AMIS0618

Certified Reference Material

Lead Concentrate, Black Mountain, Northern Cape, South Africa.

Certificate of Analysis

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

Analyte	Method	Certified (μ)[7]	(2s)[9] ±	Unit
Pb	Titration[1]	69.86	0.82	%
Pb	XRF[2]	69.74	4.30	%
SG	SG[3]	6.35	0.27	Dimensionless
S	Combustion/LECO[4]	14.16	0.35	%
S	XRF	14.12	0.68	%
Ag	4A_MICP[5]	592	53	ppm
As	4A_MICP	212	24	ppm
Ba	4A_MICP	97	14	ppm
Be	4A_MICP	0.9	0.3	ppm
Bi	4A_MICP	2863	229	ppm
Ca	4A_MICP	939	212	ppm
Cd	4A_MICP	88	8	ppm
Ce	4A_MICP	16	4	ppm
Co	4A_MICP	228	17	ppm
Cs	4A_MICP	0.8	0.1	ppm
Cu	4A_MICP	2.01	0.12	%
Cu	FUS[6]	2.15	0.17	%
Fe	4A_MICP	5.19	0.32	%
Fe	FUS	5.28	0.067	%
Ga	4A_MICP	1	0.1	ppm
In	4A_MICP	11	2	ppm
La	4A_MICP	9	1	ppm
Mg	4A_MICP	1193	173	ppm
Mn	4A_MICP	6551	388	ppm
Mo	4A_MICP	221	34	ppm
Ni	4A_MICP	73	8	ppm
Rb	4A_MICP	2	0.6	ppm
Sb	4A_MICP	175	38	ppm
Se	4A_MICP	15	2	ppm
Sn	4A_MICP	4	2	ppm
Sr	4A_MICP	3	0.8	ppm
Te	4A_MICP	2	1	ppm
Th	4A_MICP	2	0.7	ppm
Tl	4A_MICP	15	0.6	ppm
U	4A_MICP	3	0.4	ppm
W	4A_MICP	6	2	ppm
Y	4A_MICP	5	2	ppm
Zn	4A_MICP	1.98	0.061	%
Zn	FUS	2.01	0.13	%
Zn	XRF	2.04	0.22	%

Major Oxides

Certified Concentrations (at two Standard Deviations)

Analyte	Method	Certified (μ)[7]	(2s)[9] ±	Unit
Fe_2O_3	FUS	7.55	0.095	%
MgO	XRF	0.21	0.04	%
MnO	XRF	0.94	0.08	%
SiO_2	XRF	2.71	0.31	%
ZnO	XRF	2.54	0.28	%

1. Certified Concentrations and Uncertainties

AMIS0618 is a new standard material, developed and certified in June 2019. Table 1 gives the certified concentrations, confidence interval, combined and expanded uncertainty for the certified reference material. Table 2 shows the certified major oxides concentrations, two standard deviations, confidence interval, combined and expanded uncertainty.

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

Analyte	Method	Certified (μ)[7]	*N*	n	k	% RSD	(u_c)[8]	(2s)[9] ±	(CI)[10] 95%	(U)[11] ±	Unit
Pb	Titration[1]	69.86	4	31	3.182	1	0.41	0.82	0.65	1	%
Pb	XRF[2]	69.74	2	16	12.706	3	2.20	4.30	19.3	27	%
SG	SG[3]	6.35	5	40	2.776	2	0.14	0.27	0.15	0.4	Dimensionless
S	Combustion/LECO[4]	14.16	3	22	4.303	1	0.18	0.35	0.23	0.8	%
S	XRF	14.12	2	16	12.706	2	0.34	0.68	3.0	4	%
Ag	4A_MICP[5]	592	5	39	2.776	5	27	53	33	74	ppm
As	4A_MICP	212	4	32	3.182	6	12	24	18	38	ppm
Ba	4A_MICP	97	5	40	2.776	7	7	14	8	20	ppm
Be	4A_MICP	0.9	4	31	3.182	18	0.2	0.3	0.2	0.5	ppm
Bi	4A_MICP	2863	5	40	2.776	4	114	229	136	317	ppm
Ca	4A_MICP	939	4	31	3.182	11	106	212	174	337	ppm
Cd	4A_MICP	88	7	56	2.447	5	4	8	4	10	ppm
Ce	4A_MICP	16	3	24	4.303	14	2	4	5	10	ppm
Co	4A_MICP	228	5	38	2.776	4	9	17	11	24	ppm
Cs	4A_MICP	0.8	2	16	12.706	7	0.05	0.1	0.4	0.7	ppm
Cu	4A_MICP	2.01	4	32	3.182	3	0.061	0.12	0.095	0.2	%
Cu	FUS[6]	2.15	2	16	12.706	4	0.085	0.17	0.75	1	%
Fe	4A_MICP	5.19	4	32	3.182	0.0003	0.16	0.32	0.25	0.5	%
Fe	FUS	5.28	3	23	4.303	1	0.034	0.067	0.048	0.1	%
Ga	4A_MICP	1	2	16	12.706	6	0.07	0.1	0.6	0.9	ppm
In	4A_MICP	11	3	23	4.303	11	1	2	3	5	ppm
La	4A_MICP	9	4	31	3.182	8	0.7	1	1	2	ppm
Mg	4A_MICP	1193	5	38	2.776	7	87	173	100	241	ppm
Mn	4A_MICP	6551	5	40	2.776	3	194	388	231	539	ppm
Mo	4A_MICP	221	6	48	2.571	8	17	34	18	44	ppm
Ni	4A_MICP	73	7	53	2.447	6	4	8	4	10	ppm
Rb	4A_MICP	2	3	24	4.303	16	0.3	0.6	0.7	1	ppm
Sb	4A_MICP	175	4	32	3.182	11	19	38	30	61	ppm
Se	4A_MICP	15	3	23	4.303	6	1	2	1	4	ppm
Sn	4A_MICP	4	2	16	12.706	26	0.9	2	8	12	ppm
Sr	4A_MICP	3	4	32	3.182	15	0.4	0.8	0.6	1	ppm
Te	4A_MICP	2	3	24	4.303	26	0.5	1	1	2	ppm
Th	4A_MICP	2	3	23	4.303	19	0.3	0.7	0.8	1	ppm
Tl	4A_MICP	15	3	24	4.303	2	0.3	0.6	0.6	1	ppm
U	4A_MICP	3	3	23	4.303	6	0.2	0.4	0.2	0.8	ppm
W	4A_MICP	6	3	24	4.303	15	0.9	2	2	4	ppm
Y	4A_MICP	5	4	32	3.182	17	0.8	2	1	3	ppm
Zn	4A_MICP	1.98	5	38	2.776	2	0.030	0.061	0.034	0.08	%
Zn	FUS	2.01	3	24	4.303	3	0.065	0.13	0.14	0.3	%
Zn	XRF	2.04	3	24	4.303	5	0.11	0.22	0.27	0.5	%

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

Analyte	Method	Certified (μ)[7]	*N*	n	k	% RSD	(u_c)[8]	(2s)[9] ±	(CI)[10] 95%	(U)[11] ±	Unit
Fe_2O_3	FUS	7.55	3	23	4.303	1	0.047	0.095	0.066	0.2	%
MgO	XRF	0.21	3	23	4.303	9	0.02	0.04	0.05	0.09	%
MnO	XRF	0.94	3	24	4.303	4	0.04	0.08	0.1	0.2	%
SiO_2	XRF	2.71	5	38	2.776	6	0.16	0.31	0.18	0.4	%
ZnO	XRF	2.54	3	24	4.303	5	0.14	0.28	0.34	0.6	%

1. *Titration*
2. *XRF is X-ray Fluorescence*
3. *SG is Specific Gravity*
4. *Combustion/LECO*
5. *4A_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish*
6. *FUS is Fusion digestion with ICP finish*
7. *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.*
8. *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)*
9. *Two standard deviations (2s)*
10. *Confidence interval at 95% level of confidence.*
11. *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
Pb Titration	69.86 %	Pb XRF	69.74 %	Unequal Variance *(p=0.013)*	0.95	Accept H_0; certified values are equal
S Combustion/LECO	14.16 %	S XRF	14.12 %	Equal Variance *(p=0.07)*	0.839	Accept H_0; certified values are equal
Cu 4A_MICP	2.01 %	Cu FUS	2.15 %	Equal Variance *(p=0.254)*	0.074	Accept H_0; certified values are equal
Fe 4A_MICP	5.19 %	Fe FUS	5.28 %	Unequal Variance *(p=0.015)*	0.331	Accept H_0; certified values are equal
Zn XRF	2.04 %	Zn FUS	2.01 %	Equal Variance *(p=0.206)*	0.692	Accept H_0; certified values are equal
Pb Titration	69.86 %	Pb XRF	69.74 %	Unequal Variance *(p=0.013)*	0.95	Accept H_0; certified values are equal
S Combustion/LECO	14.16 %	S XRF	14.12 %	Equal Variance *(p=0.07)*	0.839	Accept H_0; certified values are equal
Cu 4A_MICP	2.01 %	Cu FUS	2.15 %	Equal Variance *(p=0.254)*	0.074	Accept H_0; certified values are equal
Fe 4A_MICP	5.19 %	Fe FUS	5.28 %	Unequal Variance *(p=0.015)*	0.331	Accept H_0; certified values are equal

3. Intended Use

AMIS0618 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 material was provided by Black Mountain Mining and is a lead concentrate made from Black Mountain Broken Hill type ore from the Northern Cape Province in South Africa. The Aggeneys copper-lead-zinc-silver deposits occur in the Precambrian metavolcanic metasedimentary Bushmanland Group which forms part of the Namaqualand Metamorphic Complex.

9. Approximate Mineral and Chemical Composition

The material comprises of concentrate grades of galena as well as sphalerite, chalcopyrite and quartz. The upper ore body is comprised of three types of iron formation: magnetite quartzite, magnetite-amphibolite and barite-magnetite. The lower ore body consists of barite to quarzitic schist with disseminated sulphides which grades into magnetite amphibolite. The footwall to the massive sulphide lenses is characterized by abundant sillimanite.

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.

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

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

The limitations of qualitative XRD analysis are as follows:

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

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

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

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

Table 5. Results of XRD analysis.

Phase	Formula	Composite
Amorphous Content		20%
Chalcopyrite	$CuFeS_2$	3%
Galena	PbS	71%
Magnetite	Fe_3O_4	1%
Quartz	SiO_2	2%
Serpentine	$Mg_3Si_2O_5(OH)_4$	1%
Sphalerite	(Zn,Fe)S	2%
Total		100%

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11. Health and Safety

The material is a very fine powder coloured dark blueish grey (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 %
0.01	0.00		0.77	0.59		58.88	99.07
0.01	0.00		0.87	0.84		66.90	99.42
0.01	0.00		0.99	1.18		76.01	99.70
0.01	0.00		1.13	1.67		86.36	99.89
0.02	0.00		1.28	2.38		98.11	100.00
0.02	0.00		1.45	3.39		111.47	100.00
0.02	0.00		1.65	4.77		126.65	100.00
0.02	0.00		1.88	6.60		143.90	100.00
0.03	0.00		2.13	8.94		163.49	100.00
0.03	0.00		2.42	11.88		185.75	100.00
0.04	0.00		2.75	15.44		211.04	100.00
0.04	0.00		3.12	19.65		239.78	100.00
0.05	0.00		3.55	24.50		272.43	100.00
0.05	0.00		4.03	29.95		309.52	100.00
0.06	0.00		4.58	35.88		351.67	100.00
0.07	0.00		5.21	42.16		399.55	100.00
0.08	0.00		5.92	48.62		453.96	100.00
0.09	0.00		6.72	55.08		515.77	100.00
0.10	0.00		7.64	61.33		586.00	100.00
0.11	0.00		8.68	67.22		665.79	100.00
0.13	0.00		9.86	72.60		756.45	100.00
0.15	0.00		11.20	77.37		859.45	100.00
0.17	0.00		12.73	81.51		976.48	100.00
0.19	0.00		14.46	85.00		1109.44	100.00
0.21	0.00		16.43	87.89		1260.50	100.00
0.24	0.00		18.66	90.25		1432.13	100.00
0.28	0.00		21.21	92.16		1627.14	100.00
0.31	0.00		24.09	93.70		1848.69	100.00
0.36	0.00		27.37	94.96		2100.42	100.00
0.41	0.00		31.10	96.00		2386.42	100.00
0.46	0.06		35.33	96.85		2711.36	100.00
0.52	0.15		40.15	97.56		3080.54	100.00
0.59	0.27		45.61	98.15		3500.00	100.00
0.68	0.41		51.82	98.65			

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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) Pb by Titration
b) Multi element scan to include all elements by Multi-acid total digestion, including HF, ICP-OES or ICP-MS
c) Majors (Include all oxides) by Lithium Borate Fusion
d) SG – gas pycnometer
e) LOI
f) Moisture

17. Information Requested of Participating Laboratories

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

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

23. Participating Laboratories

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

1. Alfred H Knight International Ltd.
2. ALS Geochemistry Vancouver
3. Argetest Mineral Processing, R&D and Analysis Services
4. Bureau Veritas Minerals Ultra Trace Pty Ltd
5. Intertek Perth
6. SGS Geosol Laboratories Ltda (Brazil)
7. SGS Mineral Services Lakefield (Canada)
8. SGS Vancouver (Canada)
9. Shiva Analyticals India
10. UIS Analytical Services (pty) Ltd.

24. Accepted Assay Data

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

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

FUS	XRF	XRF	XRF	XRF	Titration	XRF	SG	Combustion/LECO	XRF
Fe_2O_3	MgO	MnO	SiO_2	ZnO	Pb	Pb	SG	S	S
%	%	%	%	%	ppm	ppm	Dimensionless	%	%
7.57	0.23	0.96	2.57	2.40	704300	681600	6.29	14.37	13.95
7.56	0.22	0.94	2.60	2.43	704500	681800	6.29	14.21	13.94
7.63	0.24	0.98	2.60	2.41	705300	682400	6.35	14.00	13.91
7.56	0.25	0.93	2.54	2.39	704000	682200	6.21	14.16	13.88
7.57	0.23	0.97	2.72	2.43	705400	682400	6.24	14.18	13.87
7.54	0.22	0.93	2.46	2.37	700800	682400	6.27	13.98	13.85
7.62	0.22	0.95	2.43	2.40	704700	681600	6.30	13.78	13.86
7.60	0.19	0.95	2.46	2.41	695400	682800	6.33	13.96	13.82
7.55	0.20	0.89	2.84	2.68	694500	713790	6.50	14.20	14.53
7.53	0.21	0.89	3.01	2.66	694700	713541	6.42	14.25	14.24
7.52	0.20	0.90	2.99	2.69	695300	711721	6.45	13.75	14.37
7.57	0.20	0.91	2.93	2.68	694800	712570	6.55	14.20	14.27
7.58	0.21	0.89	2.94	2.69	694500	713951	6.42	14.25	14.31
7.47	0.21	0.90	2.87	2.68	694500	712300	6.55	14.20	14.29
7.45	0.20	0.89	2.78	2.69	694500	711148	6.50	14.30	14.32
7.59	0.19	0.89	2.67	2.67	696800	711431	6.55	14.30	14.49
7.56	0.19	1.00	2.72	2.55	696400		5.96	14.20	
7.56	0.19	0.96	2.79	2.54	696200		6.22	14.40	
7.45	0.22	0.97	2.70	2.54	694800		6.27	14.30	
7.55	0.20	0.97	2.74	2.54	696400		6.33	14.20	
7.55	0.19	0.96	2.73	2.55	697500		6.16	14.10	
7.55	0.19	0.97	2.68	2.54	696500		6.03	14.30	
7.55	0.19	0.97	2.61	2.54	696500		6.35		
		0.97	2.61	2.54	698100		6.11		
			2.65		698700		6.41		
			2.61		698800		6.34		
			2.63		698500		6.35		
			2.59		699000		6.40		
			2.63		699600		6.41		
			2.57		698700		6.37		
			2.64		700300		6.38		
			2.70				6.37		
			2.66				6.40		
			2.93				6.39		
			2.73				6.39		
			2.64				6.38		
			2.55				6.40		
			2.84				6.38		
							6.40		
							6.41		

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS
Ag	As	Ba	Be	Bi	Ca	Cd	Ce	Co	Cs	Cu	Cu
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
622	220	99	0.65	2768	1100	88.00	16.10	213	0.81	19300	22000
619	227	93	0.70	2786	1100	89.00	14.90	213	0.84	19400	22000
626	222	97	0.68	2747	1100	85.00	14.10	212	0.80	19300	22300
627	232	94	0.68	2697	1100	89.00	13.70	217	0.83	19400	22200
623	220	97	0.68	2699	1100	89.00	13.90	217	0.84	19400	21900
620	230	95	0.70	2741	1100	88.00	14.80	214	0.81	19300	22300
625	216	96	0.65	2737	1100	87.00	13.00	228	0.87	19400	22200
621	224	93	0.67	2683	842	88.00	13.10	223	0.85	19300	22100
606	207	104	0.82	2840	855	93.86	17.70	226	0.80	20300	20855
608	219	99	0.86	2760	844	93.80	19.15	222	0.80	20000	20877
608	208	101	0.84	2740	869	92.33	17.55	223	0.70	20100	20915
609	214	104	0.86	2840	871	91.27	18.45	227	0.80	20000	21025
613	214	97	0.84	2840	847	91.49	17.85	223	0.80	20100	21050
602	209	103	0.80	2850	854	91.27	18.10	229	0.80	20200	20897
606	210	97	0.84	2770	866	92.93	19.20	232	0.80	19800	20849
605	212	106	0.86	2850	900	91.98	19.35	238	0.70	20100	21060
571	216	110	1.11	2892	900	82.00	17.30	237		20300	
571	220	100	1.04	2972	900	83.00	16.20	236		20500	
573	211	110	1.05	2936	900	82.00	17.00	231		20700	
572	214	100	1.02	2936	900	82.00	16.50	236		20500	
577	218	100	0.96	2930	900	83.00	16.20	235		20100	
572	220	110	0.98	2919	900	82.00	16.60	236		20300	
572	212	100	0.99	2929	900	83.00	16.30	233		20500	
570	221	110	1.04	2940	900	81.00	16.50	231		20500	
601	198	91	1.00	3000	900	90.00		230		20767	
594	200	89	1.00	3050	900	90.00		228		20962	
605	192	89	1.00	2990	900	90.00		229		20699	
597	192	89	1.00	3000	900	90.00		231		20534	
607	196	91	0.90	3000	900	90.00		230		20705	
604	201	89	0.90	3000	900	90.00		229		20748	
605	201	90	0.90	2990	900	90.00		236		20854	
595	195	90		3070		90.00		238		20614	
559		90		2850		85.70		232			
563		90		2840		86.10		237			
553		90		2840		89.50		236			
552		90		2840		86.80		237			
554		100		2820		88.10		235			
556		90		2840		86.60		240			
560		90		2840		88.70					
		100		2750		86.50					
						92.70					
						92.90					
						91.10					
						92.40					
						92.10					
						89.90					
						92.80					
						95.50					
						85.50					
						83.00					
						82.00					
						83.00					
						85.00					
						85.00					
						84.00					
						83.50					

Assay Data (Cont.)

4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Fe	Fe	Ga	In	La	Mg	Mn	Mo	Ni	Rb	Sb	Se
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
52700	52945	1.12	11.04	9.00	1300	6650	206	82.00	2.00	183	14.00
53900	52875	1.11	10.93	9.10	1300	6610	203	82.00	1.90	181	17.00
53900	53364	1.09	10.99	8.60	1300	6688	202	79.00	2.20	184	14.00
53700	52875	1.09	10.87	8.90	1300	6617	207	81.00	1.90	181	16.00
53300	52945	1.08	10.73	9.20	1200	6575	209	80.00	2.10	180	14.00
53100	52735	1.05	10.77	8.60	1300	6591	207	74.41	2.00	178	16.00
53900	53294	1.15	10.78	8.90	1300	6523	209	75.85	2.30	180	16.00
53900	53154	1.17	10.53	9.20	1300	6695	206	75.00	2.10	179	15.00
51000	52800	1.20	12.50	10.00	1150	6270	219	75.31	1.90	200	17.00
50100	52600	1.20	12.75	9.00	1150	6320	217	76.06	1.80	200	15.00
50500	52600	1.20	12.45	9.70	1140	6300	217	74.84	1.80	200	16.00
50300	52900	1.20	12.75	9.70	1140	6350	222	73.92	1.90	200	16.00
50200	53000	1.20	12.75	9.40	1160	6360	218	75.19	1.90	200	15.00
50500	52200	1.20	12.30	8.80	1150	6300	216	68.00	1.80	200	17.00
49600	52100	1.20	12.70	8.20	1150	6270	218	69.00	1.90	200	17.00
50400	53100	1.20	9.98	8.30	1150	6310	218	69.00	2.00	200	15.00
53000	52900		10.00	9.80	1200	6700	237	69.00	1.60	159	15.00
53200	52900		9.94	10.70	1200	6900	239	69.00	1.40	158	15.00
52700	52100		10.20	9.60	1100	6900	246	67.00	1.60	158	15.00
52500	52800		10.40	10.00	1100	6800	233	69.00	1.60	159	15.00
52800	52800		10.40	9.70	1100	6700	235	69.00	1.60	160	15.00
52800	52800		10.30	10.00	1200	6800	237	74.00	1.40	161	15.00
53200	52800		10.40	10.70	1200	6800	238	73.00	1.60	162	15.00
52700				9.30	1200	6800	244	73.00	1.40	163	
50700				8.50	1100	6433	200	75.00		159	
52000				9.00	1100	6489	200	72.00		163	
50300				8.70	1100	6379	200	71.00		159	
50800				8.80	1100	6361	200	73.00		164	
50600				8.30	1100	6447	200	72.00		160	
50500				8.60	1100	6480	200	68.00		160	
50400				8.30	1100	6476	200	69.00		162	
51500					1100	6461	200	70.00		165	
					1300	6600	246	68.00			
					1300	6660	241	68.00			
					1200	6550	246	68.00			
					1300	6590	235	69.00			
					1300	6560	242	70.00			
					1200	6470	242	74.80			
						6540	245	74.60			
						6710	237	72.90			
							220	74.70			
							223	71.50			
							212	74.10			
							221	75.00			
							226	76.70			
							221	70.00			
							223	70.00			
							221	70.00			
								70.00			
								70.00			
								70.00			
								70.00			
								70.00			

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS	XRF
Sn	Sr	Te	Th	Tl	U	W	Y	Zn	Zn	Zn
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
4.20	2.90	1.90	1.70	14.70	3.60	6.00	4.50	19400	19500	19300
4.30	2.90	2.20	1.90	15.10	3.10	6.00	4.30	19400	19400	19500
4.40	2.91	2.40	1.90	14.80	3.60	7.00	4.40	19300	20600	19400
4.30	2.90	2.20	1.60	14.90	3.20	7.00	4.60	19200	19900	19200
4.30	2.90	2.40	2.00	15.10	3.40	7.00	4.60	19200	19500	19500
4.20	2.86	2.30	1.90	14.50	3.40	6.00	4.70	19500	20000	19000
4.40	2.89	2.20	2.00	14.70	3.00	6.00	4.30	19200	19600	19300
4.60	2.94	2.30	1.80	14.70	2.90	7.00	4.60	19400	20500	19400
3.00	3.10	2.12	2.15	14.30	3.30	6.10	4.00	19600	20781	21520
3.00	3.10	2.24	2.02	14.30	3.00	6.20	4.30	20100	20818	21360
3.00	3.30	2.07	1.99	14.25	3.10	6.10	4.00	19700	20701	21601
3.00	3.10	2.16	2.43	14.45	3.50	5.90	4.50	19900	20714	21520
3.00	3.20	2.07	1.96	14.15	3.30	6.20	4.40	19800	20938	21601
3.00	2.90	2.14	1.84	14.00	3.10	6.10	4.20	20000	20793	21520
3.00	3.20	2.27	2.21	14.25	3.30	6.50	4.60	19600	20527	21601
3.00	3.10	2.25	1.50	14.90	3.40	6.60	4.30	19900	20808	21440
	3.10	1.40	1.60	14.30	3.20	5.50	5.10	19700	19400	20500
	3.10	1.40	1.40	14.60	3.10	5.50	5.50	19900	19700	20400
	3.00	1.40	1.40	14.50	3.10	4.50	5.30	20000	20400	20400
	3.10	1.40	1.50	14.60	3.40	5.00	5.30	19800	20200	20400
	3.00	1.40	1.40	14.50	3.20	4.50	5.40	19700	19200	20500
	3.00	1.20	1.50	14.70	3.30	5.50	5.10	19700	19600	20400
	3.10	1.40	1.40	14.70	3.20	5.00	5.40	19800	19500	20400
	3.10	1.20		14.50		4.50	5.50	19900	19800	20400
	2.50						6.00	19880		
	2.50						6.10	19628		
	2.00						6.00	19841		
	2.50						6.30	19743		
	2.50						6.00	19973		
	2.50						6.10	19835		
	2.50						6.20	19915		
	1.50						6.00	19698		
								20100		
								20100		
								20200		
								19900		
								19800		
								20400		

25. Reported Values

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

26. Validation of Accuracy (Trueness)

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

27. Metrological Traceability

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

28. Period of Validity

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

29. Minimum Sample Size

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

30. Availability

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

31. Recommended use in Quality Control

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

32. Legal Notice

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

Date of Version 000: 11 June 2019

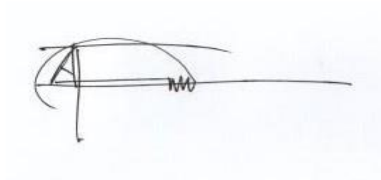
Version: *000*

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	Pb Collection	8	595.8	6.1	1	ppm
Al	4A_MICP	32	1760.9	247.7	14	ppm
Al	FUS	15	2057.1	64.9	3	ppm
Al	XRF	8	1862.5	51.8	3	ppm
Al_2O_3	4A_MICP	16	0.3	0.03	9	%
Al_2O_3	FUS	15	0.4	0.01	3	%
Al_2O_3	XRF	32	0.4	0.05	12	%
As	XRF	8	162.5	8.9	5	ppm
Ba	FUS	8	109.4	4.2	4	ppm
BaO	4A_MICP	8	0.01	0.001	4	%
BaO	XRF	16	0.02	0.003	20	%
C	Combustion/LECO	16	0.2	0.02	12	%
Ca	XRF	8	800.0	*	*	ppm
CaO	4A_MICP	16	0.1	0.02	13	%
CaO	FUS	8	0.2	0.01	3	%
CaO	XRF	24	0.1	0.02	13	%
Co	FUS	8	245.4	2.0	1	ppm
Co	XRF	8	237.7	7.0	3	ppm
Cr	4A_MICP	16	533.7	38.1	7	ppm
Cr	FUS	16	580.4	18.6	3	ppm
Cr_2O_3	4A_MICP	7	0.1	*	*	%
Cr_2O_3	XRF	24	0.1	0.03	26	%
Cu	XRF	24	20661.9	2286.8	11	ppm
CuO	XRF	24	2.6	0.3	11	%
Dy	4A_MICP	16	1.3	0.2	14	ppm
Er	4A_MICP	16	0.4	0.1	16	ppm
Eu	4A_MICP	16	0.9	0.1	8	ppm
Fe	XRF	40	52713.8	4860.0	9	ppm
Fe_2O_3	4A_MICP	8	7.1	0.2	3	%
Fe_2O_3	XRF	40	7.5	0.7	10	%
Gd	4A_MICP	16	2.4	0.1	6	ppm
Ge	4A_MICP	8	0.1	0.01	15	ppm
GOI	GOI	16	7.2	2.7	38	%
Hf	4A_MICP	8	0.2	0.1	32	ppm
Ho	4A_MICP	15	0.2	0.01	3	ppm
K	4A_MICP	24	166.7	57.7	35	ppm
K	FUS	5	580.0	44.7	8	ppm
K_2O	4A_MICP	15	0.02	0.01	32	%
K_2O	XRF	14	0.03	0.01	24	%
Li	4A_MICP	23	1.1	0.2	16	ppm
LOI	LOI	24	8.5	3.4	40	%
Lu	4A_MICP	8	0.04	*	*	ppm

Element	Generic Method	n	Mean	SD	RSD %	Unit
Mg	FUS	16	1260.0	221.0	18	ppm
MgO	4A_MICP	15	0.2	0.01	3	%
MgO	FUS	16	0.2	0.04	18	%
Mn	FUS	24	6798.0	584.7	9	ppm
MnO	4A_MICP	8	0.8	0.01	1	%
MnO	FUS	24	0.9	0.1	9	%
Moisture	Moisture	39	0.1	0.03	40	%
Na	4A_MICP	18	344.4	352.3	102	ppm
Na_2O	4A_MICP	14	0.02	0.01	36	%
Na_2O	XRF	2	0.1	0.03	22	%
Nb	4A_MICP	16	1.7	0.5	27	ppm
Nd	4A_MICP	15	7.4	0.5	6	ppm
Ni	FUS	8	103.1	7.7	7	ppm
Ni	XRF	14	61.7	3.9	6	ppm
P	4A_MICP	16	125.0	35.4	28	ppm
P_2O_5	4A_MICP	8	0.03	0.005	14	%
P_2O_5	XRF	24	0.03	0.02	48	%
Pb	4A_MICP	16	460083.4	198416.0	43	ppm
Pb	FUS	8	693750.0	16316.1	2	ppm
Pr	4A_MICP	16	1.8	0.1	7	ppm
Re	4A_MICP	16	0.1	0.01	11	ppm
S	4A_MICP	16	11.8	1.6	14	%
S	FUS	16	14.8	0.4	3	%
Sb	FUS	8	172.5	3.0	2	ppm
Sc	4A_MICP	9	0.4	0.2	62	ppm
Si	FUS	16	13727.9	595.8	4	ppm
Si	XRF	8	12212.5	124.6	1	ppm
SiO_2	4A_MICP	16	2.7	0.1	3	%
SiO_2	FUS	16	2.9	0.1	3	%
Sm	4A_MICP	16	2.2	0.2	7	ppm
Ta	4A_MICP	10	0.1	0.01	18	ppm
Tb	4A_MICP	16	0.3	0.02	7	ppm
Ti	4A_MICP	32	129.4	20.1	16	ppm
Ti	FUS	8	100.0	*	*	ppm
TiO_2	4A_MICP	13	0.02	*	*	%
TiO_2	XRF	17	0.03	0.01	56	%
Tm	4A_MICP	8	0.05	0.01	22	ppm
V	4A_MICP	21	7.1	2.4	34	ppm
Yb	4A_MICP	15	0.3	0.1	21	ppm
Zr	4A_MICP	35	7.7	3.4	43	ppm
Zr	XRF	7	682.2	30.1	4	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:

$|z|$≤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

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

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

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

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):

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

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.

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

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.

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

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.

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

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.

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

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:

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

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:

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

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 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 32) which is >0.84. Similarly, the *p*-value=0.43 which is >0.05. This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known, the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

Appendix 4. Two-standard Deviations

Two-standard deviations are calculated using the expression:

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

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:

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

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^{o}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^{o}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