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Certificate

# AMIS0857

## Certified Reference Material

### Copperbelt, Sulphide, Zambia

## *Certificate of Analysis*

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## Table of Contents

Table of Contents .....	2
List of Tables .....	3
List of Appendices .....	3
Summary Statistics .....	4
1. Certified Concentrations and Uncertainties .....	6
2. Uncertified element statistics .....	8
3. Statistical Comparison of Means .....	10
4. Intended Use .....	11
5. Abbreviations and Symbols .....	11
6. Uncertified Concentration Values .....	12
7. Units .....	12
8. Analytical and Physical Methods .....	12
9. Origin of Material .....	12
10. Approximate Mineral and Chemical Composition .....	13
11. Quantitative Analysis by X-Ray Diffraction .....	13
12. Health and Safety .....	14
13. Method of Preparation .....	14
14. Particle Size Determination .....	14
15. Handling .....	15
16. Storage information .....	15
17. Methods of Analysis Requested .....	15
18. Information Requested of Participating Laboratories .....	15
19. Certification of Mean and Estimation of Measurement Uncertainty .....	16
20. Two Standard Deviations .....	16
21. Confidence Interval .....	16
22. Expanded Uncertainty .....	16
23. Confidence Interval and Expanded Uncertainty .....	17
24. Participating Laboratories .....	17
25. Accepted Assay Data .....	18
26. Reported Values .....	24
27. Validation of Accuracy (Trueness) .....	24
28. Metrological Traceability .....	24
29. Period of Validity .....	24
30. Minimum Sample Size .....	24
31. Availability .....	24
32. Recommended use in Quality Control .....	24
33. Legal Notice .....	25
References .....	26
Appendices .....	27
End of certificate .....	35

## List of Tables

<b>Table 1.</b> Certified concentrations, two standard deviations, combined and expanded uncertainty. ....	6
<b>Table 2.</b> Certified major oxides concentrations, two standard deviations, combined and expanded uncertainty.....	7
<b>Table 3.</b> Uncertified element concentrations statistics (Before the removal of outliers). ....	8
<b>Table 4.</b> The results of a two-sample equal or unequal variance t-test (two-tailed) data sets in which different analytical methods /instrumentation were used.....	10
<b>Table 5.</b> Comparison of the mean values in which three different analytical methods are used to determine their concentration. ....	10
<b>Table 6.</b> Abbreviations, symbols, and descriptions. ....	11
<b>Table 7.</b> Results of XRD analysis. ....	14
<b>Table 8.</b> Particle Size Determination by laser diffraction. ....	15
<b>Table 9.</b> Example of replicate assay data in which the <i>CI</i> , <i>2s</i> and <i>U</i> are shown.....	17
<b>Table 10.</b> Data used to calculate the certified values after removal of outliers. ....	18
<b>Table 11.</b> A single-factor ANOVA table showing key elements. Where <i>P</i> is the total number of groups, or laboratories. <i>P</i> -1 is 1 less than number of laboratories, <i>P</i> ( <i>n</i> -1) is the number of data values minus number of groups (equals degrees of freedom for each group added together), and <i>P</i> -1 + <i>P</i> ( <i>n</i> -1) is 1 less than the number of data points. <i>MS</i> is the mean squares of between laboratories and within laboratories. After Ellison <i>et al.</i> , (2009), Table 6.2, page 61.....	30
<b>Table 12.</b> CRM certified value, quoted expanded uncertainty <i>U</i> , the coverage factor for the CRM, <i>k</i> =2.25 and mean for <i>n</i> =9 replicates and corresponding standard deviation for the replicate data. ....	31
<b>Table 13.</b> 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. ....	34
<b>Table 14.</b> Recommended reporting scheme for LOD and LOQ in fire assay.....	34
<b>Table 15.</b> T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence. ....	35

## List of Appendices

<b>Appendix 1.</b> Certification of Reference Material and Estimation of Measurement Uncertainty.....	27
<b>Appendix 2.</b> Example: Comparison of Mean and Certified Value for Validation of Accuracy .....	31
<b>Appendix 3.</b> Two-standard Deviations .....	32
<b>Appendix 4.</b> Confidence Interval.....	32
<b>Appendix 5.</b> Using the CRM in Quality Control.....	32
<b>Appendix 6.</b> Conversion to Air-dry Basis .....	33
<b>Appendix 7.</b> Example of Determination of LOD and LOQ in Fire Assay .....	34
<b>Appendix 8.</b> T-distribution table .....	35

## Summary Statistics

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

Analyte	Method	<sup>7</sup> ( $\mu$ )	<sup>9</sup> (2s) $\pm$	Unit
Cu	<sup>1</sup> 2A_MICP	9537	411	ppm
Cu	<sup>2</sup> 4A_MICP	9567	526	ppm
Cu	<sup>3</sup> FUS	9822	812	ppm
Co	2A_MICP	480	66	ppm
Co	4A_MICP	503	52	ppm
Co	FUS	458	110	ppm
C	<sup>4</sup> Combustion/LECO	3.22	0.33	%
S	Combustion/LECO	2.79	0.16	%
SG	<sup>5</sup> SG	2.80	0.054	Dimensionless
Al	4A_MICP	5.28	0.35	%
Al	FUS	5.30	0.12	%
As	2A_MICP	19	2	ppm
Ba	4A_MICP	1239	92	ppm
Be	4A_MICP	2	0.1	ppm
Bi	2A_MICP	8	2	ppm
Bi	4A_MICP	8	1	ppm
Ca	2A_MICP	5.84	0.40	%
Ca	4A_MICP	6.18	0.33	%
Cr	4A_MICP	79	16	ppm
Fe	2A_MICP	2.96	0.33	%
Fe	4A_MICP	3.06	0.23	%
Fe	FUS	3.02	0.10	%
K	2A_MICP	1.34	0.11	%
K	FUS	4.66	0.12	%
Li	4A_MICP	65	3	ppm
Mn	2A_MICP	1374	52	ppm
Mn	4A_MICP	1524	136	ppm
Mn	FUS	1563	61	ppm
Mo	2A_MICP	8	0.8	ppm
Mo	4A_MICP	9	2	ppm
Na	2A_MICP	210	13	ppm
Ni	2A_MICP	53	6	ppm
Ni	4A_MICP	59	11	ppm
P	2A_MICP	719	123	ppm
P	4A_MICP	661	67	ppm
Pb	2A_MICP	7	2	ppm
Pb	4A_MICP	9	4	ppm
Si	FUS	23.34	1.2	%
Sr	2A_MICP	124	14	ppm
Sr	4A_MICP	160	17	ppm
Ti	4A_MICP	2328	177	ppm
Ti	FUS	2943	104	ppm
V	2A_MICP	35	10	ppm
V	4A_MICP	77	5	ppm
Y	4A_MICP	15	0.9	ppm
Zn	2A_MICP	67	19	ppm
Zn	4A_MICP	63	5	ppm
Zr	4A_MICP	78	5	ppm

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

Analyte	Method	<sup>7</sup> ( $\mu$ )	<sup>9</sup> (2s) $\pm$	Unit
CuO	<sup>6</sup> XRF	1.19	0.025	%
Al <sub>2</sub> O <sub>3</sub>	XRF	9.88	0.75	%
BaO	XRF	0.14	0.02	%
CaO	XRF	8.70	0.33	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	4.28	0.25	%
K <sub>2</sub> O	XRF	5.41	0.58	%
MgO	XRF	6.14	0.22	%
MnO	XRF	0.20	0.02	%
P <sub>2</sub> O <sub>5</sub>	XRF	0.14	0.03	%
TiO <sub>2</sub>	XRF	0.48	0.03	%

**Uncertified Concentrations (at two Standard Deviation) on Table 3**

Analyte	Method	(Mean)	$\pm$ (2s)	Unit
Cu	<sup>14</sup> AS	37.1	#86.0	ppm
Cu	SAL	277.5	33.4	ppm

## 1. Certified Concentrations and Uncertainties

AMIS0857 is a new standard material, developed and certified in November 2022. 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	<sup>7</sup> ( $\mu$ )	<i>N</i>	<i>n</i>	<i>k</i>	% RSD	<sup>8</sup> ( $u_c$ )	<sup>9</sup> (2s) $\pm$	<sup>10</sup> (CI) 95%	<sup>11</sup> (U) $\pm$	Unit
Cu	<sup>1</sup> 2A_MICP	9537	7	56	2.447	2	205	411	180	503	ppm
Cu	<sup>2</sup> 4A_MICP	9567	7	56	2.447	3	263	526	233	644	ppm
Cu	<sup>3</sup> FUS	9822	4	30	3.182	4	406	812	670	1292	ppm
Co	2A_MICP	480	6	48	2.571	7	33	66	34	85	ppm
Co	4A_MICP	503	6	48	2.571	5	26	52	27	66	ppm
Co	FUS	458	3	22	4.303	12	55	110	144	237	ppm
C	<sup>4</sup> Combustion/LECO	3.22	5	40	2.776	5	0.16	0.33	0.20	0.5	%
S	Combustion/LECO	2.79	5	40	2.776	3	0.080	0.16	0.092	0.2	%
SG	<sup>5</sup> SG	2.80	3	23	4.303	1	0.027	0.054	0.061	0.1	Dimensionless
Al	4A_MICP	5.28	6	47	2.571	3	0.17	0.35	0.18	0.4	%
Al	FUS	5.30	2	14	12.706	1	0.059	0.12	0.11	0.8	%
As	2A_MICP	19	3	24	4.303	5	0.9	2	1	4	ppm
Ba	4A_MICP	1239	5	40	2.776	4	46	92	54	127	ppm
Be	4A_MICP	2	3	23	4.303	3	0.06	0.1	0.1	0.3	ppm
Bi	2A_MICP	8	3	24	4.303	11	0.9	2	2	4	ppm
Bi	4A_MICP	8	3	22	4.303	7	0.6	1	0.2	2	ppm
Ca	2A_MICP	5.84	6	44	2.571	3	0.20	0.40	0.21	0.5	%
Ca	4A_MICP	6.18	6	47	2.571	3	0.17	0.33	0.17	0.4	%
Cr	4A_MICP	79	3	24	4.303	10	8	16	20	34	ppm
Fe	2A_MICP	2.96	5	36	2.776	6	0.17	0.33	0.25	0.5	%
Fe	4A_MICP	3.06	6	47	2.571	4	0.11	0.23	0.12	0.3	%
Fe	FUS	3.02	4	32	3.182	2	0.048	0.10	0.054	0.2	%
K	2A_MICP	1.34	4	32	3.182	4	0.054	0.11	0.076	0.2	%
K	FUS	4.66	2	16	12.706	1	0.058	0.12	0.41	0.7	%
Li	4A_MICP	65	3	23	4.303	2	2	3	2	7	ppm
Mn	2A_MICP	1374	3	22	4.303	2	26	52	62	112	ppm
Mn	4A_MICP	1524	6	48	2.571	4	68	136	70	174	ppm
Mn	FUS	1563	4	30	3.182	2	30	61	45	97	ppm
Mo	2A_MICP	8	4	29	3.182	5	0.4	0.8	0.5	1	ppm
Mo	4A_MICP	9	5	39	2.776	9	0.9	2	0.9	2	ppm
Na	2A_MICP	210	2	16	12.706	3	7	13	54	85	ppm
Ni	2A_MICP	53	5	40	2.776	5	3	6	3	8	ppm
Ni	4A_MICP	59	7	55	2.447	9	5	11	5	13	ppm
P	2A_MICP	719	4	31	3.182	9	61	123	96	195	ppm
P	4A_MICP	661	4	32	3.182	5	33	67	52	106	ppm
Pb	2A_MICP	7	3	24	4.303	16	1	2	2	5	ppm
Pb	4A_MICP	9	5	38	2.776	22	2	4	2	6	ppm
Si	FUS	23.34	2	16	12.706	3	0.62	1.2	2.7	8	%
Sr	2A_MICP	124	3	24	4.303	6	7	14	16	30	ppm
Sr	4A_MICP	160	5	39	2.776	5	8	17	10	23	ppm
Ti	4A_MICP	2328	5	40	2.776	4	89	177	102	246	ppm
Ti	FUS	2943	2	16	12.706	2	52	104	381	663	ppm
V	2A_MICP	35	4	32	3.182	14	5	10	8	16	ppm
V	4A_MICP	77	6	46	2.571	3	2	5	2	6	ppm
Y	4A_MICP	15	2	16	12.706	3	0.4	0.9	4	6	ppm
Zn	2A_MICP	67	6	48	2.571	14	9	19	10	24	ppm
Zn	4A_MICP	63	6	46	2.571	4	2	5	2	6	ppm
Zr	4A_MICP	78	4	32	3.182	3	3	5	3	8	ppm

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

Analyte	Method	<sup>7</sup> ( $\mu$ )	N	n	k	% RSD	<sup>8</sup> ( $u_c$ )	<sup>9</sup> (2s) $\pm$	<sup>10</sup> (CI) 95%	<sup>11</sup> (U) $\pm$	Unit
CuO	<sup>6</sup> XRF	1.19	2	16	12.706	1	0.013	0.025	0.10	0.2	%
Al <sub>2</sub> O <sub>3</sub>	XRF	9.88	4	32	3.182	4	0.37	0.75	0.59	1	%
BaO	XRF	0.14	3	23	4.303	5	0.008	0.02	0.02	0.03	%
CaO	XRF	8.70	4	30	3.182	2	0.17	0.33	0.28	0.5	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	4.28	5	40	2.776	3	0.12	0.25	0.15	0.3	%
K <sub>2</sub> O	XRF	5.41	5	40	2.776	5	0.29	0.58	0.36	0.8	%
MgO	XRF	6.14	4	32	3.182	2	0.11	0.22	0.17	0.3	%
MnO	XRF	0.20	2	16	12.706	5	0.01	0.02	0.09	0.1	%
P <sub>2</sub> O <sub>5</sub>	XRF	0.14	4	32	3.182	10	0.01	0.03	0.02	0.05	%
TiO <sub>2</sub>	XRF	0.48	5	39	2.776	4	0.02	0.03	0.02	0.05	%

1. 2A\_MICP is a Two-acid digestion with either ICPOES/ICPMS/AAS finish
2. 4A\_MICP is a Four-acid digestion with either ICPOES/ICPMS/AAS finish
3. FUS is Fusion digestion with either ICPOES/ICPMS/AAS finish
4. Combustion/LECO
5. SG is Specific Gravity
6. XRF is X-ray Fluorescence
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. Uncertified element statistics

Uncertified element statistics are shown in Table 3.

**Table 3.** Uncertified element concentrations statistics (Before the removal of outliers).

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	2A_MICP	8	0.7	0.05	8	ppm
Ag	4A_MICP	8	0.5	0.02	4	ppm
Al	2A_MICP	40	22747.9	15196.6	67	ppm
Al <sub>2</sub> O <sub>3</sub>	FUS	8	10.4	0.05	0.5	%
As	4A_MICP	16	18.7	1.3	7	ppm
As	FUS	1	21.0	*	*	ppm
B	FUS	8	83.0	2.5	3	ppm
Ba	2A_MICP	16	111.9	48.7	44	ppm
Ba	FUS	16	1235.5	15.3	1	ppm
Be	2A_MICP	8	0.8	0.05	6	ppm
Be	FUS	8	2.0	*	*	ppm
Bi	FUS	8	8.0	0.1	2	ppm
Bi <sub>2</sub> O <sub>3</sub>	XRF	4	0.001	<0.0001	2	%
Ca	FUS	23	60421.3	9520.6	16	ppm
CaO	2A_MICP	8	8.4	0.07	0.9	%
CaO	FUS	8	9.8	0.1	1	%
Cd	4A_MICP	8	0.1	0.02	13	ppm
Cd	FUS	1	11.0	*	*	ppm
Ce	2A_MICP	8	24.5	0.5	2	ppm
Ce	4A_MICP	8	55.1	0.8	2	ppm
CeO <sub>2</sub>	XRF	2	0.007	0.006	98	%
Cl	XRF	5	100.2	30.5	30	ppm
Co	<sup>12</sup> 3A_ICPES	8	429.6	7.5	2	ppm
Co	<sup>13</sup> SAL	8	27.6	4.1	15	ppm
CoO	XRF	16	0.07	0.01	14	%
Cr	2A_MICP	24	46.4	13.7	30	ppm
Cr	FUS	8	94.8	8.7	9	ppm
Cr <sub>2</sub> O <sub>3</sub>	XRF	24	0.01	0.007	49	%
Cs	4A_MICP	8	2.3	0.05	2	ppm
Cs	FUS	8	2.2	0.08	4	ppm

Element	Generic Method	n	Mean	SD	RSD %	Unit
Cu	<sup>14</sup> AS	16	37.1	#43.0	116	ppm
Cu	SAL	8	277.5	16.7	6	ppm
CuO	SAL	8	0.03	0.008	24	%
F	XRF	2	128.4	27.6	21	ppm
Fe <sub>2</sub> O <sub>3</sub>	2A_MICP	8	4.2	0.05	1	%
Ga	4A_MICP	8	13.1	0.08	0.6	ppm
Ga	FUS	8	12.4	0.5	4	ppm
Ga <sub>2</sub> O <sub>3</sub>	XRF	8	0.001	0.0003	24	%
Gd <sub>2</sub> O <sub>3</sub>	XRF	3	0.001	<0.0001	2	%
Ge	4A_MICP	8	1.2	0.06	5	ppm
Ge	FUS	8	1.9	0.4	19	ppm
Hf	4A_MICP	8	2.3	0.07	3	ppm
Hg	2A_MICP	1	6.0	*	*	ppm
In	4A_MICP	8	1.1	0.02	2	ppm
In	FUS	8	1.1	0.05	5	ppm
K	4A_MICP	32	43475.2	3330.2	8	ppm
La	2A_MICP	8	12.9	0.3	2	ppm
La	4A_MICP	16	29.2	1.1	4	ppm
La <sub>2</sub> O <sub>3</sub>	XRF	5	0.005	0.003	53	%
Li	2A_MICP	8	30.9	1.0	3	ppm
Li	FUS	8	62.3	0.9	1	ppm
LOI	<sup>15</sup> LOI	24	11.1	2.0	18	%
LOI	XRF	8	8.3	0.05	0.7	%
Mg	2A_MICP	32	30307.9	5047.6	17	ppm
Mg	4A_MICP	56	35399.9	3431.8	10	ppm
Mg	FUS	24	33358.2	6619.7	20	ppm
MgO	2A_MICP	8	6.4	0.08	1	%
MgO	FUS	8	7.0	0.03	0.5	%
Mn <sub>3</sub> O <sub>4</sub>	XRF	8	0.2	0.02	9	%
MnO	2A_MICP	8	0.2	0.001	0.6	%

\* denotes that the results were exactly the same and SD and RSD% could not be calculated

# denotes that SD>Mean



**Table 3 (Continued)**

Element	Generic Method	n	Mean	SD	RSD %	Unit
Mo	FUS	8	10.4	3.5	34	ppm
Moisture	<sup>16</sup> Moisture	29	0.1	0.05	34	%
MoO <sub>3</sub>	XRF	5	0.0009	0.0008	80	%
Na	4A_MICP	48	3446.5	281.5	8	ppm
Na <sub>2</sub> O	XRF	40	0.4	0.06	15	%
Nb	4A_MICP	8	10.1	0.2	2	ppm
Nb <sub>2</sub> O <sub>5</sub>	XRF	4	0.01	0.01	112	%
Nd <sub>2</sub> O <sub>3</sub>	XRF	5	0.004	0.003	82	%
Ni	FUS	8	63.5	4.4	7	ppm
NiO	XRF	16	0.01	0.007	52	%
P	FUS	8	700.0	*	*	ppm
PbO	XRF	8	0.003	0.0008	29	%
Pr <sub>6</sub> O <sub>11</sub>	XRF	3	0.001	0.0006	43	%
Rb	4A_MICP	8	127.9	0.9	0.7	ppm
Rb	FUS	8	121.0	1.4	1	ppm
Rb <sub>2</sub> O	XRF	8	0.01	0.0003	2	%
Re	4A_MICP	8	0.02	0.004	18	ppm
S	2A_MICP	32	2.8	0.2	9	%
S	4A_MICP	24	2.7	0.2	6	%
S	FUS	24	3.2	1.6	51	%
Sb	2A_MICP	3	4.7	4.6	99	ppm
Sb	4A_MICP	8	0.5	0.04	7	ppm
Sb	FUS	6	0.6	0.05	10	ppm
Sb <sub>2</sub> O <sub>3</sub>	XRF	6	0.006	0.003	48	%
Sc	2A_MICP	16	3.1	0.09	3	ppm
Sc	4A_MICP	16	8.7	0.2	2	ppm
Se	4A_MICP	8	1.7	0.3	15	ppm
Si	2A_MICP	8	290573.9	9699.7	3	ppm
SiO <sub>2</sub>	FUS	8	53.5	0.3	0.5	%
SiO <sub>2</sub>	XRF	40	49.2	2.1	4	%

Element	Generic Method	n	Mean	SD	RSD %	Unit
Sm <sub>2</sub> O <sub>3</sub>	XRF	5	0.004	0.002	39	%
Sn	4A_MICP	8	2.4	0.05	2	ppm
SnO <sub>2</sub>	XRF	3	0.01	0.01	80	%
SO <sub>3</sub>	XRF	16	6.7	0.1	2	%
Sr	FUS	16	153.3	1.9	1	ppm
SrO	XRF	15	0.02	0.004	17	%
Ta	4A_MICP	8	1.1	0.03	2	ppm
Ta	FUS	8	1.5	0.3	19	ppm
Ta <sub>2</sub> O <sub>5</sub>	XRF	4	0.001	<0.0001	1	%
Te	4A_MICP	8	0.4	0.05	12	ppm
Th	4A_MICP	8	11.0	0.3	2	ppm
Th	FUS	8	12.0	0.2	2	ppm
ThO <sub>2</sub>	XRF	8	0.001	0.0005	38	%
Ti	2A_MICP	40	4520.7	#7177.1	159	ppm
Tl	4A_MICP	8	0.4	0.005	1	ppm
U	4A_MICP	8	6.3	0.3	4	ppm
U	FUS	8	6.6	0.4	7	ppm
U <sub>3</sub> O <sub>8</sub>	XRF	6	0.001	<0.0001	1	%
V	FUS	8	80.9	1.2	2	ppm
V <sub>2</sub> O <sub>5</sub>	XRF	16	0.03	0.02	58	%
W	4A_MICP	8	2.2	0.05	2	ppm
W	FUS	8	2.4	0.5	22	ppm
WO <sub>3</sub>	XRF	8	0.03	0.005	14	%
Y	2A_MICP	8	10.0	*	*	ppm
Y	FUS	8	19.0	0.1	0.7	ppm
Y <sub>2</sub> O <sub>3</sub>	XRF	8	0.004	0.0005	11	%
Zn	FUS	14	65.7	8.4	13	ppm
ZnO	XRF	16	0.01	0.009	63	%
Zr	2A_MICP	8	3.6	0.2	5	ppm
ZrO <sub>2</sub>	XRF	11	0.02	0.01	65	%

\* denotes that the results were exactly the same and SD and RSD% could not be calculated

# denotes that SD>Mean

- 12. 3A\_ICPES is a Three-acid digestion with ICPOES finish
- 13. SAL is Sulphuric Acid Leach
- 14. AS is Acid Soluble
- 15. LOI is Loss on Ignition
- 16. Moisture is residual moisture content

### 3. 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 4 and 5). This gives the analyst confidence in the certified values reported by different analytical methods on the same analyte.

**Table 4.** 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
Al 4A_MICP	5.28 %	Al FUS	5.30 %	Equal Variance ( $p=0.053$ )	0.874	Accept $H_0$ ; certified values are equal
K 4A_MICP	4.35 %	K FUS	4.66 %	Equal Variance ( $p=0.09$ )	0.328	Accept $H_0$ ; certified values are equal
Ti 4A_MICP	0.233 %	Ti FUS	0.294 %	Equal Variance ( $p=0.366$ )	0.001	Reject $H_0$ ; certified values are <i>not</i> equal
Bi 4A_MICP	0.001 %	Bi 2A_MICP	0.001 %	Unequal Variance ( $p=0.019$ )	0.295	Accept $H_0$ ; certified values are equal
Ca 4A_MICP	6.18 %	Ca 2A_MICP	5.84 %	Equal Variance ( $p=0.328$ )	0.008	Reject $H_0$ ; certified values are <i>not</i> equal
Mo 4A_MICP	0.001 %	Mo 2A_MICP	0.001 %	Equal Variance ( $p=0.095$ )	0.034	Reject $H_0$ ; certified values are <i>not</i> equal
P 4A_MICP	0.066 %	P 2A_MICP	0.072 %	Equal Variance ( $p=0.172$ )	0.138	Accept $H_0$ ; certified values are equal
Pb 4A_MICP	0.001 %	Pb 2A_MICP	0.001 %	Equal Variance ( $p=0.178$ )	0.124	Accept $H_0$ ; certified values are equal
Sr 4A_MICP	0.016 %	Sr 2A_MICP	0.012 %	Equal Variance ( $p=0.403$ )	0.001	Reject $H_0$ ; certified values are <i>not</i> equal
V 4A_MICP	0.008 %	V 2A_MICP	0.004 %	Equal Variance ( $p=0.062$ )	0.001	Reject $H_0$ ; certified values are <i>not</i> equal
Zn 4A_MICP	0.006 %	Zn 2A_MICP	0.007 %	Unequal Variance ( $p=0.003$ )	0.328	Accept $H_0$ ; certified values are equal
Ni 4A_MICP	0.006 %	Ni 2A_MICP	0.005 %	Equal Variance ( $p=0.109$ )	0.054	Accept $H_0$ ; certified values are equal

**Table 5.** Comparison of the mean values in which three different analytical methods are used to determine their concentration.

Method	Certified value	Method	Certified value	Method	Certified value	F-ANOVA $p$ -value	F ANOVA Outcome
Cu_2A MICP	0.954%	Cu_4A MICP	0.957%	Cu FUS	0.982%	0.251	Means are equal. Accept $H_0$
Co_2A MICP	0.048%	Co_4A MICP	0.050%	Co FUS	0.046%	0.223	Means are equal. Accept $H_0$
Fe_2A MICP	2.96%	Fe_4A MICP	3.06%	Fe FUS	3.02	0.527	Means are equal. Accept $H_0$
Mn_2A MICP	0.137%	Mn_4A MICP	0.152%	FUS Mn	0.156%	0.002	At least one mean is different. Reject $H_0$

## 4. Intended Use

AMIS0857 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 2). 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 5). 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.

## 5. Abbreviations and Symbols

Abbreviations and symbols used in this document are shown in Table 6.

**Table 6.** 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, <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
$p$	' $p$ -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

Abbreviation/Symbol	Description
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 $k=1$
$\mu m$	Micron, is an SI derived unit of length equaling $1 \times 10^{-6}$ of a meter

## 6. Uncertified Concentration Values

Table 3 gives uncertified concentrations for other elements present in the CRM.

## 7. Units

All results certified for major oxides are reported as oxides in percentages. All results certified for major elements analyses reported in percentages 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.

## 8. 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)

## 9. Origin of Material

The material for this CRM was sourced from the Mufulira mine, which is a sediment-hosted stratabound copper deposit in the Zambian Copperbelt. The mine site is located 10km south of the border of Democratic Republic of Congo.

## 10. Approximate Mineral and Chemical Composition

The Mufulira Mine is characterized by chalcopyrite mineralisation in Contact Shale and copper rich sections. Pyrite mineralisation increases at the expense of chalcopyrite in the upper part of the South Orebody Shale, and a zone of exclusively pyrite mineralisation occurs at the top. Bornite is typically absent from the ore formation, but minor occurrence appears on the fringes of the barren gaps, particularly in the contact shale. In order of importance, chalcopyrite, chalcocite and bornite are present in the mineralized footwall. Higher cobalt values are concentrated on either side of the geological footwall.

## 11. 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 recognized and accounted for. X-ray diffraction is effective in such a way that it allows the identification of different phases of compounds that are identical in chemistry, but have distinctly different 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.

### Sample preparation for X-Ray Diffraction

The material submitted was prepared for XRD analysis using a backloading preparation method. It was analysed with a PANalytical Aeris diffractometer with PIXcel detector and fixed slits with Fe filtered Co-K $\alpha$  radiation. The phases were identified using X'Pert Highscore plus software and PAN-ICSD and ICDD PDF4 2016 databases.

The relative phase amounts (weight %) were estimated using the Rietveld method.

### Comment

- Mineral names may not reflect the actual compositions of minerals identified, but rather the mineral group. Two mica polytypes may be present.
- Due to preferred orientation and crystallite size effects, results may not be as accurate as shown.
- Traces of additional phases may be present. Quantities below 0.5% may be unreliable.
- Amorphous phases, if present, were not taken into consideration during quantification.

**Table 7.** Results of XRD analysis.

<b>Mineral</b>	<b>Unit</b>	<b>Composite</b>
Quartz	wt%	34.6
Dolomite	wt%	8.4
Orthoclase	wt%	9.1
Chalcopyrite	wt%	1.7
Plagioclase	wt%	10.6
Calcite	wt%	3.2
Phlogopite	wt%	17.4
Muscovite	wt%	12.3
Actinolite	wt%	1.2
Talc	wt%	1.3
Chlorite	wt%	0.2
Malachite	wt%	0.1
Total		100.1%

*For informational purposes only*

## **12. Health and Safety**

The material is a very fine 5 PB 5/1 Blueish Grey coloured powder. Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

## **13. Method of Preparation**

The particle size distribution for this material was shown to have a nominal top size of 53µm (98.57% passing 53µm). 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.

## **14. 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 8.

**Table 8.** Particle Size Determination by laser diffraction.

Size (µm)	Vol. Under %
<38um	96.98
<53um	98.57
<63um	98.83
<75um	98.98
<90um	99.10
<106um	99.20
<150um	99.30

*For informational purposes only*

## 15. 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 6 for an example calculation).

## 16. 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.

## 17. Methods of Analysis Requested

The following methods of analysis were requested:

- a) Acid Soluble-Cu
- b) Sulphuric Acid Leach-Cu
- c) 2 Acid Digest for multi-element scan especially Co, & Cu
- d) 4 Acid Digest for multi-element scan especially Co, & Cu
- e) Multi-element scan by Peroxide Fusion especially Co & Cu
- f) Major oxides & LOI by XRF
- g) C & S Combustion/LECO
- h) SG – Gas Pycnometer
- i) Moisture

## 18. Information Requested of Participating Laboratories

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

- a) All aliquots used for all determinations to be stated.
- b) All results for major elements to be reported as oxides in percentage (%).
- c) All results for multi-element scans and fusion to be reported in parts per million (ppm).
- d) All QC data to include replicates, blanks and any certified reference material 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) Moisture correction factor to be used to calculate and determine the moisture content. The moisture correction factor is to be stipulated when reporting results.

- h) Results to be recorded onto the PT Reporting template provided (Include uncertainty of measurements) together with a copy of the PDF.
- i) Ensure correct PPE is used i.e., gloves, dust masks and protective clothing when handling and analyzing the samples
- j) Storage and analysis shall be conducted under controlled environmental conditions.
- k) Ensure all safety requirements as per your laboratory requirements are adhered to.
- l) Samples shall be retained for 60 days after completion of analysis, prior to being discarded.

## 19. 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 Harmonized 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 are re-calculated using all remaining data (Thompson, 2008; Carr, 2011) (see Appendix 2)

## 20. 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]).

## 21. 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 8) or MS Excel as =TINV (5%,  $df$ ).

## 22. 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]).



## 23. 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 5, "Using the CRM in Quality Control" be used, in setting the limits of the CRM. Table 9 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 9.** Example of replicate assay data in which the *CI*, 2*s* and *U* are shown.

Lab No.	Mean Au (g/t)	<i>CI</i>	0.0088
1	0.268	<b>2s</b>	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		

## 24. Participating Laboratories

The laboratories that provided timeous results are:

1. American Assay Laboratories (USA)
2. Black Mountain Mining (South Africa)
3. Compass Green Worldwide SARL - Kolwezi
4. Inspectorate Griffith India Pvt. Ltd., Gandhidham Laboratory
5. Inspectorate Griffith India Pvt. Ltd., Zavar Laboratory
6. Intertek Perth
7. Misenge Environmental and Technical Service
8. MSA Bulyanhulu
9. Parlboro Mining Company
10. RCI Analytical Services
11. SGS de México, S.A. de C.V.
12. SGS Mineral Services Lakefield (Canada)
13. Shiva Analyticals India

## 25. Accepted Assay Data

Data from the 13 laboratories used for certification are set out in Table 10.

**Table 10.** Data used to calculate the certified values after removal of outliers.

2A_MICP	4A_MICP	FUS	2A_MICP	4A_MICP	FUS	Combustion/LECO	Combustion/LECO	SG
Cu	Cu	Cu	Co	Co	Co	C	S	SG
ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	Dimensionless
9680.00	9480.00	10100.00	520.00	468.00	397.93	34200.00	2.73	2.77
9740.00	9530.00	9950.00	520.00	478.00	388.81	33600.00	2.73	2.79
9680.00	9270.00	9970.00	520.00	480.00	395.33	33900.00	2.74	2.78
9740.00	9430.00	10100.00	520.00	477.00	389.17	34400.00	2.70	2.76
9610.00	9360.00	10000.00	510.00	474.00	389.43	33800.00	2.73	2.75
9740.00	9310.00	9960.00	520.00	478.00	388.54	34300.00	2.69	2.76
9670.00	9290.00	9920.00	520.00	481.00	500.00	34100.00	2.66	2.76
9680.00	9340.00	9880.00	520.00	477.00	500.00	33400.00	2.75	2.77
9600.00	9290.00	9033.87	513.72	525.58	500.00	33600.00	2.81	2.80
9700.00	9480.00	9251.23	513.19	526.91	500.00	32100.00	2.82	2.82
9600.00	9390.00	9234.70	501.75	524.45	500.00	32100.00	2.78	2.81
9600.00	9420.00	9222.81	502.72	525.45	500.00	32300.00	2.79	2.80
9600.00	9290.00	9282.91	504.63	528.17	500.00	32100.00	2.76	2.80
9600.00	9490.00	9314.53	508.23	527.29	500.00	32700.00	2.80	2.79
9600.00	9310.00	10000.00	502.73	522.86	488.00	32800.00	2.81	2.80
9600.00	9430.00	10100.00	504.13	524.89	482.00	32800.00	2.79	2.82
9760.00	9450.00	10300.00	480.63	525.12	473.00	29848.64	2.84	2.83
9755.00	9480.00	10400.00	466.46	522.68	489.00	29005.87	2.81	2.81
9740.00	9460.00	10200.00	471.21	524.29	482.00	30022.42	2.92	2.80
9665.00	9510.00	10200.00	473.98	507.30	481.00	29197.47	2.83	2.82
9710.00	9340.00	10100.00	475.67	526.49	474.00	29382.70	2.81	2.83
9695.00	9390.00	10300.00	477.78	520.50	481.00	29896.48	2.90	2.81
9600.00	9430.00	9883.00	460.32	517.33		29419.43	2.88	2.80
9675.00	9470.00	9856.00	469.14	527.01		29866.38	2.89	
9398.70	9635.94	9867.00	460.00	460.85		32400.00	2.71	
9418.50	9539.12	9761.00	453.00	465.30		32400.00	2.70	
9359.10	9568.26	9798.00	466.00	467.35		32500.00	2.70	
9319.50	9604.00	10007.00	445.00	465.04		32700.00	2.71	
9302.40	9625.60	10081.00	463.00	470.61		32600.00	2.71	
9258.30	9625.60	9790.00	464.00	469.41		32500.00	2.69	
9311.00	9631.00		453.00	465.67		32700.00	2.73	
9228.60	9675.42		446.00	473.50		32600.00	2.72	
9602.71	9201.81		428.00	503.20		32548.00	2.87	
9377.51	9328.06		432.00	506.90		32929.00	2.90	
9503.77	9407.81		432.00	504.60		32489.00	2.88	
9421.95	9308.78		431.00	503.90		32371.00	2.83	
9344.17	9377.46		435.00	492.40		32753.00	2.90	
9419.92	9339.10		432.00	509.70		32211.00	2.86	
9191.64	9340.09		435.00	503.50		32393.00	2.86	
9408.80	9390.55		433.00	509.90		32659.00	2.79	
9180.00	9873.10		492.76	522.18				
9303.00	10084.50		490.33	525.79				
9211.00	10001.60		498.48	519.71				
9223.00	10020.00		494.71	530.64				
9322.00	9782.60		496.61	523.90				
9436.00	10078.60		498.18	527.35				
9304.00	9933.70		495.49	517.36				
9239.00	10060.40		499.24	520.65				
9764.76	9665.52							
9710.82	9812.72							
9767.55	9837.56							
9796.38	9940.60							
9722.91	9775.00							
9789.87	9841.24							
9748.95	9806.28							
9639.21	9992.12							

**Assay Data (Continued)**

XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF
CuO	Al <sub>2</sub> O <sub>3</sub>	BaO	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>
%	%	%	%	%	%	%	%	%	%
1.17	10.21	0.15	8.45	4.21	5.34	6.17	0.20	0.15	0.47
1.19	10.12	0.14	8.43	4.23	5.36	6.19	0.21	0.15	0.49
1.18	10.07	0.15	8.45	4.18	5.41	6.21	0.21	0.15	0.48
1.18	10.09	0.15	8.43	4.21	5.29	6.20	0.20	0.14	0.49
1.17	10.10	0.16	8.47	4.19	5.31	6.19	0.21	0.14	0.51
1.18	10.14	0.15	8.42	4.23	5.36	6.21	0.21	0.15	0.48
1.18	10.02	0.16	8.71	4.21	5.38	6.24	0.20	0.15	0.49
1.18	9.99	0.14	8.75	4.17	5.31	6.23	0.21	0.15	0.49
1.19	10.10	0.14	8.75	4.31	5.25	6.10	0.19	0.15	0.50
1.20	10.09	0.14	8.77	4.31	5.27	6.12	0.19	0.16	0.50
1.19	10.00	0.15	8.76	4.32	5.30	6.12	0.19	0.16	0.50
1.20	10.01	0.14	8.82	4.34	5.29	6.10	0.19	0.15	0.49
1.20	10.12	0.14	8.83	4.34	5.33	6.11	0.19	0.16	0.50
1.19	10.13	0.14	8.75	4.37	5.38	6.14	0.19	0.16	0.50
1.20	10.08	0.14	8.79	4.37	5.35	6.17	0.19	0.16	0.49
1.19	10.05	0.14	8.81	4.33	5.28	6.11	0.19	0.16	0.47
	9.32	0.15	8.82	4.38	5.78	5.98		0.12	0.49
	9.32	0.14	8.83	4.46	5.91	6.01		0.12	0.49
	9.34	0.13	8.87	4.47	5.88	5.98		0.12	0.49
	9.33	0.14	8.84	4.47	5.89	5.99		0.12	0.52
	9.33	0.14	8.83	4.46	5.86	6.01		0.12	0.50
	9.35	0.15	8.81	4.44	5.85	6.04		0.12	0.49
	9.31	0.14	8.77	4.47	5.92	5.99		0.12	0.49
	9.30		8.79	4.47	5.91	5.96		0.13	0.46
	9.98		8.80	4.16	5.08	6.21		0.15	0.46
	10.02		8.76	4.13	5.08	6.22		0.15	0.46
	10.04		8.74	4.12	5.10	6.23		0.15	0.46
	10.01		8.77	4.15	5.09	6.23		0.15	0.46
	9.99		8.84	4.15	5.12	6.21		0.15	0.46
	10.08		8.79	4.15	5.09	6.26		0.15	0.45
	10.11			4.14	5.08	6.27		0.15	0.46
	10.03			4.11	5.08	6.24		0.15	0.49
				4.28	5.45				0.49
				4.27	5.45				0.50
				4.28	5.45				0.48
				4.26	5.43				0.48
				4.25	5.42				0.50
				4.26	5.50				0.49
				4.31	5.49				0.49
				4.28	5.44				

**Assay Data (Continued)**

4A_MICP	FUS	2A_MICP	4A_MICP	4A_MICP	2A_MICP	4A_MICP	2A_MICP	4A_MICP	4A_MICP
Al	Al	As	Ba	Be	Bi	Bi	Ca	Ca	Cr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
52100.00	51639.37	19.03	1220.00	1.87	7.93	7.20	60000.00	63300.00	82.00
52600.00	53563.55	19.98	1260.00	1.92	7.46	6.98	59700.00	63900.00	85.00
51200.00	53174.39	18.80	1270.00	1.93	8.34	7.29	59700.00	61500.00	83.00
52600.00	53412.21	19.02	1240.00	1.90	6.80	7.99	59200.00	63600.00	82.00
52000.00	52990.62	20.10	1220.00	1.91	8.22	8.30	60300.00	62500.00	84.00
51600.00	52871.71	19.12	1210.00	1.90	7.65	8.40	60300.00	62900.00	83.00
52100.00	53100.00	19.10	1220.00	1.93	9.29	7.68	60300.00	63500.00	84.00
52800.00	53300.00	18.45	1240.00	1.92	9.02	8.22	60200.00	64603.20	83.00
55344.20	53000.00	18.00	1294.40	1.90	9.00	7.61	59148.00	64422.72	69.94
55526.80	52600.00	18.00	1291.50	1.90	9.00	7.81	59020.00	64451.52	69.78
55241.62	52800.00	19.00	1285.20	1.90	9.00	7.43	58445.00	64980.48	70.19
55478.38	53500.00	19.00	1298.00	1.90	9.00	8.12	58547.00	64084.80	70.17
55149.50	53900.00	19.00	1279.60	1.80	10.00	7.42	58873.00	64104.32	70.07
55682.44	52700.00	19.00	1247.50	1.80	9.00	7.54	58485.00	64168.96	70.18
55304.56		19.00	1249.60	1.90	9.00	7.00	58513.00	64455.04	68.38
55197.52		18.00	1261.40	1.90	9.00	8.00	58608.00	60589.11	69.97
53273.00		20.26	1188.99	2.02	7.17	8.00	60724.82	60677.38	84.00
53272.00		18.88	1192.41	1.98	7.40	8.00	59310.42	60819.00	85.00
53568.00		18.55	1195.38	1.97	8.00	9.00	59466.41	59983.76	83.00
51924.00		20.72	1159.20	1.85	8.00	7.00	59393.63	60738.49	84.00
53542.00		21.18	1195.65	1.98	7.00	8.00	58925.64	60997.48	82.00
53307.00		19.42	1187.28	2.03	7.82	8.00	59092.03	59953.76	84.00
52703.00		19.32	1174.86	1.94	9.00		57864.85	60954.80	83.00
53388.00		20.13	1189.71		8.00		59414.45	59729.51	84.00
49951.20			1274.50				57100.00	60351.68	
50284.00			1310.70				56500.00	60800.48	
49774.40			1282.60				57300.00	60382.26	
50096.80			1302.50				54000.00	60729.06	
50263.20			1271.00				57400.00	60259.88	
49868.00			1284.70				58000.00	59923.28	
50492.00			1290.30				55400.00	61086.07	
52723.00			1284.70				55800.00	60343.00	
52921.00			1196.82				53900.00	61382.00	
52068.00			1207.08				55300.00	60656.00	
52829.00			1206.45				56000.00	61168.00	
51442.00			1213.47				56800.00	59941.00	
53252.00			1214.91				59447.82	61132.00	
53332.00			1208.07				60536.82	60643.00	
52565.00			1207.08				60266.82	60879.00	
52838.40			1216.53				61415.82	61353.36	
53416.32							60861.82	61752.72	
53567.04							60835.82	61702.80	
53821.44							60830.82	62173.20	
53660.16							60179.82	61861.20	
53691.84								62400.72	
53400.00								61681.68	
53810.88								62085.84	

**Assay Data (Continued)**

2A_MICP	4A_MICP	FUS	2A_MICP	FUS	4A_MICP	2A_MICP	4A_MICP	FUS	2A_MICP
Fe	Fe	Fe	K	K	Li	Mn	Mn	Mn	Mo
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
30000.00	29700.00	30060.00	14041.00	47300.00	68.00	1400.00	1450.00	1600.00	9.00
29400.00	30000.00	29490.00	14105.00	46800.00	65.00	1400.00	1490.00	1560.00	8.95
29000.00	29000.00	30250.00	13559.00	47100.00	65.00	1400.00	1500.00	1560.00	8.76
29200.00	29800.00	29750.00	13686.00	47200.00	67.00	1400.00	1490.00	1580.00	8.86
29900.00	29700.00	29660.00	13823.00	47000.00	62.00	1400.00	1480.00	1570.00	9.00
29400.00	29500.00	29650.00	13880.00	47000.00	66.00	1400.00	1480.00	1570.00	8.81
29500.00	29800.00	30010.00	13555.00	46800.00	67.00	1394.82	1490.00	1540.00	8.50
29300.00	29900.00	30050.00	13858.00	46300.00	68.00	1368.29	1480.00	1540.00	8.41
28054.45	32550.72	31200.00	13310.00	46300.00	65.00	1375.87	1542.63	1520.29	8.00
28087.70	32338.56	30200.00	13110.00	46300.00	67.00	1374.60	1534.72	1540.07	8.00
27674.45	32121.60	30500.00	13270.00	46100.00	65.00	1356.92	1527.89	1562.05	8.00
27655.45	32469.12	30900.00	12440.00	45900.00	64.00	1375.88	1559.01	1524.22	9.00
27943.30	32138.88	30600.00	13370.00	46100.00	63.00	1345.54	1532.08	1525.82	8.00
27799.85	32480.32	30600.00	13380.00	46700.00	65.00	1377.13	1588.31	1520.72	8.00
27766.60	32211.20	29900.00	12190.00	47100.00	66.00	1333.00	1541.90	1600.00	8.00
27767.55	31455.16	29800.00	12960.00	45800.00	65.50	1347.00	1534.78	1600.00	8.00
33224.56	31722.88	29800.00	12788.00		64.70	1345.00	1563.20	1600.00	8.00
33053.88	31383.38	30300.00	12899.00		64.50	1350.00	1585.20	1600.00	8.00
32553.76	31426.00	30700.00	12879.00		65.10	1358.00	1583.70	1600.00	8.00
33151.40	31298.02	31300.00	12911.00		63.40	1354.00	1565.00	1600.00	9.00
29200.00	31551.00	30300.00	12997.00		64.20	1363.00	1574.10	1600.00	8.00
29200.00	31037.09	30300.00	13016.00		64.20	1351.00	1576.90	1600.00	8.71
29100.00	31580.29	30300.00	13084.00		64.70		1548.10	1555.00	8.68
29200.00	29088.59	30900.00	13035.00				1574.70	1557.00	8.54
29200.00	29212.07	30000.00	14058.16				1396.10	1552.00	8.61
29200.00	29644.66	30100.00	13720.28				1408.63	1539.00	8.52
29300.00	29315.06	29900.00	13593.91				1414.91	1547.00	8.57
29200.00	29469.54	29700.00	13848.82				1408.63	1568.00	8.55
28031.71	29242.96	29700.00	14049.68				1408.63	1562.00	8.61
28352.17	29119.40	30200.00	13752.01				1409.89	1549.00	
28273.77	29788.82	29900.00	13686.94				1403.63		
28884.31	29800.00	29900.00	13613.85				1416.15		
28744.17	30000.00						1577.00		
28492.31	29300.00						1599.00		
28661.85	30100.00						1572.00		
28284.55	29600.00						1579.00		
	30400.00						1560.00		
	29900.00						1598.00		
	30100.00						1599.00		
	30703.68						1581.00		
	30689.28						1535.65		
	30504.00						1548.19		
	30641.28						1558.26		
	30792.96						1564.15		
	31039.68						1542.97		
	30516.48						1570.71		
	30648.00						1539.83		
							1562.73		

**Assay Data (Continued)**

4A_MICP	2A_MICP	2A_MICP	4A_MICP	2A_MICP	4A_MICP	2A_MICP	4A_MICP	FUS	2A_MICP
Mo	Na	Ni	Ni	P	P	Pb	Pb	Si	Sr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
10.00	211.52	50.01	58.00	771.78	687.00	9.00	9.71	238000.00	132.19
11.00	203.00	50.29	57.00	771.55	679.00	9.00	9.58	234000.00	131.05
11.00	205.27	50.26	58.00	768.12	679.00	7.00	8.70	238000.00	127.05
11.00	207.39	50.35	58.00	771.30	679.00	7.00	8.89	228000.00	126.51
10.00	210.04	50.15	58.00	761.71	686.00	7.00	9.06	214000.00	126.37
10.00	204.00	50.46	59.00	758.97	686.00	7.00	9.18	233000.00	126.45
10.00	202.26	50.33	58.00	763.18	687.00	7.00	9.29	236000.00	126.68
9.20	206.00	50.17	56.00	762.80	691.00	7.00	10.36	229000.00	125.94
10.18	215.23	59.14	61.86	700.00	663.63	8.00	13.16	236000.00	119.00
9.04	214.44	57.93	62.63	700.00	665.10	7.00	12.66	237000.00	117.00
9.60	212.70	57.42	63.90	700.00	682.38	7.00	13.80	235000.00	119.00
8.98	219.48	57.39	63.44	700.00	659.95	9.00	13.20	233000.00	112.00
9.34	217.87	55.21	63.53	700.00	670.21	8.00	10.17	234000.00	119.00
9.68	212.02	58.41	62.57	700.00	667.36	7.00	10.53	237000.00	121.00
10.07	213.31	55.85	62.35	700.00	663.00	7.00	9.00	239000.00	110.00
9.00	212.75	57.27	62.53	634.00	680.70	8.00	12.00	233000.00	115.00
9.00		55.00	66.10	642.00	601.00	6.00	8.00		127.96
9.00		54.00	68.30	639.00	617.00	6.00	9.00		128.66
8.00		56.00	68.10	639.00	612.00	6.00	8.00		125.99
8.00		52.00	67.67	647.00	612.00	6.00	8.00		128.47
8.00		54.00	66.30	646.00	619.00	6.00	10.00		127.65
9.00		55.00	68.20	650.00	612.00	6.00	8.00		127.20
8.00		53.00	64.30	644.00	607.00	6.00	6.50		128.97
9.20		54.00	65.60	759.76	619.00	6.00	6.90		126.26
8.90		52.00	52.57	774.53	679.87		6.50		
9.10		52.00	53.20	768.88	670.61		6.60		
9.10		52.00	53.85	760.82	678.18		6.50		
9.30		52.00	53.85	770.72	664.17		6.70		
8.90		51.00	53.74	772.27	682.00		6.60		
8.80		51.00	53.46	774.92	680.00		6.80		
9.20		52.00	52.21	770.59	676.00		9.55		
11.00		51.00	53.94		687.00		8.74		
9.96		50.71	57.00				8.54		
9.66		52.44	54.00				9.68		
9.77		52.38	54.00				8.81		
9.47		52.22	54.00				8.91		
10.19		52.79	51.00				9.63		
9.59		53.06	51.00				9.14		
9.85		50.91	54.00						
		52.50	55.00						
			55.70						
			55.00						
			54.00						
			54.10						
			52.80						
			55.60						
			54.00						
			55.10						
			63.42						
			66.33						
			61.35						
			62.19						
			62.35						
			61.76						
			62.15						

**Assay Data (Continued)**

4A_MICP	4A_MICP	FUS	2A_MICP	4A_MICP	4A_MICP	2A_MICP	4A_MICP	4A_MICP
Sr	Ti	Ti	V	V	Y	Zn	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
149.00	2240.00	3000.00	40.73	75.00	14.30	75.00	65.00	75.91
151.00	2300.00	2960.00	41.07	77.00	14.60	75.50	65.00	74.89
151.00	2260.00	2990.00	38.75	78.00	14.60	74.00	63.00	76.34
152.00	2270.00	3000.00	39.29	78.00	14.60	73.00	62.00	74.60
150.00	2290.00	2980.00	40.09	77.00	14.60	71.90	65.00	77.36
150.00	2260.00	2990.00	40.20	76.00	14.40	73.50	63.00	75.88
150.00	2320.00	2930.00	38.91	76.00	14.60	70.80	66.00	73.24
152.00	2320.00	2930.00	40.16	77.00	14.70	71.90	62.83	74.80
173.47	2436.09	2900.00	31.00	74.67	15.12	73.00	60.81	84.20
173.50	2498.41	2900.00	30.00	74.71	15.17	72.00	62.74	79.30
173.00	2457.78	2900.00	31.00	74.19	15.04	70.00	65.10	81.20
173.25	2464.78	2900.00	30.00	76.32	15.23	70.00	63.50	80.10
169.41	2420.60	2900.00	31.00	74.66	14.94	70.00	64.20	78.10
172.82	2446.05	2900.00	31.00	72.36	15.37	71.00	62.18	75.80
172.04	2471.55	3000.00	30.00	73.96	15.02	71.00	63.10	77.90
153.30	2454.20	2900.00	30.00	74.48	15.31	71.00	61.31	80.30
153.19	2244.90		31.00	77.43		62.19	63.33	77.60
155.20	2226.50		31.00	77.72		61.86	61.76	81.00
153.00	2298.70		31.00	78.26		62.18	62.48	77.40
154.81	2209.00		31.00	76.99		61.45	61.89	80.00
154.16	2310.90		32.00	77.47		61.46	62.98	80.80
151.54	2287.70		32.00	76.22		62.60	61.73	79.90
155.48	2196.70		31.00	76.11		60.08	62.89	76.40
160.76	2280.90		32.00	77.05		61.19	60.00	81.70
162.92	2340.00		39.97	77.00		82.73	58.00	77.75
161.49	2385.00		38.61	74.00		79.38	59.00	75.73
163.02	2325.00		37.98	76.00		78.98	62.00	77.28
159.90	2382.00		38.98	76.00		79.62	57.00	76.61
161.94	2367.00		40.10	74.00		79.69	59.00	78.12
160.92	2435.00		39.27	75.00		80.00	58.00	76.97
162.93	2280.00		38.55	80.00		78.35	64.00	77.47
157.56	2396.00		38.18	80.00		80.75	66.00	76.92
158.99	2265.00			78.00		54.00	64.00	
159.38	2240.00			81.00		54.00	65.00	
159.78	2314.00			79.00		54.00	64.00	
158.99	2283.10			81.00		53.00	66.00	
159.41	2280.90			79.00		55.00	66.00	
158.80	2277.00			80.00		54.00	66.00	
160.51	2282.30			79.65		55.00	65.02	
	2295.30			80.53		54.00	60.80	
				79.49		63.33	64.67	
				80.42		62.31	64.78	
				80.45		62.27	64.49	
				79.51		61.64	65.06	
				79.89		62.61	62.78	
				79.43		62.08	60.85	
						61.76		
						62.65		

## **26. Reported Values**

The certified values listed in this certificate fulfil the AMIS statistical criteria (see section 19) regarding agreement for certification and have been independently validated by Allan Fraser.

## **27. 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 2 for an example on the validation of accuracy using replicate data derived from the analysis of a CRM.

## **28. Metrological Traceability**

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

## **29. Period of Validity**

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

## **30. Minimum Sample Size**

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

## **31. Availability**

This product is available in Laboratory Packs containing 1kg of material and Explorer Packs containing custom weights (from 30g to 250g) of material. The Laboratory Packs are sealed bottles delivered in sealed foil pouches. The Explorer Packs contain material in standard geochem envelopes, nitrogen flushed, and vacuum sealed in foil pouches.

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

Users should set their own limits *i.e.*, 1, 2 and 3 standard deviations from an obtained mean value based on at least 10 replicate analyses using this CRM (see Appendix 5 for detail on the use of this CRM in quality control).



### 33. Legal Notice

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

**Date of Version 000:** 06 November 2022

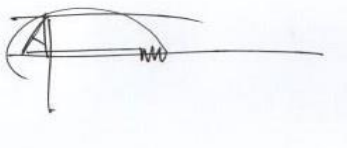
**Version:** 000

**Approving Officer:**

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

**Melesha Gopi Mungaroo (Senior Quality Specialist)**

**Certifying Officer:**

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

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

**Allan Fraser**

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

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## Appendices

Appendix 1 through 8, prepared by Allan Fraser.

### Appendix 1. 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, 2006). 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 19, an 'appropriate precision' as shown in [8] is calculated for sufficient homogeneity (Thompson, 2008):

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

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

### Total Variation (SST)

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

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

### Between Group Variation (SSB)

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

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

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

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

### Within Group Variation (SSW)

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

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

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

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

From equations [9] through [13], the ANOVA table as shown in Table 11 is developed.

**Table 11.** 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 8, 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 2. 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 12. 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 12.** 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 8, page 35) 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 3. Two-standard Deviations

Two-standard deviations are calculated using the expression:

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

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

### Appendix 4. Confidence Interval

Confidence interval is calculated as:

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

Where,  $N$  is the number of laboratories (accepted laboratory data),  $t_{critical}$  is a two-tailed value for  $N - 1$  degrees of freedom ( $df$ ) and  $s$ , is the standard deviation of the accepted laboratory means. A two-tailed critical value is found for  $N - 1$  degrees of freedom from either a  $t$ -distribution table (Appendix 8) or MS Excel as =TINV (5%,  $df$ ).

### Appendix 5. Using the CRM in Quality Control

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

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

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



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

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

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

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

#### **Appendix 6. 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:

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

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

#### **Example**

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

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

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

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

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

#### Appendix 7. Example of Determination of LOD and LOQ in Fire Assay

The limit of detection (LOD) is the minimum detectable quantity of the analyte of interest (Skoog & West, 1985). To determine the LOD in fire assay by lead collection, the minimum mass that an assay microbalance is capable of weighing ( $m$  in micrograms, and the original test sample mass,  $Mass_{assay}$  in grams) determines the LOD. The smallest prill mass most assay microbalances can measure is  $1\mu\text{g}$  or  $0.001\text{mg}$ . Even with a microscope it may be difficult to locate and pick up a prill weighing ten times that amount (*i.e.*  $0.01\text{mg}$  or  $10\mu\text{g}$ ) and weigh it. If an analyst can weigh a prill of  $1\mu\text{g}$  then the LOD becomes  $1\mu\text{g}$ . However, the concentration factor would be 50 times for a 50-gram assay sample and therefore the LOD in g/t becomes  $1\mu\text{g}$  divided by the original mass of the sample in grams taken for fire assay [24]. Therefore, the LOD in fire assay is computed as:

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

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

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

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be  $0.02\text{g/t}$ . *i.e.*  $1\mu\text{g} = 1\text{g/t}$ , therefore  $1\mu\text{g}/50\text{g} = 0.02\text{g/t}$ . If no prill was found, then the LOD result would be  $<0.02\text{g/t}$  or "not detected". Using a larger assay sample mass improves the LOD and LOQ (Table 12). Table 14 gives a recommended reporting scheme for LOD and LOQ.

**Table 13.** Mass of assay sample and corresponding limit of detection and limit of quantitation for an assay microbalance capability of smallest prill mass of  $1\mu\text{g}$  or  $0.001\text{mg}$ .

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 14.** Recommended reporting scheme for LOD and LOQ in fire assay.

Data	Report as
$<LOD$	Not detected
$<LOQ$	Detected
$\geq LOQ$	Report assay result

**Appendix 8.** T-distribution table

**Table 15.** T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence.

<i>df</i>	Two-tailed	<i>df</i>	Two-tailed
1	12.71	23	2.06
2	4.30	24	2.06
3	3.18	25	2.06
4	2.78	26	2.05
5	2.57	27	2.05
6	2.44	28	2.04
7	2.36	29	2.04
8	2.30	30	2.04
9	2.26	35	2.03
10	2.22	40	2.02
11	2.20	45	2.01
12	2.17	50	2.00
13	2.16	55	2.00
14	2.14	60	2.00
15	2.13	70	1.99
16	2.12	80	1.98
17	2.11	90	1.98
18	2.10	100	1.98
19	2.09	120	1.98
20	2.08	Infinity	1.96
21	2.08		
22	2.07		

**End of certificate**