

# **NOVEL METHOD FOR THE DETERMINATION OF RADIONUCLIDES AND THEIR PRECURSORS IN CONCRETE USING LA-ICP-MS**

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## ABSTRACT

During the decommissioning of nuclear facilities, a range of materials are generated and need careful characterisation in order to segregate them into their appropriate waste stream. The procedures involved demand significant time and investments to accurately determine the radionuclide inventory necessary to proceed. Methodology requires sampling, homogenisation, dissolution and sometimes a separation step to measure radionuclides using their decay properties.

The approach proposed here is to spatially resolve the distribution of major and trace elements in concretes, and by inference important neutron activation-induced radionuclides, using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The technique offers the possibility of an onsite sampling tool for the different concrete constituents such as aggregates and sand/cement mixes at the micron scale, with typical detection limits in the  $\text{ng.g}^{-1}$  range for most elements.

Several shielding concrete samples from Windscale (Cumbria) and CONSORT research reactor hosted by Imperial College (Silwood Park campus) are investigated. Initial work focussed on the identification and main chemistry of the aggregate types involved, using a set of chemical characteristics to fingerprint the ablated phases. Subsequently, available and manufactured calibration materials are evaluated for direct quantification purposes, together with wet chemistry reference values obtained for each concrete constituent for validation. Typical chemistry can thereafter be linked to each phase and build the overall bulk information.

Finally, the potential to measure  $^3\text{H}$  directly using ICP-MS is investigated. This theoretical approach describes the conventional analysis methods and problems with ICP-MS analysis and considers several technological advances from the original instrumentation to overcome these, including the latest instrument available and figures of merit based on practical data.

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## Glossary

AES: Atomic emission spectroscopy

AMS: Accelerator mass spectrometry

ASTM: American Society for Testing and  
Materials

BEC: Background equivalent  
concentration

BS: Bioshield

CEFAS: Centre for Environment, Fisheries  
and Aquaculture Science

CPS: Counts per second

CRC: Collision/reaction cell

C/S: Cement and sand mixture

EC: Electron capture

EDS: Energy dispersive spectrometer

H<sub>2</sub>F<sub>2</sub>: Hydrofluoric acid

H<sub>2</sub>O<sub>2</sub>: Hydrogen peroxide

HCl: Hydrochloric acid

HClO<sub>4</sub>: Perchloric acid

HLW: High level waste

HNO<sub>3</sub>: Nitric acid

HSE: Health and Safety Executive

IAEA: International Atomic Energy Agency

IAG: International Association of  
Geoanalysts

ICP: Inductively coupled plasma

IS: Internal standardisation

LA: Laser ablation

LB: Large block

LiBO<sub>2</sub>: Lithium metaborate

LLD: Lower limit of detection

LLW: Low level waste

LSC: Liquid scintillation counting

MIP: Microwave induced plasma

MS: Mass spectrometry

m/z: Mass per charge

Na<sub>2</sub>O<sub>2</sub>: Sodium peroxide

NDA: Nuclear Decommissioning Authority

NERC: Natural Environment Research  
Council

NIST: National Institute of Standards and  
Technology

NNL: National Nuclear Laboratory

NPL: National Physical Laboratory

OBT: Organically bound tritium

OES: Optical emission spectrometry

OPC: Ordinary Portland cement

REE: Rare earth element

RIFE: Radioactivity in Food and the  
Environment

RIMS: Resonance ion mass spectrometry

SA: Standard addition

SB1: Small block 1

SIMS: Secondary ion mass spectrometry

TIMS: Thermal ionisation mass  
spectrometry

TOC: Total oxide correction

USGS: United States Geological Survey

WDS: Wavelength dispersive  
spectrometer

WP1: Windscale Pile one

WP2: Windscale Pile two

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## CHAPTER I: INTRODUCTION

### 1. Background

Since the first nuclear reactor with dual capacity to produce weapon-grade plutonium and electricity went online at Calder Hall (Seascale, Cumbria) in 1956, nuclear energy evolved and grew to become an important contributor to the U.K. energy demand. This station was the first to deliver electricity at an industrial scale from nuclear energy (The Engineer, 1956). Since then, the British nuclear park saw many new plants emerge to replace the aging ones, including the latest group which has been given the 'go ahead' for construction work. From this nuclear park, 18 plants are still generating electricity, contributing to about 18% of the U.K. energy demand (World nuclear association, 2011). In 2003 the Government's Energy White Paper underlined that to meet low carbon targets required by European law, the energy sector needs to cut on fossil fuel power stations and shift its electricity production towards low carbon sources. At the same time, a diversification of the energy sources was a welcomed addition to secure the future of the energy sector. Nuclear energy, together with wind and solar energy, has been connected to a low carbon footprint, but concerns towards the technology are related to the handling of the waste generated and its legacy. Also in the views of the Fukushima Daiichi accident that happened on 11<sup>th</sup> March 2011 on the Japanese coastline, the general safety of nuclear plants has been questioned and triggered worldwide concerns and actions, from the complete termination of the national nuclear programme in Germany to a delay in the construction phase of the new plants in the U.K.

To help on the nuclear waste management front, important research outcomes and technological developments have been achieved in the areas of waste segregation, recycling, packaging, transport and disposal. At this point, the key subject of a deep geological repository for High Level Waste (HLW) has been addressed and possible locations have been put forward for assessment. For existing disposal facilities, such as the Low Level Waste (LLW) Repository near Drigg (Cumbria), the capacity to accept waste is constantly diminishing. Low Level Waste is a relatively broad category, and spans over five orders of magnitude for radioactivity levels, with some variations depending on the radionuclides involved. Construction of new repository vaults to accept the waste comes at important costs, therefore the idea to apply the waste hierarchy, from prevention to disposal of waste, is regarded as very important to implement and ease the pressure on the repository. A report published in 2010 by the Nuclear Decommissioning Authority (NDA), responsible for dealing with nuclear waste on the national scale, highlights the strategy adopted for the management of low level solid nuclear waste. One key factor is the preferred

option of implementing the waste hierarchy more efficiently on solid low level waste, which has a very significant potential for reuse and recycling of material. Figure 1.1 shows the hierarchy for nuclear waste presented.

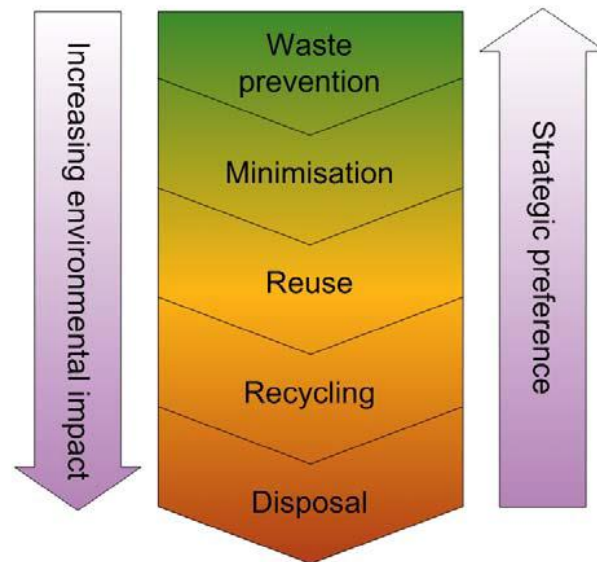


Figure 1.1: Waste hierarchy for nuclear industry (NDA, 2010).

The majority of LLW comes from the activities related to nuclear fuel cycle, including fabrication and reprocessing, activities undertaken by the Ministry of Defence and the fabrication of radioactive products for medical purposes. Finally, the decommissioning of nuclear facilities generates vast amounts of LLW, and includes general building rubble, soils and metals as well as the equipment and items used at the nuclear facility.

The decommissioning of nuclear facilities is accepted to be a process of three stages, with usually care and maintenance periods in-between. The stages include firstly the defueling of the facility and the removal of heat transport fluids, followed by the decontamination of appropriate areas and dismantling and safekeeping of certain parts on or off-site, usually not the core parts of the reactor which is sealed, and finally all remaining materials, structures and equipment are removed for appropriate storage and the land returned to unrestricted use. In order to tailor the activities required for all stages of the decommissioning process and the timescale attached to each, it is necessary to gather as much information as possible on the nature of the radiological contamination, such as the radionuclides inventory, the quantities of each, their location within the plant and the physical and chemical form. Therefore, accurate characterisation of the radiological waste before any decommissioning activity is started is paramount (Bayliss and Langley, 2003).

One such material to deal with is concrete, commonly used on nuclear sites mainly for structural buildings, but also and most importantly as a shielding material. Concrete combines good radiation absorption properties (against gamma rays and neutrons produced in the reactor core), as well as satisfactory mechanical strength, durability and presents attractive economical value during the building phase (Neville, 1981). Although the shielding concrete is not directly in contact with radioactive elements, it becomes a radioactive waste due to the activation process taking place while experiencing the intense neutron flux during the reactor operation period. Neutron activation happens when a stable isotope captures a neutron to form a new isotope at mass +1, usually a radioisotope. A second activation mechanism, more commonly referred to as fission, can occur when a stable element captures a neutron, but is too unstable under its new configuration and spontaneously splits into two or three atoms of variable atomic masses, also usually radioactive and are called fission products. Together with this fission, two more neutrons and significant energy are liberated: this is the basis of nuclear power used in reactors. Overall activation generates a range of radioisotopes produced from specific stable elements originally present in the concrete. The activation of concrete is not a constant process through the shield's thickness and the inventory of radionuclides produced will vary and needs accurate characterisation to allow for the best decommissioning approach.

The waste characterisation process used in the industry is potentially split in two phases. The initial assessment consists in surveys using radioactive dose-rate measurement tools and also taking "swabs" of contaminated surfaces. Nevertheless to enable an accurate determination of the whole inventory, samples need to be taken and processed for radionuclide specific measurements. A representative sub-sample from the bulk concrete is taken and processed to measure the radionuclides using their decay properties. For some nuclides such as gamma emitters, the process only involves a homogenisation step as the strongly penetrating rays can be measured relatively easily, with mostly the sample geometry to be of importance for accurate results. Nevertheless for alpha and beta rays emitters, the preparation can include a digestion and extraction to isolate the analyte of interest as both radiations are weaker and stopped more easily by the sample's matrix (Bayliss and Langley, 2003). In 2005, The NDA and the Health and Safety Executive (HSE) co-hosted a workshop on 'Technical Issues in Nuclear Liabilities management in the UK' to address the characterisation problems of a waste such as concrete. The outcomes were that typical issues are the reduction of measurement errors and better limits of detection, faster and cheaper methods for waste characterisation, the possibility of on-line techniques and the development of new methods for difficult-to-measure waste, especially from the nuclear legacy point of view.

The approach taken by the nuclear industry to measure radionuclides provides an accurate average of the inventory over the representative sub-sample taken, but demands lengthy sampling, preparation, separation and measurement periods. Also, potential loss of nuclides or contamination during the sampling and preparation are to be accounted for. A different method used in the industry is the application of computer codes to estimate the activation inventory, with a realistic distribution within the concrete. Such codes require the chemical composition of the concrete, take into account the total neutron flux history of the nuclear facility and natural decay of nuclides produced (Gaudry and Delmas, 2007). Commercial codes are available, such as FISPIN (Amec) and ORIGEN (Oak Ridge National Laboratory, USA) which can be used for estimation of activation products of nuclear fuel rods and applicable to nuclear structures; also many nuclear scientists developed their own codes for specific applications such as activation products prediction in concrete and concrete constituents (Evans *et al.*, 1984). To determine the composition of a material such as concrete, several analytical methods are available. These include atomic absorption spectroscopy, X-ray fluorescence, neutron activation analysis, inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ICP mass spectrometry (ICP-MS). Overall, the majority of major and trace elements present in concretes can be determined, again with a sampling and digestion process before quantification. This results in a bulk chemical composition suitable to be run with the activation codes (Gaudry and Delmas, 2007).

In the field of analytical chemistry, ICP-MS grew rapidly to become the most widely used technique for trace, ultratrace elemental analysis and precise isotopic measurements in inorganic chemistry in a variety of matrices. The technique developed with technological advances to improve sensitivity, matrix tolerance and stability of the instrumentation, at decreasing costs per sample. Alongside these developments, different sample introduction options were also tested to enlarge the instrumental capabilities and sample types range. One such alternative was the coupling of a laser ablation device with an ICP-MS, bypassing the conventional liquid introduction system to enable the direct analysis of solid samples. The first successful study reported for laser ablation (LA) ICP-MS was by Gray in 1985, where a ruby laser was fired at rock samples pressed into pellets. Again this new application attracted a lot of interest and developed to become a powerful analysis technique for samples in the fields of geology, environmental sciences, and more recently for the characterisation of medical, high purity samples such as semi-conductors and the nuclear field (Becker, 2002). The main advantages offered by LA-ICP-MS are that a minimal to no sample preparation is required, saving valuable time and avoiding extensive sample handling and digestions which may introduce contamination or analytes loss. Moreover, the technique enables the spatial characterisation of analytes at a resolution of approximately 20µm and detection limits down

to the  $\text{ng.g}^{-1}$  level. As for many analytical techniques, the instrumentation requires a calibration step in order to correlate the signal measured to a concentration. Although this is relatively straightforward for most techniques, including liquid ICP-MS, the calibration of the LA-ICP-MS system has been and remains the major hurdle to overcome for quantitative measurements (Jarvis *et al.*, 2003).

## 2. Aim and objectives

The aims of the project are:

1. To characterise the spatial distribution of lithium, uranium and other trace elements in reactor concretes using LA-ICP-MS.
2. Assess the role of stable element chemistry as a guide to locating hotspots of activation products in shielding concrete.
3. Evaluate the quantitative determination of tritium by ICP-MS.

The aims of the project will be achieved through the following objectives:

- Perform a literature search to identify the basic requirements of concrete for shielding and its evolution through time, as well as the potential composition of such concrete in terms of types of constituents (cement, sand and aggregates) and information on chemistry.
- Locate samples of suitable test material from nuclear sites.
- Identify important activation products from studies on nuclear plant decommissioning and the key stable element precursors.
- Assess existing and prepare a number of different matrices similar to concrete constituents for testing as calibration standards for LA-ICP-MS.
- Measure major and trace element chemistry of concrete components (aggregates, cement, filler) using conventional wet chemistry techniques to characterise the materials.

- Define key characteristics of different components.
- Chemically profile samples to test chemical groupings using LA-ICP-MS.
- Identify the issues linked with tritium analysis by ICP-MS and investigate possible improvements.
- Measure backgrounds and assess suitability for tritium determination using quadrupole and sector field ICP-MS instruments.

Here part of the project aims at identifying, locating and quantifying the major and trace element responsible for the formation of relevant activation products to the industry. A research through available literature, decommissioning reports and nuclear plant archives will provide the necessary information to select some of the precursor elements and information about the constituents used in shielding concrete through the different generations of designs. Also professionals involved in decommissioning, nuclear research institutions and several power plants will be approached for potential sample availability. The LA-ICP-MS instrumentation is then used to characterise the different constituents present in the acquired samples, looking at possibilities to differentiate the chemistry involved overall and in details. A calibration of the instrumentation is attempted to provide quantitative data directly. Once the major chemistry of the constituents is established, potential calibrators are investigated. There are a few certified materials available which potentially match some of the matrices found in concretes. These include the most widely used calibration standards used in LA-ICP-MS, namely the NIST 610 series. Next to this, there is a range of certified rock powders and the possibility to manufacture specific calibration materials from relatively pure or characterised materials, all of which can be pressed into pellets to change their physical characteristics.

The laser offers a spatial resolution at a very fine scale. Connected to an ICP-MS instrument, the system is able to identify very small variations in the bulk concrete. It is used to investigate the spatial distribution of these key stable isotopes in the concrete constituents (cement, fine and large aggregates) by recognising the phase they appear in using a set of chemical characteristics, or fingerprints. The connection between the phase and the key precursors is then achieved by correlating the phase to wet chemistry data performed on typical constituent examples. Thereafter it is possible to evaluate the contribution of each phase to add up to the bulk concentration of these key elements.

Finally the possibility to measure tritium, a paramount radionuclide during decommissioning, directly using ICP-MS technology is investigated. First a review of the existing quantifications procedures and levels measured is gathered, followed by the identification of the issues linked with tritium measurements. Since the use of tritium is restricted due to its radiological nature, the work focuses on the chemical behaviour of hydrogen, as a chemical analogue. And any quantification is based on estimations derived from the response of the closest stable and measureable element, here lithium.

## CHAPTER II: LITERATURE REVIEW

### 1. Concrete and concrete components

Concrete, together with steel, is most widely used structural material in the construction industry. The popularity of concrete is mainly due to three key points: its relative robustness against the weather, especially its resistance to water which allowed its use to confine water since the Roman age; secondly its versatility to be shaped in various forms and sizes, since fresh concrete mixes are relatively malleable; thirdly concrete is relatively cheap to produce and uses local materials readily available around the world (Metha, 1986). Concrete is formed of three main components, namely cement, aggregates and water. The aggregates generally are categorised as fine (sand) and large (coarse) in size. A common recipe is to use one part cement, two of sand, 3-4 of coarse aggregates and  $\frac{1}{2}$  of water. The resulting ordinary concrete has a typical density of  $2.3\text{g.cm}^{-3}$  (Profio 1979).

#### 1.1. Cement

Cement constituents are predominantly derived from lime (silicates and aluminates), and so contain large amounts of calcareous material. Cement is made by mixing a calcium and a silica source together and roasting the mix in a kiln. Common sources of calcium are naturally occurring calcium carbonates such as limestone and chalk, and the extra silica comes from clay or shale (Metha and Monteiro, 2006). The resulting powder is a mixture of predominantly four compounds, and some traces. These compounds are: tricalcium silicate, dicalcium silicate, tricalcium aluminate, tetracalcium aluminoferrite. Their chemical formula and abbreviation can be found in Table 2.1.

| Name                        | Chemical formula                                          | Abbreviation          |
|-----------------------------|-----------------------------------------------------------|-----------------------|
| Tricalcium silicate         | $3\text{CaO}.\text{SiO}_2$                                | $\text{C}_3\text{S}$  |
| Dicalcium silicate          | $2\text{CaO}.\text{SiO}_2$                                | $\text{C}_2\text{S}$  |
| Tricalcium aluminate        | $3\text{CaO}.\text{Al}_2\text{O}_3$                       | $\text{C}_3\text{A}$  |
| Tetracalcium aluminoferrite | $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ | $\text{C}_4\text{AF}$ |

Table 2.1: Main compound composition of cement (from Neville, 1981).

Commonly, the cement used in the construction industry can be separated in three categories: natural cement, Portland cement and high-alumina cement. Natural cement originates from a natural “cement” rock (clayey limestone) after calcining and grinding.

Portland cement, the name was originally given due to the resemblance in colour and quality to Portland stone (from Dorset, UK), is the most widely used today, representing about 90% of all cements used in the United Kingdom and the United States (Neville, 1981).

## 1.2 Aggregates

In concrete, aggregates represent the largest portion of the total volume, usually around 75%. Thus the choice of aggregates is important for the quality and specificities wanted for the final concrete. In the past, the aggregates were more regarded as “fillers” for the concrete, from an economic point of view. They were considered inert and of minor importance in the concrete. Nevertheless, the choice of aggregates is of prime importance, as a weak aggregate type will produce a weak concrete, and the physical, thermal and chemical properties of aggregates will affect the performance of the final concrete product (Neville, 1981).

Aggregates are defined by the American Society for Testing and Materials (ASTM, 1995) as a granular material, such as sand, gravel, crushed stone, or industrial by-products (iron blast-furnace for example) used with a cementing medium to form hydraulic-cement concrete or mortar. The size of aggregates is generally categorised in two parts, namely coarse aggregates (predominantly or wholly retained by a 4.75mm sieve) and fine aggregates (passing through 4.75mm and retained on the 0.75mm sieve). Below 0.75mm the particles are considered as silts. In the industry, the particle size distribution used in any concrete is called “grading”, for example a concrete with the whole range of particle sizes used is a low grade concrete (Neville, 1981; Metha, 1986).

### 1.2.1 Natural aggregates

Nowadays most aggregates used originate from naturally occurring rock, although it is possible to use artificially-manufactured aggregates for very specific applications. The natural rock may be either crushed to a certain particle size, or have been weathered naturally to produce the desired size range. Many properties of the aggregates can be related to the parent rock, such as mineralogy, hardness, physical and chemical stability, etc, but the aggregate shape and surface texture cannot. Although it is possible to assess the aggregates on all these different properties, it is difficult to categorise the aggregates into “good” or “bad” for concrete. Some aggregates may be of lesser quality in one of their aspects, but be suitable when used in concrete. This is mainly due to the change of matrix, as aggregates are surrounded by a layer of low permeability cementing material. Natural

aggregates may be classified as Basalt, Flint, Gabbro, Granite, Limestone, and a few others (Neville, 1981).

As aggregates are quarried, stored and transported on site for the final mixing to form fresh concrete, aggregates can be mixed with unwanted materials that can affect the concrete-making process. These can be impurities, interfering with the concrete making process, usually present as organic compounds. This is more relevant to fine aggregates rather than coarse ones, which are easier to wash. The material can also be a coating of some kind, such as clays, silts or other very fine particles, and can prevent a good bond between the surface of the aggregate and the cement paste. Also, aggregates obtained from the seabed or estuaries can contain large amounts of salts or shells and need cleaning before use to improve the quality of the aggregates. These particles are referred to as unsound and present in large quantities will affect the strength of the concrete, acting as soft parts compared to the pure aggregates (Metha, 1986).

#### 1.2.2 Artificial aggregates

Natural aggregates available to use in concrete cover a range of densities, and are usually the best option to keep the costs of making concrete low. Nevertheless, there are cases where artificial aggregates are manufactured and used, namely to obtain concrete specific densities at both ends of the usual range, either low density or high density. Another scenario where manufactured aggregates are preferred is when there is a shortage of natural appropriate aggregates, which is the case for several countries in the world, including the United Kingdom (Neville, 1981).

From the first category, the materials include clays, shales or slates (derived from shale-type sedimentary rocks), which produce gases when reaching very high temperatures. Subsequently these gases stay trapped in the melted material, and during cooling these pores remain and lower the density of the starting material. One example of artificial aggregate is resulting from the ash after the burning of domestic waste in incinerators. The ash collected at the end of the combustion process contains a proportion of metals, which are separated before the residue is homogenised into a powder, mixed with clay and processed to obtain pelletized aggregates with a low density. Also recycled concrete aggregates, which are the results of demolition works of concrete structures, becoming more and more important because of environmental impact issues, are considered artificial (Neville, 1981).

### 1.3 Additives and admixtures

It is possible to change certain properties of concrete mixes by incorporating some additives in small quantities. These additives are known as admixtures, and can be differentiated by their impact on concrete setting times, final water content or improvements on the final product. As per the ASTM Standards book on construction, concrete and aggregates (1995), admixtures can be classified and standardised as accelerating, retarding, water-reducing, super-plasticisers.

An example of accelerating admixture is calcium chloride, which is used to accelerate the setting of the concrete. The calcium chloride increases the liberation of heat within the first few hours after the mixing, promoting the hydration of the cement paste, similarly to the action of a catalyst of the reaction. It is used when a rapid repair is needed or in environments where the temperature is close to frost ( $2-4^{\circ}\text{C}$ ), usually at a proportion of 1-2% by weight of the cement; if used in larger amounts, flash setting can occur (Neville and Brooks, 1987).

Water-reducing admixtures, such as lignosulphonic acids and hydroxylated carboxylic acids and their respective salts, act on the interface of the particulates present in the mix and change their physico-chemical properties. The substance adsorbs on the cement and the active part acts as a repellent to each other because of negative charges induced. The particles have in consequence a greater mobility, and more water is available towards the workability of the concrete. The amount of water reduction is in the region of 5 to 15%.

Super-plasticisers are the modern version of water-reducing admixtures, but much more effective. They are complex compounds, with a higher dispersive action, making the concrete mix more workable and easily put in places where access is limited or a rapid placing is needed. The second use of super-plasticisers is to significantly increase the concrete strength by minimising the water/cement ratio of the concrete mix, with no improvements on the workability compared to not using an admixture. The water reduction can be between 25 and 35%, and the strength improvement can be as much as 50 to 75% after 24 hours (Neville, 1981).

## 2 Shielding concrete for nuclear sites

Reactor cores are a major source of neutrons and gamma rays. Shielding against gamma rays is straightforward, by using aggregates heavier than the range used for ordinary concrete. These heavy aggregates have a density between 2.3 and in extreme cases

4.4g.cm<sup>-3</sup> (Metha and Monteiro, 2006). Good neutron shielding is more difficult to achieve. The energetic neutrons produced may require a significant amount of low mass elements, such as hydrogen or boron, for fast neutron attenuation purposes, and high cross section absorption from the material to absorb the thermal (slow) neutrons. Concrete also has the structural strength advantage to support its own weight and was a popular choice for the biological shielding of radiation.

## 2.1 Shielding concrete in the early days

Important requirements to look for in concrete were its resistance to elevated temperatures, prolonged use and radiation protection media without loss of shielding properties, low heat conductivity and low cost of production (Jaeger *et al.*, 1975). Indeed in cases where the absorption of radiation and the possible heat transfer from the reactor core is significant, the shielding compound may require the presence of “thermal” shield to protect the biological shield (Profio, 1979). The versatility of concrete enables its properties to be changed almost at will to suit one or more of the following special needs: higher neutron shielding, higher gamma-rays shielding, higher temperature performance. To some extent, all three are of importance in nuclear radiation shielding, and thus a compromise between them is usually required.

Heavy aggregates permitting good gamma ray shielding (and in some cases additional neutron attenuation) are given in Table 2.2. Most are based on iron and barium ores, with additional water of crystallisation.

| Name             | Chemistry                           | Remarks                                                                                  |
|------------------|-------------------------------------|------------------------------------------------------------------------------------------|
| Haematite        | Fe <sub>2</sub> O <sub>3</sub>      |                                                                                          |
| Ilmenite         | FeTiO <sub>3</sub> , some Mg, Mn    | Disseminated in rock rather than major rock formation; common heavy aggregate            |
| Lepidocrocite    | FeO(OH)                             | Occurs with Goethite                                                                     |
| Goethite         | FeO(OH)                             | Same chemistry as Lepidocrocite, but different crystallisation                           |
| Limonite         | Hydrous iron mix                    |                                                                                          |
| Magnetite        | FeO, Fe <sub>2</sub> O <sub>3</sub> | Strongly magnetic, one of most widely used heavy aggregate ore                           |
| Witherite        | BaCO <sub>3</sub>                   | 2nd most common Ba ore, abundant in UK. Expected to be present in most Ba ore used in UK |
| Barite           | BaSO <sub>4</sub>                   | Most common Ba ore, accompanied of clay or CaSO <sub>4</sub> mineral.                    |
| Ferro-phosphorus | Iron phosphides mix                 | Flammable and possibly toxic gases released in concrete                                  |

Table 2.2: Heavy aggregates for use in high density concrete (adapted from ASTM, 1995).

All iron bearing minerals are a popular choice for high density concrete due to their ready availability and low cost to obtain. Few of them have the additional advantage to contain a significant amount of water of crystallisation and add to the neutron shielding (limonite and goethite). Also to consider are metallic residual by-products such as scrap iron and steel punching. For shielding concretes facing high temperatures, the use of serpentite aggregates ( $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , a form of asbestos) is preferable. It can withstand temperatures as high as almost  $500^\circ\text{C}$ , and the fixed crystallisation water content is drawn off very slowly. This type of concrete has been used at the Enrico Fermi Atomic Power Plant at Monroe, Michigan, USA (Jaeger *et al.*, 1975).

An alternative aggregates for efficient neutron shielding is the use of boron-based aggregates. The reason is that the secondary X-rays from neutron capture by boron are much less penetrating than those resulting from neutron capture by hydrogen. Its high capture capability permits the use of boron in small quantities. When used as an aggregate, as borate minerals or boron frit, it may induce a delay in the setting of concrete.

Most commercially important sources of sodium, calcium and magnesium borate are from precipitates from waters in arid volcanic regions. Some of these hydrated minerals are easily altered with change in humidity and temperature. Stable and insoluble boron minerals are usually not available in a large enough quantity to be used as aggregate, apart from the following two exceptions: Paigete and Tourmaline. The most useful boron-frit glass used for shielding contains calcium, silicon and aluminium, and a low amount of alkalies. From these elements, the amount of silica and alumina governs the solubility of the glass (the more of them the less soluble) and thus the setting times.

In most cases, it is needed to compromise between high density concrete and high neutron shielding, as both are usually present in opposite amounts. Thus mixing of scrap metal and limonite, or ore rich in boron/hydrogen with scrap iron to obtain a particularly well suited concrete against gamma rays and neutrons is feasible (Jaeger *et al.*, 1975). Other approaches have looked at the use of successive layers of high gamma and neutron shielding materials, such as iron-polyethylene, iron-water and tungsten followed by lithium hydride (Profio, 1979).

## 2.2 Shielding concrete today

Today's concrete mixes used in the nuclear industry are more reflective of the financial constraints involved in the general construction of a nuclear plant. Already the use of high density concrete to ordinary concrete increases the costs by a factor of six, from \$200 to

\$1200 per cubic metre (Profio, 1979). The arguably more appropriate specific aggregate mixes used at the dawn of nuclear energy have shifted towards the more readily available types. In most cases, when space is not considered a limiting factor for the thickness of the shielding concrete, a high density concrete containing premium specific aggregates (and thus expensive to produce) can be replaced by a slightly thicker shielding wall (around 10% extra) made of local appropriate heavy aggregates (Evans et al, 1984). Since nearly all nuclear plants in Great Britain have been constructed adjacent to the coastline, a variation in aggregates types is expected due to the variation in local geology and thus local aggregates (dolerites/basalts in the north, flints in the south). The costs involved in acquiring and transporting these to a site are significantly lower, for a final product of similar total shielding capacity. Transportation has also become more relevant regarding the environmental impact during construction and has to be accounted for in the new-built reactor generation.

Nevertheless, if a specific aggregate from a different region is necessary (can be for high-temperature resistant shield), the possibility to barge in large amounts along the coast becomes a suitable option. In the case where a local aggregate is used, the concrete mixture can be produced in large amounts, and is more likely to be used as well for the outer shell of the reactor or for other buildings on site, even if no shielding properties are required. If, based on the reactor design, a local shine path of rays in the shield is likely to be a problem, an enhanced concrete can be used (with aggregates such as magnetite or barites) for that area of the shield.

In addition to the principal components of the shielding concrete, nowadays the mixture also contains several industrial by-products, including pulverised fly ash, furnace slag, which can have EU standards for some elemental content. In general, the interest lies in the element or compounds present at the percent level in the mixtures and cement, due to their potential effects on workability, setting times and final quality of the concrete mix. Trace elements present are not of interest for a structural point of view, and thus other admixtures such as organics, sugars and molasses (present at  $<10 \text{ L.m}^{-3}$  of concrete mixture) have no legal requirements (personal communication, Halcrow meeting, 2009).

### 2.3 Shielding concrete chemistry

As mentioned in Section 1.2 of this chapter, up to 75% of the total concrete mass consists of aggregates. Therefore the selection of these can introduce significant variation in the bulk chemistry of the final product and change the amounts of potential activation products. A few studies have been looking at the chemistry of actual shielding concretes, but since the

decommissioning of nuclear installations around the world are at different stages, the availability and detail of the characterisations are limited.

### 2.3.1 Bulk concrete

In theory, it is possible to calculate the final bulk concrete chemistry using the chemical characteristics of the raw materials and the proportion of each used in the concrete making process. Nevertheless, as described earlier, the minor and trace chemical information is generally scarce and the proportions used can be approximate. Therefore a variation in the chemistry of the final product from the original component is possible. A few examples of bulk concrete chemistry have been reported.

As part of an Environmental Radioactivity Proficiency Test Exercise organised by the National Physical Laboratory (NPL) in 2008, a homogenised concrete sample was sent to over 30 institutions worldwide for radionuclides determination. As part of the process, which ultimately aimed at producing a concrete reference material (Harms and Gilligan, 2010), the report contained selected major and trace elements chemistry of the concrete powder. The values can be found in Table 2.3.

| Major components <sup>1</sup><br>(% by weight) |      | Trace elements <sup>3</sup><br>( $\mu\text{g.g}^{-1}$ ) |      |    |      |
|------------------------------------------------|------|---------------------------------------------------------|------|----|------|
| Al <sub>2</sub> O <sub>3</sub>                 | 2.17 | As                                                      | 2.46 | Ni | <150 |
| CaO                                            | 40.2 | Ba                                                      | 610  | Pb | n/a  |
| SiO <sub>2</sub>                               | 23.0 | Cd                                                      | <4.9 | Sb | 0.52 |
| Fe <sub>2</sub> O <sub>3</sub>                 | 0.93 | Ce                                                      | 12.5 | Sr | 720  |
| K <sub>2</sub> O                               | 0.66 | Co                                                      | 2.52 | Th | 1.40 |
| MgO                                            | 0.73 | Cr                                                      | 20.1 | U  | 1.70 |
| Na <sub>2</sub> O                              | 0.29 | La                                                      | 7.62 | V  | 17.7 |
| TiO <sub>2</sub>                               | 0.10 | Li                                                      | n/a  | Zn | 17.0 |
| LOI <sup>2</sup>                               | ~31  |                                                         |      |    |      |

Table 2.3: Major and trace element chemistry for concrete obtained by neutron activation analysis. <sup>1</sup> major components were calculated using elemental results; <sup>2</sup> LOI (loss on ignition) is estimated from the remaining phase to reach ~100% total components; <sup>3</sup> values less than a certain number are below detection limit given.

In the United States, a substantial report was compiled by staff from the Pacific Northwest Laboratory in Richland (WA) in 1984 on behalf of the U.S. Nuclear Regulatory Commission. The report addresses the issue of activated materials in nuclear reactor decommissioning and includes elemental composition of a range of reactor components, including concretes.

Samples from 12 sites across the U.S. were collected, in most cases concrete slabs from preliminary strength tests or subsequently cores taken from the shield. In some cases the ingredients (cement, sand, aggregates and fly ash) used to produce them were also available in order to identify the contribution of each and any significant variation in trace elements composition. Table 2.4 shows the results obtained for the analysis of 36 shielding concrete samples coming from 12 sites for selected elements.

| Major Element (%)                      | Average<br>$\pm 1SD$ | Range       | Range<br>Factor |
|----------------------------------------|----------------------|-------------|-----------------|
| Al                                     | 3.1 $\pm$ 2          | 0.53 - 6.1  | 11.5            |
| Si                                     | 16.8 $\pm$ 9.5       | 3.9 - 32.4  | 8.3             |
| Ca                                     | 18.3 $\pm$ 9.7       | 8.3 - 34.7  | 4.2             |
| Fe                                     | 3.9 $\pm$ 6.4        | 0.50 - 24.0 | 48              |
| Minor Element ( $\mu\text{g.g}^{-1}$ ) |                      |             |                 |
| Ti                                     | 2121 $\pm$ 2320      | 230 - 7900  | 34              |
| Cr                                     | 109 $\pm$ 159        | 29 - 540    | 18.6            |
| Mn                                     | 377 $\pm$ 290        | 56 - 990    | 17.7            |
| Co                                     | 9.8 $\pm$ 10.3       | 1.1 - 31    | 28              |
| Ni                                     | 38 $\pm$ 25          | 11.9 - 87.0 | 7.3             |
| Zn                                     | 75 $\pm$ 90          | 8.4 - 340   | 41              |
| Sr                                     | 438 $\pm$ 208        | 220 - 940   | 4.3             |
| Ba                                     | 950 $\pm$ 1950       | <20 - 7060  | 353             |
| La                                     | 13.0 $\pm$ 6.9       | 2.9 - 28    | 9.7             |
| Ce                                     | 24.3 $\pm$ 13.5      | 6.2 - 52    | 8.4             |
| Eu                                     | 0.55 $\pm$ 0.38      | 0.11 - 1.2  | 10.9            |
| Pb                                     | 61 $\pm$ 158         | 5.4 - 560   | 104             |
| Th                                     | 3.5 $\pm$ 3.0        | 0.75 - 120  | 160             |
| U                                      | 2.7 $\pm$ 0.9        | 1.4 - 4.4   | 3.1             |

Table 2.4: Elemental concentrations for shielding concrete from 12 U.S. nuclear sites. Range factors are calculated as the maximum over the minimum concentration measured.

From the Table, it is possible to notice the influence of aggregates on the major chemistry. For example Si, Ca and Fe have a significant range of concentrations observed, possibly reflecting if the aggregates used are mostly silicates, limestones or iron based. This variation is also visible in the trace elements, as most minor elements show a range of concentration over one order of magnitude (range factor  $\geq 10$ ) with even two orders of magnitude for Ba, Pb and Th.

Taking into account the chemistry of the bulk concrete and the individual components used to produce it at one particular site (Hartsville), the authors calculated the likely proportions used and the individual elemental contribution to the bulk chemistry. Calculated proportions were 73.4% aggregates, 4.0% fly ash and 19.7% cement. Contribution results are given in Table 2.5.

| Element | Aggregates | Fly ash | Cement |
|---------|------------|---------|--------|
| Al      | 38.5       | 28.4    | 33.1   |
| Ca      | 74.6       | 0.2     | 25.2   |
| Fe      | 22.4       | 43.4    | 34.3   |
| Ti      | 44.7       | 32.7    | 22.6   |
| Cr      | 34.6       | 34.5    | 30.9   |
| Mn      | 79.0       | 4       | 17.1   |
| Co      | 23.9       | 40.8    | 35.3   |
| Ni      | 55.6       | 17.8    | 26.7   |
| Zn      | 33.7       | 33.7    | 32.6   |
| Sr      | 64.7       | 2.9     | 32.4   |
| Ba      | 32.5       | 32.9    | 34.6   |
| Eu      | 44.4       | 27.4    | 28.3   |
| Pb      | 36.8       | 54.7    | 8.5    |
| Th      | 39.2       | 34.0    | 26.8   |
| U       | 30.0       | 53.0    | 17.0   |

Table 2.5: Contribution in % of each ingredient to the bulk concrete chemistry (from Evans et al, 1984).

Although the fly ash compound is theoretically present only at 4% by weight in the concrete, its contribution to the bulk concentration is in general close or superior to a third for most of the elements listed. This feature reflects in some way the fact that this ingredient, and its manufacturing origin, concentrates elements which would otherwise be present in a lesser amount (Evans *et al.*, 1984).

### 2.3.2 Cements

There are a few cements available commercially as reference materials, for which the concentrations of a range of elements are certified. Unfortunately in most cases the certified values are given only for major elements and not traces present in the cement. Table 2.6 shows two cements from Dillinger Hüttenwerke AG, Freiburg, Germany, and an additional sample from a proficiency test exercise. For this, information on trace elements in one type of cement has been compiled by the International Association of Geoanalysts (IAG) as part of a

bi-annual international proficiency test scheme (GeoPT program). An uncertified sample is prepared as a finely ground powder and sent to analytical laboratories around the world taking part in the scheme for major and trace elements characterisation, using the laboratories' routine analytical procedure. Results then undergo extensive statistical analysis and values are assigned to each element. The sample characterised for the second half of 2009 was an Ordinary Portland Cement (OPC) sample originating from South Africa.

| Element | Dillinger Hüttenwerke |                       | GeoPT |
|---------|-----------------------|-----------------------|-------|
|         | Portland Cement X0201 | Portland Cement X0203 | OPC   |
| As      | 5.4                   | 11.1                  | 4.56  |
| Ba      | 222.1                 | 282.2                 | 511   |
| Be      | 2.8                   | 2.6                   | 0.82* |
| Cd      | <2.5                  | <2.5                  | -     |
| Ce      | 54.6                  | 54.5                  | 48.9  |
| Co      | 4.5                   | 13.5                  | 21.38 |
| Cu      | 7                     | 36                    | 23.7* |
| La      | 27.3                  | 28.5                  | 25.93 |
| Li      | -                     | -                     | 13.1* |
| Mo      | <1.0                  | 4                     | -     |
| Ni      | 14.3                  | 29.9                  | 87*   |
| Pb      | 24.9                  | 80                    | 7.2*  |
| Sb      | <2.0                  | 3.6                   | 0.256 |
| Se      | <2.5                  | 2.3                   | -     |
| Th      | 8.6                   | 7.4                   | 3.93  |
| U       | 3.3                   | 4.3                   | 0.83  |
| V       | 100.4                 | 163.5                 | 63.97 |
| Y       | -                     | -                     | 15.5  |
| Zn      | 74                    | 474.9                 | 27.8  |

Table 2.6: Certified trace elements values for Portland cements (\*provisional values).

An extensive characterisation exercise is reported by Lawrence (1998) where the major chemical components and some trace chemistry are reported. The database consists of nearly 290 results for ordinary Portland cements. Table 2.7 shows the range of concentrations measured and mean values calculated for the major and trace components.

| Major components (in %)               | Range     | Mean | Number of results |
|---------------------------------------|-----------|------|-------------------|
| SiO <sub>2</sub>                      | 18.4-24.5 | 21.0 | 284               |
| Fe <sub>2</sub> O <sub>3</sub>        | 0.16-5.74 | 2.85 | 284               |
| Al <sub>2</sub> O <sub>3</sub>        | 3.10-7.56 | 5.04 | 284               |
| CaO                                   | 58.1-68.0 | 64.2 | 284               |
| MgO                                   | 0.02-7.10 | 1.67 | 285               |
| Na <sub>2</sub> O                     | 0-0.78    | 0.24 | 263               |
| K <sub>2</sub> O                      | 0.04-1.66 | 0.70 | 280               |
| Trace Metals (in µg.g <sup>-1</sup> ) |           |      |                   |
| Ti                                    | 0-4196    | 1059 | 288               |
| P                                     | 0-2139    | 389  | 288               |
| Mn                                    | 0-2366    | 315  | 288               |
| Sr                                    | 0-19195   | 532  | 191               |
| Ba                                    | 91-1402   | 280  | 94                |
| Ni                                    | 10-129    | 31   | 85                |
| Cr                                    | 25-422    | 76   | 94                |

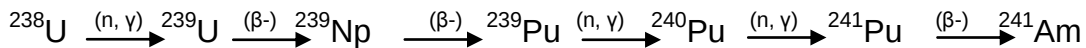
Table 2.7: Selected chemistry of cements (from Lawrence, 1998).

### 3 Shielding concrete activation

#### 3.1 Neutron activation

Neutron activation is a process where an isotope captures and incorporates a neutron to its nucleus, increasing its atomic mass by one with an additional release of a particle. This phenomenon, although having a relatively low occurrence in the natural environment, is promoted when a material is subject to an intense flux of neutrons, for example close to the core in nuclear reactors during the fission process. The most common activation reaction consists in the absorption of one neutron by an isotope, with the release of a gamma ray, noted (n,γ), with the precursor isotope and resulting activated product on their respective side of the activation mechanism. For example <sup>59</sup>Co activates to produce <sup>60</sup>Co, expressed as <sup>59</sup>Co (n,γ) <sup>60</sup>Co. Besides this typical activation process, others are possible and occur with specific stable isotopes. Although the activation is still initiated with the capture of a neutron, the associated release of particle can be different, and include proton (p), alpha particle (α) or multiple neutrons. For example, <sup>14</sup>N (n,p) <sup>14</sup>C, <sup>6</sup>Li (n,α) <sup>3</sup>H and <sup>23</sup>Na (n,2n) <sup>22</sup>Na (Gaudry and Delmas, 2007). In almost all of the described cases, the resulting product of neutron activation is a radioelement subject to decay.

In a reactor core, the flux of neutrons is such that once activation products are formed, some have the ability to absorb another neutron and activate again before decay. In this view, it is therefore possible to obtain elements and radioisotopes with possibly an atomic mass greater than the heaviest stable isotope, namely  $^{238}\text{U}$ . This series of isotopes formed by multiple n-capture and decay is called the transuranium elements series, and they are commonly found in nuclear fuel waste. This series include isotopes such as  $^{239}\text{Np}$  and  $^{241}\text{Am}$ . An example of multiple neutron capture and decays is given below for the formation of  $^{241}\text{Am}$  from stable  $^{238}\text{U}$ :



A slightly different neutron interaction with a stable nucleus is the neutron-induced fission process. In this case, the absorbed neutron and nucleus form an unstable compound that will split into smaller nuclei, releasing at the same time two or more neutrons and a significant amount of energy, which is the basis of energy source for reactors. The newly released neutrons can thereafter interact with more nuclei, and form the basis of chain reactions in nuclear fuel which contain a significant proportion of 'fissile' material ( $^{235}\text{U}$ ,  $^{239}\text{Pu}$  for example). The fission process produces in general two smaller nuclei, but their atomic mass can range from about 65 to 167 as each fission event gives a different pair of fission products. It has been shown that the fission of  $^{235}\text{U}$  generates up to 80 isotopes. The fission products are likely to fall into two groups, namely from mass 80 to 110 (light group) and 12 to 155 (heavy group). The probability of each isotope is different, and the maximum fission yield is for 95 and 139 with around 6.4% (Jevremovic, 2009).

### 3.2 Elements of interest

In the periodic table, many elements and their isotopes have the potential to activate and produce a radioelement subject to decay. Nevertheless, the interest for decommissioning purposes is only targeted at a select few radioisotopes, mainly based on the presence of the precursor isotope in materials experiencing the high neutron flux (here concrete), and also on the half-life of the radioelement. The normal decommissioning process of a commercial reactor in the U.K. usually involves a period of care and maintenance after the defueling process, normally for a period of time up to 60 years, during which the relatively short-lived radionuclides (short half-life) decay rapidly to reach very low levels, leaving relatively long-lived nuclides to be of concern. To identify a coherent set of isotopes of interest, the following literary sources have been considered.

Gaudry and Delmas (2007) produced a table of radionuclides expected in the shielding concrete of nuclear plants. In order to account for those important on the longer term, or long-lived radionuclides, the authors set a limit of one year for the lowest half-life. The radionuclides can be found in Table 2.8.

| Nuclide          | Half-life (y)     | Nuclide          | Half-life (y)       | Nuclide           | Half-life (y) |
|------------------|-------------------|------------------|---------------------|-------------------|---------------|
| <sup>3</sup> H   | 12.35             | <sup>60</sup> Co | 5.27                | <sup>109</sup> Cd | 1.27          |
| <sup>14</sup> C  | 5730              | <sup>63</sup> Ni | 100                 | <sup>134</sup> Cs | 2             |
| <sup>22</sup> Na | 2.6               | <sup>79</sup> Se | 1.1x10 <sup>6</sup> | <sup>133</sup> Ba | 10.5          |
| <sup>36</sup> Cl | 3x10 <sup>5</sup> | <sup>93</sup> Zr | 1.5x10 <sup>6</sup> | <sup>151</sup> Sm | 90            |
| <sup>41</sup> Ca | 1x10 <sup>5</sup> | <sup>94</sup> Nb | 2x10 <sup>4</sup>   | <sup>152</sup> Eu | 13.5          |
| <sup>55</sup> Fe | 2.7               | <sup>93</sup> Mo | 4x10 <sup>3</sup>   | <sup>154</sup> Eu | 8.6           |

Table 2.8: Long-lived radionuclides expected in concrete (Gaudry and Delmas, 2007).

In 2010, Harms and Gilligan developed a neutron-activated concrete powder reference material produced from the bioshield of a decommissioned nuclear reactor. The sample was sent to over 30 organisations around the world as part of a proficiency test exercise (2008) and the results processed to assign certified values to a selection of radionuclides. The list of certified values included the following elements: <sup>3</sup>H, <sup>14</sup>C, <sup>40</sup>K, <sup>55</sup>Fe, <sup>60</sup>Co, <sup>63</sup>Ni, <sup>133</sup>Ba, <sup>152</sup>Eu and <sup>154</sup>Eu. Several other nuclides were originally considered as potentially present in the activated concrete sample, including <sup>22</sup>Na, <sup>41</sup>Ca and <sup>36</sup>Cl, but were disregarded due to a lack of results from the proficiency exercise participants. This list of elements is also completed with some fission products by Hou (2007), and includes <sup>90</sup>Sr, <sup>99</sup>Tc, <sup>129</sup>I and <sup>137</sup>Cs, also confirmed in Hong *et al.* (2009) and some transuranium elements. Table 2.9 summarises information on some of these elements.

| Radioisotope      | Precursor <sup>b</sup> | Cross section neutron capture (Barnes) <sup>a</sup> | activation mode <sup>b</sup> | Half-life (years) <sup>b</sup> |
|-------------------|------------------------|-----------------------------------------------------|------------------------------|--------------------------------|
| <sup>3</sup> H    | <sup>6</sup> Li        | 953                                                 | n,α                          | 1.23E+01                       |
| <sup>14</sup> C   | <sup>14</sup> N        | 2                                                   | n,p                          | 5.70E+03                       |
| <sup>41</sup> Ca  | <sup>40</sup> Ca       | 0.2                                                 | n,γ                          | 8.00E+04                       |
| <sup>55</sup> Fe  | <sup>54</sup> Fe       | 3                                                   | n,γ                          | 2.75E+00                       |
| <sup>60</sup> Co  | <sup>59</sup> Co       | 19                                                  | n,γ                          | 5.27E+00                       |
| <sup>63</sup> Ni  | <sup>62</sup> Ni       | 15                                                  | n,γ                          | 9.87E+01                       |
| <sup>133</sup> Ba | <sup>132</sup> Ba      | 7                                                   | n,γ                          | 1.05E+01                       |
| <sup>152</sup> Eu | <sup>151</sup> Eu      | 5900                                                | n,γ                          | 1.35E+01                       |
| <sup>154</sup> Eu | <sup>153</sup> Eu      | 320                                                 | n,γ                          | 8.60E+00                       |
| <sup>137</sup> Cs | <sup>235</sup> U       | fis 577                                             | fission                      | 3.01E+01                       |
| <sup>90</sup> Sr  | <sup>235</sup> U       | fis 577                                             | fission                      | 2.88E+01                       |
| <sup>99</sup> Tc  | <sup>235</sup> U       | fis 577                                             | fission                      | 2.12E+05                       |
| <sup>129</sup> I  | <sup>235</sup> U       | fis 577                                             | fission                      | 1.61E+07                       |

Table 2.9: Selection of important radioisotopes and their precursors. Data obtained from: <sup>a</sup> Lederer et al, 1967; <sup>b</sup> Table de radionuclides, 2008.

#### 4. Conventional radionuclides measurement techniques

##### 4.1 Radiation types

###### 4.1.1 Alpha particle

An alpha decay is the emission of two protons and two neutrons, effectively a <sup>4</sup>He atom, from a parent nuclide. The decay leaves a daughter nuclide with the appropriate mass number (-4 from parent nuclide) and atomic number (-2), and possibly additional emission of gamma rays. The alpha particles are emitted with discrete energies, that is to say with a set of specific energy values for a given radionuclide (Ehmann and Vance, 1991). An example of a decay diagram is shown in Figure 2.1.

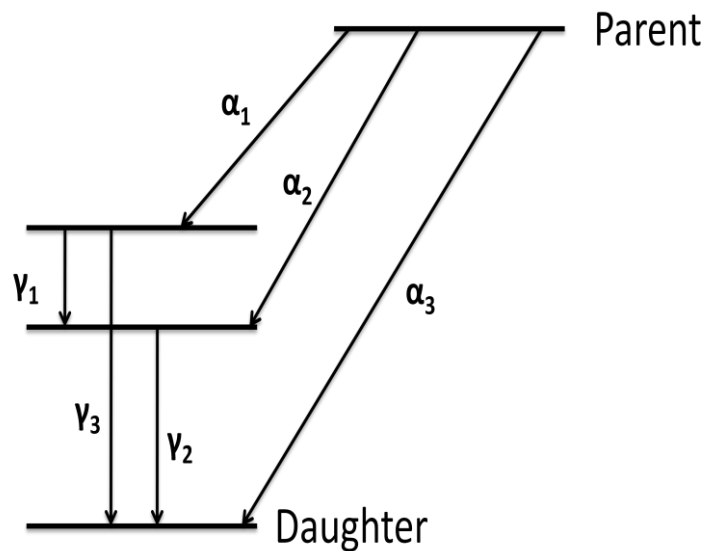


Figure 2.1: Alpha decay diagram, showing the discrete decay energies ( $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ ). Specific probabilities apply to each decay, adding to 1. The proportion of each is reflected in the energy spectrum. The relative positions of intermediate energy levels (excited) are shown between the parent and daughter levels. The transitions from these levels to the daughter ground energy level are done by spontaneous gamma emissions.

In theory direct alpha spectrometry of the sample is feasible, though the surrounding and matrix-induced energy attenuation seriously affects the resulting spectra. Here again, a separation process is required, using a yield monitor. The same steps as per beta emitter separation are used. There is a slight difference in the final source preparation before measurement, where two options are available to achieve a thin source layer: electrodeposition of the isolated nuclide on a disk (produces a robust source, but relatively time consuming), or co-precipitation as a thin layer with a rare earth fluoride (faster, but source not as robust). The final measurement is made by alpha spectrometry using ion-implanted detectors in a vacuum chamber with very low detection limits. Also gross alpha measurement is an option using gas flow proportional counters or zinc sulphide screen scintillation detectors.

#### 4.1.2 Beta particle

The beta decay can happen via three different processes, namely the emission of a negatron ( $\beta^-$ ), a positron ( $\beta^+$ ) or by electron capture (EC). The negatron, or negative electron, is produced when a proton changes into a neutron, with additional emission of an anti-neutrino and possible gamma rays. The positron, or positive electron, transforms a neutron into a proton. In electron capture decay, an orbital atomic electron is captured by the excited

nucleus. In both  $\beta^+$  and EC, neutrinos and gamma rays are also emitted. The main difference is that the decay energy available is distributed between the different emitted particles and rays and therefore the beta particle has a range of energy values, rather than discrete values as for alpha decay.

The available decay energy is split between the two, and therefore the beta particle can have energies from virtually zero to the maximum available. This makes it very difficult to analyse by spectrometry, as there are no discrete energies to identify each nuclide, and therefore a chemical separation is needed to isolate and purify the radionuclide of interest from the bulk sample. The separation process involves a combination of steps such as precipitation, solvent extraction, ion exchange and extraction chromatography. During the process, yield monitors need to be introduced to evaluate the efficiency of the separation. The activity is then measured by a gross beta counting technique, for example gas flow proportional counting, anthracene-screen scintillation or Geiger-Müller tube (NICoP, 2006). Also liquid scintillation counting is possible and preferred option for pure beta emitters with available decay energy of  $\sim 2,000\text{keV}$  or less (IAEA, 2007), or for low energy beta emitters such as  $^3\text{H}$  and  $^{14}\text{C}$  using specific energy windows.

#### 4.1.3 Gamma particle

In this decay, an electromagnetic radiation is produced as the excited nucleus makes a transition to a lower energy or ground state. There is no change in the atomic and mass numbers for the isotope, only a change in energy state.

Due to the penetrating properties of gamma rays, the quantification of gamma emitters requires minimum sample preparation. When applicable, the bulk sample is homogenised and dried (freeze-dried technique can be used) before being compacted into an appropriate container and placed on a detector. Usually the detector is made of a cooled high purity germanium detector, or sodium iodide crystal detectors can also be used, but their energy resolution is not as good as germanium detector, introducing difficulties in the spectrum interpretation. The calibration of the system is done by analysing a standard containing a range of radionuclides across the energy range required, matrix-matched with the sample's geometry and material density (to replicate potential attenuation effects). The lower limit of photon energy detected is about  $40\text{keV}$ , though it is possible to measure lower energies with appropriate energy windows fitted (NICoP, 2006). In some cases the complexity of the sample in terms of the range of gamma emitters present requires a mineralisation step of the sample and subsequent analysis with high resolution gamma spectrometry (IAEA, 2007).

## 4.2 Non radiometric analysis

Rather than using the radioactive decay of the isotope, other techniques are used, most of them (except fluorimetry) using the atomic mass of the radioelement to be determined. These techniques are more effective at the determination of long-lived radioelements and actinides at the high end of the mass range, where there are no interferences (isobaric) from stable element isotopes. These mass-dependant techniques include inductively coupled plasma mass spectrometry (quadrupole, high resolution and multi-collector instruments), thermal ionisation mass spectrometry (TIMS), secondary ion mass spectrometry (SIMS), resonance ion mass spectrometry (RIMS) and accelerator mass spectrometry (AMS).

## 4.3 Sample mineralisation

This step is necessary for accurate determination of mainly  $\alpha$ - and  $\beta$ -emitters, and the mineralisation procedure to adopt depends on the sample type and potentially the nuclides of interest. In the IAEA report on Strategy and Methodology for Radioactive Waste Characterization (2007), guidelines on such procedure are given. The general approach is to incinerate samples if possible as a first step, then a digestion with acids or a fusion with subsequent solubilisation is adopted. Due to the potential high temperature involved, elements which can form volatile compounds are not quantitatively extractable with some of the sample preparations. These elements are listed as halogens (F, Cl, Br, I, At), Tc, As, Sb, Hg, B, Ru, tritium and carbon isotopes. They are referred to as “volatiles” in the examples of sample preparations below for common matrices:

- Concrete: heated acid digestion using a combination of HCl, HNO<sub>3</sub> and H<sub>2</sub>F<sub>2</sub>. This method is not suitable for volatiles.
- Liquid inorganic waste: three processes are possible, starting with a filtration if necessary, then evaporation or co-precipitation followed by dissolution in HNO<sub>3</sub>, or adsorption on an exchange resin with mineralisation as an organic solid.
- Liquid organic waste: direct ashing in a furnace and subsequently to be dealt as incineration ashes.
- Soils, filters and combustible waste: sample is first dried and ashed in a furnace, further dealt as incineration ashes.
- Incineration ashes: the sample is fused using Na<sub>2</sub>O<sub>2</sub> flux, and the resulting glass dissolved in HNO<sub>3</sub>. Similarly to concrete sample preparation, volatiles can't be measured by this method.

The IAEA report also includes more specific separation and extraction methods for radioisotopes such as tritium,  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ , and the relevant isotopes of uranium and plutonium, as well as the possible interferences and optimum energy windows for  $\alpha$ ,  $\beta$  and  $\gamma$  spectrometry.

## 5 Laser ablation systems

### 5.1 Advantages over liquid sample introduction

The connection between a laser ablation system and an ICP-MS instrument was first achieved by Gray in 1985. It is adapted from conventional liquid sample analysis by ICP-MS by by-passing the liquid sample introduction system and introducing a straightforward connection between the LA system, used as a sampling tool, and the ion source. From the connection, it is then possible to sample a solid at a fine scale and obtain qualitative and quantitative data for major and trace elements, with excellent detection limits, from any solid sample. This overall picture attracted a lot of interest from the start of the LA-ICP-MS tool (Günther and Hattendorf, 2005).

One of the main advantages of laser ablation compared to conventional liquid ICP-MS is the possibility of spatial resolution at a scale of tens of microns. For conventional ICP-MS analysis the solid material of interest is in most cases ground to a powder before a cocktail of oxidising chemicals is used to digest it, thus only allowing a bulk characterisation. Moreover, the several steps involved in the sample preparation for liquid analysis, including the original material sampling, grinding, representative sub-sampling for digestion, digestion process, final dilution for analysis if required are as many possible sources of errors and contamination that can affect the final result. Using laser ablation, the sampling and analysis of any solid material can take place without these potential problems. Finally the time required for analysis is much reduced and therefore a greater amount of sample can be analysed.

The laser ablation system is used as a tool for direct sampling of a solid sample and replaces the liquid introduction system on a typical ICP-MS instrument. The laser beam generated is focused onto the surface of the sample and interacts with it, producing an aerosol. The aerosol is mainly composed of ions, atoms and a range of very small particles, resulting from the vaporisation of the sample. This aerosol is then flushed from the ablation cell by a gas (typically Ar or He), and fed into the ion source at the back of the ICP torch. During that travel, ions formed regroup into neutral molecules before entering the plasma.

## 5.2 Laser ablation systems available

Lasers may be classified according to the material used to generate the laser beam and can be divided into dye, gas, semiconductor diode and solid-state lasers (Sneddon and Lee, 1997). Of these four types solid-state and more recently gas lasers (Excimer) have been favoured for analytical applications. Solid-state lasers are a good compromise between energy outputs and are relatively cheap to purchase and maintain. They are also fairly compact. Although Excimer lasers are more expensive to run (ultra-pure gases used need to be changed periodically), the output energy delivered and the flat bottom shape of the beam makes them attractive for specific analytical applications (Nelms, 2005). As laser technology has evolved, almost all available wavelengths have been evaluated with ICP-MS instrumentation (Günther and Hattendorf, 2005).

## 6 ICP-MS uses in the nuclear field

### 6.1 Liquid sample

In the past two decades the use of ICP-MS instrumentation has attracted significant interests for the direct measurement of certain radionuclides in a range of sample types, including environmental, nuclear waste materials, bio-assays to name a few (Lariviere *et al.*, 2006; Boulyga, 2011). This is a direct result of the better detection limits and better sample preparation techniques developed over the years (Lariviere *et al.*, 2006) and the fact that they are difficult to measure by conventional radiometric methods. Examples of such isotopes are  $^{99}\text{Tc}$ ,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Am}$  and the natural isotopes of Th and U. Most of these nuclides are usually relatively free of a major mass-related interference (stable isotope isobaric and major polyatomic species when an appropriate purification step is added), therefore minimal background and, with the exception of  $^{99}\text{Tc}$ , are in the mass region of relatively high sensitivity for ICP-MS. Both these features permit excellent detection limits. Also, these nuclides are mainly  $\alpha$ -/ $\beta$ -emitters and long-lived (with half-lives of  $>100\text{y}$ ), and require a separation step and long counting times by conventional radiometric techniques. The favoured instrumentation used are sector field (better background and sensitivity) and multi-collector (for isotopic ratios measurement) ICP-MS together with liquid sample introduction, therefore solid samples require mineralisation prior to analysis (Hou, 2007; Varga *et al.*, 2007; McLean *et al.*, 2001; Pointurier *et al.*, 2004).

## 6.2 Laser ablation

In some cases, the measurement of radionuclides directly in the solid sample is preferred, for example if the sample of interest is difficult to dissolve, such as soils, ashes, glasses, or the material of interest is relatively difficult to handle, for example nuclear waste requiring segregation before recycling or appropriate packaging (Becker *et al.*, 2000). Radionuclides measurement in such samples has been investigated using analytical laser ablation systems, but not extensively.

In 2007, Guillon and co-workers designed a LA-ICP-MS system permitting the analysis of highly radioactive samples in an  $\alpha$ -box with the appropriate lead shielding. The laser optics was adjusted to enable the ablation to take place inside the box, with most of the equipment remaining outside to avoid deterioration from the high level of radiation from the sample. Using optimised parameters, a spent fuel sample was analysed and a mass spectrum from 230 to 260 amu was recorded, and the transuranic elements expected in the sample could be detected, though due to isobaric and polyatomic interference no accurate quantitative data was obtained.

Gastel *et al.* (1997) compared the detection limits obtained for a concrete-type matrix for several radionuclides using both quadrupole and sector field ICP-MS instruments connected to a LA system. The authors used a fine cement powder and artificially added in variable concentrations of  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ ,  $^{232}\text{Th}$ ,  $^{233}\text{U}$  and  $^{237}\text{Np}$  from stock solutions to form synthetic standards. The cured concrete matrices were then analysed, and detection limits obtained for all isotopes (except  $^{232}\text{Th}$  and  $^{129}\text{I}$ ) were in the range of 5-10 ng.g<sup>-1</sup> using quadrupole ICP-MS and about one order of magnitude lower with sector field instrument. Similarly, the same research group (Becker *et al.*, 2007) applied the same setup on doped graphite powder synthetic standards for establishing limits of detection and figures of merit for a graphite-type matrix. In both these cases, the developed standards were not tested against real samples.

## 6.3 LA-ICP-MS calibration

When analysing a sample with ICP-MS, the instrumental signal recorded is a relative number proportional to the amount of the element present in the sample. As it is the case for many other analytical techniques, the signal from the unknown samples must be correlated to the signal given by a standard or set of standards (sample containing elements at known concentrations), that is to say a calibration of the instrumental response is needed to be able to give quantitative data.

For liquid sample ICP-MS analysis, a set of synthetic standards can be produced fairly easily using stock solutions of certified elemental concentration diluted to form an appropriate range of concentrations. In these cases, the sample is in a matrix which can affect the instrumental response, matrix-matching the calibration standards with the sample is also straightforward with the addition of chemicals.

For LA-ICP-MS data, the choice of an adequate calibration material requires the understanding of the ablation process involved which can affect the accuracy of quantitative results. As the laser light interacts with the sample, the coupling of the working wavelength and the sample, the physical and chemical properties of the sample affect the response. For example a thin section of a geologic rock, a fine powder that has been pressed into a pellet or a metallic sample will interact differently with the laser and give values that are unlikely to be easy to correlate to each other. Thus in most cases, standards used to give quantitative results need to be of the same matrix to limit these differences (Van Heuzen, 1991; Van Heuzen and Morsink, 1991). It is accepted that matching the chemistry of both standards and unknowns is sufficient to obtain quantitative results (Nelms, 2005). Unfortunately, the availability of certified solid calibration material is very limited, and the analyst requires other means of appropriate calibration for the generation of quantitative data.

Also studies have been focussing on the use of pressed powder pellets to establish a calibration line, usually matching the chemistry of the sample. Examples include the use of a set of certified materials such as in Bellis *et al.* (2006), where candidate reference materials for lead in bone analysis are used to spatially resolve Pb distribution in bones. Other examples use the preparation of a synthetic calibration line by spiking the elements of interest in a relatively pure powder base or certified material to produce a set of standards with increasing concentration. The addition can take form of stock solutions containing the element or element oxides mixed into the powders. Matrices using this approach include calcium carbonates (Pearce *et al.*, 1992; Craig *et al.*, 2000), cellulose for the analysis of tree rings (Prohaska *et al.*, 1998; Pearson, 2003) and diamond (Rege *et al.*, 2005) to name a few.

Alongside matrix-matched calibration, studies looked at the use of standards of a significantly different matrix compared to the sample, or non matrix-matched calibration. An example is given by Jackson *et al.* (1992) where a silicate glass (NIST 612) is used to calibrate for the analysis of zircons, apatite, uraninite, garnet and titanite, with recoveries between 10 and 20% from the target values.

Another approach to calibration is by using the standard addition method. This method can only be applied if the sample can be crushed down to a fine powder. In this method, a known

amount of the analytes of interest is added to a subsample of the original sample to obtain a new spiked sample. The spiked-in elements can take the form of an added oxide powder, or also mixed in via the addition of liquids containing the elements. This is done at least twice with increasing concentrations, usually by doubling, quadrupling etc. the expected analyte concentration. For better accuracy when determining the elemental concentration, it is common to use three to five spiked standards. Thereafter, the set of original sample plus the spiked samples are analysed, and the response for each analyte form a line that is used to calculate back the concentration of the analyte in the original sample. This is done by plotting the signal for the original sample for an equivalent concentration of element spiked in (in this case 0), and subsequently adding the spiked sample's signals with their respective added elemental concentration. Finally, the concentration of the element in the original sample equals the negative value of the best fit line intercept on the x axis. A graphical example can be found in Figure 2.2.

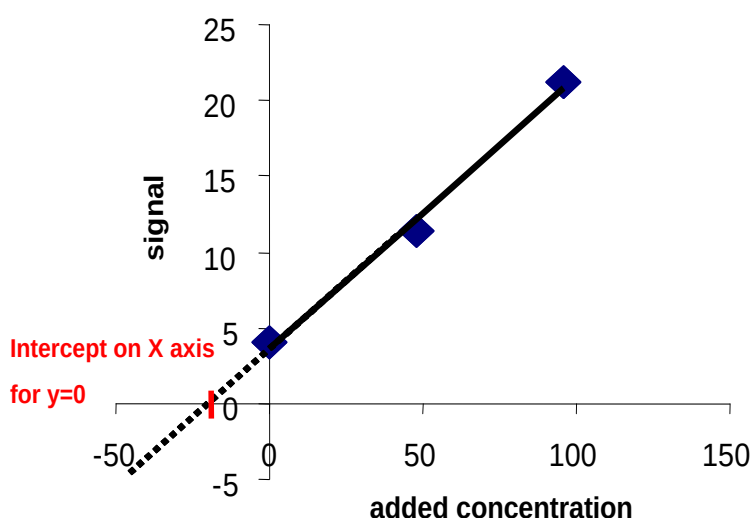


Figure 2.2: Standard addition method used when initial concentration for analyte is unknown.

The main advantage of this method is that no other sample than the original one is needed and spectral overlaps are corrected for, but it also has several drawbacks. The method is quite time consuming, and uses up to five or six analyses to obtain the concentrations of one unknown sample. Also, to prepare the spiked sample, the original sample will in almost all cases undergo a major change of its physical structure. For example, a solid material needs to be crushed down into a fine powder, the spikes added into the subsamples and the whole

set to be reformed into a similar shape, such as pressed into pellets. Thus the spatial variation of elemental distribution will be lost, and only bulk analysis will be possible.

Finally a novel and unusual approach to calibration of the LA-ICP-MS system for solid sample analysis was investigated by means of addition of a synthetic solution incorporated in the analyte gas stream. This was first reported by Chenery and Cooke in 1993 for a selection of elements only, as the fractionation effect prevents a wider use of the technique. Several studies focussed on improving this calibration method, which showed potential to measure REEs mainly in geological samples at an accuracy of 10-15% from published target values. One of the main advantages of this technique is that samples of unknown matrix can be characterised without prior measurement of an internal standard (Halicz and Günther, 2004).

#### 6.4 Elemental fractionation

Elemental fractionation can be described as the time-dependent variation in element isotope ratios measured when analysing a sample by LA-ICP-MS, even if the sample is considered homogeneous. The term comprises all non-stoichiometric effects during the whole LA-ICP-MS, including the ablation of the sample, aerosol transport, and dissociation and ionisation in the ICP leading to the variation (Guillong and Günther, 2002; Kuhn and Günther, 2004). The problem arose when differences in elemental response were observed, resulting in potential quantification issues. This feature of LA analysis was investigated from the mid 1990s, with one of the studies from Fryer and co-workers (1995) showing the relative fractionation of trace elements during a continuous ablation of homogenous NIST 610 glass. The experiment ratioed the response of about 60 elements to Ca, used an internal standard here, to produce fraction factors for each element. Results show that for although a straightforward chemical or physical explanation was not possible at this stage, lithophilic elements, including REEs, Th and U, displayed fractionation factors close to one, equivalent to negligible or no fractionation compared to Ca. On the contrary, chalcophile elements (e.g. Cu, Zn, Cd, Pb) show higher factors ( $>2$ ). Since a number of studies have been conducted to identify and describe the contributing factors to the fractionation effect. A comprehensive study by Kuhn and Günther (2003) investigated the ablation of a brass (Cu-Zn alloy) certified sample. Both elements have a significant difference in their melting and boiling points, with Cu at 1,083°C and 2,567°C, and Zn at 420°C and 907°C respectively. The authors collected ablated material in different size fractions on filters, which were subsequently mineralised and characterised with liquid ICP-MS. Also material deposited around the ablation crater was studied. The results showed that for brass sample there is a size-dependent fractionation of copper and zinc, reflecting the relatively higher volatility of Zn. Aerosol particles larger than

100nm were depleted in Zn, whereas particles less than the minimum measureable and the vapour phase were enriched in Zn. Also the deposited material around the crater showed impoverishment in Zn. The underlying factors of fractionation include the wavelength of the laser used, in respect of the interaction with the sample and the range of particles size generated, the transportation to the ICP and the incomplete vaporisation of the relatively large particles in the ICP (Kuhn and Günther, 2004).

## CHAPTER III: INSTRUMENTATION

### 1. Inductively coupled plasma mass spectrometry

ICP-MS is a versatile analytical technique for the measurement of trace elements mainly applied to liquid samples. It has the capacity to measure most elements in the periodic table, except for a few, in a very short time and with unmatched detection limits. Typically an analysis will take between three and five minutes for a sample. The length of the actual data recording is dependent on the quality of the data desired, the number of replicates, and the number of elements of interest. It is usually adding up to half of the analysis time, the remaining being sample handling and solution washout. The detection limits for most elements are in the order of few  $\text{ng.g}^{-1}$ , and are reduced to few  $\text{pg.g}^{-1}$  for elements with very low backgrounds.

The ICP-MS instrument used for this work is an Agilent 7500, which uses a quadrupole mass spectrometer for mass separation. For LA-ICP-MS analysis, the liquid sample introduction system is by-passed and the ablated material is transported directly to the back of the ICP. A schematic of the instrument is given in Figure 3.1. The instrument also includes a collision/reaction cell, placed between the lens assembly and the quadrupole (not featured in Figure 3.1), however this facility has not been used for the core work reported in this thesis.

#### 1.1 Inductively couple plasma mass spectrometry components

An ICP-MS instrument can be separated into three main components: the sample introduction system, the ion source and the separation and detection of the formed ions.

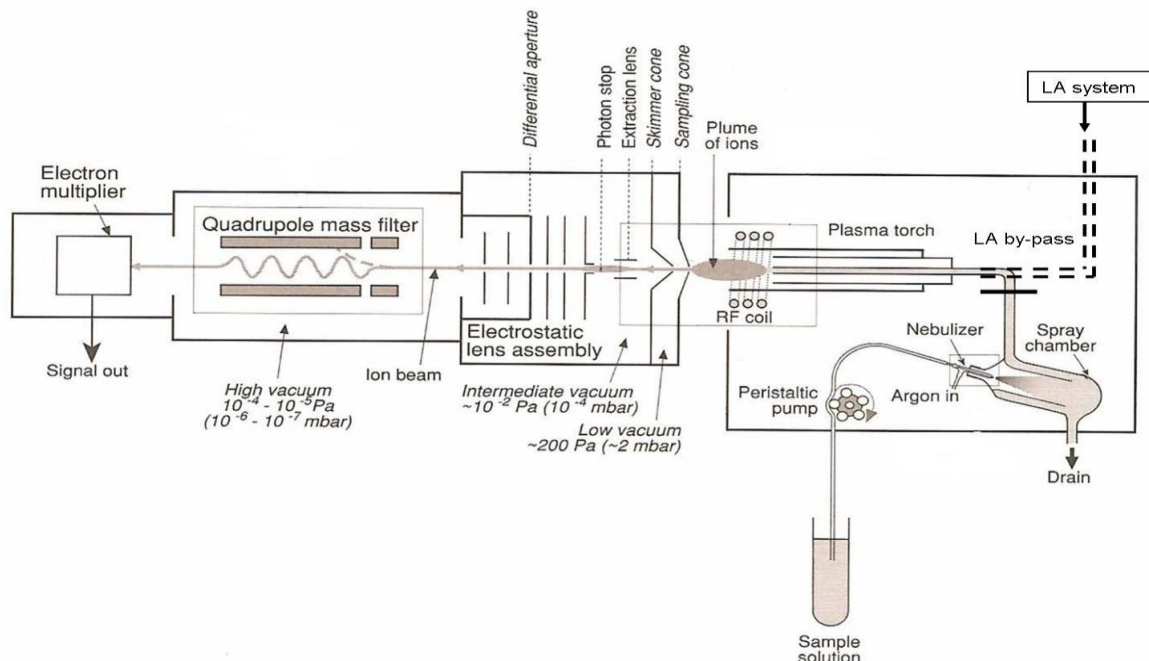


Figure 3.1: Schematic of a conventional liquid sample introduction ICP-MS instrument. The figure is altered to include the point where the laser ablated sample is introduced into the ICP-MS, by-passing the liquid system (adapted from Gill, 1997).

#### 1.1.1 Sample introduction: liquid sample

Commercial ICP-MS instruments are manufactured with a liquid sample introduction system. This consists of a peristaltic pump, a nebuliser and a spray chamber, before the connection to the back of the ICP torch. The solution, which is usually water or a solid sample digest with the appropriate dilution, needs to enter the ICP as a gas stream (Jarvis *et al.*, 2003). To that effect, the liquid sample is taken into the nebuliser via a peristaltic pump at a fixed rate, and meets the carrier gas. There are a variety of designs for nebulizers, but the main aim is to mix the carrier gas and liquid sample to produce an aerosol of the solution with a restricted range of small droplet sizes. The design used with the Agilent 7500 is a cross-flow nebuliser, where the liquid and carrier gas come into contact at a 90 degrees angle to form the aerosol.

Once the aerosol is formed it enters the spray chamber, which aims to select only the smaller fraction of droplets. The reason is that large particles may not successfully produce ions in the plasma. Most designs of spray chamber use the higher inertia of large particles to impact them on the chamber walls whereby they are removed from the system as waste. Here a Double pass Scott-type is used, which forces the spray around a 180° angle to continue towards the ICP. Only about 1% of the initial aerosol makes it to the plasma and most of the particles are below 10µm.

Another feature developed for the spray chamber is some form of cooling jacket. Uncontrolled temperature in the spray chamber affects the magnitude of the instrumental background and therefore overall performance. Lowest background was observed at low temperature (Jarvis *et al.*, 2003). The spray chamber is usually cooled by either a water jacket (circulating chilled water) or by means of a thermoelectric cooling system (Peltier cooler), which uses the Peltier effect of heat transfer from one material to another, with energy consumption. The Agilent 7500 cooling temperature is set at +2°C.

#### 1.1.2 Ion source: Inductively Coupled Plasma

A plasma is a very hot and highly ionised substance, here made of argon gas. The gas passes through a torch, where the formed aerosol is transported in the inner-most part surrounded by additional flows of argon. Near to the end of the torch, a copper coil is wound, attached to a radio frequency generator. It creates an alternating current where the gas passes, and after an electric discharge generates some Ar ions, these start to bounce against other atoms under the effect of the magnetic field originating from the coil to ionise them as well, resulting in the plasma. The maximum temperature in the plasma is about 8,000°K at its centre. As the finely selected aerosol reaches the plasma, it undergoes a few steps, firstly the desolvation of the analyte molecules, which subsequently break down to form atoms and these atoms ionise by loss of an electron to become positively charged ions (Jarvis *et al.*, 2003; Gill, 1997). This process takes only a few milliseconds and is highlighted in Figure 3.2.

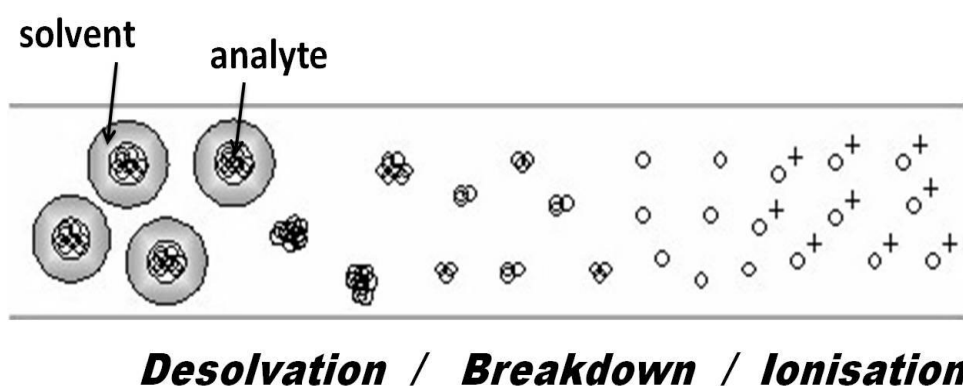


Figure 3.2: Sequence of changes undergone by the aerosol in the plasma to form ions. Typical residence time is few milliseconds (adapted from Agilent, 2000).

The relative amount of ions formed for each element is largely governed by the energy required for the ionisation process, and is different for each element and reflects their position in the periodic table and electron cloud structure. Some elements, like Na, K will

easily ionise, whereas F and He have a higher energy of first ionisation requirements than Ar, therefore not ionising at all (Emsley 1998). Table 3.1 shows the ionisation energy required and the elements concerned, and Figure 3.3 represents the degree of ionisation against this ionisation energy in an argon plasma (Jarvis *et al.*, 2003; Nelms, 2005).

| Ionisation energy (eV) | Elements                                                                                                                                           |                                    |
|------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|
| <7                     | Li, Na, Al, K, Ca, Sc, Ti, V, Cr, Ga, Rb, Sr, Y, Zr, Nb, In, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Ra, Th, U |                                    |
| 7-8                    | Mg, Mn, Fe, Co, Ni, Cu, Ge, Tc, Ru, Rh, Ag, Sn, Sb, Ta, W, Re, Pb, Bi                                                                              |                                    |
| 8-9                    | B, Si, Pd, Cd, Os, Ir, Pt, Po                                                                                                                      |                                    |
| 9-10                   | Be, Zn, As, Se, Te, Au                                                                                                                             | 2 <sup>+</sup> ions                |
| 10-11                  | P, S, I, Hg, Rn                                                                                                                                    | Ba, Ce, Pr, Nd, Ra                 |
| 11-12                  | C, Br                                                                                                                                              | Ca, Sr, La, Sm, Eu, Tb, Dy, Ho, Er |
| 12-13                  | Xe                                                                                                                                                 | Sc, Y, Gd, Tm, Yb, Th, U           |
| 13-14                  | H, O, Cl, Kr                                                                                                                                       | Ti, Zr, Lu                         |
| 14-15                  | N                                                                                                                                                  | V, Nb, Hf                          |
| 15-16                  | Ar                                                                                                                                                 | Mg, Mn, Ge, Pb                     |
| >16                    | He, F, Ne                                                                                                                                          | All other elements                 |

Table 3.1: Ionisation energy for singly and doubly charged ions at 1eV intervals (from Jarvis *et al.*, 2003).

Figure 3.3 shows how elements with first ionisation energy up to about 7eV will almost completely ionise (~100%), whereas elements above 11eV will only relatively ionise at 10% or less, influencing the instrumental response and sensitivity.

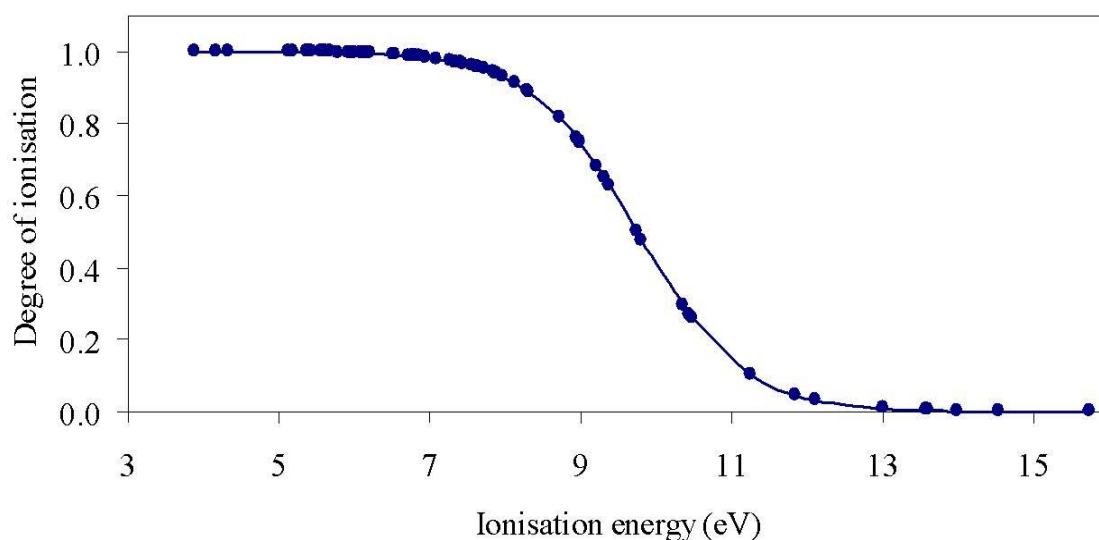


Figure 3.3: Degree of ionisation versus ionisation energy in an argon ICP (adapted from Jarvis *et al.*, 2003)

### 1.1.3 Separation and detection: mass spectrometry

Once the ion plume is formed at the end of the torch in the ICP, it enters the separation and detection process based on the ions'  $m/z$  ratio. At plasma level, the ion plume is at atmospheric pressure, but to be able to be sorted and counted efficiently in the mass spectrometer, a high vacuum is required (usually nine orders of magnitude lower than atmospheric pressure). To gradually enter the high vacuum, the ions pass through a two stage extraction interface with intermediate pressure. Firstly the ions pass through a small orifice (about 1mm) in a cone (sampling cone) tightly attached to the vacuum chamber, then through a smaller second cone (skimmer cone) with a hole of about 0.4 to 0.7mm. Once the ions have been extracted, they are focussed and reach an adequate speed to enter the mass spectrometer and be successfully separated. This is important as the maximum number of ions need to go through for reaching the excellent limits of detection of the technique. Therefore, a stack of lenses is used to shape the ion plume into a fine beam. Different electric currents are applied to the lenses to affect the ions, and only the ions. At this stage, photons and non ionized particles (neutrals) are stopped, because they will not be separated by the mass analyser and therefore only contribute to background noise as electron multiplier detectors are also sensitive to light. In the past this was generally achieved by using a charged metal disc positioned in the path of the ion beam. Only ions flow around that disc whereas photons and non charged particles collide with it. More recently, the idea of forcing

the ion beam through a chicane with again different voltages has been developed, so that the mass spectrometer's entrance is offset from the lens stack (case for Agilent 7500).

After passing through the lens stack, which focuses the ions into a fine beam, the ions enter the mass spectrometer unit for ion separation and counting. Each ion is separated based on its mass per charge ratio ( $m/z$ ) using the mass filter. This device is formed by four parallel rods (quadrupole) and equidistant to the beam of ions at its centre. Each set of opposite rods has different direct current and radio frequency settings, making the ions oscillate into a stable zone in the central channel of the four rods. Depending on the settings, only ions of one  $m/z$  will remain in the stable area and proceed to the detector. All other ions will be subject to extreme oscillation, will leave the stable zone and be lost in the vacuum vessel. The selected ion is then counted by the detector. As the ions enter the detector (electron multiplier detector for Agilent 7500), a special coating in the inside releases electrons as the ion hits the surface, starting a chain reaction with many electrons released. Thus each ion is transformed into a pulse, and the intensity of the pulse signal can be related to the number of incoming ions. To convert into concentration, a calibration curve is required, giving the relationship between a set of known elemental concentrations and their respective response signal under the same conditions as the unknown sample. The relationship is linear over up to nine orders of magnitude (Jarvis *et al.*, 2003; Gill, 1997).

The ICP-MS settings used and specifications for laser ablation mode analysis in are given Table 3.2.

| Agilent 7500                                        |                          |
|-----------------------------------------------------|--------------------------|
| Operation parameters                                |                          |
| RF power (W)                                        | 1500                     |
| Plasma gas flow (L.min <sup>-1</sup> )              | 14.95                    |
| Carrier gas in ablation cell (L.min <sup>-1</sup> ) | 1.4                      |
| Data acquisition                                    |                          |
| Acquisition mode                                    | Spectrum                 |
| Integration time (s)                                | 0.1–0.2/point            |
| Peak pattern                                        | FullQuant, 3 points/peak |
| Repetition                                          | 10                       |

Table 3.2: Operating condition of Agilent 7500 in laser ablation mode.

## 2. Laser ablation system

### 2.1 Instrumentation

The laser ablation system used here is a CETAC LSX-100 (Omaha, USA) employing a neodymium and yttrium aluminium garnet (Nd:YAG) solid-state laser. The laser produces a fundamental wavelength of 1064nm, and its frequency quadrupled to give a final working wavelength of 266nm. Figure 3.4 shows the schematic diagram of the laser ablation system.

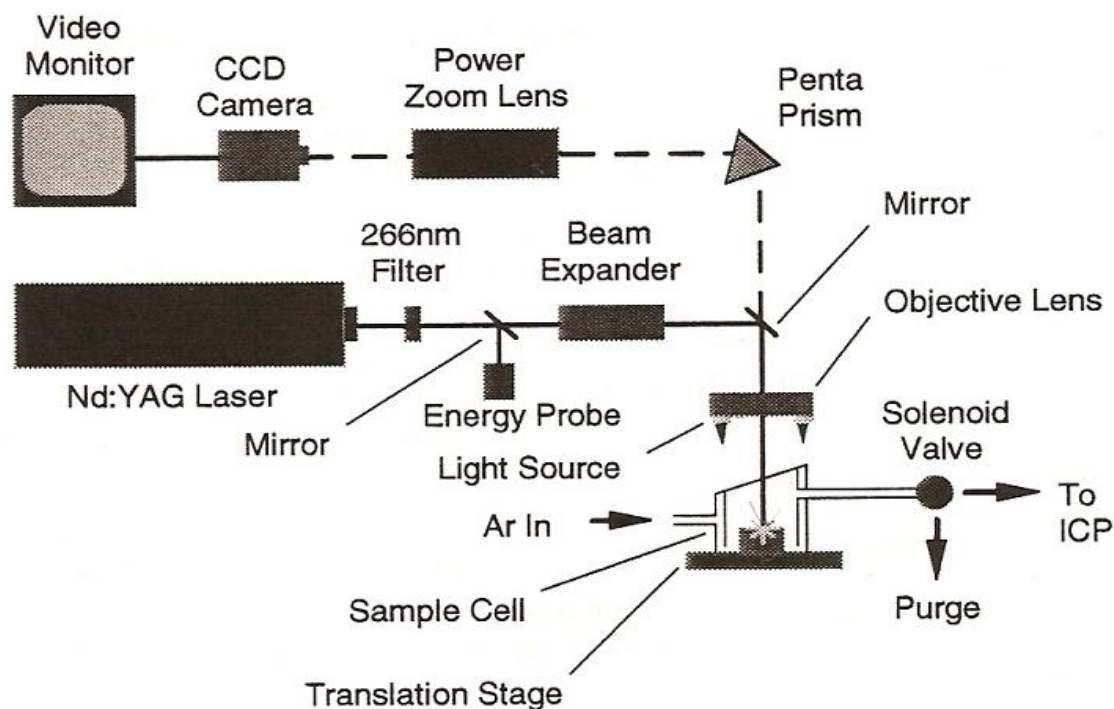


Figure 3.4: Schematic diagram of CETAC LSX-100 ablation system (CETAC, 1996).

The system includes a set of optics and a CCD camera microscope system for sample identification and focusing purposes. The sample is contained in an air-tight ablation cell measuring 50mm in diameter and 20mm high. The cell has an inlet and outlet for gas flushing and sample transport, and the stage supporting the cell is movable in three dimensions.

The laser ablation system has several operating parameters that can be configured. These include the scanning speed, the repetition rate of the laser pulse, the distance between the scanning lines and the defocusing of the laser beam. Table 3.3 shows typical parameters used for the analysis samples.

|                                         | CETAC LSX-100 |
|-----------------------------------------|---------------|
| Parameters                              |               |
| Ablation cell volume (cm <sup>3</sup> ) | 39.3          |
| Ablation mode                           | Scanning      |
| Track width (μm)                        | ~30-50        |
| Laser shot energy (mJ)                  | 0.1-0.2       |
| Frequency (Hz)                          | 10            |
| Scanning speed (μm.s <sup>-1</sup> )    | 10-30         |
| Defocusing (μm)                         | 500           |

Table 3.3: Laser ablation system parameters used for this study.

## 2.2 System optimisation and performance

Before any analysis can take place, the LA-ICP-MS system is optimised. This is a routine protocol that determines the good working conditions of the system. For this, a very well characterised solid sample is used, namely NIST 610, which is a Si-based synthetic fused glass with certified data for major and about 60 trace elements present at approximately 400μg.g<sup>-1</sup>. Using pre-determined setting for the laser ablation system that are appropriate for opaque glass samples, the signal for <sup>9</sup>Be, <sup>115</sup>In and <sup>238</sup>U is monitored and adjusted by changing the ICP-MS instrument settings (sampling depth, lens voltages, etc.) to obtain a good compromise between sensitivity and precision, as far as achievable. A short term stability test is routinely performed over four min, during which 10 replicate analyses are recorded and precision calculated for nine isotopes including <sup>9</sup>Be, <sup>24</sup>Mg, <sup>59</sup>Co, <sup>89</sup>Y, <sup>115</sup>In, <sup>140</sup>Ce, <sup>165</sup>Tm, <sup>208</sup>Pb and <sup>238</sup>U. Typical precision on NIST 610 analysis is better than 10% on corrected data.

### 2.2.1 Background

This background signal originates from stray photons hitting the detector, electronic noise in the system and from polyatomic ion species formed in the plasma from the gases present. Apart from the polyatomic species, which will depend on the sample matrix, the instrument background is usually assessed by monitoring 5m/z and 220m/z, which in theory are free of isotopic and polyatomic signal.

## 2.2.2 Oxides and doubly charged ions

Levels of oxide polyatomic interference and doubly charged ion are also quantified. Here for solution ICP-MS, this is achieved by monitoring the formation of  $\text{CeO}^+$  and  $\text{Ce}^{2+}$ . Typical target for  $\text{CeO}^+/\text{Ce}^+$  is <1% and  $\text{Ce}^{2+}/\text{Ce}^+$  of <2.5%. For laser work, the most commonly used material for testing the instrument performance is NIST 610 glass. Because the glass contains almost all elements, it is not possible to monitor the doubly charged ions, as there are isobaric interferences on nearly all  $m/z$  values. Elemental oxides are monitored using thorium signal and corresponding  $\text{ThO}$  at 248  $m/z$ . Due to the absence of a solvent such as water in LA dry plasma,  $\text{ThO}/\text{Th}$  of <0.3% is achievable here.

## 2.3 Laser data processing

### 2.3.1 Quantitative results

There are a number of stages in data processing which will determine if the data are qualitative or quantitative in nature.

The first step is to correct gross signal for background. Ideally this must be done using a matrix-matched blank sample but this is not normally possible. Instead, a gas blank measurement is made by firing the laser but with the shutter closed so that no ablation is taking place. Five replicate analyses of the blank are taken and the average signal is then deducted from all other measurements.

The second step is to remove any signal which cannot be statistically differentiated from the background signal. This is done by calculating a threshold value called the lower limit of detection (LLD). This value corresponds to three times the standard deviation ( $\sigma$ ) of the background (gas blank) signal. In normal Gaussian distribution,  $3\sigma$  include 99.7% of all measurements, and therefore any signal above that threshold can be considered as above the background and correspond to a quantifiable measurement.

The next step is to select an appropriate internal standard and account for the differential ablation efficiency. As the ablation process takes place, every laser pulse delivered hits the sample and a different amount of material is sampled. This usually gives rise to significant imprecision in replicate analysis of an homogeneous sample. An element present in both the sample and the standard, and homogeneously distributed, is identified. This element is the internal standard; its concentration in the calibration material and samples is required prior to correcting the data set and can be obtained by other analytical methods (for example

electron probe or using ICP-AES analysis after appropriate sampling and digestion step). Also it will no longer be possible to quantify this element. For NIST 610 calibration materials, useful internal standards are for example  $^{43}\text{Ca}$  or  $^{44}\text{Ca}$ ,  $^{29}\text{Si}$  or isotopes of Mg

Once the internal standard is selected, the final correction steps can be applied to obtain 'normalised' data. At this point, the internal standard signal can include differences due to the ablation efficiency, but also due to difference in the concentration of that internal standard in the materials investigated. To correct for the latter, which was measured by another technique and likely to be present at different amounts, the signals are proportionally adjusted in all measurements to reflect the concentration differences. The internal standard signals are corrected independently from all other isotopes and are now identical. Finally, the internal standard signals are now comparable to each other, and the remaining differences in the signal can now be correlated to the differential ablation rate only. By correcting the internal standard signal of each subsequent analysis to the first value to the first analysis, and all other isotopes at the same time by the same factor, the data will be fully corrected and ready for quantitative or qualitative assessment. An example of this last correction between uncorrected and normalised data is shown in Figure 3.5.

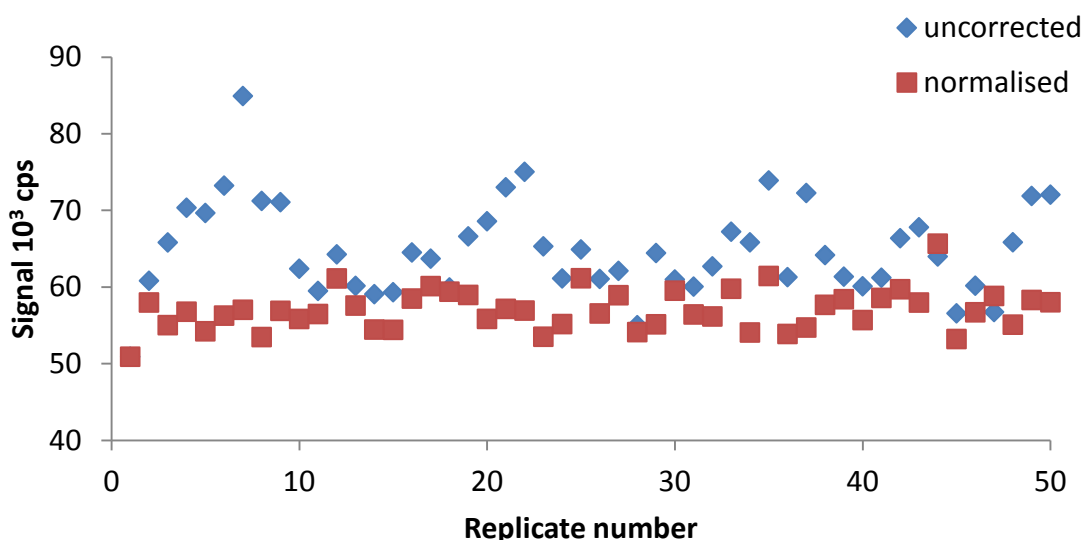


Figure 3.5: Uncorrected and normalised data example. The data represent  $^{59}\text{Co}$  signal and were acquired over 50 consecutive analysis of NIST 610 homogeneous glass, using  $^{43}\text{Ca}$  as internal standard. Relative standard deviations of uncorrected and normalised data are 9.4 and 4.6% of the mean respectively.

At this point, the response given by the sample can be directly quantified using the calibration standard signal and the corresponding concentration of the analyte of interest.

### 2.3.2 Qualitative results

In cases, an appropriate calibration standard is difficult to obtain or commonly not available. Also, quantitative data may not be required and the interest lies in the changes of the analytes within a matrix, for example variation in trace element chemistry of marine shells, tree rings and bones (Craig *et al.*, 2000; Pearsons, 2003; Bellis *et al.*, 2006). In these examples, assuming the matrix is homogeneous, the analyte and a major component signals can be ratioed directly, providing a measure of spatial variability.

### 2.4 Laser data correction for this study

As described above, one crucial feature of the sample of interest is for the matrix to be homogenous throughout and a major component element to be distributed evenly. This was not always possible with the concrete samples under investigation, with changing chemistry between the different constituents and in some cases within the same constituent. To address this, a slightly different partial correction approach was used, namely using the total major elements composition of the sample. Measurements of major elements for geological samples are usually reported in percent oxide form, adding up to nominally 100%. In some cases, for example carbonates, the CO<sub>2</sub> forms a significant part of the sample, but cannot be monitored by the instrument and needs to be evaluated and added to the total components. Therefore in principle, monitoring the major elements, converting them into their respective oxide form and correcting the data to 100% total major oxides, it is possible to correct for the ablation volume differences experienced with the laser.

In this study, the laser data are initially corrected for blank signal and instrumental detection limits, and NIST 610 glass is used as a calibration standard to generate approximate concentrations and enable the correction described above. The validity of this approach is tested and discussed in Chapter IV, Section 2.

### 2.5 Proficiency test

It is sometimes difficult to assess the quality level (accuracy and precision of results) of an analysis using a specific technique. This is the case for LA-ICP-MS, where the calibration is of prime importance to obtain reliable data. One way to assess the performance of the technique is to participate in a Proficiency Testing scheme. In 2005, the LA-ICP-MS system used in this research, which was NERC ICP facility (at Kingston University) instrumentation at the time, participated in an international proficiency testing scheme organised by the International Association of Geoanalysts (IAG) for the analysis of a synthetic homogeneous

glass sample. For this scheme, over 60 laboratories from around the world participated, and LA-ICP-MS and electron probe analysis were used for the analysis of the sample, a basaltic glass. The results obtained for the LA-ICP-MS setup used here are given in Table 3.4 together with the assigned values for the proficiency sample (NKT-1G).

| Element       | Be   | Na    | K     | Ca    | Sc    | V    | Cr    | Mn    | Co   |
|---------------|------|-------|-------|-------|-------|------|-------|-------|------|
| ICP Facility  | 2.2  | 26222 | 9802  | 85428 | 25.4  | 268  | 406   | 1386  | 57.3 |
| USGS assigned | 2.7  | 25817 | 10646 | 94399 | 22.4  | 294  | 443   | 1603  | 61.5 |
| Recovery (%)  | 83.7 | 101.6 | 92.1  | 90.5  | 113.5 | 91.4 | 91.8  | 86.5  | 93.2 |
| Element       | Cu   | Rb    | Sr    | Y     | Zr    | Mo   | Sn    | Cs    | Ba   |
| ICP Facility  | 47.9 | 29.5  | 1019  | 23.1  | 233   | 0.7  | 2.6   | 0.5   | 627  |
| USGS assigned | 49.2 | 31.2  | 1204  | 29.7  | 286   | 0.8  | 2.5   | 0.5   | 725  |
| Recovery (%)  | 97.4 | 94.4  | 84.6  | 77.9  | 81.3  | 84.7 | 102.3 | 102.0 | 86.5 |
| Element       | La   | Pr    | Nd    | Sm    | Eu    | Gd   | Tb    | Dy    | Ho   |
| ICP Facility  | 56.9 | 12.3  | 53.2  | 10.7  | 3.7   | 8.4  | 1.1   | 6.0   | 0.9  |
| USGS assigned | 64.2 | 15.0  | 61.7  | 12.0  | 3.8   | 10.9 | 1.3   | 6.7   | 1.1  |
| Recovery (%)  | 88.6 | 82.0  | 86.2  | 88.8  | 95.8  | 76.7 | 82.8  | 89.1  | 81.5 |
| Element       | Er   | Tm    | Yb    | Lu    | Hf    | Ta   | Pb    | Th    | U    |
| ICP Facility  | 2.1  | 0.2   | 1.4   | 0.2   | 5.5   | 3.3  | 2.9   | 5.8   | 1.9  |
| USGS assigned | 2.6  | 0.3   | 1.8   | 0.2   | 6.5   | 4.9  | 3.0   | 7.2   | 2.2  |
| Recovery (%)  | 78.9 | 61.5  | 76.3  | 84.0  | 84.7  | 67.8 | 96.2  | 81.1  | 86.7 |

Table 3.4: Elemental concentrations measured and assigned values (in  $\mu\text{g.g}^{-1}$ ) for the sample NKT-1G and recovery percentages.

The results were obtained by a one point calibration using NIST 610 standard and using Mg as internal standard. The Mg data were obtained by electron probe at Kingston University. In general the measured values are in excellent agreements with the assigned values for both low and high concentrations. This demonstrates the potential of the LA-ICP-MS system used for the analysis of an ideal sample, here a homogeneous glass.

### 3. ICP-Atomic Emission Spectroscopy

ICP-AES is the preferred instrumentation for the analysis of major components in geological materials. Similarly to ICP-MS, it is also equipped with a liquid sample introduction system and an ICP, though the function of the ICP and the detection method used are different. When an electron absorbs the energy delivered by the ICP, it reaches an excited state. As it regains its lower energy state, it releases light of a specific wavelength or wavelengths

particular to the element of interest. This radiation is thereafter measured, with its intensity proportional to the amount of the element present in the sample. Quantification is performed using a calibration line from known concentration of major elements (Ebdon *et al.*, 1998)

The instrument used for this work is a HORIBA Jobin Yvon Ultima 2C (JY, Longjumeau, France). Calibration of the instrument is performed by analysing certified reference materials prepared in the same way as the sample to form a calibration line of certified target values against signal response. Here two separate sets of reference materials prepared by HF/HClO<sub>4</sub> acid digest or lithium metaborate fusion are used, covering the expected range of major element concentrations to be found in the samples. Table 3.5 shows the materials used for each sample preparation method and the major element target values used.

| Major component |        | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO    | MgO  | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> |
|-----------------|--------|------------------|--------------------------------|--------------------------------|--------|------|-------|-------------------|------------------|------------------|-------------------------------|
| Fusion          | BHVO-1 | 49.94            | 13.80                          | 12.23                          | 0.168  | 7.23 | 11.40 | 2.26              | 0.52             | 2.71             | 0.273                         |
|                 | CCH-1  | 0.97             | 0.3                            | 0.17                           | 0.0007 | 2.91 | 52.12 | 0.048             | 0.082            | 0.017            | 0.051                         |
|                 | GSS-4  | 50.94            | 23.45                          | 10.30                          | 0.18   | 0.49 | 0.26  | 0.112             | 1.03             | 1.80             | 0.16                          |
|                 | JG-2   | 76.95            | 12.41                          | 0.92                           | 0.015  | 0.04 | 0.8   | 3.55              | 4.72             | 0.04             | 0.002                         |
|                 | SCO-1  | 62.78            | 13.67                          | 5.14                           | 0.053  | 2.72 | 2.62  | 0.90              | 2.77             | 0.628            | 0.206                         |
|                 | W-2*   | 52.44            | 15.35                          | 10.74                          | 0.163  | 6.37 | 10.87 | 2.14              | 0.627            | 1.06             | 0.131                         |
| Acid digests    | AGV-1  | n/a              | 17.15                          | 6.77                           | 0.09   | 1.53 | 4.94  | 4.26              | 2.92             | 1.05             | 0.49                          |
|                 | G-2    | n/a              | 15.39                          | 2.66                           | 0.03   | 0.75 | 1.96  | 4.08              | 4.48             | 0.48             | 0.14                          |
|                 | MAG-1  | n/a              | 16.37                          | 6.80                           | 0.098  | 3.00 | 1.37  | 3.83              | 3.55             | 0.751            | 0.163                         |
|                 | OPC-1  | n/a              | 4.55                           | 3.19                           | 0.404  | 2.58 | 62.9  | n/a               | 0.344            | 0.318            | 0.044                         |

Table 3.5: Reference materials and certified values used for the calibration of the ICP-AES instrument for both fusion and acid digest (HF/HClO<sub>4</sub>) sample preparation. \*W-2 used in both calibrations.

#### 4. Electron probe

This technique is used for chemical characterisation and physical mapping of samples. A schematic diagram is shown in Figure 3.6. The technique consists in a high energy electron beam focused onto a sample coated with a very thin conductive layer of gold or carbon. The technique can record the X-rays produced by the bombarded sample to obtain chemical composition as well as secondary electrons for topographic images of the sample's surface.

There are two types of X-rays analysers, namely energy-dispersive spectrometers (EDS) and wavelength-dispersive spectrometers (WDS). Both can be used for qualitative measurements of the chemistry, though WDS records only one wavelength at a time and thus relatively slow whereas EDS records the whole spectrum simultaneously. Nevertheless, to obtain quantitative data, again both spectrometers can be used, though WDS is capable of better detection limits for trace elements analysis. A combination between EDS for major elements and WDS for trace elements is possible (Potts *et al.*, 1995). The main aim is to give chemical composition for major and some trace elements present at values approximately  $>100 \mu\text{g.g}^{-1}$  (detection limit) at a resolution of about  $5 \times 5 \times 5$  micrometres.

The second feature involves the production of topographic-type images of the sample. In the case of a polished sample, back-scattered electrons are recorded and give a picture of the sample with different light, dark and shades of grey colour. This variation gives an indication of the mean atomic mass, following the principle of the brighter the colour, the higher the average mass. This feature is a quick and useful tool for the visual localisation of boundaries and possible different mineral phases with significant different major chemistry.

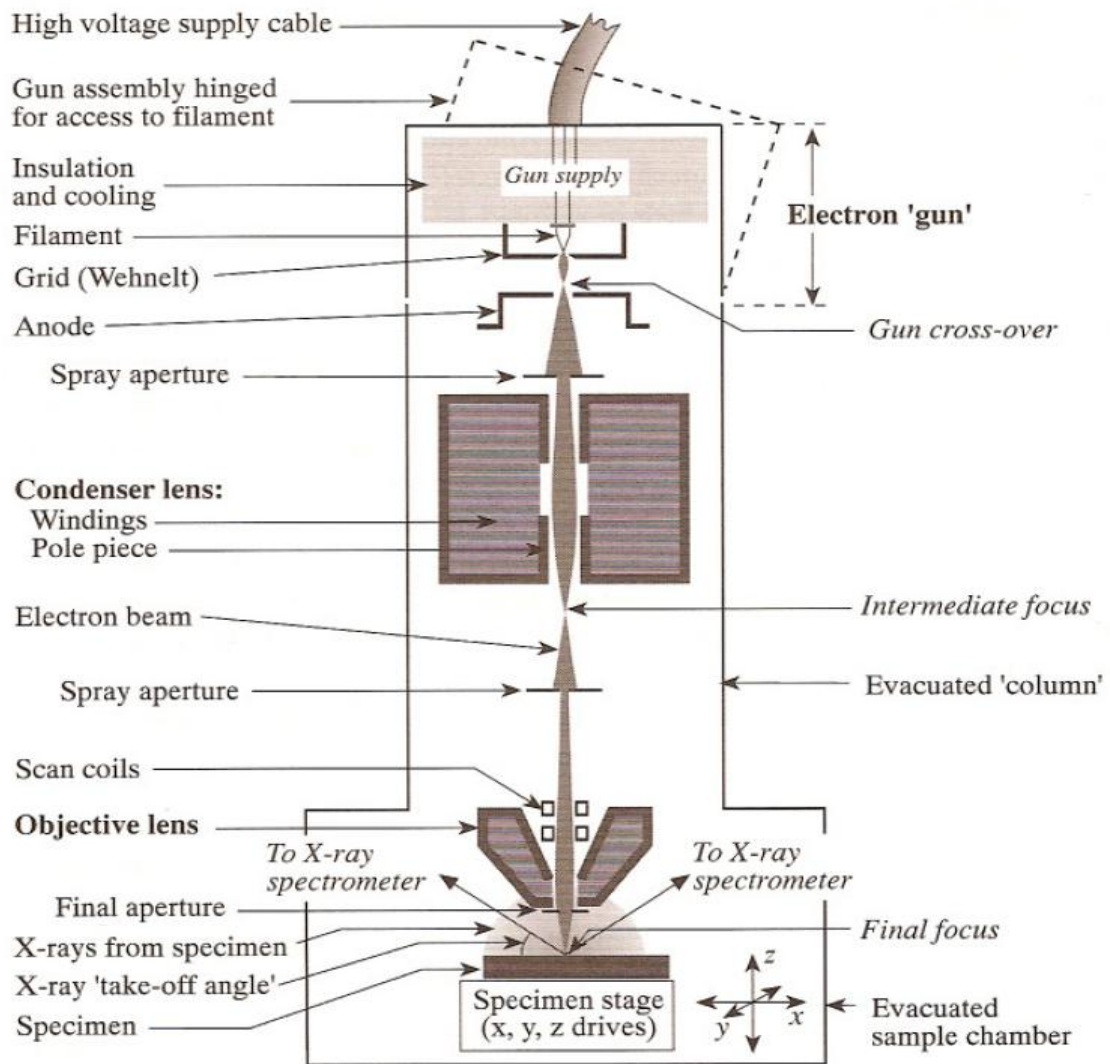


Figure 3.6: Schematic diagram of a typical electron microprobe (from Gill, 1997).

## 5. Concrete samples investigated

For this study five different samples of concrete shielding material were obtained, three originate from the CONSORT research reactor hosted by Imperial College at their Silwood Park campus, Berkshire, and the remaining two from the Windscale Piles reactors on the Sellafield site, Cumbria.

### 5.1 CONSORT samples

The CONSORT reactor started operations in 1965 and is a research reactor operating at 100kW (low power compared to commercial reactors). It is used as a source of neutrons for different applications, including a commercial neutron activation analysis facility, and was an active centre for external training and support to postgraduate level students. The reactor

was officially shutting down at the end of 2012 to enter decommissioning stage. Figure 3.7 shows a graphical representation of the reactor.

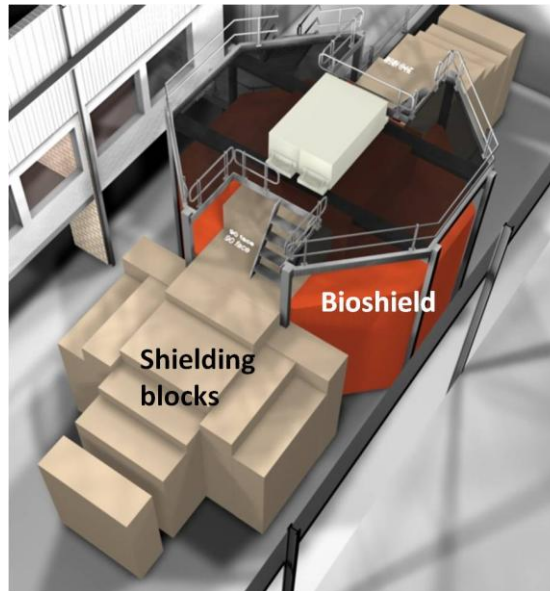


Figure 3.7: graphical representation of CONSORT reactor. The three samples come from the bioshield (in red) and from two different types of shielding blocks used as protection for the shine path on the analytical open sides of the reactor (adapted from Kafala, 2005).

### **Bioshield sample**

The main reactor shield is of octagonal shape and measures 6.17m across opposite sides. Originally designed to be a one monolithic block, closer inspection of the shield highlighted two horizontal “joints” at about 1/3 and 2/3 of the total height. These joints suggest a pouring of the concrete in three steps. A small portion of the shielding monoblock surrounding the reactor core was recovered from a previous investigation. Figure 3.8 shows this sample. The sample consisted in a mixture of powder and small portions of cement, sand and larger aggregates from a corner of the shield. The specifications found were as follow:

Dried out density: 2322.7kg.m-3

Coarse aggregates: 38.1-19.1mm, 3.0 parts by weight  
19.1-4.76mm, 1.3 parts by weight

Fine aggregates: 1.7 parts by weight

Cement: 1.0 parts by weight



Figure 3.8: CONSORT bioshield concrete sample. The red pigments are from the outer paint layer of the shield.

### **Large block**

These blocks are about 2m<sup>3</sup> in volume and are placed at the open sides of the reactor for the analytical and monitoring equipment. The sample consists in several small blocks of sand cement and aggregates together, approximately 5cm in diameter.

### **Small block**

The final sample is a portion of relatively smaller shielding blocks, weighing up to 50kg used with the large blocks for additional shielding. Figure 3.9 shows a flat section of the sample used for investigation.



Figure 3.9: Flat section of small block sample SB1. Dimensions are 4.4cm by 2.3cm

From the three samples, the small block offers a representative sample of the whole block, and was used as the test sample to develop the LA-ICP-MS methodology.

## 5.2 Windscale samples

The Windscale site, now part of the larger Sellafield site, hosted up to fairly recently two reactors for the production of plutonium. The reactors, Pile No. 1 and Pile No. 2, were constructed in the early fifties as part of the British nuclear weapons project, and started operations in October 1950 and June 1951 respectively. Unfortunately in 1957, a fire broke out in the core of Pile No. 1, resulting in the worst nuclear accident in the U.K. (Wakeford, 2007). From that point onwards the two reactors were shut down and confined before decommissioning started in the 1980s. Figure 3.10 shows the two reactors with their ventilation tower.



Figure 3.10: Windscale Piles No. 1 & 2.

### Pile No. 1 sample

This sample is a core extraction from Pile No.1 and was obtained from National Physical Laboratory (Simon Jerome, personal communication). The core is 22cm long and 5cm in diameter, and corresponds to the 12 to 34cm of the inner face of the bioshield. The sample received is shown in Figure 3.11.



Figure 3.11: Windscale Pile No.1 core sample as received from NPL.

### Pile No. 2 sample

A sample from Pile No.2 was obtained from British Nuclear Fuels Limited (BNFL, David Adamson, personal communication), as part of a concrete recycling exercise undertaken on the ventilation chimney on behalf of the British Nuclear Group. The exercise identified that from the 4,500 tonnes of concrete to be decommissioned, about 3,000 tonnes are below the threshold value of “free release” activity (here  $0.4\text{Bq.g}^{-1}$ ) with potential to be recycled.

The sample received consisted of recycled large aggregates, which were crushed and sieved from the bulk concrete. The aggregates are 14mm in diameter or less, a small proportion of them with remaining cement and sand mix attached.

## 5.3 Samples preparation

### 5.3.1 Sections

Samples are typically prepared as slices of solid material approximately  $60\mu\text{m}$  thick. At this thickness it is possible to perform some conventional light microscope investigation of sample, for example identify mineral phases or the nature of grains present. Also a minimum thickness is required to use the laser and avoid the beam to ablate through the sample and into the supporting glass slide. A section is prepared by producing a flat surface

of the sample, which is subsequently glued on a glass slide and the appropriate thickness sawn off.

### 5.3.2 Sample mineralisation

For bulk chemistry analysis, a representative portion of the concrete sample is crushed to a fine powder, typically  $<200\mu\text{m}$ , and homogenised. For concrete constituents work, the cement and sand (c/s) mixture and single aggregates were separated from each other. The main separation was performed using pliers, and a micro-drill with a cone shaped tungsten carbide head was used under a microscope (x5 magnification) to remove the remaining cement and sand mixture from the aggregates' surface. Large aggregates ( $>0.5\text{g}$ ) were crushed into a fine powder, whereas the smaller ones ( $<0.1\text{g}$ ), predominantly from sample SB1, were weighed as a whole, since crushing of such amounts is practically difficult to recover enough material for a representative analysis.

Subsequently the samples were digested using an appropriate method for the analysis of elements of interest and adapted to the sample type. Namely three methods were used and are briefly described here. The first two are widespread methods used for characterisation of Si-rich geological materials by ICP-MS and ICP-AES to give the full major and trace elements chemistry of the sample. Both are based on Thompson and Walsh (1989) and NERC ICP facility digestion methods (Appendix 1):

***HF/HClO<sub>4</sub> digests:*** basically the HF reacts with the silicon present in the sample and forms a volatile  $\text{SiF}_4$  compound. It is used especially for the determination of volatile elements (e.g. As, Pb). The procedure is not recommended for samples containing highly resistant minerals such as zircons and chromites. This method was preferred for the small aggregates from SB1, to enable the analysis of the key elements such as Li.

***LiBO<sub>2</sub> fusion:*** here the sample is mixed with a flux to lower its melting point, using a high temperature furnace ( $>1,000^\circ\text{C}$ ). The resulting glass melt is dissolved in dilute acid. This procedure enables the analysis of all major and trace elements, except volatiles and Li and B (flux components).

***HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> digests***: highly oxidising environment, appropriate for samples containing significant amounts of carbonates such as limestone and dolomite. This method was applied mainly to aggregates from sample WP1. Any residue was considered to be remaining cement and sand mixture and was not handled further.

## CHAPTER IV: CALIBRATION

The calibration of the instrumental response is paramount in LA-ICP-MS for the production of accurate quantitative data. In general quantitative data can be produced from a chemical and physical matrix-matching of the calibration material and the sample of interest. At the moment only a few certified solid reference materials are available commercially matching certain types of samples, and in most cases the manufacturing of synthetic standards to fit the chemical and physical requirements of the sample is necessary.

In this work the suitability of certified reference materials and synthetic standards is evaluated. One such calibration material, widely used around the world, is the suite of synthetic glass produced by the National Institute of Standards and Technology (NIST, USA). This suite consists of four glass discs with different concentrations of about 60 trace elements, with a matrix consisting of 72%  $\text{SiO}_2$ , 14%  $\text{Na}_2\text{O}$ , 12%  $\text{CaO}$  and 2%  $\text{Al}_2\text{O}_3$ . The trace elements are present at approximately 500 (NIST 610 standard), 50 (612), 1 (614) and  $0.02\mu\text{g.g}^{-1}$  (616). Most commonly NIST 610 and 612 are used in analytical laboratories, as calibration standard and also to perform instrumental tuning and check performance of the LA-ICP-MS system prior to analysis.

Considering the different components that may be found in concrete, the following examples and characteristics are defined: for the cement and sand matrix, it is not possible to differentiate between the cement and small aggregates used as their particle size range is below the spatial resolution capability of the LA-ICP-MS system. Based on a mixing ratio of one part cement (approximately 60%  $\text{CaO}$ , 20%  $\text{SiO}_2$ ) and two parts sand (100%  $\text{SiO}_2$ ), the resulting major chemistry is likely to be around 73%  $\text{SiO}_2$ , 20%  $\text{CaO}$  and the remaining 7% consisting of minor other oxides. The potential use of fly ash and other additives can affect the trace element composition, with minor effect on the major chemistry. For limestone aggregates, the chemistry is likely to be  $\text{CaCO}_3$  exclusively; also in case of dolomites, a significant proportion of the matrix will be  $\text{MgCO}_3$ . Other possible large aggregates are likely to have a  $\text{SiO}_2$ -based matrix, although information found in the literature on suitable aggregates for reactor shielding considers the use of aggregates containing significant iron in the matrix.

There are a number of “calibration materials” which are potentially suitable for the calibration of materials of interest described above. Firstly OPC-1, an ordinary Portland cement which has been used as a proficiency test sample (IAG, 2009), is considered for the cement and sand mixture. It is a powdered material which has been pressed into a pellet and has been

characterised for about 40 major and trace elements. The natural content is used as reference value (Appendix 2). The second material is MACS-3, a microanalytical calcium carbonate standard artificially prepared by co-precipitation and supplied by the United States Geological Survey (USGS). The standard is presented as a pressed pellet and recommended values for over 40 major and trace elements are given (Appendix 3). The third material is NIST 612 glass, which was described earlier, containing about  $50\mu\text{g.g}^{-1}$  of over 60 trace elements (Appendix 4). A number of alternative calibration strategies have been tested.

#### 1. One point calibration using NIST 610 glass

The first experiment is to use NIST 610 glass standard as a one point calibration to quantify major and trace elements in the other matrices. Here the NIST 612 glass, OPC-1 and MACS-3 are used as target samples. In this exercise, data are collected for over 50 elements over 10 successive replicate analyses. Table 4.1 shows the major element results. The table contains the target value for each element (in % by weight) of the material. Also present are the recoveries (in % from the target value) achieved using both the internal standardisation (IS), here using  $^{43}\text{Ca}$ , and the total oxides (TO) data correction methods, as described in section 2.4 in Chapter III. Here the TO method has to take into account that MACS-3 sample contains a significant amount of volatile  $\text{CO}_2$  and non-measurable by ICP-MS, which is corrected using the Ca signal. It is assumed all the Ca is present as  $\text{CaCO}_3$  and the stoichiometry is adjusted with the corresponding  $\text{CO}_2$  content. In a similar approach, the potential presence of  $\text{MgCO}_3$  was assessed using the Mg content and was calculated as equivalent to 0.3%, which is relatively negligible in the approach taken.

| Major component (%)     | NIST 612 | Recovery |      | OPC-1 | Recovery |      | MACS-3            | Recovery |     |
|-------------------------|----------|----------|------|-------|----------|------|-------------------|----------|-----|
|                         |          | IS       | TO   |       | IS       | TO   |                   | IS       | TO  |
| $\text{SiO}_2$          | 71.8     | 100      | 99.7 | 21.9  | 79.6     | 85.0 | n/a               |          |     |
| $\text{TiO}_2$          | -        |          |      | 0.3   | 70.5     | 75.0 | -                 |          |     |
| $\text{Al}_2\text{O}_3$ | 2.1      | 97.1     | 96.9 | 4.6   | 89.8     | 95.9 | n/a               |          |     |
| $\text{Fe}_2\text{O}_3$ | -        |          |      | 3.2   | 135      | 131  | 1.6               | 126      | 145 |
| MnO                     | -        |          |      | 0.4   | 115      | 123  | -                 |          |     |
| MgO                     | -        |          |      | 2.6   | 93.6     | 99.7 | -                 |          |     |
| CaO                     | 11.9     | n/a      | 99.8 | 62.9  | n/a      | 107  | 52.7              | n/a      | 115 |
| $\text{Na}_2\text{O}$   | 14.0     | 105      | 105  | n/a   |          |      | 0.8               | 94.4     | 109 |
| $\text{K}_2\text{O}$    | -        |          |      | 0.3   | 44.1     | 47.0 | n/a               |          |     |
| $\text{CO}_2$           | n/a      |          |      | n/a   |          |      | 41.4 <sup>b</sup> |          |     |
| TOTAL <sup>a</sup>      | 100      |          |      | 96.2  |          |      | 96.5              |          |     |

Table 4.1: Target values and recoveries (in %) by internal standardisation (IS) using  $^{43}\text{Ca}$  and total oxides (TO) data correction. Data below 0.2% are considered as trace elements and reported as such. <sup>a</sup>Total elemental oxide components as reported in certificates; <sup>b</sup>contains estimate of  $\text{CO}_2$  contribution based on CaO content.

Based on the results from Table 4.1, another agreement table is drawn (Table 4.2). The data are split in three categories, with recoveries considered as “good” (within +/- 20% of the target value), average (+/- 50%) and poor (>50%). For all major elements except Ca, the data obtained by internal standardisation are included, as it is the conventional data correction method used. In case of CaO, the total oxide data is used.

| Agreement | Good ( $\pm 20\%$ )                                                           | Average ( $\pm 20-50\%$ )                                               | Poor ( $>50\%$ )               |
|-----------|-------------------------------------------------------------------------------|-------------------------------------------------------------------------|--------------------------------|
| NIST 612  | SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> ,<br>CaO, Na <sub>2</sub> O |                                                                         |                                |
| OPC-1     | Al <sub>2</sub> O <sub>3</sub> , CaO,<br>MnO, MgO                             | Fe <sub>2</sub> O <sub>3</sub> ,<br>TiO <sub>2</sub> , SiO <sub>2</sub> | K <sub>2</sub> O               |
| MACS-3    | CaO, Na <sub>2</sub> O                                                        |                                                                         | Fe <sub>2</sub> O <sub>3</sub> |

Table 4.2: Summary of recoveries agreement for major components in three potential calibration materials. Recoveries agreement measured as percent bias from the target value.

Considering NIST 612 results, the table shows good agreement for all four major matrix components. This reflects the excellent matrix matching between the two NIST glasses. For OPC-1 and MACS-3, four out of eight and two out of three components respectively are in good agreement, while the remaining data show average to poor recoveries agreement. This may reflect the change in matrix, both in the chemistry and physical appearance (both are pressed pellets) compared to NIST 610 glass. Although the chemistry variations is dominated by the CaO content, this component does show good agreement for all three matrices using the TO correction. Similarly Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> results are in good agreement by IS, but Fe<sub>2</sub>O<sub>3</sub> is in both cases observed overestimated by about 30%. Tables 4.3 and 4.4 show the results for the trace elements for the same samples.

| Trace elements | NIST 612 | Recovery |      | OPC-1 | Recovery |     | MACS-3 | Recovery |     |
|----------------|----------|----------|------|-------|----------|-----|--------|----------|-----|
|                |          | IS       | TO   |       | IS       | TO  |        | IS       | TO  |
| Li             | 41.5     | 103      | 103  | 13.1  | 91       | 97  | 62.2   | 91       | 104 |
| B              | 34.7     | 146      | 146  | n/a   |          |     | n/a    |          |     |
| Mg             | 77.4     | 112      | 111  | -     |          |     | 1756   | 90       | 104 |
| K              | 66.3     | 487      | 492  | -     |          |     | n/a    |          |     |
| Ti             | 48.1     | 121      | 123  | -     |          |     | 54.9   | 87       | 102 |
| Cr             | 39.8     | 95.3     | 94.9 | n/a   |          |     | 117    | 158      | 182 |
| Mn             | 38.4     | 101      | 100  | -     |          |     | 536    | 100      | 115 |
| Fe             | 56.3     | 254      | 252  | -     |          |     | -      |          |     |
| Co             | 35.3     | 100      | 100  | 21.4  | 98       | 105 | 57.1   | 87       | 101 |
| Ni             | 38.4     | 129      | 130  | 87.0  | 86       | 92  | 57.4   | 112      | 129 |
| Cu             | 36.7     | 164      | 164  | 23.7  | 102      | 108 | 120    | 81       | 93  |
| Zn             | 37.9     | 179      | 179  | 27.8  | 130      | 136 | 111    | 80       | 92  |
| Sr             | 76.2     | 108      | 108  | 118   | 133      | 142 | 6760   | 110      | 127 |
| Ba             | 37.7     | 126      | 126  | 512   | 138      | 145 | 58.7   | 144      | 166 |
| La             | 35.8     | 111      | 111  | 25.9  | 109      | 116 | 10.4   | 103      | 119 |
| Ce             | 38.4     | 97       | 97   | 48.9  | 149      | 159 | 11.2   | 106      | 122 |
| Eu             | 34.4     | 110      | 110  | 1.00  | 135      | 144 | 11.8   | 90       | 103 |
| Pb             | 39.0     | 125      | 124  | 7.2   | 223      | 238 | 56.5   | 155      | 178 |
| Th             | 37.2     | 103      | 102  | 3.93  | 85       | 90  | 55.4   | 70       | 81  |
| U              | 37.2     | 101      | 101  | 0.83  | 95       | 101 | 1.52   | 102      | 117 |

Table 4.3: Comparison of recoveries agreement for 20 trace elements for three calibration candidates by internal standard (IS) and total oxide (TO) data correction. Target values are given for each material, with recoveries achieved expressed as percentage of the target. Elements present as major components in the matrix not included.

| Agreement | Good ( $\pm 20\%$ )                               | Average ( $\pm 20-50\%$ ) | Poor ( $> 50\%$ ) |
|-----------|---------------------------------------------------|---------------------------|-------------------|
| NIST 612  | Li, Mg, Cr, Mn, Co, Sr, La, Ce, Eu, Th, U         | B, Ti, Ni, Ba, Pb         | K, Fe, Cu, Zn     |
| OPC-1     | Li, Co, Ni, Cu, La, Th, U                         | Zn, Sr, Ba, Ce, Eu        | Pb                |
| MACS-3    | Li, Mg, Ti, Mn, Co, Ni, Cu, Zn, Sr, La, Ce, Eu, U | Ba, Th                    | Pb, Cr            |

Table 4.4: Summary of recoveries agreement for trace elements in three potential calibration materials. Recoveries agreement measured as percent bias from the target value.

Considering Table 4.4, this time the NIST 612 results show only about half of the trace elements are in good agreement with target values. The same is observed with OPC-1 sample, but here MACS-3 is showing relatively more elements in good agreement. In general, considering both major and trace elements recoveries, elements such as Li, Mg, Mn, Co, La and U all show good recoveries for all samples. For Cu, Zn and Ni, only NIST 612 shows rather average and poor recoveries whereas these elements are in line with target values for OPC-1 and MACS-3. Also the rare earth elements monitored and Th are generally in good accord, though Th in MACS-3 and Ce and Eu in OPC-1 show slight discrepancies. Possible explanations are for example that the low concentration of Eu in OPC-1 ( $1\mu\text{g.g}^{-1}$ ) is difficult to recover quantitatively and additionally both  $^{151}\text{Eu}$  and  $^{153}\text{Eu}$  can be affected by oxides of the different barium isotopes. Nevertheless, K, Fe, Ba and Pb are consistently showing average or poor recoveries, with all matrices. In the case of K, since it is adjacent to  $^{40}\text{Ar}$ , the large argon peak tails into its neighbouring masses, here affecting  $^{39}\text{K}$  by introducing a significant and variable background. For Fe, the additional presence of O allows for more  $^{40}\text{Ar}^{16}\text{O}$  and  $^{40}\text{Ar}^{16}\text{O}^1\text{H}$  to be formed and interfere with both  $^{56}\text{Fe}$  and  $^{57}\text{Fe}$ , introducing a significant interference. For Pb, the element is relatively more volatile than most others, and has shown to give mixed recoveries in general. Also for Cr in MACS-3, the overestimation observed can be linked to the fact that the matrix increases the amount of  $^{12}\text{C}$  and  $^{40}\text{Ca}$  which will combine to form ions measured at 52m/z in conjunction with the  $^{52}\text{Cr}$  present. Using  $^{53}\text{Cr}$  does not show improvement, as an additional  $^1\text{H}$  can combine with the polyatomic species.

## 2. Internal standardisation versus total oxide data correction

As highlighted earlier in chapter III, section 2.3, the usual approach to laser data correction, using an internal standard such as Ca, is only potentially successful for homogeneous matrices. Here the possibility of sample heterogeneity is assessed, and the alternative data correction using the total oxide component is tested.

“Thick” sections of concrete samples were prepared and investigated under scanning electron microprobe. The backscattered electron images obtained reflect the major chemistry homogeneity, which is present as variations in the shades of grey to bright white areas, representing the increase in the mean atomic mass. Figure 4.1 shows some examples of aggregates from sample SB1.

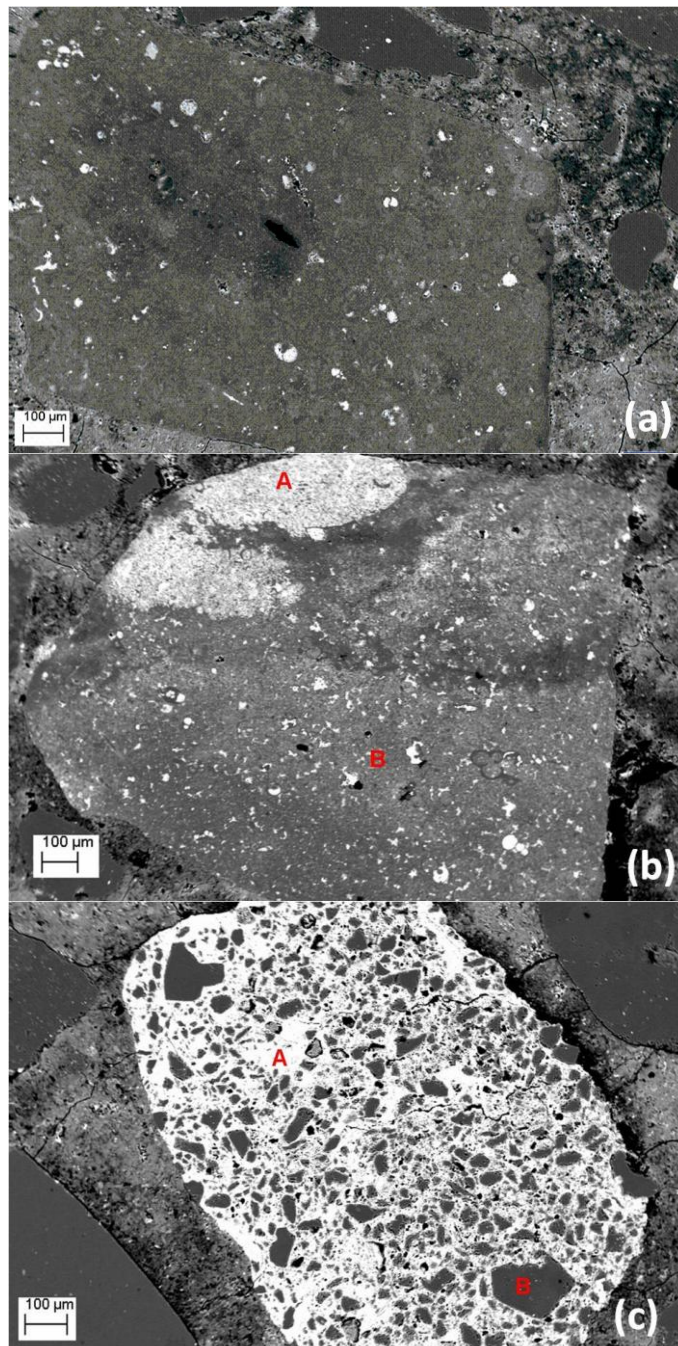


Figure 4.1: Backscattered images of three different aggregates from sample SB1. Bright spherical shapes, around 20 $\mu$ m or less in size, present especially in aggregates a and b were identified as tungsten carbide material originating from the polishing step involved during thick section preparation.

From Figure 4.1, it is possible to see that the major chemistry is likely to vary significantly from one area to another within the same aggregate. Example (a) reflects a good homogeneity throughout the aggregate, whereas (b) and (c) are made of a dominant matrix with variations in two different ways. Firstly in (b), the change occurs in a relative gradual

way from a lower average atomic mass (B) to a higher average (A) on the edge of the aggregate, whereas in (c) the variation happens as clear inclusions of a lower average (B) in a high average matrix (A). In all three cases, the areas of interest are characterised with the electron probe. Results are given in Table 4.5.

| Aggregate | Area  | SiO <sub>2</sub> | Fe oxides <sup>a</sup> | Al <sub>2</sub> O <sub>3</sub> | CaO | Others |
|-----------|-------|------------------|------------------------|--------------------------------|-----|--------|
| (a)       | Whole | 100              |                        |                                |     |        |
| (b)       | A     | 53.6             | 38.6                   | 3.5                            | 1.4 | 2.8    |
|           | B     | 93.8             | 6.2                    |                                |     |        |
| (c)       | A     | 7                | 83.6                   | 4                              | 3   | 0.4    |
|           | B     | 100              |                        |                                |     |        |

Table 4.5: Major chemistry for some aggregates encountered in sample SB1. <sup>a</sup> the electron probe does not have the capability to differentiate between the possible forms of iron oxides (FeO, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) and the results are reported as iron bearing oxides.

As suggested by the backscattered images, the chemistry within some aggregates does vary significantly. Therefore the use of an internal standard is likely to produce significantly biased sets of data. If on the contrary the total amount of major elements oxides is monitored, the correction can be applied and adapted to the variation observed. To test the method, NIST 610 glass was used as a one point calibration for the analysis of NIST 612, OPC-1 and MACS-3. Major and trace elements were determined by both the internal standardisation method and the total oxide correction. Recoveries achieved by the two methods for the major and trace elements reported for each standard in Tables 4.1 and 4.3 with values between 50 and 200% recovery are plotted in Figure 4.2.

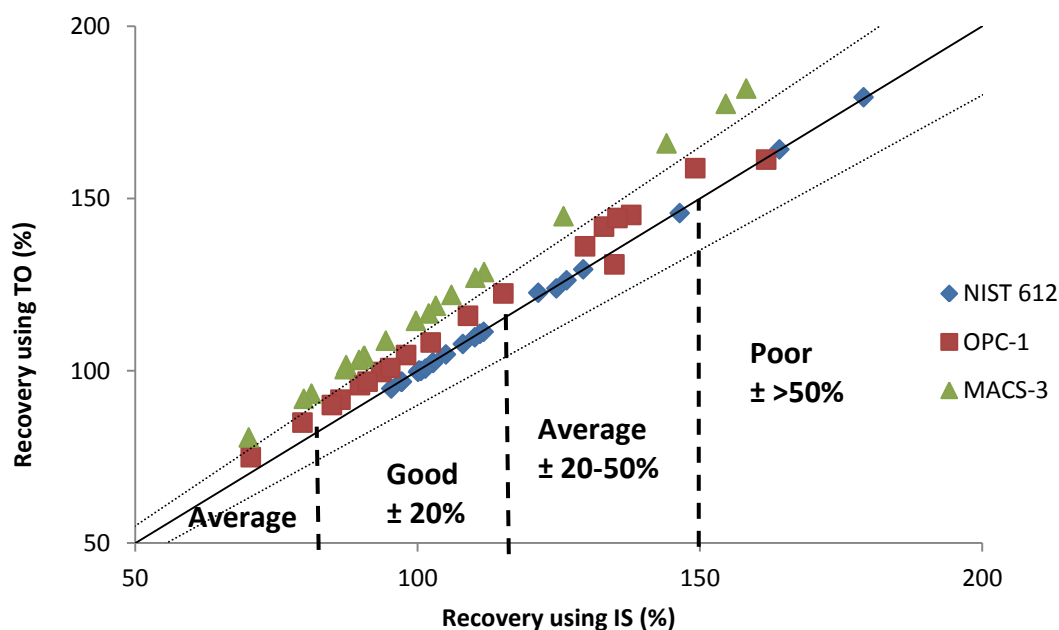


Figure 4.2: Recoveries obtained using internal standardisation (IS) and total oxide (TO) correction for a selection of major and trace elements for NIST 612, OPC-1 and MACS-3 using one point calibration by NIST 610. Solid line represents identical recoveries by both methods. Grey lines represent  $\pm 10\%$  bias from 100% recovery. Also represented are the three agreement groups: good ( $\pm 20\%$ ), average ( $\pm 20-50\%$ ) and poor ( $\pm >50\%$ ).

First observation regarding NIST 612 is that the recoveries obtained by IS and TO corrections are in good agreement with each other. Secondly, in general the recoveries range from close to 100%, with a significant number above the 125% mark without affecting the agreements, highlighting that the accuracy between target and measured value are only dependant on the instrumental response of the LA-ICP-MS system and not the correction method.

For OPC-1 and MACS-3, the recoveries show a bias towards higher TO recoveries compared to the IS method, with  $<10\%$  for OPC-1 and slightly above 10% for MACS-3 added difference. One explanation is the fact that based on the data given in Table 4.1 the major components for OPC-1 and MACS-3 add up to 96.2 and 96.5% respectively, introducing a relative positive bias of approximately  $+3-4\%$  in the accuracy results by TO. This is not the case for NIST 612, as the oxides components total 100%. Correcting for the small difference in total oxides values is likely to shift most values for OPC-1 close to the agreement line with the IS results (solid line), and also MACS-3 values within 10% of the same line.

Overall, in the case of a standard and a sample matrix-matched in chemical and physical form, such as NIST 610 and 612, the recoveries calculated using the accepted method of

internal standardisation and alternative total oxides correction are in good agreement. For samples with a different chemical and physical matrix, such as OPC-1 and MACS-3 which are both pressed pellets and have dominant CaO component, the two methods agree within about 10% from each other. As to which is most accurate, this is difficult to assess as the range of recoveries is well beyond the 100 +/-20% for a range of elements. Nevertheless, the use of total oxide correction for changing chemistry from potentially one component of concrete to another, or even variations within the same component, is appropriate to correct to some extent the laser data and can be considered as a semi-quantitative technique for analysing concrete-type samples.

### 3. Cement and sand matrix characterisation

#### 3.1 OPC-1 characterisation using standard addition method

The standard addition method is used to measure a selection of trace elements in OPC-1 standard. A set of four pellets are used, with one unspiked and three with increasing concentration of each element. The spike consists in adding a single volume of stock solution made from single element solutions. The increases in spiked concentration correspond to approximately 2x, 4x and 6x the original concentration in the unspiked material. Figure 4.3 shows the corresponding graphs for the standard addition and Table 4.6 shows the elemental addition performed and results. The elements chosen are important activation precursors and a couple of elements present in concrete components (Sr and Pb).

| Element                   | Li    | Co    | Ni    | Sr    | Ba    | Eu    | Pb    | U     |
|---------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Unspiked pellet           | 13.1  | 21.4  | 87.0  | 118   | 512   | 1.00  | 7.20  | 0.83  |
| Pellet 1 (x2)             | 25.9  | 43.0  | 175   | 238   | 1024  | 2.60  | 14.4  | 1.63  |
| Pellet 2 (x4)             | 52.3  | 85.4  | 351   | 470   | 2048  | 4.20  | 28.8  | 3.23  |
| Pellet 3 (x6)             | 78.7  | 129   | 519   | 710   | 3072  | 5.80  | 43.2  | 4.83  |
| Correlation factor, $r^2$ | 0.986 | 0.992 | 0.970 | 0.989 | 0.933 | 0.993 | 0.995 | 0.996 |
| Concentration using SA    | 2.9   | 15.1  | 68.6  | 113   | 399   | 0.62  | 5.75  | 0.41  |
| Bias (%)                  | -78   | -29   | -21   | -4    | -22   | -38   | -20   | -50   |

Table 4.6: Standard addition method for OPC-1 material. Initial concentration and successive elemental addition in  $\mu\text{g.g}^{-1}$  and designed to correspond to approximately x2, x4 and x6 the target value.

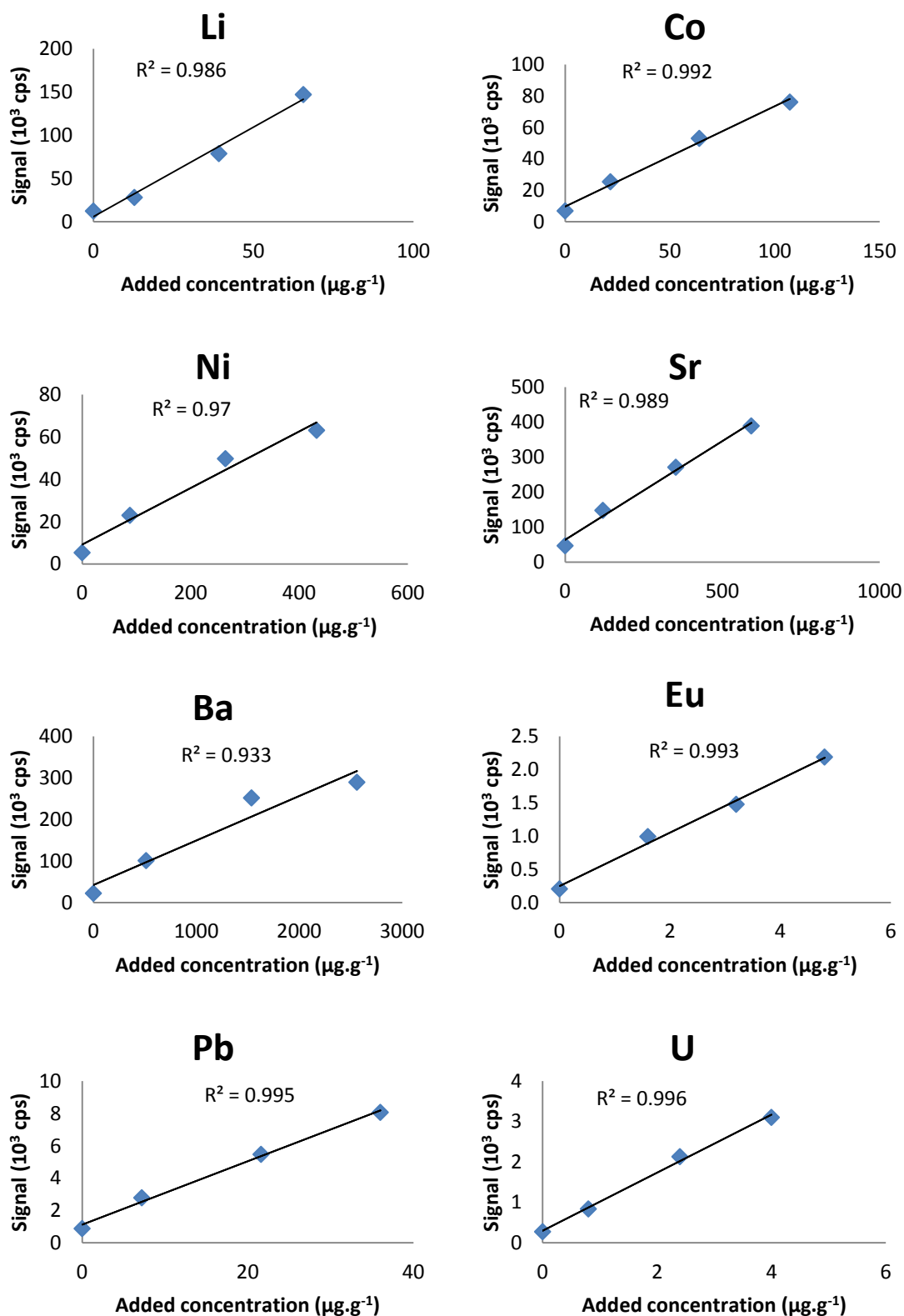


Figure 4.3: Standard addition graphs for elements of interest. Graphs represent the added concentration of a specific element to the natural content of the sample against the signal measured.

Results show excellent correlation factors for all elements ( $>0.93$ ) and linearity between the unspiked and spiked pellets. Nevertheless, a consistent negative bias is observed against target values, reflecting the possibility that elements present naturally in the material (blank) and the added elements are released differently during analysis. The elements spiked in are likely to be coated on the outer surface of each material grain, whereas the original elements are contained in the mineral lattice. A similar observation was made on  $\text{Ca}_3(\text{PO}_4)_2$  reference materials using the same SA approach (Disch, 2008). From the elements of interest, only Sr shows good accuracy, and therefore the set of unspiked and spiked pellets under investigation here are not suitable to form a suitable calibration line. A single point calibration using the unspiked material is preferable.

### 3.2 OPC-1 as external calibration standard

Here the measurement of major and trace elements in the cement/sand mixture of a sample from Windscale Pile one (WP1) is assessed using an OPC-1 pressed pellet as external calibration standard. Each laser ablation scan consists of 10 consecutive replicate analyses. The data collected are corrected using total oxide components and compared to reference data. The reference data are obtained by analysing four subsamples of cement/sand mixture by acid digests and lithium metaborate fusion followed by liquid ICP-MS and ICP-AES measurements. OPC-1 sample and another reference material from USGS, namely a granite (G-2) were prepared by both digestion methods and the accuracy of the results compared. For a selection of elements, the results given by both methods are in good agreement. Sample digestion results were used as target values and laser data are compared to these. Table 4.7 shows the results obtained for four laser scans.

Results show variable agreement between target values and laser data. For major components and trace elements showing good agreement, most often the data have relatively poor precision but the average is in line with the target value. This is applicable to  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , Li, Eu and Th. A different set of elements show significant bias overall but with some replicate data close to the target value. Two causes are identified, and are firstly the low elemental concentration to be measured, therefore relatively small variation affects the bias significantly, and the possibility of spatial variability at the ablation scale. The potential use of blast furnace residue, which is enriched in metals, within the cement and sand mixture has the potential to form hot spots and affect results by introducing relatively large variations. These elements are Co, Ni, U.

| Major component |   | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO        | MgO         | CaO         | Na <sub>2</sub> O <sup>a</sup> | K <sub>2</sub> O |
|-----------------|---|------------------|------------------|--------------------------------|--------------------------------|------------|-------------|-------------|--------------------------------|------------------|
| Target          |   | 62.9             | 0.20             | 5.21                           | 1.69                           | 0.04       | 1.13        | 14.5        | 0.73                           | 1.34             |
|                 | 1 | 46.9             | 0.29             | 5.54                           | 1.94                           | 0.07       | 2.18        | 41.2        | 0.64                           | 1.05             |
| LA data         | 2 | 52.0             | 0.17             | 5.28                           | 2.27                           | 0.10       | 1.65        | 35.7        | 1.31                           | 1.48             |
| scan            | 3 | 42.5             | 0.18             | 6.80                           | 2.38                           | 0.07       | 2.11        | 41.7        | 1.49                           | 2.52             |
|                 | 4 | 50.2             | 0.14             | 4.10                           | 2.11                           | 0.09       | 1.39        | 39.8        | 0.41                           | 0.81             |
| Average         |   | 47.9             | 0.2              | 5.4                            | 2.18                           | 0.08       | 1.8         | 39.6        | 0.96                           | 1.47             |
| Bias            |   | -24              | -3               | 4                              | 28                             | 100        | 62          | 173         | 33                             | 9                |
| Trace element   |   | Li               | Co               | Ni                             | Sr                             | Ba         | La          | Eu          | Th                             | U                |
| <b>Target</b>   |   | <b>23.8</b>      | <b>5.14</b>      | <b>20.4</b>                    | <b>742</b>                     | <b>288</b> | <b>13.3</b> | <b>0.52</b> | <b>3.63</b>                    | <b>1.41</b>      |
|                 | 1 | 31.6             | 7.16             | 27.8                           | 1558                           | 201        | 14.3        | 0.63        | 3.83                           | 1.88             |
| LA data         | 2 | 22.6             | 6.43             | 21.2                           | 1282                           | 169        | 12.7        | 0.67        | 5.73                           | 2.56             |
| scan            | 3 | 33.3             | 7.74             | 27.4                           | 1558                           | 164        | 11.3        | 0.35        | 3.77                           | 2.24             |
|                 | 4 | 21.0             | 5.59             | 20.2                           | 1155                           | 130        | 10.4        | 0.36        | 2.48                           | 2.51             |
| Average         |   | 27.1             | 6.73             | 24.2                           | 1388                           | 166        | 12.2        | 0.50        | 3.95                           | 2.30             |
| Bias            |   | 14               | 31               | 18                             | 87                             | -42        | -9          | -2          | 9                              | 63               |

Table 4.7: Major and trace elements in cement and sand matrix. <sup>a</sup> Na<sub>2</sub>O contribution estimated with NIST 610 signal.

Finally SiO<sub>2</sub>, MnO, CaO, Sr and Ba show significant bias from the target values and are present at relatively high concentration, therefore showing a discrepancy in the results. SiO<sub>2</sub> and Ba are measured with a negative bias and both CaO and Sr with a positive bias using the laser. This could mean that the laser analysis sampled relatively more cement than sand compared to the bulk chemistry, although the remaining chemistry does not reflect similar biases. As per the definition for fine aggregates such as sand, the particle size can range from 0.75 up to 4.75mm. At this level, the particle size is likely to dictate the chemistry during an analysis covering a relatively small area of the sample.

#### 4. Calcium carbonates characterisation

##### 4.1 Synthetic calibration

Here a set of synthetic calcium carbonate calibration standards are prepared and analysed. A calcium carbonate powder (99.995% purity, Sigma-Aldrich) with particle size <50µm was mixed with stock solutions containing increasing amounts of a range of trace elements, dried and pressed into pellets. The signal given by an unspiked sample was used as a blank and

subsequently deducted from the spiked samples results. The range of concentrations used for each element was based on the typical concentration expected in the concrete limestone aggregates and previously determined by wet chemistry. Examples of calibration lines are given in Figure 4.4 for elements showing correlation factors above 0.9.

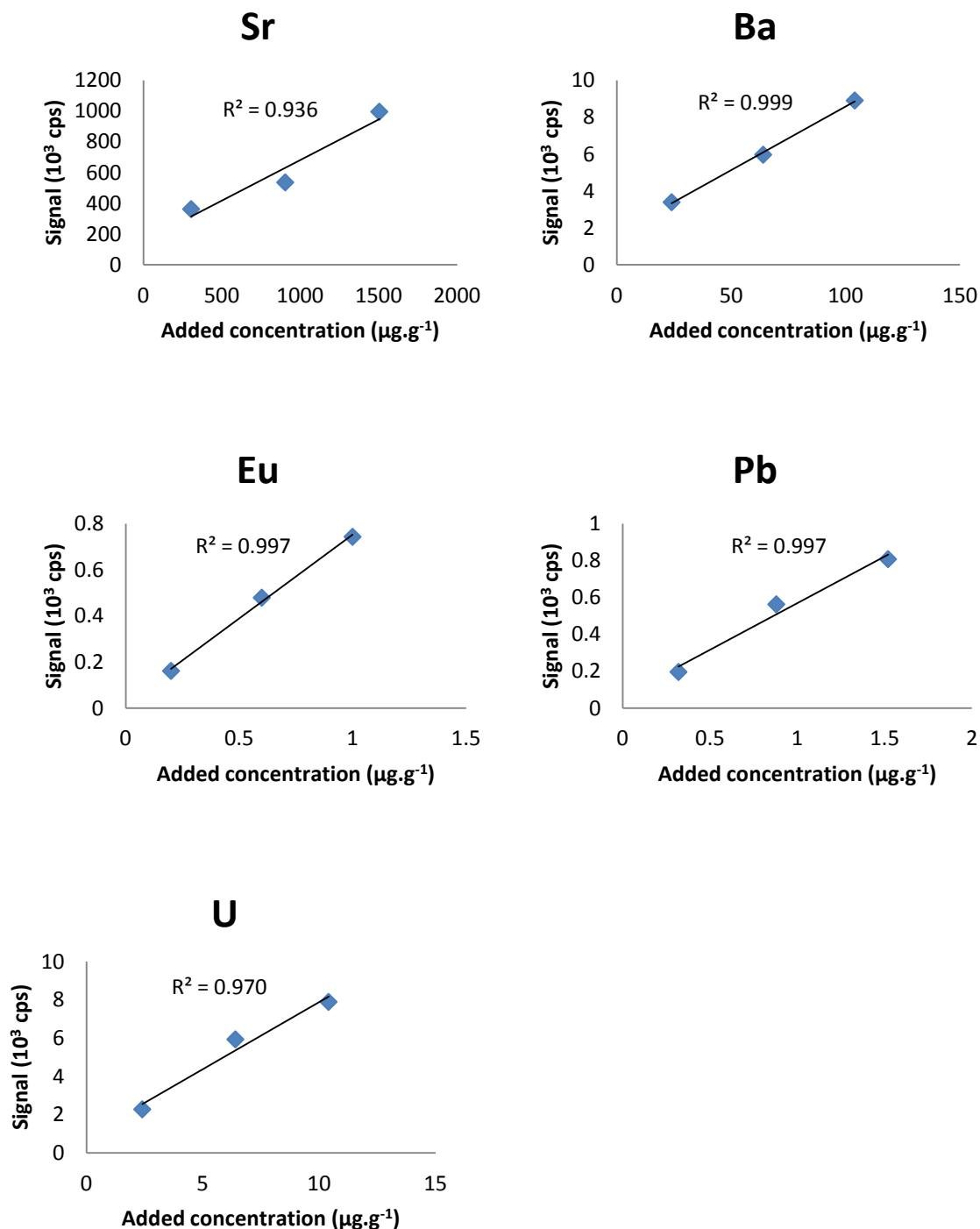


Figure 4.4: Calibration lines for a selection of elements of interest spiked in  $\text{CaCO}_3$  pressed powder pellets. The unspiked material is used as a blank sample and the corresponding signal is deducted from the spiked samples' signals.

Considering the graphs, theoretically the calibration line is a straight line passing through the origin. Although this is the case for Eu, Pb and U, there is an offset observed for Sr and Ba. To test the calibration lines, MACS-3, a microanalytical carbonate standard, is here used as an unknown. Table 4.8 shows the concentration range used and results obtained.

| Element                   | Li    | Co    | Ni    | Sr    | Ba    | Eu    | Pb    | U     |
|---------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Pellet 1                  | 0.10  | 0.64  | 0.32  | 304   | 24    | 0.2   | 0.32  | 2.4   |
| Pellet 2                  | 0.40  | 1.84  | 0.88  | 904   | 64    | 0.6   | 0.88  | 6.4   |
| Pellet 3                  | 0.80  | 3.04  | 1.52  | 1504  | 104   | 1     | 1.52  | 10.4  |
| Correlation factor, $r^2$ | 0.922 | 0.708 | <0.1  | 0.936 | 0.999 | 0.997 | 0.997 | 0.970 |
| MACS-3 targets            | 62.20 | 57.10 | 57.40 | 6760  | 59    | 11.8  | 56.50 | 1.5   |
| Recovery (%)              | n/a   | n/a   | n/a   | 175   | 194   | 63    | n/a   | 81    |

Table 4.8: Synthetic calcium carbonates standards concentrations ( $\mu\text{g.g}^{-1}$ ), correlation and recoveries of MACS-3 sample.

Correlation factors are better than 0.92 apart from Co and Ni. For Li, the results are actually negative after blank signal subtraction. It can be argued that higher concentration ranges for Li, Co and Ni potentially can improve dramatically the correlation, offering better signal to background data. Nevertheless, a good correlation is observed for Eu, Pb and to some extend U for relatively low concentrations. Concerning recovery values for MACS-3 using these calibration lines, the results show all elements except U with relatively large variations with around +/- 50% or more bias, even for elements such as Ba and U where both the correlation factors and range of concentrations covered are appropriate for a quantitative determination in MACS-3. Overall the use of spiked synthetic  $\text{CaCO}_3$  calibration standards shows variable correlation factors depending on the element of interest and overall poor accuracy, therefore not likely to be useful for quantification purposes. A possible cause is that the calcium carbonate powder is reacting with the weak acid present in the spike solution and incorporates the spiked in elements heterogeneously. Similar to the production of OPC-1, a co-precipitation potentially offers an alternative approach for standards preparation.

#### 4.2 MACS-3 as external calibration standard

In this experiment MACS-3 is used as a one point calibration for the determination of major and trace elements in limestone aggregates. The aggregates investigated are from sample

WP1. To this effect, a section of the sample core was disaggregated and the relevant large limestone aggregates were isolated and cleaned by removing any potential remaining sand and cement mix. A selection of 16 aggregates were dissolved and analysed by liquid ICP-MS and ICP-AES to provide typical elemental target values. This time the dissolution was performed by nitric acid digest only, therefore any SiO<sub>2</sub> based minerals are not digested. Laser data were collected as five set of 10 consecutive replicate analyses on four different limestone aggregates, with one aggregate analysed twice. Results can be found in Table 4.9 for major components and Table 4.10 for a selection of trace elements. Again a reference material, here a limestone (JLS-1), is used to assess the accuracy of dissolution techniques. Also, the total amount of oxides, including the contribution from CO<sub>2</sub>, reached only around 86% by dissolution method, the laser data was corrected to account for this.

| Major component            | MgO         | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | CaO         | Fe <sub>2</sub> O <sub>3</sub> |
|----------------------------|-------------|--------------------------------|------------------|-------------|--------------------------------|
| Target value (%)           | 0.18        | 0.02                           | n/a              | 47.9        | 0.09                           |
| 1A                         | 0.19        | 0.84                           | 1.06             | 46.8        | 0.17                           |
| 1B                         | 0.18        | 1.21                           | 1.46             | 46.4        | 0.22                           |
| LA data scans <sup>a</sup> |             |                                |                  |             |                                |
| 2                          | 0.11        | 0.84                           | 0.75             | 46.9        | 0.37                           |
| 3                          | 0.15        | 0.43                           | 1.15             | 47.0        | 0.12                           |
| 4                          | 0.19        | 0.61                           | 1.64             | 46.6        | 0.17                           |
| <b>Average LA data (%)</b> | <b>0.16</b> | <b>0.79</b>                    | <b>1.21</b>      | <b>46.7</b> | <b>0.21</b>                    |
| <i>Bias</i>                | -9          | 4006                           | n/a              | -2          | 130                            |

Table 4.9: Major components in calcium carbonate aggregates from sample WP1. <sup>a</sup> laser data corrected for 87% total oxides.

From the results, two major components agree well with target values, namely CaO and MgO. On the contrary, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are both overestimated by the laser data. Nevertheless these two target concentrations are relatively low in the aggregates, and slight variations can affect the accuracy greatly. One thing to keep in mind is the possibility that undigested material, containing minerals resistant to nitric acid digest such as the SiO<sub>2</sub> component, also accounts for the difference in Al and Fe. Furthermore, considering both Al and Fe laser data, the presence of significant amounts of <sup>12</sup>C, <sup>16</sup>O and <sup>40</sup>Ca from the sample matrix may affect the low concentrations expected. Interfering polyatomic species of <sup>12</sup>C<sup>14</sup>N<sup>1</sup>H, <sup>12</sup>C<sup>15</sup>N or <sup>13</sup>C<sup>14</sup>N on <sup>27</sup>Al and <sup>40</sup>Ca<sup>16</sup>O and <sup>40</sup>Ca<sup>16</sup>O<sup>1</sup>H on <sup>56</sup>Fe and <sup>57</sup>Fe respectively can contribute to the higher concentrations given with the laser. This effect was not observed

with OPC-1, as the expected concentrations of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are higher by at least one order of magnitude.

| Trace element                       |    | Li              | Co                | Ni                 | Sr     | Ba    |
|-------------------------------------|----|-----------------|-------------------|--------------------|--------|-------|
| Target value                        |    | <1 <sup>a</sup> | 1.04 <sup>a</sup> | 3.22 <sup>a</sup>  | 649    | 10.95 |
| LA data scans                       | 1A | 0.76            | 0.51              | 2.37               | 385    | 6.64  |
|                                     | 1B | 0.82            | 0.60              | 2.85               | 399    | 5.73  |
|                                     | 2  | 0.44            | 0.98              | 5.87               | 229    | 16.71 |
|                                     | 3  | 0.63            | 0.28              | 1.11               | 452    | 4.24  |
|                                     | 4  | 1.67            | 0.73              | 2.83               | 530    | 4.58  |
| Range of RSDs for 10 replicates (%) |    | 17-84           | 12-100            | 32-72              | 6-19   | 9-98  |
| Average LA data                     |    | 0.87            | 0.62              | 3.01               | 399    | 7.58  |
| RSD (%)                             |    | 55              | 42                | 58                 | 28     | 68    |
| Bias                                |    | n/a             | -41               | -7                 | -38    | -31   |
| Trace element                       |    | La              | Ce                | Eu                 | Th     | U     |
| Target value                        |    | 4.96            | 6.08              | <0.25 <sup>a</sup> | 0.29   | 2.05  |
| LA data scans                       | 1A | 2.29            | 2.27              | 0.11               | 0.15   | 1.00  |
|                                     | 1B | 2.31            | 2.36              | 0.11               | 0.18   | 1.00  |
|                                     | 2  | 0.87            | 0.87              | 0.05               | 0.02   | 0.60  |
|                                     | 3  | 2.46            | 2.46              | 0.11               | 0.09   | 1.60  |
|                                     | 4  | 5.93            | 5.39              | 0.30               | 0.35   | 1.38  |
| Range of RSDs for 10 replicates (%) |    | 9-53            | 12-44             | 16-50              | 20-120 | 13-44 |
| Average LA data                     |    | 2.77            | 2.67              | 0.14               | 0.16   | 1.12  |
| RSD (%)                             |    | 68              | 62                | 69                 | 78     | 35    |
| Bias                                |    | -44             | -56               | n/a                | -46    | -46   |

Table 4.10: Selection of trace elements in calcium carbonate aggregates from sample WP1. <sup>a</sup> laser data corrected for 87% total oxides.

The five replicate LA analyses show significant variations for each of the elements monitored and especially replicate number two shows significantly different concentrations, with higher Co, Ni and Ba, but lower values for all other elements. One particularity is also that overall, there is a negative bias in the laser data compared to the target (wet) data. This can be a reflection of a possible different surface chemistry compared to the whole aggregate.

## 5. Silicate-based aggregates characterisation

In this experiment NIST 610 is used as a one point calibration for the determination of major and trace elements in aggregates found in sample SB1. Eight aggregates with different

optical and geometry features were selected. Again as with the limestone aggregates, the sample SB1 is broken apart and the relevant aggregates isolated cleaned from potential cement and sand mix. Each aggregate then undergoes laser analysis, with 10 consecutive replicates, before digestion by HF/HClO<sub>4</sub> to generate target values. Table 4.11 shows the results for these aggregates.

| Major elements |   | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO           | MgO           | CaO           | Na <sub>2</sub> O | K <sub>2</sub> O |               |
|----------------|---|------------------|------------------|--------------------------------|--------------------------------|---------------|---------------|---------------|-------------------|------------------|---------------|
| Aggregates     | 1 | Target           | n/a              | 0.10                           | 1.4                            | 73.9          | 0.25          | 0.3           | 1.1               | 0.19             | 0.21          |
|                |   | LA data          | 11.2<br>±4.8     | 0.27<br>±0.04                  | 2.6<br>±0.3                    | 68.6<br>±8.6  | 0.39<br>±0.03 | 0.7<br>±0.1   | 21.2<br>±4.8      | 0.15<br>±0.04    | 0.26<br>±0.06 |
|                |   | Recovery         | n/a              | 265                            | 189                            | 93            | 158           | 224           | 1956              | 81               | 128           |
|                | 2 | Target           | n/a              | 0.01                           | <LLD                           | <LLD          | <LLD          | <LLD          | 0.8               | 0.46             | 0.25          |
|                |   | LA data          | 89.8<br>±4.4     | 0.04<br>±0.02                  | 0.5<br>±0.3                    | 0.3<br>±0.2   | 0.01<br>±0.01 | 0.1<br>±0.1   | 8.9<br>±3.9       | 0.09<br>±0.02    | 0.06<br>±0.01 |
|                |   | Recovery         | n/a              | 328                            | n/a                            | n/a           | n/a           | n/a           | 1121              | 21               | 25            |
|                | 3 | Target           | n/a              | <LLD                           | <LLD                           | <LLD          | <LLD          | <LLD          | <LLD              | <LLD             | <LLD          |
|                |   | LA data          | 98.3<br>±1.4     | 0.02<br>±0.02                  | 0.12<br>±0.1                   | 0.35<br>±0.57 | 0.02<br>±0.03 | 0.03<br>±0.02 | 1.3<br>±1.0       | 0.04<br>±0.01    | 0.05<br>±0.05 |
|                |   | Recovery         | n/a              | n/a                            | n/a                            | n/a           | n/a           | n/a           | n/a               | n/a              | n/a           |
|                | 4 | Target           | n/a              | <LLD                           | <LLD                           | <LLD          | <LLD          | <LLD          | 0.5               | 0.16             | 0.09          |
|                |   | LA data          | 85.8<br>±5.0     | 0.03<br>±0.01                  | 0.5<br>±0.2                    | 0.7<br>±0.2   | 0.01<br>±0.01 | 0.2<br>±0.1   | 12.5<br>±4.6      | 0.07<br>±0.01    | 0.07<br>±0.02 |
|                |   | Recovery         | n/a              | n/a                            | n/a                            | n/a           | n/a           | n/a           | 2769              | 47               | 78            |
|                | 5 | Target           | n/a              | 0.03                           | <LLD                           | <LLD          | <LLD          | <LLD          | 4.7               | 0.19             | 0.14          |
|                |   | LA data          | 96.1<br>±0.9     | 0.07<br>±0.02                  | 0.7<br>±0.3                    | 0.4<br>±0.2   | 0.01<br>±0.01 | 0.10<br>±0.04 | 2.0<br>±0.6       | 0.29<br>±0.27    | 0.15<br>±0.06 |
|                |   | Recovery         | n/a              | 230                            | n/a                            | n/a           | n/a           | n/a           | 42                | 153              | 106           |
|                | 6 | Target           | n/a              | <LLD                           | <LLD                           | <LLD          | <LLD          | <LLD          | 0.7               | <LLD             | 0.06          |
|                |   | LA data          | 92.8<br>±1.3     | 0.03<br>±0.01                  | 0.5<br>±0.1                    | 1.0<br>±0.4   | 0.01<br>±0.01 | 0.10<br>±0.03 | 5.3<br>±1.3       | 0.05<br>±0.01    | 0.08<br>±0.02 |
|                |   | Recovery         | n/a              | n/a                            | n/a                            | n/a           | n/a           | n/a           | 796               | n/a              | 124           |
|                | 7 | Target           | n/a              | 0.06                           | 1.5                            | 24.6          | 0.02          | <LLD          | 1.3               | 0.27             | 0.14          |
|                |   | LA data          | 63.5<br>±4.8     | 0.07<br>±0.04                  | 3.9<br>±1.0                    | 31.2<br>±5.6  | 0.03<br>±0.01 | 0.11<br>±0.02 | 1.8<br>±0.6       | 0.44<br>±0.06    | 0.13<br>±0.03 |
|                |   | Recovery         | n/a              | 125                            | 259                            | 127           | 160           | n/a           | 135               | 162              | 97            |
|                | 8 | Target           | n/a              | 0.06                           | 1.7                            | 19.0          | 0.04          | <LLD          | 4.6               | <LLD             | 0.07          |
|                |   | LA data          | 64.9<br>±4.4     | 0.17<br>±0.04                  | 3.1<br>±0.5                    | 16.6<br>±3.1  | 0.06<br>±0.01 | 0.24<br>±0.03 | 14.2<br>±2.3      | 0.15<br>±0.12    | 0.15<br>±0.02 |
|                |   | Recovery         | n/a              | 272                            | 187                            | 87            | 159           | n/a           | 312               | n/a              | 214           |

Table 4.11: Major components relative recoveries for aggregates in sample SB1 using NIST 610 and total oxide correction. Target and laser data in % oxides concentration, relative recoveries given in percentage from target value.

Based on the major chemistry, the chosen aggregates cover a range of composition, from nearly pure SiO<sub>2</sub> (based on LA data) to increasing component of Fe<sub>2</sub>O<sub>3</sub>. Also aggregates with predominant SiO<sub>2</sub> have relatively few other elements above detection limit. When reference data are available, the recoveries vary significantly for the same element, for example Al<sub>2</sub>O<sub>3</sub>, MnO and K<sub>2</sub>O. Nevertheless for Fe<sub>2</sub>O<sub>3</sub> and CaO, both with relatively higher concentrations present, the recoveries are quite different. Iron oxide shows in general a good to average agreement, whereas CaO is overestimated by the laser data by a large margin in most cases. It is thought that the possibility of the laser data, covering only a relatively small area on the surface of the aggregate, does not reflect the overall chemistry quantified by digestion. The higher measurements of CaO on the surface can easily be a response to remaining cement material present.

| Trace elements |   |          | Li   | Co    | Ni     | Sr       | Ba      | La       | Eu        | Th         | U         |
|----------------|---|----------|------|-------|--------|----------|---------|----------|-----------|------------|-----------|
| Aggregates     | 1 | Target   | 16   | 33    | 144    | 249      | 53      | 32       | 1.4       | 1.6        | 1.2       |
|                |   | LA data  | 28±4 | 29±2  | 145±35 | 1992±455 | 117±17  | 43±8     | 2.7±0.4   | 7.3±1.0    | 1.7±1.9   |
|                |   | Recovery | 174  | 89    | 101    | 800      | 219     | 133      | 201       | 448        | 136       |
|                | 2 | Target   | n/a  | <LLD  | <LLD   | 8        | 46      | 1        | 0.07      | 0.33       | 0.09      |
|                |   | LA data  | 19±3 | 18±12 | 41±18  | 176±103  | 35±17   | 3±2      | 0.22±0.23 | 0.46±0.20  | 0.38±0.12 |
|                |   | Recovery | n/a  | n/a   | n/a    | 2180     | 77      | 240      | 300       | 139        | 406       |
|                | 3 | Target   | n/a  | 0.03  | 0.07   | 1        | 2       | 0.18     | 0.002     | 0.004      | <LLD      |
|                |   | LA data  | 25±5 | 2±2   | 18±14  | 22±15    | 27±29   | 4.94±6.3 | 0.17±0.08 | 0.235±0.18 | 0.15±0.09 |
|                |   | Recovery | n/a  | 6254  | 26768  | 2992     | 1378    | 2689     | 7761      | 5506       | n/a       |
|                | 4 | Target   | 6    | 0.3   | 1      | 22       | 3       | 4        | 0.21      | 0.06       | 0.19      |
|                |   | LA data  | 23±2 | 21±17 | 42±19  | 282±71   | 43±13   | 10±5     | 0.54±0.27 | 0.53±0.15  | 0.42±0.05 |
|                |   | Recovery | 367  | 8359  | 4402   | 1258     | 1484    | 282      | 265       | 895        | 224       |
|                | 5 | Target   | 7    | 0.6   | 3.5    | 975      | 45      | 2.4      | 0.06      | 0.57       | 0.25      |
|                |   | LA data  | 27±3 | 5.5±6 | 44±22  | 168±46   | 46±29   | 2.7±1.3  | 0.08±0.03 | 0.43±0.20  | 0.34±0.15 |
|                |   | Recovery | 367  | 904   | 1264   | 17       | 102     | 115      | 124       | 75         | 139       |
|                | 6 | Target   | 1    | 1     | 2      | 58       | 619     | 2        | 0.17      | 0.35       | 0.38      |
|                |   | LA data  | 21±4 | 26±37 | 23±5   | 142±23   | 400±121 | 11±10    | 0.43±0.38 | 0.68±0.19  | 0.42±0.11 |
|                |   | Recovery | 1782 | 3566  | 1311   | 243      | 65      | 583      | 261       | 193        | 110       |
|                | 7 | Target   | 24   | 26    | 48     | 126      | 255     | 31       | 1.9       | 5.9        | 0.8       |
|                |   | LA data  | 53±8 | 41±9  | 84±21  | 197±43   | 237±38  | 56±19    | 3.1±0.7   | 6.6±1.9    | 1.2±0.2   |
|                |   | Recovery | 224  | 160   | 174    | 156      | 93      | 181      | 165       | 111        | 165       |
|                | 8 | Target   | 18   | 23    | 127    | 715      | 68      | 19       | 2.1       | 10         | 0.6       |
|                |   | LA data  | 49±6 | 29±4  | 132±34 | 1585±217 | 174±29  | 37±6     | 3.6±0.5   | 18±2       | 1.2±0.2   |
|                |   | Recovery | 271  | 124   | 103    | 222      | 257     | 192      | 166       | 174        | 184       |

Table 4.12: Trace elements recoveries for aggregates in sample SB1 using NIST 610 and total oxide correction. Laser data given with error of 1SD (±SD).

Results for trace elements (Table 4.12) show a large variation in the recoveries. In cases the target concentration is very low and for aggregates containing predominantly  $\text{SiO}_2$ , namely aggregate 3, 5 and 6, in general the laser data overestimate significantly the target value. The assumption here is that there is a surface chemistry difference compared to the whole aggregate chemistry. For aggregates containing relatively more  $\text{Fe}_2\text{O}_3$  (aggregates 1, 7 and 8), and with higher target values for most elements, their recoveries reach more homogeneous values, up to about 2-3 times the target values. The general comment is that it is difficult to obtain accurate data for the aggregates in sample SB1, and that it is likely the laser analysis on the surface of the aggregate reflects a different chemistry than the whole aggregate. The relatively small analysis track is affected by the likely particle size present in the aggregate and reflects the associated chemistry. For example, the proportions of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  mainly dictate the likely presence of relatively low or higher concentration of trace elements.

## 6. Conclusions

Concerning the laser data correction, using the total oxide correction approach is effective at correcting for differential ablation rates of the laser for the three matrices investigated, namely silicate-rich glass, carbonates and cement. The agreement between conventional IS and TO correction results are very good, and possible bias observed reflect instrumental response only. Also, the monitoring of the total oxide components needs careful attention, as non-measurable compounds such as  $\text{H}_2\text{O}$  or  $\text{CO}_2$  need to be accounted for in the normalisation.

The possibility to construct a calibration line for each of these matrices to generate quantitative data has proven difficult. The standard addition approach applied to cement matrix showed very good linear relationship, but failed to accurately measure the natural elemental concentration in the unspiked cement. For carbonate samples, the spiking of elements at increasing concentrations into pure calcium carbonates had mixed success, with elements showing good and mediocre correlation factors, possibly from heterogeneous distribution of the spiked-in elements.

Regarding the use of the certified materials for each matrix, namely NIST 610, OPC-1 and MACS-3, for quantification purposes of actual samples, results showed very significant variations in recoveries between target values and laser data. The variations can have several origins, and include the following examples. Many of the target values are very low concentrations, and small variations will have a significant impact on the results. The laser beam takes a sample at the surface of the aggregates investigated, representing a very

small portion of the whole compound which was digested to generate the target value. As seen on SEM imagery, there are potentially strong chemical inhomogeneities issues within aggregates. Finally, the different physical properties and heterogeneous chemistry of the aggregates are too different from the calibration material and prevent the obtaining of accurate data.

## CHAPTER V: CONCRETE CHARACTERISATION

In this chapter, the methodology used to characterise concrete samples and its constituents is presented. As discussed in Chapter IV, the calibration of the instrumentation is proving relatively inconsistent, and therefore the ability to generate quantitative data directly is difficult to achieve. Also the levels of some of the key elements of interest to the nuclear industry can be present at very low concentrations, and the precision achieved with the laser may not be of sufficient quality. To overcome this, a different approach is investigated. It consists in the segregation of the different phases present in the concrete (aggregates types, cement and sand mixture) and the ability to recognise these phases using the instrumentation and subsequently correlate them to their respective key major and trace element chemistry. The phase recognition is based on a fingerprinting exercise, in which a selection of major and trace elements is used to draw differences between aggregates and cement/sand mixture. The characteristic chemistry is assessed separately by digesting a set of the relevant concrete components to obtain solution data representative of the aggregate group or cement/sand mixture.

Most of the development work has been done using samples SB1 (small concrete block from CONSORT reactor, Silwood park) and WP1 (core sample of Windscale Pile one reactor, Cumbria) as these were available early in the project. Also both samples are considered as a representative sub-sample of the original material in terms of concrete components distribution and proportions. The aspects covered are the initial macro- and microscopic assessment of different constituents, aggregates differentiation and fingerprinting recognition, and finally a blind ablation test.

### 1. Initial microscopic examination of aggregates

As both samples were received, an initial assessment was based on visual inspection of the aggregates present in the concrete. To enable a clearer picture, thin sections were investigated using a microscope and polarised light through each sample. For mineralogists, the identification of minerals in thin sections using their characteristic birefringence colours is a well established procedure. The identification of minerals depends on the angle of the light coming through and the corresponding colours scheme displayed during rotation of the stage supporting the sample section. Although this requires some expertise in the field, the variations observed were used on a similarity basis between the different components observed in each section. Figure 5.1 represent sample SB1 and Figure 5.2 sample WP1.

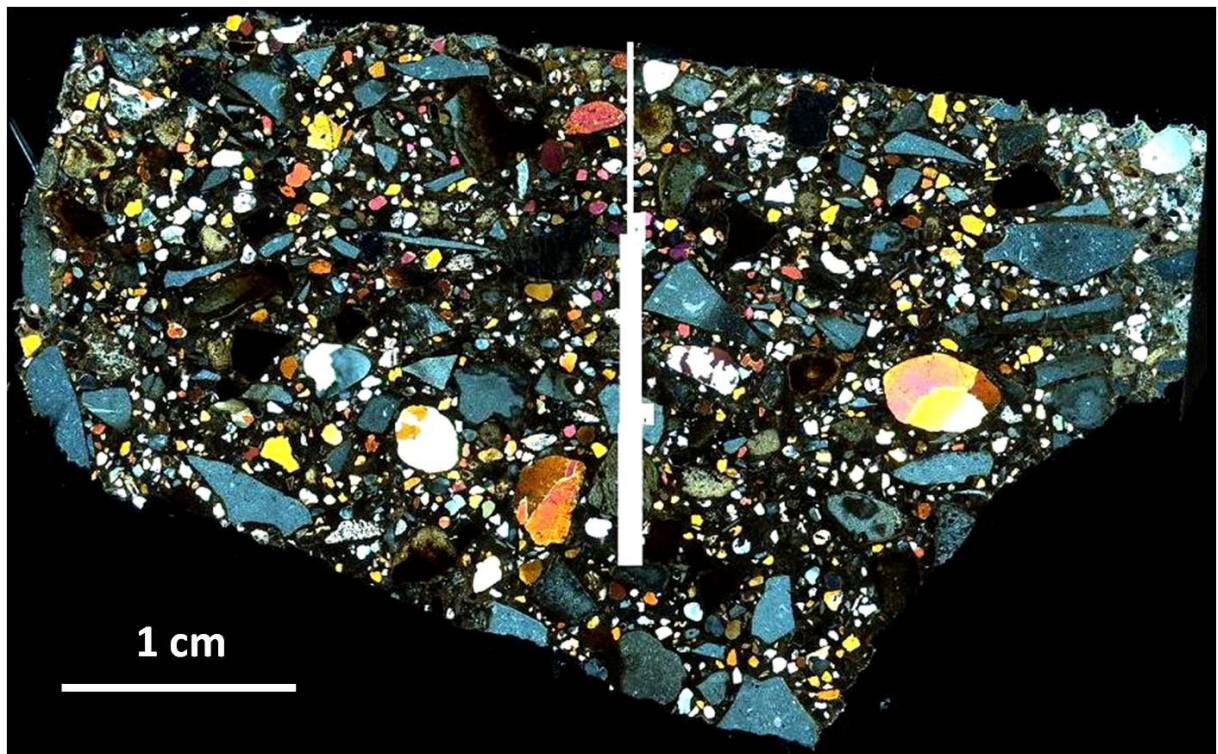


Figure 5.1: Thin section of SB1 under a microscope and polarised light. White band in the centre represents unmapped area. The different colours are a feature of the optical properties of the material.

Several features can be drawn from Figure 5.1 from sample SB1. The picture is very complex, and aggregates are present from a relatively small size ( $\leq 1\text{mm}$ ), likely to be the sand fraction, to slightly larger, approximately 2-5mm in diameter, which can represent the 'coarse fraction' of aggregates. Compared to conventional aggregates distribution (ASTM classification, Chapter II section 1.2) with coarse aggregates retained by a 4.75mm sieve, the fraction used here is relatively smaller than expected. A possible explanation is that due to the very small size of these shielding blocks. The probability for a  $\gamma$ -ray or neutron to pass through the material without interacting with enough large aggregates is relatively much higher considering larger aggregates and a wider distribution compared to smaller aggregates with a closer distribution on the scale of the blocks, keeping in mind the overall concrete density needed to remain within certain limits.

Looking at colours and shapes displayed, there is a distinctive group of aggregates which are of a grey colour, and in most cases have straight edges probably as a result of crushing. Rotating the stage does not alter the colour indicating they are polycrystalline. Some larger aggregates also have smooth edges and spherical shapes and colours displayed are yellow, pink, white and brown, sometimes within the same aggregate. These colours alternate with each other when rotating the sample stage. The shape points to the possibility of weathered natural aggregates, such as quartz beach gravel. Other aggregates are opaque to

transmitted polarised light, with colour variations between dark brown and black with no changes in colour when rotating the stage. These are likely to be oxides of iron, such as magnetite and ilmenite. Finally, the sand fraction shows a similar colour pattern to the spherical aggregates, suggesting that both are made of the same mineral.

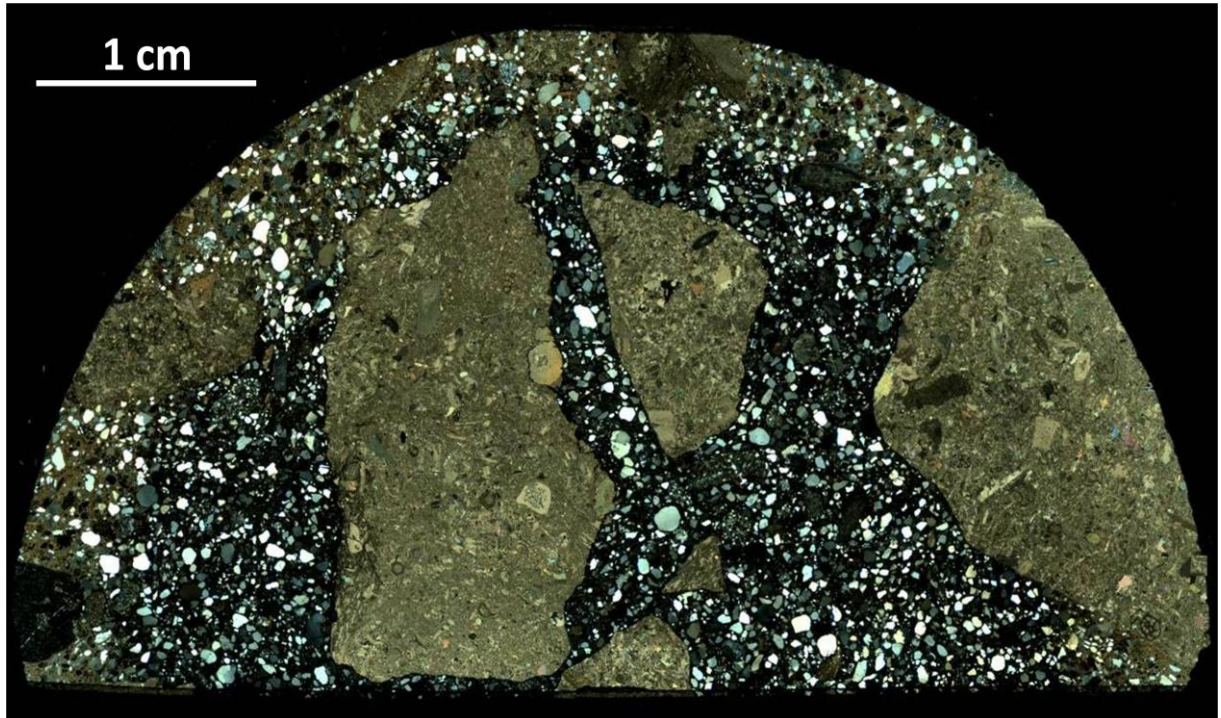


Figure 5.2: Thin section of WP1 sample under a microscope and polarised light. The different colours are a feature of the optical properties of the material.

For WP1, the size difference between coarse and fine aggregates is more significant. Also, the aggregates present significant visual heterogeneity and the presence of foraminifera, fossils from originally marine animals, suggest the aggregates are sedimentary calcium carbonates. To note is the large aggregate at the bottom left of the Figure, which displays different colour and composition, and potentially being of a different matrix. Figure 5.3 shows examples of the foraminifera found in these aggregates.

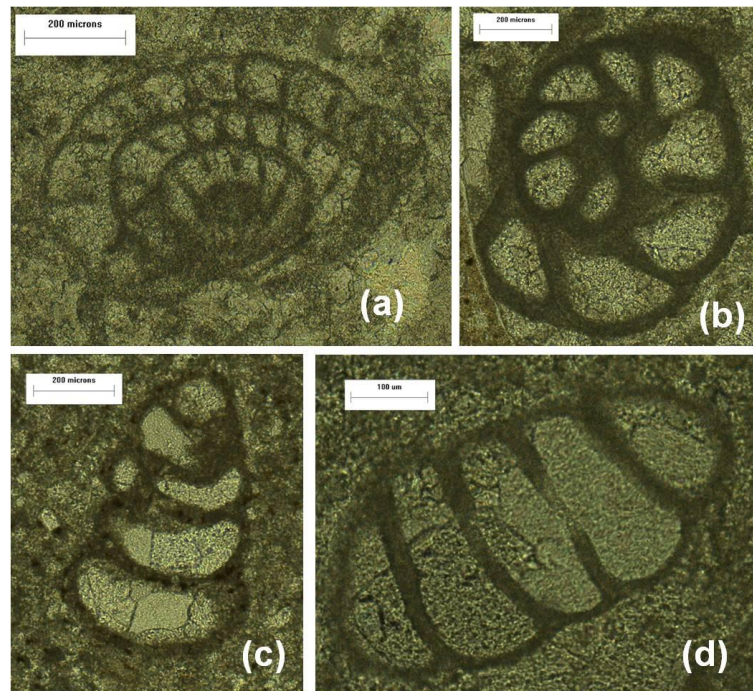


Figure 5.3: Examples of foraminifera found in aggregates from sample WP1. The relatively darker lines represent the original skeleton of the marine organism. Scale bars are 200 microns for (a), (b) and (c) and 100 microns for (d).

## 2. Major element chemistry

To highlight the variability in matrices between each aggregate type and cement and sand mixture, the LA-ICP-MS system was used to collect major and trace element data from over 70 single aggregates from sample SB1, 17 aggregates and several cement/sand from WP1. The instrument settings used were similar to those for the calibration exercise (Table 3.3 page 53 and 10 replicate analyses). The data were obtained from the central area of each aggregate, avoiding the edges. At this point there is no data available for cement and sand mixture for sample SB1. The major element data can be used to categorise the aggregates and illustrate the distinctive differences between aggregates from SB1 and WP1. Three of the major elements showing the most variability, namely  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$ , were plotted on a ternary diagram (Figure 5.4). For this purpose, the concentrations for all three components are normalised to 100%. Although their absolute value is in general less than what is represented on the diagram, the true total of the three elements is at least 80%, apart for the aggregates with high Ca (most of aggregates from WP1) where  $\text{CO}_2$  is potentially a major contributor if the component is  $\text{CaCO}_3$  and therefore not measurable.

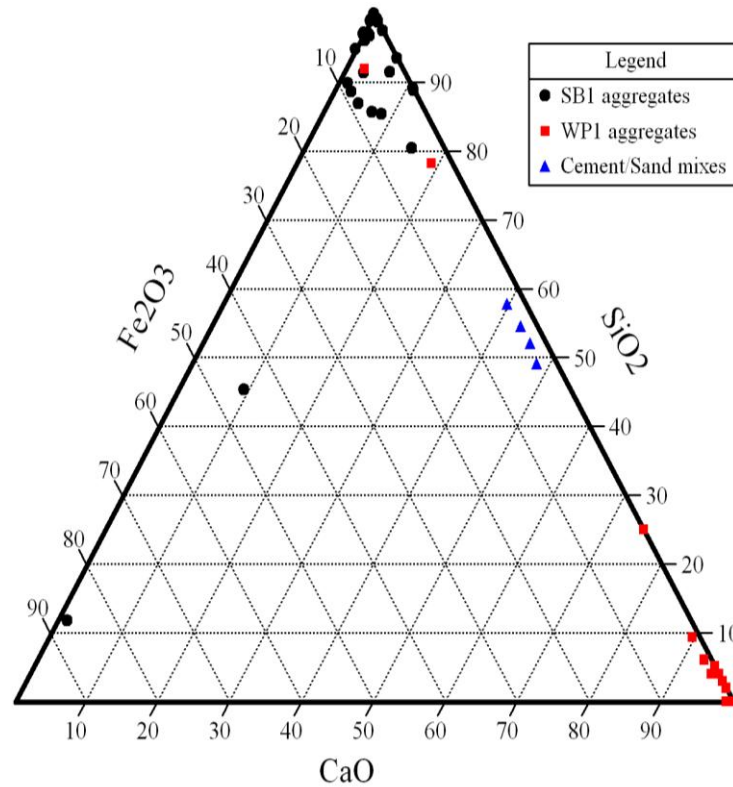


Figure 5.4: Ternary diagram based on  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  components of aggregates from sample SB1 and WP1 and cement/sand mixture of WP1. Each component's contribution is given by the dashed line in line with the value and tick outside the main triangle. For example the single point at the bottom left corner represents ~12%  $\text{SiO}_2$ , ~2%  $\text{CaO}$  and ~86%  $\text{Fe}_2\text{O}_3$ .

The majority of SB1 aggregates appear at  $\geq 95\%$   $\text{SiO}_2$  with 60 out of 75 analyses above that level. Most of the remaining aggregates show increases in  $\text{Fe}_2\text{O}_3$  and/or  $\text{CaO}$  content, up to ~10% maximum each. Two aggregates show significant differences, showing ~46% and ~86%  $\text{Fe}_2\text{O}_3$  respectively and  $\text{CaO} < 10\%$ . For WP1 aggregates, 15 out of 18 aggregates are represented with over 90%  $\text{CaO}$  and up to 10%  $\text{SiO}_2$ , and the remaining three showing increasing levels of  $\text{SiO}_2$  instead of  $\text{CaO}$ , with respectively 25, 78 and 92%  $\text{SiO}_2$  and similarly increasing levels of  $\text{Fe}_2\text{O}_3$  up to 7-8%. Finally the cement and sand mixture have variable  $\text{CaO}$  and  $\text{SiO}_2$  contents in the ranges 40-50 and 50-60% respectively, with relatively constant  $\text{Fe}_2\text{O}_3$  at 2-3%. This feature can be explained with the variation between ablating more or less sand aggregates ( $\text{SiO}_2$ ) and the cement (predominantly  $\text{CaO}$ ). Overall, aggregates from SB1 show some variations especially from nearly pure silicates to increasing levels of iron and calcium oxides. These require more in depth analysis to identify how many different types are present and their characteristics. For sample WP1, most aggregates show to contain mainly  $\text{CaO}$ , and two present similarities with the SB1 aggregates, showing a certain

percentage of aggregates contain silicates and are different from the bulk number of calcium carbonates aggregates. The cement and sand mixture from sample WP1 seem to vary for CaO and SiO<sub>2</sub> within 10% maximums, reflecting the proportion of sand and cement sampled.

At this point, the use of a ternary phase diagram consisting of SiO<sub>2</sub>, CaO and Fe<sub>2</sub>O<sub>3</sub> helps to identify mainly the presence of these three important major components in the aggregates. In the case of a nearly pure CaO signal (>90%), it is quite likely the aggregate is a carbonate and therefore needs to be corrected for the proportional CO<sub>2</sub> and potential MgCO<sub>3</sub> if not done so already during the total oxide correction.

Considering the aggregates from SB1 only and including the visual aspects described earlier, potential groups of aggregates are identified. This time all major data are incorporated and represent the values calculated by total oxide correction with the laser. Pure silicates include mostly major elements results at ≥98% SiO<sub>2</sub>, and contain aggregates identified as round and grey in their features. The possibility to separate both based on trace elements chemistry is investigated further. The remaining aggregates, with increasing amounts of iron or calcium oxides are referred to as mixed oxides. For the two aggregates showing even more predominant iron oxide in the matrix, and due to the fact that they do not transmit polarised light at all, this suggests they are of a different type of aggregates and likely to be some form of iron oxides. Finally a set of aggregates are at this stage identified as 'unknowns' because they are not displaying visually distinctive features from other groups. They potentially form another group of aggregates and will be tested for similarities in chemistry with the groups in place. Table 5.1 shows a summary of the aggregates groups so far.

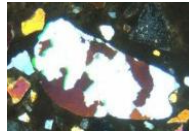
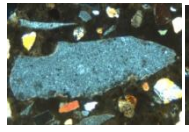
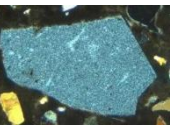
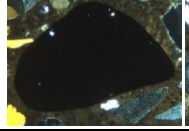
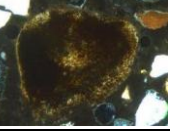
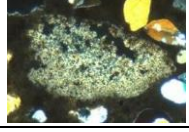
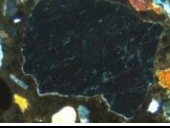
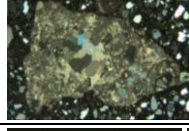
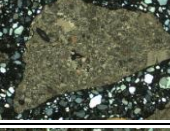
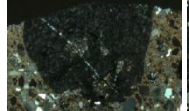
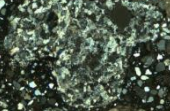
|     | Aggregate type              | Major chemistry                                                                                                           | Polarised light features                                | Examples                                                                             |                                                                                      |
|-----|-----------------------------|---------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| SB1 | Silicate                    | SiO <sub>2</sub> ≥98%                                                                                                     | Alternating between white, pink, yellow and brown       |   |   |
|     |                             |                                                                                                                           | Grey not changing                                       |   |   |
|     | Mixed oxides and iron oxide | SiO <sub>2</sub> : 8-96%<br>Fe <sub>2</sub> O <sub>3</sub> : 2-83%<br>CaO: 0-15%<br>Al <sub>2</sub> O <sub>3</sub> : 0-5% | Opaque to transmitted light, black and shades of brown. |   |   |
|     | Unknown                     | Variable chemistry, mainly SiO <sub>2</sub>                                                                               | Not displaying features from the above categories.      |   |   |
| WP1 | Calcium carbonates          | CaCO <sub>3</sub> , traces of MgCO <sub>3</sub>                                                                           | Angular and brown in colour, with foraminifera.         |   |   |
|     | Other                       | Mixture of major elements                                                                                                 | Darker colour and grained microstructure composition    |  |  |

Table 5.1: Summary of aggregate groups identified in sample SB1. The aggregate type names reflect the major chemistry observed and descriptive features. Examples of unknown and other aggregates in SB1 and WP1 respectively are given on the basis of non-conformity to observations so far, but are not excluded from any defining group and require further investigation.

### 3. Trace element chemistry

#### 3.1 Silicate aggregates

The silicate aggregates present in sample SB1 are potentially of two distinctive groups based on the optical properties and shape. After selecting appropriate aggregate to define both possible groups, trace element chemistry was investigated for possible differentiation. The aim was to find a pattern in the chemistry with the potential to separate the two sets of aggregates by plotting a relevant chemical aspect. The data were filtered through on a element concentration basis and also on the presence or absence of certain elements. A differentiating pattern in the boron data was identified between the 'round' weathered silicates and 'grey' crushed silicates based on concentration and precision over the ten replicate analyses performed for each aggregate. Figure 5.5 shows the two distinctive groups using the defining aggregates. The round aggregates show relatively low boron concentration ( $2\text{-}15\mu\text{g.g}^{-1}$ ) with corresponding higher relative precision ( $>25\%$ ) of the 10

replicate analyses, the other group representing the grey aggregates has relatively higher concentrations ( $45\text{--}110\mu\text{g.g}^{-1}$ ) and better relative precision ( $<20\%$ ). Also for the round aggregates, two of them showed no boron data above the detection limit and are not included here.

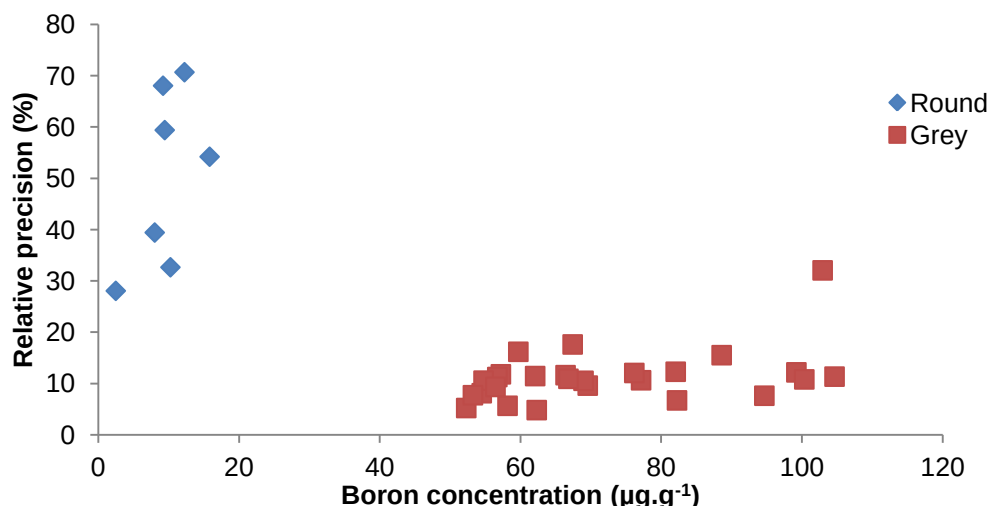


Figure 5.5: Boron content (in  $\mu\text{g.g}^{-1}$ ) against the relative precision ( $1\sigma$  in % of the mean) of 10 replicate analyses for aggregates identified as 'round' and 'grey' for sample SB1.

To test the potential discriminating factor, the set of 'unknown' aggregates, which do not display the exact visual properties and major elements characteristics of either group are put through a similar comparison. Therefore, aggregates showing  $\text{SiO}_2$  content  $\geq 98\%$  are selected and their boron characteristics added to the same graph. Figure 5.6 shows the updated distribution.

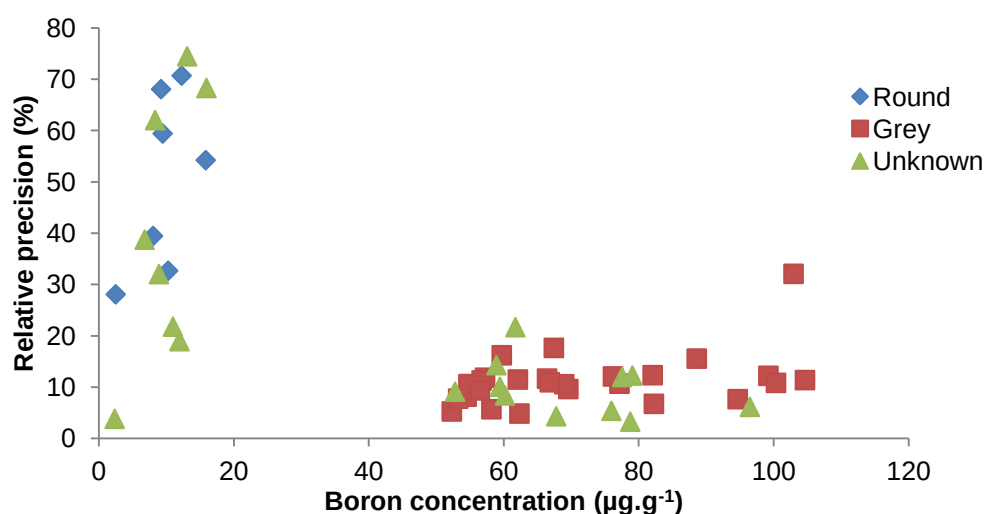


Figure 5.6: Boron content characteristics showing concentration (in  $\mu\text{g.g}^{-1}$ ) against the relative precision ( $1\sigma$  in % of the mean) of 10 replicate analyses for aggregates identified as 'round', 'grey' and 'unknown' for sample SB1.

From Figure 5.6, a set of 19 out of 27 unknown aggregates with sufficient SiO<sub>2</sub> separates successfully in two and agrees with either the round or grey aggregates defining groups. Eleven of them have similar boron chemistry than the grey aggregates and the remaining eight correlate with round aggregates boron data. A slightly different observation is the relative precision of the round aggregates which present possibly better values than previously expected (<25%), nevertheless the maximum boron concentration recorded is below 20µg.g<sup>-1</sup>.

A second discrimination factor was found for the same set of aggregates, again based on trace element chemistry, it was observed that elements such as La and U showed significant difference between the grey and round aggregates. In the first instance, both elements are present and are quantified above detection limit for almost every replicate analysis. The monitoring of a U/La ratio gives is valid (with numbers on both the numerator and denominator) in 267 out of 270 total replicate analyses, or equal to 98.9%, over the 27 grey aggregates monitored. For the three cases the ratio is invalid, this happened only to a single replicate in three different aggregates. On the contrary for the round aggregates, the U/La ratio gives a valid number in 13 out of 90 replicates, or 14.4%, with a maximum of three out of ten for any of the nine aggregates monitored. Table 5.2 summarises these observations.

| Aggregate group | Number of replicate analyses | Number of valid U/La ratio | Percentage from total | Number of valid ratio per single aggregate (10 replicates) |
|-----------------|------------------------------|----------------------------|-----------------------|------------------------------------------------------------|
| Round silicate  | 90                           | 13                         | 14.4%                 | 0-3                                                        |
| Grey silicate   | 270                          | 267                        | 98.9%                 | 9-10                                                       |

Table 5.2: Uranium and lanthanum data statistics for silicate aggregates.

Considering both sets of data, most of the time the uranium data are below the detection limit and cause an invalid ratio. Again using the parameters described above, the data obtained for the unknown aggregates is tested. For the 11 unknown aggregates showing similarities with grey aggregates, one out of the 110 replicates shows invalid U/La ratio. This concurs well with previous observations. For the eight remaining unknowns with affinity for the round aggregates, six of them agree with the previous observations. Indeed nine out of 60 replicates show a valid ratio and a maximum of three in the same aggregate. The last two aggregates show, on the contrary, valid U/La ratio for all 20 replicates, therefore showing agreement with the grey aggregates parameters. The reason why this is the case is unclear, it is possible these aggregates are slightly enriched in either U or La. Additional information

on these two aggregates shows that in Figure 5.6, the relevant results are at boron concentration of 11 and 12  $\mu\text{g.g}^{-1}$  and a relative precision of 22 and 19% respectively, which are appearing slightly below the original round aggregates data points. It is possible the laser is sampling the aggregate partially only and some cement and sand mixture is included, as both elements have higher concentrations in the mixture. Also the possibility these two aggregates are of a different type is put forward, but other trace element data such as Sr and REEs, which are significantly low, and with  $\text{CaO} < 0.2\%$  in both cases, there is a high confidence some cement chemistry would be showing and that therefore these aggregates can be assimilated to the round silicates type.

To conclude for aggregates in sample SB1 showing a major chemistry  $\text{SiO}_2$  content equal or above 98% oxide, trace boron data statistics (concentration against precision) and the validity of a La/U ratio can be used to segregate efficiently both silicates types.

### 3.2 Mixed oxides aggregates

The second general type of aggregates present in SB1 are referred to as 'mixed oxides' due to the decreasing proportion of  $\text{SiO}_2$  and increasing contribution from other major elements such as Fe, Ca and Al or a combination of all three. Based on Figure 5.4, the majority of these aggregates, with 10 out of 12, show silicate as the predominant element and with content between, 79 and 96%. The remaining two show  $\text{Fe}_2\text{O}_3$  content of respectively 83 and 43%, standing out from the group as potentially of a different matrix. Also based on optical properties, the two specific aggregates are also completely opaque to transmitted light. They will be referred as iron oxides. Based on trace element chemistry patterns, these groups of aggregates are relatively difficult to separate and show significant variations in some elements and heterogeneity within individual aggregate.

In order to facilitate the recognition of the aggregate and phase ablated by the laser, a set of major and trace elements results are used in graphical representation as a fingerprinting exercise to be able to discriminate them from each other. The discrimination diagrams include sets of elements chosen to reflect on the matrix of the ablated material and that are able to separate different aggregate groups efficiently. In all cases the differentiation is based on ratios of a major and a trace element with similar chemical behaviour but significant different amounts. The diagrams used are plots of Ca signal against Ca/Sr, Fe signal vs Fe/Mn and Fe signal vs Fe/Cr. For each graph, the ten replicates are initially corrected using the total oxide method, before the relevant data are averaged to form a single point on the discrimination diagram. Aggregates from samples SB1 and WP1 are included, as well as

cement and sand mixture from WP1. In the first instance, only the aggregates defining each group are included, and thereafter the unknown aggregates are introduced and assessed. Figures 5.7 to 5.9 show these diagrams.

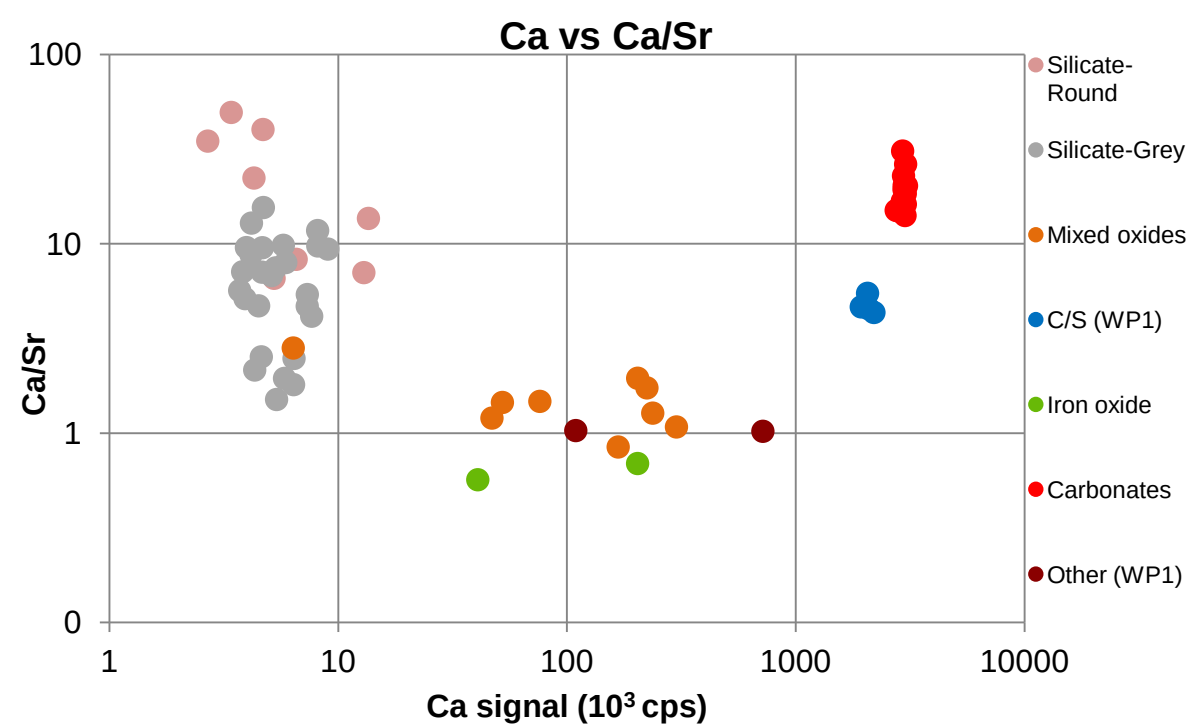


Figure 5.7: Calcium signal against Ca/Sr ratio for defining aggregates group. WP1: all 15 carbonate aggregate from that sample, and two other with different chemistry.

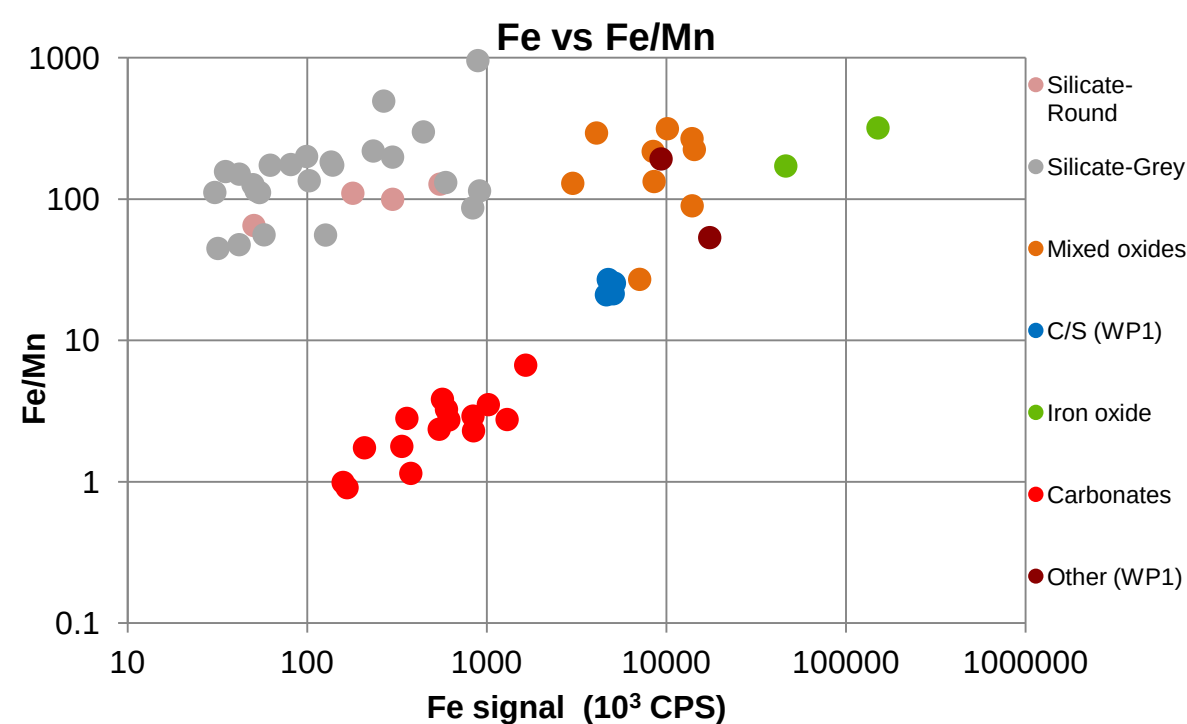


Figure 5.8: Iron signal against Fe/Mn ratio for defining aggregate groups.

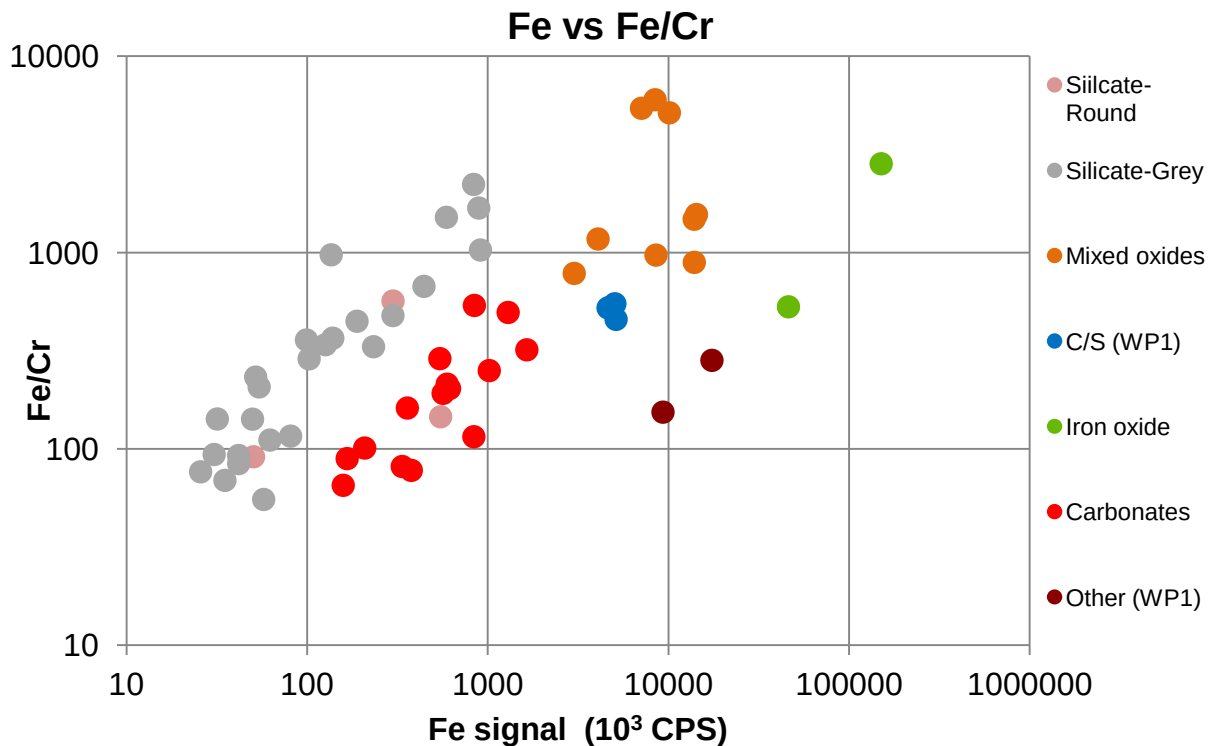


Figure 5.9: Iron signal against Fe/Cr ratio for defining aggregate groups.

Based on Figures 5.7 to 5.9, the following observations are made. The silicate group, both the round and grey aggregates, shows the lowest range of signals for both Ca and Fe. They also stand apart from the other aggregates, especially in the Fe/Mn and Ca/Sr diagrams. Nevertheless in all three diagrams it is not possible to separate the two silicate types. Therefore the use of boron data and La/U ratio are required. Mixed oxides aggregates form another group noticeably away from silicates, influenced by their Fe content in both iron-based diagrams. Considering Ca/Sr ratio and Ca signal, again the Ca levels separates them from the silicates, with signal >40kcps compared to silicates signal of <15kcps. In this instance, the Ca/Sr ratio also discriminates with a ratio of two or more for silicates and close to one for mixed oxides. Also in these diagrams, iron oxide aggregates are showing the highest iron content, with 46 and 150Mcps compared to a maximum of 14Mcps for the highest mixed oxide. The cement and sand mixture (C/S) data present relatively high precision, with all four points close together in all graphs. Together with the carbonates, the most helpful discriminating factor is Ca level where the relatively higher signal for C/S (2Mcps) and carbonates (3Mcps) is significantly above either mixed oxides or silicates. Although both show different Ca/Sr ratio in this diagram, the difference is also pronounced in the Fe/Mn diagram, where a higher ratio and Fe signal surpasses the carbonates results.

Finally the two other aggregates from sample WP1 show similarities with mixed oxides in both Fe/Mn and Ca/Sr diagrams.

Considering all components in each of the diagrams, it seems the Fe/Cr shows that with increasing Fe signal, the ratio Fe/Cr also increases steadily. On the contrary, Fe/Mn ratio stays relatively constant for all components, suggesting both Fe and Mn follow each other in abundance. Lastly, in the Ca/Sr diagram, both silicates and Ca-rich compounds show relatively constant Ca signals and more variable Ca/Sr ratio, but for mixed oxides, iron oxides and the two other aggregates from WP1, the statement in the opposite.

The next step is to include the 'unknown' aggregates from SB1 and verify the validity of original segregation based on major oxide composition. Figures 5.10 to 5.12 show the same diagrams as Figures 5.7 to 5.9, but the original data points for each aggregate group is reduced in size and the new points for three unknown (UKN) groups, namely UKN-round, UKN-grey and UKN-mixed oxides are shown. The whole UKN group of aggregates from SB1 went through the initial major oxides discrimination and boron and La/U data applied to the emerging silicate group.

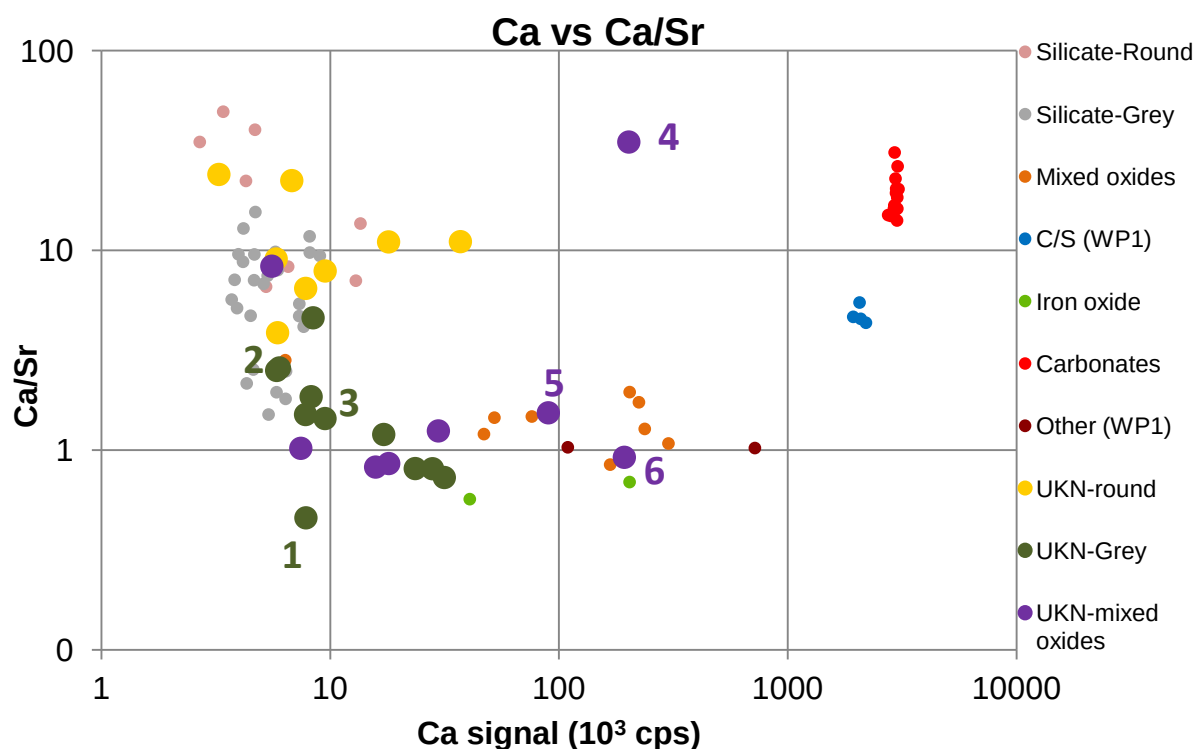


Figure 5.10: Calcium signal against Ca/Sr ratio for defining aggregates group from samples SB1, WP1 and including unknown aggregates from SB1. Numbers were allocated to some aggregates of interest for recognition purposes between the different diagrams. A more detailed investigation is applied to them.

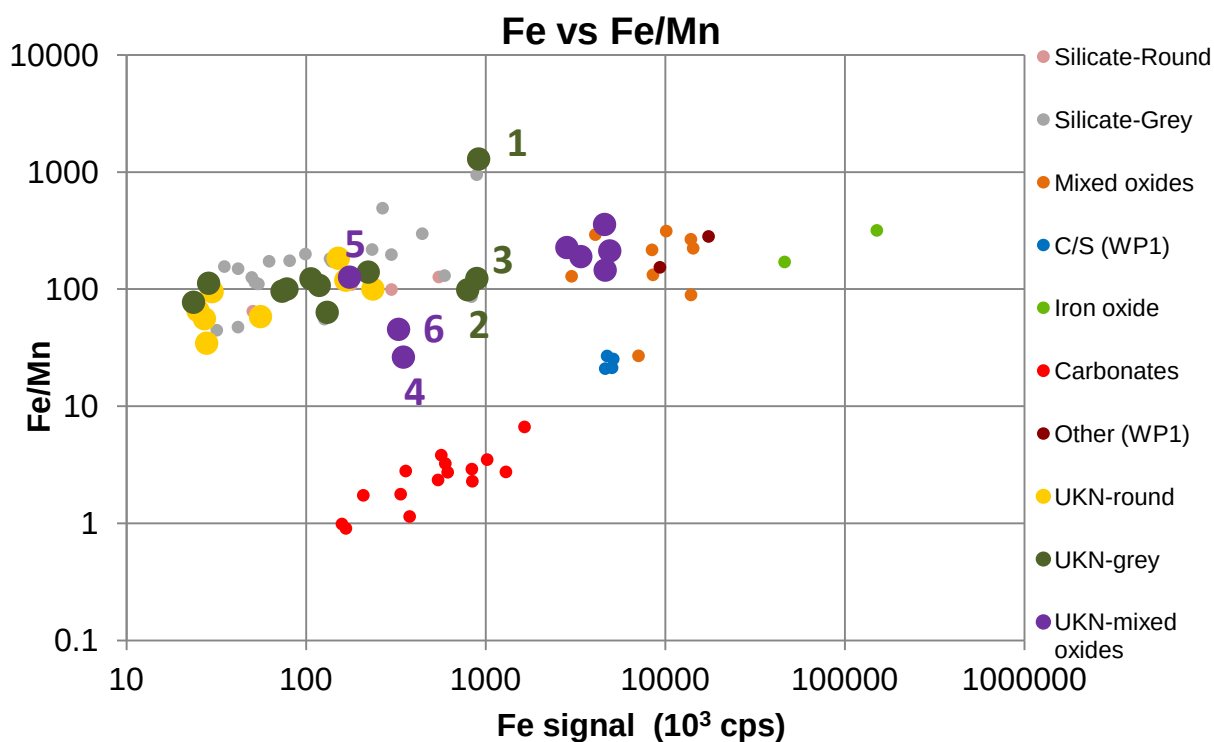


Figure 5.11: Iron signal against Fe/Mn ratio for defining aggregates group from samples SB1, WP1 and including unknown aggregates from SB1.

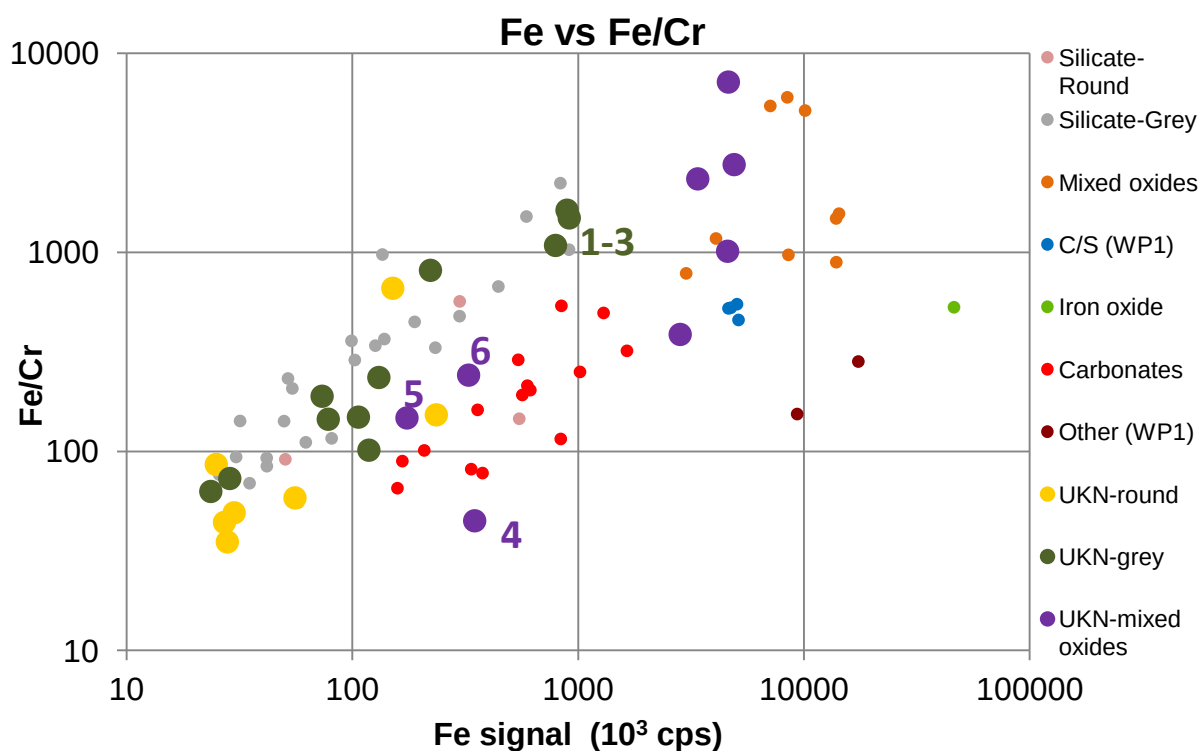


Figure 5.12: Iron signal against Fe/Cr ratio for defining aggregates group from samples SB1, WP1 and including unknown aggregates from SB1. One iron oxide data point is outside the range of Fe signal showed.

Considering the UKN-round aggregates data points only (yellow), in all three graphs the data points are in good correlation with the defining silicate group. This confirms the segregation based on SiO<sub>2</sub> content and the use of trace element data for boron, lanthanum and uranium to separate these aggregates from the other grey silicates is effective in this case.

For the UKN-grey aggregates (dark green), the majority of them agrees with the silicate groups in the Fe signal against Fe/Mn and Fe/Cr ratios diagrams within the defined spatial limits. Nevertheless, a group of three of aggregates (noted 1 to 3) are on the edge of these limits for both iron based diagrams. In the case of Fe/Mn and Ca/Sr, No. 1 shows significantly different ratio than the defining group and No. 2 and 3. By comparing the trace element data for all three of these aggregates against the typical values observed with the grey group, aggregate 2 and 3 did not show any significant differences. On the contrary, aggregate 1 consistently measured a barium concentration of ~1200µg.g<sup>-1</sup> on average, which is two orders of magnitude higher than the average observed for grey aggregates. No other element showed significant differences. Therefore aggregate 1 is likely to be of a different type, though no other characterised aggregate in sample SB1 shows similar chemistry. The remaining aggregates are in good agreement with silicates in both iron-based diagrams, but some show lowering of the Ca/Sr ratio and increase in Ca signal to branch out towards the mixed oxide defining group. Nevertheless their iron levels remain in the region of one order of magnitude below the mixed oxide group. A possible explanation is that these UKN-grey aggregates are sampled by the laser on the edge of the particle's surface and can include some cement and sand mixture. Since the cement and sand mixture of sample SB1 has not been assessed, it is not possible to predict the direction a mixture of chemistry will take in the case described above. To a certain extent, this mixed phase can also explain the non-conform optical properties observed under polarised light compared to the grey aggregates.

For the unknown mixed oxide aggregates, a mixed pattern is also present. Looking at both iron-based diagrams, a group of three aggregates (noted 4 to 6) do not present the required iron level to agree with the defining mixed oxide group, by one order of magnitude. The remaining five aggregates show similar ratios and distribution to the defining group in both plots. On the contrary, in the Ca/Sr diagram, these same five aggregates are not showing data concurring with the defining group. Also aggregates 5 and 6 are showing similar ratio and Ca level, but aggregate 4 is significantly away from any of the existing defining groups.

After a closer investigation of all aggregates from the UKN-mixed oxide group, the following information is drawn. The major chemistry of aggregate No. 4 is relatively different to all other aggregates. The total major element oxides, prior to correction, add up to <80% for all ten

replicate analyses, and decrease to 40% on two occasions. This result is comparatively low considering all other aggregates monitored in sample SB1, as all show totals close to or exceeding 100% due to differential ablation volumes. This feature points towards the presence of a non-measurable matrix compound, similar to CO<sub>2</sub> in limestone aggregates. Also, after the total oxides correction was applied, the Na<sub>2</sub>O component is present in the region of 15% to the total content, with SiO<sub>2</sub> and CaO around 70 and 10% respectively. This relatively high Na content has not been measured in any of the other aggregates, with all other Na<sub>2</sub>O data <1%. In previous analysis of the thin section, a measurement of the glue used to stick the sample onto the thin glass slide was included. A total oxide correction applied to that specific glue analysis showed a perfect match with the major chemistry observed here. Also, including the glue analysis in the Ca/Sr diagram highlighted the perfect matching with 'aggregate' No. 4. Therefore it is accepted that this specific analysis is actually a void, where originally a real aggregate can have resided, filled with glue (epoxy resin).

Considering aggregate No. 6, the replicate results also showed data issues. Using NIST 610 to generate concentrations, the 10 replicates for that aggregate show slightly variable major composition of SiO<sub>2</sub> (93 ±3%), CaO (6 ±2%) and Al<sub>2</sub>O<sub>3</sub> (1 ±1%), nevertheless after five replicates, the levels of SiO<sub>2</sub> diminish and Al<sub>2</sub>O<sub>3</sub> increases, and at the same time a number of trace elements such as Ba, La, Ce, Pb and others show a significant spike. Figure 5.13 illustrates the observation. This shows the possibility of an inclusion rich in trace elements, some of them important in terms of activation purposes.

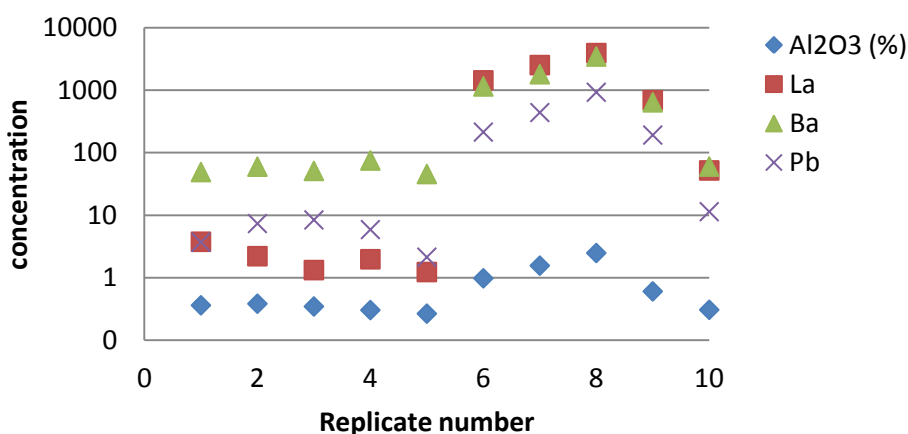


Figure 5.13: Replicate analysis data for Al<sub>2</sub>O<sub>3</sub> (in % oxide) and trace elements (in µg.g<sup>-1</sup>) for an aggregate

For aggregate No. 5, showing similarities with silicates in both iron diagrams but not for the Ca/Sr, again replicate data show a distinctive pattern. The first five replicates show chemistry which assimilates the aggregate to a silicate grey. The remaining five show increasing

contribution of Ca and Sr from potentially cement and sand mixture. Indeed this aggregate is actually relatively small, and it is likely cement and sand is included in the analysis.

The remaining aggregates from the UKN-mixed oxide group, which show good correlation with the defining group in the iron-based plots, do not display any inconsistencies with their replicate or trace element pattern. It is unclear why they are showing relatively lower Ca signal compared to the defining group in the Ca/Sr plot. Further study is required to solve this problem.

#### 4. Test concrete aggregates

As part of the concrete characterisation, the three additional concrete samples were tested. Two samples are from CONSORT reactor and are from the bioshield monoblock (BS) and large blocks (LB), and the last one from Windscale Pile 2 reactor chimney (WP2). For each sample a selection of aggregates were analysed using the laser and the data used on the plots containing the defining aggregate groups for samples SB1 and WP1. The aggregates for WP2 are shown in Figure 5.14. They consist of four aggregates with similar shape and colour (WP2 1-4), an additional two relatively smaller and different (WP2 5/6) and a portion of cement and sand (not shown). Each aggregate was analysed by three sets of 10 replicates to give a better representation of the data spread depending on the area ablated. The cement and sand was analysed twice only.

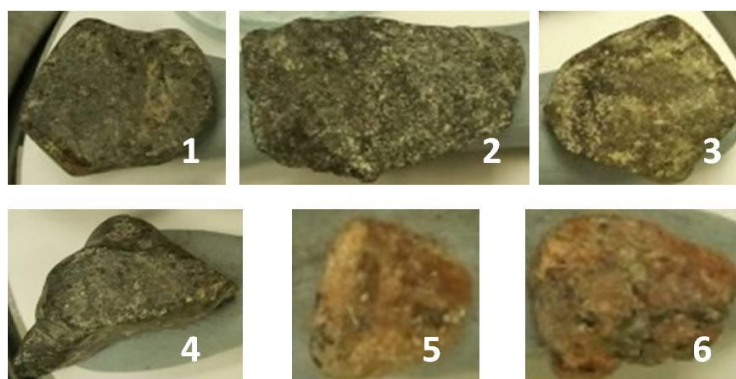


Figure 5.14: Characterised aggregates from sample Windscale Pile 2 (WP2). Aggregates 1-4 and 5/6 are significantly different in colour.

The constituents from sample LB are shown in Figure 5.15. They consist of two similar aggregates (LB 2/3), and two different aggregate (LB 1 and LB 4) and a cement and sand portion (C/S). Each component was analysed with two sets of 10 replicates. Finally the aggregates for sample BS are shown in Figure 5.16. For two of them, namely aggregates

three and four, the differently coloured areas were ablated separately. All analyses were individual sets of 10 replicates. The new plots are given in Figures 5.17 to 5.19.



Figure 5.15: Constituents of sample CONSORT large block (LB).

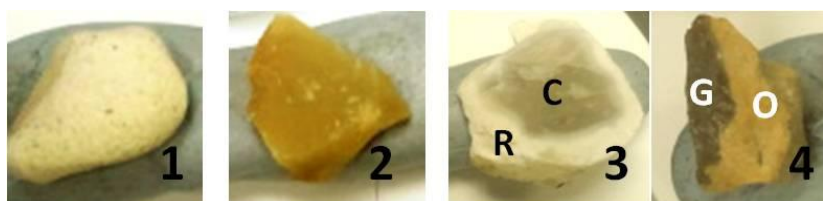


Figure 5.16: Aggregates from sample CONSORT bioshield (BS). Aggregates 3 and 4 were analysed on two sites as they showed colour differences, namely rim (R) and centre (C) for No. 3 and grey (G) and orange (O) for No. 4.

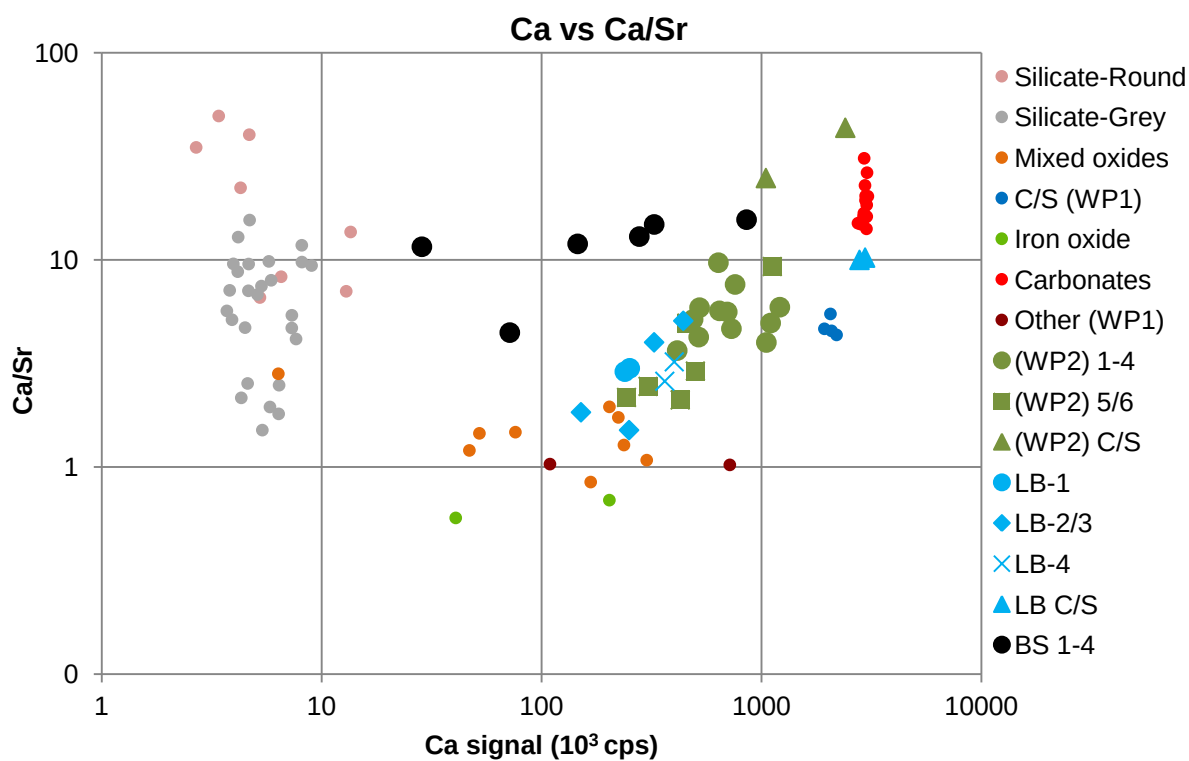


Figure 5.17: Calcium signal against Ca/Sr ratio for defining aggregates group from SB1, WP1 and including constituents from CONSORT sample large block (LB), bioshield (BS) and Windscale Pile 2 (WP2).

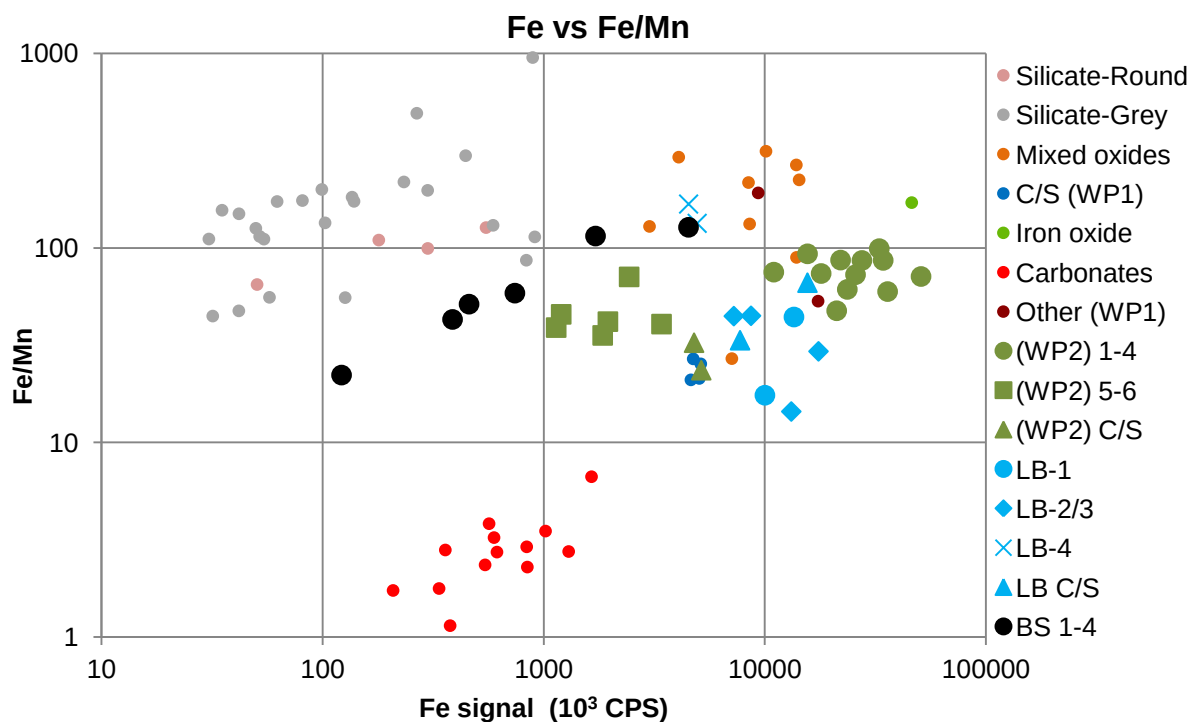


Figure 5.18: Iron signal against Fe/Mn ratio for defining aggregates group from SB1, WP1 and including constituents from samples LB, BS and WP2.

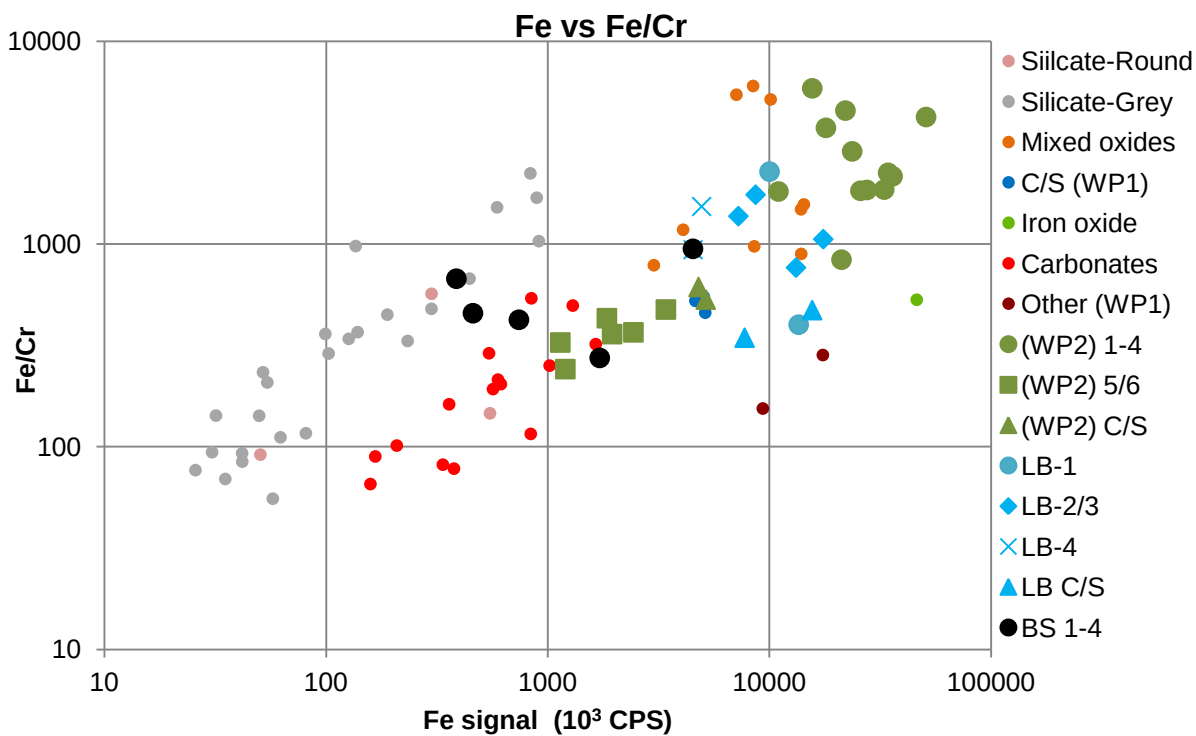


Figure 5.19: Iron signal against Fe/Cr ratio for defining aggregates group from SB1, WP1 and including constituents from samples LB, BS and WP2.

For the three discrimination diagrams, the picture is relatively complex as many constituents of different samples are considered simultaneously. In the Ca/Sr diagram, almost all the new data points show differently from the defining groups from sample SB1. All constituents from samples WP2 and LB are present between the mixed oxide and the carbonates groups. On the contrary, some aggregates from the bioshield (BS) sample show more affinity with silicate-type aggregates.

In both Fe/Mn and Fe/Cr diagrams, aggregates WP2 1-4 show to contain significant iron levels, and appear between the mixed and iron oxide defining groups. Aggregates WP2 5/6 show lower iron signal and form a distinctive group between the defining silicates, mixed oxides and cement and sand mixture. Considering C/S mixes, the results from sample WP2 are the same as C/S from WP1 for the iron based diagrams. Unfortunately this is not the case for Ca/Sr, where the duplicate data are not reproducible and does not concur with the defining C/S data.

Although the diagrams show that most of the time the new constituents do not fall within a specific defining constituent group from samples SB1 and WP1, a couple of the new data groups are tested to evaluate if the variations observed in the data spread in the diagrams significantly affect the elemental concentrations based on wet chemistry data. For this test, aggregates 1-4 from sample WP2, which show a possible mixed or iron oxide nature, and aggregate No.2/3 from sample BS, which show similarities to silicates, are chosen.

Following the protocol established for SB1 and WP1 constituents, BS-3 analysis data from both the rim and centre area in theory falls in the category of grey aggregates, although the boron data are not strictly at the required concentration (relatively too low). All other aspects, namely the SiO<sub>2</sub> content, boron precision and La/U ratio validity are good. This is not the case for aggregate No. 2, which shows only 92% SiO<sub>2</sub> and is taken out of the silicate group into the mixed oxide category. Nevertheless, based on both iron discrimination diagrams, BS-2 is showing similar behaviour to silicates, suggesting the Ca/Sr plot shows some C/S may have been ablated with the aggregate. Therefore under these circumstances, BS-2 is defined as silicate with some C/S, but in reality this is not the case. For BS-3, Fe/Cr data shows strong affinity with silicates, but Fe/Mn show the aggregate slightly below the expected ratio range. The Ca/Sr data is also not conclusive about its silicate nature, with more Ca signal than expected and variable ration between the rim and centre. The remaining laser data show that the rim has significantly more Sr and REEs from lanthanum to samarium. For the four aggregates from sample WP2, due to the relatively higher Ca and Fe signal, they stand close to mixed and iron oxide group in each plot. As a comparison, Table

5.3 shows a selection of major and trace elements from silicates, mixed oxides and iron oxides from sample SB1 and for aggregates BS 2/3 and WP2 1-4.

|                    | Major component (%) |                                |          |                                | Trace element ( $\mu\text{g.g}^{-1}$ ) |        |         |         |          |
|--------------------|---------------------|--------------------------------|----------|--------------------------------|----------------------------------------|--------|---------|---------|----------|
| Aggregate          | SiO <sub>2</sub> *  | Al <sub>2</sub> O <sub>3</sub> | CaO      | Fe <sub>2</sub> O <sub>3</sub> | Co                                     | Ni     | Sr      | Ba      | U        |
| <b>Mixed oxide</b> | 82.8                | 1.1                            | 3.4      | 12.4                           | 20.6                                   | 56.5   | 365     | 85      | 0.54     |
| <i>Range</i>       | 72-97               | 0.2-1.8                        | 0.4-6.8  | 1.6-25                         | 2-40                                   | 7-127  | 28-715  | 36-255  | 0.2-1.1  |
| <b>Iron oxide</b>  | 22.0                | 1                              | 1        | 74                             | 35                                     | 148    | 254     | 55      | 1.15     |
| <b>WP2 1-4</b>     | 50.9                | 13                             | 8        | 12                             | 31                                     | 39     | 339     | 283     | 1        |
| <i>Range</i>       | 50-51               | 12.7-13.1                      | 6.8-8.8  | 11.6-13.5                      | 20-36                                  | 28-43  | 315-360 | 239-267 | 0.5-1.6  |
| <b>Silicate-R</b>  | 100                 | N/A                            | 0.1      | N/A                            | 0.25                                   | 2.4    | 8.4     | 10.6    | 0.06     |
| <i>Range</i>       | 99.8-100            | N/A                            | N/A      | N/A                            | 0.1-0.6                                | 0.1-4  | 0.7-24  | 0.7-20  | 0.01-0.2 |
| <b>Silicate-G</b>  | 99.7                | N/A                            | 0.3      | 0.2                            | 0.4                                    | 6.4    | 16      | 28      | 0.28     |
| <i>Range</i>       | 99-100              | N/A                            | 0.05-0.8 | N/A                            | 0.1-1                                  | 2.9-10 | 5.2-34  | 2.9-134 | 0.1-0.6  |
| <b>BS-2</b>        | 99.8                | <0.01                          | 0.10     | 0.02                           | 0.4                                    | 0.6    | 8.5     | 33.0    | 0.26     |
| <b>BS-3</b>        | 99.8                | 0.10                           | 0.07     | <0.01                          | 0.1                                    | 0.3    | 16.8    | 13.4    | 0.11     |

Table 5.3: Selection of major components and trace elements concentrations determined by wet chemistry for certain aggregates from samples SB1, BS and WP2. Some of the SiO<sub>2</sub> is deducted as the remaining part of the total of all other major components to 100%.

Considering the results from WP2 aggregates 1-4, the relative range of concentrations for each element is relatively small, suggesting a good homogeneity between aggregates. Compared to the mixed and iron oxide data, the chemistry of the WP2 aggregates shows some variations. First in the major chemistry, WP2 shows significantly more Al<sub>2</sub>O<sub>3</sub>, slightly more CaO and a SiO<sub>2</sub> concentration in between mixed and iron oxide data. To some extent the iron, nickel, strontium and uranium data are closer to the mixed oxide group, although the range quoted for each of these elements is actually very large within the mixed oxide group. This suggests there may be some irregularities in this group and more data and analysis are required. Finally barium is on average significantly higher in the WP2 aggregates than in either mixed or iron oxide groups. For BS 2/3 compared to the silicates group, BS-2 show very similar levels to the silicate grey group for all elements apart from nickel, and BS-3 with the round group. Again, some elements in the grey group predominantly show a wide range

of values, especially for Ca, Sr and Ba. Overall, the two aggregates investigated from the bioshield concrete show strong similarities with the silicates groups in sample SB1, whereas the WP2 aggregates are quite different in major and some trace chemistries from either the mixed or iron oxide groups from SB1. The WP2 aggregates are likely to form a new specific group of aggregates with a specific set of concentrations. In the discrimination diagrams they appear to be close to the mixed and iron oxides. It is likely another discriminating factor is required to significantly differentiate them from the other groups, and aluminium seems to be a very good candidate in this case.

One issue concerns the relatively wide range of concentration observed in some of the groups, especially the mixed oxide aggregates. It is possible some of the values in the range are erroneous due to contamination; equally the aggregates in that group can be of different types and under the discrimination settings used at the moment, the difference is not drawn; or simply the aggregates do have that range of concentrations. In all cases, increasing the database with more analysis of the same samples and aggregates will help to identify the exact reason for the range of concentrations observed, and identify the potential new discriminators required to separate the aggregate groups.

## 5. Blind ablation test

At times the possibility to visually investigate a concrete surface before analysis takes place is restricted. Here the aim is to be able to recognise the ablated phase without visual support, by using the chemical data collected and chemistry fingerprinting to draw a picture of the different concrete components encountered. For this, two sets of 35 replicate analyses over specific concrete areas were taken. A slight difference in the laser settings is the scanning speed has been increased to  $30\mu\text{m.s}^{-1}$  instead of the usual 10 to cover more surface area. Therefore each replicate covers  $145\mu\text{m}$  and the total length of the ablated track is 5.08mm. The areas selected contained representative aggregates from the silicates and mixed oxides group, and the cement/sand mixture in-between. The data collected are plotted and assessed for component recognition. Compared to the development work, some replicate analyses are within aggregate boundaries, but also this time the replicate analyses can reflect a mixture of chemical compositions as the areas ablated are likely to be over both cement/sand mixture and specific aggregates. Also, the plots are focussing on the new data points for each track, and some data points from the defining groups are outside the plotted area to increase the resolution and spread of the track data. In each case, data showing clustering in a relevant area are tagged with the possible phase ablated. Subsequently the 35 replicate analyses of each track will be given the most likely phase ablated based on

chemical data and checked against the visual data of the ablated track Figures 5.20 to 5.22 show the results for the first set of 35 replicates (Track A).

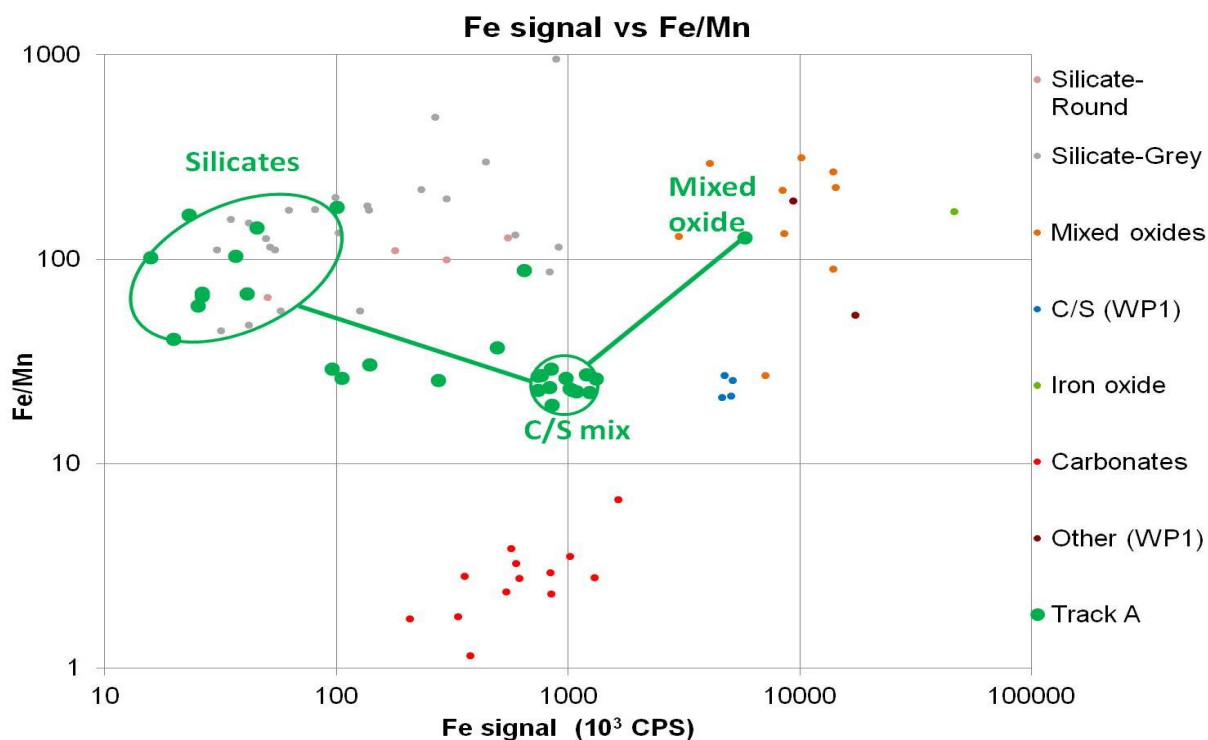


Figure 5.20: Replicate analysis of Track A and defining groups from SB1 and WP1 for Fe/Mn. Clusters of points are identified and linked to each other to highlight the likely mixed chemistry resulting from the ablation of two phases

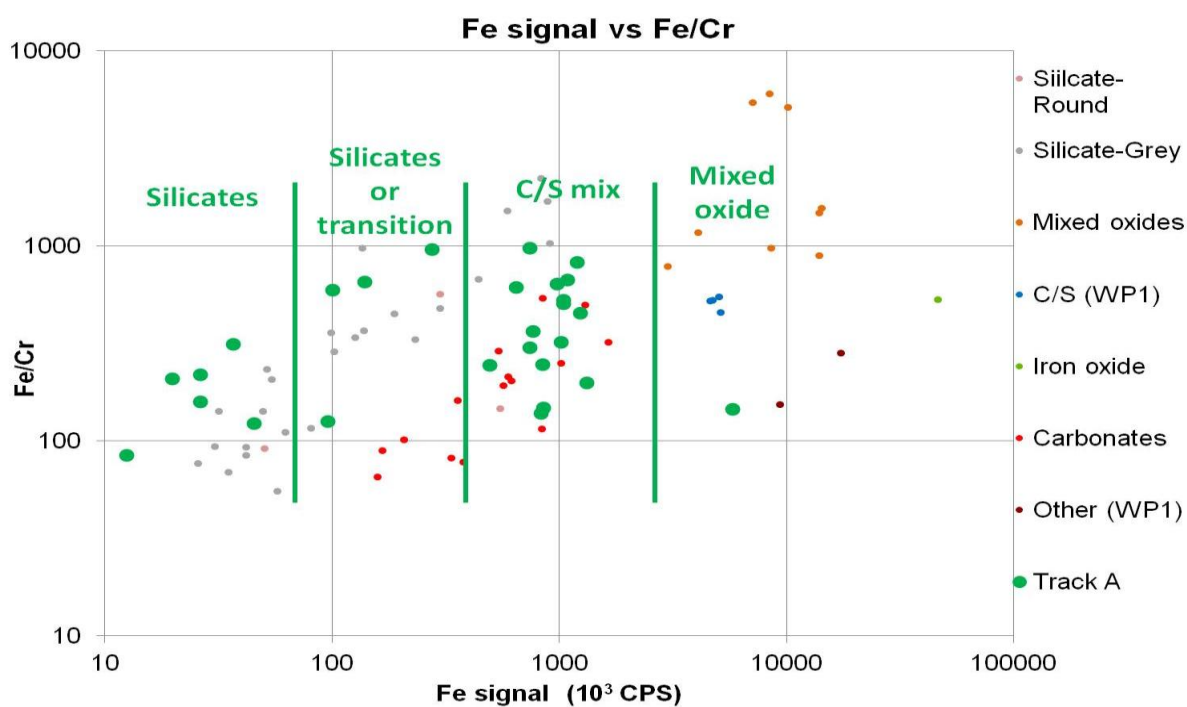


Figure 5.21: Replicate analysis of Track A and defining groups from SB1 and WP1 for Fe/Cr.

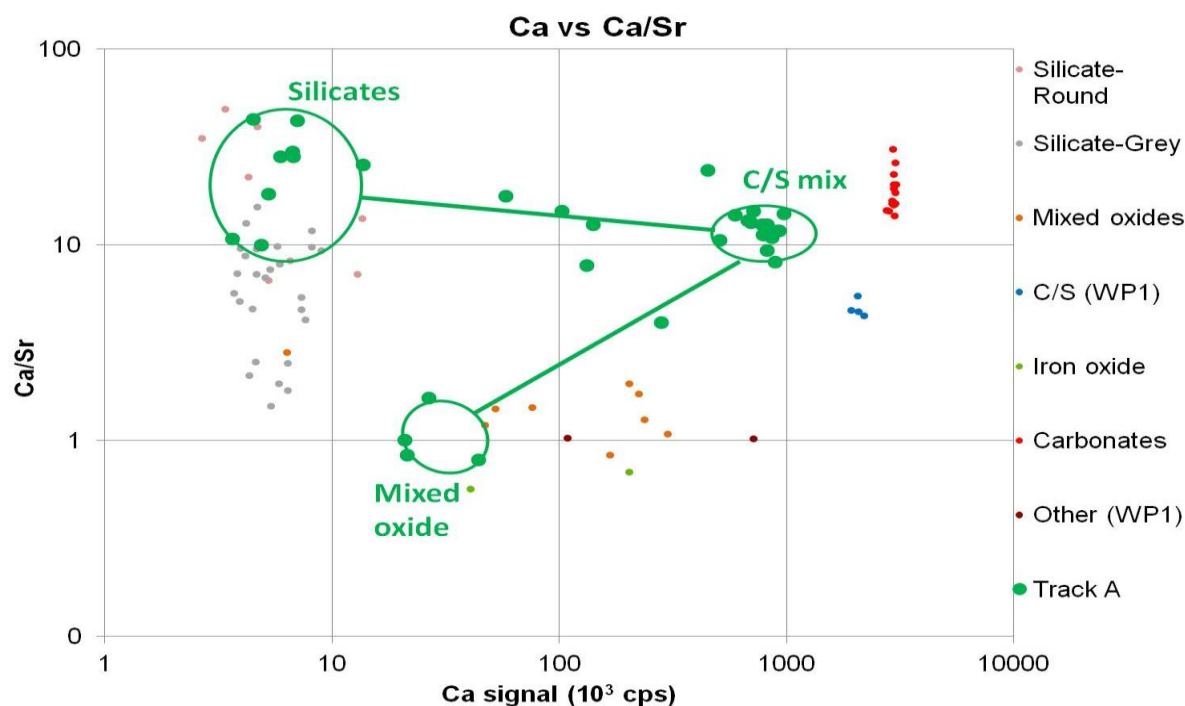


Figure 5.22: Replicate analysis of Track A and defining groups from SB1 and WP1 for Ca/Sr.

Considering all three graphs, the results show that clusters of data points are formed in certain areas. Ca/Sr and Fe/Mn plots are the most useful at potentially identifying the groups. The first group coincides well with silicate aggregates in both plots and consists in nine replicate analyses on both occasions. The second group shows similar Fe/Mn ratio to that of cement and sand mix, but with a relatively lower Fe signal. In the Ca/Sr plot, the same group shows similarities to high Ca groups such as calcium carbonates and C/S mix from WP1, although the ratio is relatively higher and signal lower. As the C/S mix from sample SB1 has not been characterised beforehand, the data observed are potentially true. Moreover, based on Fe signal intensity and position in both Fe plots, there is a possibility that at least one of the replicates is a mixed oxide and identified as such. This is supported by the presence of possibly four replicates in the mixed oxide zone on the Ca/Sr plot, although three of them are relatively outside the main defining group. Finally, a certain number of data points are present in areas generally between the three identified groups. This can be a result of a mixture of chemistry ablating one phase to another. It is expected that 'transition zones' will be present from the laser ablating from the C/S mixture to an aggregate and vice-versa, but not from aggregate to aggregate. To highlight the likely transition zones, solid lines have been drawn from the respective groups on the Ca/Sr and Fe/Mn plots.

In a similar way to Track A, a second set of 35 replicate analyses were taken over a different area of sample SB1, but this time all replicates are not in a single straight line. After approximately 25 replicates, the laser changes direction twice by a 90° angle to scan just above the existing track but backwards from the original direction. Again the ratio plots with defining aggregate groups are used and the new data plotted and assessed. Figures 5.23 to 5.25 show the plotted results for track B.

Considering Ca/Sr and Fe/Mn plots, first observation is that a potential C/S mix cluster of data points shows consistently at the same coordinates, although a potential shift towards lower Fe signal in Fe/Mn suggests variable amounts of silicate (sand) particles. Moreover a silicate large aggregate group is present, though showing relatively below the defining group in the Fe/Mn plot and inconsistent on the Ca/Sr plot. It has also relatively fewer points than Track A, suggesting less silicate aggregates present. On the contrary, there is a well defined group in the Fe/Mn plot with ratios similar to the mixed oxide defining group but with lower Fe signal, not concurring with the single replicate from Track A. This group consists in more data points, with around 7-9 replicates. In the Ca/Sr, this group has also shifted, showing similar ratio than the mixed oxide defining group but at a lower Ca signal.

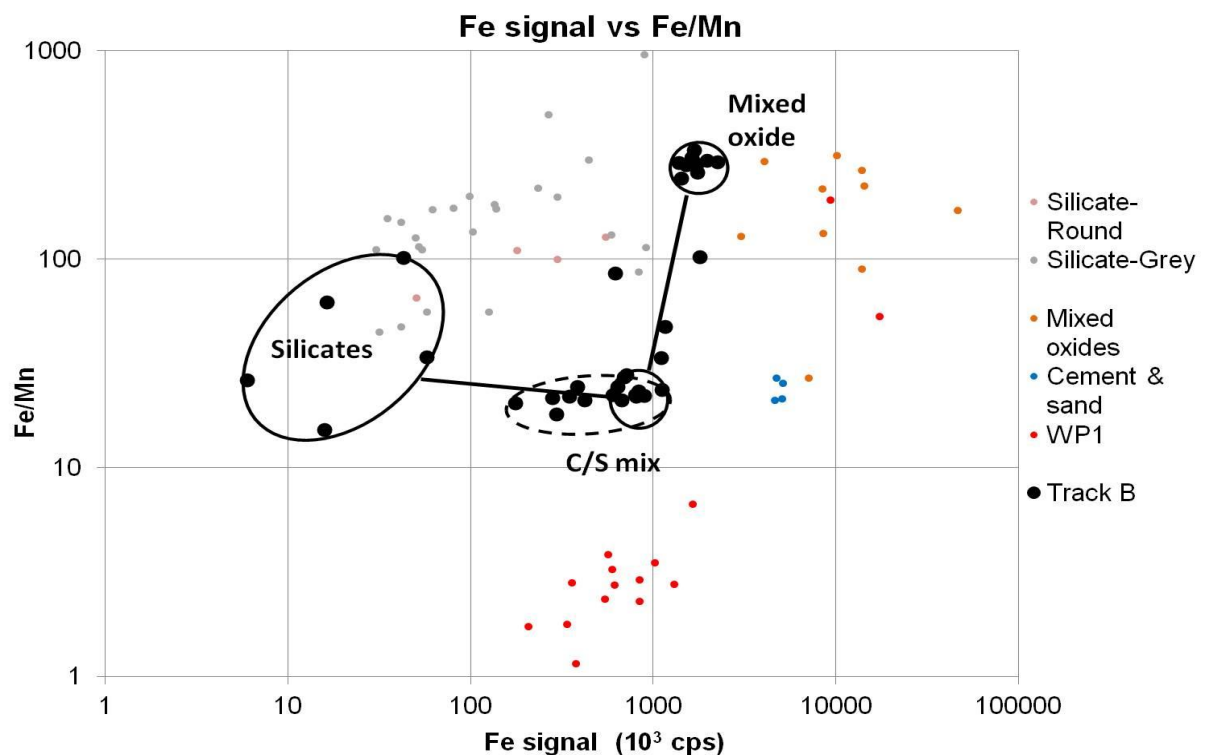


Figure 5.23: Replicate analysis of Track B and defining groups from SB1 and WP1 for Fe/Mn.

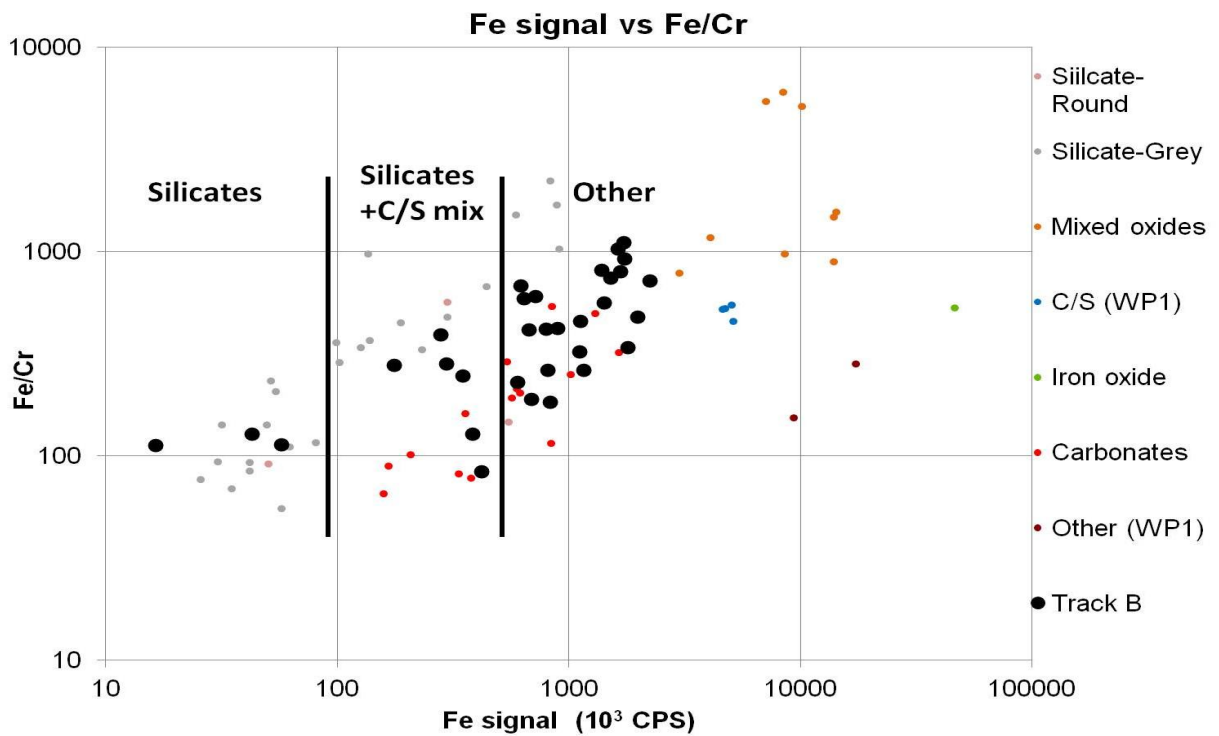


Figure 5.24: Replicate analysis of Track B and defining groups from SB1 and WP1 for Fe/Cr.

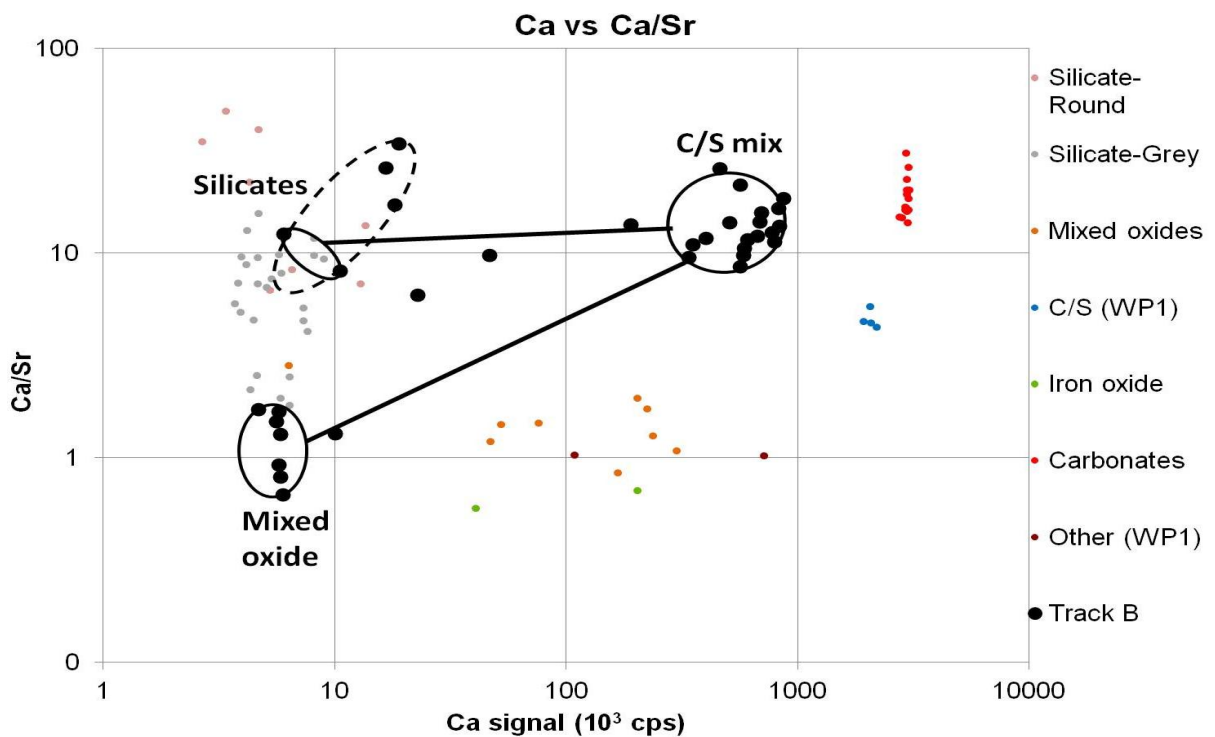


Figure 5.25: Replicate analysis of Track B and defining groups from SB1 and WP1 for Ca/Sr.

Overall between Tracks A and B, the ablated material is likely to have sampled significant amounts of cement and sand mixture, as well as silicates and mixed oxides aggregates.

There is also the possibility of a mixture of chemistry between C/S and either aggregate, as the replicate analyses can overlap the two phases. Using the chemical information and the replicates sequence, both sets of data are put in replicate order (1 to 35) and the likely phase ablated deduced from the information gathered from each discrimination diagram and also from boron concentration and U/La ratio to segregate the silicate group. Table 5.4 and 5.5 show these results for Track A and B.

| Replicate number | Chemical discrimination plots |             |       | Boron concentration | La/U ratio | Final phase     |
|------------------|-------------------------------|-------------|-------|---------------------|------------|-----------------|
|                  | Fe/Mn                         | Fe/Cr       | Ca/Sr |                     |            |                 |
| 1                | C/S                           | C/S         | C/S   | 40                  | Y          | <b>C/S</b>      |
| 2                | C/S                           | C/S         | C/S   | 39                  | Y          | <b>C/S</b>      |
| 3                | C/S                           | C/S         | C/S   | 36                  | Y          | <b>C/S</b>      |
| 4                | Tr.                           | Tr. or Sil. | Tr.   | -                   | N          | <b>C/S + R</b>  |
| 5                | Tr.                           | C/S         | Tr.   | 74                  | Y          | <b>C/S + G</b>  |
| 6                | Tr.                           | C/S         | Tr.   | 55                  | Y          | <b>C/S + G</b>  |
| 7                | C/S                           | C/S         | C/S   | 52                  | Y          | <b>C/S</b>      |
| 8                | C/S                           | C/S         | C/S   | 15                  | Y          | <b>C/S</b>      |
| 9                | C/S                           | C/S         | C/S   | 32                  | Y          | <b>C/S</b>      |
| 10               | Tr.                           | Tr. or Sil. | Tr.   | 58                  | Y          | <b>Tr.</b>      |
| 11               | Sil.                          | Tr. or Sil. | MO    | 138                 | Y          | <b>G</b>        |
| 12               | Sil.                          | Sil.        | MO    | 89                  | N          | <b>G</b>        |
| 13               | Sil.                          | Sil.        | MO    | 88                  | N          | <b>G</b>        |
| 14               | -                             | -           | MO    | 79                  | N          | <b>G</b>        |
| 15               | C/S                           | C/S         | C/S   | 38                  | Y          | <b>C/S</b>      |
| 16               | MO                            | MO          | C/S   | 36                  | Y          | <b>C/S + MO</b> |
| 17               | C/S                           | C/S         | C/S   | 25                  | Y          | <b>C/S</b>      |
| 18               | Sil.                          | -           | Sil.  | -                   | N          | <b>R</b>        |
| 19               | -                             | -           | Sil.  | -                   | N          | <b>R</b>        |
| 20               | -                             | -           | -     | -                   | N          | <b>R</b>        |
| 21               | Tr.                           | Tr. or Sil. | Tr.   | -                   | Y          | <b>Tr.</b>      |
| 22               | C/S                           | C/S         | C/S   | 30                  | Y          | <b>C/S</b>      |
| 23               | C/S                           | C/S         | C/S   | 55                  | Y          | <b>C/S</b>      |
| 24               | C/S                           | C/S         | C/S   | 34                  | Y          | <b>C/S</b>      |
| 25               | C/S                           | C/S         | C/S   | 37                  | Y          | <b>C/S</b>      |
| 26               | C/S                           | C/S         | C/S   | 39                  | Y          | <b>C/S</b>      |
| 27               | C/S                           | C/S         | C/S   | 40                  | Y          | <b>C/S</b>      |
| 28               | Tr.                           | -           | Tr.   | 71                  | Y          | <b>Tr.</b>      |
| 29               | Sil.                          | -           | Sil.  | 56                  | N          | <b>G</b>        |
| 30               | Sil.                          | -           | Sil.  | 68                  | Y          | <b>G</b>        |
| 31               | Sil.                          | Sil.        | Sil.  | 71                  | Y          | <b>G</b>        |
| 32               | Sil.                          | Sil.        | Sil.  | 69                  | Y          | <b>G</b>        |
| 33               | Sil.                          | Sil.        | Sil.  | 66                  | Y          | <b>G</b>        |
| 34               | Sil.                          | -           | Sil.  | 63                  | Y          | <b>G</b>        |
| 35               | -                             | Sil.        | Sil.  | 48                  | Y          | <b>G</b>        |

Table 5.4: Detailed phase information obtained for all 35 replicate analyses of Track A on sample SB1. C/S: cement and sand mixture; Tr: transition; Sil: silicate; MO: mixed oxide; G: grey aggregate; R: round aggregate. Boron concentration in  $\mu\text{g.g}^{-1}$  obtained from laser data. La/U ratio: Y for valid ratio, N for invalid ratio.

To explain some of the reasoning behind the choices made for the final phase determination, some examples are detailed below. In general, the information from the ratio plots is most useful from the Fe/Mn and Ca/Sr ratios. The remaining Fe/Cr, since it is relatively less resolved, is used to confirm the selection of a particular phase rather than determining it. As the boron concentration and La/U ratio have not been characterised previously in the cement and sand mixture, it is not possible to use the information in the case of a C/S phase. Therefore if all three agree on C/S phase, the result is accepted (namely replicates 1-3, 7-9 and 22-27). In the instance some of the information suggests a transition phase, though it only shows on a few replicates without confirming the change of phase, the result is accepted as C/S phase with potentially a relatively more important contribution from a specific aggregate (large sand type). To identify the nature of the aggregate, the boron and La/U information is used. Therefore replicates 4, 5 and 6 are respectively assigned a round, grey and grey aggregate. Replicates showing correlation to a silicate aggregate also are segregated on the boron and La/U data, such as replicates 11-14 and 29-35 are identified as grey, mainly due to the high and consistent boron data, and replicates 18-20 as a round aggregate. In most cases, a 'transition' replicate exists between these phase changes, collecting chemistry from both matrices, although the change can take place close to the boundary and does not reflect in the replicate sequence (example between replicate 14 and 15. Finally, replicates 15 to 17 show mostly C/S information, although a high Fe signal typical of mixed oxide aggregate is measured, therefore the final phase is marked as C/S with potentially a small mixed oxide aggregate included.

For the results obtained for Track B, given in Table 5.5, the results from the Fe/Cr plot are again for information only. Applying the same reasoning as for Track A, the presence of a larger mixed oxide aggregate is deducted. An additional information on this comes from a relatively lower La/U ratio in the mixed oxide, namely  $<10\mu\text{g.g}^{-1}$  in almost all cases.

To test both sequence of the final phases chosen for track A and B, the actual respective ablation track is shown with relevant chemistry changes occurring at each replicate analysis. The sequence is added for comparison. Figure 5.26 and 5.27 show the results for Track A and B respectively.

| Replicate number | Chemical discrimination plots |             |             | Boron concentration | La/U ratio | Final phase    |
|------------------|-------------------------------|-------------|-------------|---------------------|------------|----------------|
|                  | Fe/Mn                         | Fe/Cr       | Ca/Sr       |                     |            |                |
| 1                | C/S                           | C/S or MO   | C/S         | 23                  | Y          | <b>C/S</b>     |
| 2                | Tr.                           | C/S or MO   | Sil.        | -                   | N          | <b>R</b>       |
| 3                | Sil.                          | -           | -           | -                   | N          | <b>R</b>       |
| 4                | Sil.                          | Sil.        | Sil.        | -                   | N          | <b>R</b>       |
| 5                | C/S or Tr.                    | Sil. or Tr. | C/S         | 12                  | Y          | <b>Tr.</b>     |
| 6                | C/S                           | C/S or MO   | C/S         | 30                  | Y          | <b>C/S</b>     |
| 7                | C/S                           | C/S or MO   | C/S         | 34                  | Y          | <b>C/S</b>     |
| 8                | Sil.                          | Sil.        | Sil. or Tr. | 78                  | N          | <b>G</b>       |
| 9                | -                             | -           | Sil. or Tr. | 54                  | Y          | <b>G</b>       |
| 10               | C/S or Tr.                    | Sil. or Tr. | C/S         | 33                  | Y          | <b>Tr.</b>     |
| 11               | C/S or Tr.                    | Sil. or Tr. | C/S         | 18                  | Y          | <b>C/S + R</b> |
| 12               | C/S                           | C/S or MO   | C/S         | 30                  | Y          | <b>C/S</b>     |
| 13               | C/S                           | C/S or MO   | C/S         | 52                  | Y          | <b>C/S</b>     |
| 14               | C/S or Tr.                    | C/S or MO   | C/S         | 37                  | Y          | <b>C/S</b>     |
| 15               | Tr.                           | C/S or MO   | C/S         | 18                  | Y          | <b>Tr.</b>     |
| 16               | MO                            | C/S or MO   | Tr.         | 5                   | Y          | <b>MO</b>      |
| 17               | MO                            | C/S or MO   | MO          | 8                   | Y          | <b>MO</b>      |
| 18               | MO                            | C/S or MO   | MO          | 7                   | Y          | <b>MO</b>      |
| 19               | MO                            | C/S or MO   | MO          | -                   | Y          | <b>MO</b>      |
| 20               | MO                            | C/S or MO   | MO          | 11                  | Y          | <b>MO</b>      |
| 21               | Tr.                           | C/S or MO   | C/S         | 24                  | Y          | <b>Tr.</b>     |
| 22               | C/S                           | C/S or MO   | C/S         | 32                  | Y          | <b>C/S</b>     |
| 23               | Sil.                          | Sil.        | Tr.         | -                   | Y          | <b>R</b>       |
| 24               | C/S or Tr.                    | Sil. or Tr. | Tr.         | 6                   | Y          | <b>Tr.</b>     |
| 25               | C/S or Tr.                    | Sil. or Tr. | C/S         | 12                  | Y          | <b>C/S + R</b> |
| 26               | Tr.                           | C/S or MO   | C/S         | 73                  | Y          | <b>C/S</b>     |
| 27               | C/S                           | C/S or MO   | C/S         | 33                  | Y          | <b>C/S</b>     |
| 28               | C/S                           | C/S or MO   | C/S         | 27                  | Y          | <b>C/S</b>     |
| 29               | Sil.                          | -           | Sil. or Tr. | -                   | N          | <b>R</b>       |
| 30               | C/S                           | C/S or MO   | C/S         | 34                  | Y          | <b>C/S</b>     |
| 31               | Tr.                           | C/S or MO   | C/S         | 59                  | Y          | <b>Tr.</b>     |
| 32               | MO                            | C/S or MO   | Tr.         | 4                   | Y          | <b>MO</b>      |
| 33               | MO                            | C/S or MO   | MO          | 9                   | Y          | <b>MO</b>      |
| 34               | MO                            | C/S or MO   | MO          | 3                   | Y          | <b>MO</b>      |
| 35               | MO                            | C/S or MO   | MO          | 3                   | Y          | <b>MO</b>      |

Table 5.5: Detailed phase information obtained for all 35 replicate analyses of Track B on sample SB1. Same description as for Table 5.4 applies.

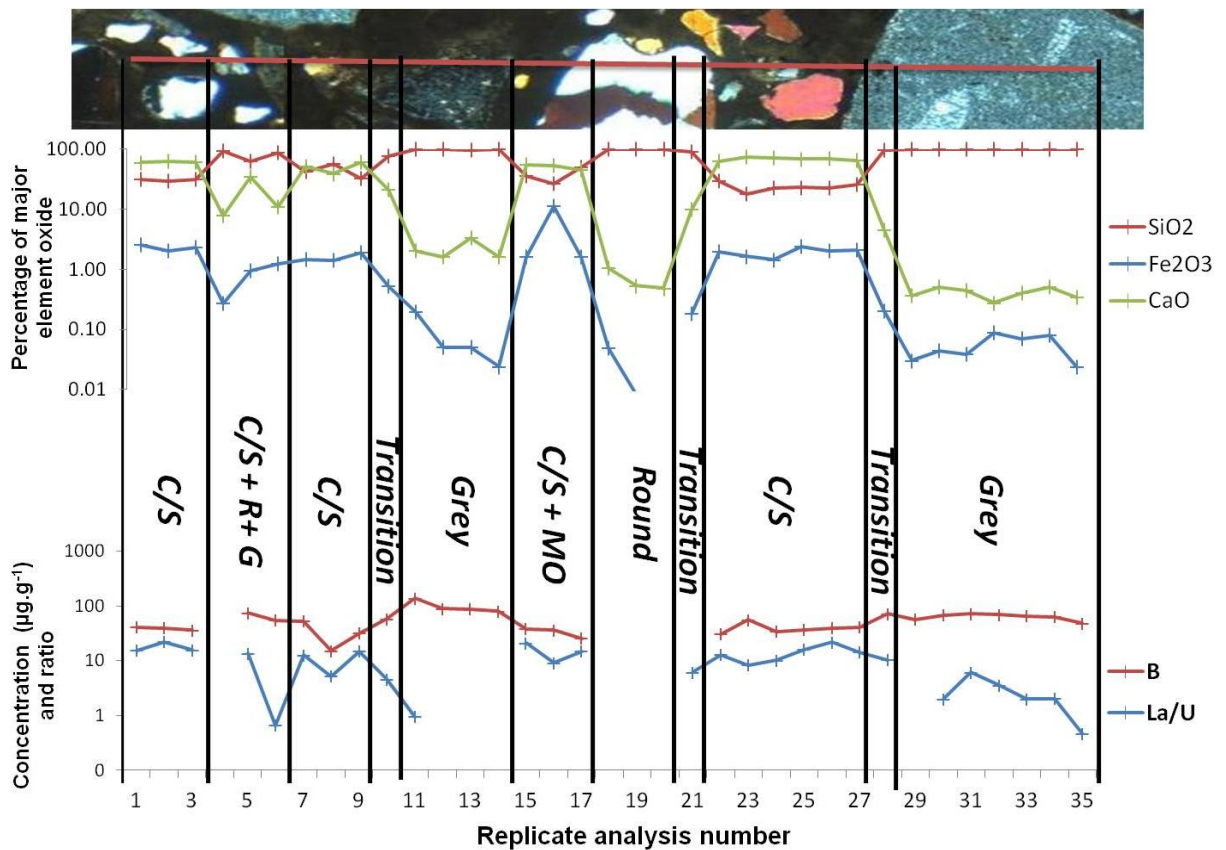


Figure 5.26: Sequence of replicate phases and visual and chemical observations for Track A. The red line represents the actual ablation track monitored. Top half lines represent major oxide composition changes for  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$ . The phase information in the middle is drawn from Table 5.4. Lower half represent boron concentration ( $\mu\text{g.g}^{-1}$ ) and La/U ratio values.

The comparison between the phase sequence exercise and the actual ablated material is in general in good agreement for Track A. Nevertheless, a couple of points are to be discussed. Replicates 15 to 17 are expected to contain a small MO aggregate due to a spike in the  $\text{Fe}_2\text{O}_3$  contribution observed. This is difficult to assess visually, as the laser track is indeed crossing over a very small aggregate, but with no other information its nature remains unknown. In most cases aggregate of this size is related to the sand fraction and therefore assimilated to a quartz grain. In case the nature of this aggregate is correctly assessed based on chemistry, then the monitoring of chemical changes is very useful on including potentially important contributors to the overall chemistry. Another point is replicate 21 which corresponds to a transition in the sequence, but visually seems to be still part of the round aggregate ablated during replicates 18-20. A possible explanation is that the laser is sample beneath the aggregate into the C/S on the edge.

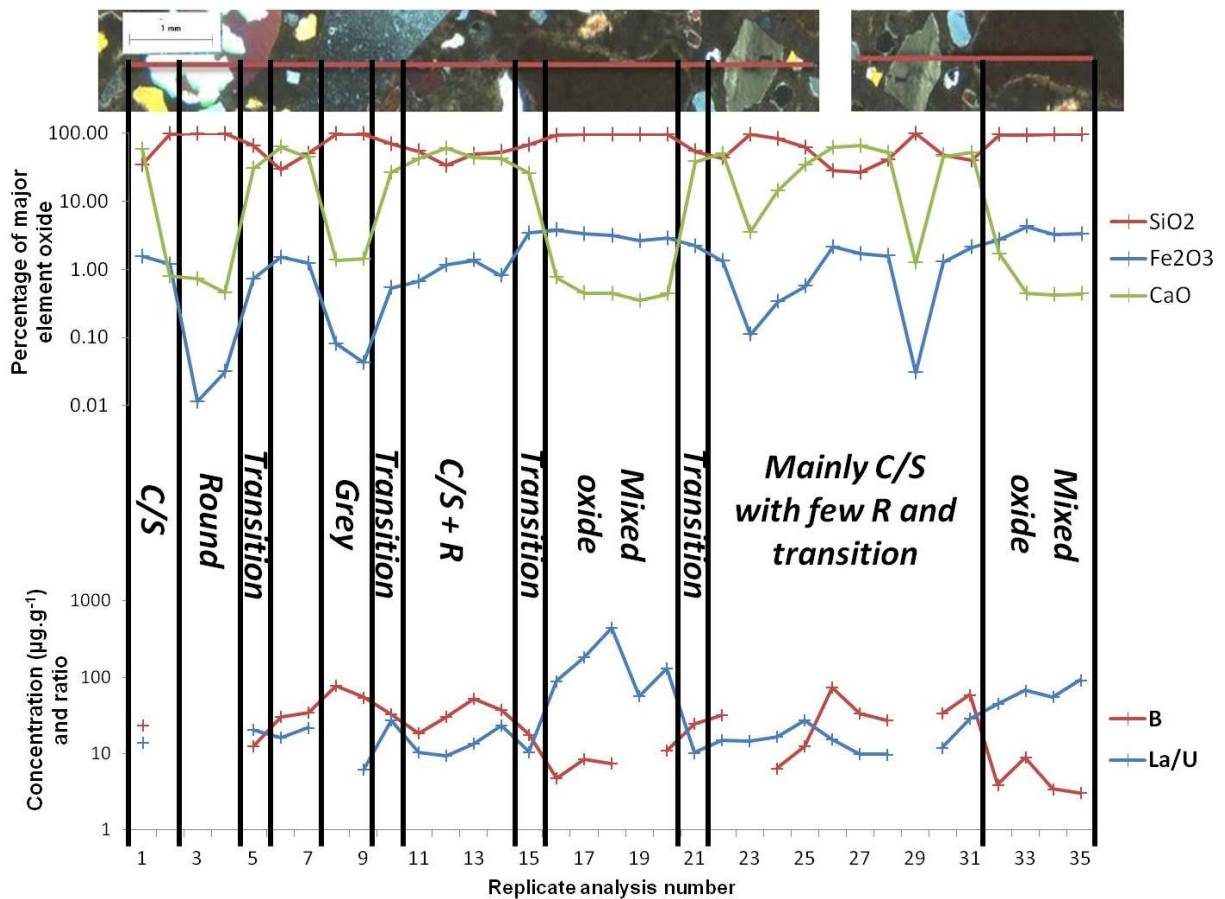


Figure 5.27: Sequence of replicate phases and visual and chemical observations for Track B. The area from replicate 22 to 31 is relatively variable and the phase sequence information is not detailed as such not to congest the diagram. The exact information is available in Table 5.5.

For Track B, the agreement is also relatively accurate, though some areas have changing chemistry for nearly each replicate, as shown by replicates 22 to 31, which increases the difficulty to accurately identify the ablated phase using the discrimination diagrams. Between these replicates, the monitoring of the major and trace elements sequence data accurately reflects the ablated phase, with a simultaneous decrease in CaO and Fe<sub>2</sub>O<sub>3</sub> and an increase in SiO<sub>2</sub> for a silicate (round) aggregate twice present. Another example is for Track A, between replicates 7 and 9, the relatively unsteady signal suggest the contribution of relatively larger sand aggregate.

## 6. Point counting exercise

This method is used to assess the overall bulk concrete chemistry of a sample based on its individual constituents group and the corresponding chemistry. The result can then be used to evaluate the total amount of the key stable isotopes present in a certain concrete structure. In this case sample SB1 is used as a test, since the majority of the aggregate

types present have been characterised. To perform the exercise, a detailed picture of specific area wide enough to be representative of the whole concrete is selected, and partitioned in relatively small squares. Subsequently one or more (if deemed necessary and more accurate) of the specific concrete components, for example round, grey aggregate or cement and sand mixture, is attributed to each square. Finally the total chemistry for each element is proportionally added using the fraction of each constituent present. For example if the concrete is made of 50% silicates (100%  $\text{SiO}_2$ ) and 50% calcium carbonate (100%  $\text{CaCO}_3$ ), then the final major element oxides composition is 50%  $\text{SiO}_2$ , 28%  $\text{CaO}$  and 22%  $\text{CO}_2$ , since  $\text{CaO}$  is 56% and  $\text{CO}_2$  44% of  $\text{CaCO}_3$ , and both are present at half (50%) the total amount in the concrete. Figure 5.28 shows the area of SB1 used and the relevant squares to be processed.

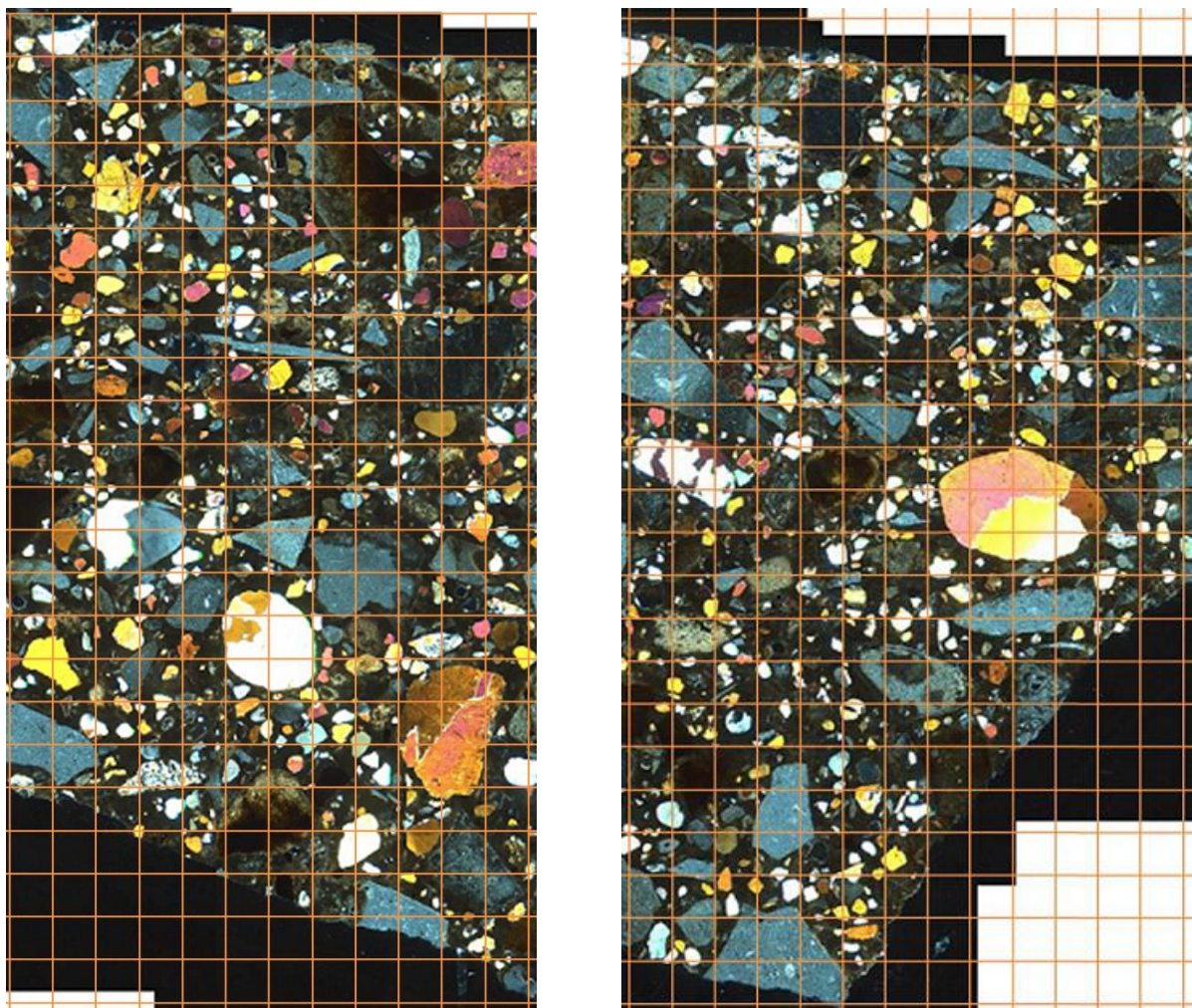


Figure 5.28: Sections of sample SB1 considered for point counting exercise. Most aggregates present have been characterised to be either round, grey or mixed oxides. First section (left) is made of 23 high and 12 wide squares, second section is 23 high by 13 wide.

Detailed results of the phases assigned to each square are given in Appendix 5 (different orientation). A summary of the proportion of each phase and totals is given in Table 5.6.

| Phase     |                         | Silicates |      | Mixed oxides | Cement and sand | Total |
|-----------|-------------------------|-----------|------|--------------|-----------------|-------|
|           |                         | Round     | Grey |              |                 |       |
| Section 1 | Counts                  | 29.5      | 22.5 | 14.5         | 165             | 231.5 |
|           | Proportion of total (%) | 12.7      | 9.7  | 6.3          | 71.3            | 100   |
| Section 2 | Counts                  | 24.5      | 32.5 | 12.5         | 167             | 236.5 |
|           | Proportion of total (%) | 10.4      | 13.7 | 5.3          | 70.6            | 100   |

Table 5.6: Summary of data obtained for the point counting exercise of the two sections of sample SB1. Results are not whole numbers as in some cases the phases present in one square are of different types, therefore half a count each for accuracy purposes.

From Table 5.6, it is possible to see that the total counts of each section are very similar and therefore comparable in proportions. Cement and sand mixture represent in both case the majority of the areas surveyed, with 71.3 and 70.6% of the total concrete respectively. Nevertheless slight differences appear for the remaining components. The influence of this variation will be assessed by comparing the final chemistry of the bulk concrete for both sections individually and together against bulk digestion data measured.

To assign a typical chemistry to each concrete component, solution data were obtained from digestion of representative aggregates and cement and sand mixture. Unfortunately the most abundant component, namely cement and sand mixture, was very difficult to separate with confidence from small aggregates, and therefore only one preparation was performed. Table 5.7 shows a selection of chemistry for each component. As the aggregates are relatively small, in most cases below 0.2g in mass, only one type of digestion was performed with each aggregate.

| Aggregate type      | Number of analyses | Major elements (% oxide) |          |                                | Trace elements ( $\mu\text{g.g}^{-1}$ ) |        |         |         |          |          |
|---------------------|--------------------|--------------------------|----------|--------------------------------|-----------------------------------------|--------|---------|---------|----------|----------|
|                     |                    | SiO <sub>2</sub>         | CaO      | Fe <sub>2</sub> O <sub>3</sub> | Co                                      | Ni     | Ba      | La      | Eu       | U        |
| Silicate Round      | 5                  | ~100                     | ~0.1     | <LLD                           | 0.25                                    | 2.4    | 10.6    | 3.3     | 0.12     | 0.06     |
|                     | Range              | 99.8-100                 | N/A      | N/A                            | 0.1-0.6                                 | 0.1-4  | 0.7-20  | 0.2-14  | 0.01-0.4 | 0.01-0.2 |
| Silicate grey       | 13                 | 99.7                     | 0.3      | 0.2                            | 0.4                                     | 6.4    | 28      | 1.9     | 0.08     | 0.28     |
|                     | Range              | 99-100                   | 0.05-0.8 | N/A                            | 0.1-1                                   | 2.9-10 | 2.9-134 | 0.9-4.1 | 0.04-0.2 | 0.1-0.6  |
| Mixed oxide         | 8                  | 82.8                     | 3.4      | 12.4                           | 20.6                                    | 56.5   | 85      | 14.2    | 1.26     | 0.54     |
|                     | Range              | 72-97                    | 0.4-6.8  | 1.6-25                         | 2-40                                    | 7-127  | 36-255  | 4-34    | 0.4-2.3  | 0.2-1.1  |
| Iron oxide          | 1                  | 22.0                     | 1        | 74                             | 35                                      | 148    | 55      | 34      | 1.4      | 1.15     |
| Cement and sand mix | 1                  | 78.1                     | 19.1     | 0.8                            | 2.6                                     | 21.5   | 48.7    | 7.6     | 0.3      | 0.6      |

Table 5.7: Average wet chemistry results for representative aggregates of sample SB1.

Using the average chemistry available from Table 5.7, the contribution of each phase to the overall chemistry was assessed. To do this, the proportions calculated in Table 5.6 are used and the expected contribution from all phases to the bulk concrete chemistry determined. Finally a sample representative of the bulk composition of SB1 was also digested, and used to assess the point counting exercise to estimate the average chemical data to be found in sample SB1. Table 5.8 shows the results for each section and the bulk chemistry.

| Trace elements ( $\mu\text{g.g}^{-1}$ ) | Co   | Ni   | Ba   | La   | Eu   | U    |
|-----------------------------------------|------|------|------|------|------|------|
| Bulk concrete                           | 77.5 | 11.1 | 72.6 | 7.97 | 0.31 | 0.55 |
| Section 1                               | 3.33 | 20.5 | 43.9 | 7.06 | 0.32 | 0.50 |
| Recovery (%)                            | 4.3  | 185  | 60   | 89   | 103  | 91   |
| Section 2                               | 3.10 | 19.9 | 43.6 | 6.84 | 0.30 | 0.50 |
| Recovery (%)                            | 4.0  | 179  | 60   | 86   | 97   | 91   |

Table 5.8: Comparison between bulk chemistry and point counting exercise results for sample SB1.

Results from Table 5.8 show a mixture of agreements. For trace elements such as La, Eu, U and to some extent Ba, the recoveries obtained by the point counting exercise concur with the wet chemistry results of the bulk sample. On the contrary, cobalt results show a significantly low recovery (4%), and nickel a relatively higher recovery (179%) than expected. Concerning U, the variation in concentration between each component (Table 5.7) is relatively small, which is not likely to affect the overall bulk concentration to a great extent. For Eu and La, there is an order of magnitude between the lowest and highest concentration for the components part, though the extreme values represent the smallest contributors, namely round and mixed oxides aggregates. For all three elements, the bulk chemistry is reflected to a certain extent by the chemistry of the major contributor, in this case cement and sand mixture (measured as ~70% of area). On the other hand, elements such as nickel and cobalt are present at a greater range of concentrations. Therefore even a small difference in a minor contributor with significantly high or low concentration is affecting the final result.

## 7. Wet chemistry data

As part of the chapter, concentration data from wet chemistry were obtained for the range of concrete components investigated. Examples were given in Tables 5.3 and 5.7. From the Tables, it appears that with increasing iron content in the material, there is also an increase in important trace elements such as Co, Ni and possibly Eu and U. To evaluate this, the trace element results of the wet chemistry database were plotted against Fe content to identify any pattern and strength of correlation. Figure 5.29 shows these graphs. Overall there is a strong correlation between Fe and Co, Ni and Eu, but not with Ba or U. Cr shows average correlation.

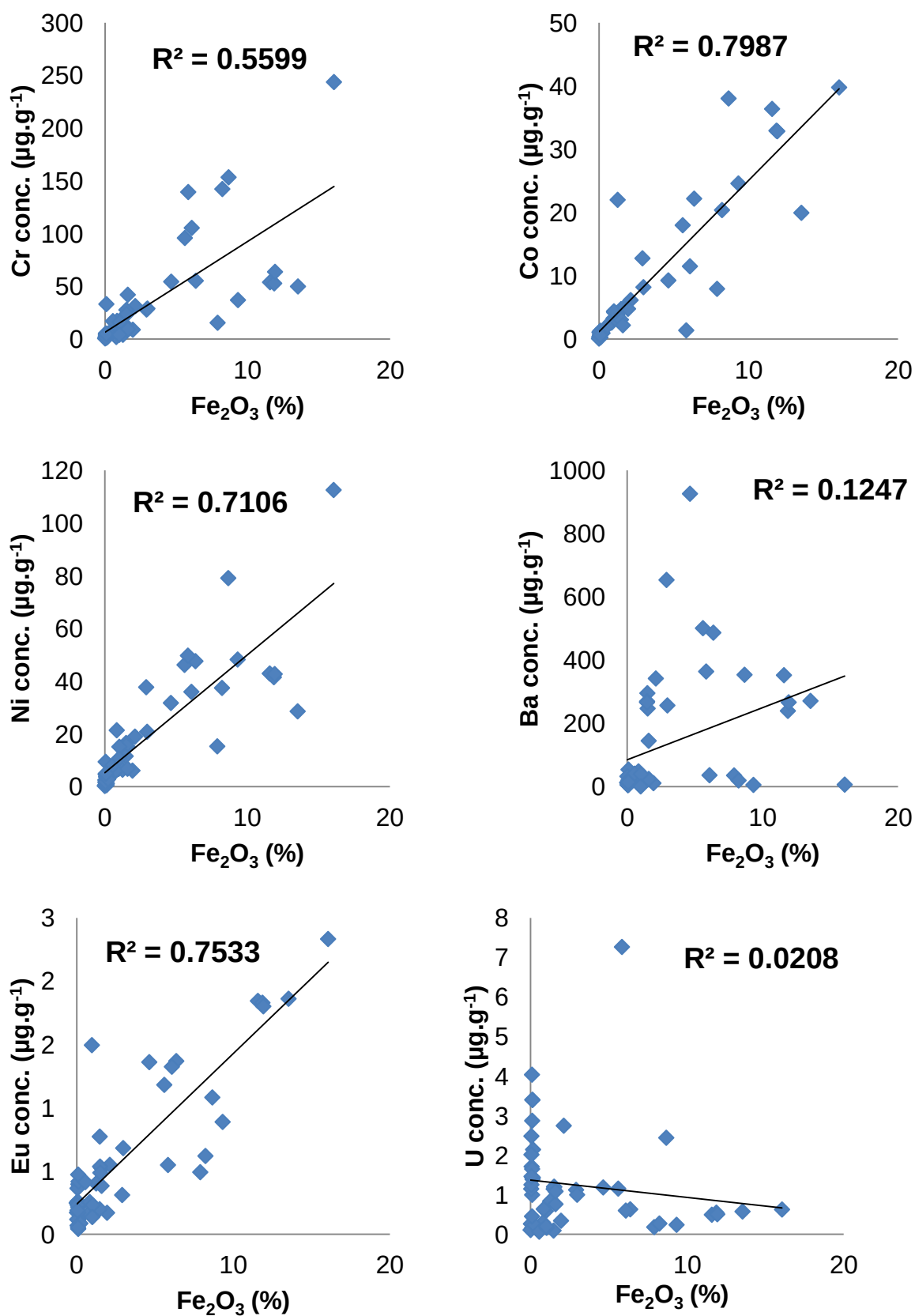


Figure 5.29: Correlation between  $\text{Fe}_2\text{O}_3$  concentration and important trace elements. Correlation factor  $R^2$  are given. All data include wet chemistry results for all individual components indiscriminately.

## 8. Conclusions

Concerning the characterisation of concrete constituents in any concrete, thin section imagery for samples investigated during the development work (SB1 and WP1) proved a helpful initial assessment. The variations in shapes, colours and transmitted polarised features identified a number of possible aggregate groups, with potentially different chemistry. Using NIST 610 glass as a one point calibration to obtain representative chemistry, a ternary phase diagram showing the three major components with the most variation (namely  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$ ) starts to separate groups from each other based on their major chemistry. Further investigation using a set of representative elements in discrimination diagrams and using data quality helps differentiate aggregates with similar major chemistry. The discrimination is based on major and trace elements with chemical similarities but present at wide concentration ranges. This enabled to set specific properties to identify the nature of aggregates with variable physical and optical properties. The same set of parameters was tested on a blind ablation run, and the collected chemistry used to draw the sequence of phases encountered. Results showed in general good agreement with actual ablated phases, with a few misjudgements. Nevertheless, monitoring in the variations in the major composition of  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  together with boron concentration and La/U ratio enables a similar if not better fit with the visual track.

The point counting exercise over the two sections shows only small differences in the proportion of each component. One feature that is not accounted for is that the cement and sand mixture is a relatively porous material, and there will be a difference between the point counting proportions and the actual true composition of crushed concrete, as the air spaces are no more included. Also the average chemistry of component groups such as the mixed oxide is produced from a relatively wider range of values for the number of wet chemistry results defining the group. The accuracy of the average values may benefit from further data.

## CHAPTER VI: TRITIUM DETERMINATION BY MASS SPECTROMETRY

### 1. Tritium levels in waste materials

The levels of tritium expected in waste material from nuclear reactors can vary significantly, depending on the size and history of the installation, as well as the chemistry of the shielding component. Several tritium concentrations have been reported and are presented in Table 6.1

| Waste type            | $^3\text{H}$ levels<br>(MBq.kg <sup>-1</sup> ) | Source                                    |
|-----------------------|------------------------------------------------|-------------------------------------------|
| Metal                 | 2.0                                            | Kim <i>et al.</i> , 2011                  |
| Shielding<br>concrete | 0.4<br>6                                       | Hou, 2005<br>Kim, 2007                    |
| Graphite<br>moderator | 10-10 <sup>3</sup><br>5-10 <sup>4</sup>        | Bushuev <i>et al.</i> , 1992<br>Hou, 2005 |
| Heavy water           | 1-3 x10 <sup>5</sup>                           | Hou, 2007                                 |

Table 6.1: Tritium levels measured in nuclear waste materials. Values represent maximums reported.

For the tritium in shielding concretes, the measured activities are from a Danish research reactor (DR-2, Hou 2005) and a steam generating heavy water reactor at Winfrith, U.K., working at 100MW (Kim, 2007). Both are relatively unusual compared with commercial facilities running at a power of several hundred megawatt equivalent, and therefore the expected tritium levels in these can vary.

### 2. Conventional tritium analysis techniques

#### 2.1 Oxidation techniques and measurement

##### 2.1.1 Wet oxidation using chemicals

This method involves a cocktail of chemicals, including acids, to decompose the sample and oxidise the tritium to form tritiated water (HTO). This method is for example used at the Centre for Environment, Fisheries & Aquaculture Science (CEFAS) for their routine monitoring of marine biota and sediment samples for the annual RIFE report (Radioactivity In

Food and the Environment). The sample oxidation is performed using chromic acid (a mixture of potassium dichromate, sulphuric acid and phosphoric acid) which decompose organic sample into water and carbon dioxide. At the end of the digestion process, a small quantity of de-ionised water is added to increase the digest volume. The water and HTO mixture is then distilled into a cold trap, and subsequently aliquots taken to measure tritium levels by liquid scintillation counting (LSC). To be able to distinguish between free HTO and organically bound tritium (OBT), each sample is oxidised as wet and dry sample, the difference between the two corresponding to the free HTO released during the drying process (McCubbin *et al.*, 2001). This method requires relatively large laboratory space and is time-consuming, and also uses hazardous chemicals, with each sample analysed wet and dry.

#### 2.1.2 Combustion furnace

A recent development in the process of sample oxidation uses a tube combustion furnace. The device consists of a furnace unit, able to apply different temperature profiles up to about 1,000°C, with a constant air or oxygen-enriched air flow passing through a certain number of parallel tubes. The sample is placed on a boat-type sample holder and placed inside the tubes. As the temperature increases, the sample decomposes, and the oxidation products pass over a catalyst bed to fully convert any gas mixtures to HTO and CO<sub>2</sub>. The HTO is finally trapped via a bubbler and analysed by LSC. This method has become the routine analysis technique for tritium determination in terrestrial foodstuff (milk and crops) by the Veterinary Laboratories Agency (Lockyer and Lally, 1993). It has also been applied to the nuclear industry, on waste materials generated during nuclear decommissioning (Warwick *et al.*, 2010). The materials analysed by the technique included irradiated steel and graphite, structural (exposed) and shielding (irradiated) concrete and bricks. Using carefully selected temperature profiles, it is also possible to assess the form of the tritium present in a sample such as shielding concrete, as demonstrated in Kim *et al.* (2008), where adsorbed HTO is released at low temperature (100°C) and strongly-bound tritium requires higher temperature (>350°C).

At the moment a typical furnace device can hold up to six tubes with samples and collect HTO. The temperature profiles applied depend on the sample of interest, and can vary from about 250 minutes up to 800 for one cycle. In some cases the possibility of memory effect has been observed (Warwick *et al.*, 2010). Therefore, including overnight quantification by LSC and instrumental purging, the sample turnover is estimated as a maximum of six in every 24H period, excluding any sample preparation time before combustion (drying and homogenisation).

### 2.1.3 Liquid scintillation counting measurements

The method is based on the interaction of radiation, mainly  $\alpha$  and low energy  $\beta$  emitters (e.g.  $^3\text{H}$  and  $^{14}\text{C}$ ), with certain materials, which cause the emission of a flash of light, subsequently detected. In liquid scintillation, an organic scintillator (also called scintillant) is mixed with a solvent (toluene and p-xylene) and the dissolved sample to analyse, all three forming the scintillation cocktail. Another compound such as dioxane can be used to facilitate the mixing of aqueous analyte samples into the organic solvent. The whole mixture is contained in a small glass vial. The decay energy produced by the radioelement is likely to be absorbed by the solvent and then passed onto the scintillator which emits a photon that can be detected. In case the photon is of too high energy, the addition of a wavelength shifter is required, absorbing the higher energy photon to re-emit another at lower energy, finally measured by the photomultiplier tube. The photons impact with a special coating in the tube, generating an electric signal that is amplified to convert into a small measurable current, proportional to the number of photons produced by the scintillation cocktail. The counting efficiency depends on the decay energy of the analyte of interest, and also some chemicals can interfere and absorb the photons emitted, reducing the signal measured. By adding a known activity of the analyte (standard addition method), the counting efficiency can be calculated to correct the data (Ehman and Vance, 1991).

## 2.2 Accelerator mass spectrometry

### 2.2.1 Principle

The basic principles of the technique are that low energy negative ions are formed (usually by means of a Cs sputter source), subsequently injected in the first part of the accelerator, stripped of one or more electrons and re-accelerated in the second part of the tandem accelerator, emerging as high energy ions (in the order of MeV). Separation is done using magnets and detectors measure specific mass per charge ratios (Wacker *et al.*, 2010). Some of the advantages of AMS compared to other mass spectrometry techniques are that the initial formation of negative ions is in some cases a way of removing possible isobaric interferences (isotopes of the same mass but from different elements), as it is for  $^{14}\text{C}$ ,  $^{41}\text{Ca}$  and  $^{129}\text{I}$ , which form stable negative ions, and respective interferences  $^{14}\text{N}$ ,  $^{41}\text{K}$  and  $^{129}\text{Xe}$  don't. Also the stripping process, removing one or more electrons, can easily produce multiple positively charged ions, and in cases polyatomic species are present, these are very unstable and break up into individual components (Hou and Roos, 2008). Detection limits are usually reported as the ratio of the isotope of interest over the most abundant stable isotope (e. g.  $^{14}\text{C}/^{12}\text{C}$  or  $^{41}\text{Ca}/^{40}\text{Ca}$ ). The very low background capabilities of the instrumentation

enable limits of detection in the order of less than  $\text{fg.g}^{-1}$  ( $10^{-15}$ ) for most isotopes (Wacker *et al.*, 2010).

### 2.2.2 Applications

In 1977, Muller developed a new way for radioisotope dating technique by using a cyclotron as a high energy mass spectrometer to measure the quantity of isotopes present rather than based on their decay characteristic. This method was originally identified as powerful for elements with low mass number, and especially good for radionuclides with long half-lives and smaller decay rates, which can require large amounts of valuable sample to be used and/or longer counting times by the conventional decay counting. Therefore  $^{10}\text{B}$ ,  $^{14}\text{C}$  and also  $^3\text{H}$  were targets for cyclotron radioisotopes dating, although, in theory, the detection of heavier nuclides ( $^{26}\text{Al}$ ,  $^{53}\text{Mn}$  and  $^{205}\text{Pb}$ ) is possible.

For tritium determination, which was also the experiment attempted by Muller at the time, the instrumentation was set to measure alternatively the tritium isotope and a stable isotope, here deuterium, for normalisation purposes, and the ratio of the two is the parameter of interest. Figures of merit included the detection level capability of  $10^{-16}$  or above, with very little to virtually no background from isobaric interferences for several isotopes (e. g.  $^3\text{He}$  and  $^1\text{H}^2\text{H}$  for  $^3\text{H}$ ).

After the first application, the trend was, as detailed in Suter (2004), to work towards improvement of the technology (ion sources, accelerators and detectors) to develop smaller AMS systems, reducing the costs and space requirements, but still able to measure a wide range of relevant isotopes including  $^{41}\text{Ca}$ ,  $^{129}\text{I}$ ,  $^{236}\text{U}$  and Pu isotopes. Many of the new developments were focussed on the radiocarbon dating (Suter *et al.*, 2000), and between 1996 and 1999, 16 new facilities were in operation, under construction or planned, with 13 of them concentrating on  $^{14}\text{C}$  determination and only one facility (Lawrence Livermore, USA) focussing on  $^3\text{H}$  analysis in biomedical and environmental samples (Fifield, 2000).

The main hurdles for tritium analysis are that natural levels are very low, and the required sample preparation is difficult (Jull and Burr, 2006). The applicability of AMS to further  $^3\text{H}$  analysis was nevertheless investigated, and pioneering work was established by Friedrich *et al.* (1997 and 2000), who used AMS for depth-profile analysis of  $^3\text{H}$  in graphite samples from the walls of fusion reactor vessels. The detection limit was about  $10^{11} \text{ atoms.cm}^{-3}$ , with depth resolution at the micrometer scale. The technique was later perfected and routine analysis of tritium in carbon samples from fusion experiments established (Friedrich *et al.*, 2004). At the same time, research was being done on pursuing the application of AMS to the biomedical

field. Roberts *et al.* (2000) developed such a small size AMS dedicated to  $^3\text{H}$  analysis for the biomedical and environmental sector. The sample size required and the time to perform an analysis were reduced, and preliminary work estimated potential improvement of detection limits by a factor of 100 to 1,000 compared to scintillation counting for a relatively cheaper investment (\$750,000 quoted) for AMS systems available at the time. Also Hughey *et al.* (2000) looked at the possibility to perform on-line analysis of  $^3\text{H}$  and  $^{14}\text{C}$  for biological samples, using an AMS as a detection system in conjunction with a gas chromatograph (GC) for the sample separation and injection as  $\text{CO}_2$ . This was later confirmed by the same research group (Skipper *et al.*, 2004), as well as the use of an HPLC introduction system. They also developed a combustion reactor-type introduction system for the analysis of  $^3\text{H}$  in He gas. The tritium sample is injected as tritiated water (HTO, reacts to form HT and  $\text{H}_2$ ) or tritium gas (HT)

## 2.3 $^3\text{He}$ ingrowth method

### 2.3.1 Principle

This method was first mentioned in Kugler and Clarke (1972), and later described by Clarke *et al.* in 1976. It consists of the measurement of the decay product of  $^3\text{H}$ ,  $^3\text{He}$ , by mass spectrometry. The water sample of interest is first completely degassed, before it is sealed and left to accumulate the so-called tritiogenic  $^3\text{He}$  over several months. The technique was first established to improve the determination of  $^3\text{He}/^4\text{He}$  ratio in water samples, with the original application to be used in shallow groundwater to investigate the presence of uranium and thorium ore deposits (Clarke and Kluger, 1973).

### 2.3.2 Applications

In a technical report from the IAEA (1981), entitled “Low-level tritium measurement”, the latest performances and facts and figures for low-level tritium measurement techniques used by different groups were presented. The  $\beta$ -decay counting techniques by conventional liquid scintillation counting or gas counting, with possible enrichment step, were compared to the growing  $^3\text{He}$  ingrowth method. At this stage, the simplicity of sample handling, and the fewer steps in preparation and analysis required, as well as comparable detection limits and better precision in the results highlighted the potential future of the ingrowth technique. Since then it has been used for many applications, for example to measure tritium levels close to nuclear facilities (Jean-Baptiste *et al.*, 2007), OBT in grass (Jean-Baptiste *et al.*, 2010), tritium levels in polar caps (Fourré *et al.*, 2006), cosmogenic tritium production rates (Brown *et al.*, 2000), and especially for its use in  $^3\text{H}/^3\text{He}$  water dating method, detailed in Cook and Solomon

(1997) and Kazemi *et al.* (2006). Here tritium is used as a tracer to investigate the hydrological cycle, looking at seawater circulation in oceanography (Schlosser *et al.*, 1995; Wallace *et al.*, 1993), groundwater age (McArthur *et al.*, 2010), cave drip water age (Kluge *et al.*, 2010) to name a few examples. Moreover the mass spectrometry instrumentation also improved for better determinations: Jean-Baptiste *et al.* (2010) report detection limit of  $0.15\text{Bq.kg}^{-1}$  for routine analysis of 20g of water sample stored for three months.

### 3. ICP-MS issues for tritium analysis

#### 3.1 Interferences

There are three types of spectral interferences in ICP-MS, namely isobaric, doubly charged ion and polyatomic ion. Polyatomic interferences are more common in the lower part of the mass spectrum and therefore heavy elements are less prone (but not immune) to interferences. The three categories are assessed in terms of interfering at  $m/z$  three.

##### 3.1.1 Isobaric

Isobaric interferences are a result of isotopes from different elements present at the same mass unit. Here for  $m/z$  three, there is a naturally occurring isotope of He, with an abundance of  $<0.0002\%$  (Emsley, 1998). In most cases this isotope is disregarded because of its very low abundance, and helium is usually referred to as mono-isotopic at  $m/z$  four. In this case here, it may be of greater importance as  $^3\text{He}$  is the decay product of  $^3\text{H}$  (by  $\beta^-$  decay radiation). Nonetheless He has a significantly higher ionisation potential than Ar, with 24.59eV compared to 15.76eV, and therefore does not produce ions in the argon plasma and is not considered further as a potential interference.

##### 3.1.2 Doubly charged ions

For doubly charged interferences (two electrons lost), the interest is at mass six for tritium applications, and also mass five and seven when using a quadrupole instrument, as the doubly charged ions centred at  $m/z$  two and half and three and a half respectively have the potential to overlap on  $m/z$  three with their peak tails. There is no element isotope at mass five, and Li is present at six and seven. The first ionisation potential for Li is 5.39eV, well below Ar, but the second ionisation potential is 75.64eV, meaning it is impossible to form doubly charged Li.

### 3.1.3 Polyatomic species

In general polyatomic species contain two atoms, in some cases three if the affinity between them is significant. Reports in the literature (For example H, being a relatively very small atom, is easier to combine with a further two other atoms to form a tri-atomic interference. Therefore, based on natural occurrence of  $^1\text{H}$  (~99.98%) and  $^2\text{H}$  (~0.02%), two polyatomic species are likely, namely  $^1\text{H}_3$  and  $^1\text{H}_1^2\text{H}_1$ . Reports in the literature (Wing *et al.*, 1976) indicate that gas phase reactions between  $\text{H}_2^+$  and  $\text{H}_2$  result in the production of  $\text{H}_3^+$  and H in thermal plasma keeping  $\text{H}_2^+$  concentrations low. It was also noted by Hirschfelder (1936) that triatomic hydrogen ions ( $\text{H}_3^+$ ) are formed in significant quantities whenever H gas is ionised. Therefore it is likely that the dominant interference at  $m/z$  three is the triatomic hydrogen ion,  $\text{H}_3^+$ .

### 3.2 Mass resolution

Quadrupole ICP-MS instruments operate with single mass unit resolution; therefore at  $3m/z$  the polyatomic interference and the tritium cannot be separated. An instrumental scan will show a unique peak made of both potential tritium ions and interfering  $^1\text{H}_3$  ions. One solution to consider is the use of a sector field instrument, which opens the possibility to resolve or separate the analyte of interest from the overlapping interference. A substantial review of the technique is given by Jakubowski and co-workers (1998) and a summary given below.

The sector field instrument uses a combination of magnetic and electric fields to separate ions with relatively small mass differences between them. The resolution required depends mainly on the mass difference, but also on the intensity of the analyte and interference peak. A definition of mass resolution is that a valley of 10% is achieved between two neighbouring peaks of equal intensity at mass  $m$  and  $m + \Delta m$ . The required resolution is usually defined as the nominal mass of interest ( $m$ ), over the mass difference between the analyte of interest and the interference ( $m_1 - m_2$ , or  $\Delta m$ ) to separate the two as described in Jakubowski *et al.*, 1998 (Equation 6.1).

$$\text{Resolution} = \frac{m}{\Delta m} \quad (\text{Equation 6.1})$$

For example,  $^{56}\text{Fe}$  has a molecular mass of 55.93494 amu and its predominant interference  $^{40}\text{Ar}^{16}\text{O}$  has a mass of  $39.96238 (^{40}\text{Ar}) + 15.99491 (^{16}\text{O}) = 55.95729$ . The difference between the two peaks is therefore 0.02235 amu. The resolution needed to efficiently resolve the two peaks is 2,500, based on Equation 6.1.

Most sector field instruments can achieve resolutions from about 300-400 up to 8,000 or 12,000. Some instruments are able to perform continuous resolution changes over these ranges, others have the possibility to select set resolution levels (low, medium and high). The trade-off with the increase in resolution is that the ion signal decreases and results in lower sensitivity. Nevertheless the instrumentation set at low resolution generally has a higher sensitivity compared to conventional quadrupole ICP-MS firstly because of better ion transmission, with large acceleration of the ion beam and enhanced ion optics, and lower ion losses due to for example the absence of a photon stop in the pass of the ion beam, which is more common for quadrupoles. It also has very low background and values of 0.1cps have been reported at low resolution (Jakubowski *et al.*, 1998).

One important factor is that considering continuous resolution and based on Equation 6.1, the peak width increases with mass. Therefore for a 300 resolution, the peak width at 6m/z is about 0.02 amu and at 238m/z it is about 0.8 amu.

In the case of tritium and its polyatomic interference, Table 6.2 shows the exact masses of both and the required resolution. In theory, resolving tritium from its interference is possible and requires only a relatively low resolution, which means that minimal loss in signal is likely to be observed and therefore relatively good detection limits are achievable.

| Interference   | mass    | $\Delta m$ | Resolution |
|----------------|---------|------------|------------|
| $^3\text{H}_1$ | 3.01605 |            |            |
| $^1\text{H}_3$ | 3.02382 | 0.00777    | 388        |

Table 6.2: resolution required to separate tritium and the triatomic hydrogen interference (from Emsley, 1998).

### 3.3 Calibration

#### 3.3.1 Mass calibration

ICP-MS instrumentation is routinely used to measure peaks from 7-238 m/z. The mass range from 1-6 m/z is not normally measured except for an assessment of background at 5m/z where there are no elemental or gas peaks present. In normal operation a mass calibration is performed across the mass range of interest using selected elements. However, for the mass range of interest here, the lowest mass element which can normally be introduced is Li with isotopes at six and seven. The experiments in this work were performed in a non-active

laboratory where the use of tritium is not permitted. It is likely that there will be a bias between the measured peak centre and the expected peak centre based on the exact mass of the species of interest. Nevertheless, it is thought the position of each peak relative to each other will remain identical to calculated values, for example the difference between the  $^1\text{H}_3$  peak and the  $^3\text{H}_1$  peak is still 0.00777 amu. Therefore a correction has been applied to the mass range so that the peak centre of the measured peak corresponds to its exact mass.

### 3.3.2 Response calibration

To be able to quantify instrumental response for a given element, it is essential that a standard of known concentration is run as well as a blank sample, both matrix-matched (here 2%  $\text{HNO}_3$  v/v) with the unknown sample of interest. Therefore for tritium determination, the issue is that the use of a standard is not permitted. To be able to estimate the sensitivity of tritium, the response for  $^7\text{Li}$  is used and extrapolated to 3m/z. To do so, the signal measured for  $^7\text{Li}$  is corrected for ionisation potential (99.8%) and isotopic abundance (92.4%), then can be further corrected considering the mass response curve of the instrument used, and finally the ionisation potential (i.e. hydrogen, 0.4%) and isotopic abundance of tritium (100%) is applied to give an equivalent net response for a tritium standard based on  $^7\text{Li}$  standard signal. The Li standards used were  $10\text{ng.ml}^{-1}$  for quadrupole ICP-MS and  $1\text{ng.ml}^{-1}$  for sector field ICP-MS, both in liquid mode of analysis, and NIST 610 glass for gas phase analysis using the laser ablation system. NIST 610 is a homogenous synthetic glass containing  $485\mu\text{g.g}^{-1}$  of Li. Finally the specific activity of tritium ( $3.63 \times 10^{14}\text{Bq.g}^{-1}$ ) is used to calculate an equivalent activity of the tritium concentrations obtained.

## 4. Quadrupole ICP-MS

### 4.1 Liquid mode

The background integration of the Li standard at 3m/z gives a value of  $\sim 38,000\text{cps}$ , using the  $^7\text{Li}$  signal, the equivalent BEC is approximately  $770\mu\text{g.l}^{-1}$  of tritium, or just short of  $280\text{GBq.kg}^{-1}$ . Three replicate measurements give a relative standard deviation of 0.2% of the mean value, equivalent to  $560\text{MBq}$ . The equivalent background concentration at 3m/z is very high in liquid mode, and therefore it is not possible to measure, with confidence, tritium-containing samples close to the exempt level of  $400\text{Bq.kg}^{-1}$  or the low-level waste limit of  $12\text{MBq.kg}^{-1}$ .

## 4.2 Gas mode

Solid samples usually undergo a dissolution step to be introduced as liquid samples into the ICP-MS instrument, in this case significantly contributing to the polyatomic interference at  $3m/z$  with increase in H from  $H_2O$  and  $HNO_3$  molecules present. One alternative sample introduction option is to sample directly the solid using a laser ablation system connected to the ICP. This will dramatically decrease the amounts of  $^1H$  into the plasma, reflecting only the content of the sample and some air entrainment.

Together with LA, another possible sample introduction method such as electro-thermal vaporisation has been used for lowering the matrix contribution to the background signal on other applications, but here the approach is very difficult to achieve as chemical behaviour of tritium is identical to that of hydrogen and will be removed in the same way.

## 4.3 Collision/reaction cell technology

### 4.3.1 Principle

Since the birth of ICP-MS, technical developments of the instrumentation improved its versatility. One recent development by all major manufacturing companies is the introduction of a chamber or small cell after the focusing lenses stack that can be filled with a gas that interacts with the beam of incoming ions. The specific name of this chamber depends on the manufacturer, but it is more or less based on the same main aim: removing interference from an analyte for detection limits improvement. The gas used in the chamber can work in two different ways, namely by colliding with the interference and lowering its kinetic energy to a point where it can be discriminated from the analyte, or by reacting in some form with the interference or the analyte. Thus the chamber is more often referred to as a collision/reaction cell, or CRC (Nelms, 2005).

The separation of the interference by collision is based on the size of the interference (mostly applicable to polyatomic species) and the analyte and the associated loss of kinetic energy from the collisions with the gas present in the chamber (for example an inert gas such as He). For example at  $m/z$  75, the  $^{40}Ar^{35}Cl$  polyatomic interference is larger in diameter than  $^{75}As$ , therefore the interference will collide more often than the analyte with the gas, losing relatively more kinetic energy, and the interference can then be filtered out from the analyte using carefully chosen instrumental settings. Figure 6.1 highlights the phenomenon described.

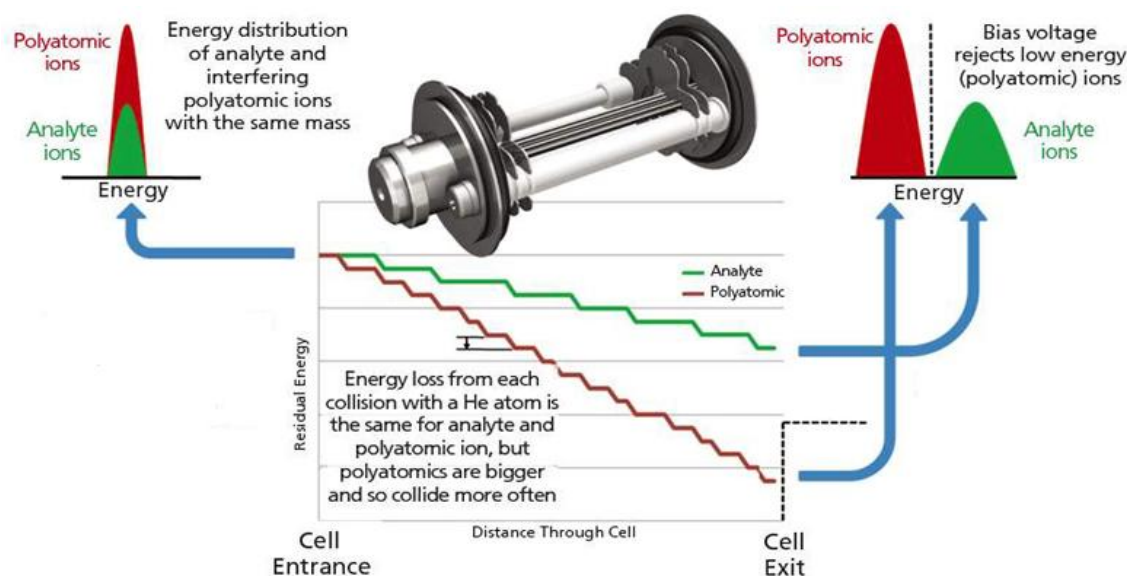


Figure 6.1: Schematic of the collision cell process with loss of kinetic energy (adapted from McCurdy *et al.*, 2010).

The second mode of use of the CRC, namely in reaction mode, has several possible mechanisms to address the problem. The processes can be broadly described as reaction of the interference with the gas, reaction of the analyte with the gas and finally the 'neutralisation' of the interference. The selective reaction of the interference with the reaction gas aims to shift the interference at a higher  $m/z$  value while the analyte remains at its original  $m/z$  value. In this case the reaction between the interference and the gas is promoted, such as, for example,  $\text{Ar}^+$  and  $\text{H}_2$  react to give  $\text{ArH}^+$  and  $\text{H}$ . Based on the same principle, it is also possible to react the analyte with the gas to move the new polyatomic molecule to a relatively background-free  $m/z$  value. For example, the reaction of  $\text{As}$  with  $\text{N}_2\text{O}$  or  $\text{O}_2$  to form  $\text{AsO}$ . Finally, the use of a reaction gas to neutralise the interference, where an electron is released from the gas and captured by the interference to become neutrally-charged and will not proceed through to the mass spectrometer. This is commonly used for  $\text{Ar}^+$  and  $\text{ArX}^+$  interferences (where  $\text{X}$  can be  $\text{H}$ ,  $\text{O}$ ,  $\text{N}$ ,  $\text{C}$ ,  $\text{Ar}$ , etc.) and the reaction gas  $\text{NH}_3$  or  $\text{CH}_4$  (Tanner *et al.*, 2002).

#### 4.3.2 Application of CRC technology to $^3\text{H}_1$ determination

##### 4.3.2. a) Interference removal using kinetic energy discrimination

Here the interest is to preferentially reduce the kinetic energy of the interference, triatomic hydrogen ions, from the tritium ions. As illustrated in Figure 6.1, the interference needs to be relatively larger in size than the analyte. To have an idea on the size of  $^1\text{H}_3^+$  and  $^3\text{H}_1^+$ ,

reported values from Hirshfelder (1938) are that an equilateral triangle shape of the three hydrogen atoms, the distance between the hydrogen nuclei is  $1.79\text{\AA}$ , or  $179\text{pm}$  ( $1\text{\AA} = 10^{-10}\text{m}$ ). For tritium, the nucleus is formed of one proton and two neutrons, and the apparent atomic size is greatly reduced as it loses its only electron, and the electron cloud disappears. The radius of ionic hydrogen is in the order of less than  $10^{-3}\text{pm}$  (Emsley, 1998; Pohl *et al.*, 2010). Therefore the difference in size between the interference (triatomic hydrogen) and the analyte is very significant, and the use of a CRC is investigated.

It is not possible to measure a tritium standard with sufficient signal to evaluate the loss in analyte signal compared to the decrease in background (due to safety issues), therefore the background at  $3m/z$  is monitored with increasing He (collision gas) flow rates, and an estimation of the loss in analyte is calculated using a Li standard. Although the  $\text{Li}^+$  is still relatively larger than  $^3\text{H}^+$ , with a radius of  $78\text{pm}$  (Hemsley, 1998), the difference in size with triatomic hydrogen will reflect what is achievable at that level. Figure 6.2 shows the evolution of the background at  $3m/z$  and  $^7\text{Li}$  standard ( $10\mu\text{g.l}^{-1}$ ) signal with increasing He flow.

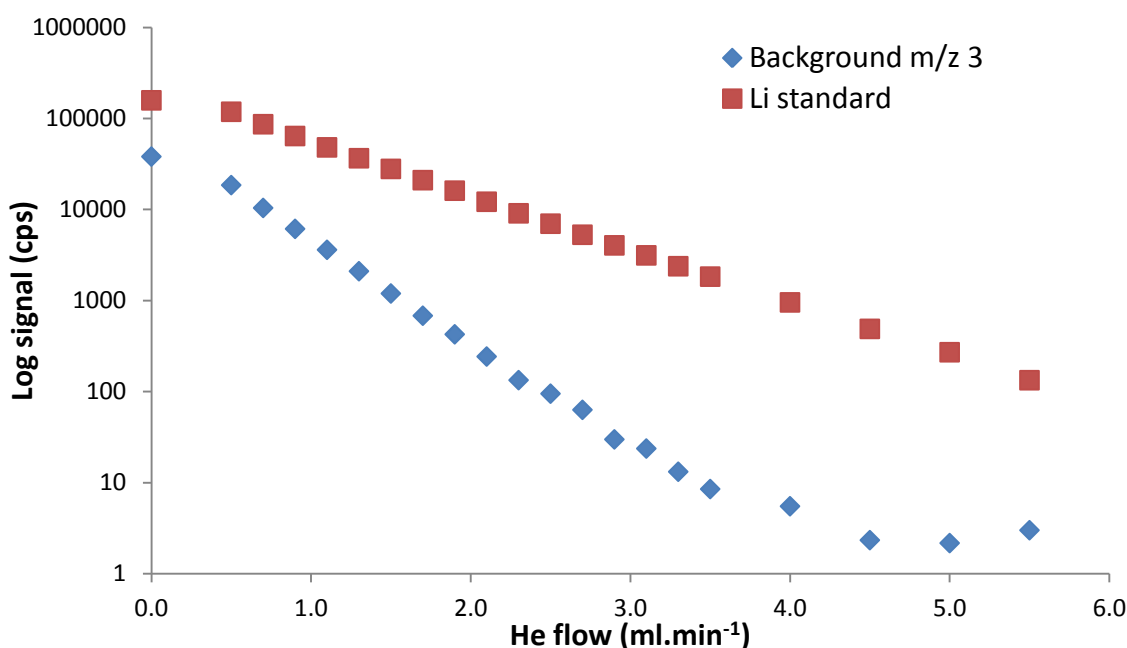


Figure 6.2: Signal obtained for increasing He flow in the CRC for background at  $m/z$  three and  $^7\text{Li}$  standard.

The Figure shows that the background at  $3m/z$  decreases at a steady rate until a flow rate of  $3.5\text{ml.min}^{-1}$ , reaching very low values ( $<10\text{cps}$ ) which can be considered to be electronic noise and the best achievable background. Similarly the Li standard signal decreases steadily, but at a lesser rate, improving the signal to background ratio with increasing He flow rates. Considering the size of the analyte only, the  $^3\text{H}$  signal decrease is likely to be at a

lesser rate than the Li signal. Nevertheless, another factor is to be considered: the relative mass of the analyte and interference compared to the collision gas. In previous examples, this factor is relatively large (e.g.  $^{75}\text{As}$  and  $^{40}\text{Ar}^{35}\text{Cl}$ , factor of  $\sim 19$ ), but here with  $^3\text{H}$ , this factor is actually  $<1$ . Considering the physics of elastic collisions, in the case where the mass of the incoming particle ( $^3\text{H}$ ) is equal to the mass of the static particle (He), the velocity of the incoming particle is completely transferred to the static particle. Therefore in this example, a single head-on collision of a  $^3\text{H}$  or  $^1\text{H}_3$  with He is likely to stop the incoming particle. This means the instrumental settings for the use of CRC with common interferences may require significant changes to adapt to this application.

To evaluate the background equivalent concentration (BEC) at  $3m/z$ , calculations are given considering a similar response for tritium to that of  $^7\text{Li}$  observed in Figure 5.2. For this, the net signal is corrected for degree of ionisation and isotopic abundance to give an equivalent net tritium signal. Subsequently the corresponding BEC is calculated and results are shown in Figure 6.3.

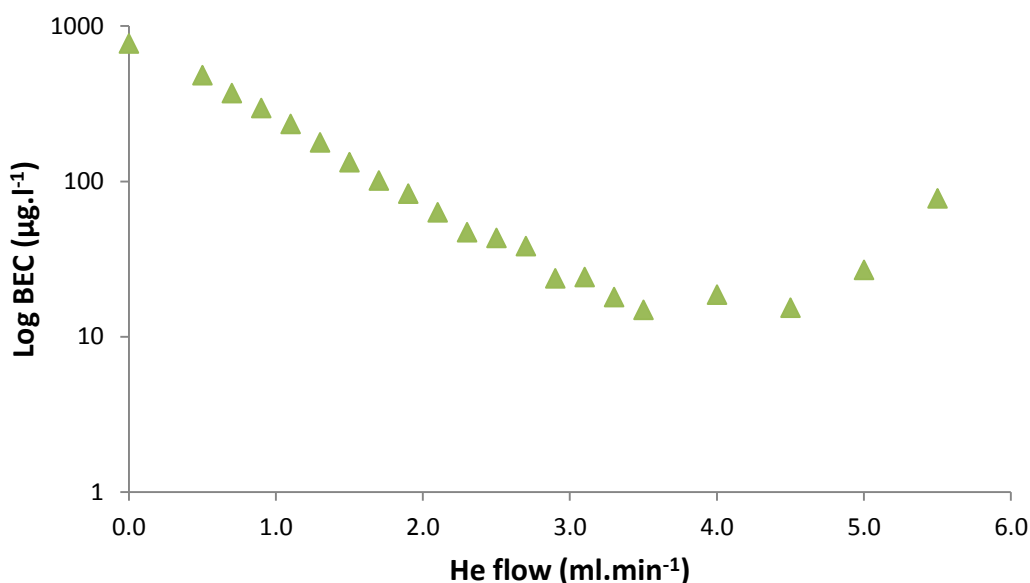


Figure 6.3: BEC estimate at  $3m/z$  using the corrected signal obtained from  $^7\text{Li}$ .

The best achievable BEC is at a He flow of 3.5 and 4.5 ml.min<sup>-1</sup> with  $\sim 15 \mu\text{g.l}^{-1}$  in both cases. Between the two values, the equivalent tritium signal of the former is about four times higher than the latter, and therefore a better choice based on counting statistics and associated precision. The BEC value of  $15 \mu\text{g.l}^{-1}$  is equal to an activity of just below  $5.4 \text{GBq.kg}^{-1}$ . Here the CRC technology has in theory improved the BEC in liquid mode from 280 to  $5.4 \text{GBq.kg}^{-1}$ ,

although the exact behaviour of the tritium ions in the presence of He in the cell is not known at this stage.

#### 4.3.2 b) Analyte reaction with oxygen

The use of the CRC is investigated in regards of promoting the reaction of tritium with an oxygenated compound to shift the newly formed charged molecule towards a relatively background-free  $m/z$  value. As highlighted in Bandura *et al.* (2001), a relatively modest conversion of the analyte to its oxide has still the potential to improve BEC and detection limits at the new  $m/z$  value if the background is very small. Their research quotes a conversion rate for Fe to FeO of about 70%. Considering the three isotopes of oxygen ( $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$ ), the TO molecules would be shifted to 19, 20 and 21  $m/z$  respectively. At these values, the background contribution from isobaric interferences is none, since the elements present, respectively  $^{19}\text{F}$ ,  $^{20}\text{Ne}$  and  $^{21}\text{Ne}$  have ionisation potential values higher than Ar (17.4 eV for F and 21.6 eV for Ne), and therefore do not form ions in an Ar plasma. For the potential background contribution from doubly charged ions, the elements of interest have masses from number 38 to 42, and are given in Table 6.3, with the values of second IPs.

| Isotope        | $^{38}\text{Ar}$ | $^{40}\text{Ar}$ | $^{39}\text{K}$ | $^{40}\text{K}$ | $^{41}\text{K}$ | $^{40}\text{Ca}$ | $^{42}\text{Ca}$ |
|----------------|------------------|------------------|-----------------|-----------------|-----------------|------------------|------------------|
| Abundance (%)  | .063             | 99.6             | 93.3            | .012            | 6.73            | 96.9             | .647             |
| Second IP (eV) | 27.6             |                  | 31.6            |                 |                 | 11.9             |                  |

Table 6.3: Isotopes considered for doubly charged ions, including second IP values which is the same for each isotope of the same element.

Based on the Table, only Ca is potentially interfering at  $m/z$  20 and 21 with K not able to form doubly charged ions. Finally, interfering polyatomic species are a combination of  $^{18}\text{O}$  and hydrogen isotopes ( $^1\text{H}_1$  and  $^2\text{H}_1$ ). The background at  $m/z$  19, 20 and 21 was measured using a 2%  $\text{HNO}_3$  de-ionised water solution, and is given in Table 6.4 with corresponding interferences.

| m/z                             | 19                                                                                                                                                                 | 20                                                                                                                                                                                                                  | 21                                                                                                                               |
|---------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|
| Signal<br>(10 <sup>3</sup> cps) | 26292                                                                                                                                                              | 1919                                                                                                                                                                                                                | 42                                                                                                                               |
| Possible Interferences          | <sup>18</sup> O <sup>1</sup> H<br><sup>17</sup> O <sup>1</sup> H <sup>1</sup> H<br><sup>17</sup> O <sup>2</sup> H<br><sup>16</sup> O <sup>2</sup> H <sup>1</sup> H | <sup>18</sup> O <sup>1</sup> H <sup>1</sup> H<br><sup>18</sup> O <sup>2</sup> H<br><sup>17</sup> O <sup>2</sup> H <sup>1</sup> H<br><sup>16</sup> O <sup>2</sup> H <sup>2</sup> H<br><sup>40</sup> Ca <sup>2+</sup> | <sup>18</sup> O <sup>2</sup> H <sup>1</sup> H<br><sup>17</sup> O <sup>2</sup> H <sup>2</sup> H<br><sup>42</sup> Ca <sup>2+</sup> |

Table 6.4: signal obtained using de-ionised water in 2% HNO<sub>3</sub> and corresponding interferences identified at 19, 20 and 21m/z.

The background from polyatomic species and doubly charged calcium is very significant at the m/z values of interest for selective reaction of tritium with oxygen, and therefore this option is not considered further for analyses of tritium using a quadrupole ICP-MS.

## 5. Sector field ICP-MS

### 5.1 Experimental details

The instrument used for this study was a Thermo Scientific Element 2 sector field instrument. The resolution settings available are low, medium and high, and correspond approximately to a resolution value of 300, 4,000 and 10,000 respectively.

### 5.2 Low resolution

The peak shown in Figure 6.4 represents the response obtained for the <sup>1</sup>H<sub>3</sub> interference peak. Also the predicted position of a tritium peak of similar intensity and width is added.

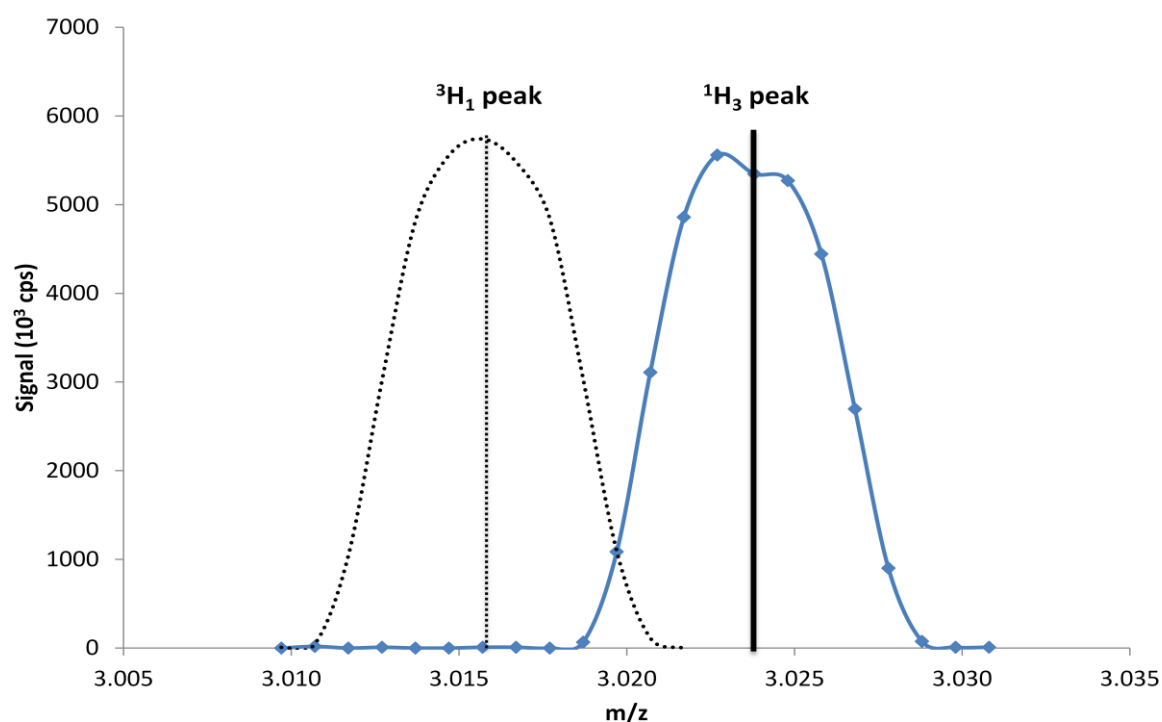


Figure 6.4: Measured interference peak (blue solid line) at low resolution. The position of the hypothetical tritium peak centre is also shown at its exact mass of 3.01605 with a similar peak width than the interference peak ( $\sim 0.01$ amu).

The interference peak is about 0.01amu wide, and agrees with the theory for a resolution of 300 from Jakubowski *et al.* (1998). Therefore, as shown by Figure 6.4, the interference peak and potential tritium peak are partially resolved. Depending on the window used to integrate the area under the peaks for quantification purposes, a better peak resolution may not be required. For example using a 0.5amu window of the whole peak width (i.e. 0.25 each side of the centre) seems to be free of interference from the tail of the adjacent peak.

The peak was measured using the Faraday detector rather than the pulse detector due to its relatively high intensity. One feature of using the Faraday detector is that the background signal, which is expected to be very low, consists of random artefact signal with random values equal to zero,  $\sim 9,500$  or  $\sim 19,000$ cps. This feature is better illustrated in Figure 6.5, where three replicates in the mass range immediately on the left of the interference peak (3.007-3.018m/z) are shown.

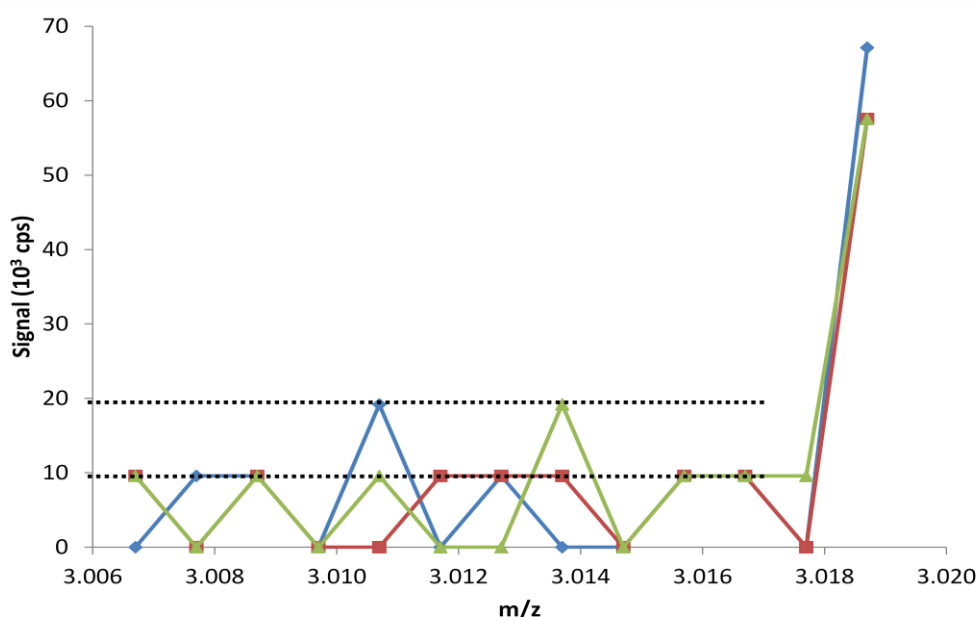


Figure 6.5: Faraday detector artefact background. Here three replicates are shown. The far right represents the beginning of the interference peak.

The implication is that it is not possible to calculate a limit of detection because the measured background in the Faraday mode does not represent the relevant ‘true’ background that is expected in pulse mode and therefore cannot be used.

To estimate the background contribution, arbitrary background levels are processed to give equivalent activity. The values are given in Table 6.5.

| Background,<br>average cps                 | 1   | 20   | 100  |
|--------------------------------------------|-----|------|------|
| Corresponding<br>BEC, MBq.kg <sup>-1</sup> | 0.6 | 12.0 | 59.8 |

Table 6.5: Potential background values and corresponding BEC (MBq.kg<sup>-1</sup>)

From the Table, a likely background of 1cps is equivalent to a BEC of 600kBq.kg<sup>-1</sup>, which is about 10,000 fold better than the best potential with quadrupole ICP-MS (using He in the CRC), and also now is below the low-level waste limit of 12MBq.kg<sup>-1</sup>. Moreover, Jakuboski and co-workers (1998) report typical background counts of 0.1 for sector field instruments. They even mention the possibility of lower values if the resolution is increased, but the associated loss in sensitivity is unlikely to overall improve the BEC.

### 5.3 Medium resolution

The same sample was run and analysed using the medium resolution setting, corresponding to approximately a resolution of 4,000. This enables to check for the presence of a  $^1\text{H}_1^2\text{H}_1$  peak (at  $m/z$  3.02204) as it is now resolved from  $^1\text{H}_3$  ( $m/z$  of 3.02382), where the required resolution is  $\sim 1,700$  using Equation 6.1. Figure 6.6 shows the interference  $^1\text{H}_3$  peak, measured with the pulse detector mode and the position of the  $^1\text{H}_1^2\text{H}_1$  interference.

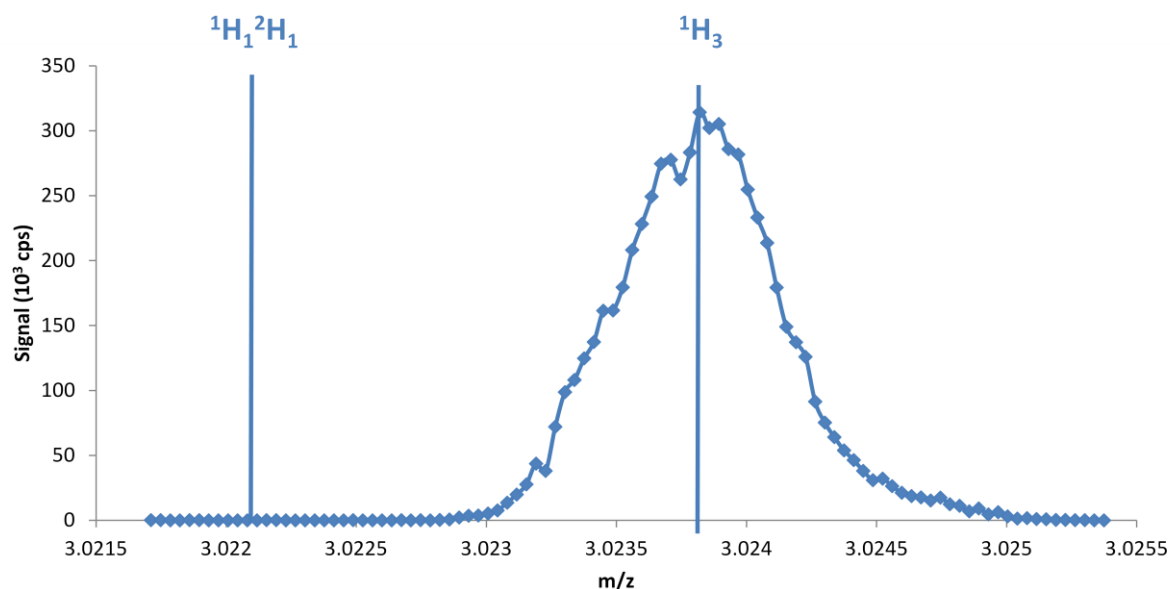


Figure 6.6:  $^1\text{H}_3$  interference peak at medium resolution. Also present is a marker at the  $m/z$  value for  $^1\text{H}_1^2\text{H}_1$  interference, showing that there is no peak present.

In this example, the signal intensities over an area of 0.5 peak width equivalent centred on the  $^1\text{H}_1^2\text{H}_1$  interference show no outline of a peak, and the average background is  $<0.1\text{cps}$  over that same area. Therefore the predominant interference is triatomic hydrogen.

In conclusion, the main interference on tritium analysis has been identified and verified to be triatomic hydrogen. Using conventional quadrupole ICP-MS in liquid mode, the corresponding BEC on this interference is relatively high, in the order of  $\text{GBq.kg}^{-1}$  and offers very limited potential for direct tritium measurements. Nevertheless, the use of a sector field instrument, with the possibility to partially resolve the interference from the tritium to be measured without loss of signal (using low resolution setting), opens a promising route for tritium analysis in solutions. The possibility to achieve BEC in the order of few  $\text{MBq.kg}^{-1}$  has been calculated.

## 6. Additional approaches for tritium analysis by ICP-MS

### 6.1 Improving degree of ionisation for hydrogen

In conventional argon ICP-MS instruments, the relative degree of ionisation for hydrogen is calculated as 0.4% due to its relatively high first ionisation energy (13.8eV, similar to oxygen) close to that of the maximum delivered by the argon plasma (1<sup>st</sup> ionisation 15.8eV). As highlighted in Figure 6.7, to be able to obtain an improved degree of ionisation, either of two options is open in theory: lower the first ionisation energy for hydrogen, which is impossible, or potentially increase the available energy in the plasma which will affect the ionisation curve. From both, the second option is investigated by the use of a helium plasma ion source with a higher first ionisation energy (24.6eV) compared to Ar and its applicability to hydrogen (hence tritium) ionisation and detection by mass spectrometry.

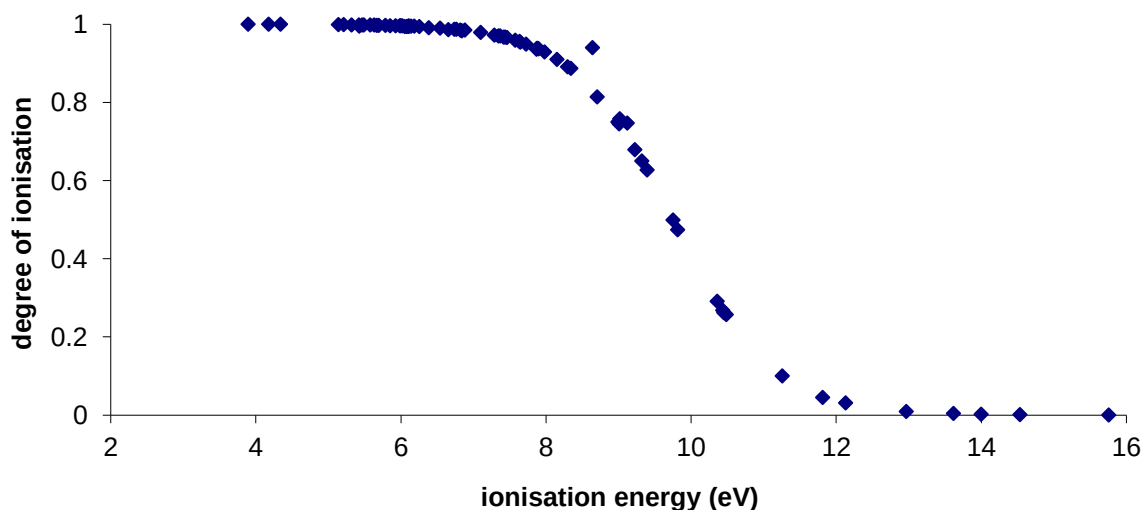


Figure 6.7: Typical elemental ionisation curve for an Ar ICP at a temperature of 7,500K and a free electron concentration of  $10^{15}\text{cm}^{-3}$ , represented as degree of ionisation against the first ionisation energy of each element (in eV). Maximum degree of ionisation is 1 and elements with higher first ionisation potentials (e.g. helium, fluorine) are not represented.

#### 6.1.1 Use of helium

The use of helium in the plasma source for mass spectrometry has been mainly of two origins. Firstly, He is now widely accepted as an alternative carrier gas or mixed with argon in laser ablation ICP-MS for the flushing and transport of the ablated material from the cell to the ICP. Experiments show that the use of helium improves the flushing of the ablation cell and the transport of the ablated material plume to the ICP (Horn and Günther, 2003). Also it

was demonstrated that the input of small quantities of helium in the argon plasma changes the plasma conditions, resulting in better ionising conditions and therefore sensitivity (Sheppard *et al.*, 1990).

More importantly, helium-based plasmas have been used as the ion source for mass spectrometry replacing the argon in an ICP (Montaser *et al.*, 1987) and in microwave-induced plasmas (MIPs, Satzger *et al.*, 1987). For both applications, the desired effects are that with the higher ionisation energy from a He plasma, elements will have an enhanced degree of ionisation, especially elements relatively hard to ionise in an Ar plasma with high first ionisation energy requirements (e.g. halogens, As, Pt, Au, Cd, etc.). Also in Ar plasma, elements such as Ca, Fe, As and Se suffer from Ar-based interferences and therefore high background signals. The use of nearly mono-isotopic He simplifies the likely background spectrum. Above 40m/z, the spectrum is relatively free of background peaks (Montaser *et al.*, 1987; Satzger *et al.*, 1987; Koppenall and Quinton, 1988). Nevertheless, trace Ar interferences are still present in the He plasma, as it is an impurity in the gas supply, but to a lesser extent. Also Creed *et al.* (1989) argue that because of the higher ionisation potential of He, elements such as krypton and xenon, also found as impurities in the He gas, now form significantly more ions and introduce new background signals at their respective set of isotopes (namely m/z=78, 80, 82-84, 86 for krypton and m/z=124, 126, 128-132, 134, 136) and have potential to affect Se measurement.

#### 6.1.2 Elemental ionisation curve

The curve represented in Figure 6.7 is a result of the Saha equation, which calculates the distribution of different ionisation states of an element, or ionisation fraction (Pradhan and Nahar, 2011). The main two variables of the equation are temperature and free electron concentration (Agilent, 2000).

An example of changes to this curve induced by plasma temperature variation for an Ar ICP is given in Figure 6.8. It is possible to see that the change in temperature can greatly influence the degree of ionisation of an element.

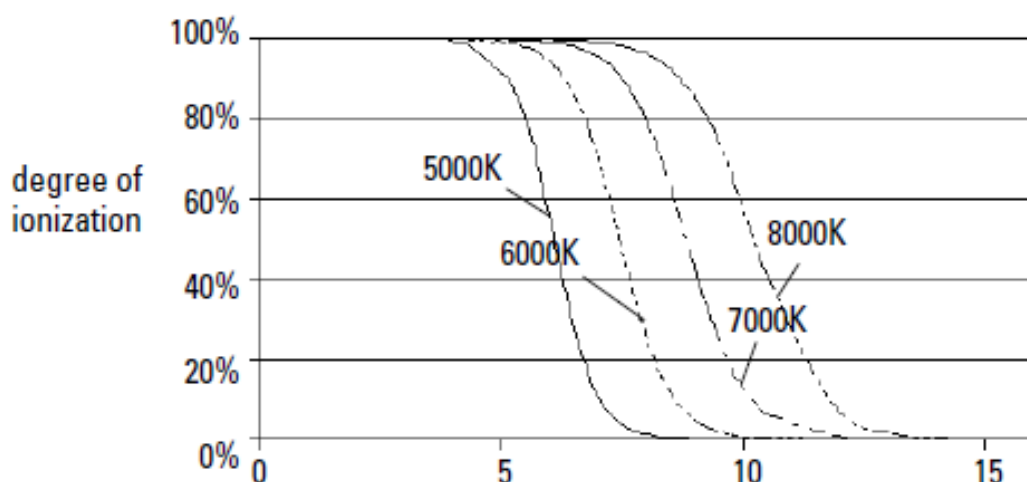


Figure 6.8: impact of temperature changes on the element ionisation curve for an Ar ICP. (from Agilent, 2000).

From the literature, the temperature of a He plasma is in general lower than of an Ar plasma. Abdallah and Mermet (1982) report a temperature of about 2,000K for He plasmas (with a power of 100W), and comment that the physical properties between a He ICP and MIP are very similar, and not comparable to a Ar ICP.

In theory the ionisation curve for a He plasma is likely to stretch further to a first ionisation potential of 24.6eV, although the potential low gas temperature will affect the curve dramatically. The temperature of 2,000k for a He plasma was generated with a power of 100W, and the literature notes possibilities to reach up to 900W for an He-ICP, which is likely to improve the gas temperature in a similar way to the observations of Ar plasma. Unfortunately no further He plasma temperature was found in the literature.

### 6.1.3 He microwave induced plasma

Microwave induced plasmas (MIPs) operate in the GHz frequency region, and were originally used as a radiation source coupled with optical emission spectrometry (OES). It was thereafter investigated as a possible ion source for mass spectrometry studies to replace the conventional inductively coupled plasma, because of lower power and gas consumption resulting in more cost-effective analyses. Study of the MIP characteristics showed that, compared to ICP, lower gas temperatures in MIP are less effective at handling wet aerosols and relatively large solid particles (laser ablation) because of inefficient matrix removal, which require high amounts of energy prior to ionising the analytes of interest. Therefore the use of MIPs with relatively dry aerosol sample introduction systems, such as electrothermal

vaporisation (ETV) and gas chromatography (GC), is more appropriate (Broekaert and Siemens, 2004; Thompson and Walsh, 1989, Abdallah and Mermet, 1982).

To that effect, Brown and co-workers (1988) studied a He-MIP is connected to a commercial ICP-MS instrument for the detection of halogens in gas phases in dry plasma. The spectrum of dry He was recorded by scanning the range 2-256m/z, with peaks identified. Peaks at the low mass end of the spectrum were at 2, 4, 5, 8m/z and above, and the likely ions were described as  $\text{H}_2^+$ ,  $\text{He}^+$ ,  $\text{HeH}^+$  and  $\text{He}_2^+$  respectively. There was no evident peak observed or identified at 3m/z, and signal measured was between 1-10 cps. Nevertheless, Creed *et al.* (1989) managed to apply the He-MIP approach to the detection of metals and non-metals in solutions. The spectrum produced by a 1%  $\text{HNO}_3$  solution gave signals at 4,5 and 8m/z, although it is unclear if m/z <4 were scanned.

In this view, the measurement of tritium with a He-MIP instrument is potentially difficult to achieve by direct solution nebulisation mode due to the low gas temperature of the plasma. Although in theory  $^3\text{H}$  is relatively easy to convert into a gas phase (HT or HTO vapour) and very low background at 3m/z is likely to produce relatively good detection limits, the chemical behaviour of  $^3\text{H}$  makes it very challenging to separate from  $^1\text{H}$ , and therefore a desolvation step is not in practice feasible unless a separation between  $^3\text{H}$  and  $^1\text{H}$  is possible.

#### 6.1.4 He-ICP

Montaser *et al.* (1987) report the first trials on the use of a He ICP ion source replacing the conventional Ar ICP in a commercial ICP-MS instrument (PlasmaQuad) and its capabilities for halogens and sulphur determination in gas samples. Previous experiments on He-ICP-AES system showed the suitability of the source for ion formation and also highlighted the significant increase in chlorine emission lines compared to Ar plasma source setup. Beside this, the use of He introduces a different set of polyatomic interferences. Figure 6.9 shows the background spectrum collected by Montaser *et al.* with the He gas only ICP.

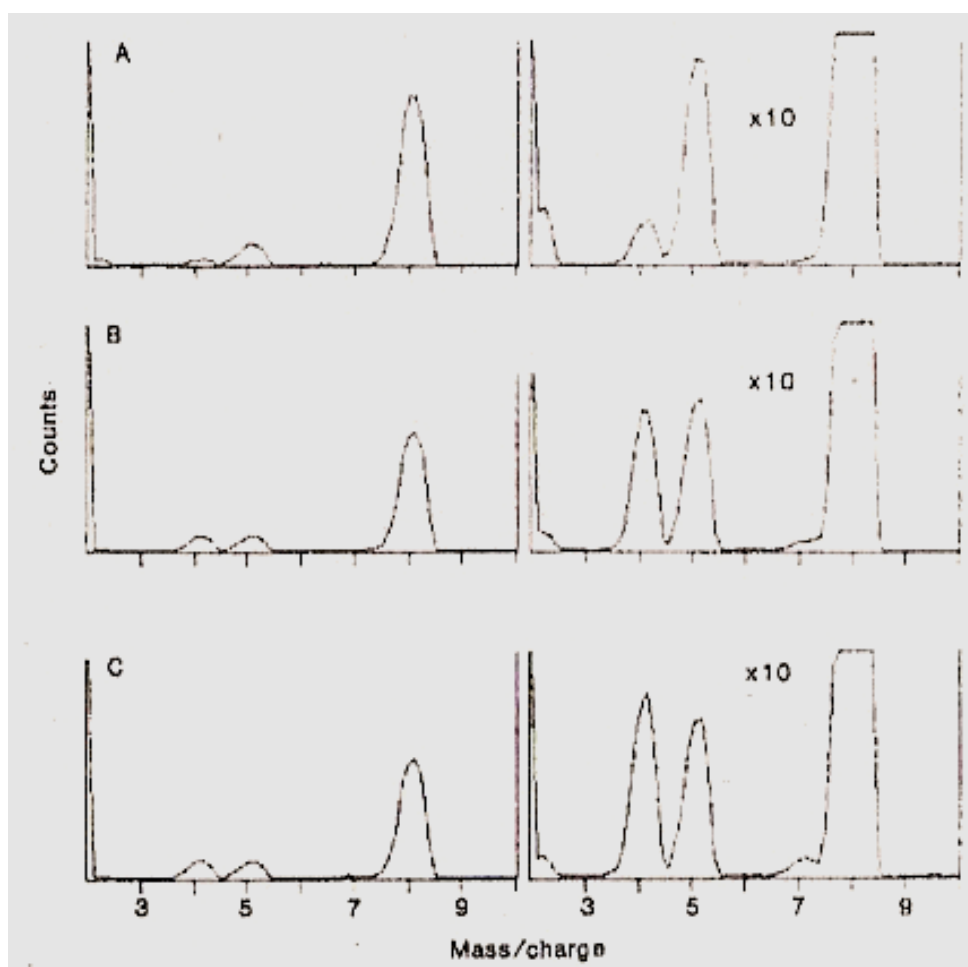


Figure 6.9: Mass spectra from  $m/z$  2 to 10 of species formed in He ICP operated at three forward powers: (A) 500 W, (B) 700 W and (C) 900 W. Full scale counts left plots 32,000; right plots 3,200 (from Montaser *et al.*, 1987).

Figure 6.9 shows that, concerning  $3m/z$ , the background is relatively very small, with no visual evidence. Also noted by Montaser and co-workers, the main three background signals observed are  $^4\text{He}^+$ ,  $^4\text{He}^1\text{H}^+$  and  $^4\text{He}_2^+$ . More intense peaks were observed at higher  $m/z$  values (e.g. 14 and 16 $m/z$ ), but are not of interest here. As the forward power increases, both the  $^4\text{He}^1\text{H}^+$  and  $^4\text{He}_2^+$  peak intensities decrease and the  $^4\text{He}^+$  peak increases, suggesting more robust plasma conditions and preferential removal of polyatomic species. This can have two effects on the background at  $3m/z$ . Firstly, the potential background from species such as  $^1\text{H}_3^+$  and  $^1\text{H}_2\text{H}^+$  for liquid samples analysis is likely to be minimised by the plasma conditions at higher forward power. Secondly, depending on the composition of the He gas used, a natural abundance of  $^3\text{He}$  (<0.0002%) will increase the background at  $3m/z$  in a higher forward power plasma, similar to the enhancement in  $^4\text{He}$  signal observed. To assess the likely contribution, considering the peak height of  $^4\text{He}^+$  in example (C) x10 (right plot) as 3,000 counts and abundance of 100%, the equivalent peak height signal for  $^3\text{He}^+$  is <0.006 counts, which is regarded as negligible. Concerning doubly charged ions, as mentioned in

section 2.1.2, Li (which doubly charged isotopes can potentially contribute to signal at 3 and 3.5m/z) has a second ionisation potential of 75.64eV, and therefore will not produce doubly charged ions in He ICP.

Overall a He plasma is offering the possibility of  $^3\text{H}$  determination, most significantly in a gas phase rather than in solution due to the relatively lower gas temperature and therefore difficulty to deal with the desolvation process. As  $^3\text{H}$  is readily vaporised, a suitable sample introduction system can produce the dry aerosol for ionisation.

## 6.2 New ICP-MS instrument

### 6.2.1 Instrument design and functionality

In 2012, Agilent launched a new instrument based on their existing technology with a variation to be the first triple quadrupole ICP-MS (ICP-QQQ). Although the instrument contains in reality only two quadrupoles, the name is following the tandem MS/MS technology used in organic mass spectrometry, where the collision cell used was originally a quadrupole but has now evolved to become a hexapole or octopole. A description of the method is given by Tanner *et al.* (2002). The core of the instruments consists of a conventional ICP-MS with a collision/reaction cell (CRC) and a quadrupole (Q2), with the addition of another quadrupole device (Q1) between the ion extraction and the cell. This new instrument is designed for rather specific applications, where the conventional CRC technology may not give adequate results

Basically the principle is that Q1 acts as a mass filter to select only one m/z value to enter the CRC, rejecting all other. This selected m/z usually includes the analyte of interest and an interference to be separated. The subsequent reaction taking place with the CRC, depending on the gas used, results in either of the following two:

- the interference preferentially reacts with the gas and is removed from the analyte and no new interference appears at the analyte's m/z measured value (Q1 rejected all other m/z values originally),
- the analyte preferentially reacts and the new molecule is shifted towards a higher m/z value (now with minimum background as Q1 rejected this specific m/z originally).

### 6.2.2 Tritium analysis application

Here the idea is to use this new instrument for the separation of  $^3\text{H}^+$  from its main interference  $\text{H}_3^+$ . The first approach is to use oxygen as reaction gas, as described in section 4.3.2.2 of this chapter, which now has the potential to shift the formed  $^3\text{HO}$  molecule to a background free  $m/z$ . Considering the formation of  $^3\text{H}^{16}\text{O}^+$  at  $19m/z$  as the most abundant species, there are still potential interferences, namely triatomic hydrogen and deuterium and hydrogen with  $^{16}\text{O}$ , although the formation of a molecule consisting of four atoms is less likely and therefore interference at  $19m/z$  is minimised. In theory all other interferences described in Table 6.4 based on hydrogen or deuterium are not considered as the initial Q1 setting prevents the 1 and 2  $m/z$

The second approach is to use  $\text{NH}_3$  in the reaction cell. Experimental data have been obtained by the company which show that certain elements react actively with  $\text{NH}_3$  to form a series of different compounds and clusters which can appear at  $m/z$  higher than the addition of a single  $\text{NH}_3$  (+17  $m/z$ ). For examples the reaction with  $^{48}\text{Ti}$  produces various clusters at increasing  $m/z$  values with intensities compared to the initial  $^{48}\text{Ti}$  spike. The experiment is performed by setting Q1 to allow only 48  $m/z$  to continue into the CRC filled with  $\text{NH}_3$  and scan all other  $m/z$  thereafter using Q2. The experimental results are visualised in Figure 6.10, and a summary of the data observed is given in Table 6.6.

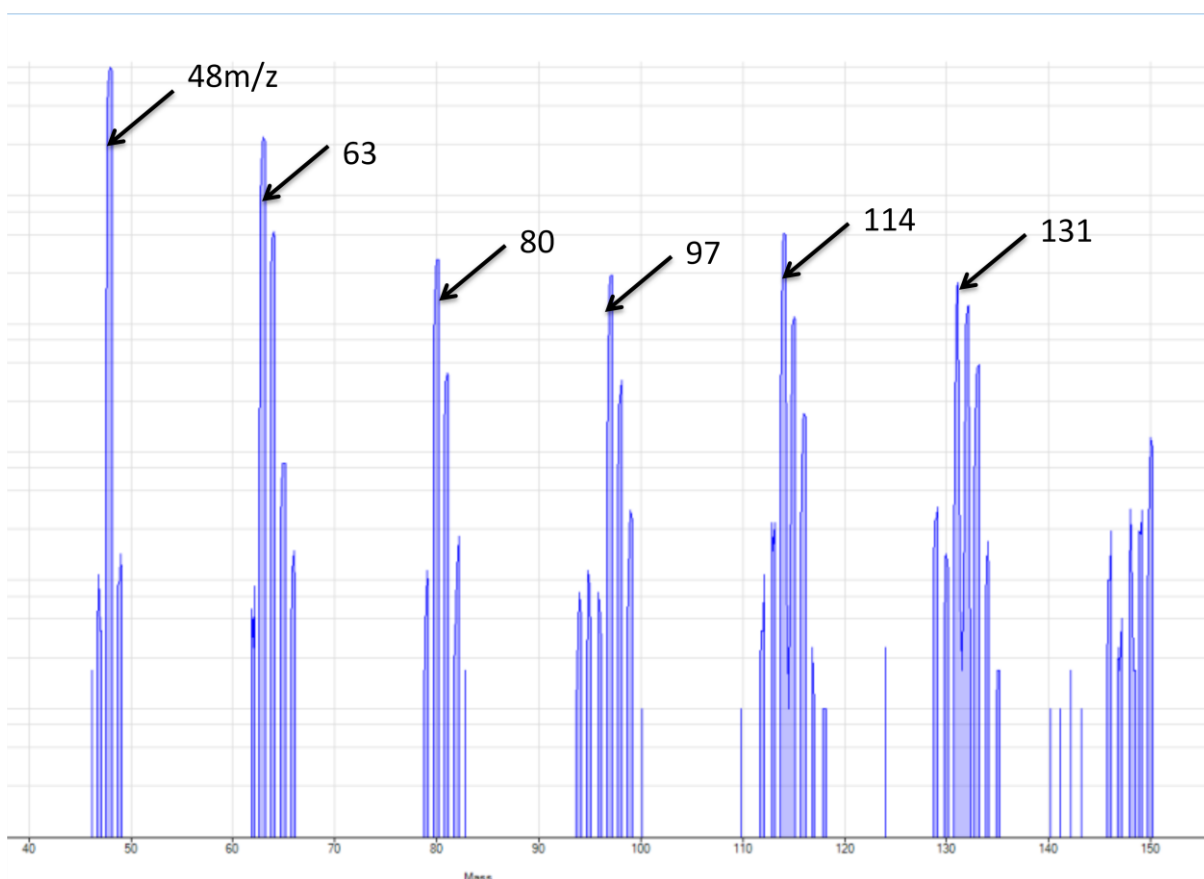


Figure 6.10: Spectrum obtained from the reaction of  $^{48}\text{Ti}$  with  $\text{NH}_3$  as reaction gas. The main peak of each cluster are consistently 17 mass units apart, starting from the first reaction cluster (63m/z), probably reflecting the addition of one extra  $\text{NH}_3$  molecule. The surrounding minor peaks in each cluster are likely results of loss and addition of H atoms from the corresponding main molecule measured, here  $^{48}\text{TiNH}(\text{NH}_3)_x$  (adapted from Agilent, 2012).

| Main peak m/z     | 48            | 63                       | 80                                    | 97                                      | 114                                     | 131                                     |
|-------------------|---------------|--------------------------|---------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| Possible identity | $\text{Ti}^+$ | $\text{Ti}(\text{NH})^+$ | $\text{Ti}[\text{NH}(\text{NH}_3)]^+$ | $\text{Ti}[\text{NH}(\text{NH}_3)_2]^+$ | $\text{Ti}[\text{NH}(\text{NH}_3)_3]^+$ | $\text{Ti}[\text{NH}(\text{NH}_3)_4]^+$ |
| Peak height (cps) | 1M            | 250k                     | 25k                                   | 25k                                     | 50k                                     | 25k                                     |

Table 6.6: Main peaks in clusters formed by  $^{48}\text{Ti}$  and  $\text{NH}_3$  at different m/z positions and their observed intensities. Several more surrounding peaks are present in each cluster but not documented.

It is possible to see from Table 6.6 that the conversion of the reaction between  $^{48}\text{Ti}$  and  $\text{NH}_3$  can be of a maximum of ~25% (peak at 63m/z) and subsequently between 5 and 2.5%.

A similar experiment is conducted with rare earth elements, and results showed that a significant difference appeared. A selection of REEs, namely La, Ce, Gd, Tb and HF, are very reactive to  $\text{NH}_3$  in the cell and actually form a more sensitive product molecule than the

original element spike. For example a La spike at about 2,000cps produces a cluster in the region 222-227m/z with the main peak at 224m/z ( $\text{La}(\text{NH}_3)_5$ ) and an intensity equivalent to 1,000,000cps. All other REEs form cluster of lesser intensity peaks than the original spike (Agilent, 2012). This is relatively unexpected as the chemistry of neighbouring REEs is very similar and it is very difficult to separate one from the other.

These experiments highlight the potential of reaction of an analyte with  $\text{NH}_3$ , with the possibility to dramatically enhance the sensitivity of a particular product molecule. A similar application to  $^3\text{H}$  has the potential to enhance the sensitivity of the analyte and the production of a unique molecule at a higher m/z value with better detection limits. Also to bear in mind, due to the shape of the response curve at the low mass end, there is the possibility of additional signal enhancement with a shift of the product molecule to a higher values from 3m/z.

## CHAPTER VII: CONCLUSIONS AND DISCUSSION

### 1. Concrete information and samples

After investigating the requirements for shielding concrete in the literature, the general idea was that the shielding specification, normally using certain types of iron- or barium-bearing heavy aggregates, may have been altered to be able to produce a cheaper equivalent with local or easy to ship-in constituents. The aim was to keep the production of vast amounts of concretes for all facilities at an economical cost. This pointed out, with the help of the engineers, that structural concrete from walls and other buildings built at the same time as the shield on site may have been constructed with the same concrete mix.

Key activation products were drawn from the literature. Some of the important precursors include  $^6\text{Li}$ ,  $^{40}\text{Ca}$ ,  $^{59}\text{Co}$ ,  $^{62}\text{Ni}$ ,  $^{132}\text{Ba}$ ,  $^{151}\text{Eu}$ ,  $^{153}\text{Eu}$  and  $^{238}\text{U}$ . From this list, several isotopes are potentially present at the percent level in materials, others remain as traces. The mixed picture comes from the fact that some of these isotopes activate relatively more (both europium isotopes for example) and others are present at such large amounts in concrete constituents ( $^{40}\text{Ca}$ ) that even a lower activation capability results in a significant amount of radionuclides.

Several samples from research reactors have been sourced for the investigation. Three of them come from the CONSORT research reactor hosted by Imperial College at their Silwood park campus (Berkshire) and two are from the Windscale site, now Sellafield (Cumbria), originally built to produce plutonium. Overall, these shielding materials may be relatively different from the concretes used in large scale commercial plants, but offered a wide range of aggregate types to investigate.

### 2. Instrument calibration

The calibration of the instrumentation is paramount to obtain quantitative data. This issue has been and remains a key factor to overcome for LA-ICP-MS analysis. Firstly, the research showed that some of the aggregates of interest displayed variable major chemistry within the aggregate's boundaries. Also, due to the heterogeneity of the concrete itself, which includes aggregates of significantly different matrices such as  $\text{SiO}_2$  or  $\text{CaCO}_3$ , the choice of a homogeneously distributed internal standard (IS) of known concentration is proving impossible to achieve. An alternative correction method was tested. It consists in calculating the proportion of major components in any constituent and normalise the total to represent 100%. Results obtained using both the IS and total oxide data correction showed that there

was no significant difference between the two, subject to an accurate normalisation step. On occasions, a bias was observed between the certified value and the concentration calculated by both methods, but this reflected only the inadequacy of the calibration material for that matrix. An important issue highlighted was also that some major components are not measureable by ICP-MS, such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and that these potential contributors to the constituent's matrix, for example in carbonate ( $\text{CaO} + \text{CO}_2$ ). Also some constituents have major oxides only adding up to about 90%, and this needs to be accounted for by using the relevant value rather than the default 100% for an accurate correction by total oxide normalisation.

Many different matrices are expected in concrete. To minimise potential matrix effects for calibration purposes, three certified materials, namely a silica-based glass (NIST 610), a cement (OPC-1) and a calcium carbonate (MACS-3) were chosen to reflect the likely matrices encountered. The attempt to construct a calibration line using standard addition on the cement resulted in straight lines with excellent correlation factors for all elements of interest ( $>0.93$ ). Nevertheless the accuracy of the certified concentrations calculated back showed a consistent negative bias and ranged from -4 to -78% for Sr and Li respectively. A carbonate sample calibration line was also attempted. Results showed that the linearity can vary from one element to another. Results on the calibration of MACS-3 used as an unknown showed variable recovery for the four elements monitored.

Each of the three certified materials was used as a one point calibration and tested against concrete samples. A range of silica-rich aggregates were measured with NIST 610, cement and sand mixture with OPC-1 and carbonates with MACS-3. Data obtained from wet chemistry were used as target values for each constituent analysed. The results, with all materials and in all matrices, showed a wide range of recoveries between laser and target. A number of causes can be defined. First and foremost, there is a difference in matrix between the sample and the calibration material and it is significant enough to preventing accurate results to be calculated. Also, the target value measured from wet chemistry is not accurate. Moreover, the laser ablation took place on the surface of the component, in reality sampling a very small amount which may not be representative of the whole component chemistry. As seen before, there can be a significant difference from one area to the next in the natural materials investigated. Ultimately, some of the target values are very low in concentration and therefore difficult to detect and quantify in general.

NIST 610 glass, used as a one point calibration and with a total oxide correction, can offer a semi-quantitative calibration approach to evaluate the concentration levels of the key stable

isotopes in the different matrices investigated. Matrices such as carbonates, cement material and silica-rich aggregates have been investigated by means of accuracy of results obtained for MACS-3, OPC-1 and NIST 612 respectively. For the major elements, CaO can be quantified within an error bracket of  $\pm 20\%$  in all three matrices with a concentration range of 10-60%. On the other hand,  $\text{Fe}_2\text{O}_3$  showed a marginal over-estimation by +20-50% at the percent level in carbonates and cement, and a much higher bias (+150%) at the trace level in the silicate glass. For the trace elements, lithium, cobalt and uranium are within  $\pm 20\%$  accuracy in all matrices. Other elements display variable accuracy, but can be estimated within reasonable error. Therefore nickel has been measured within a 30% error, chromium within 80%, barium is overestimated by between 25 and 70% and europium within 50% in all matrices. Overall this means that the key major elements can be measured with a relatively good confidence of 20%, and that most trace elements are kept within 80% of the true value. In the eventuality a rapid survey of hotspots and overall distribution of these elements in an unknown concrete as required, the laser calibrated with NIST glass can give an appropriate and relevant distribution fit for purpose, which can be an attractive initial investigation in the decommissioning process.

### 3. Concrete characterisation

Based on the small block samples from CONSORT (SB1) and the sample from Windscale Pile one reactor (WP1),  $\text{SiO}_2$ , CaO and  $\text{Fe}_2\text{O}_3$  are the principal major components showing the most variation across all the concrete components surveyed. By using a ternary diagram, it is possible to survey the likely matrices for aggregates in concrete. At this point, the data do not require total oxide correction, and a simple one calibration point using NIST 610 generates the proportions of the three major components normalised to 100. At this point, any result showing predominant CaO ( $\geq 90\%$  of the three components) requires attention, as there is a possibility that the matrix in question is actually calcium carbonate. It is important to account for the  $\text{CO}_2$  present during the total oxide data correction.

Once the dataset has been fully corrected, a handful of major and trace elements signals have been used to discriminate between them and form groups of similar chemical fingerprints. The graphical representations used Ca signal against Ca/Sr ratio, Fe signal against Fe/Mn and Fe/Cr ratios. On the Ca/Sr diagram, there is a significant difference between each aggregates groups identified. Silicates show the lowest Ca signals, compared to calcium-based components such as carbonate aggregates and cement/sand mixture. In a similar way, in both iron-based diagrams the aggregates containing significant iron separate from the remaining components. Nevertheless in all three diagrams it is not possible to

separate both silica-based aggregates, namely the quartz weathered type (“round”) and straight-edged polycrystalline type (“grey”). To achieve this, boron data and La/U ratio are used as discriminators. Boron concentration, determined by laser, plotted against the precision of the 10 replicate analyses successfully differentiated grey from round silicates. Moreover the existence (grey) or not (round) of a valid La/U ratio also directs to the appropriate aggregate type. Overall, a simple set of elements showing important variations from one concrete phase to another have been identified and need testing.

Using the discriminating information, it was possible to recognise a sequence of ablated phases in a blind test, where only the chemistry is used and validate the selection of key discriminators previously chosen. The discrimination diagrams gave an accurate recognition of the phase or mix of phases ablated for each replicate, with a few mistakes on the interpretation. These misjudgements can be rectified by also monitoring the major components variations, namely  $\text{SiO}_2$ ,  $\text{CaO}$   $\text{Fe}_2\text{O}_3$  together with boron concentration and La/U ratio, through the sequence of replicates. Therefore, using the laser to sample a representative area, together with accurate wet chemistry concentrations to be linked with each recognised component or phase, a more accurate distribution of precursor nuclides can be established.

Based on the same diagrams established with samples SB1 and WP1, the data from new components from different samples did in most cases not strictly fall into a certain defining aggregate group. Nevertheless, the same variations in Ca and Fe signals were observed, with the new components showing affinity with one group or another. The wet chemistry results for all aggregate types were compared, and it was shown that for example the affinity to the silicate defining group also presented similarly lower concentrations of the whole range of elements of interest, whereas iron-rich alike aggregates tend to contain more of these trace elements. Correlation patterns were established to support the idea that more iron present in the aggregate, more trace elements are present.

#### 4. Tritium determination by ICP-MS

The theoretical approach on the direct measurement of tritium in solution, based on some measurements, strongly suggests that it may be achievable at a certain level of concentration. A sector field ICP-MS instrument, working at low resolution (300), has the capability to separate the theoretical tritium peak from its closest interference, triatomic hydrogen. Using the most central channels and an equivalent of 0.7 of the whole peak, no background and tailing interference from the neighbouring peak should be appearing. Using Li signal, a background equivalent activity of  $0.6\text{MBq.kg}^{-1}$  is quoted based on typical

background values, which is below the low-level waste limit of  $12\text{MBq.kg}^{-1}$ . The potential to improve this value, mainly due to the poor ionisation of tritium in argon plasma, has been documented by potentially using a more energetic plasma made of helium, and also the use of a new instrument with extended capabilities.

## **FUTURE WORK**

The work achieved in this thesis presents a starting point for further investigations to take place. Several points of interest are presented.

The characterisation of more concrete samples is required, for different reasons. Firstly the types of concrete investigated so far represent a relatively small portion of the potential compositions to be found elsewhere. The possibility that shielding concrete reflects the local geology due to close-by aggregate sourcing can help to target a few key places around the country with likely very different chemistry. This way the database of chemical and ablation data can increase, with potentially the formation of denser clusters of aggregate groups, the identification of additional discriminators if required, and possibly a more accurate chemistry of the key isotopes present in each group.

In regards of a representative sampling, an assessment of sample WP1 is possible. The phase recognition based on a handful of elements can be applied to maximise the resolution capabilities of the laser. A practical test is to set the replicate analysis to measure the discriminator elements only, therefore shortening the time of each replicate, which in turn enables to increase the laser scanning speed and cover a much larger area than before. The work would establish the area, distance between lines and scanning speed required to representatively sample and quantify this type of constituent distribution in a sample.

On the tritium determination, the next step would be to test the theory proposed and be able to run tritium standards on one such sector field instrument. This will also allow for the mass calibration issue to be addressed, and quantify backgrounds levels and give a detection limit.

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## APPENDIX 1

### ***Geological sample digestion by HF and HClO<sub>4</sub>***

This digestion method is adapted from the NERC ICP Facility method entitled “The preparation of solutions for trace-element determination by ICP-MS using an open HF-HClO<sub>4</sub> digestion”. The equipment required is as follow: analytical balance, laboratory oven, fume cupboard with washdown facilities, acid-resistant hotplate capable of 250°C, 60ml *Teflon* beakers, 50ml volumetric flasks, 50ml plastic tubes, pipettes and tips for 10, 5, 2 and 1ml capacity, weighing boats.

Reagents needed are: 18MΩ deionised water, trace metal grade hydrofluoric (HF), perchloric (HClO<sub>4</sub>) and nitric (HNO<sub>3</sub>) acids.

#### ***PROCEDURE***

- (1) Dry powder or whole aggregate at 105°C for 24hrs.
- (2) Weigh 0.10g of powdered sample or whole aggregate into a weighing boat. Record exact sample weight.
- (3) Transfer sample with a few ml of deionised water in *Teflon* beaker.
- (4) Slowly add 3ml of HF followed by 2ml of HClO<sub>4</sub>.
- (5) Decompose sample on a hotplate at approximately 200°C until it reaches near dryness (a crystalline mush in the bottom of the beaker appears).
- (6) Examine sample for any undigested material and repeat steps (4) and (5) if necessary.
- (7) Add a final 2ml of HClO<sub>4</sub>. This step is to remove any remaining HF.
- (8) Evaporate to near dryness.
- (9) Add 10ml of 5M\* HNO<sub>3</sub>, allow digest to dissolve again (or until first fumes appear).
- (10) Transfer into 50ml volumetric flask, with multiple deionised water rinses, and make up to volume.

(11)                      Transfer to a new 50ml plastic tube and store.

\* This can be made up by diluting 320ml of concentrated  $\text{HNO}_3$  to 1000ml with deionised water.

### ***APPLICATIONS***

This method has been used for the analysis of major and trace elements, rare earth elements and U and Th on many geological samples, except those containing refractory minerals such as zircon, spinel and chromite which are not attacked by this procedure.

For ICP-AES analysis, sample can be analysed as it is together with appropriately prepared reference materials. For ICP-MS, a further dilution by a factor of 10 is required prior to analysis.

## APPENDIX 1 (continued)

### ***Geological sample preparation by lithium metaborate fusion***

This digestion method is adapted from the NERC ICP Facility method entitled “The preparation of solutions for ICP-MS analysis by lithium metaborate fusion in graphite crucibles”. The equipment required is as follow: analytical balance, muffle furnace capable of 1050°C, 250ml volumetric flasks, graphite crucibles (capacity ~50ml), 150ml measuring cylinder, 250ml plastic beakers with lid, magnetic stirrers and stirring plate, filter papers type *Whatman 41*, filter funnels, 50ml plastic tubes, weighing boats.

Reagents needed are: 18MΩ deionised water, trace metal grade nitric (HNO<sub>3</sub>) acids and lithium metaborate flux *Spectroflux 100A*.

### ***PROCEDURE***

- (1) Dry powder at 105°C for 24hrs.
- (2) Weigh 0.25g of powdered sample into a weighing boat. Record exact sample weight.
- (3) Weigh 1.25g of lithium metaborate flux and mix. For blank sample just use flux without sample.
- (4) Transfer into graphite crucibles, and place in furnace note positions. Fuse at 1050°C for 20min.
- (5) While fusing, prepare 250ml plastic bottles with 150ml of 0.5M\* HNO<sub>3</sub>, add magnetic stirrer bar.
- (6) Transfer fusion melt from furnace directly to bottle, with gentle swirls before pouring in stirring liquid. Check for any remaining melt in crucible.
- (7) Let mixture stir for 30min, and check for any non-dissolved glass material. Fine black particles (graphite) are likely to present but irrelevant.
- (8) Filter content into 250ml volumetric flask, with multiple rinses of bottle and filter paper. Make up to volume

- (9) Collect 50ml of final solution in plastic tube and store, discard remaining quantity.

\* This can be made up by diluting 35ml of concentrated  $\text{HNO}_3$  to 1000ml with deionised water.

### ***APPLICATIONS***

This method has been used for the analysis of major, trace and rare earth elements of geological samples, including those containing refractory minerals such as zircon, spinel and chromite. This procedure is not suitable for volatile elements such as As, Pb, Sb, Sn and Zn which are lost during fusion and elements present in the flux (Li and B).

For ICP-AES analysis, sample can be analysed as it is together with appropriately prepared reference materials. For ICP-MS, a further dilution by a factor of 25 is required prior to analysis. Also it is necessary to matrix-match calibration standards with the addition of some blank flux sample to limit matrix effects.

## APPENDIX 1 (continued)

### ***Carbonate samples digestion by $\text{HNO}_3$ and $\text{H}_2\text{O}_2$***

This digestion method is prepared based on procedure from the NERC ICP Facility entitled “The digestion of rocks and soils of high organic content for ICP-MS analysis”. The equipment required is as follow: acid-resistant hotplate capable of  $250^\circ\text{C}$ , 50ml glass beakers (preferably narrow), 50ml volumetric flasks, 50ml plastic tubes, pipettes and tips for 10, 2 and 1ml capacity, weighing boats.

Reagents needed are: 18MΩ deionised water, trace metal grade nitric ( $\text{HNO}_3$ ) acid and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

#### ***PROCEDURE***

- (1) Dry aggregate at  $105^\circ\text{C}$  for 24hrs.
- (2) Weigh accurately aggregate in weighing boat, transfer to glass beaker.
- (3) Add 2ml of 1/1 by volume of concentrated  $\text{HNO}_3$  and deionised water. Decompose at  $150^\circ\text{C}$  and check for active effervescence of sample (release of  $\text{CO}_2$ ).
- (4) In case the sample does not show significant reaction, remove sample and apply procedure detailed previously ( $\text{HF}/\text{HClO}_4$  digestion).
- (5) When reaction intensity decreases, initially slowly add 2ml of  $\text{H}_2\text{O}_2$  to revive digestion. If needed, add concentrated  $\text{HNO}_3$  further in aliquots of 1ml until effervescence does not re-initiate and sample is dissolved, to a maximum of 4ml
- (6) When sample is digested, add 10ml of deionised water.
- (7) Transfer digest to 50ml volumetric flask, rinse multiple times with deionised water and make up to volume.
- (8) Transfer content to new 50ml plastic tube.

## APPLICATIONS

This method has been used for the digestion and analysis of major, trace and rare earth elements of carbonate samples. Any remaining material was regarded as cement and sand material, and usually corresponded to a very small proportion of the original aggregate and considered insignificant. This procedure is not suitable for aggregates of different composition.

For ICP-AES analysis, the sample can be analysed as it is together with appropriately prepared reference materials (in this case using the HF/HClO<sub>4</sub> standards). For ICP-MS analysis, a dilution prior to analysis may be required depending on the likely total dissolved solids of the final preparation solution. The aggregates were weighed whole and differed in mass. A guideline on the masses recorded, the likely dissolved solids in the digested solutions (including the loss of CO<sub>2</sub> during the procedure) and dilution required to reach a value of <200µg.g<sup>-1</sup> is given in the following Table.

| Aggregate mass<br>range (g) | Approximate total<br>dissolved solids (µg.g <sup>-1</sup> ) | Dilution applied |
|-----------------------------|-------------------------------------------------------------|------------------|
| 0.09-0.18                   | 1000-2000                                                   | x10              |
| 0.24-0.34                   | 2500-4000                                                   | x20              |
| 0.42-0.66                   | 4500-7400                                                   | X40              |
| 1.3-1.7                     | 14500-19000                                                 | x100             |

# APPENDIX 2 OPC-1

|                                  | Assigned value | Uncertainty of assigned | Horwitz Target value | Uncertainty y/Target | Number of reported results | Robust mean of results | Median of results | Status      | Type of assigned value |
|----------------------------------|----------------|-------------------------|----------------------|----------------------|----------------------------|------------------------|-------------------|-------------|------------------------|
|                                  | $X_a$<br>% m/m | sdm<br>% m/m            | $H_a$<br>% m/m       | sdm/ $H_a$           | n                          | % m/m                  | % m/m             |             |                        |
| SiO <sub>2</sub>                 | 21.85          | 0.052                   | 0.275                | 0.190                | 68                         | 21.93                  | 21.85             | Assigned    | Median                 |
| TiO <sub>2</sub>                 | 0.318          | 0.002                   | 0.008                | 0.303                | 74                         | 0.318                  | 0.3193            | Assigned    | Robust Mean            |
| Al <sub>2</sub> O <sub>3</sub>   | 4.55           | 0.021                   | 0.072                | 0.283                | 71                         | 4.55                   | 4.55              | Assigned    | Robust Mean            |
| Fe <sub>2</sub> O <sub>3</sub> T | 3.19           | 0.012                   | 0.054                | 0.219                | 74                         | 3.18                   | 3.19              | Assigned    | Median                 |
| MnO                              | 0.404          | 0.003                   | 0.009                | 0.325                | 72                         | 0.404                  | 0.4045            | Assigned    | Robust Mean            |
| MgO                              | 2.58           | 0.011                   | 0.045                | 0.236                | 71                         | 2.58                   | 2.58              | Assigned    | Median                 |
| CaO                              | 62.9           | 0.126                   | 0.674                | 0.186                | 73                         | 62.9                   | 62.82             | Assigned    | Robust Mean            |
| K <sub>2</sub> O                 | 0.344          | 0.003                   | 0.008                | 0.381                | 73                         | 0.344                  | 0.342             | Assigned    | Robust Mean            |
| P <sub>2</sub> O <sub>5</sub>    | 0.044          | 0.001                   | 0.001                | 0.736                | 62                         | 0.044                  | 0.044             | Provisional | Robust Mean            |
|                                  | mg/kg          | mg/kg                   | mg/kg                |                      |                            | mg/kg                  | mg/kg             |             |                        |
| As                               | 4.6            | 0.183                   | 0.291                | 0.631                | 26                         | 4.8                    | 4.5635            | Provisional | Median                 |
| Ba                               | 512            | 6.023                   | 16.002               | 0.376                | 68                         | 506                    | 511.5             | Assigned    | Median                 |
| Be                               | 0.82           | 0.036                   | 0.068                | 0.537                | 24                         | 0.84                   | 0.82              | Provisional | Median                 |
| Ce                               | 48.9           | 0.580                   | 2.178                | 0.266                | 55                         | 49.5                   | 48.9              | Assigned    | Median                 |
| Co                               | 21.4           | 0.324                   | 1.079                | 0.300                | 55                         | 20.9                   | 21.38             | Assigned    | Median                 |
| Cs                               | 1.00           | 0.019                   | 0.080                | 0.237                | 32                         | 1.00                   | 1                 | Assigned    | Robust Mean            |
| Cu                               | 23.7           | 0.614                   | 1.179                | 0.521                | 62                         | 23.7                   | 23.615            | Provisional | Robust Mean            |
| Dy                               | 2.87           | 0.031                   | 0.196                | 0.160                | 34                         | 2.87                   | 2.87              | Assigned    | Robust Mean            |
| Er                               | 1.52           | 0.015                   | 0.114                | 0.131                | 32                         | 1.52                   | 1.54              | Assigned    | Robust Mean            |
| Eu                               | 1.00           | 0.012                   | 0.080                | 0.149                | 36                         | 1.00                   | 1                 | Assigned    | Robust Mean            |
| Ga                               | 7              | 0.111                   | 0.418                | 0.267                | 45                         | 6.9                    | 7                 | Assigned    | Median                 |
| Gd                               | 3.75           | 0.050                   | 0.246                | 0.204                | 35                         | 3.81                   | 3.75              | Assigned    | Median                 |
| Hf                               | 2.12           | 0.039                   | 0.151                | 0.255                | 35                         | 2.16                   | 2.12              | Assigned    | Median                 |
| Ho                               | 0.55           | 0.006                   | 0.049                | 0.133                | 34                         | 0.55                   | 0.5505            | Assigned    | Robust Mean            |
| La                               | 25.9           | 0.383                   | 1.271                | 0.302                | 54                         | 25.7                   | 25.9275           | Assigned    | Median                 |
| Li                               | 13.1           | 0.553                   | 0.714                | 0.775                | 27                         | 13.1                   | 13.359            | Provisional | Robust Mean            |
| Lu                               | 0.20           | 0.002                   | 0.020                | 0.096                | 34                         | 0.20                   | 0.199             | Assigned    | Robust Mean            |
| Nb                               | 4.9            | 0.137                   | 0.311                | 0.440                | 51                         | 4.9                    | 4.92              | Assigned    | Robust Mean            |
| Nd                               | 24.7           | 0.254                   | 1.219                | 0.209                | 49                         | 24.4                   | 24.7              | Assigned    | Median                 |
| Ni                               | 87.0           | 1.888                   | 3.552                | 0.531                | 67                         | 87.0                   | 87.96             | Provisional | Robust Mean            |
| Pb                               | 7.2            | 0.301                   | 0.426                | 0.707                | 52                         | 7.2                    | 7.145             | Provisional | Robust Mean            |
| Pr                               | 6.2            | 0.075                   | 0.378                | 0.199                | 36                         | 6.2                    | 6.2155            | Assigned    | Robust Mean            |
| Rb                               | 14.7           | 0.298                   | 0.783                | 0.381                | 59                         | 14.7                   | 14.7              | Assigned    | Robust Mean            |
| Sb                               | 0.26           | 0.012                   | 0.025                | 0.472                | 20                         | 0.25                   | 0.2558            | Assigned    | Median                 |
| Sm                               | 4.5            | 0.053                   | 0.289                | 0.185                | 40                         | 4.5                    | 4.515             | Assigned    | Robust Mean            |
| Sr                               | 118.2          | 1.051                   | 4.610                | 0.228                | 66                         | 118.2                  | 118.55            | Assigned    | Robust Mean            |
| Ta                               | 0.35           | 0.016                   | 0.033                | 0.480                | 30                         | 0.35                   | 0.3515            | Provisional | Robust Mean            |
| Tb                               | 0.52           | 0.006                   | 0.046                | 0.127                | 32                         | 0.52                   | 0.52              | Assigned    | Robust Mean            |
| Th                               | 3.93           | 0.064                   | 0.256                | 0.248                | 49                         | 4.25                   | 3.93              | Assigned    | Median                 |
| Tm                               | 0.21           | 0.003                   | 0.022                | 0.118                | 29                         | 0.21                   | 0.21              | Assigned    | Robust Mean            |
| U                                | 0.83           | 0.014                   | 0.068                | 0.208                | 39                         | 0.83                   | 0.831             | Assigned    | Robust Mean            |
| V                                | 64.0           | 1.066                   | 2.736                | 0.389                | 64                         | 62.6                   | 63.965            | Provisional | Median                 |
| W                                | 0.7            | 0.034                   | 0.059                | 0.576                | 19                         | 0.75                   | 0.7               | Provisional | Median                 |
| Y                                | 15.5           | 0.295                   | 0.822                | 0.359                | 58                         | 15.5                   | 15.56             | Assigned    | Robust Mean            |
| Yb                               | 1.34           | 0.015                   | 0.103                | 0.147                | 39                         | 1.34                   | 1.36              | Assigned    | Robust Mean            |
| Zn                               | 27.8           | 0.603                   | 1.349                | 0.447                | 66                         | 27.8                   | 27.65             | Provisional | Robust Mean            |
| Zr                               | 81.2           | 1.170                   | 3.352                | 0.349                | 62                         | 81.2                   | 81.45             | Assigned    | Robust Mean            |

## PRELIMINARY

# United States Geological Survey

## Certificate of Analysis

### Microanalytical Carbonate Standard, MACS-3

This reference material is designed primarily for use in the analysis of carbonate samples using techniques such as Laser Ablation ICP-MS. MACS-3 was prepared using a specially designed co-precipitation process in which forty five trace and minor elements are added to the reaction vessel and allowed to mix with the calcium carbonate precipitate. The final slurry was ground to less than 40 micron, dried at 110° C and then pressed into pellets. Recommended values are based on USGS bulk analysis using a variety of analytical techniques and confirmed by one international laboratory. Information values represent results from a single method of analysis.

## Recommended values

| Element          | Wt %  | +/-  | Oxide                              | Wt %  | +/-   |
|------------------|-------|------|------------------------------------|-------|-------|
| Ca               | 37.69 | 0.52 | CaO                                | 52.74 | 0.73  |
| Fe TOT           | 1.12  | 0.03 | Fe <sub>2</sub> O <sub>3</sub> TOT | 1.60  | 0.04  |
| Na               | 0.59  | 0.04 | Na <sub>2</sub> O                  | 0.80  | 0.014 |
| C <sub>TOT</sub> | 11.5  | 0.06 |                                    |       |       |

| Element | µg/g | +/-  | Element | µg/g | +/-  |
|---------|------|------|---------|------|------|
| Ag      | 53.3 | 1.8  | Mg      | 1756 | 136  |
| As      | 44.2 | 1.4  | Mn      | 536  | 28   |
| Ba      | 58.7 | 2.0  | Mo      | 1.21 | 0.14 |
| Be      | 56.4 | 1.7  | Nb      | 35.2 | 3.1  |
| Bi      | 19.9 | 1.6  | Nd      | 11   | 0.41 |
| Cd      | 54.6 | 2.2  | Ni      | 57.4 | 4.9  |
| Ce      | 11.2 | 0.33 | Pb      | 56.5 | 1.8  |
| Co      | 57.1 | 2    | Pr      | 12.1 | 0.23 |
| Cr      | 117  | 5    | Sb      | 20.6 | 1.1  |
| Cu      | 120  | 5    | Sc      | 21   | 0.8  |
| Dy      | 10.7 | 0.5  | Sm      | 11   | 0.27 |
| Er      | 11.2 | 0.22 | Sn      | 58.1 | 8.8  |
| Eu      | 11.8 | 0.13 | Sr      | 6760 | 350  |
| Ga      | 16.1 | 1.1  | Ta      | 20.5 | 5.3  |
| Gd      | 10.8 | 0.3  | Th      | 55.4 | 1.1  |
| Ge      | 56.9 | 4    | Ti      | 54.9 | 0.18 |
| Hf      | 4.73 | 0.21 | Tl      | 14.2 | 1.7  |
| Hg      | 10.2 | 0.4  | U       | 1.52 | 0.04 |
| Ho      | 11.3 | 0.14 | V       | 46.3 | 1.13 |
| La      | 10.4 | 0.5  | W       | 2.16 | 0.19 |
| Li      | 62.2 | 4.2  | Zn      | 111  | 5.7  |
| Lu      | 10.8 | 0.3  | Zr      | 8.67 | 0.63 |

(Over)

## Information values

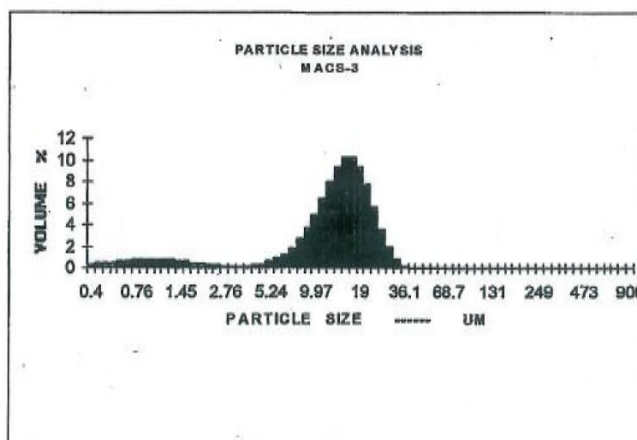
| Element | ug/g | +/- | Element | ug/g | +/- |
|---------|------|-----|---------|------|-----|
| Au      | 7.12 |     | Pd      | 3.4  |     |
| Br      | 0.44 |     | Pt      | 17.8 |     |
| Cl      | 61   | 2   | Ru      | 20.1 |     |
| I       | 20.3 |     |         |      |     |

## Isotopic Information

| Element                 | Ratios  | +/-      | N |
|-------------------------|---------|----------|---|
| Sr 87/86 (Rb corrected) | 0.70759 | 2.5e-5   | 1 |
| Sr (SRM 987)            | 0.71025 | 1.0e-5   | 1 |
|                         | Ratio   | +/- (2σ) | N |
| Pb208/204               | 38.181  | 0.002    | 1 |
| 207/204                 | 15.619  | 0.002    | 1 |
| 206/204                 | 18.390  | 0.01     | 1 |
| Pb SRM 981              |         |          |   |
| 208/204                 | 36.688  | 0.004    | 1 |
| 207/204                 | 15.488  | 0.002    | 1 |
| 206/204                 | 16.935  | 0.002    | 1 |

## Glossary

|      |                          |
|------|--------------------------|
| Wt % | Weight percent           |
| ug/g | micrograms/gram          |
| +/-  | one standard deviation   |
| N    | number of labs reporting |



## APPENDIX 4` NIST Glasses

- NIST 610 Majors

| Toronto EPMA,<br>this study,<br>average<br>(n=20) | Memorial EPMA,<br>this study,<br>average<br>(n=19) | (A)<br>average | Overall<br>average | Overall<br>average,<br>scaled | NIST<br>nominal<br>matrix        |
|---------------------------------------------------|----------------------------------------------------|----------------|--------------------|-------------------------------|----------------------------------|
| 69.895 ± 0.214                                    | 70.400 ± 0.400                                     | 69.63 ± 0.27   | 69.975 ± 0.391     | 72.276                        | 72 SiO <sub>2</sub>              |
| 0.070 ± 0.025                                     | 0.076 ± 0.012                                      | 0.08 ± 0.01    | 0.075 ± 0.005      |                               | TiO <sub>2</sub>                 |
| 1.936 ± 0.027                                     | 1.960 ± 0.090                                      | 2.22 ± 0.01    | 2.039 ± 0.157      | 2.106                         | 2 Al <sub>2</sub> O <sub>3</sub> |
| 0.059 ± 0.023                                     | 0.039 ± 0.024                                      | 0.07 ± 0.02    | 0.056 ± 0.016      |                               | FeO                              |
| 0.053 ± 0.025                                     | 0.060 ± 0.031                                      | 0.05 ± 0.03    | 0.054 ± 0.005      |                               | MnO                              |
| 0.067 ± 0.012                                     | 0.057 ± 0.006                                      | 0.07 ± 0.01    | 0.065 ± 0.007      |                               | MgO                              |
| 11.370 ± 0.083                                    | 11.270 ± 0.140                                     | 11.71 ± 0.03   | 11.450 ± 0.231     | 11.827                        | 12 CaO                           |
| 13.833 ± 0.090                                    | 8.200 ± 0.300                                      | 12.87 ± 0.08   | 13.352 ± 0.681     | 13.791                        | 14 Na <sub>2</sub> O             |
| 0.061 ± 0.019                                     | 0.057 ± 0.026                                      | 0.06 ± 0.01    | 0.059 ± 0.002      |                               | K <sub>2</sub> O                 |
| 0.047 ± 0.016                                     |                                                    |                | 0.047 ± 0.000      |                               | Cl                               |
|                                                   |                                                    | 0.12 ± 0.02    | 0.120 ± 0.000      |                               | P <sub>2</sub> O <sub>5</sub>    |
| 97.389                                            | 92.119                                             | 96.88 ± 0.13   | 97.292             | 100.000                       | 100 Total                        |

- NIST 612 Majors

| Toronto EPMA<br>this study,<br>average<br>(n=20) | (A)    | (B)<br>average<br>(n=10) | (C)<br>average | (D)<br>average | (E)<br>activation<br>analysis | (E)<br>superprobe<br>733 | Overall<br>average | Overall<br>average,<br>scaled | NIST<br>nominal<br>matrix |
|--------------------------------------------------|--------|--------------------------|----------------|----------------|-------------------------------|--------------------------|--------------------|-------------------------------|---------------------------|
| SiO <sub>2</sub> 72.29±0.22                      | 71.5   | 72.17±0.35               |                |                | 72.90±1.40                    | 70.65                    | 71.90±0.96         | 71.79                         | 72                        |
| TiO <sub>2</sub> 0.02±0.02                       |        | 0.01±0.01                |                |                |                               |                          | 0.01±0.00          |                               |                           |
| Al <sub>2</sub> O <sub>3</sub> 2.01±0.04         | 2.15   | 2.32±0.01                |                |                | 2.10±0.04                     | 1.96                     | 2.11±0.16          | 2.10                          | 2                         |
| FeO 0.01±0.02                                    | 0.027  | 0.02±0.01                |                |                |                               |                          | 0.02±0.00          |                               |                           |
| MnO 0.01±0.02                                    |        | 0.01±0.02                |                |                |                               |                          | 0.01±0.00          |                               |                           |
| MgO 0.00±0.00                                    |        |                          |                |                |                               |                          | 0.00               |                               |                           |
| CaO 11.77±0.11                                   | 11.4   | 12.09±0.50               | 12.10±0.20     | 12.30±1.00     |                               |                          | 11.93±0.22         | 11.91                         | 12                        |
| Na <sub>2</sub> O 14.18±0.10                     | 13     | 13.16±0.07               | 14.20±0.20     | 14.40±0.80     |                               |                          | 13.98±0.56         | 13.96                         | 14                        |
| K <sub>2</sub> O 0.01±0.01                       | 0.02   | 0.01±0.01                |                |                |                               |                          | 0.01±0.00          |                               |                           |
| Cl 0.02±0.02                                     |        |                          |                |                |                               |                          | 0.02               |                               |                           |
| P <sub>2</sub> O <sub>5</sub>                    |        | 0.01±0.01                |                |                |                               |                          | 0.01               |                               |                           |
| Total 100.319                                    | 98.117 | 99.8                     |                |                |                               |                          | 100.009            | 100.000                       | 100                       |

- NIST 610 Traces

| N  |    | Overall average | s     | Range  |       | Median | Geometric mean | Preferred average | s <sub>p</sub> | n  | NIST   | cl* |    |
|----|----|-----------------|-------|--------|-------|--------|----------------|-------------------|----------------|----|--------|-----|----|
|    |    |                 |       | Max    | Min   |        |                |                   |                |    |        |     |    |
| Ag | 8  | 235.4           | 29.0  | 267    | 180   | 238.5  | 233.7          | 239.4             | 18.6           | 6  | (254)  | 10  | Ag |
| As | 7  | 330.1           | 35.4  | 406    | 303   | 317    | 328.6          | 317.4             | 12.4           | 6  |        |     | As |
| Au | 7  | 22.7            | 5.3   | 31     | 15.63 | 22.6   | 22.2           | 22.5              | 3.5            | 5  | (25)   |     | Au |
| B  | 9  | 332.4           | 72.1  | 368    | 141   | 356    | 321.4          | 356.4             | 7.3            | 8  | (351)  |     | B  |
| Ba | 9  | 565.1           | 285.5 | 1160   | 382   | 424    | 518.3          | 424.1             | 29.3           | 7  |        |     | Ba |
| Be | 9  | 469.0           | 34.9  | 540.67 | 421   | 452    | 467.9          | 465.6             | 19.2           | 7  |        |     | Be |
| Bi | 10 | 326.4           | 99.7  | 430    | 113.7 | 372.5  | 307.0          | 357.7             | 49.0           | 7  |        |     | Bi |
| Cd | 6  | 269.6           | 67.1  | 393    | 187   | 259    | 263.2          | 259.4             | 4.7            | 4  |        |     | Cd |
| Ce | 12 | 462.6           | 57.6  | 611    | 384   | 451.1  | 459.6          | 447.8             | 16.8           | 9  |        |     | Ce |
| Cl | 2  | 470.0           | 0.0   | 470    | 470   | 470    | 470.0          | 470.0             | 0.0            | 2  |        |     | Cl |
| Co | 14 | 374.8           | 82.8  | 444    | 135   | 396.5  | 361.6          | 405.0             | 22.9           | 12 | (390)  |     | Co |
| Cr | 9  | 415.0           | 49.5  | 485    | 343   | 406    | 412.4          | 405.2             | 32.3           | 6  |        |     | Cr |
| Cs | 7  | 429.4           | 191.3 | 840    | 259   | 369    | 401.9          | 360.9             | 67.5           | 6  |        |     | Cs |
| Cu | 13 | 421.7           | 42.0  | 486    | 343   | 428    | 419.7          | 430.3             | 23.6           | 10 | (444)  | 4   | Cu |
| Dy | 7  | 420.2           | 39.9  | 466    | 343   | 429    | 418.5          | 426.5             | 18.0           | 5  |        |     | Dy |
| Er | 9  | 440.1           | 54.8  | 526    | 360   | 436    | 437.2          | 426.0             | 23.9           | 6  |        |     | Er |
| Eu | 9  | 479.6           | 110.1 | 731    | 357   | 442.7  | 469.9          | 461.1             | 52.1           | 7  |        |     | Eu |
| Fe | 11 | 430.3           | 79.3  | 517    | 260   | 455    | 422.2          | 457.1             | 22.2           | 8  | 458    | 9   | Fe |
| Ga | 11 | 443.8           | 28.7  | 501.3  | 395   | 436.5  | 443.0          | 438.1             | 11.3           | 8  |        |     | Ga |
| Gd | 9  | 437.2           | 69.6  | 556    | 331   | 430.53 | 432.4          | 419.9             | 25.2           | 6  |        |     | Gd |
| Ge | 5  | 433.3           | 38.8  | 496    | 391.3 | 426    | 431.9          | 426.3             | 9.5            | 3  |        |     | Ge |
| Hf | 10 | 419.1           | 50.3  | 477    | 312.7 | 418    | 416.1          | 417.7             | 28.2           | 7  |        |     | Hf |
| Ho | 8  | 445.7           | 46.4  | 511    | 358   | 444.9  | 443.5          | 449.4             | 24.6           | 6  |        |     | Ho |
| In | 7  | 423.9           | 54.7  | 474    | 319   | 449    | 420.5          | 441.4             | 32.0           | 6  |        |     | In |
| K  | 6  | 671.7           | 456.6 | 1600   | 442   | 487.5  | 591.1          | 486.0             | 45.7           | 5  | (461)  |     | K  |
| La | 12 | 509.2           | 138.0 | 794    | 386   | 448    | 494.6          | 457.4             | 72.4           | 10 |        |     | La |
| Li | 10 | 464.2           | 61.4  | 536.3  | 354   | 487.9  | 460.2          | 484.6             | 21.7           | 7  |        |     | Li |
| Lu | 11 | 431.0           | 46.9  | 497    | 332   | 440    | 428.6          | 434.7             | 31.0           | 9  |        |     | Lu |
| Mg | 5  | 465.6           | 37.0  | 511    | 421   | 472    | 464.4          | 465.3             | 26.6           | 3  |        |     | Mg |
| Mn | 11 | 419.2           | 75.4  | 495    | 216   | 440.8  | 410.9          | 433.3             | 31.8           | 9  | 485    | 10  | Mn |
| Mo | 10 | 363.5           | 57.7  | 427    | 276   | 389.5  | 359.1          | 376.8             | 45.0           | 7  |        |     | Mo |
| Nb | 8  | 373.7           | 97.8  | 458    | 225   | 428.1  | 360.9          | 419.4             | 57.6           | 6  |        |     | Nb |
| Nd | 10 | 455.6           | 79.3  | 598    | 364   | 430.6  | 449.8          | 430.8             | 37.5           | 7  |        |     | Nd |
| Ni | 11 | 437.5           | 74.9  | 603.8  | 316   | 441    | 431.7          | 443.9             | 24.2           | 8  | 458.7  | 4   | Ni |
| P  | 2  | 342.5           | 53.1  | 380    | 304.9 | 342.5  | 340.4          | 342.5             | 53.1           | 2  |        |     | P  |
| Pb | 18 | 409.0           | 31.6  | 448    | 301.4 | 417    | 407.7          | 413.3             | 15.4           | 16 | 426    | 1   | Pb |
| Pr | 9  | 432.7           | 57.6  | 505    | 318   | 441    | 429.1          | 429.8             | 30.0           | 6  |        |     | Pr |
| Rb | 10 | 435.0           | 27.4  | 501.97 | 400   | 429.5  | 434.3          | 431.1             | 11.4           | 8  | 425.7  | 0.8 | Rb |
| Re | 4  | 192.9           | 192.9 | 460.4  | 37    | 137    | 124.3          | 103.7             | 90.0           | 3  |        |     | Re |
| Sb | 6  | 345.9           | 60.5  | 394    | 233   | 362.2  | 340.7          | 368.5             | 27.5           | 5  |        |     | Sb |
| Sc | 9  | 432.1           | 47.1  | 486    | 315   | 444    | 429.4          | 441.1             | 9.6            | 7  |        |     | Sc |
| Se | 3  | 110.7           | 3.1   | 114    | 108   | 110    | 110.6          | 109.0             | 1.4            | 2  |        |     | Se |
| Sm | 9  | 484.5           | 69.9  | 610    | 417   | 458    | 480.4          | 450.5             | 20.6           | 7  |        |     | Sm |
| Sn | 5  | 391.3           | 54.5  | 458    | 309.4 | 404    | 388.1          | 396.3             | 17.8           | 3  |        |     | Sn |
| Sr | 11 | 479.6           | 44.0  | 515.5  | 377   | 498    | 477.6          | 497.4             | 18.3           | 9  | 515.5  | 0.5 | Sr |
| Ta | 11 | 365.9           | 125.7 | 525    | 134   | 340.13 | 342.0          | 376.6             | 77.6           | 7  |        |     | Ta |
| Tb | 10 | 443.5           | 75.9  | 585    | 328   | 454.9  | 437.6          | 442.8             | 22.4           | 6  |        |     | Tb |
| Th | 14 | 448.0           | 69.1  | 539    | 249   | 456.3  | 441.8          | 450.6             | 27.8           | 11 | 457.2  | 1.2 | Th |
| Ti | 13 | 428.2           | 66.5  | 524.43 | 257   | 437.3  | 422.6          | 434.0             | 14.7           | 9  | (437)  |     | Ti |
| Tl | 9  | 61.9            | 5.2   | 70     | 52    | 61.19  | 61.7           | 61.2              | 2.1            | 6  | (61.8) | 2.5 | Tl |
| Tm | 9  | 431.4           | 45.4  | 517    | 366   | 422.6  | 429.3          | 420.1             | 19.2           | 6  |        |     | Tm |
| U  | 17 | 453.2           | 27.3  | 513.3  | 413   | 461.3  | 452.5          | 457.1             | 13.6           | 11 | 461.5  | 1.1 | U  |
| V  | 12 | 422.1           | 79.3  | 494.2  | 206   | 435.1  | 412.9          | 441.7             | 42.7           | 11 |        |     | V  |
| W  | 4  | 425.5           | 44.6  | 467    | 366   | 434.5  | 423.7          | 445.3             | 25.0           | 3  |        |     | W  |
| Y  | 10 | 440.2           | 66.9  | 531.47 | 271   | 448    | 434.6          | 449.9             | 19.3           | 8  |        |     | Y  |
| Yb | 9  | 467.2           | 52.2  | 574    | 400   | 450.6  | 464.7          | 461.5             | 30.6           | 7  |        |     | Yb |
| Zn | 12 | 447.2           | 30.7  | 494.27 | 398   | 451    | 446.3          | 456.3             | 19.2           | 8  | (433)  |     | Zn |
| Zr | 10 | 435.1           | 26.6  | 482.37 | 381.3 | 435.5  | 434.3          | 439.9             | 7.8            | 7  |        |     | Zr |

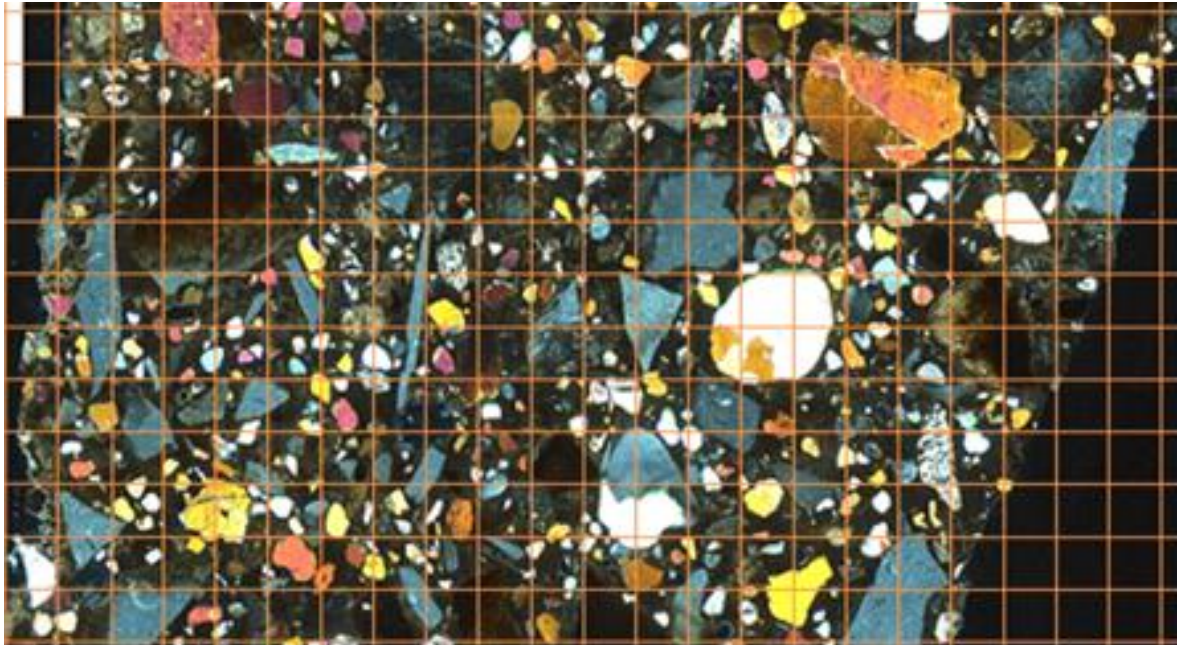
- NIST 612 Traces

| N  |    | Overall average | s      | Range  |        | Median | Geometric mean | Preferred average | s <sub>p</sub> | n  | NIST   | cl*  |    |
|----|----|-----------------|--------|--------|--------|--------|----------------|-------------------|----------------|----|--------|------|----|
|    |    |                 |        | Max    | Min    |        |                |                   |                |    |        |      |    |
| Ag | 8  | 20.44           | 8.91   | 31     | 1      | 31.26  | 15.46          | 21.92             | 3.26           | 6  | 22     | 0.3  | Ag |
| As | 7  | 38.56           | 11.11  | 58.1   | 25.2   | 35.6   | 37.29          | 37.33             | 6.56           | 5  |        |      | As |
| Au | 6  | 5.07            | 0.63   | 6      | 4.05   | 5.05   | 5.04           | 5.09              | 0.13           | 4  | (5)    |      | Au |
| B  | 11 | 33.73           | 5.83   | 43     | 25.8   | 33     | 33.26          | 34.73             | 3.21           | 6  | (32)   |      | B  |
| Ba | 11 | 3792            | 3.42   | 45     | 32.87  | 38     | 3778           | 3774              | 1.26           | 7  | (41)   |      | Ba |
| Be | 10 | 39.31           | 5.88   | 50     | 31     | 38.3   | 38.94          | 3773              | 2.41           | 7  |        |      | Be |
| Bi | 6  | 28.73           | 9.86   | 40     | 13     | 32.13  | 26.96          | 29.84             | 5.98           | 4  |        |      | Bi |
| Cd | 4  | 31.24           | 5.87   | 40     | 27.63  | 28.66  | 30.87          | 28.32             | 0.65           | 3  |        |      | Cd |
| Ce | 18 | 38.75           | 3.92   | 48.2   | 33     | 38     | 38.57          | 38.35             | 1.64           | 12 | (39)   |      | Ce |
| Co | 16 | 36.23           | 15.37  | 84     | 2      | 34.95  | 31.05          | 35.26             | 2.44           | 14 | (35.5) | 1.2  | Co |
| Cr | 10 | 51.39           | 39.11  | 155    | 19.241 | 3797   | 43.19          | 39.88             | 15.17          | 9  |        |      | Cr |
| Cs | 11 | 46.49           | 16.28  | 95     | 35.08  | 42.3   | 44.81          | 41.64             | 2.59           | 10 |        |      | Cs |
| Cu | 10 | 35.17           | 11.64  | 52.007 | 6      | 37.57  | 31.63          | 36.71             | 3.07           | 8  | (377)  | 0.9  | Cu |
| Dy | 14 | 36.03           | 2.22   | 41.7   | 31.1   | 36     | 35.97          | 35.97             | 0.82           | 12 | (35)   |      | Dy |
| Er | 13 | 3799            | 3.27   | 44.6   | 32     | 38.15  | 3786           | 3743              | 1.50           | 10 | (39)   |      | Er |
| Eu | 18 | 35.51           | 5.50   | 53     | 26     | 34.97  | 35.16          | 34.44             | 1.59           | 15 | (36)   |      | Eu |
| Fe | 7  | 64.71           | 27.14  | 115    | 37.7   | 53     | 60.56          | 56.33             | 17.14          | 6  | 51     | 2    | Fe |
| Ga | 9  | 3771            | 4.29   | 44.9   | 33     | 36.88  | 37.50          | 36.24             | 2.03           | 6  |        |      | Ga |
| Gd | 15 | 38.09           | 6.66   | 61     | 30     | 37     | 37.66          | 36.95             | 1.06           | 13 | (39)   |      | Gd |
| Ge | 2  | 34.64           | 2.64   | 36.5   | 32.77  | 34.64  | 34.58          | 34.64             | 2.64           | 2  |        |      | Ge |
| Hf | 11 | 34.29           | 9.64   | 52.29  | 12     | 35     | 32.61          | 34.77             | 3.65           | 9  |        |      | Hf |
| Ho | 11 | 3789            | 3.71   | 46     | 30     | 37.6   | 3772           | 3787              | 1.09           | 9  |        |      | Ho |
| In | 6  | 38.85           | 10.72  | 49     | 18.44  | 42.22  | 37.16          | 42.93             | 4.32           | 5  |        |      | In |
| K  | 3  | 63.84           | 4.20   | 66.52  | 59     | 66     | 63.75          | 66.26             | 0.37           | 2  | (64)   |      | K  |
| La | 17 | 36.95           | 3.92   | 48     | 33     | 35.75  | 36.77          | 35.77             | 2.15           | 13 | (36)   |      | La |
| Li | 12 | 43.17           | 6.25   | 61     | 37.9   | 41.83  | 42.81          | 41.54             | 2.87           | 11 |        |      | Li |
| Lu | 13 | 37.60           | 3.73   | 45     | 29     | 37.2   | 37.42          | 37.71             | 1.95           | 11 |        |      | Lu |
| Mg | 6  | 121.37          | 110.93 | 341    | 36     | 80.15  | 93.51          | 77.44             | 30.15          | 5  |        |      | Mg |
| Mn | 9  | 36.60           | 5.55   | 39.9   | 22     | 38.3   | 36.11          | 38.43             | 0.99           | 8  | (39.6) | 0.8  | Mn |
| Mo | 8  | 3779            | 3.15   | 43     | 33.8   | 3776   | 3767           | 38.30             | 1.65           | 5  |        |      | Mo |
| Nb | 5  | 38.74           | 3.54   | 44.5   | 35     | 38.1   | 38.61          | 38.06             | 0.86           | 3  |        |      | Nb |
| Nd | 13 | 37.52           | 8.58   | 65     | 31     | 35     | 36.86          | 35.24             | 2.44           | 12 | (36)   |      | Nd |
| Ni | 8  | 35.51           | 9.33   | 3.431  | 15     | 38.2   | 33.96          | 38.44             | 4.64           | 7  | 38.8   | 0.2  | Ni |
| P  | 2  | 55.16           | 22.71  | 71.21  | 39.1   | 55.16  | 52.77          | 55.16             | 22.71          | 2  |        |      | P  |
| Pb | 16 | 39.77           | 5.34   | 57.9   | 33     | 38.64  | 39.49          | 38.96             | 1.84           | 14 | 38.57  | 0.2  | Pb |
| Pr | 10 | 36.69           | 1.82   | 39     | 33     | 37.21  | 36.64          | 37.16             | 0.93           | 7  |        |      | Pr |
| Rb | 12 | 32.19           | 1.48   | 36     | 31.02  | 31.43  | 32.16          | 31.63             | 0.59           | 10 | 31.4   | 0.4  | Rb |
| Re | 2  | 8.12            | 3.27   | 10.43  | 5.8    | 8.12   | 7.78           | 8.12              | 3.27           | 2  |        |      | Re |
| S  | 1  | 16.00           | 0.00   | 16     | 16     | 16     | 16.00          | 16.00             | 16.00          | 1  |        |      | S  |
| Sb | 8  | 3774            | 4.46   | 45.2   | 32.2   | 38.46  | 37.51          | 38.44             | 2.26           | 5  |        |      | Sb |
| Sc | 9  | 42.25           | 7.51   | 54.6   | 34     | 40.35  | 41.68          | 41.05             | 4.09           | 5  |        |      | Sc |
| Sm | 17 | 38.50           | 7.77   | 67     | 32.7   | 36.8   | 37.96          | 36.72             | 2.63           | 16 | (39)   |      | Sm |
| Sn | 5  | 33.56           | 9.94   | 40     | 16     | 36.8   | 31.91          | 37.96             | 1.76           | 4  |        |      | Sn |
| Sr | 13 | 76.60           | 3.74   | 86.2   | 72     | 76.3   | 76.52          | 76.15             | 2.29           | 11 | 78.4   | 0.2  | Sr |
| Ta | 6  | 41.92           | 5.62   | 52.7   | 36.33  | 40.61  | 41.64          | 39.77             | 2.15           | 5  |        |      | Ta |
| Tb | 14 | 36.14           | 6.56   | 52.9   | 22     | 36.8   | 35.58          | 35.92             | 2.68           | 12 |        |      | Tb |
| Th | 14 | 36.11           | 4.41   | 42.1   | 23     | 36.99  | 35.81          | 37.23             | 0.72           | 11 | 3779   | 0.08 | Th |
| Ti | 8  | 47.68           | 7.01   | 57     | 38.2   | 47.85  | 47.22          | 48.11             | 3.01           | 4  | (50.1) | 0.8  | Ti |
| Tl | 8  | 14.06           | 2.92   | 16     | 7      | 14.91  | 13.68          | 15.07             | 0.66           | 7  | (15.7) | 0.3  | Tl |
| Tm | 10 | 36.24           | 3.01   | 39.15  | 30     | 37.01  | 36.12          | 37.55             | 1.25           | 8  |        |      | Tm |
| U  | 20 | 37.19           | 3.18   | 44.1   | 30     | 37.37  | 37.06          | 37.15             | 1.23           | 16 | 3738   | 0.08 | U  |
| V  | 10 | 40.44           | 7.54   | 58.6   | 32     | 38.1   | 39.88          | 39.22             | 3.76           | 8  |        |      | V  |
| W  | 3  | 35.20           | 7.55   | 40.1   | 26.5   | 39     | 34.61          | 39.55             | 0.78           | 2  |        |      | W  |
| Y  | 11 | 38.33           | 3.78   | 46     | 31.45  | 37.9   | 38.17          | 38.25             | 2.14           | 9  |        |      | Y  |
| Yb | 17 | 41.20           | 5.52   | 55     | 34     | 40.02  | 40.88          | 39.95             | 2.86           | 14 | (42)   |      | Yb |
| Zn | 8  | 36.24           | 10.72  | 49.4   | 13     | 37.15  | 34.18          | 37.92             | 3.86           | 6  |        |      | Zn |
| Zr | 9  | 38.01           | 3.77   | 43.5   | 33.81  | 37.3   | 37.85          | 35.99             | 1.25           | 5  |        |      | Zr |

## APPENDIX 5

### Point counting exercise results

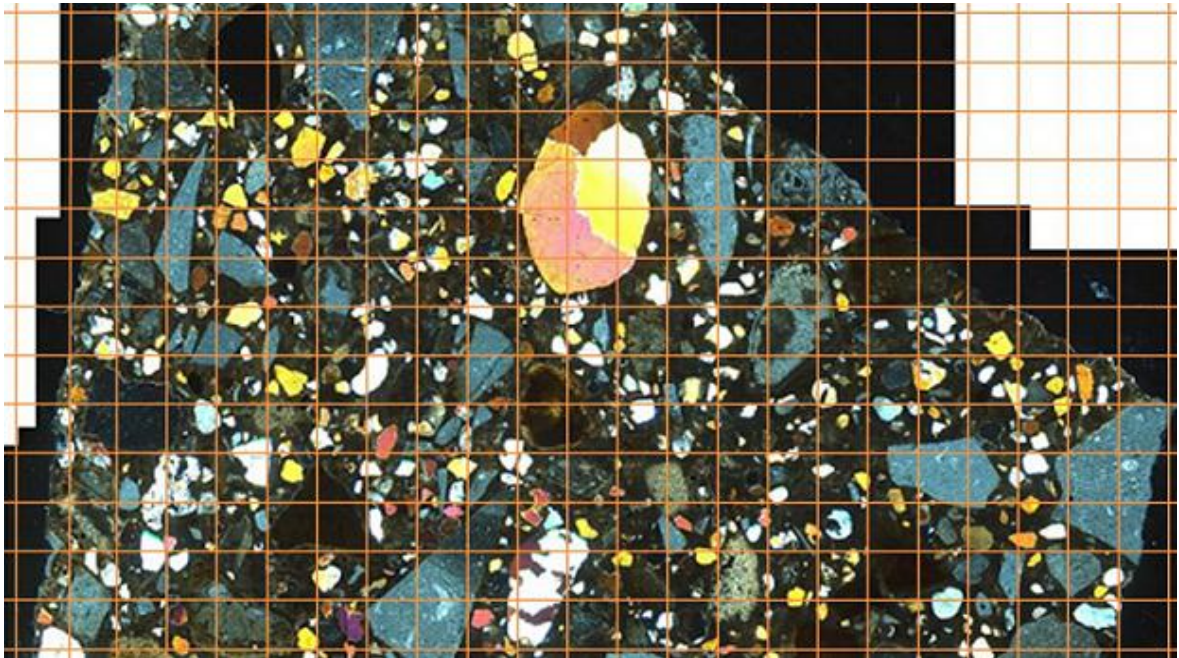
#### Section 1



|    |     |   |   |     |     |     |     |     |     |     |     |     |   |     |     |   |     |     |     |    |
|----|-----|---|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|---|-----|-----|---|-----|-----|-----|----|
|    | C   | C | R | C   | C   | C   | R   | C   | C   | C   | C   | C   | C | C/M | C   | C | C   | G/C | C   | C  |
|    | C   | C | C | R/C | C   | C   | R   | R   | C   | C/R | C   | G   | C | C/R | R   | R | R/C | G   | G   | C  |
|    | R/C | C | M | C   | C   | C   | R   | R   | C   | C   | C   | C   | C | R/C | R   | R | R/C | R/C | C   | G  |
|    | C   | C | M | M   | C   | C   | C   | C   | C   | C   | C   | G   | C | R/C | C   | C | C   | R/C | C/G | G/ |
| /C | C/G | M | M | M   | C   | C   | C   | C   | C   | C   | C   | G   | C | C/R | C   | C | C/R | C   |     |    |
| /C | G   | C | C | C   | G/C | C   | C   | C/R | C   | G/C | C/G | C   | R | R   | C   | C | M   | M/C | C   |    |
| C  | C/G | C | C | C   | C   | R/C | C   | R   | C/G | G   | C/G | C   | R | R   | C   | C | C/M | M/C | C/  |    |
| C  | R/C | G | C | G/C | C   | C   | C   | C   | C   | C   | C   | C   | G | C   | C   | C | C   | C   |     |    |
| C  | C   | C | C | C   | C   | C   | C   | C   | C   | M   | R   | C   | C | C   | C   | C | C   | C/  |     |    |
| /C | G   | C | R | R/C | R/C | C   | C   | C   | C   | C   | R   | R/C | C | C   | C   | C | C   |     |     |    |
| C  | C   | C | C | C   | R/C | C   | G/C | M/C | C   | C   | C/R | C   | C | R/C | C   | G | C/  |     |     |    |
| C  | C   | G | C | C   | C   | C/M | M/C | M   | C   | C/M | M   | C/G | C | C   | C/G | G | C/  |     |     |    |

| Component | Round - <b>R</b> | Grey - <b>G</b> | Mixed oxide - <b>M</b> | Cement and sand - <b>C</b> | Total |
|-----------|------------------|-----------------|------------------------|----------------------------|-------|
| Counts    | 29.5             | 22.5            | 14.5                   | 165                        | 231.5 |

## Section 2



|    |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |   |     |     |    |  |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|---|-----|-----|----|--|
|    |     | C   | C   | M   | C   | G   | G   | C/G | C   | C/G | C   | C   | C/  |     |     |     |     |     |   |     |     |    |  |
|    |     | G/R | R/C | M   | M/C | G   | C   | C   | C   | C   | R/C | C   | C   | C/  |     |     |     |     |   |     |     |    |  |
|    | /C  | C   | C   | C   | R/C | C   | C   | C   | C   | C   | R   | R/C | C/G | C   | C/  |     |     |     |   |     |     |    |  |
|    | /C  | C   | C   | C   | C   | R/C | R/C | C   | R/C | R   | R   | R/C | C/G | C/G | G   | G/  |     |     |   |     |     |    |  |
|    | /C  | G/C | G/C | C   | C   | C/R | C   | C   | C   | R   | R   | R/C | C/G | G/C | C   | C   | C/  |     |   |     |     |    |  |
|    | /C  | G/C | C/G | C/G | C   | G   | C   | C   | C   | C/R | R   | R/C | C   | C   | M   | C   | C   | C   |   |     |     |    |  |
|    | C   | C   | G/C | G/C | C   | C/G | C   | C   | G/C | C   | C   | G/C | C   | C   | M   | C   | C   | C   | C | C/  |     |    |  |
|    | R/C | R/C | C   | C   | R/C | C   | R/C | C   | G   | M/C | C   | C/G | C   | C   | M/C | C   | C   | R/C | C | R/C | C   | C/ |  |
|    | R   | R   | C   | C   | C   | C   | C   | G/C | C   | M   | M/C | C   | C   | C   | C   | C   | C   | C   | C | C   | R/C | G  |  |
|    | C   | C   | R/C | C/R | C   | M/C | R/C | R/C | C   | C   | M   | C   | R/C | C   | C   | C   | C/G | G   | G | C   | G   | G  |  |
| /C | C   | C/R | C   | C   | M   | M   | C   | C   | G   | C   | R/C | C   | C   | C   | C   | C   | C   | C   | C | C   | C/G | G/ |  |
| /C | C   | C   | G/C | C   | C   | C   | C   | G   | G/C | R   | R/C | C   | C   | C   | C   | C/M | C/M | C   | C | G/C | G/C |    |  |
| /C | G   | C   | C/G | G   | G/C | C   | G   | G   | C   | R   | C   | C   | C   | C   | C   | M   | C   | C   | C | R/C | C   |    |  |

| Component | Round - <b>R</b> | Grey - <b>G</b> | Mixed oxide - <b>M</b> | Cement and sand - <b>C</b> | Total |
|-----------|------------------|-----------------|------------------------|----------------------------|-------|
| Counts    | 24.5             | 32.5            | 12.5                   | 167                        | 236.5 |

## An investigation of calibration materials for the measurement of metals in ambient particulate matter on filters by LA-ICP-MS

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Three different types of simple and low-cost calibration material for the measurement of the metals content of ambient particulate matter (PM) on filters using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) have been compared: cellulose ester filters spiked with multi-element calibration solutions, pellets of compressed ambient particulate matter certified reference material (CRM), and powdered ambient particulate matter CRM adhered to a surface. Elements determined were As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn, each at approximate levels of 1000 ng per filter. Blank filters spiked with multi-elemental standards were found to be significantly more reproducible and repeatable than materials based on powdered reference materials. However, a comparison of these spiked filters with real samples of ambient PM showed that the analytical sensitivities obtained per mass of analyte were significantly different. It is concluded that the spiked filters could act as very effective quality control standards correcting, to within 1%, drifts in LA-ICP-MS measurements of up to 10%, or as indirect calibration materials supported by additional measurements using traditional wet chemical techniques.

**Keywords:** ambient air, particulate matter, metals, calibration, LA-ICP-MS

### 1. Introduction

Air pollution continues to be of great concern to the scientific and medical communities, as well as legislators and the general public. The increasing recognition of the detrimental health effects of a number of airborne pollutants has meant that the number of species requiring monitoring by national and international legislation has increased over the last decade. This monitoring is usually delivered by national air quality monitoring networks, with monitoring sites located where population exposure to identified pollutants is likely to be greatest [1]. The metals content of the breathable PM<sub>10</sub> fraction of ambient air is no exception and the European Commission (EC) has now passed legislation which limits the allowable maximum concentrations of some of the most toxic 'heavy metals', namely Pb, Ni, As and Cd in PM<sub>10</sub> throughout Member States via the Air Quality Directive [2] (covering Pb) and Fourth Air Quality Daughter Directive [3] (covering Ni, As and Cd).

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In order to improve the quality and comparability of these measurements around Europe the EC mandated the European Committee for Standardisation (CEN) to produce a standard method for making these measurements, EN14902 [4], which the EC have since adopted as the 'reference method' in support of this legislation and that Member States are now required to use. If Member States wish to use an alternative method they must first prove the equivalence of this candidate method to the reference method using a formal procedure [5]. Two main considerations drive the need to seek alternative techniques to perform these analyses. First, with ever-increasing demands on budgets there is a need to always search for more cost-effective alternatives than the method prescribed by EN14902. Second, techniques which are non-destructive, or only destructive of part of the sample are of increasing interest as the desire for multiple analyses from single samples grows.

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) [6] provides a possible alternative method as it is quicker and potentially less expensive per analysis than wet chemical ICP-MS methods. LA-ICP-MS is commonly used for the analysis of geological materials [7] and there have been a few studies of the use of LA-ICP-MS to measure metals in ambient aerosols [8–12], mostly producing results with very large uncertainties. Our recent work has used LA-ICP-MS as a relative measure of the spatial distribution of metals on filters [13], and compared the performance of LA-ICP-MS, energy dispersive X-ray fluorescence, and wet chemical ICP-MS for the measurement of metals in ambient particulate matter with an aerodynamic radius of 10 microns or less ( $PM_{10}$ ) [14]. The common theme in these studies was the difficulty of calibrating the LA-ICP-MS in order to perform absolute measurements. Indeed the LA-ICP-MS was calibrated in both cases using filters subsequently digested and measured using the EN14902 method, which rather defeats the purpose of employing alternative methods of analysis. The lack of robust and traceable calibration strategies [15] is a major hurdle, which must be overcome if LA-ICP-MS is ever going to be able to make independent quantitative measurement of metals in particulate matter. Previous calibration approaches for LA-ICP-MS have focussed on commercially available glass reference materials, pressed pellets containing reference materials, or spiked powders [16–20]. Even aqueous solutions have been considered as calibration standards [21]. Studies that have addressed the measurement of metals in ambient particulate matter have used calibration materials prepared using dust chambers to deposit powdered reference materials onto PTFE filters [22,23]. However, these techniques are high-cost and relatively complicated, producing highly non-linear calibration curves, and without comparison against real samples. Moreover these studies were performed on PTFE filters which are only very rarely used in Europe for the collection of metals in particulate matter in support of the requirements of legislation. More recently isotope dilution strategies have been used [24], however these are clearly not appropriate for some of the metals of interest in air which are mono-isotopic (such as As and Mn).

This paper addresses the problem of calibrating measurements of the metals content of particulate matter using LA-ICP-MS. The aim of this work is to investigate calibration techniques that are simple, quick and cheap and can be used to measure drifts in the calibration of LA-ICP-MS analysis of ambient particulate collected on filters. This has been done by assessing three different types of candidate materials that could be used for this purpose, namely: filters spiked with multi-element calibration solutions, pellets of compressed ambient particulate matter certified reference material (CRM), and powdered ambient particulate matter CRM adhered to a surface.

## 2. Experimental

### 2.1 Sampling

Real PM samples were taken using Partisol 2000 instruments, each fitted with a PM<sub>10</sub> sampling head operating at a calibrated flow rate, nominally of 1 m<sup>3</sup> h<sup>-1</sup>, for a period of one week onto 47 mm diameter GN Metrical membrane filters (made of cellulose ester materials). Two samples were taken at each of three sites: the UK Heavy Metals Monitoring Network [25] sites at Runcorn Weston Point, Manchester Wythenshawe, and Cardiff Llandaff. Following sampling the filters were cut in half. One half of each filter was analysed using acid digestion and ICP-MS, and the other half of each filter was analysed using LA-ICP-MS. The elements measured were As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn.

### 2.2 ICP-MS analysis

Analysis took place by acid digestion of the filters in a mixture of 8 ml of concentrated nitric acid and 2 ml of hydrogen peroxide in a microwave (Anton Parr Multiwave 3000) followed by analysis using ICP-MS (a PerkinElmer Elan DRC II), following the National Physical Laboratory's (NPL's) previously described [26,27] United Kingdom Accreditation Service (UKAS) accredited procedure, which is fully compliant with the requirements of European standard method EN14902 [4]. Measurements were calibrated using at least four matrix-matched gravimetrically prepared calibration solutions prepared from mono-elemental standard solutions (VWR, checked for total elemental composition against the NIST SRM 3100 series (mono-elemental standard solutions)) and involved several additional quality control measures [26]. In particular a quality control solution containing all the analytes of interest at roughly the same concentration and the same matrix as is expected in the unknown samples was measured every third sample during the measurement series. The series of values obtained from these measurements is then fitted to a polynomial function describing its drift over the measurement series. This function may then be used to correct for instrument drift [28]. Each sample was analysed in triplicate, each analysis consisting of five replicates. The mass of each metal in solution (and its uncertainty) was quantified by a method of generalised least squares using XLGENLINE (an NPL-developed program: [29]) to construct a calibration curve. All results were blank corrected using average measurements from a series of five blank filters. These results are shown in Table 1.

### 2.3 LA-ICP-MS analysis

The sampled filters were cut into segments with a scalpel blade and fixed to polycarbonate mounts using adhesive carbon tape. The filters were mounted in such a way that the laser ablation tracks did not impinge directly upon the mounting tape once the filter was ablated through, and it was expected that once the laser reached the base polycarbonate mount it would be sufficiently defocused to render any signal from this material not significant. The laser ablation analyses were carried out, as previously described [13] using a CETAC LSX100 Nd:YAG laser operating at 266 nm coupled to an Agilent 7500 quadrupole ICP-MS instrument using a He carrier gas flow rate of 1.38 l/min with the laser carrier line connected directly to the back of the torch. Prior to analysis of filter samples the system was optimised to give maximum sensitivity (without compromising short term

Table 1. Masses of each element on each whole filter, determined using the EN14902 wet chemical digestion ICP-MS method, for the real samples taken during this study at the UK Heavy Metals Network Monitoring sites at Runcorn Weston Point (Runcorn 1 and 2), Manchester Wythenshawe (Manchester 1 and 2) and Cardiff Llandaff (Cardiff 1 and 2). Expanded uncertainties are quoted giving a level of confidence of approximately 95%.

| Element | Mass of metal on filter/ng |               |                  |                  |               |                  |
|---------|----------------------------|---------------|------------------|------------------|---------------|------------------|
|         | Runcorn 1                  | Runcorn 2     | Manchester 1     | Manchester 2     | Cardiff 1     | Cardiff 2        |
| As      | 45 ± 15                    | 130 ± 21      | 111 ± 19         | 78 ± 17          | 71 ± 17       | 126 ± 20         |
| Cd      | 7.1 ± 1.6                  | 31 ± 4        | 22 ± 3           | 14 ± 2           | 25 ± 3        | 34 ± 4           |
| Cr      | 51 ± 32                    | 106 ± 62      | 828 ± 106        | 435 ± 82         | 349 ± 95      | 537 ± 94         |
| Cu      | 650 ± 63                   | 1450 ± 140    | 7030 ± 670       | 5480 ± 520       | 2950 ± 300    | 4630 ± 450       |
| Fe      | 16,400 ± 1700              | 34,600 ± 3340 | 200,600 ± 19,100 | 118,300 ± 11,100 | 87,000 ± 8900 | 124,700 ± 12,000 |
| Mn      | 325 ± 31                   | 824 ± 78      | 2590 ± 245       | 1340 ± 130       | 1320 ± 140    | 2360 ± 230       |
| Ni      | 47 ± 13                    | 217 ± 26      | 179 ± 22         | 52 ± 15          | 49 ± 14       | 138 ± 20         |
| Pb      | 577 ± 62                   | 1700 ± 160    | 1322 ± 130       | 823 ± 81         | 1840 ± 180    | 2620 ± 250       |
| V       | 222 ± 23                   | 661 ± 62      | 304 ± 31         | 192 ± 20         | 120 ± 16      | 271 ± 28         |
| Zn      | 1080 ± 110                 | 2750 ± 260    | 5250 ± 500       | 4560 ± 430       | 4920 ± 510    | 7850 ± 740       |

repeatability) using NIST SRM 610 glass [13]. A small in-line filter device (using glass wool) was installed in the carrier gas line about 20 cm from the ablation site, similar to ones previously described [30]. This device vastly improves the repeatability of analysis by filtering out larger particles liberated from the surface during the ablation process – although it can result in the selective loss of some analytes and particle sizes [31] and the implications of this are discussed later. Data were collected for each isotope of interest with 20 channels per peak and an integration time of 0.01 s per channel. A manual trigger was used to start each analysis, which was 13.3 s duration. The laser was operated at a power of 0.18 mJ with a scan speed of 30 μm/s and a defocusing distance of 3000 μm. The distance covered by the laser beam during each analysis was approximately 500 μm with a track width of 60 μm. Measurements of the sampled filter sections were made starting at the centre of the each filter and moving outwards along the radius of the filter to the outer sampled edge, and comprised approximately 40 to 45 separate measurements. (In routine usage it would be envisaged that fewer measurements would be taken, once homogeneity had been proved, assuring that the technique would therefore be quicker than wet-chemical methods for high throughput analysis. However, enough measurements are still required to obtain an average value for the mass on the filter with an acceptable uncertainty.) The isotopes measured were <sup>75</sup>As, <sup>111</sup>Cd, <sup>52</sup>Cr, <sup>53</sup>Cr, <sup>63</sup>Cu, <sup>65</sup>Cu, <sup>56</sup>Fe, <sup>115</sup>In (as an internal standard), <sup>55</sup>Mn, <sup>60</sup>Ni, <sup>207</sup>Pb, <sup>208</sup>Pb, <sup>51</sup>V, <sup>66</sup>Zn and <sup>68</sup>Zn. The measurement of multiple isotopes for some elements enabled internal consistency checks to ensure that variability observed in signal levels was real, as previously described [13]. Using these experimental parameters the entire depth of the filter and the PM on it is ablated during a single measurement (as evidenced by inspection of the filter following analysis).

2.4 Analytical interferences

Of the polyatomic interferences that are expected to be significant within respect to the precision of the measurement in the sample matrices considered [32]: the <sup>40</sup>Ar<sup>35</sup>Cl

interference with  $^{75}\text{As}$  was removed by mathematical correction and instrumental tuning as previously described [27]; the  $^{12}\text{C}^{40}\text{Ar}$  interference with  $^{52}\text{Cr}$ , and the  $^{13}\text{C}^{40}\text{Ar}$  interference with  $^{53}\text{Cr}$  were estimated empirically using previously described techniques which spike C-containing solvents into the sample in various quantities and also monitor the change in the  $^{52}\text{Cr}/^{53}\text{Cr}$  ratio [33]. Despite the estimated corrections for  $^{52}\text{Cr}$  and  $^{53}\text{Cr}$ , the signal to noise was sufficiently poor even after this process, that it was difficult to robustly interpret the results from this element. The results are included for completeness, but must be treated with much more caution than those for the other elements and are for information only.

## 2.5 Preparation and measurement of calibration materials

### (a) Spiked blank filters

A parent spike solution was prepared by mixing different volumes of single element standard solutions (Fisher). (The mass fractions of the elements in the final parent solution were between 10 and 50  $\mu\text{g/g}$ ). This spike solution was diluted gravimetrically to produce two daughter spike solutions, which were 5 and 20 times less concentrated than the parent, respectively. In addition an In spike was added to the parent and daughter solutions, such that it was present in the same concentration in all three solutions (10  $\mu\text{g/g}$ ). The purpose of the In spike was to act as an internal standard during analysis by dividing all analyte intensities by the relevant In intensity. A batch of blank filters of the same type used for collecting the real PM samples were taken and each filter was cut accurately into quarters. Three of the quarters in each set of four received 0.8 ml of either the parent solution or one of the daughter solutions. The fourth quarter received 0.8 ml of a blank solution containing only the In spike, present at the same concentration as in the spike solutions – this acted as the calibration point at zero analyte content. The volume added was the optimum to wet each filter quarter evenly without any solution escaping from the sides of the filter – giving confidence that all the mass added from the solution was retained by the filter. (Proof of the uniform and even distribution of the liquid and its constituent elements across in filter is shown later in Figure 3 for Ni, but was similarly good for all elements. The technique of wetting of the whole filter seemed to negate any chromatographic separation effects that might have otherwise been expected. A possible alternative method – soaking of the filters in excess solution – would have led to difficulties in measuring the exact mass of solution added to the filter.) The final masses of each element added to each filter quarter is given in Table 2 – the range of masses was chosen to cover adequately the likely loadings found on the real samples. Spiked filters were dried overnight at 60 °C. Two sub-types of spiked filters were prepared. One batch of solutions was prepared with 0.1% Triton-X (a dispersant to enable better wetting of the filter) - this created the spiked filter (SF) calibration materials. One batch of solutions was prepared without the Triton-X – this created the spiked filter without dispersant (SF(n)) calibration materials.

### (b) NIST SRM 1648a and graphite powder mixes

NIST SRM 1648a (urban particulate matter – the calculated 10, 50, and 90 percentile particle sizes (percent volume of particles smaller than the value) for NIST SRM 1648a are:  $d_{0.1} = 1.35 \mu\text{m}$ ,  $d_{0.5} = 5.85 \mu\text{m}$ , and  $d_{0.9} = 30.1 \mu\text{m}$ .), the certified reference material recommended for method validation and quality control of EN14902, was mixed with graphite powder (as a very low metal content, inert mixer material, with average particle

Table 2. Masses of each element added to each spiked filter (A-D) for both the spiked filter with dispersant (SF) and the spiked filters without dispersant (SF(n)) calibration materials. D represents the blank filter to which only the In internal standard was added.

| Element | Mass added to each spiked filter/ng |      |      |      |
|---------|-------------------------------------|------|------|------|
|         | A                                   | B    | C    | D    |
| V       | 8000                                | 1600 | 400  | 0    |
| Cr      | 8000                                | 1600 | 400  | 0    |
| Mn      | 40,000                              | 8000 | 2000 | 0    |
| Fe      | 40,000                              | 8000 | 2000 | 0    |
| Ni      | 8000                                | 1600 | 400  | 0    |
| Cu      | 8000                                | 1600 | 400  | 0    |
| Zn      | 40,000                              | 8000 | 2000 | 0    |
| As      | 8000                                | 1600 | 400  | 0    |
| Cd      | 8000                                | 1600 | 400  | 0    |
| Pb      | 8000                                | 1600 | 400  | 0    |
| In      | 8000                                | 8000 | 8000 | 8000 |

Table 3. Masses of each material added to each mixture (E-H). H represents the graphite powder blank.

| Material        | Mass added to each mixture/g |      |      |      |
|-----------------|------------------------------|------|------|------|
|                 | E                            | F    | G    | H    |
| NIST 1648a      | 0.20                         | 0.10 | 0.05 | 0.00 |
| Graphite powder | 0.20                         | 0.30 | 0.35 | 0.40 |

diameters of less than 10  $\mu\text{m}$ ) at different mass fractions to produce a range of reference material dilutions. The composition of which can be found in Table 3. Once the powders were homogenised by thorough manual mixing and grinding over prolonged periods (ensuring thorough mixing is, of course, extremely difficult and it may be that prolonged mechanical mixing techniques would be preferred in future), 4 ml of In spike was added corresponding to a mass fraction of 100  $\mu\text{g/g}$  in the final calibration material and mixed in with the powder. (The purpose of the In spike was again to act as an internal standard during analysis by dividing all analyte intensities by the relevant In intensity.) The mixtures were dried at 60°C overnight. The following day, the dry powder was scrapped off the watch glass, homogenised with a spatula, and then a metal disc (1 cm diameter) mounted with an adhesive black disc (of the type commonly used for mounting SEM samples), was pressed onto the powder to collect material. This was performed several times to ensure, as much as possible, that coverage over the adhesive disc was uniform. The excess was tapped off. This created the adhesive disc (AD) calibration material. The remaining powder was then pressed into a pellet, at 5 tonnes  $\text{cm}^{-2}$  for 1 min, with the addition of 0.02 ml of 5% by volume of Mowiol solution (an inert binder). This created the pressed pellet (PP) calibration materials.

## 2.6 Calibration material summary

Three independent sets of each calibration material were prepared. To analyse and assess the calibration materials the same LA-ICP-MS method was used, as described above, but including the measurement of In. SF and SF(n) were analysed with 40 replicates, and AD and PP with 45 replicates, covering the equivalent distance of approximately 1.5 filter radii, but transcribing chords across the material. For the candidate calibration materials the signal obtained for each analyte was ratioed to In intensity, which acted as an internal standard to correct for variations in laser power and analyser drift.

## 3. Results and discussion

### 3.1 Repeatability and reproducibility

The repeatability and reproducibility of the calibration materials were tested by construction of four point calibration curves (including a point at zero analyte content representing the blank) of response against analyte content. Comparison of the relationships was made against an expected linear profile. (This is more exacting than previous studies which used higher order calibration relationships which allowed for negative gradients at high filter loadings [23]). The linearity of the calibration relationship was expressed as the squared correlation coefficient,  $r^2$  [34,35]. The linearity of this calibration curve is a surrogate quantity to assess the reproducibility of the preparation of the material. (Equally we could have prepared several materials with nominally equal content and calculated the standard deviation of their response, or ratioed average response to content, but this approach allowed us to quantify the reproducibility from the calibration relationship concomitantly.) The repeatability of the response from the calibration materials was calculated as the average of the relative standard deviations,  $S_r$ , of the LA-ICP-MS response from repeat measurements of the non-zero calibration points. The results of this analysis are displayed in Figures 1 and 2.

It is clear from this analysis that the spiked filters are by far the superior material in terms of the linearity of the calibration curve, and therefore reproducibility, and also in the repeatability of analysis of the material. The spiked filters with the dispersant show a slightly better performance in both respects compared with those without the dispersant, presumably because the addition of this chemical allows a more homogenous wetting of the filter. (The spiked filters have the additional advantage of having a blank correction built in as a result of using the same filter material as the real samples. Robust blank correction for the powder-based materials requires a little more effort.) The pressed pellets show the next best performance overall, with the adhesive discs showing the poorest performance. The pressed pellets exhibited correlation coefficients above 0.95 for all but four elements, although two of these values were below 0.7. For the adhesive discs only three elements showed correlation coefficients above 0.8. Significant difference in performance between elements is present only for the powder-based materials, and is thought to be a result of a distribution of compositions across the different particle sizes present within the powdered reference materials. In addition, any variability in ionization potential (perhaps because of different chemical states) or plasma temperature (as a result of instrument instability, or between the different carbon-based matrices of the pressed pellet and adhesive discs) is expected to adversely affect the relative standard deviations measured from these materials. This implies that the spiked filters may be prepared reproducibly with a homogeneous distribution of analyte content (especially when using

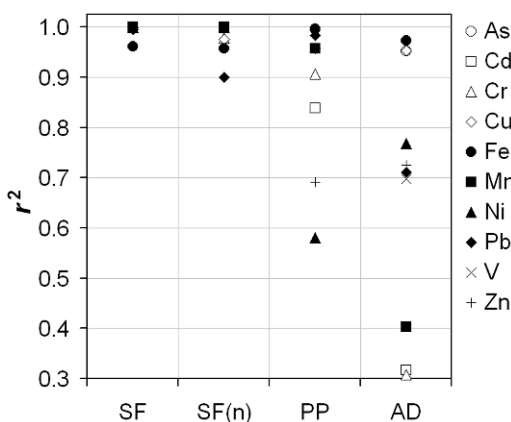


Figure 1. Squared correlation coefficient,  $r^2$ , determined for each element measured from each of the candidate calibration materials – spiked filters (SF), spiked filters without dispersant (SF(n)), pressed pellets (PP), adhesive discs (AD). (Results for Cr are included for information only).

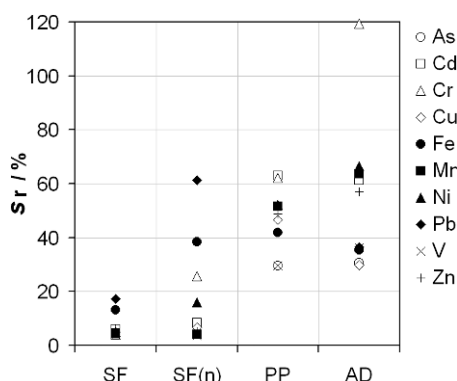


Figure 2. The relative standard deviation,  $S_r$ , determined for each element measured across the non-zero calibration points of each of the candidate calibration materials – spiked filters (SF), spiked filters without dispersant (SF(n)), pressed pellets (PP), adhesive discs (AD). (Results for Cr are included for information only).

the dispersant), whereas for the pressed pellets it is more challenging to prepare these reproducibly for analysis, and for the adhesive discs it is very difficult to prepare a reproducible material. This is not entirely surprising since the spiked filters are based on a solution preparation method, whereas the other two materials are based on the mixing of solids, which is much more difficult to perform reproducibly. In terms of the relative standard deviation of response, which gives an indication of repeatability within a calibration material, the spiked filters with dispersant show values less than 0.2 across all elements with the majority being less than 0.05 – presumably because the elements are distributed evenly across the filter. The spiked filters without dispersant show slightly worse repeatability, with three elements showing relative standard deviations of over 0.2. For the pressed pellets and adhesive discs the relative standard deviations are higher and

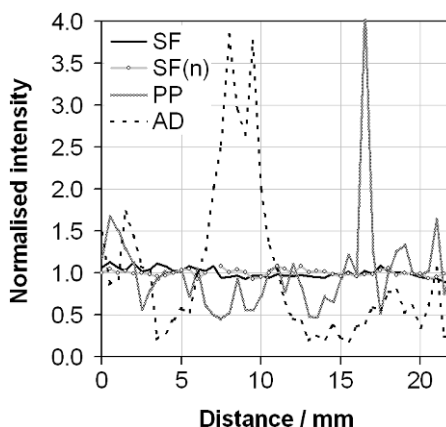


Figure 3. Measured intensity for 45 measurements of Ni across a 22.5 mm portion of each calibration material – spiked filters (SF), spiked filters without dispersant (SF(n)), pressed pellets (PP), adhesive discs (AD) – normalised to the average across each measurement series.

similar, between 0.3 and 0.7 in all cases except for Cr on the adhesive disc. The differences in spatial homogeneity of the three calibration materials are highlighted in Figure 3, which shows an example of the normalised response for 45 measurements of Ni across a 22.5 mm portion of each calibration material. This clearly shows the better spatial homogeneity of the spiked filters, and that the origin of the poor repeatability of the pressed pellets and adhesive discs is a combination of generally poorer spatial homogeneity coupled with extreme outliers of apparently very high or low analyte content. These outliers are more frequent for the adhesive discs than for the pressed pellets. It is also known [13] that the laser ablation process disturbs, and may also sample, material adjacent to the area being ablated, especially for particulate matter and similar compressed powders, thereby increasing significantly the impression of poor repeatability across the calibration material.

### 3.2 Comparison of spiked filters with EN14902 analysis

The intention of calibration is to determine the content of an unknown sample by using an instrumental sensitivity determined from the analytical responses measured from a variety of samples of known composition. If the calibration artefact and samples are not of identical matrix, this can cause problems in establishing this relationship. The requirement for the measurements discussed in this paper is to determine the mass of an element on a filter. This is because the final measurand is the mass concentration of element in ambient air, rather than mass fraction of the element in the PM collected. Although a subtle point, this is an important one since it makes the use of the reference material-based calibrants much more challenging. Whilst the NIST-based materials are of a more similar matrix to the ambient PM being measured, they are not present on a filter at a defined thickness. The spiked filters, whilst not being an entirely similar matrix to the ambient PM (although obviously similar to the filter material on which the PM is collected) still have defined thickness. Because of the nature of the laser ablation process the entire depth of the filter

and the PM on it is ablated during a single measurement (as evidenced by inspection of the filter following analysis), such that the intensity response of the instrument should be directly proportional to the entire mass of material in the cross-section sampled. The same is true for the spiked filter material and hence it is valid to make a direct comparison between sample and calibration material in this case. The obfuscating factor is the efficiency of measurements with respect to the two different matrices, as shall be demonstrated later.

The powder-based materials suffer from the opposite problem. As they are of a very similar matrix to a real PM sample, the relative efficiencies of ablation and measurement should be very similar. However, they are usually much thicker than the sampled filters meaning that the intensity response of the instrument will not be directly proportional to the entire mass of material in the cross-section sampled, because during the ablation period in one location the entire depth of the material is not necessarily sampled. Furthermore, elemental fractionation of the sample is very likely to occur under these experimental conditions meaning that the relative distribution of elements may vary between the PM sample and what it actually ejected by LA. Moreover a key parameter in LA processes are the optical properties of the irradiated materials. The LA phenomenon is dramatically affected by changes in absorption properties as well as the reflective indices of the particles. Indeed, thermal and pure laser ablation effects are often combined as a complex function of optical parameters under such situations. In addition, the use of the binders, graphite, carbon tape and polycarbonate mount is likely to add to exacerbate the elemental fractionation present.

The solution to the sample thickness issue raised above would either be to make these materials extremely thin to match the depth of the sampled PM on a filter, or use ablation conditions that were mild enough not to ablate the entire depth of the PM on the sampled filter and match these conditions during calibration. The first solution is difficult and expensive to achieve practically as so would defeat the objectives of this paper. Whilst this has been achieved practically [23] the results were scarcely better than those achieved with the simple materials described in this work. The second solution may not provide enough power to measure the sample with sufficient sensitivity, and even if it did, would then require an additional measurement of the mass of PM collected before analysis, as the response from the calibrant in this case is related to mass fraction, rather than total mass.

The above discussion and results presented indicate that spiked filters are currently the only credible possibility for the calibration independent of the EN14902 method. However, the relative analytical sensitivities obtained from the measurement of spiked filters and real PM samples still needs to be determined in order to assess whether these artefacts may really be used for quantitative determinations. This may be done by comparing the intensities measured by LA-ICP-MS from the spiked filters that have a known analyte mass, and from the real samples which have a known analyte mass as measured using EN14902. The average sensitivity of the relationships (i.e. gradients of the regression lines) produced by analysing the spiked filters (both with and without dispersant),  $\dot{V}_{\text{sf}}$ , and analysing the real samples of particulate matter,  $\dot{V}_{\text{pm}}$ , have been calculated in terms of blank-corrected LA-ICP-MS response per ng of analyte on the filter as previously described [13]. The ratio of the average sensitivities,  $\dot{V}_{\text{pm}}/\dot{V}_{\text{sf}}$ , have then been calculated and these are plotted in Figure 4. It is clear from these results that the spiked filters and real filters do not exhibit the same sensitivities. For the elements measured these sensitivity ratios range from approximately 2 to 6. The difference measured between

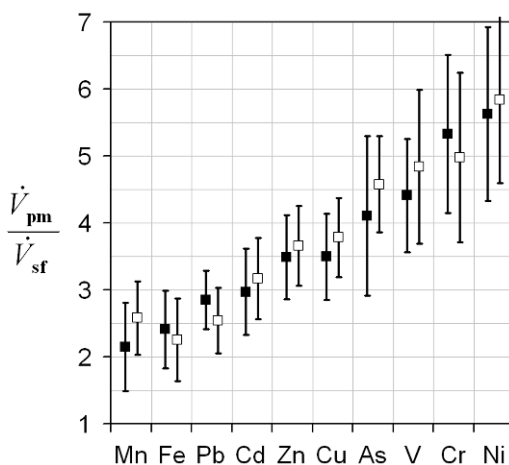


Figure 4. The ratio of the LA-ICP-MS instrumental sensitivities,  $\dot{V}_{pm}/\dot{V}_{sf}$ , produced by analysing real samples of particulate matter ( $\dot{V}_{pm}$ ) and the spiked filters ( $\dot{V}_{sf}$ ) for each element, for the spiked filters (solid squares) and the spiked filters without dispersant (open squares), displayed in ascending average numerical order – please refer to main text for full description. The error bars represent an estimate of the expanded uncertainty in these values expressed at the 95% confidence interval, estimated by adding in quadrature the uncertainty of analysis by EN14902 with the average repeatability of the LA-ICP-MS signal, and the observed standard deviation of the sensitivities within a sample type. (Results for Cr are included for information only.)

elements is again thought to be a result of a distribution of compositions within the different particle sizes present within the real samples, and the different reaction of these to the laser ablation process. The observed results suggest that a much larger analytical response is measured per ng of element in real PM than per ng of element of a spiked filter. One reason may be the different chemical forms of the metals in the spiking solution and those in the PM. A further reason for this is that the influence of the laser is not confined to the point of focus when ablating PM but disturbs, and hence dislodges and samples, surrounding material thereby resulting in higher analytical intensities - despite the in-line filter we have developed to prevent very large pieces of dislodged PM reaching the ICP-MS. This effect may be observed with the naked eye during measurement. (It is probable that the use of a 213 or 193 nm femtosecond ablating laser would result in better results as a function of producing thinner particles and fewer thermal effects.) The fact that this effect does not seem to be of the same size for all of the elements of interest gives further evidence to the theory that substantial elemental fractionation is being observed during the measurement regime. Interestingly this effect seems to dominate and override non-representative sampling of some elements caused by the in-line filter owing to loss of analyte as ablated material passes through the filter. If this effect dominated we might expect  $\dot{V}_{pm}/\dot{V}_{sf}$  of less than one, since selective loss as observed for PM measurements is not thought to be a significant problem for the spiked filters alone. Moreover the fact that the composition of particles generated by laser ablation are likely to be size dependent and chemically different for each size fraction will have significant implications for the laser ablation of a real samples as compared to a spiked filter, further emphasising the matrix mismatching problem. In this way incomplete atomisation of the larger particles during analysis would result in a range of  $\dot{V}_{pm}/\dot{V}_{sf}$  for each element depending on which size

fraction they were predominantly found in. Furthermore because of the more heavily carbon containing matrix in the PM as compared with the spiked filter the ionizing capacity of the ICP-MS will be affected, which in turn is known to (1) dramatically affect the achievable sensitivities for elements with high ionisation potentials and (2) enable a hotter plasma potentially resulting in an over reading of elements in the more highly carbon-containing matrix. These effects are thought to be the origin of the different values of  $\dot{V}_{\text{pm}}/\dot{V}_{\text{sf}}$  for different analytes. However, it is encouraging that there is better agreement of  $\dot{V}_{\text{pm}}/\dot{V}_{\text{sf}}$  values between the spiked filters and the spiked filters without dispersant – giving some confidence in the reproducibility of the results obtained in Figure 4. However the differences between the two sets of observations, plus the uncertainties on these observations, are sufficiently large to rule out the use of these spiked filters for calibration in conjunction with a fixed scaling coefficient to overcome the observed differences from 1 of the  $\dot{V}_{\text{pm}}/\dot{V}_{\text{sf}}$  ratios.

#### 4. Conclusions

From the data presented it seems that the production of low-cost and simple direct and independent calibrants of LA-ICP-MS analysis remains challenging. The main reasons for this are the difficulty in (1) producing a spatially homogenous calibration material and (2) dealing with the differences in matrix between the calibration material and real samples, which causes significant elemental fractional effects and large variations in atomisation efficiency and instrument sensitivity. The only realistic practical method for calibration and traceability is via comparative measurements with traditional techniques such as EN14902. However, this work has demonstrated the usefulness of spiked filters as both a linearity check and a quality control standard for LA-ICP-MS analysis which could be used in conjunction with an absolute calibrant (such as comparative EN 19042 measurements) to correct for drifts in sensitivity over time. As such, the spiked filters would prove very useful for laboratories performing high throughput analyses to fit-for-purpose uncertainties in support of air quality legislation. Moreover the improvement obtained in the repeatability of analysis of the calibrant materials by using an In spike as an internal standard against which to take intensity ratios suggests that using the same techniques to spike sampled filters after (or even prior to) sampling would significantly improve the repeatability of analysis of real samples.

Future work in this area should continue to focus on routes to produce artefacts that are suitable as direct and independent calibrants for LA-ICP-MS analysis of metals in PM, perhaps by depositing aerosolised particulate matter reference materials onto ambient air filters to create close-to-real samples, but with known compositions (as has been previously done for workplace air proficiency testing schemes [36]). Other certified reference materials, such as NIST SRM 2873 (air particulate on filter media), remain available for use in this context, providing they are of a very similar matrix to the material under test. However, this is a very costly method to calibrate high-throughput, routine measurements, and ideally check standards would be required in periods between uses of this material. Furthermore, a future interlaboratory comparison of possible LA-ICP-MS calibration materials would also prove extremely useful in benchmarking the inter-laboratory comparability of these proposed methods.

Whilst the production of low-cost and simple direct and independent calibrants remains challenging using a 266 nm nanosecond laser for LA-ICP-MS, it is quite possible

that the use of 213 nm or 193 nm femtosecond laser for ablation will produce better results – and would certainly result in less elemental fractionation and less powerful shockwaves within the particulate material. This should be fully investigated as part of any further work in this area.

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