

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

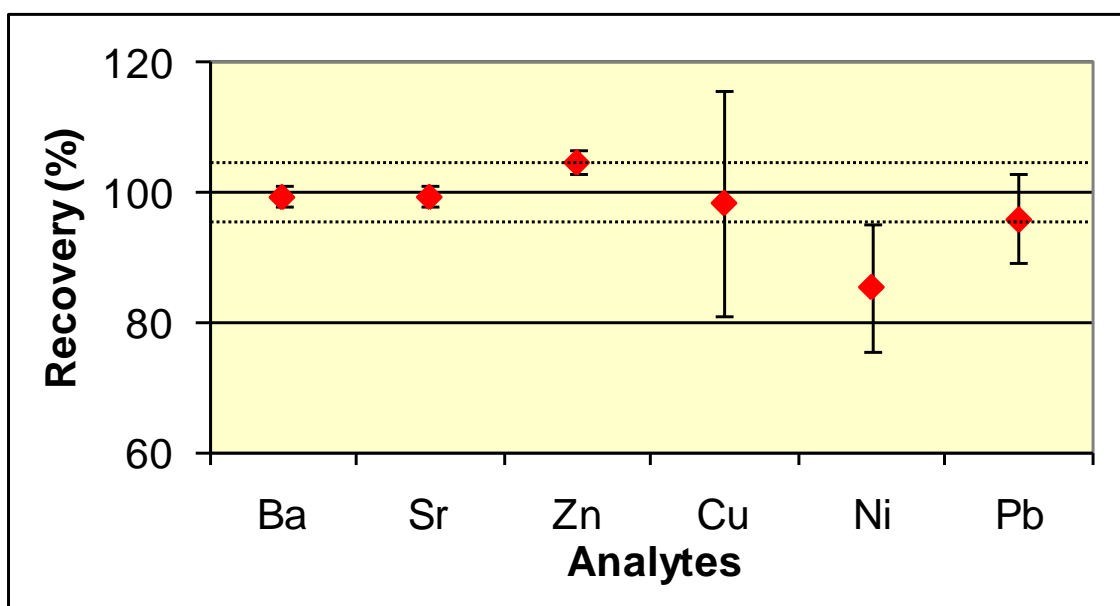


Figure 6.1: Summary of the results for the recoveries of the analytes of SY-4

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.

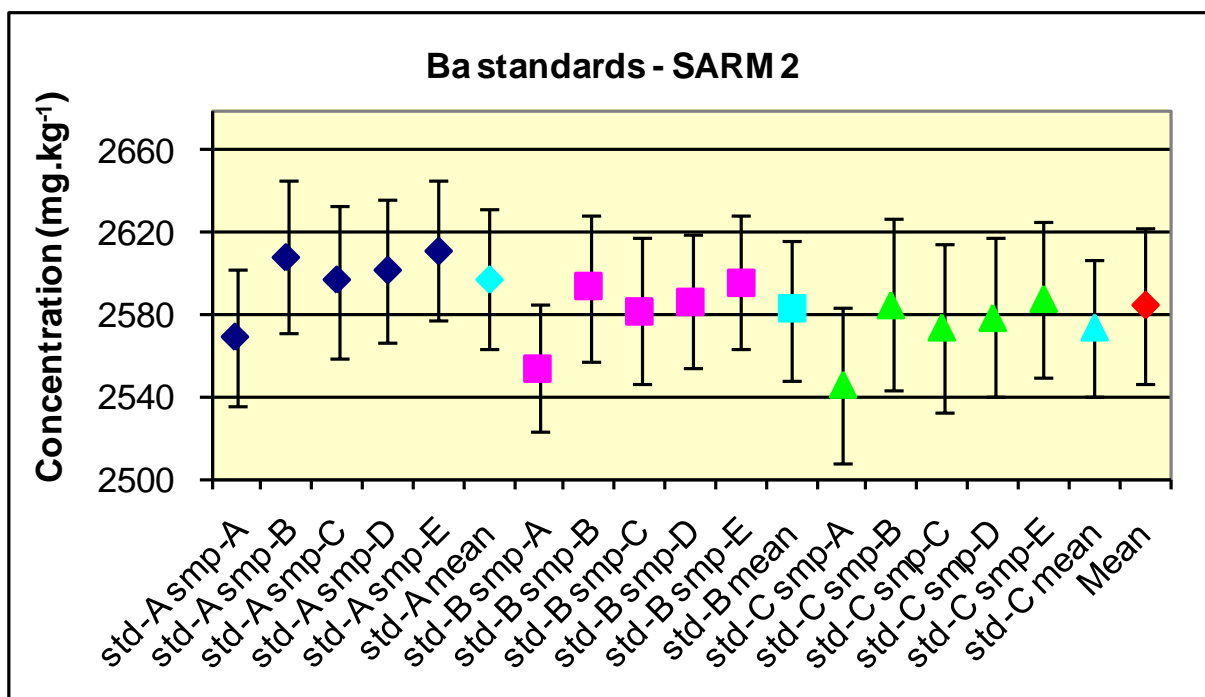


Figure 6.2: A comparison between the three primary assay standard blends for Ba in SARM 2

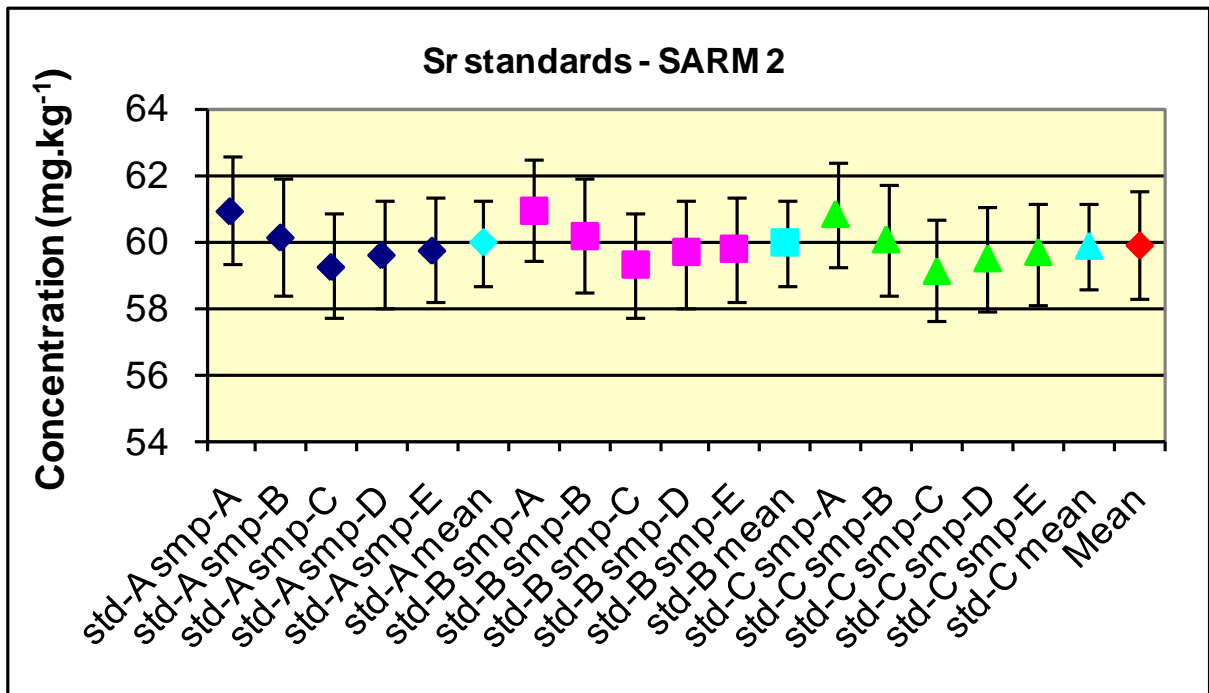


Figure 6.3: A comparison between the three primary assay standard blends for Sr in SARM 2

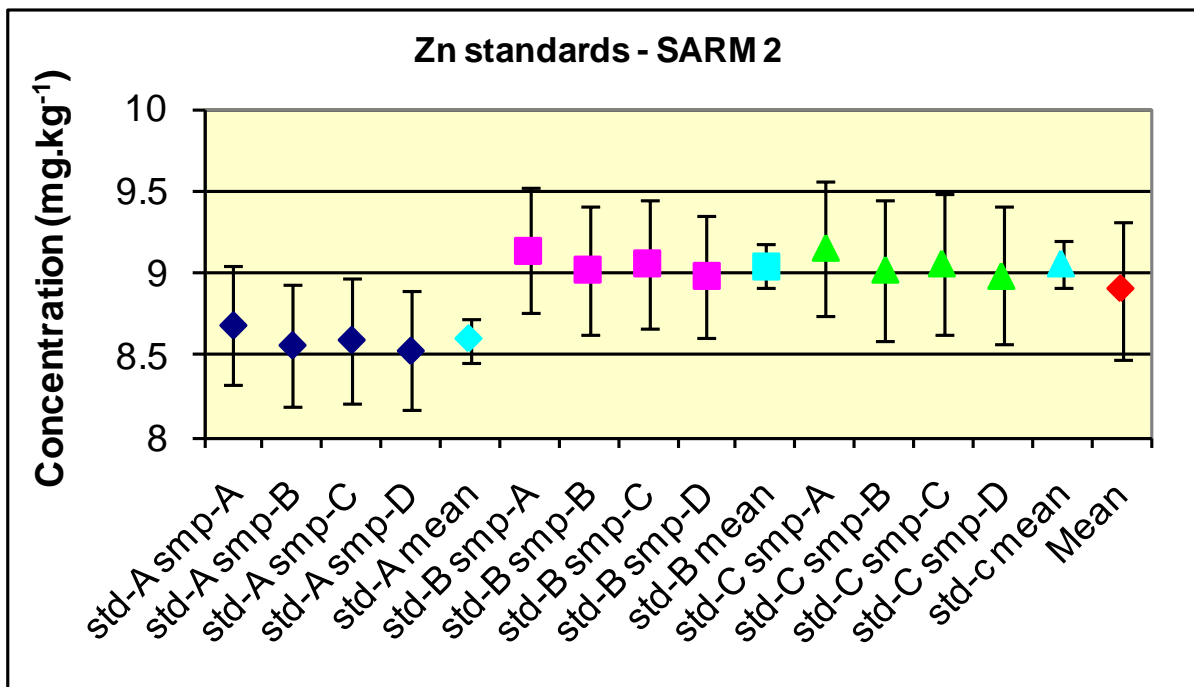


Figure 6.4: A comparison between the three primary assay standard blends for Zn in SARM 2

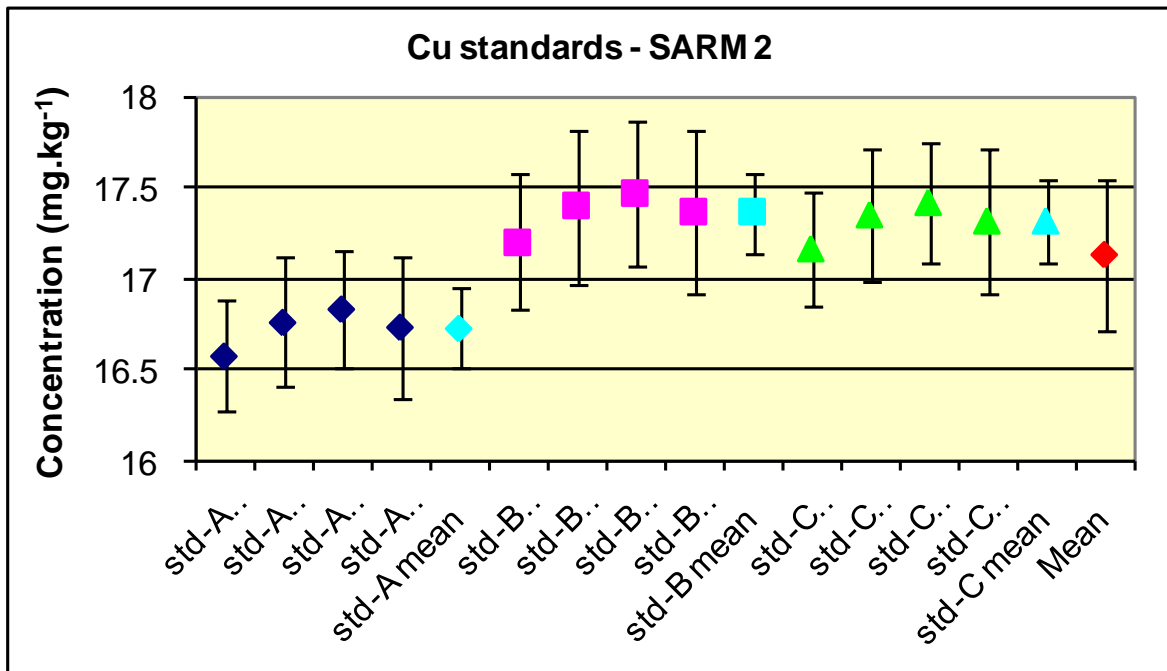


Figure 6.5: A comparison between the three primary assay standard blends for Cu in SARM 2

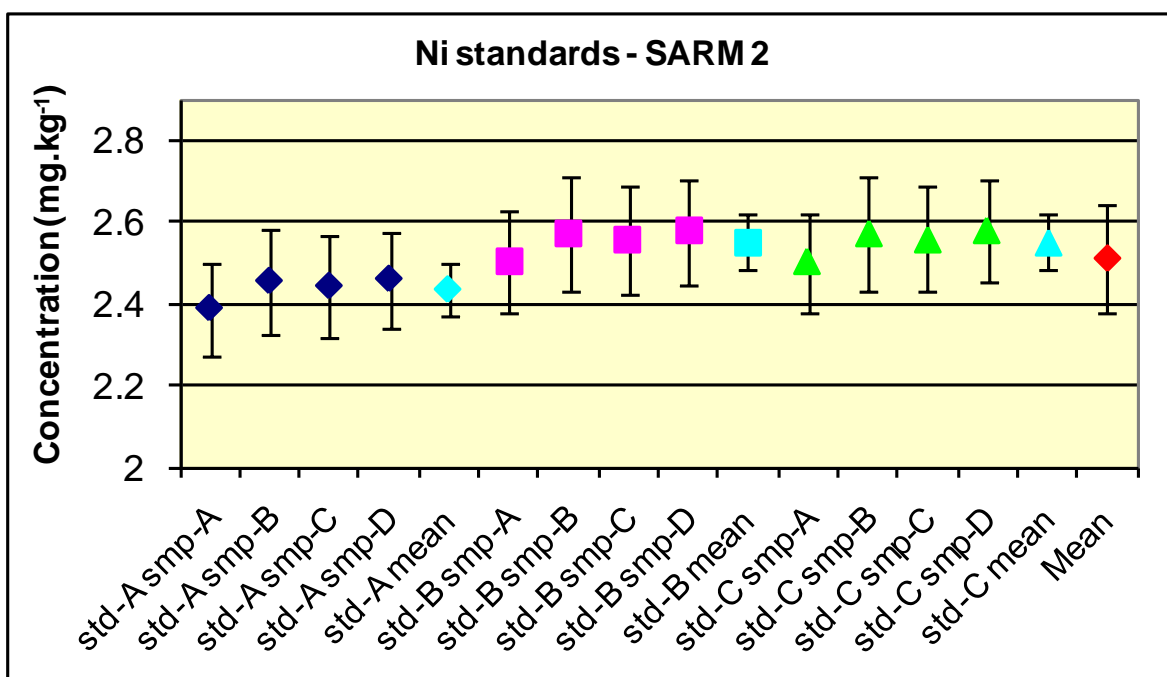


Figure 6.6: A comparison between the three primary assay standard blends for Ni in SARM 2

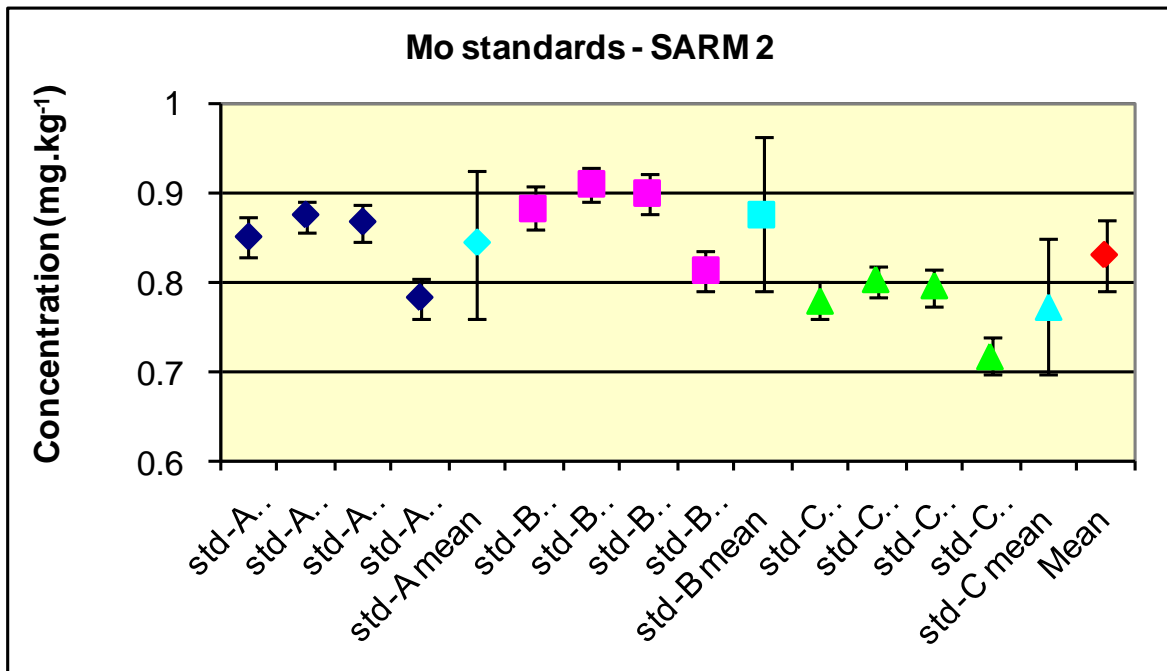


Figure 6.7: A comparison between the three primary assay standard blends for Mo in SARM 2

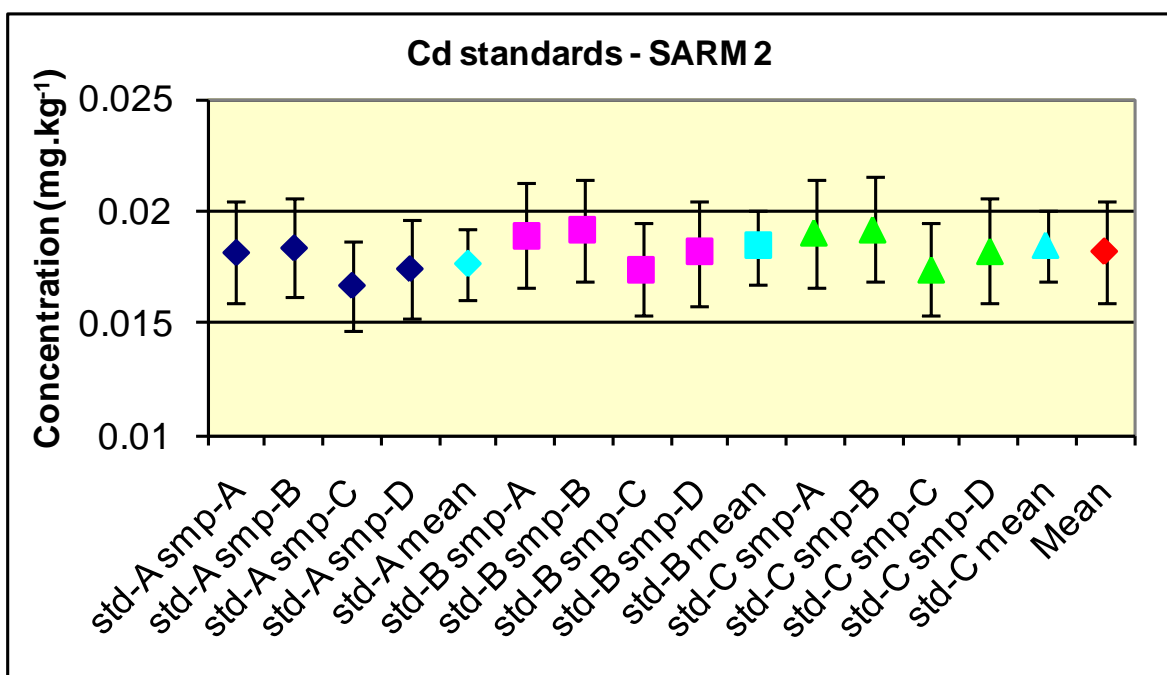


Figure 6.8: A comparison between the three primary assay standard blends for Cd in SARM 2

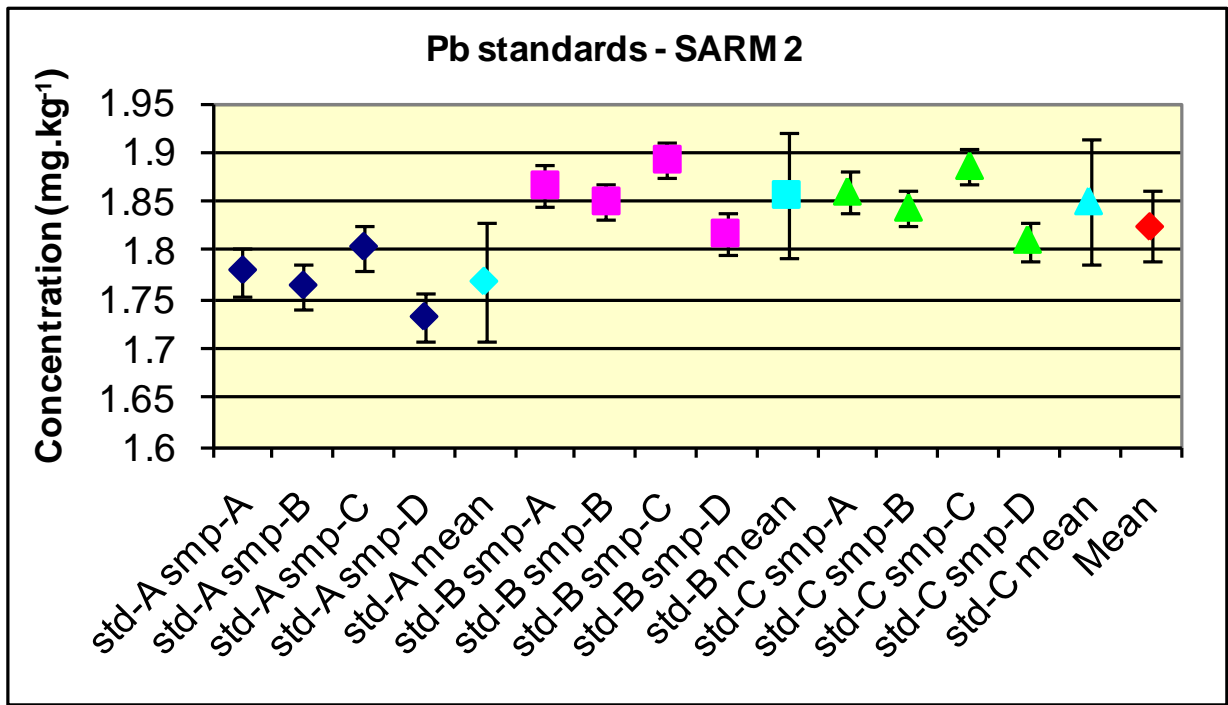


Figure 6.9: A comparison between the three primary assay standard blends for Pb in SARM 2

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.

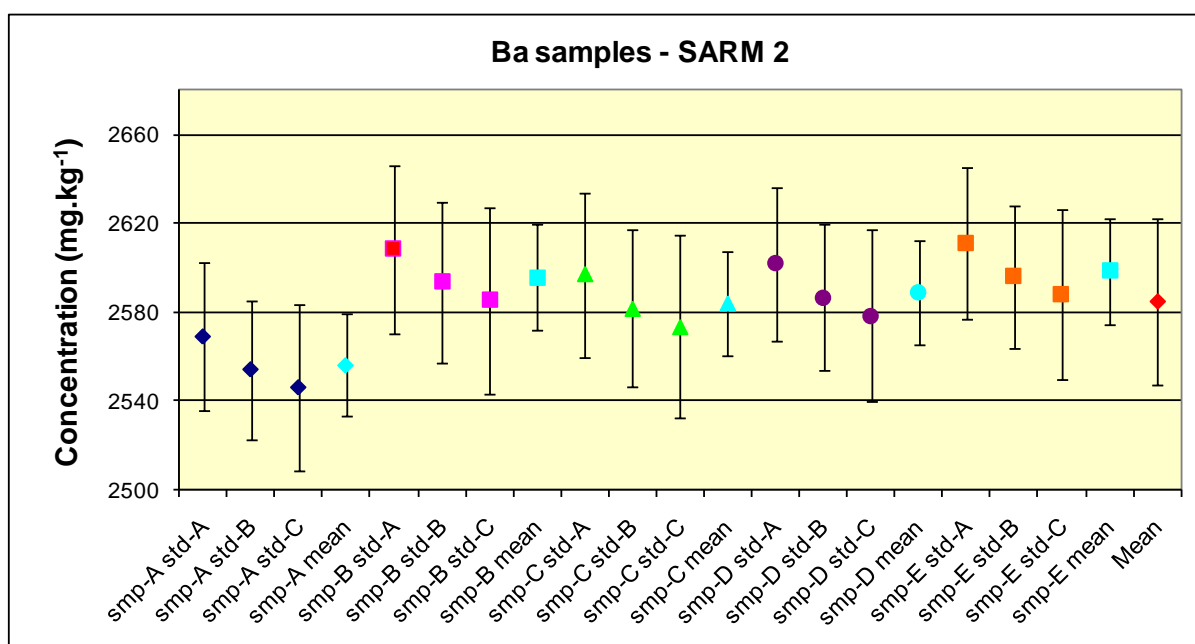


Figure 6.10: The individual determinations and mean result for Ba in SARM 2

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.

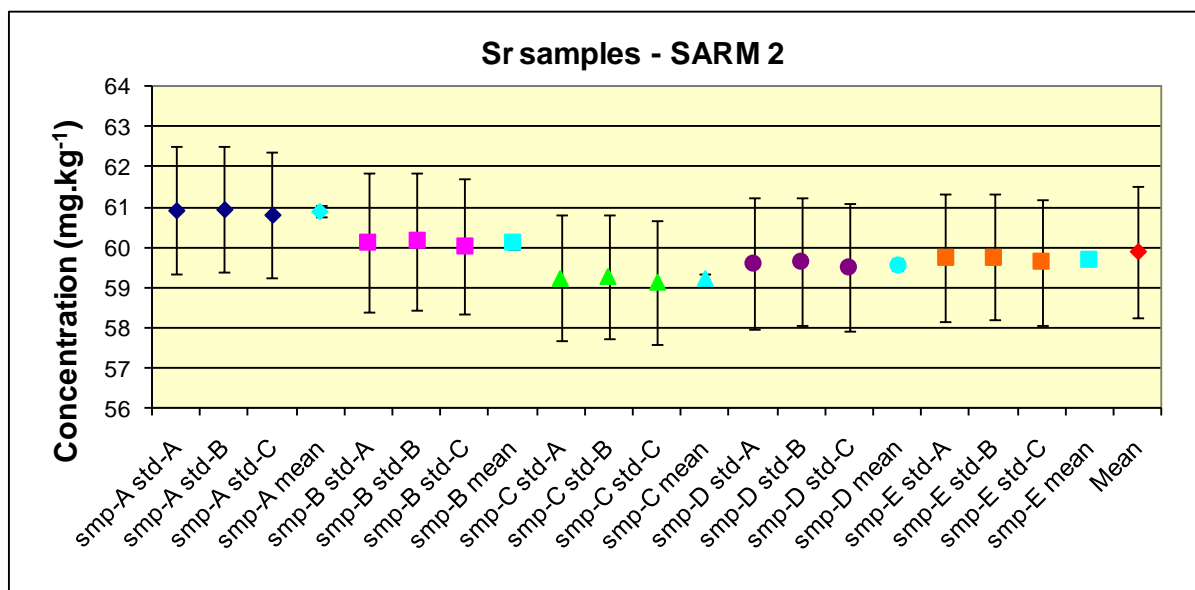


Figure 6.11: The individual determinations and mean result for Sr in SARM 2

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%.

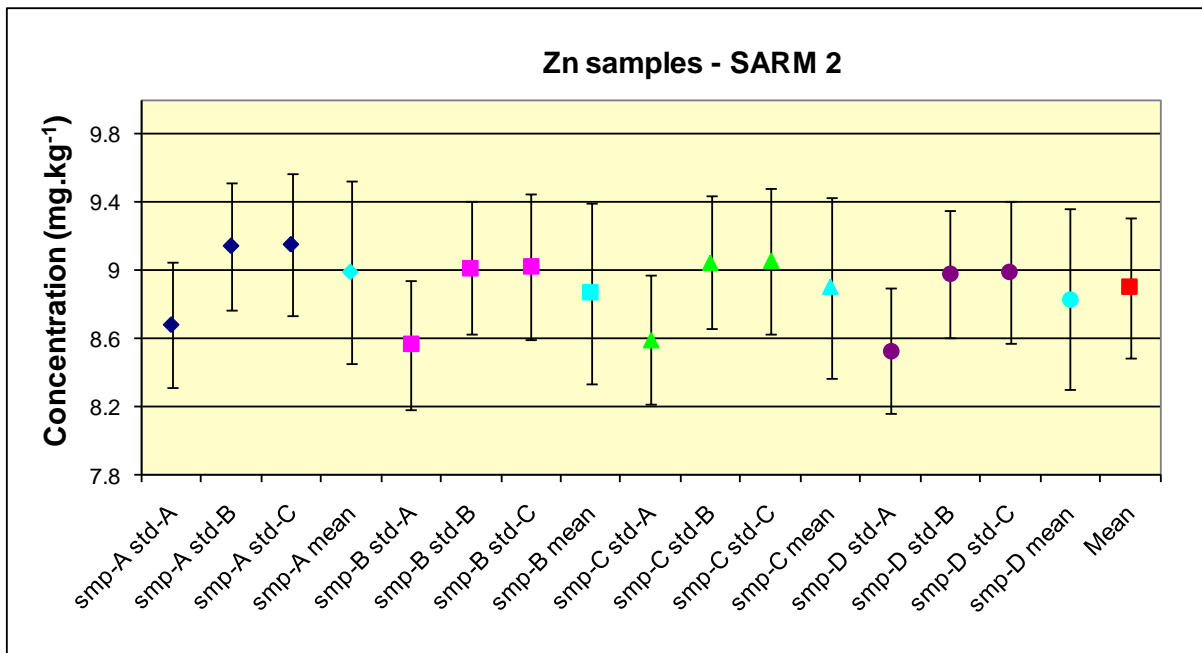


Figure 6.12: The individual determinations and mean result for Zn in SARM 2

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%.

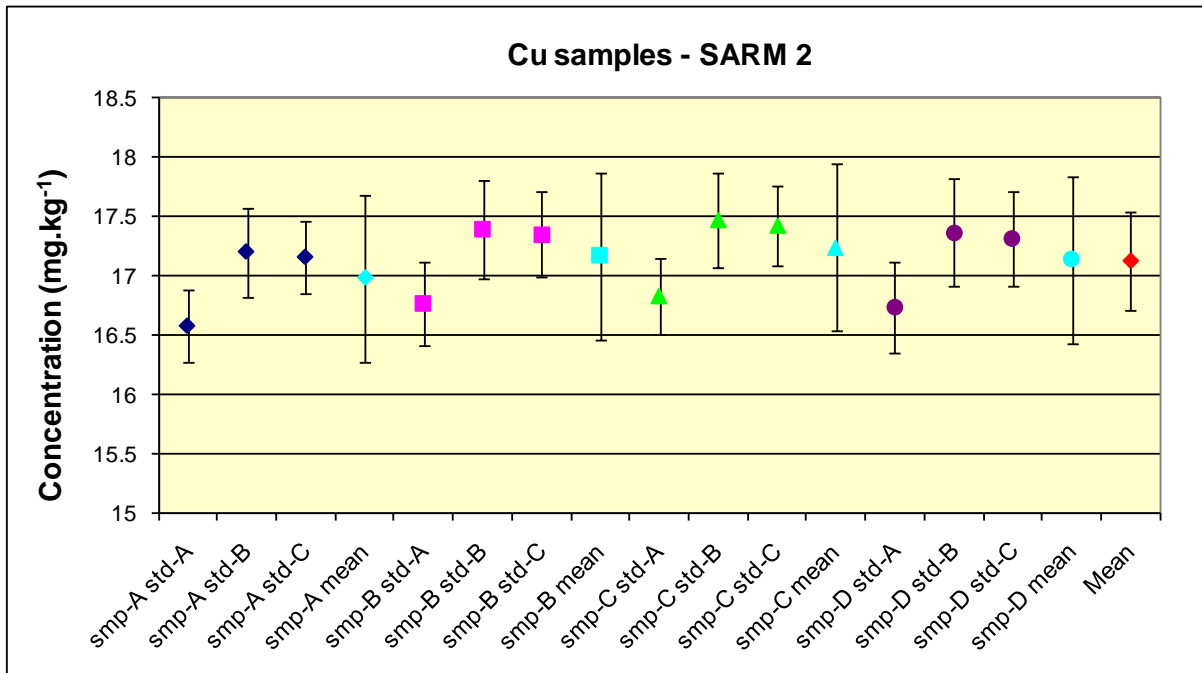


Figure 6.13: The individual determinations and mean result for Cu in SARM 2

Nickel

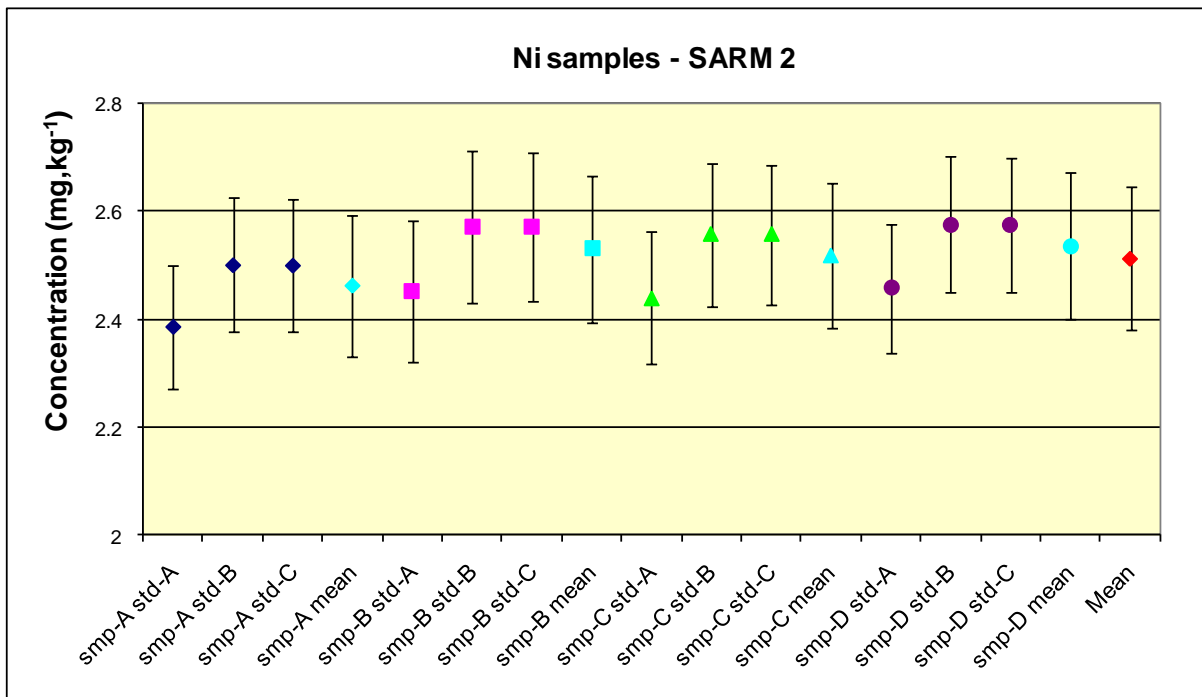


Figure 6.14: The individual determinations and mean result for Ni in SARM 2

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.

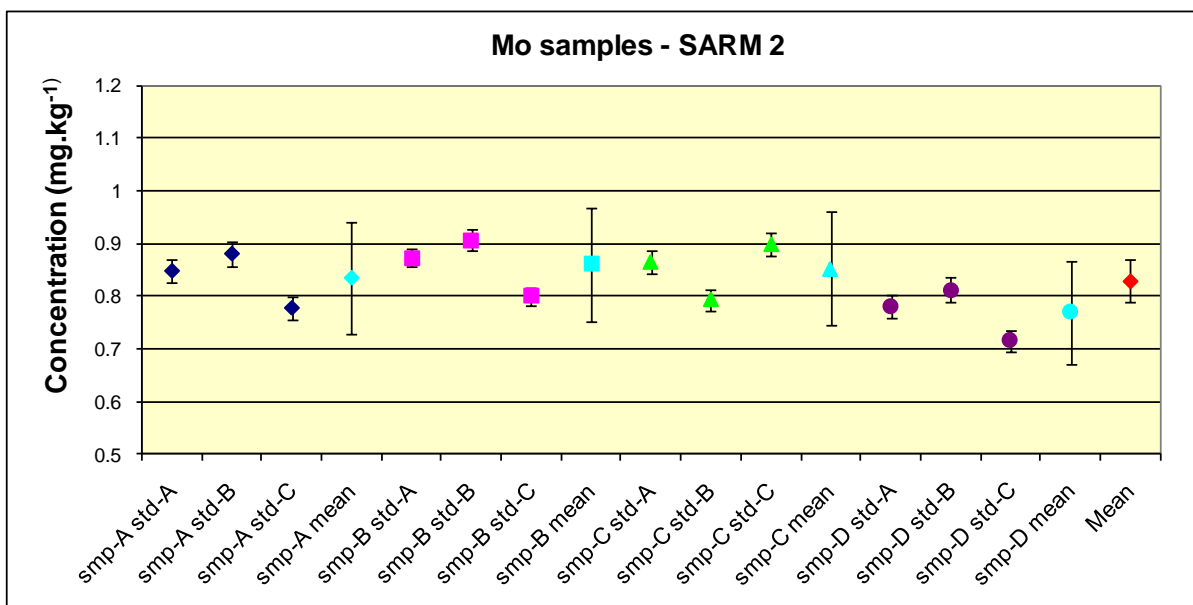


Figure 6.15: The individual determinations and mean result for Mo in SARM 2

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	

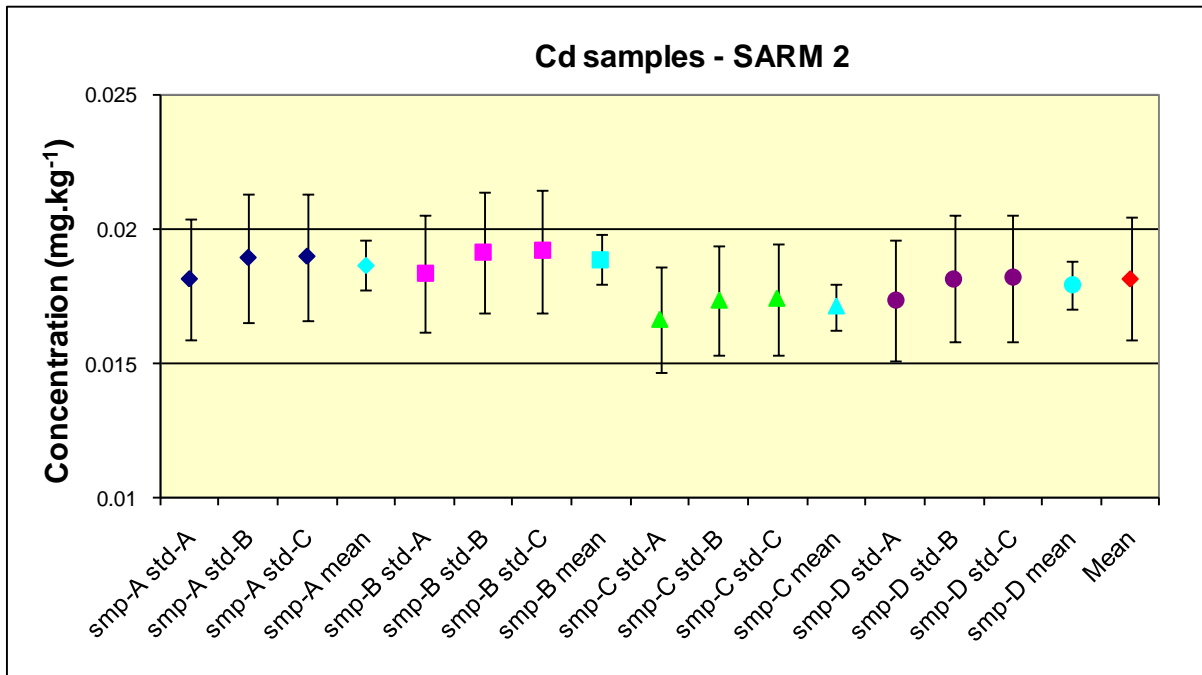


Figure 6.16: The individual determinations and mean result for Cd in SARM 2

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.

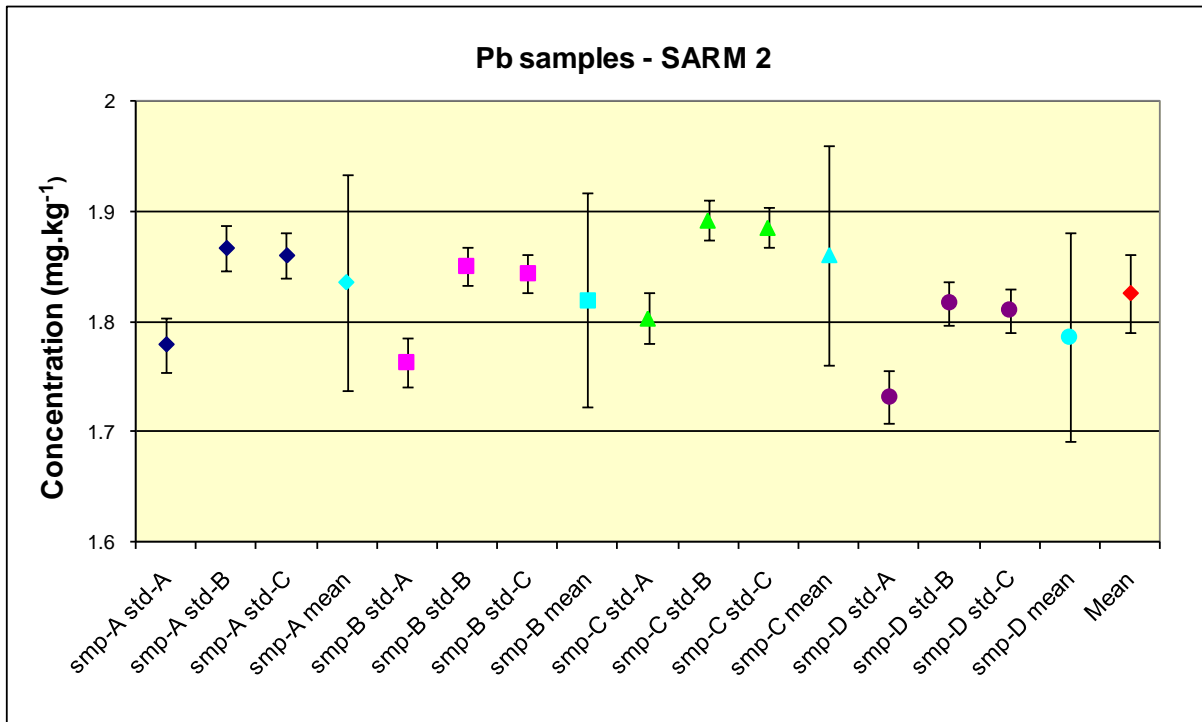


Figure 6.17: The individual determinations and mean result for Pb in SARM 2

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	

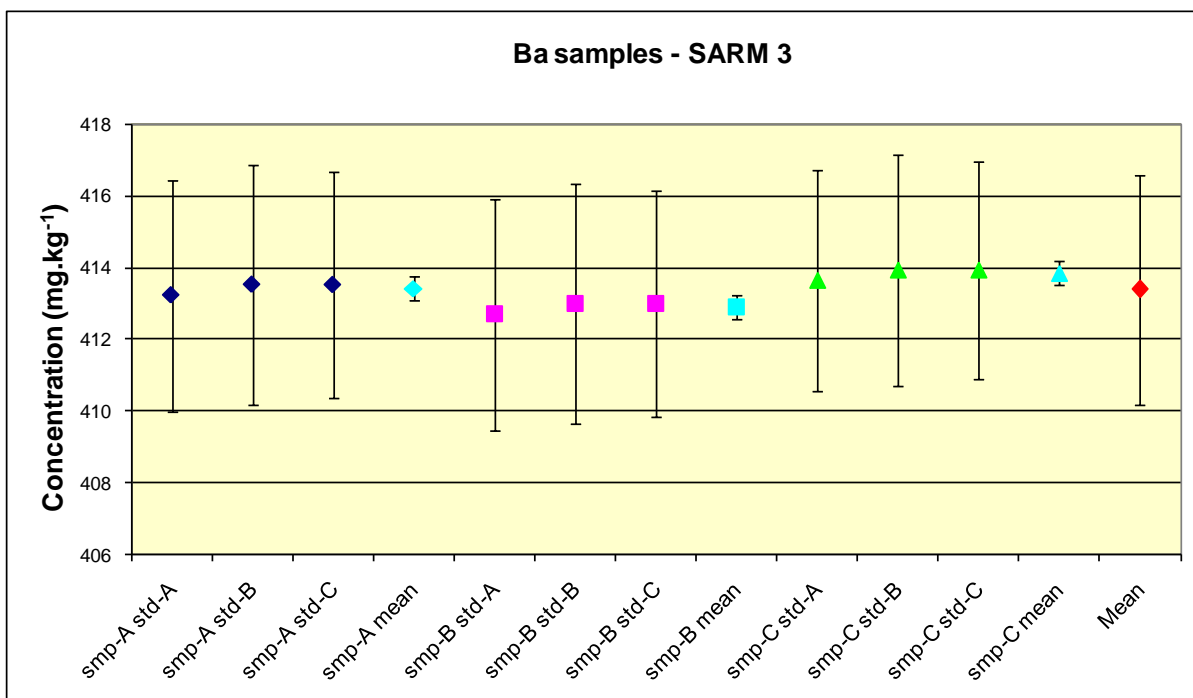


Figure 6.18: The individual determinations and mean result for Ba in SARM 3

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%.

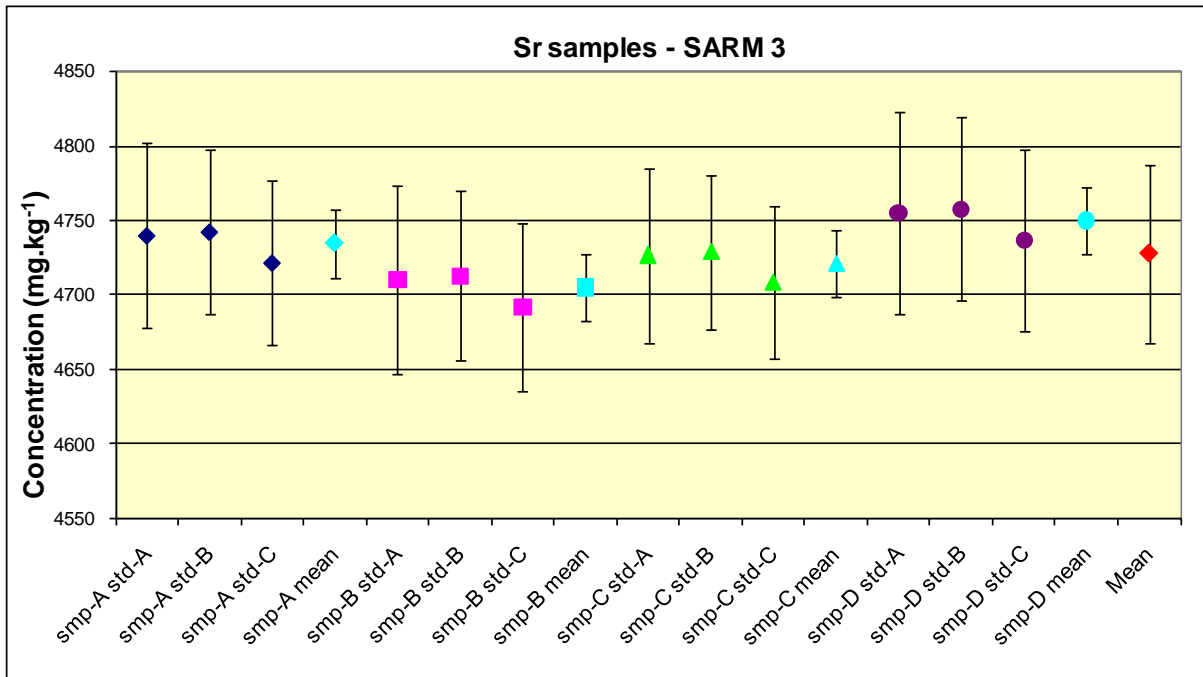


Figure 6.19: The individual determinations and mean result for Sr in SARM 3

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**).

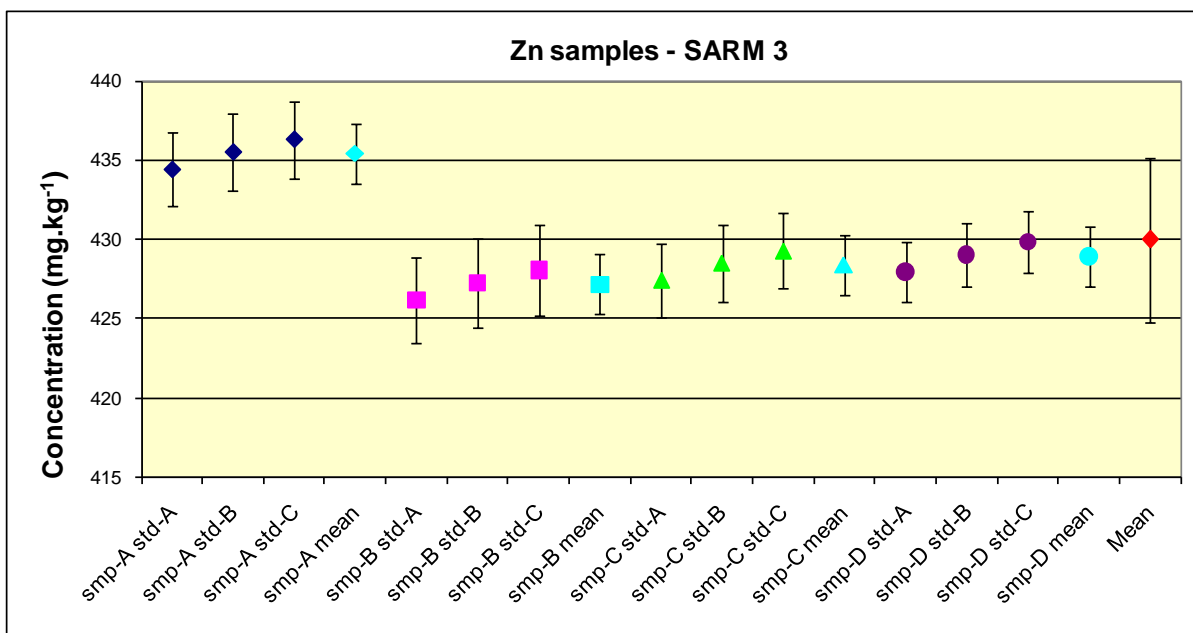


Figure 6.20: The individual determinations and mean result for Zn in SARM 3

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**.

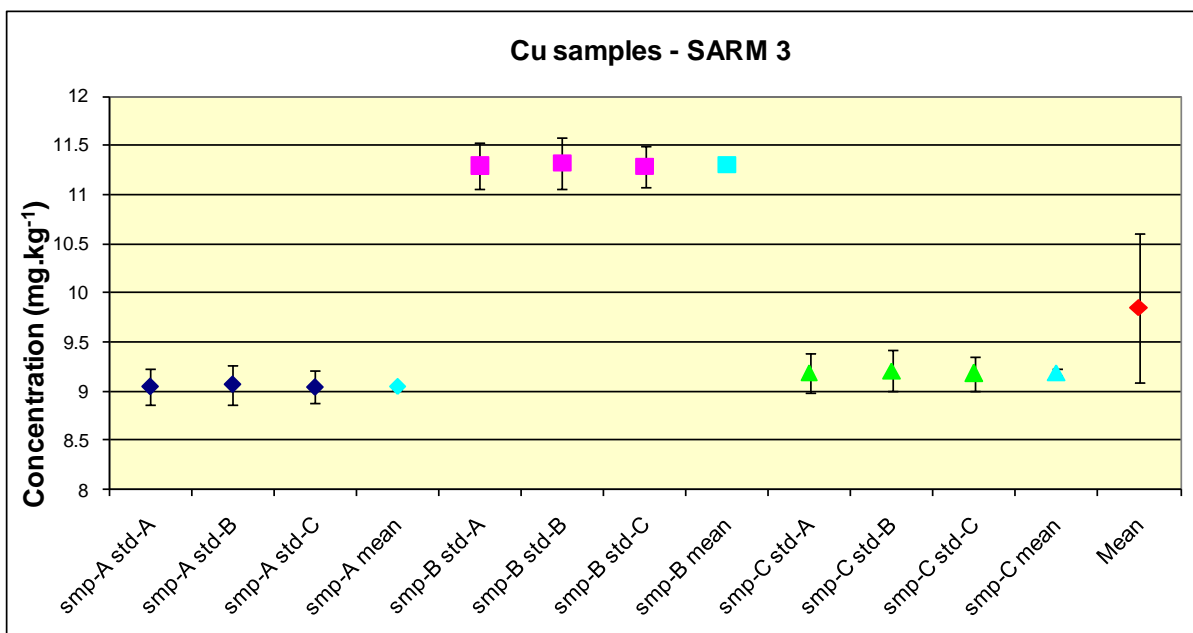


Figure 6.21: The individual determinations and mean result for Cu in SARM 3

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	

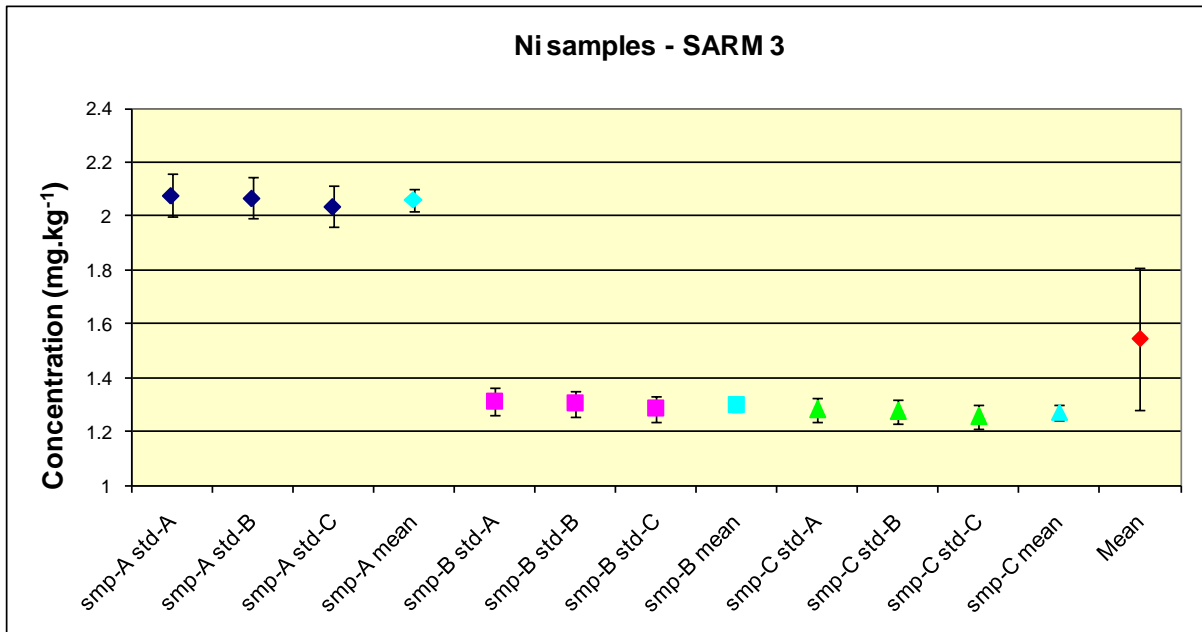


Figure 6.22: The individual determinations and mean result for Ni in SARM 3

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%.

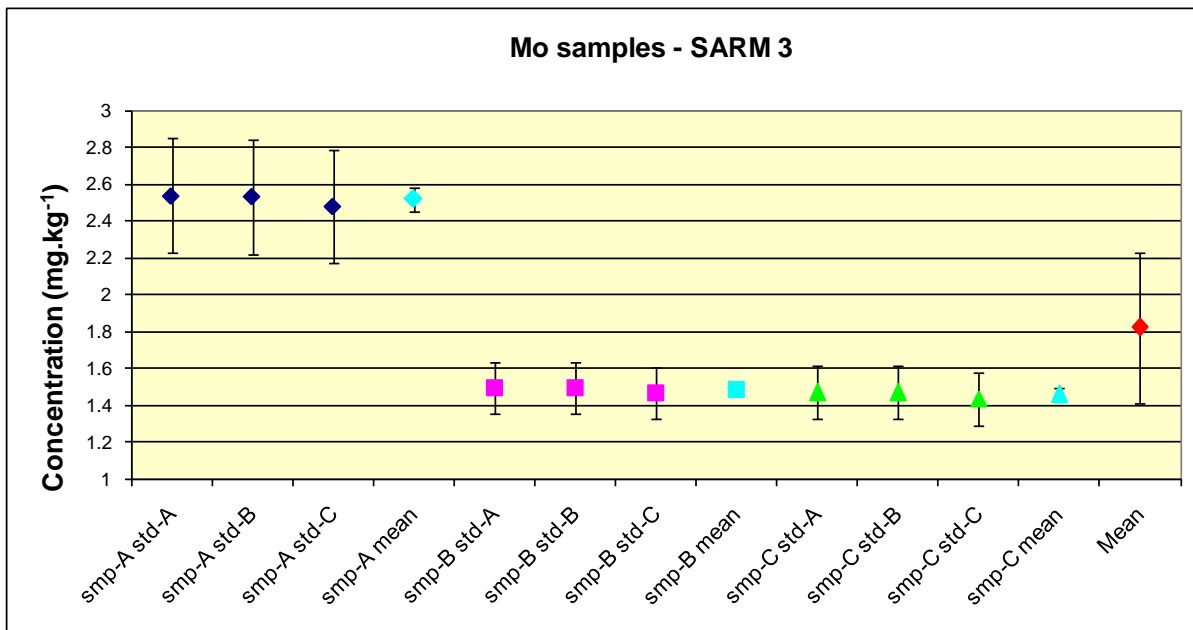


Figure 6.23: The individual determinations and mean result for Mo in SARM 3

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%.

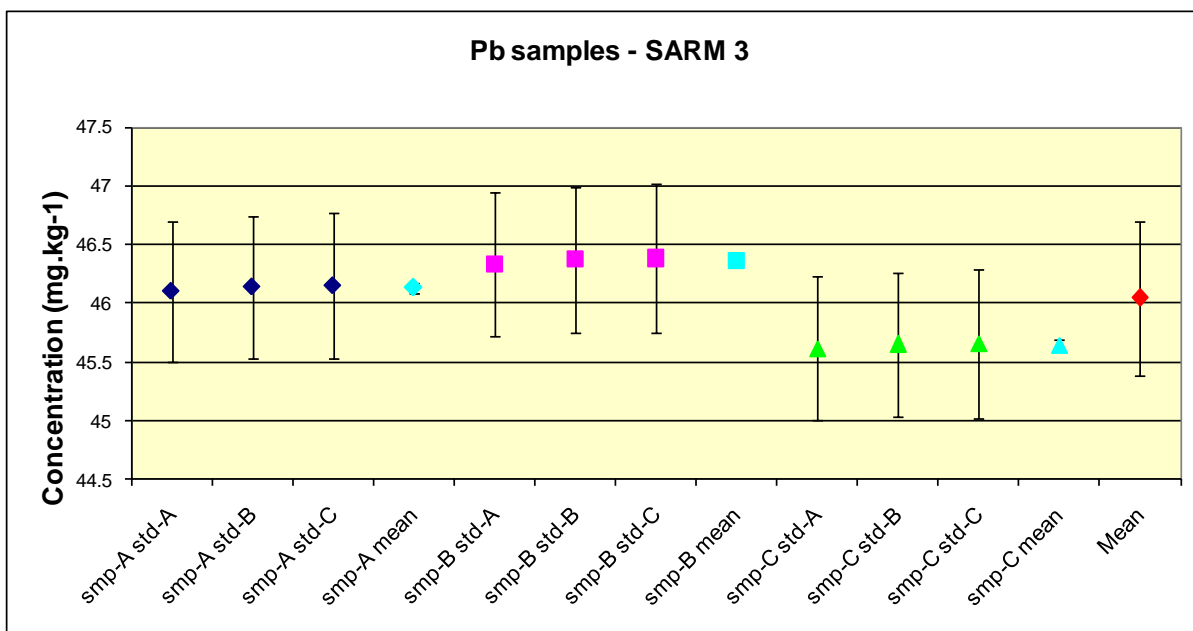


Figure 6.24: The individual determinations and mean result for Pb in SARM 3

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	

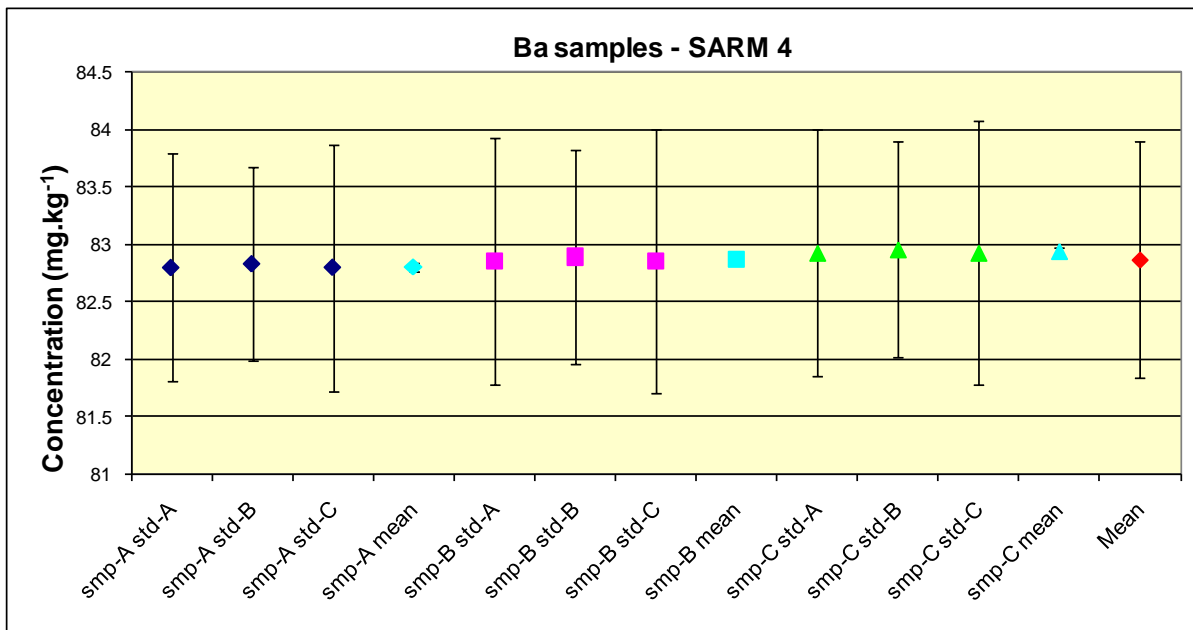


Figure 6.25: The individual determinations and mean result for Ba in SARM 4

Strontium

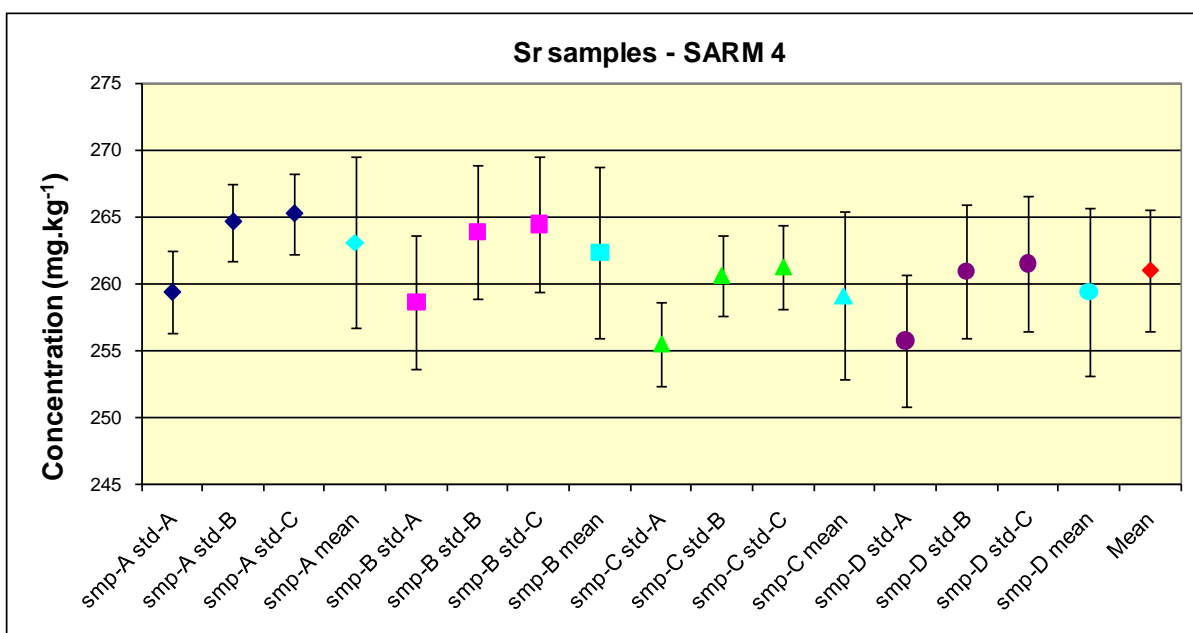


Figure 6.26: The individual determinations and mean result for Sr in SARM 4

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%.

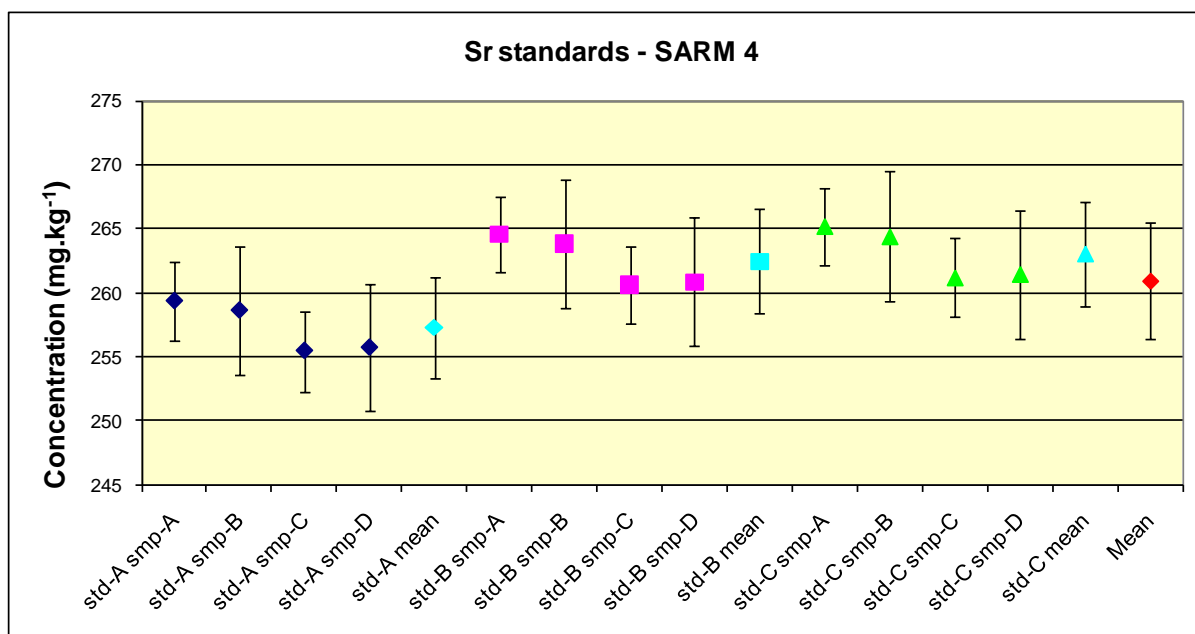


Figure 6.27: The individual determinations in relation to the primary assay standard blends for Sr in SARM 4

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%.

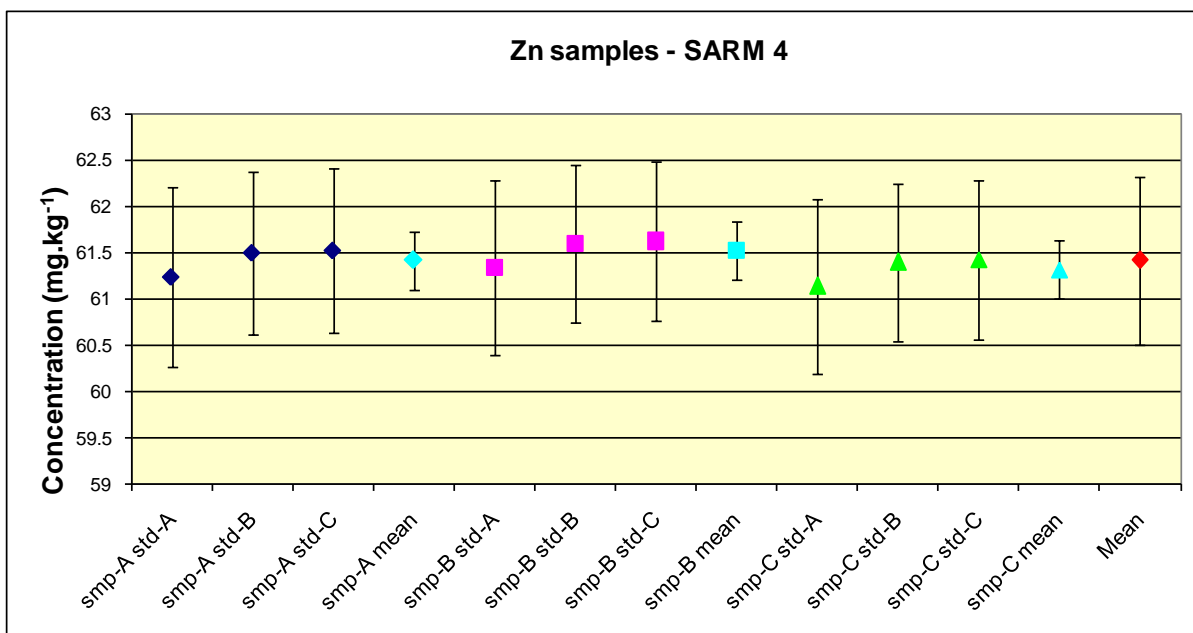


Figure 6.28: The individual determinations and mean result for Zn in SARM 4

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**.

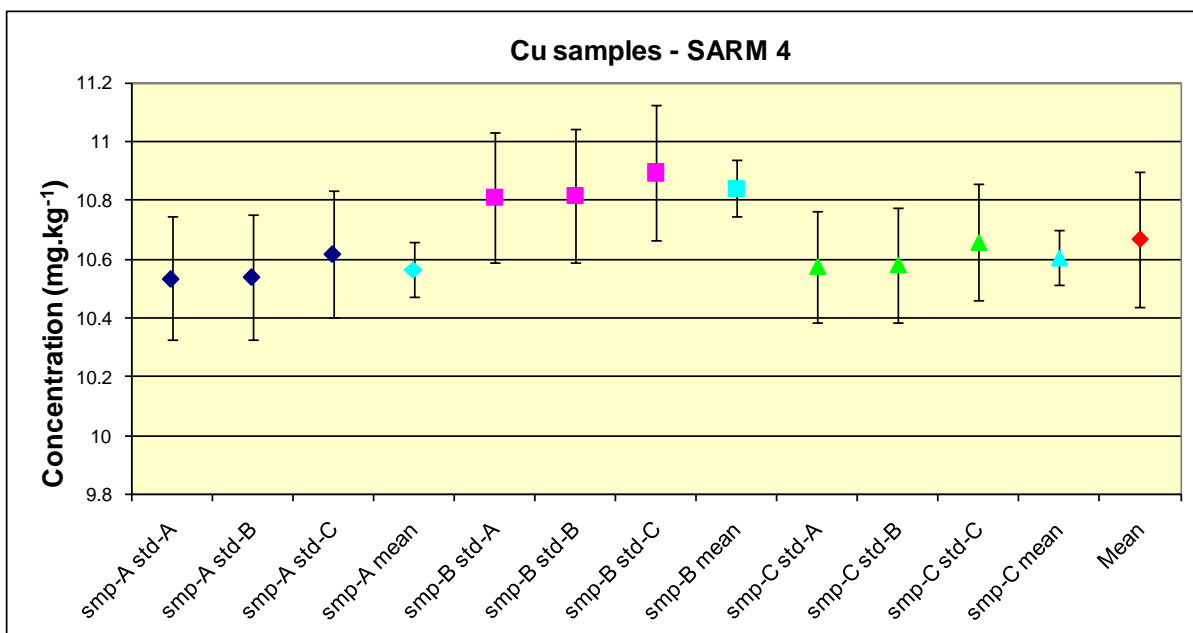


Figure 6.29: The individual determinations and mean result for Cu in SARM 4

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 Ni/ ⁶¹ Ni		⁶⁰ Ni/ ⁶¹ 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	

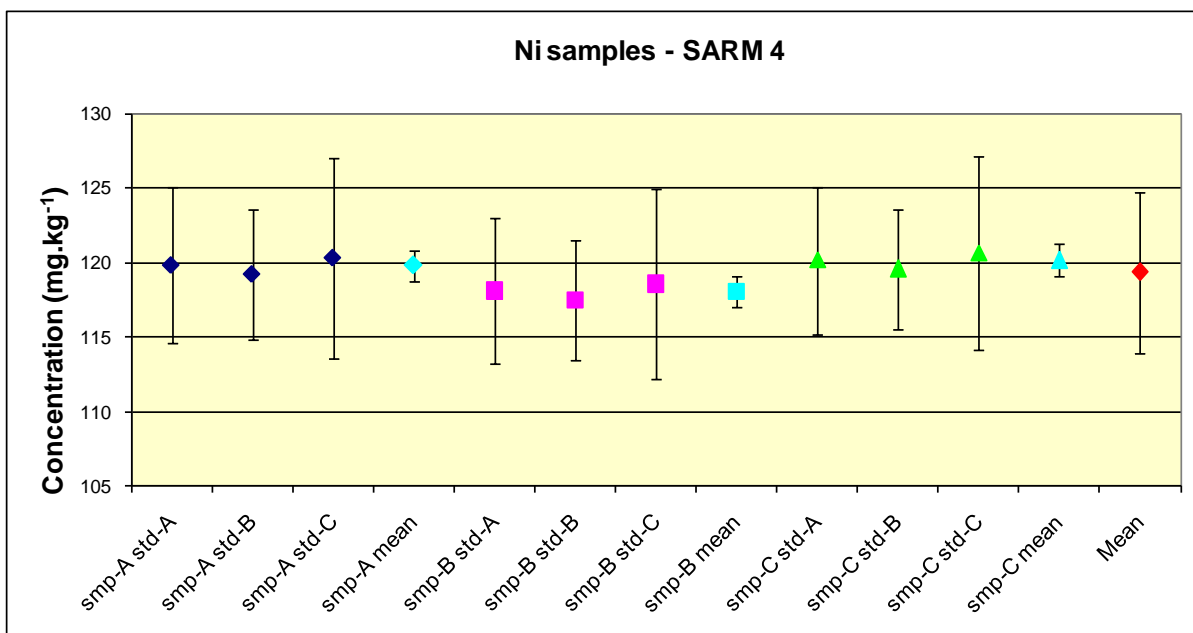


Figure 6.30: The individual determinations and mean result for Ni in SARM 4

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%.

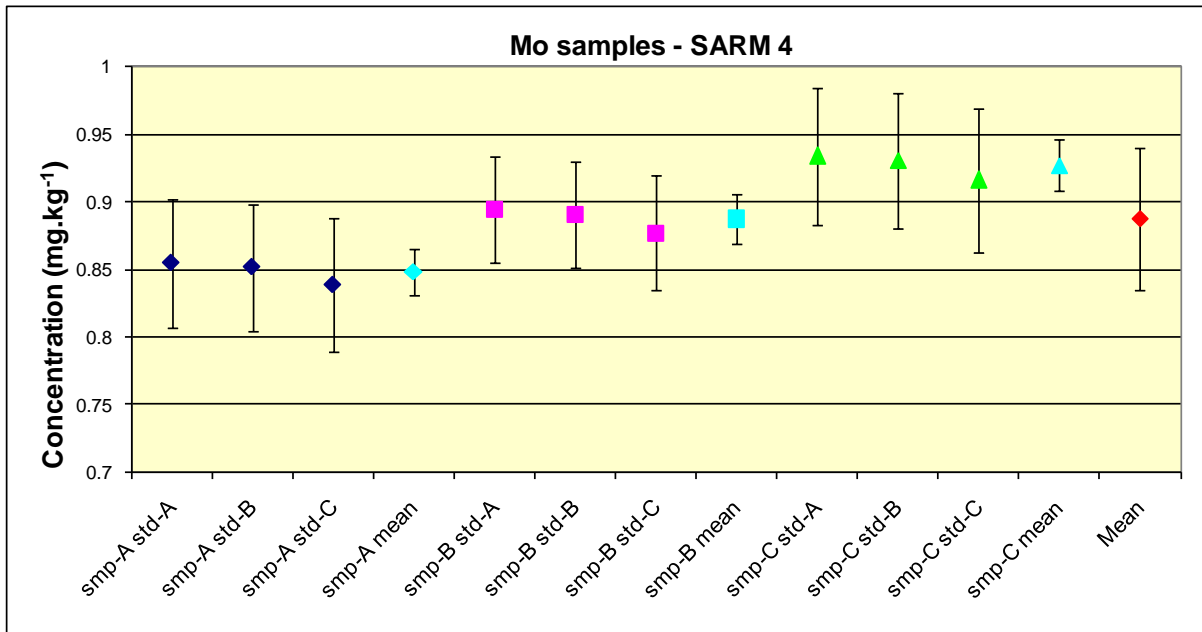


Figure 6.31: The individual determinations and mean result for Mo in SARM 4

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%.

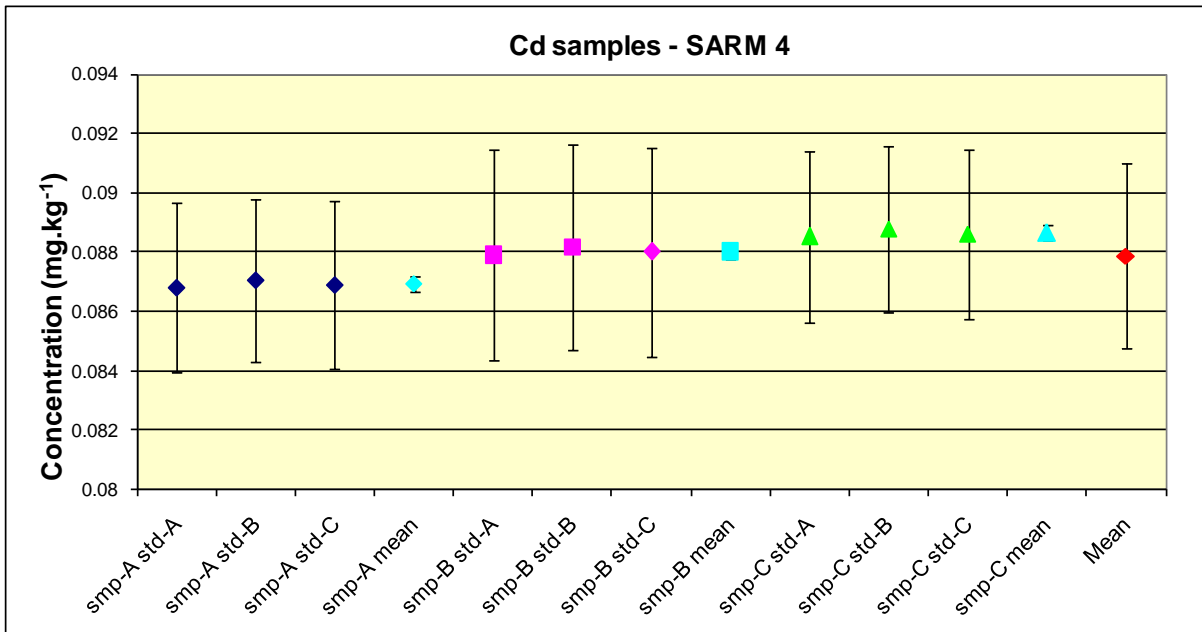


Figure 6.32: The individual determinations and mean result for Cd in SARM 4

Lead

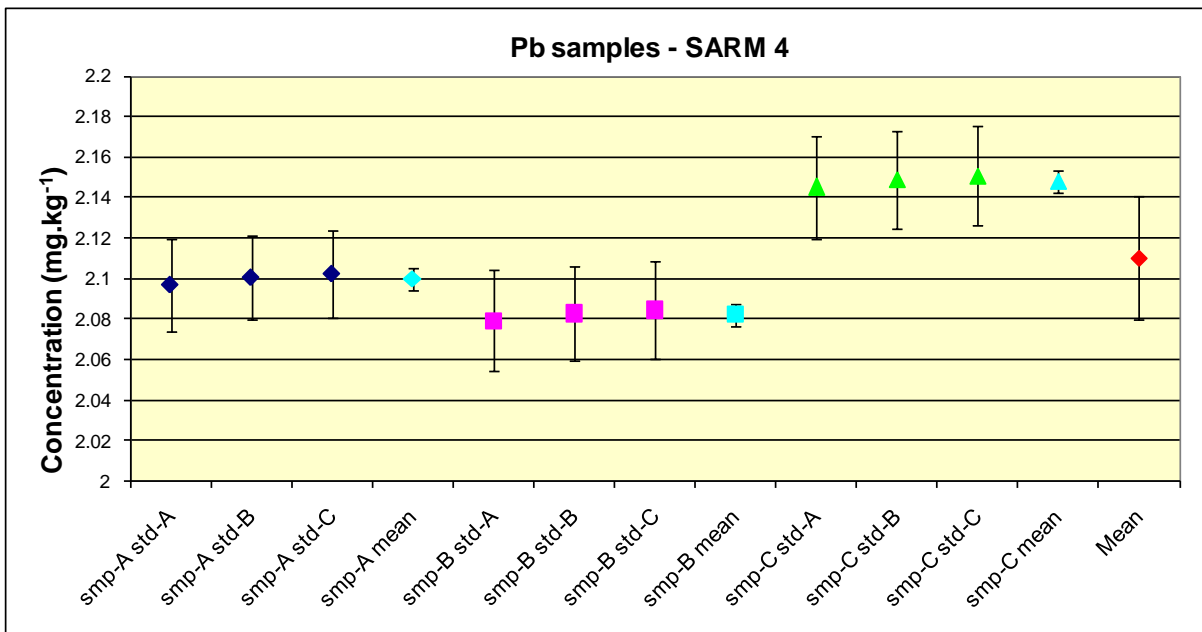


Figure 6.33: The individual determinations and mean result for Pb in SARM 4

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%.