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Certificate

# AMIS0642

## Certified Reference Material

### B2 Gold, Namibia

## *Certificate of Analysis*

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## Summary Statistics

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

Analyte	Method	Certified ( $\mu$ ) <sup>8</sup>	(2s) <sup>10</sup> $\pm$	Unit
Au	Pb Collection <sup>1</sup>	0.121	0.023	g/t
Pd	Pb Collection	0.019	0.0014	g/t
C	Combustion/LECO <sup>2</sup>	3.04	0.14	%
S	Combustion/LECO	1.16	0.079	%
S	4A_MICP <sup>3</sup>	1.18	0.15	%
LOI	LOI <sup>4</sup>	9.52	0.96	%
SG	SG <sup>5</sup>	2.78	0.13	Dimensionless
Al	FUS <sup>6</sup>	6.55	0.19	%
As	4A_MICP	33	4	ppm
Ba	4A_MICP	30	8	ppm
Be	4A_MICP	0.6	0.1	ppm
Bi	4A_MICP	0.2	0.04	ppm
Ca	4A_MICP	6.21	0.32	%
Co	4A_MICP	17	6	ppm
Cr	4A_MICP	122	11	ppm
Cr	FUS	155	14	ppm
Cs	4A_MICP	1	0.2	ppm
Cu	4A_MICP	65	16	ppm
Fe	4A_MICP	4.93	0.28	%
Fe	FUS	4.98	0.13	%
Hf	4A_MICP	3	0.9	ppm
K	4A_MICP	1532	137	ppm
La	4A_MICP	31	8	ppm
Li	4A_MICP	9	1	ppm
Mg	4A_MICP	1.78	0.031	%
Mg	FUS	1.94	0.055	%
Mn	4A_MICP	1193	87	ppm
Mn	FUS	1267	68	ppm
Na	4A_MICP	4.76	0.29	%
Ni	4A_MICP	48	8	ppm
P	4A_MICP	712	47	ppm
Pb	4A_MICP	17	4	ppm
Rb	4A_MICP	9	0.7	ppm
Sb	4A_MICP	2	0.3	ppm
Si	FUS	23.78	0.78	%
Sr	4A_MICP	108	14	ppm
Ta	4A_MICP	0.7	0.09	ppm
Th	4A_MICP	9	0.8	ppm
Ti	4A_MICP	3652	211	ppm
Ti	FUS	3908	396	ppm
U	4A_MICP	4	0.3	ppm
V	4A_MICP	136	17	ppm
Y	4A_MICP	20	5	ppm
Zn	4A_MICP	47	4	ppm
Zr	4A_MICP	115	18	ppm

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

Analyte	Method	Certified ( $\mu$ ) <sup>8</sup>	(2s) <sup>10</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	FUS	12.37	0.35	%
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>7</sup>	12.27	0.16	%
CaO	XRF	8.92	0.12	%
Cr <sub>2</sub> O <sub>3</sub>	FUS	0.022	0.003	%
Cr <sub>2</sub> O <sub>3</sub>	XRF	0.020	0.0004	%
Fe <sub>2</sub> O <sub>3</sub>	FUS	7.12	0.19	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	7.05	0.19	%
K <sub>2</sub> O	XRF	0.18	0.01	%
MgO	FUS	3.22	0.093	%
MgO	XRF	3.25	0.066	%
MnO	FUS	0.16	0.01	%
MnO	XRF	0.16	0.01	%
Na <sub>2</sub> O	XRF	6.45	0.31	%
P <sub>2</sub> O <sub>5</sub>	XRF	0.16	0.01	%
SiO <sub>2</sub>	FUS	50.87	1.7	%
SiO <sub>2</sub>	XRF	49.16	0.53	%
TiO <sub>2</sub>	FUS	0.65	0.07	%
TiO <sub>2</sub>	XRF	0.67	0.02	%

## 1. Certified Concentrations and Uncertainties

AMIS0642 is a new standard material, developed and certified in June 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>8</sup>	N	n	k	% RSD	( $u_c$ ) <sup>9</sup>	(2s) <sup>10</sup> $\pm$	(CI) <sup>11</sup> 95%	(U) <sup>12</sup> $\pm$	Unit
Au	Pb Collection <sup>1</sup>	0.121	14	108	2.160	9	0.011	0.023	0.0050	0.02	g/t
Pd	Pb Collection	0.019	3	24	4.303	4	0.00070	0.0014	0.0010	0.003	g/t
C	Combustion/LECO <sup>2</sup>	3.04	6	48	2.571	2	0.070	0.14	0.071	0.2	%
S	Combustion/LECO	1.16	8	64	2.365	3	0.039	0.079	0.031	0.09	%
S	4A_MICP <sup>3</sup>	1.18	4	30	3.182	6	0.074	0.15	0.12	0.2	%
LOI	LOI <sup>4</sup>	9.52	6	48	2.571	5	0.48	0.96	0.50	1	%
SG	SG <sup>5</sup>	2.78	5	39	2.776	2	0.066	0.13	0.080	0.2	Dimensionless
Al	FUS <sup>6</sup>	6.55	2	15	12.706	1	0.095	0.19	0.74	1	%
As	4A_MICP	33	4	32	3.182	6	2	4	2	7	ppm
Ba	4A_MICP	30	4	32	3.182	13	4	8	6	12	ppm
Be	4A_MICP	0.6	4	32	3.182	9	0.05	0.1	0.08	0.2	ppm
Bi	4A_MICP	0.2	2	16	12.706	10	0.02	0.04	0.2	0.3	ppm
Ca	4A_MICP	6.21	4	31	3.182	3	0.16	0.32	0.23	0.5	%
Co	4A_MICP	17	5	39	2.776	18	3	6	4	8	ppm
Cr	4A_MICP	122	3	24	4.303	4	5	11	11	23	ppm
Cr	FUS	155	3	23	4.303	5	7	14	16	30	ppm
Cs	4A_MICP	1	3	24	4.303	8	0.1	0.2	0.2	0.4	ppm
Cu	4A_MICP	65	5	40	2.776	13	8	16	10	23	ppm
Fe	4A_MICP	4.93	3	24	4.303	3	0.14	0.28	0.34	0.6	%
Fe	FUS	4.98	4	30	3.182	1	0.067	0.13	0.053	0.2	%
Hf	4A_MICP	3	3	24	4.303	13	0.4	0.9	1	2	ppm
K	4A_MICP	1532	5	40	2.776	4	68	137	58	190	ppm
La	4A_MICP	31	4	32	3.182	14	4	8	7	13	ppm
Li	4A_MICP	9	3	24	4.303	7	0.6	1	1	3	ppm
Mg	4A_MICP	1.78	2	16	12.706	1	0.016	0.031	0.024	0.2	%
Mg	FUS	1.94	4	30	3.182	1	0.028	0.055	0.019	0.09	%
Mn	4A_MICP	1193	4	31	3.182	4	43	87	64	138	ppm
Mn	FUS	1267	3	23	4.303	3	34	68	78	147	ppm
Na	4A_MICP	4.76	4	30	3.182	3	0.14	0.29	0.23	0.5	%
Ni	4A_MICP	48	6	46	2.571	8	4	8	4	10	ppm
P	4A_MICP	712	4	30	3.182	3	23	47	22	74	ppm
Pb	4A_MICP	17	5	39	2.776	12	2	4	2	5	ppm
Rb	4A_MICP	9	3	23	4.303	4	0.4	0.7	0.8	2	ppm
Sb	4A_MICP	2	2	16	12.706	7	0.2	0.3	1	2	ppm
Si	FUS	23.78	3	22	4.303	2	0.39	0.78	0.64	2	%
Sr	4A_MICP	108	5	39	2.776	6	7	14	8	19	ppm
Ta	4A_MICP	0.7	3	24	4.303	6	0.05	0.09	0.09	0.2	ppm
Th	4A_MICP	9	3	24	4.303	4	0.4	0.8	0.9	2	ppm
Ti	4A_MICP	3652	3	22	4.303	3	106	211	212	454	ppm
Ti	FUS	3908	4	31	3.182	5	198	396	307	631	ppm
U	4A_MICP	4	3	24	4.303	4	0.1	0.3	0.3	0.6	ppm
V	4A_MICP	136	5	38	2.776	6	8	17	10	23	ppm
Y	4A_MICP	20	3	24	4.303	13	3	5	6	11	ppm
Zn	4A_MICP	47	5	39	2.776	4	2	4	2	5	ppm
Zr	4A_MICP	115	4	32	3.182	8	9	18	14	28	ppm

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

Analyte	Method	Certified ( $\mu$ ) <sup>8</sup>	N	n	k	% RSD	( $u_c$ ) <sup>9</sup>	(2s) <sup>10</sup> $\pm$	(CI) <sup>11</sup> 95%	(U) <sup>12</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	FUS	12.37	2	15	12.706	1	0.18	0.35	1.0	2	%
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>7</sup>	12.27	6	46	2.571	1	0.082	0.16	0.079	0.2	%
CaO	XRF	8.92	5	40	2.776	1	0.060	0.12	0.057	0.2	%
Cr <sub>2</sub> O <sub>3</sub>	FUS	0.022	4	31	3.182	7	0.002	0.003	0.002	0.005	%
Cr <sub>2</sub> O <sub>3</sub>	XRF	0.020	4	30	3.182	1	0.0002	0.0004	0.0001	0.001	%
Fe <sub>2</sub> O <sub>3</sub>	FUS	7.12	4	30	3.182	1	0.096	0.19	0.076	0.3	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	7.05	6	46	2.571	1	0.096	0.19	0.10	0.2	%
K <sub>2</sub> O	XRF	0.18	6	46	2.571	4	0.006	0.01	0.006	0.02	%
MgO	FUS	3.22	4	30	3.182	1	0.046	0.093	0.030	0.1	%
MgO	XRF	3.25	6	47	2.571	1	0.033	0.066	0.031	0.09	%
MnO	FUS	0.16	3	23	4.303	3	0.004	0.01	0.01	0.02	%
MnO	XRF	0.16	5	40	2.776	2	0.004	0.01	0.002	0.01	%
Na <sub>2</sub> O	XRF	6.45	5	37	2.776	2	0.15	0.31	0.21	0.4	%
P <sub>2</sub> O <sub>5</sub>	XRF	0.16	4	32	3.182	2	0.003	0.01	0.004	0.01	%
SiO <sub>2</sub>	FUS	50.87	3	22	4.303	2	0.83	1.7	1.0	4	%
SiO <sub>2</sub>	XRF	49.16	5	40	2.776	1	0.26	0.53	0.30	0.7	%
TiO <sub>2</sub>	FUS	0.65	4	31	3.182	5	0.03	0.07	0.05	0.1	%
TiO <sub>2</sub>	XRF	0.67	6	45	2.571	2	0.01	0.02	0.009	0.03	%

1. Pb Collection
2. Combustion/LECO
3. 4A\_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
4. LOI is Loss on Ignition
5. SG is Specific Gravity
6. FUS is Fusion digestion with ICP finish
7. XRF is X-ray Fluorescence
8. 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.
9. 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. ( $u_c$ )
10. Two standard deviations (2s)
11. Confidence interval at 95% level of confidence.
12. 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:  $U = 2.36 \times 0.23 = 0.5\%$
13. The nugget effect is a geostatistical term used to describe the variability seen between samples that are closely spaced. The nugget effect is composed of a geological component, which can be thought of as inherent, and a sampling component, which is not fixed. The geological contribution to the nugget effect is described in terms of geological continuity for quart-gold reefs, kimberlites and placer deposits as these are all subject to a high nugget effect (>50%). The geological nugget effect is attributed to the heterogeneous distribution of grain sizes, grades and small to large scale structures inherent in these deposits
14. ANC is Acid Neutralizing Capacity
15. AP is Acid Potential
16. MPA is Mycophenolic Acid
17. NAGpH is Net Acid Generation pH
18. NNP is Net Neutralizing Potential
19. NP is Neutralizing Potential
20. NPR is Neutralizing Potential Ratio

## 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
S Combustion/LECO	1.16 %	S 4A_MICP	1.18 %	Unequal Variance ( $p=0.048$ )	0.702	Accept $H_0$ ; certified values are equal
Al <sub>2</sub> O <sub>3</sub> FUS	12.37 %	Al <sub>2</sub> O <sub>3</sub> XRF	12.27 %	Equal Variance ( $p=0.096$ )	0.229	Accept $H_0$ ; certified values are equal
Cr <sub>2</sub> O <sub>3</sub> FUS	0.022 %	Cr <sub>2</sub> O <sub>3</sub> XRF	0.020 %	Unequal Variance ( $p < 0.001$ )	0.081	Accept $H_0$ ; certified values are equal
Fe <sub>2</sub> O <sub>3</sub> FUS	7.12 %	Fe <sub>2</sub> O <sub>3</sub> XRF	7.05 %	Equal Variance ( $p=0.134$ )	0.228	Accept $H_0$ ; certified values are equal
MgO FUS	3.22 %	MgO XRF	3.25 %	Equal Variance ( $p=0.253$ )	0.093	Accept $H_0$ ; certified values are equal
MnO FUS	0.164 %	MnO XRF	0.161 %	Equal Variance ( $p=0.097$ )	0.205	Accept $H_0$ ; certified values are equal
SiO <sub>2</sub> FUS	50.87 %	SiO <sub>2</sub> XRF	49.16 %	Equal Variance ( $p=0.075$ )	0.001	Reject $H_0$ ; certified values are <i>not</i> equal
TiO <sub>2</sub> FUS	0.651 %	TiO <sub>2</sub> XRF	0.666 %	Unequal Variance ( $p=0.007$ )	0.441	Accept $H_0$ ; certified values are equal
Cr FUS	0.015 %	Cr 4A_MICP	0.012 %	Equal Variance ( $p=0.317$ )	0.002	Reject $H_0$ ; certified values are <i>not</i> equal
Fe FUS	4.98 %	Fe 4A_MICP	4.93 %	Unequal Variance ( $p=0.024$ )	0.591	Accept $H_0$ ; certified values are equal
Mn FUS	0.127 %	Mn 4A_MICP	0.119 %	Equal Variance ( $p=0.4$ )	0.047	Reject $H_0$ ; certified values are <i>not</i> equal
Ti FUS	0.391 %	Ti 4A_MICP	0.365 %	Equal Variance ( $p=0.167$ )	0.088	Accept $H_0$ ; certified values are equal

## 3. Intended Use

AMIS0642 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

Abbreviation/Symbol	Description
SS	Sum of squares in ANOVA
SST	Total variation in ANOVA
SSB	Between group (laboratory) variance
SSW	Within group (laboratory) variance
2s	Two times standard deviation
SI	Standard International system of units
$t_{\text{calc}}$	Calculated t statistic from a one-sample, two-tailed t-test
t-critical or $t_{\text{crit}}$	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 $k=1$
$u_c$	Combined standard uncertainty at $k=1$
$\mu\text{m}$	Micron, is an SI derived unit of length equaling $1 \times 10^{-6}$ 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

The material for this standard was sourced from the Otjikoto Gold Mine owned by B2Gold Namibia <sup>(13)</sup>. The Otjikoto Gold deposit is located within the Damara Mobile Belt, which forms part of the Pan-African Mobile Belt system. The Otjikoto Gold mine is located about 300 km north of Windhoek, in Otjozondjupa province, in Namibia.

## 9. Approximate Mineral and Chemical Composition

The Otjikoto project is located within the Neoproterozoic Damara mobile belt, which forms part of the Pan–African mobile belt system. The deposit falls under the general classification of an orogenic gold deposit and occurs in a similar stratigraphic position as the Navachab gold mine deposit. The Otjikoto deposit lithology has been divided into three principal mineralized lithostratigraphic units, from top to base, the OTC, OTB, and OTA. The OTC albitite-hornfels unit hosts most of the mineralised vein system and is underlain by a distinct marker horizon, the unmineralised OTB calcitic marble.

Gold in the main Otjikoto deposit is hosted by a north-north-east-striking sheeted sulphide (+ magnetite) –quartz and carbonate vein system. Gold occurs within the vein system as coarse native gold with a size variation from 5microns to 4000 microns. It occurs adjacent to and within sulphides, garnets on the edges of amphiboles and chlorite, as free gold in quartz and carbonates.

## 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 recognised 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.

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

Phase	Formula	Composite %
Amorphous Content		20
Amphibole	$(\text{Na,Ca})_2(\text{Fe,Mg,Al})_5(\text{Si,Al})_8\text{O}_{22}(\text{OH})_2$	3
Calcite	$\text{CaCO}_3$	4
Chlorite	$(\text{Fe,Al,Mg})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$	1
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	15
Illite	$(\text{K,Ca,Na})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$	1
Ilmenite	$\text{FeTiO}_3$	<1
Pyrite	$\text{FeS}_2$	2
Pyrrhotite	$\text{Fe}(1-x)\text{S}_x$ ( $x=0-0.2$ )	
Quartz	$\text{SiO}_2$	8
Sodium Plagioclase	$\text{NaAlSi}_3\text{O}_8$	47
Total		101 %

*For informational purposes only*

## 11. Health and Safety

The material is a very fine powder coloured pale brown (Corstor 5YR 6/2). 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 54 $\mu\text{m}$  (95% passing 54 $\mu\text{m}$ ). The procedure of preparation in brief is as follows: the material was crushed, dry-milled and air-classified to <54 $\mu\text{m}$ . 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	97.9
<54um	98.5
<63um	98.7
<75um	98.9
<90um	99.4
<100um	99.7
<106um	99.8
<150um	100

*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) Au-Pb collection finished with either ICP-OES or ICP-MS or AAS or gravimetric
- b) Multi element scan to include all elements-4-acid total digestion including HF and/or peroxide fusion finished with either ICP-OES or ICP-MS or AAS
- c) LOI and all major oxides with XRF finish and/or Peroxide fusion and/or 4 acid digest including HF finished with either ICP-OES or ICP-MS or AAS (Please specify the temperature for LOI)
- d) SG – gas pycnometer
- e) S and C Combustion/LECO
- f) Moisture
- g) Acid Rock Drainage suite:
- h) Total Sulfur %
- i) Neutralization Potential (kg CaCO<sub>3</sub>/t)
- j) Acid Generating Potential (kg H<sub>2</sub>SO<sub>4</sub>/t)
- k) (NPP) Net-acid potential

## 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 to be reported in ppm.
- d) All results for Au to be reported in ppm.
- e) Report all QC data, to include replicates, blanks and certified reference materials used.
- f) All Round robin samples must be treated the same as routine test samples.
- g) All results must be reported to maximum decimal places i.e. dependent on laboratories capabilities
- h) 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.
- i) 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.
- j) Please send excel and PDF of all results.
- k) Ensure correct PPE is used i.e. gloves, dust masks and protective clothing.
- l) 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. Antech ALS Geochemistry Arabia
2. ALS Geochemistry Ireland
3. ALS Geochemistry Vancouver
4. Antech Zimbabwe
5. Argetest Mineral Processing, R&D and Analysis Services
6. Bureau Veritas Adelaide GeoAnalytical Laboratory
7. Bureau Veritas Minerals Ultra Trace Pty Ltd
8. Intertek Perth
9. Performance Laboratories Zimbabwe
10. Ready Lead Assay Laboratory
11. SGS Ankara (Turkey)
12. SGS Geosol Laboratories Ltda (Brazil)
13. SGS South Africa
14. SGS South Africa (Pty) Ltd - Barberton
15. SGS Vancouver (Canada)
16. Shiva Analyticals India
17. Super Laboratory Services (Pty) Ltd. Springs



## 24. Accepted Assay Data

Data from the 17 laboratories used for certification are set out in Table 8.

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

FUS	XRF	XRF	FUS	XRF	FUS	XRF	XRF	FUS
Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Cr <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO
%	%	%	%	%	%	%	%	%
12.46	12.30	8.95	0.02	0.02	7.01	6.99	0.18	3.21
12.38	12.28	8.91	0.02	0.02	7.02	6.95	0.18	3.13
12.41	12.36	8.97	0.02	0.02	7.10	6.98	0.18	3.22
12.57	12.38	8.98	0.02	0.02	7.24	6.99	0.18	3.23
12.65	12.29	8.93	0.02	0.02	7.25	6.96	0.18	3.32
12.51	12.30	8.84	0.02	0.02	7.17	6.95	0.18	3.33
12.36	12.25	8.85	0.02	0.02	7.19	6.91	0.17	3.22
12.11	12.35	8.97	0.02	0.02	7.09	7.00	0.18	3.18
12.36	12.36	8.86	0.02	0.02	7.09	7.25	0.19	3.23
12.23	12.45	8.85	0.02	0.02	7.11	7.19	0.18	3.22
12.34	12.39	8.88	0.02	0.02	6.99	7.21	0.18	3.23
12.32	12.39	8.85	0.02	0.02	7.02	7.17	0.19	3.15
12.23	12.30	8.84	0.02	0.02	7.08	7.21	0.19	3.22
12.21	12.32	8.87	0.02	0.02	7.05	7.23	0.18	3.23
12.28	12.38	8.85	0.02	0.02	7.15	6.92	0.17	3.22
	12.39	8.89	0.02	0.02	6.96	6.92	0.17	3.30
	12.23	8.91	0.02	0.02	7.05	6.94	0.17	3.20
	12.21	8.98	0.02	0.02	7.01	6.93	0.17	3.22
	12.23	8.95	0.02	0.02	7.19	6.95	0.17	3.20
	12.21	8.99	0.02	0.02	7.19	6.96	0.17	3.27
	12.26	8.94	0.02	0.02	7.31	6.94	0.17	3.20
	12.26	8.95	0.02	0.02	7.02	6.96	0.17	3.22
	12.26	8.96	0.02	0.02	7.06	6.98	0.17	3.25
	12.24	8.95	0.02	0.02	7.06	7.04	0.18	3.13
	12.20	8.98	0.02	0.02	7.25	7.06	0.17	3.20
	12.20	8.99	0.02	0.02	7.16	7.08	0.17	3.20
	12.10	8.89	0.02	0.02	7.19	7.03	0.17	3.20
	12.10	9.01	0.02	0.02	7.18	7.03	0.18	3.15
	12.20	9.00	0.02	0.02	7.29	7.02	0.17	3.20
	12.10	8.95	0.02	0.02	7.13	7.03	0.17	3.23
	12.20	9.01	0.02			7.09	0.18	
	12.20	8.99				7.10	0.17	
	12.30	8.94				7.06	0.17	
	12.30	8.92				7.11	0.17	
	12.20	8.85				7.13	0.17	
	12.30	8.92				7.07	0.17	
	12.30	8.92				7.10	0.17	
	12.20	8.92				7.11	0.17	
	12.29	8.78				7.09	0.17	
	12.25	8.93				7.07	0.17	
	12.27					7.07	0.17	
	12.25					7.06	0.18	
	12.27					7.08	0.18	
	12.25					7.07	0.17	
	12.29					7.04	0.17	
	12.26					7.07	0.17	

**Assay Data (Cont.)**

XRF	FUS	XRF	XRF	XRF	FUS	XRF	FUS	XRF
MgO	MnO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	TiO <sub>2</sub>
%	%	%	%	%	%	%	%	%
3.28	0.16	0.16	6.70	0.16	50.80	49.50	0.64	0.66
3.27	0.16	0.16	6.73	0.16	50.80	49.39	0.63	0.66
3.29	0.16	0.16	6.72	0.16	51.30	49.64	0.65	0.66
3.29	0.16	0.16	6.73	0.16	51.00	49.71	0.66	0.66
3.27	0.16	0.16	6.73	0.16	50.60	49.43	0.66	0.65
3.26	0.16	0.16	6.27	0.16	50.50	49.62	0.66	0.66
3.24	0.16	0.16	6.26	0.16	51.10	49.25	0.65	0.65
3.29	0.16	0.16	6.27	0.16	50.40	49.67	0.65	0.66
3.31	0.17	0.16	6.27	0.16	49.42	48.80	0.68	0.69
3.27	0.17	0.17	6.27	0.17	49.21	48.84	0.68	0.69
3.26	0.17	0.16	6.28	0.16	51.13	48.86	0.70	0.66
3.23	0.17	0.16	6.28	0.16	50.70	48.95	0.70	0.66
3.28	0.17	0.17	6.27	0.17	51.13	48.99	0.70	0.69
3.30	0.17	0.17	6.54	0.16	51.35	48.94	0.70	0.66
3.26	0.17	0.16	6.50	0.16	49.85	48.87	0.68	0.66
3.28	0.16	0.16	6.49	0.16	50.06	48.97	0.60	0.67
3.19	0.16	0.15	6.47	0.16	51.77	49.10	0.62	0.66
3.20	0.16	0.16	6.46	0.16	51.35	49.20	0.60	0.67
3.20	0.16	0.16	6.41	0.16	51.99	48.90	0.63	0.67
3.20	0.16	0.16	6.50	0.16	51.77	48.90	0.62	0.67
3.20	0.16	0.16	6.51	0.16	51.99	48.90	0.62	0.67
3.20	0.16	0.16	6.37	0.16	49.85	49.10	0.62	0.67
3.21	0.16	0.16	6.40	0.16		48.90	0.62	0.67
3.27		0.16	6.39	0.16		49.00	0.63	0.67
3.28		0.16	6.39	0.17		49.10	0.65	0.67
3.26		0.16	6.43	0.16		49.10	0.67	0.66
3.25		0.16	6.41	0.16		49.30	0.63	0.67
3.24		0.17	6.33	0.16		49.20	0.63	0.67
3.31		0.16	6.40	0.17		49.20	0.65	0.67
3.25		0.16	6.40	0.17		49.20	0.65	0.65
3.23		0.16	6.38	0.16		49.10	0.65	0.65
3.24		0.16	6.41	0.17		49.10		0.66
3.26		0.16	6.36			49.21		0.66
3.23		0.16	6.39			49.13		0.66
3.26		0.16	6.37			49.42		0.65
3.27		0.16	6.40			49.11		0.65
3.25		0.16	6.37			49.15		0.66
3.24		0.16				49.15		0.67
3.26		0.16				49.43		0.67
3.23		0.16				49.13		0.67
3.22								0.67
3.22								0.67
3.23								0.66
3.25								0.67
3.23								0.67
3.21								
3.23								

**Assay Data (Cont.)**

Pb Collection	Pb Collection	Pb Collection	Combustion/LECO	Combustion/LECO	4A_MICP	LOI	SG	FUS	4A_MICP
Au	Au	Pd	C	S	S	LOI	SG	AI	As
g/t	g/t	g/t	ppm	%	%	%	Dimensionless	ppm	ppm
0.12	0.13	0.02	30000	1.20	1.08	10.01	2.74	66000	33.00
0.11	0.13	0.02	29900	1.20	1.05	10.02	2.76	65500	28.00
0.12	0.12	0.02	30200	1.21	1.05	9.99	2.75	65700	32.00
0.11	0.13	0.02	29800	1.21	1.09	9.95	2.74	66500	35.00
0.12	0.12	0.02	29700	1.19	1.08	10.00	2.76	67000	33.00
0.12	0.11	0.02	30000	1.19	1.06	9.89	2.75	66200	31.00
0.12	0.12	0.02	30100	1.15	1.24	9.99	2.75	65400	32.00
0.11	0.12	0.02	30000	1.20	1.26	9.99	2.73	64100	31.00
0.13	0.12	0.02	30400	1.18	1.23	8.53	2.83	65400	34.00
0.12	0.12	0.02	30300	1.17	1.25	8.53	2.77	64700	39.00
0.14	0.11	0.02	30700	1.16	1.24	8.64	2.78	65300	34.00
0.13	0.12	0.02	30800	1.16	1.26	8.69	2.78	65200	35.00
0.11	0.12	0.02	30400	1.18	1.28	8.61	2.78	64700	33.00
0.12	0.13	0.02	30400	1.17	1.22	8.60	2.84	64600	34.00
0.13	0.11	0.02	30600	1.19	1.22	8.65	2.78	65000	37.00
0.14	0.11	0.02	30700	1.18	1.20	8.59	2.76		35.00
0.13	0.12	0.02	31500	1.12	1.18	9.74	2.68		35.00
0.15	0.12	0.02	31400	1.15	1.22	9.76	2.68		33.00
0.14	0.12	0.02	31500	1.15	1.20	9.75	2.72		34.00
0.13	0.13	0.02	31300	1.12	1.18	9.72	2.71		34.00
0.12	0.11	0.02	31200	1.17	1.17	9.73	2.71		32.00
0.14	0.11	0.02	31300	1.15	1.21	9.73	2.71		30.00
0.14	0.11	0.02	31300	1.17	1.20	9.72	2.69		32.00
0.10	0.11	0.02	31200	1.15	1.21	9.74	2.66		31.00
0.14	0.11		29600	1.15	1.22	9.51	2.80		33.00
0.14	0.11		29700	1.13	1.21	9.42	2.80		35.00
0.15	0.11		29600	1.14	1.21	9.48	2.80		33.00
0.14	0.11		29300	1.14	1.21	9.48	2.80		33.00
0.13	0.10		29200	1.15	1.20	9.44	2.81		35.00
0.14	0.11		29200	1.16	1.22	9.46	2.80		33.00
0.15	0.13		29200	1.16		9.44	2.81		34.00
0.11	0.10		29400	1.16		9.50	2.80		34.00
0.11	0.10		30900	1.15		9.86	2.84		
0.12	0.09		30400	1.16		9.83	2.88		
0.11	0.11		30900	1.16		9.73	2.89		
0.11	0.10		31100	1.14		9.65	2.90		
0.12	0.12		30900	1.14		9.70	2.84		
0.12	0.12		30700	1.17		9.63	2.83		
0.11	0.12		30700	1.14		9.77	2.89		
0.10	0.12		30900	1.16		9.62			
0.12	0.12		29800	1.17		9.70			
0.13	0.13		30300	1.18		9.69			
0.12	0.12		30100	1.18		9.49			
0.13	0.13		30700	1.16		9.62			
0.12			30500	1.18		9.59			
0.13			30400	1.17		9.69			
0.12			30000	1.18		9.52			
0.12			30500	1.18		9.60			
0.13				1.22					
0.12				1.23					
0.12				1.22					
0.12				1.23					
0.12				1.22					
0.12				1.22					
0.12				1.22					
0.12				1.22					
0.13				1.13					
0.12				1.08					
0.13				1.08					
0.12				1.08					
0.13				1.12					
0.13				1.11					
0.12				1.08					
0.13				1.10					

**Assay Data (Cont.)**

4A MICP	4A MICP	4A MICP	4A MICP	4A MICP	4A MICP	FUS	4A MICP	4A MICP	4A MICP	FUS	4A MICP	4A MICP
Ba	Be	Bi	Ca	Co	Cr	Cr	Cs	Cu	Fe	Fe	Hf	K
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
34.00	0.60	0.20	63400	20.78	119	150	1.30	66.00	49980	49000	3.80	1500
35.00	0.60	0.20	63600	19.28	120	150	1.20	68.00	49860	49100	3.80	1500
35.00	0.60	0.20	62300	19.62	117	150	1.30	64.00	49830	49700	3.80	1400
35.00	0.60	0.20	62800	19.75	118	150	1.20	65.00	49880	50600	3.60	1400
36.00	0.60	0.20	63400	20.54	122	150	1.20	66.00	50060	50700	3.80	1500
36.00	0.60	0.20	61700	20.78	117	150	1.20	65.00	50590	50100	3.60	1400
35.00	0.60	0.20	64400	20.21	122	150	1.20	66.00	50120	50300	3.60	1500
34.00	0.60	0.20	62700	20.76	120	160	1.20	66.00	50110	49600	3.60	1500
29.00	0.50	0.23	65100	15.00	131	159	1.17	53.44	48500	49600	2.84	1600
28.00	0.50	0.20	63000	15.00	125	160	1.19	55.24	47300	49700	2.78	1500
29.00	0.50	0.22	64200	15.00	125	167	1.23	52.42	47000	48900	2.95	1700
27.00	0.50	0.23	62400	15.00	125	161	1.22	53.65	48400	49100	2.89	1600
28.00	0.50	0.23	62600	15.00	128	166	1.22	54.04	47600	49500	2.89	1600
28.00	0.50	0.24	62100	15.00	130	164	1.26	53.59	48100	49300	2.89	1500
28.00	0.50	0.23	63000	15.00	127	160	1.19	52.64	47600	50000	2.83	1600
28.00	0.50	0.24	63700	14.00	128	150	1.16	53.99	47300	48700	2.81	1600
25.24	0.60		60700	20.00	120	154	1.40	78.70	49900	49300	3.50	1600
27.75	0.60		59000	20.00	115	147	1.40	77.50	50100	49000	3.50	1500
26.78	0.60		60700	20.00	114	151	1.40	74.10	50300	50300	3.50	1400
27.05	0.60		60400	20.00	122	148	1.30	78.10	50200	50300	3.50	1600
28.00	0.60		60700	20.00	120	154	1.40	76.90	49800	51100	3.30	1500
25.77	0.60		59600	20.00	117	152	1.30	75.80	50100	49100	3.40	1500
25.82	0.60		59500	20.00	122	155	1.30	76.50	49800	49400	3.40	1500
26.95	0.60		61972	14.28	126		1.40	74.20	50900	49400	3.40	1500
28.00	0.60		62225	13.89				65.75		50700		1500
28.00	0.60		62093	14.27				64.44		50100		1500
29.00	0.60		62411	13.80				64.22		50300		1600
29.00	0.60		61802	13.43				65.58		50200		1500
29.00	0.60		62292	14.00				63.87		51000		1600
28.00	0.60		61355	13.49				64.09		49900		1600
29.00	0.60		63297	13.75				62.92				1600
28.00	0.60			14.90				62.52				1500
				15.30				67.00				1528
				15.30				67.00				1522
				15.20				67.00				1545
				15.30				67.00				1551
				14.90				68.00				1538
				15.50				67.00				1546
				15.10				68.00				1557
								68.00				1578

**Assay Data (Cont.)**

4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS
La	Li	Mg	Mg	Mn	Mn	Na	Ni	P	Pb	Rb	Sb	Si
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
34.60	9.00	18061	19400	1165	1210	50000	48.00	720	16.00	8.60	2.40	237000
34.70	8.50	17708	18900	1215	1220	49300	43.00	720	20.00	8.40	2.20	238000
35.40	9.00	17539	19400	1155	1230	49600	47.00	710	16.00	8.20	2.40	240000
35.90	8.50	17861	19500	1135	1250	49300	45.00	710	18.00	8.40	2.40	238000
35.90	8.50	17964	20000	1180	1250	49800	49.00	730	19.00	8.40	2.40	237000
35.60	9.00	17916	20100	1150	1270	49200	50.00	690	18.00	8.20	2.40	236000
36.70	9.00	17864	19400	1190	1230	46100	49.00	730	18.00	8.40	2.20	239000
34.30	8.50	17808	19200	1170	1240	47200	47.00	730	14.00	9.20	2.40	235000
32.90	9.97	17763	19500	1230	1300	47700	48.45	750	15.00	8.90	2.05	231000
32.20	9.18	17733	19400	1220	1300	47200	49.09	700	17.00	8.60	2.15	230000
33.60	9.29	17839	19500	1230	1300	46600	48.78	750	18.00	9.10	2.23	239000
31.80	9.71	17855	19000	1260	1300	46800	47.85	700	15.00	9.20	2.11	237000
32.40	9.66	17699	19400	1230	1300	46700	49.55	750	16.00	9.10	2.19	239000
32.30	10.11	17786	19500	1220	1300	47200	47.74	700	16.00	8.60	2.19	240000
32.00	9.82	17661	19400	1240	1300	46400	49.92	700	15.00	9.00	2.06	233000
31.60	10.12	18087	19900	1169	1220	45200	50.39	700	18.00	8.60	2.24	234000
26.05	8.70		19300	1150	1275	46300	47.00	741	18.00	8.90		242000
26.02	8.90		19400	1148	1263	46500	48.00	706	18.00	9.10		240000
25.93	9.00		19300	1160	1273	46500	44.00	664	18.00	8.90		243000
27.15	8.70		19700	1141	1275	46400	51.00	709	17.00	9.00		242000
26.43	8.80		19300	1156	1268	46100	50.00	665	17.00	9.20		243000
25.96	8.80		19400	1155	1275	45500	48.00	662	17.00	9.00		233000
26.07	8.90		19600	1112	1265	47342	48.00	710	17.00	8.70		
25.95	8.70		18900	1218		47767	45.00	714	16.44			
28.60			19300	1224		48094	50.00	717	16.29			
28.00			19300	1220		47716	50.00	727	15.48			
28.50			19300	1217		47335	55.00	717	12.97			
27.70			19000	1223		47412	55.00	719	13.30			
27.80			19300	1217		47814	55.00	725	14.50			
29.20			19500	1203		47969	55.00	724	15.49			
27.00				1245				42.77	13.13			
28.20								43.24	19.00			
								42.09	18.00			
								42.61	19.00			
								41.90	19.00			
								41.93	19.00			
								41.81	19.00			
								41.55	19.00			
								47.00	18.00			
								48.00				
								49.00				
								49.00				
								48.00				
								49.00				
								51.00				
								49.00				

**Assay Data (Cont.)**

4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Sr	Ta	Th	Ti	Ti	U	V	Y	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
109	0.80	9.30	3800	3900	3.90	142	22.20	49.00	128
113	0.80	9.20	3700	3800	3.90	139	21.50	51.00	121
106	0.70	9.40	3800	3900	4.00	139	22.70	48.00	125
108	0.80	9.00	3800	4000	3.90	139	21.70	47.00	124
111	0.80	9.30	3600	3900	3.90	141	21.80	49.00	125
110	0.80	9.20	3800	4000	3.90	137	21.50	46.00	123
111	0.80	9.00	3700	3900	3.80	143	21.30	49.00	122
109	0.80	9.10	3600	3900	3.90	141	21.40	48.00	123
113	0.75	8.60	3500	4100	4.06	122	16.85	49.89	113
111	0.71	8.50	3600	4100	4.29	122	16.69	47.40	111
109	0.75	8.60	3700	4200	4.10	125	17.09	50.66	112
106	0.77	8.60	3600	4200	4.11	121	17.28	50.19	110
110	0.75	8.60	3600	4200	4.06	124	17.22	50.08	113
110	0.71	8.80	3500	4200	4.11	131	16.69	47.82	110
112	0.67	8.60	3639	4100	4.11	122	16.90	48.56	110
107	0.75	8.70	3505	3600	4.28	145	16.38	47.92	109
119	0.72	9.35	3624	3700	4.03	145	20.90	45.00	105
116	0.72	9.46	3644	3600	4.03	145	21.00	44.00	103
119	0.72	9.28	3566	3800	4.02	150	20.40	46.00	105
117	0.72	9.38	3570	3700	4.22	145	21.00	46.00	105
117	0.70	9.15	3582	3700	3.99	145	21.10	45.00	107
114	0.72	9.52	3711	3700	4.19	145	21.00	47.00	105
115	0.71	9.03		3700	4.10	136	20.30	45.00	105
115	0.74	9.36		3800	4.05	135	20.80	49.74	105
98				3900		133		48.60	124
95				4000		133		44.64	122
99				3800		132		49.04	120
99				3800		133		47.58	120
98				3900		131		49.78	122
97				3900		131		45.32	120
97				3900		140		46.45	120
108						133		46.00	122
110						136		47.00	
108						142		46.00	
108						136		46.00	
109						136		45.00	
110						140		46.00	
109						138		47.00	
108								47.00	

## **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. Limit of Detection and Limit of Quantitation in Gravimetric Fire Assay**

In the determination of limit of detection (LOD) and limit of quantitation (LOQ) in gravimetric fire assay (*i.e.* lead collection and weighing of resulting gold prill), the minimum mass that an assay microbalance is capable of weighing and the original test sample mass determines the LOD and the LOQ in the assay (Fraser, 2015), (see Appendix 8 for an example of the calculation LOD and LOQ and Table 13 for a recommend reporting scheme for LOD and LOQ values).

## **28. 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.

## **29. 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.

## **30. Minimum Sample Size**

Most of the 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.

## **31. 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.

## **32. 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).

### 33. Legal Notice

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

**Date of Version 000:** 07 August 2019

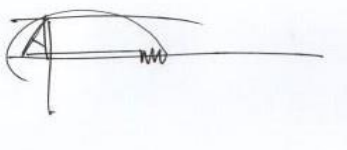
**Version:** 000

**Approving Officer:**

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

**Makhosi Khoza (Quality Specialist)**

**Certifying Officer:**

A handwritten signature in black ink, appearing to be 'A. Fraser', written over a horizontal line.

**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	1	0.1	*	*	ppm
Al	4A_MICP	32	62979.7	3969.4	6	ppm
ANC <sup>14</sup>	ANC	16	218.4	17.1	8	KgH <sub>2</sub> SO <sub>4</sub> /t
AP	NP	8	34.9	0.3	1	tCaCO <sub>3</sub> /1Kt
As	FUS	8	28.9	1.2	4	ppm
B	4A_MICP	8	187.5	18.3	10	ppm
Ba	FUS	16	29.5	2.6	9	ppm
BaO	XRF	1	0.04	*	*	%
Bi	FUS	7	0.2	*	*	ppm
C	UN_UN	7	28957.1	330.9	1	ppm
C inorganic	CALC	8	29787.5	172.7	1	ppm
C organic	IR	8	175.0	88.6	51	ppm
Ca	FUS	24	63879.2	5163.1	8	ppm
CaO	FUS	24	8.9	0.7	8	%
Cd	4A_MICP	15	0.1	0.01	11	ppm
Ce	4A_MICP	16	62.0	4.7	8	ppm
Ce	FUS	15	60.7	1.7	3	ppm
Co	FUS	24	17.2	4.0	23	ppm
Co	XRF	2	65.0	21.2	33	ppm
CO <sub>2</sub>	UN_UN	7	10.6	0.1	1	%
Cs	FUS	16	1.7	0.4	24	ppm
Cu	FUS	15	67.3	2.3	3	ppm
Dy	4A_MICP	15	4.1	0.1	2	ppm
Dy	FUS	16	5.9	0.2	3	ppm
EC	WS/MTR	7	58.8	1.0	2	mS/m
Er	4A_MICP	8	2.1	0.04	2	ppm
Er	FUS	16	3.6	0.4	12	ppm
Eu	4A_MICP	8	1.2	0.02	2	ppm
Eu	FUS	16	1.4	0.1	4	ppm
Final-pH	ANC/MTR	8	1.1	0.05	4	pH
FIZZ RATING	ANC/QUAL	8	2.6	0.5	20	NO UNIT
FIZZ RATING	NP	8	3.0	*	*	NO UNIT
Ga	4A_MICP	15	16.2	0.3	2	ppm
Ga	FUS	16	17.8	3.0	17	ppm
Gd	4A_MICP	15	5.5	0.2	3	ppm
Gd	FUS	16	6.7	0.7	10	ppm
Ge	4A_MICP	8	1.2	0.1	8	ppm
Ge	FUS	7	1.0	*	*	ppm
Hf	FUS	8	4.0	*	*	ppm
Ho	4A_MICP	15	0.7	0.02	2	ppm
Ho	FUS	15	1.1	0.1	7	ppm
In	4A_MICP	16	0.1	0.01	8	ppm
In	FUS	8	0.6	0.1	8	ppm
K	FUS	16	1500.0	516.4	34	ppm
K <sub>2</sub> O	FUS	8	0.2	*	*	%
La	FUS	16	32.1	0.8	2	ppm
Li	FUS	1	10.0	*	*	ppm
Lu	4A_MICP	8	0.3	0.01	4	ppm
Lu	FUS	16	0.5	0.1	17	ppm
Mo	4A_MICP	19	1.0	0.1	7	ppm
Moisture	Moisture	16	0.3	0.1	36	%
MPA	CALC	7	37.0	*	*	KgH <sub>2</sub> SO <sub>4</sub> /t
MPA	NAG_Ti	8	33.6	0.7	2	KgH <sub>2</sub> SO <sub>4</sub> /t
MPA <sub>2</sub>	NP	8	35.9	0.6	2	tCaCO <sub>3</sub> /1Kt
Na <sub>2</sub> O	4A_MICP	8	6.7	0.1	1	%

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

**Table 9.** Uncertified element concentrations statistics. (Continued)

Element	Generic Method	n	Mean	SD	RSD %	Unit
NAGpH	NAG	8	8.6	0.1	1	NO UNIT
Nb	4A_MICP	16	9.8	0.6	6	ppm
Nb	FUS	16	10.4	0.5	5	ppm
Nd	4A_MICP	16	30.0	0.8	3	ppm
Nd	FUS	15	29.6	0.9	3	ppm
Ni	FUS	15	49.1	0.9	2	ppm
Ni	XRF	4	90.0	11.5	13	ppm
NNP	NP	16	178.8	23.0	13	tCaCO <sub>3</sub> /1Kt
NP	NP	16	214.3	23.5	11	tCaCO <sub>3</sub> /1Kt
NPR	NP	8	5.5	0.2	3	NO UNIT
P	FUS	14	700.0	*	*	ppm
P <sub>2</sub> O <sub>5</sub>	FUS	7	0.2	*	*	%
Pb	FUS	8	17.5	0.8	4	ppm
pH	pH	7	8.6	0.04	0.4	pH
pH	WS/MTR	8	8.5	0.1	1	pH
pH Drop	ANC/MTR	8	2.8	0.05	2	pH
Pr	4A_MICP	15	7.1	0.1	2	ppm
Pr	FUS	15	7.9	0.2	3	ppm
Pt	Pb Collection	16	0.04	0.004	12	g/t
Ratio (NP:MPA)	NP	8	6.6	0.2	4	NO UNIT
Rb	FUS	8	8.7	0.3	3	ppm
S	CALC	16	1.1	0.02	2	%
S	HCl Leachable	3	0.01	*	*	%
S	TSCL	14	0.04	0.02	49	%
Sb	FUS	15	2.2	0.2	7	ppm
Sc	4A_MICP	30	14.1	3.0	22	ppm
Sc	FUS	16	13.8	1.0	8	ppm
Se	4A_MICP	8	4.0	*	*	ppm
Sm	4A_MICP	16	6.2	0.5	8	ppm
Sm	FUS	16	6.5	0.3	5	ppm
Sn	4A_MICP	16	2.6	0.4	13	ppm
Sn	FUS	8	3.0	*	*	ppm
SO <sub>3</sub>	XRF	24	2.7	0.5	18	%
Sr	FUS	7	107.9	1.9	2	ppm
SrO	XRF	8	0.01	0.0003	2	%
Ta	FUS	16	1.3	0.6	44	ppm
Tb	4A_MICP	16	0.7	0.03	4	ppm
Tb	FUS	16	1.1	0.2	14	ppm
Te	4A_MICP	8	0.3	0.1	19	ppm
Th	FUS	16	9.6	0.5	5	ppm
Tl	4A_MICP	8	0.1	0.01	7	ppm
Tl	FUS	1	0.5	*	*	ppm
Tm	4A_MICP	8	0.3	0.01	4	ppm
Tm	FUS	16	0.6	0.2	26	ppm
U	FUS	15	4.4	0.1	3	ppm
V	FUS	16	145.9	7.0	5	ppm
V <sub>2</sub> O <sub>5</sub>	XRF	16	0.03	*	*	%
W	4A_MICP	15	3.2	0.3	10	ppm
W	FUS	7	3.0	*	*	ppm
Y	FUS	15	30.7	1.3	4	ppm
Yb	4A_MICP	16	2.1	0.1	5	ppm
Yb	FUS	8	2.9	0.1	3	ppm
Zn	FUS	8	50.8	1.8	3	ppm
Zr	FUS	8	141.0	4.5	3	ppm

\*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 36) 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**