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Quality Specialist

Approver:  
Managing  
Director

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Certificate

# AMIS0656

## Certified Reference Material

### Spodumene Concentrate, Brazil.

### *Certificate of Analysis*

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#### AMIS

A: 11 Avalon Road, West Lake View, Ext 11, Modderfontein, 1609, South Africa

P: PO Box 856, Isando, 1600, Gauteng, South Africa

T: +27 (0) 11 923 0800

W: [www.amis.co.za](http://www.amis.co.za)



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## Summary Statistics

### ***Recommended Concentrations and Limits (at two Standard Deviations) Certified Concentrations***

Analyte	Method	Certified ( $\mu$ ) <sup>6</sup>	(2s) <sup>8</sup> $\pm$	Unit
Li	4A_MICP <sup>1</sup>	2.94	0.29	%
Li	FUS <sup>2</sup>	3.07	0.32	%
Ta	4A_MICP	187	35	ppm
Ta	FUS	179	26	ppm
Nb	4A_MICP	26	5	ppm
Nb	FUS	26	5	ppm
As	4A_MICP	2	1	ppm
Sb	4A_MICP	4	0.6	ppm
Sb	FUS	5	2	ppm
Sn	FUS	573	44	ppm
F	SIE <sup>3</sup>	1153	182	ppm
S	4A_MICP	0.019	0.003	%
SG	SG <sup>4</sup>	3.15	0.22	Dimensionless
Ba	4A_MICP	17	2	ppm
Be	4A_MICP	273	45	ppm
Bi	4A_MICP	2	0.5	ppm
Co	4A_MICP	3	0.5	ppm
Cs	4A_MICP	86	23	ppm
Cu	4A_MICP	25	6	ppm
Ga	4A_MICP	140	9	ppm
Hf	4A_MICP	7	2	ppm
K	4A_MICP	3262	326	ppm
Lu	4A_MICP	0.03	0.03	ppm
Mn	4A_MICP	1006	102	ppm
Mn	FUS	1043	85	ppm
Mo	4A_MICP	1	0.1	ppm
Na	4A_MICP	3879	246	ppm
Ni	4A_MICP	16	5	ppm
P	4A_MICP	1427	189	ppm
Pb	4A_MICP	24	4	ppm
Sc	4A_MICP	0.7	0.4	ppm
Si	FUS	29.72	1.1	%
Ti	4A_MICP	305	20	ppm
Tl	4A_MICP	7	0.7	ppm
V	4A_MICP	8	0.9	ppm
W	4A_MICP	1	0.4	ppm
Yb	4A_MICP	0.3	0.2	ppm
Zn	4A_MICP	58	6	ppm
Zr	4A_MICP	32	8	ppm

**Major Oxides**  
**Certified Concentrations (at two Standard Deviations)**

Analyte	Method	Certified ( $\mu$ ) <sup>6</sup>	(2s) <sup>8</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>5</sup>	25.60	0.32	%
CaO	XRF	1.06	0.022	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	1.40	0.083	%
K <sub>2</sub> O	XRF	0.38	0.01	%
Li <sub>2</sub> O	FUS	6.62	0.70	%
MnO	FUS	0.13	0.01	%
MnO	XRF	0.14	0.01	%
Na <sub>2</sub> O	XRF	0.50	0.01	%
Nb <sub>2</sub> O <sub>5</sub>	FUS	0.003	0.001	%
P <sub>2</sub> O <sub>5</sub>	XRF	0.33	0.03	%
Sb <sub>2</sub> O <sub>5</sub>	FUS	0.001	0.0003	ppm
SiO <sub>2</sub>	FUS	63.47	2.3	%
SiO <sub>2</sub>	XRF	62.71	0.99	%
SnO <sub>2</sub>	FUS	0.057	0.004	%
Ta <sub>2</sub> O <sub>5</sub>	FUS	0.022	0.003	%
TiO <sub>2</sub>	XRF	0.054	0.01	%

## 1. Certified Concentrations and Uncertainties

AMIS0656 is a new standard material, developed and certified in August 2019. Table 1 gives the certified concentrations, confidence interval, combined and expanded uncertainty for the certified reference material. Table 2 shows the certified major oxides concentrations, two standard deviations, confidence interval, combined and expanded uncertainty.

**Table 1.** Certified concentrations, two standard deviations, combined and expanded uncertainty.

Analyte	Method	Certified ( $\mu$ ) <sup>6</sup>	N	n	k	% RSD	( $u_c$ ) <sup>7</sup>	(2s) <sup>8</sup> $\pm$	(CI) <sup>9</sup> 95%	(U) <sup>10</sup> $\pm$	Unit
Li	4A_MICP <sup>1</sup>	2.94	3	24	4.303	5	0.14	0.29	0.34	0.6	%
Li	FUS <sup>2</sup>	3.07	5	39	2.776	5	0.16	0.32	0.20	0.4	%
Ta	4A_MICP	187	4	29	3.182	9	17	35	20	55	ppm
Ta	FUS	179	5	37	2.776	7	13	26	16	35	ppm
Nb	4A_MICP	26	4	32	3.182	9	2	5	4	8	ppm
Nb	FUS	26	4	32	3.182	11	3	5	3	9	ppm
As	4A_MICP	2	4	30	3.182	26	0.6	1	0.7	2	ppm
Sb	4A_MICP	4	5	38	2.776	7	0.3	0.6	0.2	0.8	ppm
Sb	FUS	5	3	24	4.303	21	1	2	2	4	ppm
Sn	FUS	573	4	31	3.182	4	22	44	29	70	ppm
F	SIE <sup>3</sup>	1153	4	29	3.182	8	91	182	133	290	ppm
S	4A_MICP	0.019	4	30	3.182	9	0.002	0.003	0.003	0.01	%
SG	SG <sup>4</sup>	3.15	3	24	4.303	3	0.11	0.22	0.26	0.5	Dimensionless
Ba	4A_MICP	17	4	32	3.182	6	1	2	1	3	ppm
Be	4A_MICP	273	4	32	3.182	8	22	45	34	71	ppm
Bi	4A_MICP	2	5	40	2.776	10	0.2	0.5	0.3	0.7	ppm
Co	4A_MICP	3	3	24	4.303	9	0.3	0.5	0.5	1	ppm
Cs	4A_MICP	86	4	32	3.182	13	11	23	18	37	ppm
Cu	4A_MICP	25	4	32	3.182	11	3	6	4	9	ppm
Ga	4A_MICP	140	5	38	2.776	3	5	9	4	13	ppm
Hf	4A_MICP	7	4	32	3.182	14	0.9	2	1	3	ppm
K	4A_MICP	3262	4	32	3.182	5	163	326	251	519	ppm
Lu	4A_MICP	0.03	2	16	12.706	41	0.01	0.03	0.1	0.2	ppm
Mn	4A_MICP	1006	5	39	2.776	5	51	102	60	142	ppm
Mn	FUS	1043	2	16	12.706	4	43	85	291	542	ppm
Mo	4A_MICP	1	5	39	2.776	5	0.07	0.1	0.05	0.2	ppm
Na	4A_MICP	3879	5	38	2.776	3	123	246	140	342	ppm
Ni	4A_MICP	16	5	36	2.776	14	2	5	3	6	ppm
P	4A_MICP	1427	4	32	3.182	7	95	189	144	301	ppm
Pb	4A_MICP	24	5	40	2.776	8	2	4	2	5	ppm
Sc	4A_MICP	0.7	3	20	4.303	29	0.2	0.4	0.6	0.9	ppm
Si	FUS	29.72	3	23	4.303	2	0.55	1.1	1.2	2	%
Ti	4A_MICP	305	4	29	3.182	3	10	20	9	32	ppm
Tl	4A_MICP	7	5	39	2.776	5	0.3	0.7	0.3	0.9	ppm
V	4A_MICP	8	4	32	3.182	6	0.5	0.9	0.6	1	ppm
W	4A_MICP	1	4	32	3.182	16	0.2	0.4	0.3	0.6	ppm
Yb	4A_MICP	0.3	2	16	12.706	39	0.1	0.2	1	1	ppm
Zn	4A_MICP	58	4	30	3.182	5	3	6	0.4	10	ppm
Zr	4A_MICP	32	5	39	2.776	12	4	8	5	11	ppm

**Table 2.** Certified major oxides concentrations, two standard deviations, combined and expanded uncertainty.

Analyte	Method	Certified ( $\mu$ ) <sup>6</sup>	N	n	k	% RSD	( $u_c$ ) <sup>7</sup>	(2s) <sup>8</sup> $\pm$	(CI) <sup>9</sup> 95%	(U) <sup>10</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	XRF	25.60	5	39	2.776	1	0.16	0.32	0.19	0.4	%
CaO	XRF	1.06	5	40	2.776	1	0.011	0.022	0.012	0.03	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	1.40	4	29	3.182	3	0.042	0.083	0.074	0.1	%
K <sub>2</sub> O	XRF	0.38	5	40	2.776	1	0.006	0.01	0.004	0.02	%
Li <sub>2</sub> O	FUS	6.62	5	39	2.776	5	0.35	0.70	0.43	1	%
MnO	FUS	0.13	2	16	12.706	4	0.005	0.01	0.04	0.07	%
MnO	XRF	0.14	5	40	2.776	4	0.005	0.01	0.005	0.01	%
Na <sub>2</sub> O	XRF	0.50	5	36	2.776	1	0.007	0.01	0.006	0.02	%
Nb <sub>2</sub> O <sub>5</sub>	FUS	0.003	5	38	2.776	17	0.001	0.001	0.001	0.002	%
P <sub>2</sub> O <sub>5</sub>	XRF	0.33	5	40	2.776	5	0.02	0.03	0.02	0.04	%
Sb <sub>2</sub> O <sub>5</sub>	FUS	0.001	3	24	4.303	21	0.0001	0.0003	0.0003	0.001	ppm
SiO <sub>2</sub>	FUS	63.47	3	23	4.303	2	1.1	2.3	2.0	5	%
SiO <sub>2</sub>	XRF	62.71	5	37	2.776	1	0.50	0.99	0.65	1	%
SnO <sub>2</sub>	FUS	0.057	4	31	3.182	4	0.002	0.004	0.003	0.01	%
Ta <sub>2</sub> O <sub>5</sub>	FUS	0.022	5	37	2.776	7	0.002	0.003	0.002	0.004	%
TiO <sub>2</sub>	XRF	0.054	6	45	2.571	11	0.006	0.01	0.005	0.02	%

1. 4A\_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
2. FUS is Fusion digestion with ICP finish
3. SIE is Selective Ion Exchange
4. SG is Specific Gravity
5. XRF is X-ray Fluorescence
6. The certified value  $\mu$ , is an unweighted grand mean of the means of N accepted sets of data from different laboratories and n number of test sample replicates. The certified value is traceable to SI units and is reported on a dry basis.
7. The combined uncertainty of the certified value is the within-laboratory reproducibility standard deviation derived from the analysis of variance of results from N number of laboratories and n number of sample replicates. ( $u_c$ )
8. Two standard deviations (2s)
9. Confidence interval at 95% level of confidence.
10. Expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty ( $u_c$ ) with a coverage factor (k) found from N-1 degrees of freedom (see Appendix 7 for t-distribution table). Example:  $U = 2.36 \times 0.23 = 0.5\%$
11. Comb/LECO is Combustion/LECO
12. Moisture
13. 4A\_ICPES is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
14. LOI is Loss on Ignition

## 2. Statistical Comparison of Means

A comparison of means for replicate data for the same element concentration determined by different analytical methods is done equating the variances between the two data sets; if the variances are found to be equal (F-test,  $p$ -value $>0.05$ ), then an equal variance t-test is applied. Should the variances be statistically significant, i.e.  $p<0.05$ , then an unequal variance t-test is performed. For either t-test, if the obtained  $p$ -value  $\geq 0.05$ , the null hypothesis that the means (certified values) are equal is accepted (Table 3). This gives the analyst confidence in the certified values reported by different analytical methods on the same analyte.

**Table 3.** The results of a two-sample equal or unequal variance t-test (two-tailed) data sets in which different analytical methods /instrumentation were used.

Method	Certified value	Method	Certified value	F-Test Outcome	$p$ -value (t-test)	t-test Outcome
Li 4A_MICP	2.94 %	Li FUS	3.07 %	Equal Variance ( $p=0.47$ )	0.283	Accept $H_0$ ; certified values are equal
Ta 4A_MICP	0.019 %	Ta FUS	0.018 %	Equal Variance ( $p=0.516$ )	0.402	Accept $H_0$ ; certified values are equal
Nb 4A_MICP	0.003 %	Nb FUS	0.003 %	Equal Variance ( $p=0.388$ )	0.760	Accept $H_0$ ; certified values are equal
Sb 4A_MICP	0.004 %	Sb FUS	0.005%	Unequal Variance ( $p=0.002$ )	0.480	Accept $H_0$ ; certified values are equal
Sn 4A_MICP	0.016 %	Sn FUS	0.057 %	Equal Variance ( $p=0.191$ )	$<0.001$	Reject $H_0$ ; certified values are <i>not</i> equal
Mn 4A_MICP	0.101 %	Mn FUS	0.104 %	Equal Variance ( $p=0.457$ )	0.386	Accept $H_0$ ; certified values are equal
MnO FUS	0.135 %	MnO XRF	0.136 %	Equal Variance ( $p=0.622$ )	0.671	Accept $H_0$ ; certified values are equal
SiO <sub>2</sub> FUS	63.47 %	SiO <sub>2</sub> XRF	62.71 %	Equal Variance ( $p=0.128$ )	0.193	Accept $H_0$ ; certified values are equal

## 3. Intended Use

AMIS0656 is a matrix matched Certified Reference Material, fit for use as a control sample in routine assay laboratory quality control when inserted within runs of test samples and measured in parallel to test samples. This material can also be used for method development, use as independent calibration verification check standard (i.e. if not used as a calibration standard in an instrument calibration), or for validation of accuracy in a method validation exercise (see Appendix 3). The recommend procedure for the use of this CRM as a control standard in laboratory quality control is to develop a Shewhart chart, where a mean value and corresponding 1, 2 and 3 standard deviations are derived from replicate measurements of the CRM (see Appendix 6). This CRM can also be used to assess inter-laboratory or instrument bias and establish within-laboratory precision and within-laboratory reproducibility. The certified concentrations and expanded uncertainty for this material are property values based on an inter-laboratory measurement campaign and reflect consensus results from the laboratories that took part in the exercise



#### 4. Abbreviations and Symbols

Abbreviations and symbols used in this document are shown in Table 4.

**Table 4.** Abbreviations, symbols and descriptions.

Abbreviation/Symbol	Description
Alpha ( $\alpha$ )	Significance level (denoted by alpha, ' $\alpha$ ') of 0.05 or 5%
ANOVA	Analysis of variance by statistical means
Bq	The becquerel is the SI derived unit of radioactivity.
BIF	Banded iron formation
CRM	Certified reference material
$df$	Degrees of freedom, typically, $n-1$ , or $N-1$
$F_{calc}$	Calculated F statistic from ANOVA or Fisher's test
F-critical or $F_{crit}$	F-critical value from F-distribution table
GOI	Gain on ignition
$H_0$	Null hypothesis
$H_1$	Alternate hypothesis
g/t	Grams per tonne
$k$	Coverage factor, e.g. $k=2$ for 95% level of confidence
LOC	Level of confidence or confidence level
LOD	Limit of detection
LOQ	Limit of quantitation
LOI	Loss on ignition
MS	Mean squares (ANOVA)
MSb	Mean squares between (ANOVA)
MSw	Mean squares within (ANOVA)
$N$	Number of labs
$n$	Number of replicates
$\mu$	Property or certified value of a CRM
$p$	' $p$ -value' a measure of the strength of evidence against $H_0$
P	Total number of data points in ANOVA
ppm	Parts per million. Equivalent to g/t
RSD	Relative standard deviation usually expressed as % at a 68% LOC
Replicates	Replication is the repetition of an experimental condition so that the variability associated with an analysis can be estimated (ASTM E1847)
$s$	Standard deviation
$s_r$	Within laboratory repeatability as derived from ANOVA
$s_s$	Between laboratory standard deviation as derived from ANOVA
SS	Sum of squares in ANOVA
SST	Total variation in ANOVA
SSB	Between group (laboratory) variance
SSW	Within group (laboratory) variance

Abbreviation/Symbol	Description
2s	Two times standard deviation
SI	Standard International system of units
t <sub>calc</sub>	Calculated t statistic from a one-sample, two-tailed t-test
t-critical or t <sub>crit</sub>	t-critical value at given alpha and degrees of freedom
Tonne	A metric ton, is a unit of mass equaling 1000 kilograms
=TINV(5%, df)	MS Excel function for t-critical value at LOC 95% and df
U	Expanded uncertainty at a given k
u	Standard uncertainty at k=1
u <sub>c</sub>	Combined standard uncertainty at k=1
µm	Micron, is an SI derived unit of length equaling 1×10 <sup>-6</sup> of a meter

## 5. Uncertified Concentration Values

Appendix 1 gives uncertified concentrations for other elements present in the CRM.

## 6. Units

All results for major oxides are reported as oxides in percentages. All results for major elements analyses reported in percentages or ppm. Results for Au and the platinum group elements are reported in g/t or ppm. Specific gravity (SG) is the ratio of the density of a substance to the density of a reference substance, *i.e.* equivalently; it is the ratio of the mass of a substance to the mass of a reference substance for the same given volume. Since specific gravity is a ratio of densities its units are therefore dimensionless.

## 7. Analytical and Physical Methods

A complete list of analytical and physical methods as generic method codes with a brief description of the methods is available on the AMIS web site [www.amis.co.za](http://www.amis.co.za)

## 8. Origin of Material

Materials made using ore sourced from the Volta Grande mine was provided by AMG Mineração S.A. ("MIBRA"), a subsidiary of AMG Advanced Metallurgical Group N.V. It is from the Volta Grande tantalum, niobium, and tin mine ("Volta Grande") in Minas Gerais state, Brazil. AMG Mineração produces Spodumene Concentrate, Tantalum Concentrate, Tin in ingots, Feldspar and Abite. The sample of spodumene concentrate was produced by flotation, after magnetic separation. The milled pegmatite was processed in a magnetic separator, to remove iron minerals, mainly silicates. The non magnetic pegmatite was floated (rougher, cleaner and recleaner).

## 9. Approximate Mineral and Chemical Composition

The Volta Grande pegmatites occur in the Archaean Barbacena greenstone belt on the Southern border of the São Francisco craton. The Volta Grande pegmatites form six sub-horizontal tabular bodies characterized by coarse to very coarse-grained spodumene, quartz, albite, microcline and muscovite. The predominant lithium mineral is spodumene.

## 10. Quantitative Analysis by X-Ray Diffraction

Both natural and synthetic materials have a specific chemistry and atomic arrangement, known as phases. Phases can be identified and quantified using X-ray diffraction (XRD) which produces a plot of the intensity of X-rays scattered at different angles by crystalline phases in a material. Essentially, an X-ray diffraction pattern is the sum of the diffraction patterns produced by each phase. Simply put, an X-ray diffraction pattern is a fingerprint that allows the identification of what is in a target sample material. Knowledge of the mineral phase composition is useful in method development with techniques such as ICP-OES and XRF as potential matrix effects and spectral interferences can be recognized and accounted for. X-ray diffraction is effective in that it allows the identification of different phases of compounds that are identical in chemistry, but have a distinctly different the atoms, e.g. quartz, cristobalite, and glass are all different phases of SiO<sub>2</sub>. Where quantitative XRD results do not correspond to results of other analytical techniques, it should be borne in mind that even though the data are quantitative they are meant to be used for indicative purposes in development of other analytical methods. Mineral names may not reflect the actual compositions of minerals identified, but rather the mineral group.

Quantification is determined from the chosen software package: this uses the full-profile Rietveld method of refining the profile of the calculated XRD pattern against the profile of the measured XRD pattern. The total calculated pattern is the sum of the calculated patterns of the individual phases. Results are given as weight % of the total crystalline phases and amorphous content. The amorphous content quantifies the amorphous material and unknown minerals or known minerals for which there is not a suitable crystal structure.

Corrections are incorporated into the process that allows for a more accurate description of the mineral's contribution to the measured pattern and to allow for variation due to atomic substitution, layer disordering, preferred orientation, and other factors that affect the acquisition of the XRD scan.

The limitations of qualitative XRD analysis are as follows:

- The detection of a phase may be dependent on its crystallinity.
- Where there exist multiple phases, overlap of diffracted reflections can occur, thus rendering some ambiguity into the interpretation.
- Overlapping reflections of a major phase can mask the presence of minor or trace phases.
- Some phases cannot be unambiguously identified as they are present in minor or trace amounts.

The limitations of quantitative XRD analysis by a full-profile Rietveld method are as follows:

- The limitations for qualitative XRD analysis apply.
- The method as described is standardless: it relies solely on the published crystallographic data available for each phase. Some data may not exactly describe the phases present.
- Particle size is important with respect to the absorption of the X-rays by the sample.
- Micronising reduces the particle size to that more suitable for quantitative analysis.

The accuracy of the analysis is dependent on sampling and sample preparation in addition to the calculated profiles being exactly representative of the chemistry of the component phases and their crystallinity. Some preferred orientation effects and reflection overlaps may occur which cannot be adequately resolved.

**Table 5.** Results of XRD analysis.

Phase	Formula	Composite %
Amorphous Content		21
Anatase	TiO <sub>2</sub>	<1
Calcite	Ca(Mg)CO <sub>3</sub>	1
Lepidolite	K(Li,Al) <sub>3</sub> (Al,Si,Rb) <sub>4</sub> O <sub>10</sub> (F,OH) <sub>2</sub>	3
Magnesite	MgCO <sub>3</sub>	<1
Potassium Feldspar	KAlSi <sub>3</sub> O <sub>8</sub>	2
Pyrite	FeS <sub>2</sub>	<1
Quartz	SiO <sub>2</sub>	4
Sodium Plagioclase	NaAlSi <sub>3</sub> O <sub>8</sub>	1
Spodumene	LiAl(SiO <sub>3</sub> ) <sub>2</sub>	69
Zeolite	e.g. (Na,K) <sub>8</sub> (Si,Al) <sub>36</sub> O <sub>72</sub> .23H <sub>2</sub> O	<1
Total		101 %

*For informational purposes only*

## 11. Health and Safety

The material is a very fine powder coloured light blueish gray (Corstor 5B 8/l). Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

## 12. Method of Preparation

The particle size distribution for this material was shown to have a nominal top size of 54µm (93% passing 54µm). The procedure of preparation in brief is as follows: the material was crushed, dry-milled and air-classified to <54µm. It was then blended in a bi-conical mixer, systematically divided and sealed into 1kg Laboratory Packs. Explorer Packs are then subdivided from the Laboratory Packs as required. Final packaged units were then selected on a random basis and submitted for analysis to an independent laboratory accredited with the ISO17025 standard of general requirements for the competence of testing and calibration laboratories. The results obtained from this laboratory are then evaluated statistically by AMIS for homogeneity.

## 13. Particle Size Determination

The sample has been analysed using a Malvern Mastersizer 2000. Particles are passed through a focused laser beam that scatter light at an angle inversely proportional to their size. The intensity of light is measured and converted to a volume in particle size distribution. The results for this standard are presented in Table 6.

**Table 6.** Particle Size Determination by laser diffraction.

Size (µm)	Vol. Under %
<45um	90.5
<63um	94.1
<75um	95.1
<90um	96.9
<100um	97.6
<106um	98.0
<150um	99.6

*For informational purposes only*

## **14. Handling**

The material is packaged in Laboratory Packs and Explorer Packs that must be shaken or otherwise agitated before use. The analyte concentrations are quoted on a dry basis; therefore, the user needs to determine the moisture content to convert any obtained assay values to an air-dry basis (see Appendix 7 for an example calculation).

## **15. Storage information**

The material should be stored in a cool dry place, in such a way that it does not compromise the integrity of the CRM. The material should be stored in conditions which will ensure it does not absorb moisture.

## **16. Methods of Analysis Requested**

The following methods of analysis were requested:

- a) Multi element scan to include Li, Ta, Nb, As, Sb, Sn. Fusion, ICP-OES or ICPMS.
- b) Multi element scan. Multi-acid digest ICP-OES or ICP-MS.
- c) F by ISE
- d) LOI and Major oxides ( Al<sub>2</sub>O<sub>3</sub>, CaO, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MgO, MnO, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, Rb<sub>2</sub>O, SiO<sub>2</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> XRF fusion
- e) SG, gas pycnometer
- f) S Combustion/LECO
- g) Moisture

## 17. Information Requested of Participating Laboratories

The following information was requested of the participating laboratories for the development of this CRM:

- a) State aliquots used for all determinations.
- b) All results for major elements to be reported as oxides in percentages.
- c) All results for multi-element scans and fusion to be reported in ppm.
- d) Report all QC data, to include replicates, blanks and certified reference materials used.
- e) All Round robin samples must be treated the same as routine test samples.
- f) All results must be reported to maximum decimal places i.e. dependent on laboratories capabilities
- g) Please ensure moisture content is determined and calculated. All results should be corrected by the moisture correction factor and this factor should be stated in the laboratory results. Please use the excel template provided by AMIS. If you require a copy, please email any of the email addresses below. Ensure all uncertainties are added to the results. Please send excel and PDF of all results. Ensure correct PPE is used i.e. gloves, dust masks and protective clothing. Analysis should be done under controlled environmental conditions

## 18. Certification of Mean and Estimation of Measurement Uncertainty

The samples used in this certification process have been selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore, all sources of uncertainty are included in the combined standard uncertainty determination. Initially the data submitted by all the laboratories are subjected to a z-score test, equation [1] to exclude outliers and the remaining data sets examined for their normality in distribution. This is followed by the exclusion of further outliers as defined by the IUPAC Harmonised Protocol of 1995 in which both Cochran and a Grubbs test are applied until all outliers are identified, equations [2] and [3]. A grand mean and standard deviation is re-calculated using all remaining data (Thompson, 2008; Carr, 2011) (see Appendix 2)

## 19. Two Standard Deviations

AMIS reports two-standard deviations (2s) with all certified values. Two -standard deviations are calculated using the expression:

$$\text{Two standard deviations} = 2 (u_c)$$

Where  $u_c$  is the standard combined uncertainty (see Appendix, equation [14]).

## 20. Confidence Interval

AMIS reports a confidence interval (CI) with all certified values. Confidence interval as used by AMIS is:

$$\text{Confidence Interval (CI)} = \frac{(t_{critical})s}{\sqrt{N}}$$

Where,  $N$  is the number of laboratories (accepted laboratory data),  $t_{critical}$  is a two-tailed value for  $N - 1$  degrees of freedom ( $df$ ) and  $s$ , is the standard deviation of the accepted laboratory means. A two-tailed critical value is found for  $N - 1$  degrees of freedom from either a  $t$ -distribution table (Appendix 9) or MS Excel as =TINV (5%,  $df$ ).

## 21. Expanded Uncertainty

ANOVA gives an estimate of the repeatability and the reproducibility of the data accepted for certification of the candidate reference material (see equations, [15] and [16], in the Appendix). Therefore, random variables (e.g., subsampling, instrument effects, interferences, operators and measurement conditions) that occur during the analysis of the candidate reference material by the various laboratories is considered. This approach does not necessarily quantify each individual source of uncertainty; however, the combined effect of random uncertainties is assessed (Ramsey & Ellison, 2007). A combined standard uncertainty is calculated from equation [14], which when multiplied by the t-critical value for  $N-1$  laboratories, gives an *expanded uncertainty* at a 95% level of confidence. The expanded uncertainty is a measure of the doubt around the certified value at a level of 95% confidence. The expanded uncertainty is used in the validation of accuracy (see equation [18]).

## 22. Confidence Interval and Expanded Uncertainty

A combined standard uncertainty will be greater than a combined *CI*. This is because ANOVA considers the within-lab repeatability (that is repeatability within each lab group) as well as the repeatability between each lab data set. This attends to random variables that contribute to the measurement of uncertainty, during the analysis of the test sample at the participating laboratories. The within-lab repeatability and the between lab repeatability is combined as the square root of the sum of squares of these two values giving a combined standard uncertainty, at a 68% confidence level. Multiplying the combined standard uncertainty by the t-critical value for  $N-1$ , gives the expanded uncertainty at 95% level of confidence. It is recommended that the procedure described in Appendix 6, “*Using the CRM in Quality Control*” be used, in setting the limits of the CRM. Table 7 below shows mean gold values obtained by fire assay lead collection, for nine different laboratories, the confidence interval, two-standard deviations and expanded uncertainty.

**Table 7.** Example of replicate assay data in which the *CI*, *2s* and *U* are shown.

Lab No.	Mean Au (g/t)
1	0.268
2	0.273
3	0.270
4	0.288
5	0.274
6	0.256
7	0.263
8	0.258
9	0.288

<b>CI</b>	0.0088
<b>2s</b>	0.031
<b>U</b>	0.04

## 23. Participating Laboratories

The laboratories that are accredited with ISO17025 and provided timeous results are:

1. Dorfner Anzaplan Analysenzentrum
2. Performance Laboratories Zimbabwe
3. Bureau Veritas Minerals Ultra Trace Pty Ltd
4. ALS Geochemistry Vancouver
5. SGS Australia Pty Ltd (Newburn) WA
6. Intertek Perth
7. SGS Geosol Laboratories Ltda (Brazil)
8. Shiva Analyticals India

## 24. Accepted Assay Data

Data from the 9 laboratories used for certification are set out in Table 8.

**Table 8.** Data used to calculate the certified values after removal of outliers.

4A_MICP	FUS	4A_MICP	FUS	4A_MICP	FUS	4A_MICP	4A_MICP	FUS	FUS	SIE	4A_MICP	SG
Li	Li	Ta	Ta	Nb	Nb	As	Sb	Sb	Sn	F	S	SG
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	Dimensionless
29157	28750	190	170	29.00	21.80	2.00	4.00	5.00	546	1110	0.02	3.11
28787	28750	204	171	28.50	23.40	3.00	4.00	5.00	550	1170	0.02	3.11
29839	29290	206	173	30.00	23.90	3.00	4.00	6.00	550	1120	0.02	3.11
29093	29100	204	173	29.00	24.70	3.00	4.00	6.00	540	1180	0.02	3.13
29278	29440	189	165	28.00	21.10	2.00	4.00	5.00	560	1090	0.02	3.11
29017	28700	210	176	28.50	23.10	2.00	4.00	6.00	570	1100	0.02	3.14
28818	28900	206	167	29.00	25.20	3.00	4.20	6.00	554	1140	0.02	3.13
28834	29500	188	171	28.50	23.50	2.00	3.80	6.00	560	1110	0.02	3.16
30200	33000	165	188	26.10	30.00	2.90	3.89	3.40	580	1000	0.02	3.27
30600	32900	193	186	26.40	25.00	2.60	3.86	3.60	570	1100	0.02	3.23
31400	32700	187	183	26.70	25.00	2.50	3.73	4.10	580	1100	0.02	3.27
31000	33400	201	180	27.90	25.00	2.50	4.35	4.00	580	1100	0.02	3.22
31200	33200	181	187	27.70	30.00	3.20	3.63	4.30	590	1100	0.02	3.31
30600	32900	217	190	25.60	25.00	2.70	4.00	4.50	590	1260	0.02	3.30
31400	32800	213	184	26.90	25.00	2.90	4.04	4.40	590	1300	0.02	3.29
31100	30800	205	191	26.50	30.00	2.40	4.51	3.60	580	1250	0.02	3.26
27902	31000	182	190	23.30	30.00	2.00	3.90	4.30	584	1260	0.02	3.05
28806	32100	181	195	25.60	25.00	2.00	4.20	4.00	590	1290	0.02	3.06
27518	31300	177	195	24.70	25.00	2.00	4.30	3.80	586	1280	0.02	3.07
28111	31100	183	185	26.10	25.00	2.00	4.50	4.10	593	1290	0.02	3.05
27891	31600	178	190	23.90	30.00	2.00	4.50	4.90	604	1260	0.02	3.07
29236	30400	179	185	27.00	25.00	2.00	4.20	4.40	597	1164	0.02	3.07
28562	31300	180	200	26.10	30.00	2.00	4.70	4.20	595	1099	0.02	3.05
27930	31156	181	189	27.10	30.00	2.00	4.10	3.80	601	1016	0.02	3.07
	30888	185	186	23.10	25.00	2.00	3.70		578	1142	0.02	
	30663	177	182	23.70	24.00	2.00	4.30		572	1190	0.02	
	30894	182	184	23.30	24.00	1.00	4.00		535	1184	0.02	
	31165	185	187	23.90	25.00	2.00	4.40		568	1116	0.02	
	31693	136	191	22.70	25.00	1.00	4.70		596	1139	0.02	
	31153		189	22.50	25.00	2.00	3.80		535		0.02	
	31141		190	23.10	24.00		4.40		554			
	30200		171	23.80	25.00		4.65					
	30500		166				4.60					
	29500		155				4.35					
	29100		158				4.36					
	28400		163				3.93					
	29500		157				4.07					
	28700						3.95					
	29000											



Assay Data (Cont.)

XRF	XRF	XRF	XRF	FUS	FUS	XRF	XRF	FUS	XRF	FUS	FUS	XRF	FUS	FUS	XRF
Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Li <sub>2</sub> O	MnO	MnO	Na <sub>2</sub> O	Nb <sub>2</sub> O <sub>5</sub>	P <sub>2</sub> O <sub>5</sub>	Sb <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	SiO <sub>2</sub>	SnO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>
%	%	%	%	%	%	%	%	%	%	ppm	%	%	%	%	%
25.82	1.06	1.47	0.38	6.19	0.13	0.13	0.50	0.00	0.30	0.00	62.47	63.28	0.05	0.02	0.06
25.79	1.07	1.47	0.39	6.19	0.13	0.13	0.51	0.00	0.30	0.00	62.47	63.32	0.06	0.02	0.06
25.79	1.06	1.47	0.38	6.30	0.13	0.13	0.51	0.00	0.30	0.00	62.26	63.32	0.06	0.02	0.06
25.86	1.06	1.46	0.38	6.26	0.13	0.13	0.50	0.00	0.30	0.00	64.18	63.29	0.05	0.02	0.06
25.84	1.06	1.47	0.38	6.34	0.13	0.13	0.51	0.00	0.31	0.00	61.83	63.26	0.06	0.02	0.06
25.75	1.07	1.40	0.38	6.18	0.14	0.13	0.50	0.00	0.30	0.00	61.83	63.33	0.06	0.02	0.06
25.74	1.06	1.39	0.39	6.22	0.13	0.14	0.51	0.00	0.30	0.00	61.61	63.34	0.06	0.02	0.06
25.78	1.07	1.39	0.38	6.35	0.13	0.13	0.50	0.00	0.30	0.00	64.61	63.31	0.06	0.02	0.06
25.41	1.05	1.39	0.38	7.10	0.14	0.14	0.51	0.00	0.33	0.00	63.97	62.58	0.06	0.02	0.06
25.39	1.05	1.39	0.38	7.08	0.14	0.14	0.50	0.00	0.33	0.00	63.97	62.33	0.06	0.02	0.06
25.37	1.05	1.39	0.38	7.04	0.14	0.14	0.51	0.00	0.33	0.00	63.97	62.27	0.06	0.02	0.06
25.41	1.04	1.39	0.38	7.19	0.14	0.14	0.50	0.00	0.33	0.00	65.47	62.28	0.06	0.02	0.05
25.44	1.05	1.39	0.38	7.15	0.13	0.14	0.50	0.00	0.33	0.00	64.40	62.38	0.06	0.02	0.06
25.40	1.05	1.37	0.38	7.08	0.13	0.14	0.49	0.00	0.33	0.00	64.82	62.31	0.06	0.02	0.06
25.41	1.05	1.37	0.38	7.06	0.14	0.14	0.49	0.00	0.33	0.00	63.33	62.44	0.06	0.02	0.05
25.45	1.05	1.36	0.38	6.63	0.14	0.14	0.50	0.00	0.33	0.00	63.69	62.39	0.06	0.02	0.06
25.50	1.08	1.36	0.38	6.67		0.14	0.50	0.00	0.33	0.00	63.70	63.00	0.06	0.02	0.05
25.60	1.07	1.38	0.39	6.91		0.14	0.50	0.00	0.32	0.00	63.78	62.90	0.06	0.02	0.06
25.50	1.08	1.37	0.38	6.74		0.14	0.49	0.00	0.33	0.00	64.01	62.90	0.06	0.02	0.05
25.40	1.07	1.36	0.39	6.69		0.13	0.49	0.00	0.33	0.00	63.67	63.00	0.06	0.02	0.05
25.50	1.08	1.36	0.38	6.80		0.14	0.50	0.00	0.34	0.00	63.67	63.00	0.06	0.02	0.05
25.50	1.08	1.38	0.39	6.54		0.14	0.51	0.00	0.33	0.00	63.72	62.80	0.06	0.02	0.05
25.60	1.06	1.36	0.39	6.74		0.14	0.51	0.00	0.33	0.00	63.50	63.00	0.06	0.02	0.05
25.50	1.06	1.38	0.38	6.71		0.14	0.51	0.00	0.33	0.00		62.90	0.06	0.02	0.05
25.69	1.06	1.37	0.39	6.65		0.14	0.51	0.00	0.34			62.91	0.06	0.02	0.05
25.66	1.07	1.38	0.39	6.60		0.14	0.50	0.00	0.34			62.98	0.06	0.02	0.05
25.69	1.06	1.37	0.39	6.65		0.14	0.51	0.00	0.33			63.15	0.05	0.02	0.05
25.65	1.06	1.38	0.38	6.71		0.14	0.50	0.00	0.34			62.83	0.06	0.02	0.05
25.63	1.06	1.37	0.39	6.82		0.14	0.49	0.00	0.33			63.01	0.06	0.02	0.05
25.69	1.06		0.38	6.71		0.14	0.50	0.00	0.34			62.83	0.05	0.02	0.05
25.76	1.07		0.39	6.70		0.14	0.50	0.00	0.34			62.95	0.06	0.02	0.05
25.65	1.06		0.38	6.50		0.13	0.50	0.00	0.33			62.78		0.02	0.06
25.49	1.07		0.37	6.56		0.13	0.49	0.00	0.34			62.07		0.02	0.05
25.60	1.07		0.38	6.35		0.14	0.50	0.00	0.34			61.97		0.02	0.05
25.55	1.07		0.38	6.26		0.13	0.50	0.00	0.34			61.99		0.02	0.05
25.49	1.07		0.38	6.11		0.13	0.50	0.00	0.34			62.05		0.02	0.05
25.71	1.08		0.38	6.35		0.13		0.00	0.34			61.85		0.02	0.06
25.59	1.07		0.38	6.18		0.14		0.00	0.34						0.06
25.68	1.07		0.38	6.24		0.13			0.34						0.04
	1.07		0.39			0.13			0.34						0.05
															0.05
															0.04
															0.05
															0.05
															0.05

**Assay Data (Cont.)**

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS
Ba	Be	Bi	Co	Cs	Cu	Ga	Hf	K	Lu	Mn	Mn
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
17.00	304	2.30	3.10	96.10	25.40	140	6.40	3300	0.04	1040	1034
17.00	296	2.20	2.90	92.60	22.60	141	5.90	3300	0.04	1040	1010
17.00	306	2.30	3.30	98.60	23.10	144	6.20	3300	0.04	1040	1013
16.00	293	2.30	3.10	92.60	24.30	141	6.10	3300	0.04	1030	1035
16.00	305	2.10	3.10	93.50	23.60	141	6.10	3200	0.04	1020	1001
16.00	301	2.10	2.80	95.30	23.10	144	6.00	3300	0.04	1020	1060
17.00	304	2.30	2.90	98.80	24.20	147	6.80	3300	0.04	1000	992
17.00	304	2.30	3.00	93.50	23.60	141	6.30	3400	0.04	1000	1014
15.00	254	2.08	2.70	69.40	24.00	148	7.40	3000	0.02	921	1085
15.00	251	2.17	2.70	67.40	22.00	140	7.67	3000	0.03	908	1085
17.00	260	2.19	2.60	67.70	23.00	140	7.30	3000	0.02	921	1085
16.00	270	2.00	2.70	71.70	22.00	148	8.06	3100	0.02	955	1085
15.00	270	2.48	2.60	70.30	23.00	145	7.22	3000	0.02	918	1008
16.00	255	1.98	2.50	68.20	25.00	140	8.06	3000	0.03	908	1008
15.00	268	2.33	2.70	74.50	23.00	148	8.67	3100	0.02	960	1085
15.00	267	2.42	2.50	70.50	21.00	144	8.44	3100	0.02	934	1085
16.00	240	2.60	2.90	80.80	28.00	128	6.30	3350		1030	
17.00	240	2.40	2.60	84.30	27.00	136	6.10	3360		1000	
16.00	265	2.70	2.60	91.20	27.00	136	5.70	3370		1000	
16.00	244	2.40	2.50	87.00	28.00	130	6.40	3460		1020	
17.00	255	2.60	2.50	84.60	29.00	143	5.70	3400		1020	
17.00	260	2.70	2.70	88.30	27.00	136	6.20	3390		1010	
16.00	258	2.50	2.80	94.40	28.00	141	5.70	3460		1040	
17.00	261	2.50	2.90	82.60	28.00	143	6.30	3460		1040	
18.00	267	2.72		91.90	29.30	137	6.54	3305		1056	
18.00	281	2.59		93.40	28.70	142	6.40	3328		1060	
18.00	273	2.64		88.80	27.90	140	6.40	3295		1056	
18.00	283	2.77		91.00	29.60	137	6.42	3308		1051	
17.00	265	2.68		90.30	29.00	140	5.51	3275		1058	
17.00	271	2.69		91.90	25.70	138	6.34	3278		1061	
18.00	278	2.50		93.60	25.00	141	6.05	3333		1067	
17.00	278	2.58		92.40	24.30	143	5.83	3314		1068	
		2.08				142				1000	
		2.18				138				1000	
		2.33				135				1000	
		2.25				145				1000	
		2.17				143				1000	
		2.41				138				1000	
		2.26								1000	
		2.07									

**Assay Data (Cont.)**

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Mo	Na	Ni	P	Pb	Sc	Si	Ti	Tl	V	W	Yb	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1.50	3900	20.00	1550	24.00	1.00	292000	300	6.90	8.00	1.50	0.35	55.00	39.00
1.50	3800	20.00	1500	25.00	1.00	292000	290	6.70	8.00	1.00	0.35	60.00	39.00
1.50	3900	20.00	1500	25.00	1.00	291000	300	6.80	8.00	1.50	0.35	60.00	39.00
1.50	3800	20.00	1500	25.00	1.00	300000	310	7.00	8.00	1.50	0.35	55.00	37.00
1.50	3800	18.20	1500	26.00	1.00	289000	300	6.90	8.00	1.50	0.35	55.00	36.00
1.50	3900	15.20	1500	25.00	1.00	289000	300	6.70	8.00	1.50	0.35	60.00	40.00
1.50	3900	15.70	1500	25.00	0.70	288000	310	6.80	8.00	1.50	0.35	60.00	40.00
1.50	4000	15.90	1500	24.00	0.60	302000	300	6.70	8.00	1.50	0.35	60.00	34.00
1.64	3700	17.30	1300	22.80	0.60	299000	310	6.19	8.00	1.10	0.20	59.00	31.40
1.52	3700	16.30	1280	22.10	0.70	299000	300	6.12	8.00	1.10	0.20	58.00	33.10
1.47	3700	15.90	1280	21.90	0.70	299000	310	6.16	9.00	1.10	0.20	58.00	33.30
1.52	3800	16.20	1340	24.60	0.60	306000	305	6.34	9.00	1.10	0.20	63.00	32.20
1.56	3700	13.00	1280	22.60	0.70	301000	295	6.32	9.00	1.00	0.20	58.00	31.70
1.45	3800	13.00	1280	22.00	0.70	303000	310	6.11	9.00	1.00	0.20	58.00	36.10
1.53	3700	13.00	1360	23.30	0.60	296000	320	6.33	9.00	1.10	0.20	59.00	32.50
1.58	3790	14.00	1310	22.50	0.60	299343	320	6.24	9.00	1.10	0.20	57.00	29.00
1.40	3800	14.00	1400	25.00	0.60	299390	329	7.20	8.00	1.30		64.00	28.00
1.40	3800	15.00	1430	24.00	0.60	299766	315	6.60	8.00	1.30		63.00	29.00
1.50	3880	14.00	1440	21.00	0.50	300847	311	6.90	8.00	1.30		58.00	30.00
1.40	3880	13.00	1400	22.00	0.60	299249	321	6.40	8.00	1.40		58.00	28.00
1.40	3850	16.00	1390	24.00		299249	293	6.90	8.00	1.20		54.00	31.00
1.40	3930	16.00	1440	23.00		299484	297	7.00	8.00	1.40		54.00	30.00
1.50	3870	16.00	1430	22.00		298450	301	7.10	8.00	1.40		61.00	30.00
1.40	3919	16.00	1390	22.00			322	6.68	8.00	1.40		63.00	28.00
1.50	3906	17.00	1500	25.00			300	6.88	9.00	1.20		54.00	30.40
1.50	3849	16.00	1524	27.00			300	6.81	8.00	1.10		59.00	28.40
1.50	3888	17.00	1480	26.00			300	6.84	8.00	1.10		58.00	30.60
1.40	3858	16.00	1537	25.00			300	6.89	9.00	1.20		57.00	26.70
1.50	3902	15.60	1424	27.00			300	7.01	8.00	1.10		56.00	27.50
1.60	3962	14.60	1425	27.00				6.87	8.00	1.00		58.00	29.00
1.60	3895	13.20	1468	26.00				6.96	8.00	1.10			30.40
1.40	4100	15.40	1494	25.00				6.42	8.00	1.10			32.90
1.61	3900	14.10		23.30				6.46					32.60
1.62	4100	13.50		22.00				7.00					31.80
1.53	3900	14.10		21.50				6.53					33.10
1.38	4100	13.20		22.00				6.24					29.90
1.52	4100			21.40				6.68					32.40
1.49	4100			22.80				6.68					31.20
1.43				23.00				6.34					30.80
				22.70									

## **25. Reported Values**

The certified values listed in this certificate fulfil the AMIS statistical criteria (see section 18) regarding agreement for certification and have been independently validated by Allan Fraser.

## **26. Validation of Accuracy (Trueness)**

This CRM can be used to validate accuracy (trueness) as required in method validation as stated in the ISO17025 standard. See Appendix 3 for an example on the validation of accuracy using replicate data derived from the analysis of a CRM.

## **27. Metrological Traceability**

The values quoted herein are based on the consensus values derived from statistical analysis of the data from an inter-laboratory measurement program. Traceability to SI units is via the standards used by the individual laboratories the majority of which are accredited to the ISO17025 general requirements for the competence of testing and calibration laboratories and who have maintained measurement traceability during the analytical process.

## **28. Period of Validity**

The certified values are valid for this product, while still sealed in its original packaging, until notification to the contrary. The stability of the material will be subject to continuous testing for the duration of the inventory. Should product stability become an issue, all customers will be notified and notification to that effect will be placed on the [www.amis.co.za](http://www.amis.co.za) website.

## **29. Minimum Sample Size**

The majority of laboratories reporting used a 0.5g sample size for the ICP-OES and a 30g sample size for the fire assay. These are the recommended minimum sample sizes for the use of this material.

## **30. Availability**

This product is available in Laboratory Packs containing 1kg of material and Explorer Packs containing custom weights (from 50 to 250g) of material. The Laboratory Packs are sealed bottles delivered in sealed foil pouches. The Explorer Packs contain material in standard geochem envelopes, nitrogen flushed, and vacuum sealed in foil pouches.

## **31. Recommended use in Quality Control**

Users should set their own limits *i.e.* 1, 2 and 3 standard deviations from an obtained mean value based on at least 10 replicate analyses using this CRM (see Appendix 6 for detail on the use of this CRM in quality control).

## 32. Legal Notice

This certificate and the reference material described in it have been prepared with due care and attention. However, AMIS, Makhosi Khoza, Melesha Gopi Mungaroo and Allan Fraser; accept no liability for any decisions or actions taken following the use of the reference material.

**Date of Version v2.00:** 07 April 2020

**Version:** v2.00

**Reason for Version v2.00:** Correction of Li<sub>2</sub>O results by FUS

**Version v2.00 replaces the all the other versions of AMIS0656 Certification**

**Date of Version v1.00:** 28 August 2019

**Version:** v1.00

**Reason for Version v1.00:** Rectification of LiO<sub>2</sub> results

**Version v1.00 replaces the original report of AMIS0656 Certification**

**Date of Version 000:** 08 August 2019

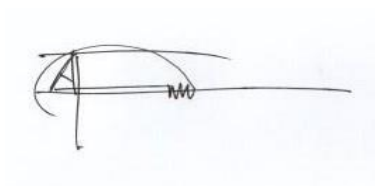
**Version:** 000

**Approving Officer:**

**African Mineral Standards:** \_\_\_\_\_

**Melesha Gopi Mungaroo (Technical Manager)**

**Certifying Officer:**

A handwritten signature in black ink, appearing to be 'AF' with a stylized flourish extending to the right.

**Geochemist:** \_\_\_\_\_

**Allan Fraser**

M.Sc. (Geology), N.D. (Analytical Chem.),  
Pr.Sci.Nat. Pr.Chem.SA

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# Appendices

## Appendix 1: Uncertified Element Statistics

Uncertified element statistics are shown in **Table 9**.

**Table 9.** Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	4A_MICP	18	0.1	0.03	33	ppm
Al	4A_MICP	16	120702.9	13921.4	1	ppm
Al	FUS	32	134400.4	9079.3	7	ppm
Al <sub>2</sub> O <sub>3</sub>	FUS	32	25.4	1.7	7	%
B	FUS	8	35.0	14.1	40	ppm
Ba	FUS	15	16.2	1.5	9	ppm
Be	FUS	16	288.1	29.1	10	ppm
Bi	FUS	15	2.6	0.2	8	ppm
C	Combustion/LECO	24	1682.5	185.8	11	ppm
Ca	4A_MICP	24	7713.6	213.7	3	ppm
Ca	FUS	16	7554.6	648.0	9	ppm
CaO	FUS	16	1.1	0.1	9	%
Cd	4A_MICP	17	0.3	0.04	15	ppm
Ce	4A_MICP	24	4.3	1.5	34	ppm
Ce	FUS	15	5.8	0.4	8	ppm
Cr	4A_MICP	32	99.9	49.2	49	ppm
Cr	FUS	15	151.8	3.4	2	ppm
Cr <sub>2</sub> O <sub>3</sub>	XRF	23	0.02	0.004	15	%
Cs	FUS	16	87.1	1.3	2	ppm
Cu	FUS	8	19.3	2.1	11	ppm
Dy	4A_MICP	16	2.1	0.2	8	ppm
Dy	FUS	15	2.3	0.1	2	ppm
Er	4A_MICP	16	0.3	0.1	25	ppm
Er	FUS	15	0.3	0.03	9	ppm
Eu	4A_MICP	9	0.1	0.01	14	ppm
Eu	FUS	9	0.1	0.01	9	ppm
F	FUS	8	1087.5	64.1	6	ppm
Fe	4A_MICP	24	8769.6	1031.7	12	ppm
Fe	FUS	32	9894.0	956.1	10	ppm
Fe	XRF	8	9700.0	53.5	1	ppm
Fe <sub>2</sub> O <sub>3</sub>	FUS	32	1.4	0.1	10	%
Ga	FUS	16	143.5	5.4	4	ppm
Gd	4A_MICP	16	3.1	0.5	16	ppm
Gd	FUS	16	3.3	0.2	7	ppm
Ge	4A_MICP	16	0.2	0.2	68	ppm
Ge	FUS	8	9.4	0.5	6	ppm
Hf	FUS	16	8.8	0.4	5	ppm
Ho	4A_MICP	16	0.1	0.02	16	ppm
Ho	FUS	16	0.2	0.04	26	ppm
In	4A_MICP	1	0.02	*	*	ppm
K	FUS	16	3294.3	567.0	17	ppm
K <sub>2</sub> O	FUS	16	0.4	0.1	17	%
La	4A_MICP	16	1.7	0.6	37	ppm
La	FUS	15	3.4	2.0	58	ppm
LOI	LOI	40	0.5	0.1	13	%
Lu	FUS	8	0.1	0.1	58	ppm

Element	Generic Method	n	Mean	SD	RSD %	Unit
Mg	4A_MICP	32	384.7	139.7	36	ppm
Mg	FUS	32	636.5	133.9	21	ppm
MgO	FUS	32	0.1	0.02	21	%
MgO	XRF	37	0.1	0.03	34	%
Mo	FUS	1	3.0	*	*	ppm
Moisture	Moisture	24	0.1	0.02	15	%
Nd	4A_MICP	16	2.6	0.3	11	ppm
Nd	FUS	15	2.8	0.3	10	ppm
Ni	FUS	8	14.9	0.6	4	ppm
P	FUS	15	1421.5	43.9	3	ppm
Pb	FUS	16	27.3	1.7	6	ppm
Pr	4A_MICP	16	0.7	0.1	18	ppm
Pr	FUS	15	0.8	0.1	10	ppm
Rb	4A_MICP	32	838.7	120.6	14	ppm
Rb	FUS	16	957.8	80.7	8	ppm
Rb <sub>2</sub> O	XRF	16	0.1	0.004	5	%
S	Combustion/LECO	32	0.02	0.003	15	%
S	XRF	8	0.02	*	*	%
Sm	4A_MICP	16	3.2	0.5	16	ppm
Sm	FUS	16	3.3	0.2	7	ppm
Sn	4A_MICP	24	156.5	9.8	6	ppm
Sn	XRF	8	577.5	10.4	2	ppm
SO <sub>3</sub>	XRF	8	0.04	0.005	11	%
Sr	4A_MICP	38	22.5	5.0	22	ppm
Sr	FUS	15	31.0	1.6	5	ppm
SrO	XRF	1	0.01	*	*	%
Tb	4A_MICP	16	0.6	0.2	42	ppm
Tb	FUS	16	0.8	0.04	5	ppm
Te	4A_MICP	12	0.1	0.02	21	ppm
Th	4A_MICP	40	3.7	1.7	47	ppm
Th	FUS	16	5.2	0.4	9	ppm
Ti	FUS	24	344.5	53.1	15	ppm
TiO <sub>2</sub>	FUS	24	0.1	0.01	15	%
Tl	FUS	15	7.0	0.5	7	ppm
Tm	4A_MICP	8	0.1	0.01	17	ppm
Tm	FUS	3	0.1	0.01	10	ppm
U	4A_MICP	40	2.8	1.3	47	ppm
U	FUS	16	4.4	0.2	6	ppm
V <sub>2</sub> O <sub>5</sub>	XRF	8	0.001	0.001	38	%
Y	4A_ICPES	8	10.0	0.3	3	ppm
Y	4A_MICP	40	6.7	2.8	42	ppm
Y	FUS	16	11.3	0.5	5	ppm
Yb	FUS	16	0.3	0.1	21	ppm
Zn	FUS	8	62.5	8.3	13	ppm
Zr	FUS	16	52.7	6.2	12	ppm
ZrO <sub>2</sub>	XRF	8	0.01	*	1	%

\* denotes that the results were too similar and SD and RSD% could not be calculated

Appendix 2 through 9, prepared by Allan Fraser.

## Appendix 2. Certification of Reference Material and Estimation of Measurement Uncertainty

In the establishment of a consensus value for the CRM, outlier tests are carried out followed by performance statistics and the estimation of the measurement uncertainty. In practice, it is highly likely that data generated by multiple laboratories as an inter-laboratory comparison of material for certification, will contain erroneous as well as extreme measurements (outliers). The influence of outliers on summary statistics needs to be minimised by the application of procedures for outlier identification on raw data. The use of z-scoring, Cochran's test for suspect repeatability variances, along with Grubbs test for suspect measurement values allows for the detection of outliers (IUPAC, 1995). Method performance in terms of precision as relative standard deviation is judged by the application of the Horwitz ratio, which gives an indication of whether the observed relative standard deviation at the concentration levels of analyte determined are acceptable (Horwitz & Albert, 2006).

In the absence of an extensive uncertainty budget, measurement uncertainty is estimated from the reproducibility standard deviation from inter-laboratory data and reported as an expanded uncertainty at a level of confidence of 95% (Miller & Miller, 2010).

The steps below give detail on the establishment of a consensus value through the elimination of outliers, method performance and estimation of measurement uncertainty using standard uncertainties and the analysis of variance.

### Z-Score

A z-score is calculated using equation [1]:

$$z = \frac{x - x_a}{s_p} \quad [1]$$

Where,  $x$  is the result of a submitted sample,  $x_a$  is the mean and  $s_p$  is the standard deviation of the submitted results from all the participating laboratories. Z-Scores are interpreted as follows:

$|z| \leq 2$  satisfactory performance  
 $2 < |z| \leq 3$  questionable performance  
 $|z| > 3$  unsatisfactory performance

(Thompson & Lowthian, 2011)

Data with z-scores exceeding two are discarded and are not included for further assessment.

### Cochran's Test

The test of Cochran (1950) as shown in equation [2] is applied to any suspect repeatability variances:

$$C_{calc} = \frac{s_{max}^2}{\sum_{i=1}^l s_i^2} \quad [2]$$

Where,  $C_{calc}$ ,  $s_{max}^2$  and  $\sum_{i=1}^l s_i^2$ , are the calculated values for Cochran's test, data set with the maximum variance and the sum of the variances of all of the participating,  $l$  laboratory datasets. The  $C_{calc}$  value is compared with a critical value,  $C_{crit}$  at a level of confidence of 95% and an alpha of 0.05% (see Ellison, *et al.*, 2009, Appendix A, Table A.3a, page 209 for a table of critical values for the test of Cochran at LOC 95%).



According to ISO 5725-2 (1999), results from a laboratory with a suspect repeatability variance can be excluded if it is shown by the Cochran test to be an outlier. Therefore, if  $C_{calc} > C_{crit}$ , the laboratory with the maximum variance is removed. The data found to be excluded should not be  $>2/9$ , or 22% of the total data.

### Grubbs Test

The test of Grubbs (1969) calculates a test statistic,  $G_{calc}$  and in the detection of a single outlier,  $G_1$  is found by using

$$G_{1\,calc} = \frac{|Suspect\ value - \bar{x}|}{s} \quad [3]$$

Where, the sample mean and standard deviation,  $\bar{x}$  and  $s$ , are calculated with the suspect value included. The  $G_{1\,calc}$  statistic is compared to a critical value for  $N$  measurements. See Ellison, *et al.*, 2009, Appendix A, Table A.2, page 208 for a table of critical values for the test of Cochran at LOC 95%.

### Method Performance

The Horwitz function is used to assess the performance of the data under consideration, with respect to precision (Horwitz & Albert, 2006). A calculated %RSD is found using the Horwitz expression

$$\%RSD = \pm 2^{(1-0.5\log C)} \quad [4]$$

where,  $C$  is the analyte concentration in percent divided by 100 and  $\log$  is the natural logarithm. The observed %RSD is calculated as

$$Observed\ \%RSD = \frac{s}{Mean} \times 100 \quad [5]$$

where  $s$  is the standard deviation of  $n$  replicates.

The ratio of the observed %RSD and the calculated %RSD gives the Horwitz ratio (HorRat):

$$HorRat = \frac{\%RSD\ Observed}{\%RSD\ Calculated} \quad [6]$$

A HorRat  $<2$  indicates that the method is of adequate precision. Should the HorRat be  $>2$  the overall data are discarded, and the candidate material considered not suitable for certification as the precision is excessive for the concentration of the analyte being determined (Nelsen & Wehling, 2008).

### Grand Mean

The grand mean ( $\bar{\bar{x}}$ ) *i.e.* the certified value of a dataset is the total of all the data values divided by the total sample size ( $n$ ):

$$\bar{\bar{x}} = \sum \frac{x}{n} \quad [7]$$

### Certified Value

From ANOVA as per the description in section 18, an 'appropriate precision' as shown in [8] is calculated for sufficient homogeneity (Thompson, 2008):

$$s_r \leq 0.3u_c \quad [8]$$

Where,  $s_r$  is the within laboratory repeatability, as determined from [14]. Once [8] is satisfied, a grand mean [7] is calculated and this is taken to be the certified value.

### Total Variation (SST)

The total variation (not the variance) comprises the sum of the squares of the differences of each mean with the grand mean.

$$SST = \sum (x - \bar{x})^2 \quad [9]$$

### Between Group Variation (SSB)

The *variation* due to the between the laboratories is denoted SSB or Sum of Squares Between laboratories and given by [10]. If the laboratory means are close to each other (and therefore the Grand Mean) SSB will be a small value. There are P samples involved with one datum value for each sample (the sample mean), so there are P-1 degrees of freedom.

$$SSB = \sum n(\bar{x} - \bar{\bar{x}})^2 \quad [10]$$

The *variance* due to the interaction between the laboratories is denoted MSB for Mean Square Between groups and is the SSB divided by its degrees of freedom.

$$MS = \frac{SSB}{n - 1} \quad [11]$$

### Within Group Variation (SSW)

The variation due to differences within individual samples is denoted SSW for Sum of Squares Within laboratories. The degrees of freedom are equal to the sum of the individual degrees of freedom for each sample. Since each sample has degrees of freedom (*df*) equal to one less than their sample sizes, and there are *k* samples, the total degrees of freedom is P less than the total sample size:  $df = n - P$ .

$$SSW = \sum df \cdot s^2 \quad [12]$$

The variance due to the differences within individual samples is denoted MSW for Mean Square Within groups. This is the within group variation divided by its degrees of freedom:

$$MSW = \frac{SSW}{P - n} \quad [13]$$

From equations [9] through [13], the ANOVA table as shown in Table 10 is developed.

**Table 10.** A single-factor ANOVA table showing key elements. Where P is the total number of groups, or laboratories. P-1 is 1 less than number of laboratories, P (n-1) is the number of data values minus number of groups (equals degrees of freedom for each group added together), and P-1 + P(n-1) is 1 less than the number of data points. MS is the mean squares of between laboratories and within laboratories. After Ellison *et al.*, (2009), Table 6.2, page 61.

Source	Sum of Squares	df	Mean Sum of Squares	F	p	F <sub>crit</sub>
Between Laboratories	SSB	P-1	MSB=SSB/df	MSB/MSW	=FDIST(x,df,df)	F-table
Within Laboratories	SSW	P(n-1)	MSW=SSW/df	–	–	–
Total	SSB+SSW	P-1 + P(n-1)	–	–	–	–

### Combined Standard Uncertainty

The combined standard uncertainty ( $u_c$ ) represents the effects of random events such as days, instruments, and analysts on the precision of the analytical procedures of all accepted data of the participating laboratories. Using the output from ANOVA, the combined standard uncertainty ( $u_c$ ) is determined from the square root of the sum of squares of the variances of the within laboratory repeatability,  $s_r$ , and the between laboratory precision,  $s_s$ :

$$u_c = \sqrt{s_r^2 + s_s^2} \quad [14]$$

Within laboratory repeatability is determined as

$$s_r = \sqrt{MSB} \quad [15]$$

and, the between laboratory precision as

$$s_s = \sqrt{\frac{(MSW - MSB)}{n}} \quad [16]$$

where  $MSW$  is the mean squares of the within laboratory variance,  $MSB$  is the mean squares for the between laboratories and  $n$  in this case, is the number of replicates in a group of the accepted data (Thompson & Lowthian, 2011).

### Expanded Uncertainty

The expanded uncertainty ( $U$ ) at a confidence level of 95% is determined by multiplication of the combined uncertainty ( $u_c$ ) by a coverage factor ( $k$ ) found from  $N-1$  degrees of freedom ( $df$ ), where  $N$  is the number of laboratory means accepted in the establishment of the certified value. The t-critical value for 5% significance can be found in a t-critical table (see Appendix 9, or from MS Excel as =TINV (5%,  $df$ )).

### Uncertainty Statement

Typically, an uncertainty statement is presented as follows: Au =0.77±0.04 g/t, where the number following the symbol ± is the numerical value of an expanded uncertainty,  $U = ku_c$ , with  $U$  determined from a combined standard uncertainty multiplied by a coverage factor  $k = 2$  or, a t-critical value for  $N-1$  accepted laboratories. Since it can be assumed that the possible estimated values of the standard are approximately normally distributed with standard uncertainty,  $u_c$ , the certified value of the CRM is believed to lie in the interval defined by  $U$  with a level of confidence of approximately 95 %, e.g. a mean value of 0.77±0.04g/t will have intervals of: 0.73≤0.77≤0.81 g/t.

### Appendix 3. Example: Comparison of Mean and Certified Value for Validation of Accuracy

According to ERM (2005); Eurolab (2007); Abzalov (2011) and Carr (2011), the validation of accuracy for a given mean and certified value requires the inclusion of the measurement uncertainty of the CRM in a t-test for statistical significance. The classical Student's t-test as shown in [17], does not consider the measurement uncertainty of the CRM. To compensate for this, Eurolab Technical Report No.1/2007 recommends equation [18] for the validation of CRMs with stated measurement uncertainties.

$$t_{calc} = \frac{|\bar{x} - \mu|}{\frac{s}{\sqrt{n}}} \quad [17]$$

$$t_{calc} = \frac{|\bar{x} - \mu|}{\sqrt{(u_{\mu})^2 + \frac{s^2}{n}}} \quad [18]$$

Where,  $t_{calc}$  is the calculated t-statistic,  $\bar{x}$  the mean of  $n$  replicates with a standard deviation of  $s$  for a CRM of  $\mu$  certified value. The standard uncertainty  $u$  is the stated expanded uncertainty ( $U$ ) of the CRM divided by the coverage factor ( $k$ ) as stated on the certificate of analysis. Note that the  $| \quad |$  bars indicate that the absolute value between the mean and the certified value is to be used, *i.e.* ignore the sign.

An example in which [18] is used for validation of accuracy is given below.

#### Example

A CRM is independently replicated nine times for  $Al_2O_3$  concentration by XRF analysis, *i.e.* 9 individual fused glass beads were prepared. The observed mean and standard deviation of the replicate data are shown with the certified value and expanded uncertainty in Table 11. In validation of accuracy, the hypothesis question is: Is the difference between the observed mean and the certified value statistically significant at a level of confidence of 95%? Alternatively put, is there sufficient evidence to conclude that the data *i.e.* replicates generated, are inaccurate?

The relevant hypotheses are:

**Null hypothesis:**  $H_0$ : Mean = Certified value of CRM with stated measurement uncertainty. The acceptance of  $H_0$  means that accuracy is demonstrated; *i.e.* insufficient evidence to reject  $H_0$ ;

**Alternate hypothesis:**  $H_1$ : Mean  $\neq$  Certified value of CRM with stated measurement uncertainty. The acceptance of  $H_1$  means that accuracy is not demonstrated, *i.e.* there is sufficient evidence to accept  $H_1$ ;

**Table 11.** CRM certified value quoted expanded uncertainty  $U$ , the coverage factor for the CRM,  $k=2.25$  and mean for  $n=9$  replicates and corresponding standard deviation for the replicate data.

CRM Certified Value	Expanded % ( $U$ )	Coverage Factor ( $k$ )	Mean ( $n=9$ )	$n$	Standard Deviation ( $s$ )
4.62%	0.08%	2.25	4.59%	9	0.01015

The standard uncertainty ( $u$ ) is found by dividing the expanded uncertainty by the coverage factor:

$$u = \frac{0.08}{2.25} = 0.0356 \%$$

Using the observed mean for the replicate data ( $n=9$ ) obtained for the CRM and substituting into [18]:

$$t_{calc} = \frac{|\bar{x} - \mu|}{\sqrt{0.0356^2 + \frac{0.01015^2}{9}}} = \frac{|4.59 - 4.62|}{\sqrt{0.00126 + 0.00001145}} = 0.84$$

Therefore,  $t_{calc} = 0.84$  and  $t_{crit}(5\%, 8) = 2.31$  ( $df$  is 8, therefore,  $t_{crit}=2.31$ , see Appendix 9, page 32) which is  $>0.84$ . Similarly, the  $p$ -value=0.43 which is  $>0.05$ . This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known, the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

#### Appendix 4. Two-standard Deviations

Two-standard deviations are calculated using the expression:

$$\text{Two standard deviations} = 2 (u_c) \quad [19]$$

Where,  $u_c$  is the standard combined uncertainty (equation [14]).

#### Appendix 5. Confidence Interval

Confidence interval is calculated as:

$$\text{Confidence Interval (CI)} = \frac{(t_{critical})s}{\sqrt{N}} \quad [20]$$

Where,  $N$  is the number of laboratories (accepted laboratory data),  $t_{critical}$  is a two-tailed value for  $N - 1$  degrees of freedom ( $df$ ) and  $s$ , is the standard deviation of the accepted laboratory means. A two-tailed critical value is found for  $N - 1$  degrees of freedom from either a  $t$ -distribution table (Appendix 9) or MS Excel as =TINV (5%,  $df$ ).

#### Appendix 6. Using the CRM in Quality Control

QC chart control limits should not be determined by the certified value and stated measurement uncertainty of the certified reference material used. These parameters although “certified” will never be known; it is only the corresponding statistical estimates, *i.e.* standard deviation and the mean calculated from replicated results that are known and these should be used in quality control charts. However, should the laboratory choose to use the certified value as the mean then the quoted  $2s$ , or  $CI$  value for the CRM can be used in the quality control chart.

It is recommended that a Shewhart chart be developed for the use if this CRM is to be used as a control sample in laboratory quality control. A Shewhart chart is a plot of sequential assay results obtained from quality control material such as an AMIS CRM. The warning and control limits are based on the standard deviation obtained from the mean of the replicates of a CRM (Ellison, *et al.*, 2009; Thompson, 2010). The procedure in preparing a Shewhart chart is as follows:

1. Analyse 10 to 15 replicates or more of the AMIS CRM.
2. Apply the Grubbs test for outliers.
3. Determine the mean of the replicates after application of the Grubbs test.
4. Determine the standard deviation, using equation [21], of the replicates following Grubbs test.
5. Calculate the standard deviation,  $s$  from:

$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n - 1}} \quad [21]$$

where,  $x_i$  is an individual measurement in the data set,  $\bar{x}$  is the mean of the data set at  $n-1$  degrees of freedom ( $df$ ) and  $n$  is the number of replicates. The sample standard deviation can be found using the MS Excel formula “=stdev.s (number1;)”.

6. Verify accuracy of the mean value using equation [18].
7. Once accuracy is verified, calculate  $\pm 2s$  and  $\pm 3s$ , where  $s$  is the standard deviation calculated from [21].
8. Construct the Shewhart control chart around the mean of  $n$  replicates.
9. Use  $\pm 2s$  as the warning limits.
10. Use  $\pm 3s$  as the control limits.
11. It is recommended that if 2 to 3 points are outside the warning limits analyse another sample and if it is then within warning limits, continue. If it is outside the warning limits, stop and troubleshoot.
12. It is recommended that if any point is outside control limits, analyse another portion (sample) of the CRM. If it is within control limits, continue. If it is outside control limits, stop and troubleshoot.
13. For reference purposes, the CRM certified value can be plotted on the Shewhart chart alongside the mean value.

On a regular basis the accuracy of the replicates of the CRM should be assessed in terms of the certified value of the CRM using equation [18].

#### **Appendix 7. Conversion to Air-dry Basis** (Prepared by Allan Fraser)

Since AMIS certified analyte values are reported on a dry-basis, the user laboratory is required to dry a portion (accurately weigh out 1.0 grams in duplicate) of the CRM material in air at 105°C in a drying oven to constant mass to determine the moisture content. Use a crucible with a flat inner surface with a surface area not smaller than 10 cm<sup>2</sup> with the CRM material spread evenly over same; this represents a 0.1 gram spread per cm<sup>2</sup>. In correcting the certified value for moisture content, a moisture correction factor is calculated:

$$\text{Moisture correction factor (MCF)} = \frac{100 - \% \text{Moisture at } 105^{\circ}C}{100} \quad [22]$$

$$\text{Air dry basis concentration} = \text{MCF} \times \text{certified value on a dry basis} \quad [23]$$

#### **Example**

The moisture content determined at 105°C on a CRM is 0.500%. The certified analyte concentration for the CRM is 12.62±0.52% (dry basis). Calculating the moisture correction factor using [22] gives:

$$\text{Moisture correction factor} = \frac{100 - 0.500}{100} = 0.995$$

Multiplying the factor of 0.995 by the certified value as stated on the certificate of analysis on a dry basis (as in [23]) gives the analyte concentration on an air-dry basis:

$$0.995 \times 12.62\% = 12.56\%$$

The stated measurement uncertainty also needs to be corrected using [22] and [23], e.g.  $0.995 \times 0.52 = 0.51_{(7)}$ , rounded to 0.52%. The air-dry basis concentration *i.e.*  $12.56 \pm 0.52\%$  is to be used as the certified value with its corresponding measurement of uncertainty.

#### Appendix 8. Example of Determination of LOD and LOQ in Fire Assay

The limit of detection (LOD) is the minimum detectable quantity of the analyte of interest (Skoog & West, 1985). To determine the LOD in fire assay by lead collection, the minimum mass that an assay microbalance is capable of weighing ( $m$  in micrograms, and the original test sample mass,  $Mass_{assay}$  in grams) determines the LOD. The smallest prill mass most assay microbalances can measure is  $1\mu\text{g}$  or  $0.001\text{mg}$ . Even with a microscope it may be difficult to locate and pick up a prill weighing ten times that amount (*i.e.*  $0.01\text{mg}$  or  $10\mu\text{g}$ ) and weigh it. If an analyst can weigh a prill of  $1\mu\text{g}$  then the LOD becomes  $1\mu\text{g}$ . However, the concentration factor would be 50 times for a 50-gram assay sample and therefore the LOD in g/t becomes  $1\mu\text{g}$  divided by the original mass of the sample in grams taken for fire assay [24]. Therefore, the LOD in fire assay is computed as:

$$LOD = \frac{m (\mu\text{g})}{Mass_{assay} (g)} (\text{g/t}) \quad [24]$$

The limit of quantitation (LOQ), is simply the LOD multiplied by 10 (Long & Winefordner, 1983):

$$LOQ = 10 \cdot \frac{m (\mu\text{g})}{Mass_{assay} (g)} (\text{g/t}) \quad [25]$$

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be  $0.02\text{g/t}$ . *i.e.*  $1\mu\text{g} = 1\text{g/t}$ , therefore  $1\mu\text{g}/50\text{g} = 0.02\text{g/t}$ . If no prill was found, then the LOD result would be  $<0.02\text{g/t}$  or "not detected". Using a larger assay sample mass improves the LOD and LOQ (Table 11). Table 13 gives a recommended reporting scheme for LOD and LOQ.

**Table 12.** Mass of assay sample and corresponding limit of detection and limit of quantitation for an assay microbalance capability of smallest prill mass of  $1\mu\text{g}$  or  $0.001\text{mg}$ .

Mass Assay Sample (g)	LOD (g/t)	LOQ (g/t)
30	0.03	0.3
50	0.02	0.2
100	0.01	0.1

**Table 13.** Recommended reporting scheme for LOD and LOQ in fire assay.

Data	Report as
<LOD	Not detected
<LOQ	Detected
$\geq\text{LOQ}$	Report assay result

**Appendix 9.** T-distribution table

**Table 14.** T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence.

<b>df</b>	<b>Two-tailed</b>	<b>df</b>	<b>Two-tailed</b>
1	12.71	23	2.06
2	4.30	24	2.06
3	3.18	25	2.06
4	2.78	26	2.05
5	2.57	27	2.05
6	2.44	28	2.04
7	2.36	29	2.04
8	2.30	30	2.04
9	2.26	35	2.03
10	2.22	40	2.02
11	2.20	45	2.01
12	2.17	50	2.00
13	2.16	55	2.00
14	2.14	60	2.00
15	2.13	70	1.99
16	2.12	80	1.98
17	2.11	90	1.98
18	2.10	100	1.98
19	2.09	120	1.98
20	2.08	Infinity	1.96
21	2.08		
22	2.07		

**End of certificate**