

# 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 14<sup>th</sup> 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

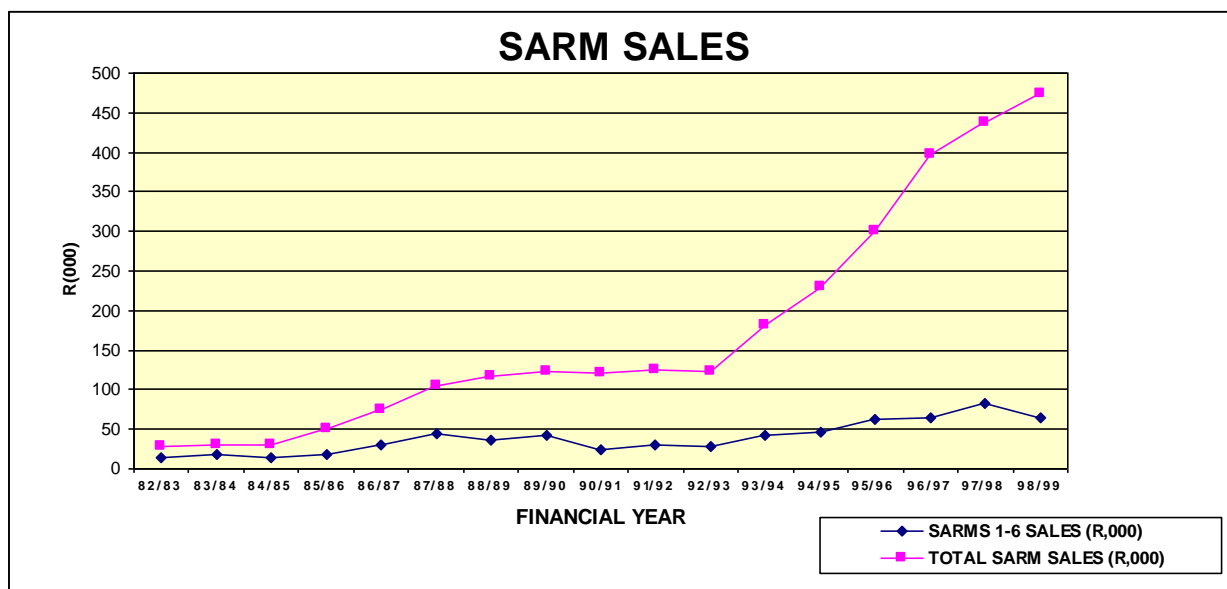
specified properties, accompanied by a certificate that states the value of the specified property, its associated uncertainty, and a statement of metrological traceability. An analogous definition for certified reference material can be found in the ISO VIM[2]. However, it is important to note that 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 <sub>2</sub>	75.70	63.63	52.40	52.64	51.10	38.96
Al <sub>2</sub> O <sub>3</sub>	12.08	17.34	13.64	16.50	4.18	0.3 <sup>?</sup>
Fe <sub>2</sub> O <sub>3</sub>	0.6 <sup>?</sup>	1.11	8.78	0.8 <sup>?</sup>	0.87	0.71
FeO	1.30	0.30	1.13	7.47	10.59	14.63
MgO	0.06 <sup>?</sup>	0.46	0.28	7.50	25.33	43.51
CaO	0.78	0.68	3.22	11.50	2.66	0.28
Na <sub>2</sub> O	3.36	0.43	8.37	2.46	0.37	0.04 <sup>?</sup>
K <sub>2</sub> O	4.99	15.35	5.51	0.25	0.09	0.01 <sup>?</sup>
MnO	-	-	0.77	0.18	0.22	0.22
TiO <sub>2</sub>	-	-	0.48	0.20	0.20	-
P <sub>2</sub> O <sub>5</sub>	-	0.12	-	-	-	-
Cr <sub>2</sub> O <sub>3</sub>	-	-	-	-	3.50	0.42
NiO	-	-	-	-	-	0.26
ZrO <sub>2</sub>	-	-	1.49	-	-	-
BaO	-	0.27	-	-	-	-
SrO	-	-	0.54	-	-	-
Nb <sub>2</sub> O <sub>5</sub>	-	-	0.14	-	-	-
Cl	-	-	0.12	-	-	-
F	0.42	-	0.44	-	-	-
H <sub>2</sub> O <sup>+</sup>	0.49	0.22	2.31	0.33	0.26	0.30
CO <sub>2</sub>	0.10 <sup>?</sup>	0.09	0.17	0.10 <sup>?</sup>	0.08 <sup>?</sup>	0.40 <sup>?</sup>
Σ	99.88 <sup>?</sup>	100.00	99.97	99.93 <sup>?</sup>	99.45 <sup>?</sup>	100.04 <sup>?</sup>
O/F.S.Cl	0.18	0.01	0.23	0.02	0.02	0.02
Σ(corrected)	99.70 <sup>?</sup>	99.99	99.56	99.91 <sup>?</sup>	99.43 <sup>?</sup>	100.02 <sup>?</sup>
OTHERS (3)*	0.29	0.14	0.29	0.22	0.23	0.11
TOTAL	99.99 <sup>?</sup>	100.13	99.85	100.13 <sup>?</sup>	99.66 <sup>?</sup>	100.13 <sup>?</sup>
TOTAL Fe as	2.00	1.40	9.91	8.97	12.70	17.00
Fe <sub>2</sub> O <sub>3</sub> (R)						
Total Fe as	2.04	1.44	10.04	9.10	12.64	16.97
Fe <sub>2</sub> O <sub>3</sub> (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 Fe<sub>2</sub>O<sub>3</sub>.

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<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> of the elements

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

**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 <sup>?</sup>	3 <sup>?</sup>	0.7 <sup>?</sup>	0.6 <sup>?</sup>	**
Zn	50	10 <sup>?</sup>	395	68	100	90
Zr	300	33 <sup>?</sup>	11000	23 <sup>?</sup>	*	*

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 <sub>2</sub>	63.63	1.08	65	63.61	0.30	6
Al <sub>2</sub> O <sub>3</sub>	17.34	0.46	69	17.15	0.44	7
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	0.43	0.11	50	0.41	0.06	6
K <sub>2</sub> O	15.35	0.92	65	15.28	0.30	5
P <sub>2</sub> O <sub>5</sub>	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 ( $\mu\text{g}\cdot\text{g}^{-1}$ )

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 ( $\text{ng}\cdot\text{g}^{-1}$ )							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 ( $\text{ng}\cdot\text{g}^{-1}$ )			1000-35000	6			16-2000	5
Ce	11.9 (9.6-14.4)	2.4		14	11.9	2.6		13
Co	3 <sup>?</sup>	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 <sup>?</sup>	0.43		6	6	0.8		9
Ni	7 <sup>?</sup>	4		24			6-116	8
Pb	5 <sup>?</sup>	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 <sup>?</sup>	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 <sup>?</sup>	0.008		6	0.07	0.026		8
Zn	10 <sup>?</sup>	6		22			9-83.15	8
Zr	33 <sup>?</sup>	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)
<b>SiO<sub>2</sub></b>	52.40	0.3	52	52.45	0.20	4
<b>Al<sub>2</sub>O<sub>3</sub></b>	13.64	0.48	57	13.40	0.08	5
<b>Fe<sub>2</sub>O<sub>3</sub></b>	9.91	0.36	67	9.96	0.38	7
<b>MgO</b>	0.28	0.10	58	0.28	0.06	5
<b>CaO</b>	3.22	0.27	72	3.12	0.14	6
<b>Na<sub>2</sub>O</b>	8.37	0.53	52	8.56	0.24	5
<b>K<sub>2</sub>O</b>	5.51	0.19	63	5.45	0.30	5
<b>TiO<sub>2</sub></b>	0.48	0.08	68	0.49	0.02	5
<b>MnO</b>	0.77	0.16	67	0.74	0.04	6
<b>P<sub>2</sub>O<sub>5</sub></b>	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 ( $\text{ng.g}^{-1}$ )			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 ( $\text{ng.g}^{-1}$ )			2000-4000	2			630-1005	3
Ce	240 <sup>?</sup>	42		18	292	64		20
Cl	1200	500		6			902-1100	2
Co			1.6-150	24	2.53	0.52		6
Cr	10 <sup>?</sup>	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 <sup>?</sup>	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 <sup>?</sup>	42		12	231	32		21
Li	48 <sup>?</sup>	20		10			39.3-55	3
Lu	0.4 <sup>?</sup>	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 <sup>?</sup>	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 <sup>?</sup>	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 <sup>?</sup>	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)
<b>U</b>	14	7		11	16.2	5.4		8
<b>V</b>	81	18		32	85	16		4
<b>W</b>			10	1			7.72-8	2
<b>Y</b>	22 (15-27)			17	20	6		11
<b>Yb</b>	3 <sup>2</sup>	1		11	2.95	0.84		15
<b>Zn</b>	395	119		30	437	32		7
<b>Zr</b>	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 <sub>2</sub>	52.64	0.74	71	52.83	0.48	6
Al <sub>2</sub> O <sub>3</sub>	16.5	0.6	74	16.50	0.30	7
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	2.46	0.17	54	2.43	0.14	7
K <sub>2</sub> O	0.25	0.07	63	0.25	0.02	6
TiO <sub>2</sub>	0.20	0.03	65	0.19	0.02	7
MnO	0.18	0.01	69	0.18	0.02	7
P <sub>2</sub> O <sub>5</sub>	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 ( $\text{ng.g}^{-1}$ )			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 <sup>?</sup>	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 <sup>?</sup>	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) <sup>#</sup>		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 <sup>?</sup>	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 <sup>?</sup>	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 <sup>2</sup>	3	3.3-13	14	6.2	1.4	5-8.7	10
Yb	0.7 <sup>2</sup>	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 <sup>2</sup>	12	6-110	11			10.5-25.7	11