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Certificate

# AMIS0556

## Certified Reference Material

Chrome bearing Norite and Feldspathic Pyroxenite  
South Africa

### *Certificate of Analysis*

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#### AMIS

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## SUMMARY STATISTICS

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

#### *Certified Concentrations Major Oxides*

Analyte	Method	<sup>5</sup> Certified (μ)	<sup>7</sup> Two Standard Deviation (2s) ±	Unit
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>1</sup>	15.0	0.42	%
Cr <sub>2</sub> O <sub>3</sub>	XRF	44.2	0.39	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	29.9	1.67	%
MgO	XRF	9.4	0.46	%
MnO	XRF	0.23	0.03	%
TiO <sub>2</sub>	XRF	0.76	0.06	%
SG	SG <sup>2</sup>	4.53	0.08	Dimensionless
GOI	LOI <sup>3</sup>	1.95	0.10	%

#### *Certified Concentrations (at two Standard Deviations)*

Analyte	Method	<sup>5</sup> Certified (μ)	<sup>7</sup> Two Standard Deviation (2s) ±	Unit
Ag	4A_MICP <sup>4</sup>	3	1	ppm
Ba	4A_MICP	31	5	ppm
Bi	4A_MICP	0.1	0.07	ppm
Cd	4A_MICP	0.1	0.06	ppm
Co	4A_MICP	284	58	ppm
Cu	4A_MICP	108	17	ppm
Dy	4A_MICP	0.1	0.03	ppm
Gd	4A_MICP	0.06	0.03	ppm
Hf	4A_MICP	0.1	0.07	ppm
La	4A_MICP	0.4	0.2	ppm
Li	4A_MICP	2	0.6	ppm
Mo	4A_MICP	0.4	0.2	ppm
Nd	4A_MICP	0.3	0.1	ppm
Pb	4A_MICP	13	3	ppm
Pr	4A_MICP	0.1	0.03	ppm
Sb	4A_MICP	3	0.6	ppm
Sc	4A_MICP	7	3	ppm
Sm	4A_MICP	0.05	0.01	ppm
Sn	4A_MICP	0.4	0.1	ppm
Sr	4A_MICP	5	2	ppm
Te	4A_MICP	0.6	0.3	ppm
Th	4A_MICP	0.1	0.09	ppm
U	4A_MICP	0.2	0.06	ppm
Y	4A_MICP	0.3	0.08	ppm

## 1. Certified Concentrations and Uncertainties

AMIS0556 is a new standard material, developed and certified in May 2018. Table 1 gives the certified concentrations of major oxides, combined and expanded uncertainty for the certified reference material. Table 2 shows the certified concentrations 4A\_MICP, two standard deviations, combined and expanded uncertainty.

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

Analyte	Method	<sup>5</sup> Certified ( $\mu$ )	N	n	k	% RSD	<sup>6</sup> Combined uncertainty ( $u_c$ )	<sup>7</sup> Two Standard Deviation (2s) $\pm$	<sup>8</sup> Expanded uncertainty (U) $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>1</sup>	15.0	7	55	2.45	1	0.212	0.42	1	%
Cr <sub>2</sub> O <sub>3</sub>	XRF	44.2	5	40	2.78	0.4	0.20	0.39	1	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	29.9	8	59	2.36	3	0.83	1.67	2	%
MgO	XRF	9.4	8	63	2.36	2	0.23	0.46	1	%
MnO	XRF	0.23	6	45	2.57	6	0.013	0.03	0.03	%
TiO <sub>2</sub>	XRF	0.76	6	48	2.57	4	0.031	0.06	0.1	%
SG	SG <sup>2</sup>	4.53	4	28	3.18	1	0.039	0.08	0.1	Dimensionless
GOI	GOI <sup>3</sup>	1.95	8	63	2.36	3	0.050	0.10	0.1	%

**Table 2.** Certified concentrations (4A\_MICP), two standard deviations, combined and expanded uncertainty.

Analyte	Method	<sup>5</sup> Certified ( $\mu$ )	N	n	k	% RSD	<sup>6</sup> Combined uncertainty ( $u_c$ )	<sup>7</sup> Two Standard Deviation (2s) $\pm$	<sup>8</sup> Expanded uncertainty (U) $\pm$	Unit
Ag	4A_MICP <sup>4</sup>	3	5	39	2.78	17	0.5	1	1	ppm
Ba	4A_MICP	31	6	45	2.57	9	3	5	7	ppm
Bi	4A_MICP	0.09	4	31	3.18	39	0.03	0.07	0.1	ppm
Cd	4A_MICP	0.1	4	25	3.18	40	0.03	0.06	0.1	ppm
Co	4A_MICP	284	6	47	2.57	10	29	58	75	ppm
Cu	4A_MICP	108	6	47	2.57	8	8	17	21	ppm
Dy	4A_MICP	0.1	4	30	3.18	22	0.01	0.03	0.04	ppm
Gd	4A_MICP	0.1	3	24	4.30	21	0.01	0.03	0.1	ppm
Hf	4A_MICP	0.1	5	33	2.78	27	0.03	0.07	0.1	ppm
La	4A_MICP	0.4	3	24	4.30	25	0.1	0.2	0.5	ppm
Li	4A_MICP	2	6	45	2.57	16	0.3	0.6	1	ppm
Mo	4A_MICP	0.4	4	29	3.18	29	0.1	0.2	0.4	ppm
Nd	4A_MICP	0.3	4	31	3.18	19	0.1	0.1	0.2	ppm
Pb	4A_MICP	13	6	46	2.57	13	2	3	4	ppm
Pr	4A_MICP	0.1	4	32	3.18	18	0.02	0.03	0.05	ppm
Sb	4A_MICP	3	5	39	2.78	12	0.3	0.6	1	ppm
Sc	4A_MICP	7	6	47	2.57	19	1	3	4	ppm
Sm	4A_MICP	0.05	3	22	4.30	11	0.006	0.01	0.03	ppm
Sn	4A_MICP	0.4	3	22	4.30	14	0.06	0.1	0.3	ppm
Sr	4A_MICP	5	6	47	2.57	15	0.8	2	2	ppm
Te	4A_MICP	0.6	5	39	2.78	25	0.1	0.3	0.4	ppm
Th	4A_MICP	0.1	4	32	3.18	33	0.04	0.09	0.1	ppm
U	4A_MICP	0.2	4	32	3.18	13	0.03	0.06	0.1	ppm
Y	4A_MICP	0.3	6	45	2.57	12	0.04	0.08	0.1	ppm

1. XRF is X-ray Fluorescence
2. SG is Specific gravity
3. GOI is Gain on ignition
4. 4A\_MICP is a Multi-acid digestion with ICP finish
5. 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.
6. 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.
7. The two standard deviations (2s) is calculated as for example:  $u_c \times 2 = 0.23 \times 2 = 0.46\%$ . See section 27, page 14, for recommended use in quality control.
8. 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:  $U = 2.36 \times 0.23 = 0.54\%$ .

## 2. Intended Use

AMIS0556 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 4). 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 participated in the exercise.

## 3. Abbreviations and Symbols

Abbreviations and symbols used in this document are shown in Table 3.

**Table 3.** 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 $N-1$
$F_{\text{calc}}$	Calculated F statistic from ANOVA or Fisher's test
F-critical or $F_{\text{crit}}$	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, <i>e.g.</i> $k=2$ 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

**Table 3** Continued.

<b>Abbreviation/Symbol</b>	<b>Description</b>
$p$	' $p$ -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
2s	Two times standard deviation
SI	Standard International system of units
$t_{calc}$	Calculated t statistic from a one-sample, two-tailed t-test
t-critical or $t_{crit}$	t-critical value at given alpha and degrees of freedom
Tonne	A metric ton, is a unit of mass equaling 1000 kilograms
=TINV(5%, $df$ )	MS Excel function for t-critical value at LOC 95% and $df$
$U$	Expanded uncertainty at a given k
$u$	Standard uncertainty at $k=1$
$u_c$	Combined standard uncertainty at $k=1$
$\mu\text{m}$	Micron, is an SI derived unit of length equaling $1 \times 10^{-6}$ of a meter

## 4. Uncertified Concentration Values

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

## 5. 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.

## 6. 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)

## 7. Origin of Material

The chromitite layers within the Critical Zone occur as three stratigraphically delineated groups. The Lower Group ("LG") consists of seven chromitite layers hosted within a feldspathic pyroxenite. Four chromitite layers contained within a norite and feldspathic pyroxenite sequence constituting the Middle Group ("MG") which is situated immediately between the Lower Group and the Upper Group of the Bushveld Complex.

## 8. Approximate Mineral and Chemical Composition

This material is a chemical grade ore mixture of MG1/MG2 with approximate concentration of 45% for Cr<sub>2</sub>O<sub>3</sub>.

## 9. 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.

### 9.1 Sample preparation for X-Ray Diffraction

The sample was micro milled for 10 minutes, with ethanol as the grinding medium. The resultant sample was lightly pressed into a back-packed sample holder.



## 9.2 XRD Results

The results from a diffractogram of this reference material is:

Spinel group, where A=Co, Cu, Fe<sup>2+</sup>, Ge, Mg, Mn<sup>2+</sup>, Ni, Ti, Zn; B=Al, Cr<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mg, Mn<sup>3+</sup>, Ti, V<sup>3+</sup>. Chromite was used in these Rietveld refinements, since it gave the best fit. Further work would be required to more accurately identify the spinel-group mineral. <sup>2</sup>Tr = trace, i.e. the mineral giving rise to the peak is estimated to be present in trace amounts. Note that other small 'unassigned' peaks in the XRD trace are spectral lines (i.e. K-β lines from the main spinel peaks).

Table 4. Mineral species identified and quantified two sub-samples of AMIS0556 using Rietveld Refinement.

Mineral	Composition	Weight %
Spinel group-chromite <sup>1</sup>	AB <sub>2</sub> O <sub>4</sub>	100
Unassigned peak <sup>2</sup>	32.7°2θ/3.17Å	Tr
%Total	—	100

## 10. Health and Safety

The material is a very fine powder coloured Dark Gray (Costor colour). Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

## 11. Method of Preparation

The particle size distribution for this material was shown to have a nominal top size of 54µm (at least 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 ISO17025:2005 standard of general requirements for the competence of testing and calibration laboratories. The results obtained from this laboratory are then evaluated by AMIS for homogeneity.

## 12. Particle Size Determination

The particle size was determined by laser diffraction. In this method, 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 5.

Table 5. Particle Size Determination by laser diffraction.

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.10	0.00	45.00	98.35	170.00	100
0.25	0.84	50.00	98.97	175.00	100
0.50	4.93	55.00	99.38	200.00	100
0.60	6.10	60.00	99.63	225.00	100
0.75	7.54	65.00	99.76	250.00	100
1.00	9.72	70.00	99.84	300.00	100
2.00	20.66	75.00	99.89	400.00	100
3.00	31.58	80.00	99.93	500.00	100
4.00	40.11	85.00	99.96	600.00	100
5.00	46.68	90.00	99.98	700.00	100
6.00	51.93	95.00	100	800.00	100
7.00	56.31	100.00	100	900.00	100
8.00	60.10	105.00	100	1000.00	100
9.00	63.44	106.00	100	1100.00	100
10.00	66.43	110.00	100	1200.00	100
12.00	71.63	115.00	100	1300.00	100
15.00	77.91	120.00	100	1400.00	100
18.00	82.81	125.00	100	1500.00	100
20.00	85.46	130.00	100	1600.00	100
25.00	90.45	135.00	100	1700.00	100
30.00	93.75	140.00	100	1800.00	100
35.00	95.94	150.00	100	1900.00	100
40.00	97.39	160.00	100	2000.00	100

### 13. 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 in order to convert any obtained assay values to an air-dry basis (see Appendix 5 for an example calculation).

### 14. 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.

### 15. Methods of Analysis Requested

The following methods of analysis were requested:

- a. Multi element scan to include all elements-4-acid total digestion, including HF, ICP-OES or ICP-MS or AAS finish
- b. All oxides to include LOI at 1000°C with XRF finish or fusion/4 acid digest with ICP/AAS finish
- c. SG – gas pycnometer
- d. S Combustion/LECO

### 16. 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.

## 17. Certification of Mean and Estimation of Measurement Uncertainty

The samples used in this certification process have been selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore, all possible sources of uncertainty are included in the combined standard uncertainty determination. Initially the data submitted by all of 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). These data are then subjected to an analysis of variance (ANOVA) as per equations, [9],[10],[11],[12] and [13] in Appendix 2. The mean squares for data within and between laboratories derived from ANOVA are used to compute the within-laboratory reproducibility, or combined standard uncertainty as shown in Appendix 2, equation [14], [15] and [16]. The Horwitz function is applied to assess the performance of the data under consideration with respect to precision as relative standard deviation (equations [4], [5] and [6]). Should the ratio of the observed %RSD and a calculated %RSD be <2, the observed %RSD is accepted (Horwitz & Albert, 2006). A final certified value is then found by calculating a grand mean of equally weighted individual laboratory means [7] (ISO Guide 35, 2003; Barwick & Pritchard, 2011).

An uncertainty statement on AMIS certificates is typically presented as:

The expanded uncertainty ( $U$ ) is determined by multiplication of the combined uncertainty ( $u_c$ ) with a coverage factor ( $k$ ) found from  $N-1$  degrees of freedom and a t-critical value at a level of confidence of 95% (EURACHEM / CITAC Guide CG 4., (2012), (see Table 12, Appendix 7 for a t-critical table).  $N$  is the number of laboratory means used in the establishment of the certified value. Since the estimated values of the CRM approximate a normal distribution with combined uncertainty,  $u_c$ , the certified value of the CRM is understood to lie in the interval defined by  $U$  with a level of confidence of 95 % (Thompson & Lowthian, 2011).

Appendix 2 gives detail on the principles used for certification of the reported assay values and estimation of measurement uncertainty.

## 18. Participating Laboratories

Five teen laboratories were each given eight randomly selected packages of the CRM. Ten laboratories submitted results in time for certification.

The 10 laboratories that provided results timeously are:

1. Shiva Analyticals India
2. SGS South Africa
3. Set Point Laboratories (Isando) SA
4. Scrooby's Lab
5. Samancor Western Chrome Mine

6. JAEC\_CPAL
7. Intertek Perth
8. Bureau Veritas Minerals Ultra Trace Pty Ltd
9. Argetest Mineral Processing, R&D and Analysis Services
10. ALS OMAC (Ireland)

## 19. Accepted Assay Data

Data from the 10 laboratories used for certification are set out in Table 6.

**Table 6.** Data used to calculate the certified values after removal of outliers.

XRF Al <sub>2</sub> O <sub>3</sub> %	XRF Cr <sub>2</sub> O <sub>3</sub> %	XRF Fe <sub>2</sub> O <sub>3</sub> %	XRF MgO %	XRF MnO %	XRF TiO <sub>2</sub> %	SG SG Dimensionless	LOI GOI %
15.00	44.40	30.00	9.45	0.22	0.78	4.51	1.97
14.90	44.20	29.80	9.39	0.22	0.76	4.51	1.94
15.00	44.40	30.00	9.45	0.23	0.79	4.50	1.96
14.80	44.10	29.80	9.31	0.23	0.76	4.49	1.96
14.90	44.20	29.90	9.35	0.21	0.76	4.50	1.95
14.80	44.00	29.80	9.33	0.23	0.76	4.51	1.96
15.00	44.40	30.20	9.45	0.22	0.76	4.51	1.93
14.90	44.10	29.80	9.39	0.24	0.76	4.51	1.96
15.18	44.23	30.83	9.28	0.25	0.76	4.46	1.97
15.21	44.18	30.74	9.34	0.25	0.80	4.59	1.96
15.12	44.19	30.93	9.37	0.24	0.83	4.52	1.96
15.38	44.27	30.36	9.23	0.22	0.84	4.52	1.96
15.07	44.24	30.61	9.30	0.23	0.77	4.48	1.96
15.06	44.23	30.87	9.25	0.25	0.78	4.56	1.96
15.29	44.12	30.81	9.29	0.24	0.83	4.57	1.96
15.15	44.21	31.14	9.33	0.24	0.79	4.57	1.96
15.40	44.10	28.00	9.52	0.24	0.75	4.58	1.94
15.50	44.10	28.10	9.92	0.24	0.76	4.60	2.00
15.40	44.10	28.00	9.41	0.24	0.77	4.55	1.84
15.50	44.10	28.10	9.56	0.24	0.77	4.59	1.91
15.50	44.10	28.00	9.65	0.23	0.76	4.49	1.68
15.20	44.10	31.29	9.26	0.24	0.76	4.52	1.93
15.10	44.00	31.31	9.24	0.23	0.78	4.53	1.91
14.91	44.10	29.97	9.67	0.23	0.77	4.53	1.98
14.84	44.55	31.43	9.50	0.23	0.78	4.50	1.99
14.96	44.64	31.52	9.72	0.23	0.78	4.53	2.00
14.85	44.65	30.66	9.70	0.23	0.76	4.53	2.01
14.92	44.60	30.02	9.75	0.23	0.77	4.53	1.98
14.89	43.76	30.03	9.91	0.23	0.76		1.96
14.91	43.80	30.05	9.93	0.23	0.76		1.87
14.86	44.18	30.03	9.35	0.21	0.76		1.95
14.80	44.24	30.07	9.33	0.21	0.77		1.95
14.80	44.14	30.02	9.32	0.21	0.72		1.99
14.80	44.13	29.88	9.32	0.20	0.72		1.99
14.80	44.42	29.96	9.38	0.21	0.70		1.98
14.80	44.38	30.10	9.34	0.21	0.73		1.97
14.80	44.31	30.10	9.34	0.20	0.72		1.99
14.80	44.38	30.10	9.33	0.24	0.70		1.94
14.80	44.31	30.10	9.34	0.24	0.70		1.98
15.02	44.29	30.10	9.43	0.24	0.73		1.93
14.90		30.10	9.43	0.24	0.78		1.96
14.93		30.20	9.44	0.24	0.78		1.95
14.97		30.10	9.40	0.24	0.76		1.99
14.69		29.36	9.40	0.24	0.77		1.97
15.00		29.16	9.40	0.24	0.78		1.97
14.97		29.44	9.39		0.78		1.94
14.79		29.53	9.40		0.77		1.96

Assay Data (Cont.)

4A_MI CP Ag ppm	4A_MI CP Ba ppm	4A_MI CP Bi ppm	4A_MI CP Cd ppm	4A_MI CP Ce ppm	4A_MI CP Co ppm	4A_MI CP Cu ppm	4A_MI CP Dy ppm	4A_MI CP Gd ppm	4A_MI CP Hf ppm	4A_MI CP La ppm	4A_MI CP Li ppm	4A_MI CP Mo ppm
2.10	33.00	0.13	0.10	0.70	242	118	0.07	0.07	0.13	0.50	1.60	0.60
2.10	33.00	0.13	0.10	0.73	245	119	0.07	0.07	0.13	0.50	1.60	0.60
2.10	33.00	0.13	0.10	0.75	244	113	0.08	0.08	0.14	0.50	1.50	0.60
2.00	33.00	0.13	0.10	0.69	243	113	0.08	0.08	0.13	0.50	1.50	0.60
2.20	33.00	0.12	0.10	0.67	246	116	0.08	0.08	0.14	0.50	1.60	0.60
2.10	32.00	0.13	0.10	0.69	249	114	0.07	0.08	0.13	0.50	1.60	0.44
2.30	33.00	0.12	0.10	0.72	244	114	0.08	0.08	0.13	0.50	1.60	0.38
3.30	33.00	0.13	0.10	0.80	242	116	0.08	0.07	0.13	0.50	1.60	0.44
3.30	35.00	0.08	0.07	0.70	248	117	0.06	0.06	0.10	0.50	2.00	0.40
3.20	36.00	0.07	0.07	0.70	244	124	0.07	0.06	0.09	0.50	2.00	0.40
3.10	37.00	0.07	0.08	0.70	284	110	0.06	0.05	0.10	0.50	2.00	0.41
3.30	37.00	0.06	0.06	0.70	262	115	0.06	0.05	0.10	0.50	2.00	0.39
3.20	32.00	0.07	0.07	0.70	249	115	0.06	0.06	0.11	0.50	2.00	0.36
3.20	30.00	0.06	0.07	0.80	268	124	0.06	0.05	0.09	0.50	2.00	0.30
3.30	29.00	0.06	0.05	0.80	239	110	0.08	0.06	0.09	0.50	2.00	0.30
3.50	28.00	0.07	0.06	0.70	282	109	0.06	0.06	0.08	0.60	1.80	0.40
3.50	28.00	0.08	0.08	0.76	290	108	0.05	0.05	0.10	0.30	1.90	0.50
3.50	29.00	0.09	0.04	0.73	285	110	0.05	0.06	0.10	0.30	1.90	0.30
3.00	28.00	0.06	0.06	0.74	288	104	0.05	0.08	0.10	0.30	1.80	0.30
3.50	27.00	0.07	0.05	0.71	294	112	0.05	0.05	0.10	0.30	1.90	0.30
3.50	29.00	0.07	0.03	0.74	282	108	0.05	0.05	0.10	0.30	1.90	0.30
3.00	28.00	0.08	0.04	0.74	289	108	0.05	0.05	0.10	0.30	1.90	0.36
3.50	28.00	0.07	0.05	0.71	296	106	0.05	0.05	0.20	0.50	1.80	0.36
3.08	28.00	0.05	0.03	0.73	295	105	0.05	0.06	0.20	0.30	2.00	0.33
2.97	28.00	0.07	0.04		300	105	0.05		0.20		2.00	0.39
3.09	28.00	0.15			290	110	0.06		0.10		2.00	0.32
3.06	28.00	0.06			295	110	0.05		0.10		2.00	0.26
2.94	28.00	0.05			295	105	0.05		0.10		2.00	0.31
2.97	28.00	0.06			290	105	0.05		0.10		2.00	0.28
3.00	30.96	0.07			290	105	0.05		0.10		2.00	
3.08	30.52	0.07			295	105			0.10		2.00	
3.40	29.12				317	107			0.10		2.55	
3.31	30.45				312	107			0.10		2.56	
3.55	30.23				311	105					2.56	
3.31	29.55				304	105					2.57	
3.32	29.64				306	104					2.59	
3.32	29.77				311	108					2.53	
3.33	30.00				307	106					2.20	
3.39	30.00				309	103					2.10	
	30.00				309	96					2.10	
	30.00				314	97					1.90	
	30.00				328	99					1.80	
	30.00				309	93					1.80	
	30.00				309	92					1.90	
	30.00				316	94					1.80	
					314	95						
					311	94						

## Assay Data (Cont.)

4A_MI CP Nd ppm	4A_MI CP Pb ppm	4A_MI CP Pr ppm	4A_MI CP Sb ppm	4A_MI CP Sc ppm	4A_MI CP Sm ppm	4A_MI CP Sn ppm	4A_MI CP Sr ppm	4A_MI CP Te ppm	4A_MI CP Th ppm	4A_MI CP U ppm	4A_MI CP Y ppm
0.40	13.00	0.10	2.49	6.90	0.05	0.40	6.30	0.70	0.19	0.21	0.30
0.39	14.00	0.10	2.51	6.80	0.06	0.40	6.30	0.60	0.19	0.21	0.30
0.40	14.00	0.10	2.59	6.90	0.06	0.30	6.50	0.70	0.19	0.21	0.30
0.40	13.00	0.10	2.57	6.80	0.05	0.40	6.30	0.70	0.20	0.25	0.30
0.39	14.00	0.11	2.72	6.90	0.05	0.40	6.50	0.70	0.20	0.25	0.30
0.39	14.00	0.10	2.71	7.00	0.06	0.40	6.40	0.70	0.20	0.20	0.30
0.40	14.00	0.10	2.48	6.90	0.06	0.40	6.40	0.70	0.20	0.25	0.30
0.39	14.00	0.10	2.57	7.00	0.05	0.50	6.50	0.70	0.20	0.18	0.30
0.40	14.70	0.08	2.30	5.10	0.05	0.40	6.00	0.62	0.12	0.23	0.30
0.40	15.80	0.08	2.30	4.80	0.05	0.30	6.50	0.63	0.11	0.24	0.30
0.40	14.00	0.08	2.10	5.60	0.05	0.40	6.00	0.66	0.10	0.22	0.30
0.40	13.50	0.08	2.40	5.20	0.05	0.40	6.30	0.63	0.12	0.22	0.30
0.40	15.80	0.08	2.50	4.90	0.05	0.40	6.00	0.68	0.11	0.22	0.30
0.30	14.80	0.07	2.80	5.30	0.05	0.40	6.10	0.62	0.12	0.24	0.40
0.40	13.50	0.09	2.50	4.70	0.06	0.40	4.90	0.65	0.13	0.24	0.40
0.40	11.00	0.08	2.30	7.00	0.05	0.50	5.00	0.49	0.10	0.21	0.40
0.25	13.00	0.06	2.20	7.00	0.04	0.50	4.80	0.70	0.10	0.20	0.40
0.25	13.00	0.06	2.60	7.00	0.06	0.50	4.90	0.40	0.20	0.20	0.30
0.25	12.00	0.06	2.20	7.00	0.05	0.50	5.20	0.60	0.10	0.20	0.30
0.25	13.00	0.06	2.60	7.00	0.06	0.40	5.10	0.70	0.10	0.20	0.30
0.25	13.00	0.08	2.40	7.00	0.06	0.40	4.90	0.30	0.10	0.20	0.30
0.30	12.00	0.08	2.40	7.00	0.06	0.40	4.90	0.40	0.10	0.20	0.30
0.35	12.00	0.08	2.20	7.00			4.70	0.40	0.10	0.20	0.30
0.30	11.00	0.06	2.20	9.00			4.50	0.80	0.10	0.20	0.30
0.30	10.00	0.08	3.14	8.00			5.00	0.40	0.12	0.20	0.30
0.30	11.00	0.09	3.13	8.00			4.50	0.40	0.13	0.20	0.30
0.30	11.00	0.09	3.07	8.00			4.50	0.40	0.16	0.30	0.30
0.40	10.00	0.08	3.03	8.00			4.50	0.40	0.11	0.20	0.30
0.30	10.00	0.09	3.14	8.00			5.00	0.40	0.12	0.30	0.30
0.30	10.00	0.09	3.00	9.00			4.50	0.40	0.12	0.20	0.37
0.30	14.18	0.09	3.07	8.00			4.50	0.40	0.11	0.20	0.39
	14.86	0.08	2.75	9.11			4.71	0.40	0.11	0.20	0.36
	14.01		2.78	8.88			4.98	0.69			0.37
	14.55		2.93	9.12			4.41	0.52			0.37
	14.79		2.47	8.51			4.67	0.62			0.38
	14.56		2.23	8.90			4.86	0.49			0.37
	14.70		2.43	8.81			4.72	0.48			0.38
	14.75		2.32	9.05			4.93	0.58			0.30
	12.10		2.61	8.95			4.58	0.49			0.30
	12.60			8.80			5.00				0.30
	13.40			9.30			5.10				0.30
	12.20			7.70			5.00				0.30
	12.30			9.00			4.90				0.30
	12.70			8.70			4.80				0.30
	11.70			8.80			5.00				0.30
	11.50			8.90			4.90				
				8.90			5.00				

## 20. Reported Values

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

## 21. Validation of Accuracy (Trueness)

This CRM can be used to validate accuracy (trueness) as required in method validation as stated in the ISO17025:2005 standard, clause 5.4. See Appendix 3 for an example on the validation of accuracy using replicate data derived from the analysis of a CRM.

## **22. 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 6 for an example of the calculation LOD and LOQ and Table 11 for a recommend reporting scheme for LOD and LOQ values).

## **23. Metrological Traceability**

The values quoted here 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 ISO17025:2005 general requirements for the competence of testing and calibration laboratories and who have maintained measurement traceability during the analytical process.

## **24. 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.

## **25. 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.

## **26. 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.

## **27. 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 4 for detail on the use of this CRM in quality control).

## **28. 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, Thivhafuni Matodzi, and Allan Fraser; accept no liability for any decisions or actions taken following the use of the reference material.

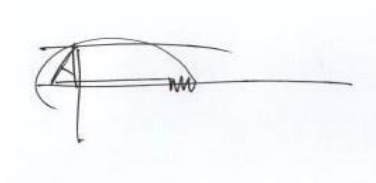
22 May 2018

Revision:000

Certifying Officers:

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

**Thivhafuni Matodzi**



Geochemist: \_\_\_\_\_

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## APPENDICES

### Appendix 1: Uncertified Element Statistics

Uncertified element statistics are shown in Table 7.

**Table 7.** Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	s	% RSD	Unit
Ag	2A_MICP	8	3.325	0.071	2.127	ppm
Al	4A_MICP	38	70666.711	12557.632	17.770	ppm
Al	FUS	8	76978.819	1899.796	2.468	ppm
Al <sub>2</sub> O <sub>3</sub>	FUS	16	10.961	1.702	15.530	%
As	4A_MICP	32	8.316	3.573	42.969	ppm
Ars	FUS	8	76978.819	1899.796	2.468	ppm
Ba	2A_MICP	8	28.750	0.707	2.460	ppm
Ba	4A_ICPES	7	32.000	<0.001	<0.001	ppm
Ba	FUS	8	33.228	2.378	7.157	ppm
BaO	XRF	3	0.010	<0.001	<0.001	%
Be	4A_MICP	9	0.114	0.027	23.164	ppm
Ca	4A_MICP	39	1325.771	178.876	13.492	ppm
Ca	FUS	6	1288.806	257.616	19.989	ppm
CaO	FUS	15	0.339	0.137	40.422	%
CaO	XRF	56	0.215	0.039	18.116	%
Ce	4A_MICP	32	0.807	0.148	18.389	ppm
Co	2A_MICP	8	16.000	<0.001	<0.001	ppm
Co	4A_ICPES	8	244.375	2.875	1.177	ppm
Co	FUS	8	266.212	7.566	2.842	ppm
CoO	XRF	8	0.040	0.001	3.401	%
Cr	4A_MICP	16	174909.529	123308.715	70.499	ppm
Cr	FUS	8	225546.039	4858.908	2.154	ppm
Cr <sub>2</sub> O <sub>3</sub>	FUS	16	45.534	1.054	2.315	%
Cr <sub>2</sub> O <sub>3</sub>	Titration	7	44.330	0.165	0.373	%
Cs	4A_MICP	13	0.082	0.024	29.977	ppm
Cu	2A_MICP	8	112.500	1.512	1.344	ppm
Cu	4A_ICPES	8	115.750	0.886	0.766	ppm
Cu	FUS	7	72.588	2.329	3.209	ppm
CuO	XRF	8	0.020	<0.001	<0.001	%
Er	4A_MICP	15	0.035	0.005	14.615	ppm
Eu	4A_MICP	9	0.024	0.005	21.561	ppm
Fe	4A_MICP	38	184137.858	37021.608	20.105	ppm
Fe	FUS	8	186537.424	4928.665	2.642	ppm
Fe <sub>2</sub> O <sub>3</sub>	FUS	8	27.254	0.062	0.229	%
FeO	FUS	8	1.799	0.162	9.025	%
FeO	XRF	8	1.799	0.162	9.025	%
Ga	4A_MICP	40	50.435	8.703	17.255	ppm
Ge	4A_MICP	32	0.282	0.228	80.919	ppm
Ho	4A_MICP	15	0.010	<0.001	<0.001	ppm
In	4A_MICP	7	0.022	0.003	11.643	ppm
K	4A_MICP	27	114.556	25.683	22.420	ppm
K <sub>2</sub> O	XRF	43	0.022	0.014	65.869	%
Lu	4A_MICP	14	0.007	0.003	37.400	ppm
Mg	4A_MICP	40	40449.394	21512.059	53.183	ppm
Mg	FUS	8	53621.182	1197.965	2.234	ppm
MgO	FUS	16	12.326	2.603	21.115	%
Mn	4A_MICP	40	1619.725	222.527	13.739	ppm
Mn	FUS	8	1821.608	42.611	2.339	ppm
MnO	FUS	16	0.536	0.242	45.041	%

Table 7 cont:

Element	Generic Method	n	Mean	s	% RSD	Unit
Na	4A_MICP	48	270.970	78.704	29.045	ppm
Na <sub>2</sub> O	XRF	24	0.490	0.621	126.627	%
Nb	4A_MICP	23	0.365	0.214	58.731	ppm
Nb	FUS	8	16.784	1.950	11.616	ppm
Ni	4A_MICP	53	933.030	161.446	17.303	ppm
Ni	FUS	8	1070.279	31.426	2.936	ppm
Ni	XRF	8	1310.125	44.315	3.383	ppm
NiO	XRF	8	0.126	0.005	4.099	%
P	4A_MICP	6	43.333	16.330	37.684	ppm
P <sub>2</sub> O <sub>5</sub>	XRF	16	0.009	0.006	62.328	%
Pb	2A_MICP	8	13.750	0.886	6.447	ppm
Rb	4A_MICP	37	1.354	1.450	107.059	ppm
Re	4A_MICP	3	0.002	<0.001	<0.001	ppm
S	4A_MICP	29	0.056	0.012	21.474	%
S	Combustion/LECO	48	0.047	0.006	13.725	%
Sc	4A_ICPES	8	7.000	<0.001	<0.001	ppm
Sc	FUS	8	5.568	0.350	6.291	ppm
Se	4A_MICP	24	21.167	17.795	84.071	ppm
Si <sub>2</sub> O <sub>3</sub>	XRF	8	1.805	0.268	14.824	%
SiO <sub>2</sub>	FUS	16	14.324	13.533	94.476	%
SiO <sub>2</sub>	XRF	56	1.709	0.169	9.873	%
SO <sub>3</sub>	XRF	22	0.123	0.019	15.325	%
Sr	2A_MICP	8	4.000	<0.001	<0.001	ppm
Sr	4A_ICPES	7	6.000	<0.001	<0.001	ppm
Sr	FUS	8	14.167	2.429	17.146	ppm
Ta	4A_MICP	23	0.088	0.096	108.333	ppm
Ta	FUS	8	77.870	3.036	3.899	ppm
Tb	4A_MICP	16	0.010	<0.001	<0.001	ppm
Ti	4A_MICP	38	0.385	0.070	18.131	%
Ti	FUS	8	0.429	0.011	2.652	%
TiO	FUS	8	0.231	0.005	2.238	%
TiO	XRF	8	0.231	0.005	2.238	%
TiO <sub>2</sub>	FUS	8	0.764	0.019	2.517	%
Tl	4A_MICP	9	0.029	0.003	11.538	ppm
Tm	4A_MICP	15	0.008	0.002	28.694	ppm
V	4A_ICPES	8	1545.000	27.749	1.796	ppm
V	4A_MICP	46	1744.597	402.681	23.082	ppm
V	FUS	8	2032.656	56.982	2.803	ppm
V <sub>2</sub> O <sub>5</sub>	FUS	7	0.402	0.002	0.376	%
V <sub>2</sub> O <sub>5</sub>	XRF	30	0.425	0.042	9.955	%
W	4A_MICP	29	1.401	2.093	149.399	ppm
Yb	4A_MICP	16	0.045	0.012	26.912	ppm
Zn	4A_ICPES	8	566.000	3.117	0.551	ppm
Zn	4A_MICP	45	621.284	123.618	19.897	ppm
Zn	FUS	8	783.478	21.010	2.682	ppm
Zn	XRF	8	822.375	17.872	2.173	ppm
ZnO	XRF	8	0.050	0.005	9.442	%
Zr	4A_MICP	36	3.696	1.317	35.636	ppm

## Appendix 2. Certification of Reference Material and Estimation of Measurement Uncertainty (Prepared by Allan Fraser)

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 application of z-scoring, Cochran test for suspect repeatability variances, along with Grubbs test as single and paired tests 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 typically 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.

### Outlier Removal

An initial purge of outliers in inter-laboratory analyses of a candidate reference material is done using z-scoring followed by the exclusion of further outliers as defined by the IUPAC Harmonised Protocol of 1995. Here both Cochran and Grubbs tests are applied until all outliers are identified.

### 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 of 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 2 are discarded and are not included for further assessment.

### Cochran 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. 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 of 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 17, an 'appropriate precision' as shown in [8] is calculated for sufficient homogeneity (Thompson, 2008):

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

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

### Total Variation (SST)

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

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

### Between Group Variation (SSB)

The *variation* due to the interaction 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 8 is developed.

**Table 8.** 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 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 7, 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  
(Prepared by Allan Fraser)

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 9. 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 9.** 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 Uncertainty ( $U$ )	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 7, page 27) 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.

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#### Appendix 4. Using the CRM in Quality Control (Prepared by Allan Fraser)

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 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 [19], of the replicates;
5. Calculate the standard deviation,  $s$  from:

$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n - 1}} \quad [19]$$

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 [19].
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 warning the limits analyse another sample and if it 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].

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**Appendix 5. 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:

$$\text{Moisture correction factor (MCF)} = \frac{100 - \% \text{Moisture at } 105^{\circ}C}{100} \quad [20]$$

$$\text{Air dry basis concentration} = \text{MCF} \times \text{certified value on a dry basis} \quad [21]$$

**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 [20] 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 [21]) 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 [20] and [21], e.g. 0.995 x 0.52 = 0.51<sub>(7)</sub>, 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 6. Example of Determination of LOD and LOQ in Fire Assay**  
Prepared by Allan Fraser

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<sub>assay</sub>* 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. Assuming that 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 [22]. Therefore, the LOD in fire assay is computed as:

$$LOD = \frac{m (\mu g)}{Mass_{assay} (g)} (g/t) \quad [22]$$

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

$$LOQ = 10 \cdot \frac{m (\mu g)}{Mass_{assay} (g)} (g/t) \quad [23]$$

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 to be weighed, then the LOD result would be <0.02 g/t or “not detected”. Table 11 gives a recommended reporting scheme for LOD and LOQ.

**Table 10.** 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 11.** Recommended reporting scheme for LOD and LOQ in fire assay.

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

**Appendix 7. T-distribution table**

Table 12. 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		