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Approver:  
Managing  
Director

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Certificate

# AMIS0639

## Certified Reference Material

B2Gold, Namibia.

### *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***

<b>Analyte</b>	<b>Method</b>	<b>Certified (μ)</b>	<b>(2s) ±</b>	<b>Unit</b>
Au	Pb Collection <sup>1</sup>	0.25	0.031	g/t
Pd	Pb Collection	0.040	0.00609	g/t
Pt	Pb Collection	0.067	0.0251	g/t
C	Combustion/LECO <sup>2</sup>	1.91	0.12	%
S	4A_MICP <sup>3</sup>	1.41	0.093	%
S	Combustion/LECO	1.41	0.11	%
LOI	LOI <sup>4</sup>	7.11	0.61	%
SG	SG <sup>5</sup>	2.86	0.29	Dimensionless
Al	4A_MICP	6.66	0.37	%
As	4A_MICP	6	2	ppm
Ba	4A_MICP	51	5	ppm
Be	4A_MICP	0.8	0.2	ppm
Ca	4A_MICP	4.00	0.31	%
Co	4A_MICP	23	7	ppm
Cr	4A_MICP	196	11	ppm
Cr	FUS <sup>6</sup>	227	63	ppm
Cu	4A_MICP	91	6	ppm
Fe	4A_MICP	5.56	0.48	%
Fe	FUS	5.59	0.26	%
Ga	4A_MICP	18	4	ppm
K	4A_MICP	2608	171	ppm
La	4A_MICP	31	2	ppm
Mg	4A_MICP	1.93	0.16	%
Mg	FUS	2.00	0.075	%
Mn	4A_MICP	1070	48	ppm
Na	4A_MICP	4.55	0.15	%
Ni	4A_MICP	69	9	ppm
P	4A_MICP	760	60	ppm
Pb	4A_MICP	37	7	ppm
Sb	4A_MICP	9	1	ppm
Sc	4A_MICP	14	2	ppm
Si	FUS	26.21	0.99	%
Sr	4A_MICP	88	5	ppm
Ti	4A_MICP	3968	267	ppm
Ti	FUS	4108	265	ppm
V	4A_MICP	147	16	ppm
Zn	4A_MICP	59	7	ppm
Zr	4A_MICP	125	22	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>	XRF <sup>7</sup>	12.52	0.16	%
CaO	XRF	5.52	0.055	%
Cr <sub>2</sub> O <sub>3</sub>	XRF	0.034	0.01	%
Fe <sub>2</sub> O <sub>3</sub>	FUS	7.94	0.44	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	7.91	0.092	%
K <sub>2</sub> O	XRF	0.30	0.01	%
MgO	FUS	3.32	0.13	%
MgO	XRF	3.33	0.053	%
P <sub>2</sub> O <sub>5</sub>	XRF	0.18	0.03	%
SiO <sub>2</sub>	FUS	56.07	2.1	%
SiO <sub>2</sub>	XRF	54.71	2.9	%
TiO <sub>2</sub>	FUS	0.69	0.04	%
TiO <sub>2</sub>	XRF	0.69	0.02	%

## 1. Certified Concentrations and Uncertainties

AMIS0639 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 ( $\mu$ )	N	n	k	% RSD	( $u_c$ )	(2s) $\pm$	(CI) 95%	(U) $\pm$	Unit
Au	Pb Collection <sup>1</sup>	0.25	10	80	2.262	6	0.0157	0.031	0.00800	0.04	g/t
Pd	Pb Collection	0.040	3	24	4.303	8	0.00304	0.00609	0.00700	0.01	g/t
Pt	Pb Collection	0.067	3	24	4.303	19	0.0125	0.0251	0.0310	0.05	g/t
C	Combustion/LECO <sup>2</sup>	1.91	6	47	2.571	3	0.061	0.12	0.064	0.2	%
S	4A_MICP <sup>3</sup>	1.41	4	32	3.182	3	0.047	0.093	0.064	0.1	%
S	Combustion/LECO	1.41	8	61	2.365	4	0.053	0.11	0.044	0.1	%
LOI	LOI <sup>4</sup>	7.11	6	45	2.571	4	0.30	0.61	0.35	0.8	%
SG	SG <sup>5</sup>	2.86	4	31	3.182	5	0.15	0.29	0.23	0.5	Dimensionless
Al	4A_MICP	6.66	3	23	4.303	3	0.185	0.37	0.4301	0.8	%
As	4A_MICP	6	4	31	3.182	14	0.9	2	0.9	3	ppm
Ba	4A_MICP	51	4	30	3.182	5	2	5	4	8	ppm
Be	4A_MICP	0.8	5	38	2.776	10	0.08	0.2	0.09	0.2	ppm
Ca	4A_MICP	4.00	3	23	4.303	4	0.157	0.31	0.3902	0.7	%
Co	4A_MICP	23	5	40	2.776	15	3	7	4	9	ppm
Cr	4A_MICP	196	4	32	3.182	3	6	11	7	18	ppm
Cr	FUS <sup>6</sup>	227	3	24	4.303	14	31	63	78	135	ppm
Cu	4A_MICP	91	5	40	2.776	3	3	6	3	8	ppm
Fe	4A_MICP	5.56	3	23	4.303	4	0.24	0.48	0.58	1	%
Fe	FUS	5.59	3	23	4.303	2	0.13	0.26	0.29	0.6	%
Ga	4A_MICP	18	3	24	4.303	10	2	4	4	8	ppm
K	4A_MICP	2608	6	46	2.571	3	85	171	80	220	ppm
La	4A_MICP	31	2	16	12.706	3	1	2	9	13	ppm
Mg	4A_MICP	1.93	2	15	12.706	4	0.082	0.16	0.72	1	%
Mg	FUS	2.00	3	23	4.303	2	0.038	0.075	0.08	0.2	%
Mn	4A_MICP	1070	4	30	3.182	2	24	48	30	77	ppm
Na	4A_MICP	4.55	4	30	3.182	2	0.07	0.15	0.09	0.2	%
Ni	4A_MICP	69	6	46	2.571	7	5	9	5	12	ppm
P	4A_MICP	760	4	31	3.182	4	30	60	33	95	ppm
Pb	4A_MICP	37	4	32	3.182	10	4	7	6	12	ppm
Sb	4A_MICP	9	3	23	4.303	8	0.7	1	1	3	ppm
Sc	4A_MICP	14	4	32	3.182	8	1	2	2	3	ppm
Si	FUS	26.21	3	24	4.303	2	0.49	0.99	0.81	2	%
Sr	4A_MICP	88	5	38	2.776	3	2	5	2	7	ppm
Ti	4A_MICP	3968	2	15	12.706	3	133	267	1129	1696	ppm
Ti	FUS	4108	3	24	4.303	3	132	265	306	569	ppm
V	4A_MICP	147	4	30	3.182	6	8	16	13	26	ppm
Zn	4A_MICP	59	5	39	2.776	6	4	7	4	10	ppm
Zr	4A_MICP	125	3	24	4.303	9	11	22	26	46	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>	XRF <sup>7</sup>	12.52	4	29	3.182	1	0.082	0.16	0.14	0.3	%
CaO	XRF	5.52	4	32	3.182	0.5	0.027	0.055	0.036	0.09	%
Cr <sub>2</sub> O <sub>3</sub>	XRF	0.034	4	32	3.182	13	0.004	0.01	0.002	0.01	%
Fe <sub>2</sub> O <sub>3</sub>	FUS	7.94	2	16	12.706	3	0.22	0.44	2.0	3	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	7.91	4	32	3.182	1	0.046	0.092	0.066	0.1	%
K <sub>2</sub> O	XRF	0.30	5	38	2.776	2	0.006	0.01	0.006	0.02	%
MgO	FUS	3.32	3	23	4.303	2	0.063	0.13	0.14	0.3	%
MgO	XRF	3.33	5	38	2.776	1	0.027	0.053	0.031	0.07	%
P <sub>2</sub> O <sub>5</sub>	XRF	0.18	4	32	3.182	9	0.02	0.03	0.02	0.05	%
SiO <sub>2</sub>	FUS	56.07	3	24	4.303	2	1.1	2.1	2.0	5	%
SiO <sub>2</sub>	XRF	54.71	4	30	3.182	3	1.5	2.9	3.0	5	%
TiO <sub>2</sub>	FUS	0.69	3	24	4.303	3	0.02	0.04	0.05	0.09	%
TiO <sub>2</sub>	XRF	0.69	4	32	3.182	1	0.01	0.02	0.01	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. AGP is Acid Generating Potential
14. ANC is Acid Neutralizing Capacity
15. AP is Acid Potential
16. MPA is Mycophenolic Acid
17. NNP is Net Neutralizing Potential
18. NP is Neutralizing Potential
19. NPP is Net Acid Potential
20. NPR is Neutralizing Potential Ratio
21. HCL Leachable
22. TSCL is Chlorination by TsCL

## 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 4A_MICP	1.41 %	S Combustion/LECO	1.41 %	Equal Variance ( $p=0.345$ )	0.912	Accept $H_0$ ; certified values are equal
Cr <sub>2</sub> O <sub>3</sub> FUS	0.033 %	Cr <sub>2</sub> O <sub>3</sub> XRF	0.034 %	Equal Variance ( $p=0.059$ )	0.722	Accept $H_0$ ; certified values are equal
Fe <sub>2</sub> O <sub>3</sub> FUS	7.94 %	Fe <sub>2</sub> O <sub>3</sub> XRF	7.91 %	Unequal Variance ( $p=0.014$ )	0.864	Accept $H_0$ ; certified values are equal
MgO FUS	3.32 %	MgO XRF	3.33 %	Equal Variance ( $p=0.084$ )	0.675	Accept $H_0$ ; certified values are equal
SiO <sub>2</sub> FUS	56.07 %	SiO <sub>2</sub> XRF	54.71 %	Equal Variance ( $p=0.167$ )	0.232	Accept $H_0$ ; certified values are equal
TiO <sub>2</sub> FUS	0.686 %	TiO <sub>2</sub> XRF	0.686 %	Equal Variance ( $p=0.091$ )	0.998	Accept $H_0$ ; certified values are equal
Cr 4A_MICP	0.020 %	Cr FUS	0.023 %	Unequal Variance ( $p=0.004$ )	0.232	Accept $H_0$ ; certified values are equal
Fe 4A_MICP	5.56 %	Fe FUS	5.59 %	Equal Variance ( $p=0.206$ )	0.853	Accept $H_0$ ; certified values are equal
Mg 4A_MICP	1.93 %	Mg FUS	2. %	Equal Variance ( $p=0.138$ )	0.245	Accept $H_0$ ; certified values are equal
Ti 4A_MICP	0.397 %	Ti FUS	0.411 %	Equal Variance ( $p=0.415$ )	0.304	Accept $H_0$ ; certified values are equal



### 3. Intended Use

AMIS0639 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, <i>e.g.</i> $k=2$ 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

Abbreviation/Symbol	Description
$p$	' $p$ -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
2s	Two times standard deviation
SI	Standard International system of units
$t_{calc}$	Calculated t statistic from a one-sample, two-tailed t-test
t-critical or $t_{crit}$	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.

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		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 light brownish gray (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 54µm (95% 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	99.8
<63um	100
<75um	100
<90um	100
<100um	100
<106um	100
<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 majors' 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:
  - Total Sulfur %
  - Neutralization Potential (kg CaCO<sub>3</sub>/t)
  - Acid Generating Potential (kg H<sub>2</sub>SO<sub>4</sub>/t)
  - (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

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. ALS Geochemistry Arabia
2. ALS Geochemistry Ireland
3. ALS Geochemistry SA
4. ALS Geochemistry Vancouver
5. Antech Zimbabwe
6. Argetest Mineral Processing, R&D and Analysis Services
7. B2 Gold (Otjikoto Lab)
8. Bureau Veritas Adelaide GeoAnalytical Laboratory
9. Bureau Veritas Minerals Ultra Trace Pty Ltd
10. Cotecna Del Peru S.A
11. Freda Rebecca Gold Mine
12. Geoangol
13. Intertek Perth
14. Performance Laboratories Zimbabwe
15. Ready Lead Assay Laboratory
16. Sci-Ba
17. SGS Ankara (Turkey)
18. SGS Inspection and Testing Services (Akyem Laboratory)
19. SGS South Africa (Pty) Ltd - Barberton
20. SGS Vancouver (Canada)
21. Shiva Analyticals India
22. Super Laboratory Services (Pty) Ltd. Springs



## 24. Accepted Assay Data

Data from the 22 laboratories used for certification are set out in Table 8.

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

Pb Collection	Pb Collection	Pb Collection	Pb Collection	Combustion/LECO	4A_MICP
Au g/t	Au g/t	Pd g/t	Pt g/t	C ppm	S %
0.25	0.25	0.04	0.06	19400	1.41
0.26	0.25	0.04	0.05	19500	1.43
0.24	0.24	0.04	0.06	19500	1.44
0.23	0.26	0.04	0.05	19400	1.44
0.24	0.24	0.04	0.05	19400	1.52
0.24	0.24	0.04	0.06	20000	1.43
0.24	0.24	0.04	0.06	19500	1.42
0.23	0.24	0.04	0.06	19100	1.45
0.23	0.26	0.04	0.08	18700	1.41
0.23	0.24	0.04	0.08	18500	1.43
0.22	0.24	0.04	0.08	18800	1.41
0.24	0.24	0.04	0.08	18500	1.41
0.23	0.24	0.04	0.08	18500	1.42
0.21	0.24	0.04	0.08	18600	1.38
0.23	0.24	0.04	0.08	18600	1.40
0.25	0.23	0.04	0.08	18800	1.40
0.27	0.24	0.04	0.07	18100	1.45
0.27	0.23	0.04	0.06	17900	1.45
0.26	0.24	0.04	0.06	18000	1.42
0.27		0.04	0.07	18000	1.41
0.27		0.04	0.07	18400	1.44
0.26		0.04	0.06	17900	1.43
0.26		0.04	0.06	18100	1.44
0.26		0.04	0.07	19700	1.46
0.22				19700	1.37
0.25				19700	1.36
0.25				19700	1.35
0.25				19700	1.36
0.29				19600	1.33
0.23				19700	1.41
0.23				19600	1.30
0.23				19300	1.36
0.25				19300	
0.24				19200	
0.25				19200	
0.24				19100	
0.23				19100	
0.24				19200	
0.24				19200	
0.23				19200	
0.30				19400	
0.26				19100	
0.26				19300	
0.26				19700	
0.28				19500	
0.24				19300	
0.26				19100	
0.28					
0.24					
0.24					
0.26					
0.24					
0.24					
0.25					
0.25					
0.24					
0.25					
0.26					
0.26					
0.25					
0.26					

Assay Data (Cont.)

Combustion/LECO	LOI	SG	4A_MICP	4A_MICP	4A_MICP	4A_MICP
S	LOI	SG	Al	As	Ba	Be
%	%	Dimensionless	ppm	ppm	ppm	ppm
1.38	7.27	2.96	66500	7.00	50.00	0.80
1.36	7.14	3.06	66700	5.00	50.00	0.80
1.38	7.34	3.03	68300	6.00	50.00	0.90
1.37	7.20	3.01	67700	9.00	50.00	0.90
1.41	6.94	3.01	67300	7.00	50.00	0.90
1.39	7.27	3.07	68100	8.00	50.00	0.80
1.43	7.13	2.95	68700	6.00	50.00	0.80
1.43	7.15	2.80	64200	6.00	49.00	0.80
1.45	7.62	2.79	65300	5.00	48.00	0.80
1.43	7.37	2.78	64000	5.00	48.00	0.80
1.44	7.50	2.80	65300	6.00	50.00	0.80
1.43	7.38	2.77	65200	6.00	48.00	0.80
1.42	7.45	2.78	64000	5.00	48.00	0.90
1.43	7.65	2.74	64000	6.00	49.00	0.80
1.42	7.42	2.75	64700	5.00	51.00	0.80
1.41	7.49	2.91	67639	6.00	51.00	0.80
1.37	7.29	3.00	67891	6.00	51.00	0.90
1.36	7.25	2.92	67283	6.00	50.00	0.90
1.36	7.33	2.95	66828	6.00	51.00	0.90
1.37	7.31	2.84	67962	6.00	50.00	0.90
1.39	7.35	2.99	67147	6.00	50.00	0.90
1.37	7.28	2.92	67352	6.00	51.00	0.90
1.35	7.28	2.98	68357	6.00	53.00	0.80
1.38	7.29	2.71		7.00	53.00	0.80
1.31	6.57	2.68		7.00	54.00	0.90
1.34	6.45	2.71		6.00	54.00	0.80
1.31	6.52	2.72		6.00	54.00	0.90
1.34	6.58	2.70		6.00	55.00	0.80
1.33	6.49	2.69		6.00	54.00	0.80
1.37	7.02	2.71		6.00	55.00	0.80
1.41	7.12	2.68		7.00		0.70
1.40	6.99					0.70
1.39	6.93					0.70
1.38	6.99					0.70
1.39	6.96					0.70
1.41	7.01					0.70
1.40	6.95					0.70
1.40	7.17					0.70
1.46	7.21					
1.43	7.15					
1.43	7.19					
1.45	7.27					
1.44	7.31					
1.42	7.06					
1.43	7.16					
1.45						
1.51						
1.51						
1.52						
1.50						
1.52						
1.48						
1.52						
1.45						
1.43						
1.46						
1.44						
1.44						
1.45						
1.42						
1.44						

**Assay Data (Cont.)**

XRF	XRF	XRF	FUS	XRF	XRF	FUS	XRF	XRF	FUS	XRF	FUS	XRF
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>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MgO	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	TiO <sub>2</sub>
%	%	%	%	%	%	%	%	%	%	%	%	%
12.65	5.51	0.03	8.11	7.89	0.31	3.37	3.36	0.17	54.77	52.33	0.72	0.69
12.62	5.48	0.04	8.11	7.84	0.30	3.40	3.34	0.17	56.48	52.38	0.72	0.68
12.63	5.46	0.04	8.05	7.82	0.30	3.43	3.33	0.17	56.48	52.26	0.72	0.68
12.67	5.52	0.03	8.12	7.90	0.31	3.35	3.36	0.17	56.48	52.32	0.70	0.68
12.65	5.52	0.03	8.05	7.88	0.31	3.33	3.36	0.17	55.41	52.34	0.70	0.68
12.47	5.47	0.04	8.08	7.83	0.30	3.33	3.33	0.17	55.41	52.41	0.70	0.68
12.50	5.48	0.04	8.05	7.84	0.30	3.30	3.34	0.17	54.13	55.75	0.70	0.68
12.48	5.49	0.04	8.18	7.83	0.30	3.32	3.34	0.17	54.98	55.82	0.72	0.68
12.51	5.51	0.03	7.78	7.95	0.31	3.20	3.34	0.20	55.80	55.79	0.67	0.70
12.53	5.52	0.03	7.80	7.96	0.31	3.26	3.37	0.20	55.60	55.74	0.66	0.70
12.54	5.52	0.03	7.71	7.97	0.31	3.28	3.36	0.20	55.90	55.73	0.67	0.69
12.50	5.51	0.04	7.82	7.93	0.30	3.26	3.36	0.20	55.70	55.79	0.68	0.70
12.47	5.52	0.04	7.75	7.94	0.31	3.24	3.35	0.20	56.00	55.71	0.67	0.70
12.42	5.52	0.03	7.75	7.95	0.31	3.24	3.38	0.20	55.70	55.76	0.67	0.70
12.47	5.51	0.04	7.82	7.94	0.30	3.29	3.30	0.20	55.90	55.42	0.67	0.69
12.42	5.52	0.03	7.90	7.94	0.30	3.35	3.31	0.20	56.00	55.49	0.69	0.70
12.42	5.52	0.03		7.92	0.30	3.35	3.29	0.17	56.48	55.43	0.67	0.68
12.45	5.54	0.03		7.94	0.30	3.35	3.29	0.17	57.34	55.45	0.67	0.69
12.46	5.54	0.04		7.93	0.30	3.35	3.29	0.17	57.76	55.50	0.68	0.69
12.44	5.54	0.03		7.94	0.30	3.35	3.29	0.17	57.55	55.42	0.68	0.68
12.42	5.53	0.03		7.94	0.30	3.33	3.29	0.17	56.91	55.49	0.68	0.69
12.48	5.52	0.04		7.92	0.30	3.30	3.30	0.17	57.98	55.45	0.68	0.68
12.48	5.53	0.03		7.93	0.30	3.38	3.31	0.17	56.48	55.40	0.67	0.68
12.48	5.54	0.04		7.94	0.30		3.32	0.17	54.34	55.10	0.67	0.69
12.48	5.54	0.03		7.94	0.30		3.31	0.17		55.30		0.68
12.49	5.55	0.03		7.88	0.30		3.31	0.17		55.30		0.68
12.48	5.51	0.03		7.91	0.30		3.32	0.17		55.20		0.69
12.48	5.52	0.03		7.88	0.30		3.30	0.17		55.30		0.68
12.47	5.54	0.03		7.86	0.30		3.33	0.17		55.20		0.67
	5.57	0.04		7.92	0.30		3.33	0.17		55.30		0.67
	5.56	0.04		7.91	0.29		3.32	0.17				0.68
	5.56	0.03		7.91	0.30		3.32	0.17				0.68
					0.30		3.34					
					0.30		3.33					
					0.29		3.34					
					0.29		3.34					
					0.29		3.33					

**Assay Data (Cont.)**

4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP
Ca	Co	Cr	Cr	Cu	Fe	Fe	Ga	K	La	Mg	Mg	Mn
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
41000	19.00	193	250	85.00	56000	56700	20.00	2500	30.00	19500	20300	1025
41600	21.00	197	250	88.00	56900	56700	20.00	2500	30.00	19700	20500	1060
42000	20.00	202	250	90.00	57700	56300	20.00	2600	30.00	20000	20700	1080
42100	21.00	206	250	92.00	57100	56800	20.00	2600	30.00	20000	20200	1060
41700	21.00	201	250	91.00	56400	56300	20.00	2500	30.00	19700	20100	1070
42100	20.00	201	250	88.00	57100	56500	20.00	2500	30.00	20000	20100	1015
42400	20.00	194	250	88.00	58000	56300	20.00	2500	30.00	20200	19900	1025
39100	21.00	193	250	87.00	52800	57200	20.00	2600	30.00	18743	20000	1065
39600	26.00	189	190	93.00	52400	54400	17.00	2600	31.70	18755	19300	1090
39000	23.00	197	190	92.00	53300	54500	17.60	2700	31.60	18643	19600	1085
39500	24.00	194	190	92.00	52800	53900	17.00	2600	31.00	19027	19800	1110
39300	24.00	196	200	94.00	52400	54700	17.20	2600	31.60	18762	19700	1075
38600	24.00	204	190	100.00	53400	54200	17.60	2600	32.00	18577	19500	1115
39000	23.00	195	190	93.00	53300	54200	17.00	2700	31.00	18614	19600	1115
39200	22.00	195	190	94.00	52600	54700	17.20	2700	31.50	18833	19900	1060
39223	22.00	195	190	95.00	56900	55300	17.20	2600	31.20		20200	1090
39316	28.10	192	241	90.00	57000	56700	16.90	2700			20200	1070
38918	28.10	187	241	90.00	56600	57200	16.50	2600			20200	1080
38506	28.90	193	244	90.00	56200	57100	17.00	2600			20200	1070
39353	28.70	190	243	90.00	57000	55900	16.60	2600			20200	1060
38926	28.80	189	238	95.00	56400	57200	16.40	2700			20100	1070
38914	29.20	190	239	90.00	56600	55800	16.60	2700			19900	1070
39509	28.30	193	232	90.00	57400	55400	16.70	2500			20400	1069
	28.30	188	235	90.00			16.90	2500				1066
	22.70	199		92.00				2500				1066
	23.00	197		92.00				2500				1056
	22.80	203		90.00				2500				1070
	22.30	194		90.00				2500				1056
	22.80	206		91.00				2500				1072
	23.20	196		90.00				2500				1078
	22.80	197		92.00				2625				
	22.70	205		92.00				2643				
	21.00			95.90				2625				
	21.00			91.20				2629				
	21.00			93.10				2680				
	21.00			90.60				2638				
	21.00			93.90				2666				
	20.00			90.30				2740				
	20.00			89.70				2700				
	20.00			92.80				2700				
								2700				
								2700				
								2700				
								2700				
								2600				
								2700				

**Assay Data (Cont.)**

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP
Na	Ni	P	Pb	Sb	Sc	Si	Sr	Ti	Ti	V	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
44700	72.00	710	40.00	9.00	13.00	256000	84.00	4000	4300	152	62.00	135
44900	73.00	770	39.00	11.00	14.00	264000	86.00	4000	4300	154	63.00	138
46200	73.00	780	40.00	9.00	14.00	264000	88.00	4100	4300	153	63.00	136
45600	76.00	800	35.00	9.00	14.00	264000	90.00	4100	4200	155	66.00	134
45700	76.00	780	42.00	10.00	15.00	259000	88.00	4000	4200	156	64.00	142
46100	74.00	760	36.00	8.00	14.00	259000	90.00	4100	4200	156	64.00	139
46400	71.00	730	40.00	10.00	14.00	253000	87.00	4100	4200	156	66.00	136
45400	69.00	750	36.00	8.60	14.00	257000	85.00	3871	4300	150	58.05	139
46100	75.00	790	38.00	8.60	14.00	261000	86.00	3860	4000	150	53.54	119
45700	76.00	790	38.00	8.40	14.00	260000	88.00	3871	4000	150	56.50	118
46300	74.00	790	37.00	9.40	13.00	261000	88.00	3921	4000	150	55.48	118
46000	74.00	790	37.00	8.40	14.00	260000	93.00	3918	4100	145	54.36	117
44900	74.00	800	37.00	8.00	13.00	262000	86.00	3836	4000	150	56.63	122
45200	75.00	770	37.00	8.20	14.00	261000	88.00	3814	4000	145	55.91	124
45000	65.14	780	37.00	8.60	13.00	261000	89.00	3944	4000	145	58.02	119
46374	65.80	750	39.00	9.90	14.00	262000	90.00		4100	146	60.00	122
46589	64.67	800	41.00	8.80	13.00	264000	88.00		4000	147	65.00	120
45796	65.33	750	40.00	8.40	13.00	268000	89.00		4000	150	60.00	118
45810	66.40	750	41.00	8.90	13.00	270000	88.00		4100	144	65.00	118
46105	64.09	750	41.00	9.40	13.00	269000	88.00		4100	155	60.00	118
45987	65.51	800	40.00	8.90	13.00	266000	90.50		4100	143	60.00	117
45672	64.85	700	42.00	9.00	13.00	271000	89.00		4100	150	60.00	119
46452	70.00	750	41.00	8.90	13.00	264000	90.50		4000	152	60.00	116
45400	65.00	738	40.00		13.00	254000	85.00		4000	138	60.00	122
44700	65.00	737	32.00		15.50		85.10			136	60.00	
45100	65.00	737	32.00		15.50		84.80			136	59.00	
44800	70.00	730	33.00		15.50		85.00			135	58.00	
45200	65.00	746	32.00		15.40		86.00			132	59.00	
43600	70.00	716	32.00		15.20		85.90			135	58.00	
44700	65.00	731	33.00		15.50		84.70			138	60.00	
	73.00	754	33.00		15.10		86.00				58.00	
	73.00		33.00		15.50		91.90				58.00	
	72.00						91.00				56.00	
	71.00						92.20				59.00	
	72.00						88.10				56.00	
	71.00						88.40				55.00	
	71.00						89.20				57.00	
	72.00						91.80				56.00	
	64.00										57.00	
	63.00											
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	65.00											

## **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

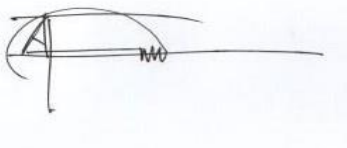
**Version:** 000

**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

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

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	4A_MICP	8	0.1	*	*	ppm
Al	FUS	16	65281.3	604.7	1	ppm
Al <sub>2</sub> O <sub>3</sub>	FUS	8	12.4	0.1	1	%
ANC	ANC/VOL	8	140.3	4.7	3	KgH <sub>2</sub> SO <sub>4</sub> /t
ANC	NAG_Ti	8	170.5	11.2	7	KgH <sub>2</sub> SO <sub>4</sub> /t
AP	NP	8	43.2	0.5	1	tCaCO <sub>3</sub> /1Kt
As	FUS	6	5.2	0.4	8	ppm
B	FUS	8	310.0	18.5	6	ppm
Ba	FUS	8	50.5	0.5	1	ppm
BaO	XRF	1	0.04	*	*	%
Bi	4A_MICP	16	0.37125	0.0318067	9	ppm
Bi	FUS	8	0.3	*	*	ppm
C	COL	8	18100.0	233.0	1	ppm
C	IR	8	100.0	*	*	ppm
Ca	FUS	16	40643.8	476.1	1	ppm
CaO	FUS	8	5.7	0.1	1	%
Cd	4A_MICP	11	0.3	0.2	75	ppm
Ce	4A_MICP	8	70.9	0.8	1	ppm
Ce	FUS	8	60.4	0.6	1	ppm
Co	FUS	8	23.0	0.7	3	ppm
CO <sub>2</sub>	COL	8	6.7	0.1	1	%
Cr <sub>2</sub> O <sub>3</sub>	FUS	16	0.03	0.005	14	%
Cs	4A_MICP	16	1.53125	0.0478714	3	ppm
Cs	FUS	8	1.5	0.1	4	ppm
Cu	FUS	8	89.6	2.2	2	ppm
Dy	4A_MICP	8	4.5	0.1	2	ppm
EC	WS/MTR	8	44.5	0.8	2	mS/m
Er	4A_MICP	8	2.36875	0.0372012	2	ppm
Er	FUS	8	3.19375	0.0417261	1	ppm
Eu	4A_MICP	8	1.275	0.0267261	2	ppm
Eu	FUS	8	1.3025	0.0296407	2	ppm
Final-pH	ANC/MTR	8	1.0	*	*	pH
FIZZ RATING	NP	8	3.0	*	*	NO UNIT
FR	ANC/QUAL	8	2.0	*	*	ppm
Ga	FUS	8	16.1	0.4	2	ppm
Gd	4A_MICP	8	6.0	0.2	3	ppm
Ge	4A_MICP	8	1.4	0.1	5	ppm
Ge	FUS	8	2.0	*	*	ppm
Hf	4A_MICP	16	3.8	0.3	8	ppm
Hf	FUS	8	4.0	*	*	ppm
Ho	4A_MICP	8	0.8	0.01	1	ppm
Ho	FUS	8	1.1	0.01	1	ppm
In	4A_MICP	16	0.1	0.01	9	ppm
K	FUS	8	2000.0	*	*	ppm
K <sub>2</sub> O	4A_MICP	8	0.3	0.01	2	%
La	FUS	8	30.0	0.4	1	ppm
Li	4A_MICP	16	9.7	0.3	3	ppm
Li	FUS	6	10.7	0.5	5	ppm
Lu	4A_MICP	8	0.3	0.01	3	ppm
Lu	FUS	8	0.4	0.01	2	ppm
Mn	FUS	16	1073.8	20.8	2	ppm
MnO	FUS	8	0.1	0.002	2	%
MnO	XRF	0	*	*	*	%
Mo	4A_MICP	20	1.1	0.2	19	ppm
Moisture	Moisture	8	0.2	0.01	4	%
MPA	CALC	8	44.1	0.4	1	KgH <sub>2</sub> SO <sub>4</sub> /t

Element	Generic Method	n	Mean	SD	RSD %	Unit
MPA	NAG_Ti	8	40.563	0.729	2	KgH <sub>2</sub> SO <sub>4</sub> /t
MPA	NP	8	42.763	0.374	1	KgH <sub>2</sub> SO <sub>4</sub> /t
Na <sub>2</sub> O	4A_MICP	8	6.015	0.093	2	%
Na <sub>2</sub> O	XRF	24	6.1317	0.034	1	%
NAE	XRF	8	99.063	0.192	0.2	%
Nb	4A_MICP	16	10.356	0.411	4	ppm
Nb	FUS	8	11.0	*	*	ppm
Nd	4A_MICP	8	31.35	0.37	1	ppm
Nd	FUS	8	28.113	0.203	1	ppm
Ni	FUS	8	75.75	1.488	2	ppm
NNP	NP	16	117.13	20.22	17	tCaCO <sub>3</sub> /1Kt
NP	NP	16	160	19.92	12	tCaCO <sub>3</sub> /1Kt
NPR	NP	8	3.27	0.111	3	NO UNIT
P	FUS	16	700	*	*	ppm
P <sub>2</sub> O <sub>5</sub>	FUS	8	0.2	0.004	2	%
Pb	FUS	8	38.75	1.753	5	ppm
pH	pH	8	9.2625	0.052	1	pH
pH Drop	ANC/MTR	8	2.825	0.046	2	pH
Pr	4A_MICP	8	7.665	0.055	1	ppm
Pr	FUS	8	7.6325	0.103	1	ppm
Ratio (NP:MPA)	NP	8	4.1813	0.129	3	NO UNIT
Rb	4A_MICP	16	13.531	0.209	2	ppm
Rb	FUS	8	14.088	0.323	2	ppm
S	CALC	16	1.4	0.02	1	%
S	HCl Leachable	4	0.01	*	*	%
S	TSCL	13	0.0338	0.019	57	%
Sb	FUS	8	7.675	0.104	1	ppm
Sc	FUS	8	14.625	0.518	4	ppm
Sm	4A_MICP	8	6.8938	0.068	1	ppm
Sm	FUS	8	6.05	0.107	2	ppm
Sn	4A_MICP	16	3.8813	0.624	16	ppm
Sn	FUS	8	4.5	0.535	12	ppm
SO <sub>3</sub>	XRF	24	3.2971	0.595	18	%
Sr	FUS	8	81.375	0.916	1	ppm
SrO	XRF	8	0.01	*	*	%
Ta	4A_MICP	16	0.8213	0.035	4	ppm
Ta	FUS	8	0.7875	0.035	4	ppm
Tb	4A_MICP	8	0.8	0.01	2	ppm
Tb	FUS	8	0.9	0.01	1	ppm
Th	4A_MICP	16	9.1375	0.166	2	ppm
Th	FUS	8	9.6	0.185	2	ppm
Tl	4A_MICP	12	0.915	2.861	313	ppm
Tm	4A_MICP	8	0.3	0.01	3	ppm
Tm	FUS	8	0.4	0.01	2	ppm
U	4A_MICP	22	5.4955	2.824	51	ppm
U	FUS	8	4.0413	0.085	2	ppm
V	FUS	8	157.38	2.446	2	ppm
V <sub>2</sub> O <sub>5</sub>	XRF	8	0.03	*	*	%
W	4A_MICP	19	3.7789	2.77	73	ppm
W	FUS	8	3	*	*	ppm
Y	4A_MICP	16	20.088	1.033	5	ppm
Y	FUS	16	25.169	5.882	23	ppm
Yb	4A_MICP	8	2.3813	0.046	2	ppm
Yb	FUS	8	2.9	0.05345	2	ppm
Zn	FUS	8	62.25	1.98206	3	ppm
Zr	FUS	8	151	3.8545	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 34) 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:

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

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

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

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.

<i>df</i>	Two-tailed	<i>df</i>	Two-tailed
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**