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Certificate

AMIS0574

Certified Reference Material

Greenstone Belt in Fairview, Barberton, South Africa

Certificate of Analysis

AMIS

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Summary Statistics

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

Analyte	Method	Certified (μ) ⁷	(2s) ⁹ \pm	Unit
Au	Pb Collection ¹	3.47	0.29	g/t
Ag	4A_MICP ²	0.9	0.2	ppm
Cu	4A_MICP	153	25	ppm
S	Combustion/LECO ³	0.31	0.03	%
S	4A_MICP	0.37	0.03	%
LOI	LOI ⁴	33.39	2.3	%
Al	4A_MICP	3149	411	ppm
Al	FUS ⁵	3300	363	ppm
As	4A_MICP	45	9	ppm
Ba	4A_MICP	29	3	ppm
Bi	4A_MICP	0.1	0.02	ppm
Ce	4A_MICP	4	0.7	ppm
Co	4A_MICP	13	3	ppm
Cr	4A_MICP	107	30	ppm
Fe	4A_MICP	5446	801	ppm
Fe	FUS	5313	465	ppm
K	4A_MICP	1119	222	ppm
La	4A_MICP	2	0.3	ppm
Li	4A_MICP	5	0.6	ppm
Mg	4A_MICP	9024	1226	ppm
Mg	FUS	9209	409	ppm
Mn	4A_MICP	5314	416	ppm
Mo	4A_MICP	2	0.3	ppm
Na	4A_MICP	557	89	ppm
Nb	4A_MICP	0.6	0.2	ppm
Ni	4A_MICP	80	9	ppm
P	4A_MICP	92	15	ppm
Pb	4A_MICP	7	0.7	ppm
Rb	4A_MICP	4	0.6	ppm
Sb	4A_MICP	5	0.9	ppm
Sc	4A_MICP	0.9	0.4	ppm
Sn	4A_MICP	2	0.4	ppm
Th	4A_MICP	0.6	0.2	ppm
Ti	4A_MICP	202	8	ppm
U	4A_MICP	0.7	0.09	ppm
V	4A_MICP	8	3	ppm
W	4A_MICP	0.5	0.1	ppm
Y	4A_MICP	2	0.1	ppm
Zn	4A_MICP	31	2	ppm
Zr	4A_MICP	7	0.6	ppm

Major Oxides
Certified Concentrations (at two Standard Deviations)

Analyte	Method	Certified (μ) ⁷	(2s) ⁹ \pm	Unit
Al ₂ O ₃	FUS	0.62	0.07	%
Al ₂ O ₃	XRF ⁶	0.60	0.03	%
CaO	XRF	57.17	1.4	%
Fe ₂ O ₃	FUS	0.76	0.07	%
Fe ₂ O ₃	XRF	0.79	0.04	%
K ₂ O	XRF	0.12	0.004	%
MgO	FUS	1.53	0.068	%
MgO	XRF	1.65	0.072	%
MnO	XRF	0.74	0.04	%
P ₂ O ₅	XRF	0.020	0.0009	%
SiO ₂	XRF	4.99	0.12	%

1. Certified Concentrations and Uncertainties

AMIS0574 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) ⁷	N	n	k	% RSD	(u_c) ⁸	(2s) ⁹ \pm	(CI) ¹⁰ 95%	(U) ¹¹ \pm	Unit
Au	Pb Collection ¹	3.47	6	48	2.571	4	0.14	0.29	0.13	0.4	g/t
Ag	4A_MICP ²	0.9	4	29	3.182	12	0.1	0.2	0.2	0.4	ppm
Cu	4A_MICP	153	5	40	2.776	8	13	25	15	35	ppm
S	Combustion/LECO ³	0.31	5	38	2.776	5	0.02	0.03	0.01	0.04	%
S	4A_MICP	0.37	5	36	2.776	4	0.01	0.03	0.02	0.04	%
LOI	LOI ⁴	33.39	5	40	2.776	3	1.2	2.3	1.0	3	%
Al	4A_MICP	3149	3	23	4.303	7	206	411	492	885	ppm
Al	FUS ⁵	3300	3	23	4.303	5	181	363	371	780	ppm
As	4A_MICP	45	4	32	3.182	10	5	9	7	14	ppm
Ba	4A_MICP	29	4	30	3.182	6	2	3	3	5	ppm
Bi	4A_MICP	0.1	3	23	4.303	8	0.009	0.02	0.02	0.04	ppm
Ce	4A_MICP	4	2	16	12.706	9	0.4	0.7	3	5	ppm
Co	4A_MICP	13	5	39	2.776	12	2	3	2	4	ppm
Cr	4A_MICP	107	2	16	12.706	14	15	30	134	192	ppm
Fe	4A_MICP	5446	3	24	4.303	7	400	801	967	1722	ppm
Fe	FUS	5313	3	23	4.303	4	232	465	405	999	ppm
K	4A_MICP	1119	4	29	3.182	10	111	222	183	353	ppm
La	4A_MICP	2	3	24	4.303	6	0.1	0.3	0.2	0.6	ppm
Li	4A_MICP	5	3	21	4.303	6	0.3	0.6	0.8	1	ppm
Mg	4A_MICP	9024	4	32	3.182	7	613	1226	918	1951	ppm
Mg	FUS	9209	2	15	12.706	2	205	409	1702	2600	ppm
Mn	4A_MICP	5314	5	39	2.776	4	208	416	233	578	ppm
Mo	4A_MICP	2	4	31	3.182	10	0.2	0.3	0.3	0.5	ppm
Na	4A_MICP	557	4	32	3.182	8	44	89	70	142	ppm
Nb	4A_MICP	0.6	4	30	3.182	17	0.1	0.2	0.2	0.4	ppm
Ni	4A_MICP	80	5	39	2.776	6	5	9	5	13	ppm
P	4A_MICP	92	5	35	2.776	8	7	15	9	20	ppm
Pb	4A_MICP	7	4	32	3.182	5	0.4	0.7	0.3	1	ppm
Rb	4A_MICP	4	4	32	3.182	8	0.3	0.6	0.4	0.9	ppm
Sb	4A_MICP	5	5	33	2.776	10	0.5	0.9	0.4	1	ppm
Sc	4A_MICP	0.9	3	24	4.303	26	0.2	0.4	0.6	1	ppm
Sn	4A_MICP	2	3	24	4.303	10	0.2	0.4	0.5	0.8	ppm
Th	4A_MICP	0.6	3	24	4.303	17	0.1	0.2	0.2	0.4	ppm
Ti	4A_MICP	202	3	24	4.303	2	4	8	9	18	ppm
U	4A_MICP	0.7	4	32	3.182	6	0.05	0.09	0.04	0.2	ppm
V	4A_MICP	8	5	38	2.776	18	2	3	2	4	ppm
W	4A_MICP	0.5	3	21	4.303	12	0.06	0.1	0.09	0.3	ppm
Y	4A_MICP	2	3	24	4.303	4	0.07	0.1	0.1	0.3	ppm
Zn	4A_MICP	31	4	31	3.182	4	1	2	1	4	ppm
Zr	4A_MICP	7	3	24	4.303	5	0.3	0.6	0.7	1	ppm

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 \pm	(CI) ¹⁰ 95%	(U) ¹¹ \pm	Unit
Al ₂ O ₃	FUS	0.62	3	23	4.303	5	0.03	0.07	0.07	0.1	%
Al ₂ O ₃	XRF ⁶	0.60	4	31	3.182	3	0.02	0.03	0.02	0.05	%
CaO	XRF	57.17	4	32	3.182	1	0.71	1.4	1.0	2	%
Fe ₂ O ₃	FUS	0.76	3	23	4.303	4	0.03	0.07	0.06	0.1	%
Fe ₂ O ₃	XRF	0.79	5	38	2.776	3	0.02	0.04	0.02	0.05	%
K ₂ O	XRF	0.12	4	28	3.182	2	0.002	0.004	0.001	0.006	%
MgO	FUS	1.53	2	15	12.706	2	0.034	0.068	0.28	0.4	%
MgO	XRF	1.65	4	32	3.182	2	0.036	0.072	0.056	0.1	%
MnO	XRF	0.74	4	32	3.182	3	0.02	0.04	0.04	0.07	%
P ₂ O ₅	XRF	0.020	4	32	3.182	2	0.0005	0.0009	0.001	0.001	%
SiO ₂	XRF	4.99	4	32	3.182	1	0.061	0.12	0.088	0.2	%

1. Pb Collection
2. 4A_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
3. Combustion/LECO
4. LOI is Loss on Ignition
5. FUS is Fusion digestion with ICP finish
6. XRF is X-ray Fluorescence
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 (u_c) with a coverage factor (k) found from N-1 degrees of freedom (see Appendix 7 for t-distribution table). Example: $U = 2.36 \times 0.23 = 0.5\%$

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	0.367 %	S Combustion/LECO	0.311 %	Equal Variance ($p=0.311$)	0.001	Reject H_0 ; certified values are <i>not</i> equal
Al ₂ O ₃ FUS	0.623 %	Al ₂ O ₃ XRF	0.596 %	Equal Variance ($p=0.15$)	0.145	Accept H_0 ; certified values are equal
Fe ₂ O ₃ FUS	0.760 %	Fe ₂ O ₃ XRF	0.791 %	Equal Variance ($p=0.214$)	0.058	Accept H_0 ; certified values are equal
MgO FUS	1.53 %	MgO XRF	1.65 %	Equal Variance ($p=0.563$)	0.015	Reject H_0 ; certified values are <i>not</i> equal
Al FUS	0.330 %	Al 4A_MICP	0.315 %	Equal Variance ($p=0.362$)	0.352	Accept H_0 ; certified values are equal
Mg FUS	0.921 %	Mg 4A_MICP	0.902 %	Equal Variance ($p=0.236$)	0.697	Accept H_0 ; certified values are equal
Fe FUS	0.531 %	Fe 4A_MICP	0.545 %	Equal Variance ($p=0.149$)	0.614	Accept H_0 ; certified values are equal

3. Intended Use

AMIS0574 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%, <i>df</i>)	MS Excel function for t-critical value at LOC 95% and <i>df</i>
<i>U</i>	Expanded uncertainty at a given k
<i>u</i>	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

Greenstone belts are zones of variably metamorphosed mafic to ultramafic volcanic sequences with associate sedimentary rocks that occur within Archaean and Proterozoic cratons between granite and gneiss bodies. Greenstone belts are primarily formed of volcanic rocks, dominated by basalt, with minor sedimentary rocks inter-leaving the volcanic formations. The material comes from the Greenstone belt in Barberton.

9. Approximate Mineral and Chemical Composition

The mineral assemblages of the samples are rich in greenschists and associated minerals. Greenschists is a generic name of minerals formed by regional metamorphism of mafic igneous rocks under the relatively low temperatures and pressures. The name greenstone originates from commonly having an abundance of green minerals such as chlorite/chamosite, Actinolite/ and amphiboles and sheets-like minerals such as biotite/muscovite. The common minerals associated with greenschists include quartz, orthoclase and calcite. The greenschists minerals are generally the pathfinders/ indicative of base metal sulphides and gold mineralisation.

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 SiO₂. 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 AMIS0569 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. The Portlandite and Calcite can undergo significant preferred orientation, which can be difficult to model. Both Calcite and Portlandite may be over or underestimated in these refinements. The results in the Table 5 should be treated as 'indicative' only.
3. Calcite was used in these Rietveld refinements. Further work would be required to better define and quantify the Calcite group mineral.
4. Tr=trace; some very small peaks are difficult to be well identified and the mineral giving rise to the peaks is assumed to be present in trace amounts.

Table 5. Results of XRD analysis.

Mineral	Mineral Composition	Composite
Quartz	SiO ₂	5
Portlandite ²	Ca(OH) ₂	28
Calcite ³	CaCO ₃	67
Total		100%

For informational purposes only

11. Health and Safety

The material is a very fine powder coloured Pale Yellowish Brown (Corstor 10YR 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	96.88	200	100
0.25	0.09	55	97.57	225	100
0.5	2.57	60	98.1	250	100
0.6	3.67	65	98.51	300	100
0.75	5.2	70	98.84	400	100
1	7.51	75	99.09	500	100
2	16.46	80	99.29	600	100
3	25.48	85	99.45	700	100
4	33.77	90	99.58	800	100
5	41	95	99.68	900	100
6	47.19	100	99.76	1000	100
7	52.46	105	99.82	1100	100
8	56.95	106	99.84	1200	100
9	60.81	110	99.88	1300	100
10	64.15	115	99.91	1400	100
12	69.67	120	99.95	1500	100
15	75.9	125	99.98	1600	100
18	80.53	130	100	1700	100
20	82.99	135	100	1800	100
25	87.66	140	100	1900	100
30	90.86	150	100	2000	100
35	93.12	160	100		
40	94.76	170	100		
45	95.97	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 or gravimetric
- b) Multi element scan to include all elements-4-acid total digestion including HF and/or peroxide fusion finished with either ICP-OES or ICP-MS or AAS
- c) LOI and all majors oxides 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

17. Information Requested of Participating Laboratories

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

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

18. Certification of Mean and Estimation of Measurement Uncertainty

The samples used in this certification process have been selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore, all sources of uncertainty are included in the combined standard uncertainty determination. Initially the data submitted by all the laboratories are subjected to a z-score test, equation [1] to exclude outliers and the remaining data sets examined for their normality in distribution. This is followed by the exclusion of further outliers as defined by the IUPAC Harmonised Protocol of 1995 in which both Cochran and a Grubbs test are applied until all outliers are identified, equations [2] and [3]. A grand mean and standard deviation is re-calculated using all remaining data (Thompson, 2008; Carr, 2011) (see Appendix 2)

19. Two Standard Deviations

AMIS reports two-standard deviations (2s) with all certified values. Two -standard deviations are calculated using the expression:

$$\text{Two standard deviations} = 2 (u_c)$$

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

20. Confidence Interval

AMIS reports a confidence interval (CI) with all certified values. Confidence interval as used by AMIS is:

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

Where, N is the number of laboratories (accepted laboratory data), $t_{critical}$ is a two-tailed value for $N - 1$ degrees of freedom (df) and s , is the standard deviation of the accepted laboratory means. A two-tailed critical value is found for $N - 1$ degrees of freedom from either a t -distribution table (Appendix 9) or MS Excel as =TINV (5%, df).

21. Expanded Uncertainty

ANOVA gives an estimate of the repeatability and the reproducibility of the data accepted for certification of the candidate reference material (see equations, [15] and [16], in the Appendix). Therefore, random variables (e.g., subsampling, instrument effects, interferences, operators and measurement conditions) that occur during the analysis of the candidate reference material by the various laboratories is considered. This approach does not necessarily quantify each individual source of uncertainty; however, the combined effect of random uncertainties is assessed (Ramsey & Ellison, 2007). A combined standard uncertainty is calculated from equation [14], which when multiplied by the t -critical value for $N - 1$ laboratories, gives an *expanded uncertainty* at a 95% level of confidence. The expanded uncertainty is a measure of the doubt around the certified value at a level of 95% confidence. The expanded uncertainty is used in the validation of accuracy (see equation [18]).

22. Confidence Interval and Expanded Uncertainty

A combined standard uncertainty will be greater than a combined *CI*. This is because ANOVA considers the within-lab repeatability (that is repeatability within each lab group) as well as the repeatability between each lab data set. This attends to random variables that contribute to the measurement of uncertainty, during the analysis of the test sample at the participating laboratories. The within-lab repeatability and the between lab repeatability is combined as the square root of the sum of squares of these two values giving a combined standard uncertainty, at a 68% confidence level. Multiplying the combined standard uncertainty by the t-critical value for *N*-1, gives the expanded uncertainty at 95% level of confidence. It is recommended that the procedure described in Appendix 6, "Using the CRM in Quality Control" be used, in setting the limits of the CRM. Table 7 below shows mean gold values obtained by fire assay lead collection, for nine different laboratories, the confidence interval, two-standard deviations and expanded uncertainty.

Table 7. Example of replicate assay data in which the *CI*, 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

<i>CI</i>	0.0088
2<i>s</i>	0.031
<i>U</i>	0.04

23. Participating Laboratories

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

1. ALS Geochemistry Arabia
2. Bureau Veritas Minerals Ultra Trace Pty Ltd
3. Intertek Mineral Tarkwa Ghana
4. Intertek Perth
5. Set Point Laboratories (Mokopane) SA
6. SGS Newburn
7. SGS Vancouver (Canada)
8. Shiva Analyticals India

24. Accepted Assay Data

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

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

FUS	XRF	XRF	FUS	XRF	XRF	FUS	XRF	XRF	XRF	XRF
Al ₂ O ₃	Al ₂ O ₃	CaO	Fe ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	MgO	MnO	P ₂ O ₅	SiO ₂
%	%	%	%	%	%	%	%	%	%	%
0.60	0.60	56.30	0.77	0.78	0.12	1.53	1.63	0.72	0.02	4.90
0.60	0.61	56.26	0.79	0.80	0.12	1.58	1.64	0.72	0.02	4.94
0.62	0.60	56.34	0.77	0.79	0.12	1.54	1.64	0.72	0.02	4.94
0.62	0.60	56.29	0.77	0.78	0.13	1.56	1.64	0.72	0.02	4.90
0.62	0.61	56.38	0.81	0.76	0.12	1.56	1.63	0.72	0.02	4.90
0.60	0.60	56.36	0.81	0.77	0.12	1.54	1.62	0.72	0.02	4.91
0.59	0.60	56.28	0.76	0.77	0.12	1.54	1.64	0.72	0.02	4.92
0.65	0.59	56.26	0.71	0.78	0.12	1.51	1.62	0.72	0.02	4.88
0.67	0.58	57.50	0.75	0.77	0.12	1.49	1.61	0.76	0.02	4.98
0.65	0.57	57.50	0.74	0.76	0.12	1.51	1.61	0.76	0.02	4.94
0.68	0.57	57.50	0.70	0.81	0.12	1.51	1.61	0.76	0.02	4.98
0.65	0.58	57.40	0.76	0.78	0.12	1.49	1.61	0.76	0.02	4.95
0.64	0.59	57.40	0.73	0.81	0.12	1.51	1.61	0.76	0.02	5.00
0.67	0.57	57.40	0.70	0.77	0.12	1.49	1.61	0.76	0.02	4.99
0.63	0.57	57.50	0.75	0.80	0.12	1.53	1.61	0.76	0.02	4.97
0.60	0.57	57.40	0.76	0.80	0.12		1.62	0.76	0.02	5.03
0.60	0.60	57.91	0.79	0.82	0.12		1.69	0.76	0.02	5.00
0.64	0.60	57.98	0.79	0.81	0.12		1.69	0.75	0.02	5.01
0.57	0.60	57.99	0.76	0.81	0.12		1.68	0.76	0.02	5.04
0.62	0.60	58.11	0.76	0.80	0.12		1.71	0.76	0.02	5.08
0.62	0.61	57.82	0.77	0.81	0.12		1.69	0.76	0.02	4.99
0.60	0.60	58.00	0.80	0.81	0.12		1.70	0.76	0.02	5.04
0.57	0.62	57.90	0.74	0.82	0.12		1.68	0.76	0.02	5.08
	0.62	57.89		0.79	0.12		1.71	0.75	0.02	5.03
	0.59	56.80		0.80	0.12		1.66	0.72	0.02	5.03
	0.61	57.10		0.80	0.12		1.65	0.72	0.02	5.03
	0.60	57.00		0.79	0.12		1.64	0.72	0.02	5.03
	0.61	57.20		0.82	0.12		1.65	0.72	0.02	5.06
	0.58	57.10		0.83			1.65	0.72	0.02	5.03
	0.61	56.80		0.81			1.64	0.73	0.02	5.03
	0.61	56.80		0.77			1.66	0.72	0.02	4.99
		56.90		0.78			1.66	0.73	0.02	4.98
				0.79						
				0.78						
				0.77						
				0.77						
				0.78						
				0.78						

Assay Data (Cont.)

Pb Collection	4A_MICP	4A_MICP	Combustion/LECO	4A_MICP	LOI	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP
Au g/t	Ag ppm	Cu ppm	S %	S %	LOI %	Al ppm	Al ppm	As ppm	Ba ppm	Bi ppm
3.37	1.00	145.00	0.28	0.35	34.61	3000	3200	51.00	31.00	0.10
3.39	1.00	160.00	0.31	0.37	34.69	3000	3200	50.00	31.00	0.10
3.41	1.00	150.00	0.28	0.37	34.60	2900	3300	49.00	31.00	0.10
3.38	1.00	155.00	0.33	0.38	34.66	3000	3300	52.00	31.00	0.10
3.27	1.00	155.00	0.32	0.37	34.70	2900	3300	51.00	31.00	0.10
3.29	0.76	155.00	0.30	0.36	34.74	2900	3200	52.00	31.00	0.10
3.33	0.74	145.00	0.30	0.36	34.62	3000	3100	49.00	30.00	0.10
3.30	0.69	155.00	0.32	0.35	34.72	3367	3445	50.00	31.00	0.10
3.62	0.73	141.00	0.33	0.35	34.37	3345	3551	43.00	30.00	0.10
3.67	0.69	140.00	0.30	0.34	34.28	3350	3445	42.00	30.00	0.10
3.59	0.79	139.00	0.30	0.34	34.37	3314	3604	40.00	30.00	0.10
3.69	0.77	139.00	0.33	0.35	34.29	3298	3445	39.00	30.00	0.10
3.67	0.75	144.00	0.32	0.38	34.36	3385	3392	40.00	30.00	0.10
3.70	0.90	137.00	0.32	0.38	34.46	3425	3551	38.00	30.00	0.10
3.63	0.90	138.00	0.33	0.38	34.32	3340	3339	40.00	30.00	0.10
3.58	0.90	145.00	0.33	0.39	34.19	3300	3200	38.00	30.00	0.11
3.56	1.00	145.00	0.32	0.38	32.30	3200	3200	45.00	30.00	0.11
3.34	0.90	140.00	0.32	0.37	32.40	3100	3400	46.00	29.00	0.12
3.53	0.90	141.00	0.29	0.36	32.40	3100	3000	45.00	30.00	0.12
3.27	0.90	139.00	0.31	0.37	32.50	3000	3300	44.00	29.00	0.11
3.51	0.90	139.00	0.30	0.38	32.40	3100	3300	43.00	29.00	0.11
3.37	0.86	142.00	0.31	0.38	32.40	3200	3200	44.00	29.00	0.12
3.43	0.87	142.00	0.33	0.38	32.30	3100	3000	44.00	29.00	0.11
3.37	0.84	151.00	0.33	0.37	32.40			43.00	29.00	
3.55	0.93	171.00	0.33	0.37	32.06			44.00	28.00	
3.51	0.88	166.00	0.32	0.38	31.98			43.00	26.00	
3.58	0.98	168.00	0.32	0.37	31.92			44.00	26.00	
3.69	0.90	167.00	0.33	0.38	32.04			42.00	27.00	
3.70	0.96	171.00	0.32	0.38	32.15			45.00	28.00	
3.49		164.00	0.33	0.38	32.17			44.00	27.00	
3.72		173.00	0.29	0.37	32.03			44.00		
3.60		169.00	0.31	0.40	32.03			46.00		
3.51		159.00	0.31	0.39	33.60					
3.44		155.00	0.31	0.37	33.80					
3.64		164.00	0.30	0.38	33.50					
3.42		157.00	0.29	0.38	33.50					
3.46		164.00	0.29		33.40					
3.41		164.00	0.30		33.60					
3.50		163.00			33.40					
3.40		168.00			33.50					
3.30										
3.29										
3.41										
3.36										
3.39										
3.31										
3.36										
3.36										

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Mo	Na	Nb	Ni	P	Pb	Rb	Sb	Sc	Sn
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1.50	600	0.50	85.00	100	7.00	4.00	4.60	1.00	2.00
1.50	600	0.50	85.00	100	7.00	4.00	5.00	1.00	2.00
1.50	600	0.50	85.00	100	7.00	4.00	4.60	1.00	2.00
1.50	600	0.50	85.00	100	7.00	4.00	4.40	1.00	2.00
1.50	600	0.50	80.00	100	7.00	3.80	5.00	1.00	2.00
1.50	600	0.50	80.00	100	7.00	4.00	4.60	1.00	2.00
1.50	600	0.70	80.00	100	8.00	3.60	4.60	1.00	2.00
1.50	600	0.70	80.00	100	7.00	3.80	4.60	1.00	2.00
1.50	500	0.80	76.00	90	8.00	3.61	5.00	1.00	1.70
1.60	500	0.70	75.00	90	7.00	3.64	5.00	1.00	1.60
1.60	500	0.70	75.00	80	7.00	3.67	4.20	1.00	1.60
1.70	500	0.70	75.00	90	8.00	3.59	4.00	1.00	1.70
1.70	500	0.70	78.00	90	7.00	3.53	5.10	1.00	1.60
1.60	500	0.80	75.00	90	7.00	3.49	5.20	1.00	1.60
1.60	500	0.60	77.00	90	7.00	3.56	4.30	1.00	1.60
1.70	500	0.70	74.00	80	7.00	3.92	4.40	1.00	1.70
1.50	590	0.60	88.00	85	7.00	3.40	5.50	0.60	1.90
1.60	600	0.60	85.00	90	7.00	3.60	3.80	0.60	1.90
1.50	590	0.60	86.00	85	7.00	3.60	4.60	0.60	1.80
1.50	570	0.60	83.00	85	7.00	3.50	4.00	0.60	1.90
1.50	585	0.60	86.00	85	7.00	3.50	3.70	0.60	1.80
1.60	560	0.60	90.00	90	7.00	3.60	4.20	0.60	1.80
1.60	585	0.70	88.00	88	7.00	3.70	4.50	0.70	1.90
1.50	575	0.70	78.00	87	6.00	3.60	4.20	0.60	1.80
1.91	549	0.70	79.00	90	7.30	4.20	3.90		
1.90	544	0.80	79.00	90	7.00	4.00	5.09		
1.84	547	0.80	78.00	84	7.00	4.10	4.92		
1.84	542	0.80	78.00	85	7.50	4.20	4.81		
1.81	538	0.70	81.00	88	7.10	4.00	4.79		
1.94	553	0.70	79.00	87	7.10	4.10	4.74		
1.85	562		80.00	100	7.50	4.30	5.06		
	549		76.70	100	7.20	4.20	4.83		
			78.30	100			5.03		
			74.10	100					
			80.70	100					
			78.20						
			77.40						
			78.20						
			77.10						

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Th	Ti	U	V	W	Y	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
0.50	200	0.70	10.00	0.50	1.80	32.00	7.00
0.50	200	0.80	10.00	0.50	1.70	31.00	7.00
0.50	200	0.80	10.00	0.50	1.80	30.00	6.70
0.50	200	0.70	10.00	0.50	1.80	31.00	7.00
0.50	200	0.70	10.00	0.50	1.70	33.00	7.20
0.50	200	0.70	10.00	0.50	1.70	31.00	6.80
0.50	200	0.80	10.00	0.60	1.60	31.00	7.20
0.50	200	0.80	10.00	0.50	1.70	32.00	7.20
0.62	209	0.74	6.00	0.50	1.71	33.00	6.50
0.58	202	0.69	6.00	0.50	1.70	32.00	6.30
0.61	202	0.74	6.00	0.50	1.73	33.00	6.50
0.57	206	0.67	6.00	0.40	1.70	31.00	6.70
0.56	212	0.72	6.00	0.50	1.70	30.00	6.20
0.57	208	0.75	6.00	0.50	1.66	30.00	6.50
0.61	207	0.78	9.00	0.60	1.63	31.00	6.70
0.58	205	0.69	8.00	0.50	1.72	31.00	6.90
0.70	200	0.69	9.00	0.50	1.80	30.00	6.90
0.70	200	0.77	9.00	0.60	1.70	30.00	6.80
0.70	200	0.76	8.00	0.70	1.70	31.00	6.90
0.70	200	0.68	8.00	0.60	1.80	31.00	7.10
0.70	200	0.72	9.00	0.50	1.80	30.00	7.20
0.70	200	0.70	8.00		1.80	30.00	7.00
0.70	200	0.66	8.00		1.80	31.00	7.20
0.70	200	0.68	8.00		1.90	29.00	6.90
		0.78	8.00			29.00	
		0.81	8.00			30.00	
		0.81	8.00			30.00	
		0.71	8.00			31.00	
		0.71	8.00			29.00	
		0.78	9.00			31.00	
		0.73	10.00			29.00	
		0.69	10.00				
			9.00				
			10.00				
			9.00				
			10.00				
			10.00				
			9.00				

25. Reported Values

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

26. Validation of Accuracy (Trueness)

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

27. Limit of Detection and Limit of Quantitation in Gravimetric Fire Assay

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

28. Metrological Traceability

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

29. Period of Validity

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

30. Minimum Sample Size

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

31. Availability

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

32. Recommended use in Quality Control

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

33. Legal Notice

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

Date of Version 000: 07 March 2019

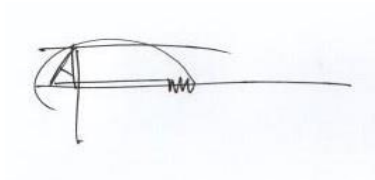
Version: 000

Approving Officer:

African Mineral Standards: _____

Makhosi Khoza (Quality Specialist)

Certifying Officer:

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

Geochemist: _____

Allan Fraser

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

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Appendices

Appendix 1: Uncertified Element Statistics

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

Table 9. Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
As	FUS	8	46.3	2.3	5	ppm
B	FUS	8	67.5	14.9	22	ppm
Ba	FS_ICPES	8	30.0	*	*	ppm
Ba	FUS	8	30.0	*	*	ppm
BaO	XRF	8	0.02	0.01	36	%
Be	4A_MICP	20	0.2	0.0	23	ppm
C	Combustion/LECO	40	68480.0	12170.4	18	ppm
Ho	4A_MICP	15	0.1	0.0	17	ppm
Ca	FUS	8	378625.0	4373.2	1	ppm
CaO	FUS	8	55.0	0.1	0.2	%
Cd	4A_MICP	15	0.1	0.0	19	ppm
K	FUS	8	1000.0	*	*	ppm
Co	FS_ICPES	8	15.0	*	*	ppm
Co	FUS	8	13.4	0.7	6	ppm
Cr	FUS	8	225.0	26.7	12	ppm
Cr2O3	XRF	23	0.02	*	*	%
Ga	4A_MICP	24	1.3	0.5	38	ppm
Cs	FUS	8	0.4	*	*	ppm
Hf	4A_MICP	15	0.2	0.0	14	ppm
Cu	FS_ICPES	8	141.9	7.0	5	ppm
Cu	FUS	8	137.5	5.3	4	ppm
Dy	4A_MICP	15	0.3	0.0	7	ppm
Dy	FUS	7	0.3	*	*	ppm
Er	4A_MICP	16	0.2	0.0	24	ppm
Eu	4A_MICP	15	0.1	0.0	12	ppm
Ca	4A_MICP	26	383315.6	22259.5	6	ppm
Gd	4A_MICP	16	0.3	0.1	24	ppm
Gd	FUS	8	0.3	*	*	ppm
Ge	4A_MICP	7	0.2	*	*	ppm
Cs	4A_MICP	14	0.3	*	*	ppm
Ce	FUS	8	4.0	0.1	4	ppm
Cu	4A_ICPES	8	145.1	2.3	2	ppm
K2O	FUS	8	0.1	0.0	3	%
La	FUS	7	2.0	0.1	3	ppm
Li	FUS	7	5.1	0.3	6	ppm
Lu	4A_MICP	21	0.02	*	*	ppm
Mn	FS_ICPES	8	5293.8	141.0	3	ppm
Mn	FUS	8	5315.0	171.8	3	ppm
MnO	FUS	8	0.6	0.0	4	%
Moisture	Moisture	16	0.8	0.1	8	%
Moisture	XRF	8	1.6	0.0	1	%

Element	Generic Method	n	Mean	SD	RSD %	Unit
Na2O	XRF	37	0.1	0.02	31	%
Nd	4A_MICP	16	1.6	0.1	8	ppm
Nd	FUS	7	1.6	0.2	10	ppm
Ni	4A_ICPES	8	79.9	1.6	2	ppm
P	FUS	7	115.7	9.8	8	ppm
Pb	4A_ICPES	8	7.1	0.8	12	ppm
Pd	Pb Collection	7	0.02	*	*	g/t
TiO2	XRF	24	0.04	0.002	5	%
Pr	FUS	8	0.5	0.1	11	ppm
Pt	Pb Collection	7	0.01	*	*	g/t
Rb	FUS	7	3.7	0.2	7	ppm
Tl	4A_MICP	15	0.05	0.004	9	ppm
Sb	FUS	8	4.5	0.3	6	ppm
SG	SG	15	2.6	0.1	3	Dimensionless
Si	FUS	16	26180.3	4159.4	16	ppm
SiO2	FUS	16	5.6	0.9	16	%
Tb	4A_MICP	15	0.04	0.01	12	ppm
Sm	FUS	7	0.3	*	*	ppm
TiO2	FUS	24	0.04	0.01	18	%
Sr	4A_ICPES	8	57.6	1.5	3	ppm
Sr	4A_MICP	39	58.6	2.6	4	ppm
Sr	FS_ICPES	8	56.3	2.3	4	ppm
Sr	FUS	7	57.0	1.3	2	ppm
SrO	XRF	7	0.01	*	*	%
Ta	4A_MICP	13	0.1	0.01	24	ppm
Pr	4A_MICP	15	0.5	0.02	5	ppm
Te	4A_MICP	3	0.1	*	*	ppm
Th	FUS	7	0.5	*	*	ppm
Ti	FUS	24	246.7	43.7	18	ppm
Sm	4A_MICP	16	0.3	0.03	8	ppm
S	FUS	8	0.4	0.03	8	%
SO3	XRF	16	0.8	0.04	5	%
Tm	4A_MICP	4	0.02	*	*	ppm
U	FUS	7	0.7	*	*	ppm
Y	FUS	8	1.7	0.1	3	ppm
Yb	4A_MICP	14	0.1	*	*	ppm
Zn	4A_ICPES	8	32.9	1.6	5	ppm
Zn	FS_ICPES	7	30.7	1.9	6	ppm
Zn	FUS	7	34.3	7.9	23	ppm
Zr	4A_ICPES	7	7.0	*	*	ppm

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

Appendix 2 through 9, prepared by Allan Fraser.

Appendix 2. Certification of Reference Material and Estimation of Measurement Uncertainty

In the establishment of a consensus value for the CRM, outlier tests are carried out followed by performance statistics and the estimation of the measurement uncertainty. In practice, it is highly likely that data generated by multiple laboratories as an inter-laboratory comparison of material for certification, will contain erroneous as well as extreme measurements (outliers). The influence of outliers on summary statistics needs to be minimised by the application of procedures for outlier identification on raw data. The use of z-scoring, Cochran's test for suspect repeatability variances, along with Grubbs test for suspect measurement values allows for the detection of outliers (IUPAC, 1995). Method performance in terms of precision as relative standard deviation is judged by the application of the Horwitz ratio, which gives an indication of whether the observed relative standard deviation at the concentration levels of analyte determined are acceptable (Horwitz & Albert, 2006).

In the absence of an extensive uncertainty budget, measurement uncertainty is estimated from the reproducibility standard deviation from inter-laboratory data and reported as an expanded uncertainty at a level of confidence of 95% (Miller & Miller, 2010).

The steps below give detail on the establishment of a consensus value through the elimination of outliers, method performance and estimation of measurement uncertainty using standard uncertainties and the analysis of variance.

Z-Score

A z-score is calculated using equation [1]:

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

Where, x is the result of a submitted sample, x_a is the mean and s_p is the standard deviation of the submitted results from all the participating laboratories. Z-Scores are interpreted as follows:

$|z| \leq 2$ satisfactory performance
 $2 < |z| \leq 3$ questionable performance
 $|z| > 3$ unsatisfactory performance

(Thompson & Lowthian, 2011)

Data with z-scores exceeding two are discarded and are not included for further assessment.

Cochran's Test

The test of Cochran (1950) as shown in equation [2] is applied to any suspect repeatability variances:

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

Where, C_{calc} , s_{max}^2 and $\sum_{i=1}^l s_i^2$, are the calculated values for Cochran's test, data set with the maximum variance and the sum of the variances of all of the participating, l laboratory datasets. The C_{calc} value is compared with a critical value, C_{crit} at a level of confidence of 95% and an alpha of 0.05% (see Ellison, *et al.*, 2009, Appendix A, Table A.3a, page 209 for a table of critical values for the test of Cochran at LOC 95%).

According to ISO 5725-2 (1999), results from a laboratory with a suspect repeatability variance can be excluded if it is shown by the Cochran test to be an outlier. Therefore, if $C_{calc} > C_{crit}$, the laboratory with the maximum variance is removed. The data found to be excluded should not be $>2/9$, or 22% of the total data.

Grubbs Test

The test of Grubbs (1969) calculates a test statistic, G_{calc} and in the detection of a single outlier, G_1 is found by using

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

Where, the sample mean and standard deviation, \bar{x} and s , are calculated with the suspect value included. The $G_{1\,calc}$ statistic is compared to a critical value for N measurements. See Ellison, *et al.*, 2009, Appendix A, Table A.2, page 208 for a table of critical values for the test of Cochran at LOC 95%.

Method Performance

The Horwitz function is used to assess the performance of the data under consideration, with respect to precision (Horwitz & Albert, 2006). A calculated %RSD is found using the Horwitz expression

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

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

$$Observed\ \%RSD = \frac{s}{Mean} \times 100 \quad [5]$$

where s is the standard deviation of n replicates.

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

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

A HorRat <2 indicates that the method is of adequate precision. Should the HorRat be >2 the overall data are discarded, and the candidate material considered not suitable for certification as the precision is excessive for the concentration of the analyte being determined (Nelsen & Wehling, 2008).

Grand Mean

The grand mean ($\bar{\bar{x}}$) *i.e.* the certified value of a dataset is the total of all the data values divided by the total sample size (n):

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

Certified Value

From ANOVA as per the description in section 18, an 'appropriate precision' as shown in [8] is calculated for sufficient homogeneity (Thompson, 2008):

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

Where, s_r is the within laboratory repeatability, as determined from [14]. Once [8] is satisfied, a grand mean [7] is calculated and this is taken to be the certified value.

Total Variation (SST)

The total variation (not the variance) comprises the sum of the squares of the differences of each mean with the grand mean.

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

Between Group Variation (SSB)

The *variation* due to the between the laboratories is denoted SSB or Sum of Squares Between laboratories and given by [10]. If the laboratory means are close to each other (and therefore the Grand Mean) SSB will be a small value. There are P samples involved with one datum value for each sample (the sample mean), so there are P-1 degrees of freedom.

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

The *variance* due to the interaction between the laboratories is denoted MSB for Mean Square Between groups and is the SSB divided by its degrees of freedom.

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

Within Group Variation (SSW)

The variation due to differences within individual samples is denoted SSW for Sum of Squares Within laboratories. The degrees of freedom are equal to the sum of the individual degrees of freedom for each sample. Since each sample has degrees of freedom (*df*) equal to one less than their sample sizes, and there are *k* samples, the total degrees of freedom is P less than the total sample size: $df = n - P$.

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

The variance due to the differences within individual samples is denoted MSW for Mean Square Within groups. This is the within group variation divided by its degrees of freedom:

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

From equations [9] through [13], the ANOVA table as shown in Table 10 is developed.

Table 10. A single-factor ANOVA table showing key elements. Where P is the total number of groups, or laboratories. P-1 is 1 less than number of laboratories, P (n-1) is the number of data values minus number of groups (equals degrees of freedom for each group added together), and P-1 + P(n-1) is 1 less than the number of data points. MS is the mean squares of between laboratories and within laboratories. After Ellison *et al.*, (2009), Table 6.2, page 61.

Source	Sum of Squares	df	Mean Sum of Squares	F	p	F _{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 $| \quad |$ bars indicate that the absolute value between the mean and the certified value is to be used, *i.e.* ignore the sign.

An example in which [18] is used for validation of accuracy is given below.

Example

A CRM is independently replicated nine times for Al_2O_3 concentration by XRF analysis, *i.e.* 9 individual fused glass beads were prepared. The observed mean and standard deviation of the replicate data are shown with the certified value and expanded uncertainty in Table 11. In validation of accuracy, the hypothesis question is: Is the difference between the observed mean and the certified value statistically significant at a level of confidence of 95%? Alternatively put, is there sufficient evidence to conclude that the data *i.e.* replicates generated, are inaccurate?

The relevant hypotheses are:

Null hypothesis: H_0 : Mean = Certified value of CRM with stated measurement uncertainty. The acceptance of H_0 means that accuracy is demonstrated; *i.e.* insufficient evidence to reject H_0 ;

Alternate hypothesis: H_1 : Mean \neq Certified value of CRM with stated measurement uncertainty. The acceptance of H_1 means that accuracy is not demonstrated, *i.e.* there is sufficient evidence to accept H_1 ;

Table 11. CRM certified value, quoted expanded uncertainty U , the coverage factor for the CRM, $k=2.25$ and mean for $n=9$ replicates and corresponding standard deviation for the replicate data.

CRM Certified Value	Expanded % (U)	Coverage Factor (k)	Mean ($n=9$)	n	Standard Deviation (s)
4.62%	0.08%	2.25	4.59%	9	0.01015

The standard uncertainty (u) is found by dividing the expanded uncertainty by the coverage factor:

$$u = \frac{0.08}{2.25} = 0.0356 \%$$

Using the observed mean for the replicate data ($n=9$) obtained for the CRM and substituting into [18]:

$$t_{calc} = \frac{|\bar{x} - \mu|}{\sqrt{0.0356^2 + \frac{0.01015^2}{9}}} = \frac{|4.59 - 4.62|}{\sqrt{0.00126 + 0.00001145}} = 0.84$$

Therefore, $t_{calc} = 0.84$ and $t_{crit}(5\%, 8) = 2.31$ (df is 8, therefore, $t_{crit}=2.31$, see Appendix 9, page 33) which is >0.84 . Similarly, the p -value= 0.43 which is >0.05 . This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known, the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

Appendix 4. Two-standard Deviations

Two-standard deviations are calculated using the expression:

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

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

Appendix 5. Confidence Interval

Confidence interval is calculated as:

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

Where, N is the number of laboratories (accepted laboratory data), $t_{critical}$ is a two-tailed value for $N - 1$ degrees of freedom (df) and s , is the standard deviation of the accepted laboratory means. A two-tailed critical value is found for $N - 1$ degrees of freedom from either a t -distribution table (Appendix 9) or MS Excel as =TINV (5%, df).

Appendix 6. Using the CRM in Quality Control

QC chart control limits should not be determined by the certified value and stated measurement uncertainty of the certified reference material used. These parameters although “certified” will never be known; it is only the corresponding statistical estimates, *i.e.* standard deviation and the mean calculated from replicated results that are known and these should be used in quality control charts. However, should the laboratory choose to use the certified value as the mean then the quoted $2s$, or CI value for the CRM can be used in the quality control chart.

It is recommended that a Shewhart chart be developed for the use if this CRM is to be used as a control sample in laboratory quality control. A Shewhart chart is a plot of sequential assay results obtained from quality control material such as an AMIS CRM. The warning and control limits are based on the standard deviation obtained from the mean of the replicates of a CRM (Ellison, *et al.*, 2009; Thompson, 2010). The procedure in preparing a Shewhart chart is as follows:

1. Analyse 10 to 15 replicates or more of the AMIS CRM.
2. Apply the Grubbs test for outliers.
3. Determine the mean of the replicates after application of the Grubbs test.
4. Determine the standard deviation, using equation [21], of the replicates following Grubbs test.
5. Calculate the standard deviation, s from:

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

where, x_i is an individual measurement in the data set, \bar{x} is the mean of the data set at $n-1$ degrees of freedom (df) and n is the number of replicates. The sample standard deviation can be found using the MS Excel formula “=stdev.s (number1;)”.

6. Verify accuracy of the mean value using equation [18].
7. Once accuracy is verified, calculate $\pm 2s$ and $\pm 3s$, where s is the standard deviation calculated from [21].
8. Construct the Shewhart control chart around the mean of n replicates.
9. Use $\pm 2s$ as the warning limits.
10. Use $\pm 3s$ as the control limits.
11. It is recommended that if 2 to 3 points are outside the warning limits analyse another sample and if it is then within warning limits, continue. If it is outside the warning limits, stop and troubleshoot.
12. It is recommended that if any point is outside control limits, analyse another portion (sample) of the CRM. If it is within control limits, continue. If it is outside control limits, stop and troubleshoot.
13. For reference purposes, the CRM certified value can be plotted on the Shewhart chart alongside the mean value.

On a regular basis the accuracy of the replicates of the CRM should be assessed in terms of the certified value of the CRM using equation [18].

Appendix 7. Conversion to Air-dry Basis (Prepared by Allan Fraser)

Since AMIS certified analyte values are reported on a dry-basis, the user laboratory is required to dry a portion (accurately weigh out 1.0 grams in duplicate) of the CRM material in air at 105°C in a drying oven to constant mass to determine the moisture content. Use a crucible with a flat inner surface with a surface area not smaller than 10 cm² with the CRM material spread evenly over same; this represents a 0.1 gram spread per cm². In correcting the certified value for moisture content, a moisture correction factor is calculated:

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

$$\text{Air dry basis concentration} = \text{MCF} \times \text{certified value on a dry basis} \quad [23]$$

Example

The moisture content determined at 105°C on a CRM is 0.500%. The certified analyte concentration for the CRM is 12.62±0.52% (dry basis). Calculating the moisture correction factor using [22] gives:

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

Multiplying the factor of 0.995 by the certified value as stated on the certificate of analysis on a dry basis (as in [23]) gives the analyte concentration on an air-dry basis:

$$0.995 \times 12.62\% = 12.56\%$$

The stated measurement uncertainty also needs to be corrected using [22] and [23], e.g. $0.995 \times 0.52 = 0.51_{(7)}$, rounded to 0.52%. The air-dry basis concentration *i.e.* $12.56 \pm 0.52\%$ is to be used as the certified value with its corresponding measurement of uncertainty.

Appendix 8. Example of Determination of LOD and LOQ in Fire Assay

The limit of detection (LOD) is the minimum detectable quantity of the analyte of interest (Skoog & West, 1985). To determine the LOD in fire assay by lead collection, the minimum mass that an assay microbalance is capable of weighing (m in micrograms, and the original test sample mass, $Mass_{assay}$ in grams) determines the LOD. The smallest prill mass most assay microbalances can measure is $1\mu\text{g}$ or 0.001mg . 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 $10\mu\text{g}$) and weigh it. If an analyst can weigh a prill of $1\mu\text{g}$ then the LOD becomes $1\mu\text{g}$. However, the concentration factor would be 50 times for a 50-gram assay sample and therefore the LOD in g/t becomes $1\mu\text{g}$ divided by the original mass of the sample in grams taken for fire assay [24]. Therefore, the LOD in fire assay is computed as:

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

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

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

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be 0.02g/t . *i.e.* $1\mu\text{g} = 1\text{g/t}$, therefore $1\mu\text{g}/50\text{g} = 0.02\text{g/t}$. If no prill was found, then the LOD result would be $<0.02\text{g/t}$ or "not detected". Using a larger assay sample mass improves the LOD and LOQ (Table 11). Table 13 gives a recommended reporting scheme for LOD and LOQ.

Table 12. Mass of assay sample and corresponding limit of detection and limit of quantitation for an assay microbalance capability of smallest prill mass of $1\mu\text{g}$ or 0.001mg .

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
$\geq\text{LOQ}$	Report assay result

Appendix 9. T-distribution table

Table 14. T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence.

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