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Certificate

AMIS0633

Certified Reference Material

Copper Tails, Kalumbila Minerals, Zambia.

Certificate of Analysis

AMIS

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Summary Statistics

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

Analyte	Method	Certified (μ) ⁸	(2s) ¹⁰ \pm	Unit
Cu	4A_MICP ¹	1219	65	ppm
Cu	FUS ²	1191	164	ppm
Co	4A_MICP	301	15	ppm
Co	FUS	317	43	ppm
Au	Pb Collection ³	0.012	0.0054	g/t
LOI	LOI ⁴	6.77	0.14	%
SG	SG ⁵	2.86	0.13	Dimensionless
C	Combustion/LECO ⁶	2.69	0.23	%
S	Combustion/LECO	1.91	0.070	%
S	4A_MICP	1.93	0.081	%
S	FUS	1.93	0.21	%
Al	4A_MICP	6.97	0.23	%
Al	FUS	8.04	0.28	%
Ba	4A_MICP	427	18	ppm
Be	4A_MICP	3	0.3	ppm
Bi	4A_MICP	0.9	0.1	ppm
Ca	4A_MICP	3540	174	ppm
Ce	4A_MICP	121	22	ppm
Cr	4A_MICP	214	20	ppm
Cr	FUS	267	69	ppm
Cs	4A_MICP	5	0.5	ppm
Fe	4A_MICP	4.20	0.30	%
Fe	FUS	4.20	0.37	%
Ga	4A_MICP	20	1	ppm
Hf	4A_MICP	4	0.4	ppm
In	4A_MICP	0.06	0.01	ppm
K	4A_MICP	2.98	0.14	%
K	FUS	3.04	0.30	%
La	4A_MICP	47	12	ppm
Li	4A_MICP	29	4	ppm
Mg	4A_MICP	1.83	0.093	%
Mn	4A_MICP	138	12	ppm
Mn	FUS	152	16	ppm
Mo	4A_MICP	10	1	ppm
Na	4A_MICP	1587	51	ppm
Nb	4A_MICP	6	0.9	ppm
Ni	4A_MICP	128	7	ppm
Ni	FUS	132	12	ppm
P	4A_MICP	498	9	ppm
Pb	4A_MICP	65	7	ppm
Rb	4A_MICP	161	14	ppm
Sb	4A_MICP	1	0.6	ppm
Sc	4A_MICP	12	1	ppm
Sn	4A_MICP	2	0.2	ppm
Sr	4A_MICP	33	3	ppm
Ta	4A_MICP	0.6	0.3	ppm
Tb	4A_MICP	0.8	0.1	ppm
Th	4A_MICP	19	2	ppm
Ti	4A_MICP	2342	94	ppm
Ti	FUS	3367	141	ppm
Tl	4A_MICP	1	0.07	ppm
U	4A_MICP	11	0.3	ppm
V	4A_MICP	125	14	ppm
W	4A_MICP	2	0.5	ppm
Y	4A_MICP	12	2	ppm
Yb	4A_MICP	1	0.3	ppm
Zn	4A_MICP	90	13	ppm
Zr	4A_MICP	126	3	ppm

Major Oxides
Certified Concentrations (at two Standard Deviations)

Analyte	Method	Certified (μ) ⁸	(2s) ¹⁰ \pm	Unit
Al ₂ O ₃	FUS	15.19	0.54	%
Al ₂ O ₃	XRF ⁷	15.35	0.42	%
CaO	XRF	0.49	0.01	%
Cr ₂ O ₃	FUS	0.039	0.01	%
Cr ₂ O ₃	XRF	0.036	0.01	%
Fe ₂ O ₃	FUS	6.01	0.53	%
Fe ₂ O ₃	XRF	6.06	0.19	%
K ₂ O	FUS	3.66	0.36	%
K ₂ O	XRF	3.64	0.034	%
MgO	FUS	3.18	0.25	%
MgO	XRF	3.22	0.10	%
MnO	FUS	0.020	0.002	%
P ₂ O ₅	XRF	0.12	0.003	%
SiO ₂	FUS	62.22	5.0	%
SiO ₂	XRF	62.69	0.60	%
SO ₃	XRF	4.66	0.42	%
TiO ₂	FUS	0.56	0.02	%
TiO ₂	XRF	0.57	0.02	%

1. Certified Concentrations and Uncertainties

AMIS0633 is a new standard material, developed and certified in May 2019. Table 1 gives the certified concentrations, confidence interval, combined and expanded uncertainty for the certified reference material. Table 2 shows the certified major oxides concentrations, two standard deviations, confidence interval, combined and expanded uncertainty.

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

Analyte	Method	Certified (μ) ⁸	N	n	k	% RSD	(u_c) ⁹	(2s) ¹⁰ ±	(CI) ¹¹ 95%	(U) ¹² ±	Unit
Cu	4A_MICP ¹	1219	4	31	3.182	3	33	65	28	103	ppm
Cu	FUS ²	1191	2	16	12.71	7	82	164	729	1042	ppm
Co	4A_MICP	301	3	24	4.303	2	7	15	16	32	ppm
Co	FUS	317	2	16	12.71	7	22	43	191	276	ppm
Au	Pb Collection ³	0.012	4	30	3.182	23	0.0027	0.0054	0.0030	0.01	g/t
LOI	LOI ⁴	6.77	5	40	2.776	1	0.071	0.14	0.075	0.2	%
SG	SG ⁵	2.86	3	22	4.303	2	0.067	0.13	0.17	0.3	Dimensionless
C	Combustion/LECO ⁶	2.69	5	40	2.776	4	0.12	0.23	0.143	0.3	%
S	Combustion/LECO	1.91	5	39	2.776	2	0.035	0.070	0.041	0.1	%
S	4A_MICP	1.93	4	31	3.182	2	0.041	0.081	0.049	0.1	%
S	FUS	1.93	2	16	12.706	6	0.11	0.21	0.95	1	%
Al	4A_MICP	6.97	3	22	4.303	2	0.11	0.23	0.15	0.5	%
Al	FUS	8.04	4	32	3.182	2	0.14	0.28	0.12	0.4	%
Ba	4A_MICP	427	3	23	4.303	2	9	18	20	38	ppm
Be	4A_MICP	3	4	30	3.182	6	0.2	0.3	0.2	0.5	ppm
Bi	4A_MICP	0.9	3	24	4.303	8	0.07	0.1	0.1	0.3	ppm
Ca	4A_MICP	3540	4	30	3.182	2	87	174	68	277	ppm
Ce	4A_MICP	121	2	16	12.71	9	11	22	97	138	ppm
Cr	4A_MICP	214	3	24	4.303	5	10	20	20	43	ppm
Cr	FUS	267	3	24	4.303	13	34	69	85	148	ppm
Cs	4A_MICP	5	3	24	4.303	5	0.2	0.5	0.6	1	ppm
Fe	4A_MICP	4.20	3	24	4.303	4	0.15	0.30	0.35	0.6	%
Fe	FUS	4.20	3	24	4.303	4	0.18	0.37	0.44	0.8	%
Ga	4A_MICP	20	3	23	4.303	3	0.6	1	1	3	ppm
Hf	4A_MICP	4	3	23	4.303	5	0.2	0.4	0.4	0.8	ppm
In	4A_MICP	0.06	2	15	12.71	5	0.003	0.01	0.008	0.04	ppm
K	4A_MICP	2.98	4	31	3.182	2	0.068	0.14	0.080	0.2	%
K	FUS	3.04	3	24	4.303	5	0.15	0.30	0.36	0.6	%
La	4A_MICP	47	3	24	4.303	13	6	12	15	26	ppm
Li	4A_MICP	29	3	24	4.303	7	2	4	4	8	ppm
Mg	4A_MICP	1.83	3	23	4.303	3	0.046	0.093	0.052	0.2	%
Mn	4A_MICP	138	3	24	4.303	5	6	12	15	27	ppm
Mn	FUS	152	3	24	4.303	5	8	16	20	35	ppm
Mo	4A_MICP	10	3	24	4.303	6	0.6	1	1	3	ppm
Na	4A_MICP	1587	3	22	4.303	2	26	51	57	111	ppm
Nb	4A_MICP	6	3	24	4.303	7	0.4	0.9	1.0	2	ppm
Ni	4A_MICP	128	4	31	3.182	3	4	7	4	12	ppm
Ni	FUS	132	2	16	12.706	4	6	12	42	74	ppm
P	4A_MICP	498	3	22	4.303	1	4	9	10	19	ppm
Pb	4A_MICP	65	4	32	3.182	6	4	7	5	12	ppm
Rb	4A_MICP	161	2	16	12.706	4	7	14	60	89	ppm
Sb	4A_MICP	1	2	16	12.706	24	0.3	0.6	3	4	ppm
Sc	4A_MICP	12	3	24	4.303	6	0.7	1	2	3	ppm
Sn	4A_MICP	2	3	23	4.303	5	0.09	0.2	0.2	0.4	ppm
Sr	4A_MICP	33	4	32	3.182	4	1	3	2	4	ppm
Ta	4A_MICP	0.6	3	24	4.303	30	0.2	0.3	0.4	0.7	ppm
Tb	4A_MICP	0.8	3	24	4.303	8	0.06	0.1	0.1	0.3	ppm
Th	4A_MICP	19	3	24	4.303	5	0.9	2	2	4	ppm
Ti	4A_MICP	2342	2	16	12.706	2	47	94	260	596	ppm
Ti	FUS	3367	4	31	3.182	2	71	141	62	225	ppm
Tl	4A_MICP	1	2	16	12.706	4	0.04	0.07	0.3	0.4	ppm
U	4A_MICP	11	3	24	4.303	2	0.2	0.3	0.2	0.7	ppm
V	4A_MICP	125	4	32	3.182	5	7	14	10	22	ppm
W	4A_MICP	2	2	16	12.706	14	0.3	0.5	2	3	ppm
Y	4A_MICP	12	3	24	4.303	8	1	2	2	4	ppm
Yb	4A_MICP	1	3	24	4.303	14	0.2	0.3	0.4	0.7	ppm
Zn	4A_MICP	90	3	24	4.303	7	6	13	15	28	ppm
Zr	4A_MICP	126	2	16	12.706	1	2	3	9	22	ppm

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

Analyte	Method	Certified (μ) ⁸	N	n	k	% RSD	(u_c) ⁹	(2s) ¹⁰ ±	(CI) ¹¹ 95%	(U) ¹² ±	Unit
Al ₂ O ₃	FUS	15.19	4	32	3.182	2	0.27	0.54	0.24	0.9	%
Al ₂ O ₃	XRF ⁷	15.35	5	40	2.776	1	0.21	0.42	0.25	0.6	%
CaO	XRF	0.49	4	32	3.182	1	0.005	0.01	0.006	0.02	%
Cr ₂ O ₃	FUS	0.039	3	24	4.303	13	0.005	0.01	0.01	0.02	%
Cr ₂ O ₃	XRF	0.036	4	32	3.182	13	0.005	0.01	0.008	0.02	%
Fe ₂ O ₃	FUS	6.01	3	24	4.303	4	0.26	0.53	0.62	1	%
Fe ₂ O ₃	XRF	6.06	4	32	3.182	2	0.094	0.19	0.15	0.3	%
K ₂ O	FUS	3.66	3	24	4.303	5	0.18	0.36	0.43	0.8	%
K ₂ O	XRF	3.64	4	31	3.182	0	0.017	0.034	0.021	0.05	%
MgO	FUS	3.18	4	32	3.182	4	0.13	0.25	0.18	0.4	%
MgO	XRF	3.22	5	40	2.776	2	0.052	0.10	0.063	0.1	%
MnO	FUS	0.020	3	24	4.303	5	0.001	0.002	0.003	0.005	%
P ₂ O ₅	XRF	0.12	4	28	3.182	1	0.002	0.003	0.002	0.01	%
SiO ₂	FUS	62.22	4	32	3.182	4	2.5	5.0	4.0	8	%
SiO ₂	XRF	62.69	5	38	2.776	0	0.30	0.60	0.34	0.8	%
SO ₃	XRF	4.66	3	24	4.303	4	0.21	0.42	0.52	0.9	%
TiO ₂	FUS	0.56	4	31	3.182	2	0.01	0.02	0.01	0.04	%
TiO ₂	XRF	0.57	5	40	2.776	1	0.008	0.02	0.008	0.02	%

1. 4A_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
2. FUS is Fusion digestion with ICP finish
3. Pb Collection
4. LOI is Loss on Ignition
5. SG is Specific Gravity
6. Combustion/LECO
7. XRF is X-ray Fluorescence
8. The certified value μ , is an unweighted grand mean of the means of N accepted sets of data from different laboratories and n number of test sample replicates. The certified value is traceable to SI units and is reported on a dry basis.
9. 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)
10. Two standard deviations (2s)
11. Confidence interval at 95% level of confidence.
12. Expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (u_c) with a coverage factor (k) found from N-1 degrees of freedom (see Appendix 7 for t-distribution table). Example: $U = 2.36 \times 0.23 = 0.5\%$

2. Statistical Comparison of Means

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

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

Method	Certified value	Method	Certified value	F-Test Outcome	p -value (t-test)	t-test Outcome
Cu FUS	0.119 %	Cu 4A_MICP	0.122 %	Unequal Variance ($p=0.019$)	0.707	Accept H_0 ; certified values are equal
Co FUS	0.032 %	Co 4A_MICP	0.03 %	Equal Variance ($p=0.082$)	0.280	Accept H_0 ; certified values are equal
Al FUS	8.04 %	Al 4A_MICP	6.97 %	Equal Variance ($p=0.408$)	0.001	Reject H_0 ; certified values are <i>not</i> equal
Cr FUS	0.027 %	Cr 4A_MICP	0.021 %	Equal Variance ($p=0.053$)	0.060	Accept H_0 ; certified values are equal
Fe FUS	4.20 %	Fe 4A_MICP	4.20 %	Equal Variance ($p=0.388$)	0.985	Accept H_0 ; certified values are equal
K FUS	3.04 %	K 4A_MICP	2.98 %	Equal Variance ($p=0.06$)	0.451	Accept H_0 ; certified values are equal
Mn FUS	0.015 %	Mn 4A_MICP	0.014 %	Equal Variance ($p=0.363$)	0.078	Accept H_0 ; certified values are equal
Ni FUS	0.013 %	Ni 4A_MICP	0.013 %	Equal Variance ($p=0.194$)	0.234	Accept H_0 ; certified values are equal

Table 3 continued.

Method	Certified value	Method	Certified value	F-Test Outcome	p-value (t-test)	t-test Outcome
Ti FUS	0.337 %	Ti 4A_MICP	0.234 %	Equal Variance ($p=0.489$)	0.001	Reject H_0 ; certified values are <i>not</i> equal
Al ₂ O ₃ FUS	15.19 %	Al ₂ O ₃ XRF	15.35 %	Equal Variance ($p=0.331$)	0.252	Accept H_0 ; certified values are equal
CaO FUS	0.463 %	CaO XRF	0.494 %	Unequal Variance ($p<0.001$)	0.804	Accept H_0 ; certified values are equal
Fe ₂ O ₃ FUS	6.01 %	Fe ₂ O ₃ XRF	6.06 %	Equal Variance ($p=0.07$)	0.726	Accept H_0 ; certified values are equal
K ₂ O FUS	3.66 %	K ₂ O XRF	3.64 %	Unequal Variance ($p<0.001$)	0.828	Accept H_0 ; certified values are equal
MgO FUS	3.18 %	MgO XRF	3.22 %	Equal Variance ($p=0.078$)	0.484	Accept H_0 ; certified values are equal
Ti FUS	0.337 %	Ti 4A_MICP	0.234 %	Equal Variance ($p=0.489$)	0.001	Reject H_0 ; certified values are <i>not</i> equal

Table 4. ANOVA applied to three data sets for the determination of Sulphur by three different methods gives an F-ANOVA p -value of 0.89, which suggests that there is no significant statistical difference between the mean values of the three different methods at a 95% level of confidence. s is the standard deviation.

Method	% S	s
LECO comb.	1.91	0.033
4A_MICP	1.93	0.031
Fus	1.93	0.11
F-ANOVA p -value	0.89	—

3. Intended Use

AMIS0633 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 (α)	Significance level (denoted by alpha, ' α ') of 0.05 or 5%
ANOVA	Analysis of variance by statistical means
Bq	The becquerel is the SI derived unit of radioactivity.
BIF	Banded iron formation
CRM	Certified reference material
df	Degrees of freedom, typically, $n-1$, or $N-1$
F_{calc}	Calculated F statistic from ANOVA or Fisher's test
F-critical or F_{crit}	F-critical value from F-distribution table
GOI	Gain on ignition
H_0	Null hypothesis
H_1	Alternate hypothesis
g/t	Grams per tonne
k	Coverage factor, e.g. $k=2$ for 95% level of confidence
LOC	Level of confidence or confidence level
LOD	Limit of detection
LOQ	Limit of quantitation
LOI	Loss on ignition
MS	Mean squares (ANOVA)
MSb	Mean squares between(ANOVA)
MSw	Mean squares within (ANOVA)
N	Number of labs
n	Number of replicates
μ	Property or certified value of a CRM
p	' p -value' a measure of the strength of evidence against H_0
P	Total number of data points in ANOVA
ppm	Parts per million. Equivalent to g/t
RSD	Relative standard deviation usually expressed as % at a 68% LOC
Replicates	Replication is the repetition of an experimental condition so that the variability associated with an analysis can be estimated (ASTM E1847)
s	Standard deviation
s_r	Within laboratory repeatability as derived from ANOVA
s_s	Between laboratory standard deviation as derived from ANOVA
SS	Sum of squares in ANOVA
SST	Total variation in ANOVA
SSB	Between group (laboratory) variance
SSW	Within group (laboratory) variance

Abbreviation/Symbol	Description
2s	Two times standard deviation
SI	Standard International system of units
t_{calc}	Calculated t statistic from a one-sample, two-tailed t-test
t-critical or t_{crit}	t-critical value at given alpha and degrees of freedom
Tonne	A metric ton, is a unit of mass equaling 1000 kilograms
=TINV(5%, 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 $k=1$
μm	Micron, is an SI derived unit of length equaling 1×10^{-6} of a meter

5. Uncertified Concentration Values

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

6. Units

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

7. Analytical and Physical Methods

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

8. Origin of Material

The material was sourced from the Sentinel Copper Mine owned by Kalumbila Minerals Limited (KML), a First Quantum subsidiary. The Sentinel copper mine is situated on the southern portion of the Trident copper project area. The mine is a stratabound, sediment hosted copper-nickel-cobalt deposit. Sentinel is approximately 150 kilometers west of the town of Solwezi in North Western Province of Zambia.

9. Approximate Mineral and Chemical Composition

The Sentinel copper deposit is a structurally modified sediment hosted copper deposit. Copper mineralisation is hosted within a phyllite package. Copper mineralisation is dominated by chalcopyrite which occurs as fine to coarse disseminations and or veinlets, with extensive zones of pyrite, particularly in the hanging wall, and with pyrrhotite occurring throughout. The copper sulphides are focused in a relatively carbon-rich zone in the center of the phyllite hosted orebody. The host phyllite is very fine grained, with quartz, muscovite, biotite and iron sulphides present.

10. Quantitative Analysis by X-Ray Diffraction

Both natural and synthetic materials have a specific chemistry and atomic arrangement, known as phases. Phases can be identified and quantified using X-ray diffraction (XRD) which produces a plot of the intensity of X-rays scattered at different angles by crystalline phases in a material. Essentially, an X-ray diffraction pattern is the sum of the diffraction patterns produced by each phase. Simply put, an X-ray diffraction pattern is a fingerprint that allows the identification of what is in a target sample material. Knowledge of the mineral phase composition is useful in method development with techniques such as ICP-OES and XRF as potential matrix effects and spectral interferences can be recognised and accounted for. X-ray diffraction is effective in that it allows the identification of different phases of compounds that are identical in chemistry, but have a distinctly different the atoms, e.g. quartz, cristobalite, and glass are all different phases of SiO₂. Where quantitative XRD results do not correspond to results of other analytical techniques, it should be borne in mind that even though the data are quantitative they are meant to be used for indicative purposes in development of other analytical methods. Mineral names may not reflect the actual compositions of minerals identified, but rather the mineral group.

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

1. Note that these QXRD results are 'unvalidated' (i.e. assay data were not provided to determine the accuracy of these results).
2. Where A=Al, Fe²⁺, Fe³⁺, Li, Mg, Mn²⁺, Ni, Zn; Z=Al, B, Fe³⁺, Si. Chamosite was used in this QXRD refinement
3. Where A=Au, Co, Cu, Fe, Mn, Ni, Os, Pd, Pt, Ru; X and Y=As, Bi, S, Sb, Se, Te. Pyrite was used in this QXRD refinement
4. Where X=Ba, Ca, Cs, (H₃O), K, Na, (NH₄); Y=Al, Cr³⁺, Fe²⁺, Fe³⁺, Li, Mg, Mn²⁺, Mn³⁺, V³⁺, Zn; Z=Al, Be, Fe³⁺, Si. Muscovite and Biotite were used in this QXRD refinement

Table 6. Results of XRD analysis.

Mineral	Mineral Composition	Composite
Quartz	SiO ₂	62
Chlorite Group ²	A ₄₋₆ Z ₄ O ₁₀ (OH, O) ₈	3
Pyrite Group ³	AXY	1
Mica Group ⁴	XY ₂₋₃ Z ₄ O ₁₀ (OH,F) ₂	34
Total		100%

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11. Health and Safety

The material is a very fine powder coloured medium dark brown. 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	95.46	200	100
0.25	0	55	96.52	225	100
0.5	1.35	60	97.3	250	100
0.6	2.1	65	97.89	300	100
0.75	3.25	70	98.33	400	100
1	5.19	75	98.66	500	100
2	12.74	80	98.92	600	100
3	19.42	85	99.12	700	100
4	25.17	90	99.29	800	100
5	30.22	95	99.41	900	100
6	34.72	100	99.52	1000	100
7	38.8	105	99.61	1100	100
8	42.57	106	99.62	1200	100
9	46.06	110	99.68	1300	100
10	49.33	115	99.74	1400	100
12	55.28	120	99.8	1500	100
15	62.95	125	99.84	1600	100
18	69.34	130	99.88	1700	100
20	72.98	135	99.91	1800	100
25	80.26	140	99.95	1900	100
30	85.52	150	99.99	2000	100
35	89.3	160	100		
40	92.04	170	100		
45	94.01	175	100		

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14. Handling

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

15. Storage information

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

16. Methods of Analysis Requested

The following methods of analysis were requested:

- a) Au-Pb collection finished with either ICP-OES or ICP-MS or AAS or gravimetric
- b) Multi element scan to include all elements and oxides by Peroxide Fusion
- c) Multi element scan to include all elements and oxides by 4 acid digests with any finish
- d) Cu-Acid soluble
- e) LOI and all major oxides with XRF finish (Please specify the temperature for LOI)
- f) SG – gas pycnometer
- g) S and C Combustion/LECO
- h) Moisture

17. Information Requested of Participating Laboratories

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

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

18. Certification of Mean and Estimation of Measurement Uncertainty

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

19. Two Standard Deviations

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

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

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

20. Confidence Interval

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

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

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

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

23. Participating Laboratories

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

1. ALS Geochemistry Arabia
2. ALS Geochemistry Vancouver
3. Bureau Veritas Minerals Ultra Trace Pty Ltd
4. Intertek Perth
5. Samancor Western Chrome Mine
6. SGS Vancouver (Canada)

24. Accepted Assay Data

Data from the 6 laboratories used for certification are set out in Table 9.

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

4A_MICP	FUS	4A_MICP	FUS	Pb Collection	LOI	SG	Combustion/LECO	Combustion/LECO	4A_MICP	FUS
Cu	Cu	Co	Co	Au	LOI	SG	C	S	S	S
ppm	ppm	ppm	ppm	g/t	%	Dimensionless	ppm	%	%	%
1233	1251	309	301	0.02	6.73	2.90	26300	1.85	1.88	1.82
1237	1229	304	302	0.01	6.71	2.92	26300	1.88	1.87	1.80
1244	1240	309	301	0.01	6.88	2.91	26100	1.87	1.91	1.86
1234	1247	310	303	0.01	6.72	2.95	26100	1.85	1.87	1.87
1242	1268	309	299	0.01	6.79	2.96	26400	1.85	1.88	1.87
1221	1237	310	302	0.01	6.77	2.95	26200	1.87	1.85	1.85
1225	1266	304	304	0.01	6.80	2.85	26800	1.86	1.93	1.86
1219	1245	303	302	0.01	6.80	2.84	26300	1.94	1.88	1.87
1210	1148	302	333	0.01	6.72	2.84	26300	1.96	1.95	2.00
1180	1111	298	333	0.02	6.75	2.85	26400	1.96	1.91	2.00
1180	1136	301	336	0.02	6.67	2.83	26800	1.96	1.92	2.00
1220	1137	305	329	0.01	6.80	2.84	26300	1.95	1.98	2.00
1250	1133	297	339	0.02	6.73	2.83	26500	1.95	1.90	2.00
1170	1129	299	330	0.02	6.80	2.79	26700	1.95	1.94	2.00
1170	1124	304	319	0.01	6.74	2.81	26300	1.95	1.98	2.00
1170	1147	298	336	0.01	6.74	2.81	26500	1.91	1.94	2.00
1190		300		0.01	6.70	2.80	28000	1.94	1.94	
1180		290		0.01	6.70	2.81	28100	1.89	1.94	
1210		290		0.01	6.70	2.81	28100	1.91	1.92	
1250		295		0.01	6.71	2.80	27900	1.95	1.94	
1250		290		0.01	6.70	2.78	28700	1.93	1.95	
1240		290		0.01	6.68	2.79	27900	1.92	1.97	
1280		300		0.01	6.65		28200	1.90	1.98	
1180		300		0.01	6.69		28400	1.95	1.99	
1192				0.01	6.80		25400	1.91	1.98	
1187				0.01	6.82		25600	1.93	1.97	
1239				0.01	6.83		25300	1.91	1.93	
1283				0.01	6.83		25300	1.88	1.93	
1244				0.01	6.83		25600	1.90	1.91	
1229				0.01	6.89		25600	1.92	1.89	
1231					6.87		25900	1.90	1.96	
					6.86		25400	1.94		
					6.86		28100	1.93		
					6.89		28100	1.91		
					6.86		27700	1.93		
					6.80		27700	1.92		
					6.77		28100	1.91		
					6.79		28200	1.92		
					6.79		28300	1.93		
					6.81		28100			

Assay Data (Cont.)

FUS	XRF	XRF	FUS	XRF	FUS	XRF	FUS	XRF	FUS	XRF	FUS	XRF	FUS	XRF	XRF	FUS	XRF
Al ₂ O ₃	Al ₂ O ₃	CaO	Cr ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	Fe ₂ O ₃	K ₂ O	K ₂ O	MgO	MgO	MnO	P ₂ O ₅	SiO ₂	SiO ₂	SO ₃	TiO ₂	TiO ₂
%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
15.15	15.43	0.50	0.04	0.04	6.19	6.12	3.49	3.63	3.12	3.22	0.02	0.12	62.70	62.57	4.49	0.56	0.58
15.15	15.30	0.50	0.04	0.04	6.02	6.14	3.49	3.65	3.11	3.19	0.02	0.12	62.30	61.97	4.42	0.57	0.57
15.10	15.26	0.50	0.04	0.04	6.18	6.12	3.49	3.64	3.08	3.17	0.02	0.12	61.60	62.20	4.42	0.55	0.57
15.00	15.36	0.50	0.04	0.04	5.99	6.12	3.49	3.64	3.05	3.19	0.02	0.12	61.20	62.31	4.42	0.55	0.57
15.20	15.38	0.49	0.04	0.04	6.08	6.10	3.49	3.64	3.08	3.20	0.02	0.12	62.30	62.08	4.43	0.56	0.58
15.10	15.23	0.50	0.04	0.04	6.16	6.10	3.49	3.63	3.11	3.15	0.02	0.12	62.00	62.26	4.40	0.56	0.57
14.40	15.32	0.50	0.04	0.04	6.23	6.09	3.37	3.64	2.90	3.18	0.02	0.12	61.80	62.88	4.40	0.55	0.57
14.95	15.32	0.50	0.04	0.04	6.09	6.11	3.49	3.64	3.03	3.20	0.02	0.12	64.20	62.67	4.40	0.57	0.57
15.27	15.47	0.49	0.04	0.04	6.23	5.92	3.66	3.63	3.10	3.18	0.02	0.12	64.18	62.83	4.81	0.57	0.56
15.25	15.43	0.49	0.04	0.04	6.06	5.93	3.65	3.63	3.10	3.19	0.02	0.12	63.33	62.93	4.79	0.57	0.56
15.42	15.48	0.49	0.04	0.04	6.09	5.93	3.70	3.64	3.13	3.17	0.02	0.12	64.18	62.66	4.76	0.57	0.56
15.44	15.42	0.50	0.04	0.04	6.20	5.95	3.73	3.60	3.15	3.17	0.02	0.12	64.82	62.76	4.72	0.57	0.57
15.40	15.43	0.49	0.04	0.04	6.23	5.88	3.69	3.62	3.13	3.18	0.02	0.12	63.97	62.74	4.79	0.57	0.56
15.42	15.46	0.50	0.04	0.04	6.26	5.90	3.70	3.62	3.13	3.19	0.02	0.12	64.18	62.81	4.75	0.57	0.57
15.55	15.47	0.49	0.04	0.04	6.12	5.91	3.72	3.64	3.15	3.17	0.02	0.12	64.61	62.91	4.81	0.57	0.57
15.30	15.46	0.49	0.04	0.04	6.26	5.93	3.65	3.67	3.10	3.17	0.02	0.12	63.75	62.85	4.71	0.58	0.56
15.29	15.00	0.49	0.03	0.03	5.62	6.11	3.85	3.67	3.22	3.29	0.02	0.12	63.75	62.93	4.80	0.55	0.56
15.00	15.00	0.49	0.04	0.03	5.65	6.12	3.85	3.66	3.20	3.28	0.02	0.12	63.33	63.15	4.79	0.55	0.56
14.96	15.00	0.49	0.03	0.03	5.69	6.12	3.73	3.65	3.18	3.29	0.02	0.12	63.33	62.70	4.80	0.57	0.56
15.29	15.00	0.49	0.03	0.03	5.75	6.11	3.85	3.65	3.23	3.30	0.02	0.12	64.61	62.99	4.82	0.57	0.56
15.27	15.00	0.49	0.03	0.03	5.90	6.09	3.85	3.65	3.18	3.29	0.02	0.12	64.61	62.70	4.77	0.57	0.57
15.36	15.00	0.49	0.03	0.03	5.75	6.10	3.85	3.66	3.23	3.29	0.02	0.12	63.97	63.21	4.79	0.57	0.57
14.96	15.00	0.49	0.03	0.03	5.73	6.11	3.73	3.64	3.13	3.28	0.02	0.12	62.68	62.82	4.78	0.58	0.56
15.40	15.00	0.49	0.03	0.03	5.68	6.11	3.85	3.63	3.23	3.31	0.02	0.12	63.33	62.82	4.80	0.53	0.57
14.87	15.47	0.50		0.04		6.11		3.63	3.35	3.19		0.12	58.19	62.80		0.58	0.57
15.70	15.54	0.50		0.04		6.08		3.62	3.45	3.19		0.12	59.26	62.78		0.57	0.58
15.55	15.49	0.49		0.04		6.06		3.63	3.37	3.19		0.12	58.62	62.87		0.55	0.57
14.93	15.54	0.49		0.04		6.09		3.66	3.27	3.19		0.12	59.26	62.86		0.55	0.57
15.34	15.42	0.49		0.04		6.08		3.65	3.38	3.17			59.05	62.84		0.55	0.57
15.25	15.43	0.49		0.04		6.10		3.61	3.32	3.19			57.34	62.83		0.55	0.57
14.74	15.50	0.49		0.03		6.08		3.64	3.27	3.18			59.48	62.60		0.55	0.57
15.17	15.47	0.50		0.04		6.08			3.18	3.18			59.26	62.80			0.57
	15.50									3.25				62.40			0.55
	15.50									3.27				62.60			0.55
	15.40									3.23				63.00			0.56
	15.40									3.25				62.90			0.56
	15.50									3.26				62.20			0.55
	15.50									3.27				62.80			0.56
	15.40									3.22							0.57
	15.60									3.27							0.55

Assay Data (Cont.)

4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP
Al ppm	Al ppm	Ba ppm	Be ppm	Bi ppm	Ca ppm	Ce ppm	Cr ppm	Cr ppm	Cs ppm	Fe ppm	Fe ppm	Ga ppm	Hf ppm
70374	80295	427	2.60	0.95	3465	115	219	300	4.60	42500	43300	18.74	3.90
71217	80295	426	2.78	0.97	3469	114	219	300	4.60	42500	42100	19.22	3.94
71210	80030	427	2.60	0.96	3508	114	219	300	4.82	43000	43200	19.12	3.93
71012	79500	425	2.65	0.95	3510	114	216	300	4.70	43200	41900	18.71	3.74
70376	80560	424	2.77	0.99	3531	116	220	300	4.79	43000	42500	19.31	3.94
69588	80030	426	2.54	0.89	3584	113	219	300	4.65	43600	43100	19.06	3.81
69760	76320	427	2.71	0.88	3552	113	215	300	4.68	43500	43600	19.19	3.77
69721	79235	423	2.65	0.89	3595	113	223	300	4.66	44000	42600	20.00	3.69
70200	80800	440	2.50	0.80	3500	128	200	269	4.50	40600	43600	20.00	3.80
69000	80700	430	2.50	0.80	3400	129	198	273	4.60	39500	42400	20.00	4.00
69000	81600	440	2.50	0.80	3400	129	198	262	4.50	39800	42600	20.00	4.00
70200	81700	430	2.50	0.90	3600	130	214	264	4.60	41500	43400	20.00	4.00
68200	81500	440	2.50	0.80	3400	131	201	265	4.60	39400	43600	20.00	3.80
68700	81600	440	2.40	0.90	3500	131	207	274	4.40	40700	43800	20.00	4.00
70300	82300	430	2.50	0.80	3600	127	211	261	4.60	41300	42800	20.00	4.00
69100	81000	419	2.40	0.80	3600	128	207	274	4.50	40800	43800	20.20	3.80
67700	80900	420	2.80	0.86	3600		218	225	5.00	41800	39300	20.20	4.18
67500	79400	420	2.80	0.84	3600		226	242	5.00	42100	39500	19.60	4.09
71700	79200	424	2.80	0.84	3500		217	235	5.00	42500	39800	20.40	4.01
70200	80900	425	2.90	0.85	3500		222	231	5.00	42100	40200	20.40	4.10
69700	80800	417	2.80	0.86	3600		209	234	5.00	43200	41300	20.40	4.25
69500	81300	418	2.80	0.88	3700		221	227	5.00	42600	40200	19.80	4.31
	79200	412	2.50	0.88	3600		230	225	5.00	41900	40100	20.20	4.18
	81500		2.50	0.85	3700		202	235	5.00	42700	39700		
	78700		2.50		3400								
	83100		2.60		3500								
	82300		2.60		3700								
	79000		2.60		3600								
	81200		2.70		3500								
	80700		2.80		3500								
	78000												
	80300												

Assay Data (Cont.)

4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP
In ppm	K ppm	K ppm	La ppm	Li ppm	Mg ppm	Mn ppm	Mn ppm	Mo ppm	Na ppm	Nb ppm	Ni ppm	Ni ppm	P ppm
0.06	29666	29000	48.74	27.60	18659	140	155	10.30	1543	6.72	132	136	493
0.06	29698	29000	49.59	27.20	18688	140	155	10.20	1537	6.63	133	134	489
0.06	29983	29000	48.67	27.40	18682	139	155	10.50	1560	6.47	133	133	490
0.06	30120	29000	48.03	27.60	18554	141	155	10.20	1547	6.58	132	141	495
0.06	30106	29000	49.27	27.70	18647	141	155	10.40	1555	6.47	133	133	492
0.06	30389	29000	47.49	26.40	18261	141	155	10.60	1572	6.41	132	139	496
0.06	30461	28000	47.26	26.70	18332	140	155	10.30	1575	6.51	130	137	493
0.07	30763	29000	46.85	27.10	18285	140	155	9.80	1595	6.49	129	132	494
0.06	29100	30400	40.00	30.00	18000	133	143	9.00	1600	6.50	131	138	500
0.06	28800	30300	40.00	31.00	17700	132	146	9.50	1600	6.50	126	132	500
0.06	28700	30700	40.00	30.00	17700	129	143	9.00	1600	6.00	126	127	500
0.06	30000	31000	40.00	30.50	18700	134	144	9.00	1600	6.50	127	127	500
0.06	29500	30600	40.00	31.50	17600	130	141	9.50	1600	6.50	123	125	500
0.06	29800	30700	40.00	30.00	18300	130	144	9.50	1600	6.00	125	129	500
0.06	29600	30900	40.00	31.50	18600	133	141	9.00	1600	6.50	129	128	500
	29200	30300	40.00	30.00	18400	131	142	9.00	1600	6.50	122	126	500
	29400	32000	51.00	28.00	17200	144	159	9.77	1600	5.60	130		500
	29000	32000	51.70	30.00	17600	142	156	9.53	1600	5.80	125		500
	29200	31000	52.10	27.00	18100	142	156	9.60	1600	5.60	130		500
	29000	32000	52.50	28.00	19100	144	160	9.72	1600	6.10	125		500
	29700	32000	52.60	29.00	18500	142	162	9.91	1600	6.00	130		500
	29500	32000	51.80	28.00	18400	142	159	10.00	1600	5.50	130		500
	29900	31000	51.40	27.00	18400	144	156	10.27		6.20	130		
	30500	32000	50.00	27.00		146	159	10.15		5.60	135		
	30200										129		
	29500										126		
	30900										126		
	31100										126		
	30900										125		
	29200										123		
	30100										125		

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS
Pb	Rb	Sb	Sc	Sn	Sr	Ta	Tb	Th	Ti	Ti
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
62.80	156	1.31	11.90	1.90	33.09	0.73	0.71	18.63	2353	3360
63.50	156	1.44	12.50	1.90	33.19	0.73	0.75	18.79	2316	3420
62.50	157	1.50	12.30	1.90	33.04	0.77	0.73	18.29	2350	3300
61.60	158	1.39	12.30	1.80	32.51	0.73	0.73	18.25	2323	3300
62.40	156	1.41	12.10	1.90	32.97	0.70	0.70	18.63	2319	3360
63.00	155	1.46	12.40	1.80	32.88	0.71	0.72	18.46	2291	3360
60.60	155	1.40	12.30	1.80	33.05	0.78	0.70	18.30	2316	3300
61.30	154	1.51	11.90	1.90	32.39	0.69	0.75	18.53	2305	3400
63.00	163	1.00	12.00	2.00	34.00	0.70	0.78	20.00	2400	3400
61.00	169	1.20	12.00	2.00	33.00	0.50	0.76	20.00	2300	3400
64.00	163	1.00	12.00	2.00	33.00	0.50	0.76	20.00	2300	3400
68.00	169	1.00	12.00	2.00	35.00	0.60	0.76	20.00	2400	3400
64.00	166	1.00	12.00	2.00	33.00	0.50	0.76	20.00	2300	3400
62.00	166	1.00	12.00	2.00	34.00	0.50	0.76	20.00	2400	3400
64.00	165	1.00	12.00	2.00	35.00	0.60	0.76	20.00	2400	3400
62.00	162	1.00	12.00	1.80	34.00	0.60	0.74	20.00	2400	3500
70.00			13.00	1.90	31.50	0.31	0.84	18.00		3300
71.00			13.20	1.80	32.00	0.39	0.80	18.70		3300
71.00			12.60	1.80	31.00	0.32	0.83	18.80		3400
69.00			13.20	1.90	31.50	0.37	0.80	18.90		3400
70.00			13.40	1.90	32.00	0.48	0.86	19.00		3400
71.00			13.50	1.90	31.00	0.47	0.87	18.70		3400
70.00			13.50	1.90	31.50	0.48	0.86	18.40		3500
67.00			13.60		31.00	0.43	0.85	18.60		3200
66.10					32.90					3500
62.00					34.00					3400
62.60					32.00					3300
63.40					33.90					3300
64.40					34.80					3300
67.50					34.60					3300
64.00					33.40					3300
64.80					32.90					

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Tl	U	V	W	Y	Yb	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
0.95	10.65	124	1.90	11.72	1.09	89.00	125
0.97	10.45	126	2.00	11.79	1.04	87.00	125
0.96	10.63	125	2.00	11.25	1.10	86.00	126
0.95	10.48	120	2.00	11.34	1.04	89.00	125
0.93	10.49	122	2.00	11.53	1.09	87.00	125
0.95	10.43	122	1.90	11.60	1.02	88.00	124
0.95	10.56	122	2.00	11.25	1.00	86.00	122
0.95	10.28	119	1.90	11.22	1.05	85.00	126
1.00	10.60	121	1.60	13.60	1.30	87.00	128
1.00	10.60	119	1.60	13.80	1.40	86.00	128
1.00	10.70	119	1.60	13.60	1.40	86.00	125
1.00	10.40	121	1.50	13.00	1.25	85.00	125
1.00	10.70	118	1.70	13.20	1.25	85.00	127
1.00	10.40	119	1.70	13.30	1.35	87.00	127
1.00	10.40	120	1.60	13.20	1.20	87.00	123
1.00	10.50	119	1.60	13.20	1.30	84.00	127
	10.52	125		11.70	1.00	100.00	
	10.52	125		11.80	1.00	100.00	
	10.27	120		11.50	1.00	90.00	
	10.70	125		11.50	1.00	95.00	
	10.88	125		12.20	1.10	95.00	
	10.85	130		12.70	1.10	100.00	
	10.60	125		12.60	1.10	95.00	
	10.89	125		12.10	1.10	100.00	
		137					
		136					
		135					
		134					
		135					
		133					
		131					
		136					

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 website.

29. 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.

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

Date of Version 000: 30 May 2019

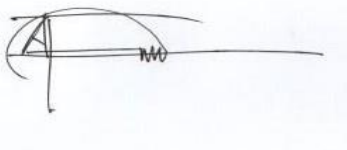
Version: 000

Approving Officer:

African Mineral Standards: _____

Makhosi Khoza (Quality Specialist)

Certifying Officer:

A handwritten signature in black ink, appearing to be 'AF' followed by a stylized flourish.

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	16	0.1	0.01	12	ppm
Al	4A_ICPES	8	72320.8	849.6	1	ppm
As	FUS	7	86.1	36.7	43	ppm
As	4A_MICP	12	3.0	*	*	ppm
B	4A_MICP	8	170.0	10.7	6	ppm
B	FUS	8	161.3	1.9	1	ppm
Ba	FUS	16	423.3	13.4	3	ppm
BaO	XRF	16	0.05	0.02	34	%
Be	FUS	16	3.0	*	*	ppm
Bi	FUS	16	0.9	0.1	10	ppm
Ca	FUS	16	3309.3	999.0	30	ppm
CaO	FUS	16	0.5	0.1	30	%
Cd	4A_MICP	15	0.3	0.03	12	ppm
Cd	FUS	8	0.3	0.1	28	ppm
Ce	FUS	8	107.8	0.9	1	ppm
Co	4A_ICPES	8	292.8	2.0	1	ppm
Cs	FUS	15	4.5	0.2	4	ppm
Cu	CL	8	318.3	5.7	2	ppm
Cu	FS_ICPMS	8	1211.4	9.7	1	ppm
Cu	SAL	16	46.9	4.8	10	ppm
Dy	4A_MICP	16	3.4	0.2	6	ppm
Dy	FUS	8	6.2	0.1	2	ppm
Er	4A_MICP	16	1.3	0.2	16	ppm
Er	FUS	8	3.7	0.1	2	ppm
Eu	4A_MICP	16	1.3	0.03	3	ppm
Eu	FUS	8	1.3	0.03	3	ppm
FeO	FUS	8	6.1	0.04	1	%
Ga	FUS	16	19.2	1.0	5	ppm
Gd	4A_MICP	16	6.3	0.2	3	ppm
Gd	FUS	8	6.7	0.2	3	ppm
Ge	4A_MICP	8	2.4	0.1	5	ppm
Ge	FUS	16	3.0	*	*	ppm
Ho	4A_MICP	16	0.5	0.1	12	ppm
Ho	FUS	8	1.2	0.02	2	ppm
La	FUS	8	46.9	1.1	2	ppm
Li	FUS	15	28.9	2.2	8	ppm
Lu	4A_MICP	14	0.2	0.02	14	ppm
Lu	FUS	8	0.5	0.01	2	ppm
Mg	FUS	37	19940.2	1701.3	9	ppm

Element	Generic Method	n	Mean	SD	RSD %	Unit
Mo	FUS	15	10.7	0.8	7	ppm
Moisture	Moisture	16	0.5	0.1	13	%
Na ₂ O	XRF	28	0.3	0.2	50	%
Nb	FUS	16	13.0	*	*	ppm
Nd	4A_MICP	15	45.2	0.8	2	ppm
Nd	FUS	8	43.1	0.3	1	ppm
P	FUS	7	600.0	*	*	ppm
Pb	FUS	19	72.6	13.1	18	ppm
Pd	Pb Collection	15	0.05	0.002	5	g/t
Pr	4A_MICP	16	12.0	0.1	1	ppm
Pr	FUS	8	11.7	0.2	2	ppm
Pt	Pb Collection	15	0.1	0.004	5	g/t
Rb	FUS	15	152.5	2.0	1	ppm
Re	4A_MICP	8	0.01	0.003	28	ppm
S	4A_ICPES	8	1.9	0.01	1	%
Sb	FUS	16	1.4	0.4	26	ppm
Se	4A_MICP	8	1.4	0.1	10	ppm
Si	FUS	40	299646.7	21371.6	7	ppm
Sm	4A_MICP	16	8.6	0.5	6	ppm
Sm	FUS	8	8.0	0.2	2	ppm
Sn	FUS	7	9.0	*	*	ppm
Sr	FUS	16	38.3	2.2	6	ppm
SrO	XRF	1	0.01	*	*	%
Ta	FUS	16	1.4	0.1	7	ppm
Tb	FUS	8	1.0	0.02	2	ppm
Te	4A_MICP	8	0.1	0.01	10	ppm
Th	FUS	16	17.7	0.6	3	ppm
TiO	FUS	8	0.6	0.01	1	%
Tl	FUS	16	0.9	0.1	10	ppm
Tm	4A_MICP	16	0.2	0.03	17	ppm
Tm	FUS	8	0.5	0.01	1	ppm
U	FUS	16	10.6	0.3	3	ppm
V	FUS	16	134.9	5.4	4	ppm
V ₂ O ₅	XRF	8	0.02	0.01	31	%
W	FUS	8	7.3	2.1	28	ppm
Y	FUS	16	33.7	0.7	2	ppm
Yb	FUS	8	3.6	0.1	2	ppm
Zn	FUS	15	88.0	15.7	18	ppm

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

Appendix 2 through 9, prepared by Allan Fraser.

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

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

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

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

Z-Score

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

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

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

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

(Thompson & Lowthian, 2011)

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

Cochran's Test

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

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

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

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

Grubbs Test

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

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

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

Method Performance

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

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

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

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

where s is the standard deviation of n replicates.

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

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

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

Grand Mean

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

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

Certified Value

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

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

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

Total Variation (SST)

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

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

Between Group Variation (SSB)

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

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

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

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

Within Group Variation (SSW)

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

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

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

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

From equations [9] through [13], the ANOVA table as shown in Table 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 _{crit}
Between Laboratories	SSB	P-1	MSB=SSB/df	MSB/MSW	=FDIST(x,df,df)	F-table
Within Laboratories	SSW	P(n-1)	MSW=SSW/df	–	–	–
Total	SSB+SSW	P-1 + P(n-1)	–	–	–	–

Combined Standard Uncertainty

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

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

Within laboratory repeatability is determined as

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

and, the between laboratory precision as

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

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

Expanded Uncertainty

The expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (u_c) by a coverage factor (k) found from $N-1$ degrees of freedom (df), where N is the number of laboratory means accepted in the establishment of the certified value. The t-critical value for 5% significance can be found in a t-critical table (see Appendix 9, or from MS Excel as =TINV (5%, df)).

Uncertainty Statement

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

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

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

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

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

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

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

Example

A CRM is independently replicated nine times for Al_2O_3 concentration by XRF analysis, *i.e.* 9 individual fused glass beads were prepared. The observed mean and standard deviation of the replicate data are shown with the certified value and expanded uncertainty in Table 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 33) which is >0.84 . Similarly, the p -value=0.43 which is >0.05 . This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known, the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

Appendix 4. Two-standard Deviations

Two-standard deviations are calculated using the expression:

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

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

Appendix 5. Confidence Interval

Confidence interval is calculated as:

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

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

Appendix 6. Using the CRM in Quality Control

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

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

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

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

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

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

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

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

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

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

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

Example

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

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

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

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

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

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

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

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

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

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

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be 0.02g/t . *i.e.* $1\mu\text{g} = 1\text{g/t}$, 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 0.001mg .

Mass Assay Sample (g)	LOD (g/t)	LOQ (g/t)
30	0.03	0.3
50	0.02	0.2
100	0.01	0.1

Table 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 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.

<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