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Director

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Certificate

# AMIS0631

## Certified Reference Material

### Tin Concentrate, Afritin Mining, Namibia

## *Certificate of Analysis*

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#### AMIS

A: 11 Avalon Road, West Lake View, Ext 11, Modderfontein, 1609, South Africa

P: PO Box 856, Isando, 1600, Gauteng, South Africa

T: +27 (0) 11 923 0800

W: [www.amis.co.za](http://www.amis.co.za)



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## Summary Statistics

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

Analyte	Method	( $\mu$ ) <sup>7</sup>	(2s) <sup>9</sup> ±	Unit
Sn	FUS <sup>1</sup>	3427	275	ppm
Li	4A_MICP <sup>2</sup>	2663	91	ppm
Li	FUS	2653	233	ppm
Rb	4A_MICP	1098	122	ppm
Rb	FUS	1168	134	ppm
Rb	FUSA <sup>3</sup>	1223	95	ppm
Ta	FUS	128	16	ppm
Ta	FUSA	152	31	ppm
LOI	LOI <sup>4</sup>	3.31	0.44	%
SG	SG <sup>5</sup>	2.69	0.19	Dimensionless
Al	FUS	9.29	0.94	%
Al	FUSA	8.95	0.38	%
As	4A_MICP	7	1	ppm
Ba	FUS	44	7	ppm
Ba	FUSA	49	4	ppm
Be	FUS	179	18	ppm
Be	FUSA	195	12	ppm
Bi	4A_MICP	2	0.5	ppm
Bi	FUS	2	0.7	ppm
Ca	4A_MICP	9969	920	ppm
Ca	FUS	9992	1092	ppm
Cd	4A_MICP	5	2	ppm
Co	4A_MICP	4	1	ppm
Cs	4A_MICP	35	7	ppm
Cs	FUS	34	6	ppm
Cu	4A_MICP	82	4	ppm
Fe	FUS	3656	370	ppm
Ga	4A_MICP	36	7	ppm
Ga	FUSA	39	3	ppm
Hf	4A_MICP	1	0.3	ppm
K	4A_MICP	1.67	0.17	%
K	FUS	1.71	0.21	%
Mn	4A_MICP	294	50	ppm
Mo	4A_MICP	0.9	0.2	ppm
Na	4A_MICP	2.37	0.28	%
Nb	FUSA	131	38	ppm
Ni	4A_MICP	11	1	ppm
Pb	FUS	358	38	ppm
Pb	FUSA	348	26	ppm
S	FUSA	0.1	0.02	%
Sb	4A_MICP	0.8	0.1	ppm
Sb	FUS	0.8	0.4	ppm
Si	FUS	32.03	0.77	%
Sr	4A_MICP	459	41	ppm
Sr	FUS	473	80	ppm
Tl	4A_MICP	9	1	ppm
Tl	FUS	9	1	ppm
Tl	FUSA	9	1	ppm
U	FUS	14	4	ppm
Zn	4A_MICP	1580	169	ppm
Zn	FUSA	1622	145	ppm
Zr	4A_MICP	12	4	ppm

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

Analyte	Method	( $\mu$ ) <sup>7</sup>	(2s) <sup>9</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	FUS	17.52	1.8	%
Al <sub>2</sub> O <sub>3</sub>	FUSA	16.91	0.74	%
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>6</sup>	17.75	1.8	%
BaO	FUSA	0.005	0.0005	%
CaO	FUS	1.34	0.19	%
CaO	XRF	1.38	0.055	%
Fe <sub>2</sub> O <sub>3</sub>	FUS	0.52	0.05	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	0.50	0.04	%
K <sub>2</sub> O	FUS	2.07	0.25	%
K <sub>2</sub> O	XRF	2.02	0.11	%
MnO	XRF	0.042	0.01	%
Na <sub>2</sub> O	XRF	3.21	0.081	%
Nb <sub>2</sub> O <sub>5</sub>	FUSA	0.02	0.005	%
Pb <sub>3</sub> O <sub>4</sub>	FUSA	0.04	0.003	%
Rb <sub>2</sub> O	FUSA	0.1	0.01	%
SiO <sub>2</sub>	FUS	68.27	2.0	%
SiO <sub>2</sub>	XRF	67.98	2.2	%
SrO	FUS	0.058	0.004	%
Ta <sub>2</sub> O <sub>5</sub>	FUSA	0.02	0.004	%
ZnO	FUSA	0.2	0.02	%

## 1. Certified Concentrations and Uncertainties

AMIS0631 is a new standard material, developed and certified in May 2019. Table 1 gives the certified concentrations, confidence interval, combined and expanded uncertainty for the certified reference material. Table 2 shows the certified major oxides concentrations, two standard deviations, confidence interval, combined and expanded uncertainty.

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

Analyte	Method	( $\mu$ ) <sup>7</sup>	N	n	k	% RSD	( $u_c$ ) <sup>8</sup>	(2s) <sup>9</sup> ±	(CI) <sup>10</sup> 95%	(U) <sup>11</sup> ±	Unit
Sn	FUS <sup>1</sup>	3427	3	23	4.303	4	138	275	283	592	ppm
Li	4A_MICP <sup>2</sup>	2663	4	31	3.182	2	46	91	51	145	ppm
Li	FUS	2653	3	23	4.303	4	117	233	250	502	ppm
Rb	4A_MICP	1098	3	22	4.303	6	61	122	142	263	ppm
Rb	FUS	1168	3	23	4.303	6	67	134	160	288	ppm
Rb	FUSA <sup>3</sup>	1223	2	16	12.706	4	47	95	409	602	ppm
Ta	FUS	128	3	23	4.303	6	8	16	18	35	ppm
Ta	FUSA	152	3	24	4.303	10	16	31	38	67	ppm
LOI	LOI <sup>4</sup>	3.31	5	40	2.776	7	0.22	0.44	0.27	0.6	%
SG	SG <sup>5</sup>	2.69	5	39	2.776	4	0.095	0.19	0.12	0.3	Dimensionless
Al	FUS	9.29	4	32	3.182	5	0.47	0.94	0.74	1	%
Al	FUSA	8.95	3	24	4.303	2	0.19	0.38	0.45	0.8	%
As	4A_MICP	7	5	40	2.776	8	0.5	1	0.2	2	ppm
Ba	FUS	44	3	23	4.303	8	3	7	5	15	ppm
Ba	FUSA	49	2	15	12.706	4	2	4	17	26	ppm
Be	FUS	179	3	23	4.303	5	9	18	16	39	ppm
Be	FUSA	195	3	24	4.303	3	6	12	13	25	ppm
Bi	4A_MICP	2	3	24	4.303	9	0.2	0.5	0.5	1	ppm
Bi	FUS	2	3	24	4.303	15	0.3	0.7	0.8	1	ppm
Ca	4A_MICP	9969	2	16	12.706	5	460	920	4058	5848	ppm
Ca	FUS	9992	4	30	3.182	5	546	1092	456	1738	ppm
Cd	4A_MICP	5	3	24	4.303	15	0.8	2	2	3	ppm
Co	4A_MICP	4	3	24	4.303	12	0.5	1	1	2	ppm
Cs	4A_MICP	35	4	31	3.182	11	4	7	6	12	ppm
Cs	FUS	34	2	15	12.706	9	3	6	26	38	ppm
Cu	4A_MICP	82	4	32	3.182	3	2	4	2	7	ppm
Fe	FUS	3656	5	37	2.776	5	185	370	188	513	ppm
Ga	4A_MICP	36	4	32	3.182	10	4	7	6	12	ppm
Ga	FUSA	39	3	24	4.303	4	1	3	2	6	ppm
Hf	4A_MICP	1	4	31	3.182	11	0.2	0.3	0.2	0.5	ppm
K	4A_MICP	1.67	4	32	3.182	5	0.087	0.17	0.13	0.3	%
K	FUS	1.71	3	24	4.303	6	0.10	0.21	0.25	0.4	%
Mn	4A_MICP	294	5	40	2.776	9	25	50	29	70	ppm
Mo	4A_MICP	0.9	4	31	3.182	13	0.1	0.2	0.2	0.4	ppm
Na	4A_MICP	2.37	5	40	2.776	6	0.14	0.28	0.16	0.4	%
Nb	FUSA	131	2	16	12.706	14	19	38	170	241	ppm
Ni	4A_MICP	11	4	32	3.182	6	0.7	1	0.9	2	ppm
Pb	FUS	358	3	24	4.303	5	19	38	35	82	ppm
Pb	FUSA	348	3	24	4.303	4	13	26	26	55	ppm
S	FUSA	0.1	3	22	4.303	10	0.01	0.02	0.01	0.05	%
Sb	4A_MICP	0.8	3	24	4.303	8	0.06	0.1	0.1	0.3	ppm
Sb	FUS	0.8	3	24	4.303	25	0.2	0.4	0.5	0.9	ppm
Si	FUS	32.03	4	29	3.182	1	0.38	0.77	0.38	1	%
Sr	4A_MICP	459	3	24	4.303	4	20	41	47	88	ppm
Sr	FUS	473	3	23	4.303	8	40	80	100	172	ppm
Tl	4A_MICP	9	4	31	3.182	8	0.7	1	1	2	ppm
Tl	FUS	9	2	15	12.706	7	0.6	1	5	8	ppm
Tl	FUSA	9	2	15	12.706	6	0.5	1	5	7	ppm
U	FUS	14	3	24	4.303	15	2	4	5	9	ppm
Zn	4A_MICP	1580	6	45	2.571	5	85	169	95	217	ppm
Zn	FUSA	1622	4	32	3.182	4	72	145	110	230	ppm
Zr	4A_MICP	12	6	48	2.571	16	2	4	2	5	ppm

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

Analyte	Method	( $\mu$ ) <sup>7</sup>	N	n	k	% RSD	( $u_c$ ) <sup>8</sup>	(2s) <sup>9</sup> ±	(CI) <sup>10</sup> 95%	(U) <sup>11</sup> ±	Unit
Al <sub>2</sub> O <sub>3</sub>	FUS	17.52	4	32	3.182	5	0.89	1.8	1.0	3	%
Al <sub>2</sub> O <sub>3</sub>	FUSA	16.91	3	24	4.303	2	0.37	0.74	0.88	2	%
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>6</sup>	17.75	4	31	3.182	5	0.89	1.8	1.0	3	%
BaO	FUSA	0.005	2	15	12.706	4	0.0002	0.0005	0.002	0.003	%
CaO	FUS	1.34	3	24	4.303	7	0.095	0.19	0.23	0.4	%
CaO	XRF	1.38	4	29	3.182	2	0.028	0.055	0.048	0.09	%
Fe <sub>2</sub> O <sub>3</sub>	FUS	0.52	5	37	2.776	5	0.03	0.05	0.03	0.07	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	0.50	5	38	2.776	4	0.02	0.04	0.02	0.05	%
K <sub>2</sub> O	FUS	2.07	3	24	4.303	6	0.13	0.25	0.31	0.5	%
K <sub>2</sub> O	XRF	2.02	4	28	3.182	3	0.055	0.11	0.10	0.2	%
MnO	XRF	0.042	4	30	3.182	10	0.004	0.01	0.006	0.01	%
Na <sub>2</sub> O	XRF	3.21	4	32	3.182	1	0.041	0.081	0.059	0.1	%
Nb <sub>2</sub> O <sub>5</sub>	FUSA	0.02	2	16	12.706	14	0.003	0.005	0.02	0.03	%
Pb <sub>3</sub> O <sub>4</sub>	FUSA	0.04	3	24	4.303	4	0.001	0.003	0.003	0.006	%
Rb <sub>2</sub> O	FUSA	0.1	2	16	12.706	4	0.005	0.01	0.05	0.07	%
SiO <sub>2</sub>	FUS	68.27	3	24	4.303	1	0.99	2.0	2.0	4	%
SiO <sub>2</sub>	XRF	67.98	4	31	3.182	2	1.1	2.2	2.0	3	%
SrO	FUS	0.058	2	16	12.706	4	0.002	0.004	0.02	0.03	%
Ta <sub>2</sub> O <sub>5</sub>	FUSA	0.02	3	24	4.303	10	0.002	0.004	0.005	0.008	%
ZnO	FUSA	0.2	4	32	3.182	4	0.009	0.02	0.01	0.03	%

1. FUS is Fusion digestion with either ICPOES/ICPMS/AAS finish
2. 4A\_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
3. FUSA is Fusion digestion with additional time and acid for digestion finished with either ICPOES/ICPMS/AAS
4. LOI is Loss on Ignition
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:  $U = 2.36 \times 0.23 = 0.5\%$
12. FS\_ICPMS is Fusion digestion with ICPMS finish
13. Moisture
14. Combustion/LECO

## 2. Statistical Comparison of Means

A comparison of means for replicate data for the same element concentration determined by different analytical methods is done equating the variances between the two data sets; if the variances are found to be equal (F-test,  $p$ -value $>0.05$ ), then an equal variance t-test is applied. Should the variances be statistically significant, i.e.  $p<0.05$ , then an unequal variance t-test is performed. For either t-test, if the obtained  $p$ -value  $\geq 0.05$ , the null hypothesis that the means (certified values) are equal is accepted (Table 3). This gives the analyst confidence in the certified values reported by different analytical methods on the same analyte.

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

Method	Certified value	Method	Certified Value	F-test Outcome	p-value (test)	t-test Outcome
Li 4A_MICP	0.266 %	Li FUS	0.265 %	Unequal Variance ( $p=0.048$ )	0.882	Accept $H_0$ ; certified values are equal
Bi 4A_MICP	2 ppm	Bi FUS	2 ppm	Equal Variance ( $p=0.313$ )	0.506	Accept $H_0$ ; certified values are equal
Ca 4A_MICP	0.997 %	Ca FUS	0.999 %	Equal Variance ( $p=0.213$ )	0.943	Accept $H_0$ ; certified values are equal
Cs 4A_MICP	0.003 %	Cs FUS	0.003 %	Equal Variance ( $p=0.505$ )	0.699	Accept $H_0$ ; certified values are equal
K 4A_MICP	1.67 %	K FUS	1.71 %	Equal Variance ( $p=0.365$ )	0.583	Accept $H_0$ ; certified values are equal
Sb 4A_MICP	0.001 %	Sb FUS	0.001%	Equal Variance ( $p=0.064$ )	0.507	Accept $H_0$ ; certified values are equal
Sr 4A_MICP	0.046 %	Sr FUS	0.047 %	Equal Variance ( $p=0.18$ )	0.626	Accept $H_0$ ; certified values are equal
Ta FUS	0.013 %	Ta FUSA	0.015 %	Equal Variance ( $p=0.185$ )	0.067	Accept $H_0$ ; certified values are equal
Al FUS	9.29 %	Al FUSA	8.95 %	Equal Variance ( $p=0.134$ )	0.296	Accept $H_0$ ; certified values are equal
Ba FUS	0.004 %	Ba FUSA	0.005 %	Equal Variance ( $p=0.409$ )	0.088	Accept $H_0$ ; certified values are equal
Be FUS	0.018 %	Be FUSA	0.019 %	Equal Variance ( $p=0.411$ )	0.029	Reject $H_0$ ; certified values are not equal



Method	Certified value	Method	Certified Value	F-test Outcome	p-value (test)	t-test Outcome
Pb FUS	0.036 %	Pb FUSA	0.035 %	Equal Variance (p=0.367)	0.35	Accept H <sub>0</sub> ; certified values are equal
Ga 4A_MICP	0.004 %	Ga FUSA	0.004 %	Unequal Variance (p=0.047)	0.292	Accept H <sub>0</sub> ; certified values are equal
Zn 4A_MICP	0.158 %	Zn FUSA	0.162 %	Equal Variance (p=0.345)	0.456	Accept H <sub>0</sub> ; certified values are equal

**Table 4.** Comparison of the mean values for different elements in which three different analytical methods are used to determine their concentration.

Method	Element/Oxide	Grand Mean	Units	ANOVA p-value	Outcome
4A_MICP	Rb	1098	ppm	0.15	Accept H <sub>0</sub> , means are equal
FUS	Rb	1168	ppm		
FUS A	Rb	1223	ppm		
4A_MICP	Tl	9.(1)	ppm	0.49	Accept H <sub>0</sub> , means are equal
FUS	Tl	8.(8)	ppm		
FUS A	Tl	9.(4)	ppm		
FUS	Al <sub>2</sub> O <sub>3</sub>	18	ppm	0.41	Accept H <sub>0</sub> , means are equal
XRF	Al <sub>2</sub> O <sub>3</sub>	18	ppm		
FUS A	Al <sub>2</sub> O <sub>3</sub>	17	ppm		

### 3. Intended Use

AMIS0631 is a matrix matched Certified Reference Material, fit for use as a control sample in routine assay laboratory quality control when inserted within runs of test samples and measured in parallel to test samples. This material can also be used for method development, use as independent calibration verification check standard (*i.e.* if not used as a calibration standard in an instrument calibration), or for validation of accuracy in a method validation exercise (see Appendix 3). The recommend procedure for the use of this CRM as a control standard in laboratory quality control is to develop a Shewhart chart, where a mean value and corresponding 1, 2 and 3 standard deviations are derived from replicate measurements of the CRM (see Appendix 6). This CRM can also be used to assess inter-laboratory or instrument bias and establish within-laboratory precision and within-laboratory reproducibility. The certified concentrations and expanded uncertainty for this material are property values based on an inter-laboratory measurement campaign and reflect consensus results from the laboratories that took part in the exercise.

#### 4. Abbreviations and Symbols

Abbreviations and symbols used in this document are shown in Table 5.

**Table 5.** Abbreviations, symbols and descriptions.

Abbreviation/Symbol	Description
Alpha ( $\alpha$ )	Significance level (denoted by alpha, ' $\alpha$ ') of 0.05 or 5%
ANOVA	Analysis of variance by statistical means
Bq	The becquerel is the SI derived unit of radioactivity.
BIF	Banded iron formation
CRM	Certified reference material
$df$	Degrees of freedom, typically, $n-1$ , or $N-1$
$F_{calc}$	Calculated F statistic from ANOVA or Fisher's test
F-critical or $F_{crit}$	F-critical value from F-distribution table
GOI	Gain on ignition
$H_0$	Null hypothesis
$H_1$	Alternate hypothesis
g/t	Grams per tonne
$k$	Coverage factor, e.g. $k=2$ for 95% level of confidence
LOC	Level of confidence or confidence level
LOD	Limit of detection
LOQ	Limit of quantitation
LOI	Loss on ignition
MS	Mean squares (ANOVA)
MSb	Mean squares between (ANOVA)
MSw	Mean squares within (ANOVA)
$N$	Number of labs
$n$	Number of replicates
$\mu$	Property or certified value of a CRM
$p$	' $p$ -value' a measure of the strength of evidence against $H_0$
P	Total number of data points in ANOVA
ppm	Parts per million. Equivalent to g/t
RSD	Relative standard deviation usually expressed as % at a 68% LOC
Replicates	Replication is the repetition of an experimental condition so that the variability associated with an analysis can be estimated (ASTM E1847)
$s$	Standard deviation
$s_r$	Within laboratory repeatability as derived from ANOVA
$s_s$	Between laboratory standard deviation as derived from ANOVA
SS	Sum of squares in ANOVA
SST	Total variation in ANOVA
SSB	Between group (laboratory) variance
SSW	Within group (laboratory) variance
2s	Two times standard deviation

Abbreviation/Symbol	Description
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

## 5. Uncertified Concentration Values

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

## 6. Units

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

## 7. Analytical and Physical Methods

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

## 8. Origin of Material

The locality is Uis Tin Mine, Namibia. The material is from the V1/V2 pegmatite of the Uis pegmatite Swarm, Cape Cross-Uis pegmatite belt. The material was blended with high grade cassiterite material to obtain the required grade.

## 9. Approximate Mineral and Chemical Composition

The material is pegmatitic or, better yet, granitic. The dominant mineralogy includes:

Plagioclase, orthoclase, perthite, microcline (feldspars), muscovite and quartz. I would say that these minerals make up about 98% of the modal abundance. Accessory mineralogy may include: Apatite, cassiterite, columbite-group minerals, tourmaline, petalite, amblygonite, cookite, beryl, lepidolite, zircon, monazite. Other secondary phases which are generally precipitates in fractures within the pegmatites are Fe-Mn-oxides (some weird mineral that constitutes both Fe and Mn) and calcite. Hematite may also be present in fractures and alteration zones as well as some primary occurrences.

## 10. Quantitative Analysis by X-Ray Diffraction

Both natural and synthetic materials have a specific chemistry and atomic arrangement, known as phases. Phases can be identified and quantified using X-ray diffraction (XRD) which produces a plot of the intensity of X-rays scattered at different angles by crystalline phases in a material. Essentially, an X-ray diffraction pattern is the sum of the diffraction patterns produced by each phase. Simply put, an X-ray diffraction pattern is a fingerprint that allows the identification of what is in a target sample material. Knowledge of the mineral phase composition is useful in method development with techniques such as ICP-OES and XRF as potential matrix effects and spectral interferences can be recognized 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.

The sample was micro milled for 10 minutes, with ethanol as the grinding liquid. The resultant sample was lightly pressed into a back-packed sample holder. These results unvalidated and not certified, they are to be used for informational purposes only. The results from a diffractogram of the material gave the following results:

Table 6. Mineral species identified and quantified two sub-samples of AMIS0631 using Rietveld Refinement.

1. Note that these QXRD results are 'unvalidated' (i.e. assay data were not provided to determine the accuracy of these results).
2. A<sup>2+</sup>=Ca, Cd, Co, Fe, Mg, Mn, Ni, Zn. Siderite was used in these Rietveld refinements. It was assumed that the peak at 37.3°2θ/2.80Å arose from Siderite.
3. Albite was used in these Rietveld refinements. Further work would be required to better define and quantify the Plagioclase mineral.
4. Microcline was used in these Rietveld refinements. Further work would be required to better define and quantify the K-feldspar group mineral.
5. A=Al, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Li, Mg, Mn<sup>2+</sup>, Ni, Zn; Z=Al, B, Fe<sup>3+</sup>, Si. Chamosite was used in these Rietveld refinements. Further work would be required to better define and quantify the Chlorite-group mineral
6. Montmorillonite was used in these Rietveld refinements. Further work would be required to confirm and/or better define the Smectite-group minerals.
7. X=Ba, Ca, Cs, (H<sub>3</sub>O), K, Na, (NH<sub>4</sub>); Y=Al, Cr<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Li, Mg, Mn<sup>2+</sup>, Mn<sup>3+</sup>, V<sup>3+</sup>, Zn; Z=Al, Be, Fe<sup>3+</sup>, Si. Biotite and Muscovite were used in these Rietveld refinements. Further work would be required to confirm and/or better define the mica-group minerals

**Table 6.** Results of XRD analysis.

Mineral	Mineral Composition	Composite
Quartz	SiO <sub>2</sub>	46
Calcite group <sup>2</sup>	A <sub>2+</sub> (CO <sub>3</sub> )	<1
Plagioclase <sup>3</sup>	(Na, Ca) Al(Al, Si)Si <sub>2</sub> O <sub>8</sub>	37
K-feldspar <sup>4</sup>	KAlSi <sub>3</sub> O <sub>8</sub>	11
Chlorite group <sup>5</sup>	A <sub>4-6</sub> Z <sub>4</sub> O <sub>10</sub> (OH, O) <sub>8</sub>	2
Smectite group <sup>6</sup>	Varying Composition	<1
Mica group <sup>7</sup>	XY <sub>2-3</sub> Z <sub>4</sub> O <sub>10</sub> (OH, F) <sub>2</sub>	3
Total		100

*For informational purposes only*

## 11. Health and Safety

The material is a very fine powder coloured very light gray (Corstor 5YR 8/I). Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

## 12. Method of Preparation

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

## 13. Particle Size Determination

The sample has been analysed using a Malvern Mastersizer 2000. Particles are passed through a focused laser beam that scatter light at an angle inversely proportional to their size. The intensity of light is measured and converted to a volume in particle size distribution. The results for this standard are presented in Table 7.

**Table 7.** Particle Size Determination by laser diffraction.

Size (µm)	Vol. Under %	Size (µm)	Vol. Under %	Size (µm)	Vol. Under %
0.1	0	50	96.04	200	99.99
0.25	0	55	96.61	225	100
0.5	1.87	60	97.08	250	100
0.6	3.12	65	97.46	300	100
0.75	5.15	70	97.79	400	100
1	8.67	75	98.06	500	100
2	21.66	80	98.29	600	100
3	31.53	85	98.49	700	100
4	39.15	90	98.67	800	100
5	45.41	95	98.82	900	100
6	50.77	100	98.96	1000	100
7	55.45	105	99.08	1100	100
8	59.58	106	99.1	1200	100
9	63.24	110	99.18	1300	100
10	66.48	115	99.28	1400	100
12	71.94	120	99.36	1500	100
15	78.11	125	99.44	1600	100
18	82.53	130	99.5	1700	100
20	84.78	135	99.57	1800	100
25	88.81	140	99.62	1900	100
30	91.38	150	99.72	2000	100
35	93.13	160	99.8		
40	94.38	170	99.86		
45	95.31	175	99.89		

*For informational purposes only*

## 14. Handling

The material is packaged in Laboratory Packs and Explorer Packs that must be shaken or otherwise agitated before use. The analyte concentrations are quoted on a dry basis; therefore, the user needs to determine the moisture content to convert any obtained assay values to an air-dry basis (see Appendix 7 for an example calculation).

## 15. Storage information

The material should be stored in a cool dry place, in such a way that it does not compromise the integrity of the CRM. The material should be stored in conditions which will ensure it does not absorb moisture.

## 16. Methods of Analysis Requested

The following methods of analysis were requested:

- a) Multi element scan to include all elements especially Li, Sn, Ta, Nb and Rb -Peroxide fusion finished with either ICP-OES or ICP-MS or AAS
- b) Multi element scan to include all elements-4 acid digest finished with either ICP-OES or ICP-MS or AAS
- c) Multi element scan to include all elements especially Li, Sn, Ta, Nb and Rb -Peroxide fusion finished with either ICP-OES or ICP-MS or AAS. NOTE: Kindly digest for longer and use excess acid during the acid leach stage of the process to ensure that the Sn and other elements precipitate are completely in solution.
- d) LOI and all major oxides with XRF finish and/or Peroxide fusion and/or 4 acid digest including HF finished with either ICP-OES or ICP-MS or AAS (Please specify the temperature for LOI)
- e) SG – gas pycnometer
- f) S and C Combustion/LECO
- g) Moisture

## 17. Information Requested of Participating Laboratories

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

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

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

The samples used in this certification process have been selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore, all sources of uncertainty are included in the combined standard uncertainty determination. Initially the data submitted by all the laboratories are subjected to a z-score test, equation [1] to exclude outliers and the remaining

data sets examined for their normality in distribution. This is followed by the exclusion of further outliers as defined by the IUPAC Harmonised Protocol of 1995 in which both Cochran and a Grubbs test are applied until all outliers are identified, equations [2] and [3]. A grand mean and standard deviation is re-calculated using all remaining data (Thompson, 2008; Carr, 2011) (see Appendix 2)

## 19. Two Standard Deviations

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

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

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

## 20. Confidence Interval

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

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

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

## 21. Expanded Uncertainty

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

## 22. Confidence Interval and Expanded Uncertainty

A combined standard uncertainty will be greater than a combined  $CI$ . This is because ANOVA considers the within-lab repeatability (that is repeatability within each lab group) as well as the repeatability between each lab data set. This attends to random variables that contribute to the measurement of uncertainty, during the analysis of the test sample at the participating laboratories. The within-lab repeatability and the between lab repeatability is combined as the square root of the sum of squares of these two values giving a combined standard uncertainty, at a 68% confidence level. Multiplying the combined standard uncertainty by the  $t$ -critical value for  $N-1$ , gives the expanded uncertainty at 95% level of confidence. It is recommended that the procedure described in Appendix 6, "Using the CRM in Quality Control" be used, in setting the limits of the CRM. Table 8 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 8.** Example of replicate assay data in which the *CI*, *2s* and *U* are shown.

<b>Lab No.</b>	<b>Mean Au (g/t)</b>
1	0.268
2	0.273
3	0.270
4	0.288
5	0.274
6	0.256
7	0.263
8	0.258
9	0.288

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

### **23. Participating Laboratories**

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

1. ALS Geochemistry Vancouver
2. Argetest Mineral Processing, R&D and Analysis Services
3. Bureau Veritas Minerals Ultra Trace Pty Ltd
4. Intertek Perth
5. SGS Geosol Laboratories Ltda (Brazil)
6. SGS South Africa
7. Shiva Analyticals India



## 24. Accepted Assay Data

Data from the 7 laboratories used for certification are set out in Table 9.

**Table 9.** Data used to calculate the certified values after removal of outliers.

SG	FUS	XRF	FUS	XRF	FUS	XRF	FUS	XRF	XRF	XRF	FUS	XRF	FUS
SG	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	CaO	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	K <sub>2</sub> O	MnO	Na <sub>2</sub> O	SiO <sub>2</sub>	SiO <sub>2</sub>	SrO
Dimensionless	%	%	%	%	%	%	%	%	%	%	%	%	%
2.72	16.80	17.10	1.23	1.35	0.54	0.50	1.93	2.02	0.04	3.18	68.00	68.02	0.06
2.72	16.65	17.00	1.26	1.36	0.53	0.50	1.93	2.01	0.04	3.22	67.60	68.44	0.06
2.73	16.55	17.10	1.26	1.36	0.52	0.50	1.93	2.03	0.04	3.22	67.40	68.74	0.06
2.79	16.65	17.00	1.26	1.36	0.53	0.49	1.93	2.02	0.04	3.21	67.20	68.66	0.06
2.71	16.65	17.10	1.23	1.35	0.55	0.50	1.93	2.03	0.04	3.19	67.40	68.64	0.06
2.72	16.65	17.10	1.15	1.36	0.51	0.49	1.93	2.02	0.04	3.22	67.20	68.83	0.06
2.73	16.65	17.00	1.29	1.36	0.55	0.50	1.93	2.01	0.04	3.23	67.60	68.79	0.06
2.75	16.55	17.00	1.20	1.36	0.53	0.47	1.93	1.98	0.04	3.23	67.40	68.58	0.06
2.61	17.46	17.50	1.38	1.36	0.48	0.47	2.10	1.97	0.04	3.24	68.27	68.20	0.06
2.68	17.13	17.40	1.34	1.37	0.49	0.47	2.14	2.00	0.04	3.28	68.07	68.30	0.06
2.65	17.15	17.50	1.40	1.36	0.46	0.47	2.15	1.99	0.04	3.26	68.15	68.30	0.06
2.64	17.25	17.50	1.38	1.38	0.48	0.47	2.12	1.99	0.04	3.24	68.28	68.30	0.06
2.71	17.29	17.40	1.42	1.36	0.51	0.47	2.18	1.94	0.04	3.26	68.33	68.20	0.06
2.68	17.15	17.40	1.40	1.37	0.53	0.47	2.21	1.97	0.04	3.24	68.26	68.20	0.06
2.64	17.51	17.40	1.36	1.36	0.50	0.52	2.24	1.97	0.04	3.26	68.11	68.20	0.06
2.68	17.34	17.50	1.40	1.36	0.53	0.50	2.21	1.98	0.04	3.28	68.32	68.30	0.06
2.54	18.62	17.46	1.40	1.38	0.53	0.52	2.10	1.99	0.04	3.22	69.74	68.89	
2.56	18.87	17.42	1.40	1.37	0.53	0.52	2.10	2.01	0.04	3.20	70.60	68.73	
2.54	18.75	17.54	1.40	1.38	0.51	0.51	2.10	2.00	0.05	3.19	69.53	68.82	
2.55	18.63	17.43	1.40	1.37	0.53	0.52	2.10	2.01	0.04	3.20	69.10	68.71	
2.59	18.77	17.33	1.40	1.37	0.51	0.50	2.10	2.00	0.04	3.19	69.32	68.62	
2.53	18.90	17.39	1.40	1.38	0.52	0.51	2.10	2.00	0.04	3.19	68.46	68.84	
2.51	18.72	17.33	1.40	1.37	0.53	0.52	2.10	2.00	0.04	3.21	68.89	68.53	
2.72	18.61	17.37	1.40	1.38	0.56	0.51	2.10	2.01	0.05	3.20	67.18	68.74	
2.70	17.59	19.17		1.41	0.50	0.52		2.02	0.05	3.15		66.28	
2.69	17.74	19.06		1.43	0.56	0.51		2.01	0.05	3.21		66.33	
2.73	17.47	19.09		1.43	0.50	0.52		1.96	0.05	3.17		66.54	
2.69	17.36	19.08		1.44	0.54	0.52		1.99	0.05	3.18		66.37	
2.73	17.44	19.17		1.41	0.51	0.51		1.98	0.05	3.17		66.31	
2.73	17.23	19.04			0.57	0.50		2.00	0.05	3.18		66.36	
2.75	17.36	19.13			0.50	0.51		2.00		3.13		66.27	
2.77	17.06				0.56	0.50		1.99		3.16			
2.75					0.54	0.51		2.13					
2.77					0.53	0.51		2.12					
2.83					0.53	0.53		2.13					
2.80					0.57	0.50		2.11					
2.82					0.54	0.50							
2.84						0.51							
2.78													

**Assay Data (Cont.)**

SG	FUS	XRF	FUS	XRF	FUS	XRF	FUS	XRF	XRF	XRF	FUS	XRF	FUS
SG	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	CaO	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	K <sub>2</sub> O	MnO	Na <sub>2</sub> O	SiO <sub>2</sub>	SiO <sub>2</sub>	SrO
Dimensionless	%	%	%	%	%	%	%	%	%	%	%	%	%
2.72	16.80	17.10	1.23	1.35	0.54	0.50	1.93	2.02	0.04	3.18	68.00	68.02	0.06
2.72	16.65	17.00	1.26	1.36	0.53	0.50	1.93	2.01	0.04	3.22	67.60	68.44	0.06
2.73	16.55	17.10	1.26	1.36	0.52	0.50	1.93	2.03	0.04	3.22	67.40	68.74	0.06
2.79	16.65	17.00	1.26	1.36	0.53	0.49	1.93	2.02	0.04	3.21	67.20	68.66	0.06
2.71	16.65	17.10	1.23	1.35	0.55	0.50	1.93	2.03	0.04	3.19	67.40	68.64	0.06
2.72	16.65	17.10	1.15	1.36	0.51	0.49	1.93	2.02	0.04	3.22	67.20	68.83	0.06
2.73	16.65	17.00	1.29	1.36	0.55	0.50	1.93	2.01	0.04	3.23	67.60	68.79	0.06
2.75	16.55	17.00	1.20	1.36	0.53	0.47	1.93	1.98	0.04	3.23	67.40	68.58	0.06
2.61	17.46	17.50	1.38	1.36	0.48	0.47	2.10	1.97	0.04	3.24	68.27	68.20	0.06
2.68	17.13	17.40	1.34	1.37	0.49	0.47	2.14	2.00	0.04	3.28	68.07	68.30	0.06
2.65	17.15	17.50	1.40	1.36	0.46	0.47	2.15	1.99	0.04	3.26	68.15	68.30	0.06
2.64	17.25	17.50	1.38	1.38	0.48	0.47	2.12	1.99	0.04	3.24	68.28	68.30	0.06
2.71	17.29	17.40	1.42	1.36	0.51	0.47	2.18	1.94	0.04	3.26	68.33	68.20	0.06
2.68	17.15	17.40	1.40	1.37	0.53	0.47	2.21	1.97	0.04	3.24	68.26	68.20	0.06
2.64	17.51	17.40	1.36	1.36	0.50	0.52	2.24	1.97	0.04	3.26	68.11	68.20	0.06
2.68	17.34	17.50	1.40	1.36	0.53	0.50	2.21	1.98	0.04	3.28	68.32	68.30	0.06
2.54	18.62	17.46	1.40	1.38	0.53	0.52	2.10	1.99	0.04	3.22	69.74	68.89	
2.56	18.87	17.42	1.40	1.37	0.53	0.52	2.10	2.01	0.04	3.20	70.60	68.73	
2.54	18.75	17.54	1.40	1.38	0.51	0.51	2.10	2.00	0.05	3.19	69.53	68.82	
2.55	18.63	17.43	1.40	1.37	0.53	0.52	2.10	2.01	0.04	3.20	69.10	68.71	
2.59	18.77	17.33	1.40	1.37	0.51	0.50	2.10	2.00	0.04	3.19	69.32	68.62	
2.53	18.90	17.39	1.40	1.38	0.52	0.51	2.10	2.00	0.04	3.19	68.46	68.84	
2.51	18.72	17.33	1.40	1.37	0.53	0.52	2.10	2.00	0.04	3.21	68.89	68.53	
2.72	18.61	17.37	1.40	1.38	0.56	0.51	2.10	2.01	0.05	3.20	67.18	68.74	
2.70	17.59	19.17		1.41	0.50	0.52		2.02	0.05	3.15		66.28	
2.69	17.74	19.06		1.43	0.56	0.51		2.01	0.05	3.21		66.33	
2.73	17.47	19.09		1.43	0.50	0.52		1.96	0.05	3.17		66.54	
2.69	17.36	19.08		1.44	0.54	0.52		1.99	0.05	3.18		66.37	
2.73	17.44	19.17		1.41	0.51	0.51		1.98	0.05	3.17		66.31	
2.73	17.23	19.04			0.57	0.50		2.00	0.05	3.18		66.36	
2.75	17.36	19.13			0.50	0.51		2.00		3.13		66.27	
2.77	17.06				0.56	0.50		1.99		3.16			
2.75					0.54	0.51		2.13					
2.77					0.53	0.51		2.12					
2.83					0.53	0.53		2.13					
2.80					0.57	0.50		2.11					
2.82					0.54	0.50							
2.84						0.51							
2.78													

**Assay Data (Cont.)**

4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP
Cd	Co	Cs	Cs	Cu	Fe	Ga	Hf	K	K	Mn	Mo	Na
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
4.01	4.06	34.50	31.80	82.64	3800	34.30	1.45	15600	16000	298	0.97	21600
4.10	4.22	33.40	31.60	82.84	3700	33.60	1.41	15200	16000	290	0.96	21300
4.14	4.12	34.10	31.30	85.52	3600	34.30	1.47	15300	16000	284	0.97	21500
3.99	4.12	34.80	30.80	84.60	3700	34.40	1.45	15900	16000	304	1.04	22000
4.12	4.09	33.00	32.60	83.06	3900	33.00	1.42	15900	16000	296	0.91	22100
3.97	3.98	34.10	31.30	84.31	3600	35.80	1.43	15700	16000	304	1.03	21900
4.10	4.08	33.80	31.40	84.19	3900	35.10	1.45	15300	16000	286	0.95	21600
4.13	4.00	34.20	35.10	83.27	3700	34.50	1.47	15700	16000	292	0.98	22000
5.75	4.50	31.41	35.90	85.00	3373	42.40	1.62	16400	17430	269	0.98	23600
5.57	4.60	31.34	36.00	85.00	3448	40.40	1.69	16500	17762	257	0.93	23500
5.35	4.50	31.00	37.50	80.00	3242	41.20	1.51	16600	17845	259	1.10	23000
5.43	4.70	30.95	36.30	80.00	3376	42.20	1.67	16600	17596	260	0.95	22200
5.62	4.30	31.43	34.80	85.00	3585	41.40	1.61	16600	18094	275	1.02	23500
5.77	4.50	30.86	35.10	85.00	3700	42.40	1.67	16700	18343	267	1.00	23400
5.41	4.50	30.89	34.10	85.00	3500	41.00	1.54	16700	18592	265	1.03	23600
5.36	4.30	30.30		80.00	3700	41.40	1.20	16600	18343	294	1.00	23300
5.00	3.74	40.40		80.00	3700	35.40	1.20	16915	17300	276	1.00	23700
5.07	3.46	37.90		81.00	3700	35.40	1.20	16614	17500	286	1.00	23500
4.93	3.48	41.10		80.00	3600	34.60	1.20	16860	17300	262	1.00	23900
5.16	3.44	40.80		80.00	3700	36.20	1.40	16323	17300	280	1.00	23800
5.01	3.52	38.20		82.00	3600	33.10	1.40	17191	17300	258	1.00	23700
4.97	3.44	40.70		83.00	3637	33.90	1.40	17251	17000	274	1.00	23700
5.10	3.55	40.20		81.00	3707	33.40	1.40	16767	17100	292	1.00	23500
5.02	3.49	35.50		83.00	3917	33.70	1.40	17488	17100	276	0.80	23700
		35.90		80.82	3497	35.67	1.50	17680		329	0.80	24347
		34.50		83.64	3917	34.69	1.40	17620		321	0.70	24065
		36.10		82.53	3497	35.00	1.50	17620		326	0.80	24040
		32.70		80.64	3777	34.66	1.30	17590		319	0.70	23758
		34.00		79.59	3567	34.14	1.40	17570		330	0.70	24899
		33.40		79.09	4000	32.75	1.20	17580		333	0.80	24939
		33.40		83.17	3500	33.66	1.30	17650		322	0.80	24298
				80.77	3900	34.31		17450		334		25452
					3800					306.1		25780
					3700					307.8		26090
					3700					303.1		25470
					4000					308.7		25570
					3800					308.3		24720
										307.5		24780
										307.5		24690
										307.8		24650

Assay Data (Cont.)

4A_MICP	FUS	4A_MICP	FUS	FUS	4A_MICP	FUS	4A_MICP	FUS	FUS	4A_MICP	4A_MICP
Ni	Pb	Sb	Sb	Si	Sr	Sr	Tl	Tl	U	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
10.40	350	0.76	0.70	319600	424	430	8.30	8.46	12.20	1550	11.10
10.70	340	0.79	0.80	317720	458	420	8.10	8.08	12.00	1560	10.90
10.60	365	0.73	0.60	316780	425	430	8.20	8.20	11.60	1570	12.10
11.00	366	0.80	0.80	315840	431	440	8.40	8.55	11.90	1580	11.90
10.10	368	0.82	0.80	316780	433	430	8.10	8.28	12.00	1640	11.00
10.40	326	0.76	0.60	315840	428	430	8.40	8.47	12.10	1630	12.00
10.60	403	0.79	0.60	317720	442	420	8.60	8.49	11.60	1580	10.90
10.50	347	0.81	0.80	316780	458	508	8.40	9.20	10.60	1590	10.80
10.59	370	0.64	0.80	313000	468	508	8.89	9.10	15.50	1401	11.68
10.65	380	0.74	0.70	322000	469	508	9.13	9.50	16.00	1395	10.22
10.61	380	0.71	0.80	322000	473	508	8.74	9.10	15.50	1397	10.06
10.29	370	0.74	0.80	323000	475	508	9.03	9.00	16.00	1406	10.56
10.76	370	0.72	0.90	323000	472	508	9.24	9.00	15.50	1477	9.93
10.30	370	0.72	0.50	320869	466	508	9.01	9.20	16.00	1600	9.85
11.25	370	0.65	0.80	319929	472	508	9.13	9.50	15.50	1570	10.01
10.27	370	0.69	0.70	320305	473	480	8.90		16.00	1590	10.10
12.00	348	0.80	1.00	320916	464	476	10.10		13.00	1560	10.00
11.00	350	0.80	1.00	321151	471	482	9.90		13.40	1600	11.00
11.00	344	0.70	1.10	320822	465	485	9.80		13.20	1580	11.00
12.00	336	0.80	1.10	320117	471	488	10.20		13.40	1570	12.00
12.00	353	0.80	1.10	321104	470	474	10.20		13.20	1560	12.00
12.00	345	0.80	1.10	326000	473	479	9.90		13.50	1685	11.00
11.00	338	0.80	0.90	330000	470	491	10.20		13.20	1675	12.00
12.00	343	0.80	1.10	325000	469		9.14		13.40	1648	11.00
10.10				323000			9.16			1654	14.00
10.55				324000			8.94			1709	14.00
10.19				320000			9.32			1645	15.00
10.85				322000			8.86			1664	14.00
9.85				314000			8.66			1688	15.00
10.67							9.00			1644	15.00
10.39							8.74			1657	15.00
9.92										1643	15.00
										1615	11.00
										1669	10.90
										1687	10.30
										1628	11.00
										1701	8.90
										1609	10.10
										1565	8.70
										1548	9.00
										1600	10.94
										1536	14.06
										1558	13.93
										1605	12.20
										1544	11.92
											12.03
											12.42
											11.93

Assay Data (Cont.)

FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA	FUSA
Nb	Nb <sub>2</sub> O <sub>5</sub>	Rb	Rb <sub>2</sub> O	Ta	Ta <sub>2</sub> O <sub>5</sub>	S	Al <sub>2</sub> O <sub>3</sub>	BaO	Pb <sub>3</sub> O <sub>4</sub>	ZnO	Al	Ba	Be	Ga	Pb	Tl	Zn
ppm	%	ppm	%	ppm	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm
117.00	0.017	1167.40	0.13	156.00	0.019	0.11	16.35	0.0056	0.038	0.20	86655.00	50.00	195.00	38.00	340.00	9.00	1590.00
116.00	0.017	1181.20	0.13	155.00	0.019	0.11	16.45	0.0056	0.040	0.19	87185.00	50.00	204.00	40.00	360.00	9.00	1530.00
115.00	0.016	1189.20	0.13	159.00	0.019	0.12	16.50	0.0056	0.040	0.19	87450.00	50.00	201.00	40.00	360.00	9.00	1520.00
119.00	0.017	1193.50	0.13	160.00	0.020	0.14	16.60	0.0056	0.040	0.19	87980.00	50.00	202.00	38.00	360.00	9.00	1520.00
120.00	0.017	1203.90	0.13	155.00	0.019	0.13	16.50	0.0056	0.038	0.19	87450.00	50.00	200.00	38.00	340.00	9.00	1550.00
120.00	0.017	1193.90	0.13	162.00	0.020	0.11	16.55	0.0056	0.038	0.19	87715.00	50.00	200.00	38.00	340.00	9.00	1550.00
117.00	0.017	1205.50	0.13	156.00	0.019	0.11	16.50	0.0056	0.038	0.19	87450.00	50.00	201.00	40.00	340.00	9.00	1540.00
116.00	0.017	1191.00	0.13	160.00	0.020	0.11	16.55	0.0051	0.040	0.19	87715.00	46.00	202.00	40.00	360.00	9.90	1560.00
145.00	0.021	1260.00	0.14	138.40	0.017	0.10	17.18	0.0052	0.039	0.20	90900.00	47.00	185.00	36.00	358.00	9.80	1600.00
144.00	0.021	1250.00	0.14	135.20	0.017	0.12	17.10	0.0054	0.039	0.20	90500.00	48.00	194.00	36.00	358.00	9.70	1600.00
144.00	0.021	1280.00	0.14	131.80	0.016	0.10	17.31	0.0054	0.039	0.19	91600.00	48.00	190.00	37.00	355.00	9.90	1550.00
146.00	0.021	1240.00	0.14	135.70	0.017	0.10	17.31	0.0052	0.039	0.20	91600.00	47.00	192.00	39.00	357.00	9.70	1600.00
144.00	0.021	1250.00	0.14	136.20	0.017	0.13	16.89	0.0054	0.039	0.19	89400.00	48.00	189.00	39.00	354.00	9.80	1550.00
143.00	0.020	1260.00	0.14	136.50	0.017	0.10	17.01	0.0051	0.040	0.20	90000.00	46.00	191.00	39.00	362.00	9.60	1600.00
144.00	0.021	1270.00	0.14	134.00	0.016	0.10	17.06	0.0054	0.039	0.20	90300.00	48.00	188.00	38.00	358.00	9.70	1600.00
144.00	0.021	1230.00	0.13	131.70	0.016	0.11	17.29		0.039	0.20	91500.00		190.00	37.00	354.00		1600.00
				163.00	0.020	0.11	17.06		0.038	0.21	90300.00		193.00	39.00	341.00		1700.00
				164.00	0.020	0.11	16.99		0.036	0.21	89900.00		192.00	38.00	330.00		1700.00
				163.00	0.020	0.11	16.99		0.038	0.21	89900.00		193.00	39.00	349.00		1700.00
				166.00	0.020	0.11	17.25		0.037	0.21	91300.00		194.00	39.00	333.00		1700.00
				164.00	0.020	0.11	17.14		0.037	0.21	90700.00		196.00	41.00	336.00		1700.00
				165.00	0.020	0.11	17.23		0.036	0.21	91200.00		193.00	41.00	326.00		1700.00
				164.00	0.020		17.04		0.037	0.21	90200.00		194.00	39.00	339.00		1700.00
				165.00	0.020		16.95		0.037	0.21	89700.00		196.00	36.00	335.00		1700.00
										0.21							1670.00
										0.21							1650.00
										0.20							1620.00
										0.20							1610.00
										0.20							1630.00
										0.21							1690.00
										0.21							1680.00
										0.21							1690.00

## **25. Reported Values**

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

## **26. Validation of Accuracy (Trueness)**

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

## **27. Metrological Traceability**

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

## **28. Period of Validity**

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

## **29. Minimum Sample Size**

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

## **30. Availability**

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

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

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

## 32. Legal Notice

This certificate and the reference material described in it have been prepared with due care and attention. However, AMIS, Makhosi Khoza, 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 v0.02:** 14 May 2020

**Version:** v0.02

**Reason for Version v0.02:** Correction of conversion factor for Li<sub>2</sub>O FUSA value on appendix one.

**Version v0.02 replaces previous versions of AMIS0631 Certification**

**Date of Version v0.01:** 19 December 2019

**Version:** v0.01

**Reason for Version v0.01:** Addition of a new certified method i.e. FUSA

**Version v0.01 replaces the original report of AMIS0631 Certification**

**Date of Version 000:** 21 May 2019

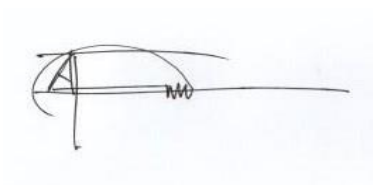
**Version:** 000

**Approving Officer:**

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

**Melesha Gopi Mungaroo (Technical Manager)**

**Certifying Officer:**



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

**Allan Fraser**

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

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# Appendices

## Appendix 1: Uncertified Element Statistics

Uncertified element statistics are shown in **Table 10**.

**Table 10.** Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	4A_MICP	22	0.5	0.04	9	ppm
Al	4A_MICP	16	77171.1	13301.2	17	ppm
As	FS_ICPMS <sup>12</sup>	7	7.7	0.5	6	ppm
As	FUS	5	100.0	*	*	ppm
As	FUSA	5	10.0	*	*	ppm
B	FUS	7	80.0	*	*	ppm
B	FUSA	7	56.4	16.4	29	ppm
Ba	4A_MICP	24	41.1	7.8	19	ppm
BaO	XRF	8	0.02	*	*	%
Be	4A_MICP	32	191.7	36.0	19	ppm
Bi	FUSA	16	2.4	0.4	16	ppm
C	Combustion/LECO <sup>13</sup>	24	845.8	237.3	28	ppm
Ca	FUSA	24	10462.5	937.2	9	ppm
CaO	FUSA	24	1.5	0.1	9	%
Cd	FUSA	8	5.0	*	*	ppm
Ce	4A_MICP	8	0.3	0.05	14	ppm
Ce	FUS	10	0.4	0.1	23	ppm
Ce	FUSA	4	0.5	*	*	ppm
Co	FS_ICPMS	5	4.5	0.2	4	ppm
Co	FUS	4	8.9	7.4	84	ppm
Co	FUSA	2	20.0	*	*	ppm
Cr	FUS	16	100.0	*	*	ppm
Cr	FUSA	8	100.0	*	*	ppm
Cr <sub>2</sub> O <sub>3</sub>	XRF	11	0.01	0.003	27	%
Cs	FUSA	16	36.1	3.5	10	ppm
Cu	FS_ICPMS	8	80.0	5.3	7	ppm
Cu	FUS	15	80.9	4.0	5	ppm
Cu	FUSA	16	94.4	8.9	9	ppm
Dy	4A_MICP	16	0.1	0.02	20	ppm
Dy	FUS	17	0.1	0.02	19	ppm
Er	FUS	6	0.05	0.04	89	ppm
Eu	FUS	2	0.1	0.04	64	ppm
Fe	4A_MICP	16	3281.4	369.2	11	ppm
Fe	FS_ICPMS	8	3475.0	237.5	7	ppm
Fe	FUSA	24	3750.0	725.3	19	ppm
Fe <sub>2</sub> O <sub>3</sub>	FUSA	24	0.5	0.1	19	%
FeO	XRF	8	0.02	*	*	%
Ga	FUS	15	35.0	0.8	2	ppm
Gd	4A_MICP	8	0.1	*	*	ppm
Gd	FUS	18	0.1	0.02	25	ppm
Ge	4A_MICP	8	5.7	0.2	3	ppm
Ge	FUS	8	5.9	0.4	6	ppm
Hf	FUS	8	2.6	0.1	5	ppm
Hf	FUSA	8	2.5	0.05	2	ppm
Ho	FUS	7	0.01	*	*	ppm
In	FUSA	7	0.4	0.08	20	ppm
K	FS_ICPMS	7	16628.6	468.0	3	ppm
K	FUSA	16	16443.8	637.9	4	ppm
K <sub>2</sub> O	FUSA	23	2.1	0.3	13	%
La	4A_MICP	8	0.2	*	*	ppm
La	FUS	15	0.2	0.1	32	ppm
La	FUSA	8	0.3	0.07	22	ppm
Li	FUSA	24	2946.2	366.7	12	ppm
Li <sub>2</sub> O	FUSA	24	0.63	0.08	12	%
Mg	4A_MICP	8	592.2	15.6	3	ppm
Mg	FUS	37	581.6	73.3	13	ppm
Mg	FUSA	16	528.8	102.8	19	ppm
MgO	FUS	37	0.1	0.01	13	%
MgO	FUSA	16	0.09	0.02	19	%
MgO	XRF	39	0.1	0.01	12	%
Mn	FUS	16	343.8	62.2	18	ppm
Mn	FUSA	16	355.0	63.6	18	ppm
MnO	FUS	16	0.05	0.01	16	%
MnO	FUSA	16	0.05	0.008	18	%
Mo	FUS	8	6.5	3.9	60	ppm
Moisture	Moisture <sup>14</sup>	8	0.4	0.1	26	%
Na <sub>2</sub> O	4A_MICP	8	3.1	0.05	2	%
Nb	4A_MICP	15	81.8	4.2	5	ppm
Nb	FUS	16	92.4	26.5	29	ppm
Nd	4A_MICP	8	0.1	0.02	21	ppm
Nd	FUS	21	0.2	0.1	31	ppm
Nd	FUSA	6	0.2	0.1	68	ppm
Ni	FS_ICPMS	8	25.0	9.3	37	ppm
Ni	FUS	7	25.7	5.3	21	ppm
Ni	FUSA	6	26.7	8.2	31	ppm
P	4A_MICP	24	8368.2	730.3	9	ppm
P	FUS	8	8100.0	*	*	ppm
P	FUSA	8	7862.5	51.8	0.7	ppm
P <sub>2</sub> O <sub>5</sub>	FUS	8	1.8	0.04	2	%
P <sub>2</sub> O <sub>5</sub>	XRF	31	1.9	0.2	9	%
Pb	4A_MICP	16	362.5	50.1	14	ppm
Pb	FS_ICPMS	7	313.7	3.0	1	ppm
Pr	4A_MICP	8	0.04	0.01	26	ppm
Pr	FUS	13	0.1	0.02	32	ppm
Re	FUS	1	0.01	*	*	ppm
S	4A_MICP	16	0.1	0.01	6	%
S	Combustion/LECO	24	0.1	0.02	14	%
S	FUS	15	0.1	0.01	11	%
Sb	FUSA	8	0.7	0.06	9	ppm
Si	FUSA	16	319500.0	4531.4	1	ppm
SiO <sub>2</sub>	FUSA	7	68.5	0.3	0.5	%
Sm	FUS	3	0.1	0.02	25	ppm
Sn	4A_MICP	8	188.9	1.0	1	ppm
Sn	FUSA	16	3417.3	129.9	4	ppm
SnO <sub>2</sub>	XRF	15	0.5	0.01	1	%
SO <sub>3</sub>	XRF	16	0.2	0.04	16	%
Sr	FUSA	16	459.9	33.7	7	ppm
SrO	XRF	8	0.1	*	*	%
Ta	4A_MICP	16	49.2	24.9	51	ppm
Ta <sub>2</sub> O <sub>5</sub>	XRF	8	0.02	0.001	2	%
Tb	FUS	5	0.01	*	*	ppm
Te	4A_MICP	8	0.1	*	*	ppm
Te	FUSA	1	1.0	*	*	ppm
Th	4A_MICP	16	0.4	0.1	22	ppm
Th	FUS	16	0.5	0.1	14	ppm
Th	FUSA	7	0.5	*	*	ppm
Ti	4A_MICP	16	81.2	19.5	24	ppm
Ti	FUS	10	74.0	15.1	20	ppm
Ti	FUSA	8	262.5	226.4	86	ppm
TiO <sub>2</sub>	FUS	16	0.02	0.01	52	%
TiO <sub>2</sub>	FUSA	8	0.02	0.005	26	%
TiO <sub>2</sub>	XRF	28	0.02	0.004	26	%
Tm	FUS	3	0.02	0.01	69	ppm
U	4A_MICP	16	11.6	2.0	17	ppm
U	FUSA	16	13.1	0.3	3	ppm
V	4A_MICP	24	2.6	0.8	30	ppm
V	FUS	7	3.4	0.5	16	ppm
W	4A_MICP	16	2.6	0.6	21	ppm
W	FUS	16	2.8	0.2	7	ppm
W	FUSA	9	3.2	0.7	21	ppm
Y	4A_MICP	16	0.4	0.1	22	ppm
Y	FUS	21	0.5	0.1	13	ppm
Y	FUSA	7	0.6	0.2	29	ppm
Yb	4A_MICP	8	0.1	0.03	38	ppm
Yb	FUS	8	0.04	0.02	42	ppm
Zn	FS_ICPMS	7	1480.0	25.2	2	ppm
Zn	FUS	16	1499.4	113.4	8	ppm
Zr	FUS	8	18.8	1.8	10	ppm
Zr	FUSA	8	14.3	0.7	5	ppm
ZrO <sub>2</sub>	XRF	8	0.02	*	*	%

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

Appendix 2 through 9, prepared by Allan Fraser.

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

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

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

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

### Z-Score

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

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

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

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

(Thompson & Lowthian, 2011)

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

### Cochran's Test

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

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

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

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

### Grubbs Test

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

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

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

### Method Performance

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

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

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

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

where  $s$  is the standard deviation of  $n$  replicates.

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

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

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

### Grand Mean

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

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

### Certified Value

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

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

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

### Total Variation (SST)

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

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

### Between Group Variation (SSB)

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

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

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

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

### Within Group Variation (SSW)

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

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

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

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

From equations [9] through [13], the ANOVA table as shown in Table 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 9, or from MS Excel as =TINV (5%,  $df$ )).

### Uncertainty Statement

Typically, an uncertainty statement is presented as follows: Au =0.77±0.04 g/t, where the number following the symbol ± is the numerical value of an expanded uncertainty,  $U = ku_c$ , with  $U$  determined from a combined standard uncertainty multiplied by a coverage factor  $k = 2$  or, a t-critical value for  $N-1$  accepted laboratories. Since it can be assumed that the possible estimated values of the standard are approximately normally distributed with standard uncertainty,  $u_c$ , the certified value of the CRM is believed to lie in the interval defined by  $U$  with a level of confidence of approximately 95 %, e.g. a mean value of 0.77±0.04g/t will have intervals of: 0.73≤0.77≤0.81 g/t.

### Appendix 3. Example: Comparison of Mean and Certified Value for Validation of Accuracy

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

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

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

Where,  $t_{calc}$  is the calculated t-statistic,  $\bar{x}$  the mean of  $n$  replicates with a standard deviation of  $s$  for a CRM of  $\mu$  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 9, page 34) which is  $>0.84$ . Similarly, the  $p$ -value=0.43 which is  $>0.05$ . This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known, the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

#### Appendix 4. Two-standard Deviations

Two-standard deviations are calculated using the expression:

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

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

#### Appendix 5. Confidence Interval

Confidence interval is calculated as:

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

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

#### Appendix 6. Using the CRM in Quality Control

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

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

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

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

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

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

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

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

Since AMIS certified analyte values are reported on a dry-basis, the user laboratory is required to dry a portion (accurately weigh out 1.0 grams in duplicate) of the CRM material in air at 105°C in a drying oven to constant mass to determine the moisture content. Use a crucible with a flat inner surface with a surface area not smaller than 10 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 8. Example of Determination of LOD and LOQ in Fire Assay

The limit of detection (LOD) is the minimum detectable quantity of the analyte of interest (Skoog & West, 1985). To determine the LOD in fire assay by lead collection, the minimum mass that an assay microbalance is capable of weighing ( $m$  in micrograms, and the original test sample mass,  $Mass_{assay}$  in grams) determines the LOD. The smallest prill mass most assay microbalances can measure is  $1\mu\text{g}$  or  $0.001\text{mg}$ . 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
$\geq\text{LOQ}$	Report assay result

**Appendix 9.** 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.

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

**End of certificate**