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Certificate

**AMIS0619**

**Certified Reference Material**

**Copper Concentrate, Black Mountain, Northern  
Cape, South Africa.**

***Certificate of Analysis***

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## Summary Statistics

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

Analyte	Method	Certified ( $\mu$ ) <sup>7</sup>	(2s) <sup>9</sup> $\pm$	Unit
Cu	Titration <sup>1</sup>	24.80	1.5	%
Cu	4A_MICP <sup>2</sup>	25.14	1.8	%
Cu	FUS <sup>3</sup>	25.68	1.8	%
SG	SG <sup>4</sup>	4.28	0.20	Dimensionless
LOI	LOI <sup>5</sup>	13.57	1.3	%
S	Combustion/LECO <sup>6</sup>	31.14	2.4	%
Ag	4A_MICP	311	28	ppm
Al	FUS	1439	244	ppm
As	4A_MICP	154	34	ppm
Ba	4A_MICP	57	5	ppm
Bi	4A_MICP	318	43	ppm
Ca	4A_MICP	4276	283	ppm
Ca	FUS	4332	505	ppm
Cd	4A_MICP	40	4	ppm
Co	4A_MICP	476	32	ppm
Fe	4A_MICP	34.22	2.0	%
In	4A_MICP	57	6	ppm
La	4A_MICP	4	2	ppm
Mg	4A_MICP	1490	195	ppm
Mg	FUS	1610	328	ppm
Mn	4A_MICP	3213	164	ppm
Mn	FUS	3400	560	ppm
Mo	4A_MICP	1098	104	ppm
Ni	4A_MICP	330	29	ppm
Pb	4A_MICP	2.72	0.16	%
Sb	4A_MICP	117	30	ppm
Sr	4A_MICP	4	2	ppm
Ti	4A_MICP	98	6	ppm
Y	4A_MICP	2	0.6	ppm
Zn	4A_MICP	1.24	0.059	%
Zn	FUS	1.29	0.11	%

**Major Oxides**  
***Certified Concentrations (at two Standard Deviations)***

Analyte	Method	Certified ( $\mu$ ) <sup>7</sup>	(2s) <sup>9</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	FUS	0.27	0.04	%
CaO	FUS	0.58	0.06	%
MnO	FUS	0.44	0.07	%

## 1. Certified Concentrations and Uncertainties

AMIS0619 is a new standard material, developed and certified in May 2019. Table 1 gives the certified concentrations, confidence interval, combined and expanded uncertainty for the certified reference material. Table 2 shows the certified major oxides concentrations, two standard deviations, confidence interval, combined and expanded uncertainty.

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

Analyte	Method	Certified ( $\mu$ ) <sup>7</sup>	N	n	k	% RSD	( $u_c$ ) <sup>8</sup>	(2s) <sup>9</sup> $\pm$	(CI) <sup>10</sup> 95%	(U) <sup>11</sup> $\pm$	Unit
Cu	Titration <sup>1</sup>	24.80	5	37	2.776	3	0.77	1.5	1.1	2	%
Cu	4A_MICP <sup>2</sup>	25.14	6	48	2.571	4	0.89	1.8	0.90	2	%
Cu	FUS <sup>3</sup>	25.68	2	16	12.706	3	0.90	1.8	7.9	11	%
SG	SG <sup>4</sup>	4.28	3	24	4.303	2	0.10	0.20	0.21	0.4	Dimensionless
LOI	LOI <sup>5</sup>	13.57	3	24	4.303	5	0.63	1.3	2.0	3	%
S	Combustion/LECO <sup>6</sup>	31.14	5	40	2.776	4	1.2	2.4	1.0	3	%
Ag	4A_MICP	311	7	55	2.447	5	14	28	13	35	ppm
Al	FUS	1439	4	31	3.182	8	122	244	181	388	ppm
As	4A_MICP	154	4	32	3.182	11	17	34	26	55	ppm
Ba	4A_MICP	57	4	32	3.182	4	2	5	3	7	ppm
Bi	4A_MICP	318	3	24	4.303	7	21	43	52	92	ppm
Ca	4A_MICP	4276	7	54	2.447	3	142	283	119	347	ppm
Ca	FUS	4332	3	23	4.303	6	252	505	431	1086	ppm
Cd	4A_MICP	40	5	39	2.776	5	2	4	2	6	ppm
Co	4A_MICP	476	8	60	2.365	3	16	32	14	38	ppm
Fe	4A_MICP	34.22	5	37	2.776	3	0.99	2.0	1.2	3	%
In	4A_MICP	57	2	16	12.706	5	3	6	26	38	ppm
La	4A_MICP	4	3	24	4.303	21	0.8	2	2	4	ppm
Mg	4A_MICP	1490	6	48	2.571	7	98	195	100	251	ppm
Mg	FUS	1610	4	30	3.182	10	164	328	271	522	ppm
Mn	4A_MICP	3213	6	47	2.571	3	82	164	79	211	ppm
Mn	FUS	3400	4	32	3.182	8	280	560	436	890	ppm
Mo	4A_MICP	1098	8	62	2.365	5	52	104	44	123	ppm
Ni	4A_MICP	330	7	56	2.447	4	15	29	13	36	ppm
Pb	4A_MICP	2.72	7	56	2.447	3	0.080	0.16	0.069	0.20	%
Sb	4A_MICP	117	4	32	3.182	13	15	30	23	47	ppm
Sr	4A_MICP	4	4	32	3.182	23	1	2	2	3	ppm
Ti	4A_MICP	98	5	40	2.776	3	3	6	3	8	ppm
Y	4A_MICP	2	3	23	4.303	14	0.3	0.6	0.7	1	ppm
Zn	4A_MICP	1.24	7	56	2.447	2	0.030	0.059	0.021	0.07	%
Zn	FUS	1.29	3	23	4.303	4	0.053	0.11	0.13	0.2	%

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

Analyte	Method	Certified ( $\mu$ ) <sup>7</sup>	N	n	k	% RSD	( $u_c$ ) <sup>8</sup>	(2s) <sup>9</sup> ±	(CI) <sup>10</sup> 95%	(U) <sup>11</sup> ±	Unit
Al <sub>2</sub> O <sub>3</sub>	FUS	0.27	4	31	3.182	8	0.02	0.04	0.03	0.07	%
CaO	FUS	0.58	3	22	4.303	5	0.03	0.06	0.07	0.1	%
MnO	FUS	0.44	4	32	3.182	8	0.04	0.07	0.06	0.1	%

1. Titration
2. 4A\_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
3. FUS is Fusion digestion with ICP finish
4. SG is Specific Gravity
5. LOI is Loss on Ignition
6. Combustion/LECO
7. The certified value  $\mu$ , is an unweighted grand mean of the means of N accepted sets of data from different laboratories and n number of test sample replicates. The certified value is traceable to SI units and is reported on a dry basis.
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  $\geq 0.05$ , the null hypothesis that the means (certified values) are equal is accepted (Table 3). This gives the analyst confidence in the certified values reported by different analytical methods on the same analyte.

**Table 3.** The results of a two-sample equal or unequal variance t-test (two-tailed) data sets in which different analytical methods /instrumentation were used.

Method	Certified value	Method	Certified value	F-Test Outcome	$p$ -value (t-test)	t-test Outcome
Ca FUS	0.433 %	Ca 4A_MICP	0.428 %	Equal Variance ( $p=0.24$ )	0.576	Accept $H_0$ ; certified values are equal
Mg FUS	0.161 %	Mg 4A_MICP	0.149 %	Equal Variance ( $p=0.123$ )	0.188	Accept $H_0$ ; certified values are equal
Mn FUS	0.340 %	Mn 4A_MICP	0.321 %	Unequal Variance ( $p=0.008$ )	0.277	Accept $H_0$ ; certified values are equal
Zn FUS	1.29 %	Zn 4A_MICP	1.24 %	Unequal Variance ( $p=0.048$ )	0.26	Accept $H_0$ ; certified values are equal

## 3. Intended Use

AMIS0619 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 4). 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 7). This CRM can also be used to assess inter-laboratory or instrument bias and establish within-laboratory precision and within-laboratory reproducibility. The certified concentrations and expanded uncertainty for this material are property values based on an inter-laboratory measurement campaign and reflect consensus results from the laboratories that took part in the exercise



#### 4. Abbreviations and Symbols

Abbreviations and symbols used in this document are shown in Table 4.

**Table 4.** Abbreviations, symbols and descriptions.

Abbreviation/Symbol	Description
Alpha ( $\alpha$ )	Significance level (denoted by alpha, ' $\alpha$ ') of 0.05 or 5%
ANOVA	Analysis of variance by statistical means
Bq	The becquerel is the SI derived unit of radioactivity.
BIF	Banded iron formation
CRM	Certified reference material
$df$	Degrees of freedom, typically, $n-1$ , or $N-1$
$F_{calc}$	Calculated F statistic from ANOVA or Fisher's test
F-critical or $F_{crit}$	F-critical value from F-distribution table
GOI	Gain on ignition
$H_0$	Null hypothesis
$H_1$	Alternate hypothesis
g/t	Grams per tonne
$k$	Coverage factor, 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
$\mu$	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 $k=1$
$\mu m$	Micron, is an SI derived unit of length equaling $1 \times 10^{-6}$ of a meter

## 5. Uncertified Concentration Values

Appendix 1 gives uncertified concentrations for other elements present in the CRM.

## 6. Units

All results for major oxides are reported as oxides in percentages. All results for major elements analyses reported in percentages or ppm. Results for Au and the platinum group elements are reported in g/t or ppm. Specific gravity (SG) is the ratio of the density of a substance to the density of a reference substance, *i.e.* equivalently; it is the ratio of the mass of a substance to the mass of a reference substance for the same given volume. Since specific gravity is a ratio of densities its units are therefore dimensionless.

## 7. Analytical and Physical Methods

A complete list of analytical and physical methods as generic method codes with a brief description of the methods is available on the AMIS web site [www.amis.co.za](http://www.amis.co.za)

## 8. Origin of Material

The material 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

Ore at the Black Mountain Mine is more copper-rich, in contrast to the other deposits to the east which are all more zinc-rich. This deposit comprises two superposed massive sulphide bodies namely the thicker upper ore body and a thinner lower ore body. Both ore bodies, which also carry disseminated sulphides, are hosted in the banded iron formation.

## 10. Quantitative Analysis by X-Ray Diffraction

Both natural and synthetic materials have a specific chemistry and atomic arrangement, known as phases. Phases can be identified and quantified using X-ray diffraction (XRD) which produces a plot of the intensity of X-rays scattered at different angles by crystalline phases in a material. Essentially, an X-ray diffraction pattern is the sum of the diffraction patterns produced by each phase. Simply put, an X-ray diffraction pattern is a fingerprint that allows the identification of what is in a target sample material. Knowledge of the mineral phase composition is useful in method development with techniques such as ICP-OES and XRF as potential matrix effects and spectral interferences can be recognised and accounted for. X-ray diffraction is effective in that it allows the identification of different phases of compounds that are identical in chemistry, but have a distinctly different the atoms, e.g. quartz, cristobalite, and glass are all different phases of SiO<sub>2</sub>. Where quantitative XRD results do not correspond to results of other analytical techniques, it should be borne in mind that even though the data are quantitative they are meant to be used for indicative purposes in development of other analytical methods. Mineral names may not reflect the actual compositions of minerals identified, but rather the mineral group.

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

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

The limitations of qualitative XRD analysis are as follows:

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

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

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

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

**Table 5.** Results of XRD analysis.

Phase	Formula	Composite
Amorphous Content		4
Chalcopyrite	CuFeS <sub>2</sub>	70
Galena	PbS	1
Molybdenite	MoS <sub>2</sub>	<1
Pyrrhotite	Fe <sub>1-x</sub> S <sub>x</sub>	21
Quartz	SiO <sub>2</sub>	1
Serpentine	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	<1
Sphalerite	(Zn,Fe)S	2
Total		99

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## 11. Health and Safety

The material is a very fine powder coloured dark grey. Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

## 12. Method of Preparation

The particle size distribution for this material was shown to have a nominal top size of 54µm (95% passing 54µm). The procedure of preparation in brief is as follows: the material was crushed, dry-milled and air-classified to <54µm. It was then blended in a bi-conical mixer, systematically divided and sealed into 1kg Laboratory Packs. Explorer Packs are then subdivided from the Laboratory Packs as required. Final packaged units were then selected on a random basis and submitted for analysis to an independent laboratory accredited with the ISO17025 standard of general requirements for the competence of testing and calibration laboratories. The results obtained from this laboratory are then evaluated statistically by AMIS for homogeneity.

## 13. Particle Size Determination

The sample has been analysed using a Malvern Mastersizer 2000. Particles are passed through a focused laser beam that scatter light at an angle inversely proportional to their size. The intensity of light is measured and converted to a volume in particle size distribution. The results for this standard are presented in Table 6.

**Table 6.** Particle Size Determination by laser diffraction.

Size (µm)	Vol. Under %
<45um	77.4
<63um	81.2
<75um	83.4
<90um	85.6
<100um	86.7
<106um	87.4
<150um	93.5

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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 8 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) Cu 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 and LOI) XRF fusion or Peroxide Fusion
- 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) 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.
- i) Please send excel and PDF of all results.
- j) Ensure correct PPE is used i.e. gloves, dust masks and protective clothing.
- k) 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 recalculated 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 10) 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 7, “Using the CRM in Quality Control” be used, in setting the limits of the CRM. Table 7 below shows mean gold values obtained by fire assay lead collection, for nine different laboratories, the confidence interval, two-standard deviations and expanded uncertainty.

**Table 7.** Example of replicate assay data in which the *CI*, *2s* and *U* are shown.

Lab No.	Mean Au (g/t)	<i>CI</i>	0.0088
1	0.268	<i>2s</i>	0.031
2	0.273	<i>U</i>	0.04
3	0.270		
4	0.288		
5	0.274		
6	0.256		
7	0.263		
8	0.258		
9	0.288		

### 23. Participating Laboratories

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

1. Alfred H Knight International Ltd.
2. ALS Geochemistry Arabia
3. ALS Geochemistry SA
4. Argetest Mineral Processing, R&D and Analysis Services
5. Intertek Perth
6. SGS Geosol Laboratories Ltda (Brazil)
7. SGS India (Chennai)
8. SGS Mineral Services Lakefield (Canada)
9. SGS Vancouver (Canada)
10. Shiva Analyticals India

## 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.

Titration	4A_MICP	FUS	SG	LOI	Combustion/LECO	FUS	FUS	FUS
Cu	Cu	Cu	SG	LOI	S	Al <sub>2</sub> O <sub>3</sub>	CaO	MnO
ppm	ppm	ppm	Dimensionless	%	%	%	%	%
239200	251000	265400	4.20	14.24	31.90	0.30	0.56	0.40
237600	251000	262500	4.20	14.37	31.70	0.26	0.59	0.39
237600	255000	264900	4.20	14.32	31.60	0.29	0.55	0.42
238600	251000	259500	4.20	14.27	31.90	0.26	0.56	0.40
234600	257000	262300	4.20	14.16	31.70	0.27	0.52	0.39
237600	256000	261900	4.20	14.23	31.80	0.28	0.56	0.40
237800	253000	263800	4.20	14.30	31.90	0.28	0.55	0.40
238700	259000	263600	4.20	14.28	31.60	0.28	0.60	0.40
251100	259700	249035	4.37	13.00	30.17	0.27	0.60	0.48
250200	262400	249618	4.55	12.99	30.02	0.26	0.60	0.48
250000	263500	249789	4.33	13.07	30.29	0.28	0.60	0.49
247400	264000	249338	4.33	13.50	30.50	0.29	0.60	0.50
249200	261000	247869	4.49	13.18	30.87	0.28	0.60	0.49
249200	264000	252205	4.31	13.16	30.53	0.27	0.60	0.49
249900	262900	254157	4.26	13.30	30.54	0.28	0.60	0.48
250100	263600	252958	4.34	12.85	30.27	0.27	0.60	0.48
261500	253474		4.26	13.40	32.24	0.29	0.60	0.44
260800	251441		4.29	13.30	32.35	0.29	0.60	0.44
261700	254234		4.30	13.30	32.57	0.29	0.60	0.43
260600	252608		4.23	13.30	32.68	0.29	0.60	0.44
260300	252299		4.27	13.30	32.42	0.30	0.60	0.43
246200	253710		4.29	13.40	32.58	0.29	0.60	0.43
247500	255470		4.29	13.20	32.12	0.29		0.44
246000	252898		4.31	13.20	32.79	0.29		0.43
246600	258000				31.70	0.25		0.43
246800	259000				31.80	0.24		0.43
246600	258000				31.10	0.25		0.43
246600	255000				31.40	0.24		0.44
246300	254000				31.60	0.24		0.45
246000	252000				31.20	0.23		0.44
243400	259000				31.80	0.24		0.43
245000	252000				31.50			0.44
245600	243300				30.40			
244800	241300				28.80			
246800	243100				29.60			
244800	242800				29.50			
244900	241400				30.60			
	239300				29.60			
	239800				28.70			
	239000				29.40			
	245000							
	239000							
	244000							
	240000							
	244000							
	238000							
	236000							
	243000							



**Assay Data (Cont.)**

4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS
Ag	Al	As	Ba	Bi	Ca	Ca	Cd	Co	Fe	In	La	Mg	Mg
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
309	1590	128	56.3	302	4300	4200	37.86	459	324600	59.74	2.90	1500	1560
309	1380	132	56.0	301	4300	4370	36.84	457	322100	59.85	3.20	1400	1510
309	1520	130	55.2	298	4300	4110	36.59	459	326700	59.08	3.10	1500	1620
307	1380	134	55.3	296	4300	4190	37.83	463	327100	60.17	3.70	1500	1530
310	1440	130	56.1	294	4300	3870	37.40	455	324400	58.72	3.40	1500	1520
307	1480	130	55.4	292	4300	4160	36.73	462	326300	59.56	3.30	1500	1520
308	1460	126	56.7	290	4400	4080	37.52	456	347000	60.09	3.50	1500	1530
309	1500	132	54.8	288	4300	4648	36.41	460	343000	59.10	3.10	1500	1520
300	1431	167	52.9	339	4270	4505	39.00	461	343000	56.00	4.40	1460	1800
289	1378	164	55.8	334	4350	4362	39.00	447	350000	55.00	4.20	1410	1800
295	1484	159	57.6	332	4400	4290	38.00	452	348000	56.00	3.90	1440	1800
291	1537	170	57.3	338	4240	4362	37.00	450	355000	56.00	4.00	1420	1920
294	1484	160	57.9	337	4410	4648	40.00	455	346000	56.00	3.90	1440	1920
296	1431	160	58.0	336	4380	4290	38.00	462	342000	55.00	3.60	1460	1920
300	1484	166	58.8	341	4350	4719	37.00	465	348500	55.00	3.70	1460	1600
294	1431	166	56.2	331	4230	4290	42.30	449	345100	54.00	3.70	1440	1600
335	1500	167	57.0	330	4400	5005	41.10	469	347900		5.10	1600	1500
335	1600	152	56.0	320	4300	4290	42.40	470	345400		4.80	1600	1600
338	1600	158	55.0	320	4400	4290	42.40	468	345100		5.30	1600	1600
334	1500	158	55.0	330	4300	4290	42.20	465	346000		4.70	1600	1500
336	1600	152	57.0	330	4400	4290	41.10	466	349100		4.70	1600	1600
335	1600	150	54.0	320	4300	4290	43.00	473	346100		4.70	1600	1500
334	1500	160	56.0	320	4400	4290	41.30	467	343000		4.80	1600	1446
298	1500	152	55.0	320	4400		40.00	465	347000		4.90	1700	1446
301	1325	163	60.0		4100		40.00	488	332000			1600	1464
291	1272	157	60.0		4000		40.00	490	342000			1600	1500
298	1325	176	60.0		4000		40.00	479	336000			1600	1488
291	1272	163	60.0		4100		40.00	488	343000			1600	1536
290	1272	165	60.0		4000		40.00	484	345000			1600	1452
295	1219	170	60.0		4200		40.00	486	345000			1600	1494
293	1272	167	60.0		4100		40.00	491	351000			1600	
308		174	60.0		4000		41.60	481	358000			1600	
309					4300		39.60	466	344000			1400	
310					4200		41.70	466	349000			1400	
311					4100		39.00	465	349000			1400	
310					4200		40.00	465	354000			1400	
310					4100		39.70	467	350000			1400	
309					4100		40.20	468				1400	
308					4200		41.20	464				1400	
322					4200			460				1400	
322					4300			486				1400	
320					4500			484				1400	
324					4500			474				1400	
317					4500			479				1400	
316					4400			478				1400	
323					4500			473				1400	
319					4400			482				1400	
316					4200			484				1400	
311					4300			495					
314					4300			472					
310					4100			494					
311					4200			487					
306					4200			494					
305					4200			491					
314								488					
								485					
								505					
								509					
								491					
								511					

**Assay Data (Cont.)**

4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS
Mn	Mn	Mo	Ni	Pb	Sb	Sr	Ti	Y	Zn	Zn
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
3135	3130	997	320	26300	109	5.97	97	2.30	12200	13800
3168	3040	1004	315	26500	109	5.70	94	2.00	12200	13400
3116	3290	998	318	26300	111	5.47	94	2.10	12300	13600
3130	3090	1003	323	26600	107	5.61	93	2.10	12300	13200
3125	3050	999	321	26700	111	6.07	94	2.10	12300	13400
3123	3070	1007	317	26500	109	5.46	95	2.10	12300	13500
3159	3100	999	320	26400	110	5.48	97	2.20	12700	13400
3145	3080	1140	319	26400	110	5.87	96	2.10	12200	12600
3280	3720	1110	316	27900	132	3.43	96	2.10	12200	12800
3280	3720	1120	306	28400	133	3.40	94	1.90	12200	12500
3320	3798	1100	306	28100	130	3.61	93	1.90	12600	12700
3250	3875	1130	307	27800	133	3.55	96	1.90	12100	12500
3310	3798	1130	312	27900	134	3.59	94	2.00	12900	12600
3290	3798	1140	314	27500	132	3.62	95	1.90	12700	12300
3330	3720	1120	313	27800	131	3.70	97	1.90	12400	13100
3310	3720	1151	310	27800	129	3.47	97	1.90	12700	12385
3304	3382	1182	331	27711	100	4.20	100	2.60	12800	12557
3268	3384	1157	333	27392	100	4.00	100	2.50	12900	12442
3257	3313	1190	332	27630	100	4.20	100	2.40	13200	12571
3263	3429	1149	335	27404	100	3.80	100	2.40	12700	12513
3262	3311	1193	332	27378	100	4.00	100	2.50	12700	12546
3259	3307	1185	332	27534	100	3.90	100	2.60	12500	12620
3287	3420	1137	334	27768	100	4.10	100	2.60	12400	12546
3277	3302	1152	330	27485	100	4.30	100		12700	
3200	3348	1104	346	26200	128	3.90	100		12660	
3200	3356	1138	354	26100	127	3.80	100		12559	
3200	3294	1124	355	25900	123	4.10	100		12613	
3200	3402	1126	353	26400	131	3.60	100		12419	
3100	3457	1130	354	26300	126	3.70	100		12071	
3100	3371	1107	342	26600	127	3.90	100		12098	
3100	3325	1100	347	26700	125	4.00	100		12482	
3100	3387	1100	355	26500	125	4.10	100		12396	
3190		1100	318	27700			100		12700	
3190		1100	318	27600			100		12600	
3120		1100	317	27500			100		12500	
3130		1100	321	27600			100		12600	
3150		1100	322	27100			100		12600	
3100		1100	324	27000			100		12600	
3170		1095	327	27700			100		12400	
3140		1070	321	27000			100		12400	
3230		1080	339	28361					12400	
3350		1075	334	29089					12300	
3250		1065	323	28333					12200	
3210		1065	332	27731					12400	
3290		1085	323	28398					12000	
3310		1095	325	28251					12000	
3290		1059	334	27730					12200	
		1022	337	28156					12200	
		1065	355	27000					12300	
		1067	338	26700					12100	
		1086	348	26700					12100	
		1065	340	26800					12150	
		1054	339	26900					12100	
		1056	341	26200					11800	
		1150	345	26000					11750	
		1115	342	26700					12100	
		1145								
		1125								
		1120								
		1130								
		1120								
		1100								

## **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 4 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](http://www.amis.co.za) website.

## **29. Minimum Sample Size**

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

## **30. Availability**

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

## **31. Recommended use in Quality Control**

Users should set their own limits *i.e.* 1, 2 and 3 standard deviations from an obtained mean value based on at least 10 replicate analyses using this CRM (see Appendix 7 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:** 13 May 2019

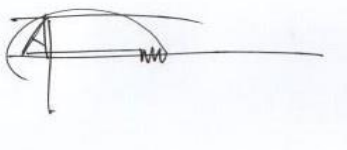
**Version:** 000

**Approving Officer:**

**African Mineral Standards:** \_\_\_\_\_

**Makhosi Khoza (Quality Specialist)**

**Certifying Officer:**

A handwritten signature in black ink, appearing to be 'AF', is written over a horizontal line. The signature is stylized and somewhat abstract.

**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	2A_MICP	7	304.4	3.9	1	ppm
Ag	FUS	8	263.1	29.1	11	ppm
Al	2A_MICP	7	1000.0	*	*	ppm
Al	4A_MICP	47	1422.3	173.8	12	ppm
Al <sub>2</sub> O <sub>3</sub>	XRF	8	0.3	0.01	2	%
As	2A_MICP	8	160.9	5.2	3	ppm
Au	2A_MICP	8	0.2	0.02	8	g/t
B	2A_MICP	2	10.0	*	*	ppm
Ba	2A_MICP	8	40.0	*	*	ppm
Ba	FUS	7	55.3	1.1	2	ppm
Be	2A_MICP	8	0.4	0.02	6	ppm
Be	4A_MICP	19	0.5	0.03	6	ppm
Bi	2A_MICP	8	291.8	8.4	3	ppm
C	Combustion/LECO	52	2375.2	329.7	14	ppm
Ca	2A_MICP	7	3914.3	37.8	1	ppm
CaO	XRF	8	0.4	0.01	2	%
Cd	2A_MICP	8	38.2	0.7	2	ppm
Ce	2A_MICP	8	4.8	0.2	4	ppm
Ce	4A_MICP	16	8.3	1.0	12	ppm
Co	2A_MICP	8	447.4	15.6	3	ppm
Co	FUS	16	438.4	43.2	10	ppm
Cr	2A_MICP	8	23.0	0.5	2	ppm
Cr	4A_MICP	32	65.4	22.7	35	ppm
Cr	FUS	9	109.7	11.3	10	ppm
Cr <sub>2</sub> O <sub>3</sub>	FUS	9	0.02	0.002	10	%
Cr <sub>2</sub> O <sub>3</sub>	XRF	8	0.01	*	*	%
Cs	2A_MICP	8	0.5	0.01	2	ppm
Cs	4A_MICP	15	0.6	0.02	3	ppm
Cu	2A_ICPES	7	237142.9	1951.8	1	ppm
Cu	2A_MICP	8	241500.0	5682.1	2	ppm
Cu	XRF	8	246250.0	3615.4	1	ppm
Dy	4A_MICP	8	0.5	0.1	10	ppm
Er	4A_MICP	7	0.2	0.1	34	ppm
Eu	4A_MICP	8	0.4	0.1	12	ppm
Fe	2A_MICP	8	352750.0	11853.3	3	ppm
Fe	FUS	24	344502.0	22574.5	7	ppm
Fe	XRF	8	328837.5	965.0	0.3	ppm
Fe <sub>2</sub> O <sub>3</sub>	FUS	24	49.3	3.2	7	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	16	36.1	12.1	33	%
Ga	2A_MICP	8	0.8	0.02	2	ppm
Ga	4A_MICP	15	0.9	0.1	14	ppm
Gd	4A_MICP	8	1.1	0.1	12	ppm
Ge	2A_MICP	7	0.4	0.01	2	ppm
Ge	4A_MICP	8	0.3	0.03	10	ppm
Hf	2A_MICP	1	0.02	*	*	ppm
Hf	4A_MICP	8	0.1	*	*	ppm
Hg	2A_MICP	8	0.3	0.02	5	ppm
In	2A_MICP	8	48.9	1.0	2	ppm
K <sub>2</sub> O	FUS	1	0.1			%
K <sub>2</sub> O	XRF	4	0.01	*	*	%
La	2A_MICP	8	2.5	0.1	5	ppm
Li	2A_MICP	8	0.7	0.1	8	ppm
Li	4A_MICP	7	1.3	0.1	5	ppm

Element	Generic Method	n	Mean	SD	RSD %	Unit
Mg	2A_MICP	7	500.0	*	*	ppm
MgO	FUS	30	0.3	0.03	10	%
MgO	XRF	8	0.3	0.01	3	%
Mn	2A_MICP	7	2612.9	25.6	1	ppm
MnO	XRF	7	0.3	0.01	2	%
Mo	2A_MICP	8	536.3	20.3	4	ppm
Mo	FUS	8	1200.0	78.9	7	ppm
Moisture	Moisture	24	0.2	0.1	29	%
Na	4A_MICP	19	184.5	202.8	110	ppm
Nb	2A_MICP	8	0.6	0.03	5	ppm
Nb	4A_MICP	16	1.7	0.1	8	ppm
Nd	4A_MICP	8	3.5	0.2	6	ppm
Ni	2A_MICP	8	307.4	8.6	3	ppm
Ni	FUS	7	336.0	8.2	2	ppm
P	2A_MICP	8	137.5	7.1	5	ppm
P	4A_MICP	16	120.0	28.5	24	ppm
P <sub>2</sub> O <sub>5</sub>	XRF	8	0.03	*	*	%
Pb	2A_MICP	7	27142.9	340.9	1	ppm
Pb	FUS	16	26450.0	915.1	3	ppm
Pb	XRF	8	27512.5	691.7	3	ppm
Pr	4A_MICP	8	0.9	0.1	8	ppm
Rb	2A_MICP	8	1.1	*	*	ppm
Rb	4A_MICP	15	1.3	0.1	5	ppm
Re	2A_MICP	8	0.2	0.01	4	ppm
Re	4A_MICP	14	0.4	0.01	3	ppm
S	2A_MICP	8	6.5	0.3	5	%
S	4A_MICP	24	24.1	7.1	29	%
S	FUS	8	32.2	0.2	1	%
Sb	2A_MICP	8	110.9	2.5	2	ppm
Sc	2A_MICP	8	0.2	*	*	ppm
Sc	4A_MICP	16	1.7	1.5	92	ppm
Se	2A_MICP	7	2.8	0.2	5	ppm
Se	4A_MICP	8	4.0	0.8	19	ppm
Si	FUS	24	6587.5	1916.6	29	ppm
Si	XRF	8	6403.8	65.2	1	ppm
SiO <sub>2</sub>	FUS	24	1.5	0.4	29	%
SiO <sub>2</sub>	XRF	8	1.4	0.02	1	%
Sm	4A_MICP	8	1.1	0.1	13	ppm
Sn	2A_MICP	8	5.3	0.1	2	ppm
Sn	4A_MICP	16	6.0	0.1	2	ppm
Sr	2A_MICP	8	3.6	0.1	3	ppm
Sr	FUS	5	11.0	*	*	ppm
Ta	2A_MICP	8	0.01	*	*	ppm
Ta	4A_MICP	8	0.1	0.01	12	ppm
Tb	4A_MICP	8	0.1	0.01	5	ppm
Te	2A_MICP	8	0.3	0.03	8	ppm
Te	4A_MICP	10	0.3	0.1	27	ppm
Th	2A_MICP	8	0.5	0.05	9	ppm
Th	4A_MICP	16	0.6	0.1	12	ppm
Ti	FUS	9	91.1	7.3	8	ppm
TiO <sub>2</sub>	FUS	9	0.02	0.001	8	%
Tl	2A_MICP	8	2.9	0.1	2	ppm
Tl	4A_MICP	16	3.0	1.8	61	ppm

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

## Appendix 2: Uncertified Element Statistics (continued)

Element	Generic Method	n	Mean	SD	RSD %	Unit
U	2A_MICP	8	0.7	0.1	8	ppm
U	4A_MICP	15	0.7	0.1	9	ppm
V	2A_MICP	8	6.3	0.9	14	ppm
V	4A_MICP	24	7.8	2.0	26	ppm
W	2A_MICP	8	4.8	0.1	2	ppm
W	4A_MICP	16	5.4	0.4	7	ppm
Y	2A_MICP	8	1.6	0.04	2	ppm
Yb	4A_MICP	2	0.1	*	*	ppm
Zn	2A_MICP	7	12028.6	26.7	0.2	ppm
Zn	XRF	8	12412.5	235.7	2	ppm
Zr	4A_MICP	16	8.6	8.0	92	ppm

Appendix 2 through 9, prepared by Allan Fraser.

## Appendix 3. 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.

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

## Between Group Variation (SSB)

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

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

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

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

## Within Group Variation (SSW)

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

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

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

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

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

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

Source	Sum of Squares	df	Mean Sum of Squares	F	p	F <sub>crit</sub>
Between Laboratories	SSB	P-1	MSB=SSB/df	MSB/MSW	=FDIST(x,df,df)	F-table
Within Laboratories	SSW	P(n-1)	MSW=SSW/df	–	–	–
Total	SSB+SSW	P-1 + P(n-1)	–	–	–	–

### Combined Standard Uncertainty

The combined standard uncertainty ( $u_c$ ) represents the effects of random events such as days, instruments, and analysts on the precision of the analytical procedures of all accepted data of the participating laboratories. Using the output from ANOVA, the combined standard uncertainty ( $u_c$ ) is determined from the square root of the sum of squares of the variances of the within laboratory repeatability,  $s_r$  and the between laboratory precision,  $s_s$ :

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

Within laboratory repeatability is determined as

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

and, the between laboratory precision as

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

where  $MSW$  is the mean squares of the within laboratory variance,  $MSB$  is the mean squares for the between laboratories and  $n$  in this case, is the number of replicates in a group of the accepted data (Thompson & Lowthian, 2011).

### Expanded Uncertainty

The expanded uncertainty ( $U$ ) at a confidence level of 95% is determined by multiplication of the combined uncertainty ( $u_c$ ) by a coverage factor ( $k$ ) found from  $N-1$  degrees of freedom ( $df$ ), where  $N$  is the number of laboratory means accepted in the establishment of the certified value. The t-critical value for 5% significance can be found in a t-critical table (see Appendix 10, or from MS Excel as =TINV (5%,  $df$ )).

## Uncertainty Statement

Typically, an uncertainty statement is presented as follows:  $Au = 0.77 \pm 0.04$  g/t, where the number following the symbol  $\pm$  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  $0.77 \pm 0.04$ g/t will have intervals of:  $0.73 \leq 0.77 \leq 0.81$  g/t.

## Appendix 4. Example: Comparison of Mean and Certified Value for Validation of Accuracy

According to ERM (2005); Eurolab (2007); Abzalov (2011) and Carr (2011), the validation of accuracy for a given mean and certified value requires the inclusion of the measurement uncertainty of the CRM in a t-test for statistical significance. The classical Student's t-test as shown in [17], does not consider the measurement uncertainty of the CRM. To compensate for this, Eurolab Technical Report No.1/2007 recommends equation [18] for the validation of CRMs with stated measurement uncertainties.

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

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

Where,  $t_{calc}$  is the calculated t-statistic,  $\bar{x}$  the mean of  $n$  replicates with a standard deviation of  $s$  for a CRM of  $\mu$  certified value. The standard uncertainty  $u$  is the stated expanded uncertainty ( $U$ ) of the CRM divided by the coverage factor ( $k$ ) as stated on the certificate of analysis. Note that the  $| \quad |$  bars indicate that the absolute value between the mean and the certified value is to be used, *i.e.* ignore the sign.

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

### Example

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

The relevant hypotheses are:

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

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

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

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

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

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

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

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

Therefore,  $t_{calc} = 0.84$  and  $t_{crit}(5\%, 8) = 2.31$  ( $df$  is 8, therefore,  $t_{crit}=2.31$ , see Appendix 10, page 31) which is  $>0.84$ . Similarly, the  $p$ -value=0.43 which is  $>0.05$ . This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known, the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

#### Appendix 5. 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 6. 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 10) or MS Excel as =TINV (5%,  $df$ ).

## Appendix 7. 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 *C*/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 8. Conversion to Air-dry Basis (Prepared by Allan Fraser)

Since AMIS certified analyte values are reported on a dry-basis, the user laboratory is required to dry a portion (accurately weigh out 1.0 grams in duplicate) of the CRM material in air at 105°C in a drying oven to constant mass to determine the moisture content. Use a crucible with a flat inner surface with a surface area not smaller than 10 cm<sup>2</sup> with the CRM material spread evenly over same; this represents a 0.1 gram spread per cm<sup>2</sup>. In correcting the certified value for moisture content, a moisture correction factor is calculated:

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

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

### 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 x 0.52 = 0.517, 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 9. 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,  $Mass_{\text{assay}}$  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:

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

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

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

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be 0.02g/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.

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

**Appendix 10.** 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.

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