Certificate

AMIS0605

Certified Reference Material

Gold Ore - High grade, Navachab Gold Mine, Namibia

Certificate of Analysis

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

Analyte	Method	Certified (μ)[6]	(2s)[8] ±	Unit
Au	Pb Collection[1]	0.783	0.11	g/t
Cu	4A_MICP[2]	466	20	ppm
C	Combustion/LECO[3]	3630	363	ppm
LOI	LOI[4]	2.57	0.26	%
S	Combustion/LECO	0.47	0.03	%
S	4A_MICP	0.47	0.04	%
Al	4A_MICP	6.92	0.27	%
As	4A_MICP	3	0.9	ppm
Ba	4A_MICP	659	120	ppm
Be	4A_MICP	11	2	ppm
Bi	4A_MICP	57	15	ppm
Ca	4A_MICP	3.47	0.37	%
Ce	4A_MICP	68	17	ppm
Cr	4A_MICP	179	17	ppm
Cs	4A_MICP	41	4	ppm
Fe	4A_MICP	5.32	0.21	%
Ga	4A_MICP	20	2	ppm
Hf	4A_MICP	4	1	ppm
In	4A_MICP	0.1	0.03	ppm
K	4A_MICP	3.42	0.14	%
La	4A_MICP	32	4	ppm
Li	4A_MICP	169	10	ppm
Lu	4A_MICP	0.4	0.05	ppm
Mg	4A_MICP	2.37	0.13	%
Mn	4A_MICP	3334	385	ppm
Mo	4A_MICP	8	0.9	ppm
Na	4A_MICP	5698	905	ppm
Nb	4A_MICP	15	1	ppm
Ni	4A_MICP	114	15	ppm
P	4A_MICP	1071	126	ppm
Pb	4A_MICP	12	1	ppm
Rb	4A_MICP	259	11	ppm
Sb	4A_MICP	2	0.4	ppm
Sc	4A_MICP	14	1	ppm
Sn	4A_MICP	4	0.6	ppm
Sr	4A_MICP	166	16	ppm
Ta	4A_MICP	6	1	ppm
Tb	4A_MICP	0.9	0.1	ppm
Te	4A_MICP	0.5	0.08	ppm
Th	4A_MICP	10	2	ppm
Ti	4A_MICP	4494	237	ppm
Tl	4A_MICP	2	0.2	ppm
U	4A_MICP	5	0.5	ppm
V	4A_MICP	158	19	ppm
W	4A_MICP	53	12	ppm
Y	4A_MICP	26	3	ppm
Yb	4A_MICP	3	0.2	ppm
Zn	4A_MICP	64	12	ppm
Zr	4A_MICP	137	23	ppm

Major Oxides

Certified Concentrations (at two Standard Deviations)

Analyte	Method	Certified (μ)[6]	(2s)[8] ±	Unit
Al_2O_3	XRF[5]	13.86	0.85	%
CaO	XRF	5.16	0.094	%
Fe_2O_3	XRF	7.85	0.16	%
K_2O	XRF	4.17	0.26	%
MgO	XRF	4.13	0.10	%
MnO	XRF	0.45	0.01	%
Na_2O	XRF	0.77	0.05	%
P_2O_5	XRF	0.26	0.03	%
SiO_2	XRF	59.06	1.6	%
TiO_2	XRF	0.76	0.03	%

1. Certified Concentrations and Uncertainties

AMIS0605 is a new standard material, developed and certified in March 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 (µ)[6]	*N*	n	k	% RSD	(u_c)[7]	(2s)[8] ±	(CI)[9] 95%	(U)[10] ±	Unit
Au	Pb Collection[1]	0.783	5	40	2.776	7	0.055	0.11	0.060	0.2	g/t
Cu	4A_MICP[2]	466	4	31	3.182	2	10	20	10	31	ppm
C	Combustion/LECO[3]	3630	3	22	4.303	5	181	363	404	780	ppm
LOI	LOI[4]	2.57	4	31	3.182	5	0.13	0.26	0.20	0.4	%
S	Combustion/LECO	0.47	3	24	4.303	3	0.01	0.03	0.03	0.06	%
S	4A_MICP	0.47	3	24	4.303	5	0.02	0.04	0.05	0.09	%
Al	4A_MICP	6.92	2	15	12.706	2	0.13	0.27	0.85	2	%
As	4A_MICP	3	3	24	4.303	18	0.5	0.9	0.3	2	ppm
Ba	4A_MICP	659	3	24	4.303	9	60	120	147	258	ppm
Be	4A_MICP	11	3	24	4.303	9	1	2	3	4	ppm
Bi	4A_MICP	57	3	24	4.303	13	8	15	19	33	ppm
Ca	4A_MICP	3.47	3	24	4.303	5	0.18	0.37	0.45	0.8	%
Ce	4A_MICP	68	3	24	4.303	13	9	17	21	37	ppm
Cr	4A_MICP	179	3	23	4.303	5	9	17	18	37	ppm
Cs	4A_MICP	41	3	23	4.303	5	2	4	4	8	ppm
Fe	4A_MICP	5.32	3	23	4.303	2	0.11	0.21	0.15	0.5	%
Ga	4A_MICP	20	3	24	4.303	5	0.9	2	2	4	ppm
Hf	4A_MICP	4	3	23	4.303	17	0.7	1	2	3	ppm
In	4A_MICP	0.1	3	24	4.303	10	0.01	0.03	0.03	0.06	ppm
K	4A_MICP	3.42	4	31	3.182	2	0.068	0.14	0.085	0.2	%
La	4A_MICP	32	4	31	3.182	6	2	4	3	6	ppm
Li	4A_MICP	169	4	31	3.182	3	5	10	7	16	ppm
Lu	4A_MICP	0.4	3	24	4.303	6	0.03	0.05	0.06	0.1	ppm
Mg	4A_MICP	2.37	3	23	4.303	3	0.066	0.13	0.093	0.3	%
Mn	4A_MICP	3334	4	32	3.182	6	193	385	294	613	ppm
Mo	4A_MICP	8	4	30	3.182	6	0.4	0.9	0.6	1	ppm
Na	4A_MICP	5698	3	24	4.303	8	452	905	1108	1946	ppm
Nb	4A_MICP	15	3	24	4.303	4	0.6	1	1	3	ppm
Ni	4A_MICP	114	4	31	3.182	7	8	15	12	25	ppm
P	4A_MICP	1071	3	24	4.303	6	63	126	153	271	ppm
Pb	4A_MICP	12	3	24	4.303	4	0.5	1	0.9	2	ppm
Rb	4A_MICP	259	3	21	4.303	2	5	11	8	23	ppm
Sb	4A_MICP	2	2	15	12.706	8	0.2	0.4	2	3	ppm
Sc	4A_MICP	14	3	23	4.303	4	0.6	1	1	3	ppm
Sn	4A_MICP	4	2	16	12.706	8	0.3	0.6	3	4	ppm
Sr	4A_MICP	166	3	23	4.303	5	8	16	19	33	ppm
Ta	4A_MICP	6	4	32	3.182	10	0.6	1	0.9	2	ppm
Tb	4A_MICP	0.9	3	24	4.303	7	0.06	0.1	0.1	0.3	ppm
Te	4A_MICP	0.5	2	16	12.706	8	0.04	0.08	0.2	0.5	ppm
Th	4A_MICP	10	3	23	4.303	10	1	2	2	4	ppm
Ti	4A_MICP	4494	2	16	12.706	3	119	237	874	1507	ppm
Tl	4A_MICP	2	3	24	4.303	8	0.1	0.2	0.3	0.5	ppm
U	4A_MICP	5	4	30	3.182	6	0.3	0.5	0.4	0.9	ppm
V	4A_MICP	158	4	32	3.182	6	9	19	14	30	ppm
W	4A_MICP	53	4	32	3.182	11	6	12	9	19	ppm
Y	4A_MICP	26	3	24	4.303	5	1	3	3	6	ppm
Yb	4A_MICP	3	3	24	4.303	3	0.09	0.2	0.1	0.4	ppm
Zn	4A_MICP	64	3	24	4.303	9	6	12	13	25	ppm
Zr	4A_MICP	137	2	16	12.706	8	11	23	101	145	ppm

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

Analyte	Method	Certified (μ)[6]	*N*	n	k	% RSD	(u_c)[7]	(2s)[8] ±	(CI)[9] 95%	(U)[10] ±	Unit
Al_2O_3	XRF[5]	13.86	4	32	3.182	3	0.43	0.85	0.68	1	%
CaO	XRF	5.16	3	24	4.303	1	0.047	0.094	0.11	0.2	%
Fe_2O_3	XRF	7.85	3	24	4.303	1	0.078	0.16	0.19	0.3	%
K_2O	XRF	4.17	4	32	3.182	3	0.13	0.26	0.21	0.4	%
MgO	XRF	4.13	3	24	4.303	1	0.049	0.10	0.12	0.2	%
MnO	XRF	0.45	3	24	4.303	1	0.004	0.01	0.005	0.02	%
Na_2O	XRF	0.77	4	31	3.182	3	0.02	0.05	0.04	0.08	%
P_2O_5	XRF	0.26	3	24	4.303	6	0.02	0.03	0.04	0.06	%
SiO_2	XRF	59.06	3	24	4.303	1	0.78	1.6	2.0	3	%
TiO_2	XRF	0.76	3	24	4.303	2	0.01	0.03	0.03	0.06	%

1. *Pb Collection*
2. *4A_MICP is a Multi-acid digestion with ICP/MICP/AA finish*
3. *Combustion/LECO*
4. *LOI is Loss on Ignition*
5. *XRF is X-ray Fluorescence*
6. *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.*
7. *The combined uncertainty of the certified value is the within-laboratory reproducibility standard deviation derived from the analysis of variance of results from N number of laboratories and n number of sample replicates. (u_c)*
8. *Two standard deviations (2s)*
9. *Confidence interval at 95% level of confidence.*
10. *Expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (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
S 4A_MICP	0.470 %	S Combustion/LECO	0.469 %	Equal Variance *(p=0.239)*	0.928	Accept H_0; certified values are equal

3. Intended Use

AMIS0605 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 (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

The raw material of AMIS0604 was sourced from QKR Namibia, Navachab Gold Mine, situated in Namibia, 10km southwest of Karibib and 170km west northwest of Windhoek. The orebody is located in the Central Zone of the Pan-African Damara Orogen.

9. Approximate Mineral and Chemical Composition

The major gangue minerals are dolomite, calcite, feldspar and quartz with minor garnet, hornblende, diopside, ilmenite, biotite and tremolite. Sulphides comprise pyrrhotite; subordinate pyrite, chalcopyrite and traces of bismuth, bismuthinite, sphalerite and galena. Gold occurs as free gold with minor maldonite (gold-bismuth alloy).

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 5**.** Mineral species identified and quantified two sub-samples of AMIS0605 using Rietveld Refinement.

1. Note that these QXRD results are ‘unvalidated’ (i.e. assay data were not provided to determine the accuracy of these results).
2. It was assumed that the peak at 34.3°2Ɵ/3.03Å arose from Calcite. Further work would be required to better define and quantify the mineral from this peak.
3. Albite was used in these Rietveld refinements. Further work would be required to better define the Plagioclase group minerals.
4. Orthoclase was used in these Rietveld refinements. Further work would be required to better define the K-feldspar group minerals present in these samples.
5. A=Ca, Na, K, Pb; B=Ca, Fe^{2+}, Li, Mg, Mn^{2+}, Na; Y=Al, Cr^{3+}, Fe^{2+}, Fe^{3+}, Mg, Mn^{2+}, Ti, Z=Al, Be, Si, Ti. Magnesiohornblende was used in these Rietveld refinements. Further work would be required to better define the Amphibole group minerals.
6. A=Al, Fe^{2+}, Fe^{3+}, Li, Mg, Mn^{2+}, Ni, Zn; Z=Al, B, Fe^{3+}, Si. Clinochlore was used in these Rietveld refinements. Further work would be required to better define the Chlorite-group mineral.
7. 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, Fe3+, Si. Muscovite and Biotite were used in these Rietveld refinements. Further work would be required to better define the mica-group minerals. Mica might be over/under-estimated.

Table 5. Results of XRD analysis.

Mineral	Mineral Composition	Composite
Quartz	SiO_2	42
Calcite	$CaCO_3$	2
Plagioclase[3]	$(Na,Ca)Al(Al,Si)Si_2O_8$	10
K feldpsar[4]	$KAlSi_3O_8$	22
Amphibole group[5]	$A0\text{-}1B_2Y_5Z_8O_{22}(OH, F, Cl)_2$	7
Chlorite group[6]	$(X_5Al)(AlSi_3)O_{10}(OH)_8$	1
Mica group[7]	$X_2Y_{4-6}Z_8O_{20}(OH,F)4$	16
Total		100%

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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 %		Size (µm)	Vol. Under %		Size (µm)	Vol. Under %
0.1	0		50	96.31		200	100
0.25	0		55	97.17		225	100
0.5	2.19		60	97.82		250	100
0.6	3.52		65	98.32		300	100
0.75	5.6		70	98.7		400	100
1	9.05		75	99		500	100
2	20.88		80	99.23		600	100
3	29.51		85	99.4		700	100
4	36.1		90	99.54		800	100
5	41.52		95	99.65		900	100
6	46.17		100	99.74		1000	100
7	50.28		105	99.81		1100	100
8	53.94		106	99.82		1200	100
9	57.25		110	99.87		1300	100
10	60.25		115	99.91		1400	100
12	65.48		120	99.94		1500	100
15	71.83		125	99.97		1600	100
18	76.83		130	100		1700	100
20	79.59		135	100		1800	100
25	84.99		140	100		1900	100
30	88.83		150	100		2000	100
35	91.62		160	100			
40	93.66		170	100			
45	95.18		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 or ICP-MS or AAS
b) Multi element scan to include all elements-4-acid total digestion including HF and/or peroxide fusion finished with either ICP-OES or ICP-MS or AAS
c) LOI and all major oxides excluding U_3O_8 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) 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.

17. 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)

18. 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]).

19. 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).

20. 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]).

21. 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*, 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

22. Participating Laboratories

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

1. Antech Zimbabwe
2. Argetest Mineral Processing, R&D and Analysis Services
3. Bureau Veritas Minerals Ultra Trace Pty Ltd
4. SGS Newburn
5. SGS Vancouver (Canada)
6. Super Laboratory Services (Pty) Ltd. Springs

23. Accepted Assay Data

Data from the 6 laboratories used for certification are set out in Table 8.

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

XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF
Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
%	%	%	%	%	%	%	%	%	%
14.40	5.11	7.78	4.37	4.09	0.45	0.81	0.28	58.21	0.75
14.46	5.10	7.77	4.36	4.07	0.45	0.81	0.27	58.42	0.75
14.55	5.11	7.79	4.39	4.08	0.45	0.82	0.27	58.17	0.75
14.46	5.11	7.78	4.37	4.07	0.45	0.81	0.27	58.28	0.75
14.54	5.12	7.78	4.37	4.09	0.45	0.81	0.27	58.22	0.75
14.49	5.12	7.78	4.35	4.10	0.45	0.79	0.27	58.28	0.75
14.49	5.11	7.78	4.36	4.08	0.45	0.81	0.28	58.26	0.75
14.56	5.12	7.77	4.34	4.10	0.45	0.75	0.28	58.02	0.75
13.60	5.18	7.84	4.08	4.11	0.45	0.76	0.25	59.20	0.77
13.60	5.19	7.82	4.08	4.12	0.45	0.76	0.25	59.20	0.78
13.50	5.18	7.86	4.09	4.12	0.45	0.76	0.25	59.20	0.77
13.60	5.19	7.84	4.09	4.11	0.45	0.76	0.25	59.20	0.77
13.60	5.19	7.84	4.09	4.11	0.45	0.76	0.25	59.20	0.78
13.60	5.18	7.83	4.09	4.11	0.44	0.77	0.25	59.20	0.77
13.60	5.19	7.82	4.08	4.10	0.44	0.75	0.25	59.10	0.78
13.60	5.19	7.82	4.08	4.12	0.45	0.75	0.25	59.20	0.77
13.65	5.20	7.91	4.13	4.17	0.45	0.76	0.25	59.73	0.75
13.66	5.17	7.91	4.13	4.19	0.44	0.76	0.24	59.84	0.75
13.68	5.19	7.95	4.13	4.20	0.45	0.76	0.25	59.79	0.75
13.64	5.21	7.93	4.12	4.17	0.45	0.76	0.25	59.71	0.75
13.68	5.15	7.91	4.13	4.18	0.45	0.75	0.24	59.78	0.75
13.64	5.20	7.95	4.13	4.16	0.45	0.76	0.25	59.73	0.75
13.63	5.21	7.95	4.13	4.20	0.44	0.75	0.25	59.74	0.75
13.68	5.22	7.94	4.13	4.15	0.44	0.78	0.25	59.85	0.76
13.60			4.10			0.78			
13.70			4.14			0.76			
13.80			4.12			0.76			
13.70			4.10			0.78			
13.70			4.10			0.77			
13.70			4.10			0.77			
13.70			4.12			0.77			
13.70			4.11						

Assay Data (Cont.)

Pb Collection	4A_MICP	Combustion/LECO	LOI	Combustion/LECO	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Au	Cu	C	LOI	S	S	Al	As	Ba	Be
g/t	ppm	ppm	%	%	%	ppm	ppm	ppm	ppm
0.79	459	3710	2.67	0.48	0.46	69700	2.61	729	11.00
0.71	453	3660	2.76	0.47	0.47	69700	3.00	720	10.70
0.74	455	3980	2.72	0.46	0.46	70000	2.95	725	10.90
0.74	461	3700	2.76	0.47	0.45	69900	2.61	722	10.70
0.76	461	4030	2.67	0.45	0.47	69700	2.73	735	10.80
0.75	464	3810	2.77	0.46	0.46	70100	2.62	730	10.80
0.74	459	3600	2.77	0.46	0.46	69900	2.83	724	10.80
0.74	462	3600	2.42	0.47	0.47	67200	2.67	716	10.80
0.80	461	3600	2.46	0.48	0.50	69700	3.00	598	12.20
0.80	476	3500	2.46	0.49	0.49	68800	2.00	603	12.30
0.73	488	3500	2.45	0.48	0.49	66700	3.00	612	12.30
0.76	478	3400	2.45	0.49	0.49	68900	2.00	633	12.50
0.69	473	3700	2.44	0.48	0.49	67800	3.00	606	12.40
0.72	477	3600	2.51	0.47	0.50	71000	3.00	620	12.30
0.77	462	3580	2.41	0.49	0.50	68000	3.00	611	12.20
0.77	465	3520	2.46	0.48	0.48		2.00	604	12.30
0.74	460	3500	2.51	0.46	0.45		2.00	639	9.90
0.80	460	3500	2.50	0.46	0.46		2.00	632	10.40
0.71	460	3560	2.48	0.46	0.45		3.00	631	10.70
0.73	475	3400	2.50	0.46	0.45		2.00	643	10.50
0.77	470	3490	2.49	0.46	0.46		2.00	649	10.20
0.76	460	3540	2.49	0.46	0.46		3.00	648	10.40
0.74	460		2.51	0.46	0.45		3.00	635	10.20
0.74	445		2.60	0.46	0.46		3.00	645	10.80
0.82	471		2.58						
0.82	476		2.61						
0.85	456		2.66						
0.80	473		2.55						
0.79	460		2.64						
0.79	483		2.64						
0.78	460		2.57						
0.84									
0.85									
0.85									
0.86									
0.86									
0.86									
0.85									
0.86									
0.86									

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
Bi	**Ca**	**Ce**	**Cr**	**Cs**	**Fe**	**Ga**	**Hf**	**In**	**K**	**La**
ppm	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
50.08	35200	62.30	176	40.80	53300	20.69	3.59	0.13	34900	32.50
47.55	34900	62.50	174	40.40	53300	20.51	3.43	0.14	35300	32.00
48.11	35200	61.90	174	37.90	53200	19.96	3.69	0.13	34500	32.20
49.04	35200	61.20	175	41.10	54100	21.02	3.66	0.13	34400	32.20
49.40	35100	63.00	173	38.40	53600	20.85	3.42	0.13	35100	32.30
47.58	34900	62.50	174	38.20	53000	20.74	3.60	0.12	34900	32.40
51.50	34900	60.80	175	39.70	53400	20.66	3.45	0.13	34700	31.70
48.00	34900	60.10	170	40.60	52800	19.96	3.32	0.13	34800	31.70
59.30	36100	77.60	185	40.80	51300	18.60	4.80	0.16	33000	30.50
58.70	36200	77.30	190	40.50	51200	19.00	4.60	0.14	32900	30.60
62.40	36200	77.20	195	40.70	52900	18.40	4.80	0.16	33300	28.70
60.90	36000	77.80	185	42.20	55000	19.00	4.60	0.14	34500	30.80
60.20	36700	78.90	180	42.10	51500	19.40	4.80	0.16	33600	29.40
60.00	36400	78.40	190	41.10	52900	19.40	4.80	0.16	34200	28.60
58.90	36100	76.90	185	41.20	52800	18.60	4.80	0.14	33200	29.90
60.70	36200	78.80	190	42.00	52300	19.00	3.44	0.16	34000	33.40
62.92	31900	62.61	170	43.00	52700	18.90	3.58	0.13	34000	33.20
63.80	33100	65.08	166	44.00	54400	19.60	3.71	0.13	33600	33.00
64.52	33100	66.20	186	42.00	53600	20.00	3.56	0.14	34200	33.20
63.19	32500	64.57	176	42.00	52200	19.00	3.60	0.13	34800	34.20
61.50	32200	62.67	174	44.00	53600	19.00	3.64	0.13	34800	34.50
65.29	32100	64.43	177	43.00	54700	19.70	3.64	0.13	34500	33.10
64.16	33300	66.17	184	43.00	54400	19.60	3.67	0.13	34000	33.80
59.37	33300	66.46				20.30		0.15	35000	29.40
									34300	30.70
									34000	31.50
									33900	30.00
									34300	29.90
									33600	30.70
									34600	31.00
									34900	31.70

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Li	**Lu**	**Mg**	**Mn**	**Mo**	**Na**	**Nb**	**Ni**	**P**	**Pb**
ppm	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
167	0.42	23700	3499	7.39	6300	15.60	119	1000	11.53
169	0.43	23800	3526	7.15	6200	14.70	125	1000	12.16
167	0.4	23900	3585	6.66	6200	15.10	127	1000	11.53
165	0.43	23900	3567	6.74	6200	15.70	124	1000	11.48
170	0.43	23800	3553	7.21	6100	15.40	123	1000	11.95
169	0.45	23500	3546	6.96	6200	15.00	122	1000	11.77
165	0.43	23600	3577	7.40	6200	15.50	125	1000	12.10
168	0.43	23900	3516	7.90	6300	14.40	112	1000	11.11
169	0.42	22400	3320	7.80	5400	14.00	111	1100	11.00
170	0.42	22800	3340	7.70	5400	14.50	109	1100	11.00
172	0.42	23600	3410	7.90	5540	14.50	112	1100	11.00
175	0.42	24600	3520	7.50	5590	14.00	116	1150	11.00
171	0.44	22800	3450	7.60	5360	15.00	116	1150	12.00
172	0.44	23400	3460	8.00	5470	14.50	113	1100	11.00
170	0.42	23600	3420	7.50	5330	15.00	109	1100	11.00
165	0.42	23500	3330	7.50	5260	14.50	115	1100	11.00
162	0.38	23100	3220	8.00	5500	15.30	115	1100	11.50
163	0.39	24800	3250	8.00	5500	15.50	110	1100	12.00
161	0.39	25000	3250	8.50	5400	15.90	115	1100	12.20
168	0.38	23800	3240	8.00	5400	15.00	110	1100	11.80
165	0.38	24700	3320	8.00	5500	15.10	110	1100	11.50
162	0.39	23800	3320	8.00	5500	15.80	110	1100	12.10
160	0.39	23400	3280	7.47	5500	15.50	115	1100	11.90
175	0.38		3280	8.00	5400	15.50	103	1100	11.40
174			3100	7.69			104		
175			3160	7.60			108		
172			3050	7.34			101		
172			3000	7.70			104		
173			3070	7.93			113		
176			3100	7.72			104		
172			3230				109		
			3210						

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Rb	Sb	Sc	Sn	Sr	Ta	Tb	Te	Th
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
258	2.50	14.28	4.00	169	5.01	0.89	0.50	8.70
256	2.50	14.38	4.00	171	5.03	0.96	0.50	8.65
256	2.60	14.47	4.00	169	5.00	1.00	0.50	8.45
262	2.50	14.68	4.00	170	4.86	0.97	0.40	8.68
255	2.60	14.61	4.00	172	5.15	0.94	0.50	8.27
263	2.50	14.54	4.00	173	5.07	1.00	0.50	8.98
265	2.50	14.15	4.00	169	4.86	0.90	0.50	8.32
262	2.70	14.23	4.00	170	4.93	0.94	0.50	10.20
259	2.24	15.00	3.50	170	6.22	0.84	0.52	10.90
265	2.36	15.00	3.60	171	5.71	0.82	0.57	10.70
264	2.30	14.00	3.60	170	6.05	0.80	0.50	10.40
258	2.24	15.00	3.60	170	6.45	0.82	0.57	11.00
266	2.26	15.00	3.50	172	6.43	0.86	0.50	10.40
250	2.29	15.00	3.60	171	5.98	0.86	0.53	10.40
258	2.25	15.00	3.60	171	6.06	0.86	0.50	10.60
267		15.00	3.50	171	5.85	0.84	0.52	9.50
253		13.40		161	6.30	0.86		9.80
249		14.00		155	6.10	0.88		9.80
260		14.10		158	6.30	0.93		9.60
257		13.50		154	6.00	0.87		9.70
262		13.50		155	6.20	0.87		9.80
		14.00		159	5.70	0.90		9.80
		13.90		157	6.10	0.91		9.80
					5.90	0.97		
					5.99			
					6.10			
					5.99			
					5.69			
					6.00			
					6.09			
					6.21			
					6.75			

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Ti	Tl	U	V	W	Y	Yb	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
4400	1.60	4.70	168.20	45.06	26.30	2.70	62.10	145
4400	1.70	4.60	166.50	44.83	26.10	2.70	62.00	147
4500	1.60	4.80	168.90	46.05	27.70	2.90	61.20	146
4400	1.60	4.80	170.30	46.33	28.10	2.90	61.30	142
4400	1.70	4.60	170.70	46.60	26.30	2.70	60.00	143
4400	1.60	4.80	171.00	45.71	27.80	2.80	62.50	144
4500	1.60	4.90	168.30	46.21	26.80	2.70	59.90	146
4400	1.60	4.70	168.20	46.48	25.80	2.70	58.20	146
4400	1.40	5.41	160.00	56.10	26.30	2.85	74.00	125
4600	1.40	4.95	158.00	56.20	26.10	2.85	67.00	130
4600	1.40	5.53	161.00	57.60	26.20	2.85	67.00	131
4500	1.40	5.14	166.00	57.10	26.20	2.90	68.00	128
4600	1.40	5.18	164.00	59.70	26.50	2.90	66.00	132
4500	1.50	5.26	165.00	57.70	26.80	2.85	74.00	128
4700	1.40	4.90	162.00	56.30	26.20	2.90	73.00	129
4600	1.50	5.00	159.00	59.80	26.50	2.85	73.00	129
	1.39	5.00	150.00	50.00	23.60	2.70	61.00	
	1.46	4.80	150.00	50.50	24.70	2.70	62.00	
	1.51	5.40	150.00	49.50	25.60	2.90	58.00	
	1.43	5.20	155.00	48.00	24.00	2.80	62.00	
	1.42	5.00	160.00	51.50	23.90	2.70	60.00	
	1.47	5.20	155.00	52.00	24.70	2.80	61.00	
	1.47	4.65	150.00	50.00	24.50	2.80	61.00	
	1.60	4.73	155.00	51.00	25.90	2.80	63.00	
		4.81	144.00	56.00				
		4.73	149.00	57.80				
		4.76	149.00	58.70				
		4.76	145.00	56.10				
		5.16	149.00	55.90				
		4.87	154.00	56.90				
			148.00	59.00				
			158.00	59.20				

24. Reported Values

The certified values listed in this certificate fulfil the AMIS statistical criteria (see section 17) regarding agreement for certification and have been independently validated by Allan Fraser.

25. 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.

26. 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).

27. Metrological Traceability

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

28. Period of Validity

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

29. Minimum Sample Size

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

30. Availability

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

31. Recommended use in Quality Control

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

32. Legal Notice

This certificate and the reference material described in it have been prepared with due care and attention. However, AMIS, a division of Torre Analytical Services (Pty) Ltd, 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: 13 March 2019

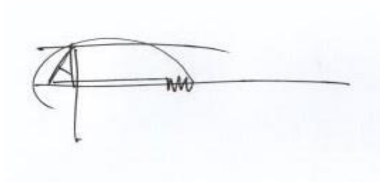
Version: *000*

Approving Officer:

African Mineral Standards: ____

Makhosi Khoza (Quality Specialist)

Certifying Officer:



Geochemist:____

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

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Appendices

Appendix 1: Uncertified Element Statistics

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

Table 9. Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	4A_MICP	15	0.4	0.02	5	ppm
Al	FUS	8	72625.0	443.2	1	ppm
Au	4A_MICP	7	0.7	0.01	2	g/t
B	4A_MICP	8	55.0	9.3	17	ppm
Ba	XRF	8	600.0	*	*	ppm
Cd	4A_MICP	14	0.6	0.4	62	ppm
Co	4A_MICP	24	18.8	4.1	22	ppm
Cr	FUS	7	300.0	*	*	ppm
Cr	XRF	8	300.0	*	*	ppm
Cr_2O_3	XRF	24	0.04	0.01	17	%
Cu	4A_ICPES	8	485.5	19.0	4	ppm
Cu	XRF	8	500.0	*	*	ppm
Dy	4A_MICP	16	5.4	0.2	3	ppm
Er	4A_MICP	16	3.1	0.1	4	ppm
Eu	4A_MICP	15	1.3	0.04	3	ppm
Fe	FUS	8	55175.0	455.9	1	ppm
Gd	4A_MICP	15	6.1	0.2	3	ppm
Ho	4A_MICP	16	1.0	0.05	5	ppm
Mg	FUS	8	24625.0	243.5	1	ppm
Moisture	Moisture	8	0.2	0.01	3	%
Nd	4A_MICP	15	33.2	1.0	3	ppm
Ni	XRF	8	100.0	*	*	ppm
Pd	Pb Collection	15	0.5	0.02	4	g/t
Pr	4A_MICP	16	8.2	0.4	4	ppm
Pt	Pb Collection	15	1.0	0.03	3	g/t
S	XRF	8	0.5	0.002	0.5	%
SG	SG	8	2.8	0.04	1	Dimensionless
Si	FUS	8	278000.0	1690.3	1	ppm
Sm	4A_MICP	16	6.8	0.4	6	ppm
Ti	FUS	8	4737.5	91.6	2	ppm
Tm	4A_MICP	16	0.4	0.02	4	ppm
V	XRF	8	200.0	*	*	ppm
V_2O_5	XRF	8	0.03	*	*	%

* 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:

$|z|$≤2 satisfactory performance
2<$|z|$≤3 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

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

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

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

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

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

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 17, 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.

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

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 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_{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:

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

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 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 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 ≠ 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 31) 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:

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

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

Appendix 5. Confidence Interval

Confidence interval is calculated as:

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

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 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:

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

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 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^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:

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

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

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:

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

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 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 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 13. 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 14. 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