Certificate

AMIS0624

Certified Reference Material

HG Copper from MMG, DRC

Certificate of Analysis

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

Analyte	Method	[9](μ)	[11] (2s) ±	Unit
Cu	4A_MICP [1]	4.17	0.13	%
Cu	SAL [2]	3.90	0.34	%
Cu	XRF [3]	4.15	0.29	%
Co	4A_MICP	898	58	ppm
Co	FUS [4]	903	172	ppm
C	Combustion/LECO [5]	1.52	0.12	%
S	4A_MICP	0.24	0.02	%
SG	SG [6]	2.77	0.15	Dimensionless
LOI	LOI [7]	7.94	0.57	%
Au	Pb Collection [8]	0.014	0.006	g/t
Al	4A_MICP	6.83	0.47	%
As	4A_MICP	29	4	ppm
Ba	4A_MICP	128	7	ppm
Be	4A_MICP	5	1	ppm
Ca	4A_MICP	1003	110	ppm
Ce	4A_MICP	219	21	ppm
Cr	4A_MICP	121	16	ppm
Fe	4A_MICP	3.71	0.35	%
Ga	4A_MICP	34	7	ppm
Hf	4A_MICP	7	1	ppm
In	4A_MICP	2	0.1	ppm
K	4A_MICP	1.89	0.17	%
La	4A_MICP	119	18	ppm
Li	4A_MICP	176	8	ppm
Mg	4A_MICP	3.18	0.28	%
Mn	4A_MICP	292	33	ppm
Mo	4A_MICP	4	1	ppm
Nb	4A_MICP	29	2	ppm
Ni	4A_MICP	71	6	ppm
P	4A_MICP	872	131	ppm
Pb	4A_MICP	23	4	ppm
Rb	4A_MICP	67	8	ppm
Sb	4A_MICP	3	0.3	ppm
Sc	4A_MICP	13	2	ppm
Se	4A_MICP	10	2	ppm
Sn	4A_MICP	4	1	ppm
Sr	4A_MICP	71	9	ppm
Ta	4A_MICP	2	0.4	ppm
Th	4A_MICP	19	4	ppm
Tl	4A_MICP	0.2	0.02	ppm
U	4A_MICP	11	1	ppm
V	4A_MICP	239	16	ppm
Y	4A_MICP	31	3	ppm
Zn	4A_MICP	47	4	ppm
Zr	4A_MICP	217	34	ppm

Major Oxides
Certified Concentrations (at two Standard Deviations)

Analyte	Method	[9](μ)	[11] (2s) ±	Unit
Al_2O_3	XRF	13.14	0.21	%
Fe_2O_3	XRF	5.45	0.12	%
K_2O	XRF	2.32	0.051	%
MgO	XRF	5.60	0.13	%
MnO	XRF	0.039	0.004	%
P_2O_5	XRF	0.22	0.01	%
SiO_2	XRF	58.19	1.0	%
TiO_2	XRF	0.85	0.02	%

1. Certified Concentrations and Uncertainties

AMIS0624 is a new standard material, developed and certified in December 2018. 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	[9](μ)	*N*	n	k	% RSD	[10](u_c)	[11] (2s) ±	[12] (CI) 95%	[13] (U) ±	Unit
Cu	4A_MICP [1]	4.17	7	53	2.447	2	0.065	0.13	0.034	0.2	%
Cu	SAL [2]	3.90	6	47	2.571	4	0.17	0.34	0.18	0.4	%
Cu	XRF [3]	4.15	2	16	12.706	3	0.14	0.29	1.3	2	%
Co	4A_MICP	898	6	46	2.571	3	29	58	25	75	ppm
Co	FUS [4]	903	3	24	4.303	10	86	172	211	370	ppm
C	Combustion/LECO [5]	1.52	6	48	2.571	4	0.061	0.12	0.063	0.2	%
S	4A_MICP	0.24	6	47	2.571	5	0.01	0.02	0.01	0.03	%
SG	SG [6]	2.77	5	40	2.776	3	0.074	0.15	0.088	0.2	Dimensionless
LOI	LOI [7]	7.94	5	40	2.776	4	0.28	0.57	0.34	1	%
Au	Pb Collection [8]	0.014	6	45	2.571	22	0.003	0.006	0.003	0.01	g/t
Al	4A_MICP	6.83	6	47	2.571	3	0.23	0.47	0.21	1	%
As	4A_MICP	29	7	52	2.447	7	2	4	0.5	5	ppm
Ba	4A_MICP	128	6	43	2.571	3	3	7	3	9	ppm
Be	4A_MICP	5	7	51	2.447	7	0.4	1	0.4	1	ppm
Ca	4A_MICP	1003	7	55	2.447	5	55	110	44	135	ppm
Ce	4A_MICP	219	3	24	4.303	5	10	21	24	44	ppm
Cr	4A_MICP	121	5	40	2.776	7	8	16	10	23	ppm
Fe	4A_MICP	3.71	5	40	2.776	5	0.17	0.35	0.20	0.5	%
Ga	4A_MICP	34	6	48	2.571	11	4	7	2	10	ppm
Hf	4A_MICP	7	3	24	4.303	7	0.5	1	1	2	ppm
In	4A_MICP	2	3	22	4.303	2	0.05	0.1	0.04	0.2	ppm
K	4A_MICP	1.89	5	40	2.776	4	0.083	0.17	0.10	0.2	%
La	4A_MICP	119	6	47	2.571	7	9	18	9	23	ppm
Li	4A_MICP	176	3	24	4.303	2	4	8	6	18	ppm
Mg	4A_MICP	3.18	5	38	2.776	4	0.14	0.28	0.16	0.4	%
Mn	4A_MICP	292	7	52	2.447	6	16	33	17	40	ppm
Mo	4A_MICP	4	7	56	2.447	9	0.4	1	0.2	1	ppm
Nb	4A_MICP	29	2	16	12.706	3	1	2	2	10	ppm
Ni	4A_MICP	71	6	46	2.571	5	3	6	3	8	ppm
P	4A_MICP	872	6	46	2.571	7	65	131	69	168	ppm
Pb	4A_MICP	23	5	40	2.776	8	2	4	1	5	ppm
Rb	4A_MICP	67	3	23	4.303	6	4	8	7	17	ppm
Sb	4A_MICP	3	3	24	4.303	7	0.2	0.3	0.2	1	ppm
Sc	4A_MICP	13	6	48	2.571	6	1	2	1	2	ppm
Se	4A_MICP	10	3	22	4.303	10	1	2	2	4	ppm
Sn	4A_MICP	4	2	16	12.706	13	0.5	1	4	6	ppm
Sr	4A_MICP	71	6	47	2.571	6	5	9	5	12	ppm
Ta	4A_MICP	2	2	16	12.706	9	0.2	0.4	2	2	ppm
Th	4A_MICP	19	5	40	2.776	11	2	4	3	6	ppm
Tl	4A_MICP	0.2	2	16	12.706	5	0.01	0.02	0.08	0.1	ppm
U	4A_MICP	11	3	24	4.303	3	0.4	1	1	2	ppm
V	4A_MICP	239	7	52	2.447	3	8	16	5	20	ppm
Y	4A_MICP	31	3	23	4.303	5	2	3	4	7	ppm
Zn	4A_MICP	47	7	54	2.447	4	2	4	1	5	ppm
Zr	4A_MICP	217	3	24	4.303	8	17	34	41	74	ppm

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

Analyte	Method	[9](μ)	*N*	n	k	% RSD	[10](u_c)	[11] (2s) ±	[12] (CI) 95%	[13] (U) ±	Unit
Al_2O_3	XRF	13.14	5	40	2.776	1	0.11	0.21	0.12	0.3	%
Fe_2O_3	XRF	5.45	5	40	2.776	1	0.061	0.12	0.072	0.2	%
K_2O	XRF	2.32	5	40	2.776	1	0.025	0.051	0.030	0.1	%
MgO	XRF	5.60	5	40	2.776	1	0.066	0.13	0.075	0.2	%
MnO	XRF	0.039	4	32	3.182	5	0.002	0.004	0.001	0.01	%
P_2O_5	XRF	0.22	4	32	3.182	3	0.006	0.01	0.009	0.02	%
SiO_2	XRF	58.19	5	40	2.776	1	0.52	1.0	0.59	1	%
TiO_2	XRF	0.85	5	36	2.776	1	0.01	0.02	0.02	0.03	%

1. *4A_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AA finish*
2. *SAL=Sulphuric Acid Leach*
3. *XRF is X-ray Fluorescence*
4. *FUS is Fusion digestion with ICP finish*
5. *Combustion/LECO*
6. *SG is Specific Gravity*
7. *LOI is Loss on Ignition*
8. *Pb Collection is Lead Collection*
9. *The certified value μ, 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.*
10. *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)*
11. *Two standard deviations (2s)*
12. *Confidence interval at 95% level of confidence.*
13. *Expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (uc) with a coverage factor (k) found from N-1 degrees of freedom (see Appendix 7 for t-distribution table). Example: U = 2.36 x 0.23=0.5%*

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 ≥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
Co 4A_MICP	0.090 %	Co FUS	0.090 %	Unequal Variance *(p=0.010)*	0.90	Accept H_0; certified values are equal

Table 4. Comparison of the mean values for copper in which three different analytical methods are used to determine their concentration. The F-ANOVA *p*-value of 0.005, indicates that at least one of the mean values is different to the others.

	Method	***Method***	***Method***	**F-ANOVA**	**Outcome**
Element	**4A_MICP**	**SAL**	**XRF**	***p*-value**	
% Cu	4.17 %	3.90 %	4.15 %	0.005	Reject H_0, at least one mean is different

Table 5. Tukey Honest Significant Difference (HSD) test results show that the mean values of 4.17 % and 4.15 % copper by 4A_MICP and XRF, respectively, are equal (*p*>0.05).

Method versus Method	p-value	Outcome
4A_MICP vs SAL	<0.05	means are not equal
4A_MICP vs XRF	>0.05	means are equal
SAL vs XRF	<0.05	means are not equal

3. Intended Use

AMIS0624 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 6.

Table 6. Abbreviations, symbols and descriptions.

Abbreviation/Symbol	Description
Alpha (α)	Significance level (denoted by alpha, 'α') 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
µ	Property or certified value of a CRM
p	'*p*-value' a measure of the strength of evidence against H_0
P	Total number of data points in ANOVA
ppm	Parts per million. Equivalent to g/t
RSD	Relative standard deviation usually expressed as % at a 68% LOC
Replicates	Replication is the repetition of an experimental condition so that the variability associated with an analysis can be estimated (ASTM E1847)
s	Standard deviation
s_r	Within laboratory repeatability as derived from ANOVA
s_s	Between laboratory standard deviation as derived from ANOVA
SS	Sum of squares in ANOVA
SST	Total variation in ANOVA
SSB	Between group (laboratory) variance
SSW	Within group (laboratory) variance

Abbreviation/Symbol	Description
2s	Two times standard deviation
SI	Standard International system of units
t_{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
µm	Micron, is an SI derived unit of length equaling 1×10^{-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

8. Origin of Material

Material is from the Kinsevere Cu deposit located in the Central African Copper-belt. The deposit is hosted within the Mine Series rocks of the Roan Group belonging to the Katangan Supergroup.

9. Approximate Mineral and Chemical Composition

The Kinsevere deposit consists of a supergene oxide deposit occurring in dolomites and calcareous siltstones and shales as malachite, chrysocolla, cuprite, chalcocite, native copper and minor azurite. Hypogene mineralization occurs largely as quartz ± carbonate ± apatite veins with chalcopyrite ± bornite ± carrollite emplaced into carbonaceous shales, siltstones, and dolomites.

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_2. 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.

The sample was micro milled for 10 minutes, with ethanol as the grinding liquid. The resultant sample was lightly pressed into a back-packed sample holder. These results unvalidated and not certified, they are to be used for informational purposes only***.*** The results from a diffractogram of the material gave the following results:

Table 7**.** Mineral species identified and quantified two sub-samples of AMIS0624 using Rietveld Refinement.

1. A=Al, Fe^{2+}, Fe^{3+}, Li, Mg, Mn^{2+}, Ni, Zn; Z=Al, B, Fe^{3+}, Si. Chamosite was used in this Rietveld refinement. Further work would be required to more accurately define, and quantify, the chloritegroup minerals.
2. X=Ba, Ca, Cs, (H_3O), K, Na, (NH_4); Y=Al, Cr^{3+}, Fe^{2+}, Fe^{3+}, Li, Mg, Mn^{2+}, Mn^{3+}, V^{3+}, Zn; Z=Al, Be, Fe^{3+}, Si. Muscovite was used in this Rietveld refinement. Further work would be required to more accurately define, and quantify, the mica-group minerals.
3. M=Al and various other cations. Goethite was assumed to give rise to the peak at 24.7°2ϴ/4.18Å. Further work would be required to more accurately define, and quantify, the mineral giving rise to this peak.
4. Tr = trace, i.e. the mineral giving rise to this peak is assumed to be present in trace amounts.
5. Note that these QXRD results are 'unvalidated' (i.e. assay data were not provided to determine the accuracy of these results).

Table 7. Results of XRD analysis.

Mineral	Mineral Composition	Composite
Quartz	SiO_2	52
Malachite	$Cu_2(OH)_2(CO_3)$	6
Chlorite group[1]	$A_{4\text{-}6}Z_4O_{10}(OH,O)_8$	20
Mica group[2]	$XY_{2\text{-}3}Z_4O_{10}(OH,F)_2$	19
Goethite[3]	$(Fe_xM_{1-x})O(OH)$	3
Unassigned peak[4]	23.1°2ϴ/4.46Å	Tr
Unassigned peak[4]	26.0°2ϴ/3.98Å	Tr
Unassigned peak[4]	32.0°2ϴ/3.24Å	Tr
Total		100

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11. Health and Safety

The material is a very fine powder coloured Dark Gray. 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 8.

Table 8. Particle Size Determination by laser diffraction.

Size (µm)	Vol. Under %		Size (µm)	Vol. Under %		Size (µm)	Vol. Under %
0.1	0		50	97.05		200	100
0.25	0		55	97.75		225	100
0.5	2.28		60	98.28		250	100
0.6	3.62		65	98.68		300	100
0.75	5.74		70	98.99		400	100
1	9.39		75	99.23		500	100
2	23.21		80	99.42		600	100
3	33.76		85	99.56		700	100
4	41.59		90	99.67		800	100
5	47.72		95	99.75		900	100
6	52.76		100	99.82		1000	100
7	57.02		105	99.87		1100	100
8	60.7		106	99.88		1200	100
9	63.92		110	99.91		1300	100
10	66.76		115	99.93		1400	100
12	71.56		120	99.96		1500	100
15	77.14		125	99.98		1600	100
18	81.39		130	100		1700	100
20	83.68		135	100		1800	100
25	88.06		140	100		1900	100
30	91.12		150	100		2000	100
35	93.32		160	100			
40	94.94		170	100			
45	96.14		175	100			

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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
b) 0.4g sample, 3 acid digest on a hotplate → Hydrochloric, Nitric and Perchloric AAS finish – Cu, Co, Mn, Ca, Mg, Pb, Fe only
c) Multi element scan to include all elements especially Cu and Co-4-acid total digestion including HF finished with either ICP-OES or ICP-MS or AAS
d) Major oxides and/or Cu and Co by Peroxide fusion finished with either ICP-OES or ICP-MS or AAS
e) LOI and all major oxides excluding U3O8 with XRF finish (Please specify the temperature for LOI)
f) SG – gas pycnometer
g) S and C Combustion/LECO
h) 0.5g sample, leached with 5% sulphuric acid at room temperature AAS finish – Cu
i) Moisture

17. Information Requested of Participating Laboratories

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

a) State aliquots used for all determinations.
b) All results for major elements to be reported as oxides in percentages.
c) All results for multi-element scans and fusion to be reported in ppm.
d) 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:

$$Two\ standard\ deviations = 2\ (u_c)$$

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:

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

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 Contro*l" be used, in setting the limits of the CRM. Table 9 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 9. Example of replicate assay data in which the *CI*, 2*s* 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

CI	0.0088
2s	0.031
U	0.04

23. Participating Laboratories

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

1. ALS Geochemistry Brisbane
2. ALS Geochemistry Ireland
3. ALS Geochemistry Peru
4. ALS Geochemistry Vancouver
5. Bureau Veritas Minerals Ultra Trace Pty Ltd
6. Mimosa Mine Laboratory Zimbabawe
7. SGS Ankara (Turkey)
8. SGS Brazil

24. Accepted Assay Data

Data from the 8 laboratories used for certification are set out in Table 10.

Table 10. Data used to calculate the certified values after removal of outliers.

4A_MICP	SAL	XRF	4A_MICP	FUS	Combustion/LECO	4A_MICP	SG	LOI	Pb Collection
Cu	**Cu**	**Cu**	**Co**	**Co**	**C**	**S**	**SG**	**LOI**	**Au**
ppm	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**%**	**Dimensionless**	**%**	**g/t**
41100	38900	40300	850	883	15500	0.22	2.75	7.98	0.01
41200	39500	40400	857	874	15900	0.23	2.74	8.18	0.01
42100	39400	40400	886	861	15400	0.23	2.71	7.98	0.02
40700	39300	40700	862	885	15600	0.23	2.75	8.09	0.02
40700	39800	40300	889	900	15600	0.23	2.70	7.89	0.02
42300	39700	40800	889	892	15700	0.23	2.78	7.89	0.02
42100	39300	40700	882	900	15700	0.23	2.70	7.90	0.02
43000	40000	40700	867	894	15700	0.23	2.68	8.10	0.01
41600	37400	42800	894	980	15800	0.24	2.85	8.37	0.01
41500	38200	42500	922	1000	16100	0.24	2.87	8.17	0.01
42500	38400	42200	899	980	15800	0.24	2.86	8.24	0.01
42300	38500	42600	904	1000	15700	0.24	2.86	8.26	0.01
41700	38400	42700	912	1020	15900	0.24	2.85	8.30	0.01
42100	38400	42200	928	1000	16000	0.25	2.85	8.29	0.01
42400	37600	42600	929	980	16100	0.24	2.87	8.21	0.01
42100	38000	42700	923	1000	15900	0.24	2.85	8.18	0.01
42200	39500		914	858	14300	0.245	2.82	8.13	0.01
41700	39900		925	808	14200	0.249	2.79	8.12	0.02
42500	39900		879	819	14300	0.24	2.81	8.12	0.01
43000	39300		904	803	14300	0.246	2.80	8.13	0.01
42500	39700		968	842	14100	0.244	2.77	8.14	0.01
41900	39900		943	827	14200	0.248	2.79	8.11	0.01
42000	40000		951	827	14300	0.263	2.80	8.16	0.01
41300	39300		890	840	14400	0.246	2.79	8.14	0.01
41000	38700		890		15200	0.25	2.79	7.54	0.02
40600	38800		900		15200	0.25	2.77	7.58	0.01
41500	38600		890		15000	0.25	2.73	7.58	0.01
41300	38600		950		15100	0.25	2.77	7.57	0.01
41900	38700		920		15300	0.24	2.84	7.56	0.01
41600	38500		890		15300	0.25	2.82	7.59	0.01
41400	38600		910		15200	0.25	2.83	7.58	0.01
40900	38600		890		15400	0.25	2.79	7.59	0.02
41000	41800		930		15200	0.24	2.67	7.78	0.02
42200	41300		910		15200	0.245	2.68	7.79	0.02
41500	42000		885		15200	0.24	2.68	7.80	0.02
41600	41500		925		15500	0.23	2.67	7.85	0.02
41900	42200		875		15400	0.245	2.69	7.65	0.02
41200	41500		915		15400	0.23	2.67	7.66	0.02
41400	41400		905		15500	0.24	2.66	7.71	0.02
42400	41300		846		15600	0.235	2.67	7.80	0.02
41600	37000		871		14700	0.22			0.02
42100	36500		859		14500	0.22			0.02
41800	36600		878		15000	0.22			0.02
41900	36500		867		14600	0.22			0.02
42000	36700		879		14900	0.22			0.02
42562	36600		870		15000	0.22			
41732	35700				14600	0.22			
40248					14900				
40767									
42472									
40733									
41488									
40568									

Assay Data (Cont.)

XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Al_2O_3	Fe_2O_3	K_2O	MgO	MnO	P_2O_5	SiO_2	TiO_2	Al	As	Ba	Be	Ca
%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm
13.25	5.50	2.34	5.67	0.04	0.21	58.70	0.87	66500	28.10	130.00	4.89	900
13.30	5.53	2.35	5.66	0.04	0.21	58.70	0.87	68000	29.60	120.00	4.92	900
13.25	5.55	2.35	5.67	0.04	0.21	58.70	0.87	70100	29.40	130.00	4.67	1000
13.25	5.53	2.35	5.67	0.04	0.21	58.70	0.87	67700	29.00	130.00	4.67	900
13.25	5.50	2.33	5.63	0.04	0.21	58.60	0.86	69800	28.70	130.00	4.73	1000
13.30	5.53	2.34	5.65	0.04	0.21	58.80	0.87	69200	28.80	130.00	4.83	900
13.25	5.53	2.35	5.65	0.04	0.21	58.70	0.86	68700	30.10	130.00	5.03	900
13.25	5.53	2.34	5.66	0.04	0.21	58.70	0.87	66700	28.30	130.00	4.74	900
13.03	5.37	2.34	5.49	0.04	0.22	57.60	0.85	68800	27.00	129.00	5.10	1000
13.03	5.37	2.33	5.49	0.04	0.22	57.63	0.85	64100	29.00	130.00	5.20	1000
13.06	5.37	2.34	5.50	0.04	0.22	57.67	0.85	66700	32.00	128.00	5.20	1000
13.07	5.38	2.34	5.50	0.04	0.22	57.77	0.85	67400	31.00	131.00	5.10	1000
13.01	5.36	2.33	5.49	0.04	0.22	57.61	0.85	67700	28.00	130.00	5.10	1000
13.06	5.38	2.34	5.50	0.04	0.22	57.87	0.85	69000	31.00	131.00	5.30	1000
13.09	5.38	2.34	5.52	0.04	0.22	58.00	0.85	68800	27.00	131.00	5.30	1000
13.05	5.36	2.34	5.49	0.04	0.22	57.74	0.85	68700	31.00	130.00	5.20	1000
13.11	5.47	2.29	5.64	0.04	0.21	58.80	0.84	69900	27.00	130.00	5.30	1100
13.03	5.44	2.28	5.62	0.04	0.21	58.40	0.85	66800	30.00	120.00	5.40	1000
13.08	5.45	2.29	5.64	0.04	0.21	58.71	0.84	67800	33.00	130.00	5.10	1100
13.06	5.45	2.28	5.64	0.04	0.21	58.43	0.85	64200	28.00	130.00	5.30	1100
12.93	5.42	2.27	5.58	0.04	0.22	58.21	0.84	67000	32.00	130.00	5.20	1100
13.02	5.45	2.28	5.62	0.04	0.22	58.51	0.85	70800	25.00	130.00	5.30	1100
13.07	5.44	2.29	5.64	0.04	0.21	58.69	0.85	68900	25.00	130.00	5.60	1100
13.04	5.45	2.29	5.62	0.04	0.21	58.60	0.84	69800	29.00	130.00	5.50	1100
13.20	5.45	2.31	5.64	0.04	0.22	57.96	0.85	70600	29.00	130.00	5.70	1000
13.26	5.46	2.33	5.68	0.04	0.22	57.99	0.85	70400	31.00	130.00	5.20	1000
13.20	5.41	2.31	5.63	0.04	0.22	57.86	0.86	70000	32.00	130.00	5.30	1000
13.08	5.41	2.30	5.56	0.04	0.22	57.32	0.84	72400	29.00	127.00	5.10	1000
13.18	5.45	2.31	5.64	0.04	0.22	57.84	0.85	69500	26.00	126.00	5.30	1100
13.08	5.38	2.31	5.56	0.03	0.22	57.40	0.86	71300	29.00	125.00	5.60	1000
13.14	5.41	2.31	5.60	0.04	0.22	57.35	0.85	71700	26.00	125.00	5.40	1000
13.12	5.40	2.31	5.61	0.04	0.22	57.50	0.85	70500	28.00	126.00	5.50	1000
13.28	5.50	2.33	5.66			58.72	0.84	69100	29.00	126.00	5.30	1000
13.19	5.47	2.31	5.59			58.36	0.83	71400	30.00	127.00	5.40	1000
13.28	5.48	2.32	5.61			58.51	0.83	70200	29.00	124.00	5.30	1000
13.23	5.50	2.32	5.64			58.70	0.84	69200	30.00	120.47	5.50	1000
13.14	5.46	2.30	5.60			58.29		70000	29.00	122.29	5.20	1000
13.04	5.42	2.29	5.54			57.86		69300	29.00	124.13	5.40	1000
13.10	5.46	2.30	5.60			58.20		69800	27.00	123.48	5.40	1000
13.16	5.44	2.31	5.57			58.06		70000	29.00	125.35	5.40	1000
								64600	27.00	121.38	6.10	1000
								65900	27.00	125.60	6.00	1000
								64200	29.00	124.68	6.00	1000
								64900	29.00		6.10	1000
								64000	32.34		4.75	1000
								65200	28.75		5.17	1000
								66200	27.88		4.55	1000
									27.75		4.67	900
									28.81		4.86	1000
									28.83		4.92	1000
									27.90		5.10	1000
									28.97			1000
												1000
												1000
												1000

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Ce	Cr	Fe	Ga	Hf	In	K	La	Li	Mg
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
214.00	119.00	34200	36.10	6.70	2.08	17700	115.50	180.50	30900.00
222.00	123.00	34700	36.40	6.40	2.07	17700	121.00	179.50	31400.00
226.00	122.00	35800	36.50	6.60	2.05	18400	123.00	178.50	32300.00
225.00	114.00	34600	35.20	6.70	2.00	17700	123.50	174.00	31200.00
221.00	122.00	35600	36.20	6.90	2.03	18300	119.50	173.50	32100.00
221.00	127.00	35700	35.70	6.80	2.04	18000	119.00	176.00	32200.00
223.00	118.00	35100	37.20	6.60	2.13	18200	122.50	182.00	31500.00
218.00	116.00	34300	36.30	6.50	2.01	17700	117.00	174.00	30900.00
227.00	130.00	35900	30.00	7.00	2.08	18600	110.00	172.00	33000.00
228.00	125.00	36400	30.00	7.00	2.02	18500	110.00	176.00	32000.00
225.00	126.00	36600	30.00	6.80	2.00	19300	110.00	171.00	32200.00
226.00	125.00	36700	30.00	7.00	2.02	18900	110.00	176.00	32200.00
224.00	122.00	36900	30.00	6.80	2.00	19000	110.00	169.00	32200.00
225.00	124.00	37800	30.00	6.60	2.04	19800	110.00	178.00	33100.00
230.00	126.00	37500	40.00	6.80	2.06	19600	110.00	169.00	33200.00
228.00	122.00	37400	30.00	6.60	2.02	19200	114.00	176.00	33000.00
204.36	118.00	36400	40.00	7.34	2.07	19700	114.00	171.77	32800.00
214.98	116.00	35100	30.00	7.47	2.10	19900	108.00	178.22	33400.00
208.74	115.00	36300	30.00	7.52	1.93	19700	116.00	182.58	31600.00
209.12	119.00	37400	30.00	7.62	2.00	20400	113.00	176.65	33000.00
215.41	119.00	34500	30.00	7.67	2.00	19600	115.00	178.00	34900.00
202.85	118.00	38000	40.00	7.44	2.05	20000	124.00	177.16	34000.00
203.89	122.00	36900	30.00	7.36		20000	115.00	180.18	34300.00
203.31	115.00	37000	40.00	7.53		19800	120.00	181.87	30000.00
	131.00	39600	40.00			19400	110.00		28700.00
	131.00	39700	30.00			19800	110.00		29600.00
	132.00	38900	30.00			19400	110.00		31100.00
	134.00	38500	40.00			18900	110.00		31500.00
	132.00	39100	30.00			19300	120.00		30400.00
	134.00	38800	30.00			19300	120.00		30800.00
	133.00	39200	40.00			19300	120.00		30111.34
	132.00	39700	30.00			19400	120.00		30965.46
	109.76	36600	35.20			17800	120.00		31344.44
	110.49	37900	35.00			18300	120.00		30655.09
	112.00	38800	35.40			18700	120.00		30980.59
	110.30	37700	34.80			18200	120.00		30699.65
	113.81	37900	35.40			18300	120.00		31307.46
	109.42	37800	35.20			18300	120.00		31574.43
	114.08	38300	35.60			18500	120.00		
	112.64	38900	34.80			18800	136.00		
			30.54				136.00		
			32.96				134.00		
			33.20				133.00		
			28.97				133.00		
			30.82				134.00		
			30.90				136.00		
			34.54				134.00		
			33.26						

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Mn	**Mo**	**Nb**	**Ni**	**P**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sn**
ppm	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
276.00	4.64	27.90	69.50	860.00	21.90	60.50	3.13	12.50	11.00	3.30
280.00	4.70	29.90	71.30	880.00	21.90	65.50	2.49	12.40	11.00	3.40
283.00	4.74	28.70	72.20	910.00	22.00	66.00	2.55	12.50	10.00	3.30
283.00	4.70	30.00	71.20	880.00	22.20	66.10	2.76	12.50	10.00	3.20
286.00	4.76	28.60	70.80	910.00	22.10	65.20	2.67	12.50	10.00	3.30
287.00	4.57	30.00	69.90	910.00	21.10	59.50	2.52	12.30	10.00	3.30
282.00	4.73	29.70	72.20	880.00	22.20	67.10	2.52	12.90	11.00	3.40
279.00	4.54	29.50	69.50	870.00	21.70	69.40	2.95	12.30	11.00	3.30
289.00	5.00	28.00	69.00	910.00	26.00	68.20	2.60	13.00	10.00	3.77
291.00	4.00	29.00	68.00	930.00	28.00	70.60	2.60	12.00	10.00	4.32
292.00	4.00	29.00	70.00	890.00	21.00	69.00	2.60	12.00	10.00	3.90
292.00	4.00	28.50	69.00	880.00	23.00	70.80	2.40	12.00	10.00	3.83
297.00	4.00	28.50	69.00	890.00	23.00	70.20	2.40	13.00	10.00	4.02
304.00	5.00	29.00	71.00	920.00	23.00	70.20	2.40	13.00	10.00	3.86
302.00	4.00	30.00	73.00	910.00	24.00	70.20	2.60	13.00	10.00	3.89
298.00	4.00	30.00	70.00	910.00	20.00	60.38	2.60	13.00	10.00	3.94
297.00	5.00		72.00	850.00	23.00	71.11	2.55	14.30	8.41	
300.00	4.00		71.00	820.00	21.00	67.88	2.51	14.40	8.60	
299.00	5.00		69.00	830.00	19.00	62.00	2.65	13.60	7.73	
304.00	4.00		71.00	815.00	20.00	64.46	2.56	14.20	9.01	
303.00	4.00		70.00	805.00	18.00	64.40	2.69	14.00	9.13	
298.00	4.00		72.00	828.00	24.00	69.52	2.65	14.20	8.91	
326.00	5.00		76.00	830.00	23.00	68.02	2.79	15.20		
315.00	4.00		72.00	817.00	22.00		2.74	14.30		
320.00	5.00		72.00	950.00	23.00			14.00		
291.00	4.00		74.00	940.00	22.00			13.00		
299.00	5.00		74.00	940.00	22.00			13.00		
283.00	5.00		76.00	970.00	23.00			13.00		
295.00	4.00		73.00	930.00	23.00			13.00		
309.00	4.00		73.00	940.00	23.00			14.00		
303.00	4.00		73.00	950.00	23.00			13.00		
304.00	4.00		73.00	960.00	22.00			13.00		
300.00	5.00		75.00	850.00	23.37			13.00		
300.00	4.00		75.00	900.00	23.88			13.00		
300.00	5.00		70.00	900.00	23.95			13.00		
300.00	5.00		75.00	900.00	24.32			14.00		
300.00	5.00		70.00	900.00	24.03			13.00		
300.00	5.00		75.00	850.00	23.77			13.00		
300.00	4.00		75.00	950.00	23.78			14.00		
300.00	4.00		70.00	950.00	24.01			13.00		
308.00	4.50		64.87	755.71				13.00		
310.00	4.50		64.62	751.02				13.00		
306.00	4.50		66.41	762.46				13.00		
306.00	4.50		63.91	785.02				13.00		
310.00	4.50		66.71	771.13				13.00		
310.00	4.50		64.69	764.40				14.00		
306.00	4.50							14.00		
312.00	4.50							14.00		
253.53	4.13									
259.59	4.34									
255.50	4.31									
253.38	4.05									
	4.05									
	4.27									
	4.06									
	4.46									

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Sr	Ta	Th	Tl	U	V	Y	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
68.40	1.85	20.00	0.20	11.20	224.00	31.90	44.00	225.00
69.50	2.02	20.00	0.20	11.20	224.00	32.80	45.00	228.00
70.50	1.96	20.00	0.20	11.30	228.00	34.00	45.00	236.00
69.20	1.95	20.00	0.20	11.10	223.00	33.10	45.00	231.00
69.70	1.87	20.00	0.20	11.10	230.00	32.30	46.00	232.00
69.80	1.98	20.00	0.20	10.70	236.00	32.50	46.00	235.00
70.10	1.89	20.00	0.20	11.40	233.00	33.60	44.00	234.00
68.70	1.97	20.00	0.20	10.60	242.00	31.70	45.00	231.00
71.00	2.20	20.00	0.22	10.80	239.00	31.60	47.00	197.00
71.00	2.20	20.00	0.22	10.70	238.00	31.60	46.00	202.00
69.00	2.10	20.00	0.21	10.40	231.00	31.20	47.00	198.00
70.00	2.30	20.00	0.22	10.80	230.00	31.20	48.00	195.00
70.00	2.20	20.00	0.21	10.90	242.00	31.80	47.00	204.00
71.00	2.20	20.00	0.20	10.60	241.00	31.60	48.00	197.00
72.00	2.20	20.00	0.20	10.90	232.00	32.00	49.00	204.00
71.00	2.20	20.00	0.22	10.70	239.00	32.10	47.00	195.00
72.90		20.00		10.25	244.00	28.85	46.00	218.26
72.50		20.00		10.70	232.00	30.34	44.00	225.79
70.70		20.00		10.40	231.00	29.83	45.00	206.82
75.70		20.00		10.55	248.00	28.27	44.00	218.57
73.80		20.00		10.45	254.00	28.72	44.00	229.04
72.90		20.00		10.30	230.00	30.35	46.00	219.99
72.40		20.00		10.50	239.00	31.87	47.00	223.23
78.00		20.00		10.70	227.00		47.00	225.25
78.00		15.60			235.00		47.00	
77.00		15.70			247.00		48.00	
79.00		15.50			244.00		44.00	
76.00		16.00			247.00		48.00	
78.00		16.00			241.00		50.00	
78.00		15.70			239.00		48.00	
78.00		15.60			240.00		48.00	
68.00		15.60			247.00		47.00	
68.50		16.86			238.00		48.00	
67.50		17.26			244.00		44.00	
67.50		16.76			243.00		48.00	
69.50		16.88			240.00		45.00	
69.50		16.75			250.00		47.00	
70.00		16.44			250.00		47.00	
68.00		17.02			240.00		46.00	
62.49		16.95			235.00		50.00	
64.02					235.00		50.00	
65.82					245.00		50.00	
63.77					250.00		45.00	
64.49					250.00		50.00	
63.53					239.98		50.00	
65.56					246.98		50.00	
66.95					224.68		46.97	
					241.61		48.16	
					249.59		48.76	
					239.43		47.52	
					245.82		45.52	
					243.91		47.64	
							47.90	
							50.61	

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 15 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 website.

30. Minimum Sample Size

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

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, a division of Torre Analytical Services (Pty) Ltd, Melesha Mungaroo, and Allan Fraser; accept no liability for any decisions or actions taken following the use of the reference material.

Date of Version 001: 17 January 2019

Version: *001*

Reason for Version 001: Incorrect Grade indicated in title

Version 001 replaces the original report of AMIS0624 Certification

Date of Version 000: 21 December 2018

Version: *000*

Approving Officer:

African Mineral Standards: ____

Melesha Mungaroo (Technical Project Specialist)

Certifying Officer:

Geochemist:____

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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 11**.

Table 11. Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	4A_MICP	11	0.4	0.2	45	ppm
Ag	FUS	7	3.0	*	*	ppm
Al	4A_ICPES	7	69814	684	1	ppm
Al	FUS	16	67613	3267	5	ppm
Al_2O_3	4A_MICP	7	13	0.1	1	%
Al_2O_3	FUS	7	14	0.1	1	%
As	4A_ICPES	7	30	1	4	ppm
As	FUS	1	32	*	*	ppm
B	4A_MICP	8	320	19	6	ppm
Ba	4A_ICPES	8	130	5	4	ppm
Ba	FUS	8	152	5	3	ppm
BaO	XRF	31	0.02	0.01	31	%
Be	4A_ICPES	7	5.2	0.1	1	ppm
Be	FUS	6	5.5	1	10	ppm
Bi	4A_ICPES	8	18	4	23	ppm
Bi	4A_MICP	42	6.0	2.1	35	ppm
Bi	FUS	8	5.0	0.1	2	ppm
Ca	3A_ICPES	8	963	52	5	ppm
Ca	4A_ICPES	7	1000	*	*	ppm
Ca	FUS	7	1336	42	3	ppm
CaO	4A_MICP	8	0.1	*	*	%
CaO	FUS	7	0.1	0.01	4	%
Cd	4A_MICP	16	0.2	0.02	11	ppm
Ce	FUS	8	244	5	2	ppm
CeO_2	XRF	8	0.02	0.0	32	%
Co	2A_AA	7	1035	9	1	ppm
Co	3A_ICPES	8	909	20	2	ppm
Co	4A_ICPES	15	932	13	1	ppm
Co	XRF	15	900	*	*	ppm
Cr	4A_ICPES	7	129	2	2	ppm
Cr	FUS	8	149	12	8	ppm
Cr	XRF	8	100	*	*	ppm
Cr_2O_3	FUS	8	0.02	0.0000000002	0.000001	%
Cr_2O_3	XRF	21	0.02	*	*	%
Cs	4A_MICP	15	1.6	0.02	1	ppm
Cs	FUS	8	1.5	0.1	5	ppm

Element	Generic Method	n	Mean	SD	RSD %	Unit
Cu	2A_AA	8	43813	559	1	ppm
Cu	3A_ICPES	8	41650	382	1	ppm
Cu	4A_ICPES	8	41701	852	2	ppm
Cu	FUS	15	42413	479	1	ppm
Dy	4A_MICP	8	6.8	0.1	1	ppm
Dy	FUS	8	8.5	0.3	3	ppm
Er	4A_MICP	8	4.0	0.1	2	ppm
Er	FUS	8	4.7	0.2	4	ppm
Eu	4A_MICP	8	1.0	0.03	3	ppm
Eu	FUS	8	1.1	0.03	3	ppm
Fe	3A_ICPES	8	38250	540	1	ppm
Fe	4A_ICPES	15	38380	516	1	ppm
Fe	FUS	24	37092	3185	9	ppm
Fe	XRF	8	38663	106	0.3	ppm
Fe_2O_3	FUS	24	5.3	0.5	9	%
Ga	4A_ICPES	8	36	5	14	ppm
Ga	FUS	8	29	1	2	ppm
Gd	4A_MICP	8	7.1	0.1	2	ppm
Gd	FUS	8	8.7	0.3	3	ppm
Ge	4A_MICP	8	0.3	0.04	14	ppm
Ge	FUS	7	1.0	*	*	ppm
Hf	FUS	8	7.5	1	7	ppm
Hg	Trace	8	0.1	0.004	3	ppm
Ho	4A_MICP	8	1.3	0.01	1	ppm
Ho	FUS	8	1.7	0.1	4	ppm
In	FUS	8	1.9	0.05	2	ppm
K	4A_ICPES	7	19657	162	1	ppm
K	FUS	16	19264	645	3	ppm
K_2O	FUS	8	2.3	0.1	3	%
La	4A_ICPES	8	114	5	5	ppm
La	FUS	8	135	3	2	ppm
Li	FUS	8	203	3	1	ppm
Lu	4A_MICP	16	0.5	0.1	12	ppm
Lu	FUS	8	0.6	0.03	4	ppm
Mg	3A_ICPES	8	32163	421	1	ppm
Mg	4A_ICPES	15	34000	444	1	ppm

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

Continued

Element	Generic Method	n	Mean	SD	RSD %	Unit
Mg	FUS	16	32037	2395	7	ppm
MgO	FUS	16	5.3	0.4	7	%
Mn	3A_ICPES	8	309	2	1	ppm
Mn	4A_ICPES	15	303	5	2	ppm
Mn	FUS	8	296	4	1	ppm
Mn	XRF	8	300	*	*	ppm
MnO	FUS	8	0.04	0.002	4	%
Mo	4A_ICPES	7	5.0	*	*	ppm
Mo	FUS	8	9.0	1	8	ppm
Moisture	Moisture	16	1.1	0.4	34	%
Na	4A_ICPES	8	400	*	*	ppm
Na	4A_MICP	48	400	*	*	ppm
Na_2O	4A_MICP	7	0.1	*	*	%
Na_2O	XRF	32	0.1	0.04	50	%
Nb	FUS	8	30	1	3	ppm
Nd	4A_MICP	8	92	1	1	ppm
Nd	FUS	8	102	3	3	ppm
Ni	2A_AA	8	66	2	3	ppm
Ni	4A_ICPES	7	74	1	1	ppm
Ni	FUS	8	67	5	7	ppm
Ni	XRF	5	64	11	18	ppm
P	4A_ICPES	8	925	24	3	ppm
P	FUS	8	940	63	7	ppm
P_2O_5	FUS	7	0.2	*	*	%
Pb	3A_ICPES	8	21	1	3	ppm
Pb	4A_ICPES	16	22	2	11	ppm
Pb	FUS	1	20	*	*	ppm
Pb	XRF	8	163	52	32	ppm
Pr	4A_MICP	8	27	0.3	1	ppm
Pr	FUS	8	28	1	2	ppm
Rb	FUS	8	65	2	3	ppm
Rb	XRF	8	66	12	18	ppm
Re	4A_MICP	8	0.02	0.003	16	ppm
S	4A_ICPES	8	0.2	0.01	2	%
S	Combustion/LECO	48	0.2	0.02	11	%
S	XRF	16	0.2	0.03	17	%

Element	Generic Method	n	Mean	SD	RSD %	Unit
Sb	4A_ICPES	5	6.0	2	37	ppm
Sb	FUS	8	2.2	0.1	5	ppm
Sc	4A_ICPES	7	13	*	*	ppm
Sc	FUS	8	12	1	4	ppm
Si	FUS	7	278286	1496	1	ppm
SiO_2	FUS	15	59	1	1	%
Sm	4A_MICP	8	12	0.3	3	ppm
Sm	FUS	8	13	0.5	4	ppm
Sr	4A_ICPES	7	74	0.5	1	ppm
Sr	FUS	8	73	1	2	ppm
SrO	XRF	16	0.01	*	*	%
Tb	4A_MICP	15	1.1	0.02	2	ppm
Tb	FUS	8	1.5	0.05	3	ppm
Te	4A_MICP	16	0.1	0.01	16	ppm
Th	4A_ICPES	8	20	*	*	ppm
Th	FUS	8	16	1	4	ppm
Ti	4A_ICPES	8	4250	93	2	ppm
Ti	4A_MICP	37	3632	406	11	ppm
Ti	FUS	24	4948	478	10	ppm
TiO_2	FUS	24	0.8	0.1	10	%
Tl	4A_ICPES	5	10.0	*	*	ppm
Tm	4A_MICP	8	0.6	0.01	2	ppm
Tm	FUS	8	0.7	0.04	6	ppm
U	FUS	8	11	0.3	3	ppm
V	4A_ICPES	8	233	5	2	ppm
V	FUS	8	223	7	3	ppm
V	XRF	8	263	52	20	ppm
W	4A_MICP	30	5.0	3.7	74	ppm
W	XRF	6	10.0	*	*	ppm
Y	FUS	8	39	1	3	ppm
Yb	4A_MICP	16	3.5	0.3	8	ppm
Yb	FUS	8	4.3	0.1	3	ppm
Zn	4A_ICPES	8	46	2	5	ppm
Zn	FUS	3	53	4	8	ppm
Zr	XRF	8	300	*	*	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]:

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

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:

$|z|\leq2$ satisfactory performance
$2<|z|\leq3$ questionable performance
$|z|>2$ 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:

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

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

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

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

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

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

$$Observed\ \%RSD = \frac{s}{Mean} x100 \qquad [5]$$

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

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

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

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*):

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

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):

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

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.

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

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.

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

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:

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

From equations [9] through [13], the ANOVA table as shown in Table 12 is developed.

Table 12. 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_{crit}
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:

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

Within laboratory repeatability is determined as

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

and, the between laboratory precision as

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

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.

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

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

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 μ 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 | | 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 13. 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 ≠ 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 13. 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:

$$Two\ standard\ deviations = 2\ (u_c) \qquad [19]$$

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

Appendix 5. Confidence Interval

Confidence interval is calculated as:

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

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 to15 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 ±2s and ±3s, where *s* is the standard deviation calculated from [21].
8. Construct the Shewhart control chart around the mean of *n* replicates.
9. Use ±2s as the warning limits.
10. Use ±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 105ºC 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^2 with the CRM material spread evenly over same; this represents a 0.1 gram spread per cm^2. In correcting the certified value for moisture content, a moisture correction factor is calculated:

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

$$Air\ dry\ basis\ concentration = MCF\ x\ certified\ value\ on\ a\ dry\ basis \quad [23]$$

Example

The moisture content determined at 105ºC 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:

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

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:

$$0.995\ x\ 12.62\% = 12.56\%$$

The stated measurement uncertainty also needs to be corrected using [22] and [23], *e.g.* 0.995 x 0.52 = $0.51_{(7)}$, rounded to 0.52%. The air-dry basis concentration *i.e.* 12.56±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 1µg or 0.001mg. Even with a microscope it may be difficult to locate and pick up a prill weighing ten times that amount (*i.e.* 0.01mg or 10µg) and weigh it. If an analyst can weigh a prill of 1µg then the LOD becomes 1µg. However, the concentration factor would be 50 times for a 50-gram assay sample and therefore the LOD in g/t becomes 1µg divided by the original mass of the sample in grams taken for fire assay [24]. Therefore, the LOD in fire assay is computed as:

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

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

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

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be 0.02g/t. *i.e.* 1µg = 1g/t, therefore 1µg/50g = 0.02g/t. If no prill was found, then the LOD result would be <0.02 g/t or “not detected”. Using a larger assay sample mass improves the LOD and LOQ (Table 13). Table 15 gives a recommended reporting scheme for LOD and LOQ.

Table 14. Mass of assay sample and corresponding limit of detection and limit of quantitation for an assay microbalance capability of smallest prill mass of 1µg or 0.001mg.

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 15. Recommended reporting scheme for LOD and LOQ in fire assay.

Data	Report as
<LOD	Not detected
<LOQ	Detected
≥LOQ	Report assay result

Appendix 9. T-distribution table

Table 16. T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence.

df	Two-tailed	*df*	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