

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

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

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.

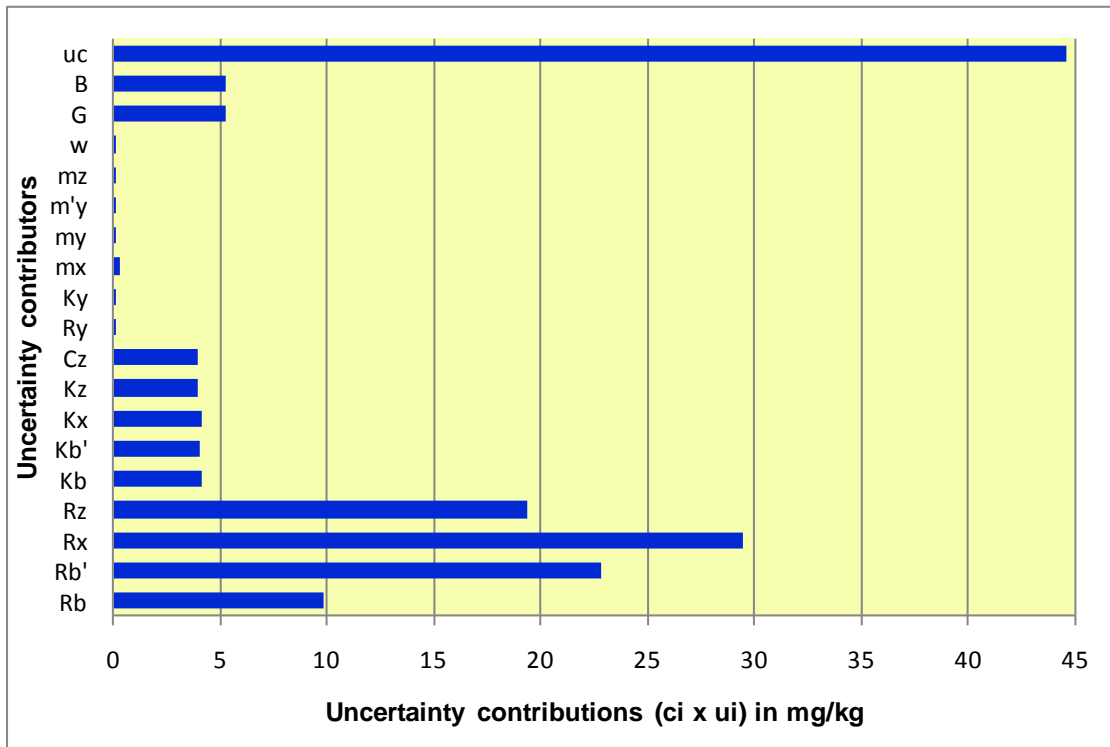


Figure 5.1: Comparison of the magnitude of the individual uncertainty contributions from the different influence quantities of the double isotope dilution experiment

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