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

by

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

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

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

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

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List of abbreviations

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

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



H_3BO_3	boric acid
HNO_3	nitric acid
HCl	hydrochloric acid
$\text{m}\ell$	millilitre
g	gram
kg	kilogram
mm	millimetre
$\text{mg}\cdot\text{kg}^{-1}$	milligram per kilogram
$\mu\text{g}\cdot\text{g}^{-1}$	microgram per gram
$\text{ng}\cdot\text{m}\ell^{-1}$	nanogram per millilitre
$\mu\text{g}\cdot\text{m}\ell^{-1}$	microgram per millilitre
$\ell\cdot\text{min}^{-1}$	litre per minute
ns	nanosecond
W	Watt
K	mass bias correction factor
R	mass resolution

Summary

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

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

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

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

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

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

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

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