AMIS0643

Certified Reference Material

B2 Gold, Namibia

Certificate of Analysis

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

Table of Contents

List of Tables

List of Appendices

Summary Statistics

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

Analyte	Method	Certified (μ)[8]	(2s)[10] ±	Unit
Au	Pb Collection[1]	0.079	0.018	g/t
Pd	Pb Collection	0.014	0.0028	g/t
C	Combustion/LECO[2]	2	0.1	ppm
S	Combustion/LECO	0.15	0.03	%
S	4A_MICP[3]	0.16	0.01	%
LOI	LOI[4]	7.93	0.48	%
SG	SG[5]	2.76	0.10	Dimensionless
Al	4A_MICP	6.38	0.52	%
Al	FUS[6]	6.20	0.21	%
Be	4A_MICP	1	0.2	ppm
Ca	4A_MICP	5.88	0.17	%
Ca	FUS	5.99	0.69	%
Cd	4A_MICP	1	0.4	ppm
Co	4A_MICP	17	4	ppm
Cr	4A_MICP	116	18	ppm
Cr	FUS	144	17	ppm
Cs	4A_MICP	1	0.1	ppm
Cu	4A_MICP	129	22	ppm
Fe	4A_MICP	5.77	0.19	%
Fe	FUS	5.62	0.20	%
Ga	4A_MICP	17	5	ppm
Hf	4A_MICP	4	1	ppm
K	4A_MICP	4177	403	ppm
La	4A_MICP	31	2	ppm
Mg	FUS	5955	180	ppm
Mn	4A_MICP	818	20	ppm
Mn	FUS	826	26	ppm
Mo	4A_MICP	2	0.7	ppm
Na	4A_MICP	3.48	0.18	%
Ni	4A_MICP	44	7	ppm
Pb	4A_MICP	48	8	ppm
Rb	4A_MICP	24	5	ppm
Sb	4A_MICP	3	0.4	ppm
Sc	4A_MICP	12	1	ppm
Si	FUS	26.30	1.07	%
Sr	4A_MICP	156	6	ppm
Ta	4A_MICP	0.6	0.08	ppm
Te	4A_MICP	0.7	0.3	ppm
Ti	FUS	4235	199	ppm
U	4A_MICP	3	0.1	ppm
V	4A_MICP	158	12	ppm
W	4A_MICP	9	3	ppm
Y	4A_MICP	17	0.7	ppm
Zn	4A_MICP	120	5	ppm
Zr	4A_MICP	137	14	ppm

Major Oxides
Certified Concentrations (at two Standard Deviations)

Analyte	Method	Certified (µ)[8]	(2s)[10] ±	Unit
Al_2O_3	FUS	11.72	0.39	%
Al_2O_3	XRF[7]	12.20	0.16	%
CaO	FUS	8.38	0.97	%
CaO	XRF	8.29	0.14	%
Cr_2O_3	FUS	0.021	0.003	%
Cr_2O_3	XRF	0.020	0.004	%
Fe_2O_3	FUS	8.03	0.29	%
Fe_2O_3	XRF	8.05	0.15	%
K_2O	FUS	0.49	0.03	%
K_2O	XRF	0.49	0.01	%
MgO	FUS	0.99	0.03	%
MgO	XRF	1.03	0.042	%
MnO	FUS	0.11	0.004	%
MnO	XRF	0.11	0.01	%
Na_2O	XRF	4.66	0.11	%
P_2O_5	XRF	0.17	0.01	%
SiO_2	FUS	56.28	2.3	%
SiO_2	XRF	54.84	2.7	%
SO_3	XRF	0.42	0.01	%
TiO_2	FUS	0.71	0.03	%
TiO_2	XRF	0.71	0.02	%

1. Certified Concentrations and Uncertainties

AMIS0643 is a new standard material, developed and certified in June 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
Au	Pb Collection[1]	0.079	10	80	2.262	11	0.0089	0.018	0.0060	0.02	g/t
Pd	Pb Collection	0.014	3	24	4.303	10	0.0014	0.0028	0.0030	0.01	g/t
C	Combustion/LECO[2]	2	5	40	2.776	4	0.07	0.1	0.08	0.2	ppm
S	Combustion/LECO	0.15	8	60	2.365	11	0.02	0.03	0.02	0.04	%
S	4A_MICP[3]	0.16	5	39	2.776	3	0.005	0.01	0.005	0.01	%
LOI	LOI[4]	7.93	5	40	2.776	3	0.24	0.48	0.29	0.7	%
SG	SG[5]	2.76	4	30	3.182	2	0.048	0.10	0.075	0.2	Dimensionless
Al	4A_MICP	6.38	2	16	12.706	4	0.26	0.52	2.3	3	%
Al	FUS[6]	6.20	2	16	12.706	2	0.10	0.21	0.79	1	%
Be	4A_MICP	1	4	31	3.182	9	0.1	0.2	0.2	0.4	ppm
Ca	4A_MICP	5.88	3	22	4.303	1	0.084	0.17	0.14	0.4	%
Ca	FUS	5.99	3	24	4.303	6	0.35	0.69	0.84	1	%
Cd	4A_MICP	1	4	32	3.182	17	0.2	0.4	0.3	0.7	ppm
Co	4A_MICP	17	5	39	2.776	11	2	4	2	5	ppm
Cr	4A_MICP	116	3	24	4.303	8	9	18	22	39	ppm
Cr	FUS	144	2	16	12.706	6	8	17	74	107	ppm
Cs	4A_MICP	1	3	22	4.303	7	0.07	0.1	0.1	0.3	ppm
Cu	4A_MICP	129	5	40	2.776	9	11	22	13	31	ppm
Fe	4A_MICP	5.77	2	16	12.706	2	0.097	0.19	0.85	1	%
Fe	FUS	5.62	4	31	3.182	2	0.10	0.20	0.13	0.3	%
Ga	4A_MICP	17	3	23	4.303	15	3	5	6	11	ppm
Hf	4A_MICP	4	2	16	12.706	14	0.5	1	5	6	ppm
K	4A_MICP	4177	4	32	3.182	5	202	403	311	642	ppm
La	4A_MICP	31	3	23	4.303	3	1	2	2	4	ppm
Mg	FUS	5955	4	30	3.182	2	90	180	52	286	ppm
Mn	4A_MICP	818	2	16	12.706	1	10	20	69	129	ppm
Mn	FUS	826	2	16	12.706	2	13	26	60	167	ppm
Mo	4A_MICP	2	2	15	12.706	16	0.4	0.7	3	4	ppm
Na	4A_MICP	3.48	4	31	3.182	3	0.091	0.18	0.13	0.3	%
Ni	4A_MICP	44	5	39	2.776	8	4	7	4	10	ppm
Pb	4A_MICP	48	5	40	2.776	8	4	8	4	10	ppm
Rb	4A_MICP	24	3	24	4.303	9	2	5	6	9.83	ppm
Sb	4A_MICP	3	3	24	4.303	6	0.2	0.4	0.2	0.8	ppm
Sc	4A_MICP	12	4	32	3.182	5	0.6	1	0.8	2	ppm
Si	FUS	26.30	3	23	4.303	2	0.54	1.07	0.83	2	%
Sr	4A_MICP	156	4	30	3.182	2	3	6	3	10	ppm
Ta	4A_MICP	0.6	2	15	12.706	6	0.04	0.08	0.3	0.5	ppm
Te	4A_MICP	0.7	2	16	12.706	23	0.2	0.3	2	2.14	ppm
Ti	FUS	4235	4	31	3.182	2	99	199	139	316	ppm
U	4A_MICP	3	2	16	12.706	3	0.07	0.1	0.5	0.9	ppm
V	4A_MICP	158	3	24	4.303	4	6	12	13	26	ppm
W	4A_MICP	9	2	16	12.706	15	1	3	12	17	ppm
Y	4A_MICP	17	2	16	12.706	2	0.3	0.7	1	4	ppm
Zn	4A_MICP	120	5	37	2.776	2	2	5	1	7	ppm
Zr	4A_MICP	137	3	24	4.303	5	7	14	16	31	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_2O_3	FUS	11.72	2	16	12.706	2	0.19	0.39	1.0	2	%
Al_2O_3	XRF[7]	12.20	4	32	3.182	1	0.082	0.16	0.12	0.3	%
CaO	FUS	8.38	3	24	4.303	6	0.49	0.97	1.0	2	%
CaO	XRF	8.29	5	40	2.776	1	0.072	0.14	0.087	0.2	%
Cr_2O_3	FUS	0.021	2	16	12.706	6	0.001	0.003	0.01	0.02	%
Cr_2O_3	XRF	0.020	4	32	3.182	10	0.002	0.004	0.001	0.01	%
Fe_2O_3	FUS	8.03	4	31	3.182	2	0.14	0.29	0.19	0.5	%
Fe_2O_3	XRF	8.05	5	40	2.776	1	0.077	0.15	0.090	0.2	%
K_2O	FUS	0.49	2	16	12.706	3	0.01	0.03	0.1	0.2	%
K_2O	XRF	0.49	5	40	2.776	1	0.005	0.01	0.005	0.01	%
MgO	FUS	0.99	4	30	3.182	2	0.02	0.03	0.01	0.05	%
MgO	XRF	1.03	5	40	2.776	2	0.021	0.042	0.024	0.06	%
MnO	FUS	0.11	2	16	12.706	2	0.002	0.004	0.008	0.02	%
MnO	XRF	0.11	4	32	3.182	3	0.003	0.01	0.002	0.01	%
Na_2O	XRF	4.66	5	40	2.776	1	0.055	0.11	0.065	0.2	%
P_2O_5	XRF	0.17	4	32	3.182	2	0.004	0.01	0.006	0.01	%
SiO_2	FUS	56.28	3	23	4.303	2	1.1	2.3	2.0	5	%
SiO_2	XRF	54.84	6	45	2.571	2	1.4	2.7	2.0	3	%
SO_3	XRF	0.42	2	16	12.706	1	0.006	0.01	0.04	0.07	%
TiO_2	FUS	0.71	4	31	3.182	2	0.02	0.03	0.02	0.05	%
TiO_2	XRF	0.71	5	39	2.776	1	0.008	0.02	0.009	0.02	%

1. *Pb Collection*
2. *Combustion/LECO*
3. *4A_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish*
4. *LOI is Loss on Ignition*
5. *SG is Specific Gravity*
6. *FUS is Fusion digestion with ICP finish*
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 (uc) with a coverage factor (k) found from N-1 degrees of freedom (see Appendix 7 for t-distribution table). Example: U = 2.36 x 0.23=0.5%*
13. *The nugget effect is a geostatistical term used to describe the variability seen between samples that are closely spaced. The nugget effect is composed of a geological component, which can be thought of as inherent, and a sampling component, which is not fixed. The geological contribution to the nugget effect is described in terms of geological continuity for quart-gold reefs, kimberlites and placer deposits as these are all subject to a high nugget effect (>50%). The geological nugget effect is attributed to the heterogeneous distribution of grain sizes, grades and small to large scale structures inherent in these deposits*
14. *ANC is Acid Neutralizing Capacity*
15. *MPA is Mycophenolic Acid*
16. *NAGpH is Net Acid Generation pH*
17. *NNP is Net Neutralizing Potential*
18. *NP is Neutralizing Potential*
19. *NPR is Neutralizing Potential Ratio*

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 ≥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
S 4A_MICP	0.164 %	S Combustion/LECO	0.154 %	Unequal Variance *(p=0.004)*	0.150	Accept H_0; certified values are equal
Al_2O_3 XRF	12.2 %	Al_2O_3 FUS	11.72 %	Equal Variance *(p=0.117)*	0.006	Reject H_0; certified values are *not* equal
CaO XRF	8.29 %	CaO FUS	8.38 %	Unequal Variance *(p=0.002)*	0.784	Accept H_0; certified values are equal
Cr_2O_3 XRF	0.020 %	Cr_2O_3 FUS	0.021 %	Equal Variance *(p=0.111)*	0.154	Accept H_0; certified values are equal
Fe_2O_3 XRF	8.05 %	Fe_2O_3 FUS	8.03 %	Equal Variance *(p=0.176)*	0.736	Accept H_0; certified values are equal
K_2O XRF	0.487 %	K_2O FUS	0.491 %	Unequal Variance *(p=0.03)*	0.716	Accept H_0; certified values are equal
MgO XRF	1.03 %	MgO FUS	0.987 %	Unequal Variance *(p=0.047)*	0.008	Reject H_0; certified values are *not* equal
MnO XRF	0.109 %	MnO FUS	0.107 %	Equal Variance *(p=0.484)*	0.066	Accept H_0; certified values are equal
SiO_2 XRF	54.84 %	SiO_2 FUS	56.28 %	Equal Variance *(p=0.19)*	0.171	Accept H_0; certified values are equal
TiO_2 XRF	0.707 %	TiO_2 FUS	0.706 %	Equal Variance *(p=0.101)*	0.927	Accept H_0; certified values are equal
Al FUS	6.20 %	Al 4A_MICP	6.38 %	Equal Variance *(p=0.21)*	0.458	Accept H_0; certified values are equal
Cr FUS	0.014 %	Cr 4A_MICP	0.012 %	Equal Variance *(p=0.551)*	0.037	Reject H_0; certified values are *not* equal
Fe FUS	5.62 %	Fe 4A_MICP	5.77 %	Equal Variance *(p=0.344)*	0.114	Accept H_0; certified values are equal
Mn FUS	0.083 %	Mn 4A_MICP	0.082 %	Equal Variance *(p=0.457)*	0.363	Accept H_0; certified values are equal

3. Intended Use

AMIS0643 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 4.

Table 4. 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 for this standard was sourced from the Otjikoto Gold Mine owned by B2Gold Namibia[13]. The Otjikoto Gold deposit is located within the Damara Mobile Belt, which forms part of the Pan-African Mobile Belt system. The Otjikoto Gold mine is located about 300 km north of Windhoek, in Otjozondjupa province, in Namibia.

9. Approximate Mineral and Chemical Composition

The Otjikoto project is located within the Neoproterozoic Damara mobile belt, which forms part of the Pan–African mobile belt system. The deposit falls under the general classification of an orogenic gold deposit and occurs in a similar stratigraphic position as the Navachab gold mine deposit. The Otjikoto deposit lithology has been divided into three principal mineralized lithostratigraphic units, from top to base, the OTC, OTB, and OTA . The OTC albitite-hornfels unit hosts most of the mineralised vein system and is underlain by a distinct marker horizon, the unmineralised OTB calcitic marble.
Gold in the main Otjikoto deposit is hosted by a north-north-east-striking sheeted sulphide (+ magnetite) –quartz and carbonate vein system. Gold occurs within the vein system as coarse native gold with a size variation from 5microns to 4000 microns. It occurs adjacent to and within sulphides, garnets on the edges of amphiboles and chlorite, as free gold in quartz and carbonates.

10. Quantitative Analysis by X-Ray Diffraction

Both natural and synthetic materials have a specific chemistry and atomic arrangement, known as phases. Phases can be identified and quantified using X-ray diffraction (XRD) which produces a plot of the intensity of X-rays scattered at different angles by crystalline phases in a material. Essentially, an X-ray diffraction pattern is the sum of the diffraction patterns produced by each phase. Simply put, an X-ray diffraction pattern is a fingerprint that allows the identification of what is in a target sample material. Knowledge of the mineral phase composition is useful in method development with techniques such as ICP-OES and XRF as potential matrix effects and spectral interferences can be recognised and accounted for. X-ray diffraction is effective in that it allows the identification of different phases of compounds that are identical in chemistry, but have a distinctly different the atoms, e.g. quartz, cristobalite, and glass are all different phases of SiO_2. Where quantitative XRD results do not correspond to results of other analytical techniques, it should be borne in mind that even though the data are quantitative they are meant to be used for indicative purposes in development of other analytical methods. Mineral names may not reflect the actual compositions of minerals identified, but rather the mineral group.

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

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

The limitations of qualitative XRD analysis are as follows:

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

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

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

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

Table 5. Results of XRD analysis.

Phase	Formula	Composite %
Amorphous Content		23
Calcite	$CaCO_3$	10
Dolomite	$CaMg(CO_3)_2$	1
Expanding clay		3
Goethite	$FeO(OH)$	2
Illite/Muscovite	$K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$	5
Ilmenite	$FeTiO_3$	<1
Kaolin	$Al_2Si_2O_5(OH)_4$	2
Mixed layer clay		2
Pyrite	FeS_2	<1
Quartz	SiO_2	18
Sodium Calcium Plagioclase	$(Na,Ca)(Al,Si)_2Si_2O_8$	33
Total		99 %

For informational purposes only

11. Health and Safety

The material is a very fine powder coloured light brown (Corstor 5YR 6/4). 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 (87% 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 6. Particle Size Determination by laser diffraction.

Size (µm)	Vol. Under %
<45um	86.6
<63um	89.6
<75um	90.9
<90um	92.3
<100um	93.0
<106um	93.4
<150um	96.2

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) Au-Pb collection finished with either ICP-OES or ICP-MS or AAS or gravimetric
b) Multi element scan to include all elements-4-acid total digestion including HF and/or peroxide fusion finished with either ICP-OES or ICP-MS or AAS
c) 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)
d) SG – gas pycnometer
e) S and C Combustion/LECO
f) Moisture
g) Acid Rock Drainage suite:
h) Total Sulfur %
i) Neutralization Potential (kg $CaCO_3$/t)
j) Acid Generating Potential (kg H_2SO_4/t)
k) (NPP) Net-acid potential

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 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 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:

$$Two\ standard\ deviations = 2\ (u_c)$$

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:

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

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 Contro*l" be used, in setting the limits of the CRM. Table 7 below shows mean gold values obtained by fire assay lead collection, for nine different laboratories, the confidence interval, two-standard deviations and expanded uncertainty.

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

Lab No.	Mean Au (g/t)
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

CI	0.0088
2s	0.031
U	0.04

23. Participating Laboratories

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

1. ALS Geochemistry Arabia
2. ALS Geochemistry Ireland
3. ALS Geochemistry Vancouver
4. Argetest Mineral Processing, R&D and Analysis Services
5. Bureau Veritas Adelaide GeoAnalytical Laboratory
6. Bureau Veritas Minerals Ultra Trace Pty Ltd
7. Intertek Perth
8. Performance Laboratories Zimbabwe
9. Ready Lead Assay Laboratory
10. SGS Ankara (Turkey)
11. SGS South Africa
12. SGS South Africa (Pty) Ltd - Barberton
13. SGS Vancouver (Canada)
14. Shiva Analyticals India
15. Super Laboratory Services (Pty) Ltd. Springs

24. Accepted Assay Data

Data from the 15 laboratories used for certification are set out in Table 8.

Table 8. Data used to calculate the certified values after removal of outliers.

FUS	XRF	FUS	XRF	FUS	XRF	FUS	XRF	FUS	XRF	FUS	XRF
Al_2O_3	Al_2O_3	CaO	CaO	Cr_2O_3	Cr_2O_3	Fe_2O_3	Fe_2O_3	K_2O	K_2O	MgO	MgO
%	%	%	%	%	%	%	%	%	%	%	%
11.58	12.18	8.79	8.32	0.02	0.02	8.24	8.13	0.50	0.49	0.97	1.04
11.64	12.21	8.87	8.34	0.02	0.02	8.12	8.16	0.50	0.49	1.00	1.04
11.58	12.21	8.86	8.35	0.02	0.02	8.22	8.15	0.50	0.49	0.99	1.04
11.71	12.18	8.93	8.34	0.02	0.02	8.20	8.13	0.50	0.49	0.98	1.03
11.70	12.20	8.89	8.31	0.02	0.02	8.03	8.10	0.50	0.49	0.96	1.03
11.47	12.20	8.94	8.33	0.02	0.02	7.98	8.13	0.50	0.49	0.96	1.03
11.60	12.18	8.76	8.30	0.02	0.02	8.16	8.09	0.50	0.49	0.99	1.03
11.53	12.17	8.60	8.32	0.02	0.02	7.91	8.12	0.50	0.49	0.98	1.03
12.09	12.31	8.26	8.28	0.02	0.02	8.06	7.96	0.48	0.49	0.99	1.04
11.85	12.29	8.40	8.28	0.02	0.02	8.02	7.97	0.48	0.49	0.98	1.04
11.75	12.34	8.26	8.31	0.02	0.02	8.16	7.99	0.48	0.49	0.99	1.04
11.83	12.28	8.54	8.29	0.02	0.02	8.25	7.97	0.48	0.49	0.99	1.03
11.94	12.26	8.54	8.26	0.02	0.02	8.11	7.90	0.48	0.49	0.98	1.02
11.70	12.35	8.40	8.33	0.02	0.02	8.32	8.02	0.48	0.49	0.99	1.04
11.73	12.34	8.54	8.33	0.02	0.02	8.19	8.01	0.48	0.49	1.01	1.04
11.79	12.32	8.54	8.32	0.02	0.02	7.86	7.98	0.48	0.49	0.99	1.04
	12.10	7.98	8.38		0.02	7.93	8.13		0.49	0.98	1.05
	12.10	7.92	8.40		0.02	7.95	8.15		0.48	0.99	1.03
	12.20	7.88	8.38		0.01	7.92	8.12		0.49	0.99	1.05
	12.10	7.84	8.38		0.02	8.01	8.15		0.49	0.98	1.04
	12.20	7.88	8.39		0.02	7.95	8.11		0.49	0.98	1.05
	12.20	7.98	8.40		0.02	7.93	8.16		0.49	0.98	1.05
	12.20	7.81	8.39		0.02	7.96	8.11		0.48	1.01	1.05
	12.20	7.78	8.40		0.02	8.05	8.14		0.49	0.99	1.07
	12.12		8.24		0.02	7.93	8.05		0.48	0.99	1.00
	12.16		8.23		0.02	7.92	8.01		0.48	0.96	1.01
	12.12		8.25		0.02	7.88	8.04		0.48	0.96	1.01
	12.12		8.24		0.02	7.92	8.01		0.48	0.99	1.01
	12.14		8.24		0.02	7.91	8.03		0.48	1.01	1.01
	12.18		8.24		0.02	7.86	8.02		0.48	1.01	1.00
	12.16		8.24		0.02	7.88	8.05		0.49		1.02
	12.14		8.22		0.02		8.04		0.48		1.01
			8.22				8.02		0.49		1.01
			8.22				7.97		0.49		1.00
			8.22				8.01		0.49		1.01
			8.23				8.00		0.48		1.00
			8.18				7.96		0.48		0.99
			8.25				8.08		0.48		1.00
			8.19				7.98		0.48		1.00
			8.21				8.01		0.48		1.01

Assay Data (Cont.)

FUS	XRF	XRF	XRF	FUS	XRF	XRF	FUS	XRF
MnO	MnO	Na_2O	P_2O_5	SiO_2	SiO_2	SO_3	TiO_2	TiO_2
%	%	%	%	%	%	%	%	%
0.11	0.11	4.64	0.17	56.30	55.74	0.41	0.72	0.70
0.11	0.11	4.66	0.17	56.70	55.90	0.41	0.72	0.71
0.11	0.11	4.68	0.17	56.20	55.95	0.42	0.73	0.70
0.11	0.11	4.66	0.17	56.70	55.84	0.41	0.71	0.71
0.10	0.11	4.65	0.17	56.60	55.85	0.41	0.70	0.70
0.11	0.11	4.67	0.17	56.30	55.96	0.42	0.71	0.71
0.11	0.11	4.65	0.17	56.40	55.82	0.42	0.71	0.71
0.10	0.11	4.66	0.17	56.50	55.82	0.41	0.69	0.70
0.11	0.11	4.71	0.17	56.91	55.66	0.42	0.68	0.70
0.11	0.11	4.71	0.17	55.62	55.55	0.42	0.68	0.70
0.11	0.11	4.73	0.17	57.76	55.85	0.42	0.68	0.70
0.11	0.11	4.71	0.17	58.19	55.58	0.42	0.68	0.70
0.11	0.10	4.68	0.17	58.41	55.51	0.42	0.70	0.70
0.11	0.11	4.73	0.17	56.48	55.93	0.42	0.68	0.70
0.11	0.11	4.73	0.17	54.77	55.88	0.42	0.70	0.70
0.11	0.11	4.72	0.17	57.12	55.78	0.42	0.68	0.70
	0.11	4.66	0.17	54.98	55.50		0.72	0.70
	0.11	4.67	0.17	55.41	55.70		0.72	0.71
	0.10	4.70	0.17	55.62	55.80		0.73	0.70
	0.11	4.66	0.17	56.91	55.50		0.73	0.71
	0.11	4.64	0.17	54.55	55.60		0.72	0.70
	0.10	4.66	0.17	54.98	55.50		0.72	0.70
	0.11	4.67	0.17	54.34	55.60		0.72	0.70
	0.11	4.65	0.17		55.70		0.70	0.69
	0.11	4.56	0.17		55.84		0.70	0.71
	0.11	4.58	0.17		55.71		0.72	0.71
	0.11	4.57	0.17		55.76		0.70	0.71
	0.11	4.57	0.16		55.72		0.70	0.71
	0.11	4.55	0.16		55.74		0.70	0.71
	0.11	4.58	0.16		55.76		0.70	0.71
	0.11	4.59	0.16		55.77		0.70	0.71
	0.11	4.57	0.17		55.75			0.71
		4.68			52.03			0.72
		4.72			52.12			0.71
		4.67			52.24			0.72
		4.63			51.97			0.71
		4.64			52.14			0.72
		4.68			53.90			0.72
		4.66			54.00			0.72
		4.67			54.00			
					54.00			
					53.80			
					54.00			
					54.00			
					54.00			

Assay Data (Cont.)

Pb Collection	Pb Collection	Combustion/LECO	Combustion/LECO	4A_MICP	LOI	SG	4A_MICP	FUS	4A_MICP
Au	Pd	C	S	S	LOI	SG	Al	Al	Be
g/t	g/t	ppm	%	%	%	Dimensionless	ppm	ppm	ppm
0.07	0.01	1.82	0.16	0.17	8.02	2.80	65390	61300	1.50
0.08	0.01	1.82	0.17	0.17	8.00	2.82	65540	61600	1.50
0.07	0.01	1.82	0.17	0.17	7.99	2.85	65932	61300	1.50
0.08	0.01	1.83	0.17	0.17	8.01	2.80	65935	62000	1.40
0.07	0.01	1.83	0.17	0.17	8.02	2.81	65400	61900	1.50
0.07	0.01	1.83	0.17	0.17	7.96	2.79	64885	60700	1.50
0.08	0.01	1.82	0.17	0.17	8.06	2.68	65701	61400	1.50
0.08	0.01	1.83	0.17	0.17	8.00	2.69	65711	61000	1.40
0.08	0.01	1.72	0.14	0.17	7.59	2.71	61300	64000	1.20
0.08	0.01	1.71	0.14	0.17	7.50	2.70	62600	62700	1.20
0.08	0.01	1.72	0.14	0.16	7.42	2.70	62500	62200	1.20
0.08	0.01	1.72	0.15	0.17	7.43	2.69	62600	62600	1.20
0.08	0.01	1.73	0.13	0.17	7.68	2.71	61500	63200	1.20
0.08	0.01	1.71	0.14	0.17	7.54	2.69	61550	61900	1.20
0.08	0.01	1.72	0.14	0.17	7.48	2.78	61000	62100	1.20
0.07	0.01	1.72	0.14	0.17	7.43	2.76	62600	62400	1.30
0.09	0.02	1.81	0.19	0.16	8.00	2.75			1.30
0.08	0.02	1.80	0.19	0.16	8.04	2.76			1.30
0.09	0.02	1.80	0.19	0.16	8.00	2.76			1.40
0.08	0.02	1.81	0.19	0.17	8.00	2.77			1.30
0.08	0.02	1.81	0.15	0.16	7.99	2.78			1.30
0.08	0.02	1.80	0.14	0.16	8.01	2.72			1.30
0.08	0.02	1.81	0.15	0.16	8.03	2.75			1.40
0.09	0.02	1.81	0.13	0.16	8.01	2.75			1.50
0.08		1.77	0.15	0.17	8.02	2.75			1.50
0.07		1.76	0.14	0.17	8.04	2.75			1.40
0.08		1.76	0.15	0.17	8.05	2.76			1.40
0.08		1.77	0.15	0.17	8.05	2.75			1.40
0.08		1.78	0.16	0.17	8.03	2.75			1.40
0.08		1.78	0.15	0.16	8.06	2.76			1.40
0.08		1.78	0.15	0.16	8.03				1.40
0.07		1.77	0.15	0.17	8.02				
0.06		1.65	0.15	0.17	8.10				
0.06		1.65	0.15	0.16	8.10				
0.06		1.67	0.15	0.15	8.08				
0.06		1.65	0.15	0.15	8.09				
0.06		1.66	0.16	0.16	8.06				
0.06		1.66	0.16	0.16	8.06				
0.06		1.66	0.15	0.16	8.05				
0.06		1.67	0.16		8.07				
0.08			0.15						
0.08			0.15						
0.08			0.16						
0.08			0.15						
0.08			0.14						
0.09			0.15						
0.08			0.15						
0.09			0.15						
0.07			0.15						
0.08			0.15						
0.07			0.14						
0.08			0.15						
0.08			0.13						
0.08			0.14						
0.08			0.14						
0.08			0.14						
0.09			0.14						
0.09			0.12						
0.09			0.13						
0.09			0.13						
0.09									
0.08									
0.09									
0.09									
0.09									
0.09									
0.09									
0.09									
0.09									
0.09									
0.09									
0.09									
0.09									
0.08									

Assay Data (Cont.)

4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP
Ca	Ca	Cd	Co	Cr	Cr	Cs	Cu	Fe	Fe	Ga	Hf
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
57727	62800	1.35	17.60	113.00	137.00	1.10	133.00	56800	57600	16.90	4.00
58062	63400	1.43	17.30	113.00	136.00	1.10	133.00	56900	56800	16.60	4.00
58458	63300	1.48	17.40	115.00	136.00	1.00	133.00	57300	57500	16.00	4.00
58414	63800	1.37	17.10	114.00	137.00	1.10	134.00	57200	57400	16.60	4.00
58105	63500	1.39	17.50	114.00	136.00	1.00	133.00	56700	56200	16.30	4.00
57624	63900	1.37	17.20	113.00	140.00	0.90	133.00	57000	55800	16.20	4.00
58475	62600	1.44	17.20	115.00	144.00	1.00	133.00	57000	57100	16.60	4.00
58471	61400	1.39	16.90	114.00	141.00	1.00	134.00	57300	55300	16.20	4.00
58200	59000	1.00	16.00	109.00	150.00	0.90	141.00	58820	56400	20.00	3.30
59900	60000	1.00	16.00	111.00	150.00	0.90	146.00	57960	56100	20.00	3.43
59300	59000	1.00	16.00	110.00	150.00	1.00	141.00	58650	57100	20.00	3.25
59300	61000	1.00	16.00	111.00	150.00	0.90	144.00	58230	57700	20.00	3.20
58700	61000	1.00	16.00	108.00	150.00	0.90	143.00	58270	56700	20.00	3.41
58200	60000	1.00	16.00	106.00	150.00	1.00	142.00	58420	58200	20.00	3.28
58200	61000	1.00	16.00	106.00	150.00	0.92	139.00	58440	57300	20.00	3.18
59300	61000	1.00	16.00	108.00	150.00	0.99	140.00	58070	55000	15.40	3.24
57900	57000	1.50	15.00	124.80		0.93	126.00		55500	15.40	
60100	56600	1.50	15.00	126.40		0.91	131.00		55600	14.80	
58200	56300	1.50	15.00	125.60		0.97	129.00		55400	14.60	
60400	56000	1.50	15.00	128.10		1.01	130.00		56000	14.80	
59100	56300	1.50	15.00	130.40		0.93	125.00		55600	15.20	
59800	57000	1.50	15.00	124.70		0.93	125.00		55500	14.80	
	55800	1.50	14.00	122.50			123.00		55700	15.40	
	55600	1.50	15.00	123.80			128.00		56300		
		1.30	20.00				130.00		55500		
		1.41	20.00				135.00		55400		
		1.34	20.00				135.00		55100		
		1.31	20.00				130.00		55400		
		1.37	20.00				130.00		55300		
		1.41	20.00				135.00		55000		
		1.30	20.00				135.00		55100		
		1.36	18.00				130.00				
			18.10				114.00				
			18.10				112.70				
			17.80				112.60				
			18.40				112.30				
			18.20				114.70				
			17.90				111.50				
			17.60				112.20				
							110.70				

Assay Data (Cont.)

4A_MICP	4A_MICP	FUS	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	FUS
K	La	Mg	Mn	Mn	Mo	Na	Ni	Pb	Rb	Sb	Sc	Si
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
4198	30.00	5900	812	830	2.00	34430	45.00	52.00	26.70	2.80	12.00	263000
4176	30.00	6000	817	830	2.00	34601	45.00	52.00	26.70	3.10	12.00	265000
4186	30.00	6000	814	830	2.00	34785	45.00	51.00	26.60	2.90	12.00	263000
4192	30.00	5900	819	840	2.00	35079	46.00	52.00	26.70	2.80	12.00	265000
4173	30.00	5800	807	810	2.00	34445	45.00	52.00	26.50	3.00	12.00	264000
4163	30.00	5800	806	810	2.00	34699	46.00	52.00	26.50	3.20	12.00	263000
4194	30.00	6000	808	820	2.00	35015	44.00	52.00	26.40	2.70	12.00	264000
4212	32.60	5900	814	800	2.50	34507	45.00	52.00	26.20	3.00	12.00	264000
3900	32.50	6000	824	821	2.50	36100	46.00	44.00	23.20	2.80	12.00	266000
4000	32.10	5900	840	821	2.50	35900	45.00	45.00	22.60	3.00	12.00	260000
4000	31.50	6000	824	832	2.50	35400	44.00	44.00	21.20	2.60	12.00	270000
4100	31.00	6000	816	847	2.50	36000	43.00	45.00	21.60	2.60	13.00	272000
3900	31.90	5900	824	837	2.50	36000	45.00	46.00	21.60	3.00	12.00	273000
3900	31.20	6000	816	821	2.50	36300	46.00	48.00	22.40	2.80	12.00	264000
3900	32.40	6100	812	842	2.50	36000	44.00	43.00	21.80	2.80	12.00	256000
4000	31.10	6000	828	825		35300	45.00	45.00	22.40	2.80	12.00	267000
4100	30.70	5900				33500	41.00	49.00	23.40	3.08	13.00	257000
4200	30.30	6000				33800	47.00	53.00	25.00	2.93	14.00	259000
4200	30.90	6000				34200	45.00	49.00	24.70	2.61	13.00	260000
4200	31.30	5900				34800	44.00	52.00	23.60	3.07	13.00	266000
4100	30.80	5900				33600	43.00	49.00	25.20	2.66	13.00	255000
4100	30.10	5900				33400	41.00	48.00	24.00	2.87	13.00	257000
4000	31.30	6100				34200	42.00	53.00	23.30	2.61	12.00	254000
4100		6000				34200	46.00	51.00	24.20	2.59	13.00	
4459		6000				35600	50.00	46.00			11.50	
4379		5800				35200	50.00	43.00			12.20	
4419		5800				34800	50.00	44.00			12.20	
4434		6000				34800	50.00	42.00			11.90	
4457		6100				34100	50.00	43.00			12.00	
4412		6100				33600	50.00	43.00			11.70	
4426						34700	45.00	44.00			11.50	
4477							45.00	44.00			11.90	
							38.53	49.10				
							39.35	49.10				
							40.14	48.10				
							40.34	47.60				
							39.98	49.10				
							39.68	51.40				
							38.83	46.10				
								48.20				

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Sr	Ta	Te	Ti	U	V	W	Y	Zn	Zr
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
159.20	0.60	0.60	4300	2.78	159	10.00	17.20	120	131
157.50	0.60	0.60	4300	2.73	155	10.00	16.90	119	128
158.80	0.60	0.60	4400	2.67	156	10.00	17.40	119	131
158.90	0.60	0.60	4300	2.74	161	10.00	17.50	119	131
156.00	0.60	0.60	4200	2.58	160	10.00	17.50	118	131
158.90	0.60	0.60	4200	2.61	155	10.00	17.30	117	128
158.90	0.60	0.60	4300	2.70	160	10.00	17.00	119	131
156.30	0.60	0.60	4200	2.66	158	10.00	16.90	120	129
157.00	0.68	0.83	4100	2.60	151	8.00	17.40	118	145
161.00	0.66	0.86	4100	2.60	153	8.00	17.50	123	141
154.00	0.65	0.85	4100	2.60	154	8.50	16.90	122	142
152.00	0.65	0.83	4100	2.60	157	8.00	16.40	119	137
159.00	0.65	0.83	4200	2.60	151	8.00	16.70	119	141
157.00	0.65	0.82	4100	2.60	149	8.00	17.20	116	148
155.00	0.64	0.81	4200	2.60	150	8.00	17.00	119	139
156.00		0.87	4100	2.70	154	8.00	16.90	117	145
150.00			4300		160			119	138
155.00			4300		170			122	142
154.00			4400		165			123	144
156.00			4400		165			120	136
151.00			4300		165			118	138
154.00			4300		160			118	135
157.00			4300		160			122	135
159.00			4200		160			120	145
153.00			4200					120	
153.00			4300					125	
150.00			4200					120	
156.00			4200					120	
152.00			4200					115	
155.00			4200					118	
			4200					123	
								124	
								125	
								121	
								120	
								122	
								119	

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. Limit of Detection and Limit of Quantitation in Gravimetric Fire Assay

In the determination of limit of detection (LOD) and limit of quantitation (LOQ) in gravimetric fire assay (*i.e.* lead collection and weighing of resulting gold prill), the minimum mass that an assay microbalance is capable of weighing and the original test sample mass determines the LOD and the LOQ in the assay (Fraser, 2015), (see Appendix 8 for an example of the calculation LOD and LOQ and Table 13 for a recommend reporting scheme for LOD and LOQ values).

28. Metrological Traceability

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

29. Period of Validity

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

30. Minimum Sample Size

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

31. Availability

This product is available in Laboratory Packs containing 1kg of material and Explorer Packs containing custom weights (from 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.

32. Recommended use in Quality Control

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

33. Legal Notice

This certificate and the reference material described in it have been prepared with due care and attention. However, AMIS, 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: 07 August 2019

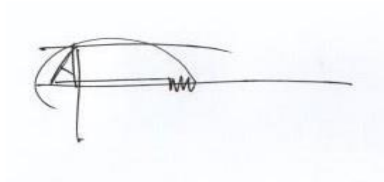
Version: *000*

Approving Officer:

African Mineral Standards: ____

Makhosi Khoza (Quality Specialist)

Certifying Officer:



Geochemist:____

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

References

Abzalov, M. (2011). Sampling Errors and Control of Assay Data Quality in Exploration and Mining Geology, Applications and Experiences of Quality Control. Ivanov, O., (Ed.), InTech, DOI: 10.5772/14965. Available from: http://www.intechopen.com/books/applications-and-experiences-of-quality-control/sampling-errors-and-control-of-assay-data-quality-in-exploration-and-mining-geology. Accessed 25th September, 2016.

ASTM E122-09e1, Standard Practice for Calculating Sample Size to Estimate, With Specified Precision, the Average for a Characteristic of a Lot or Process, ASTM International, West Conshohocken, PA, 2011, www.astm.org

Barwick V.J., Pritchard E. (Eds). (2011). Eurachem Guide; Terminology in Analytical Measurement – Introduction to VIM 3 (2011). ISBN 978-0-948926-29-7.

Carr R.H. (2011). Estimating errors using graphs and taking good data. California State University Los Angeles. March 2011. 14. http://web.calstatela.edu/faculty/kaniol/Err-Gph-Meas-IBooklet.pdf. Retrieved: 29 August, 2016.

Cochran, W.G. (1950). The Comparison of Percentages in Matched Samples. Biometrika, 37, 256-66.

Ellison, S., Barwick, V., Duguid Farrant, T. (2009). *Practical statistics for the analytical scientist, a bench guide. 2nd Edition.* RSC Publishing. 25-172.

ERM Application Note 1. (2005). Comparison of a measurement value with a certified value. European Commission – Joint Research Centre Institute for Reference Materials and Measurements (IRMM). 1-2.

EURACHEM / CITAC Guide CG 4. (2012). Quantifying uncertainty in analytical measurement. 3rd Edition. Editors: Ellison, S. L. R., Williams, A. 4-121.

Eurolab Technical Report No.1/2007. (2007). Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation. European Federation of National Associations of Measurement, Testing and Laboratories. 43-46.

Fraser, A.W. (2015). Minimising uncertainty in measurement and improving limit of detection in gold bearing ores from concentrations predicted by linear regression in atomic absorption spectrometry. M.Sc. thesis (unpublished), University of Johannesburg: 199 pages.

Grubbs, F.E. (1969). Procedures for detecting outlying observations in samples. *Technometrics*, 11, 1969. 1-21.

Horwitz, W., Albert, R. (2006). The Horwitz Ratio (HorRat): A useful index of method performance with respect to precision, Journal of Association of Official Analytical Chemists International, 89: 1095-1109.

ISO/IEC 17025:2005(E).(2005). *General requirements for the competence of testing and calibration laboratories.* 2nd Edition*:* 14-59.

ISO Guide 35 (2003). Certification of reference materials — General and Statistical principles, 3rd edition. ISO/REMCO WG 1.

ISO 5725-2:1994. Accuracy (trueness and precision) of measurement methods and results -- Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.

Long, J., Winefordner, J. (1983). Limit of detection - a closer look at the IUPAC definition. Analytical Chemistry 55: 712A - 724A.

Miller, J., Miller, J. (2010). *Statistics for analytical chemistry.* 6th Edition. New York: Ellis Horwood.36-126.

Nelsen T.C., Wehling P. (2008). Collaborative studies for quantitative chemical analytical methods. AACC International Report. Cereal Foods World. September – October 2008, Vol. 53, No. 5. 285-288.

Skoog, D., West, D. (1982). *Fundamentals of analytical chemistry.* 4th Edition. CBS College Publishing. Holt Saunders International Editions:39-73.

Thompson, M. (Ed.) (2008). Test for 'sufficient homogeneity' in a reference material. Analytical Methods Committee, AMCTB 17A, ISSN 1757-5958.

Thompson, M. (Ed.) (2010). Internal quality control in routine analysis. AMC Technical Brief. Analytical Methods Committee. AMCTB No.46. 2010. Issn 1757-5958.

Thompson, M., Lowthian, P. (2011). *Notes on statistics and data quality for analytical chemists.* Imperial College Press: 15-115.

Appendices

Appendix 1: Uncertified Element Statistics

Uncertified element statistics are shown in **Table 9**.

Table 9. Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	4A_MICP	22	0.6	0.1	16	ppm
ANC[14]	ANC	15	154.5	9.4	6	KgH_2SO_4/t
AP	NP	7	2.5	0.2	10	$tCaCO_3/1Kt$
As	4A_MICP	20	4.9	1.5	30	ppm
B	FUS	8	305.0	14.1	5	ppm
Ba	4A_MICP	24	210.8	37.7	18	ppm
Ba	FUS	16	194.9	4.0	2	ppm
BaO	XRF	16	11.5	11.9	103	%
Bi	4A_MICP	28	6.9	2.2	32	ppm
Bi	FUS	8	5.2	0.1	1	ppm
C	CALC	8	1.6	0.0	1	ppm
C inorganic	CALC	7	1.8	0.004	0.2	ppm
C organic	IR	4	0.010	*	*	ppm
Cd	FUS	15	1.4	0.1	5	ppm
Ce	4A_MICP	16	70.1	5.7	8	ppm
Ce	FUS	15	64.7	1.1	2	ppm
Co	FUS	8	16.3	0.4	2	ppm
CO_2	CALC	8	6.0	0.1	2	%
Cs	FUS	16	0.9	0.1	6	ppm
Cu	FUS	8	130.0	3.9	3	ppm
Dy	4A_MICP	16	3.7	0.1	3	ppm
Dy	FUS	16	5.2	0.7	13	ppm
EC	WS/MTR	8	27.2	0.2	1	mS/m
Er	4A_MICP	8	1.8	0.1	3	ppm
Er	FUS	8	3.5	0.1	2	ppm
Eu	4A_MICP	8	1.3	0.0	3	ppm
Eu	FUS	8	1.3	0.0	3	ppm
Final-pH	ANC/MTR	8	1.0	0.1	6	pH
FIZZ RATING	FR	16	3.0	*	*	NO UNIT
Ga	FUS	16	16.1	0.6	4	ppm
Gd	4A_MICP	8	5.6	0.2	3	ppm
Gd	FUS	15	6.4	0.2	3	ppm
Ge	4A_MICP	8	1.6	0.1	4	ppm
Ge	FUS	8	1.6	0.5	32	ppm
Hf	FUS	8	5.0	*	*	ppm
Ho	4A_MICP	15	0.6	0.0	3	ppm
Ho	FUS	15	1.1	0.1	5	ppm
In	4A_MICP	16	0.1	0.01	9	ppm
K	FUS	0	0.000	0.000	0.000	ppm
La	FUS	16	31.5	0.7	2	ppm
Li	4A_MICP	16	7.5	1.2	16	ppm
Lu	4A_MICP	15	0.3	0.0	3	ppm
Lu	FUS	16	0.4	0.1	14	ppm
Mg	4A_MICP	15	5534.1	64.1	1	ppm
Mo	FUS	7	3.0	*	*	ppm
Moisture	Moisture	8	1.0	0.005	0.5	%
MPA[15]	CALC	8	5.0	*	*	KgH2SO4/t
MPA	NAG_Ti	8	4.2	0.4	9	KgH2SO4/t
MPA_2	NP	8	4.6	0.2	5	tCaCO3/1Kt
Na_2O	4A_MICP	8	4.8	0.0	1	%

Table 10. Uncertified element concentrations statistics (Continued)

Element	Generic Method	n	Mean	SD	RSD %	Unit
NAGpH[16]	NAG	8	8.8	0.1	1	NO UNIT
Nb	4A_MICP	16	8.1	0.6	7	ppm
Nb	FUS	8	11.4	0.7	7	ppm
Nd	4A_MICP	16	32.3	1.5	5	ppm
Nd	FUS	15	31.2	0.5	2	ppm
Ni	FUS	16	40.0	5.1	13	ppm
NNP[17]	NP	15	139.1	3.2	2	$tCaCO_3/1Kt$
NP[18]	NP	16	142.2	4.6	3	$tCaCO_3/1Kt$
NPR[19]	NP	7	56.1	5.3	9	NO UNIT
P	4A_MICP	14	745.3	9.0	1	ppm
P	FUS	15	700.0	*	*	ppm
P_2O_5	FUS	15	0.2	0.005	3	%
Pb	FUS	7	49.1	0.4	1	ppm
pH	pH	8	8.4	0.1	1	pH
pH	WS/MTR	7	8.5	*	*	pH
pH Drop	ANC/MTR	6	3.8	0.1	2	pH
Pr	4A_MICP	15	7.9	0.2	2	ppm
Pr	FUS	16	8.0	0.3	3	ppm
Pt	Pb Collection	16	0.02	0.003	13	g/t
Ratio (NP:MPA)	NP	7	31.7	1.1	4	NO UNIT
Rb	FUS	16	22.9	1.4	6	ppm
S	CALC	16	0.1	0.01	16	%
S	HCl Leachable	6	0.01	0.01	39	%
S	TSCL	15	0.1	0.01	10	%
Sb	FUS	14	2.8	0.1	5	ppm
Sc	FUS	16	12.4	1.5	12	ppm
Se	4A_MICP	8	4.0	*	*	ppm
Sm	4A_MICP	16	6.8	0.5	8	ppm
Sm	FUS	16	6.6	0.2	2	ppm
Sn	4A_MICP	15	3.0	0.1	2	ppm
Sn	FUS	8	4.0	0.5	13	ppm
Sr	FUS	8	149.4	1.1	1	ppm
SrO	XRF	16	0.02	0.001	5	%
Ta	FUS	16	1.0	0.2	15	ppm
Tb	4A_MICP	16	0.7	0.1	12	ppm
Tb	FUS	16	1.0	0.03	3	ppm
Th	4A_MICP	15	9.7	0.2	2	ppm
Th	FUS	8	10.5	0.1	1	ppm
Ti	4A_MICP	15	3347.7	86.3	3	ppm
Tl	4A_MICP	16	0.3	*	*	ppm
Tm	4A_MICP	16	0.2	0.01	6	ppm
Tm	FUS	15	0.5	0.03	7	ppm
U	FUS	16	3.2	0.1	3	ppm
V	FUS	16	165.5	9.3	6	ppm
V_2O_5	FUS	16	0.03	0.002	6	%
V_2O_5	XRF	13	0.03	*	*	%
W	FUS	8	11.0	*	*	ppm
WtSamp	Moisture	8	99.2	0.3	0.3	g
WtTotal	Moisture	7	100.5	0.2	0.2	g
Y	FUS	8	32.7	0.5	2	ppm
Yb	4A_MICP	8	1.9	0.1	3	ppm
Yb	FUS	8	3.2	0.1	2	ppm
Zn	FUS	16	118.2	5.9	5	ppm
Zr	FUS	8	188.1	5.6	3	ppm

*denotes that 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]:

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

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:

$|z|\leq2$ satisfactory performance
$2<|z|\leq3$ questionable performance
$|z|>2$ 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:

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

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

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

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

$$\%RSD = \pm 2^{(1-0.5logC)} \qquad [4]$$

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

$$Observed\ \%RSD = \frac{s}{Mean} x100 \qquad [5]$$

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

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

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

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*):

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

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):

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

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.

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

Between Group Variation (SSB)

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

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

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:

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

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

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

Source	**Sum of Squares**	***df***	**Mean Sum of Squares**	***F***	***p***	F_{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:

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

Within laboratory repeatability is determined as

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

and, the between laboratory precision as

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

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 laboratories 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 | | bars indicate that the absolute value between the mean and the certified value is to be used, *i.e.* ignore the sign.

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

Example

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

The relevant hypotheses are:

Null hypothesis: H_0: Mean = Certified value of CRM with stated measurement uncertainty. The acceptance of H_0 means that accuracy is demonstrated; *i.e.* insufficient evidence to reject H_0;
Alternate hypothesis: H_1: Mean ≠ Certified value of CRM with stated measurement uncertainty. The acceptance of H_1 means that accuracy is not demonstrated, *i.e.* there is sufficient evidence to accept H_1;

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

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

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

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

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

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

Therefore, t_{calc}= 0.84 and $t_{crit}(5\%, 8) = 2.31$ (*df* is 8, therefore, t_{crit}=2.31, see Appendix 9, page 37) 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:

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

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

Appendix 5. Confidence Interval

Confidence interval is calculated as:

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

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 to15 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:

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

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 ±2s and ±3s, where *s* is the standard deviation calculated from [21].
8. Construct the Shewhart control chart around the mean of *n* replicates.
9. Use ±2s as the warning limits.
10. Use ±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^2 with the CRM material spread evenly over same; this represents a 0.1 gram spread per cm^2. In correcting the certified value for moisture content, a moisture correction factor is calculated:

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

$$Air\ dry\ basis\ concentration = MCF\ x\ certified\ value\ on\ a\ dry\ basis \qquad [23]$$

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:

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

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:

$$0.995\ x\ 12.62\% = 12.56\%$$

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

Appendix 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 1µg or 0.001mg. Even with a microscope it may be difficult to locate and pick up a prill weighing ten times that amount (*i.e.* 0.01mg or 10µg) and weigh it. If an analyst can weigh a prill of 1µg then the LOD becomes 1µg. However, the concentration factor would be 50 times for a 50-gram assay sample and therefore the LOD in g/t becomes 1µg divided by the original mass of the sample in grams taken for fire assay [24]. Therefore, the LOD in fire assay is computed as:

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

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

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

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be 0.02g/t. *i.e.* 1µg = 1g/t, therefore 1µg/50g = 0.02g/t. If no prill was found, then the LOD result would be <0.02 g/t or “not detected”. Using a larger assay sample mass improves the LOD and LOQ (Table 11). Table 13 gives a recommended reporting scheme for LOD and LOQ.

Table 12. Mass of assay sample and corresponding limit of detection and limit of quantitation for an assay microbalance capability of smallest prill mass of 1µg or 0.001mg.

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

Table 13. Recommended reporting scheme for LOD and LOQ in fire assay.

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

Appendix 9. T-distribution table

Table 14. T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence.

df	**Two-tailed**	***df***	**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