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The quantitative characterisation of geological reference materials by isotope dilution inductively coupled plasma mass spectrometry (ICP-MS)

by

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I, Angelique Botha, declare that the thesis/dissertation, which I hereby submit for the degree Ph. D (Chemistry) at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

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Psalm 138:8 “Die Here sal vir my alles goed laat afloop.

Aan u liefde, Here, is daar geen einde nie.

Moet tog nie die werk van u hande laat vaar nie.”

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List of abbreviations

SI	International System of Units
CIPM	International Committee for Weights and Measures
BIPM	International Bureau of Weights and Measures
IUPAC	International Union for Pure and Applied Chemistry
IUPAP	International Union for Pure and Applied Physics
ISO	International Organisation for Standardisation
CCQM	Consultative Committee for Amount of Substance
NMI	National Metrology Institute
NBS	United States National Bureau of Standards
SABS	South African Bureau of Standards
CSIR	Council for Scientific and Industrial Research
NIM	National Institute of Metallurgy
MINTEK	Council for Mineral Technology
SARM	South African Reference Material
SACCRM	South African Committee for Certified Reference Materials
ISO/REMCO	ISO Technical Committee on Reference materials
CRM	Certified Reference Material
IEC	International Electrotechnical Commission
GML	Government Metallurgical Laboratory
NMISA	National Metrology Institute of South Africa
ISO GUM	ISO Guide to the Expression of Uncertainty of Measurement
VIM	Vocabulary of Metrology – Basic General Concepts and Associated Terms
CANMET	Canada Centre for Mineral and Energy Technology

NIST	National Institute of Science and Technology
CITAC	Cooperation on International Traceability in Analytical Chemistry
ISO/TAG4	ISO Technical Advisory Group on Metrology
AAS	atomic absorption spectrometry
ICP	inductively coupled plasma
MS	mass spectrometry
ID-ICP-MS	isotope dilution inductively coupled plasma mass spectrometry
HR-ICP-MS	high resolution inductively coupled plasma mass spectrometry
XRF	X-ray fluorescence
INAA	instrumental neutron activation analysis
UV/VIS	ultraviolet/visible light
ICP-OES	inductively coupled plasma optical emission spectrometry
IDMS	isotope dilution mass spectrometry
DCM	dominant cluster mode
MAD	median absolute deviation
m/z	mass-to-charge ratio
cps	counts per second
HF	hydrofluoric acid
Na ₂ O ₂	sodium peroxide
LiBO ₂	lithium borate
Li ₂ B ₄ O ₇	lithium metaborate
Na ₂ B ₄ O ₇	sodium metaborate
NaOH	sodium hydroxide
KOH	potassium hydroxide



H_3BO_3	boric acid
HNO_3	nitric acid
HCl	hydrochloric acid
mℓ	millilitre
g	gram
kg	kilogram
mm	millimetre
mg.kg ⁻¹	milligram per kilogram
μg.g ⁻¹	microgram per gram
ng.mℓ ⁻¹	nanogram per millilitre
μg.mℓ ⁻¹	microgram per millilitre
ℓ.min ⁻¹	litre per minute
ns	nanosecond
W	Watt
<i>K</i>	mass bias correction factor
<i>R</i>	mass resolution

Summary

The geology and mining industries rely heavily on reliable quantitative data on the elemental composition of various rocks and minerals. The analytical accuracy of the best measurement systems are, however, limited to the accuracy with which the composition of a generally accepted reference sample is known, which serves to calibrate an instrument or validate a method. Thus, there is an established market for well-characterised reference materials which trade internationally as value added commodities. International organisations prepare strict procedures for the preparation and certification of these reference materials.

ISO/REMCO is the ISO Committee on Reference Materials that carries out and encourages a broad international effort for the harmonisation and promotion of reference materials, their production and their application. In view of recent developments in ISO/REMCO related to updated guides and changes in definitions, SARM 1 to 6 (the NIMROCs) are in danger of losing their status as certified reference materials (CRMs).

Due to the continued popularity of the NIMROCs and the availability of bulk sample, the National Metrology Institute of South Africa (NMISA) embarked on a project to re-certify three materials from the suite of six igneous rock samples, i.e. SARM 2 (Syenite), SARM 3 (Lujavrite) and SARM 4 (Norite). The aim of the re-certification project was to re-certify the materials with a single primary reference measurement procedure in a single laboratory to comply with one of the possible routes to the establishment of metrological traceability as described in ISO Guide 34.

Eight elements (Ba, Sr, Cd, Mo, Cu, Ni, Pb and Zn) of SARM 2, SARM 3 and SARM 4 were value assigned during this study to ensure that they comply with the ISO Guide 30 and ISO GUM requirements for traceability and measurement uncertainty. Traceability to the SI units of mass and amount of substance at the highest level of accuracy was established by employing the definitive technique of double isotope dilution ICP-MS, with primary assay standards traceable to the NIST SRM 3100 series and gravimetrically prepared samples.

For the first time assigned values with uncertainty statements for these elements in these reference materials were calculated according to the ISO GUM and CITAC/EURACHEM guidelines for expression of the uncertainty of measurement. The uncertainties of the assigned values for all elements were within the target of 5%

relative set during the development of the methodology, except for elements in concentrations below 10 mg.kg^{-1} .

The ID-ICP-MS results are supported by good comparability with results reported in the literature since 1978, as well as the original certified values published in 1978. The results from this study for all elements in these reference materials have the potential to become new certified values in accordance with the requirements of ISO Guides 34 and 35. This will improve the usefulness of these reference materials to the South African and international geology and mining communities for the purposes of analytical quality control and method validation in exploration and geochemical analysis. Confirmation of the homogeneity and stability of the remaining units of the reference materials is considered necessary to complete the re-certification project.

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Chapter 1

Introduction

1.1 Background

Commercial and public pressures demand more reliable measurements in chemistry: areas of concern include environmental monitoring, international trade in food and drugs, clinical practice, human health and safety, forensic medicine, advanced materials research and energy.

The most direct way to establish comparability of measurement results on a global scale is through an interlaboratory comparison, but this is a very expensive exercise that can never be accomplished for every measurement.

The simplest way to ensure comparability of results is to link the results firmly to the unchanging constants of nature. This is best done by linking all measurements to the International System of Units (SI). A base unit for the amount of substance (chemistry) was introduced by the 14th Conférence Générale of the CIPM (International Committee for Weights and Measures) in 1971 following requests from the International Union of Pure and Applied Chemistry (IUPAC), the International Union of Pure and Applied Physics (IUPAP) and the International Organisation for Standardisation (ISO)[1].

The mole is the amount of substance as a system which contains as many elementary entities as there are atoms in 0.012 kg of carbon-12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles or specified groups of such particles.

The international importance of metrology in chemistry was recognised with the formulation of the terms of reference of the CCQM (Consultative Committee for Amount of Substance) of the CIPM in 1993. Through the CCQM the international community concerned with the accuracy of measurement is establishing infrastructure to determine the existing level of measurement equivalence between national metrology institutes (NMIs). Mechanisms, such as metrological traceability, are also being developed for the improvement of the comparability of quantitative chemical measurement results on a global scale.

Metrological traceability[2] is the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty. *Measurement uncertainty*[2] is the non-negative parameter characterising the dispersion of the quantity values being attributed to a measurand (analyte), based on the information used.

At the level of NMIs the focus is on the establishment of metrological traceability at the highest level of accuracy, which is directly related to the SI units. Strictly, traceability to the SI in measurements of amount of substance requires that the measurements be made using a *primary reference measurement procedure*[2], which is correctly applied and stated with an evaluated uncertainty. There may be other, indirect ways of establishing traceability to the SI, and these are under study by the CCQM.

A *primary reference measurement procedure* is a reference measurement procedure used to obtain a measurement result without relation to a measurement standard for a quantity of the same kind, i.e. a procedure of which the measurement result is accepted without reference to a standard of the quantity being measured.

The application of the definition of a primary reference measurement procedure (method) to measurements of amount of substance is complicated. The CCQM laid down two conditions for a method to be considered primary. First, it must be a method which is specific for a defined substance and second, the values of all parameters, or corrections which depend on other species or the matrix, must be known or calculable with appropriate uncertainty. These methods must not have chemically-dependent constants or functions that require access to an independent chemical standard of the same analyte. The methods that the CCQM[1] identified as having the potential to be primary are:

- a. isotope-dilution mass spectrometry
- b. coulometry
- c. gravimetry (with gas mixtures or gravimetric analysis)
- d. titrimetry, and
- e. a group of colligative methods, including the lowering of the vapour pressure, the raising of the freezing point, the lowering of the boiling point temperature and the osmotic pressure.

However, primary reference measurement procedures can hardly be applied by routine laboratories. The capital investment in equipment is high, their operating costs are high, they are labour-intensive and a high level of expertise is required from the operator. Typically other routes to metrological traceability for accurate measurements will be employed by routine laboratories. These may include the use of a pure substance of

the analyte as in the case of spiking studies (standard addition), the use of an empirical method, or most typically the use of a certified reference material. A *certified reference material*[3] is a reference material characterised by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability.

Reference materials first appeared in South Africa around 1969. At a meeting of a committee of the International Organisation for Standardisation (ISO) in that year the US National Bureau of Standards (NBS) stated that it would be unable to continue to supply reference materials indefinitely to all, and that the National Standards Bodies should put their own houses in order. A meeting of users and interested bodies in South Africa was convened in Pretoria to discuss the NBS suggestion. The South African Bureau of Standards (SABS), agreed to be the secretariat for ISO in South Africa, and a select committee was formed, which comprised of the SABS, Council for Scientific and Industrial Research (CSIR), and National Institute of Metallurgy (NIM), now the Council for Mineral Technology (MINTEK).

MINTEK has prepared and certified over 70 South African Reference Materials (SARMs) to date. The materials range from igneous rocks, sedimentary and metamorphic rocks, minerals, ore and semi-processed ore materials, as well as coal, uranium, gold-bearing and heavy mineral processed materials. The SARMs were previously produced and issued under the guidance and control of the South African Committee for Certified Reference Materials (SACCRM). The committee concentrated on the production of certified reference materials specific to minerals, ores, intermediate and final products produced in, and exported from, South Africa. Another important criterium for the selected reference materials was that no equivalent internationally recognised certified reference materials were available at the time.

ISO/REMCO is the ISO Committee on Reference Materials that carries out and encourages a broad international effort for the harmonisation and promotion of reference materials, their production and their application. Its vision is to be the global centre of excellence with respect to issues relating to reference materials.

So far, the committee has developed six guides, i.e. ISO Guides 30 to 35. ISO/REMCO activities focus on procedures for the production and use of reference materials.

In view of recent developments in ISO/REMCO related to updated guides and changes in definitions, SARM 1 to 6 are in danger of losing their status as certified reference materials (CRMs). ISO Guide 30[3] states that a certified reference material is a reference material, characterised by a metrologically valid procedure for one or more

specified properties, accompanied by a certificate that states the value of the specified property, its associated uncertainty, and a statement of metrological traceability. An analogous definition for certified reference material can be found in the ISO VIM[2]. However, it is important to note that the definition in ISO Guide 30 applies to reference materials for both quantitative analysis and the testing of nominal properties, whereas the definition in the ISO VIM focuses on reference materials for quantitative analysis.

All measurements contain errors. As a result, the true value of the parameter being measured, can never be known. Since most of science and engineering revolves around measurement, it stands to reason that it is important to determine, by estimation, the size of the error associated with the measurement in order for it to be meaningful. Whilst an error, which remains constant, (systematic error), can be corrected for, an error due to randomly changing factors cannot. This form of error is best referred to as an “Uncertainty of Measurement” and can be analysed using a number of methodologies, the most commonly used one being the “ISO Guide to the expression of uncertainty in measurement” (ISO GUM)[4]. Once analysed using this methodology, the estimated “Uncertainty of Measurement” provides a numerical value describing the range, within which the true value of the measured parameter is expected to lie, with a specified level of confidence. This then makes it possible to use the measurement result, in spite of the fact that the true value is not known.

According to ISO Guide 34[5] there are several technically valid approaches for the characterisation of a reference material, such as a single (primary) method in a single laboratory; two or more independent reference methods in one or several laboratories; one or more methods of demonstrable accuracy, performed by a network of competent laboratories; an approach providing method-specific, operationally defined property values, using a network of competent laboratories. Compliance with ISO/IEC 17025[6] is stated as the measure for the competence of the laboratories.

Certified reference material production in South Africa was initiated and maintained for many years, largely through the efforts of one man, the late Trevor Steele, director of the Analytical Science Division of originally the Government Metallurgical Laboratory (GML), which then became the National Institute for Metallurgy (NIM), and finally changed to MINTEK. Trevor Steele was also a member of the International Study Group for Reference Materials (ISGRM), and a founder member of the ISO Technical Committee on reference materials (ISO/REMCO). Through his international involvement in setting standards for the production of reference materials, he obtained international recognition for South African reference materials, in particular the first set of reference materials produced by South Africa, the NIMROCs (SARM 1 to 6).

SARM 1 to 6 are very well-known and popular, being sought after locally as well as internationally. During the past three decades the NIMROCs maintained their status as high quality CRMs. Large numbers of units have been sold locally, as well as internationally. In **Figure 1.1** (see **Appendix A** for the full details) it can be seen that there has been a steady decline in the sales of SARM 1 to 6 since 1987. This may be due, in part, to the fact that several other CRMs of the more common minerals (such as granite and syenite) have become available. However, the lack of uncertainty budgets associated with the certified values of SARM 1 to 6 cannot be ignored as a possible contributing factor to the decrease in sales. It should be noted that the first edition of ISO Guide 35, which stipulates the importance of uncertainty budgets for assigned values was developed during the period from 1986 and published in 1989.

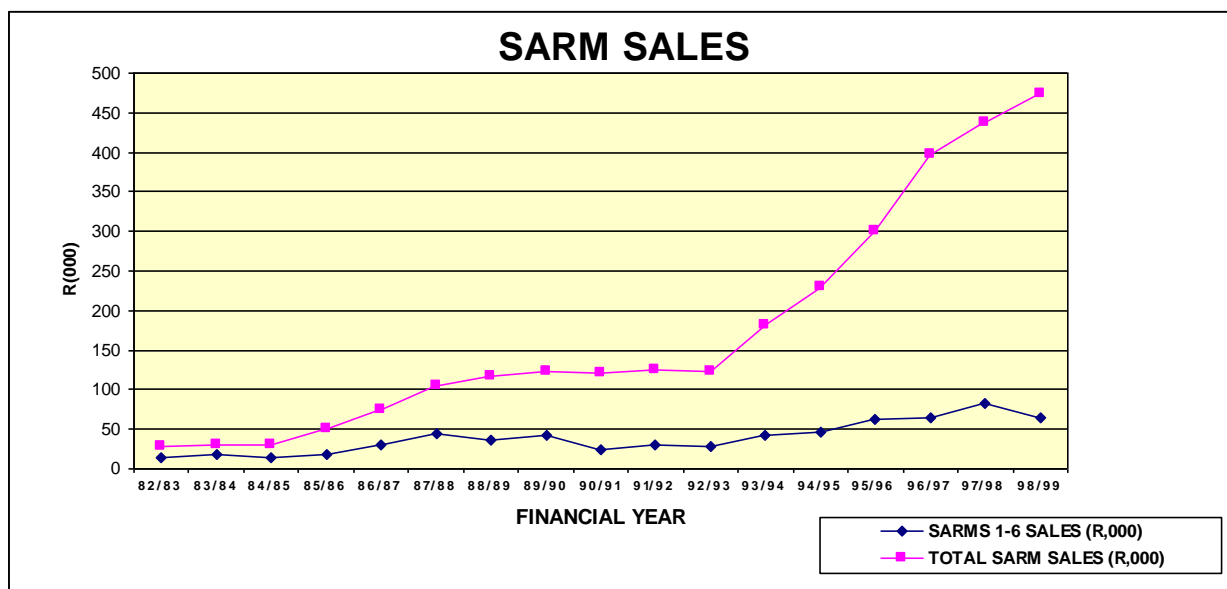


Figure 1.1: Summary of the sales statistics for the SARMS from 1982 to 1999

SARM 1 to 6 were previously certified in the period between 1972 and 1979[7, 8]. The analysis of the rare-earth elements was concluded in 1984[9]. Originally SARM 1 to 6 were certified through the use of an interlaboratory study with approximately 25 participating laboratories. However, at that stage, there was no strict requirement for accreditation to ISO/IEC 17025, the standard did not even exist. The ‘certified values’ which were reported for the reference materials also did not include any estimation of the uncertainty of measurement. In the original certification reports the data of participating laboratories were evaluated statistically, but not in accordance with the ISO GUM[10-12]. During the preparation of the materials the homogeneity was evaluated,

and it was concluded that the materials were homogeneous for the purpose of the preparation of reference materials[13].

During the past two decades new analytical techniques for the analysis of geological samples have been developed and the older techniques, such as atomic absorption spectroscopy (AAS), have improved, resulting in increased sensitivity, lower detection limits and better resolution. These improved capabilities for quantitative chemical analysis will result in higher accuracy for the determination of especially the minor and trace elements in SARM 1 to 6.

An added advantage is that there are large stocks of the prepared bulk sample of these six reference materials still available at MINTEK (see **Table 1.1**). The preparation of the bulk sample encompasses more than 50% of the effort involved with the production of a reference material. Assigning the certified values is technically more intricate and requires more organisational skills. The certification is the value adding step in the production of a CRM.

Table 1.1: Stocks available of SARM 1 to 6

Sample	Number of units prepared (100 g)	Number of units still available
SARM 1	2200	1000
SARM 2	2200	1400
SARM 3	2200	1100
SARM 4	2200	1300
SARM 5	2200	1150
SARM 6	2200	1200

All six bulk samples have been milled to the required degree of fineness, and blended. However, they are at different stages of the final preparation steps necessary to convert them into saleable units. For SARM 2 and 5 the milled and blended bulk materials are stored in bags, each containing approximately 23 kg of material. Further preparation work required involves the following steps:

Step 1: Re-blending of all bags of bulk material, in case any segregation has taken place within the bags.

Step 2: Manually dividing blended material sequentially into 10 kg portions in buckets.

Step 3: Thorough cleaning of rotary splitter and beakers, with a final rinse with distilled water.

Step 4: Rinsing (new) bottles with distilled water and drying.

Step 5: Labelling of required number of bottles.

Step 6: Splitting the material into 100 g portions in successive steps using a vibrating rotary feed splitter.

Step 7: Bottling the portions.

Step 8: Assigning the correct split number to each bottle, for purposes of traceability.

SARM 1 and 6 are each currently stored in 10 kg portions, ten of SARM 1 and twelve of SARM 6. Further preparation of SARM 1 and 6 involves steps 3 to 8 above. All the above steps have been completed for SARM 3 and 4.

1.2 Aim of this study

South Africa is recognised as a world leader in the mining industry. SARM 1 to 6 are silent ambassadors, which enhance the status of South Africa in the international mining community. The re-certification of SARM 1 to 6 will allow South Africa to maintain these reference materials as ambassadors, and grow our expertise and status in the arena of reference material production.

In view of the continued popularity of the NIMROCs and the availability of bulk sample, the National Metrology Institute of South Africa (NMISA) embarked on a project to re-certify some of the materials. Three samples were selected from the suite of six igneous rock samples of SARM 1 to SARM 6, i.e., SARM 2 (Syenite), SARM 3 (Lujavrite) and SARM 4 (Norite). As pointed out already, the materials in their current state of certification had several shortcomings.

The aim of the re-certification project was to first assign values to as many of the minor and trace elements of the materials with a single primary reference measurement procedure in a single laboratory to comply with the ISO Guide 34 requirement for metrological traceability. The NMISA has established its capability in the technique of double isotope dilution inductively coupled plasma sectorfield mass spectrometry (ID-

ICP-MS) through participation in several international comparisons of the CCQM (CCQM-K13, CCQM-P12, CCQM-K24, CCQM-P25, CCQM-K14, CCQM-K33, CCQM-P72, CCQM-P64, CCQM-P85, CCQM-P86, CCQM-K30, CCQM-P12.1, CCQM-K56, CCQM-P106, CCQM-K60, CCQM-P119, CCQM-K75, CCQM-P118)[14].

The materials were to be characterised for selected trace elements and would include the complete evaluation of the measurement uncertainties associated with the methods used in accordance with the requirements of ISO Guides 30, 31, 34 and 35 and the ISO GUM[3-5, 15, 16]. Algorithms were to be developed for the calculation of the amount of content and all the possible uncertainty contributions associated with the measurement technique were to be evaluated thoroughly for the estimation of the measurement uncertainty.

As part of the development of the methodology, the NMISA was to develop sample preparation procedures for the complete decomposition of these silicate rock type samples. During the development of the methodology the focus would be on the establishment of an effective microwave digestion method. The methodology would also be validated through the use of an established certified reference material (CRM).

Experimental designs would be developed for optimum isotope ratios for the elements of interest in the sample blends, using a multi-element isotope spike blend. This would require careful optimisation of the high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) measurement procedures to obtain sufficient counting statistics for optimum precision of the different isotope ratios.

Chapter 2

History of SARM 1 to 6

2.1 Origin and mineralogy[13]

SARM 1: NIM-G Granite

SARM 1 was excavated from the acid portion of the Bushveld Igneous Complex. The specimen consists mainly of several large blocks collected from a small, shallow quarry that was developed for masonry stone. The reference material is a granitic rock-type which consists mainly of quartz and K-feldspar, and has smaller amounts of mica and Na-feldspar. The reference material is used in the analysis of rock samples, some non-metalliferous ores, and geochemical samples.

SARM 2: NIM-S Syenite

SARM 2 was excavated from the Palabora Igneous Complex. A few large blocks from the quarry at Brekerkop were cracked with sledge-hammers. The specimen is slightly inhomogeneous and consists predominantly of alkali-feldspar with pods and schlieren of green alkali pyroxene. The material is a syenitic rock-type which consists mainly of K-feldspar and has minor amounts of quartz, Na-feldspar, and alkali-amphiboles. The material is used in the analysis of silicate samples, but can also be used as a reference material in the analysis of non-metalliferous raw materials and geochemical prospecting samples.

SARM 3: NIM-L Lujavrite

SARM 3 was excavated from the green foyaite group of the Pilanesberg Alkaline Complex. The rock-type is a lujavrite and is an undersaturated igneous rock which consists of nepheline, sphene, aegrine, magnetite, and some feldspar. This reference material is useful in the analysis of silicate rocks, but can also be used in the analysis of some non-metalliferous ores and as a geochemical exploration reference material. Because of its unusual trace element concentrations it is also a valuable trace element reference material.

SARM 4: NIM-N Norite (Gabbro)

SARM 4 was excavated from the Main Zone of the Bushveld Igneous Complex. This rock-type is a norite which consists of orthopyroxene, plagioclase, magnetite, ilmenite, and clinopyroxene and minor amounts of quartz and alteration products. It is a useful silicate reference material for intermediate rocks, but is also used in the analysis of geochemical exploration samples.

SARM 5: NIM-P Pyroxenite

SARM 5 was excavated from the Critical Zone of the Bushveld Igneous Complex. The specimen consists of loose blocks collected from the waste dump of the Ruighoek Chrome Mine, and the material is from the lower end of No. 1 Incline Shaft, 400 feet vertically below the surface. This rock-type is a pyroxenite which consists of orthopyroxene, clinopyroxene and plagioclase and minor amounts of olivine and chromite. This reference material is used in the analysis of mafic silicate rocks, and can also be used in the analysis of geochemical exploration samples.

SARM 6: NIM-D Chrysolite Dunite

SARM 6 was excavated from an ultrabasic pipe transecting the Critical Zone of the Bushveld Igneous Complex. This specimen consists of loose blocks collected from the waste dump of the Driekop Platinum Mine and is from the No. 5 Drive, 500 feet below the surface. This rock-type is a dunite and consists of olivine and orthopyroxene, and minor amounts of clinopyroxene, plagioclase and chromite. This reference material is used in the analysis of basic silicate rock samples, and can also be used in the analysis of non-metalliferous ores, as well as geochemical exploration samples.

2.2 Original certification study

In 1972, a preliminary report[13, 17] was issued by NIM that gave the analytical results from 32 laboratories, for elements ranging in concentration from major to trace amounts in SARM 1 to 6. The data for the major and minor constituents were plotted in the form of histograms. Statistical rejection procedures were applied and the resultant data listed and discussed. A table of mean and median values was provided in the report. Because the results for most trace elements were insufficient for a statistical evaluation, these results were only tabulated, and standard values were not recommended in the report.

Although satisfactory precision was shown by the results obtained for some of the constituents of the NIMROC samples, further analytical work was required before statistically valid certified values could be recommended for all major and minor

constituents. It was expected that, as soon as sufficient additional results were received, standard values would be recommended for the major and minor constituents of all samples, and at least a statistical analysis for the trace constituents would be made.

In the preliminary report[13] results were given for 68 elements in one or more of the rocks. For the sets of results where all the values fell within 3 standard deviations of the overall mean, this overall mean was given for 20 elements in one or more samples (13 elements for all 6 samples), and it was suggested that these values could be used in the absence of any firm recommendation by the investigators. Because of the scarcity of the results, no commitment was made for what amounted to 70 percent of the sets of results for the various elements, in one or more of the samples. In 1973, values were given under the term 'averages' for major, minor and a few trace elements, and under 'magnitudes' for the remainder of the trace elements, but 'averages' and 'magnitudes' were not defined.

Regarding the NIMROC samples, results that fell outside 3 standard deviations of the mean were excluded in the calculation of the average[10, 11]. It was intended that 'magnitude' for the NIMROC samples should be interpreted as 'somewhere in the region of' the given value. A further set of values, referred to as 'usable' values, was given in a paper at a later date[17]. Since there were so many elements for which recommended values could not be given, the usefulness of the NIMROC samples as reference materials was limited. Since the publication of the preliminary report, many more results were received from a total of 79 contributing laboratories. In February 1978 another report was published by MINTEK[11], which dealt with the elements whose concentration range was 1 percent or less, which were the elements most in need of revision. In this report, the results from the 79 laboratories were published and evaluated statistically with the goal to increase the usefulness of the NIMROC samples as CRMs.

The samples were prepared at a time when the importance of an 'experimental design', or the need for detailed instructions to the analyst on the reporting of his results was not fully appreciated and, consequently, as with the preliminary report, it was not possible to give a detailed statistical analysis of the data.

In the 1978 report there were 97 sets of results, covering 25 trace and minor elements in the NIMROC samples, for which recommended values could be given, a considerable improvement on the data reported in 1972. Results were received for the following elements, for which there were no results in the previous report: silver, arsenic, bismuth, carbon, erbium, mercury, holmium, indium, praseodymium, platinum, tellurium, thallium,

and thulium. However, because there were too few results, recommended values could not be given for these elements.

Although further results were received, recommended values could not be given for the following elements: gold, beryllium, bromine, cadmium, chlorine, chromium, dysprosium, europium, gadolinium, germanium, hafnium, lutetium, molybdenum, neodymium, antimony, scandium, samarium, tin, tantalum, terbium, and tungsten.

There were also many elements for which recommended values could be given for only some of the samples; for example, lanthanum, sulphur, and ytterbium in one of the materials and fluorine, lithium, niobium, and uranium in two of the materials. It is surprising that, even for the commonly determined elements phosphorus and nickel, recommended values could not be given for NIM-G and NIM-L, respectively.

In May 1979 another report was published by MINTEK[10] which gave the data received up to February 1978 for the constituents which occur in major concentrations in the NIMROC samples. Subsequently, the results of these two reports were also published in two separate papers[7, 8].

Several estimators were used to assist in the assignment of recommended values. In addition to the mean, median, and dominant cluster mode (DCM) that were used on the trace elements[11, 18], three other estimators of central tendency were used for the data on major and minor constituents: the gamma central value[19, 20], a trimmed mean[20], and a modification of the median described by J. Gastwirth and referred to as the Gastwirth median[20].

In 1984 a final report was published by MINTEK[12] with all the analytical results submitted by the contributing laboratories before July 1983 for thorium, yttrium, lanthanum, and the rare-earth elements in the six NIMROC reference materials (SARM 1 to 6). According to the report, the procedure for the certification of a reference material as practised at MINTEK at that stage required that, for any constituent, all the following criteria must be met:

- i) There must be a minimum of ten results after the rejection of gross outliers.
- ii) The robust relative standard deviation, s_r , must be less than 33%.

$$Robust(s_r) = \frac{Robust(s)}{Median} \dots\dots\dots (2.1)$$

where

$$Robust(s) = \frac{UpperHexile - LowerHexile}{2} \dots\dots\dots(2.2)$$

- iii) The distribution of the results must not be bimodal i.e. the results must not have two peaks when plotted as a histogram.
- iv) There must be good agreement between the four indicators for central tendency.

Recommended values were assigned to data sets meeting all these criteria. For those sets with a distribution that was only slightly skewed (i.e. with a positive or negative skewness value smaller than 0.5), the Gastwirth median (which is considered to be more robust than the median) was assigned as the recommended value. For the data sets that satisfied the criteria, but with a moderate or definite skewness (i.e. a positive or negative skewness value greater than 0.5), the DCM was assigned as the recommended value. For recommended values assigned in accordance with the Gastwirth median, the confidence limits were calculated according to Nair's method. Confidence limits were calculated according to Ellis, where the DCM was assigned to elements as the recommended value[18].

The materials were certified through interlaboratory studies, where the participants were reputable national and international laboratories, specialising in geochemical analysis. During the early 1970s the certified values were reported as single values without uncertainty statements, and later the 95% confidence limits of the standard deviation of the mean of means of the reported values were included in the certificates, along with the certified values (see **Tables 2.1** and **2.2**).

Table 2.1: Certified and uncertified values for the major elements in SARM 1 to 6, in % oxide

Constituent	SARM 1	SARM 2	SARM 3	SARM 4	SARM 5	SARM 6
SiO ₂	75.70	63.63	52.40	52.64	51.10	38.96
Al ₂ O ₃	12.08	17.34	13.64	16.50	4.18	0.3 [?]
Fe ₂ O ₃	0.6 [?]	1.11	8.78	0.8 [?]	0.87	0.71
FeO	1.30	0.30	1.13	7.47	10.59	14.63
MgO	0.06 [?]	0.46	0.28	7.50	25.33	43.51
CaO	0.78	0.68	3.22	11.50	2.66	0.28
Na ₂ O	3.36	0.43	8.37	2.46	0.37	0.04 [?]
K ₂ O	4.99	15.35	5.51	0.25	0.09	0.01 [?]
MnO	-	-	0.77	0.18	0.22	0.22
TiO ₂	-	-	0.48	0.20	0.20	-
P ₂ O ₅	-	0.12	-	-	-	-
Cr ₂ O ₃	-	-	-	-	3.50	0.42
NiO	-	-	-	-	-	0.26
ZrO ₂	-	-	1.49	-	-	-
BaO	-	0.27	-	-	-	-
SrO	-	-	0.54	-	-	-
Nb ₂ O ₅	-	-	0.14	-	-	-
Cl	-	-	0.12	-	-	-
F	0.42	-	0.44	-	-	-
H ₂ O ⁺	0.49	0.22	2.31	0.33	0.26	0.30
CO ₂	0.10 [?]	0.09	0.17	0.10 [?]	0.08 [?]	0.40 [?]
Σ	99.88 [?]	100.00	99.97	99.93 [?]	99.45 [?]	100.04 [?]
O/F.S.Cl	0.18	0.01	0.23	0.02	0.02	0.02
Σ(corrected)	99.70 [?]	99.99	99.56	99.91 [?]	99.43 [?]	100.02 [?]
OTHERS (3)*	0.29	0.14	0.29	0.22	0.23	0.11
TOTAL	99.99 [?]	100.13	99.85	100.13 [?]	99.66 [?]	100.13 [?]
TOTAL Fe as	2.00	1.40	9.91	8.97	12.70	17.00
Fe ₂ O ₃ (R)						
Total Fe as	2.04	1.44	10.04	9.10	12.64	16.97
Fe ₂ O ₃ (c)						

(3)* See key to Table 2.1.

(R) Certified value obtained by using the reported analytical results for total Fe.

(c) Certified value obtained by calculation from the certified values for FeO and Fe₂O₃.

Key to Table 2.1:

1. A question mark indicates an uncertified value.
2. Where there are dashes, the values are given in mg.kg⁻¹ of the elements in Table 2.2.
3. "OTHERS" is the sum of the oxides of trace constituents that are present in concentrations large enough to affect the summation. They are reported individually as mg.kg⁻¹ of the elements in Table 2.2.

Table 2.2: Certified and uncertified values for the minor and trace elements in SARM 1 to 6, in mg.kg⁻¹ of the elements

Element	SARM 1	SARM 2	SARM 3	SARM 4	SARM 5	SARM 6
Ba	120 [?]	2400	450	102	46 [?]	10 [?]
Ce	195(190-203)	11.9(9.6-14.4)	240 [?]	6 [?]	**	**
Co	*	3 [?]	*	58	110	208
Cr	12	12	10 [?]	30 [?]	24000	2900
Cu	12	19	13	14	18	10
Dy	17 [?]	0.4 [?]	**	**	**	**
Eu	0.35(0.34-0.47)	0.30(0.27-0.38)	1.2(1.0-1.5)	0.63(0.59-0.69)	0.2 [?]	**
F	4200	*	4400	*	*	*
Ga	27	11	54 [?]	16	8 [?]	*
Gd	14 [?]	**	**	**	**	**
La	109(100-116)	5 [?]	250 [?]	3 [?]	2 [?]	0.2 [?]
Li	12 [?]	*	48 [?]	*	*	*
Lu	2 [?]	**	0.4 [?]	0.2 [?]	**	**
Mn	160	80	6000	1400	1700	1700
Nb	53	*	960	*	*	*
Nd	72(67-84)	6 [?]	48(35-57)	3 [?]	**	**
Ni	8 [?]	7 [?]	*	120	555	2040
P	*	520	260	130 [?]	90	40 [?]
Pb	40	5 [?]	43	*	*	8
Rb	325	530	190	*	*	*
S	*	*	650 [?]	*	*	*
Sm	15.8(14.0-18.0)	1 [?]	5 [?]	0.8 [?]	**	**
Sr	10	62	4600	260	32	3 [?]
Tb	3.0(2.4-3.5)	**	0.7 [?]	**	**	**
Th	51(48-55)	1.0(0.5-1.0)	66(58-72)	**	**	**
Ti	540	265	2900	1200	1200	120
Tm	2 [?]	**	**	**	**	**
U	15 [?]	*	14	*	*	*
V	2 [?]	10	81	220	230	40
Y	143(120-159)	**	22(15-27)	7 [?]	5 [?]	**

Table 2.2: Cont.

Element	SARM 1	SARM 2	SARM 3	SARM 4	SARM 5	SARM 6
Yb	14.2(12.8-16.0)	0.07 [?]	3 [?]	0.7 [?]	0.6 [?]	**
Zn	50	10 [?]	395	68	100	90
Zr	300	33 [?]	11000	23 [?]	*	*

Key to Table 2.2:

1. Figures in brackets are the 95% confidence limits of the certified value.
 2. A question mark indicates an uncertified, or tentative value.
 3. Where no value is given, no certified or uncertified value has been assigned.
- * Indicates that an order of magnitude for this element can be ascertained from the data in NIM report No. 1975[11]. Orders of magnitude are similarly available for Ag, As, Au, B, Be, Bi, Cd, Cl, Cs, Hf, Mo, Sb, Sc and Ta.
- ** Indicates that an order of magnitude for this element can be ascertained from the data in MINTEK Report No M134[12]. Orders of magnitude are similarly available for Er, Ho and Pr.

2.3 Compilation of data from 1978 to the present.

The ultimate aim in the assessment of analytical data on reference materials is the assignment of a 'true value'. According to the "Vocabulary of Metrology – Basic General Concepts and Associated Terms", the true value of a quantity is a value consistent with the definition of the particular quantity[2]. This value can only be obtained by a perfect measurement and is therefore, by nature, indeterminate. As the ideal of a true value cannot be met, the alternative is the assignment of a value representing consensus of the analysts who have taken part in the analysis. Instead of 'consensus value', use is made of the term 'recommended value', which is more or less synonymous with terms such as 'preferred value', 'estimate' or 'usable value' used by producers of geological reference materials, and with the ISO definition of reference value.

For the statistical evaluation of the compiled data for SARM 2, 3 and 4 published in the period from 1978 to 2005, the non-parametric estimator, the median, was used. The median absolute deviation (*MAD*) was used as the non-parametric estimator of the standard deviation. This is given by the median of all absolute deviations of each test result and the median (**equation 2.3**):

$$MAD = median(|x_i - median|) \dots \dots \dots (2.3)$$

To confer equivalence to the standard deviation of a normal distribution, the MAD was multiplied by a factor of 1.483. This value is known as the MAD_e [21]. The range of the published values are reported as the median, with the MAD_e multiplied by a coverage factor of two, to provide for a result with an expanded uncertainty which approximates a confidence level of 95.45%. An expanded uncertainty (U) is usually the uncertainty reported with a measurement result and consists of the combination of all the uncertainty contributions to the measurement result with a level of confidence [2].

Tables 2.3 to 2.8 summarise the results from the compilation of the published data for the three materials that were analysed during this study, and also compares the compilation data with the results from the original certification study. The data for the published results for the individual elements of SARM 2 to 4 are summarised in **Appendix B to D**, respectively.



Table 2.3: Statistical evaluation of the literature values compared with the originally certified values for the major elements of SARM 2 (%)

Elements	Originally certified values			Literature values from 1978 to 2006		
	Concentration	Standard deviation	Number of values (n)	Median	Expanded uncertainty, k=2	Number of values (n)
SiO ₂	63.63	1.08	65	63.61	0.30	6
Al ₂ O ₃	17.34	0.46	69	17.15	0.44	7
Fe ₂ O ₃	1.4	0.2	69	1.40	0.08	7
MgO	0.46	0.19	58	0.47	0.04	7
CaO	3.22	0.27	72	3.12	0.14	6
Na ₂ O	0.43	0.11	50	0.41	0.06	6
K ₂ O	15.35	0.92	65	15.28	0.30	5
P ₂ O ₅	0.12	0.03	38	0.11	0.06	8

Table 2.4: Statistical evaluation of the literature values compared with the originally certified values for the minor and trace elements of SARM 2 ($\mu\text{g.g}^{-1}$)

Elements	Originally certified values				Literature values from 1978 to 2006			
	Concentration	Standard deviation	Range	Number of values (n)	Median	Expanded uncertainty, k=2	Range	Number of values (n)
Ag			0.083	1			0.1-2	3
As			0.21	1			0.25-6	4
Au (ng.g^{-1})							0.062-3000	4
B			8.9-14.0	7			8.8-15.4	2
Ba	2400	360		29	2565	428		6
Be			1.099-2.0	11	1.62	0.12		5
Bi			400	1			17-2500	4
Cd (ng.g^{-1})			1000-35000	6			16-2000	5
Ce	11.9 (9.6-14.4)	2.4		14	11.9	2.6		13
Co	3 [?]	2		22	2.87	0.24		5
Cr	12	4		29			5.52-134	6
Cs			5.7-10.14	10	6.47	0.42		3
Cu	19	5		29	20.5	6.2		5
Dy			0.3-0.63	3	0.4	0.14		9
Er			0.068	1	0.12	0.02		6
Eu	0.3 (0.27-0.38)	0.06		14	0.27	0.04		10
F			86-370	10			76-135.5	3
Ga	11	4		12			10-11.3	2
Gd			0.56-0.59	3	0.81	0.18		10
Hf			0.2-41	5	0.46	0.02		3
Hg			<10	1			9.4-35	4
Ho			0.048	1	0.055	0.010		4
Ir							0.01-2500	4
La	5	1.3		9	5.60	1.98		14
Li			1.38-4.0	11			<2	2
Lu			0.006-0.3	6	0.010	0.002		5
Mo			0.29-10	13			0.76-3	3
Nb			3.0-5.0	12			0.25-4.5	5
Nd	6 [?]	0.43		6	6	0.8		9
Ni	7 [?]	4		24			6-116	8
Pb	5 [?]	4		18			2-13	4
Pd							0.067-6	2
Pr			1	1	1.45	0.34		8
Rb	530	58		23	537	26		6
Ru							0.3-3000	4
Sb			0.17-0.7	7			0.05-18	4
Sc			3.0-8.0	13			3.6-13.5	5
Sm	1 [?]	0.25		8	1.3	0.32		10
Sn			0.5-10	11			0.11-3	3
Sr	62	14		30	62	6		9
Ta			0.03-0.3	5	0.043	0.030		4
Tb			0.05-0.11	4	0.10	0.04		3
Th	1.0 (0.5-1.0)			15			0.691-25	7
Tm			0.011	1			0.01-0.5	4
U			0.1-5.0	13	0.5	0.38		4

Table 2.4: Cont.

Elements	Originally certified values				Literature values from 1978 to 2006			
	Concentration	Standard deviation	Range	Number of values (n)	Median	Expanded uncertainty, k=2	Range	Number of values (n)
V	10	4		18			1-139	4
W	<10			2			<1	3
Y			1.5-50	10			1.1-16.2	11
Yb	0.07 [?]	0.008		6	0.07	0.026		8
Zn	10 [?]	6		22			9-83.15	8
Zr	33 [?]	20		10	20	12		11



Table 2.5: Statistical evaluation of the literature values compared with the originally certified values for the major elements of SARM 3 (%)

Elements	Originally certified values			Literature values from 1978 to 2006		
	Concentration	Standard deviation	Number of values (n)	Median	Expanded uncertainty, k=2	Number of values (n)
SiO₂	52.40	0.3	52	52.45	0.20	4
Al₂O₃	13.64	0.48	57	13.40	0.08	5
Fe₂O₃	9.91	0.36	67	9.96	0.38	7
MgO	0.28	0.10	58	0.28	0.06	5
CaO	3.22	0.27	72	3.12	0.14	6
Na₂O	8.37	0.53	52	8.56	0.24	5
K₂O	5.51	0.19	63	5.45	0.30	5
TiO₂	0.48	0.08	68	0.49	0.02	5
MnO	0.77	0.16	67	0.74	0.04	6
P₂O₅	0.06	0.04	34	0.06	0.02	6

Table 2.6: Statistical evaluation of the literature values compared with the originally certified values for the minor and trace elements of SARM 3 ($\mu\text{g.g}^{-1}$)

Elements	Originally certified values				Literature values from 1978 to 2006			
	Concentration	Standard deviation	Range	Number of values (n)	Median	Expanded uncertainty, k=2	Range	Number of values (n)
Ag			0.11-2.0	2			9.45	2
As			1.0-14	4			1.70-1.92	3
Au (ng.g^{-1})			4.4	1			0.64	1
B			3.2	1			3.3-8.37	2
Ba	450	140		33	420.5	49.0		9
Be			2.0-31.0	8	25.8	4.4		5
Bi			0.4	1			0.25-1.76	3
Cd (ng.g^{-1})			2000-4000	2			630-1005	3
Ce	240 [?]	42		18	292	64		20
Cl	1200	500		6			902-1100	2
Co			1.6-150	24	2.53	0.52		6
Cr	10 [?]	14		27	12	6		7
Cs			2.1-9	8	2.71	0.52		4
Cu	13	6		33	10.8	4.4		4
Dy			1.9-3.719	2	2.9	0.6		12
Er			1.2-2.3	9	2.28	0.38		10
Eu	1.2 (1.0-1.5)			15	1.07	0.22		16
F	4400	1500		11			3185-5500	3
Ga	54 [?]	98		14			51.1-54	2
Gd			1.799-3.6	2	3.60	1.68		14
Ge							0.76-0.89	2
Hf			148-274	5	226	16		4
Hg							23.9-44.5	3
Ho			0.42-0.9	2	0.62	0.28		8
La	250 [?]	42		12	231	32		21
Li	48 [?]	20		10			39.3-55	3
Lu	0.4 [?]	0.2		7	0.47	0.18		13
Mo			0.920-5	6			0.75-1.3	2
Nb	960	570		12	985	50		5
Nd	48 (35-57)			11	48	12		17
Ni			2-150	26			2.16-57	6
Pb	43	17		28			44-68	3
Pr			15-21.5	2	18.5	4.6		12
Rb	190	350		24	198	20		7
S	650 [?]	170		10			537	1
Sb			0.190-2.469	4			0.11-0.36	4
Sc			0.260-80	7			0.186-4	6
Sm	5 [?]	2		10	4.5	2.0		16
Sn			0.720-12	6			6.9-12	3
Sr	4600	1000		34	4685	600		10
Ta			21-26.2	8	22.9	4.6		4
Tb	0.7 [?]	0.2		9	0.60	0.16		8
Th	66 (58-72)			21	64	12		7
Tm			0.230-0.900	4	0.38	0.08		6

Table 2.6: Cont.

Elements	Originally certified values				Literature values from 1978 to 2006			
	Concentration	Standard deviation	Range	Number of values (n)	Median	Expanded uncertainty, k=2	Range	Number of values (n)
U	14	7		11	16.2	5.4		8
V	81	18		32	85	16		4
W			10	1			7.72-8	2
Y	22 (15-27)			17	20	6		11
Yb	3 [?]	1		11	2.95	0.84		15
Zn	395	119		30	437	32		7
Zr	11000	5000		31	11329	1100		11



Table 2.7: Statistical evaluation of the literature values compared with the originally certified values for the major elements of SARM 4 (%)

Elements	Originally certified values			Literature values from 1978 to 2006		
	Concentration	Standard deviation	Number of values (n)	Median	Expanded uncertainty, k=2	Number of values (n)
SiO ₂	52.64	0.74	71	52.83	0.48	6
Al ₂ O ₃	16.5	0.6	74	16.50	0.30	7
Fe ₂ O ₃	8.97	0.90	73	8.96	0.38	8
MgO	7.5	0.7	74	7.47	0.18	8
CaO	11.5	0.4	78	11.45	0.10	8
Na ₂ O	2.46	0.17	54	2.43	0.14	7
K ₂ O	0.25	0.07	63	0.25	0.02	6
TiO ₂	0.20	0.03	65	0.19	0.02	7
MnO	0.18	0.01	69	0.18	0.02	7
P ₂ O ₅	0.03	0.02	33	0.03	0.02	8

Table 2.8: Statistical evaluation of the literature values compared with the originally certified values for the minor and trace elements of SARM 4 ($\mu\text{g.g}^{-1}$)

Elements	Originally certified values				Literature values from 1978 to 2006			
	Concentration	Standard deviation	Range	Number of values (n)	Median	Expanded uncertainty (k=2)	Range	Number of values (n)
Ag			0.13 - 17	6			0.76-9.45	4
As			0.46	6			0.4-6	4
Au (ng.g^{-1})			4	3			0.65-6000	4
B			2.5-9	7			2.7-4.76	2
Ba	102	21	60-300	22	89.9	17.8	80.3-200	8
Be			0.26-3	11			0.27-419	5
Bi			0.6	5			0.01-1	4
Cd			1-4	6			0.047-2	3
Ce	6 [?]	3	3.6-24	13	5.9	0.88	4.8-39	19
Cl			40-300	5			34	1
Co	58	10	40-100	34	57.7	4.8	51-59.5	6
Cr	30 [?]	8	7.7-340	34	31.1	9	9-42.05	7
Cs			0.2-4	8	0.23	0.02	0.23-0.24	3
Cu	14	4	5-200	34	12.0	3.6	8-15	7
Dy			1.099-1.929	3	1.1	0.2	0.98-5	14
Er			0.620	1	0.665	0.052	0.5-0.9	12
Eu	0.63 (0.59-0.69) [#]		0.300-0.690	14	0.59	0.06	0.4-1.9	15
F			10-530	10			22-59.4	3
Ga	16	3	12-22	13	16.2	3.6	15-18	3
Gd			0.12-0.74	4	0.94	0.08	0.6-5	13
Ge			1.0-1.4	3			1.54-1.67	2
Hf			0.2-5	4	0.36	0.06	0.1-0.38	3
Hg			<10	1			12.8-54	3
Ho			0.22	1	0.22	0.02	0.20-0.24	6
La	3 [?]	0.4	2.3-3.4	11	3.05	1.24	2.4-11	16
Li			4-9	11			2-7.2	3
Lu	0.2	0.1	0.11-0.8	7	0.110	0.02	0.09-0.3	10
Mo			0.84-60	13			0.93-4	3
Nb			2-3	12			0.27-4	10
Nd	3	2	0.4-7.5	7	3	0.36	2-3.32	13
Ni	120	22	27-230	44	119.5	7.4	101-122.9	9
Pb			0.8-26	28			2.48-21	3
Pr			0.72	1	0.72	0.08	0.48-2.43	12
Rb			2.4-18	23			1-191.1	7
S			42-140	10			50	1
Sb			0.07-0.49	6			0.05-18	4
Sc			31-130	15	38.7	3.2	36-39.8	5
Sm	0.8 [?]	0.2	0.5-1.0	9	0.8	0.08	0.77-1.5	12
Sn			0.3-5	11			0.23-3	4
Sr	260	39	160-700	34	264	14	250-269	9
Ta			0.06-4	5	0.08	0.04	0.064-0.16	4
Tb			0.1-0.16	3	0.162	0.006	0.15-0.2	5
Th			0.2-5	16	0.42	0.24	0.34-3.6	5
Tm			0.1	2	0.100	0.002	0.099-0.5	6
U			0.26-5	11	0.4	0.2	0.28-20	7
V	220	37	40-280	31	215	16	201.3-225	5

Table 2.8: Cont.

Elements	Originally certified values				Literature values from 1978 to 2006			
	Concentration	Standard deviation	Range	Number of values (n)	Median	Expanded uncertainty (k=2)	Range	Number of values (n)
W			10-400	3			2-7	3
Y	7 [?]	3	3.3-13	14	6.2	1.4	5-8.7	10
Yb	0.7 [?]	0.5	0.42-2.4	10	0.70	0.14	0.6-2.6	17
Zn	68	19	32-410	29	63	3	54-68	8
Zr	23 [?]	12	6-110	11			10.5-25.7	11

Chapter 3

The measurement technique of isotope dilution inductively coupled plasma mass spectrometry (ICP-MS)

3.1 Introduction

Total metal analysis, including trace and ultra trace elemental analysis of geological materials, have traditionally been performed using analysis methods such as atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA)[22]. Other methods include flame emission spectrometry, spectrophotometric analysis, ion selective electrode potentiometry, UV/VIS spectroscopy, candoluminescence, etc[10, 11]. Over the past 30 years more versatile measurement techniques have been developed in the form of inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

The first requirement for this study was to re-certify SARM 1 to 6 using a definitive technique with the potential to be a primary reference measurement procedure (primary method) as defined in Chapter 1[2]. Firstly, the method must be performed at the highest level of accuracy (trueness and precision)[2, 23]. Secondly, a complete measurement model must be defined in terms of SI units to facilitate the complete evaluation of all contributions to the measurement uncertainty in accordance with the Guide to the Expression of Uncertainty of Measurement (ISO GUM)[4].

Isotope dilution mass spectrometry is a direct ratio method which has been identified by the Consultative Committee for Amount of Substance (CCQM) of the International Committee for Weights and Measures (CIPM) to have the potential to be a primary method [1]. Isotope dilution measurements can be made with inductively coupled plasma mass spectrometry (ICP-MS), which is specifically suited to trace and ultra trace elemental analysis of geological materials.

3.2 Isotope dilution mass spectrometry (IDMS)

The principle of isotope dilution can be explained with the following illustration: In a large box you have a mixture of white soccer balls and rugby balls, where the one cannot be distinguished from the other. We want to know the number of soccer

balls, but there are too many to count. So, what kind of method can we use to determine the number of soccer balls?

Put 100 red soccer balls into the box with the white soccer balls and rugby balls, and mix them completely. By doing this, the original white soccer balls are diluted with the red ones. Now, take 50 soccer balls out of the box and count the number of red ones. If the number is 5, then we know the ratio of the red soccer balls to all the soccer balls is $0.1 (= \frac{5}{50})$. This ratio does not change before or after taking the

soccer balls out of the box. Before taking the soccer balls out of the box, the number of red soccer balls in the box was 100, so the total number of soccer balls in the box had to be a 1000, suggesting that the original number of white soccer balls was 900. Thus we are able to establish the total number (though it is an approximate value) by measuring the ratio of the marked (red) soccer balls to the unmarked (white) soccer balls in a sample from the box, after mixing them.

This is the principle of isotope dilution analysis, where the white soccer balls correspond to the analyte in the sample and the red soccer balls correspond to the spiked analyte, which is added to the sample in a known quantity. The rugby balls correspond to the matrix.

Isotopes of an element are the atoms which have the same atomic number as the element, but have different mass numbers (numbers of neutrons in their nuclei). They are classified as stable isotopes and radioisotopes. In isotope dilution analysis, an enriched radioisotope or stable isotope is used as the 'marked' analyte. It behaves in the same way as the analyte and is called a 'spike' (also a 'marker' or a 'label'). The analyte in the sample is mixed with a defined amount of spiked analyte (then called the diluent). By measuring the specific activities or isotope ratio of the diluent and the diluted sample, it is possible to know the degree of dilution and calculate the quantity of the analyte in the sample. There is essentially no difference between the principles of radio and stable isotope dilution analysis. But, in the case of stable isotope dilution analysis, there is no corresponding radioactivity to measure, so the degree of dilution must be measured mainly by using mass spectrometry. Therefore, the development of stable isotope dilution analysis coincided with improvements in mass spectrometers.

Isotope dilution mass spectrometry (IDMS)[24] is based on addition of a known amount of enriched isotope (called the 'spike') to a sample. After equilibration of the spike isotope with the natural isotope of the element in the sample, mass spectrometry (MS) is used to measure the altered isotopic ratio(s). The measured isotope ratio (R_m) of isotope A to isotope B can be calculated as follows:

Basic equation:

$$R_m = \frac{A_x C_x W_x + A_s C_s W_s}{B_x C_x W_x + B_s C_s W_s} \dots\dots\dots (3.1)$$

where

A_x, B_x = the atom fractions of isotopes A and B in the sample, relative to all isotopes

A_s, B_s = the atom fractions of isotopes A and B in the spike

C_x, C_s = the elemental mass concentrations in the sample and the spike,
respectively

W_x, W_s = the weights of the sample and the spike, respectively

The concentration of the element in the sample can then be calculated from this ratio:

$$C_x = \left(\frac{C_s W_s}{W_x} \right) \cdot \left(\frac{A_s - R_m B_s}{R_m B_x - A_x} \right) \dots\dots\dots (3.2)$$

A major advantage of the technique is that chemical separations, if required for accurate ratio measurement, need not be quantitative (after equilibration). In addition, ratios can be measured very reproducibly and, thus, concentrations can be determined very precisely. The technique is based directly on primary standards and the processes of weighing and mass spectrometric isotope ratio measurement. Thus, the weighing process ties the technique to the fundamental SI unit, the kilogram. The mass spectrometric isotope ratio measurement process ties the technique to the relative atomic masses of the elements, linking mass to amount of substance and thus to the mole, the fundamental unit of chemistry.

Accurate quantification with IDMS requires calibration of the isotopic abundances and concentration of the enriched stable isotope spike. Typically the enrichment of the stable isotope spike is known, but the concentration may not be accurately known. The concentration of the spike is then determined by a reverse isotope dilution procedure: The spike is mixed with known amounts of the natural material of the analyte of interest using solutions prepared from primary standards or high-purity materials of the analyte of interest. The isotopic composition of the natural material samples must also be determined for the few elements for which natural variations are expected (e.g., Pb).

The direct link between the amount content of an element in an unknown sample and a primary chemical standard is illustrated in **Figures 3.1** and **3.2**. The accurately known chemical composition of the primary assay standard (a standard with accurately known isotopic abundances as well as quantitative chemical composition), is used to obtain an accurate value of concentration for the spike solution by isotope ratio measurement of a mixture of these two solutions. This procedure is called “spike calibration”, and the process of quantitatively diluting the highly-enriched ^{206}Pb atom fraction in the spike solution with the isotopically natural assay standard, is often referred to as “reverse isotope dilution” or “double isotope dilution”. The spike calibration is an important and integral part of the isotope dilution process, making the analysis of the sample a “double ratio” process, through the spike, to the primary assay standard.

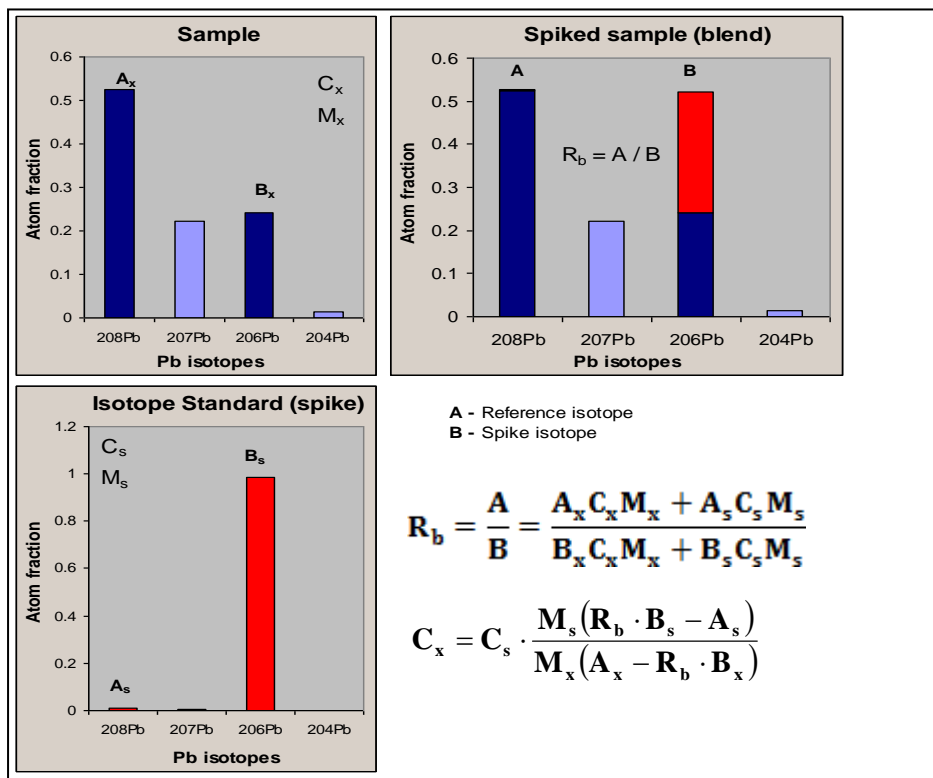


Figure 3.1: Illustration of the natural sample which is spiked with the enriched stable isotope standard to produce a stable isotope sample spike blend

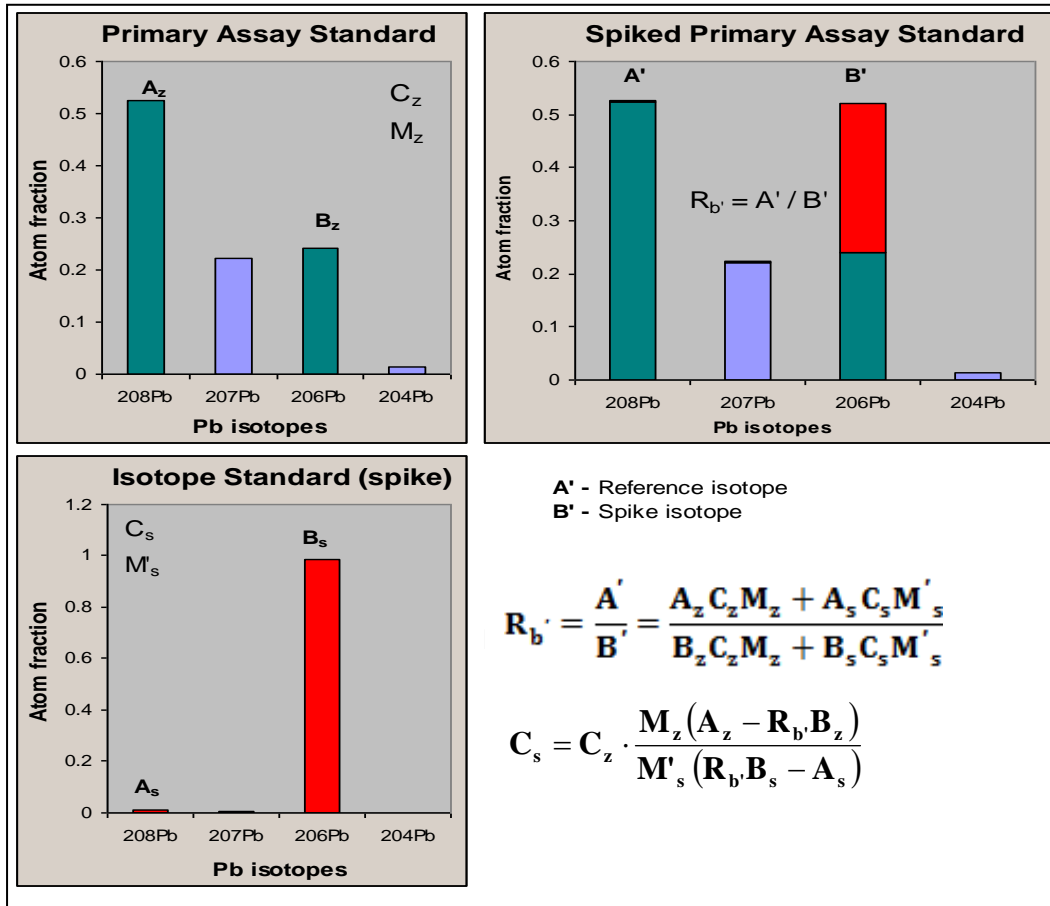


Figure 3.2: Illustration of the primary assay standard which is spiked with the enriched stable isotope standard to produce a stable isotope primary assay standard spike blend

The double isotope dilution technique is based on the use of a primary assay standard. The accurately known concentration of the primary assay standard is utilised to obtain an accurate value of the elemental concentration for the spike isotope standard through the measurement of the isotope ratio (R_b) of a mixture of these solutions. Therefore, double isotope dilution analysis requires accurate measurement of the isotope ratios of two mixtures (blend solutions), i.e. spike:unknown (R_b) and spike:assay standard (R_b').

$$R_b = \frac{A}{B} = \frac{A_x C_x M_x + A_s C_s M_s}{B_x C_x M_x + B_s C_s M_s} \dots\dots\dots(3.3)$$

If you make C_x the subject of the equation, then

$$C_x = C_s \cdot \frac{M_s (R_b \cdot B_s - A_s)}{M_x (A_x - R_b \cdot B_x)} \dots\dots\dots(3.4)$$

$$R_{b'} = \frac{A'}{B'} = \frac{A_z C_z M_z + A_s C_s M_s'}{B_z C_z M_z + B_s C_s M_s'} \dots\dots\dots (3.5)$$

If you make C_s the subject of the equation, then

$$C_s = C_z \cdot \frac{M_z (A_z - R_{b'} B_z)}{M_s' (R_{b'} B_s - A_s)} \dots\dots\dots (3.6)$$

Then you substitute C_s in **equation 3.4**

$$C_x = C_z \cdot \frac{M_z (A_z - R_{b'} B_z) M_s (R_{b'} B_s - A_s)}{M_s' (R_{b'} B_s - A_s) M_x (A_x - R_b B_x)} \dots\dots\dots (3.7)$$

If the conditions of ratio measurement are consistent between the spike calibration and the sample measurement, and assuming accurate weighing, potential systematic errors in the measurement process are cancelled or minimised in the final result. The calculation of the mass fraction of the analyte in the unknown sample is carried out according to the final equation (**equation 3.8**):

$$C_x = C_z \cdot \frac{M_z M_s (A_z - R_{b'} B_z) (R_{b'} B_s - A_s)}{M_s' M_x (R_{b'} B_s - A_s) (A_x - R_b B_x)} \dots\dots\dots (3.8)$$

where,

x - index for the sample

s - index for the spike

z - index for the primary assay standard

b - index for the blend of fractions of sample and spike

b' - index for the blend of fractions of the primary assay standard and spike

C_z - Amount content or mass fraction of the primary assay standard

M_s - Mass of the spike in blend b

M_z - Mass of the primary assay standard in blend b'

M_x - Mass of the sample in blend b

M_s' - Mass of the spike in blend b'

R_b - Determined isotope ratio of blend b

$R_{b'}$ - Determined isotope ratio in blend b'

A_x, B_x = the atom fractions of isotopes A and B in the sample, relative to all isotopes

A_s, B_s = the atom fractions of isotopes A and B in the spike

A_z, B_z = the atom fractions of isotopes A and B in the assay standard

Equation 3.8 can be simplified further by substituting atom fractions with ratios.

$$C_x = C_z \cdot \frac{M_z \cdot M_s \cdot (R_z - R_{b'}) \cdot (R_b - R_s)}{M_{s'} \cdot M_x \cdot (R_{b'} - R_s) \cdot (R_x - R_b)} \dots\dots\dots (3.9)$$

where

R_b = Determined isotope ratio in the sample blend, b

$R_{b'}$ = Determined isotope ratio in the standard blend, b'

R_x = Determined isotope ratio in the sample

R_z = Determined isotope ratio in the assay standard

A typical experiment for double isotope dilution analysis of a single sample requires the preparation and analysis of six solutions. The set of six sample solutions (see **Figure 3.3**) are prepared under identical conditions and includes: rock sample, rock sample with added isotope spikes, primary standard, and primary standard with added isotope spikes, reagent blank and reagent blank with added isotope spikes.

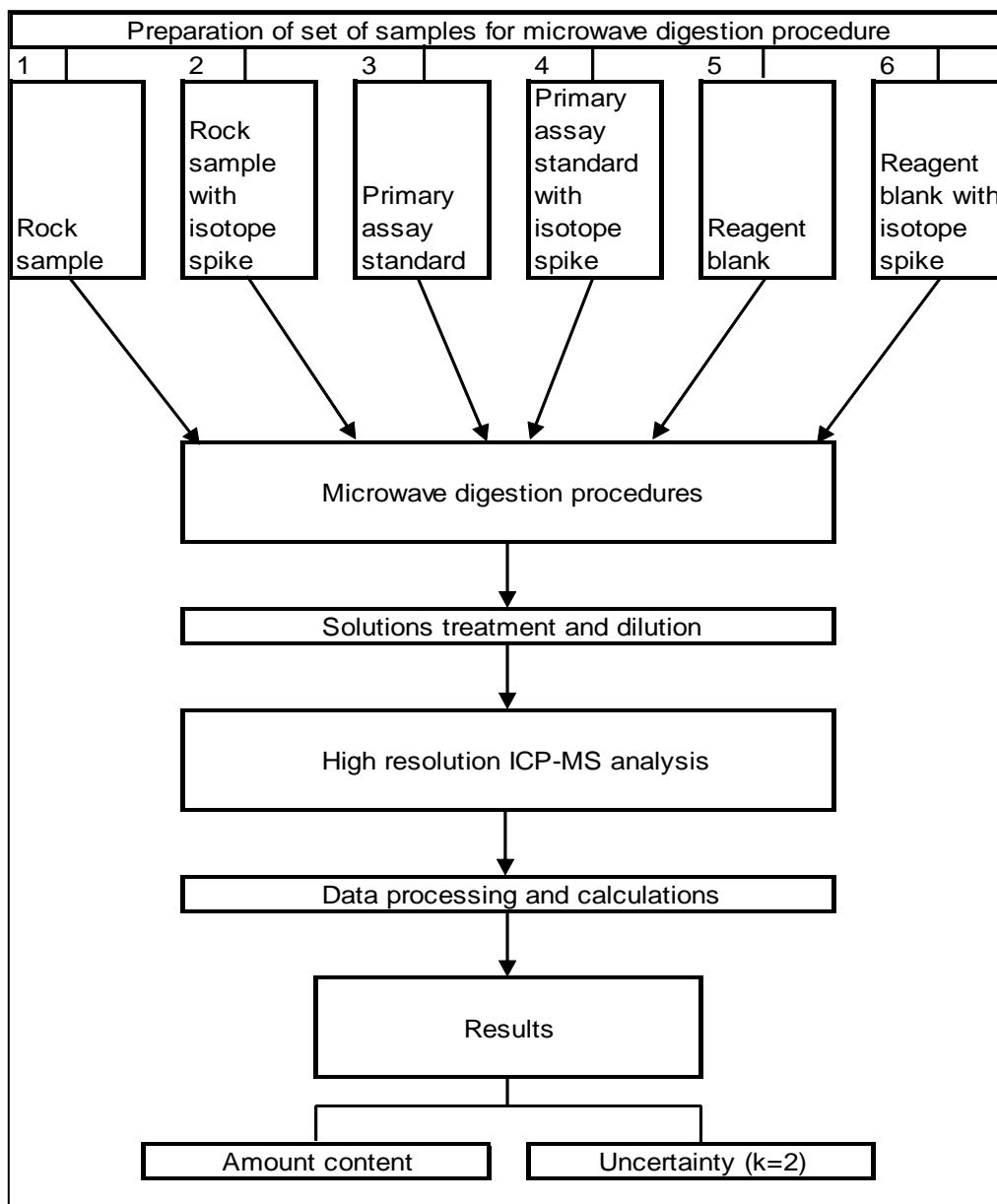


Figure 3.3: General scheme for the double isotope dilution HR-ICPMS analysis

There are three possible sources of systematic error in IDMS[24], i.e. sample preparation, mass spectrometric analysis, and the concentration of the spike standard solution, which must be accurately known and therefore traceable. Because double ID ICP-MS requires equilibration of the spike isotope and the natural isotope(s), the spiked sample must be completely dissolved into solution. During this stage of the procedure the analyst must be aware of pitfalls. If the sample does not completely dissolve, if the spike or sample isotopes are selectively lost before equilibration, or if contamination occurs in the dissolution process, the measured isotopic ratio will not reflect the accurate ratio of added spike atoms to sample atoms for that element. One advantage of IDMS is that the chemical separation of an element need not be quantitative. Once equilibration is achieved,

the isotopic ratio defines the elemental concentration and this ratio will not change with non-isotope selective element loss.

There are two dominant aspects of accurate isotopic ratio measurements[24], i. e., isobaric interferences and instrumental discrimination/fractionation effects. Isobaric interferences can result from elemental interferences, molecular ion interferences that can arise from the sample, residual gases in the mass spectrometer, or multiply-charged ions. It is difficult to generalise about the potential effects of isobaric interferences because they are dependent on the specificity of the mass spectrometric method, and the sample. Isobaric interferences, which result from the sample matrix itself, present greater difficulties. Measurement of natural isotopic abundances for the unspiked samples should be a prerequisite for accurate isotope dilution analysis.

The best IDMS measurements require an optimum mixture of the spike and sample. The error magnification factor (the propagation of the uncertainty in concentration from the uncertainty in ratio measurement) can be calculated[25] and becomes large if the spiked sample ratio approaches the spike ratio ('overspiking') or the natural ratio ('underspiking'). The effect of the error magnification factor is dependent on the mass spectrometric precision, and the relative enrichment of the spike isotope and natural isotope. From an error propagation standpoint alone, the 'best' mole ratio occurs when the determined ratio, R_m , equals the square root of the product of the ratios of the spike and the natural isotope. In practice, other factors are considered. For example, the best mass spectrometric precision is achieved for ratios near one. When the element to be determined is near the detection limit, the ratio of spike isotope to natural isotope should be greater than one (≈ 10), so that noise contributes only to the uncertainty of the natural isotope and not to the spike isotope[25].

Several sources of noise exist in any analytical measurement performed by ICP-MS. The two major sources of noise that can have an impact on the ultimate precision obtained for an isotope ratio measurement are flicker noise and shot noise. Flicker noise is a non-fundamental source of noise relating primarily to the sample introduction system and the ICP. Sources of flicker noise include peristaltic pump pulsation and changing droplet size distributions for solution nebulisation. Sources of flicker noise for solid sampling include shot to shot laser fluctuations and changing particle size distribution from one moment to the next. These and other effects cause a fluctuation in the number of analyte ions that generate the signal used for analytical purposes. Flicker noise increases directly with increasing signal level. For example, if a given signal has a strength of 1000 and a standard deviation of 100 ($RSD=(100/1000) \times 100 = 10\%$), a corresponding signal of 10 000 would have a standard deviation of 1000 or an RSD of 10% as well.

Shot noise, otherwise known as Poisson Statistics or Counting Statistics, is a much different and fundamental source of noise that is directly proportional to the square

root of the signal. Shot noise is due to the random arrival rate of particles (photons, electrons, ions) at a detector. Using the previous example of signal strength of 1000, the shot noise component would be $1000^{1/2}$ or 31.6 yielding an RSD of 3.16% and a signal of 10 000 could give an RSD of 1%. It is evident from this simple example that increasing the amount of signal accumulated will improve the shot noise component of the overall statistical variance of a measurement.

Ultimately, the noise of any measurement depends on which source of noise becomes the dominant limiting factor towards the precision of the measurement result. Shot noise usually becomes the precision limiting source of noise with very low signals. Conversely, the contribution of shot noise to the overall noise level in high signals becomes small, and flicker noise dominates the precision of the measurement result.

Thus,

$$\text{Flicker noise: } \sigma \propto s \dots\dots\dots(3.10)$$

$$\text{Shot noise: } \sigma \cdot s^{1/2} \dots\dots\dots(3.11)$$

$$\text{RSD} = \frac{\sigma}{s} \dots\dots\dots(3.12)$$

where

σ = standard deviation (noise)

s = signal required

At the shot noise limit, substituting (3.11) into (3.12) yields

$$\text{RSD} = s^{-1/2} \dots\dots\dots(3.13)$$

Measurement of high precision isotope ratios presents unique challenges for ICP-MS. When an isotope ratio is taken, not only are the isotopes of interest measured, but also the flicker noise component is minimised. Ideally, the only noise component is from shot noise; flicker noise is completely eliminated. Using a sequential ICP-MS device, this ideal condition is sought by peak hopping very rapidly between the two isotopes of interest. The rapid peak hopping process is necessary in order to minimise the time between the measurement of the isotopes of interest. This is done to minimise flicker noise, but it introduces higher levels of shot noise since the amount of signal collected during each measurement sequence is reduced as the integration time for each isotope is kept small. Using a sequential ICP-MS system the result is a conundrum. One must introduce elevated levels of shot noise in order to remove flicker noise.

Similar to the single signal case, the shot noise or theoretical lowest limit of a ratio ($RSD_{A/B}$), can be calculated from the following equations.

$$RSD_{A/B}^2 = RSD_A^2 + RSD_B^2 \dots\dots\dots (3.14)$$

Substituting in equation (3.13) yields

$$RSD_{A/B}^2 = \left[\left(s_A^{-1/2} \right)^2 + \left(s_B^{-1/2} \right)^2 \right] \dots\dots\dots (3.15)$$

or

$$RSD_{A/B} = \left(s_A^{-1} + s_B^{-1} \right)^{1/2} \dots\dots\dots (3.16)$$

From equation (3.16), it can be seen that the $RSD_{A/B}$ will become smaller as s_A and s_B increase. There are several ways for the signal required for each of the isotopes to increase. First, the concentration of the isotopes can be increased. Second, since s_A and s_B represent the total signal measured and not the signal rate, the integration time of the measurement can be increased.

Increasing the concentration of the isotopes can be done to a certain extent and is a valuable tool for improving the ratio measurement. The original sample, sampling conditions, and detector saturation considerations will undoubtedly dictate the concentration regime that can be used in any measurement.

Increasing the integration time is a very effective tool for improving the measured precision of an isotope ratio for a simultaneous measurement system. However, the fact remains that a sequential system must peak hop or scan very rapidly in order to minimise flicker noise. The impact of this peak hopping or scanning can be very dramatic on the quality of the data. Plasma conditions cannot be completely matched at each moment in time. This implies that atomisation and ionisation conditions, polyatomic formation and dissociation, ion extraction and ion transmission parameters fluctuate on a very rapid time-scale. Thus, even when rapid peak hopping is incorporated, deviation from the ideal precision of the measurement is observed.

Example 1: 1:1 isotope ratio (Similar to $^{107}\text{Ag}:^{109}\text{Ag}$ where ^{107}Ag is 51.8% naturally abundant and ^{109}Ag is 48.2% naturally abundant).

Count rate for A = 10 000 counts per second (cps)

Count rate for B = 10 000 cps

Integration time = 1 second

$$s_A = 10\,000 \text{ counts}$$

$$s_B = 10\,000 \text{ counts}$$

$$\text{RSD}_{A/B} = (10\,000^{-1} + 10\,000^{-1})^{1/2}$$

$$\text{RSD}_{A/B} = 0.014 = 1.4\%$$

The above calculation indicates that the theoretical lower limit of the precision for this isotope ratio is 1.4% using a 1 second integration time. When the integration time is increased:

Example 2: 1:1 isotope ratio

Count rate for A = 10 000 counts per second (cps)

Count rate for B = 10 000 cps

Integration time = 10 seconds

$$s_A = 100\,000 \text{ counts}$$

$$s_B = 100\,000 \text{ counts}$$

$$\text{RSD}_{A/B} = (100\,000^{-1} + 100\,000^{-1})^{1/2}$$

$$\text{RSD}_{A/B} = 0.0044 = 0.44\%$$

The improvement in precision demonstrated is from 1.4% to 0.44% (improved by $10^{1/2}$) by increasing the integration time from 1 second to 10 seconds with the same count rate. Increasing the concentration (count rate) by the same factor of 10 and leaving the integration time at 1 second would have had an identical effect.

Another point that should be brought out from equation (3.16) is the effect of the ratio itself. In **Examples 1** and **2**, a total of 10 000 cps + 10 000 cps = 20 000 cps were taken. However, if the ratio changes, the theoretical limit of the RSD also changes.

Example 3: Ratio = 3:1

$$s_A = 15\,000 \text{ cps}$$

$$s_B = 5\,000 \text{ cps}$$

Integration time = 1 second

$$\text{RSD}_{A/B} = (15\,000^{-1} + 5\,000^{-1})^{1/2}$$

$$\text{RSD}_{A/B} = 0.0163 = 1.63\%$$

3.3 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS has matured into one of the most successful methods in atomic spectrometry, because of its sensitivity and ability to make multi-element measurements[26]. Since it was introduced for elemental analysis, the ICP has developed into one of the most successful sources. Initially, it had been used as an electronic excitation source, primarily in combination with emission spectroscopy. During the past 20 years, it has been widely used as an ion source for mass spectrometry (MS). Certain technological problems related to the sampling of ions had to be resolved for a successful combination of ICP and MS into ICP-MS.

In the ICP, ions are generated at atmospheric pressure; whereas for operating a mass spectrometer, a pressure of less than 10^{-5} mbar is a prerequisite. The bottleneck in between is the interface, which is used for ion extraction and pressure reduction. In the early days of ICP-MS, this was realised simply by a single, water-cooled, nozzle-like orifice with a diameter of only 50 to 70 μm . The problem with this arrangement was that, in the cool boundary layer in front of the cone, many different molecular ions were generated. This problem was overcome by increasing the diameter of the entrance orifice to about 1 mm, so that the boundary layer is punctured and ions are directly sampled from the “undisturbed” plasma. This technique became known as continuum sampling, and therefore the cone became known as the “sampler”.

Because the gas flow through this sampler is much larger than before, the pressure must be reduced by differential pumping in two or more steps. This is why a second nozzle is placed downstream of the sampler and the space in between is evacuated by a fore pump with a high pumping rate. Because of the high difference in pressure between the ICP and the first pumping stage, the ions are sucked into the interface and accelerated to supersonic velocities.

To avoid turbulence at the second cone, it was machined with sharp edges to skim the ions from the supersonic beam, and therefore the name “skimmer” became widely used. The arrangement, consisting of a sampler and a skimmer cone with diameters of about 1 mm, became known as the “interface”. This was the breakthrough in ICP-MS that made ion extraction more effective, and thus improved intensity, and decreased spectral interferences by orders of magnitude.

Although ICP-MS is much less prone to spectral interference compared to ICP-OES, these nevertheless occur and must be eliminated as far as possible for the successful implementation of ID-ICP-MS. Spectrometric interferences are caused by atomic or molecular ions having the same nominal mass as the analyte isotope of

interest. The resulting signal may disturb, or even obscure, the true analytical signal; so the accuracy of the determination as well as the detection limits may be considerably deteriorated. The sources from which the interfering species may arise are many; so far, no generally accepted model exists to explain all of the contributing factors, but it is now well accepted that the interface still plays an important role in the appearance of molecular species.

Spectrometric interferences may be subdivided into isobaric atomic ions, multiply-charged ions, intense adjacent signals, and polyatomic ions of various origins. Isobaric overlap exists when isotopes of different elements coincide at the same nominal mass. For each element, with the exception of indium (In), at least one isotope can be found that is free from isobaric overlap, but in many cases this will not be the most abundant isotope. Multiply-charged ions will be found in the mass spectrum at a position m/z . Mainly, doubly charged ions of the major matrix components, and multiply-charged ions of the discharge gas argon, contribute to the mass spectrum. The signals of neighbouring ions with a very high intensity, such as those coming from a matrix element, may contribute to the signal of an adjacent isotope by tailing, if the abundance sensitivity i.e. the ratio of a signal intensity at m/z ($m+1$) to that at m , is not sufficient. Polyatomic ions may consist of atoms of the discharge gas and its contaminants, plus components of the solvent and matrix.

Of all these different groups of spectrometric interferences, polyatomic ions cause the most severe problems. Polyatomic ion interferences may be introduced by the analytical sample itself. For example, oxides can survive passage through the hot zone of the plasma, because of their higher bond strength. The majority of polyatomic interferences arising from the sample do so because of the water introduced with the sample. Laser ablation and solvent desolvation introduction systems substantially reduce oxide interferences. Polyatomic ions may also be produced as contaminants from either the chemical pre-treatment stage, or from the discharge gas, or possibly from air trapped in the plasma. Spectroscopic interferences of this kind can, in principle, be separated from the affected analyte isotope by high mass resolution.

A mass spectral interference will be resolved from the analyte signal depending on their mass difference and the instrument resolution. Mass resolution (R) is generally defined as $\frac{m}{\Delta m}$, in which Δm is the mass difference necessary to achieve a valley of 10% between two neighbouring peaks of identical intensity at a mass m and mass $m + \Delta m$. Because the intensities of neighbouring peaks are rarely identical, an alternative definition will be much more useful. In this definition, Δm is derived from the peak width at the points in the profile that correspond to 5% of the height. This approach will lead to the same value as in the 10% definition mentioned before, if the neighbouring peaks are equally high. It should be pointed out that, in general, the theoretical value is only a lower estimation for the resolution required, because most

often the signal intensity of the interfering species exceeds the analyte intensity by orders of magnitude.

One of the most often discussed examples of a spectral interference is $^{56}\text{Fe}^+$ and $^{40}\text{Ar}^{16}\text{O}^+$. The latter is a product created from the discharge gas argon and from oxygen contained in the solvent used. In this example, the isotopes $^{54}\text{Fe}^+$, $^{57}\text{Fe}^+$ and $^{58}\text{Fe}^+$ can be used alternatively for analysis, but the $^{58}\text{Fe}^+$ is isobarically interfered with by the isotope $^{58}\text{Ni}^+$. Whereas, the others are interfered with, to a certain extent, by $^{40}\text{Ar}^{14}\text{N}^+$ or $^{40}\text{Ar}^{16}\text{O}^{1}\text{H}^+$, the best choice overall is to use $^{57}\text{Fe}^+$. However, as its natural abundance is only 2.2 %, the detection limit for this element is extremely poor if low resolution instruments are used. Nevertheless, a resolution of less than 2500 is sufficient to separate the spectral interference from the $^{40}\text{Ar}^{16}\text{O}^+$ ion from the interfered analyte isotope at a m/z of 56.

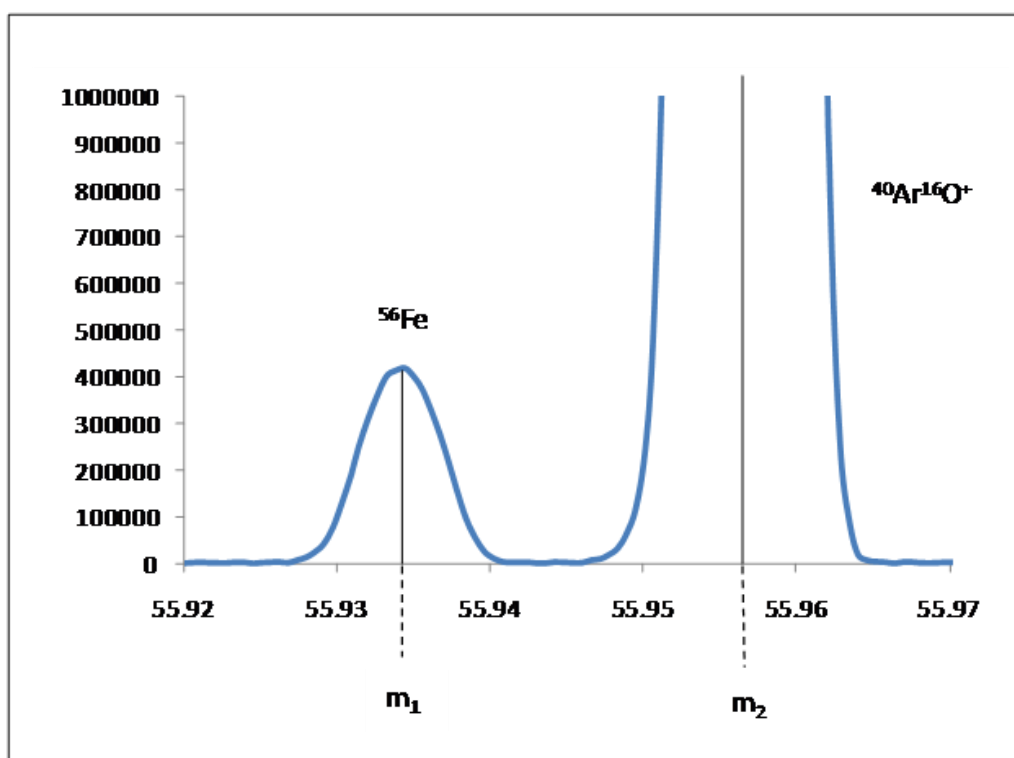


Figure 3.4: A schematic illustration of the effective resolution of the Finnigan Mat ELEMENT2 applied to the example of ^{56}Fe and $^{40}\text{Ar}^{16}\text{O}^+$

In **Figure 3.4** the nuclidic mass of $^{40}\text{Ar}^{16}\text{O}^+$ is $m_2 = 55.9565$ and the nuclidic mass of ^{56}Fe is $m_1 = 55.9345$, then $\Delta m = m_2 - m_1 = 55.9565 - 55.9345 = 0.022$. Thus, the needed resolution for the instrument is calculated as $R = \frac{m}{\Delta m} = 2543$.

A more problematic example is $^{75}\text{As}^+$, if chloride ($^{40}\text{Ar}^{35}\text{Cl}^-$) is present in the analyte sample. In the case of a mono-isotopic element, no alternative isotope can be chosen and the required resolution must be increased to about 7800. However, a resolution of 3000 will be sufficient to eliminate more than 90% of the interferences

caused by polyatomic ions. Commercial high-resolution magnetic sector field ICP-MS instruments have a maximum resolution somewhere between 7 500 and 12 000.

3.4 High resolution inductively coupled plasma magnetic sector field-mass spectrometry (HR-ICP-MS)

High mass resolution is usually achieved with a double-focusing instrument on the basis of combining magnetic and electric sector fields[26]. These instruments have an even longer tradition in mass spectrometry than do quadrupoles, but they are technically more sophisticated and therefore more expensive. The heart of a double-focusing instrument is a magnetic sector field. If ions of uniform kinetic energy and different mass are injected perpendicular to a magnetic sector field, they pass the field on a circular trajectory because of the Lorentz force. The radius of the trajectory depends on the mass of the ion, leading to a mass dispersion.

If the ion beam diverges from an entrance slit with a certain angle, then the beam focuses (directional focusing) behind the magnetic sector. Mass separation can now be realised if a slit is positioned behind the sector field just at this focus point, resulting in a well-defined radius and selection of a specific mass. Decreasing the slit width can be used to increase the mass resolution, but only if the ions are mono-energetic, because any spread in energy will deteriorate the beam width at the focus point itself. From this point of view, the ICP is not an ideal ion source. The energy distribution of ions is far too broad to be accepted by a magnetic sector device operated in high mass-resolution mode.

Therefore, the energy dispersion of an electric sector field is used to exactly compensate for the energy dispersion of the magnet so that, in the whole device, only mass dispersion is left. Both magnetic and electric sector instruments have angular focusing properties, and the combined system focuses by angle and energy. This is why these instruments are called double focusing.

Different geometries for combining a magnetic and an electric sector are possible, but double-focusing conditions can be realised with a well-defined combination of electric and magnetic sector angles only. The position sequence of the two analyser components is optional. Traditionally, the electric sector is placed before the magnetic sector field. A 90° electrostatic sector combined with a 60° magnetic sector became widely known as Nier-Johnson geometry. Nowadays, the so-called “reverse geometry” with the electric sector behind the magnetic sector is usually considered advantageous, because the high ion currents from the source are first reduced by mass analysis, and only ions of the selected mass are subjected to the subsequent energy analysis. This configuration helps improve abundance sensitivity as well as reduce noise.

In normal sector field arrangements, double-focusing conditions are obtainable at only one point, where the exit slit is located. Some very special arrangements have been developed, which guarantee double focusing in a whole plane. Such arrangements have been used for simultaneous detection by photoplates or by multicollector Farraday cup equipment. The latter is advantageous, especially for high-precision (small relative standard deviation) isotope ratio measurements, because all isotopes of an element can be measured simultaneously. Therefore, precision is not limited by time-dependent fluctuations of the source. Although often not designed for high mass-resolution, precise isotope ratio measurements with double-focusing instruments are an important application, for example in dating geological samples or taking measurements at nuclear power plants.

A schematic of an ICP double-focusing MS instrument is shown in **Figure 3.5**. An ion source, a sampling interface, and a subsequent lens system are necessary, similarly to standard, low-resolution quadrupole-based instruments. A major difference is the need for an accelerating voltage of up to 8000 V. A special lens system is normally used, shaping beams and focusing ions into the mass analyser.

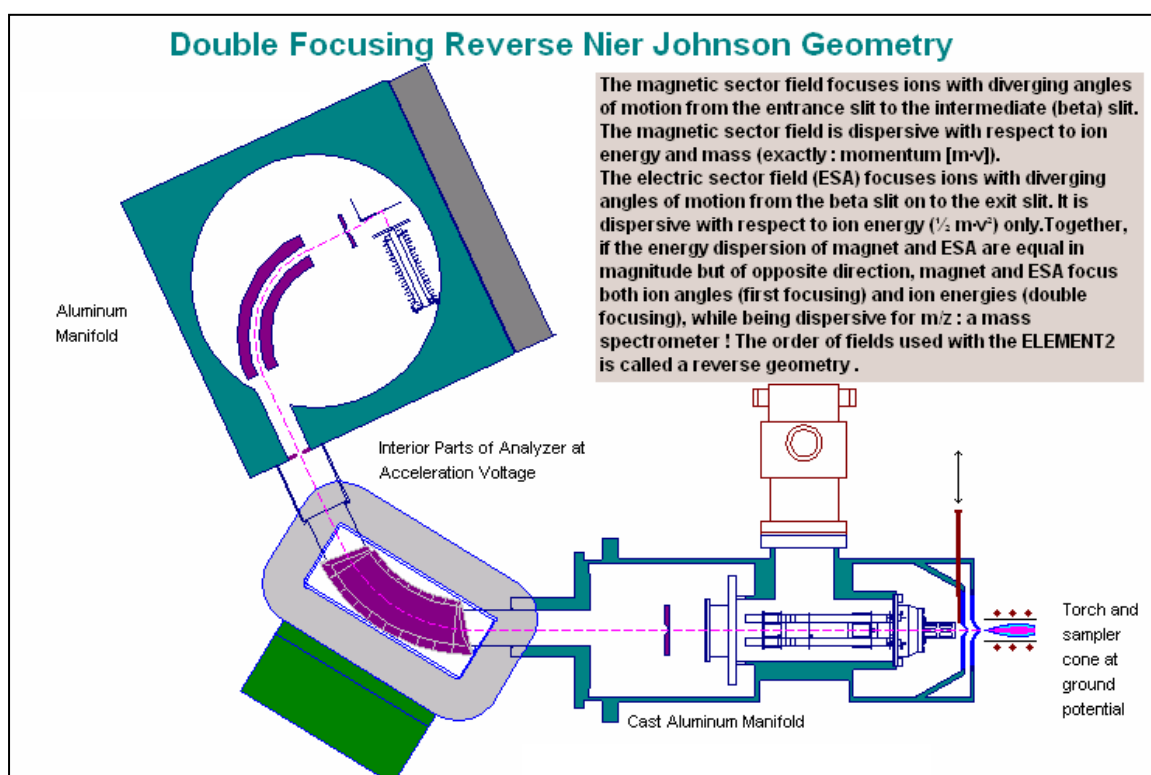


Figure 3.5: A schematic diagram of the ion optics of the Thermo FINNIGAN MAT Element 2 HR-ICP-MS

The resulting bent geometry of double-focusing instruments provides certain advantages when compared with the linear geometry of quadrupoles, because it keeps the noise level low and guarantees a high transmission. No ion losses occur

at otherwise offset lens systems or photon stop arrangements, as is the case with quadrupole instrumentation. For these reasons, sensitivities of up to 10^9 cps (counts per second) per $\mu\text{g}\cdot\text{m}^{-1}$ for the low-resolution mode and noise levels of less than 0.1 cps have been reported. Reducing noise and improving sensitivity can improve detection limits by orders of magnitude, even when the instruments are operated in low-resolution mode.

The first HR-ICP-MS instrument with Nier-Johnson geometry on the market was the Plasmatrace I, introduced in 1988 by VG Elemental. Design of the ion source and the interface was based on quadrupole ICP-MS systems by the same manufacturer. Nowadays, double-focusing instruments with high-resolution capabilities are available from different manufacturers.

Some peculiarities of double-focusing instruments should be mentioned. At first, the peak shape looks different compared to those from quadrupoles. Quadrupoles are operated with constant peak width and therefore linearly increasing resolution with mass. However, double-focusing instruments are operated (for a fixed slit width) with constant resolution, and therefore the absolute peak width increases with mass. For normal-resolution settings, the peaks have a trapezoidal peak shape, which looks needle-like at low masses, and are broader at high masses. The scan speed with which a mass spectrum can be acquired is lower than that obtainable with quadrupoles, even with modern laminated magnets, because double-focusing instruments require a longer settling time for achieving stable magnetic-field conditions. This limits the number of isotopes that can be investigated when data acquisition is by special sample introduction systems such as laser ablation.

Of course the most important capability of double-focusing instruments is high mass resolution. Increasing resolution results in decreased peak width. The interfering molecule can be separated from the analytical isotope, but not without a reduction in sensitivity. It should be noted that increasing the resolution from 400 to 4 000 decreases sensitivity by about 1 order of magnitude. Even in this case, the detection limits are better than that of quadrupole instruments by an order of magnitude.

Chapter 4

Experimental: Sample preparation and isotope ratio measurements

4.1 Development of the methodology for sample preparation

The analysis technique used during this study was double isotope dilution inductively coupled plasma magnetic sector field mass spectrometry (ID-ICP-MS). For the isotope dilution analysis it was a requirement to convert the rock samples to solutions. The two most common approaches to the decomposition of geological samples are acid digestion and fusion[22]. Other decomposition methods include slurry nebulisation (where the sample is introduced to the ICP in a semi-solid state), solvent extraction, pyrolysis, combustion, etc.

A slurry may be defined as a uniform suspension of small particles[22]. The slurry must be of low viscosity to be of practical use as a method of introducing samples into an ICP. The transport properties of a slurry should be similar to those of an aqueous solution, since the behaviour of the slurry in the spray chamber, torch and plasma will then be similar to that of a solution. If these criteria are fulfilled, it should then be possible to calibrate the system using aqueous calibration solutions. However, depending on the samples, matrix effects could be pronounced and internal standardisation will typically be required. In an ideal slurry, all particles would be of uniform small size ($< 5 \mu\text{m}$) so that they will remain suspended in a fluid medium during an analytical run.

In ICP-AES applications, slurries are typically analysed at concentrations between 1 and 30 % m/v. However, for analysis by ICP-MS it is necessary to limit the levels of total solids (or total dissolved solids) to less than $2000 \mu\text{g}\cdot\text{mL}^{-1}$ in order to prevent blocking of the sampling cone orifice. For good accuracy and precision, samples need to be very homogeneous, which could be problematic to achieve for geological samples, which are generally polymineralic.

Slurry nebulisation is a useful alternative method of sample introduction for the direct analysis of solids. Provided that the sample can be reduced to a sufficiently small and uniform particle size, measured data should be of comparable quality to that obtained by solution nebulisation. The technique is best applied to materials for which alternative methods of sample preparation are unsuitable and for the determination of elements which are lost as volatile species during other methods of

sample preparation. Problems of contamination and particle size reduction currently limit the widespread application of slurry nebulisation.

Fusion is usually employed when the matrix does not allow for complete decomposition of the sample by acid digestion. Fusion can be performed using a wide range of fluxes specifically suited to the matrix of the sample. Fluxes include sodium peroxide (Na_2O_2), lithium borate (LiBO_2) lithium metaborate ($\text{Li}_2\text{B}_4\text{O}_7$) and sodium metaborate ($\text{Na}_2\text{B}_4\text{O}_7$) for acidic rocks, which are igneous rocks containing more than two thirds silicon dioxide (SiO_2), and sodium hydroxide (NaOH), potassium hydroxide (KOH) for basic rocks, which are silicate minerals or rocks that are rich in magnesium and iron, etc. The major disadvantage of fusion for trace and ultra trace analysis at high levels of accuracy is the limited levels of purity of the fluxes.

The hotplate was traditionally used for acid digestion with different combinations of acids specifically suited to decompose the matrix of the sample. For example, a combination of hydrofluoric acid (HF), nitric (HNO_3) and hydrochloric acid (HCl) can be used for silicate rocks similar to the samples analysed during this study. Acid digestion was also performed in an open or closed configuration on the hotplate. In open acid digestion the samples with the acids were left open on the hotplate and the acids were allowed to evaporate to dryness. When a closed configuration of acid digestion on the hotplate (atmospheric pressure refluxing) was performed, the beakers with the samples and acids were covered with watch glasses to allow for dissolution of the samples under reflux of the acids.

With the advent of microwave technology, industrial microwave ovens were developed for specific application in acid digestion of samples for chemical analysis. A variety of microwave procedures were developed either in closed or open configuration for the decomposition of geological samples[27].

During this study a method was developed for the decomposition of the rock samples with acid digestion in a microwave oven with a high temperature and pressure programme. An attempt was made to develop a one step method for the complete dissolution of the samples. The idea was to have a simple digestion method to prevent loss of sample and to facilitate the use of the methodology for more routine applications. Some measure of pre-concentration of the samples was also required for the accurate determination of the low concentrations of especially nickel, cadmium and molybdenum in the samples.

The samples were first digested with the one step method proposed by Barbaro *et al.*[28]. Aliquots of 0.5 g sample of SARM 3 and SARM 4 were dissolved in a microwave oven using 2 ml HCl , 5 ml HNO_3 and 6 ml HF under pressure. Afterwards the samples were dried on hotplate before the samples were diluted with 10% HNO_3 . SARM 4 did not dissolve completely during the one step microwave digestion, most probably due to the high concentration of silica, as well as calcium-,

magnesium- and iron oxide, compared to SARM 3 and SARM 2. After evaporation on the hotplate, the samples also did not completely redissolve in 10% HNO₃. Experiments were done with different amounts of HF to see if the samples would dissolve in a one step digestion procedure. Care was taken to keep the amount of acid added to the samples to a minimum to prevent the samples from venting during the microwave procedure. Different amounts of HF did not improve the dissolution of the samples. HF is a very dangerous and corrosive reagent. The amount of HF in the acid mixture was kept to a minimum for safety reasons and also to protect the glassware and sample introduction system of the ICP.

A two step microwave digestion procedure was then developed[29], where the sample aliquot was reduced to 0.2 g. During the first step the samples were digested with 4 ml HNO₃, 3 ml HCl and 1 ml HF. During the second step another 1 ml HF was added with 15 ml 5% H₃BO₃ to dissolve the precipitate of fluorosilicates that precipitated during the digestion of SARM 4. The boric acid reacted with the fluorosilicates that precipitated during the digestion of SARM 4 to form borofluorosilicates in solution to produce a clear solution after the two-step digestion procedure. A possible drawback with the addition of a high volume of boric acid is the possibility of contamination, this necessitates the use of super-boiled or ultra-pure boric acid in these experiments.

4.2 Experimental work

4.2.1 Instrumentation

- High resolution inductively coupled plasma mass spectrometer, Element 2, Thermo Finnigan GmbH, Bremen, Germany.
- Self-aspirating nebuliser of 100 or 50 $\mu\text{l}\cdot\text{min}^{-1}$, suitable for nebulisation of solutions containing HF, an HF-resistant spray chamber and appropriate nebuliser tube for solutions containing HF.
- Desolvating sample introduction system, Aridus, Cetac Technologies Inc., Omaha, USA.
- Autosampler, ASX-100, Cetac Technologies Inc, Omaha, USA.
- Semi-micro analytical balance, Model: Genius ME215P, Sartorius AG, Goettingen, Germany.
- Eppendorf Variable Reference micropipettes (10 to 100 μl and 100 to 1000 μl) and Eppendorf Variable Research Pro (100 to 5000 μl), Eppendorf-Netheler-Hinz GmbH, Hamburg, Germany.

- Microwave Digestion System, Ethos 1600, Milestone S.r.l., Sorisole, Italy, with automatic temperature control.
- Drying oven, Ecoterm, Labotec.
- Water purification systems, Option 7/15 Plus and Elgastat Maxima Analytical, USF Elga, Bucks,UK.



Figure 4.1: Sartorius GENIUS ME215P semi-micro analytical balance

4.2.2 Test samples and certified reference material (CRM)

Experimental work was carried out using the following rock-type materials:

SY-4, Diorite Gneiss, Canadian Certified Reference Material, CANMET

SARM 2, Syenite, South African Reference Material (NIM-S)

SARM 3, Lujavrite, South African Reference Material (NIM-L)

SARM 4, Norite, South African Reference Material (NIM-N)

4.2.3 Reagents, standards and laboratory ware

4.2.3.1 Reagents

- Nitric acid 65%, Ultrapur, Merck KGaA, Darmstadt, Germany.

- Hydrochloric acid 30%, Ultrapur, Merck KGaA, Darmstadt, Germany.
- Hydrofluoric acid 40%, Environmental grade, Merck KGaA, Darmstadt, Germany.
- Boric acid 99,9999%, Suprapur, Merck KGaA, Darmstadt, Germany , and 5% solution.
- Deionised water, 18 Mohm.cm.

4.2.3.2 *Standards*

- Certified single element ICP-MS calibration standard, NIST SRM 3136; Lot no. 000612; $9.738 \pm 0.022 \text{ mg.g}^{-1}$ Ni; $k=2,31$.
- Certified single element ICP-MS calibration standard, NIST SRM 3114; Lot no. 011017; $9.993 \pm 0.016 \text{ mg.g}^{-1}$ Cu; $k=1,99$.
- Certified single element ICP-MS calibration standard, NIST SRM 3128; Lot no. 991504; $9.98 \pm 0.03 \text{ mg.g}^{-1}$ Pb; $k=2$.
- Certified single element ICP-MS calibration standard, NIST SRM 3134; Lot no. 891307; $9.99 \pm 0.03 \text{ mg.g}^{-1}$ Mo; $k=2$.
- Certified single element ICP-MS calibration standard, NIST SRM 3108; Lot no. 890312; $9.116 \pm 0.025 \text{ mg.g}^{-1}$ Cd; $k=2,36$.
- Certified single element ICP-MS calibration standard, NIST SRM 3168a; Lot no. 001402; $9.99 \pm 0.02 \text{ mg.g}^{-1}$ Zn; $k=2,05$.
- Certified single element ICP-MS calibration standard, NIST SRM 3104a; Lot no. 992907; $9.93 \pm 0.03 \text{ mg.g}^{-1}$ Ba; $k=2$.
- Certified ICP-MS calibration standard, Lot no. 219323, $1000 \pm 3 \text{ }\mu\text{g.l}^{-1}$ Sr, High Purity Standards, USA. The standard concentration has been certified by spectrometric analysis against an independent source, which is directly traceable to NIST SRM 3153a, Lot no. 990906 Density $1.01010 \text{ g.ml}^{-1}$ at 20°C .
- Certified ICP-MS Calibration Standard M, Lot no. 510217, High Purity Standards, USA. The standard concentration has been certified by spectrometric analysis against an independent source, which is directly traceable to NIST SRM no. 3100 series.

- ^{206}Pb stable isotope standard solution of $10 \text{ mg}\cdot\text{l}^{-1}$, Claritas PPT, Spex CertiPrep, USA.
- ^{135}Ba stable isotope standard solution of $10 \text{ mg}\cdot\text{l}^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{67}Zn stable isotope standard solution of $10 \text{ mg}\cdot\text{l}^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{65}Cu stable isotope standard solution of $10 \text{ mg}\cdot\text{l}^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{61}Ni stable isotope standard solution of $10 \text{ mg}\cdot\text{l}^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{86}Sr stable isotope standard solution of $10 \text{ mg}\cdot\text{l}^{-1}$, Spectrascan, Teknolab A/S, Norway.
- ^{97}Mo stable isotope standard solution of approximately $3233 \text{ mg}\cdot\text{l}^{-1}$ prepared by nitric acid digestion of the pure metal, Cambridge Isotope Laboratories, USA.
- ^{111}Cd stable isotope standard solution of $10.7965 \text{ mg}\cdot\text{l}^{-1}$, IRMM, Belgium.

The isotopic compositions of the stable isotope standards are given in **Appendix E**.

The general procedure for IDMS to be used in this study was the exact matching method where the samples would be spiked with an enriched isotope standard of the elements of interest to obtain a calculated isotope ratio close to 1. This could be achieved with relative ease during this study, because from the original certification study for SARM 1 to 6 the concentrations of the elements of interest in this study was fairly accurately known. However, the idea was to prepare a multi-element isotope standard spike solution containing all the elements of interest instead of spiking each sample with each spike isotope standard solution separately, to simplify the procedure.

Wherever necessary, intermediate isotope standard solutions were prepared from the stock isotope standards, using appropriate dilutions with high-purity deionised water and nitric acid. A multi-element isotope standard spike solution containing ^{61}Ni , ^{65}Cu , ^{67}Zn , ^{97}Mo , ^{111}Cd and ^{206}Pb in optimal concentrations, was prepared from the corresponding source spike solutions for the four samples.

Due to the high concentrations of barium and strontium in SARM 2 and SY-4, strontium and zinc in SARM 3 and the strontium in SARM 4 it was not practically possible or economical to add the isotope spike to the sample aliquots before

digestion. Individual ^{135}Ba and ^{86}Sr spikes were performed after digestion to accurately weighed aliquots of the digested sub-samples of SARM 2 and SY-4 due to the high concentrations of these elements present in the respective samples. For SARM 3 the ^{86}Sr and ^{67}Zn spikes were added after digestion and for SARM 4 only the ^{86}Sr spike was added after digestion.

It was still expected that complete equilibration between the naturally occurring isotopes and the enriched spike isotopes would occur even if the spike is added after digestion, because the chemical form of the elements in the digested solution was nitrates due to the dominance of nitric acid in the digestion reagents and the isotope spikes were also added to the digested samples in the chemical form of nitrates.

4.2.3.3 Laboratory ware

- PTFE (Teflon®) and polypropylene vials, 3 cm³ volume capacity.
- Stainless steel weighing boat.
- Microwave digestion PTFE vessels with caps.
- Polypropylene graduated test tubes with caps.
- Polypropylene micropipette tips for Eppendorf Reference and Research Pro micropipettes.
- Weighing glass bottles with caps.
- Set of calibrated mass pieces, traceable to the SI unit, the kilogram.

4.3 Sample preparation procedures

4.3.1 Moisture content

The procedure used for the determination of the moisture content in the test samples was as follows:

- Approximately 1 to 3 g of the solid test samples were weighed on an analytical balance with 5 significant digits in suitable glass weighing bottles. The samples were capped immediately after the transfer took place.
- The weighing bottles (with caps removed) were placed in a drying oven at 105 °C for a minimum of 24 hours.

- After drying, the weighing bottles with samples were closed and the bottles were transferred directly into a desiccator. The vessels were left to cool down to room temperature (22 ± 1 °C) and were then weighed several times.
- The moisture content (as % moisture and dry mass correction factor) was calculated from the difference in the sample weights found. The uncertainty includes contributions from the weighing process and the uncertainty of the mean of the weighings. The standard uncertainty associated with the weighing of materials in various mass ranges, was derived from experimental data, taking into account the repeatability and absolute bias in the weight measurements (see **Section 5.3.3**).

4.3.2 Preparation of isotope dilution samples prior to microwave digestion

The test samples for this study were obtained from one bottle of each of the reference materials. The bottles were homogenised prior to taking the samples by shaking the sample bottles. During the development of the microwave digestion method, the experiments started with a sample aliquot of 0.5 g. However, a clear completely dissolved sample solution could not be obtained with any of the tested methodologies and the sample aliquot was then reduced to 0.2 g.

During the original certification study the homogeneity of the SARM 1 to 6 materials were tested with three different methods: the chemical analysis of a synthetic mix, X-ray fluorescence analysis and gamma-scintillation counting[13]. A new check on the between bottle homogeneity of the materials was not performed during this study, but is a proposal for further work towards the complete re-certification of the remaining units of SARM 1 to 6.

The set of samples for each isotope dilution experiment were prepared gravimetrically, using an analytical balance with 5 significant digits, prior to microwave digestion. All samples, primary assay standards, reagents and blends were subjected to the same treatment conditions throughout the analysis to minimise the uncertainty.

All microwave vessels utilised in the preparation of the test samples were cleaned with a mixture of acids and a specific microwave program prior to use. When not in use, the vessels were stored filled with high purity water. The vessels were thoroughly rinsed with high purity water prior to use. The procedure for preparation of samples prior to microwave digestion was as follows:

The accuracy of the analytical balance was confirmed with a set of calibrated mass pieces with stated traceability.

- Microwave digestion vessel no.1: Rock sample.

Approximately 0.2 g of sample was accurately weighed to 5 significant digits (± 0.01 mg) into a tared sample boat. The reading was recorded. The sample was then transferred to the first microwave vessel and the empty boat was re-weighed. The reading was recorded again and the actual sample weight transferred was calculated.

- Microwave digestion vessel no.2: Rock sample with multi-element isotope spike.

The procedure for microwave digestion vessel no. 1 was repeated for microwave vessel no.2 with the same solid sample. The weighing of the multi-element isotope spike standard was performed using clean Teflon® vials. The actual mass of the aliquots were calculated after re-weighing the empty vials.

- Microwave digestion vessel no.3: Primary assay standard.

An aliquot of the primary assay standard was accurately weighed in a Teflon® vial according to the experimental design. The content of the vial was transferred into microwave vessel no.3 and the empty vial was re-weighed.

- Microwave digestion vessel no.4: Primary assay standard with multi-element isotope spike.

The procedure for microwave vessel no. 2 was repeated for microwave vessel no.4. The aliquot of the multi-element isotope spike standard, as reflected in the experimental design, was added. The weighing of the isotope standard spike was performed using a clean Teflon® vial. The actual mass of the aliquot was calculated after re-weighing the empty vial.

- Microwave digestion vessel no.5: Reagent blank with multi-element isotope spike as for microwave vessel no. 4.
- Microwave digestion vessel no.6: Reagent blank.

Reserved for reagent blank only.

The reagents (4 ml nitric acid (HNO_3), 3 ml hydrochloric acid (HCl) and 1 ml hydrofluoric acid (HF)) were added to all the microwave digestion vessels using a micropipette and changing tips for every reagent. The volume of the solutions in each vessel was calculated and appropriate volumes of deionised water were added to each vessel to ensure that all vessels contained the same volume of liquid.

4.3.3 Microwave digestion procedure

The samples prepared in the microwave vessels as described above were covered with the microwave Teflon® caps and placed in safety housing shields. The vessels were then introduced to the rotor segment and tightened using a torque wrench. The rotor segment was inserted into the microwave cavity, and the temperature sensor, positioned into vessel no.1 (rock sample), was connected to the temperature control unit.

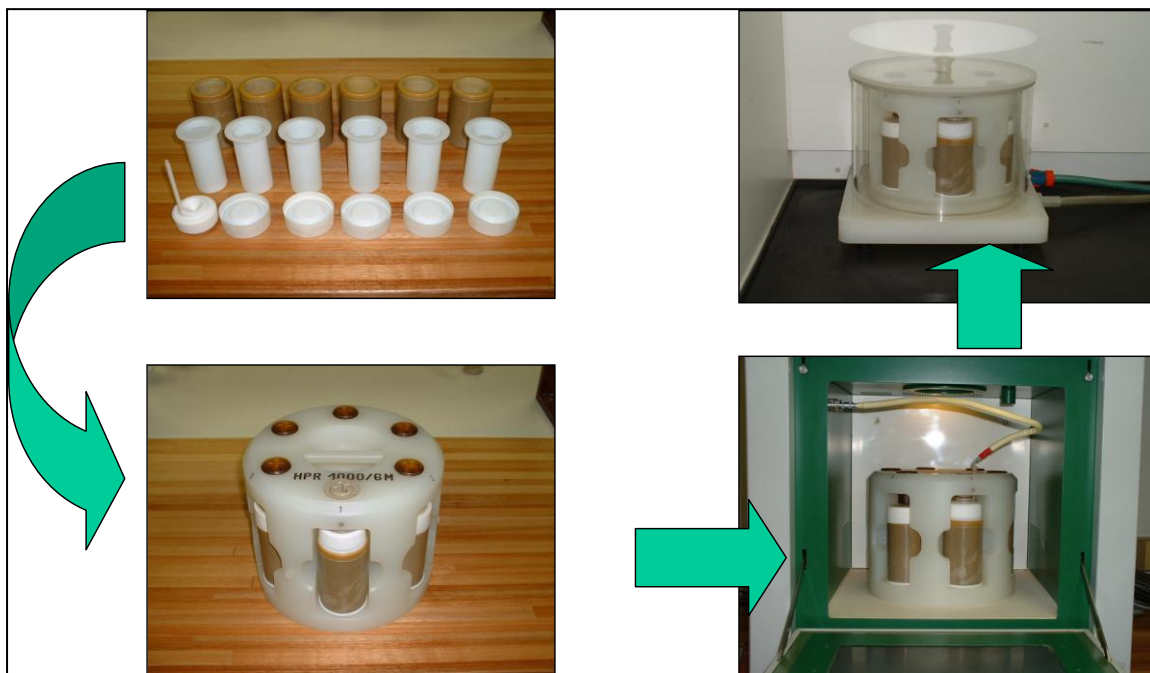


Figure 4.2: Milestone ETHOS 1600 microwave digestion system

The complete digestion of the samples was achieved using a two-stage microwave program. After the first microwave digestion cycle (see **Table 4.1**), the vessels were removed from the microwave system, cooled down in a water bath for approximately 45 minutes and carefully opened under a fume cupboard. Then 1 ml hydrofluoric acid (HF) and 15 ml 5% boric acid (H_3BO_3) were added to all samples. The sample vessels were closed again and put back into the microwave system for the second microwave program (see **Table 4.2**).

For the microwave digestion, high pressure vessels with a maximum working pressure of 100 bar, were used. The temperature during the digestion process was monitored and automatically controlled to follow the temperature profile of the microwave programs (see **Figure 4.3**) by means of the temperature probe inserted into vessel no.1.

After the first stage of the microwave digestion procedure, a residue due to the precipitation of metal fluorides and fluorosilicates was formed. In order to obtain a complete digestion the second stage of microwave treatment was performed with the additions of H_3BO_3 and HF. The additions of HF and H_3BO_3 resulted in the formation

of HBF_4 , which acted as a releasing agent, the boric acid reacted with the precipitate of metal fluorides and fluorosilicates to form borofluorosilicates, which dissolved in the sample digest to produce a clear sample solution after digestion. After completion, the vessels were cooled down, opened and the solutions quantitatively transferred into clean 50 ml polypropylene graduated tubes. The solutions were left for several hours to reach room temperature ($22 \pm 1 \text{ }^\circ\text{C}$) and brought to the mark as per the experimental design for the final dilution of the digested sample with deionised water. Appropriate dilutions were prepared according to the experimental designs created for each of the four reference materials. The concentrations of the different analytes in the final measurement solutions ranged from 0.3 to 3.0 $\text{ng}\cdot\text{ml}^{-1}$ depending on the concentrations of the analytes in the different solid samples. On all occasions, nitric acid was added to the diluted samples to correspond to 2% of the total solution volume.

Table 4.1: Microwave program 1

Step	Time (minutes)	Temperature ($^\circ\text{C}$)	Microwave power (W)
1	10	140	Up to 1000
2	15	185	Up to 1000
3	10	185	Up to 1000
4	10	Venting	0

Table 4.2: Microwave program 2

Step	Time (minutes)	Temperature ($^\circ\text{C}$)	Microwave power (W)
1	10	175	Up to 1000
2	8	175	Up to 1000
3	10	Venting	0

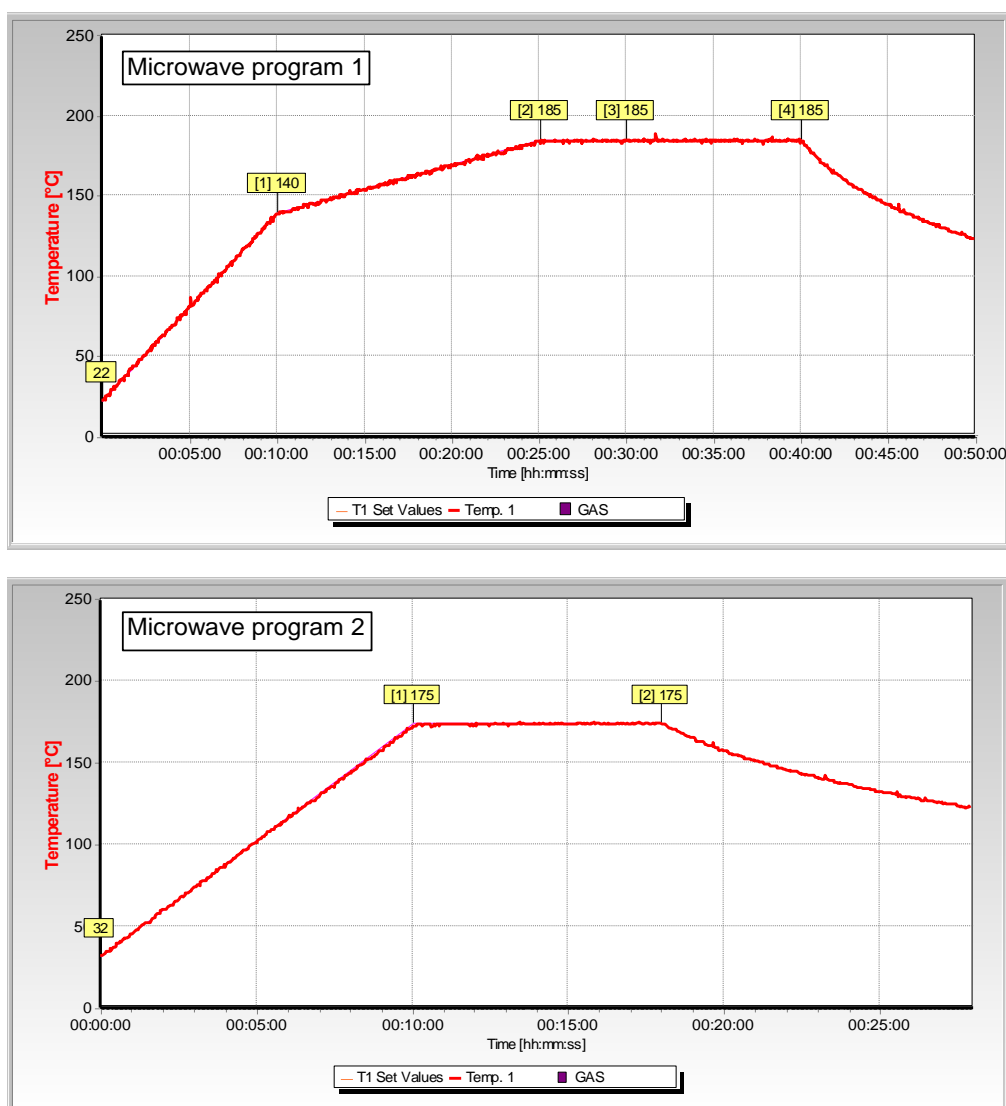


Figure 4.3: Experimental microwave digestion temperature profiles

4.4 ID-ICP-MS analysis and isotope ratio measurements

After appropriate dilutions relevant to every element, the sample digests were subjected to analysis using a magnetic sector (HR) ICP-MS and an autosampler system (AXS-100) with a 24 position sample rack. A self-aspirating nebuliser of 100 or 50 $\mu\text{l}\cdot\text{min}^{-1}$, suitable for nebulisation of solutions containing HF, an HF-resistant spray chamber and appropriate nebuliser tube for solutions containing HF was used to prevent corrosion of the sample introduction system due to the HF content in the sample solutions. A desolvating sample introduction system (Aridus) was used to minimise polyatomic interferences due to the introduction of oxides from the water in the samples into the plasma.



Figure 4.4: ThermoFinnigan MAT Element 2 inductively coupled plasma magnetic sector field-mass spectrometer

4.4.1 HR-ICP-MS parameters

The nature of the IDMS method employed during this study is an approximate matching method similar to the method used by Catterick, *et al.*[30] based on the philosophy of the iterative ‘exact matching’ method proposed by Henrion[31]. In this study, the ‘match’ between the isotope ratios for the analytes in the spiked sample blends and the spiked primary assay standard blends was aimed to be within 10% of the ratio of one for optimum counting statistics and mass spectrometric precision.

The mass bias correction factor (K) for each element, was determined by repeated measurements of a natural isotopic abundance standard for all the elements, except for Pb, where the NIST SRM 982-1 certified isotopic standard was used. In the analysis sequence the duplicate analysis of each sample was bracketed by the measurement of the mass bias standard, which in turn was bracketed by the measurement of the wash solution (see **Appendix F**). The measured isotopic ratios of the mass bias standard were individually compared either to the corresponding certified isotopic ratio values of the standard or to the theoretical isotopic ratio values derived from the IUPAC isotopic abundance data (when an isotopic standard with certified isotopic ratios was not available). During this experiment the mass bias

correction factor that was applied to each isotope ratio measurement was calculated from the average of the ratios measured for the mass bias standard throughout the measurement sequence.

The classical experiment for a double isotope dilution analysis of a single sample requires the preparation and analysis of six solutions. The set of six sample solutions is prepared under identical conditions and includes: the sample to be analysed and the sample with added isotope spikes; the primary assay standard and the primary assay standard with added isotope spikes; the reagent blank and the reagent blank with added isotope spikes.

During this experiment only the sample and sample with stable isotope spike standard blends, as well as one primary assay standard and stable isotope spike standard for each of SARM 2 and SY-4 were digested. All the other solutions required for the double isotope dilution analysis such as the primary assay standard and two additional blends of primary assay standard and stable isotope spike standard for both SARM 2 and SY-4, as well as the blend of the reagent blank and the stable isotope spike standard, were prepared off-line without going through the digestion process. No significant difference was found for the different sample blends between the off-line and digested standard blends.

The aliquots of multi-element stable isotope spike standard, as well as the spikes for Ba and Sr that were added to the samples for the preparation of the sample and stable isotope standard spike blends were varied to within approximately -10% to +10% of the exact matching amount.

Optimisation of the plasma conditions, torch position as well as the peak shapes and mass calibrations, were performed prior to every analysis. The ratios of the following pairs of isotopes for barium, copper, nickel, lead, zinc, cadmium, molybdenum and strontium were measured using separate methods: $^{137}\text{Ba}/^{135}\text{Ba}$, as well as $^{138}\text{Ba}/^{135}\text{Ba}$; $^{63}\text{Cu}/^{65}\text{Cu}$; $^{60}\text{Ni}/^{61}\text{Ni}$; $^{208}\text{Pb}/^{206}\text{Pb}$; $^{66}\text{Zn}/^{67}\text{Zn}$; $^{112}\text{Cd}/^{111}\text{Cd}$, as well as $^{114}\text{Cd}/^{111}\text{Cd}$; $^{95}\text{Mo}/^{97}\text{Mo}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ (i.e. reference isotope/spike isotope). For some elements the results from two sets of ratios were compared to provide additional information, either to improve the precision of the results, or to overcome the effect of isobaric interference on the reference isotope.

The parameters common to all measurement methods are summarised in **Table 4.3**.

Table 4.3: ICP magnetic sector field MS measurement parameters

	Low resolution	Medium resolution
Coolant gas flow	13.5 l.min ⁻¹	13.5 l.min ⁻¹
Auxiliary gas flow	0.75 l.min ⁻¹	0.75 l.min ⁻¹
Carrier gas flow	1.1 l.min ⁻¹	1.1 l.min ⁻¹
RF forward power	1200 W	1200 W
Runs	1	1
Passes	200	200
Mass window	10 %	120 %
Number of samples per peak	1	24
Sample time	0.01-0.1 s	0.01-0.1 s
Scan type	E-Scan	E-Scan
Detection mode	Counting	Counting
Detector dead time correction	25 ns	25 ns
Measurands	Ba,Sr,Pb,Cd,Mo	Cu,Ni,Zn
Peak integration	80%	80%
Acquisition time, min	3	3

At high count rates, two effects cause counting modes of the detector systems to record fewer counts than actually occur. The most important of these two effects in the Finnigan MAT ELEMENT detection system is dead time. After an ion generates an electron pulse at the conversion dynode, and subsequently an electron pulse in a multiplier, there is a finite time during which the system is incapable of recording another event. The system is effectively “dead” (i.e. unable to process another event) in this interval. There are several reasons for the dead time:

1. Finite width of the output pulse of the multiplier
2. Amplifier discriminator requires an interval to process the data
3. The discriminator emits a pulse of finite width
4. The pulse must be recorded by the data system

A correction should be applied to all ion count rates (counting detection mode) to compensate for this dead time. The detector dead time correction can become significant when accurate isotope ratios are required or for quantitative analysis for samples with high count rates.

The dead time correction of the Counting Mode uses the following equation:

$$I_{corr} = \frac{I_{meas}}{1 - I_{meas} \cdot \tau_{dead}} \dots\dots\dots (4.1)$$

where

I_{corr} = corrected intensity (cps)

I_{meas} = measured intensity (cps)

τ_{dead} = dead time value (s)

For the determination of the dead time correction for the Finnigan MAT ELEMENT 2 ICP-MS spectrometer that was used during this study, four standards were prepared for each element of interest over the expected concentration of the elements in the final solution. The intensities of the reference and spike isotopes of the individual elements were measured with the ICP-MS spectrometer and then a spreadsheet method was used to determine the deadtime correction for each element. In the spreadsheet the calculated ratios of the measured isotope intensities were plotted on a best curve fit. The dead time correction factor was then calculated iteratively on the spreadsheet until the slope of the fitted curve became 0, i.e., the curve became a horizontal line. This horizontal line indicated comparable precision of the determined isotope ratios over the expected concentration ranges of the elements in the final solutions.

The mass window is the scanning range of the instrument around a peak. It is defined with respect to the centre of the peak and its value is entered as a percentage. A mass window of 100% means that, starting from the centre of the peak, half of the peak width on either side of the centre, i.e., one peak width in total is scanned (100% of the peak width). The mass window is also sometimes referred to as the scan window or the mass range. The peak width depends on the mass of the isotope measured and the selected resolution (peak width = m/R), e.g. for ^{63}Cu at mass 62.92 and resolution (R) 3000, the peak width is 0.02097, i.e., this would define a mass window of 100%. Furthermore, the mass range scanned for ^{63}Cu with mass 62.92, peak width 0.02097 and mass window 100%, will be 62.9095 to 62.9304.

The determinations of Sr, Ba, Pb, Cd and Mo were carried out in low-resolution mode. Interference corrections were performed on ^{86}Sr for the isobaric interference of ^{86}Kr in the argon carrier gas. This involved measuring the ^{83}Kr isotope together with ^{86}Kr , ^{86}Sr and ^{88}Sr . The interference correction was calculated with the following equation:

$$R_{corr} = \frac{I_{^{88}\text{Sr}}}{I_{^{86}\text{Sr}}^{corr}} = \frac{I_{^{88}\text{Sr}}}{I_{^{86}\text{Sr}} - I_{^{83}\text{Kr}} \times \frac{A_{^{86}\text{Kr}}}{A_{^{83}\text{Kr}}}} \dots\dots\dots (4.2)$$

where

$I_{^{88}\text{Sr}}$ = the measured intensity for the ^{88}Sr isotope

$I_{^{86}\text{Sr}}$ = the measured intensity for the ^{86}Sr isotope

$I_{^{83}\text{Kr}}$ = the measured intensity for the ^{83}Kr isotope

$A_{^{86}\text{Kr}}$ = the IUPAC abundance of the ^{86}Kr isotope

$A_{^{83}\text{Kr}}$ = the IUPAC abundance of the ^{83}Kr isotope

The isobaric interference correction on the measured intensity for ^{86}Sr was made for several aliquots of each sample, as well as sample and spike isotope standard blends over the span of the measurement sequence. The corrected ratios for the samples compared well with the primary assay standards and the variations in the measured intensities of the different isotopes were taken into account with the interference correction calculation for each of the aliquots. The contributions to uncertainty from the abundances of the ^{86}Kr and ^{83}Kr isotopes are negligible compared to the precision of the measured intensities for the different isotopes. Therefore, no additional correction factor or uncertainty contribution for the isobaric interference correction was required.

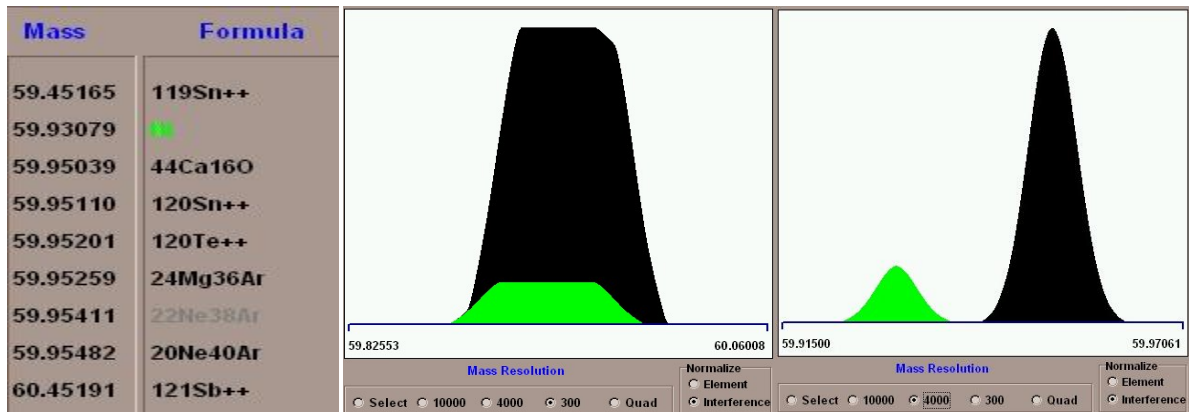
The measurements for $^{63}\text{Cu}/^{65}\text{Cu}$, $^{60}\text{Ni}/^{61}\text{Ni}$ and $^{66}\text{Zn}/^{67}\text{Zn}$ isotope ratios were performed in medium resolution mode in order to eliminate possible spectral interferences as shown in **Table 4.2**.

Table 4.2: Most probable spectral interferences on the measurements of Ni, Cu and Zn isotopes of interest in the samples

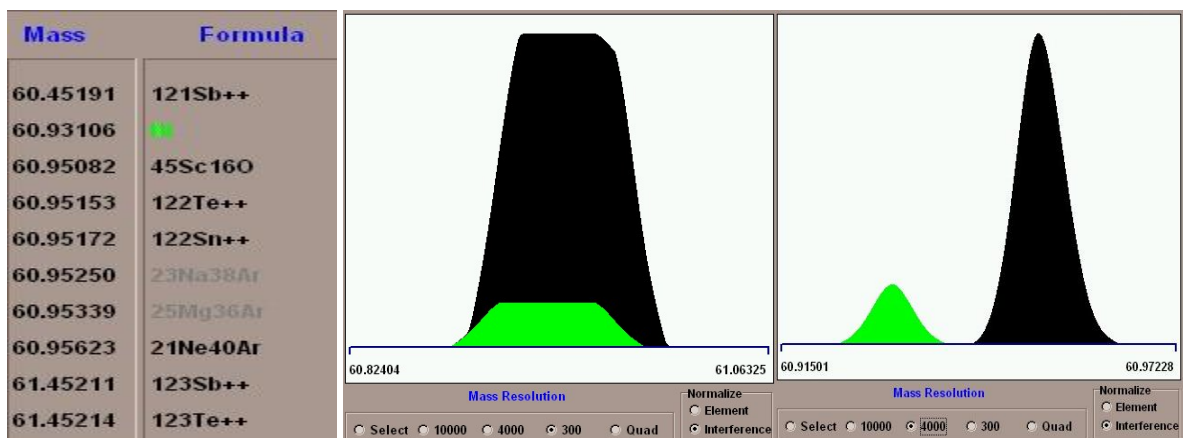
Isotope	Isotope mass	Possible spectral interference	Interference mass
^{60}Ni	59.930788	$^{44}\text{Ca}^{16}\text{O}$	59.95039
		$^{24}\text{Mg}^{36}\text{Ar}$	59.95259
^{61}Ni	60.931058	$^{23}\text{Na}^{38}\text{Ar}$	60.95250
		$^{25}\text{Mg}^{36}\text{Ar}$	60.95339
^{62}Ni	61.92835	$^{24}\text{Mg}^{38}\text{Ar}$	61.94778
		$^{24}\text{Mg}^{38}\text{Ar}$	61.95014
^{63}Cu	62.939598	$^{25}\text{Mg}^{38}\text{Ar}$	62.94857
		$^{27}\text{Al}^{36}\text{Ar}$	62.94909
		$^{23}\text{Na}^{40}\text{Ar}$	62.95215
^{65}Cu	64.927793	$^{29}\text{Si}^{36}\text{Ar}$	64.94405
		$^{27}\text{Al}^{38}\text{Ar}$	64.94427
		$^{25}\text{Mg}^{40}\text{Ar}$	64.94822
^{66}Zn	65.926034	$^{28}\text{Si}^{38}\text{Ar}$	65.93966
		$^{30}\text{Si}^{36}\text{Ar}$	65.94132
		$^{26}\text{Mg}^{40}\text{Ar}$	65.94498
^{67}Zn	66.927129	$^{29}\text{Si}^{38}\text{Ar}$	66.93923
		$^{27}\text{Al}^{40}\text{Ar}$	66.94392
		$^{134}\text{Ba}^{++}$	66.95225
^{68}Zn	67.92485	$^{28}\text{Si}^{40}\text{Ar}$	67.93931
		$^{136}\text{Ba}^{++}$	67.95228

In **Figure 4.5** the effect of the use of medium resolution for the measurement of Ni is illustrated. For the isotopes of ^{60}Ni , ^{61}Ni and ^{62}Ni in low resolution ($R = 300$) the signals are swamped by interferences from polyatomic ions such as $^{44}\text{Ca}^{16}\text{O}$ and $^{24}\text{Mg}^{36}\text{Ar}$, $^{23}\text{Na}^{38}\text{Ar}$ and $^{25}\text{Mg}^{36}\text{Ar}$, $^{24}\text{Mg}^{38}\text{Ar}$ and $^{24}\text{Mg}^{38}\text{Ar}$, respectively. In medium resolution ($R = 4000$), the nickel peaks are resolved from the peaks of the polyatomic ions. The same effect of medium mass resolution is illustrated for Cu and Ni in **Figures 4.6** and **4.7**. The major interference from Ba^{++} on Zn was eliminated through the use of medium resolution. The other possible interferences on Zn even in medium resolution mode were not likely in these samples because of their low abundance.

Ni-60



Ni-61



Ni-62

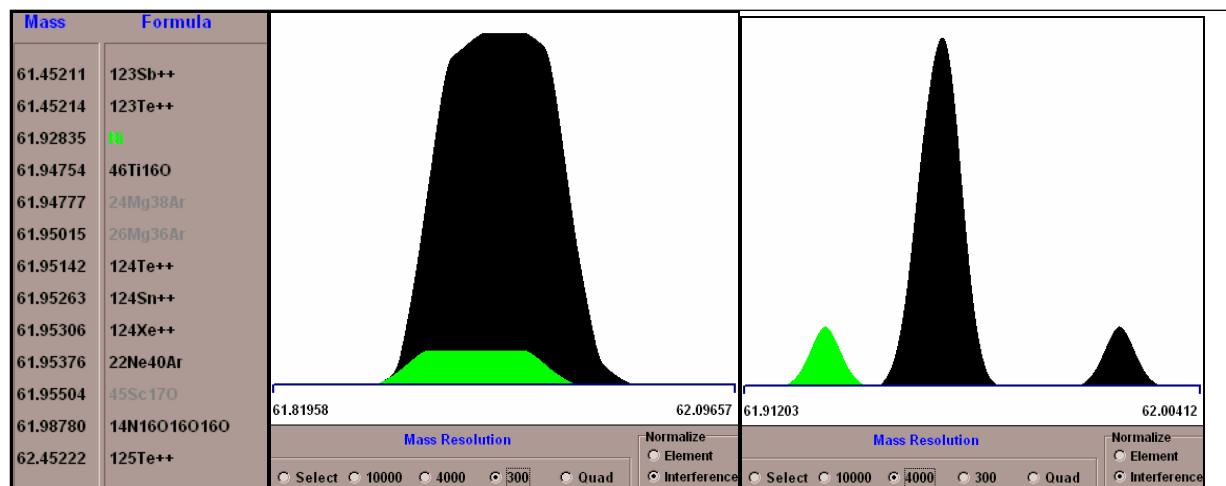
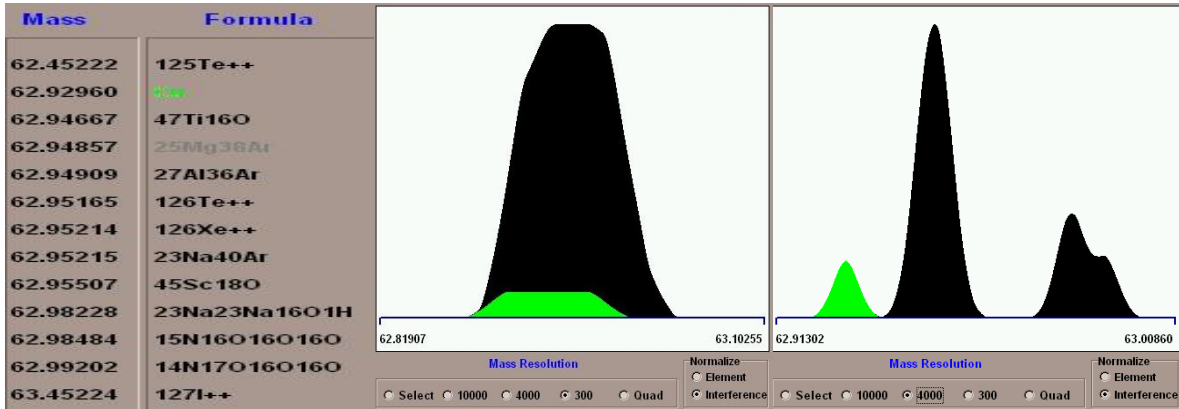


Figure 4.5: Schematic presentation of the effect of medium mass resolution for Ni (Green peak = Ni; Black peaks are the interferences; the peaks represent the same masses and abundances of the analyte and the individual interferences)

Cu-63



Cu-65

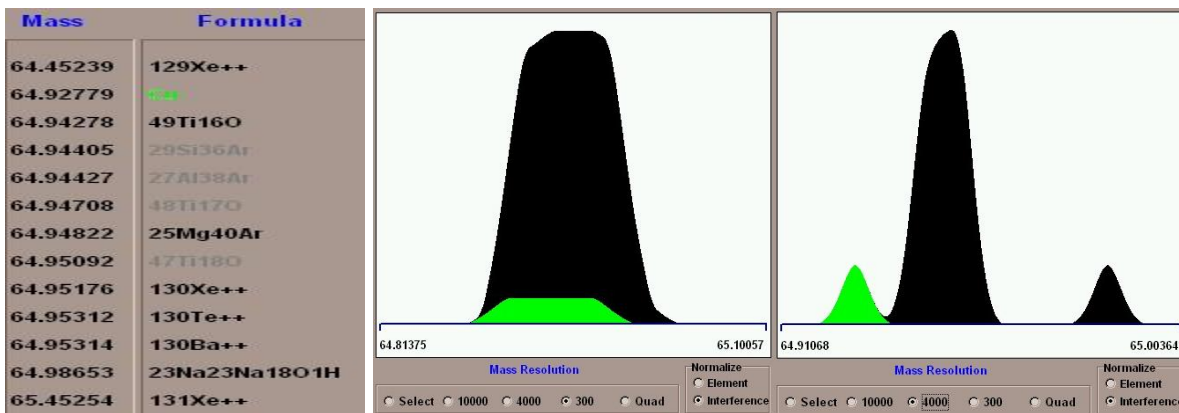
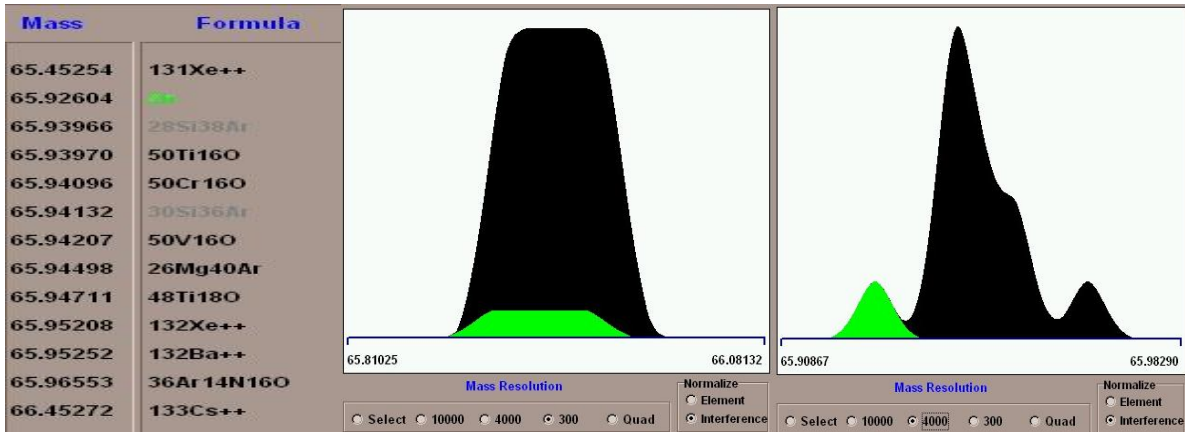
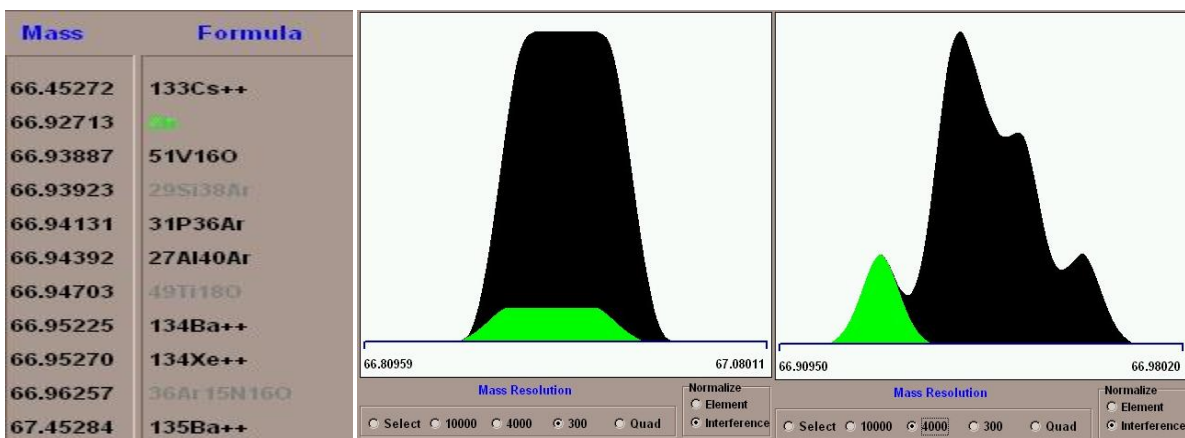


Figure 4.6: Schematic presentation of the effect of medium mass resolution for Cu (Green peak = Cu; Black peaks are the interferences; the peaks represent the same amounts and abundances of the analyte and the individual interferences)

Zn-66



Zn-67



Zn-68

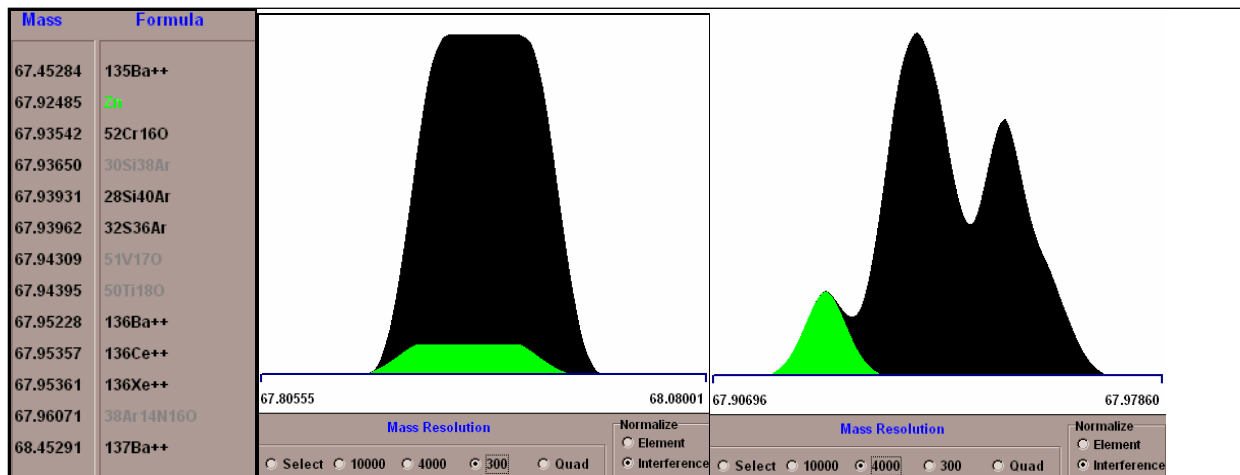


Figure 4.7: Schematic presentation of the effect of medium mass resolution for Zn (Green peak = Zn; Black peaks are the interferences; the peaks represent the same amounts and abundances of the analyte and the individual interferences)

For low resolution each sample solution was split into two independent sample aliquots for analysis and every aliquot was measured in duplicate. In the analysis

sequence every sample was bracketed by a wash solution of 2% nitric acid and a mass bias standard of comparable concentration to the sample (see **Appendix F**). The measurements of this standard throughout the sequence were performed in order to calculate the mass bias correction factor for every analyte. The mass bias correction factor was used to monitor the isotopic ratios of the analyte during the analysis sequence to allow for off-line correction of any possible drift in the mass calibration. The samples with natural isotopic abundances were always analysed before the spiked solutions. Each analyte was determined separately on individual samples.

Every sample is measured with autosampling parameters: Wash time: 140 s (2% nitric acid prior to uptake of sample); Uptake time: 110 s.

4.5 Experimental designs for SARM 2, SARM 3, SARM 4 and SY-4

As part of the developed methodology, experimental designs were created for the determination of Ba, Sr, Zn, Cu, Ni, Mo, Cd and Pb in SARM 2, SARM 3, SARM 4 and SY-4. For optimal precision in the isotope ratio measurements, the necessary spikes of the enriched isotopes were calculated for the ratio of the measured pair of isotopes in the final blend solutions (prior to analysis) to be close to unity. Samples were diluted according to the diagrams presented in **Appendix G** so that the solutions subjected for analysis contained element concentrations suitable to perform measurements in medium (Ni, Cu, Zn) and low (Ba, Sr, Mo, Cd, Pb) resolution.

Chapter 5

Uncertainty of measurement

5.1 Introduction

During 1977 to 1981 the need for an internationally accepted consensus on the procedure for expressing measurement uncertainty was recognised by several international organisations. A document was developed based on the recommendation of the BIPM (International Bureau of Weights and Measures) working group on the 'Statement of Uncertainties'. The document was developed by working group 3 of ISO/TAG4, the ISO Technical Advisory Group on Metrology, with the participation of 6 international organisations.

The Guide to the Expression of Uncertainty of Measurement (ISO GUM)[4] was published in 1993 for the first time, and was then reprinted in 1995. The document is widely accepted internationally and many simplified versions have been developed by standardisation and accreditation bodies around the world. It is the only reference for the estimation of uncertainties being used in the standard ISO/IEC 17025[6], for the quality assessment of the competence of calibration and testing laboratories.

The purpose of the ISO GUM is to establish general rules and procedures for the evaluation and expression of uncertainty of measurement, primarily to provide a basis for international comparison of measurement results. The applicability of the Guide ranges over a broad spectrum of measurements at various levels of accuracy. It is intended for use within standardisation, the accreditation of calibration and testing laboratories, metrology and scientific research.

Uncertainty is defined in the International Vocabulary of Terms in Metrology (ISO VIM)[2] as "a parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand" and is typically expressed as

$$Y = y \pm U \quad \text{e.g. } m = 1000.00250 \pm 0.00050 \text{ g}$$

The result of the measurement is the best estimate of the value of the measurand (analyte), and all the components of uncertainty that contribute to the dispersion of the values. A measurement result is not considered valid, and is not acceptable, without an uncertainty statement according to the definition in the ISO VIM.

The definition for uncertainty of measurement is an operational one, which is consistent with other concepts that factor on unknowable quantities, such as 'true value' and 'error'. A measure of the possible error in the best estimate of the measurand is provided by the result of the measurement with its stated uncertainty. It could also be interpreted that the measurement result with its stated uncertainty, characterises the range of values within which the 'true value' of the measurand is expected to lie.

Uncertainty always exists in measurement. At best it can be reduced, but it can never be eliminated. Uncertainty of measurement reflects the lack of exact knowledge of the 'true value' of the measurand, which is limited by the present state of science and technology. It is an indicator of the accuracy or quality of a measurement, and reflects the technical competence of the laboratory which performed the measurement. The proper evaluation of measurement uncertainty will help to identify major sources of error, and provide direction for improvement in a laboratory.

The general procedure for the evaluation of the uncertainty of a measurement method consists of five steps.

Step 1: The specification of the measurand and the modelling of the measurement system.

Step 2: Evaluation of the standard uncertainties of all the uncertainty contributions.

Step 3: Determining the combined standard uncertainty.

Step 4: Determining the expanded uncertainty.

Step 5: Reporting the measurement result with its uncertainty.

5.2 Specification and modeling

Isotope dilution mass spectrometry (IDMS) has been considered to be a definitive method for over 50 years, offering the potential for small uncertainties. The basis for trace metal analysis using isotope dilution is the addition of an isotopically enriched material (known as the 'spike'), which acts as an internal standard. Provided the enriched isotope is present in an equilibrated and equivalent state to the natural isotope, it can perform the role of the ideal internal standard. Thus the added isotope should enable exact compensation to be made for all stages of the analysis, from sample digestion through to the end determination.

Once the spike has been added and fully equilibrated within the sample, sources of error due to sample loss, matrix suppression and dilutions, are rectified by the presence of the spike. However, care must be taken in the selection of the isotopes

used to avoid interferences from polyatomic or isobaric spectral overlaps. Provided these interferences are negligible, the accuracy of the isotope dilution determinations is dependent on the accuracy of the isotope ratio measurements.

In the determination of the isotope ratios by ICP-MS a number of factors must be considered, including: mass bias, detector linearity and detector dead time. In addition, the uncertainties associated with the characterisation of the enriched spike material will also contribute to the overall uncertainty of the final results. The double isotope dilution technique employed during this study was an approximate matching method similar to the method used by Catterick, *et al.*[30] and based on the philosophy of the 'exact matching' method proposed by Henrion[31]. The aim was to obtain isotope ratios for the analytes in the blend solution as close to one as possible for optimum counting statistics and mass spectrometric precision. Under these conditions many of the uncertainties mentioned above are significantly reduced or negated.

The double isotope dilution analysis of a test sample, requires the accurate determination of the ratios between the spike and reference isotopes, after measurement of the isotope intensities, for any particular element in two blend solutions: the spiked sample and the spiked primary assay standard. The accurately known concentration of the primary assay standard was utilised to obtain an accurate estimate for the concentration of the spike isotope standard. The calculation of the mass fraction of the analyte in the test sample can therefore be obtained from the following equation (derived from **equation 3.9** in **Chapter 3** with additional factors to take into consideration mass bias correction, blank correction, dry mass correction, etc.):

$$C_x = C_z \times \frac{M_z \cdot M_s (K_z \cdot R_z - K_{b'} \cdot R_{b'}) \cdot (K_b \cdot R_b - K_s \cdot R_s)}{M_{s'} \cdot M_x \cdot (K_{b'} \cdot R_{b'} - K_s \cdot R_s) \cdot (K_x \cdot R_x - K_b \cdot R_b)} \cdot \frac{\sum (K_{ix} \cdot R_{ix}) \cdot B \cdot G}{\sum (K_{iz} \cdot R_{iz}) \cdot W} \dots\dots\dots (5.1)$$

where,

x - index for the sample

s - index for the spike

z - index for the primary assay standard

b - index for the blend of fractions of sample and spike

b' - index for the blend of fractions of the primary assay standard and spike

C_x - Mass fraction of the analyte in the sample

C_z - Mass fraction of the primary assay standard

M_x - Mass of the sample in blend b

M_s - Mass of the spike in sample blend b

M_z - Mass of the primary assay standard in blend b'

M_s' - Mass of the spike in standard blend b'

R_b - Determined isotope amount ratio of blend b

$R_{b'}$ - Determined isotope amount ratio in blend b'

R_x - Determined isotope amount ratio in the sample

R_s - Determined isotope amount ratio in the spike

R_z - Determined isotope amount ratio in the primary assay standard

K_b - Mass bias correction factor of R_b

$K_{b'}$ - Mass bias correction factor of $R_{b'}$

K_x - Mass bias correction factor of R_x

K_s - Mass bias correction factor for R_s

K_z - Mass bias correction factor of R_z

G - Digestion correction factor

B - Blank correction factor

w - Dry mass correction factor

$\sum K_{ix} \cdot R_{ix}$ - Sum of all isotope ratios of the analyte in the sample

$\sum K_{iz} \cdot R_{iz}$ - Sum of all isotope ratios of the analyte in the primary assay standard

5.3 Calculation of the standard uncertainties of the input quantities

The standard uncertainties associated with the individual uncertainty contributors to the ID-ICP-MS method, were calculated using the ISO GUM and EURACHEM/CITAC guidelines[32], and included contributions from all input parameters in the measurement equation (**equation 5.1**), as well as variation between the independent determinations.

5.3.1 Standard uncertainty of the determined isotope ratios, $u_{Ri(s)}$

Each sample solution was analysed in duplicate. The standard uncertainty associated with a particular isotope ratio (i) for a solution, $u_{Ri(s)}$, was defined by the standard deviation, $s_{Ri(s)}$, i.e. $u_{Ri(s)} = s_{Ri(s)}$.

In low resolution two aliquots (aliquots ‘a’ and ‘b’) of the samples and standard solutions were analysed in duplicate. Two approaches were possible for the calculation of the standard uncertainty, $u_{Ri(s)}$, of the determined ratios. The first approach was to calculate the mean, $R_{i(s)}$ and standard deviation, $s_{Ri(s)}$, of the four results, and then use the standard deviation as the standard uncertainty as explained above, $u_{Ri(s)} = s_{Ri(s)}$. The second approach was to calculate the mean, $R_{i(s)}$, and standard deviation, $s_{Ri(s)}$, of each aliquot and then calculate the mean of means and the standard deviation of the mean for the sample. The standard uncertainty is then calculated using the following equation.

$$u_{Ri(s)} = \sqrt{\left(\frac{s_{Ri(a)}^2 + s_{Ri(b)}^2}{2}\right) + u_{mean}^2} \dots\dots\dots(5.2)$$

where

$u_{Ri(s)}$ = the standard uncertainty of the determined ratio

$s_{Ri(a)}$ = the standard deviation of the mean of aliquot a

$s_{Ri(b)}$ = the standard deviation of the mean of aliquot b

u_{mean} = the standard deviation of the mean of the two aliquots

In **Table 5.1** the difference between the two approaches are summarised for the elements measured in low resolution in SARM 2.

Table 5.1: Comparison between the two approaches for calculating the uncertainty of the determined ratios

SARM 2	Standards				Samples			
	Approach 1		Approach 2		Approach 1		Approach 2	
	Mean	Standard uncertainty	Mean	Standard uncertainty	Mean	Standard uncertainty	Mean	Standard uncertainty
Ba	1.719	0.002772	1.719	0.002780	1.720	0.001462	1.720	0.001704
Sr	8.495	0.019718	8.495	0.024079	8.511	0.086679	8.511	0.088861
Pb	2.110	0.002398	2.110	0.000866	2.086	0.004489	2.086	0.003478
Mo	1.641	0.001797	1.641	0.001498	1.652	0.009497	1.652	0.008208
Cd	1.859	0.004209	1.859	0.004520	9.087	0.575177	9.087	0.520904

In general the standard uncertainties for the determined ratios, $u_{Ri(s)}$, calculated with the two different approaches were comparable. The second approach was selected as the approach to be used in this study, since it was most consistent with the calculation of the standard uncertainties for the other ratios, and with the requirements of the ISO GUM[4].

For all the elements in **Table 5.1** the ratios of the standards and samples are close to each other as it is expected to be for an ID-ICP-MS experiment, but Cd is the one exception. For the Cd standards the determined ratios are close to the ratio calculated from the published IUPAC abundances, but the ratios for the samples are 5 times higher. There are several possible reasons for this discrepancy in the expected isotope ratios determined for the SARM 2 samples.

When the intensity data for the Cd isotopes were studied it was found that the signal of the ^{112}Sn interference was very large compared to the ^{112}Cd signal and even more so when compared to the ^{111}Cd signal. From the intensity data for the different isotopes, it was finally concluded that due to the very low ^{111}Cd signal and the very large ^{112}Sn signal, proper interference corrections could not be calculated.

The possibility of polyatomic interference from $^{95}\text{Mo}^{16}\text{O}$ was disregarded, because typically, if this interference was present in the sample, the calculated ratios for $^{112}\text{Cd}/^{111}\text{Cd}$, as well as $^{114}\text{Cd}/^{111}\text{Cd}$ would have been lower than the ratios for the standards as well as the ratio calculated from the IUPAC abundances, because the ^{111}Cd signal would have been higher due to the interference. The multi-element standard that was also used during the study (Certified ICP-MS Calibration Standard M, Lot no. 510217, High Purity Standards, USA) had equal concentrations of Cd and Mo and also did not show any $^{95}\text{Mo}^{16}\text{O}$ interference.

This also confirms the efficiency of the ARIDUS solvent desolvating, which was used as part of the sample introduction, to reduce the amount of water introduced to the plasma and therefore limit the formation of polyatomic oxide interferences.

5.3.2 Standard uncertainty of the mass bias correction factor, $u_{K_{mean}}$

Due to differential ion transmission efficiency, the isotope ratio calculated from the intensities measured for the two isotopes of interest for each element could differ from the true isotope ratio. This difference between the true isotope ratio and determined isotope ratio of the isotope pair of interest is intrinsic to each spectrometer and is termed the mass bias.

Instrument drift is a term used to describe changes in the determined isotope ratio during the measurement sequence due to possible changes in the instrument temperature (electronics or plasma components) and/or other effects that could result in a change in the peak shape of the measured isotope signals, mass calibration effects or a change in the instrument sensitivity.

A mass bias/drift standard was used to correct for both the intrinsic mass bias and instrument drift during this study. For the double ID-ICP-MS experiment the instrument drift is expected to be the dominant contributor to possible changes in the determined isotope ratio. In the single IDMS experiment the absolute isotope ratio is important and therefore the intrinsic mass bias of the mass spectrometer must be accurately known.

During the measurement sequence the determined isotope ratios of the analyte may change due to a drift in the mass positions of the measured isotopes over time. A mass bias/drift standard, with an adequate concentration to provide sufficiently high isotope signals, is repeatedly measured throughout the measurement sequence to monitor the change in the determined isotope ratios. Any observed deviations can be corrected using the data from the mass bias standard measurements. Mass bias correction factors for each analyte were calculated using the determined isotope ratios of the mass bias standard, compared to a reference ratio calculated from the corresponding IUPAC isotope abundance data.

$$K_i = \frac{R_i}{R_{IUPAC}} \dots\dots\dots(5.3)$$

where

K_i = the mass bias correction factor from individual determined isotope ratios of the mass bias standard

R_i = determined isotope ratio in the mass bias standard

R_{IUPAC} = isotope ratio calculated from the isotopic abundances published by IUPAC[33]

In the case of Pb the mass bias correction factor was calculated compared to the isotopic abundances published for NIST SRM 982.

The mean mass bias factor K_{mean} is calculated using all individual mass bias factors.

The standard uncertainty, $u_{K_{mean}}$, of the mean mass bias correction factor, K_{mean} , for any particular isotope ratio, was then defined as the experimental standard deviation of the mean mass bias correction factor K_{mean} :

$$u_{K_{mean}} = \frac{s_{(K_i)}}{\sqrt{m}} \dots\dots\dots(5.4)$$

where

$u_{K_{mean}}$ = the standard uncertainty of the mean mass bias correction factor, K_{mean}

$s_{(K_i)}$ = the standard deviation calculated for the individual mass bias correction factors K_i

m = the total number of individual mass bias correction factors K_i

5.3.3 Standard uncertainty of the weighing process, u_m

The standard uncertainty associated with the weighing of materials in various mass ranges, was derived from experimental data, taking into account the repeatability and absolute bias in the weight measurements. The standard uncertainty data for the weighing process was calculated as follows:

$$u_m = \sqrt{u_{repeat}^2 + u_{bias}^2 + u_{masspieces}^2} \dots\dots\dots (5.5)$$

where

u_m = combined standard uncertainty of the weighing process

u_{repeat} = repeatability (standard deviation of the experimental data)

u_{bias} = bias (difference between mean and certified value of mass pieces used)

$u_{masspieces}$ = certified standard uncertainty of the mass pieces used

A summary of the final combined standard uncertainty values (as calculated for the individual mass ranges) with experimental data collected over a period of six months are given in **Table 5.2**, below.

Table 5.2: The standard uncertainties calculated for the balance

Weighing Range (g)		Standard Uncertainty (g)
From	To	
0.01000	2.99999	0.00002
3.00000	10.99999	0.00006
11.0000	100.99999	0.00019
101.00000	210.00000	0.00030

5.3.4 Standard uncertainty of the dry mass correction factor, u_w

The dry mass correction factors for the samples were calculated as follows:

$$Moisture = \frac{Drysample}{Wetsample} \dots\dots\dots(5.6)$$

The uncertainty of the dry mass correction factor took into account the uncertainty contributions associated with the balance measurements of the original, and dried samples:

$$u_w = \sqrt{u_{dry}^2 + u_{orig}^2} \dots\dots\dots(5.7)$$

where

u_w = Standard uncertainty of the dry mass correction factor

u_{dry} = Standard uncertainty associated with the weight of the dried sample

u_{orig} = Standard uncertainty associated with the weight of the original sample

The uncertainty contributions for u_{dry} and u_{orig} was determined through weighing by difference and already include the uncertainty contribution from the empty sample vessel.

5.3.5 Combined standard uncertainty of the primary assay standard,

$$u_{Cz(1)}$$

The combined uncertainty of the primary assay standard, from which aliquots were taken in the preparation of the primary assay standard blends, was calculated by taking into account uncertainty contributions associated with the source primary assay standard, and the weighing process of the preparation of the intermediate standard. The standard uncertainty of the source primary assay standard was typically determined from the statement of uncertainty provided by NIST (or generally from the producer of the certified reference material), using the coverage factor or the level of confidence provided, otherwise a rectangular distribution was assumed for the manufacturer's specification in accordance with the requirements of the GUM[4].

5.3.5.1 *The uncertainty of the density factor, applied for correction (if necessary), u_D*

If the concentration of the analyte in the primary assay standard was presented in the units $\mu\text{g}\cdot\text{m}\ell^{-1}$, or equivalent, a density factor for conversion to units of mass fraction was applied. The density factor was experimentally determined, and its uncertainty included contributions from the uncertainty of the density measurement, as well as the standard deviation associated with variations in the density value, due to temperature variations in the range of 21 ± 2 °C. The latter could have been an over-estimation, but specifically took into consideration possible variations in the temperature of the laboratory temperature.

The combined standard uncertainty for a density factor of any aqueous primary assay standard solution, which was typically measured in the range of 0.9 to 1.3 $\text{g}\cdot\text{m}\ell^{-1}$, was determined as follows:

$$u_D = \sqrt{u_{Dm}^2 + u_{Dtm}^2} \dots\dots\dots(5.8)$$

where

u_D = standard uncertainty of the density factor

u_{Dm} = standard uncertainty of the density instrument, 0.00005 (type B)

u_{Dtm} = standard deviation of density measurements of pure water obtained for a temperature interval of 21 ± 2 °C

The combined standard uncertainty of the primary assay standard, taking into account all the abovementioned uncertainty contributions, was calculated using the different approaches to be discussed in the following section.

5.3.6 Standard uncertainty for the sum of ratios, $u_{(\sum(K_{ix} \cdot R_{ix}))}$ and $u_{(\sum(K_{iz} \cdot R_{iz}))}$

The uncertainty for the sum of ratios was calculated only for the determination of Pb, because the natural abundance of Pb across the earth is not constant. A separate analysis sequence for Pb, consisting of the test sample and Pb primary assay standard, as well as the mass bias isotope standard (NIST SRM 982), was run for the calculation of the corresponding sum of ratios for Pb. The uncertainties associated with the determination of all possible Pb isotope ratios in the test sample and the standard, R_{ix} and R_{iz} , were calculated as described above, where $u_{R_{ix}} = s_{R_{ix}}$ and $u_{R_{iz}} = s_{R_{iz}}$. The uncertainties associated with the mass bias correction factors for the corresponding isotope ratios in the test sample and the primary assay standard, K_{ix} and K_{iz} respectively, were calculated as described earlier, and compared to the corresponding certified isotope ratios of the isotopic standard NIST SRM 982:

$$u_{K_{ix}} = \frac{s(K_{ix})}{\sqrt{m}} \text{ and } u_{K_{iz}} = \frac{s(K_{iz})}{\sqrt{m}} \dots\dots (5.9)$$

where

$u_{K_{ix}}$ = standard uncertainty for the mass bias correction factors for the sample

$u_{K_{iz}}$ = standard uncertainty for the mass bias correction factors for the standard

$s(K_{ix})$ = the corresponding standard deviation of the mean mass bias correction factor for each of the Pb isotope ratios in the test sample

$s(K_{iz})$ = the corresponding standard deviation of the mean mass bias correction factor for each of the Pb isotope ratios in the primary assay standard

m = the number of mass bias standard measurements in the analysis sequence

The combined standard uncertainty for the sum of isotope ratios for Pb in the test sample and the primary assay standard, were calculated using the different approaches to be discussed in the following section.

5.3.7 Standard uncertainty of the blank correction factor, u_B

All amounts of the reagents used in the preparation of the individual solutions were kept relatively constant. It was assumed therefore that the effect on the isotope ratios of the spiked samples and primary assay standards would be nearly identical and cancel out. However, since small differences in the amounts of the added reagents may exist, the blank may affect the uncertainty of the measurement result

of an individual determination. Therefore, a blank correction factor of 1, with an assigned relative standard uncertainty of 0.2% was introduced and included in the measurement equation based on the experience gained by the laboratory during the development and validation of different methodologies.

5.3.8 Standard uncertainty associated with the digestion process, u_G

Based on the experience gained by the laboratory during the development and validation of different methodologies, a digestion correction factor of 1, with an estimated relative standard uncertainty of 0.2%. This digestion correction factor takes into account any possible variations in the sample matrix, and discrimination effects that might have occurred in the equilibration process during digestion between the naturally occurring and spike isotopes.

5.4 Calculation of the combined standard uncertainty

A detailed evaluation of the uncertainty contributions towards the combined standard uncertainty in the determination of the analytes, revealed that the major sources of uncertainty were associated with the measurement of the isotope ratios, the calculation of the mass bias correction factors and the assigned uncertainty of the primary assay standards (see **Figure 5.1**). Some of these major contributors confirm the findings of a previous study[34]. All these uncertainty contributions, with the exception of the amount content of the primary assay standard, are type A uncertainties based on experimental data. It is possible then that by improving the counting statistics through longer acquisition times, the precision of the isotope ratio measurements could improve, subsequently reducing the measurement uncertainty of the individual determinations.

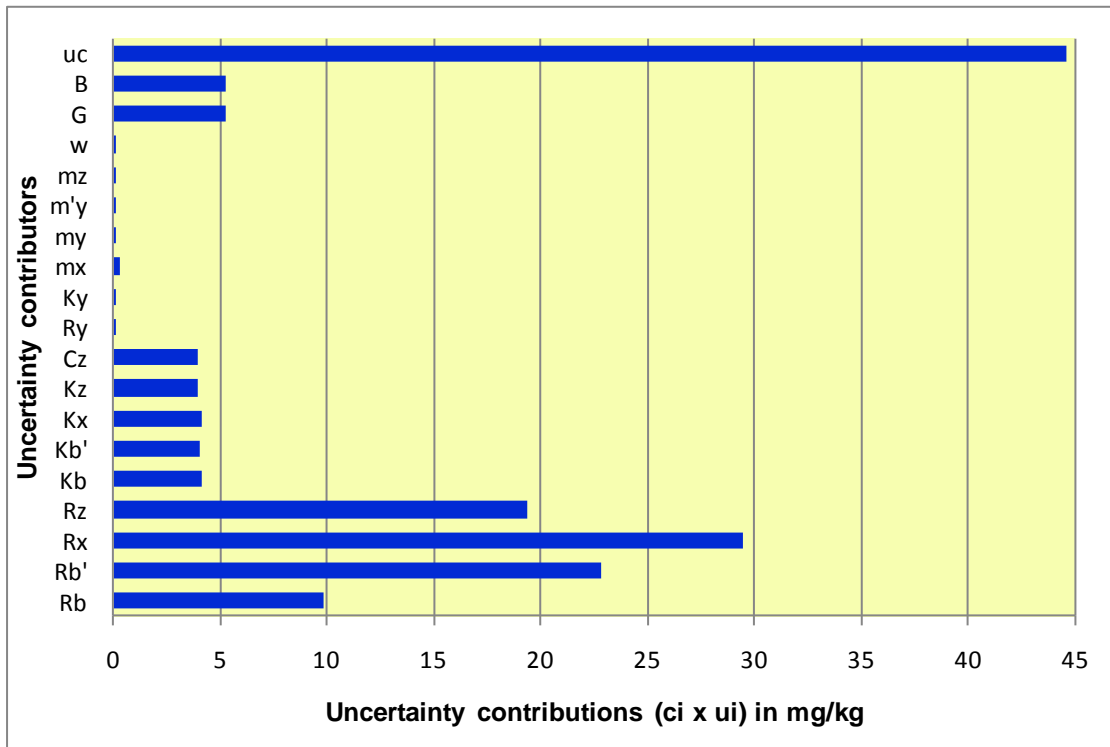


Figure 5.1: Comparison of the magnitude of the individual uncertainty contributions from the different influence quantities of the double isotope dilution experiment

Three approaches are generally used for the calculation of the combined standard uncertainty and were compared during this study.

5.4.1 Sensitivity coefficients calculated with partial derivatives

The combined standard uncertainty associated with the ID-ICP-MS results of Ba, Sr, Cd, Pb, Mo, Zn, Cu and Ni for any independent determination were calculated in accordance with the ISO GUM[4] and EURACHEM/CITAC guidelines[32] for quantifying uncertainty of measurement. The following expression was used, which corresponds to the law of propagation of uncertainty applied to the equation for the double isotope dilution determination (see **equation 5.1**):

$$u_{c(C_x)} = \sqrt{c_i \cdot u_{(p_i)}} \dots\dots\dots (5.10)$$

where, $c_i = \frac{\partial C_x}{\partial p_i}$ (sensitivity coefficients) can be calculated from the partial derivatives of C_x to each uncertainty component p_i .

The sensitivity coefficients describe how the output estimate, C_x , varies with changes in the values of the input quantities as detailed in **equation 5.1**. **Appendix H** summarises the calculation of the combined standard uncertainties of several of

the uncertainty contributors and the combined standard uncertainty of the double isotope dilution experiment for Ba in SARM 2.

5.4.2 Sensitivity coefficients calculated with the numerical approximation method

In the instance where the skills to derive partial derivatives are not available in a laboratory, the sensitivity coefficients can be approximated numerically. The sensitivity coefficients describe how the output estimate, y , varies with changes in the input quantities x_1, x_2, \dots, x_N , where y is defined as $y = f(x_1, x_2, \dots, x_N)$ and can be numerically approximated by

$$c_i = \frac{\Delta y}{\Delta x_i} = \frac{\Delta f(x_i)}{\Delta x_i} \dots\dots\dots (5.11)$$

Thus, the sensitivity coefficients can be evaluated numerically by changing the value of an input quantity by a small amount and determining the effect it has on the estimate of the measurand. The numerical approximation of the sensitivity coefficients can be determined either by calculation, if the measurement system is well-defined, or otherwise it can also be determined experimentally.

Spreadsheet software was developed by Kragten[35], with a procedure that takes advantage of an approximate numerical method of differentiation. The procedure requires knowledge of the mathematical model (measurement equation) for the calculation of the final measurement result, including any correction factors, or other influence quantities, as well as the numerical values of the best estimates of all the uncertainty contributions and their standard uncertainties.

The assumption is made that the sensitivity coefficients can be approximated by

$$c_i \approx \frac{\Delta y}{\Delta x_i} = \frac{y(x_i + u(x_i)) - y(x_i)}{u(x_i)} \dots (5.12)$$

Provided that either y is linear in x_i or $u(x_i)$ is small compared to x_i . In **Appendix I** an example is given for the calculation of the combined standard uncertainties for some of the uncertainty contributors and the double isotope dilution experiment for Ba in SARM 2 with the numerical approximation method.

5.4.3 Power Law

If Y is of the form $Y = cX_1^{p_1} X_2^{p_2} \dots X_N^{p_N}$, and the exponents p_i are known positive or negative numbers having negligible uncertainties, the combined variance, $u_c^2(y)$ can be expressed as

$$\left(\frac{u_c(y)}{y}\right)^2 = \sum_{i=1}^N \left(\frac{p_i u(x_i)}{x_i}\right)^2 \dots\dots\dots (5.13)$$

This is of the same form as **equation 5.10**, but with the combined variance, $u_c^2(y)$, expressed as a relative combined variance, $\left(\frac{u_c(y)}{y}\right)^2$, and the estimated variance, $u^2(x_i)$, associated with each input estimate expressed as an estimated relative variance, $\left(\frac{u(x_i)}{x_i}\right)^2$. Thus, the relative combined standard uncertainty is $\frac{u_c(y)}{y}$, and the relative standard uncertainty of each input estimate is $\frac{u(x_i)}{x_i}$. If each p_i is either +1 or -1, **equation 5.13** becomes

$$\left(\frac{u_c(y)}{y}\right)^2 = \sum_{i=1}^N \left(\frac{u(x_i)}{x_i}\right)^2 \dots\dots\dots (5.14)$$

This special case shows that the relative combined variance associated with the estimate of y , is simply equal to the sum of the estimated relative variances associated with the input estimates x_i . In **Appendix J** the power law was used for the calculation of the combined standard uncertainties of some of the uncertainty contributors and the double isotope dilution experiment for Ba in SARM 2.

The combined standard uncertainties, for the individual determinations of the eight elements in the four reference materials, were calculated using all three approaches to the calculation of the combined standard uncertainties (see **Table 5.3**). The combined standard uncertainties calculated with the partial derivatives and the numerical approximation methods were comparable. The combined standard uncertainties calculated with the power law were mostly comparable with the results for the other two approaches. For some of the elements the results from the calculations with the power law was double to three times larger. This was probably due to the fact that the measurement equation for the double ID-ICPMS experiment does not strictly adhere to the definition of the measurement model for the power law. While the power for most of the input quantities is +1 or -1, other operations,

such as subtraction, is also found in the measurement equation (**equation 5.1**) and therefore the power law approach is invalid.

It is important to note that the calculation of the combined standard uncertainty is much simplified with the use of the power law. For applications where the requirements for highest level of accuracy are not as stringent, the use of the power law for a simplification of the calculation may be justified.

In this study the use of partial derivatives for the calculation of the sensitivity coefficients were used to obtain the final results, in an attempt to follow the requirements of the ISO GUM as strictly as possible.

Table 5.3: Comparison between the different methods for the calculation of the combined standard uncertainty

		Sensitivity coefficients			Numerical approximation			Power law		
		Mean	Uncertainty (k=2)	Relative uncertainty (%)	Mean	Uncertainty (k=2)	Relative uncertainty (%)	Mean	Uncertainty (k=2)	Relative uncertainty (%)
SARM 2	Ba	2585	38	1.5	2585	37	1.4	2585	41	1.6
	Sr	59.9	1.6	2.7	59.9	1.7	2.8	59.9	1.8	3.0
	Zn	8.90	0.41	4.7	8.90	0.41	4.6	8.90	0.38	4.3
	Cu	17.13	0.41	2.4	17.13	0.41	2.4	17.1	1.1	6.2
	Ni	2.51	0.13	5.3	2.51	0.13	5.2	2.51	0.13	5.3
	Mo	0.830	0.040	4.8	0.830	0.040	4.8	0.830	0.089	10.8
	Cd	0.0182	0.0023	12.6	0.0182	0.0023	12.5	0.0182	0.0022	12.4
SARM 3	Pb	1.826	0.036	2.0	1.826	0.041	2.2	1.826	0.038	2.1
	Ba	413.4	3.2	0.8	413.4	3.2	0.8	413.4	7.5	1.8
	Sr	4728	60	1.3	4728	66	1.4	4728	96	2.0
	Zn	430.0	5.2	1.2	430.0	5.2	1.2	430	10	2.4
	Cu	9.85	0.76	7.7	9.85	0.76	7.7	9.85	0.94	9.6
	Ni	1.54	0.26	17.1	1.54	0.26	17.1	1.54	0.26	17.1
	Mo	1.82	0.41	22.5	1.82	0.41	22.5	1.82	0.40	22.1
SARM 4	Pb	46.04	0.65	1.4	46.04	1.14	2.5	46.04	0.76	1.7
	Ba	82.9	1.0	1.2	82.9	1.0	1.2	82.9	1.3	1.5
	Sr	260.9	4.5	1.7	260.9	4.4	1.7	260.9	5.8	2.2
	Zn	61.42	0.90	1.5	61.42	0.90	1.5	61.4	1.6	2.5
	Cu	10.67	0.23	2.2	10.67	0.23	2.1	10.67	0.65	6.1
	Ni	119.3	5.4	4.5	119.3	5.3	4.5	119.3	3.8	3.2
	Mo	0.888	0.052	5.9	0.888	0.052	5.9	0.888	0.094	10.6
Cd	0.0879	0.0031	3.5	0.0879	0.0031	3.5	0.0879	0.0028	3.1	
Pb	2.110	0.031	1.5	2.110	0.036	1.7	2.110	0.041	1.9	

5.5 Calculation of the uncertainty of the mean result

The combined standard uncertainty of the end result (the mean of the independent determinations) was calculated according to the following equation:

$$u_c = \sqrt{\frac{u_c(1)^2 + \dots + u_c(n)^2}{n}} + u_{mean}^2 \dots \dots \dots (5.15)$$

where

u_c = combined standard uncertainty of the mean result (of the independent determinations)

$u_c(1)$ = combined standard uncertainty for determination 1

$u_c(n)$ = combined standard uncertainty for determination n

u_{mean} = experimental standard deviation of the mean result

n = the total number of determinations

5.6 Calculation of the expanded uncertainty, U

The expanded uncertainty, U , was obtained by multiplying the combined standard uncertainty with a coverage factor of 2, to provide a 95.45% level of confidence for the ID-ICP-MS result. The uncertainty budget consists of a combination of various different uncertainty contributors. Some of the contributors were evaluated as Type A uncertainties from experimental data through the use of statistical analysis with frequency based probability distributions and a finite number of degrees of freedom. Other contributors were evaluated as Type B uncertainties through the use of a priori probability distributions. The effective degrees of freedom of the combined standard uncertainty of all the Type A and Type B uncertainty contributions was calculated with the Welch-Satterthwaite[4] equation.

$$v_{eff} = \frac{u_c^4(y)}{\sum_{i=1}^N \frac{(c_i u_i)^4}{v_i}} \dots\dots\dots (5.16)$$

where

v_{eff} = effective degrees of freedom

$u_c(y)$ = combined standard uncertainty of the individual determination

$c_i u_i$ = the uncertainty contribution of a particular contributor, i

v_i = the degrees of freedom of a particular uncertainty contributor, i

Chapter 6

Results and discussion

6.1 Method validation

The developed methodology for ID-ICP-MS analysis of rock samples and the applied experimental designs, were also applied in the analysis of the rock type CRM SY-4 (Diorite Gneiss)[36]. The certification of the CRM was completed in 1995 with an interlaboratory comparison study of eighty nine international laboratories.

Homogeneity testing was performed on twenty two bottles of the SY-4 samples by a stratified random sampling scheme. The chosen bottles were analysed by the Mineral Resources Division of the Geological Survey of Canada (GSC) by wavelength dispersive X-ray fluorescence spectrometry and rapid chemical methods for a wide range of whole-rock constituents along with barium, strontium, rubidium and zirconium.

The elements of interest were independently determined from three digestions (Cu, Ni, Pb, Zn, Cd and Mo) or four digestions (Sr and Ba). The measured concentrations and associated uncertainties from the ID-ICPMS analyses are presented in **Table 6.1**, together with the certification values. Any possible biases between the measured and certified values for the elements of interest, were evaluated through the calculation of the recoveries as well as the E_n -values[37].

$$E_n = \left| \frac{\bar{x}_{measured} - \bar{x}_{certified}}{U_{measured}^2 + U_{certified}^2} \right| \dots\dots\dots (6.1)$$

where

E_n = a measure of the comparability of two results

$\bar{x}_{measured}$ = the mean of the measured value in the laboratory

$\bar{x}_{certified}$ = the certified value

$U_{measured}$ = the expanded uncertainty reported by the laboratory

$U_{certified}$ = the expanded uncertainty reported for the reference material

The E_n -values compares the differences between the measured and the certified values for the elements taking into account the reported uncertainties. E_n -values smaller than one signify that the measured and certified values are comparable.

The uncertainties in the recoveries as displayed in **Figure 6.1** were calculated through the combination of the relative uncertainties of the certified values and the measured values.

$$u(\text{recovery}) = \text{Recovery} \times \sqrt{\left(\left(\frac{u(\text{certifiedvalue})}{\text{Certifiedvalue}} \right)^2 + \left(\frac{u(\text{measuredvalue})}{\text{Measuredvalue}} \right)^2 \right)} / 2 \quad (6.2)$$

For all the elements in SY-4 where the recoveries could be calculated the results were within the 95% level of confidence, except for Ni where the recoveries were lower. SY-4 has been used on several occasions for the validation of methodology developed for the determination of Ni in rocks and sediments, the Ni results for SY-4 by ID-ICP-MS has been consistently lower on all these occasions. In the case of SARM 4 the ID-ICP-MS result for Ni was in very good agreement with the previously certified value as well as the median calculated for the literature values published since 1978. It was therefore decided not to correct the measurement results for Ni in SARM 2, SARM 3 and SARM 4 for the lower recovery of Ni in SY-4.

All the E_n -values, except for Zn were better than 1 indicating good comparability between the measured and certified values within the calculated uncertainties. The recoveries for Cd and Mo could not be calculated, because certified values were not provided for these elements in the certificate of analysis, only a range of expected values were provided.

Table 6.1: Comparison of certified and measured values for SY-4

Element	Certified		Measured		Recovery (%)	E_n -values
	Value mg.kg ⁻¹	Uncertainty ^a (k=2) mg.kg ⁻¹	Value mg.kg ⁻¹	Uncertainty (k=2) mg.kg ⁻¹		
Ba	340	5	338.2	5.8	99.5	0.24
Cd	0.1-2 ^b		0.18	0.06		
Cu	7	1	6.9	1.4	98.6	0.06
Mo	0.2-3 ^b		0.28	0.03		
Ni	9	1	7.7	0.9	85.6	0.97
Pb	10	1	9.6	0.1	96.0	0.40
Sr	1191	12	1185	26	99.5	0.21
Zn	93	2	97.5	1.3	104.8	1.9

^a Calculated from the experimental standard deviation of the mean with a coverage factor k=2

^b Range of expected values

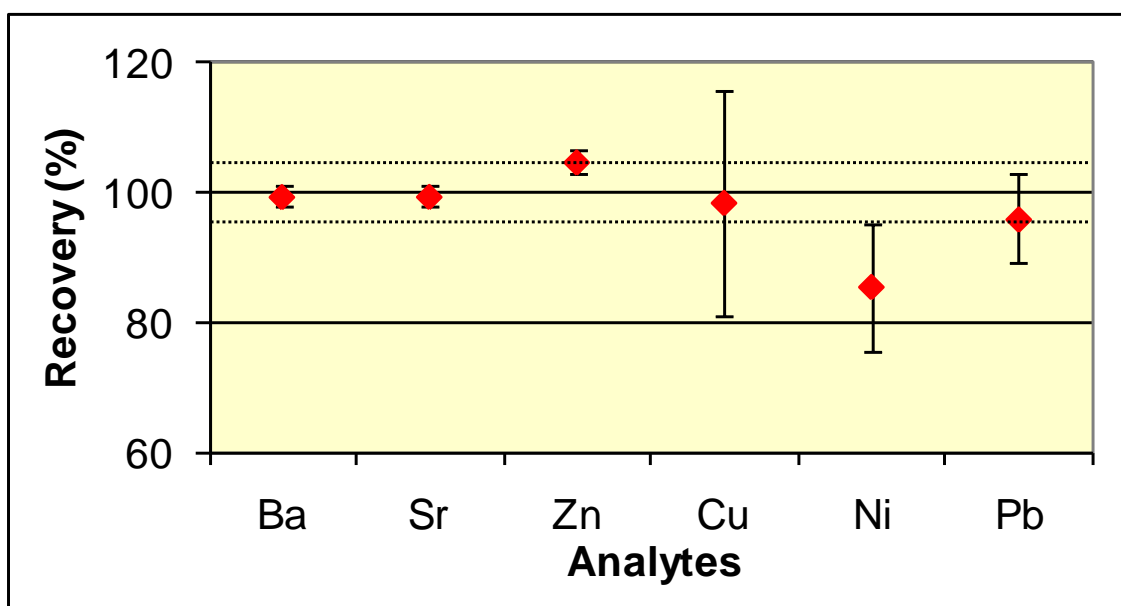


Figure 6.1: Summary of the results for the recoveries of the analytes of SY-4

6.2 Evaluation of the flexibility of the ID-ICP-MS methodology

During the experiment, three aliquots of the primary assay standard and the stable isotope spike blend were prepared for each sample. Only one aliquot of the blend was digested with the samples. The other two aliquots of the blend were prepared off-line and did not go through the microwave digestion cycle with the samples. The comparisons between the results from the different primary assay standard blends for the eight elements in SARM 2 are illustrated in **Figures 6.2 to 6.9**.

In **Figures 6.2, 6.3, 6.6, 6.7** and **6.8** it can be seen that there are no differences between the results for the digested primary assay standard and spike blend compared to the two blends that were prepared without digestion for Ba, Sr, Ni, Mo and Cd. For Zn, Cu and Pb the results for the digested primary assay standard blend appears to measure lower than the other two blends, as can be seen in **Figures 6.4, 6.5** and **6.9**, respectively. However, the results with the calculated uncertainties between all the primary assay standard blends still show enough overlap to be considered as part of the same sample population and not biased.

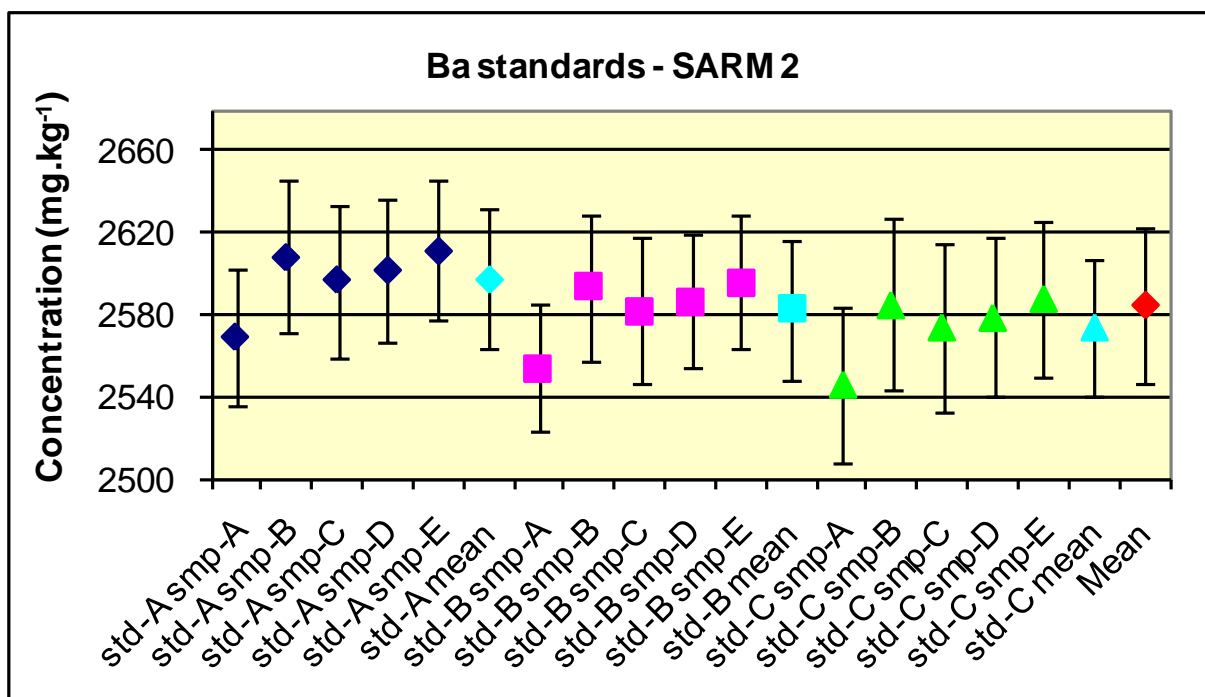


Figure 6.2: A comparison between the three primary assay standard blends for Ba in SARM 2

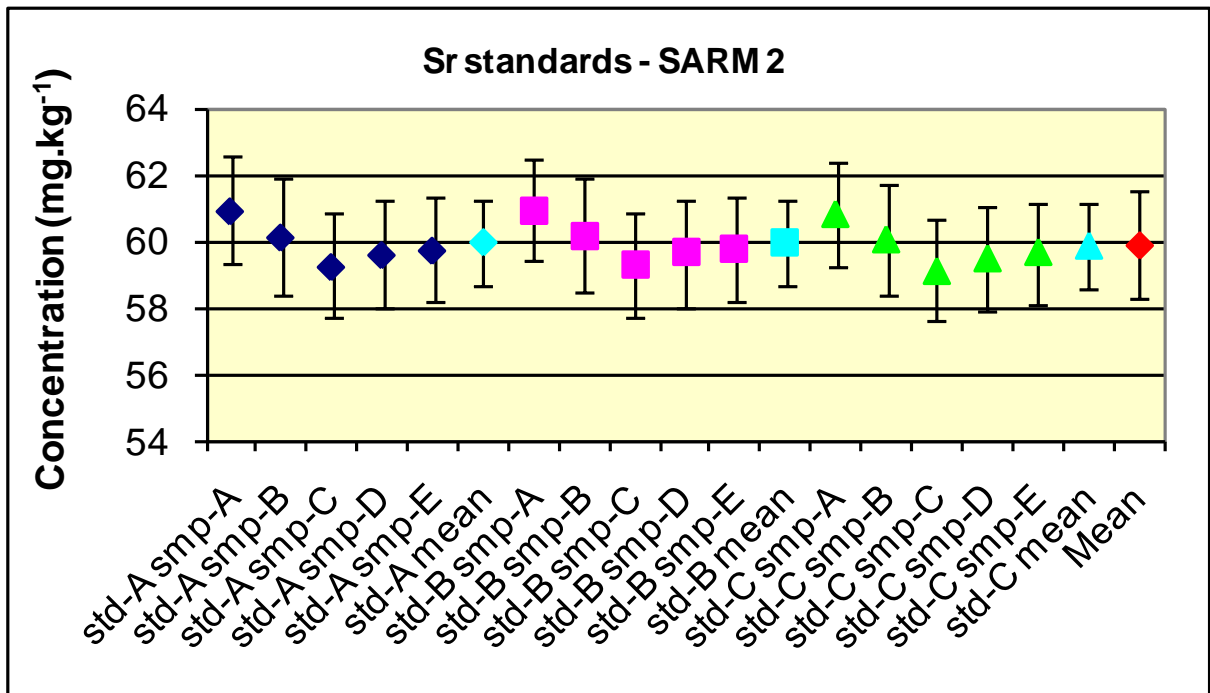


Figure 6.3: A comparison between the three primary assay standard blends for Sr in SARM 2

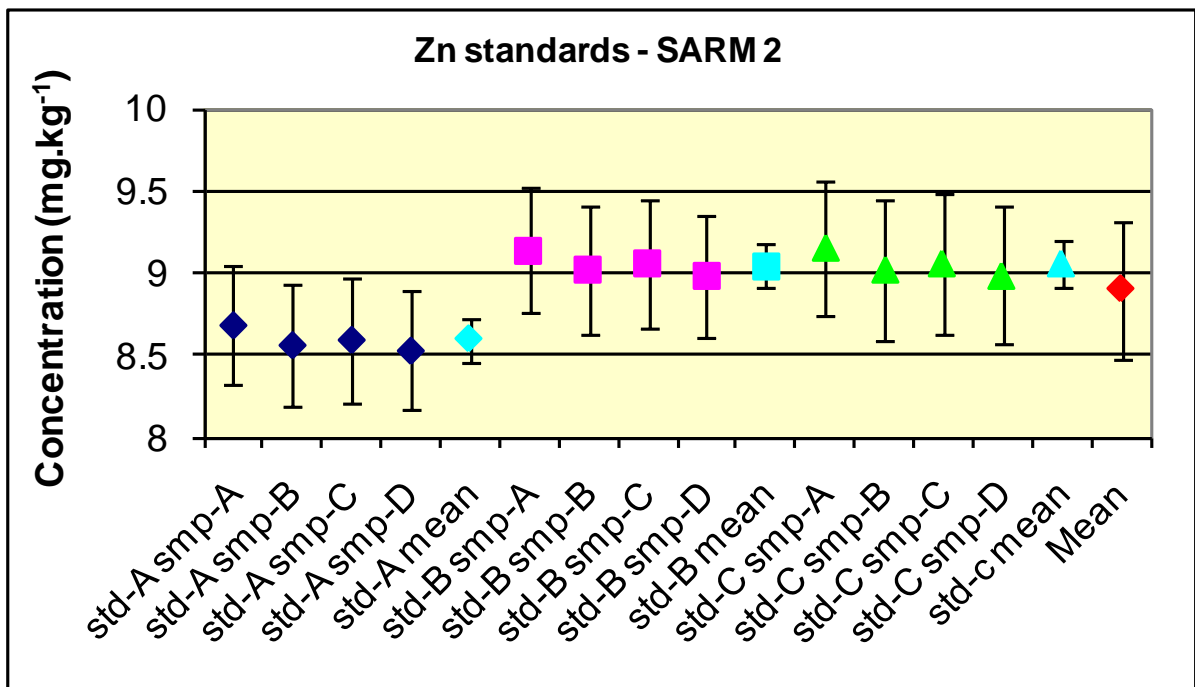


Figure 6.4: A comparison between the three primary assay standard blends for Zn in SARM 2

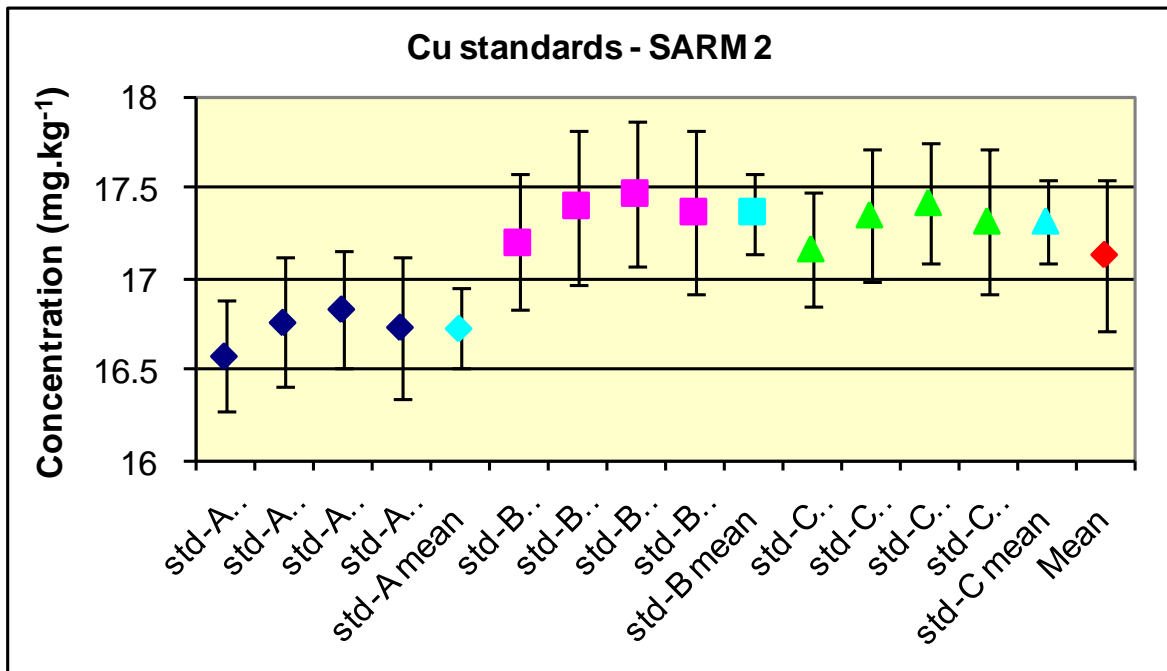


Figure 6.5: A comparison between the three primary assay standard blends for Cu in SARM 2

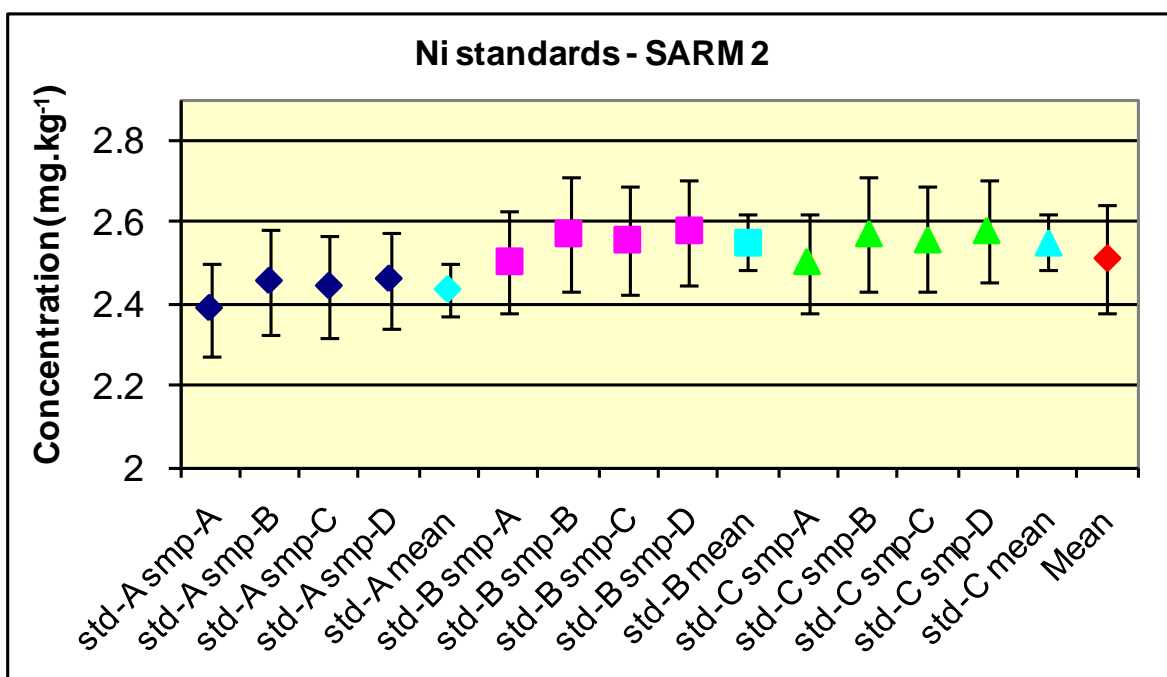


Figure 6.6: A comparison between the three primary assay standard blends for Ni in SARM 2

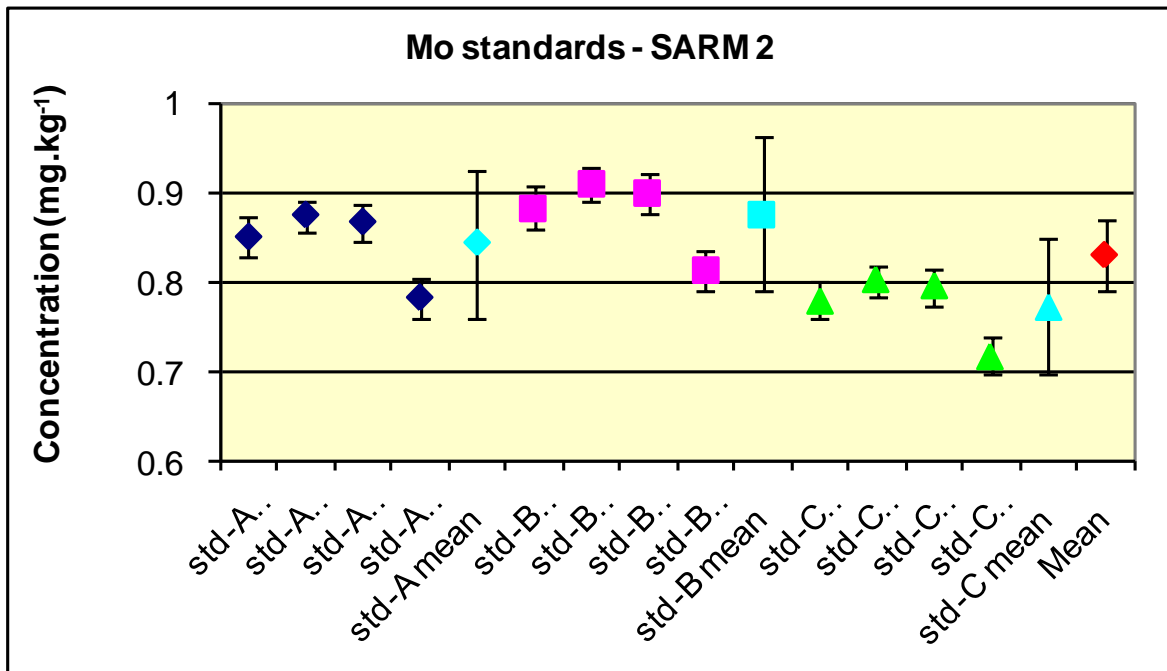


Figure 6.7: A comparison between the three primary assay standard blends for Mo in SARM 2

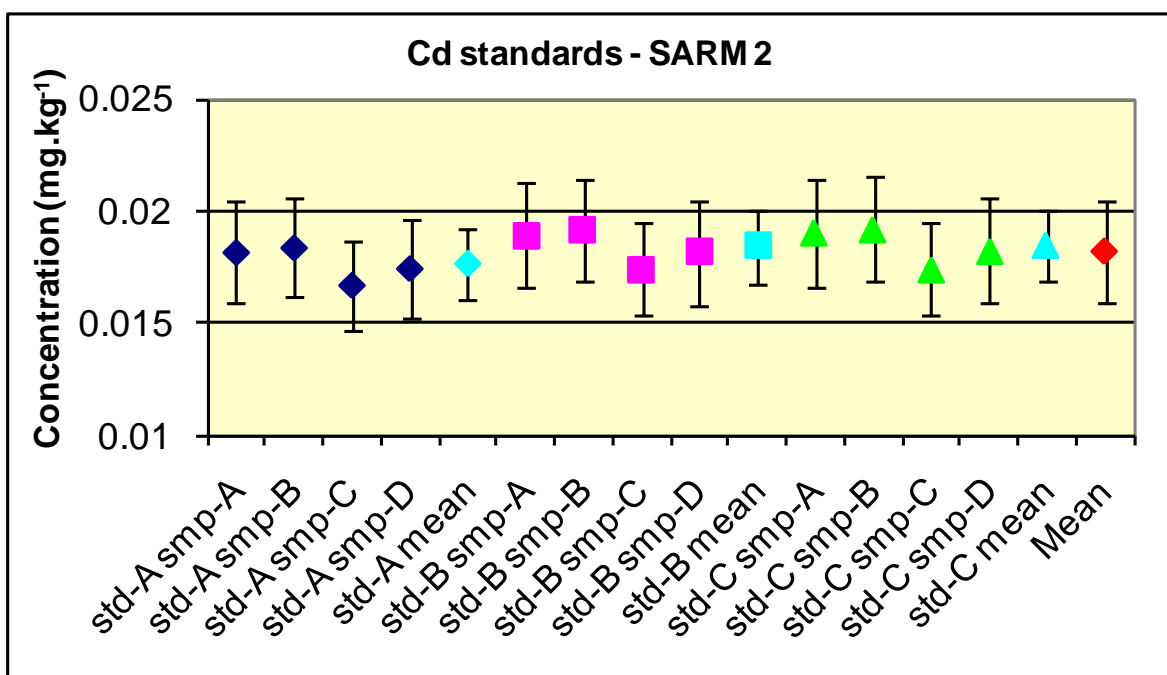


Figure 6.8: A comparison between the three primary assay standard blends for Cd in SARM 2

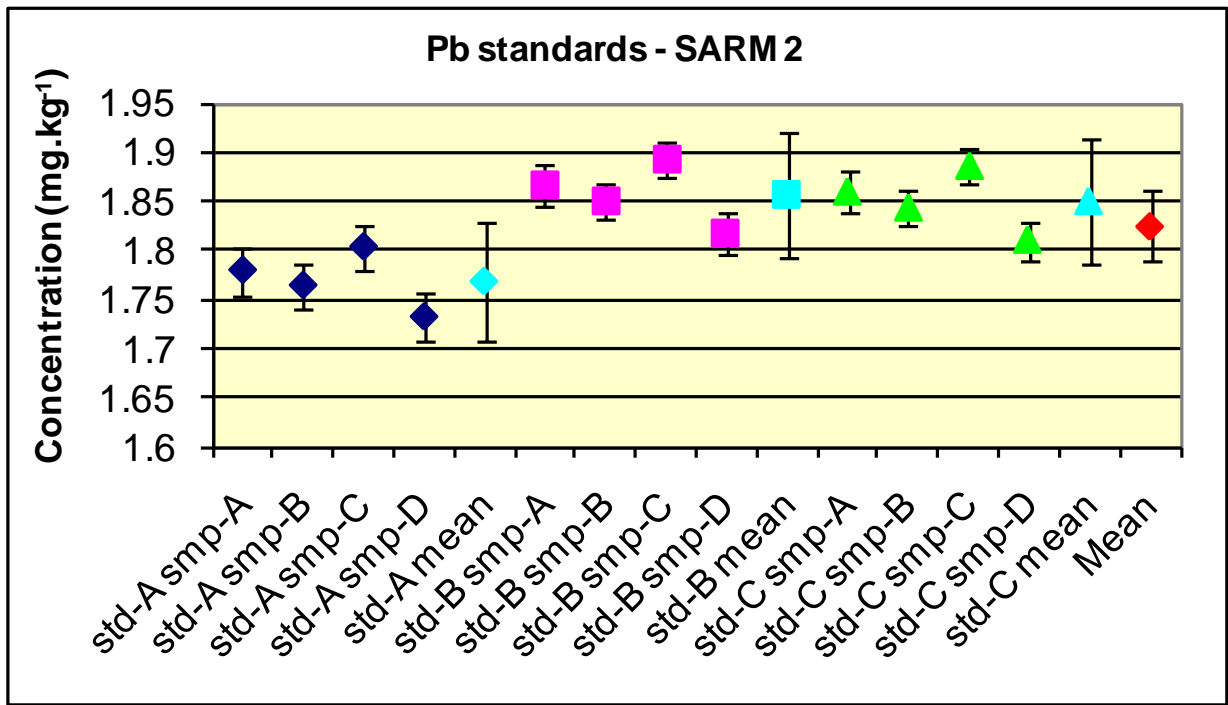


Figure 6.9: A comparison between the three primary assay standard blends for Pb in SARM 2

Table 6.2: Comparison between the on-line and off-line standard blends for SARM 2

Element	On-line standard blend		Off-line standard blend		Mean	
	Value $\mu\text{g}\cdot\text{g}^{-1}$	Uncertainty (k=2) $\mu\text{g}\cdot\text{g}^{-1}$	Value $\mu\text{g}\cdot\text{g}^{-1}$	Uncertainty (k=2) $\mu\text{g}\cdot\text{g}^{-1}$	Value $\mu\text{g}\cdot\text{g}^{-1}$	Uncertainty (k=2) $\mu\text{g}\cdot\text{g}^{-1}$
Ba	2597	38	2578	38	2585	38
Sr	59.9	1.8	59.9	1.6	59.9	1.6
Cd	0.018	0.002	0.018	0.002	0.018	0.002
Pb	1.77	0.06*	1.86	0.06*	1.83	0.06*
Mo	0.85	0.04	0.83	0.06	0.83	0.04
Zn	8.6	0.4	9.1	0.4	8.9	0.4
Cu	16.7	0.4	17.3	0.4	17.1	0.4
Ni	2.43	0.12	2.55	0.14	2.51	0.14

* 2 x standard deviation(s)

The comparison between the results for the digested primary assay standard blends and the other blends are also summarised in **Table 6.2**. The difference between the different blends appears to be the most pronounced for Pb. However, a *t*-test shows that the difference noted between the results for the digested blend and the other two blends for Pb, Zn or Cu is not significant.

For Ba and Sr five aliquots of the sample and stable isotope spike blend were prepared, and for all the other elements four aliquots of the sample and spike blend were prepared. The amount of spike to be added was varied from the exact matching amount (i.e the amount of spike to be added to obtain a ratio of 1 in the sample and spike blend) to some degree for each aliquot of the sample and spike blend. The comparison between the effect of the variation in the addition of the amount of spike on the precision of the results for each element is summarised in **Table 6.3**.

Table 6.3: Comparison between the effect of the variation in the addition of the amount of spike on the precision of the results for SARM 2

Element	%Difference between amount of spike and exact matching amount	%Difference between each sample blend and mean of the results	Result		
			Value $\mu\text{g}\cdot\text{g}^{-1}$	Uncertainty (k=2) $\mu\text{g}\cdot\text{g}^{-1}$	Relative uncertainty (k=2) %
Ba	+0.2 to +14.8	0.03 to 1.10	2585	38	1.5
Sr	+0.4 to +32.4	0.3 to 1.7	59.9	1.6	2.7
Cd	-10.4 to +9.3	1.3 to 5.6	0.018	0.002	11.1
Pb	-10.4 to +9.3	0.3 to 2.1	1.83	0.04	2.2
Mo	-10.4 to +9.3	0.8 to 7.2	0.83	0.04	4.8
Zn	-10.4 to +9.3	0.03 to 1.1	8.9	0.4	4.5
Cu	-10.4 to +9.3	0.05 to 0.90	17.1	0.4	2.3
Ni	-10.4 to +9.3	0.3 to 2.0	2.51	0.13	5.2

For all the elements, except for Mo, the range of differences between each sample blend and the mean of the results is smaller than the relative uncertainty of the result.

For Ba and Cd in SARM 2, the isotope ratios of $^{138}\text{Ba}/^{135}\text{Ba}$ and $^{114}\text{Cd}/^{111}\text{Cd}$ were determined, in addition to the ratios of $^{137}\text{Ba}/^{135}\text{Ba}$ and $^{112}\text{Cd}/^{111}\text{Cd}$ for which the method was optimised. The comparison of the results for the different ratios are summarised in **Table 6.4**.

Table 6.4: Comparison between different isotope ratio measurements for the same elements in SARM 2

Element	Result		
	Value $\mu\text{g}\cdot\text{g}^{-1}$	Uncertainty (k=2) $\mu\text{g}\cdot\text{g}^{-1}$	Relative uncertainty (k=2) %
$^{137}\text{Ba}/^{135}\text{Ba}$	2585	38	1.5
$^{138}\text{Ba}/^{135}\text{Ba}$	2624	103	3.9
$^{112}\text{Cd}/^{111}\text{Cd}$	0.018	0.002	11.1
$^{114}\text{Cd}/^{111}\text{Cd}$	0.022	0.012	54.5

For both Ba and Cd the other isotope ratio determinations confirmed the results of the optimised method, but the precision deteriorated for the non-optimum isotope ratios.

The presence of an unresolved poly-atomic interference was suspected for the isotope ratio measurements for Mo in SARM 2, in low resolution, and the measurement sequence was repeated in medium resolution (see **Table 6.5**).

Table 6.5: Comparison between low resolution and medium resolution for the isotope ratio determinations of Mo in SARM 2

Element	Result		
	Value $\mu\text{g}\cdot\text{g}^{-1}$	Uncertainty (k=2) $\mu\text{g}\cdot\text{g}^{-1}$	Relative uncertainty (k=2) %
Low resolution	0.83	0.04	4.8
Medium resolution	0.83	0.05	6.0

The medium resolution determination of the isotope ratios for Mo in SARM 2 confirmed the results of the isotope ratios measured in low resolution, but due to the loss of sensitivity for the samples in the medium resolution the precision deteriorated slightly in medium resolution.

6.3 Results

A summary of the individual determinations for the eight elements in SARM 2, SARM 3 and SARM 4 is given in **Appendix K**.

SARM 2

Barium

Due to the high concentration of Ba in SARM 2 the ^{135}Ba spike was only added to a diluted sample after digestion. The most important requirement to reap the full benefit of the IDMS approach is complete equilibration of the spike isotope and the natural isotope(s), therefore the samples must be completely dissolved. The best way to obtain full equilibration between the spike isotope and the natural isotope(s) is when the spike isotope solution is added to the sample prior to digestion so that the natural isotopes and enriched spike isotopes can reach equilibration through the chemical conversion process of the digestion. In the case of Ba in SARM 2 the amount of ^{135}Ba spike that was required to add to the sample prior to digestion to obtain the optimum sample to spike ratio of one, was calculated to be 2.4070 mL, which was not practically possible in this study.

Although the spike was only added to an aliquot of the sample after digestion, it is believed that full equilibration between the spike isotopes and natural isotopes was still obtained, because the sample was digested in a nitric acid matrix and the spike isotope was also added to the aliquot of the sample in the form of a nitrate, thus the spike isotope and the natural isotope(s) were both in the same chemical form when the spike was added. Thorough mixing of the sample aliquot and the spike solution also facilitated complete equilibration. It is also important to note that only one of the primary assay standards were spiked and digested for each element for each sample. The rest of the primary assay standard and isotope spike blends were prepared without digestion.

Any possible losses that could have occurred during the digestion process that would not have happened the same way to the natural isotopes in the sample compared to the spike isotope due to the spiking after digestion, would be accounted for with the digestion factor in the uncertainty budget. The uncertainty contribution from the extra weighing of the aliquot taken from the digested sample prior to spiking is also accounted for in the uncertainty budget.

Two isotope ratios ($^{137}\text{Ba}/^{135}\text{Ba}$ and $^{138}\text{Ba}/^{135}\text{Ba}$) were determined in low resolution mode. A *t*-test showed that there was no significant difference between the two calculated ratios. However, due to the fact that the experimental design was not optimised for the ratio of $^{138}\text{Ba}/^{135}\text{Ba}$, the counting statistics and mass spectrometric precision were also not optimised. This resulted in calculated uncertainties of

measurement for the $^{138}\text{Ba}/^{135}\text{Ba}$ ratio determinations that were double the uncertainties calculated for the $^{137}\text{Ba}/^{135}\text{Ba}$ ratio determinations (see **Table 6.6**).

Table 6.6: Comparison between the two ratio experiments for Ba in SARM 2

		$^{137}\text{Ba}/^{135}\text{Ba}$		$^{138}\text{Ba}/^{135}\text{Ba}$	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	2569	17	2775	64
	std-spkB	2554	16	2763	68
	std-spkC	2546	19	2754	59
smp-spkB	std-spkA	2609	19	2626	43
	std-spkB	2593	18	2615	48
	std-spkC	2585	21	2607	36
smp-spkC	std-spkA	2597	19	2572	42
	std-spkB	2582	18	2562	47
	std-spkC	2574	21	2553	35
smp-spkD	std-spkA	2602	17	2585	44
	std-spkB	2587	16	2574	49
	std-spkC	2578	19	2566	37
smp-spkE	std-spkA	2611	17	2611	45
	std-spkB	2596	16	2600	49
	std-spkC	2588	19	2591	38
Mean		2585		2624	
Standard deviation		18		76	
Expanded uncertainty (k=2)		38		103	
Relative uncertainty (%)		1.5		3.9	

The mean result for Ba in SARM 2 was determined from a combination of 5 sample blends and 3 primary assay standard blends, for a total of 15 determinations. The primary assay standard was prepared from single element standards of the NIST

SRM 3100 series, as discussed in **Chapter 3**. One of the primary assay standard blends was digested with the samples, while the other two blends were prepared without digestion, and matrix matched to 2% ultrapure nitric acid. As discussed, no significant difference was found between the three blends (see **Section 5.2**).

Figure 6.10 presents the individual determinations for Ba in SARM 2. The expanded uncertainty ($k=2$) for the individual determinations calculated with sensitivity coefficients, as discussed in **Chapter 4**, are presented with the mean of the determinations and its expanded uncertainty. The final result for Ba in SARM 2 was $2585 \pm 38 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 1.5%.

Since the ^{135}Ba spike was added after digestion, an aliquot was taken from the digest of the pure sample, and an additional sample and spike blend was prepared for barium from this aliquot. In **Figure 6.10** it can be seen that the determinations of the additional spike (smp-A) was slightly lower than the other sample blends.

In **Figure 6.10** it can also be seen that the uncertainty calculated for each individual determination is comparable with the standard deviation of the mean of the result, which is an indication of good homogeneity for Ba in the bottle from which the samples were taken.

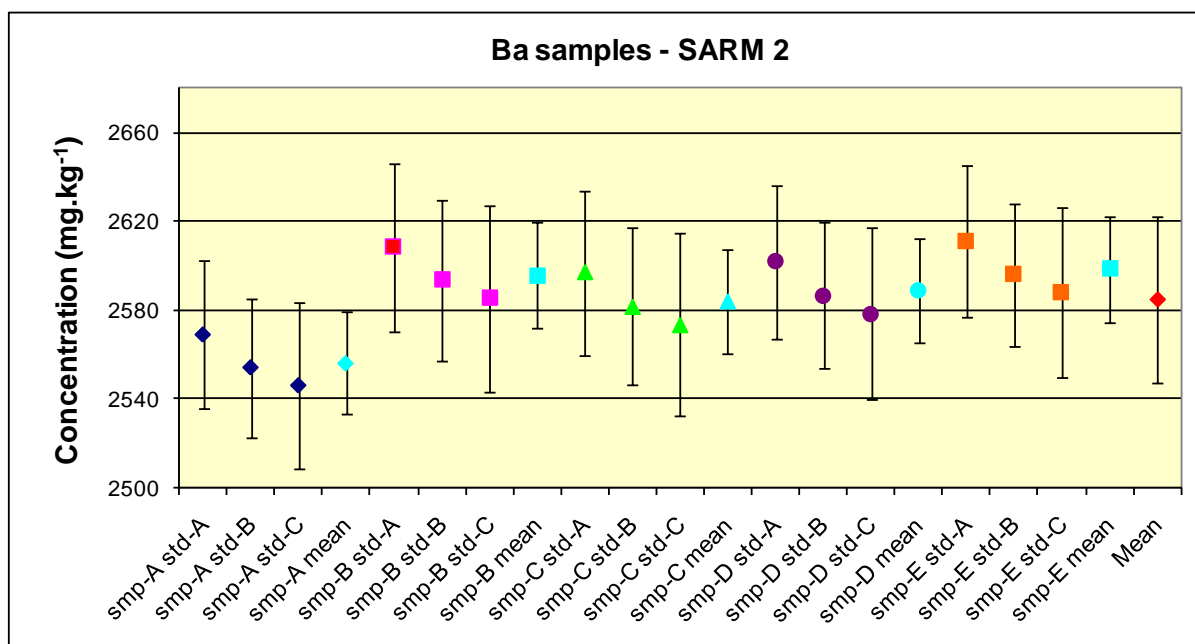


Figure 6.10: The individual determinations and mean result for Ba in SARM 2

Strontium

The concentration of Sr in SARM 2 was also too high to facilitate spiking before digestion. Diluted samples were spiked after digestion as for Ba. The determined

isotope ratios were corrected off-line for isobaric interference from ^{86}Kr in the Ar carrier gas.

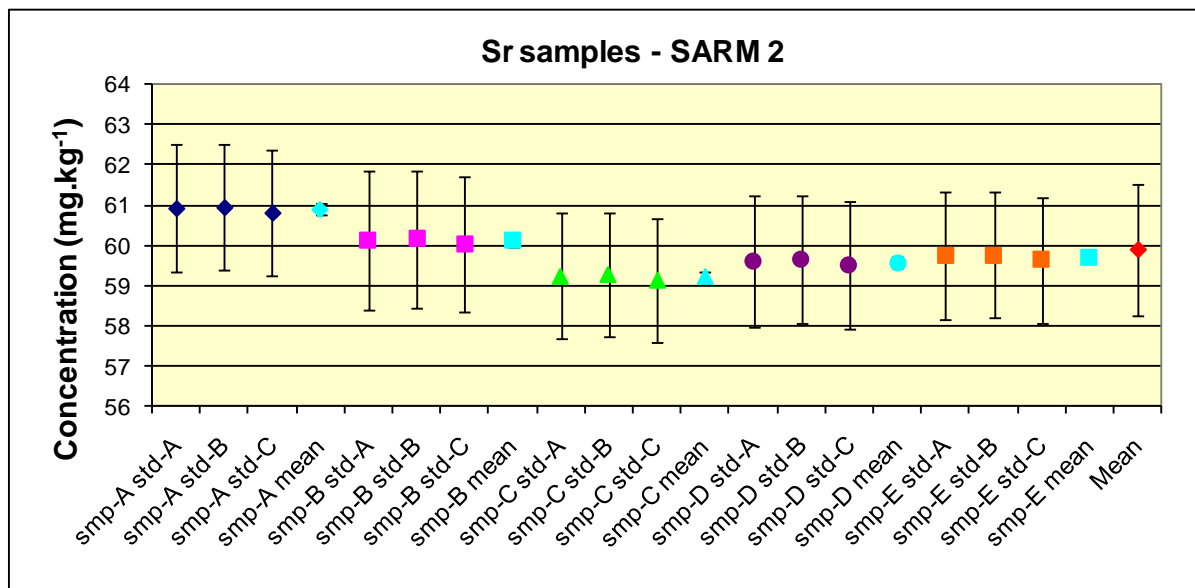


Figure 6.11: The individual determinations and mean result for Sr in SARM 2

The mean result for Sr in SARM 2 was also calculated from 15 determinations in the same way as for Ba. The individual determinations are presented in **Figure 6.11** and show good agreement between all the sample and primary assay standard blends. The comparability between the uncertainty for each individual measurement and the uncertainty calculated for the mean result also indicate good homogeneity for Sr in the sample bottle. The final result for Sr in SARM 2 was calculated as $59.9 \pm 1.7 \text{ mg.kg}^{-1}$ ($k=2$) with a relative uncertainty of 2.8%.

Zinc

The isotope ratio determinations for Zn in SARM 2 was performed in medium resolution, mainly due to the isobaric interference of the doubly charged Ba^{++} as discussed in **Chapter 3**.

The mean result for Zn in SARM 2 was calculated from 12 determinations, which consisted of a combination of 4 sample blends and 3 primary assay standard blends. In **Figure 6.12** it can be seen that the first result for each sample is lower. This is as a result of the first primary assay standard blend that measured lower, as discussed in the previous section (see **Figure 6.3**). Once again the magnitude of the combined standard uncertainties calculated for the individual determinations were comparable with the calculated standard deviation of the mean. The final result calculated for Zn in SARM 2 was $8.90 \pm 0.42 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 4.7%.

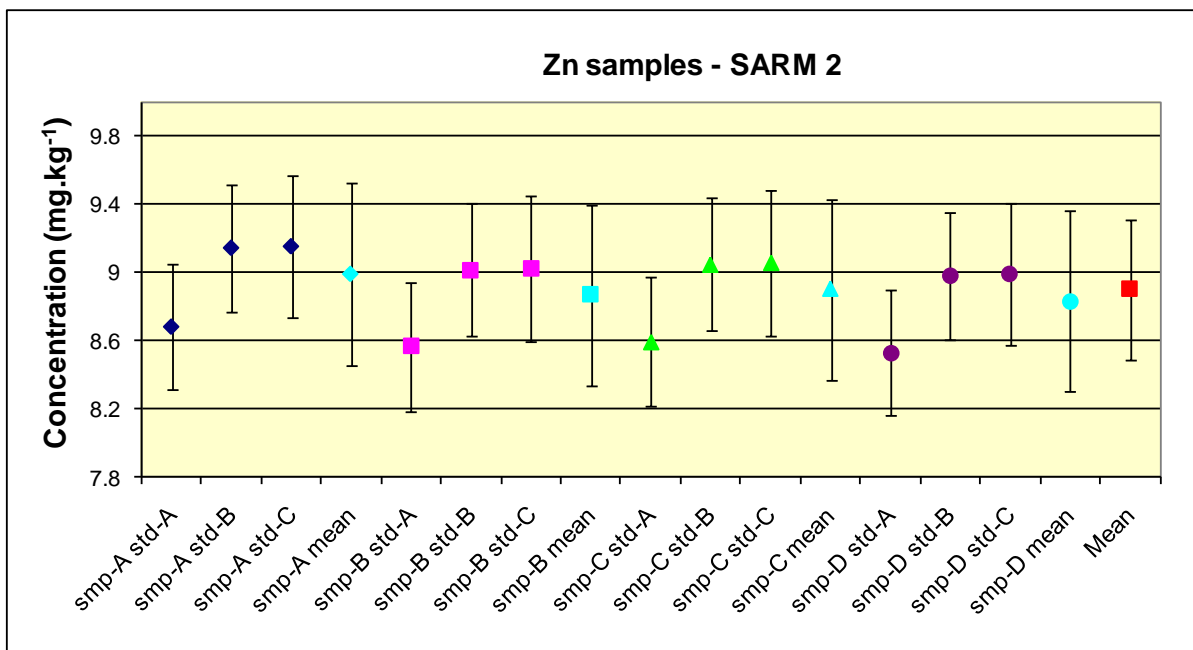


Figure 6.12: The individual determinations and mean result for Zn in SARM 2

Copper

The isotope ratio determinations for copper were performed in medium resolution mode due to polyatomic interferences as discussed in **Chapter 3**. The mean result for Cu in SARM 2 was also calculated from 12 independent determinations in the same way as for Zn. The results for the first primary assay standard blend was also lower (see **Figure 6.4**), which resulted in a lower result for the first determination for each sample. The final result for Cu in SARM 2 was calculated as 17.13 ± 0.42 mg.kg⁻¹ (k=2) with a relative uncertainty of 2.5%.

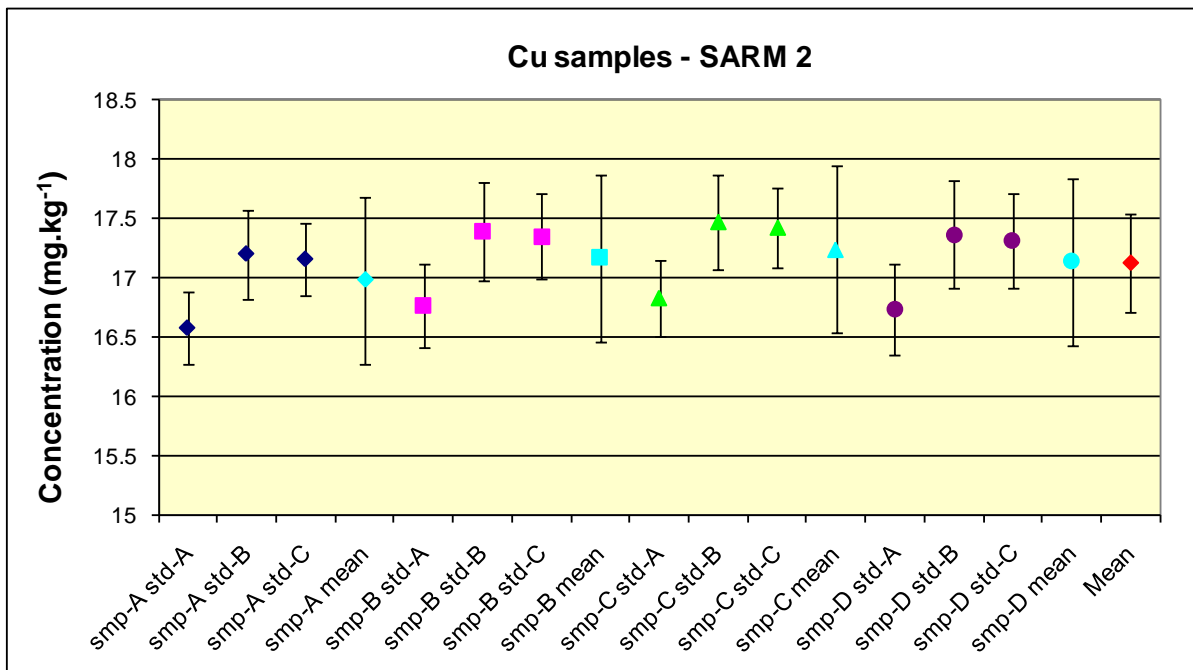


Figure 6.13: The individual determinations and mean result for Cu in SARM 2

Nickel

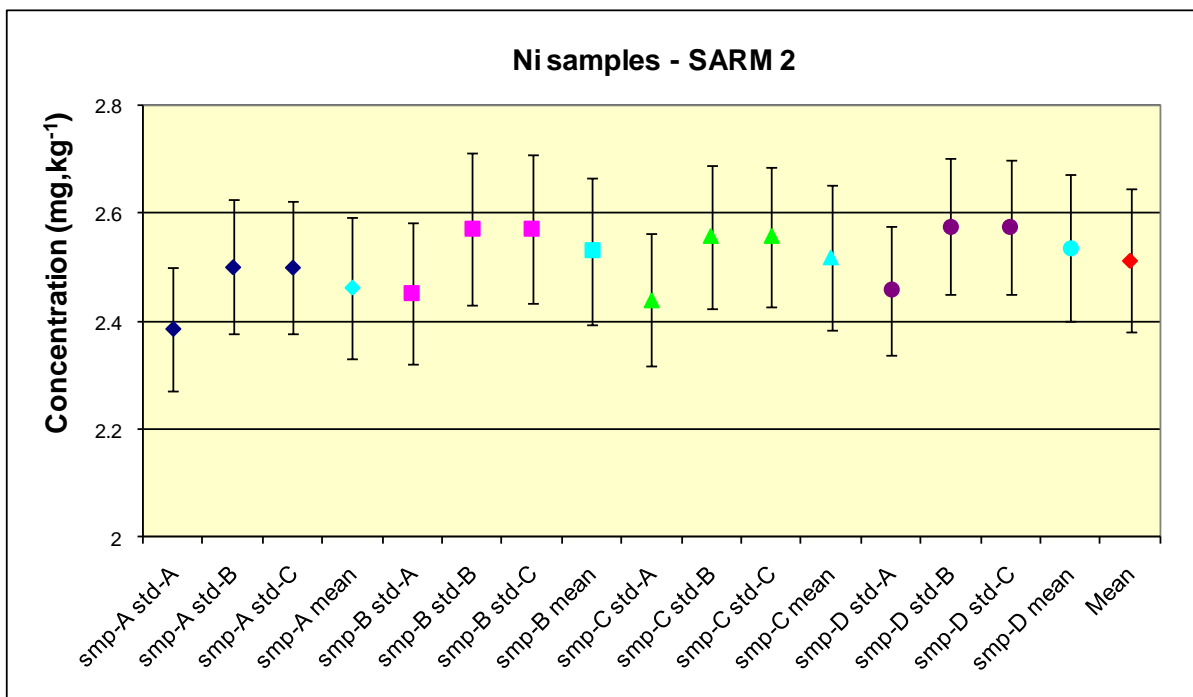


Figure 6.14: The individual determinations and mean result for Ni in SARM 2

The isotope ratio determinations for Ni in SARM 2 were also performed in medium resolution due to polyatomic interferences, as discussed in **Chapter 3**. The mean result for Ni in SARM 2 was also calculated from 12 independent determinations in

the same way as for Cu and Zn. The first result for each sample was also lower. However, in **Figure 5** the digested primary assay standard blend does not appear to be significantly different from the off-line blends.

The final result for Ni in SARM 2 was calculated as $2.51 \pm 0.14 \text{ mg.kg}^{-1}$ ($k=2$) with a relative uncertainty of 5.6%.

Molybdenum

No certified value for Mo in SARM 2 was available and very few measurement results for Mo in SARM 2 have been reported in the literature since the certification. The experimental design for the double isotope dilution-ICP-MS experiment to determine Mo in SARM 2 was based on the range of values reported during the initial certification study, and the two values reported in the literature. The determined isotope ratios in the sample blends were still significantly smaller than one, approximately 0.3.

The result for Mo is still considered to be a good one based on the following two conclusions. Firstly, the combined standard uncertainties calculated for the individual determinations were about double the standard deviation of the mean result, and thus comparable. Secondly, the relative uncertainty calculated for the final result was below 5%, which was the initial uncertainty target for this study.

At these low concentration levels of Mo in the sample the heterogeneity of the sample has a significant impact on the uncertainty of the mean result for the 12 determinations of the analyte in SARM 2. The standard deviation of the mean is significantly larger than the combined standard uncertainty calculated for each determination and forms the major component of the reported uncertainty for Mo in SARM 2.

As discussed above (see **Table 6.5**) Mo in SARM 2 was measured in both low and medium resolution to monitor the possibility of polyatomic interferences in low resolution. The mean result calculated for the determinations in low resolution was confirmed by the mean result for the determinations in medium resolution. However, due to the loss in sensitivity in medium resolution the precision of the isotope ratio determinations deteriorated. The combined standard uncertainties calculated for the individual determinations were larger in medium resolution and impacted negatively on the uncertainty calculated for the mean result for Mo in SARM 2.

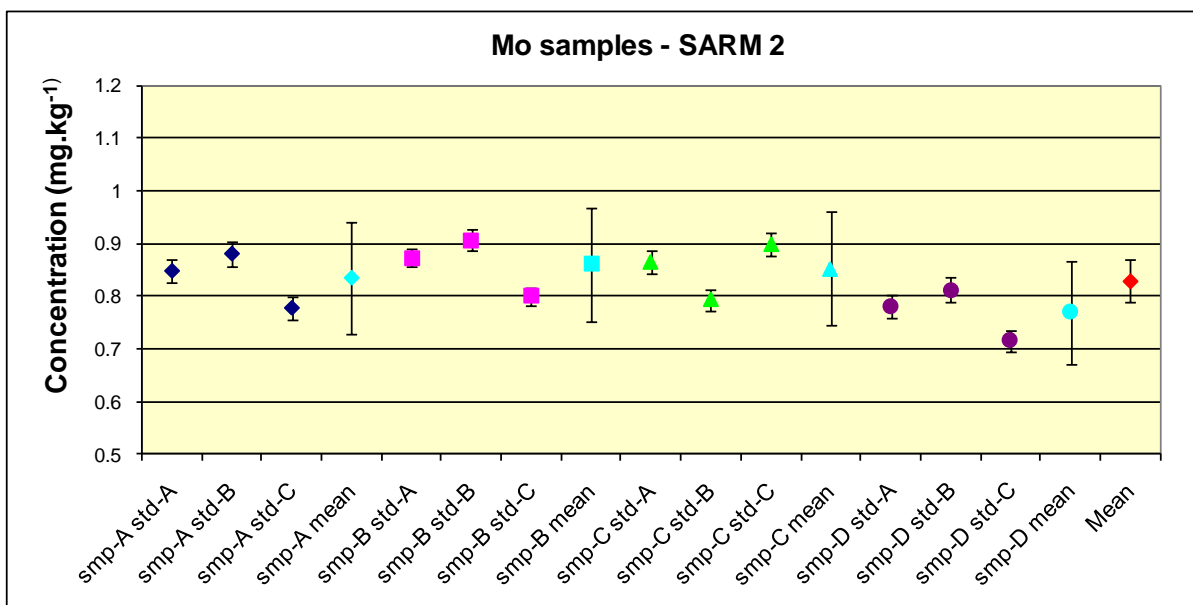


Figure 6.15: The individual determinations and mean result for Mo in SARM 2

The final result for Mo in SARM 2 was $0.830 \pm 0.040 \text{ mg.kg}^{-1}$ ($k=2$) with a relative uncertainty of 4.8%.

Cadmium

Due to the many possibilities for polyatomic and other interferences, two sets of isotope ratio determinations were performed for Cd in SARM 2 ($^{112}\text{Cd}/^{111}\text{Cd}$ and $^{114}\text{Cd}/^{111}\text{Cd}$). A t -test performed on the data from the two isotope ratios showed that there was a significant difference between the two ratios. Due to the fact that the experimental design was not optimised for the ratio of $^{114}\text{Cd}/^{111}\text{Cd}$, the calculated uncertainties of the Cd results from the $^{114}\text{Cd}/^{111}\text{Cd}$ ratio determinations were approximately three times the uncertainties calculated for the results from the $^{112}\text{Cd}/^{111}\text{Cd}$ ratio determinations (see **Table 6.7**).

The isotope ratio determinations were also corrected for the isobaric interference of ^{112}Sn . For the Cd standards in the SARM 2 experiment, the determined ratios were close to the ratio calculated from the published IUPAC abundances, but the ratios for the samples were approximately 5 times higher. There are several possible reasons for this discrepancy in the expected isotope ratios determined for the SARM 2 samples.

When the intensity data for the Cd isotopes were studied it was found that the signal of the ^{112}Sn interference was very large compared to the ^{112}Cd signal and even more so when compared to the ^{111}Cd signal. From the intensity data for the different isotopes, it was finally concluded that due to the very low ^{111}Cd signal and the very large ^{112}Sn signal, proper interference corrections could not be calculated.

The possibility of polyatomic interference from $^{95}\text{Mo}^{16}\text{O}$ was disregarded, because typically if this interference was present in the sample the calculated ratios for $^{112}\text{Cd}/^{111}\text{Cd}$, as well as $^{114}\text{Cd}/^{111}\text{Cd}$ would have been lower than the ratios for the standards as well as the ratio calculated from the IUPAC abundances, because the ^{111}Cd signal would have been higher due to the interference. The multi-element standard that was also used during the study (Certified ICP-MS Calibration Standard M, Lot no. 510217, High Purity Standards, USA) had equal concentrations of Cd and Mo and also did not show any $^{95}\text{Mo}^{16}\text{O}$ interference.

Very good results were calculated for Cd in SARM 2, even at these low concentration levels. The combined standard uncertainties calculated for the individual determinations, compared well with the standard deviation of the mean.

The final result for Cd in SARM 2 was $18.2 \pm 2.3 \mu\text{g}\cdot\text{kg}^{-1}$ ($k=2$), with a relative uncertainty of 12.6%.

Table 6.7: Comparison between the two ratio experiments for Cd in SARM 2

		¹¹² Cd/ ¹¹¹ Cd		¹¹⁴ Cd/ ¹¹¹ Cd	
		Concentration μg.kg ⁻¹	Standard uncertainty (u _c) μg.kg ⁻¹	Concentration μg.kg ⁻¹	Standard uncertainty (u _c) μg.kg ⁻¹
smp-spkA	std-spkA	18.2	1.1	14	4
	std-spkB	18.2	1.1	14	4
	std-spkC	18.2	1.1	14	4
smp-spkB	std-spkA	18.2	1.1	14	4
	std-spkB	18.2	1.1	14	4
	std-spkC	18.2	1.1	14	4
smp-spkC	std-spkA	18.2	1.1	14	4
	std-spkB	18.2	1.1	14	4
	std-spkC	18.2	1.1	14	4
smp-spkD	std-spkA	18.2	1.1	14	4
	std-spkB	18.2	1.1	14	4
	std-spkC	18.2	1.1	14	4
Mean		18.2		14	
Standard deviation		0.8		5	
Expanded uncertainty (k=2)		2.3		12	
Relative uncertainty (%)		12.6		53.5	

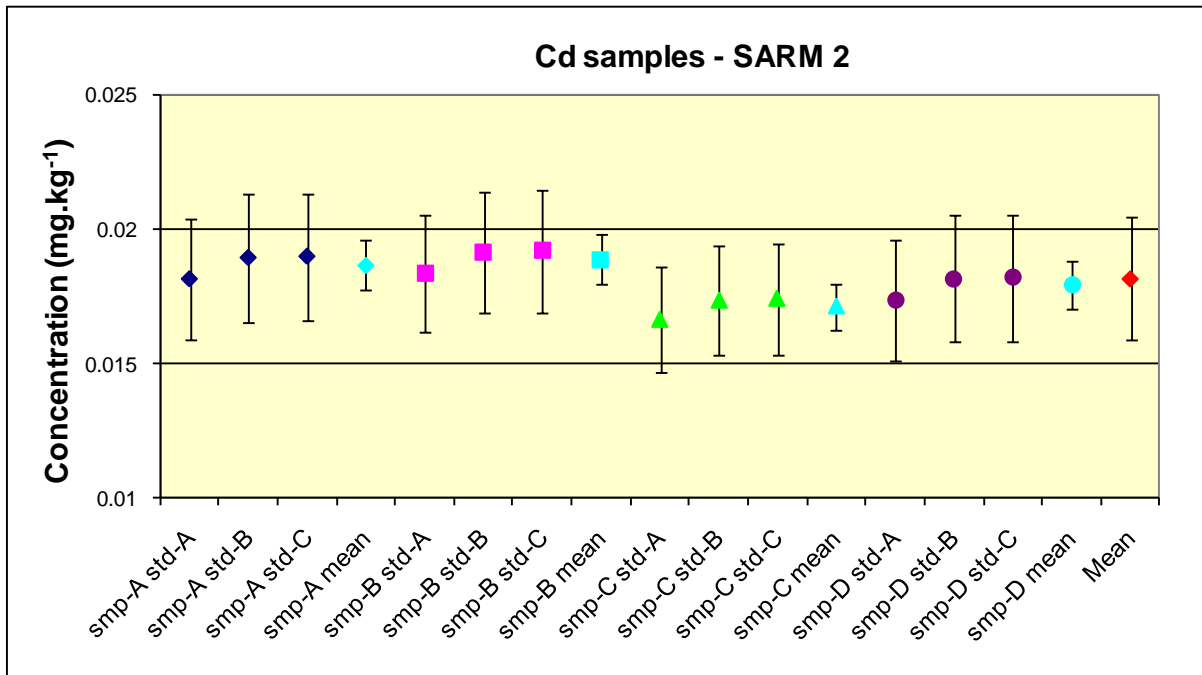


Figure 6.16: The individual determinations and mean result for Cd in SARM 2

Lead

The lower results for the digested primary assay standard blend compared to the two blends that were prepared without microwave digestion treatment, were again clearly seen in the lower results for the first determination of every sample for Pb in SARM 2. From **Table 6.2**, the difference between the different blends appears to be the most pronounced for Pb in SARM 2. However, a *t*-test showed that the difference noted between the results for the digested blend and the other two blends for Pb, Zn or Cu is not significant.

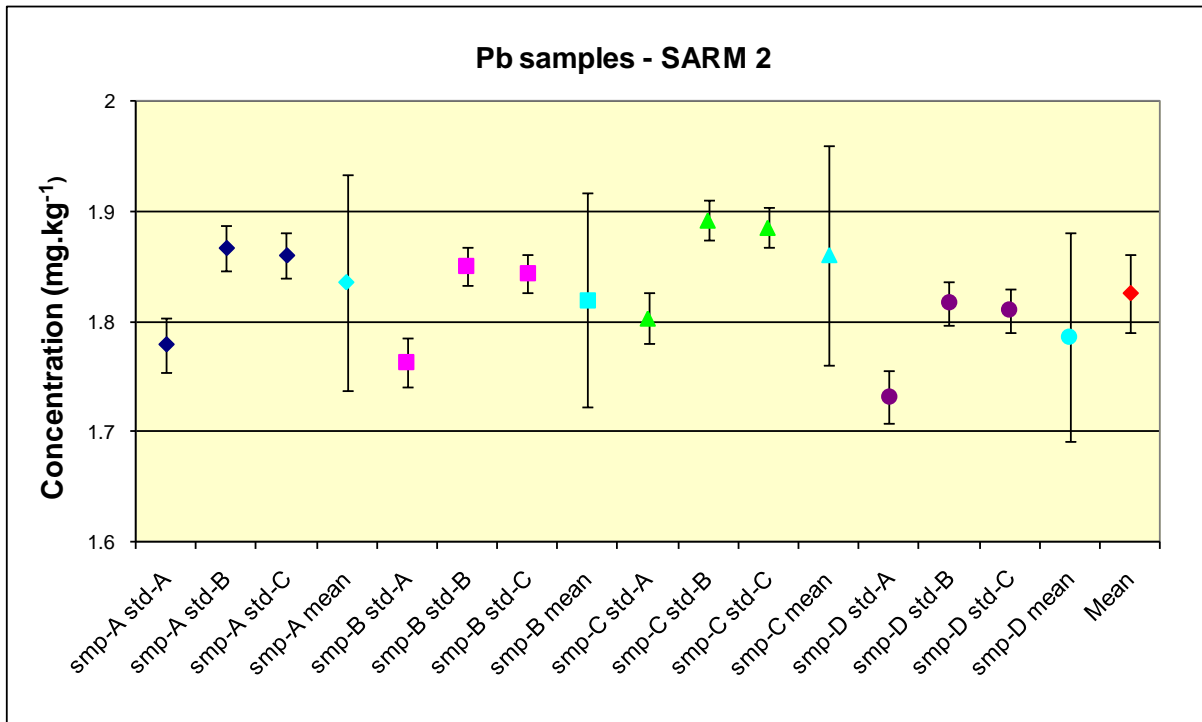


Figure 6.17: The individual determinations and mean result for Pb in SARM 2

The final result for Pb in SARM 2 was $1.826 \pm 0.036 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 2.0%.

SARM 3

Barium

Ba in SARM 3 was measured in low resolution mode and two isotope ratios were determined ($^{137}\text{Ba}/^{135}\text{Ba}$ and $^{138}\text{Ba}/^{135}\text{Ba}$). The results from the two experiments were comparable, a *t*-test performed on the data showed no significant difference, but once again because the experimental design was optimised for the $^{137}\text{Ba}/^{135}\text{Ba}$ ratio, the calculated measurement uncertainty was a factor of 2 smaller than the uncertainties calculated for the results of the $^{138}\text{Ba}/^{135}\text{Ba}$ experiment (see **Table 6.8**).

The mean result for Ba in SARM 3 was determined from a combination of 3 sample blends and 3 primary assay standard blends for a total of 9 determinations. All 3 primary assay standard blends were prepared without microwave digestion. The standard deviation of the mean of the results was smaller than the combined standard uncertainties calculated for the individual determinations. This leads to the conclusion that the major uncertainty contribution for the result is associated with the measurement method rather than the variations between the sample and standard blends.

Table 6.8: Comparison between the two ratio experiments for Ba in SARM 3

		¹³⁷ Ba/ ¹³⁵ Ba		¹³⁸ Ba/ ¹³⁵ Ba	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	413.2	1.6	412.3	2.7
	std-spkB	413.5	1.7	413.1	3.4
	std-spkC	413.5	1.6	407.6	3.2
smp-spkB	std-spkA	412.7	1.6	416.5	2.7
	std-spkB	413.0	1.7	417.3	3.4
	std-spkC	413.0	1.6	411.8	3.2
smp-spkC	std-spkA	413.6	1.5	417.2	2.6
	std-spkB	413.9	1.6	418.0	3.3
	std-spkC	413.9	1.5	412.6	3.1
Mean		413.4		414.0	
Standard deviation		0.4		3.4	
Expanded uncertainty (k=2)		3.2		6.6	
Relative uncertainty (%)		0.8		1.6	

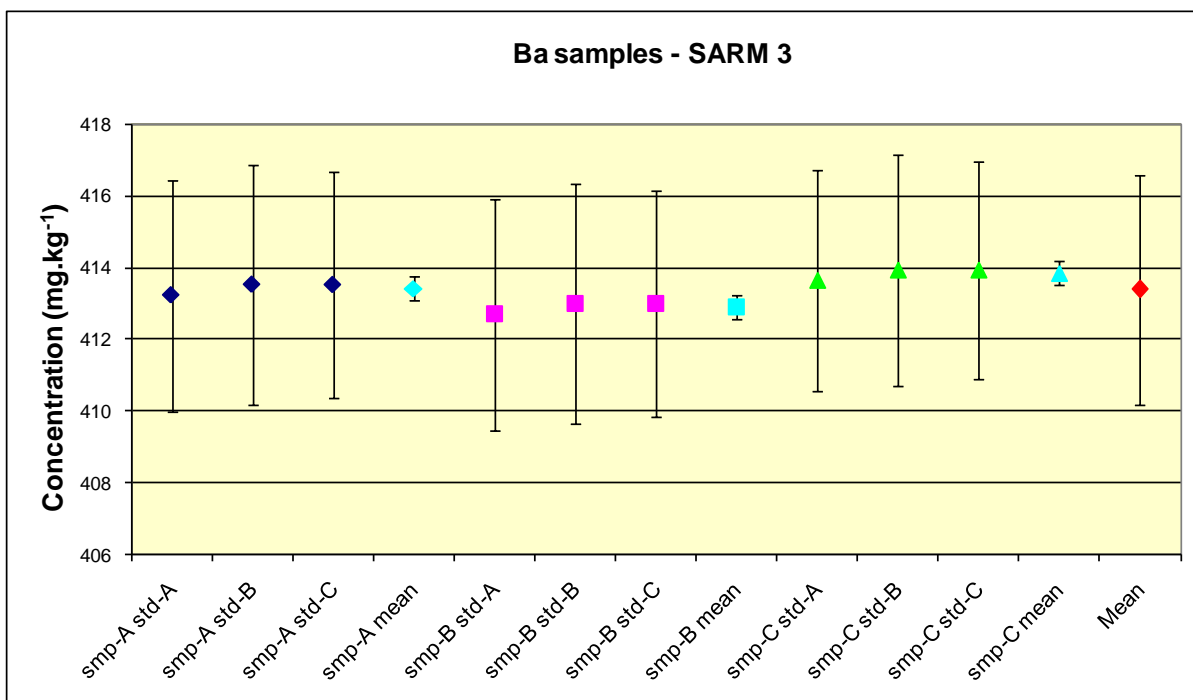


Figure 6.18: The individual determinations and mean result for Ba in SARM 3

The final result for Ba in SARM 3 was $413.4 \pm 3.3 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 0.8%.

Strontium

The concentration of Sr in SARM 3 was too high to facilitate spiking of the weighed sample aliquot. The ^{86}Sr spike was therefore only added to the diluted sample after digestion. The isotope ratios was measured in low resolution and corrected off-line for the isobaric interference of ^{86}Kr in the argon carrier gas.

The mean result for Sr in SARM 3 was calculated from 12 determinations. There was one extra sample blend, because the spiking with the ^{86}Sr standard was performed after digestion to the diluted sample, an extra aliquot was taken out of the pure sample solution for an additional sample blend. As can be seen from the results in **Figure 19**, the magnitude of the combined standard uncertainties is comparable to the magnitude of the standard deviation of the mean of the results, and both contribute equally to the combined standard uncertainty of the mean result.

The final result for Sr in SARM 3 was $4728 \pm 60 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 1.3%.

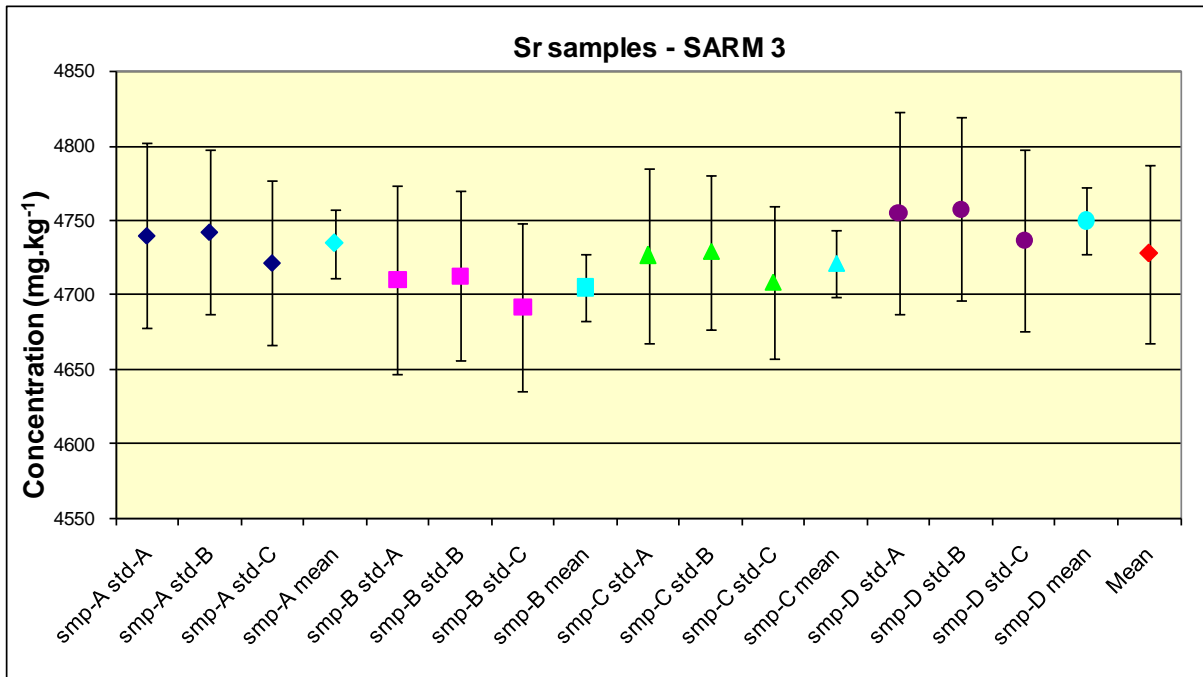


Figure 6.19: The individual determinations and mean result for Sr in SARM 3

Zinc

Table 6.9: Comparison between the two ratio experiments for Zn in SARM 3

		$^{66}\text{Zn}/^{67}\text{Zn}$		$^{68}\text{Zn}/^{67}\text{Zn}$	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	434.4	2.3	435.3	4.3
	std-spkB	435.5	2.4	435.2	3.8
	std-spkC	436.3	2.4	434.8	4.0
smp-spkB	std-spkA	426.2	2.7	427.0	3.8
	std-spkB	427.3	2.8	426.9	3.2
	std-spkC	428.1	2.8	426.5	3.5
smp-spkC	std-spkA	427.4	2.3	430.4	4.1
	std-spkB	428.5	2.4	430.3	3.6
	std-spkC	429.3	2.4	429.9	3.8
smp-spkD	std-spkA	427.9	1.9	430.7	4.2
	std-spkB	429.0	2.0	430.6	3.8
	std-spkC	429.8	2.0	430.2	3.9
Mean		430.0		430.6	
Standard deviation		3.4		3.1	
Expanded uncertainty (k=2)		5.2		7.9	
Relative uncertainty (%)		1.2		1.8	

The isotope ratio determinations for Zn in SARM 3 was also performed in medium resolution mainly due to the interference of the doubly charged Ba⁺⁺ as discussed in **Chapter 3**. Two isotope ratios were determined for Zn in SARM 3, i.e. $^{66}\text{Zn}/^{67}\text{Zn}$ and $^{68}\text{Zn}/^{67}\text{Zn}$. The results from the two experiments were very comparable, because although the experimental design was optimised for the $^{66}\text{Zn}/^{67}\text{Zn}$ ratio measurements, the difference between the two ratios is small (see **Table 6.9**).

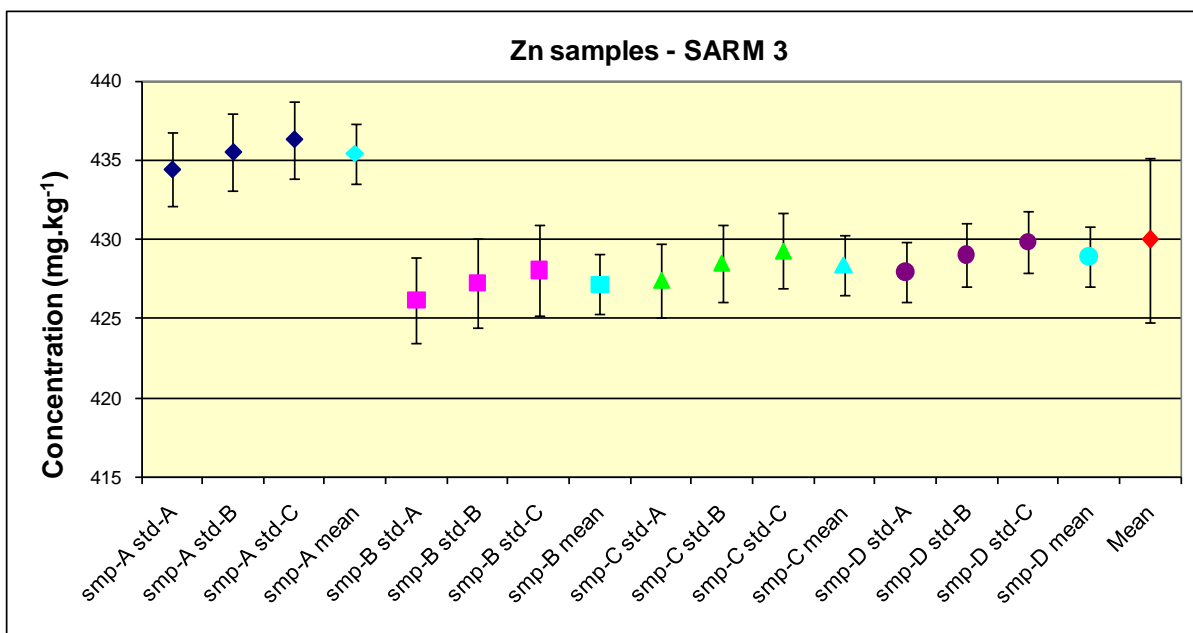


Figure 6.20: The individual determinations and mean result for Zn in SARM 3

The spiking of Zn in SARM 3 was also performed after digestion, because the concentration of Zn in SARM 3 was too high to facilitate spiking of the pure sample before digestion. As for Sr, an additional sample and spike blend was prepared for Zn in SARM 3 from the solution of the pure digested sample. However, in the case of Zn the results for the additional spike were higher than for the other three sample blends (see **Figure 6.20**).

The final result for Zn in SARM 3 was $430.0 \pm 5.2 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 1.2%.

Copper

The isotope ratio determinations for Cu were performed in medium resolution mode due to polyatomic interferences as discussed in **Chapter 3**.

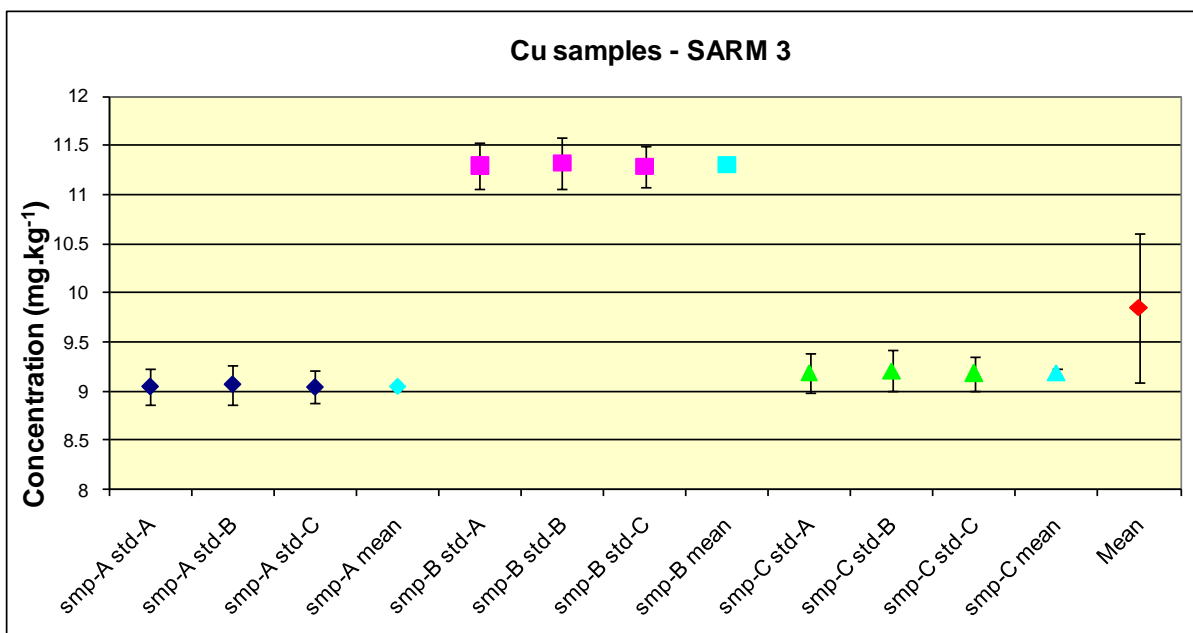


Figure 6.21: The individual determinations and mean result for Cu in SARM 3

One of the three sample blends of Cu in SARM 3 gave a higher result compared to the other two. This could be due to heterogeneity of the sample in the sample bottle and might require a full homogeneity study of the remaining material to also determine the adequate sub-sample size.

The final result for Cu in SARM 3 was $9.85 \pm 0.76 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 7.7%.

Nickel

The isotope ratio determinations for Ni in SARM 3 were also performed in medium resolution due to polyatomic interferences as discussed in **Chapter 3**. The mean result was determined from 9 determinations resulting from combinations of 3 sample blends and 3 primary assay standard blends.

Two isotope ratios were determined for Ni in SARM 3, i.e. $^{60}\text{Ni}/^{61}\text{Ni}$ and $^{62}\text{Ni}/^{61}\text{Ni}$. The experimental design for Ni in SARM 3 was optimised for the $^{60}\text{Ni}/^{61}\text{Ni}$ ratio, and because the two ratios are very different the precisions of the two experiments also differed greatly (see **Table 6.10**).

A higher result was also observed for one of the sample blends for Ni in SARM 3, but in this instance it was a different sample from Cu. These differences are probably due to inhomogeneity of the sample in the sample bottle and might require a full homogeneity study of the remaining material to also determine the adequate sub-sample size.

The final result for Ni in SARM 3 was $1.54 \pm 0.27 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 17.5 %.

Table 6.10: Comparison between the two ratio experiments for Ni in SARM 3

		$^{60}\text{Ni}/^{61}\text{Ni}$		$^{62}\text{Ni}/^{61}\text{Ni}$	
		Concentration mg.kg^{-1}	Standard uncertainty (u_c) mg.kg^{-1}	Concentration mg.kg^{-1}	Standard uncertainty (u_c) mg.kg^{-1}
smp-spkA	std-spkA	2.08	0.04	2.03	0.07
	std-spkB	2.07	0.04	2.02	0.07
	std-spkC	2.04	0.04	2.00	0.07
smp-spkB	std-spkA	1.31	0.02	1.30	0.04
	std-spkB	1.31	0.02	1.30	0.04
	std-spkC	1.29	0.02	1.28	0.04
smp-spkC	std-spkA	1.28	0.02	1.20	0.04
	std-spkB	1.28	0.02	1.20	0.04
	std-spkC	1.26	0.02	1.18	0.04
Mean		1.54		1.50	
Standard deviation		0.39		0.39	
Expanded uncertainty (k=2)		0.26		0.28	
Relative uncertainty (%)		17.1		18.6	

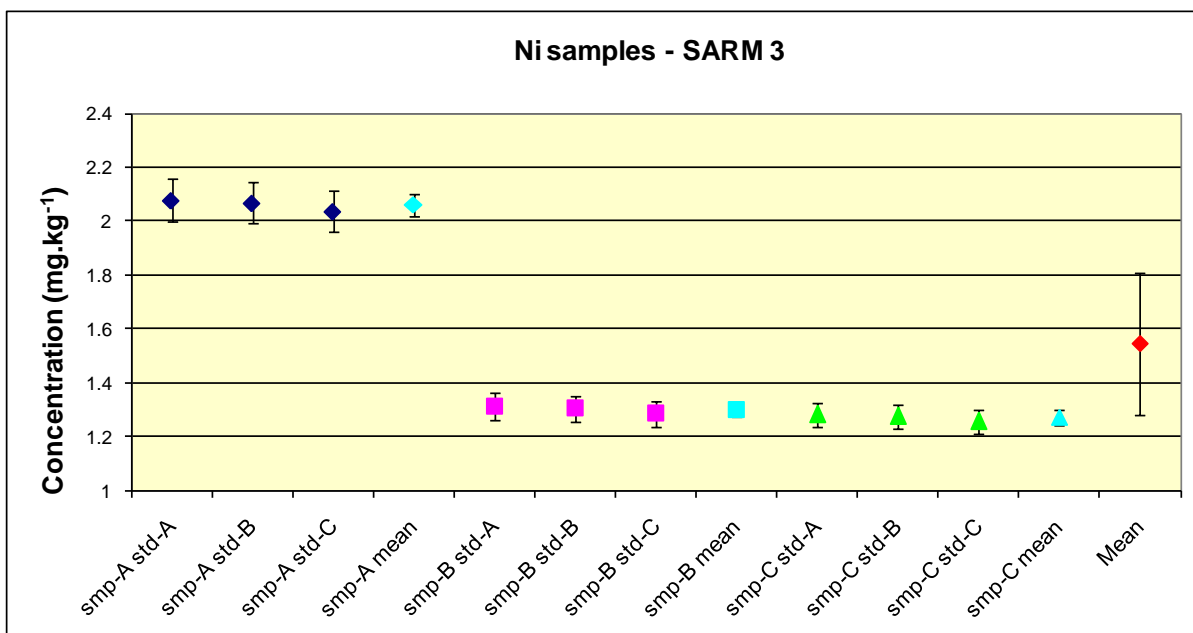


Figure 6.22: The individual determinations and mean result for Ni in SARM 3

Molybdenum

The isotope ratio determinations for Mo in SARM 3 were performed in low resolution mode. The mean of the results were calculated from 9 determinations consisting of a combination of 3 sample and 3 primary assay standard blends.

The first sample blend for Mo in SARM 3 also gave a higher result from the other two blends similarly to Ni (see **Figures 6.23** and **6.22**). The combined standard uncertainties calculated for the individual determinations were also higher for the first sample. These differences are probably due to inhomogeneity of the sample in the sample bottle and might require a full homogeneity study of the remaining material to also determine the adequate sub-sample size.

The final result for Mo in SARM 3 was $1.82 \pm 0.41 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 22.5%.

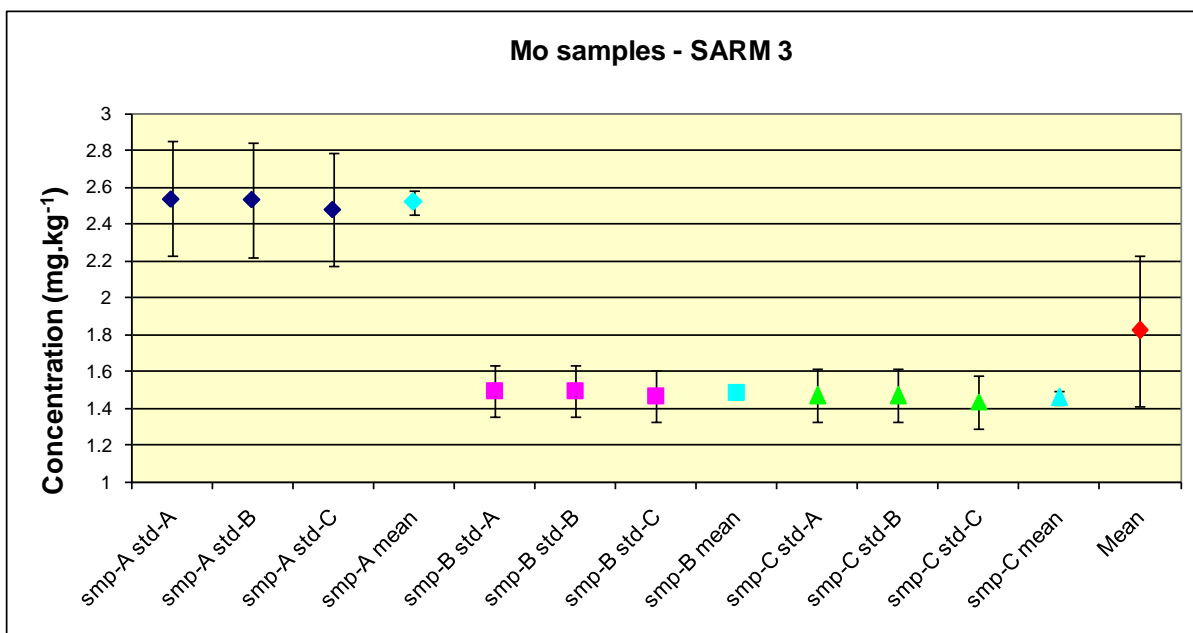


Figure 6.23: The individual determinations and mean result for Mo in SARM 3

Cadmium

Due to some interference that could not be identified or resolved, Cd in SARM 3 could not be determined during the ID-ICP-MS experiment.

Lead

The results for the 9 determinations of Pb in SARM 3 show good agreement. Although the results for the third sample blend were slightly lower than for the other two there were still good overlap of the calculated combined standard uncertainties between all the determinations.

The final result for Pb in SARM 3 was $46.04 \pm 0.66 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 1.4%.

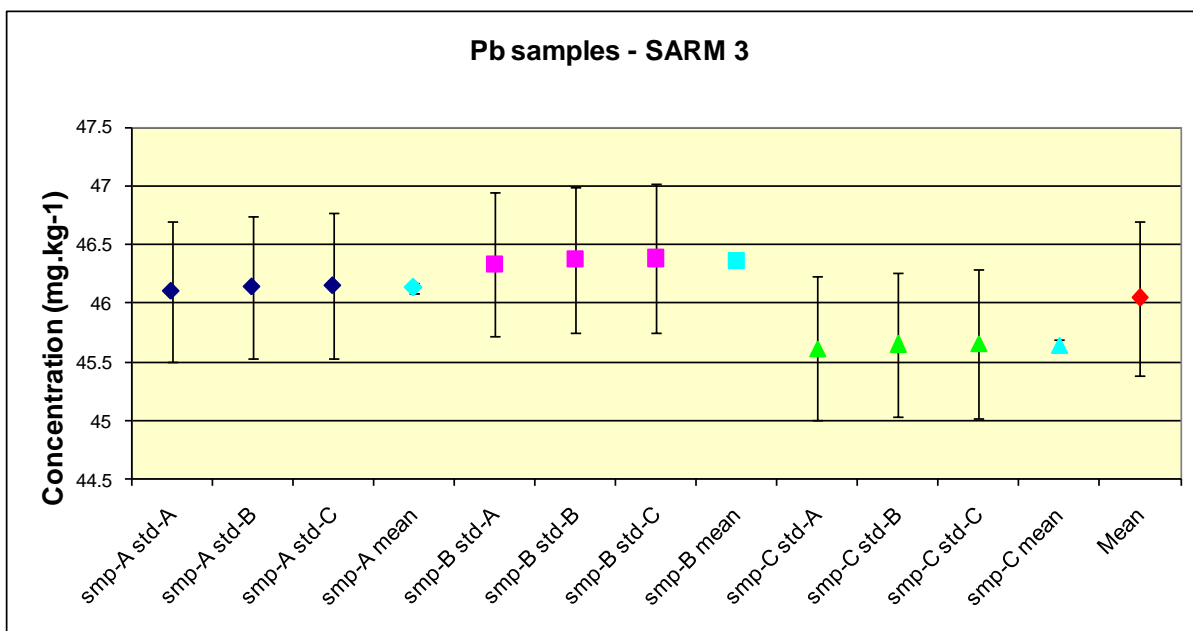


Figure 6.24: The individual determinations and mean result for Pb in SARM 3

SARM 4

Barium

Ba in SARM 4 was measured in low resolution mode and two isotope ratio experiments were carried out ($^{137}\text{Ba}/^{135}\text{Ba}$ and $^{138}\text{Ba}/^{135}\text{Ba}$) as for SARM 3. A *t*-test showed that there was a significant difference between the two experiments (see **Table 6.11**). The experimental design was optimised for the $^{137}\text{Ba}/^{135}\text{Ba}$ ratio.

The mean result for Ba in SARM 4 was determined from a combination of 3 sample blends and 3 primary assay standard blends for a total of 9 determinations. All three primary assay standard blends were prepared without microwave digestion. The standard deviation of the mean of the results was again much smaller than the combined standard uncertainties calculated for the individual determinations. This leads to the conclusion that the major uncertainty contribution for the result is associated with the measurement method rather than the variations between the samples and standards. An additional conclusion from the experimental results is that the Ba is very homogeneous in the sample bottle used for the experiment.

The final result for Ba in SARM 4 was $82.9 \pm 1.1 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 1.3%.

Table 6.11: Comparison between the two ratio experiments for Ba in SARM 4

		¹³⁷ Ba/ ¹³⁵ Ba		¹³⁸ Ba/ ¹³⁵ Ba	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp- spkA	std-spkA	82.8	0.5	87.3	0.8
	std-spkB	82.8	0.4	87.8	0.8
	std-spkC	82.8	0.5	87.7	0.8
smp- spkB	std-spkA	82.9	0.5	87.4	0.5
	std-spkB	82.9	0.5	88.0	0.6
	std-spkC	82.9	0.6	87.8	0.5
smp- spkC	std-spkA	82.9	0.5	83.1	0.5
	std-spkB	83.0	0.5	83.7	0.7
	std-spkC	82.9	0.6	83.5	0.6
Mean		82.9		86.3	
Standard deviation		0.1		2.1	
Expanded uncertainty		1.0		1.9	
Relative uncertainty (%) (k=2)		1.2		2.2	

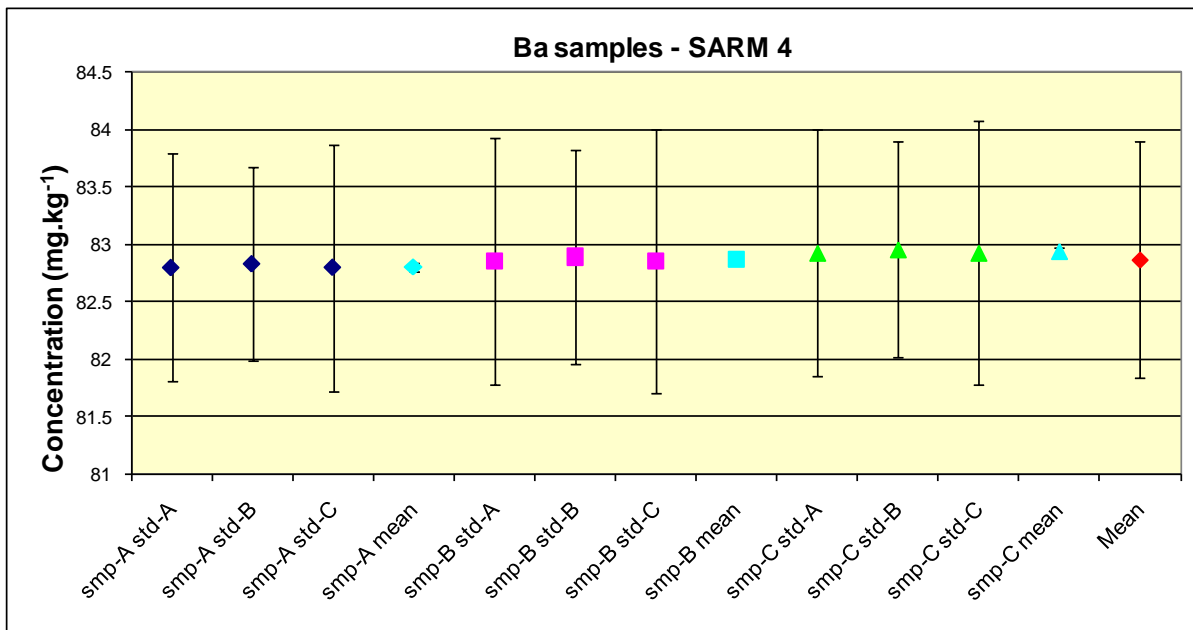


Figure 6.25: The individual determinations and mean result for Ba in SARM 4

Strontium

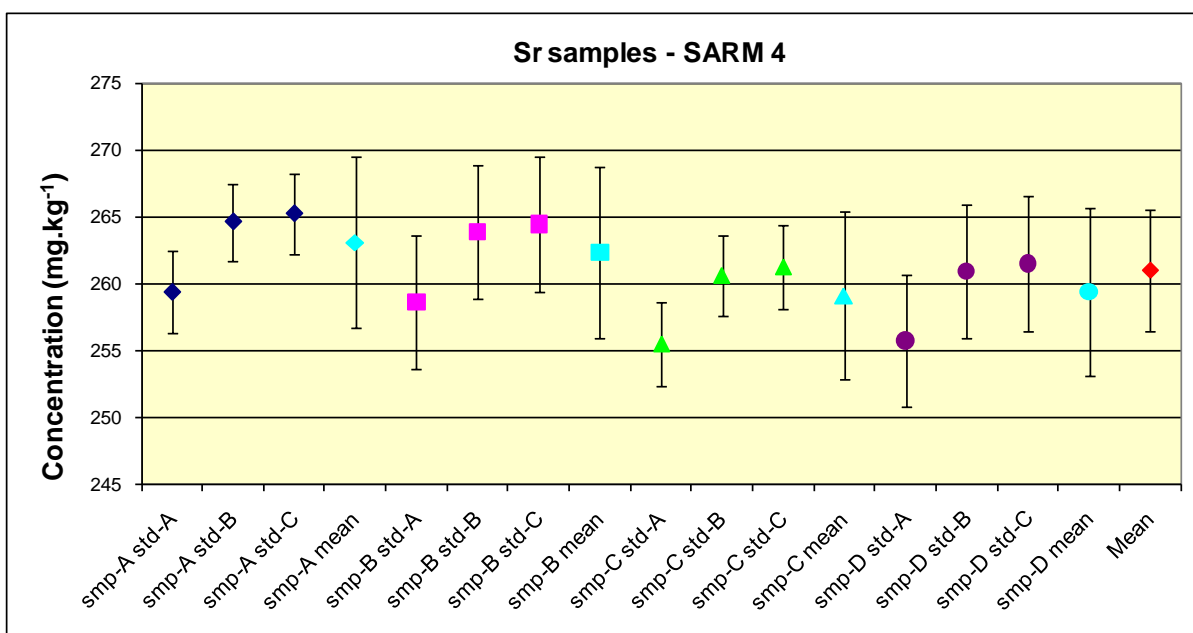


Figure 6.26: The individual determinations and mean result for Sr in SARM 4

The concentration of Sr in SARM 4 was also too high to facilitate spiking of the weighed sample aliquot. The ⁸⁶Sr spike was therefore only added to the diluted sample after digestion. The isotope ratios was measured in low resolution and corrected off-line for the isobaric interference of ⁸⁶Kr in the argon carrier gas.

The mean result for Sr in SARM 4 was calculated from 12 determinations. There was one extra sample blend, because the spiking with the ^{86}Sr standard was performed after digestion to the diluted sample, an extra aliquot was taken out of the pure sample solution, for an additional sample blend. As can be seen from the results in **Figure 6.26**, the results from the four sample blends were comparable. However, the first determination of every sample blend was lower every time. This was as a result of the first primary assay standard blend that gave lower results compared to the other two (see **Figure 6.27**).

The final result for Sr in SARM 4 was $260.9 \pm 4.6 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 1.8%.

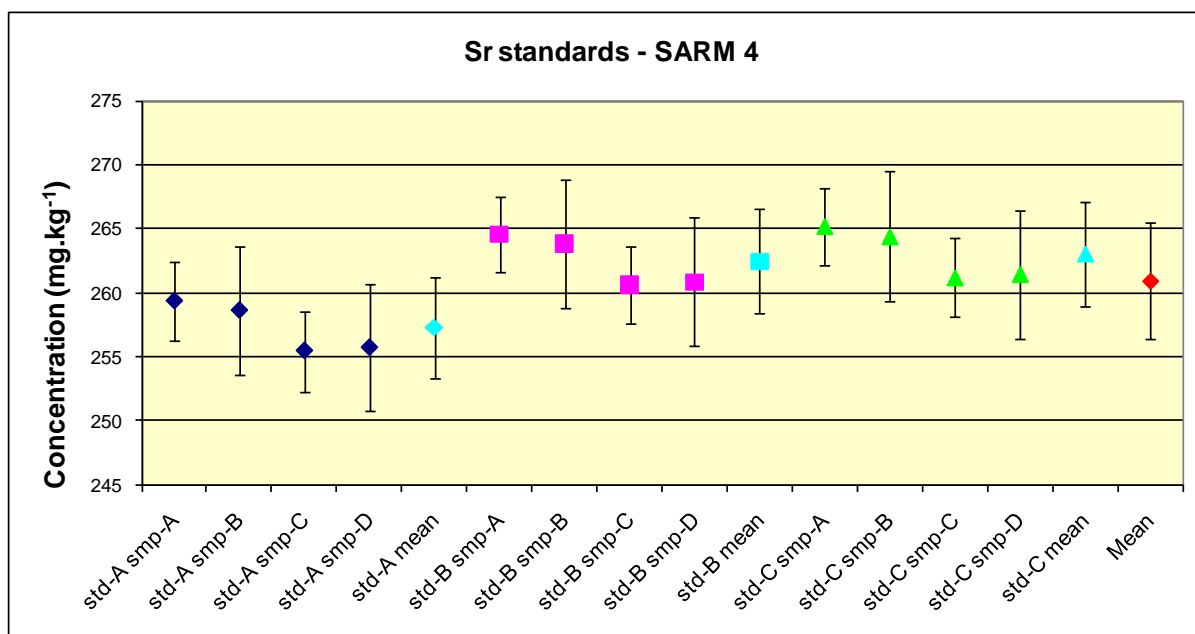


Figure 6.27: The individual determinations in relation to the primary assay standard blends for Sr in SARM 4

Zinc

Table 6.12: Comparison between the two ratio experiments for Zn in SARM 4

		$^{66}\text{Zn}/^{67}\text{Zn}$		$^{68}\text{Zn}/^{67}\text{Zn}$	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	61.23	0.49	62.83	0.39
	std-spkB	61.49	0.44	62.90	0.41
	std-spkC	61.51	0.44	62.95	0.59
smp-spkB	std-spkA	61.34	0.47	63.02	0.44
	std-spkB	61.60	0.43	63.09	0.45
	std-spkC	61.62	0.43	63.14	0.62
smp-spkC	std-spkA	61.14	0.47	62.76	0.43
	std-spkB	61.39	0.43	62.84	0.45
	std-spkC	61.42	0.43	62.89	0.61
Mean		61.42		62.93	
Standard deviation		0.16		0.13	
Expanded uncertainty		0.90		1.00	
Relative uncertainty (%) (k=2)		1.5		1.6	

The isotope ratio determinations for Zn in SARM 4 were also performed in medium resolution mainly due to the interference of the doubly charged Ba⁺⁺ as discussed in **Chapter 3**. Two isotope ratios were determined for Zn in SARM 4, i.e. $^{66}\text{Zn}/^{67}\text{Zn}$ and $^{68}\text{Zn}/^{67}\text{Zn}$. The results from the two experiments were very comparable, because although the experimental design was optimised for the $^{66}\text{Zn}/^{67}\text{Zn}$ ratio measurements the difference between the two ratios is small (see **Table 12**).

The final result for Zn in SARM 4 was $61.42 \pm 0.91 \text{ mg.kg}^{-1}$ (k=2), with a relative uncertainty of 1.5%.

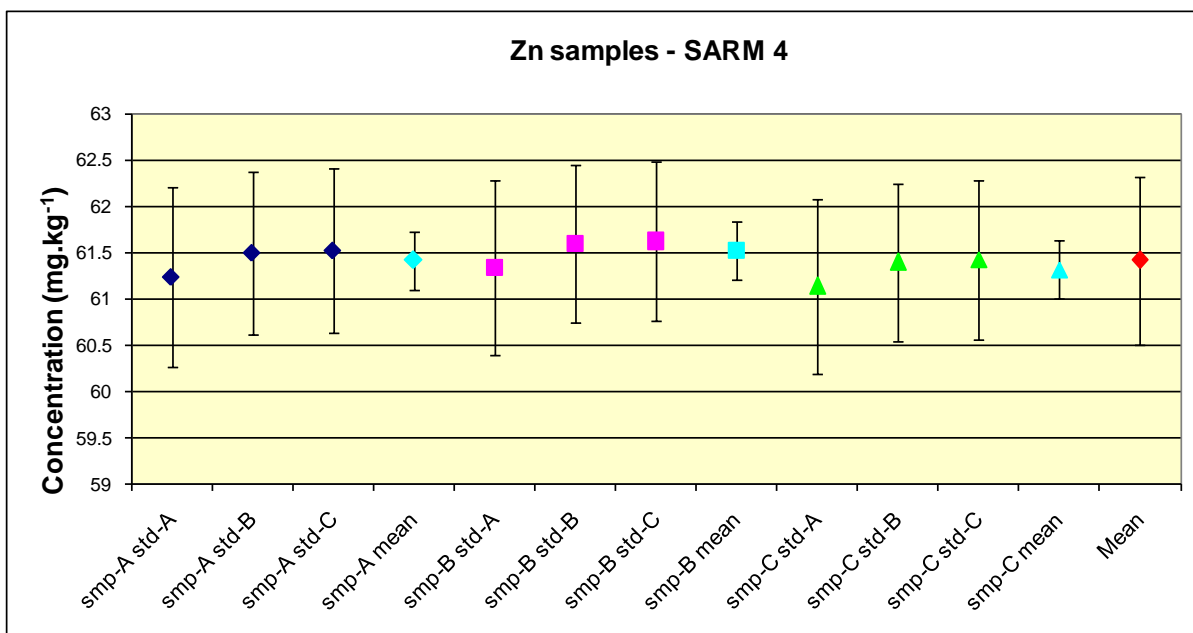


Figure 6.28: The individual determinations and mean result for Zn in SARM 4

Copper

The isotope ratio determinations for copper were performed in medium resolution mode due to polyatomic interferences as discussed in **Chapter 3**.

The standard deviation of the mean of the results was comparable to the combined standard uncertainties calculated for the individual determinations as can be seen in **Figure 6.29**.

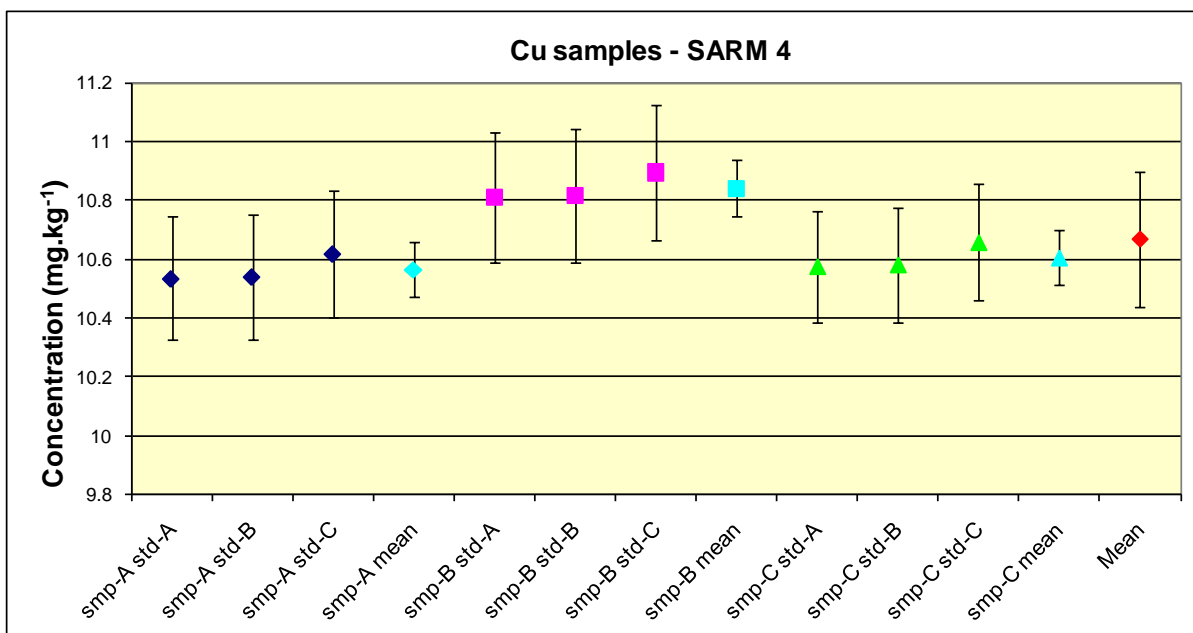


Figure 6.29: The individual determinations and mean result for Cu in SARM 4

The final result for Cu in SARM 4 was $10.67 \pm 0.23 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 2.2%.

Nickel

The isotope ratio determinations for Ni in SARM 4 were also performed in medium resolution due to polyatomic interferences as discussed in **Chapter 3**. The mean result was determined from 9 determinations, resulting from combinations of 3 sample blends and 3 primary assay standard blends.

Two isotope ratios were determined for Ni in SARM 4, i.e. $^{60}\text{Ni}/^{61}\text{Ni}$ and $^{62}\text{Ni}/^{61}\text{Ni}$, a t -test showed no significant difference between the two isotope ratio experiments. The experimental design for Ni in SARM 4 was optimised for the $^{62}\text{Ni}/^{61}\text{Ni}$ ratio to minimise the amount of ^{61}Ni spike to be added to the weighed sample aliquot, because the concentration of Ni in SARM 4 was quite high. The abundances for the three isotopes are very different; therefore the ratios measured in the two experiments were very different (see **Table 6.13**). The ratios determined for the blends in the $^{60}\text{Ni}/^{61}\text{Ni}$ experiment was close to 7.0 and for the $^{62}\text{Ni}/^{61}\text{Ni}$ experiment it was close to unity as for an optimised double isotope dilution analysis.

The final result for Ni in SARM 4 was $119.3 \pm 5.4 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 4.5%.

Table 6.13: Comparison between the two ratio experiments for Ni in SARM 4

		$^{62}\text{Ni}/^{61}\text{Ni}$		$^{60}\text{Ni}/^{61}\text{Ni}$	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp- spkA	std-spkA	119.8	2.6	112.5	1.8
	std-spkB	119.2	2.2	121.1	1.8
	std-spkC	120.3	3.4	121.1	1.9
smp- spkB	std-spkA	118.1	2.4	111.9	1.7
	std-spkB	117.5	2.0	120.5	1.7
	std-spkC	118.6	3.2	120.4	1.9
smp- spkC	std-spkA	120.2	2.5	111.6	1.8
	std-spkB	119.6	2.0	120.2	1.8
	std-spkC	120.7	3.2	120.2	1.9
Mean		119.3		117.7	
Standard deviation		1.1		4.3	
Expanded uncertainty		5.4		4.6	
Relative uncertainty (%) (k=2)		4.5		3.9	

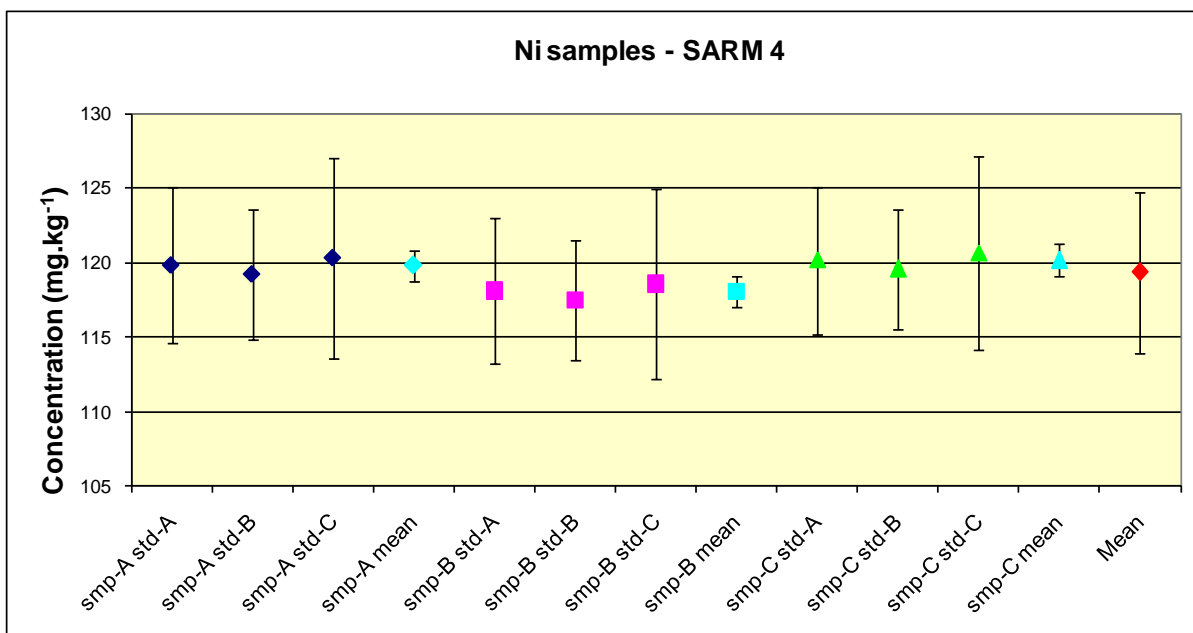


Figure 6.30: The individual determinations and mean result for Ni in SARM 4

Molybdenum

The isotope ratio determinations for Mo in SARM 4 were performed in low resolution mode. The mean of the results were calculated from 9 determinations consisting of a combination of 3 sample blends and 3 primary assay standard blends.

The variation between the three sample blends were larger, but still comparable to the combined standard uncertainties calculated for the individual determinations.

The final result for Mo in SARM 4 was $0.888 \pm 0.053 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 6.0%.

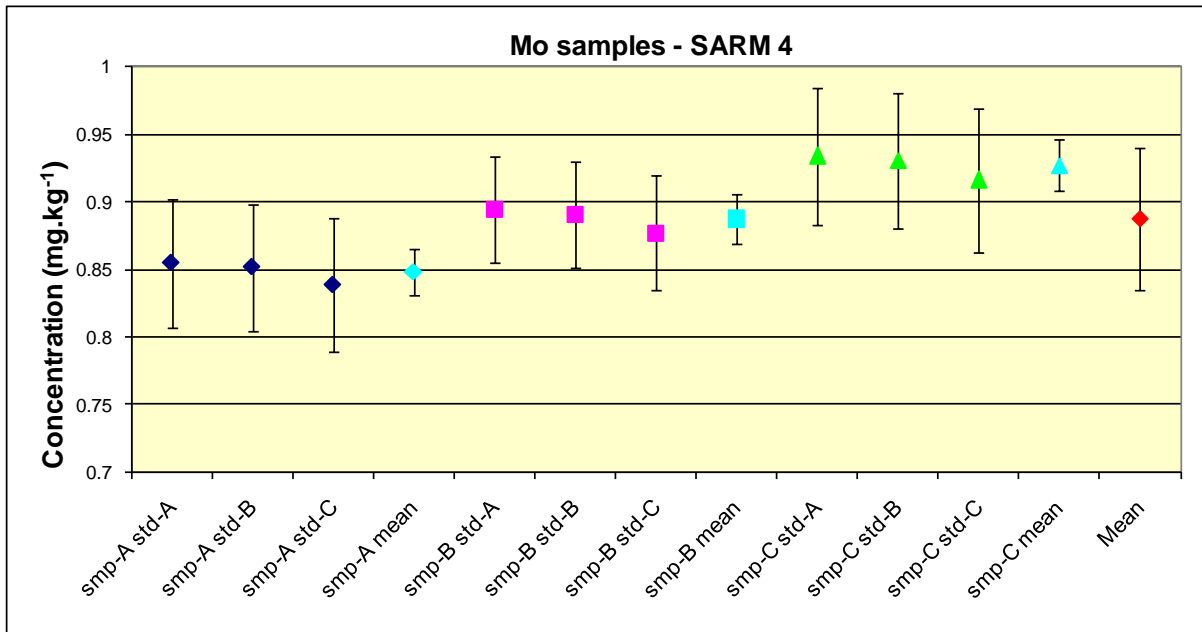


Figure 6.31: The individual determinations and mean result for Mo in SARM 4

Cadmium

The isotope ratio measurements for Cd in SARM 4 were performed in low resolution mode and were corrected off-line for the isobaric interference of ¹¹²Sn.

Very good results were calculated even at these low concentration levels. The combined standard uncertainties calculated for the individual determinations were the major uncertainty contribution to the final result. The standard deviation of the mean was a factor of two smaller than the combined standard uncertainties (see **Figure 6.32**).

The final result for Cd in SARM 4 was $87.9 \pm 3.2 \mu\text{g.kg}^{-1}$ ($k=2$), with a relative uncertainty of 3.6%.

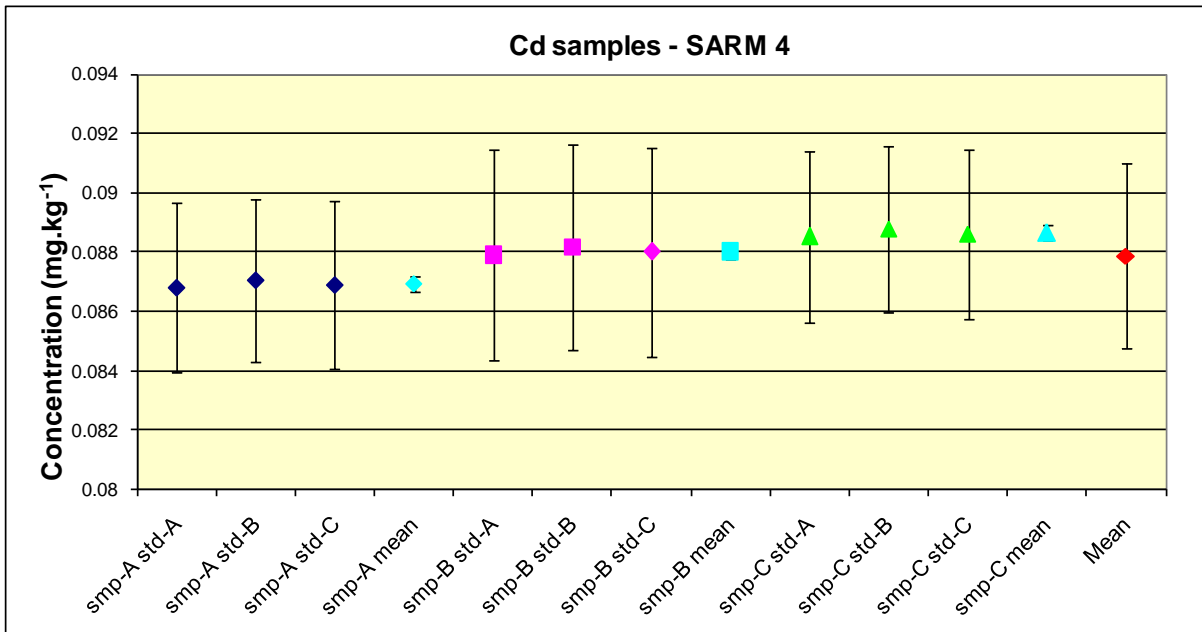


Figure 6.32: The individual determinations and mean result for Cd in SARM 4

Lead

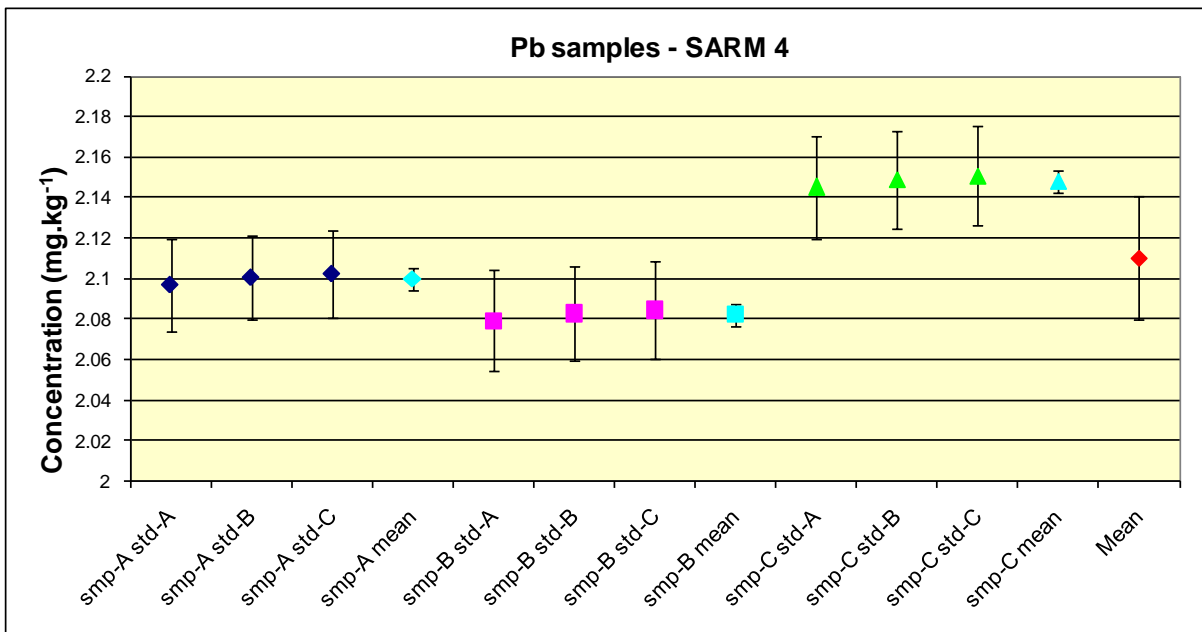


Figure 6.33: The individual determinations and mean result for Pb in SARM 4

The results for the 9 determinations of Pb in SARM 4 show good agreement. The results for the third sample blend were slightly higher than for the other two (see **Figure 6.33**). The standard deviation of the mean result was a factor of 2 larger than the combined standard uncertainties calculated for the individual results. This

difference is probably due to inhomogeneity of the sample in the sample bottle and might require a full homogeneity study of the remaining material to also determine the adequate sub-sample size.

The final result for Pb in SARM 4 was $2.110 \pm 0.031 \text{ mg.kg}^{-1}$ ($k=2$), with a relative uncertainty of 1.5%.

Chapter 7

Summary of the results and conclusions

7.1 Summary of the results

A compilation of data for SARM 2, SARM 3 and SARM 4, including the initial certification values, the published results since 1978, as well as the ID-ICP-MS results from the present study is presented in **Tables 7.1, 7.2 and 7.3**, respectively.

SARM 2

Although there is no sufficient basis for a correct statistical comparison between the data, certain observations on the data in **Table 7.1** for SARM2 can be made.

First, the initial certification values (Ba, Sr, Cu) do not have associated uncertainty statements. The values for Pb, Zn and Ni are only provisional and Mo and Cd are presented only with information on the range of expected concentrations.

Secondly, the published literature data for the majority of analytes in this study were either insufficient or exhibit a range of values too wide to facilitate a justifiable conclusion, or application of the robust statistics approach. Median values and median absolute deviations corrected for normally distributed data were only meaningful and calculated for Ba and Sr (see **Figures 7.1 to 7.6**). The expanded uncertainties associated with the median values are calculated for a level of confidence of 95.45%. The light blue bars in the figures are the individual results that were reported in the literature; on the x -axis the technique used is indicated. The median was calculated from these literature values.

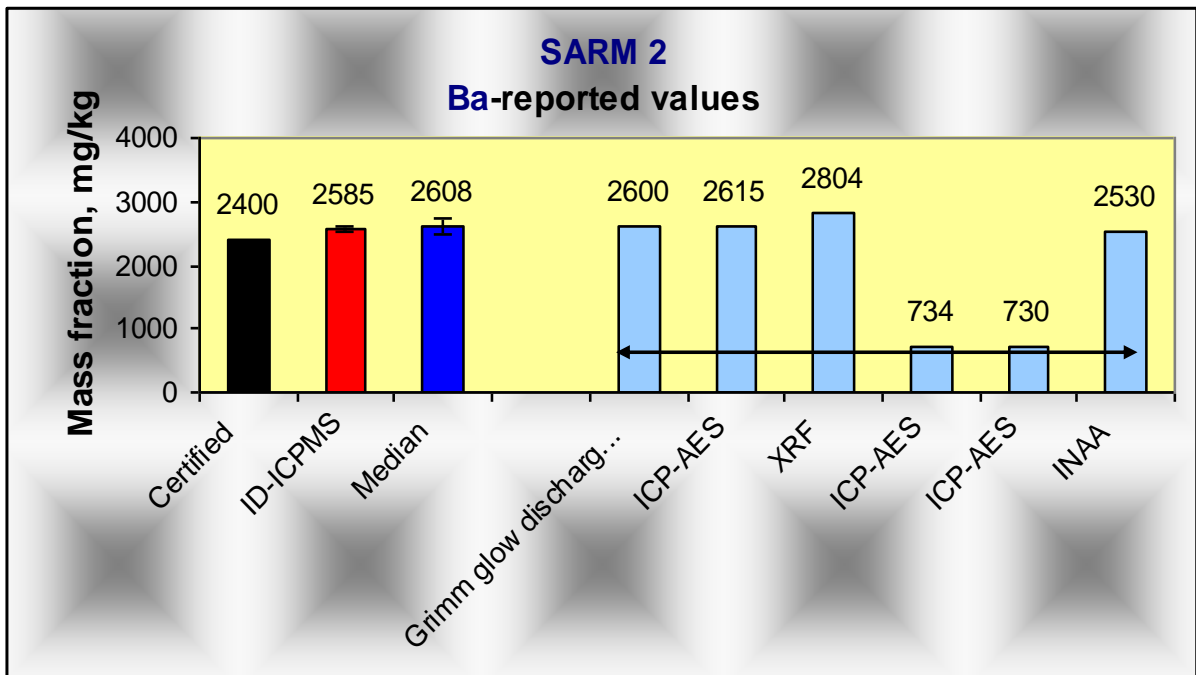


Figure 7.1: Summary of all the results for Ba in SARM 2

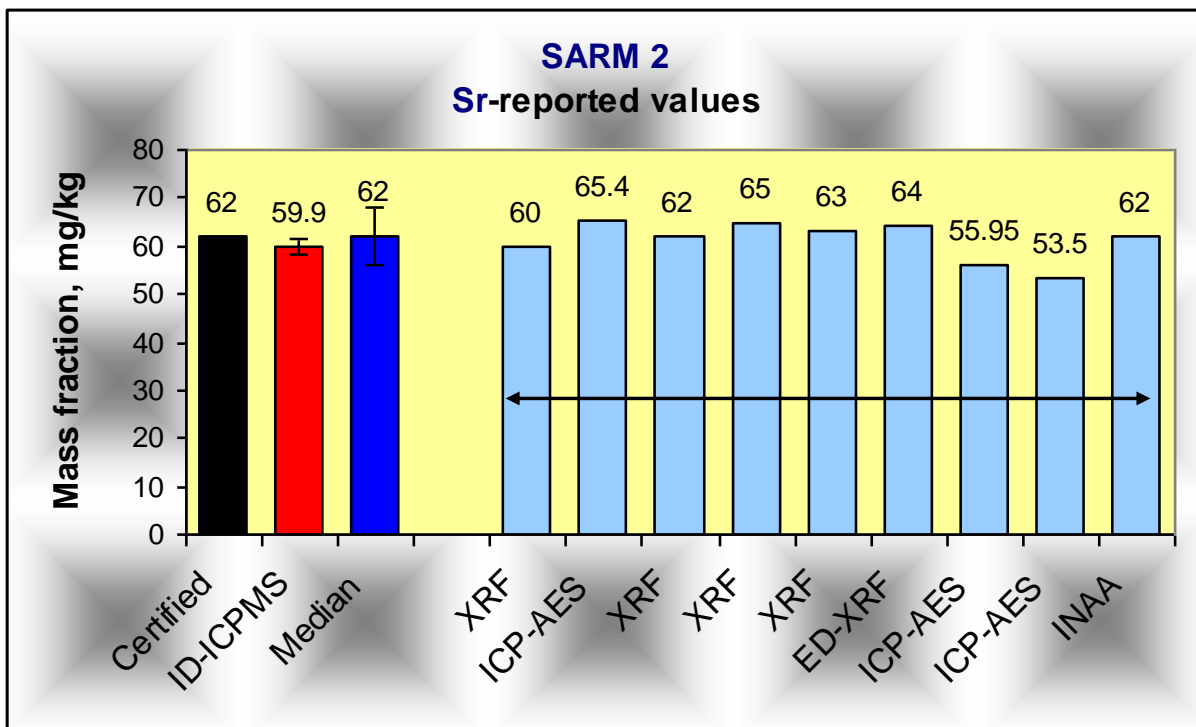


Figure 7.2: Summary of all the results for Sr in SARM 2

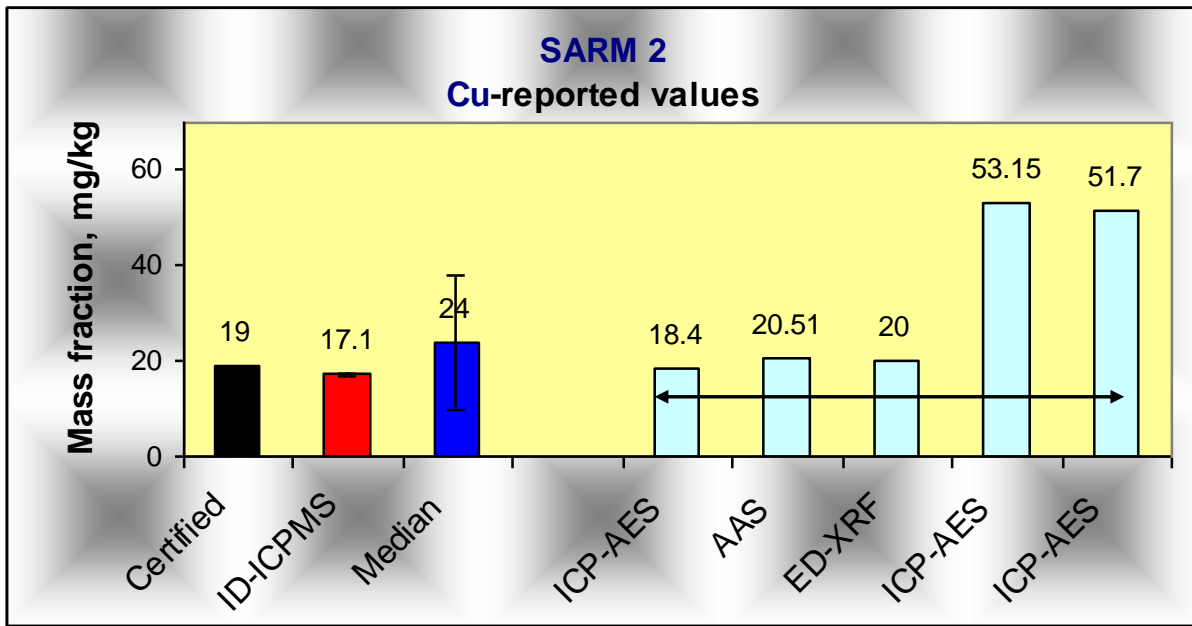


Figure 7.3: Summary of all the results for Cu in SARM 2

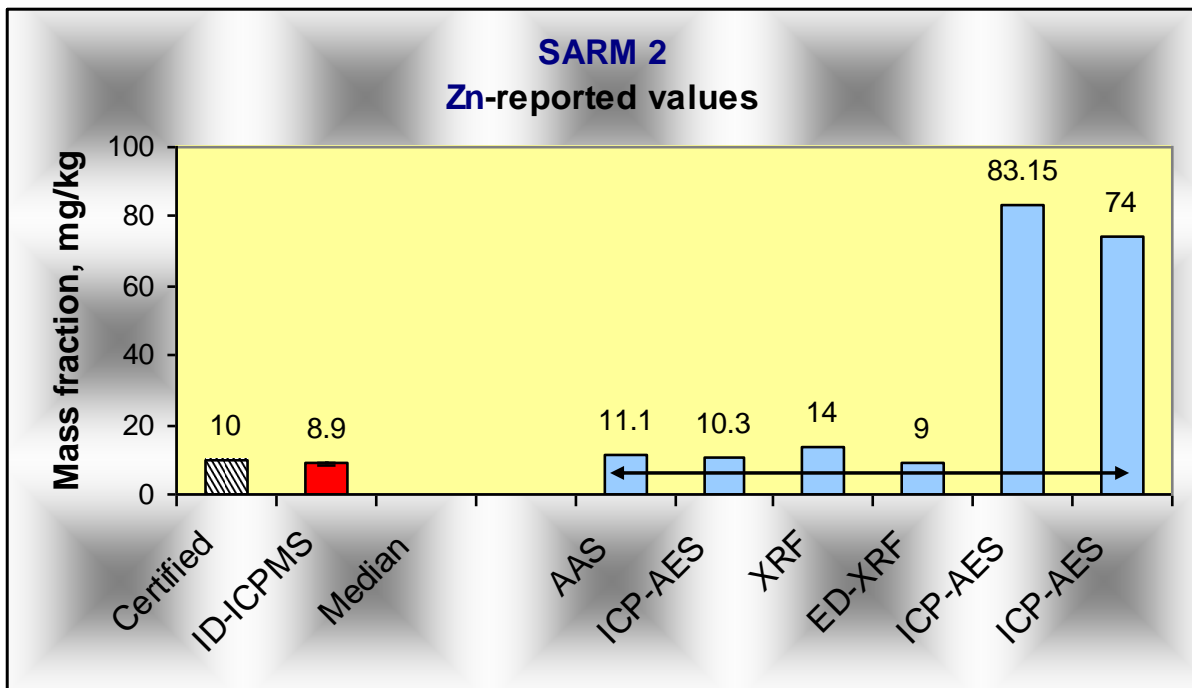


Figure 7.4: Summary of all the results for Zn in SARM 2

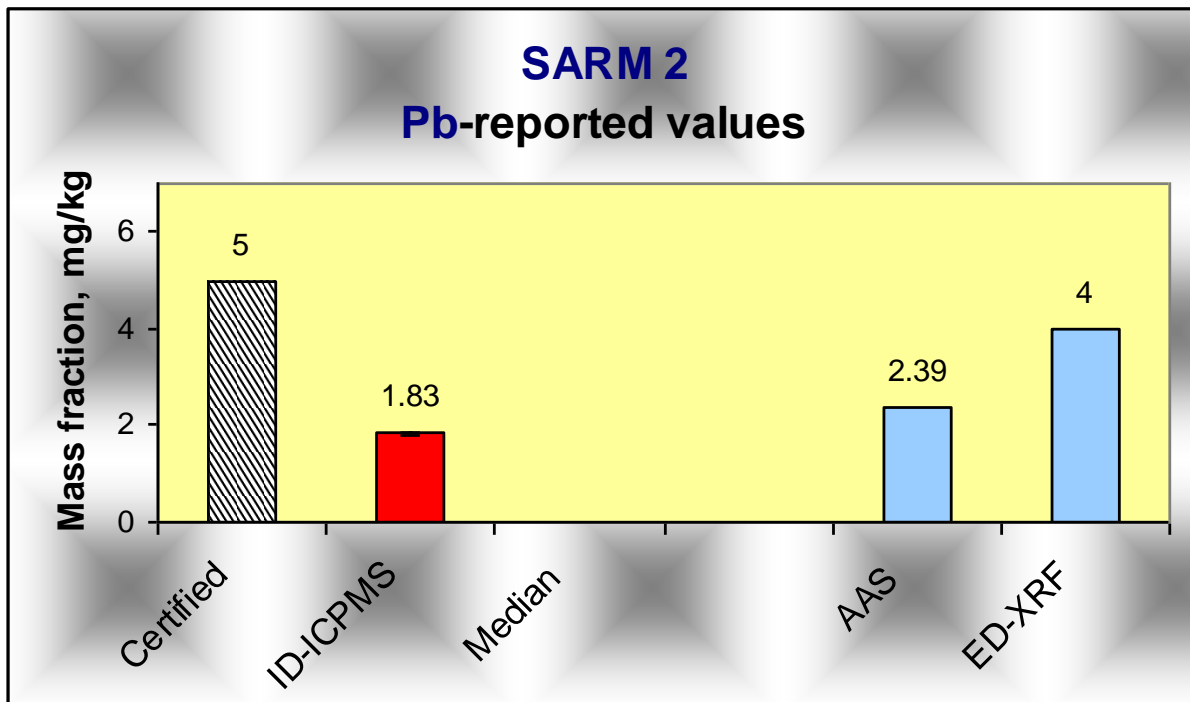


Figure 7.5: Summary of all the results for Pb in SARM 2

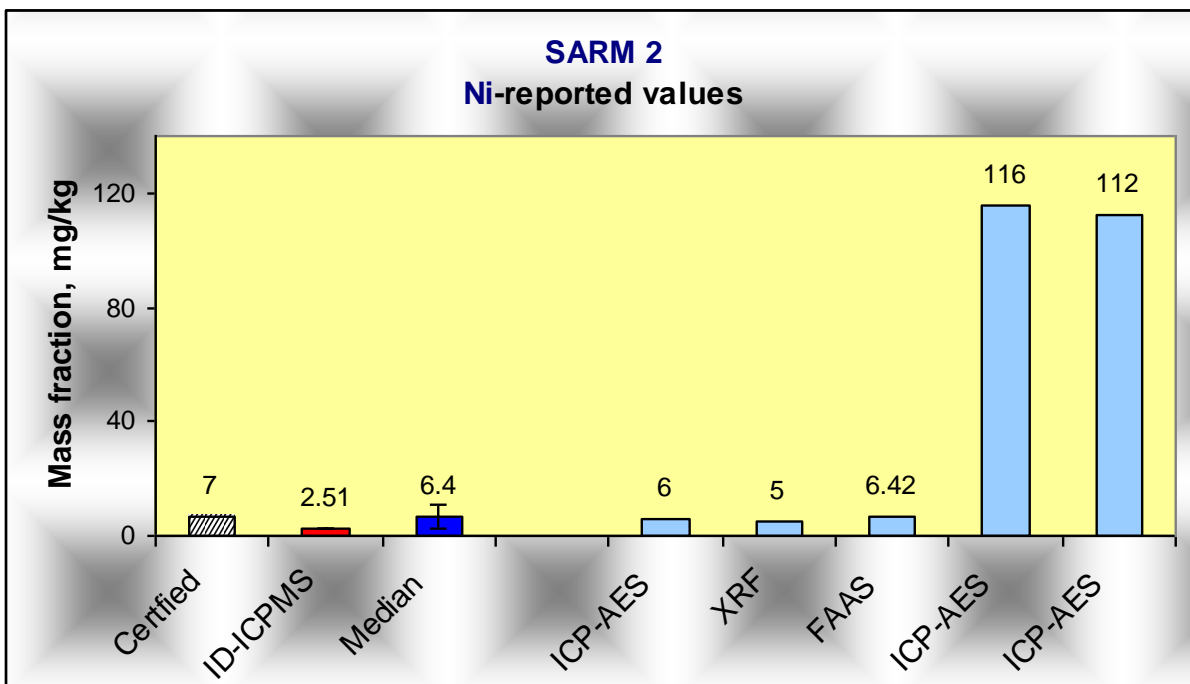


Figure 7.6: Summary of all the results for Ni in SARM 2

Each ID-ICP-MS result is based on 12 to 15 measurements from 4 or 5 spiked sub-samples in combination with 3 independent primary assay standard blends. The

combined standard uncertainty incorporates contributions from all input parameters in the measurement equation, as well as the experimental standard deviation of the mean. The results are directly traceable to the SI unit of mass, through the gravimetric preparation of the blend solutions, and via the NIST SRMs used for the preparation of the primary assay standard. In the case of Ba and Sr, there is very good agreement between the corresponding median values based on the published data and the present ID-ICP-MS results at 95.45% level of confidence.

Table 7.1: Summary of data for SARM 2: initial certification, published values since 1978 and ID-ICP-MS results from this study

	Ba	Sr	Cd	Pb	Mo	Zn	Cu	Ni
	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹
Initial certification ^a , provisional ^b and information ^c values	2400	62	1-35 ^c	5 ^b	0.290-10 ^c	10 ^b	19	7 ^b
Range of published ^d values since certification (1978)	730-2804	53.5-65.4	0.69-43	2.39-44	0.76	9-720	18.4-53.15	5-116
Median (published data, 1978-2006)	2608	62	-	-	-	-	24	6.4
Uncertainty ^e (k=2) associated with the median	126	6	-	-	-	-	14	4.2
ID-ICP-MS result (this study)	2585	59.9	0.018	1.83	0.83	8.9	17.1	2.51
Combined uncertainty	19	0.8	0.001	0.02	0.02	0.2	0.2	0.65
Uncertainty (k=2)	38	1.6	0.002	0.04	0.04	0.4	0.4	0.13
Relative uncertainty (%)	1.5	2.7	11.1	2.2	4.8	4.5	2.3	5.2
Number of measurements	15	15	12	12	12	12	12	12
Number of sample blends	5	5	4	4	4	4	4	4
Number of standard blends	3	3	3	3	3	3	3	3

^a No uncertainty associated with the certified values

^b Provisional values

^c Information concentration range

^d The number of results for the analytes of interest published in the period from 1978 to 2006 were the following: Ba (4), Sr (9), Cd (5), Pb (6), Mo (3), Zn (10), Cu (7) and Ni (5)

^e Calculated using the median absolute deviation for the range of published values corrected for normally distributed data and a coverage factor of 2 for a level of confidence of 95.45%

SARM 3

The data in **Table 7.2** for SARM 3 show initial certified values for Ba, Sr, Pb, Zn and Cu. Cd and Ni are only presented with information on the range of concentrations reported by the participating laboratories during the initial certification study. No figure is presented for the Pb data, because there was no certified value during the initial certification study, only a provisional value. No median was calculated for Pb, because the reported literature values were only a few and very widely dispersed.

From the published literature data, median values with associated expanded uncertainties, calculated from the median absolute deviations corrected for normally distributed data, were calculated for Ba, Sr, Zn and Cu (see **Figures 7.7 to 7.10**).

Each ID-ICP-MS result is based on 9 to 12 measurements, from 3 to 4 spiked sub-samples in combination with 3 independent primary assay standard blends.

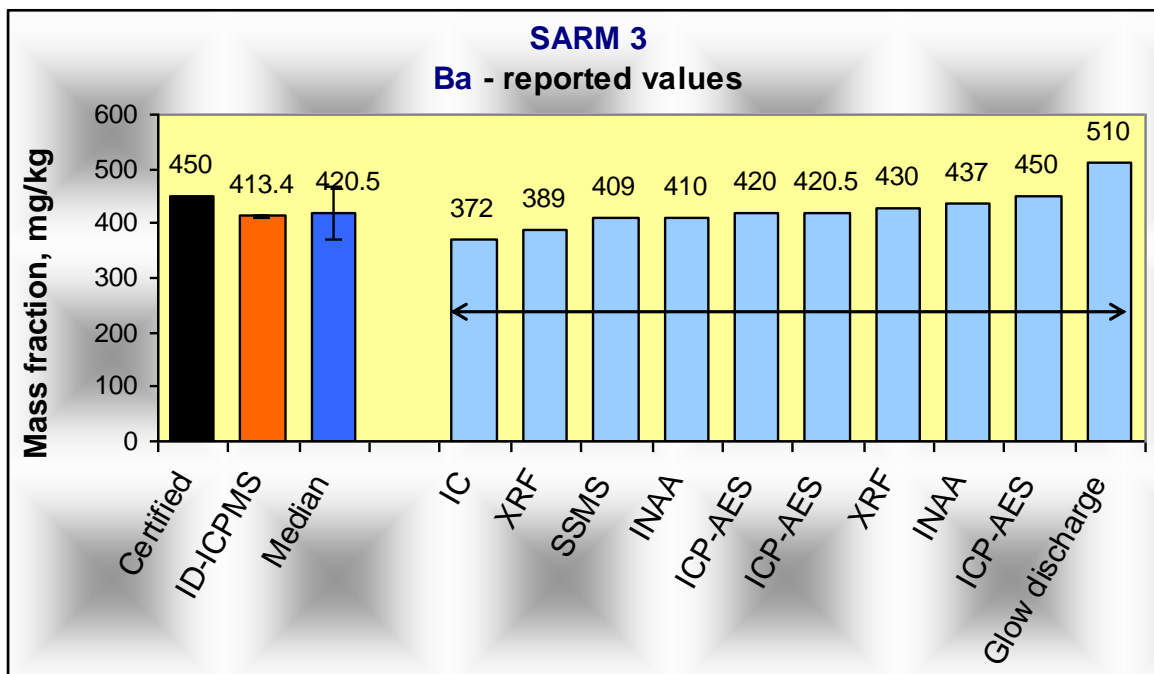


Figure 7.7: Summary of all the results for Ba in SARM 3

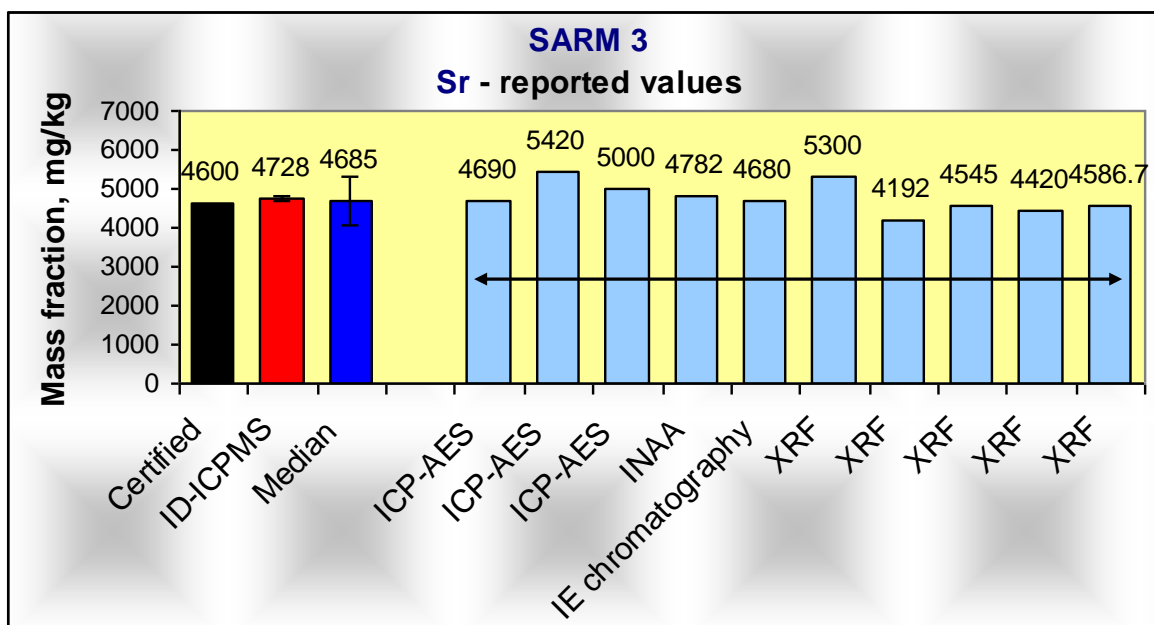


Figure 7.8: Summary of all the results for Sr in SARM 3

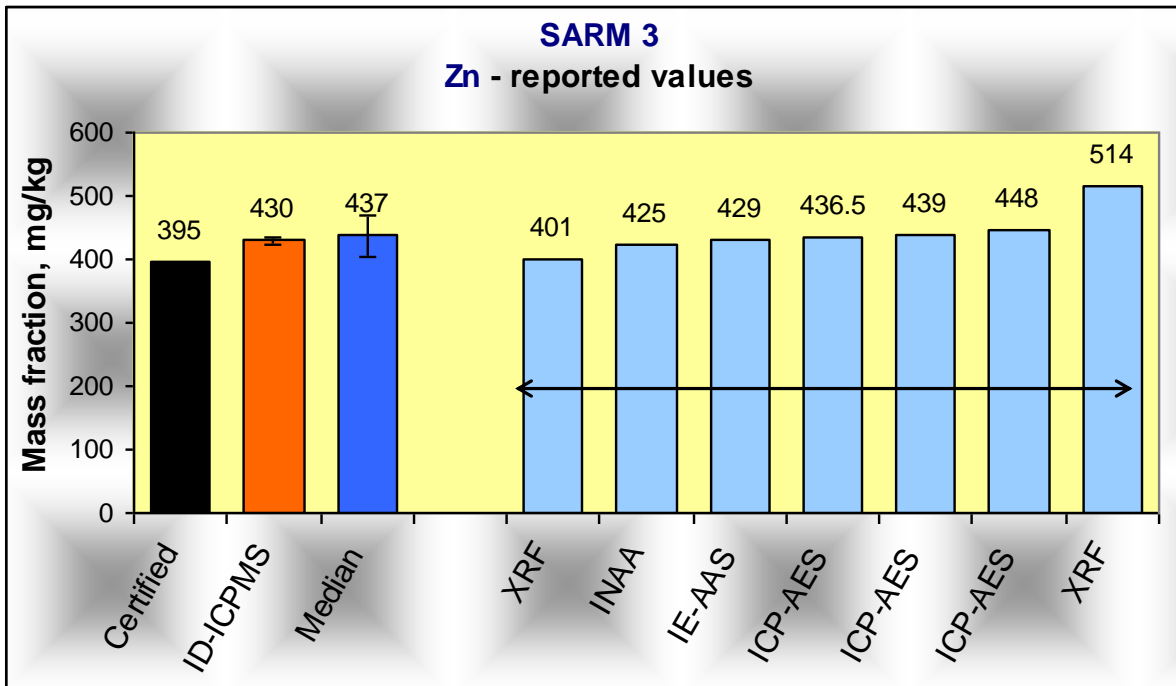


Figure 7.9: Summary of all the results for Zn in SARM 3

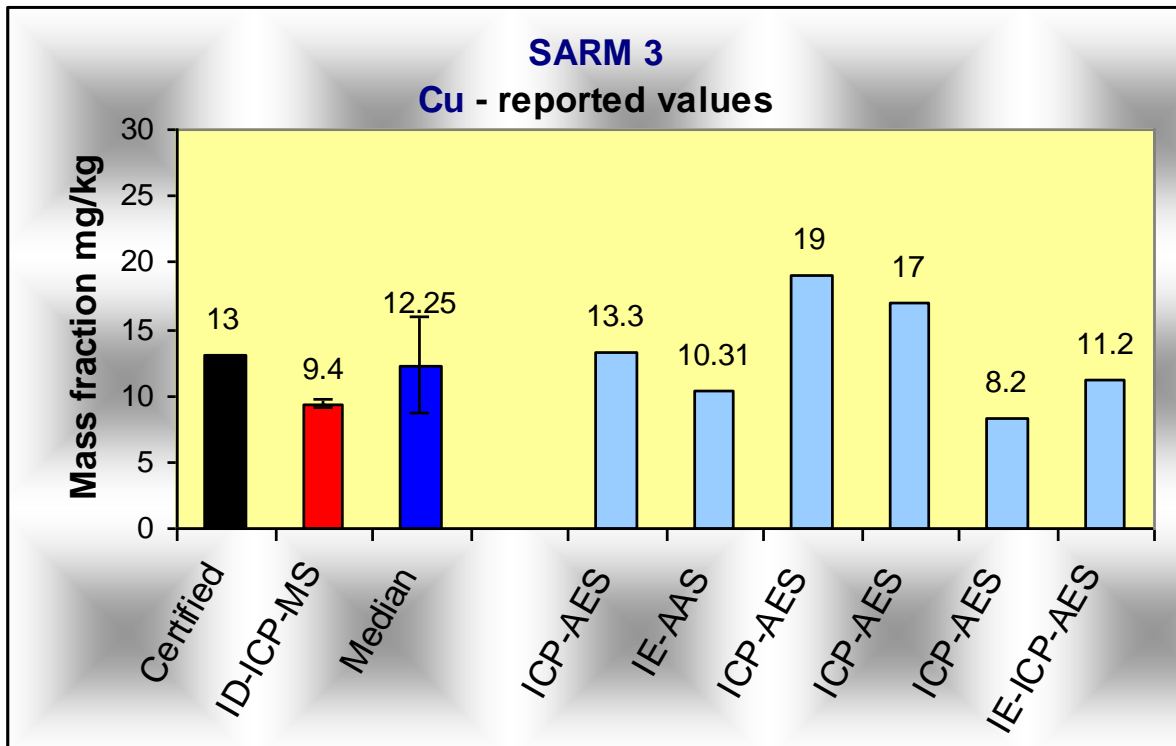


Figure 7.10: Summary of all the results for Cu in SARM 3

Table 7.2: Summary of data for SARM 3: initial certification, published values since 1978 and ID-ICP-MS results from this study

	Ba	Sr	Cd	Pb	Mo	Zn	Cu	Ni
	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹
Initial certification ^a , provisional ^b and information ^c values	450	4600	2-4 ^c	43	0.920-5 ^c	395	13	2-150 ^c
Range of published ^d values since certification (1978)	372-510	4192-5420	0.630-2	44-68	0.75-5	401-514	2-13.3	2.16-57
Median (published data, 1978-2006)	420.5	4685	-	-	-	437	10.8	-
Uncertainty ^e (k=2) associated with the median	49.0	600	-	-	-	32	4.4	-
ID-ICP-MS result (this study)	413.4	4728	-	46.04	1.82	430.0	9.85	1.54
Combined uncertainty		30	-	0.33		2.7	0.38	
Uncertainty (k=2)	3.3	60	-	0.66	0.41	5.2	0.76	0.27
Relative uncertainty (%)	0.8	1.3	-	1.4	22.5	1.2	7.7	17.5
Number of measurements	9	12	-	9	9	12	9	9
Number of sample blends	3	4	-	3	3	4	3	3
Number of standard blends	3	3	-	3	3	3	3	3

^a No uncertainty associated with the certified values

^b Provisional values

^c Information concentration range

^d The number of results for the analytes of interest published in the period from 1978 to 2006 were the following: Ba (4), Sr (9), Cd (5), Pb (6), Mo (3), Zn (10), Cu (7) and Ni (5)

^e Calculated using the median absolute deviation for the range of published values corrected for normally distributed data and a coverage factor of 2 for a level of confidence of 95.45%

SARM 4

Table 7.3 shows certified values for Ba, Sr, Zn, Cu and Ni in SARM 4. Cd, Pb and Mo are only presented with information on the range of concentrations reported by the participating laboratories during the initial certification study.

Table 7.3: Summary of data for SARM 4: initial certification, published values since 1978 and ID-ICP-MS results from this study

	Ba	Sr	Cd	Pb	Mo	Zn	Cu	Ni
	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹	mg.kg ⁻¹
Initial certification ^a , provisional ^b and information ^c values	102	260	1-4 ^c	0.8-26 ^c	0.84-60 ^c	68	14	120
Range of published ^d values since certification (1978)	80.3-200	250-269	0.047-2	2.48-21	0.93-4	54-65.9	8-15	101-122.9
Median (published data, 1978-2006)	89.9	264	-	-	-	62.5	12.0	119.5
Uncertainty ^e (k=2) associated with the median	17.8	14	-	-	-	3.2	3.6	7.4
ID-ICP-MS result (this study)	82.9	260.9	0.0879	2.110	0.888	61.42	10.67	119.3
Combined uncertainty		2.3	0.0016					2.7
Uncertainty (k=2)	1.1	4.6	0.0032	0.031	0.053	0.91	0.23	5.4
Relative uncertainty (%)	1.3	1.8	3.6	1.5	6.0	1.5	2.2	4.5
Number of measurements	9	12	9	9	9	9		9
Number of sample blends	3	4	3	3	3	3		3
Number of standard blends	3	3	3	3	3	3		3

^a No uncertainty associated with the certified values

^b Provisional values

^c Information concentration range

^d The number of results for the analytes of interest published in the period from 1978 to 2006 were the following: Ba (4), Sr (9), Cd (5), Pb (6), Mo (3), Zn (10), Cu (7) and Ni (5)

^e Calculated using the median absolute deviation for the range of published values corrected for normally distributed data and a coverage factor of 2 for a level of confidence of 95.45%

From the published literature data, median values, with associated expanded uncertainties, could only be calculated for the five elements with certified values (see **Figures 7.11 to 7.15**).

Each ID-ICP-MS result is based on 9 to 12 measurements, from 3 to 4 spiked sub-samples, in combination with 3 independent primary assay standard blends.

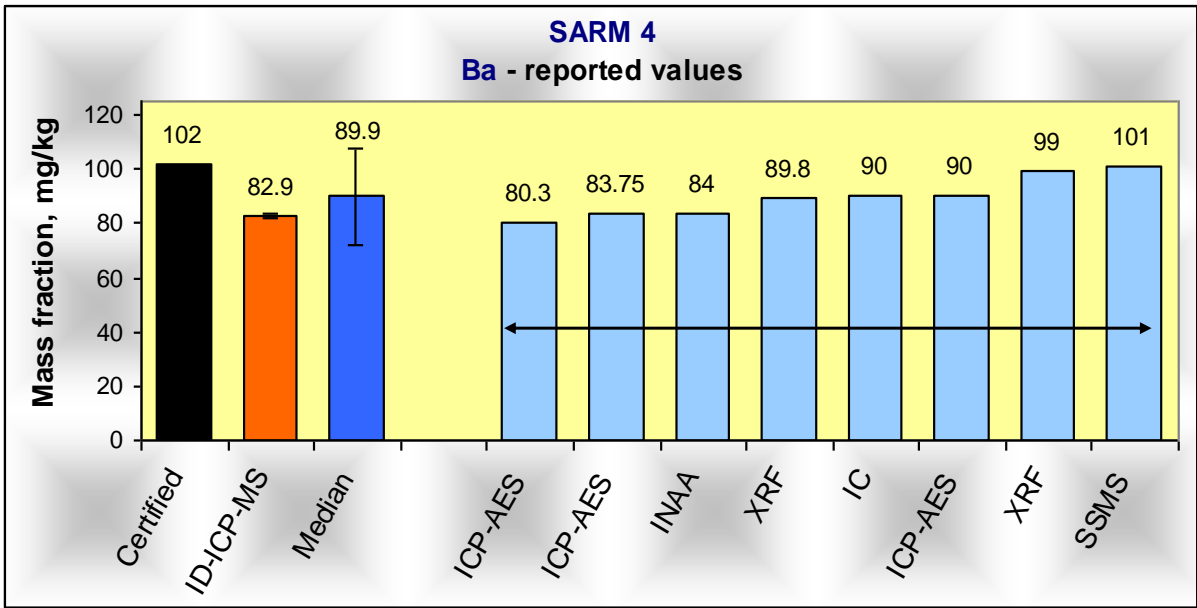


Figure 7.11: Summary of all the results for Ba in SARM 4

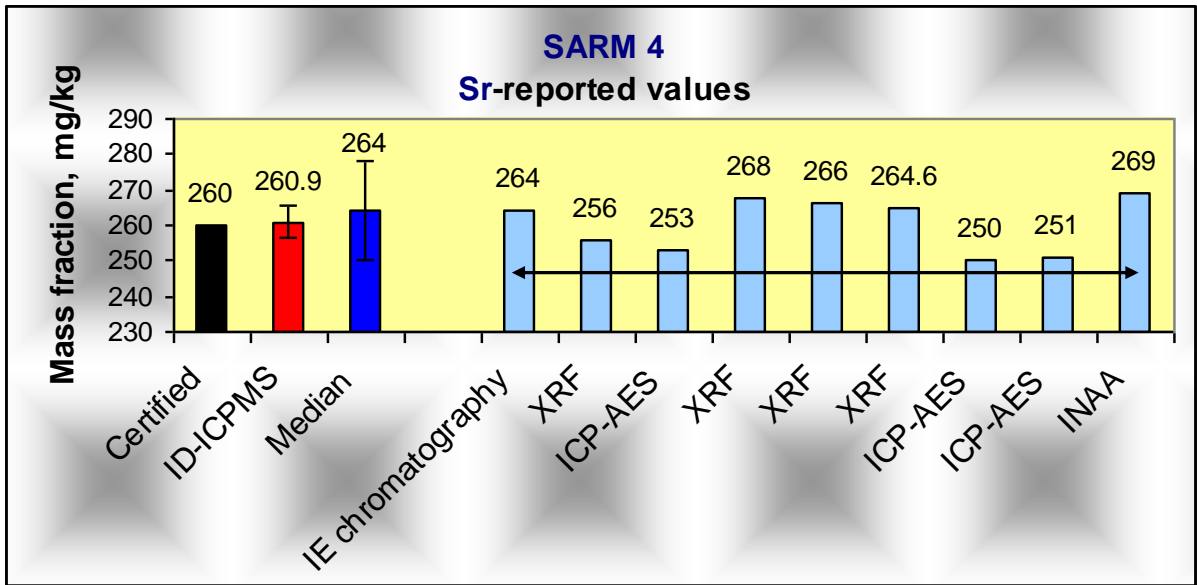


Figure 7.12: Summary of all the results for Sr in SARM 4

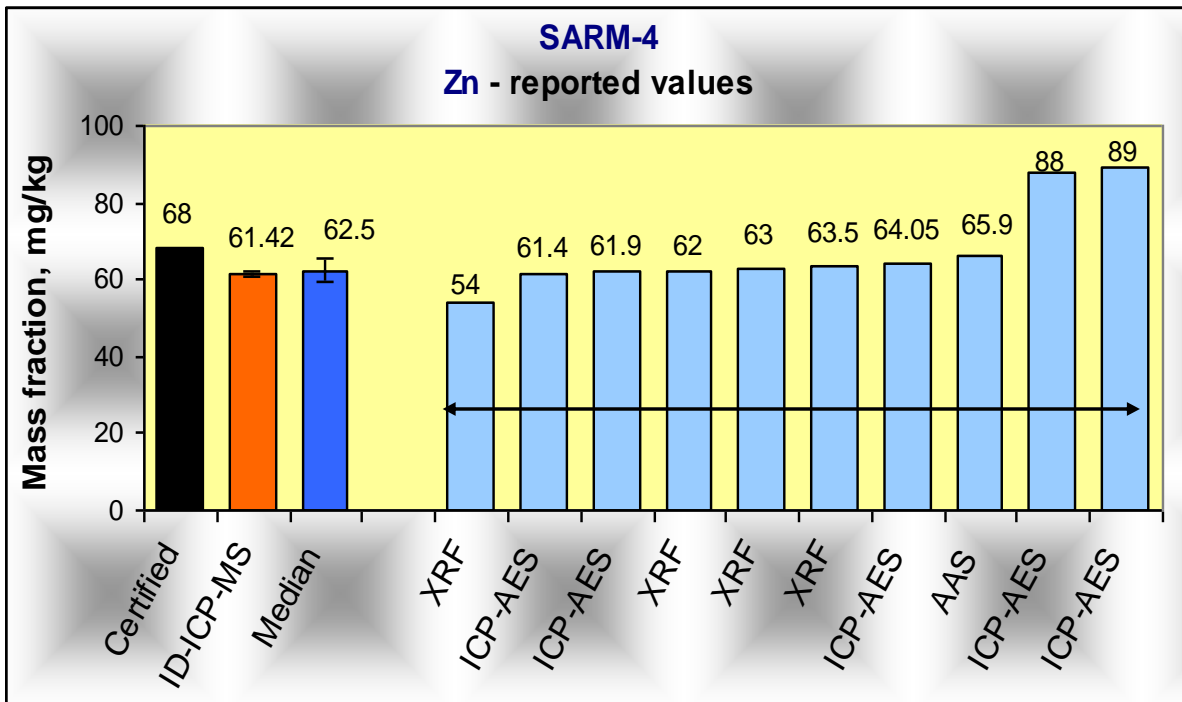


Figure 7.13: Summary of all the results for Zn in SARM 4

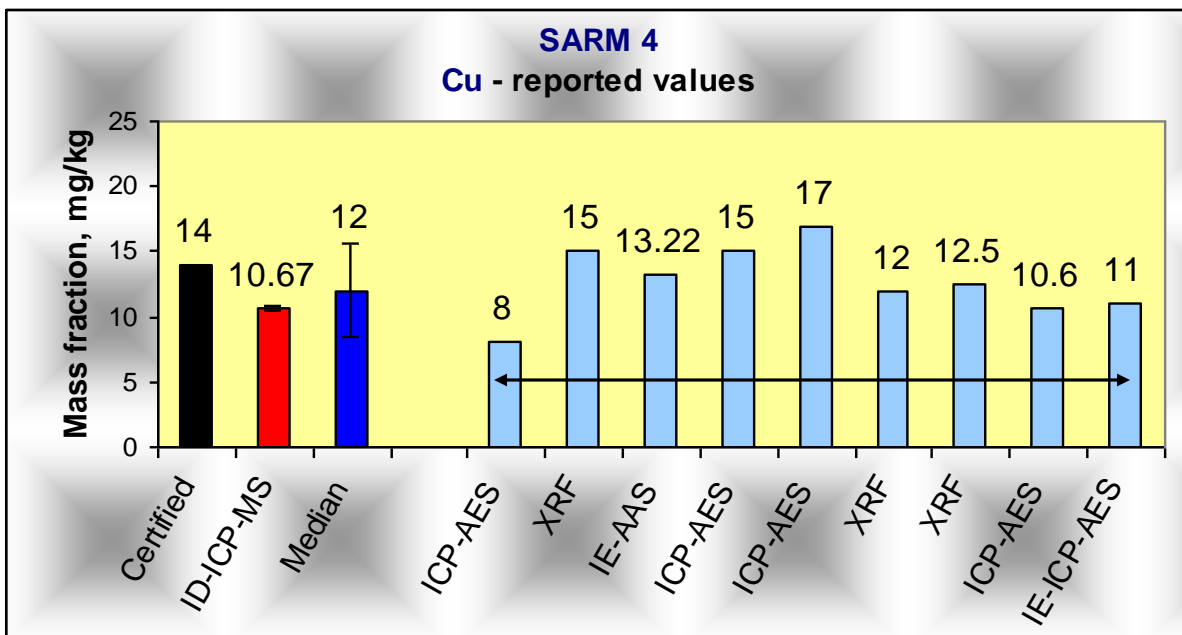


Figure 7.14: Summary of all the results for Cu in SARM 4

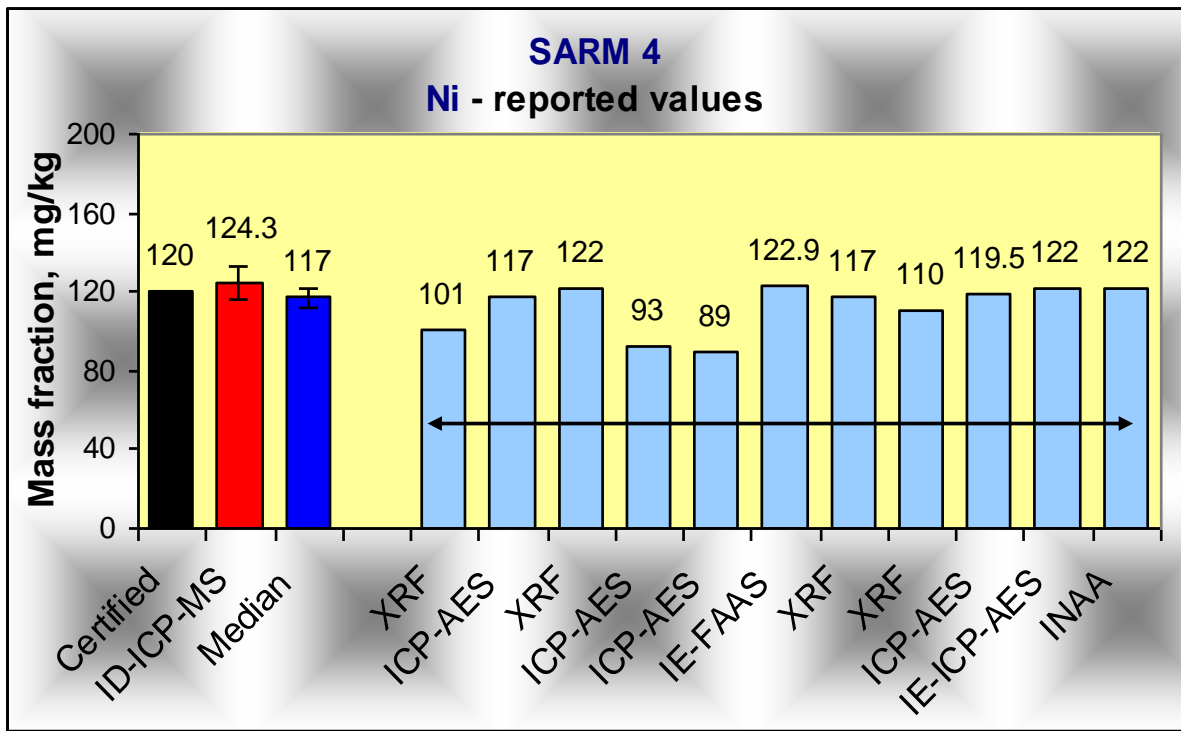


Figure 7.15: Summary of all the results for Ni in SARM 4

7.2 Conclusions

Eight elements (Ba, Sr, Cd, Mo, Cu, Ni, Pb and Zn) of SARM 2 (Syenite), SARM 3 (Lujavrite) and SARM 4 (Norite) were value assigned during this study to ensure that these South African Reference Materials comply with the ISO Guide 30 and ISO GUM requirements for traceability and measurement uncertainty. Traceability to the SI units of mass and amount of substance at the highest level of accuracy was established by employing the definitive technique of double isotope dilution ICP-MS, with primary assay standards traceable to the NIST SRM 3100 series and gravimetrically prepared samples.

For the first time uncertainty statements for these elements in these reference materials were calculated according to the ISO GUM[4] and CITAC/EURACHEM guidelines for expression of the uncertainty of the measurement[32]. The uncertainties for all elements were within the target of 5% relative set during the development of the methodology, except for elements in concentrations below 10 mg.kg⁻¹: Cd and Ni in SARM 2, Mo, Cu and Ni in SARM 3 as well as Mo in SARM 4. Due to the very low concentration of Cd in SARM 3 and the large isobaric interference on the isotope ratios of ¹¹²Cd/¹¹¹Cd and ¹¹⁴Cd/¹¹¹Cd from tin, this element could not be quantified with this method. The very low concentrations of Cd in SARM 2 and SARM 4 along with a similar large interference from tin also complicated the accurate quantification of Cd in these two materials.

The methodology was validated through a parallel analysis of SY-4 (Diorite Gneiss), a Canadian certified reference material. The statistical analysis of the data proved the recovery was quantitative and the average experimental values were statistically identical to the corresponding certified results at a 95% level of confidence. SY-4 was the best CRM available to our laboratory to match with the matrices of our SARM samples and with certified values and information values for the elements of interest in this study.

An effective microwave-assisted acid digestion method was developed for the complete decomposition of the silicate rock materials. It incorporated a two step acid digestion procedure with a mixture of HNO₃, HCl and HF (4:3:1) followed by a treatment with HF and 5% H₃BO₃ (1:15) for dissolution of the precipitation of fluorosilicates.

Experimental designs were developed for optimum isotope ratios for the elements of interest in the sample blends using a multi-element stable isotope spike solution. An approximation of the isotope ratios for the sample blend and the primary assay standard blend to be close to one, proved to be reliable for achieving optimal precision in the isotope ratio measurements.

The HR-ICP-MS measurement parameters and conditions were optimised for every element and pair of isotopes measured. The corresponding isotopes for Ni, Cu and Zn were measured in medium resolution mode due to spectral interferences.

Three alternative approaches for the calculation of the combined standard uncertainty were applied and compared. The use of partial derivatives, or the numerical approximation method - developed by Kragten[35], for the calculation of the sensitivity coefficients was found to be comparable. The combined standard uncertainty calculated with the assumption of the Power Law for the simplification of the measurement model, gave more conservative, but still reasonably comparable results for the combined standard uncertainties for the individual determinations.

The ID-ICP-MS results are supported by good comparability with results reported in the literature since 1978, as well as the original certified values published in 1978. For elements Cd and Mo in SARM 2, Cd, Mo and Ni in SARM 3, as well as Cd, Mo and Pb in SARM 4 only information values were available after the original certification study. Other elements such as Pb, Ni, and Zn in SARM 2 had only provisional values after the original certification.

The results from this study for all elements in these reference materials have the potential to become new certified values in accordance with the requirements of ISO Guide 34 and ISO Guide 35 and improve the usefulness of these reference materials to the South African and international geology and mining communities for the purposes of analytical quality control and method validation in exploration and geochemical analysis. During this study the sub-samples were taken from one bottle of each reference material and the data for especially Cu, Ni and Mo in SARM 3, as

well as Pb in SARM 4 indicated that there could be a problem with homogeneity of the samples that needs to be investigated. A confirmation of the homogeneity and stability of the remaining units of reference materials is considered necessary. The results were communicated to the international community through two peer reviewed publications in international journals (see **Appendix L**) and a conference presentation (Geoanalysis 2009, Drakensberg Sports Resort, South Africa, September 2009).

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Appendix A

Summary of SARM 1 to 6 sales from 1982 to 1999

Financial year	SARMs 1-6 units sold	SARMs 1-6 Sales (R)	Total SARMs Sales (R)
1982/1983	274	14 457	28 388
1983/1984	292	17 254	31 111
1984/1985	197	14 629	30 255
1985/1986	155	17 753	49 694
1986/1987	315	30 990	74 165
1987/1988	453	44 799	104 121
1988/1989	258	35 910	117 278
1989/1990	266	42 460	123 989
1990/1991	142	24 769	120 751
1991/1992	165	30 268	125 396
1992/1993	152	28 390	122 099
1993/1994	137	42 509	180 874
1994/1995	130	45 645	230 396
1995/1996	161	62 135	300 157
1996/1997	131	63 802	397 763
1997/1998	163	83 209	436 911
1998/1999	91	65 211	472 934
TOTAL	3 482	664 190	2 946 282

Appendix B

Compilation of SARM 2

Table 1: Summary of the published data for SiO₂ in SARM 2

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
63.8	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
63.6	not reported	ICP-AES	Walsh 1980[39]
63.61	0.15	WD-XRF	Stork <i>et al.</i> 1987[40]
64.61	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
63.22	not reported	XRF	Couture <i>et al.</i> 1993[42]
63.6*	not reported	ICP-AES	Cantagrel and Pin 1994[43]
63.61 (n=6) 0.15 0.30 0.5		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
63.63 (n=65)	1.08	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 2: Summary of the published data for Al₂O₃ in SARM 2

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
17.2	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
16.61	not reported	ICP-AES	Walsh 1980[39]
17.42*	0.63	ICP-AES	Church 1981[44]
17.11	0.05	WD-XRF	Stork <i>et al.</i> 1987[40]
17.62	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
17.15	not reported	XRF	Couture <i>et al.</i> 1993[42]
17*	not reported	ICP-AES	Cantagrel and Pin 1994[43]
17.15 (n=7) 0.22 0.44 2.6		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
17.34 (n=69)	0.46	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 3: Summary of the published data for total Fe as Fe₂O₃ in SARM 2

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
1.39	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
1.37	not reported	ICP-AES	Walsh 1980[39]
1.49*	0.03	ICP-AES	Church 1981[44]
1.42	0.03	WD-XRF	Stork <i>et al.</i> 1987[40]
1.4	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
1.37	not reported	XRF	Couture <i>et al.</i> 1993[42]
1.45*	not reported	ICP-AES	Cantagrel and Pin 1994[43]
1.40 (n=7) 0.04 0.08 5.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
1.40 (n=69)	0.2	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 4: Summary of the published data for MgO in SARM 2

Published values	Standard deviation	Analysis technique	Reference
(% oxide)	(% oxide)		
0.47	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
0.43	not reported	ICP-AES	Walsh 1980[39]
0.47	0.02	ICP-AES	Church 1981[44]
0.48	0.02	WD-XRF	Stork <i>et al.</i> 1987[40]
0.57	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.43	not reported	XRF	Couture <i>et al.</i> 1993[42]
0.46	not reported	ICP-AES	Cantagrel and Pin 1994[43]
0.47 (n=7)		Median	
0.02		MADe	
0.04		Expanded uncertainty, k=2	
8.5		Relative expanded uncertainty, %	
0.46 (n=58)	0.19	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 5: Summary of the published data for CaO in SARM 2

Published values	Standard deviation	Analysis technique	Reference
(% oxide)	(% oxide)		
3.05	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
3.15*	0.1	ICP-AES	Church 1981[44]
3.14	0.02	WD-XRF	Stork <i>et al.</i> 1987[40]
3.09	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
3.21*	0.01	ICP-AES	Cantagrel and Pin 1994[43]
2.94	not reported	INAA	Korotev 1996[45]
3.12 (n=6)		Median	
0.07		MADe	
0.14		Expanded uncertainty, k=2	
4.5		Relative expanded uncertainty, %	
3.22 (n=72)	0.27	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 6: Summary of the published data for Na₂O in SARM 2

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.4	not reported	ICP-AES	Walsh 1980[39]
0.433*	0.02	ICP-AES	Church 1981[44]
0.54	0.03	WD-XRF	Stork <i>et al.</i> 1987[40]
0.3	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.4	not reported	XRF	Couture <i>et al.</i> 1993[42]
0.42*	0.003	ICP-AES	Cantagrel and Pin 1994[42]
0.41 (n=6) 0.03 0.06 14.6		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.43 (n=50)	0.11	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 7: Summary of the published data for K₂O in SARM 2

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
14.74	not reported	ICP-AES	Walsh 1980[39]
>10*	not reported	ICP-AES	Church 1981[44]
15.18	0.18	WD-XRF	Stork <i>et al.</i> 1987[40]
15.28	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
15.28	not reported	XRF	Couture <i>et al.</i> 1993[42]
15.4*	0.12	ICP-AES	Cantagrel and Pin 1994[43]
15.28 (n=5) 0.15 0.30 2.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
15.35 (n=65)	0.92	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 8: Summary of the published data for TiO₂ in SARM 2

Published values	Standard deviation	Analysis technique	Reference
(% oxide)	(% oxide)		
0.04	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
0.04	not reported	ICP-AES	Walsh 1980[39]
0.041*	0.001	ICP-AES	Church 1981[44]
0.04	0.01	WD-XRF	Stork <i>et al.</i> 1987[40]
0.06	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.04	not reported	XRF	Couture <i>et al.</i> 1993[42]
0.04*	not reported	ICP-AES	Cantagrel and Pin 1994[43]
0.04 (n=7)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 9: Summary of the published data for MnO in SARM 2

Published values	Standard deviation	Analysis technique	Reference
(% oxide)	(% oxide)		
0.01	0.001	WD-XRF	Stork <i>et al.</i> 1987[40]
0.01	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.01	not reported	XRF	Couture <i>et al.</i> 1993[42]
0.01*	not reported	ICP-AES	Cantagrel and Pin 1994[43]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 10: Summary of the published data for P₂O₅ in SARM 2

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.118	not reported	Spectrophotometric	Watkins 1979[46]
0.11	not reported	ICP-AES	Walsh 1980[39]
0.012*	0.001	ICP-AES	Church 1981[44]
0.12	0.003	WD-XRF	Stork <i>et al.</i> 1987[40]
0.12	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.15	not reported	XRF	Couture <i>et al.</i> 1993[42]
0.071	not reported	ICP-AES	Cantagrel and Pin 1994[43]
0.076	0.004	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.11 (n=8) 0.03 0.06 54.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.12 (n=38)	0.03	Originally certified value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 11: Summary of the published data for Ag in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<2*	not reported	ICP-AES	Church 1981[44]
0.1*	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
<1 [#]	not reported	INAA	Korotev 1996[45]
0.083		Reported during certification	Steele <i>et al.</i> 1978[7]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	

* Incomplete dissolution

[#] Primary method

Table 12: Summary of the published data for As in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<6*	not reported	ICP-AES	Church 1981[44]
0.25	not reported	FAAS, Hydride generation	Terashima 1986[48] Jarvis and Williams 1989[47]
<DL*	not reported	SN-ICP-MS	1989[47]
0.26	not reported	INAA	Korotev 1996[45]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Reported during certification	Steele <i>et al.</i> 1978[7]
0.21			

* Incomplete dissolution

DL =detection limit

Table 13: Summary of the published data for Au in SARM 2

Published values ($\text{ng}\cdot\text{g}^{-1}$)	Standard deviation ($\text{ng}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<3000*	not reported	ICP-AES	Church 1981[44]
0.29	0.02	Flameless AAS (GTA)	Terashima 1988[49]
<2000 [#]	not reported	INAA	Korotev 1996[45]
0.062	not reported	ICP-MS	Plessen and Erzinger 1998[50]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

[#] Primary method

Table 14: Summary of the published data for B in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
8.8*	not reported	ICP-AES	Walsh 1985[51]
15.4*	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
8.9-14.0 (n=7)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 15: Summary of the published data for Ba in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
2600	not reported	Grimm glow discharge lamp	Bubert and Hagenah 1981[52]
2615*	52	ICP-AES	Church 1981[44]
2804	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
734	not reported	ICP-AES	Cantagrel and Pin 1994[43]
730	34	IE-ICP-AES	Cantagrel and Pin 1994[43]
2530 [#]	76	INAA	Korotev 1996[45]
2565 (n=6) 214 428 16.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
2400 (n=29) 2585	360 38	Originally certified value ID-ICP-MS	Steele <i>et al.</i> 1978[7] Botha <i>et al.</i> 2007[53]

* Incomplete dissolution

[#] Primary method

Table 16: Summary of the published data for Be in SARM 2

Published values ($\mu\text{g.g}^{-1}$)	Standard deviation ($\mu\text{g.g}^{-1}$)	Analysis technique	Reference
1.61*	0.03	ICP-AES	Church 1981[44]
2.1*	0.36	SE-Flameless AAS	Vilcsek and Lohmann 1982[54]
1.48	not reported	ICP-AES	Watkins and Thompson[55] 1983
1.62	not reported	ICP-AES	Watkins and Thompson 1983[55]
1.66*	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
1.62 (n=5) 0.06 0.12 7.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
1.099-2.0 (n=11)		Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 17: Summary of the published data for Bi in SARM 2

Published values (ng.g^{-1})	Standard deviation (ng.g^{-1})	Analysis technique	Reference
39	not reported	Flameless AAS	Heinrichs 1979[56]
<2500*	not reported	ICP-AES	Church 1981[44]
17	not reported	Flameless AAS (hydride generation)	Terashima 1984[57]
500*	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
400		Reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 18: Summary of the published data for Cd in SARM 2

Published values (ng.g ⁻¹)	Standard deviation (ng.g ⁻¹)	Analysis technique	Reference
43	not reported	Flameless AAS	Heinrichs 1979[56]
16	82	ID-MS	Rosman and De Laeter 1980[58]
<2000*	not reported	ICP-AES	Church 1981[44]
690*	not reported	ICP-MS	Jarvis and Williams 1989[47]
Not analysed [#]	not reported	INAA	Korotev 1996[45]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
1000-35000 (n=6)		Range reported during certification	Steele <u>et al.</u> 1978[7]
0.018	0.002	ID-ICP-MS	Botha <u>et al.</u> 2007[53]

* Incomplete dissolution

∞ Primary method

Table 19: Summary of the published data for Ce in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
16	2	Candoluminescence ES	Mazzucotelli and Vannucci 1980[59]
20*	4	ICP-AES	Church 1981[44]
11.5 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
<35	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
ND	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
10.7	0.5	IE-ICP-AES	Jarvis and Jarvis 1988[62]
12.2	0.1	IE-ICP-AES	Roelandts 1990[63]
11	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
9.5	0.9	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
12	2	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
62.35	not reported	ICP-AES	Cantagrel and Pin 1994[43]
63.6	3.9	IE-ICP-AES	Cantagrel and Pin 1994[43]
11.9	0.2	IE-ICP-AES	Cantagrel and Pin 1994[43]
11.7 [#]	0.3	INAA	Korotev 1996[45]
11.5	0.2	IE-ICP-AES	Rucandio 1997[66]
11.9 (n=13)		Median	
1.3		MADe	
2.6		Expanded uncertainty, k=2	
21.8		Relative expanded uncertainty, %	
11 (n=9)	2	Provisional value	Steele <i>et al.</i> 1978[7]
11.9 (9.6-14.4) [#] (n=14)	2.4	Revised value	Hansen and Ring 1985[9]

* Incomplete dissolution

[∞] Primary method

[#] 95 % confidence interval

Table 20: Summary of the published data for Co in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
2.5*	1	ICP-AES	Church 1981[44]
2.8 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60] Anderson and Victor 1986[67]
2.97	0.03	IE-FAAS	Victor 1986[68]
2.95	0.01	IE-FAAS	Korotev 1996[45]
2.87 [#]	0.08	INAA	
2.87 (n=5) 0.12 0.24 8.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
3 (n=22)	2	Provisional value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

[#] Primary method**Table 21:** Summary of the published data for Cr in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
12.7*	1	ICP-AES	Church 1981[44] Jarvis and Williams 1989[47]
5.52*	not reported	SN-ICP-MS	Stork <i>et al.</i> 1987[40]
ND	not reported	WD-XRF	Cantagrel and Pin 1994[43]
123.5	not reported	ICP-AES	Cantagrel and Pin 1994[43]
134	15	IE-ICP-AES	Korotev 1996[45]
12.5	0.4	INAA	
12 (n=29)	4	Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

ND not detected

Table 22: Summary of the published data for Cs in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
6.33	0.05	Flame emission	Goguel 1981[69]
6.68	not reported	Flame emission	Terashima and Mita 1981[70]
6.47 [#]	0.19	INAA	Korotev 1996[45]
6.47 (n=3) 0.21 0.42 6.5		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
5.7-10.14 (n=10)		Range reported during certification	Steele <u>et al.</u> 1978[7]

[#] Primary method

Table 23: Summary of the literature data for Cu in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
18.4*	1	ICP-AES	Church 1981[44]
20.51	0.07	IE-AAS	Victor 1983[71]
20	not reported	ED-XRF	Webb <u>et al.</u> 1990[72]
53.15	not reported	ICP-AES	Cantagrel and Pin 1994[43]
51.7	2.0	IE-ICP-AES	Cantagrel and Pin 1994[43]
20.5 (n=5) 3.1 6.2 30.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
19 (n=29)	5	Originally certified value	Steele <u>et al.</u> 1978[7]
17.1	0.4	ID-ICP-MS	Botha <u>et al.</u> 2007[53]

* Incomplete dissolution

Table 24: Summary of the published data for Dy in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.45 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
<4	not reported	IE-CP-AES	Bolton <i>et al.</i> 1983[61]
0.33	0.02	IE-CP-AES	Jarvis and Jarvis 1988[62]
0.48	0.01	IE-CP-AES	Roelandts 1990[63] Watkins and Nolan
0.3	not reported	IE-CP-AES	1990[64]
0.37	0.03	IE-CP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.4	0.1	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.3	0.01	IE-CP-AES	Cantagrel and Pin 1994[43]
0.39 [#]	not reported	INAA	Korotev 1996[45]
0.32	not reported	IE-CP-AES	Rucandio 1997[66]
0.37 (n=9) 0.07 0.14 37.8		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.3-0.63 (n=3)		Range reported during certification	Steele <i>et al.</i> 1978[7]

[#] Primary method

Table 25: Summary of the published data for Er in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.13 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.12	0.02	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.12	0.02	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
<0.2	not reported	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.41	0.14	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.12 [#]	not reported	INAA	Korotev 1996[45]
0.074	0.07	IE-ICP-AES	Rucandio 1997[66]
0.12 (n=6) 0.01 0.02 16.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.068		Reported during certification	Steele <i>et al.</i> 1978[7]

[#] Primary method

Table 26: Summary of the published data for Eu in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<0.6*	not reported	ICP-AES	Church 1981[44]
0.27 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
1.3	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
0.27	0.01	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.28	0.01	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
0.24	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.24	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.5	0.2	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.26	0.01	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.259 [#]	0.008	INAA	Korotev 1996[45]
0.28	0.01	IE-ICP-AES	Rucandio 1997[66]
0.27 (n=10) 0.02 0.04 14.8 0.30 (0.27-0.38) [#] (n=14)	0.06	Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Revised value	Hansen and Ring 1985[9]

* Incomplete dissolution

∞ Primary method

95 % confidence interval

Table 27: Summary of the published data for F in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
76	2	Ion selective electrode	Troll and Farzenah 1978[73]
135.5 [#]	8.1	INAA	Esprit <i>et al.</i> 1984[74]
146	not reported	PIGE	Roelandts <i>et al.</i> 1985[75]
86-370 (n=10)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

∞ Primary method

Table 28: Summary of the published data for Ga in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
11.3	0.2	IE-FAAS	Van der Walt and Strelow 1984[76]
10	not reported	ED-XRF	Webb et al. 1990[72]
11 (n=12)	4	Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele et al. 1978[7]

Table 29: Summary of the published data for Gd in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<2*	not reported	ICP-AES	Church 1981[44]
0.79 [#]	not reported	INAA	Potts et al. 1981[60]
6	not reported	IE-ICP-AES	Bolton et al. 1983[61]
0.83	0.08	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.87	0.01	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
0.72	not reported	IE-ICP-AES	Bauer-Wolf et al. 1993[65]
0.87	0.1	IE-ICP-AES	Bauer-Wolf et al. 1993[65]
0.9	0.3	IE-XRF	Bauer-Wolf et al. 1993[65]
0.79	0.03	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.75 [#]	not reported	INAA	Korotev 1996[45]
0.75	0.02	IE-ICP-AES	Rucandio 1997[66]
0.81 (n=10) 0.09 0.18 22.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele et al. 1978[7]
0.56-0.59 (n=3)			

* Incomplete dissolution

[#] Primary method

Table 30: Summary of the published data for Hf in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.46 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.3	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
0.466 [#]	0.01	INAA	Korotev 1996[45]
0.46 (n=3) 0.01 0.02 4.3		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.2-41 (n=5)		Range reported during certification	Steele <i>et al.</i> 1978[7]

[#] Primary method

Table 31: Summary of the published data for Hg in SARM 2

Published values ($\text{ng}\cdot\text{g}^{-1}$)	Standard deviation ($\text{ng}\cdot\text{g}^{-1}$)	Analysis technique	Reference
26.1	1.9	Flameless AAS	Flanagan <i>et al.</i> 1982[77]
9.4	0.4	Flameless AAS (Hydride generation)	Chan and Bina 1989[78]
35	3	Cold vapor AAS	Terashima 1994[79]
Not analysed [#]		INAA	Korotev 1996[45]
<10		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
		Reported during certification	Steele <i>et al.</i> 1978[7]

[#] Primary method

Table 32: Summary of the published data for Ho in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.07 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.05	0.02	IE-ICP-AES	Jarvis and Jarvis 1988[62] Watkins and Nolan 1990[64]
ND	not reported	IE-ICP-AES	1990[64]
<0.25	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
<0.2	not reported	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.059 [#]	not reported	INAA	Korotev 1996[45]
0.05	0.01	IE-ICP-AES	Rucandio 1997[66]
0.055 (n=4) 0.005 0.010 18.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.048		Reported during certification	Steele <i>et al.</i> 1978[7]

[∞] Primary method

ND not detected

Table 33: Summary of the published data for Ir in SARM 2

Published values ($\text{ng}\cdot\text{g}^{-1}$)	Standard deviation ($\text{ng}\cdot\text{g}^{-1}$)	Analysis technique	Reference
2500	not reported	ETV-ICP-MS	Sen Gupta and Gregoire 1989[80]
2000	not reported	SN-ICP-MS	Sen Gupta and Gregoire 1989[80]
Not analysed [#]	not reported	INAA	Korotev 1996[45]
0.01	not reported	ICP-MS	Plessen and Erzinger 1998[50]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
		Reported during certification	Steele <i>et al.</i> 1978[7]

[∞] Primary method

Table 34: Summary of the published data for La in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
6*	1	ICP-AES	Church 1981[44]
5.1 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
13	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
7	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
4.47	0.15	IE-ICP-AES	Jarvis and Jarvis 1988[62]
5.4	0.1	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
4.9	not reported	IE-ICP-AES	
5.5	0.3	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
5.8	0.4	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
33.25	not reported	ICP-AES	Cantagrel and Pin 1994[43]
34.8	0.8	IE-ICP-AES	Cantagrel and Pin 1994[43]
5.69	0.4	IE-ICP-AES	Cantagrel and Pin 1994[43]
4.95 [#]	0.1	INAA	Korotev 1996[45]
4.79	0.03	IE-ICP-AES	Rucandio 1997[66]
5.60 (n=14) 0.99 1.98 35.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
5 (n=9)	1.3	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

[#] Primary method

Table 35: Summary of the published data for Li in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
2	not reported	Grimm glow discharge lamp	Bubert and Hagenah 1981[52]
<2*	not reported	ICP-AES	Church 1981[44]
1.38-4.0 (n=11)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele et al. 1978[7]

* Incomplete dissolution

Table 36: Summary of the published data for Lu in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.006 [#]	not reported	INAA	Potts et al. 1981[60]
0.01	not reported	IE-ICP-AES	Jarvis and Jarvis 1988[62]
<0.05	not reported	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
ND	not reported	IE-ICP-AES	Bauer-Wolf et al. 1993[65]
0.01	not reported	IE-ICP-AES	Bauer-Wolf et al. 1993[65]
<0.2	not reported	IE-XRF	Bauer-Wolf et al. 1993[65]
ND	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.011 [#]	not reported	INAA	Korotev 1996[45]
0.016	0.003	IE-ICP-AES	Rucandio 1997[66]
0.010 (n=5) 0.001 0.002 38.3		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during revision	Hansen and Ring 1985[9]
0.006-0.3 (n=6)			

Table 37: Summary of the published data for Mo in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.76	not reported	Spectrophotometry	Terashima 1980[81]
<3*	not reported	ICP-AES	Church 1981[44]
<DL	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
0.29-10 (n=13)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.83	0.04	Range reported during certification ID-ICP-MS	Steele <i>et al.</i> 1978[7] Botha <i>et al.</i> 2007[53]

* Incomplete dissolution

Table 38: Summary of the published data for Nb in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
4.5	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
1.3	2	WD-XRF	Stork <i>et al.</i> 1987[40]
0.46	not reported	ICP-MS	Jarvis and Williams 1989[47]
2	not reported	ED-XRF	Webb <i>et al.</i> 1990[72]
0.25	not reported	ICP-MS	Poitrasson <i>et al.</i> 1993[83]
3.0-5.0 (n=12)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 39: Summary of the published data for Nd in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<20*	not reported	ICP-AES	Church 1981[44]
6.5 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
<30	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
ND	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
6.16	0.09	IE-ICP-AES	Jarvis and Jarvis 1988[62]
6.7	0.1	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
6.3	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
6.3	1	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
5.4	0.2	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
6.26	0.01	IE-ICP-AES	Cantagrel and Pin[43]
6.6 [#]	0.2	INAA	Korotev 1996[45]
5.92	0.08	IE-ICP-AES	Rucandio 1997[66]
6.3 (n=9)		Median	
0.4		MADe	
0.8		Expanded uncertainty, k=2	
12.7		Relative expanded uncertainty, %	
6 (n=6)	0.43	Provisional value	Hansen and Ring 1985[9]

* Incomplete dissolution

[#] Primary method

ND not detected

Table 40: Summary of the published data for Ni in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
ND	not reported	XRF	Vié le Sage <i>et al.</i> 1979[82]
6*	1	ICP-AES	Church 1981[44]
5	1	XRF	Stork <i>et al.</i> 1987[40]
6.42	0.13	IE-FAAS	Victor 1987[84]
ND	not reported	ED-XRF	Webb <i>et al.</i> 1990[72]
116	not reported	ICP-AES	Cantagrel and Pin 1994[43]
112	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
<20 [#]	not reported	INAA	Korotev 1996[45]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
7 (n=24)	4	Provisional value	Steele <i>et al.</i> 1978[7]
2.51	0.13	ID-ICP-MS	Botha <i>et al.</i> 2007[53]

ND not detected

* Incomplete dissolution

[∞] Primary method

Table 41: Summary of the published data for Pb in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
2.39	0.05	IE-AAS	Victor and Strelow 1980[85]
<13	not reported	ICP-AES	Church 1981[44]
<2	not reported	XRF	Stork <i>et al.</i> 1987[40]
4	not reported	ED-XRF	Webb <i>et al.</i> 1990[72]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
5 (n=18)	4	Provisional value	Steele <i>et al.</i> 1978[7]
1.83	0.04	ID-ICP-MS	Botha <i>et al.</i> 2007[53]

^{*} Incomplete dissolution

Table 42: Summary of the published data for Pd in SARM 2

Published values (ng.g ⁻¹)	Standard deviation (ng.g ⁻¹)	Analysis technique	Reference
6	not reported	GF-AAS	Sen Gupta and Gregoire 1989[80]
0.067	not reported	ICP-MS	Plessen and Erzinger 1998[50]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
		Originally certified value	Steele et al. 1978[7]

* Incomplete dissolution

Table 43: Summary of the published data for Pr in SARM 2

Published values (µg.g ⁻¹)	Standard deviation (µg.g ⁻¹)	Analysis technique	Reference
1.5 [#]	not reported	INAA	Potts et al. 1981[60]
<15	not reported	WD-XRF	Robinson and Bennett 1981[86]
1.39	0.04	ICP-AES	Jarvis and Jarvis 1988[62]
1.19	not reported	ICP-AES	Watkins and Nolan 1990[64]
1.7	0.3	ICP-AES	Bauer-Wolf et al. 1993[65]
1.5	0.3	IE-XRF	Bauer-Wolf et al. 1993[65]
1.27	0.15	ICP-AES	Cantagrel and Pin 1994[43]
1.5 [#]	not reported	INAA	Korotev 1996[45]
1.25	0.06	ICP-AES	Rucandio 1997[66]
1.45 (n=8) 0.17 0.34 23.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
1		Reported during certification	Steele et al. 1978[7]

[∞] Primary method

Table 44: Summary of the published data for Rb in SARM 2

Published values ($\mu\text{g.g}^{-1}$)	Standard deviation ($\mu\text{g.g}^{-1}$)	Analysis technique	Reference
298	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
680	not reported	Grimm glow discharge lamp	Bubert and Hagenah 1981[52]
543	not reported	WD-XRF	Robinson and Bennett 1981[86]
531	4	WD-XRF	Stork <i>et al.</i> 1987[40]
546	not reported	ED-XRF	Webb <i>et al.</i> 1990[72]
528 [#]	15	INAA	Korotev 1996[45]
537 (n=6) 13 26 4.8		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
530 (n=23)	58	Originally certified value	Steele <i>et al.</i> 1978[7]

[#] Primary method

Table 45: Summary of the published data for Ru in SARM 2

Published values (ng.g^{-1})	Standard deviation (ng.g^{-1})	Analysis technique	Reference
3000	not reported	ETV-ICP-MS	Sen Gupta and Gregoire 1989[80]
2600	not reported	SN-ICP-MS	Sen Gupta and Gregoire 1989[80]
2600	not reported	GF-AAS	Sen Gupta and Gregoire 1989[80]
<0.3	not reported	ICP-MS	Plessen and Erzinger 1998[50]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
		Originally certified value	Steele <i>et al.</i> 1978[7]

Table 46: Summary of the published data for Sb in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<18*	not reported	ICP-AES	Church 1981[44]
<DL*	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
0.05	not reported	FAAS, Hydride generation	Terashima 1986[48]
0.05 [#]	0.02	INAA	Korotev 1996[45]
0.17-0.7 (n=7)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <u>et al.</u> 1978[7]

* Incomplete dissolution

DL detection limit

[∞] Primary method**Table 47:** Summary of the published data for Sc in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
6	not reported	IE-ICP-AES	Bolton <u>et al.</u> 1983[61]
3.6	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
13	not reported	ICP-AES	Cantagrel and Pin 1994[43]
13.5	1.3	IE-ICP-AES	Cantagrel and Pin 1994[43]
3.78 [#]	0.11	INAA	Korotev 1996[45]
3.0-8.0 (n=13)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <u>et al.</u> 1978[7]

[∞] Primary method

Table 48: Summary of the published data for Sm in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<5*	not reported	ICP-AES	Church 1981[44]
1.36 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60] Robinson and Bennett 1981[86]
<10	not reported	WD-XRF	1981[86]
<15	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
1.14	0.01	IE-ICP-AES	Jarvis and Jarvis 1988[62]
1.14	0.01	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
1.18	not reported	IE-ICP-AES	1990[64]
1.5	0.1	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
1.4	0.2	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
1.21	0.04	IE-ICP-AES	Cantagrel and Pin 1994[43]
1.287 [#]	0.038	INAA	Korotev 1996[45]
1.1	0.04	IE-ICP-AES	Rucandio 1997[66]
1.25 (n=10) 0.16 0.32 25.6		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
1 (n=8)	0.25	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

[#] Primary method**Table 49:** Summary of the published data for Sn in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<3*	not reported	ICP-AES	Church 1981[44]
0.48	not reported	SE-AAS	Terashima 1982[87] Jarvis and Williams 1989[47]
0.11*	not reported	SN-ICP-MS	1989[47]
0.5-10 (n=11)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 50: Summary of the published data for Sr in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
60	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
65.4*	1.3	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
62	not reported	WD-XRF	Sørensen 1981[88]
65	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
63	1	ED-XRF	Webb <i>et al.</i> 1990[72]
64	not reported	ICP-AES	Cantagrel and Pin 1994[43]
55.95	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
53.5	1.7	INAA	Korotev 1996[45]
62 [#]	2		
62 (n=9)		Median	
3		MADe	
6		Expanded uncertainty, k=2	
9.7		Relative expanded uncertainty, %	
62 (n=30)	14	Originally certified value	Steele <i>et al.</i> 1978[7]
59.9	1.6	ID-ICP-MS	Botha <i>et al.</i> 2007[53]

* Incomplete dissolution

[#] Primary method**Table 51:** Summary of the published data for Ta in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.03 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60] Jarvis and Williams 1989[47]
0.2*	not reported	SN-ICP-MS	Poitrasson <i>et al.</i> 1993[83]
0.05	not reported	ICP-MS	Korotev 1996[45]
0.036 [#]	0.002		
0.043 (n=4)		Median	
0.015		MADe	
0.030		Expanded uncertainty, k=2	
69.8		Relative expanded uncertainty, %	
0.03-0.3 (n=5)		Range reported during certification	Steele <i>et al.</i> 1978[7]

[#] Primary method

* Incomplete dissolution

Table 52: Summary of the published data for Tb in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.1 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
<0.19	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
<0.2	not reported	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.088 [#]	0.003	INAA	Korotev 1996[45]
1.7	0.4	IE-ICP-AES	Rucandio 1997[66]
0.10 (n=3) 0.02 0.04 40.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.05-0.11 (n=4)		Range reported during certification	Steele <i>et al.</i> 1978[7]

[∞] Primary method

Table 53: Summary of the published data for Th in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<25 [*]	not reported	ICP-AES	Church 1981[44]
0.73 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
<3	not reported	WD-XRF	Robinson and Bennett 1981[86]
1.41 [*]	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
2	2	WD-XRF	Stork <i>et al.</i> 1987[40]
ND	not reported	ED-XRF	Webb <i>et al.</i> 1990[72]
0.691 [#]	0.020	INAA	Korotev 1996[45]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.9 (n=9)	0.3	Provisional value	Steele <i>et al.</i> 1978[7]
1.0 (0.5-1.0) [#] (n=15)		Revised value	Hansen and Ring 1985[9]

^{*} Incomplete dissolution

[∞] Primary method

ND not detected

[#] 95% confidence interval

Table 54: Summary of the published data for Tm in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.01 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
<0.5	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
<0.2	not reported	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.013 [#]	not reported	INAA	Korotev 1996[45]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.011		Reported during certification	Steele <i>et al.</i> 1978[7]

[∞] Primary method

Table 55: Summary of the published data for U in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<20 [*]	not reported	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
4	not reported	WD-XRF	
0.39	0.03	Fluorimetry	Kanai <i>et al.</i> 1986[89]
ND	not reported	WD-XRF	Stork <i>et al.</i> 1987[40] Jarvis and Williams 1989[47]
0.65 [*]	not reported	SN-ICP-MS	
ND	not reported	ED-XRF	Webb <i>et al.</i> 1990[72]
0.41 [#]	0.02	INAA	Korotev 1996[45]
0.53 (n=4) 0.19 0.38 71.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.1-5.0 (n=13)		Range reported during certification	Steele <i>et al.</i> 1978[7]

^{*} Incomplete dissolution

ND not detected

[∞] Primary method

Table 56: Summary of the published data for V in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
10*	1	ICP-AES	Church 1981[44]
<1	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
137.5	not reported	ICP-AES	Cantagrel and Pin 1994[43]
139	10	IE-ICP-AES	Cantagrel and Pin 1994[43]
10 (n=18)	4	Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 57: Summary of the published data for W in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<7*	not reported	ICP-AES	Church 1981[44] Jarvis and Williams 1989[47]
<DL*	not reported	SN-ICP-MS	1989[47]
<1 [#]	not reported	INAA	Korotev 1996[45]
<10 (n=2)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

DL detection limit

[∞] Primary method

Table 58: Summary of the published data for Y in SARM 2

Published values ($\mu\text{g.g}^{-1}$)	Standard deviation ($\mu\text{g.g}^{-1}$)	Analysis technique	Reference
16	not reported	WD-XRF	Robinson and Bennett 1981[86]
3	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
7	3	WD-XRF	Stork <i>et al.</i> 1987[40]
1.14	0.04	IE-ICP-AES	Jarvis and Jarvis 1988[62] Watkins and Nolan 1990[64]
1.1	not reported	IE-ICP-AES	1990[64]
8	not reported	ED-XRF	Webb <i>et al.</i> 1990[72]
14.3	not reported	ICP-AES	Cantagrel and Pin 1994[43]
16.2	0.9	IE-ICP-AES	Cantagrel and Pin 1994[43]
1.44	0.08	IE-ICP-AES	Cantagrel and Pin 1994[43]
1.4 [#]	not reported	INAA	Korotev 1996[45]
1.17	0.08	IE-ICP-AES	Rucandio 1997[66]
1.5-50 (n=10)		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during revision	Hansen and Ring 1985[9]

Table 59: Summary of the published data for Yb in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<0.2*	not reported	ICP-AES	Church 1981[44]
0.06 [#]	not reported	INAA	Potts <i>et al.</i> 1981[60]
<1	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
0.08	0.01	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.1	0.01	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
0.06	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.12	0.01	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
<0.2	not reported	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.07	0.01	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.067 [#]	0.007	INAA	Korotev 1996[45]
0.06	0.01	IE-ICP-AES	Rucandio 1997[66]
0.069 (n=8) 0.013 0.026 37.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.07 (n=6)	0.008	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

[#] Primary method

Table 60: Summary of the published data for Zn in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
ND	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
11.1	0.1	IE-AAS	Victor and Strelow 1980[85]
10.3*	1	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
14	not reported	WD-XRF	
9	not reported	ED-XRF	Webb <i>et al.</i> 1990[72]
83.15	not reported	ICP-AES	Cantagrel and Pin 1994[43]
74	7	IE-ICP-AES	Cantagrel and Pin 1994[43]
Not analysed [#]		INAA	Korotev 1996[45]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
10 (n=22)	6	Provisional value	Steele <i>et al.</i> 1978[7]
8.9	0.4	ID-ICP-MS	Botha <i>et al.</i> 2007[53]

* Incomplete dissolution

[∞] Primary method

Table 61: Summary of the published data for Zr in SARM 2

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
24	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
17*	1	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
16	not reported	WD-XRF	Watkins and Thompson 1983[55]
15	not reported	ICP-AES	Watkins and Thompson 1983[55]
15	not reported	ICP-AES	1983[55]
22	1	WD-XRF	Stork <i>et al.</i> 1987[40]
24	not reported	ED-XRF	Webb <i>et al.</i> 1990[72]
20	3	Spectrophotometric	Okai 1991[90]
129	not reported	ICP-AES	Cantagrel and Pin 1994[43]
124	9	IE-ICP-AES	Cantagrel and Pin 1994[43]
15 [#]	1	INAA	Korotev 1996[45]
20 (n=11) 6 12 60.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
33 (n=10)	20	Provisional value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

[∞] Primary method

Appendix C

Compilation of SARM 3

Table 1: Summary of the published data for SiO₂ in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
52.5	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
52.53	0.07	WD-XRF	Stork <i>et al.</i> 1987[40]
51.25	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
52.4*	0.4	ICP-AES	Cantagrel and Pin 1994[43]
52.45 (n=4) 0.10 0.20 0.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
52.40 (n=52)	0.3	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 2: Summary of the published data for Al₂O₃ in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
13.35	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
13.43*	0.48	ICP-AES	Church 1981[44]
13.6	0.07	WD-XRF	Stork <i>et al.</i> 1987[40]
13.4	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
13.4*	not reported	ICP-AES	Cantagrel and Pin 1994[43]
13.40 (n=5) 0.04 0.08 0.6		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
13.64 (n=57)	0.48	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 3: Summary of the published data for total Fe as Fe₂O₃ in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
9.7	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
10.22*	0.23	ICP-AES	Church 1981[44]
10.09	0.07	WD-XRF	Stork <i>et al.</i> 1987[40]
10.09	0.04	INAA	Bedard and Barnes 1990[91]
9.7	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
9.96*	0.09	ICP-AES	Cantagrel and Pin 1994[43]
9.92	not reported	INAA	Korotev 1996[45]
9.96 (n=7) 0.19 0.38 3.8		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
9.91 (n=67)	0.36	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 4: Summary of the published data for MgO in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.24	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
0.263*	0.008	ICP-AES	Church 1981[44]
0.28	0.01	WD-XRF	Stork <i>et al.</i> 1987[40]
0.34	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.28*	0.01	ICP-AES	Cantagrel and Pin 1994[43]
0.28 (n=5) 0.03 0.06 21.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.28 (n=58)	0.10	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 5: Summary of the published data for CaO in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
3.05	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
3.15*	0.1	ICP-AES	Church 1981[44]
3.14	0.02	WD-XRF	Stork <i>et al.</i> 1987[40]
3.09	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
3.21*	0.01	ICP-AES	Cantagrel and Pin 1994[43]
2.94	not reported	INAA	Korotev 1996[45]
3.12 (n=6) 0.07 0.14 4.5		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
3.22 (n=72)	0.27	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 6: Summary of the published data for Na₂O in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
8.56*	0.27	ICP-AES	Church 1981[44] Bedard and Barnes 1990[91]
8.58	0.02	INAA	Verma <i>et al.</i> 1992[41]
8.11	not reported	WD-XRF	Cantagrel and Pin 1994[43]
8.18*	0.27	ICP-AES	Korotev 1996[45]
8.64	not reported	INAA	
8.56 (n=5) 0.12 0.24 2.8		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
8.37 (n=52)	0.53	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 7: Summary of the published data for K₂O in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
5.45*	0.14	ICP-AES	Church 1981[44]
5.55	not reported	WD-XRF	Galson <i>et al.</i> 1983[92]
5.39	0.02	WD-XRF	Stork <i>et al.</i> 1987[40]
5.24	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
5.57*	0.25	ICP-AES	Cantagrel and Pin 1994[43]
5.45 (n=5) 0.15 0.30 5.5		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
5.51 (n=63)	0.19	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 8: Summary of the published data for TiO₂ in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.48	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
0.493*	0.012	ICP-AES	Church 1981[44]
0.5	0.01	WD-XRF	Stork <i>et al.</i> 1987[40]
0.49	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.48*	0.01	ICP-AES	Cantagrel and Pin 1994[43]
0.49 (n=5) 0.01 0.02 4.1		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.48 (n=68)	0.08	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 9: Summary of the published data for MnO in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.73	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
0.77*	0.02	ICP-AES	Church 1981[44]
0.73	0.01	WD-XRF	Stork <i>et al.</i> 1987[40]
0.72	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.75*	0.02	ICP-AES	Cantagrel and Pin 1994[43]
0.75	not reported	Spectrophotometry	Rao 1994[93]
0.74 (n=6)		Median	
0.02		MADe	
0.04		Expanded uncertainty, k=2	
5.4		Relative expanded uncertainty, %	
0.77 (n=67)	0.16	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 10: Summary of the published data for P₂O₅ in SARM 3

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.056	not reported	Spectrophotometry	Watkins 1979[46]
0.064*	0.003	ICP-AES	Church 1981[44]
0.05	0.005	WD-XRF	Stork <i>et al.</i> 1987[40]
0.05	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.076	not reported	ICP-AES	Cantagrel and Pin 1994[43]
0.085	0.004	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.06 (n=6)		Median	
0.01		MADe	
0.02		Expanded uncertainty, k=2	
33.3		Relative expanded uncertainty, %	
0.06 (n=34)	0.04	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 11: Summary of the published data for Ag in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<2*	not reported	ICP-AES	Church 1981[44]
9.45	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
0.11-2.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 12: Summary of the published data for As in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<5*	not reported	ICP-AES	Church 1981[44]
1.92	not reported	HG-FAAS	Terashima 1986[48]
1.88	0.03	SN-ICP-MS	Jarvis and Williams 1989[47]
<DL	not reported	INAA	Bedard and Barnes 1990[91]
1.70	not reported	INAA	Korotev 1996[45]
1.0-14		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

DL =detection limit

Table 13: Summary of the published data for Au in SARM 3

Published values (ng.g ⁻¹)	Standard deviation (ng.g ⁻¹)	Analysis technique	Reference
<4000*	not reported	ICP-AES	Church 1981[44]
0.64*	0.1	GF-AAS	Terashima 1988[49]
<10	not reported	INAA	Korotev 1996[45]
4.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Reported during certification	Steele <u>et al.</u> 1978[7]

* Incomplete dissolution

Table 14: Summary of the published data for B in SARM 3

Published values (µg.g ⁻¹)	Standard deviation (µg.g ⁻¹)	Analysis technique	Reference
3.3*	not reported	ICP-AES	Walsh 1985[51] Jarvis and Williams 1989[47]
8.37	0.62	SN-ICP-MS	
3.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Reported during certification	Steele <u>et al.</u> 1978[7]

* Incomplete dissolution

Table 15: Summary of the published data for Ba in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
372	4	IEC	Strelow <i>et al.</i> 1978[94]
510	not reported	Grimm GDL	Bubert and Hagenah 1981[52]
420*	8.4	ICP-AES	Church 1981[44]
389	not reported	WD-XRF	Robinson and Bennett 1981[86]
430	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
437 [∞]	23	INAA	Bedard and Barnes 1990[91]
420.5	not reported	ICP-AES	Cantagrel and Pin 1994[43]
450	2.25	IE-ICP-AES	Cantagrel and Pin 1994[43]
410 [∞]	not reported	INAA	Korotev 1996[45]
420.5 (n=9)		Median	
24.5		MADe	
49.0		Expanded uncertainty, k=2	
11.7		Relative expanded uncertainty, %	
450 (n=33)	140	Originally certified value	Steele <i>et al.</i> 1978[7]
413.4 [∞]	3.3	ID-ICP-MS	This work

* Incomplete dissolution

[∞] Primary method**Table 16:** Summary of the published data for Be in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
25.8	0.5	IEC	Strelow <i>et al.</i> 1978[94]
29.7*	0.6	ICP-AES	Church 1981[44]
27	not reported	ICP-AES	Watkins and Thompson 1983[55]
24.3	1.2	SE-Spectrophotometry	Sauerer and Troll 1984[95]
24.2	0.82	SN-ICP-MS	Jarvis and Williams 1989[47]
25.8 (n=5)		Median	
2.2		MADe	
4.4		Expanded uncertainty, k=2	
17.1		Relative expanded uncertainty, %	
2.0-31.0		Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 17: Summary of the published data for Bi in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.25	not reported	FD-AAS	Heinrichs 1979[56]
<25*	not reported	ICP-AES	Church 1981[44]
0.468	not reported	SE-HG-AAS	Terashima 1984[57]
1.76	0.22	SN-ICP-MS	Jarvis and Williams 1989[47]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.4		Reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 18: Summary of the published data for Cd in SARM 3

Published values ($\text{ng}\cdot\text{g}^{-1}$)	Standard deviation ($\text{ng}\cdot\text{g}^{-1}$)	Analysis technique	Reference
630	not reported	FD-Flameless AAS	Heinrichs 1979[56]
1005 [∞]	82	IE-ID-MS	Rosman and De Laeter[58] 1980
<2000*	not reported	ICP-AES	Church 1981[44]
930	10	SN-ICP-MS	Jarvis and Williams 1989[47]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
2000-4000		Range reported during certification	Steele <i>et al.</i> 1978[7]

[∞] Primary method

* Incomplete dissolution

Table 19: Summary of the published data for Ce in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
210	5	IE-CES	Mazzucotelli and Vannucci 1980[59]
311*	6.2	ICP-AES	Church 1981[44]
308	not reported	INAA	Potts <i>et al.</i> 1981[60] Robinson and Bennett 1981[86]
313	not reported	WD-XRF	
307	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61] Date and Hutchinson 1987[96]
300	not reported	ICP-MS	
245	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
262	13	IE-ICP-AES	Jarvis and Jarvis 1988[62]
231	not reported	SN-ICP-MS	Jarvis 1989[97]
272	1	INAA	Bedard and Barnes 1990[91]
292	2	IE-ICP-AES	Roelandts 1990[63]
270	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
257	7	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
639.5	not reported	ICP-AES	Cantagrel and Pin 1994[43]
693	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
298	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
249	6	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
293	not reported	INAA	Korotev 1996[45]
291	8	IE-ICP-AES	Rucandio 1997[66]
248	not reported	ICP-MS	Brenner <i>et al.</i> 1999[99]
292 (n=20)		Median	
32		MADe	
64		Expanded uncertainty, k=2	
21.9		Relative expanded uncertainty, %	
230 (n=13)	43	Provisional value	Steele <i>et al.</i> 1978[7]
240 (n=18)	42	Revised value	Hansen and Ring 1985[9]

* Incomplete dissolution

Table 20: Summary of the published data for Cl in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
902	not reported	LE-CIC (LECO)	Evans and Moore 1980[100]
1100	not reported	SN-ICP-MS	Jarvis 1992[101]
1200 (n=6)	500	Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele and Hansen 1979[8]

Table 21: Summary of the published data for Co in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<1*	not reported	ICP-AES	Church 1981[44]
2.4	not reported	INAA	Potts <i>et al.</i> 1981[60]
4	not reported	WD-XRF	Robinson and Bennett 1981[86]
2.61	0.11	IE-FAAS	Anderson and Victor 1986[67]
2.44	0.04	IE-FAAS	Victor 1986[68]
3.5	0.4	INAA	Bedard and Barnes 1990[91]
2.3	not reported	INAA	Korotev 1996[45]
2.53 (n=6) 0.26 0.52 20.6		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 22: Summary of the published data for Cr in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
12.1*	1.2	ICP-AES	Church 1981[44]
10	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
12	0.42	SN-ICP-MS	Jarvis and Williams 1989[47]
11 [∞]	2	INAA	Bedard and Barnes 1990[91]
15.15	not reported	ICP-AES	Cantagrel and Pin 1994[43]
14.8	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
9	not reported	INAA	Korotev 1996[45]
12 (n=7) 3 6 50.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
10 (n=27)	14	Provisional value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 23: Summary of the published data for Cs in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
2.43	0.09	Flame emission	Goguel 1981[69]
2.78	not reported	Flame emission	Terashima and Mita 1981[70]
3.4	0.2	INAA	Bedard and Barnes 1990[91]
2.63	not reported	INAA	Korotev 1996[45]
2.71 (n=4) 0.26 0.52 19.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
2.1-9		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 24: Summary of the literature data for Cu in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
13.3*	1.3	ICP-AES	Church 1981[44]
<2	not reported	WD-XRF	Robinson and Bennett 1981[86]
10.31	0.03	IE-AAS	Victor 1983[71]
8.2	not reported	ICP-AES	Cantagrel and Pin 1994[43]
11.2	0.3	IE-ICP-AES	Cantagrel and Pin 1994[43]
10.8 (n=4) 2.2 4.4 40.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
13 (n=33)	6	Originally certified value	Steele <i>et al.</i> 1978[7]
9.85	0.76	ID-ICP-MS	This work

* Incomplete dissolution

Table 25: Summary of the published data for Dy in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
10	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
2.9	not reported	ICP-MS	Date and Hutchinson 1987[96]
3.1	0.22	IE-ICP-AES	Jarvis and Jarvis 1988[62]
2.69	not reported	SN-ICP-MS	Jarvis 1989[97]
3.3	0.1	IE-ICP-AES	Roelandts 1990[63]
2.75	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
2.6	0.3	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
2.69	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
3.01	0.23	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
3.1	not reported	INAA	Korotev 1996[45]
2.9	0.3	IE-ICP-AES	Rucandio 1997[66]
2.9	not reported	ICP-MS	Brenner <i>et al.</i> 1999[99]
2.9 (n=12)		Median	
0.3		MADe	
0.6		Expanded uncertainty, k=2	
20.7		Relative expanded uncertainty, %	
1.9-3.719		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 26: Summary of the published data for Er in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
2.1	not reported	ICP-MS	Date and Hutchinson 1987[96]
2.58	0.24	IE-ICP-AES	Jarvis and Jarvis 1988[62]
2.26	not reported	SN-ICP-MS	Jarvis 1989[97]
1.55	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
2.23	0.04	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
2.6	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
2.45	0.21	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
2.3	not reported	INAA	Korotev 1996[45]
2.3	0.2	IE-ICP-AES	Rucandio 1997[66]
2.2	not reported	ICP-MS	Brenner <i>et al.</i> 1999[99]
2.28 (n=10)		Median	
0.19		MADe	
0.38		Expanded uncertainty, k=2	
16.7		Relative expanded uncertainty, %	
1.2-2.3		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 27: Summary of the published data for Eu in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
2.1*	0.2	ICP-AES	Church 1981[44]
0.9	not reported	IE-GF-AAS	Horsky and Fletcher 1981[102]
1.15	not reported	INAA	Potts <i>et al.</i> 1981[60]
3.8	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
1	not reported	ICP-MS	Date and Hutchinson 1987[96]
1.05	0.07	IE-ICP-AES	Jarvis and Jarvis 1988[62]
1*	not reported	SN-ICP-MS	Jarvis 1989[97]
1	0.2	INAA	Bedard and Barnes 1990[91]
1.16	0.01	IE-ICP-AES	Roelandts 1990[63]
0.95	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
1	0.08	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
1.06	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
1.13	0.13	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
1.082	not reported	INAA	Korotev 1996[45]
1.21	0.04	IE-ICP-AES	Rucandio 1997[66]
1.4	not reported	ICP-MS	Brenner <i>et al.</i> 1999[99]
1.07 (n=16)		Median	
0.11		MADe	
0.22		Expanded uncertainty, k=2	
20.6		Relative expanded uncertainty, %	
1.2 (1.0-1.5) # (n=15)		Revised value	Hansen and Ring 1985[9]

* Incomplete dissolution

95 % confidence interval

Table 28: Summary of the published data for F in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
3185	10	ISE	Troll and Farzenah 1978[73]
5500 ^{oo}	230	INAA	Esprit <i>et al.</i> 1984[74]
4783	not reported	PIGE	Roelandts <i>et al.</i> 1985[75]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
4400 (n=11)	1500	Originally certified value	Steele and Hansen 1979[8]

Table 29: Summary of the published data for Ga in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
54	not reported	WD-XRF	Robinson and Bennett 1981[86]
51.1	0.4	IE-FAAS	Van der Walt and Strelow 1984[76]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
54 (n=12)	98	Provisional value	Steele <i>et al.</i> 1978[7]

Table 30: Summary of the published data for Gd in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
3*	0.3	ICP-AES	Church 1981[44]
3.6	not reported	INAA	Potts <i>et al.</i> 1981[60]
7	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61] Date and Hutchinson 1987[96]
4	not reported	ICP-MS	Jarvis and Jarvis 1988[62]
3.59	0.44	IE-ICP-AES	Jarvis 1989[97]
4.13	not reported	SN-ICP-MS	Roelandts 1990[63] Watkins and Nolan 1990[64]
3	0.1	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
2.35	not reported	IE-ICP-AES	Cantagrel and Pin 1994[43]
4.4	0.5	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
2.5	0.1	IE-ICP-AES	Korotev 1996[45]
3.18	0.34	IE-ICP-AES	Rucandio 1997[66]
2.6	not reported	INAA	Brenner <i>et al.</i> 1999[99]
3.8	0.9	IE-ICP-AES	
4	0.04	ICP-MS	
3.60 (n=14)		Median	
0.84		MADe	
1.68		Expanded uncertainty, k=2	
46.7		Relative expanded uncertainty, %	
1.799-3.6		Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 31: Summary of the published data for Ge in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.76	0.02	SN-ICP-MS	Jarvis and Williams 1989[47]
0.89	0.05	SE-HG-ICP-AES	Halicz 1990[103]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele <i>et al.</i> 1978[7]

Table 32: Summary of the published data for Hf in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
231	not reported	INAA	Potts <i>et al.</i> 1981[60]
220.2	0.4	INAA	Bedard and Barnes 1990[91]
220	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
235	not reported	INAA	Korotev 1996[45]
226 (n=4) 8 16 7.1		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]
148-274			

Table 33: Summary of the published data for Hg in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
23.9	0.85	FAAS	Flanagan <i>et al.</i> 1982[77]
44.5*	1.2	HG-FAAS	Chan and Bina 1989[78]
24	2	CV-AAS	Terashima 1994[79]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
		Originally certified value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 34: Summary of the published data for Ho in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.5	not reported	ICP-MS	Date and Hutchinson 1987[96]
0.91	0.12	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.64	not reported	SN-ICP-MS	Jarvis 1989[97] Watkins and Nolan 1990[64]
0.55	not reported	IE-ICP-AES	1990[64]
<0.7	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.77	0.13	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.74	not reported	INAA	Korotev 1996[45]
0.59	0.07	IE-ICP-AES	Rucandio 1997[66]
0.6	0.01	ICP-MS	Brenner <i>et al.</i> 1999[99]
0.62 (n=8) 0.14 0.28 45.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.42-0.9		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 35: Summary of the published data for La in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
300	not reported	Grimm GDL	Bubert and Hagenah 1981[52]
232*	4.6	ICP-AES	Church 1981[44] Horsky and Fletcher 1981[102]
123	not reported	IE-GF-AAS	
228	not reported	INAA	Potts <i>et al.</i> 1981[60] Robinson and Bennett 1981[86]
268	not reported	WD-XRF	
236	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
250	not reported	Revised value	Hansen and Ring 1985[9] Date and Hutchinson 1987[96]
240	not reported	ICP-MS	
219	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
201	9	IE-ICP-AES	Jarvis and Jarvis 1988[62]
160	not reported	SN-ICP-MS	Jarvis 1989[97] Bedard and Barnes 1990[91]
222.3	0.4	INAA	
232	1	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
215	not reported	IE-ICP-AES	
288	8	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
223.5	not reported	ICP-AES	Cantagrel and Pin 1994[43]
234	13	IE-ICP-AES	Cantagrel and Pin 1994[43]
231	3	IE-ICP-AES	Cantagrel and Pin 1994[43]
242	10	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
228	not reported	INAA	Korotev 1996[45]
217	5	IE-ICP-AES	Rucandio 1997[66]
248	2	ICP-MS	Brenner <i>et al.</i> 1999[99]
231 (n=21) 16 32 13.9		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
250 (n=12)	42	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

Table 36: Summary of the published data for Li in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
43.4	0.6	IEC	Strelow <i>et al.</i> 1978[94]
55	not reported	Grimm GDL	Bubert and Hagenah 1981[52]
39.3*	0.78	ICP-AES	Church 1981[44]
48 (n=10)	20	Provisional value	Steele <i>et al.</i> 1978[7]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	

* Incomplete dissolution

Table 37: Summary of the published data for Lu in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.41 [∞]	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.5	not reported	ICP-MS	Date and Hutchinson 1987[96]
0.38	0.02	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.41	not reported	SN-ICP-MS	Jarvis 1989[97]
0.55	0.02	INAA	Bedard and Barnes 1990[91]
0.51	0.01	IE-ICP-AES	Roelandts 1990[63]
0.7	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
0.53	0.06	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.47	0.04	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.47	0.06	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.47	not reported	INAA	Korotev 1996[45]
0.48	0.02	IE-ICP-AES	Rucandio 1997[66]
0.4	0.01	ICP-MS	Brenner <i>et al.</i> 1999[99]
0.47 (n=13) 0.09 0.18 38.3		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.4 (n=7)	0.2	Revised value (provisional)	Hansen and Ring 1985

Table 38: Summary of the published data for Mo in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<5*	not reported	ICP-AES	Church 1981[44]
1.3	0.14	SE-ICP-AES	Thompson and Zao 1985[104]
0.75	0.08	SN-ICP-MS	Jarvis and Williams 1989[47]
0.920-5 1.82	0.41	Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification ID-ICP-MS	Steele <i>et al.</i> 1978[7] This work

* Incomplete dissolution

Table 39: Summary of the published data for Nb in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
1002	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
991	not reported	WD-XRF	Robinson and Bennett 1981[86]
985	42	WD-XRF	Stork <i>et al.</i> 1987[40]
932	22	SN-ICP-MS	Jarvis and Williams 1989[47]
953.7	not reported	WD-XRF	Harvey 1992[105]
985 (n=5) 25 50 5.1		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele <i>et al.</i> 1978[7]
960 (n=12)	570		

Table 40: Summary of the published data for Nd in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
49*	10	ICP-AES	Church 1981[44]
54.8	not reported	INAA	Potts <i>et al.</i> 1981[60] Robinson and Bennett 1981[86]
59	not reported	WD-XRF	
60	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61] Date and Hutchinson 1987[96]
52	not reported	ICP-MS	
50	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
43.1	2.1	IE-ICP-AES	Jarvis and Jarvis 1988[62]
39.6	not reported	SN-ICP-MS	Jarvis 1989[97] Bedard and Barnes 1990[91]
44	1	INAA	
52	1	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
45.5	not reported	IE-ICP-AES	
45	1	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
47.2	0.8	IE-ICP-AES	Cantagrel and Pin 1994[43]
50.3	4.6	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
48	not reported	INAA	Korotev 1996[45]
48	0.3	IE-ICP-AES	Rucandio 1997[66]
43	0.2	ICP-MS	Brenner <i>et al.</i> 1999[99]
48 (n=17)		Median	
6		MADe	
12		Expanded uncertainty, k=2	
25.0		Relative expanded uncertainty, %	
48 (35-57) [#] (n=11)		Revised value	Hansen and Ring 1985[9]

* Incomplete dissolution

[#] 95% confidence interval

Table 41: Summary of the published data for Ni in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
57	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
7*	1	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
<3	not reported	WD-XRF	1981[86]
3	1	WD-XRF	Stork <i>et al.</i> 1987[40]
2.16	0.29	IE-FAAS	Victor 1987[84] Bedard and Barnes 1990[91]
<DL	not reported	INAA	1990[91]
4.25	not reported	ICP-AES	Cantagrel and Pin 1994[43]
4.1	1.5	IE-ICP-AES	Cantagrel and Pin 1994[43]
<50	not reported	INAA	Korotev 1996[45]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
2-150		Range reported during certification	Steele <i>et al.</i> 1978[7]
1.54	0.27	ID-ICP-MS	This work

Table 42: Summary of the published data for Pb in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
48.6	0.3	IE-AAS	Victor and Strelow 1980[85]
68*	7	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
44	not reported	XRF	1981[86]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
43 (n=28)	17	Originally certified value	Steele <i>et al.</i> 1978[7]
46.04	0.66	ID-ICP-MS	This work

* Incomplete dissolution

Table 43: Summary of the published data for Pr in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
2.43	0.09	Flame emission	Goguel 1981[69]
21.5	not reported	INAA	Potts <i>et al.</i> 1981[60]
<15	not reported	WD-XRF	Robinson and Bennett 1981[86]
21	not reported	ICP-MS	Date and Hutchinson 1987[96]
16.4	1.1	IE-ICP-AES	Jarvis and Jarvis 1988[62]
16.9	not reported	SN-ICP-MS	Jarvis 1989[97]
19	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
16.8	0.7	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
19.9	0.5	IE-ICP-AES	Cantagrel and Pin 1994[43]
17.4	0.8	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
20	not reported	INAA	Korotev 1996[45]
19	2	IE-ICP-AES	Rucandio 1997[66]
18	0.1	ICP-MS	Brenner <i>et al.</i> 1999[99]
18.5 (n=12)		Median	
2.3		MADe	
4.6		Expanded uncertainty, k=2	
24.9		Relative expanded uncertainty, %	
15-21.5		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 44: Summary of the published data for Rb in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
248	not reported	XRF	Vié le Sage <i>et al.</i> 1979[82]
293	not reported	Grimm GDL	Bubert and Hagenah 1981[52]
201	not reported	XRF	Robinson and Bennett 1981[86]
191.1	not reported	XRF	Galson <i>et al.</i> 1983[92]
198	3	XRF	Stork <i>et al.</i> 1987[40]
191 ^o	4	INAA	Bedard and Barnes 1990[91]
198 ^o	not reported	INAA	Korotev 1996[45]
198 (n=7)		Median	
10		MADe	
20		Expanded uncertainty, k=2	
10.1		Relative expanded uncertainty, %	
190 (n=24)	350	Originally certified value	Steele <i>et al.</i> 1978[7]

Table 45: Summary of the published data for S in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
537	not reported	Infrared photometry	Terashima 1978[106]
		Median	
		MADe	
		Expanded uncertainty, k=2	
		Relative expanded uncertainty, %	
650 (n=10)	170	Provisional value	Steele <i>et al.</i> 1978[7]

Table 46: Summary of the published data for Sb in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<14*	not reported	ICP-AES	Church 1981[44]
0.13	not reported	HG-FAAS	Terashima 1986[48]
0.36	0.06	SN-ICP-MS	Jarvis and Williams 1989[47]
0.19	0.03	INAA	Bedard and Barnes 1990[91]
0.11	not reported	INAA	Korotev 1996[45]
0.16 (n=4) 0.06 0.12 75.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.190-2.469		Range reported during certification	Steele <u>et al.</u> 1978[7]

* Incomplete dissolution

Table 47: Summary of the published data for Sc in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
4	not reported	IE-ICP-AES	Bolton <u>et al.</u> 1983[61]
0.22	0.01	INAA	Bedard and Barnes 1990[91]
0.5	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
1.925	not reported	ICP-AES	Cantagrel and Pin 1994[43]
1.87	0.19	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.186	not reported	INAA	Korotev 1996[45]
1.19 (n=6) 1.26 2.52 211.8		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.260-80		Range reported during certification	Steele <u>et al.</u> 1978[7]

Table 48: Summary of the published data for Sm in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
7.5*	1.5	ICP-AES	Church 1981[44]
6.2	not reported	IE-GF-AAS	Horsky and Fletcher 1981[102]
5.6	not reported	INAA	Potts <i>et al.</i> 1981[60]
<10	not reported	WD-XRF	Robinson and Bennett 1981[86]
15	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
4.6	not reported	ICP-MS	Date and Hutchinson 1987[96]
3.53	0.42	IE-ICP-AES	Jarvis and Jarvis 1988[62]
3.76	not reported	SN-ICP-MS	Jarvis 1989[97]
5.18	0.02	INAA	Bedard and Barnes 1990[91]
4.4	0.1	IE-ICP-AES	Roelandts 1990[63]
3.8	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
3.1	0.2	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
4.22	0.03	IE-ICP-AES	Cantagrel and Pin 1994[43]
4.7	0.4	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
4.48	not reported	INAA	Korotev 1996[45]
4.9	0.6	IE-ICP-AES	Rucandio 1997[66]
4.2	0.06	ICP-MS	Brenner <i>et al.</i> 1999[99]
4.5 (n=16)		Median	
1.0		MADe	
2.0		Expanded uncertainty, k=2	
44.4		Relative expanded uncertainty, %	
5 (n=10)	2	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

Table 49: Summary of the published data for Sn in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
12 [*]	2	ICP-AES	Church 1981[44]
7.4	not reported	SE-AAS	Terashima 1982[87]
6.9	0.16	SN-ICP-MS	Jarvis and Williams 1989[47]
0.720-12		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 50: Summary of the published data for Sr in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
4680	10	IEC	Strelow <i>et al.</i> 1978[94]
5300	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
4690 [*]	94	ICP-AES	Church 1981[44]
4192	not reported	WD-XRF	Robinson and Bennett 1981[86]
4545	not reported	WD-XRF	Sørensen 1981[88]
4420	27	WD-XRF	Stork <i>et al.</i> 1987[40]
4586.7	not reported	WD-XRF	Harvey 1992[105]
5420	not reported	ICP-AES	Cantagrel and Pin 1994[43]
5000	325	IE-ICP-AES	Cantagrel and Pin 1994[43]
4782	not reported	INAA	Korotev 1996[45]
4685 (n=10) 300 600 12.8		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele <i>et al.</i> 1978[7]
4600 (n=34) 4728	1000 60	ID-ICP-MS	This work

* Incomplete dissolution

Table 51: Summary of the published data for Ta in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
25.2	not reported	INAA	Potts <i>et al.</i> 1981[60]
18.8	0.62	SN-ICP-MS	Jarvis and Williams 1989[47]
23.7	0.2	INAA	Bedard and Barnes 1990[91]
22.1	not reported	INAA	Korotev 1996[45]
22.9 (n=4) 2.3 4.6 20.1		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
21-26.2		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 52: Summary of the published data for Tb in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.54 [∞]	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.6	not reported	ICP-MS	Date and Hutchinson 1987[96]
0.43	not reported	SN-ICP-MS	Jarvis 1989[97]
0.65	0.09	INAA	Bedard and Barnes 1990[91]
<0.5	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.64	0.07	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.45	not reported	INAA	Korotev 1996[45]
0.82	0.09	IE-ICP-AES	Rucandio 1997[66]
0.6	0.001	ICP-MS	Brenner <i>et al.</i> 1999[99]
0.60 (n=8) 0.08 0.16 26.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.7 (n=9)	0.2	Revised value (provisional)	Hansen and Ring 1985[9]

Table 53: Summary of the published data for Th in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
55 [*]	8.3	ICP-AES	Church 1981[44]
69	not reported	INAA	Potts <i>et al.</i> 1981[60] Robinson and Bennett 1981[86]
68	not reported	WD-XRF	Galson <i>et al.</i> 1983[92]
63.9	not reported	WD-XRF	Jarvis and Williams 1989[47]
58.3	2.4	SN-ICP-MS	Bedard and Barnes 1990[91]
66.9	0.2	INAA	
61.4	not reported	INAA	Korotev 1996[45]
64 (n=7)		Median	
6		MADe	
12		Expanded uncertainty, k=2	
18.8		Relative expanded uncertainty, %	
65 (n=18)	24	Originally certified value	Steele <i>et al.</i> 1978[7]
66 (58-72) [#] (n=21)		Revised value	Hansen and Ring 1985[9]

^{*} Incomplete dissolution

[#] 95% confidence interval

Table 54: Summary of the published data for Tm in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
0.27	not reported	INAA	Potts <i>et al.</i> 1981[60] Date and Hutchinson 1987[96]
0.4	not reported	ICP-MS	Jarvis 1989[97]
0.37	not reported	SN-ICP-MS	Bauer-Wolf <i>et al.</i> 1993[65]
<1.3	not reported	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.17	0.03	IE-ICP-AES	Korotev 1996[45]
0.38	not reported	INAA	
0.4	0.01	ICP-MS	Brenner <i>et al.</i> 1999[99]
0.38 (n=6)		Median	
0.04		MADe	
0.08		Expanded uncertainty, k=2	
21.1		Relative expanded uncertainty, %	
0.230-0.900		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 55: Summary of the published data for U in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
14	not reported	Originally certified value	Steele <i>et al.</i> 1978[7]
12.9	0.4	IEC	Strelow <i>et al.</i> 1978[94]
<20*	not reported	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
15	not reported	WD-XRF	Galson <i>et al.</i> 1983[92]
13.49	not reported	WD-XRF	
15.3	1.4	Fluorimetry	Kanai <i>et al.</i> 1986[89]
17	1	Extractive photometry	Kanai <i>et al.</i> 1986[89] Jarvis and Williams 1989[47]
18.1	0.8	SN-ICP-MS	Bedard and Barnes 1990[91]
17.9	0.2	INAA	
18.3	not reported	INAA	Korotev 1996[45]
16.2 (n=8) 2.7 5.4 33.3		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
14 (n=11)	7	Originally certified value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 56: Summary of the published data for V in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
72.4	0.5	IEC	Strelow <i>et al.</i> 1978[94]
82*	2.5	ICP-AES	Church 1981[44]
88.65	not reported	ICP-AES	Cantagrel and Pin 1994[43]
92.5	4	IE-ICP-AES	Cantagrel and Pin 1994[43]
85 (n=4) 8 16 18.8		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
81 (n=32)	18	Originally certified value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 57: Summary of the published data for W in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
<8*	not reported	ICP-AES	Church 1981[44] Jarvis and Williams 1989[47]
7.72	0.19	SN-ICP-MS	1989[47]
8	not reported	INAA	Korotev 1996[45]
10		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 58: Summary of the published data for Y in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
19	not reported	WD-XRF	Robinson and Bennett 1981[86]
24	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
13	14	WD-XRF	Stork <i>et al.</i> 1987[40]
17	1	IE-ICP-AES	Jarvis and Jarvis 1988[62]
16.6	not reported	SN-ICP-MS	Jarvis 1989[97] Watkins and Nolan 1990[64]
18.8	not reported	IE-ICP-AES	1990[64]
21.85	not reported	ICP-AES	Cantagrel and Pin 1994[43]
22.9	0.6	IE-ICP-AES	Cantagrel and Pin 1994[43]
20.1	0.9	IE-ICP-AES	Cantagrel and Pin 1994[43]
22	not reported	INAA	Korotev 1996[45]
22	9	IE-ICP-AES	Rucandio 1997[66]
20 (n=11) 3 6 30.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
25 (n=11)	17	Provisional value	Steele <i>et al.</i> 1978[7]
22 (15-27) [#] (n=17)		Revised value	Hansen and Ring 1985[9]

[#] 95% confidence interval

Table 59: Summary of the published data for Yb in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
3*	0.1	ICP-AES	Church 1981[44] Horsky and Fletcher 1981[102]
3.8	not reported	IE-GF-AAS	
3.4	not reported	INAA	Potts <i>et al.</i> 1981[60]
4	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61] Date and Hutchinson 1987[96]
2.4	not reported	ICP-MS	
2.45	0.19	IE-ICP-AES	Jarvis and Jarvis 1988[62]
2.67	not reported	SN-ICP-MS	Jarvis 1989[97]
3.14	0.04	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
2.6	not reported	IE-ICP-AES	
2.7	0.1	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
2.95	0.05	IE-ICP-AES	Cantagrel and Pin 1994[43]
2.86	0.12	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
2.84	not reported	INAA	Korotev 1996[45]
3.2	0.6	IE-ICP-AES	Rucandio 1997[66]
3.6	0.02	ICP-MS	Brenner <i>et al.</i> 1999[99]
2.95 (n=15) 0.42 0.84 28.5		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
3 (n=11)	1	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

Table 60: Summary of the published data for Zn in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
514	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
429	1	IE-AAS	Victor and Strelow 1980[85]
439 [*]	13	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
401	not reported	WD-XRF	1981[86]
436.5	not reported	ICP-AES	Cantagrel and Pin 1994[43]
448	11	IE-ICP-AES	Cantagrel and Pin 1994[43]
425	not reported	INAA	Korotev 1996[45]
437 (n=7) 16 32 7.3		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
395 (n=30)	119	Originally certified value	Steele <i>et al.</i> 1978[7]
430.0	5.2	ID-ICP-MS	This work

^{*} Incomplete dissolution

Table 61: Summary of the published data for Zr in SARM 3

Published values ($\mu\text{g}\cdot\text{g}^{-1}$)	Standard deviation ($\mu\text{g}\cdot\text{g}^{-1}$)	Analysis technique	Reference
15900	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
11600*	350	ICP-AES	Church 1981 Watkins and Thompson 1983[55]
12000	not reported	ICP-AES	1983[55]
10000	110	WD-XRF	Stork <i>et al.</i> 1987[40] Bedard and Barnes 1990[91]
11189	109	INAA	1990[91]
11400	100	Spectrometric	Okai 1991[90]
10950.7	not reported	WD-XRF	Harvey 1992[105]
9900	not reported	ICP-AES	Cantagrel and Pin 1994[43]
11700	470	IE-ICP-AES	Cantagrel and Pin 1994[43]
11329	not reported	INAA	Korotev 1996[45]
11329 (n=11) 550 1100 9.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
11000 (n=31)	5000	Originally certified value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Appendix D

Compilation of SARM 4

Table 1: Summary of the published data for SiO₂ in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
52.6	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
53.6	not reported	ICP-AES	Walsh 1980[39]
52.68	0.15	WD-XRF	Stork <i>et al.</i> 1987[40]
52.82	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
52.83	not reported	XRF	Couture <i>et al.</i> 1993[42]
53*	0.4	ICP-AES	Cantagrel and Pin 1994[43]
52.83 (n=6) 0.24 0.48 0.9		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
52.64 (n=71)	0.74	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 2: Summary of the published data for Al₂O₃ in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
16.5	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
16.37	not reported	ICP-AES	Walsh 1980[39]
16.39*	0.59	ICP-AES	Church 1981[44]
16.58	0.05	WD-XRF	Stork <i>et al.</i> 1987[40]
16.74	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
16.6	not reported	XRF	Couture <i>et al.</i> 1993[42]
16.5*	not reported	ICP-AES	Cantagrel and Pin 1994[43]
16.50 (n=7) 0.15 0.30 1.8		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
16.5 (n=74)	0.6	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 3: Summary of the published data for total Fe as Fe₂O₃ in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
8.85	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
8.76	not reported	ICP-AES	Walsh 1980[39]
8.71*	0.19	ICP-AES	Church 1981[44]
9.1	0.05	WD-XRF	Stork <i>et al.</i> 1987[40]
9.22	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
8.99	not reported	XRF	Couture <i>et al.</i> 1993[42]
8.96*	0.06	ICP-AES	Cantagrel and Pin 1994[43]
8.96	not reported	INAA	Korotev 1996[45]
8.96 (n=8) 0.19 0.38 4.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
8.97 (n=73)	0.90	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 4: Summary of the published data for MgO in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
7.47	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
7.37	not reported	ICP-AES	Walsh 1980[39]
7.53*	0.23	ICP-AES	Church 1981[44]
7.51	0.05	WD-XRF	Stork <i>et al.</i> 1987[40]
7.58	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
7.41	not reported	XRF	Couture <i>et al.</i> 1993[42]
7.29*	0.07	ICP-AES	Cantagrel and Pin 1994[43]
7.47 (n=8) 0.09 0.18 2.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
7.5 (n=74)	0.7	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 5: Summary of the published data for CaO in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
11.43	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
11.46	not reported	ICP-AES	Walsh 1980[39]
10.94*	0.36	ICP-AES	Church 1981[44]
11.4	0.3	WD-XRF	Stork <i>et al.</i> 1987[40]
11.45	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
11.58	not reported	XRF	Couture <i>et al.</i> 1993[42]
11.7*	not reported	ICP-AES	Cantagrel and Pin 1994[43]
11.45	not reported	INAA	Korotev 1996[45]
11.45 (n=8) 0.05 0.10 0.9		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
11.5 (n=78)	0.4	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 6: Summary of the published data for Na₂O in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
2.38	not reported	ICP-AES	Walsh 1980[39]
2.47*	0.08	ICP-AES	Church 1981[44]
2.43	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
2.28	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
2.54	not reported	XRF	Couture <i>et al.</i> 1993[42]
2.42*	0.08	ICP-AES	Cantagrel and Pin 1994[43]
2.48	not reported	INAA	Korotev 1996[45]
2.43 (n=7) 0.07 0.14 5.8		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
2.46 (n=54)	0.17	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 7: Summary of the published data for K₂O in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.47	not reported	ICP-AES	Walsh 1980[39]
0.258*	0.007	ICP-AES	Church 1981[44]
0.24	0.01	WD-XRF	Stork <i>et al.</i> 1987[40]
0.25	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.24	not reported	XRF	Couture <i>et al.</i> 1993[42]
0.25*	0.07	ICP-AES	Cantagrel and Pin 1994[43]
0.25 (n=6) 0.01 0.02 8.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.25 (n=63)	0.07	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 8: Summary of the published data for TiO₂ in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.19	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
0.19	not reported	ICP-AES	Walsh 1980[39]
0.185*	0.005	ICP-AES	Church 1981[44]
0.2	0.01	WD-XRF	Stork <i>et al.</i> 1987[40]
0.49	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.2	not reported	XRF	Couture <i>et al.</i> 1993[42]
0.19*	0.006	ICP-AES	Cantagrel and Pin 1994[43]
0.19 (n=7) 0.01 0.02 10.5		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.20 (n=65)	0.03	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 9: Summary of the published data for MnO in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.18	not reported	ICP-AES	Brenner <i>et al.</i> 1980[38]
0.17	not reported	ICP-AES	Walsh 1980[39]
0.18*	0.005	ICP-AES	Church 1981[44]
0.18	0.002	WD-XRF	Stork <i>et al.</i> 1987[40]
0.19	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.19	not reported	XRF	Couture <i>et al.</i> 1993[42]
0.18*	0.006	ICP-AES	Cantagrel and Pin 1994[43]
0.18 (n=7) 0.01 0.02 11.1		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.18 (n=69)	0.01	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 10: Summary of the published data for P₂O₅ in SARM 4

Published values (% oxide)	Standard deviation (% oxide)	Analysis technique	Reference
0.035	not reported	Spectrophotometric	Watkins 1979[46]
0.03	not reported	ICP-AES	Walsh 1980[39]
0.018*	0.002	ICP-AES	Church 1981[44]
0.02	0.005	WD-XRF	Stork <i>et al.</i> 1987[40]
0.02	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
0.03	not reported	XRF	Couture <i>et al.</i> 1993[42]
0.051	not reported	ICP-AES	Cantagrel and Pin 1994[43]
0.049	0.005	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.03 (n=8) 0.01 0.02 66.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.03 (n=33)	0.02	Originally certified value	Steele and Hansen 1979[8]

* Incomplete dissolution

Table 11: Summary of the published data for Ag in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<3*	not reported	ICP-AES	Church 1981[44]
9.45	not reported	HG-FAAS	Terashima 1986[48]
0.76	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
<2	not reported	INAA	Korotev 1996[45]
0.13 - 17		Median MADe Expanded uncertainty, k=2 Relative uncertainty, % Range reported during certification	Steele <u>et al.</u> 1978[7]

* Incomplete dissolution

Table 12: Summary of the published data for As in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<6*	not reported	ICP-AES	Church 1981[44]
0.4	not reported	HG-FAAS	Terashima 1986[48]
<DL	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
<1	not reported	INAA	Korotev 1996[45]
0.46		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Reported during certification	Steele <u>et al.</u> 1978[7]

* Incomplete dissolution

DL = detection limit

Table 13: Summary of the published data for Au in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<3*	not reported	ICP-AES	Church 1981[44]
0.76*	0.06	SE-FAAS (GTA)	Terashima 1988[49]
<6	not reported	INAA	Korotev 1996[45]
0.00065	0.000145	NiS Fire assay ICP-MS	Plessen and Erzinger 1998[50]
0.004		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 14: Summary of the published data for B in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
2.7*	not reported	ICP-AES	Walsh 1985[51]
4.76	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
2.5 - 9		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 15: Summary of the published data for Ba in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
90	7	IEC	Strelow et al. 1978[94]
200	not reported	Grimm GDL	Bubert and Hagenah 1981[52]
80.3*	1.6	ICP-AES	Church 1981[44]
99	not reported	XRF	Robinson and Bennett 1981[86]
89.8	3.3	XRF	Verma et al. 1992[41]
83.75	not reported	ICP-AES	Cantagrel and Pin 1994[43]
90	5.2	IE-ICP-AES	Cantagrel and Pin 1994[43]
84	not reported	INAA	Korotev 1996[45]
89.9 (n=8)		Median	
8.9		MADe	
17.8		Expanded uncertainty, k=2	
19.8		Relative expanded uncertainty, %	
102 (n=22)	21	Originally certified value	Steele et al.1978[7]
82.9	1.1	ID-ICP-MS	This work

* Incomplete dissolution

Table 16: Summary of the published data for Be in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.27	0.02	IEC	Strelow et al. 1978[94]
0.43*	0.02	ICP-AES	Church 1981[44]
419*	43	SE-FAAS	Vilcsek and Lohmann 1982[54]
0.38	not reported	ICP-AES	Watkins and Thompson 1983[55]
1.04	0.82	SN-ICP-MS	Jarvis and Williams1989[47]
		Median	
		MADe	
		Expanded uncertainty, k=2	
		Relative expanded uncertainty, %	
0.26 - 3		Range reported during certification	Steele et al. 1978[7]

* Incomplete dissolution

Table 17: Summary of the published data for Bi in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.01	not reported	FD-FAAS	Heinrichs 1979[56]
<25*	not reported	ICP-AES	Church 1981[44]
11	not reported	SE-HG-FAAS	Terashima 1984[57]
<DL*	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.6		Reported during certification	Steele <u>et al.</u> 1978[7]

* Incomplete dissolution

DL = detection limit

Table 18: Summary of the published data for Cd in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.047		FD-FAAS	Heinrichs 1979[56]
<2*		ICP-AES	Church 1981[44]
<DL		SN-ICP-MS	Jarvis and Williams 1989[47]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
1 – 4		Range reported during certification	Steele <u>et al.</u> 1978[7]
0.0879	0.0032	ID-IP-MS	This work

* Incomplete dissolution

DL = detection limit

Table 19: Summary of the published data for Ce in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
10	3	IE-CES	Mazzucotelli and Vannucci 1980[59]
<15*	not reported	ICP-AES	Church 1981[44]
5.9	not reported	INAA	Potts <i>et al.</i> 1981[60]
<10	not reported	XRF	Robinson and Bennett 1981[86]
39	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
<12	not reported	XRF	Juras <i>et al.</i> 1987[107]
6.32	0.4	IE-ICP-AES	Jarvis and Jarvis 1988[62]
5.69	not reported	HPIC - light detector	Le Roex and Watkins 1990[108]
6.32	not reported	ICP-AES	Le Roex and Watkins 1990[108]
4.8	0.1	IE-ICP-AES	Roelandts 1990[63]
5.5	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
5	0.7	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
7.3	3	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
5.85	not reported	ICP-AES	Cantagrel and Pin 1994[43]
5.9	1.8	IE-ICP-AES	Cantagrel and Pin 1994[43]
5.74	0.02	IE-ICP-AES	Cantagrel and Pin 1994[43]
5.87	0.39	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
5.62	not reported	INAA	Korotev 1996[45]
5.8	0.03	IE-ICP-MS	Pin and Joannon 1997[109]
5.86 (n=19)		Median	
0.44		MADe	
0.88		Expanded uncertainty, k=2	
15.0		Relative expanded uncertainty, %	
6 (n=13)	3	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

Table 20: Summary of the published data for Cl in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
34	not reported	IE-CIC (LECO)	Evans and Moore 1980[100]
40 - 300		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele and Hansen 1979[8]

Table 21: Summary of the published data for Co in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
56.4*	1.7	ICP-AES	Church 1981[44]
59	not reported	INAA	Potts <i>et al.</i> 1981[60] Robinson and Bennett 1981[86]
51	not reported	XRF	Victor 1986[68]
59.5	0.1	IE-FAAS	Verma <i>et al.</i> 1992[41]
51	1.2	XRF	Korotev 1996[45]
59.2	not reported	INAA	
57.7 (n=6) 2.4 4.8 8.3		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
58 (n=34)	10	Originally certified value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 22: Summary of the published data for Cr in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
31.1*	1.6	ICP-AES	Church 1981[44]
28	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
37.5	2.5	WD-XRF	Verma <i>et al.</i> 1992[41]
42.05	not reported	ICP-AES	Cantagrel and Pin 1994[43]
32.8	3	IE-ICP-AES	Cantagrel and Pin 1994[43]
30	not reported	XRF	Class <i>et al.</i> 1994[110]
9	not reported	INAA	Korotev 1996[45]
31.1 (n=7) 4.6 9.2 29.6		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
30 (n=34)	8	Originally certified value (provisional)	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 23: Summary of the published data for Cs in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.23	0.02	Flame emission	Goguel 1981[69]
0.22	not reported	Flame emission	Terashima and Mita 1981[70]
0.24	not reported	INAA	Korotev 1996[45]
0.23 (n=3) 0.01 0.02 8.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.2-4		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 24: Summary of the published data for Cu in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
8*	1	ICP-AES	Church 1981[44]
15	not reported	XRF	Robinson and Bennett 1981[86]
13.22	0.09	IE-AAS	Victor 1983[71]
12	not reported	XRF	Webb <i>et al.</i> 1990[72]
12.5	1.1	XRF	Verma <i>et al.</i> 1992[41]
10.6	not reported	ICP-AES	Cantagrel and Pin 1994[43]
11	0.3	IE-ICP-AES	Cantagrel and Pin 1994[43]
12.0 (n=7)		Median	
1.8		MADe	
3.6		Expanded uncertainty,	
30.0		k=2	
		Relative expanded uncertainty, %	
14 (n=34)	4	Originally certified value	Steele <i>et al.</i> 1978[7]
10.67	0.23	ID-ICP-MS	This work

* Incomplete dissolution

Table 25: Summary of the published data for Dy in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
1.1	not reported	INAA	Potts <i>et al.</i> 1981[60]
5	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
1.4	not reported	IE-GF-AAS (GTA)	Juras <i>et al.</i> 1987[107]
1	0.01	IE-ICP-AES	Jarvis and Jarvis 1988[62]
1.1	not reported	HPIC - light detector	Le Roex and Watkins 1990[108]
1	not reported	ICP-AES	Le Roex and Watkins 1990[108]
1.2	0.1	IE-ICP-AES	Roelandts 1990[63]
1.06	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
1.12	0.2	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
1.3	0.2	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
1.05	0.01	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.98	0.23	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
1.1	not reported	INAA	Korotev 1996[45]
1.06	0.007	IE-ICP-MS	Pin and Joannon 1997[109]
1.1 (n=14)		Median	
0.1		MADe	
0.2		expanded uncertainty, k=2	
18.2		Relative expanded uncertainty, %	
1.099-1.929		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 26: Summary of the published data for Er in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.66	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.9	not reported	IE-FAAS (GTA)	Juras <i>et al.</i> 1987[107]
0.67	0.04	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.64	not reported	HPIC - light detector	Le Roex and Watkins 1990[108]
0.67	not reported	ICP-AES	Le Roex and Watkins 1990[108]
0.67	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
0.71	0.08	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.5	0.2	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.84	0.02	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.63	0.1	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.66	not reported	INAA	Korotev 1996[45]
0.655	0.007	IE-ICP-MS	Pin and Joannon 1997[109]
0.665 (n=12)		Median	
0.026		MADe	
0.052		Expanded uncertainty, k=2	
7.8		Relative expanded uncertainty, %	
		Originally certified value	Steele <i>et al.</i> 1978[7]

Table 27: Summary of the published data for Eu in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<0.6*	not reported	ICP-AES	Church 1981[44] Horsky and Fletcher 1981[102]
0.8	not reported	IE-GF-AAS	
0.59	not reported	INAA	Potts <i>et al.</i> 1981[60]
1.9	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
0.4	not reported	IE-FAAS (GTA)	Juras <i>et al.</i> 1987[107]
0.57	0.01	IE-ICP-AES	Jarvis and Jarvis 1988[62] Le Roex and Watkins 1990[108]
0.6	not reported	HPIC - light detector	Le Roex and Watkins 1990[108]
0.57	not reported	ICP-AES	1990[108]
0.65	0.01	IE-ICP-AES	Roelandts 1990[63]
0.58	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
0.52	0.15	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.5	0.2	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.6	0.02	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.62	0.05	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.589	not reported	INAA	Korotev 1996[45]
0.58	0.002	IE-ICP-MS	Pin and Joannon 1997[109]
0.59 (n=15) 0.03 0.06 10.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.63 (0.59- 0.69) [#] (n=14)		Revised value	Hansen and Ring 1985[9]

[#] 95% confidence interval

Table 28: Summary of the published data for F in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
22	1	ISE	Troll and Farzaneh 1978[73]
59.4	5	INAA	Esprit <i>et al.</i> 1984[74]
35	not reported	PIGE	Roelandts <i>et al.</i> 1985[75]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele and Hansen 1979[8]
10-530			

Table 29: Summary of the published data for Ga in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
18	not reported	XRF	Robinson and Bennett 1981[86]
16.2	0.2	IE-FAAS	Van der Walt and Strelow 1984[76]
15	not reported	XRF	Webb <i>et al.</i> 1990[72]
16.2 (n=3) 1.8 3.6 22.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
16 (n=13)	3	Originally certified value	Steele <i>et al.</i> 1978[7]

Table 30: Summary of the published data for Gd in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<2*	not reported	ICP-AES	Church 1981[44]
0.99	not reported	INAA	Potts <i>et al.</i> 1981[60]
5	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
0.91	0.03	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.93	not reported	HPIC-light detector	Le Roex and Watkins 1990[108]
0.91	not reported	ICP-AES	Le Roex and Watkins 1990[108]
0.8	0.01	IE-ICP-AES	Roelandts 1990[63]
0.96	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
0.98	0.1	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.6	0.2	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.91	0.04	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.97	0.11	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.94	not reported	INAA	Korotev 1996[45]
1.01	0.03	IE-ICP-MS	Pin and Joannon 1997[109]
0.94 (n=13) 0.04 0.08 8.5 0.12-0.74		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 31: Summary of the published data for Ge in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
1.67	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
1.54	0.03	SE-HG-ICP-AES	Halicz 1990[103]
1.0-1.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 32: Summary of the published data for Hf in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.38	not reported	INAA	Potts et al. 1981[60] Watkins and Nolan 1990[64]
0.1	not reported	IE-ICP-AES	
0.36	not reported	INAA	Korotev 1996[45]
0.36 (n=3) 0.03 0.06 16.7 0.2-5		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele et al. 1978[7]

Table 33: Summary of the published data for Hg in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
20.4	0.89	FAAS	Flanagan et al. 1982[77]
12.8*	0.63	HG-FAAS	Chan and Bina 1989[78]
54	3	CV-AAS	Terashima 1994[79]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele et al. 1978[7]

* Incomplete dissolution

Table 34: Summary of the published data for Ho in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.23	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.22	not reported	IE-ICP-AES	Jarvis and Jarvis 1988[62] Watkins and Nolan 1990[64]
0.22	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
<0.25	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
<0.2	not reported	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.22	0.03	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.24	not reported	INAA	Korotev 1996[45]
0.227	0.002	IE-ICP-MS	Pin and Joannon 1997[109]
0.22 (n=6)		Median	
0.01		MADe	
0.02		Expanded uncertainty, k=2	
9.1		Relative expanded uncertainty, %	
0.22		Reported during certification	Steele <i>et al.</i> 1978[7]

Table 35: Summary of the published data for La in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<5*	not reported	ICP-AES	Church 1981[44]
2.6	not reported	INAA	Potts <i>et al.</i> 1981[60] Robinson and Bennett 1981[86]
<5	not reported	WD-XRF	1981[86]
11	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
<3	not reported	XRF	Juras <i>et al.</i> 1987[107]
5	not reported	WD-XRF	Stork <i>et al.</i> 1987[40]
3.09	0.61	IE-ICP-AES	Jarvis and Jarvis 1988[62] Le Roex and Watkins 1990[108]
2.67	not reported	HPIC-light detector	1990[108] Le Roex and Watkins 1990[108]
3.09	not reported	ICP-AES	1990[108]
3.9	0.1	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
2.8	not reported	IE-ICP-AES	1990[64]
3.9	0.1	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
2.4	1	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
2.5	not reported	ICP-AES	Cantagrel and Pin 1994[43]
3.1	1.3	IE-ICP-AES	Cantagrel and Pin 1994[43]
3.65	0.55	IE-ICP-AES	Cantagrel and Pin 1994[43]
3.01	0.09	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
2.84	not reported	INAA	Korotev 1996[45]
2.87	0.02	IE-ICP-MS	Pin and Joannon 1997[109]
3.05 (n=16) 0.62 1.24 40.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
3 (n=11)	0.4	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

Table 36: Summary of the published data for Li in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
5.1	0.3	IEC	Strelow <i>et al.</i> 1978[94] Bubert and Hagenah 1981[52]
7.2	not reported	Grimm GDL	Church 1981[44]
<2*	0.78	ICP-AES	
4-9		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 37: Summary of the published data for Lu in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.11	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.11	not reported	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.11	0.01	IE-ICP-AES	Roelandts 1990[63] Watkins and Nolan 1990[64]
0.1	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.17	0.05	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.3	0.1	IE-XRF	Cantagrel and Pin 1994[43]
0.09	0.01	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.17	0.03	IE-ICP-AES	Korotev 1996[45]
0.101	not reported	INAA	Pin and Joannon 1997[109]
0.112	0.001	IE-ICP-MS	
0.11 (n=10) 0.01 0.02 18.2		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Revised value (provisional)	Hansen and Ring 1985[9]
0.2 (n=7)	0.1		

Table 38: Summary of the published data for Mo in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<4*	not reported	ICP-AES	Church 1981[44]
0.93	not reported	SE-ICP-AES	Thompson and Zao 1985[104]
<DL	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]
0.84-60 0.888	0.053	ID-ICP-MS	This work

* Incomplete dissolution

DL = detection limit

Table 39: Summary of the published data for Nb in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
4	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
<2	not reported	WD-XRF	Robinson and Bennett 1981[86]
0.68	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
0.3	0.02	SSMS	Jochum <i>et al.</i> 1990[111]
0.3	0.02	XRF	Jochum <i>et al.</i> 1990[111]
2	not reported	XRF	Webb <i>et al.</i> 1990[72]
0.97	0.03	WD-XRF	Verma <i>et al.</i> 1992[41]
0.63	0.02	ICP-MS	Poitrasson <i>et al.</i> 1993[83]
0.36	0.01	IE-HPLC	Rèhkamper 1994[112]
0.27	not reported	WD-XRF	Etoubleau <i>et al.</i> 1999[113]
0.32	not reported	IE-WD-XRF	Etoubleau <i>et al.</i> 1999[113]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]
2-3			

Table 40: Summary of the published data for Nd in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<20*	not reported	ICP-AES	Church 1981[44]
3.2	not reported	INAA	Potts <i>et al.</i> 1981[60] Robinson and Bennett 1981[86]
<12	not reported	WD-XRF	Bolton <i>et al.</i> 1983[61]
<30	not reported	IE-ICP-AES	Juras <i>et al.</i> 1987[107]
8	not reported	XRF	Jarvis and Jarvis 1988[62]
3.32	0.25	IE-ICP-AES	Le Roex and Watkins 1990[108]
3.22	not reported	HPIC-light detector	Le Roex and Watkins 1990[108]
3.32	not reported	ICP-AES	Roelandts 1990[63]
3.1	0.1	IE-ICP-AES	Watkins and Nolan 1990[64]
3.9	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
3.1	0.3	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
2	0.6	IE-XRF	Cantagrel and Pin 1994[43]
3.03	0.09	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
2.97	0.21	IE-ICP-AES	Korotev 1996[45]
3.2	not reported	INAA	Pin and Joannon 1997[109]
3.18	0.01	IE-ICP-MS	
3.20 (n=13)		Median	
0.18		MADe	
0.36		Expanded uncertainty, k=2	
11.3		Relative expanded uncertainty, %	
3 (n=7)	2	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

Table 41: Summary of the published data for Ni in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
101	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
117*	3.5	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
122	not reported	WD-XRF	Victor 1987[84]
122.9	0.3	IE-FAAS	Victor 1987[84]
117	not reported	XRF	Webb <i>et al.</i> 1990[72]
110	not reported	WD-XRF	Verma <i>et al.</i> 1992[41]
119.5	not reported	ICP-AES	Cantagrel and Pin 1994[43] Cantagrel and Pin 1994[43]
122	5	IE-ICP-AES	1994[43]
122	not reported	INAA	Korotev 1996[45]
119.5 (n=9)		Median	
3.7		MADe	
7.4		Expanded uncertainty, k=2	
6.2		Relative expanded uncertainty, %	
120 (n=44)	22	Originally certified value	Steele <i>et al.</i> 1978[7]
119.3	5.4	ID-ICP-MS	This work

* Incomplete dissolution
DL = detection limit

Table 42: Summary of the published data for Pb in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
2.48	0.05	IE-AAS	Victor and Strelow 1980[85]
<13*	not reported	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
21	not reported	WD-XRF	1981[86]
		Median	
		MADe	
		Expanded uncertainty, k=2	
		Relative expanded uncertainty, %	
0.8-26		Range reported during certification	Steele <i>et al.</i> 1978[7]
2.110	0.031	ID-ICP-MS	This work

* Incomplete dissolution

Table 43: Summary of the published data for Pr in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
2.43	0.09	Flame emission	Goguel 1981[69]
0.74	not reported	INAA	Potts <i>et al.</i> 1981[60]
<15	not reported	WD-XRF	Robinson and Bennett 1981[86]
0.77	0.04	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.75	not reported	HPIC-light detector	Le Roex and Watkins 1990[108]
0.77	not reported	ICP-AES	Le Roex and Watkins 1990[108]
0.67	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
0.7	0.1	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.7	0.3	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.48	0.16	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.69	0.12	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.71	not reported	INAA	Korotev 1996[45]
0.73	0.005	IE-ICP-MS	Pin and Joannon 1997[109]
0.72 (n=12)		Median	
0.04		MADe	
0.08		Expanded uncertainty, k=2	
11.1		Relative expanded uncertainty, %	
0.72		Reported during certification	Steele <i>et al.</i> 1978[7]

Table 44: Summary of the published data for Rb in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
1	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
8.8	not reported	Grimm GDL	Bubert and Hagenah 1981[52]
7	not reported	WD-XRF	Robinson and Bennett 1981[86]
191.1	not reported	XRF	Galson <i>et al.</i> 1983[92]
5	not reported	XRF	Webb <i>et al.</i> 1990[72]
3.9	0.2	WD-XRF	Verma <i>et al.</i> 1992[41]
4.9	not reported	INAA	Korotev 1996[45]
2.4-18		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 45: Summary of the published data for S in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
50	not reported	Combustion/Infrared photometry	Terashima 1978[106]
42-140		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 46: Summary of the published data for Sb in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<18 [*]	not reported	ICP-AES	Church 1981[44]
0.05	not reported	HG-FAAS	Terashima 1986[48] Jarvis and Williams 1989[47]
<DL	not reported	SN-ICP-MS	1989[47]
0.06	not reported	INAA	Korotev 1996[45]
0.07-0.49		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Originally certified value	Steele et al. 1978[7]

^{*} Incomplete dissolution

DL = detection limit

Table 47: Summary of the published data for Sc in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
36	not reported	IE-ICP-AES	Bolton et al. 1983[61]
37.4	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
38.7	not reported	ICP-AES	Cantagrel and Pin 1994[43]
39.4	2.1	IE-ICP-AES	Cantagrel and Pin 1994[43]
39.8	not reported	INAA	Korotev 1996[45]
38.7 (n=5) 1.6 3.2 8.3 31-130		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele et al. 1978[7]

Table 48: Summary of the published data for Sm in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<5*	not reported	ICP-AES	Church 1981[44]
<1	not reported	IE-GF-AAS	Horsky and Fletcher 1981[102]
0.91	not reported	INAA	Potts <u>et al.</u> 1981[60]
<10	not reported	WD-XRF	Robinson and Bennett 1981[86]
<15	not reported	IE-ICP-AES	Bolton <u>et al.</u> 1983[61]
1.5	not reported	IE-GF-AAS (GTA)	Juras <u>et al.</u> 1987[107]
0.78	0.06	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.85	not reported	HPIC-light detector	Le Roex and Watkins 1990[108]
0.78	not reported	ICP-AES	Le Roex and Watkins 1990[108]
0.88	0.01	IE-ICP-AES	Roelandts 1990[63]
0.82	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
<1.2	not reported	IE-ICP-AES	Bauer-Wolf <u>et al.</u> 1993[65]
0.8	0.2	IE-XRF	Bauer-Wolf <u>et al.</u> 1993[65]
0.77	0.01	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.84	0.09	IE-ICP-AES	Fariñas <u>et al.</u> 1995[98]
0.837	not reported	INAA	Korotev 1996[45]
0.807	0.004	IE-ICP-MS	Pin and Joannon 1997[109]
0.83 (n=12)		Median	
0.04		MADe	
0.08		Expanded uncertainty,	
9.6		k=2	
		Relative expanded uncertainty, %	
0.8 (n=9)	0.2	Revised value (provisional)	Hansen and Ring 1985[9]

* Incomplete dissolution

Table 49: Summary of the published data for Sn in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<3*	not reported	ICP-AES	Church 1981[44]
0.27	not reported	SE-AAS	Terashima 1982[87]
0.28	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
0.23	not reported	SSMS	Jochum <i>et al.</i> 1993[114]
0.3-5		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 50: Summary of the published data for Sr in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
264	1	IEC	Strelow <i>et al.</i> 1978[94]
256	not reported	XRF	Vié le Sage <i>et al.</i> 1979[82]
253*	5.1	ICP-AES	Church 1981[44]
268	not reported	WD-XRF	Robinson and Bennett 1981[86]
266	not reported	XRF	Webb <i>et al.</i> 1990[72]
264.6	1.2	WD-XRF	Verma <i>et al.</i> 1992[41]
250	not reported	ICP-AES	Cantagrel and Pin 1994[43]
251	6.8	IE-ICP-AES	Cantagrel and Pin 1994[43]
269	not reported	INAA	Korotev 1996[45]
264 (n=9) 7 14 5.3		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
260 (n=34) 260.9	39 4.6	Originally certified value ID-ICP-MS	Steele <i>et al.</i> 1978[7] This work

* Incomplete dissolution

Table 51: Summary of the published data for Ta in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.07	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.09	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
0.16	not reported	ICP-MS	Poitrasson <i>et al.</i> 1993[83]
0.064	not reported	INAA	Korotev 1996[45]
0.08 (n=4) 0.02 0.04 50.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.06-0.4		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 52: Summary of the published data for Tb in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.17	not reported	INAA	Potts <i>et al.</i> 1981[60]
0.15	not reported	HPIC-light detector	Le Roex and Watkins 1990[108]
<0.19	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
<0.2	not reported	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.16	0.02	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.164	not reported	INAA	Korotev 1996[45]
0.162	0.0004	IE-ICP-MS	Pin and Joannon 1997[109]
0.162 (n=5) 0.003 0.006 3.7		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.1-0.16		Range reported during certification	Steele <i>et al.</i> 1978[7]

Table 53: Summary of the published data for Th in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<25*	not reported	ICP-AES	Church 1981[44]
0.42	not reported	INAA	Potts <i>et al.</i> 1981[60]
<3	not reported	XRF	Robinson and Bennett 1981[86]
3.6	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
0.34	not reported	INAA	Korotev 1996[45]
0.42 (n=3) 0.12 0.24 57.1		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.2-5		Range reported during original certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 54: Summary of the published data for Tm in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.1	not reported	INAA	Potts <i>et al.</i> 1981[60]
<0.5	not reported	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
<0.2	not reported	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.1	0.01	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.099	not reported	INAA	Korotev 1996[45]
0.106	0.001	IE-ICP-MS	Pin and Joannon 1997[109]
0.100 (n=4) 0.001 0.002 2.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.1		Reported during certification	Steele <i>et al.</i> 1978[7]



Table 55: Summary of the published data for U in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.4	0.1	IEC	Strelow <i>et al.</i> 1978[94]
<20*	not reported	ICP-AES	Church 1981[44]
<2	not reported	WD-XRF	Robinson and Bennett 1981[86]
0.32	not reported	DNC	Massey 1983[115]
0.28	0.03	IE-Fluorimetry	Kanai <i>et al.</i> 1986[89]
0.93	not reported	SN-ICP-MS	Jarvis and Williams 1989[47]
0.4	not reported	INAA	Korotev 1996[45]
0.4 (n=5) 0.1 0.2 50.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.26-5		Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 56: Summary of the published data for V in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
217	2.2	IEC	Strelow <i>et al.</i> 1978[94]
225*	6.8	ICP-AES	Church 1981[44]
201.3	1.3	WD-XRF	Verma <i>et al.</i> 1992[41]
209.5	not reported	ICP-AES	Cantagrel and Pin 1994[43]
215	1	IE-ICP-AES	Cantagrel and Pin 1994[43]
215 (n=5) 8 16 7.4		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
220 (n=31)	37	Originally certified value	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 57: Summary of the published data for W in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
<7*	not reported	ICP-AES	Church 1981[44] Jarvis and Williams 1989[47]
<DL	0.19	SN-ICP-MS	1989[47]
<2	not reported	INAA	Korotev 1996[45]
10-400		Median MADe Uncertainty, k=2 Relative uncertainty, % Range reported during certification	Steele <i>et al.</i> 1978[7]

* Incomplete dissolution

Table 58: Summary of the published data for Y in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
5	not reported	WD-XRF	Robinson and Bennett 1981[86]
6	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61] Jarvis and Jarvis 1988[62]
5.67	0.16	IE-ICP-AES	Watkins and Nolan 1990[64]
5.5	not reported	IE-ICP-AES	1990[64]
8	not reported	XRF	Webb <i>et al.</i> 1990[72]
7.3	0.2	WD-XRF	Verma <i>et al.</i> 1992[41]
6.47	not reported	ICP-AES	Cantagrel and Pin 1994[43]
6.68	0.41	IE-ICP-AES	Cantagrel and Pin 1994[43]
5.89	0.18	IE-ICP-AES	Cantagrel and Pin 1994[43]
6.5	not reported	INAA	Korotev 1996[45]
6.2 (n=10) 0.7 1.4 22.6		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
6 (n=13)	3	Originally certified value	Steele <i>et al.</i> 1978[7] Hansen and Ring 1985[9]
7 (n=14)	3	Revised value (provisional)	1985[9]

Table 59: Summary of the published data for Yb in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
0.97 [*]	0.05	ICP-AES	Church 1981[44]
0.95	not reported	IE-GF-AAS	Horsky and Fletcher 1981[102]
1.1	not reported	IE-GF-AAS	Horsky and Fletcher 1981[102]
0.67 [∞]	not reported	INAA	Potts <i>et al.</i> 1981[60]
2	not reported	IE-ICP-AES	Bolton <i>et al.</i> 1983[61]
0.7	not reported	IE-FAAS (GTA)	Juras <i>et al.</i> 1987[107]
0.65	0.02	IE-ICP-AES	Jarvis and Jarvis 1988[62]
0.68	not reported	HPIC-light detector	Le Roex and Watkins 1990[108]
0.65	not reported	ICP-AES	Le Roex and Watkins 1990[108]
0.66	0.04	IE-ICP-AES	Roelandts 1990[63]
2.6	not reported	IE-ICP-AES	Watkins and Nolan 1990[64]
0.71	0.06	IE-ICP-AES	Bauer-Wolf <i>et al.</i> 1993[65]
0.6	0.2	IE-XRF	Bauer-Wolf <i>et al.</i> 1993[65]
0.7	0.006	IE-ICP-AES	Cantagrel and Pin 1994[43]
0.79	0.13	IE-ICP-AES	Fariñas <i>et al.</i> 1995[98]
0.657 [∞]	not reported	INAA	Korotev 1996[45]
0.688	0.008	IE-ICP-MS	Pin and Joannon 1997[109]
0.70 (n=17) 0.07 0.14 20.0		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
0.7 (n=10)	0.5	Revised value (provisional)	Hansen and Ring 1985[9]

^{*} Incomplete dissolution

[∞] Primary method

Table 60: Summary of the published data for Zn in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
54	not reported	WD-XRF	Vié le Sage et al. 1979[82]
65.9	0.2	IE-AAS	Victor and Strelow 1980[85]
61.9*	3.1	ICP-AES	Church 1981[44]
62	not reported	WD-XRF	Robinson and Bennett 1981[86]
63	not reported	XRF	Webb et al. 1990[72]
63.5	1.1	WD-XRF	Verma et al. 1992[41]
64.05	not reported	ICP-AES	Cantagrel and Pin 1994[43]
61.4	2.9	IE-ICP-AES	Cantagrel and Pin 1994[43]
62.5 (n=8)		Median	
1.6		MADe	
3.2		Expanded uncertainty, k=2	
5.1		Relative expanded uncertainty, %	
68 (n=29)	19	Originally certified value	Steele et al. 1978[7]
61.42	0.91	ID-ICP-MS	This work

* Incomplete dissolution

Table 61: Summary of the published data for Zr in SARM 4

Published values	Standard deviation	Analysis technique	Reference
$\mu\text{g}\cdot\text{g}^{-1}$	$\mu\text{g}\cdot\text{g}^{-1}$		
ND	not reported	WD-XRF	Vié le Sage <i>et al.</i> 1979[82]
17*	1	ICP-AES	Church 1981[44] Robinson and Bennett 1981[86]
23	not reported	WD-XRF	Watkins and Thompson 1983[55]
20	not reported	ICP-AES	Jochum <i>et al.</i> 1990[111]
10.5	0.5	SSMS	Jochum <i>et al.</i> 1990[111]
10.5	0.5	XRF	Webb <i>et al.</i> 1990[72]
23	not reported	XRF	Verma <i>et al.</i> 1992[41]
13.6	0.1	WD-XRF	Cantagrel and Pin 1994[43]
25.7	not reported	ICP-AES	Cantagrel and Pin 1994[43]
11	3	IE-ICP-AES	Cantagrel and Pin 1994[43]
<80	not reported	INAA	Korotev 1996[45]
		Median MADe Expanded uncertainty, k=2 Relative expanded uncertainty, %	
23 (n=11)	12	Originally certified value (provisional)	Steele <i>et al.</i> 1978[7]

ND = not detected

* Incomplete dissolution

Appendix E

Isotopic composition of the isotope enriched standards used for the HR-ICP-MS analysis

¹³⁵ Ba standard	Abundance, %	Specification	Standard uncertainty
¹³⁰ Ba	<0.010		
¹³² Ba	0.057	0.00	0.000000
¹³⁴ Ba	0.466	0.00	0.000000
¹³⁵ Ba	93.380	0.02	0.011547005
¹³⁶ Ba	1.640	0.01	0.005773503
¹³⁷ Ba	0.890	0.01	0.005773503
¹³⁸ Ba	3.560	0.02	0.011547005

⁸⁶ Sr standard	Abundance, %	Specification	Standard uncertainty
⁸⁴ Sr	0.08	0.01	0.005773503
⁸⁶ Sr	97.02	0.04	0.023094011
⁸⁷ Sr	0.78	0.01	0.005773503
⁸⁸ Sr	2.12	0.03	0.017320508

⁶⁷ Zn standard	Abundance, %	Specification	Standard uncertainty
⁶⁴ Zn	1.113	0.00	0.000000
⁶⁶ Zn	1.95	0.02	0.011547005
⁶⁷ Zn	94.6	0.03	0.017320508
⁶⁸ Zn	2.28	0.01	0.005773503
⁷⁰ Zn	0.054	0.00	0.000000

⁶⁵ Cu standard	Abundance, %	Specification	Standard uncertainty
⁶³ Cu	0.39	0.02	0.011547005
⁶⁵ Cu	99.61	0.02	0.011547005

⁶¹ Ni standard	Abundance, %	Specification	Standard uncertainty
⁵⁸ Ni	3.45	0.04	0.023094011
⁶⁰ Ni	6.12	0.06	0.034641016
⁶¹ Ni	88.84	0.1	0.057735027
⁶² Ni	1.40	0.01	0.005773503
⁶⁴ Ni	0.20	0.01	0.005773503

⁹⁷ Mo standard	Abundance, %	Specification	Standard uncertainty
⁹² Mo	0.22	0.05	0.028867513
⁹⁴ Mo	0.24	0.05	0.028867513
⁹⁵ Mo	0.59	0.05	0.028867513
⁹⁶ Mo	1.34	0.05	0.028867513
⁹⁷ Mo	94.25	0.10	0.057735027
⁹⁸ Mo	3.07	0.10	0.057735027
¹⁰⁰ Mo	0.30	0.05	0.028867513

¹¹¹ Cd standard	Abundance, %	Specification	Standard uncertainty
¹⁰⁶ Cd	<0.005		0
¹⁰⁸ Cd	<0.005		0
¹¹⁰ Cd	0.4250	0.0400	0.023094011
¹¹¹ Cd	95.7400	0.0420	0.024248711
¹¹² Cd	2.0809	0.0094	0.005427093
¹¹³ Cd	0.5570	0.0054	0.003117691
¹¹⁴ Cd	1.0411	0.0084	0.004849742
¹¹⁶ Cd	0.1560	0.0042	0.002424871

²⁰⁶ Pb standard	Abundance, %	Standard deviation	Standard uncertainty
²⁰⁴ Pb	0.032	0.0032	0.0032
²⁰⁶ Pb	98.41	0.01	0.01
²⁰⁷ Pb	0.548	0.0033	0.0033
²⁰⁸ Pb	1.00	0.008	0.008

Appendix F

Sequence of HR-ICP-MS sample analysis

Wash-1

Standard-1

Wash-2

Reagent-blank-1

Reagent-blank-2

Wash-3

Standard-2

Wash-4

Primary standard-1

Primary standard-2

Wash-5

Standard-3

Wash-6

Sample-1

Sample-2

Wash-7

Standard-4

Wash-8

Reagent-blank + spike-1

Reagent-blank + spike-2

Wash-9

Standard-5

Wash-10

Primary standard + spike-1

Primary standard + + spike-2

Wash-11

Standard-6

Wash-12

Sample + spike-1

Sample + spike-2

Wash-13

Standard-7

Wash-14

Appendix G

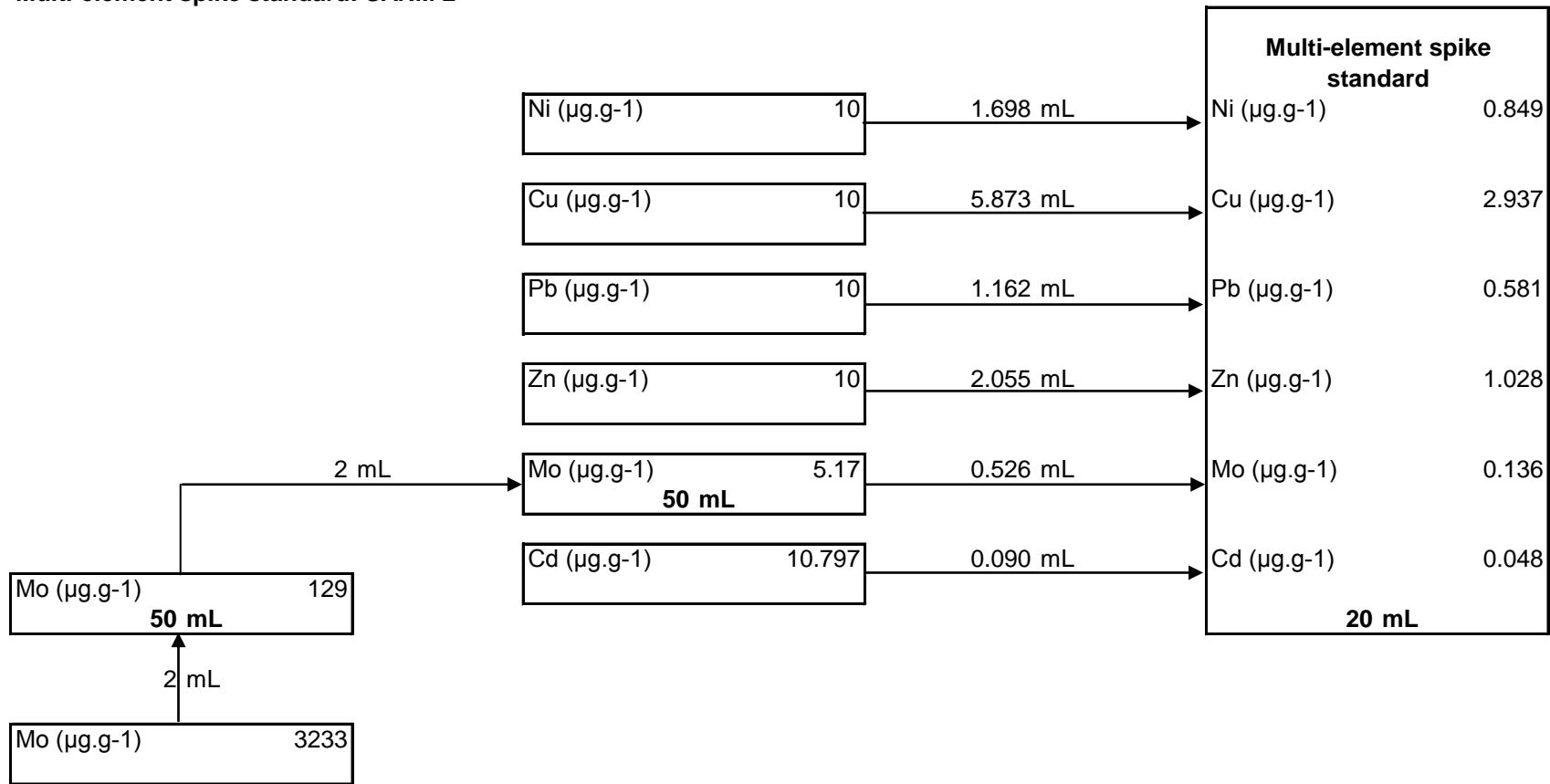
Experimental designs

SARM 2

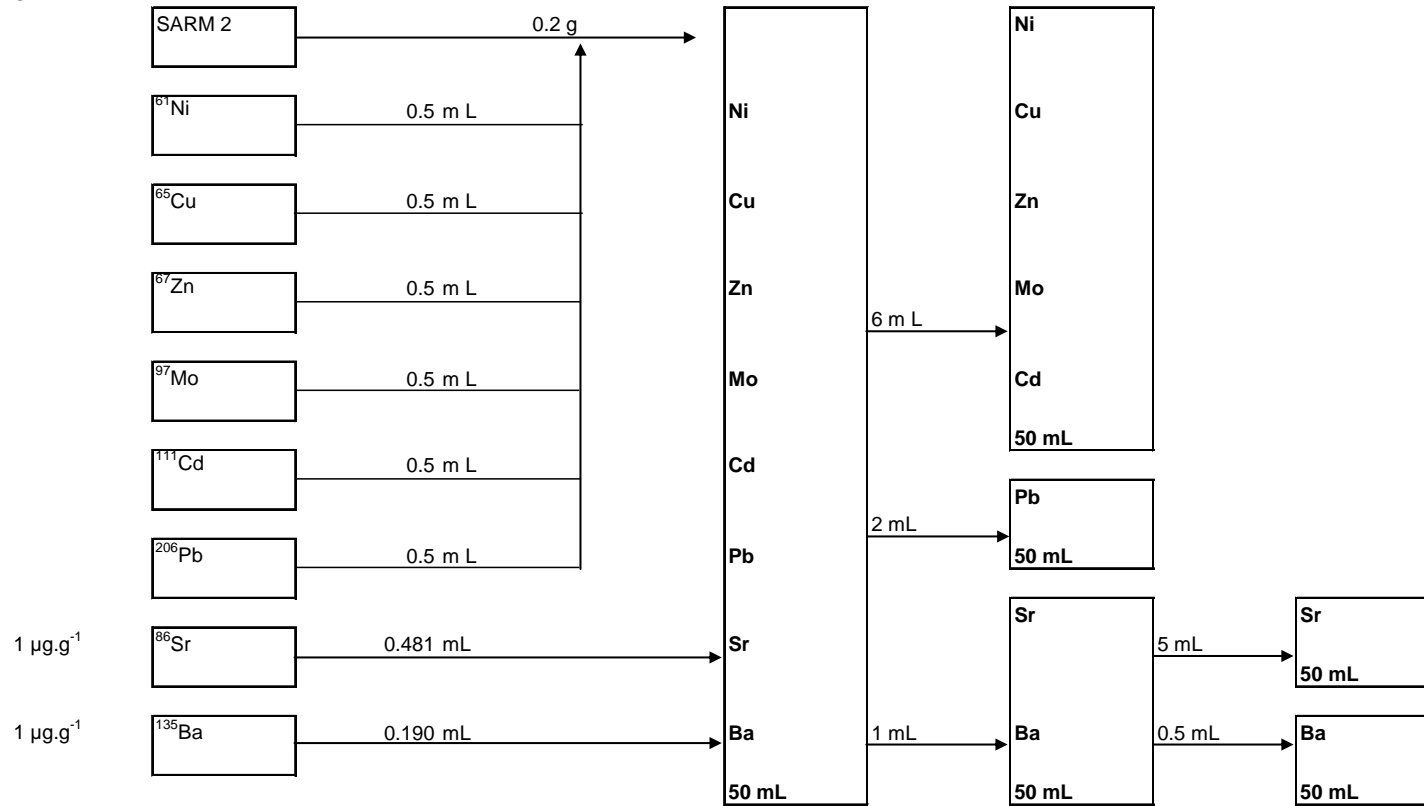
Elements	Expected concentration in SARM 2 $\mu\text{g.g}^{-1}$	Solid sample aliquot g	Amount of analyte in solid sample μg	Ratio	Required spike isotope addition for optimum ratio prior to digestion		Required multi-element spike standard concentration, $\mu\text{g.g}^{-1}$	(Required) Spike stock standard concentration $\mu\text{g.g}^{-1}$	Source spike stock standard concentration	Amount of spike standard addition mL	Volume of intermediate spike standard mL	Intermediate spike stock standard concentration	Amount of spike standard addition mL	Volume of intermediate spike standard mL	Amount of spike standard addition mL	Volume of spike standard mL	Volume-1 volume after digestion	Aliquot-1 ml	Volume-2 ml	Aliquot-2 ml	Volume-3	Expected working sample concentration ng.ml^{-1}
					$\frac{C_{\text{sample}}}{C_{\text{spike}}}$	Aliquot μg																
Ni	7	0.2	1.4	60Ni/61Ni	3.298245614	0.424	0.5	0.849	10		20				1.698	20	50	6	50			4.4
Cu	19	0.2	3.8	63Cu/65Cu	2.587897757	1.468	0.5	2.937	10		20				5.873	20	50	6	50			12.6
Pb	5	0.2	1	208Pb/206Pb	3.44204947	0.291	0.5	0.581	10		20				1.162	20	50	2	50			1.0
Zn	10	0.2	2	66Zn/67Zn	3.892857143	0.514	0.5	1.028	10		20				2.055	20	50	6	50			6.0
137Ba	2400	0.2	480	137Ba/135Ba	19.94178525	24.070			1		20				0.481	20	50	1	50	0.5	50	2.0
Mo	5	0.2	1	95Mo/97Mo	14.7032967	0.068	0.5	0.136	5.173333333	3233.333333	2	50	129.3333333	2	50	0.526	20	50	6	50		2.6
Cd	1	0.2	0.2	112Cd/111Cd	8.26646955	0.024	0.5	0.048	10.797		20				0.090	20	50	6	50			0.5
88Sr	62	0.2	12.4	88Sr/86Sr	1.305005501	9.502			1		20				0.190	20	50	1	50	5	50	0.9



Multi-element spike standard: SARM 2



SARM 2



Reference isotope	Spike isotope
⁶⁰ Ni	⁶¹ Ni
⁶³ Cu	⁶⁵ Cu
²⁰⁸ Pb	²⁰⁶ Pb
⁶⁶ Zn	⁶⁷ Zn
¹³⁷ Ba	¹³⁵ Ba
⁹⁵ Mo	⁹⁷ Mo
¹¹² Cd	¹¹¹ Cd
⁸⁸ Sr	⁸⁶ Sr

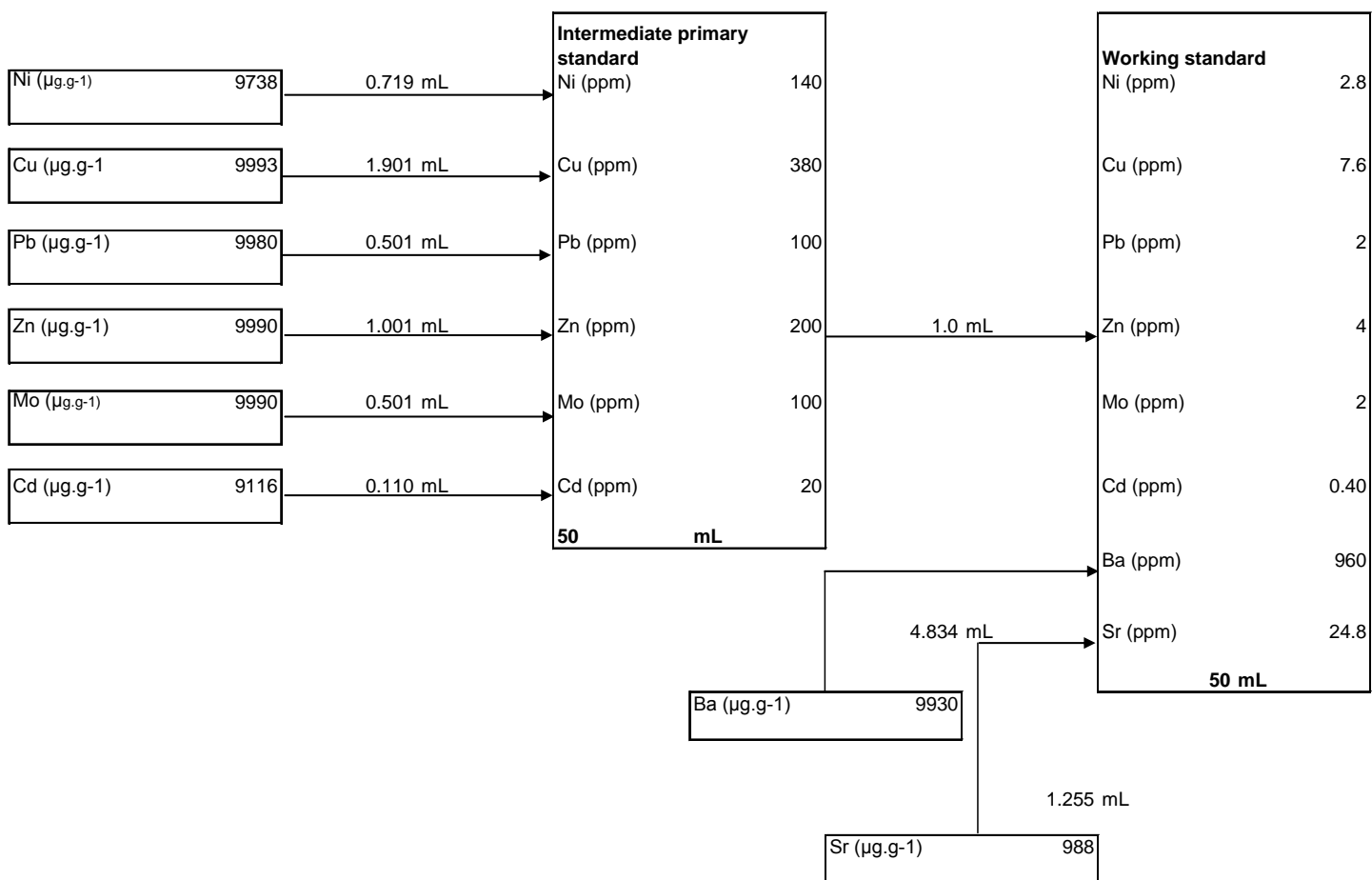


Single element standard: SARM 2

Elements	Amount of element required to match sample		Required concentration of each analyte in the final primary standard (working standard) $\mu\text{g.g}^{-1}$	Source primary standard concentration $\mu\text{g.g}^{-1}$	Uncertainty of source primary standard concentration (k=2) $\mu\text{g.g}^{-1}$		Amount of source primary standard added to IMPS $\mu\text{g.g}^{-1}$	Volume of primary standard added to IMPS $\mu\text{g.g}^{-1}$	Volume of intermediate primary standard $\mu\text{g.g}^{-1}$	Required concentration of intermediate primary standard $\mu\text{g.g}^{-1}$	Amount of IMPS to be added to working standard $\mu\text{g.g}^{-1}$	Volume of working standard $\mu\text{g.g}^{-1}$	Ratio $\frac{C_{\text{sample}}}{C_{\text{spike}}}$	Required spike isotope addition for optimum ratio prior to digestion μg	Required multielement spike standard concentration, for 0.5 ml $\mu\text{g.g}^{-1}$	Spike stock standard concentration $\mu\text{g.g}^{-1}$	Amount of spike standard addition to 10 multielement spike standard $\mu\text{g.g}^{-1}$	Volume-1 volume after digestion	Aliquot-1 ml	Volume-2 ml	Aliquot-2 ml	Volume-3 ml	Expected working sample concentration ng.ml^{-1}
	μg	mL																					
Ni	1.4	0.5	2.8	9 738	22	0.718833436	50	140	1.0	50	60Ni/61Ni	3.298245614	0.424	0.849	10	0.849	50						28
Cu	3.8	0.5	7.6	9993	16	1.901330932	50	380	1.0	50	63Cu/65Cu	2.587897757	1.468	2.937	10	2.937	50	10	50				15.2
Pb	1	0.5	2	9980	30	0.501002004	50	100	1.0	50	208Pb/206Pb	3.44204947	0.291	0.581	10	0.581	50	3	50				1.2
Zn	2	0.5	4	9990	20	1.001001001	50	200	1.0	50	66Zn/67Zn	3.892857143	0.514	1.028	10	1.028	50						40
Ba	480	0.5	960	9930	30			4.833836858		50	137Ba/135Ba	19.94178525	24.070	48.140	10	48.140	50	1	50	1	50		3.84
Mo	1	0.5	2	9990	30	0.500500501	50	100	1.0	50	95Mo/97Mo	14.7032967	0.068	0.136	10	0.136	50	5	50				2
Cd	0.2	0.5	0.40	9116	25	0.109697236	50	20	1.0	50	112Cd/111Cd	8.26646955	0.024	0.048	10	0.048	50	5	50				0.4
Sr	12.4	0.5	24.8	988	3			1.255060729		50	88Sr/86Sr	1.305005501	9.502	19.004	10	19.004	50	5	50	5	50		2.48



Single element primary standard: SARM 2

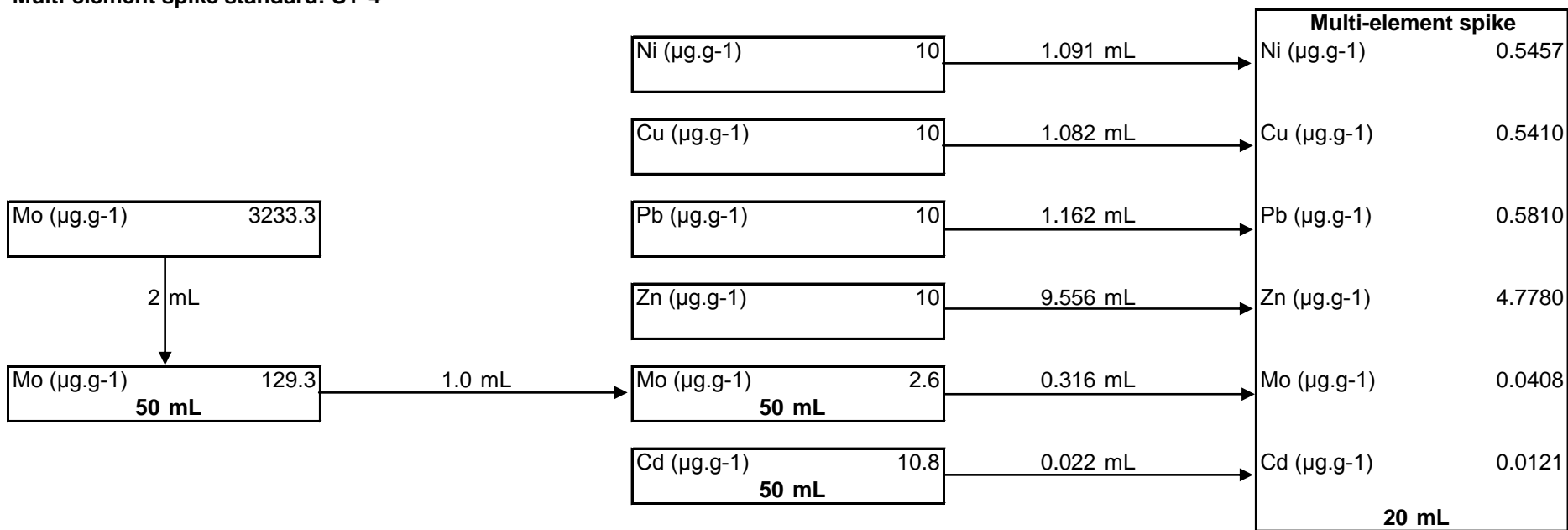


Reference isotope	Spike isotope
⁶⁰ Ni	⁶¹ Ni
⁶³ Cu	⁶⁵ Cu
²⁰⁸ Pb	²⁰⁶ Pb
⁶⁶ Zn	⁶⁷ Zn
¹³⁷ Ba	¹³⁵ Ba
⁹⁵ Mo	⁹⁷ Mo
¹¹² Cd	¹¹¹ Cd
⁸⁸ Sr	⁸⁶ Sr

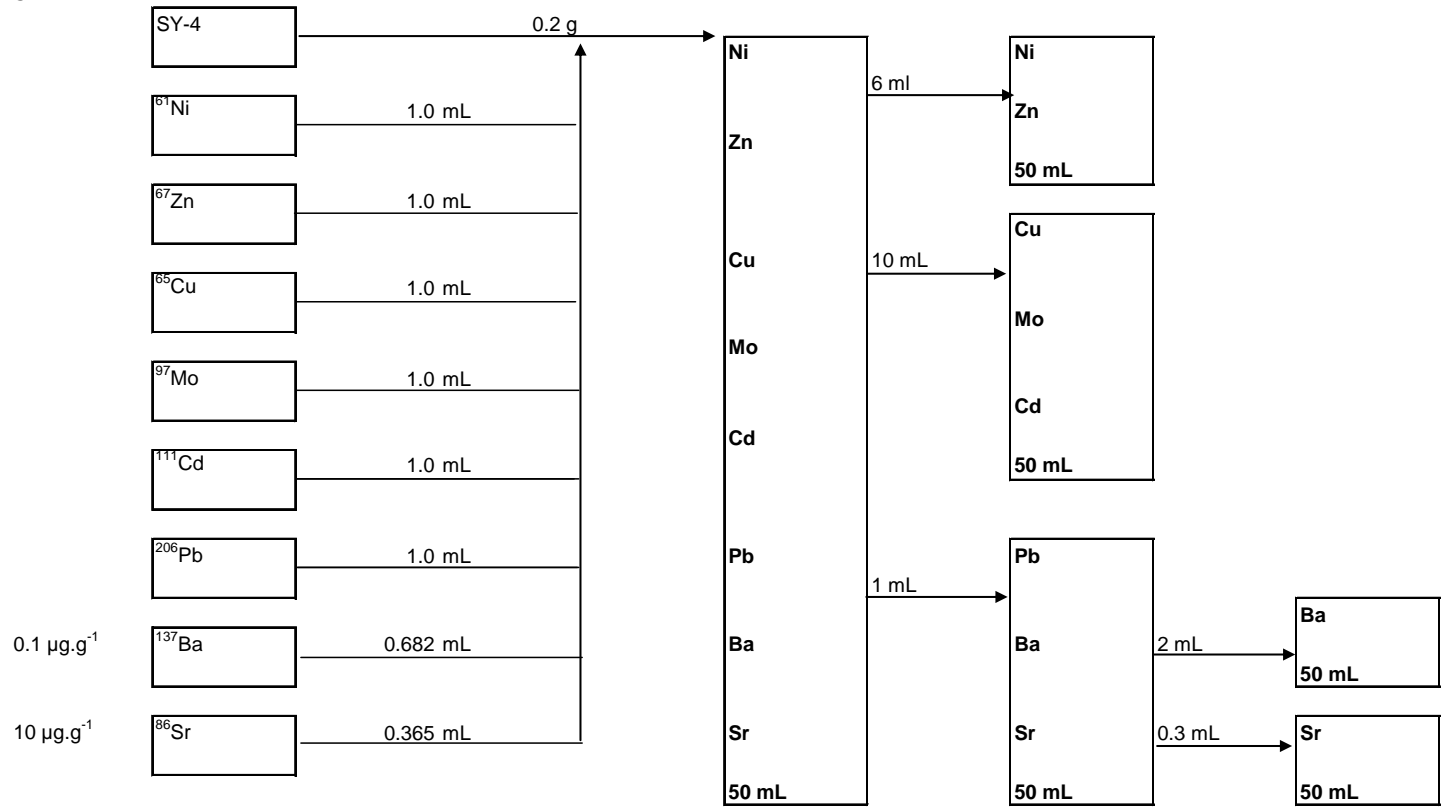
SY 4

Elements	Expected concentration in SY 4 $\mu\text{g.g}^{-1}$	Solid sample aliquot g	Amount of analyte in solid sample μg	Ratio	$\frac{C_{\text{sample}}}{C_{\text{spike}}}$	Required spike isotope addition for optimum ratio prior to digestion		Required multielement spike standard concentration, $\mu\text{g.g}^{-1}$	Spike stock standard concentration $\mu\text{g.g}^{-1}$	Source spike stock standard concentration	Amount of spike standard addition mL	Volume of intermediate spike standard mL	Intermediate spike stock standard concentration	Amount of spike standard addition mL	Volume of intermediate spike standard mL	Amount of spike standard addition mL	Volume of spike standard mL	Volume-1 volume after digestion	Aliquot-1 ml	Volume-2 ml	Aliquot-2 ml	Volume-3	Expected working sample concentration ng.ml^{-1}	
						μg	mL																	
Ni	9	0.2	1.8	60Ni/61Ni	3.298245614	0.5457	1.0	0.5457	10								1.091	20	50	6	50		5.6	
Cu	7	0.2	1.4	63Cu/65Cu	2.587897757	0.5410	1.0	0.5410	10								1.082	20	50	10	50		7.8	
Pb	10	0.2	2	208Pb/206Pb	3.44204947	0.5810	1.0	0.5810	10								1.162	20	50	1	50		1.0	
Zn	93	0.2	18.6	66Zn/67Zn	3.892857143	4.7780	1.0	4.7780	10								9.556	20	50	6	50		56.1	
137Ba	340	0.2	68	137Ba/135Ba	19.94178525	3.4099			0.1								0.682		50	1	50	2	50	1.1
Mo	3	0.2	0.6	95Mo/97Mo	14.7032967	0.0408	1.0	0.0408	2.586666667	3233.333333	2	50	129.3333333	1	50		0.316	20	50	10	50		2.6	
Cd	0.5	0.2	0.1	112Cd/111Cd	8.26646955	0.0121	1.0	0.0121	10.797								0.022	20	50	10	50		0.4	
88Sr	1191	0.2	238.2	88Sr/86Sr	1.305005501	182.5280			10								0.365		50	1	50	0.3	50	1.0

Multi-element spike standard: SY-4



SY-4



Reference isotope	Spike isotope
⁶⁰ Ni	⁶¹ Ni
⁶³ Cu	⁶⁵ Cu
²⁰⁸ Pb	²⁰⁶ Pb
⁶⁶ Zn	⁶⁵ Zn
¹³⁵ Ba	¹³⁷ Ba
⁹⁵ Mo	⁹⁷ Mo
¹¹² Cd	¹¹¹ Cd
⁸⁸ Sr	⁸⁶ Sr

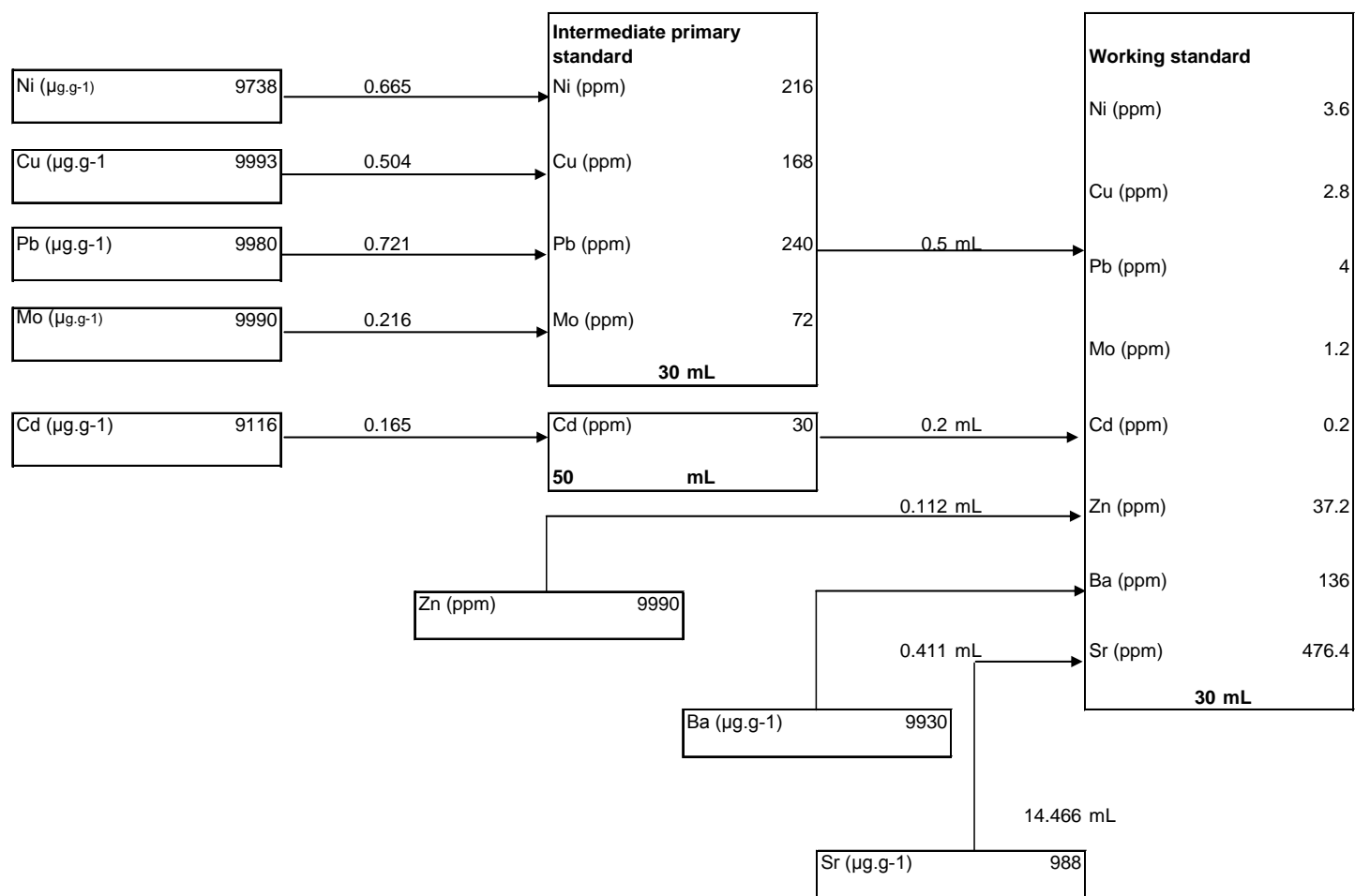


Single element standard: SY-4

Elements	Amount of element required to match sample		Required concentration of each analyte in the final primary standard (working standard) $\mu\text{g.g}^{-1}$	Source primary standard concentration $\mu\text{g.g}^{-1}$	Uncertainty of source primary standard concentration (k=2) $\mu\text{g.g}^{-1}$		Amount of source primary standard added to IMPS mL	Volume of primary standard mL	Volume of intermediate primary standard added to working standard mL	Required concentration of intermediate primary standard $\mu\text{g.g}^{-1}$	Amount of IMPS to be added to working standard mL	Volume of working standard mL	Ratio $\frac{C_{\text{sample}}}{C_{\text{spike}}}$	Required spike isotope addition for optimum ratio prior to digestion μg	Required multielement spike standard concentration, for 0.5 ml $\mu\text{g.g}^{-1}$	Spike stock standard concentration $\mu\text{g.g}^{-1}$	Amount of spike standard addition to 10 multielement spike standard mL	Volume-1 volume after digestion	Aliquot-1 ml	Volume-2 ml	Aliquot-2 ml	Volume-3	Expected working sample concentration ng.ml^{-1}
	μg	Aliquot mL																					
Ni	1.8	0.5	3.6	9 738	22	0.665	30	216	0.5	30	60Ni/61Ni	3.298245614	0.546	1.091	10	1.091	50						36
Cu	1.4	0.5	2.8	9993	16	0.504	30	168	0.5	30	63Cu/65Cu	2.587897757	0.541	1.082	10	1.082	50						28
Pb	2	0.5	4	9980	30	0.721	30	240	0.5	30	208Pb/206Pb	3.44204947	0.581	1.162	10	1.162	50	2		50			1.6
Zn	18.6	0.5	37.2	9990	20			0.112		30	66Zn/67Zn	3.892857143	4.778	9.556	10	9.556	50	10		50			74.4
Ba	68	0.5	136	9930	30			0.411		30	137Ba/135Ba	19.94178525	3.410	6.820	10	6.820	50	2		50	2	50	2.176
Mo	0.6	0.5	1.2	9990	30	0.216	30	72	0.5	30	95Mo/97Mo	14.7032967	0.041	0.082	10	0.082	50	10		50			2.4
Cd	0.1	0.5	0.2	9116	25	0.165	50	30	0.2	30	112Cd/111Cd	8.26646955	0.012	0.024	10	0.024	50	20		50			0.8
Sr	238.2	0.5	476.4	988	3			14.466		30	87Sr/86Sr	-33.65034965	-7.079	-14.157	10	-14.157	50	0.2		50	5	50	1.9056



Single element primary standard: SY-4



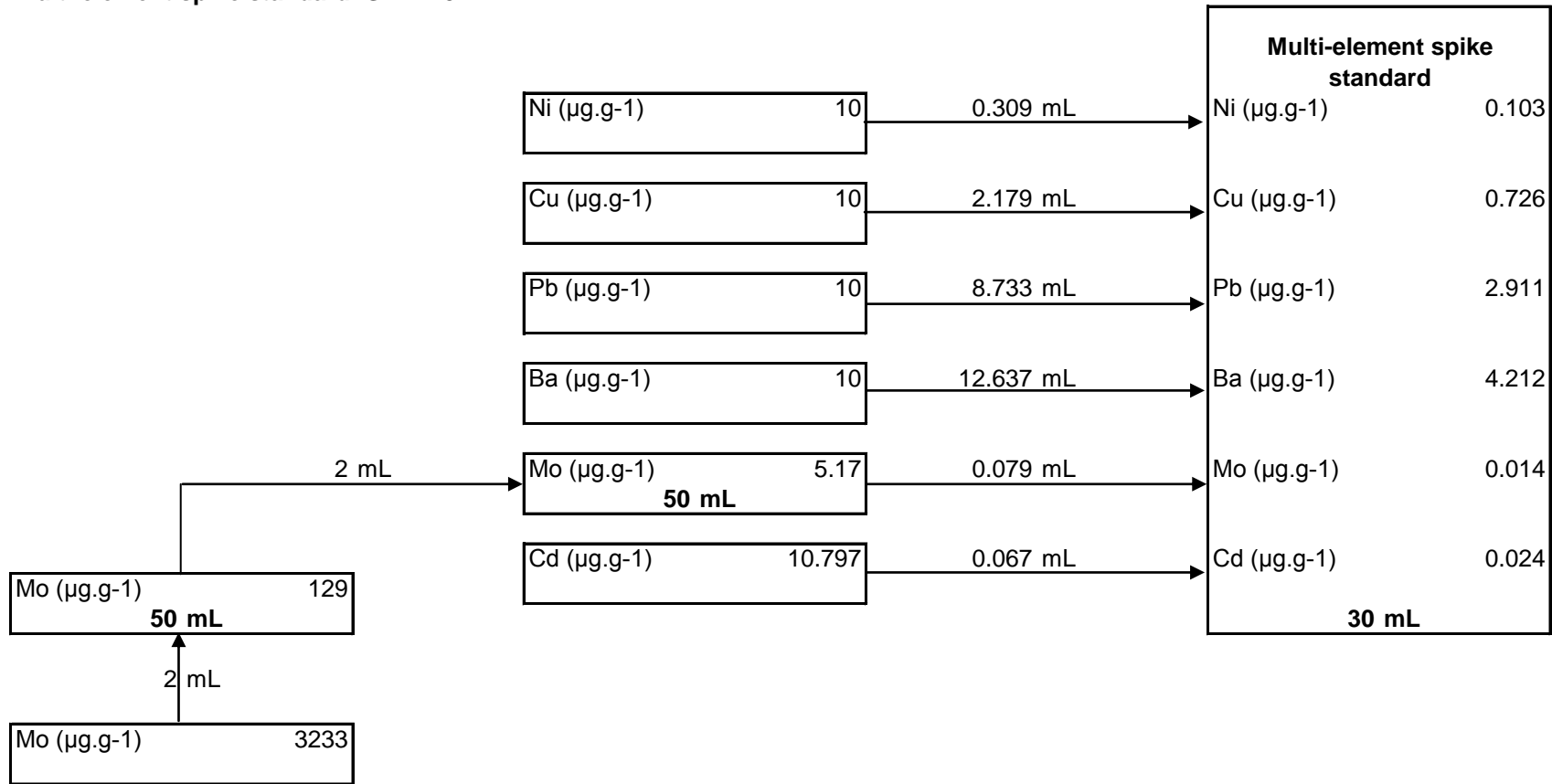
Reference isotope	Spike isotope
⁶⁰ Ni	⁶¹ Ni
⁶³ Cu	⁶⁵ Cu
²⁰⁸ Pb	²⁰⁶ Pb
⁶⁶ Zn	⁶⁷ Zn
¹³⁷ Ba	¹³⁵ Ba
⁹⁵ Mo	⁹⁷ Mo
¹¹² Cd	¹¹¹ Cd
⁸⁸ Sr	⁸⁶ Sr

SARM 3

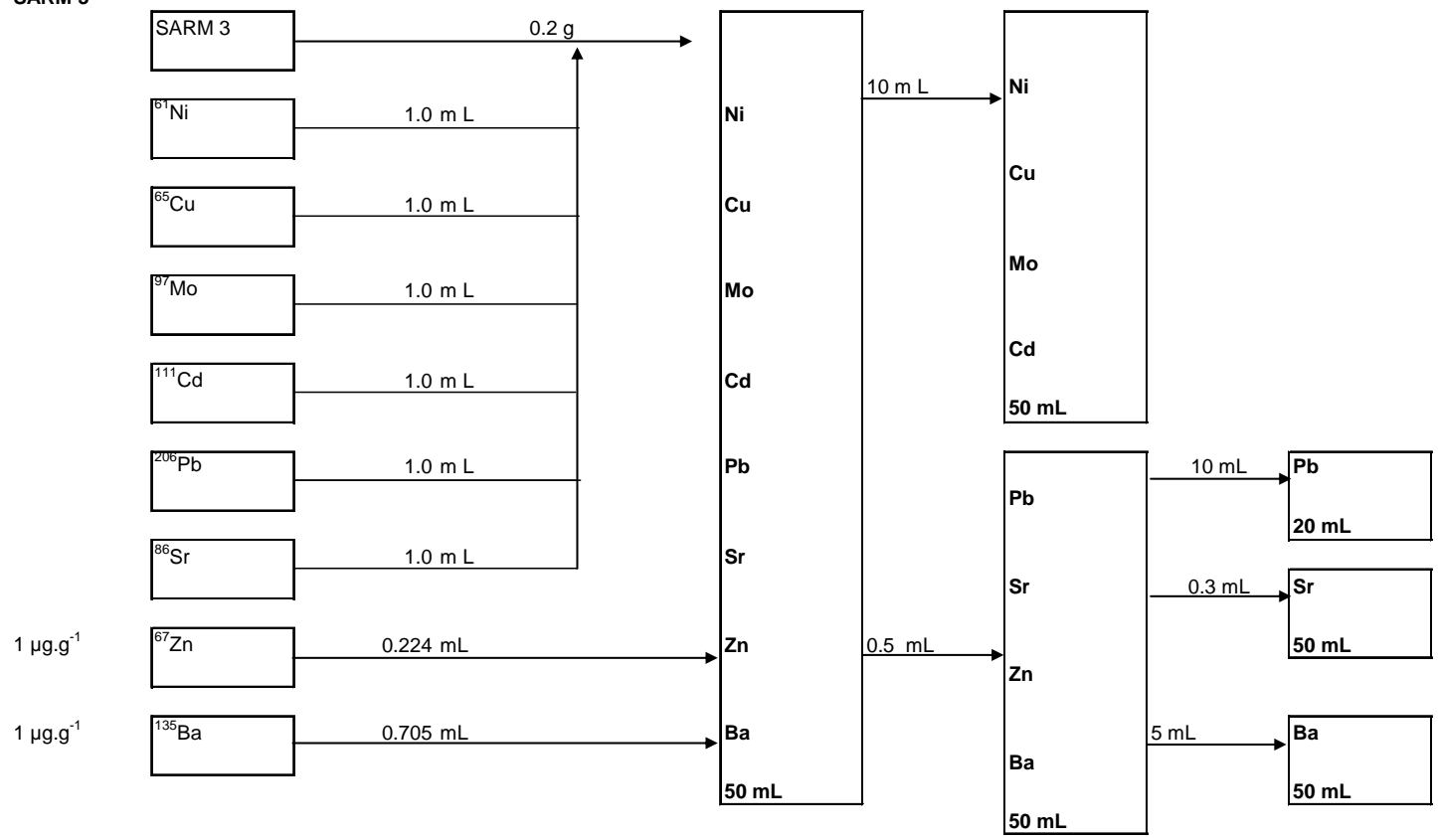
Elements	Expected concentration in SARM 3 $\mu\text{g.g}^{-1}$	Solid sample aliquot g	Amount of analyte in solid sample μg	Ratio	Required spike isotope addition for optimum ratio prior to digestion		Aliquot μL	Required multielement spike standard concentration, $\mu\text{g.g}^{-1}$	(Required) Spike stock standard concentration $\mu\text{g.g}^{-1}$	Source spike stock standard concentration	Amount of spike standard addition mL	Volume of intermediate spike standard mL	Intermediate spike stock standard concentration	Amount of spike standard addition mL	Volume of intermediate spike standard mL	Amount of spike standard addition mL	Volume of spike standard mL	Volume-1 volume after digestion	Aliquot-1 ml	Volume-2 ml	Aliquot-2 ml	Volume-3	Expected working sample concentration ng.ml^{-1}
					$\frac{C_{\text{sample}}}{C_{\text{spike}}}$	Required spike addition for optimum ratio prior to digestion μg																	
Ni	1.7	0.2	0.34	60Ni/61Ni	3.298245614	0.103	1.0	0.103	10			20				0.309	30	50	10	50			1.8
Cu	9.4	0.2	1.88	63Cu/65Cu	2.587897757	0.726	1.0	0.726	10			20				2.179	30	50	10	50			10.4
Pb	50.1	0.2	10.02	208Pb/206Pb	3.44204947	2.911	1.0	2.911	10			20				8.733	30	50	0.5	50	10	20	1.3
Zn	435.5	0.2	87.1	66Zn/67Zn	3.892857143	22.374			1.0							0.224	30	50	0.5	50			21.9
137Ba	420	0.2	84	137Ba/135Ba	19.94178525	4.212	1.0	4.212	10			20				12.637	30	50	0.5	50	5	50	1.8
Mo	1	0.2	0.2	95Mo/97Mo	14.7032967	0.014	1.0	0.014	5.173333333	3233.333333	2	50	129.3333333	2	50	0.079	30	50	10	50			0.9
Cd	1	0.2	0.2	112Cd/111Cd	8.26646955	0.024	1.0	0.024	10.797			20				0.067	30	50	10	50			0.9
88Sr	4600	0.2	920	88Sr/86Sr	1.305005501	704.978			10							0.705	30	50	0.5	50	0.3	50	1.9



Multi-element spike standard: SARM 3



SARM 3



Reference isotope	Spike isotope
^{60}Ni	^{61}Ni
^{63}Cu	^{65}Cu
^{208}Pb	^{206}Pb
^{66}Zn	^{67}Zn
^{137}Ba	^{135}Ba
^{95}Mo	^{97}Mo
^{112}Cd	^{111}Cd
^{88}Sr	^{86}Sr

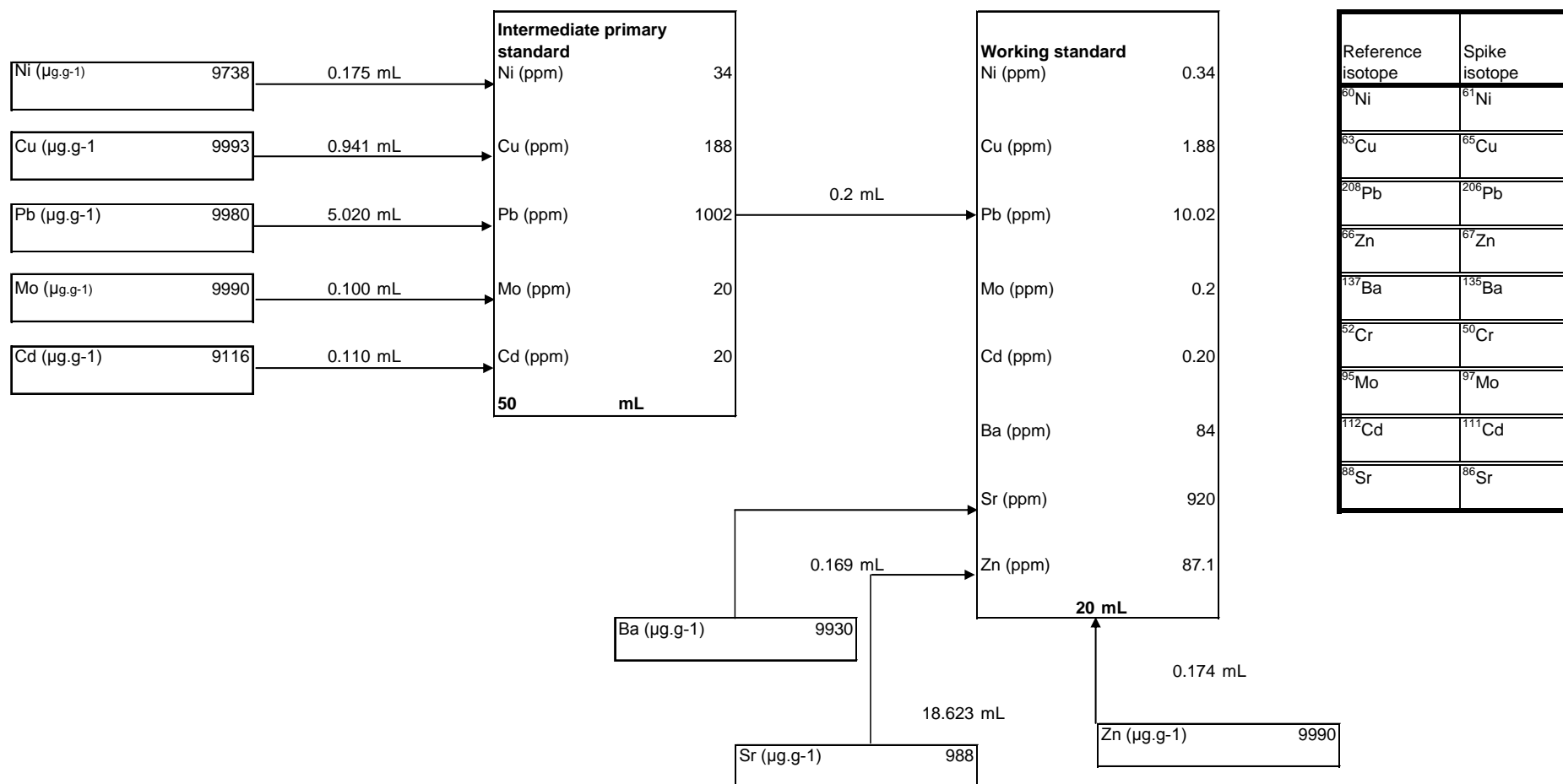


Single element standard: SARM 3

Elements	Amount of element required to match sample		Required concentration of each analyte in the final primary standard (working standard) $\mu\text{g.g}^{-1}$	Source primary standard concentration $\mu\text{g.g}^{-1}$	Uncertainty of source primary standard concentration (k=2) $\mu\text{g.g}^{-1}$		Amount of source primary standard added to IMPPS standard		Volume of primary intermediate standard	Required concentration of primary standard $\mu\text{g.g}^{-1}$	Amount of IMPPS to be added to working standard	Volume of working standard mL	Ratio $\frac{C_{\text{sample}}}{C_{\text{spike}}}$	Required spike isotope addition for optimum ratio prior to digestion μg	Required multielement spike standard concentration, for 0.5 ml $\mu\text{g.g}^{-1}$		Amount of spike standard addition to 10 multielement spike standard mL		Volume-1 volume after digestion			Expected working sample concentration ng.ml^{-1}
	μg	Aliquot mL			$\mu\text{g.g}^{-1}$	$\mu\text{g.g}^{-1}$	mL	mL							$\mu\text{g.g}^{-1}$	mL	$\mu\text{g.g}^{-1}$	$\mu\text{g.g}^{-1}$	Volume-1 mL	Aliquot-1 ml	Volume-2 ml	
Ni	0.34	1.0	0.34	9738	22	0.175	50	34	0.2	20	⁶⁰ Ni/ ⁶¹ Ni	3.298245614	0.103	0.206	10	0.206	50					6.8
Cu	1.88	1.0	1.88	9993	16	0.941	50	188	0.2	20	⁶³ Cu/ ⁶⁵ Cu	2.587897757	0.726	1.453	10	1.453	50	10	50			7.52
Pb	10.02	1.0	10.02	9980	30	5.020	50	1002	0.2	20	²⁰⁸ Pb/ ²⁰⁶ Pb	3.44204947	2.911	5.822	10	5.822	50	3	50			12.024
Zn	87.1	1.0	87.1	9990	20	43.594	50	8710	0.2	20	⁶⁶ Zn/ ⁶⁷ Zn	3.892857143	22.374	44.749	10	44.749	50					1742
Ba	84	1.0	84	9930	30				0.169	20	¹³⁷ Ba/ ¹³⁵ Ba	19.94178525	4.212	8.425	10	8.425	50	1	50	1	50	0.672
Mo	0.2	1.0	0.2	9990	30	0.100	50	20	0.2	20	⁹⁵ Mo/ ⁹⁷ Mo	14.7032967	0.014	0.027	10	0.027	50	5	50			0.4
Cd	0.2	1.0	0.20	9116	25	0.110	50	20	0.2	20	¹¹² Cd/ ¹¹¹ Cd	8.26646955	0.024	0.048	10	0.048	50	5	50			0.4
Sr	920	1.0	920	988	3				18.623	20	⁸⁸ Sr/ ⁸⁶ Sr	1.305005501	704.978	1409.956	10	1409.956	50	5	50	5	50	184



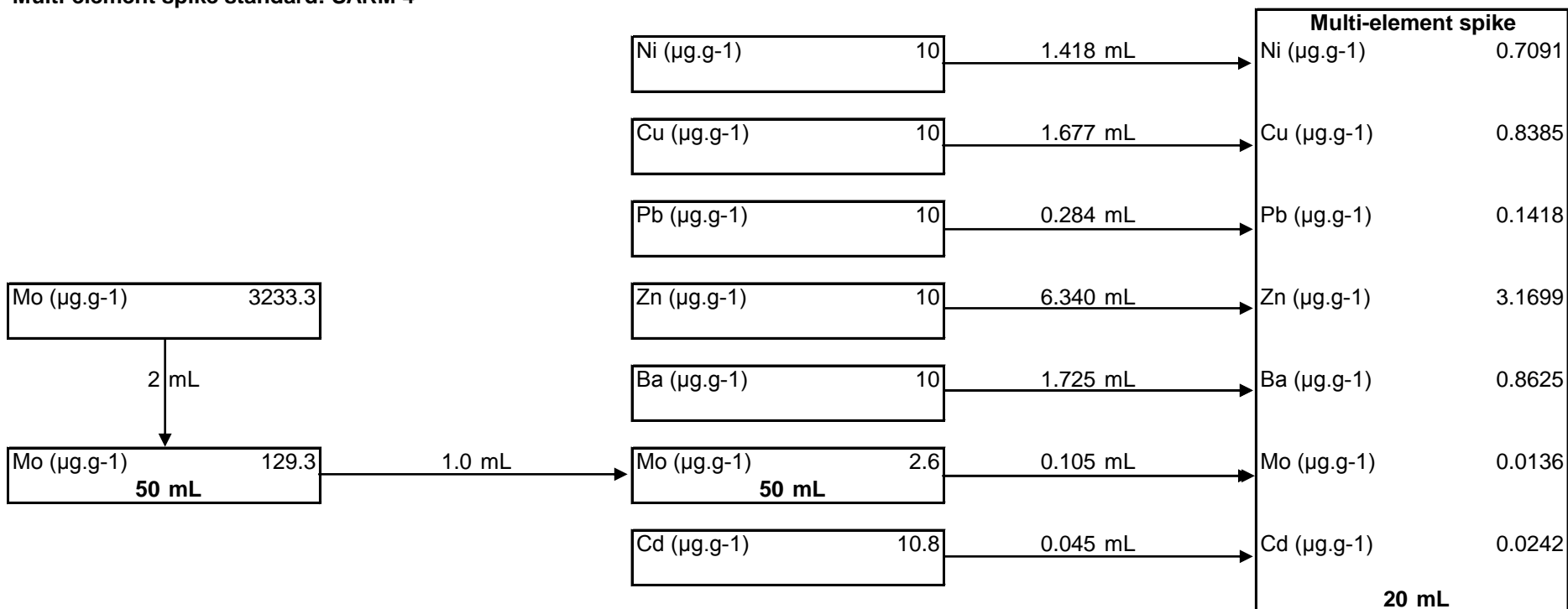
Single element primary standard: SARM 3



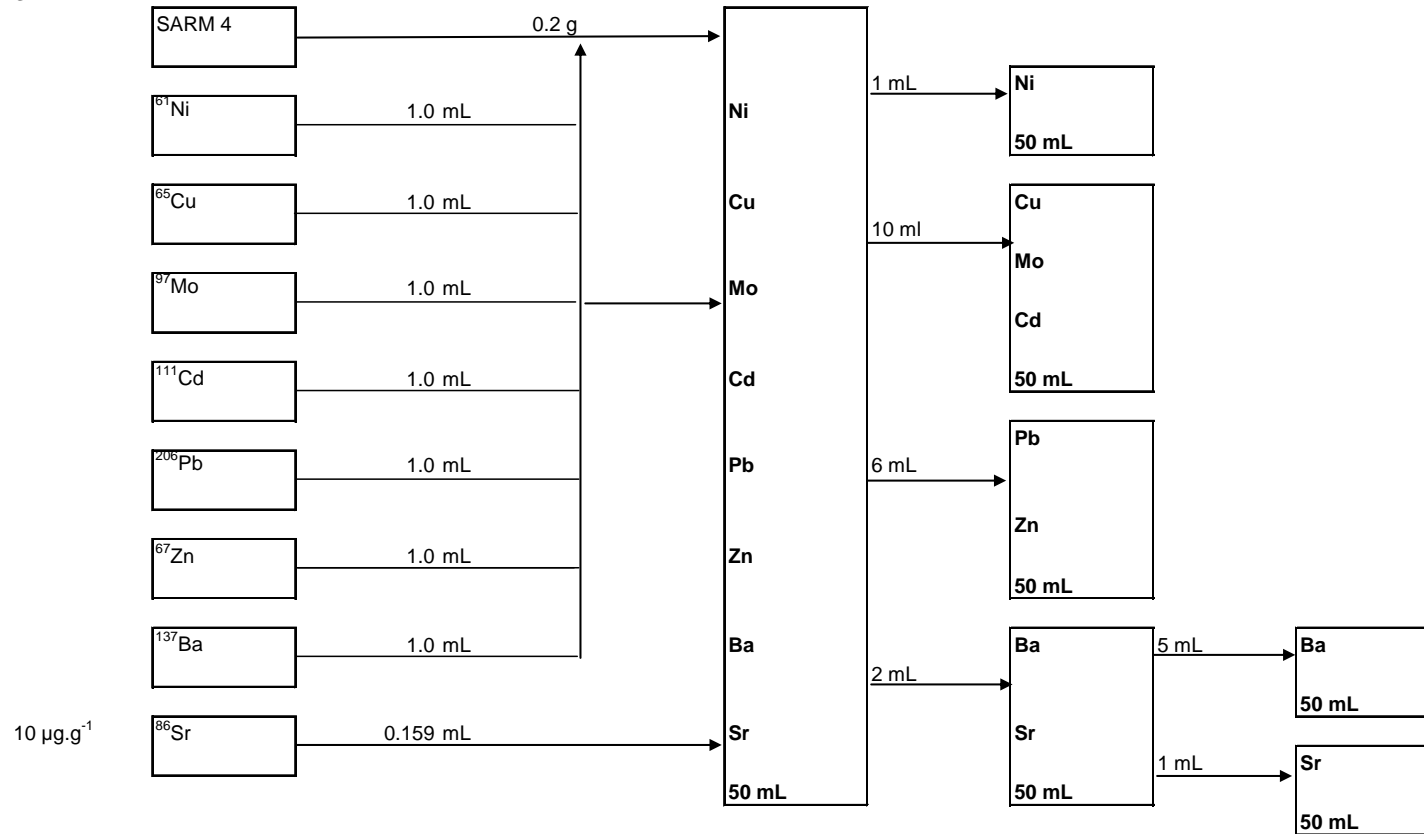
SARM 4

Elements	Expected concentration in SARM 4 $\mu\text{g.g}^{-1}$	Solid sample aliquot g	Amount of analyte in solid sample μg	Ratio $\frac{C_{\text{sample}}}{C_{\text{spike}}}$	Required spike isotope addition for optimum ratio prior to digestion		Required multi-element spike standard concentration, $\mu\text{g.g}^{-1}$	Spike stock standard concentration $\mu\text{g.g}^{-1}$	Source spike stock standard concentration	Amount of spike standard addition mL	Volume of intermediate spike standard mL	Intermediate spike stock standard concentration	Amount of spike standard addition mL	Volume of intermediate spike standard mL	Amount of spike standard addition mL	Volume of spike standard mL	Volume-1 volume after digestion	Aliquot-1 ml	Volume-2 ml	Aliquot-2 ml	Volume-3	Expected working sample concentration ng.ml^{-1}
					μg	mL																
⁶² Ni/ ⁶¹ Ni	124.3	0.2	24.86	⁶² Ni/ ⁶¹ Ni	35.06014435	0.7091	1.0	0.7091	10						1.418	20	50	1	50			10.2
Cu	10.85	0.2	2.17	⁶³ Cu/ ⁶⁵ Cu	2.587897757	0.8385	1.0	0.8385	10						1.677	20	50	10	50			12.0
Pb	2.44	0.2	0.488	²⁰⁸ Pb/ ²⁰⁶ Pb	3.44204947	0.1418	1.0	0.1418	10						0.284	20	50	6	50			1.5
Zn	61.7	0.2	12.34	⁶⁶ Zn/ ⁶⁷ Zn	3.892857143	3.1699	1.0	3.1699	10						6.340	20	50	6	50			37.2
¹³⁷ Ba	86	0.2	17.2	¹³⁷ Ba/ ¹³⁵ Ba	19.94178525	0.8625	1.0	0.8625	10						1.725	20	50	2	50	5	50	1.4
Mo	1	0.2	0.2	⁹⁵ Mo/ ⁹⁷ Mo	14.7032967	0.0136	1.0	0.0136	2.586666667	3233.333333	2	50	129.3333333	1	50	0.105	20	50	10	50		0.9
Cd	1	0.2	0.2	¹¹² Cd/ ¹¹¹ Cd	8.26646955	0.0242	1.0	0.0242	10.797						0.045	20	50	10	50			0.9
⁸⁸ Sr	260	0.2	52	⁸⁸ Sr/ ⁸⁶ Sr	1.305005501	39.8466			10						0.159		50	2	50	1	50	1.5

Multi-element spike standard: SARM 4



SARM 4



Reference isotope	Spike isotope
^{60}Ni	^{61}Ni
^{63}Cu	^{65}Cu
^{208}Pb	^{206}Pb
^{66}Zn	^{65}Zn
^{135}Ba	^{137}Ba
^{95}Mo	^{97}Mo
^{112}Cd	^{111}Cd
^{88}Sr	^{86}Sr

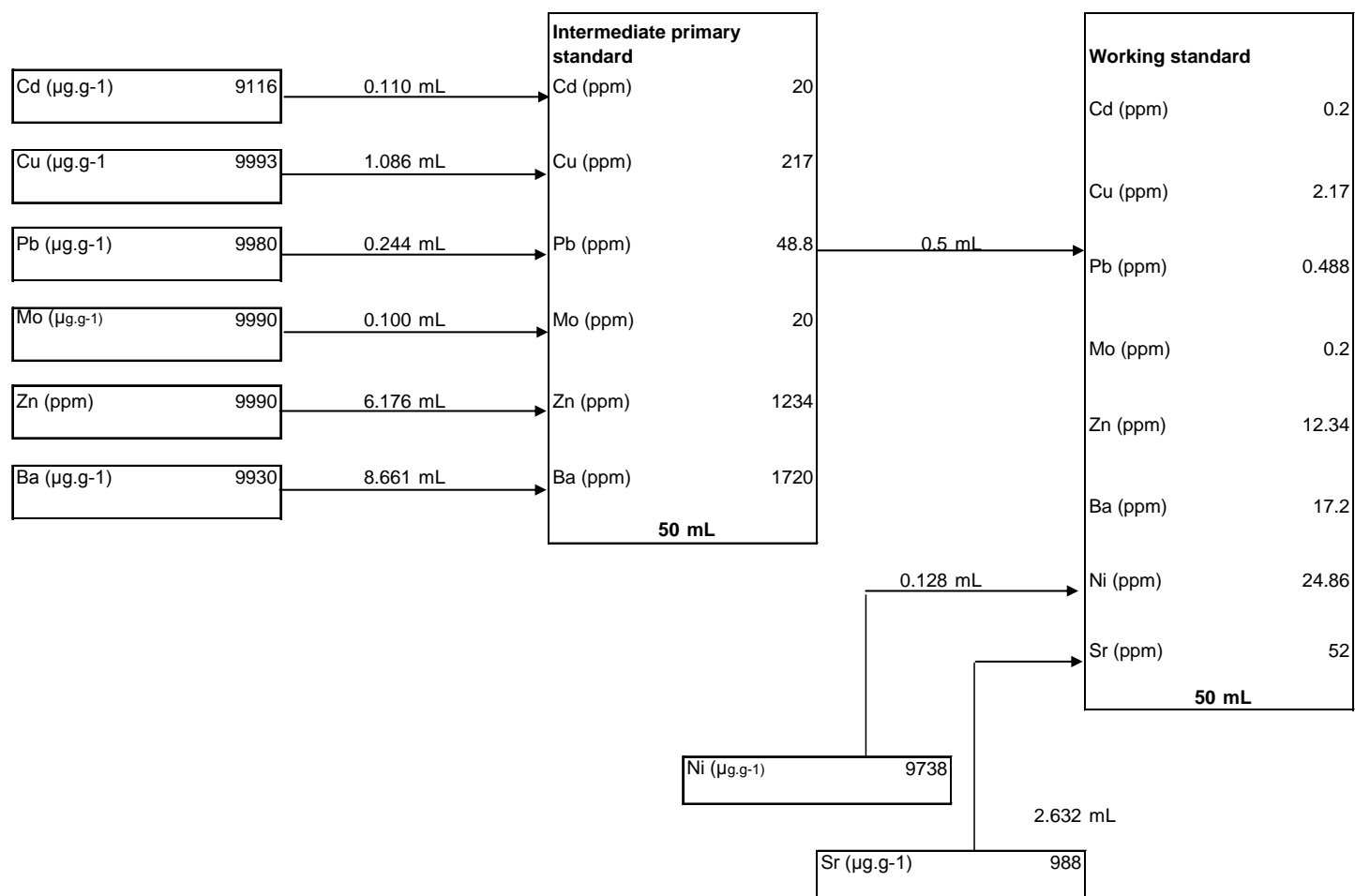


Single element standard: SARM 4

Elements	Amount of element required to match sample		Required concentration of each analyte in the final primary standard (working standard) $\mu\text{g.g}^{-1}$	Source primary standard concentration $\mu\text{g.g}^{-1}$	Uncertainty of source primary standard concentration (k=2) $\mu\text{g.g}^{-1}$		Amount of source primary standard added to IMPPS standard mL	Volume of primary intermediate standard mL	Required concentration of intermediate primary standard $\mu\text{g.g}^{-1}$	Amount of IMPPS to be added to working standard mL	Volume of working standard mL	Ratio	$\frac{C_{\text{sample}}}{C_{\text{spike}}}$	Required spike isotope addition for optimum ratio prior to digestion μg	Required multielement spike standard concentration, for 0.5 ml $\mu\text{g.g}^{-1}$	Spike stock standard concentration $\mu\text{g.g}^{-1}$	Amount of spike standard addition to 10 multielement spike standard mL	Volume-1 volume after digestion	Aliquot-1 ml	Volume-2 ml	Aliquot-2 ml	Volume-3	Expected working sample concentration ng.ml^{-1}	
	μg	Aliquot mL																						
Ni	24.86	1.0	24.86	9738	22					0.128	50	$^{60}\text{Ni}/^{61}\text{Ni}$	3.298245614	7.537	15.075	10	15.075	50						497.2
Cu	2.17	1.0	2.17	9993	16	1.086	50	217	0.5	50	$^{63}\text{Cu}/^{65}\text{Cu}$	2.587897757	0.839	1.677	10	1.677	50							43.4
Pb	0.488	1.0	0.488	9980	30	0.244	50	48.8	0.5	50	$^{208}\text{Pb}/^{206}\text{Pb}$	3.44204947	0.142	0.284	10	0.284	50							0.3904
Zn	12.34	1.0	12.34	9990	20	6.176	50	1234	0.5	50	$^{66}\text{Zn}/^{67}\text{Zn}$	3.892857143	3.170	6.340	10	6.340	50	10	50					49.36
Ba	17.2	1.0	17.2	9930	30	8.661	50	1720	0.5	50	$^{137}\text{Ba}/^{135}\text{Ba}$	19.94178525	0.863	1.725	10	1.725	50	2	50		2	50		0.5504
Mo	0.2	1.0	0.2	9990	30	0.100	50	20	0.5	50	$^{95}\text{Mo}/^{97}\text{Mo}$	14.7032967	0.014	0.027	10	0.027	50	10	50					0.8
Cd	0.2	1.0	0.2	9116	25	0.110	50	20	0.5	50	$^{112}\text{Cd}/^{111}\text{Cd}$	8.26646955	0.024	0.048	10	0.048	50	20	50					1.6
Sr	52	1.0	52	988	3					2.632	50	$^{88}\text{Sr}/^{86}\text{Sr}$	1.305005501	39.847	79.693	10	79.693	50	0.2	50	5	50		0.416



Single element primary standard: SARM 4



Reference isotope	Spike isotope
^{60}Ni	^{61}Ni
^{63}Cu	^{65}Cu
^{208}Pb	^{206}Pb
^{66}Zn	^{67}Zn
^{137}Ba	^{135}Ba
^{95}Mo	^{97}Mo
^{112}Cd	^{111}Cd
^{88}Sr	^{86}Sr

Appendix H

Example of the use of partial derivatives as the sensitivity coefficients for the calculation of the combined standard uncertainty

Table 1: Calculation of the combined standard uncertainty of sample blend A for SARM 2 spiked after digestion

Model:
$$m_x = \frac{Aliquot-1}{Volume-1} \times Aliquot-2$$

Parameter	Estimate	Specification	Probability distribution	Divisor	Standard uncertainty u_i	Sensitivity coefficient c_i	Sensitivity coefficient c_i	Uncertainty contribution $c_i \times u_i$	Type A/B	Degrees of freedom
Aliquot-1 (g)	0.20088				0.00002	$\frac{\partial m_x}{\partial Aliquot-1} = \frac{1}{Volume-1} \times Aliquot-2$	0.020147306	4.02946E-07	B	∞
Volume-1 (g)	52.72417				0.00019	$\frac{\partial m_x}{\partial Volume1} = \frac{-Aliquot1}{Volume1^2} \times Aliquot2$	-7.67616E-05	-1.45847E-08	B	∞
Aliquot-2 (g)	1.06225				0.00002	$\frac{\partial m_x}{\partial Aliquot-2} = \frac{Aliquot-1}{Volume-1}$	0.003810017	7.62003E-08	B	∞
								4.10347E-07		

m_x	0.004047191
u_c	4.10347E-07
v_{eff}	∞
k	2
U	8.20694E-07

Table 2: Combined standard uncertainty calculated with partial derivatives for the measured ratio of the ¹³⁵Ba spike

Model: $Ratio = \frac{A(^{137}Ba)}{A(^{135}Ba)}$

Parameter	Estimate	Specification	Probability distribution	Divisor	Std uncertainty	Sensitivity coefficient	Uncertainty contribution	Type A/B	Degrees of freedom
A(¹³⁵ Ba)	93.39	0.02	Rectangular	$\sqrt{3}$	0.011547005	-0.000102044	-1.17831E-06	B	infinity
A(¹³⁷ Ba)	0.89	0.01	Rectangular	$\sqrt{3}$	0.005773503	0.010707785	6.18214E-05	B	infinity
							6.18327E-05		

$Ratio$	0.009529928
u_c	6.18327E-05
v_{eff}	infinity
k	2
U	0.000123665

Table 3: Calculation of the combined standard uncertainty of the moisture determination of SARM 2 with partial derivatives

$$\text{Moisture} = \frac{\text{Dry}_{\text{sample}}}{\text{Wet}_{\text{sample}}}$$

Model:

Parameter	Estimate	Specification	Probability distribution	Divisor	Standard uncertainty u_i	Sensitivity coefficient c_i	Sensitivity coefficient c_i	Uncertainty contribution $c_i \times u_i$	Type A/B	Degrees of freedom
$\text{Wet}_{\text{sample}}$	2.65319				0.00002	$\frac{\partial \text{Moisture}}{\partial \text{Wet}_{\text{sample}}} = \frac{-\text{Dry}_{\text{sample}}}{\text{Wet}_{\text{sample}}^2}$	-0.376433153	-7.52866E-06	B	∞
$\text{Dry}_{\text{sample}}$	2.64987				0.00002	$\frac{\partial \text{Moisture}}{\partial \text{Dry}_{\text{sample}}} = \frac{1}{\text{Wet}_{\text{sample}}}$	0.376904783	7.5381E-06	B	∞
								1.06538E-05		

Moisture 0.998748676
 u_c 1.06538E-05
 v_{eff} ∞
k 2
U 2.13076E-05
RSU 0.002133431



Table 4: Calculation of the combined standard uncertainty of the amount content, Cz, of the primary assay standard with partial derivatives as the sensitivity coefficients.

$$C_{PS} = C_{source} \times \frac{Aliquot - 1}{Volume - 1}$$

Model:

Parameter	Estimate	Specification	Probability distribution	Divisor	Standard uncertainty ui	Sensitivity coefficient ci	Sensitivity coefficient ci	Uncertainty contribution ci x ui	Type A/B	Degrees of freedom
C_{source}	9930	30	Normal	2	15	$\frac{\partial C_{PS}}{\partial C_{source}} = \frac{Aliquot - 1}{Volume - 1}$	0.097909698	1.468645472	B	∞
Aliquot-1 (g)	4.93136				0.00006	$\frac{\partial C_{PS}}{\partial Aliquot - 1} = \frac{C_{source}}{Volume - 1}$	197.1552072	0.011829312	A	∞
Volume-1 (g)	50.36641				0.00019	$\frac{\partial C_{PS}}{\partial Volume - 1} = \frac{-C_{source} \times Aliquot - 1}{Volume - 1^2}$	-19.30340683	-0.003667647	A	∞
								1.468697691		

$$C_{PS} = 972.2433026 \mu\text{g.g}^{-1}$$

$$u_c = 1.468697691$$

$$v_{eff} = \infty$$

$$k = 2$$

$$U = 2.937395382$$

Cz, Amount content of Ba in the primary assay standard blend

$$C_z = C_{PS} \times \frac{Aliquot - 1}{Volume - 1}$$

Model:

Parameter	Estimate	Specification	Probability distribution	Divisor	Standard uncertainty ui	Sensitivity coefficient ci	Sensitivity coefficient ci	Uncertainty contribution ci x ui	Type A/B	Degrees of freedom
C_{PS}	972.2433026	2.937395382	Normal	k=2	1.468697691	$\frac{\partial C_z}{\partial C_{PS}} = \frac{Aliquot - 1}{Volume - 1}$	0.009604921	0.014106726	A/B	∞
Aliquot-1(g)	0.49843				0.00002	$\frac{\partial C_z}{\partial Aliquot - 1} = \frac{C_{PS}}{Volume - 1}$	18.73546996	0.000374709	A	∞
Volume-1(g)	51.89319				0.00019	$\frac{\partial C_z}{\partial Volume - 1} = \frac{-C_{PS} \times Aliquot - 1}{Volume - 1^2}$	-0.179952712	-3.4191E-05	A	∞
								0.014111743		

$$C_z = 9.338320295$$

$$u_c = 0.014111743$$

$$v_{eff} = \infty$$

$$k = 2$$

$$U = 0.028223485$$

$$RSU = 0.302232998$$



Table 5: Calculation of the combined standard uncertainty of the isotope dilution experiment for Ba in SARM 2 with partial derivatives

$$C_x = C_z \times \frac{M_y \cdot M_z (K_y \cdot R_y - K_b \cdot R_b) \cdot (K_b \cdot R_b' - K_z \cdot R_z)}{w \cdot M_x \cdot M_y \cdot (K_b \cdot R_b - K_x \cdot R_x) \cdot (K_y \cdot R_y - K_b \cdot R_b')}$$

Model:

	Parameter	Estimate	Specification	Probability distribution	Divisor	Std uncertainty	Sensitivity coefficient	Uncertainty contribution	Type A/B	Degrees of freedom
Rb	Measured ratio in the blend b	6.453850				0.04405	1021.88309	45.01676 A		398
Rb'	Measured ratio in the blend b'	6.450050				0.023688	-1023.30283	-24.24008 A		398
Rx	Measured ratio in the sample	11.161800				0.05141	-589.38448	-30.30220 A		796
Rz	Measured ratio in the primary standard	11.148725				0.03486	590.54790	20.58517 A		796
Kb	Mass bias correction factor for Rb	1.019742				0.00066	6467.39807	4.24753 A		23
Kb'	Mass bias correction factor for Rb'	1.019742				0.00066	-6472.57020	-4.25093 A		23
Kx	Mass bias correction factor for Rx	1.019742				0.00066	-6451.22880	-4.23691 A		23
Kz	Mass bias correction factor for Rz	1.019742				0.00066	6456.39135	4.24030 A		23
Cz	Amount content of element in the sample, ug/g	9.338320				0.01411	297.14045	4.19317		infinity
Ry	Measured ratio in the spike	0.038124				0.00012	0.25632	0.00003 B		infinity
Ky	Mass bias correction factor for Ry	1.019742				0.00066	0.00958	0.00001 A		23
mx	Mass of sample in blend b, g	0.004047191				4.10347E-07	-685609.53884	-0.28134		infinity
my	Mass of spike in blend b, g	0.55215				0.00002	5025.43271	0.10051 B		infinity
m'y	Mass of spike in blend b', g	0.48306				0.00002	-5744.19880	-0.11488 B		infinity
mz	Mass of primary standard in blend b', g	1.05224				0.00002	2637.03402	0.05274 B		infinity
w	Dry mass correction	0.998749				0.00001	-2778.26919	-0.02960		infinity
G	Digestion correction factor	1.000000				0.002000	2774.79267	5.54959 B		infinity
B	Blank correction factor	1.000000				0.002000	2774.79267	5.54959 B		infinity

64.08893

Cx	Cx	2774.792673
uc	uc	64.088931
veff	veff	1346.731296
k	k	2
U	U	128.177862
REU	REU(%)	4.61937



Appendix I

Example of the use of numerical approximation for the calculation of the sensitivity coefficients to be used for the calculation of the combined standard uncertainty

Table 1: Calculation combined standard uncertainty of the aliquot of a SARM 2 sample blend with the numerical approximation method

	Parameter	Value	SU	$Y_{pi(n)}$	$V-V*0.99$	Aliquot-1 (g)	Volume-1 (g)	Aliquot-2 (g)
Aliquot-1 (g)	Aliquot-1 (g)	0.200620	0.000020	249	0.00201	0.20263	0.20062	0.20062
Volume-1 (g)	Volume-1 (g)	52.474600	0.000190	249	0.52475	52.47460	52.99935	52.47460
Aliquot-2 (g)	Aliquot-2 (g)	1.053230	0.000020	249	0.01053	1.05323	1.05323	1.06376
Concentration (ug/g)		0.004026691				0.004067	0.003987	0.004067
Combined uncertainty		0.000000409			#	0.000004	-0.000004	0.000004
Exp. Unc		0.000000818			$C_{pi}=\#/(V-V*0.99)$	0.020007	-0.000008	0.00382
					$C_{pi}*u_{pi}$	0.000000	0.000000	0.000000
	SUM of $(C_{pi}*u_{pi})^2$	0.000000			$(C_{pi}*u_{pi})^2$	0.000000	0.000000	0.000000
	SQRT (SUM $(C_{pi}*u_{pi})^2$)	0.000000						
					$(C_{pi}*u_{pi})^4$	0.000000	0.000000	0.000000
	SUM of $(C_{pi}*u_{pi})^4 / Y_{pi}$	0.000000			$(C_{pi}*u_{pi})^4 / Y_{pi}$	0.000000	0.000000	0.000000
	$Y_{eff(n)}$, total degree of freedom	267.71158	k=1.984, 95%					



Table 2: Calculation of the measured ratio of the ¹³⁵Ba spike with the numerical approximation method

	Parameter	Value	SU	Y _{pi(n)}	V-V*0.99	A(137Ba)	A(135Ba)
A(¹³⁷ Ba)	A(¹³⁷ Ba)	0.89	0.02	249	0.00890	0.89890	0.89000
A(¹³⁵ Ba)	A(¹³⁵ Ba)	93.39	0.010000	249	0.93390	93.39000	94.32390
Ratio		0.009529928				0.009625228	0.009435573
Combined uncertainty		0.000214158			#	0.00010	-0.00009
Exp. Unc		0.000428316			C _{pi} =#/(V-V*0.99)	0.01071	-0.00010
					C _{pi} *u _{pi}	0.00021	0.00000
	SUM of (C _{pi} *u _{pi}) ²	0.00000			(C _{pi} *u _{pi}) ²	0.00000	0.00000
	SQRT (SUM (C _{pi} *u _{pi}) ²)	0.00021			(C _{pi} *u _{pi}) ⁴	0.00000	0.00000
	SUM of (C _{pi} *u _{pi}) ⁴ / Y _{pi}	0.00000			(C _{pi} *u _{pi}) ⁴ / Y _{pi}	0.00000	0.00000
	Y_{eff (n)}, total degree of freedom	249.01108	k=1.984, 95%				

Table 3: Calculation of the combined standard uncertainty of the moisture determination of SARM 2 with the numerical approximation method

	Parameter	Value	SU	Y _{pi(n)}	V-V*0.99	Dry sample (g)	Wet sample (g)
Dry sample (g)	Dry sample (g)	2.649870	0.000020	249	0.02650	2.67637	2.64987
Wet sample (g)	Wet sample (g)	2.653190	0.000190	249	0.02653	2.65319	2.67972
Concentration (ug/g)		0.998748676				1.008736163	0.988860075
Combined uncertainty		0.000071214			#	0.00999	-0.00989
Exp. Unc		0.000142428			C _{pi} =#/(V-V*0.99)	0.37690	-0.37271
					C _{pi} *u _{pi}	0.00001	-0.00007
	SUM of (C _{pi} *u _{pi}) ²	0.00000			(C _{pi} *u _{pi}) ²	0.00000	0.00000
	SQRT (SUM (C _{pi} *u _{pi}) ²)	0.00007			(C _{pi} *u _{pi}) ⁴	0.00000	0.00000
	SUM of (C _{pi} *u _{pi}) ⁴ / Y _{pi}	0.00000			(C _{pi} *u _{pi}) ⁴ / Y _{pi}	0.00000	0.00000
	Y_{eff (n)}, total degree of freedom	254.64231	k=1.984, 95%				



Table 4: Calculation of the combined standard uncertainty for the amount content, Cz, of Ba in SARM 2 with the numerical approximation method

	Parameter	Value	SU	$Y_{pi(n)}$	V-V*0.99	Csource	Aliquot-1 (g)	Volume-1 (g)
Csource	Csource	9930.000000	15.000000	249	99.30000	10029.30000	9930.00000	9930.00000
Aliquot-1 (g)	Aliquot-1 (g)	4.931360	0.000060	249	0.04931	4.93136	4.98067	4.93136
Volume-1 (g)	Volume-1 (g)	50.366410	0.000190	249	0.50366	50.36641	50.36641	50.87007
Concentration (ug/g)		972.243303				981.965736	981.965736	962.617131
Combined uncertainty		1.468698		#		9.72243	9.72243	-9.62617
Exp. Unc		2.937395		$C_{pi}=\#/(V-V*0.99)$		0.09791	197.15521	-19.11228
				$C_{pi}*u_{pi}$		1.46865	0.01183	-0.00363
	SUM of $(C_{pi}*u_{pi})^2$	2.15707		$(C_{pi}*u_{pi})^2$		2.15692	0.00014	0.00001
	SQRT (SUM $(C_{pi}*u_{pi})^2$)	1.46870		$(C_{pi}*u_{pi})^4$		4.65230	0.00000	0.00000
	SUM of $(C_{pi}*u_{pi})^4 / Y_{pi}$	0.01868		$(C_{pi}*u_{pi})^4 / Y_{pi}$		0.01868	0.00000	0.00000
	$Y_{eff(n)}$, total degree of freedom	249.03535	k=1.984, 95%					

Cz, Amount content of Ba in the spiked aliquot of primary standard

	Parameter	Value	SU	$Y_{pi(n)}$	V-V*0.99	Cps	Aliquot-1 (g)	Volume-1 (g)
Cps	Cps	972.243303	1.468698	249	9.72243	981.96574	972.24330	972.24330
Aliquot-1(g)	Aliquot-1 (g)	0.498430	0.000020	249	0.00498	0.49843	0.50341	0.49843
Volume-1(g)	Volume-1 (g)	51.893190	0.000190	249	0.51893	51.89319	51.89319	52.41212
Concentration (ug/g)		9.338320				9.431703	9.431703	9.245862
Combined uncertainty		0.014112		#		0.09338	0.09338	-0.09246
Exp. Unc				$C_{pi}=\#/(V-V*0.99)$		0.00960	18.73547	-0.17817
				$C_{pi}*u_{pi}$		0.01411	0.00037	-0.00003
	SUM of $(C_{pi}*u_{pi})^2$	0.00020		$(C_{pi}*u_{pi})^2$		0.00020	0.00000	0.00000
	SQRT (SUM $(C_{pi}*u_{pi})^2$)	0.01411		$(C_{pi}*u_{pi})^4$		0.00000	0.00000	0.00000
	SUM of $(C_{pi}*u_{pi})^4 / Y_{pi}$	0.00000		$(C_{pi}*u_{pi})^4 / Y_{pi}$		0.00000	0.00000	0.00000
	$Y_{eff(n)}$, total degree of freedom	249.35424	k=1.984, 95%					

Table 5: Calculation of the combined standard uncertainty of the double isotope dilution experiment for Ba in SARM 2 with the numerical approximation method

Parameter	Value	SU	Y _{rel}	V-V*0.99	Rb	Rb'	Rx	Rz	Kb	Kb'	Kx	Kz	Cz	Ry	Ky	mx	my	m'y	mz	w	G	B	
Rb	Measured ratio in the blend b	6.453850	0.044053	249	0.06454	6.51899	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	6.45385	
Rb'	Measured ratio in the blend b'	6.450050	0.023689	249	0.06450	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	6.45005	
Rx	Measured ratio in the sample	11.161800	0.051413	249	0.11162	11.16180	11.16180	11.27342	11.16180	11.16180	11.16180	11.16180	11.16180	11.16180	11.16180	11.16180	11.16180	11.16180	11.16180	11.16180	11.16180	11.16180	
Rz	Measured ratio in the primary standard	11.148725	0.034858	249	0.11149	11.14873	11.14873	11.14873	11.26021	11.14873	11.14873	11.14873	11.14873	11.14873	11.14873	11.14873	11.14873	11.14873	11.14873	11.14873	11.14873	11.14873	
Kb	Mass bias correction factor for Rb	1.019742	0.000657	20	0.01020	1.01974	1.01974	1.01974	1.01974	1.02294	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	
Kb'	Mass bias correction factor for Rb'	1.019742	0.000657	20	0.01020	1.01974	1.01974	1.01974	1.01974	1.02294	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	
Kx	Mass bias correction factor for Rx	1.019742	0.000657	20	0.01020	1.01974	1.01974	1.01974	1.01974	1.01974	1.02294	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	
Kz	Mass bias correction factor for Rz	1.019742	0.000657	20	0.01020	1.01974	1.01974	1.01974	1.01974	1.01974	1.02294	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	
Cz	Amount content of element in the sample, ug/g	9.518368	0.000396	100	0.09518	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	9.51837	
Ry	Measured ratio in the spike	0.038124	0.000214	249	0.00388	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	0.03812	
Ky	Mass bias correction factor for Ry	1.019742	0.000657	18	0.01020	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	1.01974	
mx	Mass of sample in blend b, g	0.004047191	4.10347E-07	100	0.00004	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	0.00405	
my	Mass of spike in blend b, g	0.55215	0.00002	100	0.00552	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	0.55215	
m'y	Mass of spike in blend b', g	0.48306	0.00002	100	0.00483	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	0.48306	
mz	Mass of primary standard in blend b', g	1.05224	0.00002	100	0.01052	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	1.05224	
w	Dry mass correction	0.998749	0.000102	1	0.00989	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	0.99875	
G	Digestion correction factor	1.000000	0.002000	100	0.01000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	
B	Blank correction factor	1.00000	0.002000	1	0.01000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	
Concentration (ug/g)		2828.292177				2896.448866	2761.686070	2762.790805	2895.400142	2896.448866	2761.686070	2762.790805	2895.400142	2896.448866	2761.686070	2762.790805	2895.400142	2896.448866	2761.686070	2762.790805	2895.400142	2896.448866	
Combined uncertainty		65.199349				68.15669	-66.60611	-65.50137	67.10796	68.15669	-66.60611	-65.50137	67.10796	68.15669	-66.60611	-65.50137	67.10796	68.15669	-66.60611	-65.50137	67.10796	68.15669	
Exp. Unc						Cp1=#/(V-V*0.99)	1056.06249	-1032.64482	-586.83521	601.93399	6683.71611	-6531.65990	-6423.32517	6580.87406	297.14045	0.26128	0.00977	#####	5122.32578	-5796.98026	2687.87746	-2803.79774	-2800.28928
						Cp2*ub	46.52246	-24.46137	-30.17113	20.98207	4.89660	-4.28973	-4.21858	4.32206	0.11756	0.00006	0.00001	-0.28392	0.10245	-0.11594	0.05376	-0.28474	-5.60058
						(Cp2*ub)^2	2164.33923	598.35863	910.29738	440.24717	19.26857	18.40181	17.79645	18.68016	0.01382	0.00000	0.00000	0.08061	0.01050	-0.01344	0.00289	0.08108	
						(Cp2*ub)^4	4684364.28395	#####	828641.32638	19381.57024	371.27780	338.62674	316.71354	348.94848	0.00019	0.00000	0.00000	0.00650	0.00011	0.00018	0.00001	0.00657	
						(Cp2*ub)^4 / Yp	18812.70797	1437.88374	3327.87661	778.38382	18.56389	16.93134	15.83566	17.44742	0.00000	0.00000	0.00000	0.00006	0.00000	0.00000	0.00000	0.00657	
Y _{rel} (95%)	total degree of freedom	709.78517	k=1.984, 95%																				



Appendix J

Example of the use of the power law for the calculation of the combined standard uncertainty

Table 1: Calculation of the combined standard uncertainty of an aliquot of SARM 2 with the Power Law

Parameter	Estimate	Specification	Probability distribution	Divisor	Standard uncertainty u_i	Relative uncertainty	Type A/B	Degrees of freedom
Aliquot-1 (g)	0.20088				0.00002	9.95619E-05	A	infinity
Volume-1 (g)	52.72417				0.00019	3.60366E-06	A	infinity
Aliquot-2 (g)	1.06225				0.00002	1.8828E-05	A	infinity
						0.000101391		

m_x	0.004047191
u_c	4.10347E-07
v_{eff}	∞
k	2
U	8.20694E-07

Table 2: Calculation of the combined standard uncertainty of the ^{135}Ba spike ratio with the Power Law

Parameter	Estimate	Specification	Probability distribution	Divisor	Std uncertainty	Relative uncertainty	Type A/B	Degrees of freedom
$A(^{135}\text{Ba})$	93.39	0.02	Rectangular	$\sqrt{3}$	0.011547005	0.000123643	B	infinity
$A(^{137}\text{Ba})$	0.89	0.01	Rectangular	$\sqrt{3}$	0.005773503	0.006487082	B	infinity
						0.00648826		

$Ratio$	0.009529928
u_c	6.18327E-05
v_{eff}	infinity
k	2
U	0.000123665

Table 3: Calculation of the combined standard uncertainty of the moisture determination of SARM 2 with the Power Law

Parameter	Estimate	Specification	Probability distribution	Divisor	Standard uncertainty u_i	Relative uncertainty	Type A/B	Degrees of freedom
<i>Wet sample</i>	2.65319				0.00002	7.5381E-06	B	∞
<i>Dry sample</i>	2.64987				0.00002	7.54754E-06	B	∞
						1.06672E-05		

%Moisture	0.998748676
u_c	1.06538E-05
v_{eff}	∞
k	2
U	2.13076E-05
RSU	0.002133431



Table 4: Calculation of the combined standard uncertainty of the amount content, C_z , of Ba in SARM 2 with the Power Law

Parameter	Estimate	Specification	Probability distribution	Divisor	Standard uncertainty u_i	Relative uncertainty	Type A/B	Degrees of freedom
C_{source}	9930	30	Normal	2	15	0.001510574	B	∞
Aliquot-1 (g)	4.93136				0.00006	1.2167E-05	A	∞
Volume-1 (g)	50.36641				0.00019	3.77236E-06	A	∞

0.001510628

C_{PS} 972.2433026 $\mu\text{g}\cdot\text{g}^{-1}$

u_c 1.468697691

v_{eff} ∞

k 2

U 2.937395382

Appendix K

Summary of the results for SARM 2, SARM 3 and SARM 4

Table 1: Summary of results for Ba in SARM 2

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	2568.892365	16.57507145	2568.892365	16.20503356	2568.892365	19.57460024
	std-spkB	2554.069191	15.6134572	2554.069191	15.53274898	2554.069191	19.32964303
	std-spkC	2545.961837	18.73401394	2545.961838	18.20090311	2545.961837	19.8922341
smp-spkB	std-spkA	2608.503064	18.92047248	2608.503064	18.88465264	2608.503064	20.20385939
	std-spkB	2593.451326	18.03357045	2593.451326	17.58172692	2593.451326	19.95542255
	std-spkC	2585.218962	20.86278531	2585.218962	20.41540336	2585.218962	20.51556167
smp-spkC	std-spkA	2596.728096	18.69608839	2596.728097	18.6543611	2596.728096	20.07031822
	std-spkB	2581.744303	17.80798537	2581.744303	17.34827638	2581.744303	19.82296841
	std-spkC	2573.549101	20.6449028	2573.549101	20.19154609	2573.549101	20.38199984
smp-spkD	std-spkA	2601.716176	17.31686059	2601.716176	17.22248494	2601.716176	19.8678515
	std-spkB	2586.7036	16.36815901	2586.7036	15.81193189	2586.7036	19.61980771
	std-spkC	2578.492655	19.43562761	2578.492656	18.90750987	2578.492655	20.18810284
smp-spkE	std-spkA	2611.150591	16.99036188	2611.150591	16.56250174	2611.150591	19.88686042
	std-spkB	2596.083576	16.01989847	2596.083576	15.08828539	2596.083576	19.6378637
	std-spkC	2587.842856	19.1662701	2587.842857	18.33387488	2587.842856	20.21004538
Mean		2584.673847		2584.673847		2584.673847	
Standard deviation		18.48000908		18.48000909		18.48000908	
Combined standard uncertainty		18.76256245		18.36312291		20.50904722	
k		2		2		2	
Expanded uncertainty		37.5251249		36.72624582		41.01809443	
Relative uncertainty(%)		1.451832112		1.420923799		1.58697371	

Table 2: Summary of results for Sr in SARM 2

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	60.92795502	0.79949085	60.92795503	0.827089187	60.92795502	0.882975257
	std-spkB	60.95234587	0.781334923	60.95234587	0.809933987	60.95234587	0.870968583
	std-spkC	60.81577045	0.776411875	60.81577045	0.805071497	60.81577045	0.868308865
smp-spkB	std-spkA	60.13813526	0.866903882	60.13813526	0.891802456	60.13813526	0.92406287
	std-spkB	60.16220992	0.850684052	60.16220993	0.876387201	60.16220992	0.912935452
	std-spkC	60.02740495	0.845943399	60.02740496	0.871689167	60.02740495	0.910231685
smp-spkC	std-spkA	59.24906267	0.786810928	59.24906268	0.813058589	59.24906267	0.858977864
	std-spkB	59.27278141	0.769377421	59.27278142	0.796566464	59.27278141	0.847306901
	std-spkC	59.13996938	0.764613763	59.13996939	0.791870266	59.13996938	0.844719991
smp-spkD	std-spkA	59.60855784	0.810521396	59.60855785	0.83614074	59.60855784	0.872416938
	std-spkB	59.6324205	0.793416097	59.63242051	0.819930407	59.6324205	0.86079404
	std-spkC	59.49880262	0.788659114	59.49880263	0.815242136	59.49880262	0.858179452
smp-spkE	std-spkA	59.74289145	0.799650759	59.74289146	0.825698872	59.74289145	0.865757098
	std-spkB	59.76680789	0.782218204	59.76680789	0.809194424	59.76680789	0.853983312
	std-spkC	59.63288889	0.777429696	59.6328889	0.804478788	59.63288889	0.851375391
Mean		59.90453361		59.90453361		59.90453361	
Standard deviation		0.595829696		0.595829696		0.595829696	
Combined standard uncertainty		0.814783911		0.840986291		0.885987446	
k		2		2		2	
Expanded uncertainty		1.629567821		1.681972581		1.771974893	
Relative uncertainty(%)		2.720274616		2.807755072		2.957997978	

Table 3: Summary of results for Zn in SARM 2

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	8.683713307	0.18298093	8.683713308	0.181691787	8.683713307	0.16838273
	std-spkB	9.142124261	0.187980629	9.142124262	0.186674915	9.142124261	0.174257677
	std-spkC	9.15093464	0.207503759	9.150934641	0.205947212	9.15093464	0.188702768
smp-spkB	std-spkA	8.563769433	0.188742996	8.563769434	0.187535393	8.563769433	0.172066217
	std-spkB	9.015848581	0.19431775	9.015848582	0.193097765	9.015848581	0.178282749
	std-spkC	9.024537267	0.212779699	9.024537268	0.211311234	9.024537267	0.192063115
smp-spkC	std-spkA	8.595510819	0.189734779	8.59551082	0.180838555	8.595510819	0.171915139
	std-spkB	9.049265587	0.195352589	9.049265588	0.185849154	9.049265587	0.178099654
	std-spkC	9.057986477	0.213856265	9.057986478	0.204827909	9.057986477	0.191990389
smp-spkD	std-spkA	8.530386146	0.182776038	8.530386147	0.181436296	8.530386146	0.165532075
	std-spkB	8.980702999	0.187924884	8.980703001	0.186562843	8.980702999	0.171311981
	std-spkC	8.989357815	0.206806549	8.989357816	0.205206845	8.989357815	0.185492218
Mean		8.898678111		8.898678112		8.898678111	
Standard deviation		0.233821714		0.233821714		0.233821714	
Combined standard uncertainty		0.207484108		0.20434583		0.190737649	
k		2		2		2	
Expanded uncertainty		0.414968216		0.408691661		0.381475298	
Relative uncertainty(%)		4.663256848		4.592723275		4.28687602	

Table 4: Summary of results for Cu in SARM 2

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	16.57436679	0.152099722	16.57436668	0.150807746	16.57436679	0.500014407
	std-spkB	17.20080603	0.187958982	17.20080603	0.186272795	17.20080603	0.521801399
	std-spkC	17.15598068	0.155409439	17.15598068	0.154083263	17.15598068	0.517445086
smp-spkB	std-spkA	16.75885734	0.175973604	16.75885734	0.174867472	16.75885734	0.507720986
	std-spkB	17.39226951	0.209755357	17.39226951	0.20837878	17.39226951	0.529819159
	std-spkC	17.34694521	0.180359701	17.34694521	0.179385581	17.34694521	0.525421306
smp-spkC	std-spkA	16.83175708	0.162011887	16.83175708	0.160376901	16.83175708	0.507975657
	std-spkB	17.46792455	0.197503994	17.46792455	0.195655661	17.46792455	0.530107281
	std-spkC	17.42240309	0.165735101	17.42240309	0.164223373	17.42240309	0.525683959
smp-spkD	std-spkA	16.73272938	0.194466737	16.73272938	0.19349446	16.73272938	0.508107775
	std-spkB	17.36515403	0.226588583	17.36515403	0.225341984	17.36515403	0.530209335
	std-spkC	17.31990039	0.199678445	17.3199004	0.198827838	17.31990039	0.525822119
Mean		17.13075784		17.13075784		17.13075784	
Standard deviation		0.317064976		0.317064976		0.317064976	
Combined standard uncertainty		0.206638537		0.205469938		0.527281407	
k		2		2		2	
Expanded uncertainty		0.413277074		0.410939876		1.054562814	
Relative uncertainty(%)		2.412485647		2.398842364		6.155961247	

Table 5: Summary of results for Ni in SARM 2

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	2.385817676	0.057789727	2.385817676	0.057308973	2.385817676	0.058190043
	std-spkB	2.500887378	0.062027244	2.500887379	0.061502412	2.500887378	0.06215182
	std-spkC	2.500163388	0.060675134	2.500163388	0.060167192	2.500163388	0.061072555
smp-spkB	std-spkA	2.452783851	0.065502568	2.452783851	0.065041157	2.452783851	0.063946957
	std-spkB	2.57108338	0.070017097	2.57108338	0.069512451	2.57108338	0.068143525
	std-spkC	2.570339068	0.068749983	2.570339069	0.06826272	2.570339068	0.067101811
smp-spkC	std-spkA	2.440427699	0.061886865	2.440427699	0.061389905	2.440427699	0.061379738
	std-spkB	2.558131282	0.066290388	2.558131282	0.065749067	2.558131282	0.065486669
	std-spkC	2.55739072	0.064966266	2.55739072	0.064441899	2.55739072	0.064414372
smp-spkD	std-spkA	2.457925844	0.059276472	2.457925845	0.058735688	2.457925844	0.059672834
	std-spkB	2.576473376	0.063636316	2.576473376	0.063049708	2.576473376	0.063746443
	std-spkC	2.575727504	0.062237587	2.575727504	0.061667464	2.575727504	0.062629687
Mean		2.512262597		2.512262597		2.512262597	
Standard deviation		0.065392955		0.065392955		0.065392955	
Combined standard uncertainty		0.066424202		0.065927844		0.065981407	
k		2		2		2	
Expanded uncertainty		0.132848405		0.131855688		0.131962814	
Relative uncertainty(%)		5.287998353		5.248483523		5.252747628	

Table 6: Summary of results for Mo in SARM 2

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	0.848795962	0.011282869	0.848795962	0.011230954	0.848795962	0.042355716
	std-spkB	0.881831439	0.011831596	0.88183144	0.01174419	0.881831439	0.044010904
	std-spkC	0.777878207	0.010351398	0.777878207	0.010344631	0.777878207	0.03881133
smp-spkB	std-spkA	0.873092435	0.008901954	0.873092435	0.008864731	0.873092435	0.04315825
	std-spkB	0.907073541	0.009394937	0.907073541	0.009253269	0.907073541	0.04484493
	std-spkC	0.800144685	0.008173182	0.800144686	0.008141951	0.800144685	0.0395466
smp-spkC	std-spkA	0.865448961	0.010810303	0.865448961	0.010784918	0.865448961	0.043044606
	std-spkB	0.793139831	0.009919197	0.793139831	0.009898178	0.793139831	0.039442536
	std-spkC	0.89913258	0.011349914	0.89913258	0.01123988	0.89913258	0.04472676
smp-spkD	std-spkA	0.781648866	0.011236616	0.781648866	0.011225811	0.781648866	0.039120954
	std-spkB	0.812070952	0.011767351	0.812070952	0.011690316	0.812070952	0.040649697
	std-spkC	0.716341319	0.010307298	0.716341319	0.010299164	0.716341319	0.035847288
Mean		0.829716565		0.829716565		0.829716565	
Standard deviation		0.058322244		0.058322244		0.058322244	
Combined standard uncertainty		0.019843727		0.019816727		0.044677842	
k		2		2		2	
Expanded uncertainty		0.039687454		0.039633454		0.089355685	
Relative uncertainty(%)		4.783254398		4.776746143		10.76942281	

Table 7: Summary of results for Cd in SARM 2

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	0.018152426	0.001133372	0.018152426	0.001123386	0.018152426	0.001098816
	std-spkB	0.018944023	0.001185655	0.018944023	0.001175198	0.018944023	0.001148262
	std-spkC	0.018991044	0.001185954	0.018991044	0.001175503	0.018991044	0.001185954
smp-spkB	std-spkA	0.018365148	0.001088237	0.018365148	0.001077526	0.018365148	0.001067058
	std-spkB	0.019166022	0.00113874	0.019166022	0.001127527	0.019166022	0.001115201
	std-spkC	0.019213594	0.001138749	0.019213594	0.001127539	0.019213594	0.001138749
smp-spkC	std-spkA	0.016652815	0.000982824	0.016652815	0.000973083	0.016652815	0.000964857
	std-spkB	0.017379017	0.001028456	0.017379017	0.00101826	0.017379017	0.001008397
	std-spkC	0.017422153	0.001028444	0.017422153	0.00101825	0.017422153	0.001028444
smp-spkD	std-spkA	0.017414202	0.001123824	0.017414202	0.001114493	0.017414202	0.001082289
	std-spkB	0.018173606	0.001175485	0.018173606	0.001165713	0.018173606	0.001130914
	std-spkC	0.018218715	0.001175949	0.018218715	0.001166183	0.018218715	0.001175949
Mean		0.018174397		0.018174397		0.018174397	
Standard deviation		0.000823128		0.000823128		0.000823128	
Combined standard uncertainty		0.001142404		0.00113239		0.001122781	
k		2		2		2	
Expanded uncertainty		0.002284808		0.002264781		0.002245562	
Relative uncertainty(%)		12.57157352		12.46138131		12.3556358	

Table 8: Summary of results for Pb in SARM 2

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	1.779271776	0.0124501	1.779271776	0.014813577	1.779271776	0.012464852
	std-spkB	1.867277958	0.01049398	1.867277958	0.013501605	1.867277958	0.012433491
	std-spkC	1.860544145	0.010456223	1.860544145	0.013452982	1.860544145	0.01238865
smp-spkB	std-spkA	1.763723075	0.011148497	1.763723075	0.014778459	1.763723075	0.011667758
	std-spkB	1.850960188	0.008794791	1.850960188	0.013497495	1.850960188	0.011562589
	std-spkC	1.844285221	0.008763177	1.844285221	0.013448886	1.844285221	0.011520888
smp-spkC	std-spkA	1.803219836	0.011539228	1.803219836	0.015215588	1.803219836	0.011979844
	std-spkB	1.892410535	0.00918778	1.892410535	0.013927662	1.892410535	0.011877963
	std-spkC	1.885586089	0.009154749	1.885586089	0.013877503	1.885586089	0.011835125
smp-spkD	std-spkA	1.731522429	0.011968488	1.731522429	0.015299268	1.731522429	0.011965151
	std-spkB	1.817166837	0.010018976	1.817166837	0.014196716	1.817166837	0.011917293
	std-spkC	1.810613736	0.009982932	1.810613736	0.01414558	1.810613736	0.011874313
Mean		1.825548485		1.825548485		1.825548485	
Standard deviation		0.050122209		0.050122209		0.050122209	
Combined standard uncertainty		0.017818038		0.02026944		0.018772983	
k		2		2		2	
Expanded uncertainty		0.035636076		0.04053888		0.037545965	
Relative uncertainty(%)		1.952075006		2.220641115		2.056695041	

Table 9: Summary of results for Ba in SARM 3

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	413.2315713	1.616311512	413.2315713	1.584471249	413.2315713	3.806802649
	std-spkB	413.5301135	1.676065583	413.5301135	1.643836041	413.5301135	3.813570305
	std-spkC	413.5213386	1.580304012	413.5213386	1.548133832	413.5213386	3.806648376
smp-spkB	std-spkA	412.7025844	1.614423097	412.7025844	1.582628239	412.7025844	3.697029468
	std-spkB	413.0007445	1.674094488	413.0007445	1.641910609	413.0007445	3.703828334
	std-spkC	412.9919808	1.578466068	412.9919808	1.546341962	412.9919808	3.696723699
smp-spkC	std-spkA	413.6494067	1.548574137	413.6494067	1.51323631	413.6494067	3.700260295
	std-spkB	413.9482508	1.61086788	413.9482508	1.575307388	413.9482508	3.707073763
	std-spkC	413.939467	1.510774192	413.939467	1.474959765	413.939467	3.699942943
Mean		413.3906064		413.3906064		413.3906064	
Standard deviation		0.436650186		0.436650186		0.436650186	
Combined standard uncertainty		1.608505454		1.575467044		3.740058487	
k		2		2		2	
Expanded uncertainty		3.217010908		3.150934089		7.480116974	
Relative uncertainty (%)		0.77820126		0.762217148		1.809454994	

Table 10: Summary of results for Sr in SARM 3

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	4740.01397	31.05688421	4740.01397	34.06310124	4740.01397	48.54291665
	std-spkB	4742.437394	27.66949036	4742.437394	31.07386773	4742.437394	47.0062788
	std-spkC	4721.671362	27.44699244	4721.671362	30.8495053	4721.671362	46.75460267
smp-spkB	std-spkA	4710.480311	31.75306316	4710.480311	34.6661365	4710.480311	48.67332778
	std-spkB	4712.888636	28.49308447	4712.888636	31.77274545	4712.888636	47.16073767
	std-spkC	4692.25199	28.27114464	4692.25199	31.54834546	4692.25199	46.90910344
smp-spkC	std-spkA	4726.725351	29.39801631	4726.725351	32.53693238	4726.725351	47.66548397
	std-spkB	4729.141982	25.81338375	4729.141982	29.40978124	4729.141982	46.10773358
	std-spkC	4708.434167	25.59230567	4708.434167	29.18821561	4708.434167	45.85935945
smp-spkD	std-spkA	4755.301505	33.78133279	4755.301505	36.58782372	4755.301505	49.99224488
	std-spkB	4757.732745	30.67797486	4757.732745	33.80644949	4757.732745	48.49311214
	std-spkC	4736.899738	30.45168185	4736.899738	33.57675218	4736.899738	48.23604527
Mean		4727.831596		4727.831596		4727.831596	
Standard deviation		19.77156485		19.77156485		19.77156485	
Combined standard uncertainty		29.84531677		32.98928568		47.97145809	
k		2		2		2	
Expanded uncertainty		59.69063353		65.97857137		95.94291618	
Relative uncertainty (%)		1.262537219		1.395535565		2.029321778	

Table 11: Summary of results for Zn in SARM 3

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	434.3954379	2.335415637	434.3954379	2.334210977	434.3954379	5.170798385
	std-spkB	435.5007432	2.442141413	435.5007432	2.439008041	435.5007432	5.215177226
	std-spkC	436.3033348	2.428868186	436.3033348	2.42606213	436.3033348	5.219249398
smp-spkB	std-spkA	426.1782647	2.738086461	426.1782647	2.738561339	426.1782647	5.226049754
	std-spkB	427.2626616	2.828311991	427.2626616	2.82713342	427.2626616	5.269086566
	std-spkC	428.0500711	2.818767523	428.0500711	2.817875652	428.0500711	5.273520366
smp-spkC	std-spkA	427.4152213	2.299342047	427.4152213	2.298159416	427.4152213	5.088262415
	std-spkB	428.5027657	2.404296448	428.5027657	2.401217066	428.5027657	5.131926231
	std-spkC	429.2924606	2.39124931	429.2924606	2.388491835	429.2924606	5.135934568
smp-spkD	std-spkA	427.9378925	1.860502197	427.9378925	1.857186818	427.9378925	4.968268821
	std-spkB	429.0267668	1.986699806	429.0267668	1.981219736	429.0267668	5.012441323
	std-spkC	429.8174273	1.969120974	429.8174273	1.963998281	429.8174273	5.016085755
Mean		429.9735873		429.9735873		429.9735873	
Standard deviation		3.435891039		3.435891039		3.435891039	
Combined standard uncertainty		2.592239312		2.590128499		5.239595339	
k		2		2		2	
Expanded uncertainty		5.184478623		5.180256998		10.47919068	
Relative uncertainty (%)		1.205766767		1.204784933		2.437170791	

Table 12: Summary of results for Cu in SARM 3

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	9.047151801	0.093587384	9.047151801	0.092947273	9.047151801	0.273660582
	std-spkB	9.069305113	0.100546366	9.069305113	0.099817071	9.069305113	0.275015292
	std-spkC	9.040867056	0.082335862	9.040867056	0.081845546	9.040867056	0.27246111
smp-spkB	std-spkA	11.29380202	0.119398036	11.29380202	0.118429647	11.29380202	0.341485702
	std-spkB	11.32145659	0.12792231	11.32145659	0.12685406	11.32145659	0.34317683
	std-spkC	11.2859566	0.105690602	11.2859566	0.104885071	11.2859566	0.339987972
smp-spkC	std-spkA	9.187556197	0.097226709	9.187556197	0.096617981	9.187556197	0.278126591
	std-spkB	9.210053311	0.104155294	9.210053311	0.103454313	9.210053311	0.279502316
	std-spkC	9.181173918	0.086087923	9.181173918	0.085634359	9.181173918	0.276909162
Mean		9.848591401		9.848591401		9.848591401	
Standard deviation		1.090650037		1.090650037		1.090650037	
Combined standard uncertainty		0.377810633		0.377610664		0.470980697	
k		2		2		2	
Expanded uncertainty		0.755621266		0.755221329		0.941961395	
Relative uncertainty (%)		7.672379073		7.66831822		9.564427606	



Table 13: Summary of results for Ni in SARM 3

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	2.077479504	0.039368724	2.077479504	0.03902681	2.077479504	0.038858694
	std-spkB	2.067695862	0.038680619	2.067695862	0.038346551	2.067695862	0.038269005
	std-spkC	2.036465065	0.038155486	2.036465065	0.037825712	2.036465065	0.03773873
smp-spkB	std-spkA	1.312582543	0.024602739	1.312582543	0.024397058	1.312582543	0.024592772
	std-spkB	1.306401092	0.024165728	1.306401092	0.023965132	1.306401092	0.024220439
	std-spkC	1.286669008	0.023838556	1.286669008	0.023640623	1.286669008	0.023884725
smp-spkC	std-spkA	1.282566959	0.022130184	1.282566959	0.021911211	1.282566959	0.022566599
	std-spkB	1.276526862	0.021684671	1.276526862	0.021470577	1.276526862	0.022193226
	std-spkC	1.257246004	0.021397394	1.257246004	0.021186219	1.257246004	0.021889393
Mean		1.5448481		1.5448481		1.5448481	
Standard deviation		0.387252597		0.387252597		0.387252597	
Combined standard uncertainty		0.132347134		0.13229062		0.132332137	
k		2		2		2	
Expanded uncertainty		0.264694267		0.264581241		0.264664274	
Relative uncertainty (%)		17.13399961		17.12668325		17.13205813	

Table 14: Summary of results for Mo in SARM 3

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	2.536625786	0.155782744	2.536625786	0.156316174	2.536625786	0.133533179
	std-spkB	2.534047345	0.156068	2.534047345	0.156589413	2.534047345	0.133484508
	std-spkC	2.47952539	0.153471286	2.47952539	0.153980977	2.47952539	0.130593329
smp-spkB	std-spkA	1.496088539	0.069446097	1.496088539	0.069123453	1.496088539	0.077978192
	std-spkB	1.494567788	0.06972101	1.494567788	0.069392761	1.494567788	0.077950791
	std-spkC	1.462411026	0.068812826	1.462411026	0.068495722	1.462411026	0.076262208
smp-spkC	std-spkA	1.46810651	0.072408574	1.46810651	0.072309011	1.46810651	0.076958883
	std-spkB	1.466614202	0.072654151	1.466614202	0.072548183	1.466614202	0.076931257
	std-spkC	1.435058883	0.071638179	1.435058883	0.071536491	1.435058883	0.075264888
Mean		1.819227274		1.819227274		1.819227274	
Standard deviation		0.52368518		0.52368518		0.52368518	
Combined standard uncertainty		0.204531338		0.204614997		0.200673519	
k		2		2		2	
Expanded uncertainty		0.409062676		0.409229994		0.401347037	
Relative uncertainty (%)		22.48551801		22.49471516		22.06140171	

Table 15: Summary of results for Pb in SARM 3

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	46.10283106	0.300879437	46.10283106	0.554373554	46.10283106	0.364815943
	std-spkB	46.1393789	0.300882	46.1393789	0.554684813	46.1393789	0.365105816
	std-spkC	46.14917985	0.310322468	46.14917985	0.559841015	46.14917985	0.367353562
smp-spkB	std-spkA	46.33530992	0.308378632	46.33530992	0.560490759	46.33530992	0.368053399
	std-spkB	46.37204207	0.308390162	46.37204207	0.560806985	46.37204207	0.368345839
	std-spkC	46.38189243	0.317702194	46.38189243	0.565960138	46.38189243	0.370596982
smp-spkC	std-spkA	45.61286683	0.306664767	45.61286683	0.553497799	45.61286683	0.363186467
	std-spkB	45.64902626	0.306680886	45.64902626	0.553810876	45.64902626	0.363475037
	std-spkC	45.65872304	0.315759045	45.65872304	0.558868553	45.65872304	0.365686162
Mean		46.04458337		46.04458337		46.04458337	
Standard deviation		0.320269562		0.320269562		0.320269562	
Combined standard uncertainty		0.326405946		0.568171085		0.381538279	
k		2		2		2	
Expanded uncertainty		0.652811893		1.13634217		0.763076559	
Relative uncertainty (%)		1.417782169		2.467917151		1.657255866	

Table 16: Summary of results for Ba in SARM 4

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	82.79975088	0.495569358	82.79975088	0.489498738	82.79975088	0.624998916
	std-spkB	82.83247942	0.4202034	82.83247942	0.414682733	82.83247942	0.615591462
	std-spkC	82.80196291	0.536325334	82.80196291	0.529931727	82.80196291	0.630880157
smp-spkB	std-spkA	82.85936536	0.536175294	82.85936536	0.531741685	82.85936536	0.631648091
	std-spkB	82.89211746	0.467332088	82.89211746	0.463722287	82.89211746	0.6223326
	std-spkC	82.86157898	0.574110287	82.86157898	0.569235888	82.86157898	0.637476662
smp-spkC	std-spkA	82.92621099	0.537889343	82.92621099	0.533406049	82.92621099	0.632095061
	std-spkB	82.95898952	0.469179985	82.95898952	0.465513596	82.95898952	0.622771067
	std-spkC	82.9284264	0.575770509	82.9284264	0.570849364	82.9284264	0.637928904
Mean		82.87343132		82.87343132		82.87343132	
Standard deviation		0.057043248		0.057043248		0.057043248	
Combined standard uncertainty		0.515268109		0.510398901		0.628740816	
k		2		2		2	
Expanded uncertainty		1.030536217		1.020797802		1.257481632	
Relative uncertainty (%)		1.243506152		1.231755203		1.517351957	



Table 17: Summary of results for Sr in SARM 4

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	259.3512596	1.511671527	259.3512596	1.69604061	259.3512596	2.583171662
	std-spkB	264.5747189	1.449003096	264.5747189	1.649447689	264.5747189	2.595252282
	std-spkC	265.175227	1.496710331	265.175227	1.691566629	265.175227	2.619952992
smp-spkB	std-spkA	258.6157705	2.497834384	258.6157705	2.614945787	258.6157705	3.098879739
	std-spkB	263.8244166	2.493208588	263.8244166	2.616254276	263.8244166	3.128261606
	std-spkC	264.4232218	2.524794379	264.4232218	2.646416777	264.4232218	3.150896346
smp-spkC	std-spkA	255.4676738	1.570311474	255.4676738	1.743665759	255.4676738	2.581049781
	std-spkB	260.6129158	1.515245577	260.6129158	1.702724738	260.6129158	2.59425155
	std-spkC	261.2044318	1.559967883	261.2044318	1.742695578	261.2044318	2.618399809
smp-spkD	std-spkA	255.7177251	2.493501616	255.7177251	1.745737708	255.7177251	2.583826072
	std-spkB	260.8680032	2.489930695	260.8680032	1.704780616	260.8680032	2.59704961
	std-spkC	261.4600982	2.520967169	261.4600982	1.744783382	261.4600982	2.621220283
Mean		260.9412885		260.9412885		260.9412885	
Standard deviation		3.264105673		3.264105673		3.264105673	
Combined standard uncertainty		2.274442578		2.19419766		2.8980377	
k		2		2		2	
Expanded uncertainty		4.548885156		4.388395319		5.7960754	
Relative uncertainty (%)		1.743260019		1.681755825		2.221218203	

Table 18: Summary of results for Zn in SARM 4

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	61.23076818	0.485087366	61.23076818	0.48380138	61.23076818	0.786756784
	std-spkB	61.48974794	0.440206075	61.48974794	0.439757951	61.48974794	0.771329694
	std-spkC	61.51417382	0.444057888	61.51417382	0.443541052	61.51417382	0.773048408
smp-spkB	std-spkA	61.33888373	0.474176983	61.33888373	0.472811525	61.33888373	0.783200153
	std-spkB	61.59832077	0.427870164	61.59832077	0.4273571	61.59832077	0.767603348
	std-spkC	61.62278978	0.431835482	61.62278978	0.431252161	61.62278978	0.769332437
smp-spkC	std-spkA	61.1355937	0.471999982	61.1355937	0.470634975	61.1355937	0.780348491
	std-spkB	61.39417091	0.425775326	61.39417091	0.425260559	61.39417091	0.76479596
	std-spkC	61.41855882	0.429733192	61.41855882	0.429148326	61.41855882	0.766519702
Mean		61.41588974		61.41588974		61.41588974	
Standard deviation		0.162191292		0.162191292		0.162191292	
Combined standard uncertainty		0.451629441		0.45082158		0.775581821	
k		2		2		2	
Expanded uncertainty		0.903258881		0.90164316		1.551163642	
Relative uncertainty (%)		1.47072506		1.468094274		2.52567153	



Table 19: Summary of results for Cu in SARM 4

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	10.5339098	0.104950118	10.5339098	0.104569695	10.5339098	0.31836011
	std-spkB	10.54030116	0.1069636	10.54030116	0.106549832	10.54030116	0.318752566
	std-spkC	10.61757964	0.108386848	10.61757964	0.10795794	10.61757964	0.321164914
smp-spkB	std-spkA	10.8087292	0.110576249	10.8087292	0.110235004	10.8087292	0.326929732
	std-spkB	10.81528731	0.112592674	10.81528731	0.112217087	10.81528731	0.327332423
	std-spkC	10.89458191	0.114057429	10.89458191	0.113666643	10.89458191	0.329809578
smp-spkC	std-spkA	10.57385182	0.095686328	10.57385182	0.095099851	10.57385182	0.318627751
	std-spkB	10.58026742	0.097895055	10.58026742	0.097276962	10.58026742	0.319021715
	std-spkC	10.65783892	0.099315896	10.65783892	0.098681643	10.65783892	0.321436544
Mean		10.66914969		10.66914969		10.66914969	
Standard deviation		0.135240178		0.135240178		0.135240178	
Combined standard uncertainty		0.114992575		0.114572588		0.32554519	
k		2		2		2	
Expanded uncertainty		0.229985149		0.229145177		0.651090381	
Relative uncertainty (%)		2.155608985		2.147736076		6.10255175	

Table 20: Summary of results for Ni in SARM 4

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	119.8126946	2.611188415	119.8126946	2.591935617	119.8126946	1.833909211
	std-spkB	119.2177532	2.196293431	119.2177532	2.182440055	119.2177532	1.580331041
	std-spkC	120.3036896	3.350320987	120.3036896	3.322147031	120.3036896	2.299825538
smp-spkB	std-spkA	118.1018312	2.44620502	118.1018312	2.425033602	118.1018312	1.725348821
	std-spkB	117.5153853	2.013014286	117.5153853	1.996884306	117.5153853	1.462355639
	std-spkC	118.5858151	3.203132481	118.5858151	3.173571161	118.5858151	2.201318186
smp-spkC	std-spkA	120.1626862	2.468605332	120.1626862	2.446681498	120.1626862	1.74056231
	std-spkB	119.5660069	2.023687848	119.5660069	2.006829735	119.5660069	1.470447294
	std-spkC	120.6551155	3.243433794	120.6551155	3.213053756	120.6551155	2.227980766
Mean		119.3245531		119.3245531		119.3245531	
Standard deviation		1.063803955		1.063803955		1.063803955	
Combined standard uncertainty		2.687496359		2.66513985		1.897317714	
k		2		2		2	
Expanded uncertainty		5.374992718		5.3302797		3.794635428	
Relative uncertainty (%)		4.504515273		4.467043507		3.180096074	



Table 21: Summary of results for Mo in SARM 4

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	0.854926489	0.023689395	0.854926489	0.02371742	0.854926489	0.044186979
	std-spkB	0.851828678	0.023598	0.851828678	0.023626188	0.851828678	0.044026874
	std-spkC	0.838398872	0.024661028	0.838398872	0.024660933	0.838398872	0.043566218
smp-spkB	std-spkA	0.894339297	0.019832053	0.894339297	0.019797267	0.894339297	0.045313744
	std-spkB	0.891098675	0.019753262	0.891098675	0.019718593	0.891098675	0.045149557
	std-spkC	0.877049743	0.021287922	0.877049743	0.02122372	0.877049743	0.044686844
smp-spkC	std-spkA	0.934364123	0.02527527	0.934364123	0.025300121	0.934364123	0.048100852
	std-spkB	0.930978472	0.025177751	0.930978472	0.02520252	0.930978472	0.047926566
	std-spkC	0.916300801	0.026384833	0.916300801	0.026378702	0.916300801	0.047427134
Mean		0.88769835		0.88769835		0.88769835	
Standard deviation		0.035051904		0.035051904		0.035051904	
Combined standard uncertainty		0.026162871		0.026161486		0.047100624	
k		2		2		2	
Expanded uncertainty		0.052325743		0.052322973		0.094201247	
Relative uncertainty (%)		5.894540927		5.89422892		10.61185336	

Table 22: Summary of results for Cd in SARM 4

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	0.086803128	0.001418944	0.086803128	0.001405457	0.086803128	0.001255951
	std-spkB	0.087053353	0.001371	0.087053353	0.001358388	0.087053353	0.001245607
	std-spkC	0.086893507	0.001401773	0.086893507	0.001388468	0.086893507	0.001252235
smp-spkB	std-spkA	0.087907242	0.001770207	0.087907242	0.0017597	0.087907242	0.001524764
	std-spkB	0.08816065	0.001733101	0.08816065	0.001723167	0.08816065	0.001517382
	std-spkC	0.087998769	0.001756754	0.087998769	0.001746452	0.087998769	0.00152211
smp-spkC	std-spkA	0.088530371	0.001446862	0.088530371	0.001433032	0.088530371	0.001279569
	std-spkB	0.088785575	0.001398323	0.088785575	0.001385011	0.088785575	0.001268999
	std-spkC	0.088622547	0.001429345	0.088622547	0.0014157	0.088622547	0.001275772
Mean		0.087861682		0.087861682		0.087861682	
Standard deviation		0.000766582		0.000766582		0.000766582	
Combined standard uncertainty		0.001554987		0.001543013		0.001378571	
k		2		2		2	
Expanded uncertainty		0.003109974		0.003086026		0.002757141	
Relative uncertainty (%)		3.539624619		3.512368944		3.138047193	

Table 23: Summary of results for Pb in SARM 4

		Sensitivity coefficients		Numerical approximation		Power Law	
		Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹	Concentration mg.kg ⁻¹	Standard uncertainty (u _c) mg.kg ⁻¹
smp-spkA	std-spkA	2.096982064	0.01134865	2.096982064	0.019253317	2.096982064	0.017536015
	std-spkB	2.100595517	0.010440	2.100595517	0.010439881	2.100595517	0.017401983
	std-spkC	2.102394924	0.010748769	2.102394924	0.010748769	2.102394924	0.01746895
smp-spkB	std-spkA	2.079232349	0.012488613	2.079232349	0.01985553	2.079232349	0.01768207
	std-spkB	2.082815217	0.011687588	2.082815217	0.011687588	2.082815217	0.017552417
	std-spkC	2.084599394	0.011961805	2.084599394	0.011961805	2.084599394	0.0176182
smp-spkC	std-spkA	2.145120368	0.012773436	2.145120368	0.020412468	2.145120368	0.01818961
	std-spkB	2.148816773	0.011938941	2.148816773	0.011938941	2.148816773	0.018055274
	std-spkC	2.150657487	0.012224402	2.150657487	0.012224402	2.150657487	0.01812325
Mean		2.110134899		2.110134899		2.110134899	
Standard deviation		0.029664055		0.029664055		0.029664055	
Combined standard uncertainty		0.015362509		0.017819288		0.020308488	
k		2		2		2	
Expanded uncertainty		0.030725018		0.035638576		0.040616976	
Relative uncertainty (%)		1.456068887		1.688924059		1.924852092	

Appendix L

Publications from this work