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Certificate

AMIS0553

Certified Reference Material

Gold and Uranium Ore
Witwatersrand, South Africa

Certificate of Analysis

AMIS

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SUMMARY STATISTICS

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

Analyte	Method	⁸ Certified (μ)	⁹ Two Standard Deviation (2s) \pm	Unit
Au	Pb Collection ¹	26.75	3.02	g/t
U	4A_MICP ²	629	109	ppm
U	XRF ³	660	40	ppm
U ₃ O ₈	XRF	0.078	0.005	%
LOI	LOI ⁴	2.10	0.15	%
S	4A_MICP	1.94	0.27	%
S	Combustion/LECO ⁵	1.90	0.059	%
SG	SG ⁶	2.76	0.070	Dimensionless
Ag	4A_MICP	2.89	0.59	ppm
As	4A_MICP	203	20	ppm
Ba	4A_MICP	62	7	ppm
Be	4A_MICP	0.5	0.1	ppm
Bi	4A_MICP	2	0.2	ppm
Ca	4A_MICP	488	50	ppm
Cd	4A_MICP	3	0.5	ppm
Ce	4A_MICP	45	13	ppm
Co	4A_MICP	56	6	ppm
Cr	4A_MICP	379	55	ppm
Cs	4A_MICP	1	0.1	ppm
Cu	4A_MICP	80	12	ppm
Dy	4A_MICP	6	1	ppm
Er	4A_MICP	3	1	ppm
Eu	4A_MICP	1	0.2	ppm
Fe	4A_MICP	32758	1853	ppm
Ga	4A_MICP	4	1	ppm
Gd	4A_MICP	5	0.5	ppm
Hf	4A_MICP	2	0.9	ppm
Ho	4A_MICP	1	0.4	ppm
In	4A_MICP	0.1	0.02	ppm
K	4A_MICP	2959	164	ppm
La	4A_MICP	22	5	ppm
Li	4A_MICP	5	1	ppm
Lu	4A_MICP	0.2	0.1	ppm
Mg	4A_MICP	1628	103	ppm
Mn	4A_MICP	137	7	ppm
Mo	4A_MICP	3	0.5	ppm
Na	4A_MICP	859	186	ppm
Nb	4A_MICP	3	1	ppm
Nd	4A_MICP	20	4	ppm
Ni	4A_MICP	114	8	ppm
Pb	4A_MICP	225	19	ppm
Pr	4A_MICP	5	1	ppm
Rb	4A_MICP	13	3	ppm
Sb	4A_MICP	7	2	ppm
Sc	4A_MICP	3	0.6	ppm
Sm	4A_MICP	5	0.6	ppm
Sn	4A_MICP	1	0.5	ppm
Sr	4A_MICP	30	2	ppm
Tb	4A_MICP	1	0.3	ppm
Te	4A_MICP	0.5	0.1	ppm
Th	4A_MICP	49	3	ppm
Tl	4A_MICP	0.2	0.1	ppm
Tm	4A_MICP	0.3	0.1	ppm
V	4A_MICP	16	4	ppm
W	4A_MICP	1	0.2	ppm
Y	4A_MICP	18	7	ppm
Yb	4A_MICP	2	0.4	ppm
Zn	4A_MICP	335	27	ppm
Zr	4A_MICP	98	23	ppm

Major Oxides
Certified Concentrations (at two Standard Deviations)

Analyte	Method	⁸ Certified (μ)	⁹ Two Standard Deviation (2s) \pm	Unit
Al ₂ O ₃	FUS ⁷	3.03	0.11	%
Al ₂ O ₃	XRF	3.14	0.068	%
CaO	XRF	0.057	0.01	%
Cr ₂ O ₃	XRF	0.066	0.01	%
Fe ₂ O ₃	FUS	4.39	0.22	%
Fe ₂ O ₃	XRF	4.50	0.10	%
K ₂ O	XRF	0.350	0.0083	%
MgO	FUS	0.262	0.039	%
MgO	XRF	0.269	0.033	%
SiO ₂	XRF	88.67	1.50	%
TiO ₂	XRF	0.155	0.010	%

1. Certified Concentrations and Uncertainties

AMIS0553 is a new standard material, developed and certified in August 2018. Table 1 gives the certified concentrations, combined and expanded uncertainty for the certified reference material. Table 2 shows the certified major oxides concentrations, two standard deviations, combined and expanded uncertainty.

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

Analyte	Method	⁸ Certified (μ)	N	n	k	% RSD	⁸ Combined uncertainty (u _c)	⁹ Two Standard Deviation (2s) ±	¹⁰ Expanded uncertainty (U) ±	Unit
Au	Pb Collection ¹	26.75	12	96	2.20	6	1.5	3.02	3	g/t
U	4A_MICP ²	629	5	40	2.78	9	55	109	152	ppm
U	XRF ³	660	4	32	3.18	3	20	40	64	ppm
U ₃ O ₈	XRF	0.078	4	32	3.18	3	0.002	0.005	0.01	%
LOI	LOI ⁴	2.10	7	56	2.45	4	0.074	0.15	0.2	%
S	4A_MICP	1.94	5	40	2.78	7	0.13	0.27	0.4	%
S	Combustion/LECO ⁵	1.90	5	39	2.78	2	0.030	0.059	0.08	%
SG	SG ⁶	2.76	6	45	2.57	1	0.035	0.070	0.09	Dimensionless
Ag	4A_MICP	3	4	32	3.18	10	0.3	0.6	0.9	ppm
As	4A_MICP	203	5	39	2.78	5	10	20	28	ppm
Ba	4A_MICP	62	6	45	2.57	6	4	7	9	ppm
Be	4A_MICP	0.5	4	26	3.18	11	0.05	0.1	0.2	ppm
Bi	4A_MICP	2	4	32	3.18	5	0.1	0.2	0.3	ppm
Ca	4A_MICP	488	4	32	3.18	5	25	50	80	ppm
Cd	4A_MICP	3	4	32	3.18	8	0.3	0.5	0.8	ppm
Ce	4A_MICP	45	4	32	3.18	15	7	13	21	ppm
Co	4A_MICP	56	6	48	2.57	5	3	6	8	ppm
Cr	4A_MICP	379	4	29	3.18	7	27	55	87	ppm
Cs	4A_MICP	1	4	32	3.18	6	0.06	0.1	0.2	ppm
Cu	4A_MICP	80	6	44	2.57	8	6	12	16	ppm
Dy	4A_MICP	6	3	24	4.30	6	0.3	1	1	ppm
Er	4A_MICP	3	3	23	4.30	9	0.3	1	1	ppm
Eu	4A_MICP	1	3	24	4.30	11	0.1	0.2	0.5	ppm
Fe	4A_MICP	32758	5	40	2.78	3	927	1853	2573	ppm
Ga	4A_MICP	4	4	31	3.18	13	1	1	2	ppm
Gd	4A_MICP	5	3	24	4.30	5	0.3	0.5	1	ppm
Hf	4A_MICP	2	5	40	2.78	18	0.5	0.9	1	ppm
Ho	4A_MICP	1	3	24	4.30	22	0.2	0.4	0.9	ppm
In	4A_MICP	0.1	4	30	3.18	13	0.009	0.02	0.03	ppm
K	4A_MICP	2959	5	38	2.78	3	82	164	227	ppm
La	4A_MICP	22	5	40	2.78	10	2	5	6	ppm
Li	4A_MICP	5	4	30	3.18	6	0.3	1	1	ppm
Lu	4A_MICP	0.2	3	24	4.30	22	0.05	0.1	0.2	ppm
Mg	4A_MICP	1628	4	31	3.18	3	52	103	164	ppm
Mn	4A_MICP	137	5	37	2.78	3	3	7	10	ppm
Mo	4A_MICP	3	5	40	2.78	10	0.3	0.5	0.8	ppm
Na	4A_MICP	859	5	40	2.78	11	93	186	258	ppm
Nb	4A_MICP	3	4	32	3.18	17	0.5	1	2	ppm
Nd	4A_MICP	20	3	24	4.30	9	2	4	8	ppm
Ni	4A_MICP	114	6	48	2.57	4	4	8	11	ppm
Pb	4A_MICP	225	6	45	2.57	4	9	19	24	ppm
Pr	4A_MICP	5	3	24	4.30	11	1	1	3	ppm
Rb	4A_MICP	13	4	32	3.18	12	2	3	5	ppm
Sb	4A_MICP	7	3	23	4.30	11	1	2	3	ppm
Sc	4A_MICP	3	4	32	3.18	10	0.3	0.6	1	ppm
Sm	4A_MICP	5	3	24	4.30	7	0.3	0.6	1	ppm
Sn	4A_MICP	1	3	23	4.30	22	0.3	0.5	1	ppm
Sr	4A_MICP	30	6	45	2.57	4	1	2	3	ppm
Tb	4A_MICP	1	3	24	4.30	19	0.2	0.3	1	ppm
Te	4A_MICP	0.5	3	24	4.30	14	0.1	0.1	0.3	ppm
Th	4A_MICP	49	5	40	2.78	3	2	3	5	ppm
Tl	4A_MICP	0.2	3	24	4.30	39	0.1	0.1	0.3	ppm
Tm	4A_MICP	0.3	3	24	4.30	21	0.1	0.1	0.3	ppm
V	4A_MICP	16	6	47	2.57	13	2	4	5	ppm
W	4A_MICP	1	3	23	4.30	16	0.1	0.2	0.4	ppm
Y	4A_MICP	18	4	32	3.18	21	4	7	12	ppm
Yb	4A_MICP	2	4	32	3.18	8	0.2	0.4	1	ppm
Zn	4A_MICP	335	6	48	2.57	4	14	27	35	ppm
Zr	4A_MICP	98	4	32	3.18	12	11	23	36	ppm

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

Analyte	Method	⁸ Certified (μ)	N	n	k	% RSD	⁸ Combined uncertainty (u_c)	⁹ Two Standard Deviation (2s) \pm	¹⁰ Expanded uncertainty (U) \pm	Unit
Al ₂ O ₃	FUS ⁷	3.03	3	23	4.30	2	0.053	0.11	0.2	%
Al ₂ O ₃	XRF	3.14	6	48	2.57	1	0.034	0.068	0.09	%
CaO	XRF	0.057	7	54	2.45	9	0.005	0.01	0.01	%
Cr ₂ O ₃	XRF	0.066	6	47	2.57	7	0.005	0.01	0.01	%
Fe ₂ O ₃	FUS	4.39	3	23	4.30	2	0.11	0.22	0.5	%
Fe ₂ O ₃	XRF	4.50	6	48	2.57	1	0.052	0.10	0.1	%
K ₂ O	XRF	0.350	6	48	2.57	1	0.0041	0.0083	0.01	%
MgO	FUS	0.262	3	23	4.30	8	0.020	0.039	0.08	%
MgO	XRF	0.269	7	56	2.45	6	0.017	0.033	0.04	%
SiO ₂	XRF	88.67	6	48	2.57	1	0.75	1.50	2	%
TiO ₂	XRF	0.155	7	53	2.45	3	0.0052	0.010	0.01	%

1. *Pb collection is fire assay by lead collection*
2. *4A_MICP is a Multi-acid digestion with ICP finish*
3. *XRF is X-ray Fluorescence*
4. *LOI is Loss on Ignition*
5. *Comb/LECO is analysis by Combustion infra-red*
6. *SG is Specific Gravity*
7. *FUS is Fusion digestion with ICP finish*
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.*
10. *The two standard deviations (2s) is calculated as for example: $u_c \times 2 = 0.23 \times 2 = 0.46\%$. See section 29 page 21, for recommended use in quality control.*
11. *Expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (u_c) with a coverage factor (k) found from N-1 degrees of freedom (see Appendix 7 for t-distribution table). Example: $U = 2.36 \times 0.23 = 0.54\%$.*

2. Statistical Comparison of Means

Comparison of means for the same element between different analytical methods was done by first comparing the variances between the two data sets using an F-test. If the variances were found to be equal (F-test, p -value ≥ 0.05), then an equal variance t-test was applied. In converse, if the variances are found to be statistically significant, then an unequal variance t-test was performed (Table 4). With a p -value ≥ 0.05 , the null hypothesis that the means (certified values) are equal is accepted (Table 3).

Table 3. Results of a two-sample equal variance t-test (two-tailed) on data sets demonstrating equal variances.

Method	Certified value	Method	Certified value	p -value (t-test)	t-test outcome
Al ₂ O ₃ XRF	3.14 %	Al ₂ O ₃ Fus	3.03%	<0.001	Reject H ₀ , means are <i>not</i> equal.
MgO XRF	0.269 %	MgO Fus	0.262 %	0.55	Accept H ₀ , means are equal.
Fe ₂ O ₃ XRF	4.50 %	Fe ₂ O ₃ Fus	4.39 %	0.024	Reject H ₀ , means are <i>not</i> equal.
U 4A_MICP	629 ppm	U XRF	660 ppm	0.31	Accept H ₀ , means are equal.

Table 4. Results of a two-sample unequal variance t-test (two-tailed) on data sets demonstrating unequal variances.

Method	Certified value	Method	Certified value	p -value (t-test)	t-test outcome
S Comb (Leco)	1.90 %	S 4A_MICP	1.94 %	0.001	Reject H ₀ , means are <i>not</i> equal.

3. Intended Use

AMIS0553 is a matrix matched Certified Reference Material, fit for use as a control sample in routine assay laboratory quality control when inserted within runs of test samples and measured in parallel to test samples. This material can also be used for method development, use as independent calibration verification check standard (*i.e.* if not used as a calibration standard in an instrument calibration), or for validation of accuracy in a method validation exercise (see Appendix 3). The recommend procedure for the use of this CRM as a control standard in laboratory quality control is to develop a Shewhart chart, where a mean value and corresponding 1, 2 and 3 standard deviations are derived from replicate measurements of the CRM (see Appendix 4). This CRM can also be used to assess inter-laboratory or instrument bias and establish within-laboratory precision and within-laboratory reproducibility. The certified concentrations and expanded uncertainty for this material are property values based on an inter-laboratory measurement campaign and reflect consensus results from the laboratories that 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
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

This standard is made from uranium bearing gold ore originating from the Ventersdorp, Contact Reef, Carbon Leader Reef and Vaal Reef. The uranium bearing ore was blended with low grade material of similar matrix to obtain the required grade.

9. Approximate Mineral and Chemical Composition

Throughout the Witwatersrand, gold ores occur in sheets or reefs originally deposited horizontally under water. The thickness of the reefs range between a lie of grit to several meters, with an average of 300mm. The sediments were also intersected by dykes and sills of dolomite, diabase and syenite intruding existing faults. The reefs can be in the form of either coarse conglomerates, rock pebbles and cemented in a silicate matrix. Pebbles usually derived from vein quartz, may also consist of quartzitic, chert jasper and quartz porphyry. The matrix consists of pure silica, but also contains minute flakes of muscovite and pyrophyllite as well as visible pyrite and other sulphides. The gold is usually confined to the matrix and tends to be concentrated along bedding planes (Vermeulen, 2001).

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.

Sample preparation for X-Ray Diffraction

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

XRD Results

The results from a diffractogram of the material gave the following results:

1. Chlorite group, where A=Al, Fe²⁺, Fe³⁺, Li, Mg, Mn²⁺, Ni, Zn; Z=Al, B, Fe³⁺, Si. It was assumed that the peaks at $7.3^{\circ}2\theta/14.13\text{\AA}$ and $14.6^{\circ}2\theta/7.06\text{\AA}$ arose from chamosite. Further work would be required to confirm this.
2. Mica group, 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. It was assumed that the peak at $10.2^{\circ}2\theta/10.05\text{\AA}$ arose from muscovite. Further work would be required to confirm this.
3. Tr = trace, i.e. the mineral giving rise to this peak is assumed to be present in trace amounts.

Table 6. Mineral species identified and quantified two sub-samples of AMIS0553 using Rietveld Refinement.

Mineral	Composition	Wt. (%)
Quartz	SiO ₂	94
Chlorite group ¹	A ₄₋₆ Z ₄ O ₁₀ (OH, O) ₈	<1
Mica group ²	X ₂ Y ₄₋₆ Z ₈ O ₂₀ (OH, F) ₄	3
Pyrite	FeS ₂	3
Unassigned peak ³	11.2°2θ/9.18Å	Tr
Unassigned peak ³	23.2°2θ/4.44Å	Tr
Unassigned peak ³	34.0°2θ/3.06Å	Tr
Total		100

11. Health and Safety

The material is a very fine powder coloured Medium Dark Gray. 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 ISO17025:2005 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 particle size was determined by laser diffraction. In this method, particles are passed through a focused laser beam that scatter light at an angle inversely proportional to their size. The intensity of light is measured and converted to a volume in particle size distribution. The results for this standard are presented in Table 7.

Table 7. Particle size determination by laser diffraction.

Size (µm)	Vol. Under %	Size (µm)	Vol. Under %	Size (µm)	Vol. Under %
0.1	0.00	45	98.06	170	100
0.25	0.00	50	98.73	175	100
0.5	1.69	55	99.19	200	100
0.6	2.84	60	99.5	225	100
0.75	4.73	65	99.71	250	100
1	8.07	70	99.84	300	100
2	21.00	75	99.92	400	100
3	30.94	80	99.96	500	100
4	38.41	85	100	600	100
5	44.43	90	100	700	100
6	49.55	95	100	800	100
7	54.04	100	100	900	100
8	58.06	105	100	1000	100
9	61.67	106	100	1100	100

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
10	64.94	110	100	1200	100
12	70.59	115	100	1300	100
15	77.29	120	100	1400	100
18	82.38	125	100	1500	100
20	85.09	130	100	1600	100
25	90.12	135	100	1700	100
30	93.42	140	100	1800	100
35	95.60	150	100	1900	100
40	97.07	160	100	2000	100

14. Radioactivity

Shipments of this material require special labelling and placarding. AMIS0553 contains U (8.25 Bq/g) and Th 0.20 Bq/g) and is classified as EXEMPT MATERIAL in terms of "Safety Standards Series No. TS-R-1: *Regulations for the Safe Transport of Radioactive Material, International Atomic Energy Agency, 2005, para 403, Table 1*".

15. Handling

The material is packaged in Laboratory Packs and Explorer Packs that must be shaken or otherwise agitated before use. The analyte concentrations are quoted on a dry basis; therefore, the user needs to determine the moisture content in order to convert any obtained assay values to an air-dry basis (see Appendix 5 for an example calculation).

16. Storage information

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

17. Methods of Analysis Requested

The following methods of analysis were requested:

- a) 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 including U₃O₈ with XRF finish and/or Peroxide fusion and/or 4 acid digest including HF finished with either ICP-OES or ICP-MS or AAS (specify the temperature for LOI)
- d) SG – gas pycnometer
- e) S and C Combustion/LECO

18. 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.

19. Certification of Mean and Estimation of Measurement Uncertainty

The samples used in this certification process have been selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore, all sources of uncertainty are included in the combined standard uncertainty determination. Initially the data submitted by all of the laboratories are subjected to a z-score test, equation [1] to exclude outliers and the remaining data sets examined for their normality in distribution. This is followed by the exclusion of further outliers as defined by the IUPAC Harmonised Protocol of 1995 in which both Cochran and a Grubbs test are applied until all outliers are identified, equations [2] and [3]. A grand mean and standard deviation is re-calculated using all remaining data (Thompson, 2008; Carr, 2011) (see Appendix 2). These data are then subjected to an analysis of variance (ANOVA) as per equations, [9],[10],[11],[12] and [13] in Appendix 2. The mean squares for data within and between laboratories derived from ANOVA are used to compute the within-laboratory reproducibility, or combined standard uncertainty as shown in Appendix 2, equation [14], [15] and [16]. The Horwitz function is applied to assess the performance of the data under consideration with respect to precision as relative standard deviation (equations [4], [5] and [6]). Should the ratio of the observed %RSD and a calculated %RSD be <2, the observed %RSD is accepted (Horwitz & Albert, 2006). A final certified value is then found by calculating a grand mean of equally weighted individual laboratory means [7] (ISO Guide 35, 2003; Barwick & Pritchard, 2011).

An uncertainty statement on AMIS certificates is typically presented as:

The expanded uncertainty (U) is determined by multiplication of the combined uncertainty (u_c) with a coverage factor (k) found from $N-1$ degrees of freedom and a t-critical value at a level of confidence of 95% (EURACHEM / CITAC Guide CG 4., (2012), (see Table 14, Appendix 7 for a t-critical table). N is the number of laboratory means used in the establishment of the certified value. Since the estimated values of the CRM approximate a normal distribution with combined uncertainty, u_c , the certified value

of the CRM is understood to lie in the interval defined by U with a level of confidence of 95 % (Thompson & Lowthian, 2011).

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

20. Participating Laboratories

Eighteen laboratories were each given eight randomly selected packages of the CRM. Fourteen ISO17025 accredited laboratories submitted results in time for certification.

The 14 laboratories that provided results timeously are:

1. Anglo Gold Ashanti - Vaal River Laboratory SA
2. ALS Arabia
3. ALS (Vancouver) - Analytical Laboratory Services - Vancouver, Canada
4. Argetest Mineral Processing, R&D and Analysis Services
5. Bureau Veritas Minerals Ultra Trace Pty Ltd
6. Chromatech Services
7. Intertek Perth
8. Nesch Mintec Lab Tanzania
9. Set Point Laboratories (Mokopane) SA
10. SGS South Africa (Pty) Ltd - Barberton
11. SGS Mineral Services Lakefield (Canada)
12. SGS South Africa
13. Shiva Analyticals India
14. Sibanye Gold SA

21. Accepted Assay Data

Data from the 14 laboratories used for certification are set out in Table 8.

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

Pb Collection Au g/t	Pb Collection Au g/t	FUS Al ₂ O ₃ %	XRF Al ₂ O ₃ %	XRF CaO %	XRF Cr ₂ O ₃ %	FUS Fe ₂ O ₃ %	XRF Fe ₂ O ₃ %	XRF K ₂ O %	LOI LOI %	FUS MgO %
25.05	27.19	2.97	3.16	0.06	0.06	4.24	4.55	0.35	2.05	0.27
25.38	27.04	3.17	3.10	0.06	0.06	4.56	4.50	0.35	2.03	0.27
26.49	25.02	3.12	3.11	0.05	0.06	4.52	4.50	0.35	2.05	0.27
26.25	27.03	2.96	3.15	0.06	0.06	4.32	4.48	0.35	2.04	0.25
25.51	25.87	2.94	3.16	0.05	0.06	4.28	4.47	0.35	2.00	0.25
27.80	27.61	3.00	3.12	0.06	0.07	4.34	4.47	0.35	2.09	0.27
24.34	26.74	2.97	3.18	0.06	0.06	4.37	4.51	0.35	2.01	0.25
26.37	28.20	3.04	3.15	0.06	0.06	4.27	4.56	0.35	2.03	0.26
23.92	26.90	3.04	3.17	0.06	0.07	4.30	4.54	0.35	2.22	0.24
23.68	26.00	3.06	3.12	0.06	0.07	4.33	4.54	0.35	2.28	0.25
24.16	26.00	3.06	3.13	0.05	0.07	4.33	4.50	0.35	2.24	0.24
23.81	26.30	3.06	3.12	0.06	0.07	4.32	4.71	0.35	2.16	0.24
25.72	26.20	3.06	3.14	0.06	0.07	4.29	4.55	0.35	2.15	0.25
25.74	26.70	3.04	3.13	0.06	0.07	4.30	4.53	0.34	2.21	0.25
25.70	27.30	3.04	3.14	0.05	0.07	4.32	4.49	0.35	2.22	0.24
26.15	26.70	3.01	3.10	0.05	0.06	4.50	4.50	0.36	2.19	0.24
25.00	26.10	3.07	3.14	0.05	0.07	4.47	4.48	0.35	2.09	0.28
25.00	26.32	3.03	3.10	0.05	0.07	4.45	4.51	0.35	2.09	0.28
25.00	26.19	3.03	3.13	0.05	0.07	4.46	4.48	0.35	2.09	0.29
24.00	26.35	2.98	3.16	0.05	0.07	4.44	4.53	0.35	2.17	0.28
25.00	26.29	3.00	3.11	0.05	0.06	4.50	4.52	0.35	2.14	0.28
24.00	26.33	2.98	3.12	0.06	0.06	4.48	4.52	0.35	2.14	0.28
25.00	26.17	3.02	3.12	0.05	0.07	4.51	4.48	0.35	2.12	0.28
24.00	26.43		3.08	0.06	0.06		4.43	0.34	2.14	
28.10	27.30		3.15	0.06	0.06		4.43	0.35	2.06	
27.50	27.60		3.16	0.06	0.06		4.44	0.35	2.05	
25.10	27.40		3.16	0.06	0.06		4.43	0.36	2.03	
28.80	27.00		3.16	0.06	0.06		4.46	0.35	1.99	
28.50	27.50		3.16	0.06	0.06		4.44	0.35	2.00	
28.30	27.40		3.17	0.06	0.06		4.48	0.35	2.03	
27.80	26.50		3.18	0.06	0.06		4.48	0.35	2.03	
26.10	26.90		3.18	0.06	0.07		4.43	0.36	2.00	
27.16	29.30		3.10	0.06	0.07		4.48	0.35	2.10	
27.46	29.08		3.09	0.06	0.07		4.47	0.35	2.08	
27.46	29.65		3.09	0.06	0.07		4.46	0.34	2.12	
27.21	29.49		3.08	0.06	0.07		4.48	0.34	2.01	
27.03	28.68		3.09	0.06	0.07		4.47	0.34	2.06	
27.08	29.29		3.10	0.06	0.07		4.47	0.35	2.15	
27.47	28.78		3.09	0.06	0.07		4.47	0.35	2.19	
27.83	29.79		3.09	0.06	0.07		4.45	0.35	2.15	
26.30			3.18	0.06	0.07		4.56	0.35	2.15	
26.70			3.18	0.06	0.07		4.55	0.35	2.15	
27.00			3.16	0.06	0.07		4.54	0.35	2.16	
26.30			3.16	0.06	0.07		4.55	0.35	2.15	
25.70			3.17	0.06	0.07		4.54	0.35	2.16	
25.20			3.17	0.06	0.07		4.56	0.35	2.15	
26.90			3.18	0.05	0.07		4.54	0.35	2.16	
26.50			3.17	0.05			4.54	0.35	2.13	
27.50				0.05					2.07	
28.00				0.05					2.08	
27.90				0.05					2.03	
28.60				0.05					2.05	
29.40				0.05					2.02	
29.40				0.05					2.07	
29.50									2.07	
26.10									2.05	

Assay Data (Cont.)

XRF SiO ₂ %	XRF TiO ₂ %	4A_MICP U ppm	XRF U ppm	XRF U ₃ O ₈ %	SG SG Dimensionless	4A_MICP Ag ppm	4A_MICP As ppm	4A_MICP Ba ppm	4A_MICP Be ppm	4A_MICP Bi ppm
88.84	0.15	639	678	0.08	2.79	3.20	210	61.00	0.50	2.05
88.94	0.16	627	678	0.08	2.77	2.90	201	62.00	0.50	2.11
89.02	0.15	632	678	0.08	2.77	3.40	211	63.00	0.50	2.02
88.82	0.16	625	678	0.08	2.80	3.10	206	63.00	0.50	2.00
88.87	0.16	625	678	0.08	2.78	3.20	203	60.00	0.50	2.08
88.91	0.15	617	678	0.08	2.77	3.20	208	62.00	0.50	2.01
88.68	0.16	617	678	0.08	2.78	3.00	203	63.00	0.50	2.04
88.81	0.15	617	678	0.08	2.73	3.30	197	62.00	0.50	2.06
90.50	0.15	630	669	0.08	2.76	3.20	218	66.00	0.50	2.18
89.90	0.15	630	660	0.08	2.76	3.00	212	65.00	0.50	2.10
89.70	0.15	650	665	0.08	2.75	3.00	200	66.00	0.50	2.14
89.70	0.16	620	675	0.08	2.75	3.10	220	65.00	0.50	2.27
89.50	0.16	640	672	0.08	2.76	2.90	212	66.00	0.50	2.27
89.60	0.15	630	679	0.08	2.75	3.00	207	67.00	0.50	2.24
89.60	0.15	650	675	0.08	2.74	3.10	211	68.00	0.50	2.15
89.40	0.15	640	685	0.08	2.77	2.80	216	68.00	0.50	2.17
88.80	0.16	693	650	0.08	2.75	2.78	208	60.00	0.50	2.00
88.80	0.16	675	650	0.08	2.76	2.93	212	60.00	0.50	2.00
88.30	0.16	693	650	0.08	2.75	2.92	210	60.00	0.40	1.90
89.10	0.16	686	650	0.08	2.76	2.56	208	60.00	0.41	1.90
88.50	0.15	681	660	0.08	2.75	2.76	215	60.00	0.40	1.90
88.70	0.15	685	650	0.08	2.76	2.85	208	60.00	0.41	2.00
88.30	0.16	682	660	0.08	2.75	2.96	217	60.00	0.41	2.00
87.00	0.15	673	650	0.08	2.76	2.97	215	57.50	0.40	2.00
87.93	0.15	541	633	0.07	2.74	2.50	188	55.00	0.40	2.02
88.36	0.15	546	636	0.08	2.74	2.50	193	58.30	0.40	2.02
88.45	0.15	542	634	0.07	2.74	2.50	191	55.50		2.01
88.36	0.15	536	633	0.07	2.74	2.50	190	56.00		2.01
88.28	0.15	538	639	0.08	2.74	2.50	184	54.10		2.03
88.38	0.16	546	637	0.08	2.74	2.50	193	61.00		2.00
88.59	0.16	536	635	0.07	2.74	2.50	185	62.00		2.06
88.84	0.16	538	635	0.07	2.74	3.00	198	61.00		2.02
87.73	0.16	658			2.70		201	61.00		
87.78	0.16	658			2.69		196	61.00		
87.40	0.16	657			2.73		194	63.00		
87.71	0.16	659			2.72		199	61.00		
87.79	0.16	662			2.72		204	63.00		
87.69	0.15	660			2.79		197	64.00		
87.67	0.15	657			2.81		205	64.00		
87.64	0.15	656			2.83			65.00		
89.01	0.15				2.82			65.00		
88.99	0.15				2.79			64.00		
88.84	0.15				2.85			65.00		
88.85	0.15				2.80			65.00		
88.81	0.15				2.82			65.00		
88.83	0.16									
88.91	0.16									
88.87	0.15									
	0.16									
	0.16									
	0.16									
	0.16									
	0.16									

Assay Data (Cont.)

4A_MICP Ca ppm	4A_MICP Cd ppm	4A_MICP Ce ppm	4A_MICP Co ppm	4A_MICP Cr ppm	4A_MICP Cs ppm	4A_MICP Cu ppm	4A_MICP Dy ppm	4A_MICP Er ppm	4A_MICP Eu ppm	4A_MICP Fe ppm	4A_MICP Ga ppm
463	3.24	36.70	54.20	408.00	1.10	77.00	5.67	2.46	1.01	34200	3.40
438	3.38	36.40	52.90	419.00	1.00	74.00	5.41	2.48	1.01	33000	3.40
454	3.47	36.20	56.50	377.00	1.00	75.00	5.26	2.58	0.91	34400	3.40
486	3.20	36.50	53.90	368.00	1.10	75.00	5.44	2.51	0.99	33800	3.40
445	3.12	35.90	53.00	343.00	1.00	75.00	5.31	2.33	0.96	33600	3.40
435	3.34	37.80	55.30	345.00	1.00	72.00	5.21	2.50	0.94	32700	3.30
465	3.07	38.40	52.80	419.00	1.00	74.00	5.26	2.49	0.98	32700	3.40
434	3.16	35.90	55.80	392.00	1.00	76.00	5.57	3.00	1.00	31900	4.20
500	3.40	42.91	52.00	389.00	1.11	75.00	5.85	2.95	0.95	33100	4.10
500	3.30	42.38	50.00	396.00	1.11	73.00	5.95	3.05	0.90	33300	3.90
500	3.40	42.83	55.00	389.00	1.06	80.00	5.95	2.90	0.95	33200	4.40
500	3.30	43.40	54.00	396.00	1.11	81.00	5.85	3.05	0.95	33600	4.20
500	3.30	44.27	49.00	390.00	1.15	72.00	5.85	3.05	0.95	32900	4.10
500	3.40	43.79	53.00	391.00	1.08	77.00	5.95	3.05	0.95	33400	4.20
500	3.50	43.38	54.00	394.00	1.12	79.00	5.80	2.90	0.95	32900	4.30
500	3.40	41.97	49.00	390.40	1.11	74.00	5.65	2.77	0.95	33600	3.80
500	3.00	45.00	55.00	394.90	1.00	73.60	5.95	2.76	1.13	31500	3.80
500	3.50	45.30	55.00	396.70	1.10	73.40	5.96	2.81	1.15	31300	3.80
500	3.00	45.20	57.00	392.00	1.00	74.50	6.07	2.75	1.15	32200	3.80
500	3.00	45.50	55.00	389.10	1.00	80.40	6.04	2.80	1.16	31300	3.80
500	3.50	45.80	57.00	390.50	1.10	74.90	5.98	2.78	1.15	32000	4.00
500	3.50	46.70	56.00	394.10	1.10	72.50	5.96	2.77	1.12	31300	3.80
500	3.00	45.30	57.00	393.70	1.00	74.00	5.98	2.78	1.14	32100	3.80
500	3.00	46.50	57.00	330.00	1.00	74.60	5.99		1.14	31900	4.60
500	3.71	52.61	58.59	390.00	1.13	74.00				33500	4.80
500	3.65	52.58	59.76	370.00	1.12	74.00				33700	4.80
500	3.71	53.63	58.60	330.00	1.12	77.00				33500	4.70
500	3.73	52.54	58.96	320.00	1.13	73.00				33400	4.40
500	3.68	52.85	58.81	350.00	1.15	76.00				33800	4.40
500	3.68	52.76	59.34		1.13	75.00				33000	4.60
500	3.68	52.62	58.81		1.16	75.00				33600	4.60
500	3.68	52.54	58.64		1.13	74.00				33400	
			60.00			84.11				31800	
			60.00			84.95				32400	
			55.00			84.04				31600	
			60.00			83.01				32100	
			55.00			82.80				31800	
			60.00			83.18				32400	
			60.00			83.75				32100	
			60.00			82.92				32300	
			56.00			80.00					
			55.70			80.00					
			56.10			75.00					
			55.80			80.00					
			55.70			75.00					
			56.00			75.00					
			56.20			75.00					
			56.20			80.00					
						92.00					
						92.00					
						92.00					
						92.00					

Assay Data (Cont.)

4A_MI CP Gd ppm	4A_MI CP Ho ppm	4A_MI CP In ppm	4A_MI CP K ppm	4A_MI CP La ppm	4A_MI CP Li ppm	4A_MI CP Lu ppm	4A_MI CP Mg ppm	4A_MI CP Mn ppm	4A_MI CP Mo ppm	4A_MI CP Na ppm	4A_MI CP Nb ppm	4A_MI CP Nd ppm
5.04	0.72	0.06	3033	21.60	4.90	0.20	1664	140	2.80	781	2.80	21.00
5.16	0.72	0.07	3109	21.30	4.80	0.19	1600	143	2.40	767	2.70	20.80
4.72	0.64	0.07	3089	18.80	4.90	0.17	1662	141	2.60	836	2.40	18.90
5.11	0.72	0.06	3030	21.40	4.90	0.19	1665	142	2.80	746	2.40	20.50
5.01	0.69	0.07	3034	20.90	4.90	0.19	1637	137	2.40	789	2.70	20.90
4.88	0.67	0.06	2908	19.70	4.90	0.17	1599	140	2.40	771	2.50	19.60
5.01	0.69	0.07	2900	22.60	4.80	0.19	1597	131	2.70	750	2.50	20.70
5.06	0.70	0.07	2800	21.40	5.10	0.19	1600	130	2.40	824	2.40	20.90
4.80	1.10	0.07	2900	20.00	5.00	0.28	1600	138	3.01	800	2.40	17.90
4.80	1.08	0.08	3000	20.00	5.00	0.28	1600	136	2.93	800	2.60	17.50
4.60	1.08	0.08	2900	20.00	5.00	0.28	1700	136	2.71	800	2.10	17.80
4.80	1.06	0.07	2900	20.00	5.00	0.26	1600	132	3.14	900	2.30	17.80
4.80	1.06	0.07	2800	20.00	5.00	0.28	1600	143	3.12	800	2.30	17.70
4.60	1.10	0.07	2900	20.00	5.00	0.28	1600	134	2.88	800	2.20	18.70
5.00	1.08	0.06	2900	20.00	5.00	0.28	1600	136	3.12	800	3.00	17.80
4.80	1.04	0.06	2900	20.00	5.50	0.26	1600	135	3.02	800	2.90	18.60
5.31	1.04	0.08	3000	23.08	5.50	0.29	1600	139	3.00	800	3.50	21.97
5.31	1.01	0.06	2800	23.01	5.50	0.28	1600	134	3.09	800	3.00	22.03
5.27	1.04	0.06	2900	23.61	5.50	0.28	1600	136	2.99	800	3.50	21.07
5.30	1.02	0.06	2900	22.81	5.50	0.29	1600	134	2.91	800	3.50	21.24
5.27	1.04	0.06	2900	22.23	5.50	0.29	1600	138	2.92	800	3.50	21.00
5.33	1.04	0.06	2900	23.01	5.50	0.28	1600	135	3.00	800	3.50	21.15
5.20	1.00	0.08	2900	23.00	5.60	0.28	1600	140	2.94	800	3.50	21.04
5.26	1.06	0.08	3000	23.11	5.40	0.28	1600	141	3.00	800	3.50	21.05
		0.08	3000	21.10	5.60		1600	141	2.50	1000	3.08	
		0.08	2900	21.20	5.80		1600	137	2.50	1000	2.99	
		0.08	3100	21.20	5.40		1600	138	2.50	1000	3.04	
		0.08	3000	21.00	5.40		1600	141	2.50	1000	3.04	
		0.08	2900	21.20	5.50		1600	138	2.50	1000	2.97	
		0.08	3000	21.80	5.40		1600	134	2.50	1000	2.96	
			3000	20.90			1700	140	2.50	1000	3.04	
			3000	21.60			1700	136	2.50	1000	3.00	
			3000	25.53			1700	140	2.95	900		
			3000	25.64			1700	138	2.95	900		
			3000	25.61			1700	132	2.95	900		
			3000	25.74			1700	134	2.99	900		
			3000	25.20			1700	136	2.97	900		
			3000	25.60			1700		3.10	900		
				25.50					2.96	900		
				25.64					3.04	900		

Assay Data (Cont.)

4A MI CP Ni ppm	4A MI CP Pb ppm	4A MI CP Pr ppm	4A MI CP Rb ppm	4A MI CP Sb ppm	4A MI CP Sc ppm	4A MI CP Sm ppm	4A MI CP Sn ppm	4A MI CP Sr ppm	4A MI CP Tb ppm	4A MI CP Te ppm	4A MI CP Th ppm	4A MI CP Hf ppm
117	233	5.61	12.30	7.40	3.00	4.80	1.10	30.50	0.70	0.50	48.44	2.90
112	227	5.55	12.30	7.00	3.00	4.70	1.10	30.40	0.70	0.40	47.79	2.50
119	233	5.01	12.60	7.30	3.00	4.40	1.00	31.80	0.63	0.50	48.78	2.50
113	230	5.63	12.60	8.20	3.00	4.90	1.10	30.60	0.71	0.40	48.58	2.50
116	228	5.51	13.10	8.40	3.00	4.80	1.30	29.40	0.70	0.40	48.14	2.50
114	227	5.17	12.60	6.50	3.00	4.50	1.10	30.60	0.67	0.50	47.76	2.50
115	228	5.90	12.40	6.60	3.00	4.80	1.10	30.20	0.70	0.40	47.92	2.50
112	236	5.55	11.30	7.61	3.00	4.80	1.00	29.50	0.70	0.50	47.68	2.70
112	227	4.70	13.28	6.99	2.80	4.40	1.50	30.60	0.86	0.51	51.00	2.10
108	230	4.70	14.65	6.28	2.70	4.25	1.40	28.40	0.88	0.52	51.10	2.13
120	231	4.74	13.99	7.73	2.80	4.35	1.60	30.10	0.88	0.50	47.70	1.89
119	243	4.76	13.54	7.21	3.00	4.30	1.50	32.20	0.84	0.53	49.70	2.10
105	243	4.74	13.56	6.80	2.90	4.55	1.40	31.60	0.88	0.52	50.50	2.02
114	227	4.82	12.85	7.50	2.80	4.55	1.60	30.40	0.90	0.53	49.90	1.93
117	225	4.72	13.45	7.71	2.80	4.50	1.50	29.90	0.84	0.50	50.20	1.93
109	225	4.82	14.25	5.80	2.90	4.35	1.00	30.70	0.88	0.50	50.10	2.05
108	232	5.85	11.00	6.20	3.13	5.04	1.00	31.00	0.98	0.40	50.00	2.99
106	230	5.90	11.20	6.40	3.01	5.05	1.00	32.00	0.99	0.40	50.00	2.46
109	241	5.88	11.00	6.40	3.12	5.06	1.00	32.00	1.03	0.40	50.00	2.32
106	226	5.91	10.80	6.40	3.05	5.02	1.00	30.00	1.07	0.40	50.00	2.06
110	235	5.90	11.00	6.60	2.94	4.91	1.00	32.00	1.00	0.40	50.00	2.27
107	226	5.86	11.20	6.00	3.12	4.95	1.00	31.00	1.00	0.40	50.00	2.30
110	236	5.93	10.80	6.40	3.01	4.93	1.00	31.00	0.99	0.40	50.00	2.37
109	231	5.87	11.00		2.97	5.00		31.00	1.01	0.40	50.00	2.31
117	227		14.60		3.50			31.77			46.36	3.00
117	223		14.50		3.40			32.03			47.05	3.20
116	227		14.40		3.80			31.36			45.21	3.20
118	231		14.80		3.60			31.32			46.69	3.20
117	231		14.60		3.40			32.02			45.83	3.00
117	225		14.60		3.40			32.27			46.80	3.20
117	229		14.50		3.40			31.76			47.10	3.20
117	227		14.50		3.50			31.59			46.82	3.20
120	215							28.00			50.00	2.25
115	217							28.00			49.00	2.26
115	216							28.00			50.00	2.24
115	221							28.50			50.00	2.31
120	220							28.50			50.00	2.22
115	214							30.80			49.00	2.22
120	217							30.60			50.00	2.23
115	222							30.60			50.00	2.27
114	206							30.70				
113	209							30.60				
113	206							30.50				
111	218							30.60				
112	209							30.60				
111												
112												
114												

Assay Data (Cont.)

4A_MICP Ti ppm	4A_MICP Tm ppm	4A_MICP V ppm	4A_MICP W ppm	4A_MICP Y ppm	4A_MICP Yb ppm	4A_MICP Zn ppm	4A_MICP Zr ppm	Combustion/LECO S %
0.14	0.27	14.00	0.50	16.50	2.20	357	91.90	1.93
0.13	0.27	14.00	0.50	15.90	2.20	336	90.90	1.93
0.13	0.24	14.00	0.50	16.20	2.10	356	89.10	1.93
0.13	0.28	14.00	0.50	15.70	2.10	353	85.50	1.91
0.13	0.25	14.00	0.50	15.80	2.50	345	86.10	1.91
0.14	0.24	14.00	0.40	16.20	2.20	327	86.90	1.92
0.15	0.26	14.00	0.50	15.80	2.30	328	84.90	1.92
0.16	0.26	16.00	0.50	16.20	2.20	329	88.90	1.88
0.10	0.38	17.00	0.60	14.30	2.02	342	91.30	1.86
0.10	0.38	16.00	0.70	13.80	2.16	327	92.10	1.88
0.10	0.38	17.00	0.60	12.70	2.09	326	87.30	1.86
0.10	0.36	17.00	0.70	13.80	2.07	356	89.80	1.87
0.10	0.36	16.00	0.60	13.60	2.11	347	91.60	1.86
0.10	0.38	16.00	0.60	13.20	2.02	331	88.90	1.88
0.10	0.38	17.00	0.60	13.40	2.10	321	89.60	1.87
0.10	0.38	14.00	0.60	14.00	2.12	338	88.70	1.90
0.21	0.38	14.00	0.50	21.40	2.50	338	108.00	1.87
0.21	0.38	14.00	0.50	20.20	2.50	336	108.00	1.88
0.22	0.38	14.00	0.50	20.70	2.60	340	109.00	1.90
0.22	0.39	14.00	0.50	20.40	2.40	329	112.00	1.87
0.21	0.38	14.00	0.50	21.30	2.55	339	110.00	1.85
0.21	0.38	14.00	0.50	21.80	2.45	333	118.00	1.85
0.22	0.38	14.00	0.50	20.60	2.45	340	113.00	1.90
0.21	0.38	16.66		20.10	2.50	337	116.00	1.90
		16.78		21.00	2.30	351	104.00	1.91
		16.71		21.00	2.33	353	104.00	1.89
		16.30		21.20	2.28	352	102.00	1.90
		15.95		21.10	2.31	356	102.00	1.85
		16.41		20.90	2.33	355	102.00	1.87
		16.62		21.00	2.34	350	101.00	1.94
		16.12		21.10	2.34	352	103.00	1.88
		15.00		21.00	2.33	355	103.00	1.86
		20.00				325		1.93
		20.00				325		1.93
		20.00				315		1.90
		15.00				315		1.93
		20.00				320		1.95
		15.00				320		1.92
		20.00				320		1.90
		18.00				320		
		18.00				324		
		18.00				330		
		18.00				324		
		17.00				326		
		18.00				328		
		18.00				324		
		18.00				326		
						326		

22. Reported Values

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

23. Validation of Accuracy (Trueness)

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

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

In the determination of limit of detection (LOD) and limit of quantitation (LOQ) in gravimetric fire assay (*i.e.* lead collection and weighing of resulting gold prill), the minimum mass that an assay microbalance is capable of weighing and the original test sample mass determines the LOD and the LOQ in the assay (Fraser, 2015), (see Appendix 6 for an example of the calculation LOD and LOQ and Table 13 for a recommend reporting scheme for LOD and LOQ values).

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

26. 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.

27. Minimum Sample Size

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

28. 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.

29. Recommended use in Quality Control

Users should set their own limits *i.e.* 1, 2 and 3 standard deviations from an obtained mean value based on at least 10 replicate analyses using this CRM (see Appendix 4 for detail on the use of this CRM in quality control).

30. Legal Notice

This certificate and the reference material described in it have been prepared with due care and attention. However, AMIS, a division of Torre Analytical Services (Pty) Ltd, Thivhafuni Matodzi, and Allan Fraser; accept no liability for any decisions or actions taken following the use of the reference material.

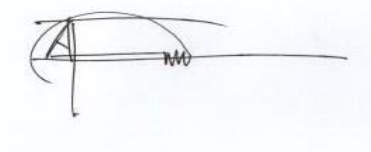
02 August 2018

Revision:00

Certifying Officers:

African Mineral Standards: _____

Thivhafuni Matodzi (Quality Specialist)

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

Geochemist: _____

Allan Fraser

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

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APPENDICES

Appendix 1: Uncertified Element Statistics

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

Table 9. Uncertified element concentrations statistics.

Element	Generic Method	<i>n</i>	Mean	SD	RSD %	Unit
BaO	XRF	11	0.010	<0.001	<0.001	%
CaO	FUS	5	0.072	0.004	6.211	%
Cr ₂ O ₃	FUS	8	0.064	0.005	8.118	%
K ₂ O	FUS	8	0.405	0.009	2.286	%
MnO	FUS	16	0.020	<0.001	<0.001	%
Na ₂ O	4A_MICP	8	0.120	<0.001	<0.001	%
S	FUS	8	1.830	0.024	1.306	%
SiO ₂	FUS	16	87.969	0.836	0.950	%
SrO	XRF	3	0.010	<0.001	<0.001	%
TiO ₂	FUS	14	0.160	<0.001	<0.001	%
Au	4A_MICP	8	24.634	0.457	1.854	g/t
Pd	Pb Collection	7	0.017	<0.001	2.242	g/t
Pt	Pb Collection	9	0.030	0.004	14.035	g/t
As	FUS	8	225.000	46.291	20.574	ppm
Ba	4A_ICPES	8	65.125	1.126	1.729	ppm
Co	4A_ICPES	7	56.000	<0.001	<0.001	ppm
Co	FUS	8	57.500	4.629	8.051	ppm
Cr	FUS	8	500.000	<0.001	<0.001	ppm
Cu	4A_ICPES	8	92.625	0.518	0.559	ppm
Cu	FUS	16	65.313	5.747	8.799	ppm
Fe	FUS	8	30137.500	140.789	0.467	ppm
Ge	4A_MICP	16	0.348	0.308	88.607	ppm
K	FUS	8	3000.000	<0.001	<0.001	ppm
Ni	4A_ICPES	8	114.375	1.847	1.615	ppm
Ni	FUS	15	104.800	13.790	13.159	ppm
Pb	FUS	7	100.000	<0.001	<0.001	ppm
Sr	4A_ICPES	8	30.250	0.463	1.530	ppm
Ta	4A_MICP	16	0.870	0.152	17.442	ppm
Zn	4A_ICPES	8	325.500	1.414	0.434	ppm
Zn	FUS	8	317.500	7.071	2.227	ppm
Zr	4A_ICPES	7	102.286	0.488	0.477	ppm

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

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

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

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

Outlier Removal

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

Z-Score

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

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

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

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

(Thompson & Lowthian, 2011)

Data with z-scores exceeding 2 are discarded and are not included for further assessment.

Cochran Test

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

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

Where, C_{calc} , s_{max}^2 and $\sum_{i=1}^l s_i^2$, are the calculated values for Cochran's test, data set with the maximum variance and the sum of the variances of all of the participating l laboratory datasets. The C_{calc} value is

compared with a critical value, C_{crit} at a level of confidence of 95% and an alpha of 0.05% (see Ellison, *et al.*, 2009, Appendix A, Table A.3a, page 209 for a table of critical values for the test of Cochran at LOC 95%).

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

Grubbs Test

The test of Grubbs (1969) calculates a test statistic, G. In the detection of a single outlier, G_1 is found by using

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

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

Method Performance

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

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

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

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

where s is the standard deviation of n replicates.

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

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

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

Grand Mean

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

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

Certified Value

From ANOVA as per the description in section 19, an 'appropriate precision' as shown in [8] is calculated for sufficient homogeneity (Thompson, 2008):

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

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

Total Variation (SST)

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

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

Between Group Variation (SSB)

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

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

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

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

Within Group Variation (SSW)

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

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

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

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

From equations [9] through [13], the ANOVA table as shown in Table 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 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 7, or from MS Excel as =TINV (5%, df)).

Uncertainty Statement

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

Appendix 3. Example: Comparison of Mean and Certified Value for Validation of Accuracy
(Prepared by Allan Fraser)

According to ERM (2005); Eurolab (2007); Abzalov (2011) and Carr (2011), the validation of accuracy for a given mean and certified value requires the inclusion of the measurement uncertainty of the CRM in a t-test for statistical significance. The classical Student's t-test as shown in [17], does not take into account 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 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 \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 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 Uncertainty (U)	Coverage Factor (k)	Mean ($n=9$)	n	Standard Deviation (s)
4.62%	0.08%	2.25	4.59	9	0.01015

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

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

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

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

Therefore, $t_{calc} = 0.84$ and $t_{crit}(5\%, 8) = 2.31$ (df is 8, therefore, $t_{crit}=2.31$, see Appendix 7, page 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.

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

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

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

1. Analyse 10 to 15 replicates or more of the AMIS CRM;
2. Apply the Grubbs test for outliers;
3. Determine the mean of the replicates after application of the Grubbs test;
4. Determine the standard deviation, using equation [19], of the replicates;
5. Calculate the standard deviation, s from:

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

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

6. Verify accuracy of the mean value using equation [18];
7. Once accuracy is verified, calculate $\pm 2s$ and $\pm 3s$, where s is the standard deviation calculated from [19].
8. Construct the Shewhart control chart around the mean of n replicates;
9. Use $\pm 2s$ as the warning limits;
10. Use $\pm 3s$ as the control limits;
11. It is recommended that if 2 to 3 points are outside warning the limits analyse another sample and if it then within warning limits, continue. If it is outside the warning limits, stop and troubleshoot;

12. It is recommended that if any point is outside control limits, analyse another portion (sample) of the CRM. If it is within control limits, continue. If it is outside control limits, stop and troubleshoot;
13. For reference purposes, the CRM certified value can be plotted on the Shewhart chart alongside the mean value.

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

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Appendix 5. Conversion to Air-dry Basis
(Prepared by Allan Fraser)

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

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

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

Example

The moisture content determined at 105°C on a CRM is 0.500%. The certified analyte concentration for the CRM is 12.62±0.52% (dry basis). Calculating the moisture correction factor using [20] gives:

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

Multiplying the factor of 0.995 by the certified value as stated on the certificate of analysis on a dry basis (as in [21]) gives the analyte concentration on an air-dry basis:

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

The stated measurement uncertainty also needs to be corrected using [20] and [21], e.g. 0.995 x 0.52 = 0.51(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 6. Example of Determination of LOD and LOQ in Fire Assay
Prepared by Allan Fraser

The limit of detection (LOD) is the minimum detectable quantity of the analyte of interest (Skoog & West, 1985). In order 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. Assuming that an analyst can weigh a prill of 1µg then the LOD becomes 1µg. However, the concentration factor would be 50 times for a 50-gram assay sample and therefore the LOD in g/t becomes 1µg divided by the original mass of the sample in grams taken for fire assay [22]. Therefore, the LOD in fire assay is computed as:

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

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

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

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be 0.02g/t. *i.e.* 1µg = 1g/t, therefore 1µg/50g = 0.02g/t. If no prill was found to be weighed then the LOD result would be <0.02 g/t or “not detected”. Table 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 7. 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.

<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		

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