	RSD	26	25	10	55	38	45	55	22	39	27
Benzo[a] anthracene/ Chrysene	$\bar{x}$	0.065	0.087	0.089	0.101	0.060	0.293	0.125	0.057	0.138	0.073
	RSD	6.0	18	2.7	42	0.38	41	39	25	21	23
Benzo[b] fluoranthene	$\bar{x}$	0.065	0.199	0.275	0.194	0.152	0.471	0.111	0.081	0.118	0.122
	RSD	9.2	5.4	27	18	8.2	33	62	37	26	0.91
Benzo[a] pyrene	$\bar{x}$	0.037	0.119	0.090	0.139	0.152	0.255	0.108	0.082	0.107	0.060
	RSD	0.36	15	24	13	11	29	/	/	37	25

The results showed that sample 6 was the most contaminated for each of the eight analytes, whereas samples 1, 8 and 10 showed the least contamination. There are few specific regulatory targets for the concentrations of PAH in environmental solid substrates, with the Environmental Agency still working on its Soil Guideline Value report[99]. The Ministry of Housing, Spatial Planning and the Environment in the Netherlands published a standard target of 1 mg/ kg in soil/ sediment and set a level of 40 mg/ kg as an intervention value when concentrations indicate human health problems[38]. The values are based on the sum of ten PAH analytes including, naphthalene, anthracene, phenanthrene, fluoranthene, benzo[a]anthracene, chrysene, benzo[a]pyrene, benzo[g,h,i]perylene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene. The sum of the analyte concentrations reported for the ten samples were close to the standard target with values between 0.65 – 3.4 mg/ kg and subsequently showed no indication of a human health hazard when compared to the intervention value.

The triplicate sub-samples of the ten dust samples were simultaneously analysed with sub-samples of a reference material, LGC6188, which is certified for the PAH analytes of interest. The results for the recoveries of PAH from the certified reference material are listed in Table 7-8.

Table 7-8 – Mean concentration (mg kg^{-1}), standard deviation and recoveries for eight PAHs in Certified Reference Material LCG6188

Analytes	$\bar{x}$	s	RSD	Target Value	Recovery
Fluorene	0.058	0.009	16	0.12	48
Phenanthrene	0.071	0.022	31	1.04	6.9
Anthracene	0.042	0.005	12	0.36	12
Fluoranthene	0.159	0.063	40	1.79	8.9
Pyrene	0.089	0.015	17	1.48	6.0
Benz[a]anthracene/ Chrysene	0.085	0.017	20	0.83	10
Benzo[b]fluoranthene	0.260	0.035	14	0.82	32
Benzo[a]pyrene	0.084	0.018	22	0.65	13

The results indicated that inefficient extraction occurred for the eight analytes that where detectable in the dust samples, although it is possible that losses could occur during clean-up, pre-concentration and/or analysis. Assuming under-extraction only a fraction of the total analytes were removed from the sample using the MAME procedure. Subsequently, the concentrations of PAH determined in the RDS samples gave low recoveries, compared to those reported in the literature (generally 80 – 100 %)[113]. The quantification of PAH in the samples was therefore not possible using the method as developed; however it could be used for screening purposes. The ratio between the certified target results and the determined result could be used as a correction factor for the sample results. This assumes that the partitioning of the analytes in all the samples throughout the extraction and analysis is relative similar and therefore can only be used a qualitative screening method to roughly compare results to the regulatory targets and other substrates. Table 7-9 shows the concentrations of each PAH corrected as stated above.

Table 7-9 – Average concentration (mg/ kg) – corrected using recoveries of reference material - of eight PAH analytes in ten dust samples from Glasgow

	Sample									
Analytes	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Fluorene		0.3	0.2	0.2	0.2	0.3	0.3		0.4	
Phenanthrene	1.7	2.2	2.3	3.5	1.2	5.6	1.7	1.3	3.4	1.3
Anthracene	0.4	0.4	0.5	0.8	0.5	1.2	0.2	0.2	0.6	0.2
Fluoranthene	2.9	3.0	4.0	4.9	2.5	10.7	4.4	1.0	4.1	1.7
Pyrene	1.8	2.8	2.5	5.1	3.0	12.7	3.0	2.0	4.8	2.2
Benzo[a] anthracene/ Chrysene	0.6	0.9	0.9	1.0	0.6	2.9	1.2	0.6	1.4	0.7
Benzo[b] fluoranthene	0.2	0.6	0.9	0.6	0.5	1.5	0.3	0.3	0.4	0.4
Benzo[a] pyrene	0.3	0.9	0.7	1.1	1.2	2.0	0.8	0.6	0.8	0.5
PAH (Sum of 8)	7.9	11.0	11.9	17.2	9.6	36.9	12.0	5.9	15.8	6.9

These screening results would indicate that phenanthrene, fluoranthene and pyrene are potentially the most concentrated PAHs in the ten sediment samples. This is in agreement with a previous study of soils in Glasgow[93] which found phenanthrene, fluoranthene and pyrene to be the most concentrated PAHs with values of 1.9, 0.25 and 1.8 mg kg^{-1}. Although the corrected results should be treated with care this agreement would indicate that reasonable assumptions could be made.

The results also showed that samples 4, 6 and 9 had the highest potential levels of contamination, with sample 6 showing levels close to the Dutch intervention value. Samples 4 (Great Western Road) and 6 (Hope Street) are both busy roads and therefore traffic emission could be a major source for PAH pollutants. Sample 6 also showed relatively high levels for most of the metals determined. Correlation co-efficient calculated for metals and PAHs determined in the ten dust samples are shown in Table 7-10.

Table 7-10 - Correlation co-efficient between metal and total PAH (sum of eight) concentrations from the same locations

Correlation co-efficient (R)								
Al	**Ba**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
-0.1568	0.2273	0.2772	-0.1568	-0.1568	-0.1568	-0.1568	0.1901	-0.1568

The correlation co-efficients do not highlight any clear relationships between the metals and PAHs. However, as the PAH data is not quantifiable further studies would be needed to make any real conclusions.

7.3.8 Conclusions

The applied sequential method has allowed for the quantification of PTE and screening of PAH in urban sediment samples from Glasgow. The use of both pseudo-total and BCR sequential extraction procedures as steps in the method has generated quantitative data that could be used to study relationships between metals and their potential behaviour in urban sediment.

The fractionation within the dusts showed aluminium, chromium, iron, manganese and nickel are all mainly associated with the residual phase and indicates they are predominantly geogenic. Barium was mainly associated with steps 2 and 4. Copper was generally evenly distributed between steps 2-4. The reducible phase dominated the fractionation for lead, although recoveries were found to be lower than *aqua regia* digestion values. Zinc was found to be evenly distributed between the four steps, although the exchangeable phase was dominant. These results were generally comparable to those found in the literature for RDS.

Overall the results and known behaviours would indicate that Al, Fe and Mn are due to geogenic sources, and levels in RDS samples may be due to soil dispersion. The other analytes, Ba, Cr, Cu, Ni, Pb and Zn, would appear to be due to anthropogenic sources. Cu, Pb and Zn have previously been highlighted as "common urban metals" in soil. The relative concentrations of Cu and Zn (along with strong positive correlations) would indicate these analytes are also common in RDS. In contrast Pb would not seem to show the same commonality in the RDS samples and this may be due to fewer anthropogenic sources of Pb. The only RDS sampling sites indicating environmental concern were Blythswood Square, Hope Street and Cathedral Street particularly with observed levels of Cu and Zn being close to or exceeding some of the SGVs. As these sites are relatively busy, and often slow moving, city centre

streets this could indicate vehicular traffic as major anthropogenic sources for these locations. The soil sampled from Househill Park also showed high levels for the sampling and analysis performed during the previous study, some of which exceeded SGVs.

The screening of PAH showed that phenanthrene, fluoranthene and pyrene were potentially present at highest concentrations which was in agreement with a previous investigation of urban soil in Glasgow.

8 Conclusions and Further work

8.1 Conclusions

A method for the potential determination of both PTE and PAH in a single sample was investigated. It was initially evaluated for the quantification of PTE, by *aqua regia* digestion and FAAS, after the sample had been treated with a micellar reagent (POLE) for the potential extraction of PAH.

Certified and secondary reference materials were analysed with and without the micellar treatment to determine if quantification was effected. It was found that there were generally no statistical differences whether or not the sample was treated with POLE for copper, iron, lead and zinc.

The analysis of manganese showed statistical difference when a secondary reference material from Glasgow was treated with POLE compared to treatment only with acid. However, determination of manganese in other substrates was not affected.

As prior extraction of PAH using POLE appeared to not affect the determination of PTE for these five metals, the method was further evaluated and developed by investigation of more analytes and expanding the procedure. The analytes studied were increased to include aluminium, barium, cadmium, chromium, copper, iron, manganese, nickel, lead and zinc using ICP-OES analysis. Results determined for cadmium were always below the detection limits and were not further evaluated. The PTE digestion was also expanded by replacing *aqua regia* digestion with the BCR sequential extraction procedure and analysing the four steps with and without MAME.

The mass balance of the sum of BCR sequential extraction steps and the pseudo-total concentration showed agreement for most analytes, with an average recovery of 82-111 %. There was nearly always leaching of PTE into the micellar reagent when it was applied which resulted in lower recoveries of step 1. This only significantly

affected the results when step 1 was the dominant fraction. Subsequently it was important to determine the concentration of each analyte in the micellar reagent to correct the concentration of step 1.

The MAME extraction has been shown to statistically affect the determination of some analytes using the BCR sequential extraction procedure, however, the fractionation was not significantly affected and environmental interpretations could still be made.

Once it had been demonstrated to be possible to quantify PTEs when using *aqua regia* and BCR sequential extraction methods, the analysis of PAHs was investigated. A method for the determination of PAH was evaluated using MAME and HPLC-UV. The method was optimized for the detection of 16 analytes highlighted as priority pollutants by the United States Environmental Protection Agency.

A solid phase extraction method was investigated for the pre-concentration and clean-up of micellar extracts. A CN/SiOH sorbent was found to show pre-concentration for the 16 analytes in micellar extracts after elution using 40:60 mixture of acetonitrile and dichloromethane. However, immiscibility of the micellar extract and dichloromethane meant there were inconsistencies regarding the actual volume of the eluate. The dichloromethane layer analysed was of smaller volume than expected and this caused overestimation in calculations.

A further pre-concentration method, evaporating the extract under nitrogen, was evaluated. This allowed the final extract volume to be controlled. The nitrogen "blow down" method was investigated to determine the effect evaporation to different volumes had on the recovery of an eluate spike (6 mL). The results showed that reduction in volume to 2 mL or less affected the recovery of the smallest and largest PAHs. Evaporation of the volume to 3 mL allowed for recovery of the analytes, while also allowing for further pre-concentration.

The evaluation of the method resulted in a procedure of microwave-assisted micellar extraction (12.5 mL), followed by clean-up using SPE to a 6 mL eluate and finally evaporation under nitrogen to 3 mL. This procedure was applied to a CRM soil certified for concentration of the 15 analytes investigated. Recoveries were found to be low and quantification using the MAME procedure, in contrast to the literature[113], was not possible. Therefore the method could only be used to screen samples for the prescience of the PAH analytes and indentify samples containing high relative concentrations.

The developed procedure was applied for the quantification of PTEs and screening of PAHs in ten urban roadside and pavement sediment samples from Glasgow. The samples were collected from locations that had previously been used in an investigation of urban soils[171].

The average concentration of each PTE was found not to be statistically different from average concentrations determined for urban soils. This indicated that soil was a major component of the sediments collected. Correlation coefficients calculated between the soil and sediment data showed the strongest correlations were for aluminium, chromium, iron and manganese. These were also the analytes most predominantly associated with the residual phase in the sequential extraction. These results indicate that these four analytes are present in sediment due to soil and are most probably predominantly geogenic metals.

The fractionation of aluminium, chromium, iron and manganese was in agreement with results obtained from the literature and the previous soil data. Copper, nickel, lead and zinc also showed fractionation patterns which were in agreement with both the literature and soil data.

The screening of PAH showed that phenanthrene, fluoranthene and pyrene were potentially present at higher concentrations than other analytes, which was in agreement with a previous investigation of soil in Glasgow.

8.2 Further Work

The method developed could be further improved through adaption to both the PAH extraction and PTE digestion steps of the sequential procedure. The MAME procedure, obtained from the literature, was originally developed using the MDS-2000 microwave digestion system and was applied to work undertaken in this research. However, failure of the MDS-2000 system led to the requirement to use the new MARS Xpress system for the later part of the work. Time constraints did not allow enough time for the optimization of the new system and the method from the MDS-2000 was transferred directly across. The extraction efficiency could potentially be improved via the optimization of the MAME method for the MARS Xpress. This could be achieved by optimising factors such as the surfactant concentration, extraction temperature, programme time, and microwave power to obtain maximum recovery of PAH.

The MAME procedure investigated in this work indicated particularly low recoveries for the PAH analytes of interest. Although optimization mention above could improve this, the use of an internal standard could allow for correction in the quantification of analytes after the extraction and sample workup is applied.

Although POLE has been used in a number of investigations for the extraction of PAH from environmental solids, there have been other surfactants applied to the extraction of PAH and other organic pollutants. Different surfactants could be investigated to determine their efficiency in the extraction of PAH from urban environmental solids.

Alternative clean-up and pre-concentration methods for the MAME extracts could also be investigated. The surfactants applied to organic extraction are generally used in aqueous solution and so the extract could be treated as a water sample. The extract from the MAME procedure could be diluted to volume which would reduce the surfactant concentration below the critical micellar concentration and subsequently the micelles would break open potentially releasing any extracted PAHs. The diluted aqueous solution could then be treated with liquid-liquid

extraction using DCM, partitioning the PAH in the non-polar solvent. The DCM layer could then be separated, pre-concentrated and if required cleaned-up using SPE.

There are several other "green" extraction methods, such as SFE and sub-critical water extraction (section 1.4.2.4), which could be used to replace the MAME procedure. These methods could be applied for PAH extraction, from solid substrates, before *aqua regia* pseudo-total digestion and investigated to determine if they affect the quantification of metals.

The quantification of both PAHs and PTEs could be improved by using an alternative analytical technique, with potentially better detection limits, for analysis. This could be achieved using HPLC-fluorescence, LC-MS or GC-MS for PAH analysis and ICP-MS for PTE analysis.

The sequential procedure developed in this work has was applied to urban soils and RDS. It could be further investigated by applying the method to other samples, such as airborne particles. Airborne particles, where the amount of sample is potential very small, is a substrate type that could benefit from a sequential approach in order to maximise the data. The analytes concentrations in airborne particles are often low, although the use of mass spectrometry couple techniques would allow for their determination.

The application of the sequential procedure to more samples would allow further investigation into the correlation of PTE and PAHs in a variety of urban solid substrates. Sampling of urban substrates from roadsides and public areas such as city centres, residential roads, retail parks, urban parklands and industrial estates would allow for comparison of analytes across different areas with different potential pollution sources. The sampling of soil, dust and airborne particles at the same locations would also allow investigation of variation between different environmental compartments. The application of chemometric methods to this type of investigation would be particularly beneficial.

Further analytes could also be investigated, such as expanding the number of metals determined or the analysing of more organic species. The use of modern ICP instruments means that many metals and some other elements can be analysed sequentially, the limiting factor is often the time to process the data rather than the acquisition time. A number of the "green" techniques previously mentioned, including MAME procedures, have been used to extract other organic species and different clean-up methods can be applied to isolate single or combinations of species, for example SPE can be used to separate aromatic and non-aromatic hydrocarbons. The use of mass spectrometry coupled chromatography techniques can be beneficial in identifying and quantifying multiple species, by monitoring for specific species.

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Appendix A

Table A-1 to A-5 show the pseudo-total digest metal content, for the two applied procedures, from CRM BCR-143R; Glasgow (GLA), Torino (TOR), Ljubljana (LJB) and Sevilla (SEV) urban soil secondary reference materials (URM).

Table A-1 – Mean concentrations (mg kg^{-1}), standard deviation and RSD values for copper in pseudo-total digestions (with [B] and without [A] initial microwave-assisted micellar extraction) of investigated samples (n=3).

Sample	Procedure	$\bar{x}$ ± s	RSD / %
BCR-143R	A	118 ± 2.16	1.83
	B	121 ± 2.37	1.96
GLA-URM	A	110 ± 7.80	7.08
	B	104 ± 4.44	4.28
TOR-URM	A	40.1 ± 1.09	2.71
	B	38.6 ± 0.370	0.96
LJB-URM	A	27.9 ± 2.13	7.62
	B	24.1 ± 0.603	2.50
SEV-URM	A	16.4 ± 1.16	7.06
	B	20.8 ± 9.16	44.1

Table A-2 – Mean concentrations (%), standard deviation and RSD values for iron in pseudo-total digestions (with [B] and without [A] initial microwave-assisted micellar extraction) of investigated samples (n=3).

Sample	Procedure	$\bar{x}$ ± s	RSD / %
BCR-143R	A	3.09 ± 0.045	1.47
	B	3.20 ± 0.270	8.46
GLA-URM	A	3.33 ± 0.155	4.65
	B	3.41 ± 0.101	2.97
TOR-URM	A	3.11 ± 0.069	2.22
	B	2.90 ± 0.081	2.79
LJB-URM	A	2.74 ± 0.180	6.55
	B	2.72 ± 0.071	2.60
SEV-URM	A	1.51 ± 0.053	3.52
	B	1.41 ± 0.032	2.26

Table A-3 – Mean concentrations (mg kg^{-1}), standard deviation and RSD values for manganese in pseudo-total digestions (with [B] and without [A] initial microwave-assisted micellar extraction) of investigated samples (n=3).

Sample	Procedure	$\bar{x}$ ± s	RSD / %
BCR-143R	A	723 ± 39.3	5.44
	B	706 ± 6.34	0.90
GLA-URM	A	453 ± 25.9	5.71
	B	341 ± 38.0	11.1
TOR-URM	A	828 ± 22.8	2.75
	B	788 ± 18.5	2.35
LJB-URM	A	423 ± 6.37	1.51
	B	388 ± 31.3	8.07
SEV-URM	A	265 ± 11.3	4.25
	B	247 ± 6.09	2.47

Table A-4 – Mean concentrations (mg kg^{-1}), standard deviation and RSD values for lead in pseudo-total digestions (with [B] and without [A] initial microwave-assisted micellar extraction) of investigated samples (n=3).

Sample	Procedure	$\bar{x}$ ± s	RSD / %
BCR-143R	A	186 ± 6.44	3.46
	B	169 ± 2.42	1.43
GLA-URM	A	371 ± 28.2	7.60
	B	355 ± 20.9	5.88
TOR-URM	A	34.4 ± 1.47	4.28
	B	32.8 ± 2.45	7.47
LJB-URM	A	51.7 ± 3.47	6.70
	B	57.0 ± 3.01	5.28
SEV-URM	A	<DL	N/A
	B	<DL	N/A

Table A-5 – Mean concentrations (mg kg^{-1}), standard deviation and RSD values for zinc in pseudo-total digestions (with [B] and without [A] initial microwave-assisted micellar extraction) of investigated samples (n=3).

Sample	Procedure	$\bar{x}$ ± s	RSD / %
BCR-143R	A	968 ± 1.51	0.16
	B	976 ± 3.84	0.39
GLA-URM	A	163 ± 3.88	2.38
	B	179 ± 2.06	1.15
TOR-URM	A	85.7 ± 3.51	4.10
	B	84.5 ± 4.93	5.83
LJB-URM	A	123 ± 4.52	3.67
	B	108 ± 4.20	3.90
SEV-URM	A	56.0 ± 0.569	1.02
	B	57.5 ± 2.25	3.92

Appendix B

Table B-1 to B-9 show the BCR sequential extraction and pseudo-total digest metal content from CRM BCR-601, Glasgow soil and composite dust samples.

Table B-1 – Mean concentrations (mg kg^{-1}), RSD values and recoveries for aluminium in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of investigated samples (n=3).

		Step 1			**Step 2**		
Sample	**Procedure**	**mean**	**RSD/ %**	**R /%**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	667	0.9		2128	0.6	
	B	320	8.6		1682	9.7	
Composite Dust	A	270	5.9		1577	7.2	
	B	254	3.6		1458	15	
		Step 3			**Step 4**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	771	3.6		17252	2.3	
	B	1398	7.9		16383	5.6	
Composite Dust	A	433	6.8		8653	3.6	
	B	623	11		10116	5.2	
		Sum of Steps 1-4			**pseudo-total**		
		mean	**RSD / %**	**R/ %**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	20818	1.9	93.6	22232	3.9	181
	B	19940	4.0	89.7			
Composite Dust	A	10933	8.7	122	8929	2.7	\
	B	12450	8.6	139			

Table B-2 - Mean concentrations (mg kg^{-1}), RSD values and recoveries for barium in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of investigated samples (n=3).

		Step 1			Step 2		
Sample	**Procedure**	**mean**	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	43.7	2.3		42.3	3.1	
	B	25.3	6.8		41.5	9.8	
Composite Dust	A	23.4	2.2		38.2	6.5	
	B	6.42	11		47.1	7.2	
		Step 3			**Step 4**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	51.4	5.9		49.0	4.4	
	B	50.0	8.5		54.5	8.8	
Composite Dust	A	10.2	11		67.8	18	
	B	12.3	5.9		65.3	5.0	
		Sum of Steps 1-4			**pseudo-total**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	186	2.2	87	214	4.2	126
	B	193	8.8	90			
Composite Dust	A	140	9.2	119	118	13	
	B	131	6.0	111			

Table B-3 - Mean concentrations (mg kg^{-1}), RSD values and recoveries for chromium in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of investigated samples (n=3).

		Step 1			Step 2		
Sample	**Procedure**	**mean**	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	0.678	8.10	106	5.01	1.64	160
	B	<DL			3.31	16.0	105
Composite Dust	A	0.749	18.6		6.67	6.94	
	B	0.657	24.5		5.31	2.1	
		Step 3			**Step 4**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	7.02	7.05	72.3	42.7	7.0	154
	B	11.0	12.0	113	42.6	10.7	153
Composite Dust	A	3.36	3.93		35.2	10.1	
	B	3.24	4.4		33.1	12.5	
		Sum of Steps 1-4			**pseudo-total**		
		mean	**RSD / %**	**%R**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	55.4	5.72	85.1	65	9.2	151
	B	57.4	8.06	88.2			
Composite Dust	A	46.0	9.10	106	43	4.1	
	B	42.3	13.7	97.6			

Table B-4 - Mean concentrations (mg kg^{-1}), RSD values and recoveries for copper in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of investigated samples (n=3).

		Step 1			Step 2		
Sample	**Procedure**	**mean**	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	10.1	3.40	96.4	73.5	2.63	101
	B	2.43	10.2	23.1	73.0	2.71	100
Glasgow Soil	A	10.3	0.81	112	51.5	1.72	182
	B	3.78	8.9	41.2	36.8	8.01	130
Composite Dust	A	44.6	5.3		68.5	28.3	
	B	16.2	6.02		52.8	24.7	
		Step 3			**Step 4**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	55.5	3.45%	70.6	52.7	7.30	87.3
	B	64.9	6.85%	82.6	48.2	2.86	79.8
Glasgow Soil	A	17.7	3.82%	53.3	25.6	5.10	99.0
	B	29.7	7.73%	89.4	29.4	26.7	114
Composite Dust	A	21.0	31.6%		22.7	18.4	
	B	31.0	11.1%		17.6	26.7	
		Sum of Steps 1-4			**pseudo-total**		
		mean	**RSD / %**	**R/ %**	**mean**	**RSD / %**	**R /%**
BCR-601	A	192		86.4			
	B	189		84.9			
Glasgow Soil	A	105	3.04	82.5	127	8.9	115
	B	104	6.06	81.6			
Composite Dust	A	157	19.7	110	142	4.2	
	B	118	17.5	82.8			

Table B-5 - Mean concentrations (mg kg^{-1}), RSD values and recoveries for iron in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of investigated samples (n=3).

		Step 1			Step 2		
Sample	**Procedure**	**mean**	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	145	1.8	90.6	7992	1.86	119
	B	143	14	89.5	4878	20.3	72.4
Composite Dust	A	446	12		4300	2.78	
	B	605	23		3742	17.9	
		Step 3			**Step 4**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	398	14.2	33.4	20480	1.64	95.7
	B	998	8.24	83.9	21758	6.44	102
Composite Dust	A	1194	3.91		30372	5.43	
	B	1591	13.7		29998	6.82	
		Sum of Steps 1-4			**pseudo-total**		
		mean	**RSD / %**	**%R**	**mean**	**RSD / %**	**R /%**
Glasgow Soil	A	29015	0.83	92.8	31253	4.7	102
	B	29016	3.29	92.8			
Composite Dust	A	36312	4.95	103	35338	4.0	
	B	35936	6.62	102			

Table B-6 - Mean concentrations (mg kg^{-1}), RSD values and recoveries for manganese in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of investigated samples (n=3).

		Step 1			Step 2		
Sample	**Procedure**	**mean**	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	281	0.37		211	4.55	
	B	202	0.45		137	1.86	
Glasgow Soil	A	121	1.47	98.6	146	3.55	109
	B	6.29	27.2	5.11	61.0	12.2	45.5
Composite Dust	A	77.6	4.49		82.2	3.18	
	B	56.0	13.4		79.6	13.3	
		Step 3			**Step 4**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	40.0	1.10		221	2.71	
	B	47.2	3.11		231	0.53	
Glasgow Soil	A	15.0	5.31	59.1	144	6.61	98.2
	B	32.0	11.4	127	156	2.18	106
Composite Dust	A	20.5	2.02		321	7.62	
	B	26.1	12.9		366	7.43	
		Sum of Steps 1-4			**pseudo-total**		
		mean	**RSD / %**	**R/ %**	**mean**	**RSD / %**	**R /%**
BCR-601	A	753					
	B	617					
Glasgow Soil	A	427	5.12	91.6	466	7.2	105
	B	375	7.82	80.6			
Composite Dust	A	501	5.79	90.5	554	18.7	
	B	527	5.03	95.2			

Table B-7 - Mean concentrations (mg kg^{-1}), RSD values and recoveries for nickel in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of investigated samples (n=3).

		Step 1			**Step 2**		
Sample	**Procedure**	**mean**	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	5.19	7.31	66.3	9.34	7.58	88.1
	B	3.23	4.57	41.4	8.13	5.96	76.7
Glasgow Soil	A	2.34	4.64	114	2.99	4.15	98.6
	B	<DL			1.55	23.8	51.2
Composite Dust	A	2.00	14.5		4.58	9.38	
	B	1.10	22.1		3.60	18.3	
		Step 3			**Step 4**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	<DL			47.9	3.60	94.8
	B	4.01	37.2	66.3	43.8	2.75	86.7
Glasgow Soil	A	3.72	5.76	79.1	45.0	6.62	112
	B	6.23	4.50	133	45.7	7.81	114
Composite Dust	A	4.13	2.90		20.3	10.9	
	B	4.27	2.64		18.1	6.75	
		Sum of Steps 1-4			**pseudo-total**		
		mean	**RSD / %**	**R/ %**	**mean**	**RSD / %**	**R /%**
BCR-601	A	62.4		83.2			
	B	59.2		78.9			
Glasgow Soil	A	54.1	5.25	83.4	65	3.0	133
	B	54.9	8.95	84.7			
Composite Dust	A	31.0	5.87	95.6	32	10.6	
	B	27.0	7.85	83.5			

Table B-8 - Mean concentrations (mg kg^{-1}), RSD values and recoveries for lead in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of investigated samples (n=3).

		Step 1			Step 2		
Sample	**Procedure**	**mean**	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	<DL			200	2.70	97.3
	B	<DL			162	2.68	79.1
Glasgow Soil	A	24.9	0.93	99.2	263	1.03	112
	B	10.7	7.43	42.5	218	6.42	92.6
Composite Dust	A	8.38	16.7		37.4	8.61	
	B	2.37	24.1		36.9	10.4	
		Step 3			**Step 4**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	7.75	0.04	39.3	18.8	0.2	49.4
	B	29.8	19.7	151	26.9	0.8	70.9
Glasgow Soil	A	36.1	2.32	68.2	76.3	9.08	104
	B	44.9	13.0	84.9	84.4	17.0	115
Composite Dust	A	3.51	17.6		8.21	4.08	
	B	4.26	23.1		6.21	14.3	
		Sum of Steps 1-4			**pseudo-total**		
		mean	**RSD / %**	**R/ %**	**mean**	**RSD / %**	**R /%**
BCR-601	A	226		85.3			
	B	219		82.6			
Glasgow Soil	A	400	1.70	93.0	430	5.4%	111
	B	366	4.60	85.1			
Composite Dust	A	57.5	8.07	76.6	75	27.2%	
	B	49.8	7.89	66.4			

Table B-9 - Mean concentrations (mg kg^{-1}), RSD values and recoveries for zinc in BCR sequential extracts (with [B] and without [A] initial microwave-assisted micellar extraction) and pseudo-total digestions of investigated samples (n=3).

		Step 1			**Step 2**		
Sample	**Procedure**	**mean**	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	273	0.84	105	282	2.53	106
	B	210	7.64	80.3	276	2.62	104
Glasgow Soil	A	13.9	1.63	90.0	19.3	1.08	73.2
	B	3.05	42.2	19.8	11.1	17.6	42.0
Composite Dust	A	212	2.96		66.3	6.19	
	B	94.4	7.35		63.5	20.8	
		Step 4			**Step 3**		
		mean	**RSD / %**	**R /%**	**mean**	**RSD / %**	**R /%**
BCR-601	A	110	9.87	103	89.6	6.55	55.6
	B	136	11.1	129	88.3	8.50	54.8
Glasgow Soil	A	22.0	11.9	80.7	115	9.42	97.4
	B	30.8	11.5	113	118	8.38	99.7
Composite Dust	A	37.5	14.1		56.6	13.9	
	B	37.8	4.02		58.2	13.1	
		Sum of Steps 1-4			**pseudo-total**		
		mean	**RSD / %**	**R/ %**	**mean**	**RSD / %**	**R /%**
BCR-601	A	754		94.9			
	B	710		89.4			
Glasgow Soil	A	170	7.86	107	159	35.5	90.0
	B	175	3.59	110			
Composite Dust	A	372	8.07	98.3	379	10.2	
	B	254	7.89	67.1			

Appendix C

Table C-1 to C-9 show the BCR sequential extraction and pseudo-total digest metal content from 10 Glasgow dust samples.

Table C-1 - Mean concentrations (mg kg^{-1}) and standard deviations for aluminium in sequential extracts (MAME and BCR procedures) and pseudo-total digestions of ten Glasgow dust samples (n=3). Recovery (R/ %) = 100 * (sum of steps/ pseudo-total)

Samples	MAME			Step 1			Step 2		
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD
1		<dl		265	27.1	10.2	1044	81.9	7.84
2	1.81	0.607	33.5	256	19.7	7.73	1297	105	8.06
3		<dl		398	78.6	19.8	1924	145	7.54
4		<dl		228	9.95	4.36	756	20.2	2.67
5	0.98	0.403	41.1	173	7.23	4.18	689	27.0	3.92
6	3.33	0.850	25.5	245	14.3	5.84	1068	24.0	2.24
7	1.98	0.674	34.0	198	15.6	7.86	827	46.6	5.63
8	4.13	0.614	14.9	227	21.6	9.54	1977	172	8.69
9	1.97	0.679	34.5	92.6	6.38	6.89	1256	119	9.50
10	2.84	0.723	25.5	83.5	8.67	10.4	1546	40.9	2.65

Samples	Step 3			Step 4			pseudo-total			R (%)
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	640	107	16.8	7336	370	5.04	11206	358	3.19	82.9
2	674	60.0	8.90	9512	539	5.66	12200	507	4.16	96.2
3	889	93.6	10.5	19442	767	3.95	23254	709	3.05	97.4
4	542	70.8	13.0	8567	229	2.67	10228	745	7.28	98.7
5	471	35.9	7.63	7027	232	3.31	8439	961	11.4	99.1
6	751	81.8	10.9	8489	378	4.45	11942	939	7.86	88.4
7	808	28.8	3.57	8229	330	4.00	9929	621	6.25	101
8	1284	134	10.5	9646	530	5.50	15041	1246	8.28	87.3
9	1495	492	32.9	9014	799	8.87	11551	2344	20.3	103
10	1852	152	8.18	11263	459	4.08	15428	463	3.00	95.6

Table C-2 - Mean concentrations (mg kg^{-1}) and standard deviations for barium in sequential extracts (MAME and BCR procedures) and pseudo-total digestions of ten Glasgow dust samples (n=3). Recovery (R/ %) = 100 * (sum of steps/ pseudo-total)

Samples	MAME			Step 1			Step 2			
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	0.236	0.020	8.54	8.57	0.841	9.80	34.1	2.11	6.17	
2	0.058	0.004	7.45	4.75	0.575	12.1	42.5	3.25	7.65	
3		<dl			<dl		101	10.8	10.6	
4	0.302	0.025	8.26	3.49	0.305	8.70	29.0	1.62	5.58	
5	0.277	0.025	8.95	2.12	0.324	15.3	25.9	3.68	14.2	
6	0.937	0.044	4.74	3.40	0.350	10.3	60.7	4.60	7.58	
7	0.512	0.200	38.9	5.52	0.495	9.0	38.0	0.69	1.83	
8	0.507	0.065	12.8	12.2	0.890	7.32	60.4	3.88	6.43	
9	0.580	0.059	10.1	8.29	0.818	9.87	45.7	4.23	9.26	
10	0.634	0.058	9.20	7.41	0.952	12.9	74.5	1.50	2.02	
Samples	**Step 3**			**Step 4**			**pseudo-total**			**R (%)**
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	13.8	1.96	14.2	57.4	10.6	18.5	122	12.4	10.2	93.5
2	13.9	1.97	14.2	56.0	12.6	22.4	118	4.97	4.22	99.7
3	38.2	5.29	13.8	92.3	5.38	5.83	228	41.0	18.0	102
4	10.7	1.01	9.42	65.2	11.1	17.1	112	12.2	11.0	97.5
5	10.9	0.46	4.24	52.2	14.3	27.4	72.1	9.62	13.3	127
6	21.6	5.45	25.2	82.4	26.2	31.8	140	13.1	9.41	121
7	14.6	0.71	4.87	59.4	12.5	21.0	100	3.50	3.49	118
8	18.3	0.41	2.21	35.9	4.28	11.9	136	16.7	12.3	93.5
9	23.8	7.21	30.3	53.3	1.9	3.50	134	27.4	20.5	99
10	31.5	0.48	1.53	50.9	2.65	5.22	156	26.6	17.0	106

Table C-3 - Mean concentrations (mg kg^{-1}) and standard deviations for chromium in sequential extracts (MAME and BCR procedures) and pseudo-total digestions of ten Glasgow dust samples (n=3). Recovery (R/ %) = 100 * (sum of steps/ pseudo-total)

Samples	MAME			Step 1			Step 2		
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD
1		<dl		0.770	0.108	14.1	6.26	0.85	13.5
2		<dl			<dl		2.37	0.69	29.1
3		<dl			<dl		1.16	0.24	20.9
4		<dl		0.979	0.094	9.62	0.99	0.35	35.9
5		<dl		0.817	0.480	58.7		<dl	
6	0.151	0.023	15.5%	1.17	0.212	18.0	7.04	1.96	27.9
7	0.111	0.020	17.9%	1.60	0.204	12.7	4.60	1.27	27.5
8		<dl			<dl		2.28	0.20	8.77
9		<dl			<dl		2.53	0.26	10.1
10		<dl			<dl		0.57	0.09	15.4

Samples	Step 3			Step 4			pseudo-total			R (%)
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	3.12	0.97	31.2	50.8	7.86	15.5	69.5	3.88	5.58	87.7
2	1.71	0.77	45.1	51.0	8.3	16.2	50.3	1.30	2.58	110
3		<dl		17.8	0.88	4.96	21.5	1.57	7.32	88.2
4	2.18	0.44	20.2	34.7	3.80	10.9	44.7	2.51	5.62	87.0
5	2.59	0.46	17.6	36.4	9.19	25.2	44.9	6.26	14.0	88.7
6	4.79	1.26	26.2	33.4	2.72	8.13	50.0	1.73	3.46	93.2
7	3.71	0.61	16.5	23.0	4.25	18.5	38.7	3.96	10.2	85.2
8	1.97	0.22	11.0	17.6	2.07	11.8	28.4	3.53	12.4	76.7
9	4.01	0.47	11.6	35.8	2.98	8.33	47.7	6.24	13.1	88.7
10	4.44	0.84	19.0	12.5	0.54	4.34	20.6	2.31	11.2	84.9

Table C-4 - Mean concentrations (mg kg^{-1}) and standard deviations for copper in sequential extracts (MAME and BCR procedures) and pseudo-total digestions of ten Glasgow dust samples (n=3). Recovery (R/ %) = 100 * (sum of steps/ pseudo-total)

Samples	MAME			Step 1			Step 2		
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD
1	1.57	0.044	2.80	16	2.32	14.8	48.5	9.76	20.1
2	1.52	0.160	10.5	13.0	3.53	27.1	18.7	2.18	11.7
3	0.14	0.005	3.70		<dl		8.28	0.36	4.36
4	0.57	0.051	8.93	26.6	1.48	5.57	18.3	5.51	30.1
5	0.91	0.039	4.22	25.7	11.6	45.2	25.2	3.51	13.9
6	1.53	0.063	4.11	34.5	1.02	2.96	114	16.8	14.7
7	0.70	0.112	16.2	47.6	9.10	19.1	40.6	4.33	10.7
8	0.56	0.111	19.6		<dl		7.72	0.49	6.32
9	1.58	0.145	9.15		<dl		24.8	3.37	13.6
10	0.76	0.045	5.94		<dl		9.86	1.53	15.5

Samples	Step 3			Step 4			pseudo-total			R (%)
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	45.1	6.04	13.4	70.0	6.91	9.87	184	73.1	39.7	98.1
2	16.5	1.80	10.9	25.1	3.36	13.4	76.6	6.57	8.57	97.6
3	5.86	2.63	44.8	31.8	3.70	11.7	45.6	4.27	9.36	101
4	26.8	5.95	22.2	23.8	6.00	25.2	68.6	25.0	36.4	140
5	35.6	16.3	45.7	21.4	2.80	13.0	72.6	22.1	30.4	150
6	133	50.7	38.0	35.2	10.3	29.3	316	41.4	13.1	101
7	33.8	6.16	18.2	17.6	2.06	11.7	231	22.9	9.91	60.6
8	10.5	2.32	22.1	12.6	2.00	15.9	29.7	2.14	7.19	106
9	28.1	8.60	30.6	43.4	3.59	8.27	111	6.92	6.22	88.0
10	27.8	5.09	18.3	13.9	2.29	16.5	50.9	8.84	17.4	103

Table C-5 - Mean concentrations (mg kg^{-1}) and standard deviations for iron in sequential extracts (MAME and BCR procedures) and pseudo-total digestions of ten Glasgow dust samples (n=3). Recovery (R/ %) = 100 * (sum of steps/ pseudo-total)

Samples	MAME			Step 1			Step 2			
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	2.41	0.262	10.9	270	40.7	15.1	1594	106	6.63	
2	2.99	0.948	31.7	153	14.2	9.29	1466	81.5	5.56	
3	3.67	0.272	7.42	193	26.0	13.5	1921	284	14.8	
4	0.72	0.023	3.17	262	30.3	11.6	1348	60.1	4.46	
5	2.92	0.825	28.2	181	10.3	5.71	1281	89.5	6.99	
6	2.79	0.293	10.5	791	69.0	8.73	245	10.0	4.08	
7	0.99	0.456	45.9	221	25.9	11.7	166	8.24	4.97	
8	1.77	0.189	10.7	45.1	4.98	11.1	189	11.6	6.13	
9	5.19	0.341	6.57	124	5.81	4.70	1760	155	8.78	
10	11.7	1.032	8.80	183	10.2	5.54	4155	247	5.95	
Samples	**Step 3**			**Step 4**			**pseudo-total**			**R (%)**
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	1172	121	10.3	23269.9	2399	10.3	26892.9	3106	11.5	97.8
2	951	125	13.2	29162.2	2886	9.90	31021.1	2953	9.52	102
3	926	78.9	8.51	32375.5	3136	9.69	35277.5	3814	10.8	100
4	964	104	10.8	28531.2	2460	8.62	29784.7	2731	9.17	104
5	842	141	16.8	25075.4	1759	7.01	26443.3	2163	8.18	104
6	1588	153	9.60	26690.7	1893	7.09	31657.9	3445	10.9	92.6
7	1253	133	10.6	25783.9	1635	6.34	31001.9	3465	11.2	88.5
8	1623	103	6.34	22867.8	1406	6.15	26276.1	2621	10.0	94.1
9	1851	228	12.3	21658.1	2840	13.1	23139.1	5934	25.6	110
10	4172	368	8.83	25282.5	1512	5.98	33048.8	3563	10.8	102

Table C-6 - Mean concentrations (mg kg^{-1}) and standard deviations for manganese in sequential extracts (MAME and BCR procedures) and pseudo-total digestions of ten Glasgow dust samples (n=3). Recovery (R/ %) = 100 * (sum of steps/ pseudo-total)

Samples	MAME			Step 1			Step 2			
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	1.30	0.138	10.6	68.3	4.51	6.61	50.4	6.25	12.4	
2	1.10	0.258	23.6	75.8	4.01	5.29	72.9	4.82	6.62	
3	0.61	0.099	16.4	50.2	4.05	8.07	64.5	10.0	15.6	
4	0.25	0.030	12.1	74.1	6.43	8.67	72.5	15.0	20.7	
5	1.14	0.093	8.11	46.8	4.01	8.58	43.9	1.98	4.51	
6	0.76	0.105	13.8	74.2	10.6	14.2	56.5	6.69	11.8	
7	0.62	0.390	62.6	59.4	4.56	7.68	54.7	5.34	9.76	
8	1.52	0.271	17.8	179	11.4	6.40	159.1	6.26	3.94	
9	2.10	0.264	12.5	62.4	9.34	15.0	53.6	4.35	8.13	
10	3.35	0.363	10.8	51.8	0.82	1.59	94.2	4.13	4.39	
Samples	**Step 3**			**Step 4**			**pseudo-total**			**R (%)**
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	21.9	1.88	8.59	254	22.7	8.93	389	16.2	4.18	102
2	25.7	1.05	4.08	349	18.5	5.30	500	24.4	4.88	105
3	34.7	2.25	6.48	386	30.2	7.83	530	5.78	1.09	101
4	28.5	3.50	12.3	345	23.8	6.89	481	16.8	3.49	108
5	21.3	2.57	12.1	275	23.1	8.40	383	45.9	12.0	101
6	28.7	4.45	15.5	315	22.0	6.98	464	36.8	7.93	102
7	30.0	0.57	1.91	311	21.4	6.89	499	136	27.3	91.0
8	28.7	2.90	10.1	246	19.4	7.90	621	67.2	10.8	98.5
9	23.6	6.68	28.3	183	21.7	11.8	301	70.8	23.5	107
10	47.6	4.24	8.91	287	19.6	6.85	434	14.3	3.30	111

Table C-7 - Mean concentrations (mg kg^{-1}) and standard deviations for nickel in sequential extracts (MAME and BCR procedures) and pseudo-total digestions of ten Glasgow dust samples (n=3). Recovery (R/ %) = 100 * (sum of steps/ pseudo-total)

Samples	MAME			Step 1			Step 2			
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	0.081	0.024	29.3	0.998	0.110	11.0	2.91	0.059	2.02	
2		<dl		0.637	0.090	14.2	2.22	0.246	11.1	
3		<dl		1.08	0.181	16.8	4.08	0.583	14.3	
4		<dl		0.600	0.106	17.7		<dl		
5		<dl		0.429	0.066	15.3		<dl		
6	0.098	0.038	38.4	1.47	0.262	17.8	2.39	0.076	3.20	
7	0.065	0.020	30.2	0.647	0.158	24.4	1.62	0.309	19.0	
8		<dl		0.852	0.131	15.3	2.08	0.244	11.8	
9	0.146	0.024	16.4	1.09	0.079	7.25	2.51	0.084	3.36	
10	0.145	0.029	20.2	0.859	0.071	8.25	1.50	0.087	5.83	

Samples	Step 3			Step 4			pseudo-total			R (%)
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	5.07	0.338	6.67	28.4	7.52	26.5	33.4	4.21	12.6	112
2	4.83	0.086	1.78	29.4	3.14	10.7	35.4	2.05	5.80	105
3	8.87	0.492	5.54	40.0	1.35	3.38	53.0	1.55	2.93	102
4	4.26	0.041	0.96	22.2	2.02	9.07	32.2	3.61	11.2	84.2
5	3.13	0.167	5.34	18.6	1.32	7.10	24.9	2.13	8.57	89.1
6	3.88	0.854	22.0	18.9	0.92	4.87	28.8	1.66	5.75	92.7
7	3.46	0.218	6.29	16.5	0.92	5.57	24.9	1.88	7.55	89.3
8	5.13	0.068	1.32	17.6	0.66	3.77	26.3	1.02	3.89	97.2
9	5.93	0.446	7.53	26.1	3.82	14.6	33.9	9.54	28.2	105
10	4.51	0.062	1.37	17.3	1.10	6.34	23.7	1.90	8.05	102

Table C-8 - Mean concentrations (mg kg^{-1}) and standard deviations for lead in sequential extracts (MAME and BCR procedures) and pseudo-total digestions of ten Glasgow dust samples (n=3). Recovery (R/ %) = 100 * (sum of steps/ pseudo-total)

Samples	MAME			Step 1			Step 2			
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1		<dl		7.57	1.59	21.0	52.7	6.94	13.2	
2		<dl		2.05	0.674	32.8	28.6	5.26	18.4	
3		<dl			<dl		21.7	3.38	15.6	
4		<dl		2.39	0.389	16.2	19.1	1.91	10.0	
5		<dl		1.24	0.594	47.9	15.0	5.30	35.3	
6	0.09496	0.022	23.2	4.56	0.228	5.01	54.8	3.45	6.29	
7	0.179	0.041	22.7	16.6	1.42	8.57	53.5	16.93	31.7	
8		<dl		1.34	0.172	12.8	36.1	2.13	5.90	
9	0.286	0.022	7.9	3.68	0.101	2.74	117	29.0	24.7	
10	0.107	0.028	26.5	0.376	0.114	30.4	41.4	6.00	14.5	
Samples	**Step 3**			**Step 4**			**pseudo-total**			**R (%)**
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	7.94	0.95	11.9	10.4	2.46	23.6	111	5.21	4.68	70.7
2	4.55	0.48	10.5	8.21	0.80	9.80	70.0	4.28	6.12	62.0
3	3.68	0.92	25.0	4.41	0.65	14.7	53.0	1.55	2.93	56.2
4	3.44	0.78	22.6	7.13	0.67	9.39	72.1	5.64	7.82	44.6
5	2.90	0.94	32.4	4.90	1.04	21.2	44.0	3.67	8.34	54.7
6	9.53	2.38	24.9	7.16	2.33	32.6	117	16.5	14.2	65.1
7	7.19	0.62	8.63	5.67	0.35	6.14	80.0	7.20	9.00	104
8	7.12	0.72	10.1	7.05	0.97	13.7	85.3	3.24	3.80	60.6
9	24.2	7.10	29.3	13.4	1.00	7.45	200	50.9	25.5	79.4
10	14.1	2.39	16.9	11.2	0.00	0.04	89.9	3.31	3.68	74.6

Table C-9 - Mean concentrations (mg kg^{-1}) and standard deviations for zinc in sequential extracts (MAME and BCR procedures) and pseudo-total digestions of ten Glasgow dust samples (n=3). Recovery (R/ %) = 100 * (sum of steps/ pseudo-total)

Samples	MAME			Step 1			Step 2		
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD
1	1.12	0.369	32.9	136	3.35	2.47	54.0	1.40	2.59
2	1.02	0.291	28.4	46.4	2.13	4.58	28.3	2.48	8.79
3	4.1	0.093	2.25	16.4	2.96	18.0	17.7	2.63	14.9
4	3.97	0.095	2.39	46.3043	1.97	4.26	20.0	0.79	3.93
5	1.92	0.343	17.8	113	30.2	26.7	38.7	3.06	7.92
6	4.08	0.822	20.2	290	49.7	17.1	70.2	2.90	4.14
7	2.51	0.877	34.9	108	8.23	7.63	39.1	3.79	9.69
8	6.16	0.108	1.75	38.1	5.46	14.3	36.6	3.39	9.27
9	1.08	0.189	17.5	79.6015	14.70	18.5	50.4	6.06	12.0
10	2.09	0.051	2.45	114	4.36	3.81	95.2	13.4	14.0

Samples	Step 3			Step 4			pseudo-total			R (%)
	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	$\bar{x}$	s	RSD	
1	35.0	2.15	6.13	45.6	6.84	15.0	348	24.3	6.99	77.6
2	22.8	1.99	8.74	54.5	5.08	9.33	148	9.34	6.31	103
3	8.00	1.71	21.3	57.3	4.68	8.17	113	7.35	6.52	88.2
4	17.1	1.60	9.32	49.4	2.18	4.42	163	17.8	10.9	81.3
5	31.0	1.14	3.69	42.0	1.94	4.63	185	9.88	5.33	121
6	47.5	7.06	14.9	52.9	5.90	11.2	414	16.8	4.06	111
7	24.0	0.89	3.71	45.7	5.92	13.0	219	22.9	10.5	98.9
8	33.0	1.49	4.51	54.6	3.51	6.44	156	4.00	2.56	104
9	32.1	2.93	9.11	42.5	3.25	7.65	222	42.3	19.0	92.0
10	118	9.73	8.27	60.9	1.42	2.34	353	41.0	11.6	110