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Certificate

# AMIS0385

## Certified Reference Material

Ni 1.77% Cu 0.96% Co 0.09% Ultramafic AU

### *Certificate of Analysis*

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## Summary Statistics

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

Analyte	Method	Certified ( $\mu$ ) <sup>8</sup>	(2s) <sup>10</sup> $\pm$	Unit
Ni	2A_MICP <sup>1</sup>	1.73	0.12	%
Ni	4A_MICP <sup>2</sup>	1.76	0.079	%
Ni	FUS <sup>3</sup>	1.77	0.071	%
Cu	2A_MICP	9511	468	ppm
Cu	4A_MICP	9629	359	ppm
Cu	FUS	9603	377	ppm
Au	Pb Collection <sup>4</sup>	0.031	0.009	g/t
Pd	Pb Collection	0.120	0.018	g/t
Pt	Pb Collection	0.029	0.013	g/t
SG	SG <sup>5</sup>	3.31	0.12	Dimensionless
S	Combustion/LECO <sup>6</sup>	13.05	0.68	%
S	2A_MICP	12.60	0.80	%
Ag	2A_MICP	3	0.9	ppm
Ag	4A_MICP	3	0.9	ppm
Al	4A_MICP	4.64	0.55	%
Al	FUS	4.53	0.23	%
Bi	4A_MICP	2	0.8	ppm
Ca	4A_MICP	2.25	0.25	%
Ca	FUS	2.44	0.33	%
Co	2A_MICP	888	131	ppm
Co	4A_MICP	934	58	ppm
Co	FUS	957	58	ppm
Cr	4A_MICP	1419	104	ppm
Cr	FUS	1668	129	ppm
Fe	2A_MICP	21.38	1.4	%
Fe	4A_MICP	25.23	1.7	%
Fe	FUS	24.78	1.8	%
Hf	4A_MICP	0.7	0.2	ppm
In	4A_MICP	0.2	0.06	ppm
Mg	4A_MICP	1.87	0.24	%
Mg	FUS	1.94	0.10	%
Mn	4A_MICP	952	107	ppm
Na	4A_MICP	6161	368	ppm
Nb	4A_MICP	4	0.2	ppm
P	4A_MICP	237	34	ppm
Sc	4A_MICP	13	1	ppm
Se	4A_MICP	21	3	ppm
Si	FUS	15.33	1.1	%
Sr	4A_MICP	100	5	ppm
Te	4A_MICP	1	0.3	ppm
Ti	4A_MICP	2293	407	ppm
Ti	FUS	2191	163	ppm
V	4A_MICP	115	31	ppm
W	4A_MICP	0.9	0.2	ppm
Y	4A_MICP	12	2	ppm
Zn	2A_MICP	58	16	ppm
Zn	4A_MICP	116	21	ppm

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

Analyte	Method	Certified ( $\mu$ ) <sup>8</sup>	(2s) <sup>10</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	FUS	8.56	0.43	%
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>7</sup>	8.85	0.36	%
CaO	XRF	3.22	0.11	%
Cr <sub>2</sub> O <sub>3</sub>	FUS	0.24	0.02	%
Fe <sub>2</sub> O <sub>3</sub>	FUS	35.44	2.6	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	35.82	0.91	%
K <sub>2</sub> O	XRF	1.00	0.070	%
MgO	FUS	3.22	0.15	%
MgO	XRF	3.30	0.15	%
MnO	XRF	0.12	0.02	%
Na <sub>2</sub> O	XRF	0.86	0.09	%
SiO <sub>2</sub>	FUS	32.74	2.6	%
SiO <sub>2</sub>	XRF	32.32	1.7	%
TiO <sub>2</sub>	FUS	0.37	0.03	%
TiO <sub>2</sub>	XRF	0.38	0.03	%

## 1. Certified Concentrations and Uncertainties

AMIS0385 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 ( $\mu$ ) <sup>8</sup>	N	n	k	% RSD	( $u_c$ ) <sup>9</sup>	(2s) <sup>10</sup> $\pm$	(CI) <sup>11</sup> 95%	(U) <sup>12</sup> $\pm$	Unit
Ni	2A_MICP <sup>1</sup>	1.73	6	48	2.571	3	0.060	0.12	0.061	0.2	%
Ni	4A_MICP <sup>2</sup>	1.76	11	86	2.228	2	0.040	0.079	0.026	0.09	%
Ni	FUS <sup>3</sup>	1.77	6	48	2.571	2	0.036	0.071	0.031	0.09	%
Cu	2A_MICP	9511	11	87	2.228	2	234	468	142	521	ppm
Cu	4A_MICP	9629	13	102	2.179	2	179	359	95	391	ppm
Cu	FUS	9603	6	48	2.571	2	189	377	164	485	ppm
Au	Pb Collection <sup>4</sup>	0.031	9	71	2.306	14	0.0043	0.009	0.0030	0.01	g/t
Pd	Pb Collection	0.120	11	84	2.228	7	0.0089	0.018	0.0050	0.02	g/t
Pt	Pb Collection	0.029	11	84	2.228	22	0.0064	0.013	0.0040	0.01	g/t
SG	SG <sup>5</sup>	3.31	13	102	2.179	2	0.059	0.12	0.033	0.1	Dimensionless
S	Combustion/LECO <sup>6</sup>	13.05	15	119	2.145	3	0.34	0.68	0.18	0.7	%
S	2A_MICP	12.60	2	16	12.706	3	0.40	0.80	3.0	5	%
Ag	2A_MICP	3	4	29	3.182	16	0.4	0.9	0.1	1	ppm
Ag	4A_MICP	3	6	47	2.571	17	0.5	0.9	0.4	1	ppm
Al	4A_MICP	4.64	8	61	2.365	6	0.27	0.55	0.23	0.6	%
Al	FUS	4.53	2	16	12.706	3	0.12	0.23	0.94	1	%
Bi	4A_MICP	2	3	24	4.303	17	0.4	0.8	1	2	ppm
Ca	4A_MICP	2.25	8	63	2.365	6	0.13	0.25	0.11	0.3	%
Ca	FUS	2.44	2	16	12.706	7	0.17	0.33	1.5	2	%
Co	2A_MICP	888	12	93	2.201	7	66	131	43	144	ppm
Co	4A_MICP	934	15	118	2.145	3	29	58	15	62	ppm
Co	FUS	957	7	54	2.447	3	29	58	20	71	ppm
Cr	4A_MICP	1419	4	32	3.182	4	52	104	75	166	ppm
Cr	FUS	1668	4	30	3.182	4	64	129	86	205	ppm
Fe	2A_MICP	21.38	6	48	2.571	3	0.68	1.4	0.67	2	%
Fe	4A_MICP	25.23	8	64	2.365	3	0.84	1.7	0.67	2	%
Fe	FUS	24.78	5	37	2.776	4	0.89	1.8	1.2	2	%
Hf	4A_MICP	0.7	3	23	4.303	13	0.09	0.2	0.1	0.4	ppm
In	4A_MICP	0.2	3	22	4.303	11	0.03	0.06	0.06	0.1	ppm
Mg	4A_MICP	1.87	7	55	2.447	6	0.12	0.24	0.11	0.3	%
Mg	FUS	1.94	3	24	4.303	3	0.052	0.10	0.11	0.2	%
Mn	4A_MICP	952	9	72	2.306	6	53	107	37	123	ppm
Na	4A_MICP	6161	6	48	2.571	3	184	368	175	473	ppm
Nb	4A_MICP	4	2	16	12.706	2	0.09	0.2	0.6	1	ppm
P	4A_MICP	237	5	39	2.776	7	17	34	17	48	ppm
Sc	4A_MICP	13	6	48	2.571	5	0.7	1	0.6	2	ppm
Se	4A_MICP	21	2	15	12.706	8	2	3	15	22	ppm
Si	FUS	15.33	3	24	4.303	4	0.57	1.1	1.4	2	%
Sr	4A_MICP	100	6	48	2.571	2	2	5	2	6	ppm
Te	4A_MICP	1	3	23	4.303	14	0.2	0.3	0.3	0.7	ppm
Ti	4A_MICP	2293	3	24	4.303	9	204	407	498	876	ppm
Ti	FUS	2191	3	22	4.303	4	81	163	168	350	ppm
V	4A_MICP	115	7	54	2.447	14	16	31	15	38	ppm
W	4A_MICP	0.9	3	23	4.303	10	0.09	0.2	0.1	0.4	ppm
Y	4A_MICP	12	4	32	3.182	11	1	2	2	4	ppm
Zn	2A_MICP	58	5	39	2.776	14	8	16	9	23	ppm
Zn	4A_MICP	116	9	71	2.306	9	10	21	7	24	ppm

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

Analyte	Method	Certified ( $\mu$ ) <sup>8</sup>	N	n	k	% RSD	( $u_c$ ) <sup>9</sup>	(2s) <sup>10</sup> $\pm$	(CI) <sup>11</sup> 95%	(U) <sup>12</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	FUS	8.56	2	16	12.706	2	0.21	0.43	2.0	3	%
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>7</sup>	8.85	6	47	2.571	2	0.18	0.36	0.19	0.5	%
CaO	XRF	3.22	5	39	2.776	2	0.056	0.11	0.070	0.2	%
Cr <sub>2</sub> O <sub>3</sub>	FUS	0.24	4	30	3.182	4	0.009	0.02	0.01	0.03	%
Fe <sub>2</sub> O <sub>3</sub>	FUS	35.44	5	37	2.776	4	1.3	2.6	2.0	4	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	35.82	4	31	3.182	1	0.45	0.91	0.72	1	%
K <sub>2</sub> O	XRF	1.00	6	48	2.571	3	0.035	0.070	0.036	0.09	%
MgO	FUS	3.22	3	23	4.303	2	0.075	0.15	0.17	0.3	%
MgO	XRF	3.30	5	40	2.776	2	0.077	0.15	0.092	0.2	%
MnO	XRF	0.12	5	40	2.776	7	0.008	0.02	0.009	0.02	%
Na <sub>2</sub> O	XRF	0.86	3	24	4.303	5	0.04	0.09	0.1	0.2	%
SiO <sub>2</sub>	FUS	32.74	3	24	4.303	4	1.3	2.6	3.0	6	%
SiO <sub>2</sub>	XRF	32.32	5	37	2.776	3	0.83	1.7	1.0	2	%
TiO <sub>2</sub>	FUS	0.37	3	22	4.303	4	0.01	0.03	0.03	0.06	%
TiO <sub>2</sub>	XRF	0.38	5	40	2.776	4	0.02	0.03	0.02	0.04	%

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

## 2. Statistical Comparison of Means

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

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

Method	Certified value	Method	Certified value	F-Test Outcome	$p$ -value (t-test)	t-test Outcome
S Combustion/LECO	13.05 %	S 2A_MICP	12.6 %	Equal Variance ( $p=0.265$ )	0.087	Accept $H_0$ ; certified values are equal
Al <sub>2</sub> O <sub>3</sub> FUS	8.56 %	Al <sub>2</sub> O <sub>3</sub> XRF	8.85 %	Equal Variance ( $p=0.351$ )	0.098	Accept $H_0$ ; certified values are equal
Fe <sub>2</sub> O <sub>3</sub> FUS	35.44 %	Fe <sub>2</sub> O <sub>3</sub> XRF	35.82 %	Equal Variance ( $p=0.054$ )	0.606	Accept $H_0$ ; certified values are equal
MgO FUS	3.22 %	MgO XRF	3.30 %	Equal Variance ( $p=0.496$ )	0.205	Accept $H_0$ ; certified values are equal
TiO <sub>2</sub> FUS	0.365 %	TiO <sub>2</sub> XRF	0.379 %	Equal Variance ( $p=0.365$ )	0.251	Accept $H_0$ ; certified values are equal
SiO <sub>2</sub> FUS	32.74 %	SiO <sub>2</sub> XRF	32.32 %	Equal Variance ( $p=0.278$ )	0.601	Accept $H_0$ ; certified values are equal
Ag 2A_MICP	3 ppm	Ag 4A_MICP	3 ppm	Unequal Variance ( $p=0.013$ )	0.734	Accept $H_0$ ; certified values are equal
Zn 2A_MICP	0.006 %	Zn 4A_MICP	0.012 %	Equal Variance ( $p=0.366$ )	$<0.001$	Reject $H_0$ ; certified values are <i>not</i> equal
Al FUS	4.53 %	Al 4A_MICP	4.64 %	Equal Variance ( $p=0.289$ )	0.624	Accept $H_0$ ; certified values are equal
Ca FUS	2.44 %	Ca 4A_MICP	2.25 %	Equal Variance ( $p=0.24$ )	0.112	Accept $H_0$ ; certified values are equal
Cr FUS	0.167 %	Cr 4A_MICP	0.142 %	Equal Variance ( $p=0.421$ )	$<0.001$	Reject $H_0$ ; certified values are <i>not</i> equal
Mg FUS	1.94 %	Mg 4A_MICP	1.87 %	Equal Variance ( $p=0.14$ )	0.373	Accept $H_0$ ; certified values are equal
Ti FUS	0.219 %	Ti 4A_MICP	0.229 %	Equal Variance ( $p=0.102$ )	0.447	Accept $H_0$ ; certified values are equal



**Table 4.** ANOVA outcome for comparison of means.

<b>Method</b>	<b>Average (ppm)</b>	<b>s</b>
Ni 2A_MICP	17292	584
Ni 4A_MICP	17587	390
Ni Fus	17708	297
<b>F-ANOVA p-value=0.240</b>		
<b>Method</b>	<b>Average (ppm)</b>	<b>s</b>
Cu 2A_MICP	9511	212
Cu 4A_MICP	9629	157
Cu Fus	9603	157
<b>F-ANOVA p-value=0.276</b>		
<b>Method</b>	<b>Average (ppm)</b>	<b>s</b>
Co 2A_MICP	888	68
Co 4A_MICP	934	28
Co Fus	957	22
<b>F-ANOVA p-value=0.007</b>		
At least one of the means is different		
<b>Method</b>	<b>Average (%)</b>	<b>s</b>
Fe 2A_MICP	21.38	0.64
Fe 4A_MICP	25.23	0.80
Fe_Fus	24.78	0.93
<b>F-ANOVA p-value&lt;0.001</b>		
Fe 4A_MICP mean=Fe Fus mean		

### 3. Intended Use

AMIS0385 is a matrix matched Certified Reference Material, fit for use as a control sample in routine assay laboratory quality control when inserted within runs of test samples and measured in parallel to test samples. This material can also be used for method development, use as independent calibration verification check standard (*i.e.* if not used as a calibration standard in an instrument calibration), or for validation of accuracy in a method validation exercise (see Appendix 3). The recommend procedure for the use of this CRM as a control standard in laboratory quality control is to develop a Shewhart chart, where a mean value and corresponding 1, 2 and 3 standard deviations are derived from replicate measurements of the CRM (see Appendix 6). This CRM can also be used to assess inter-laboratory or instrument bias and establish within-laboratory precision and within-laboratory reproducibility. The certified concentrations and expanded uncertainty for this material are property values based on an inter-laboratory measurement campaign and reflect consensus results from the laboratories that took part in the exercise.

#### 4. Abbreviations and Symbols

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

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

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

Abbreviation/Symbol	Description
2s	Two times standard deviation
SI	Standard International system of units
t <sub>calc</sub>	Calculated t statistic from a one-sample, two-tailed t-test
t-critical or t <sub>crit</sub>	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 <sub>c</sub>	Combined standard uncertainty at k=1
µm	Micron, is an SI derived unit of length equaling 1×10 <sup>-6</sup> of a meter

## 5. Uncertified Concentration Values

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

## 6. Units

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

## 7. Analytical and Physical Methods

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

## 8. Origin of Material

The material for AMIS0385 was provided by SGS Minerals from the Savannah Nickel Mine (previously known as the Sally Malay Mine) which is owned and operated by Panoramic Resources Limited. The Sally Malay deposit is situated about 100 kilometres north of Halls Creek in Western Australia.

## 9. Approximate Mineral and Chemical Composition

The Sally Malay nickel deposit is hosted by one of an extensive suite of mafic and ultramafic intrusives within the late Palaeoproterozoic Halls Creek Mobile Zone in northern Western Australia, formed on the eastern margin of the Kimberley Block. The late Palaeoproterozoic host intrusive comprises a rhythmically layered body of olivine gabbro, troctolite, norite and minor anorthosites and other ultramafics, with ultramafic basal zones containing nickel sulphides. This intrusive was emplaced into granulite facies rocks, as were most of the mineralised intrusives in the district. The ore is dominantly composed of pyrrhotite /chalcopyrite /pentlandite and occurs as two, steeply dipping lenses of massive sulphide (>40% total sulphide) of 3 to 40 metres in thickness, hosted by the basal norite zone within the layered ultramafic complex.

## **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<sub>2</sub>. Where quantitative XRD results do not correspond to results of other analytical techniques, it should be borne in mind that even though the data are quantitative they are meant to be used for indicative purposes in development of other analytical methods. Mineral names may not reflect the actual compositions of minerals identified, but rather the mineral group.

## **11. Health and Safety**

The material is a very fine powder coloured dark grey (Corstor 5YR 6/2). Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

## **12. Method of Preparation**

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

## **13. 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).

## **14. 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.

## 15. Methods of Analysis Requested

The following methods of analysis were requested:

- a) Pt, Pd and Au. Pb collection with Ag as a co-collector, ICP-OES or ICP-MS.
- b) Multi element scan to include Co, Cu and Ni. Multi-acid total digestion, including HF, ICP-OES or ICP-MS.
- c) Co, Cu and Ni. Aqua regia digestion with ICP-OES or ICP-MS.
- d) Co, Cu and Ni. Fusion AAS.
- e) Majors (Al<sub>2</sub>O<sub>3</sub>, CaO, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MgO, MnO, Na<sub>2</sub>O, SiO<sub>2</sub>, TiO<sub>2</sub>. LOI.) XRF fusion.
- f) S – combustion analysis.
- g) SG – gas pycnometer

## 16. Information Requested of Participating Laboratories

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

- a) State and provide brief description of analytical techniques used.
- b) State aliquots used for all determinations.
- c) Results for individual analyses to be reported.
- d) All results for individual PGM's to be reported in ppb.
- e) All results for base metals to be reported in ppm.
- f) Report all QC data, to include replicates, blanks and certified reference materials used.

## 17. 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)

## 18. Two Standard Deviations

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

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

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

## 19. Confidence Interval

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

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

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

## 20. 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]).

## 21. Confidence Interval and Expanded Uncertainty

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

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

## **22. Participating Laboratories**

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

1. ACME Analytical Laboratories Ltd CA
2. ALS Geochemistry Brisbane
3. ALS Geochemistry Ireland
4. ALS Geochemistry Perth
5. ALS Geochemistry SA
6. ALS Geochemistry Vancouver
7. Genalysis Laboratory Services (South Africa) Pty
8. Intertek Perth
9. Intertek Utama Services (Indonesia)
10. Labtium Inc Finland
11. Set Point Laboratories (Isando) SA
12. SGS Australia Pty Ltd (Newburn) WA
13. SGS Geosol Laboratories Ltda (Brazil)
14. SGS Mineral Services Callao (Peru)
15. SGS Mineral Services Lakefield (Canada)
16. SGS South Africa
17. SGS Vancouver (Canada)
18. Ultra Trace (Pty) Ltd WA

## 23. Accepted Assay Data

Data from the 18 laboratories used for certification are set out in Table 7.

**Table 7.** Data used to calculate the certified values after removal of outliers.

2A_MICP	4A_MICP	FUS	2A_MICP	4A_MICP	FUS	Pb Collection	Pb Collection	Pb Collection	SG	Combustion/LECO
Ni	Ni	Ni	Cu	Cu	Cu	Au	Pd	Pt	SG	S
ppm	ppm	ppm	ppm	ppm	ppm	g/t	g/t	g/t	Dimensionless	%
18050	17300	17300	9710	9570	9200	0.03	0.12	0.03	3.33	12.95
18000	17550	17700	9650	9720	9500	0.03	0.12	0.03	3.32	13.30
17650	17600	17600	9460	9600	9600	0.03	0.12	0.03	3.32	12.60
17900	17550	16900	9580	9670	9400	0.03	0.12	0.03	3.32	12.65
17950	17550	17700	9450	9600	9500	0.03	0.12	0.03	3.32	13.00
17900	17350	17100	9530	9550	9500	0.03	0.12	0.03	3.34	13.25
18100	17150	17500	9670	9530	9400	0.03	0.12	0.03	3.32	13.20
18050	17500	17200	9680	9540	9200	0.03	0.12	0.02	3.32	12.75
17300	17700	17641	9390	9703	9540	0.03	0.13	0.03	3.29	13.80
17250	17700	17579	9440	9571	9545	0.03	0.14	0.02	3.31	13.60
17300	17950	17722	9430	9884	9545	0.03	0.12	0.03	3.31	13.70
17100	17900	17790	9250	9880	9620	0.03	0.12	0.04	3.32	13.70
17500	17850	17404	9470	9852	9442	0.03	0.13	0.03	3.26	13.80
17200	17900	17613	9280	9754	9440	0.03	0.13	0.02	3.30	13.70
17300	17900	17756	9430	9808	9628	0.03	0.13	0.02	3.31	13.70
17400	17850	17643	9370	9860	9547	0.03	0.13	0.03	3.31	12.50
16607	18300	17950	9696	9560	9380	0.03	0.13	0.03	3.20	12.80
16697	18100	18150	9683	9640	9270	0.03	0.13	0.03	3.24	13.00
16724	18000	18200	9725	9640	9750	0.03	0.13	0.03	3.19	12.80
16814	18100	17650	9720	9770	9800	0.03	0.13	0.03	3.23	12.90
16604	18200	18050	9732	9700	9550	0.03	0.13	0.03	3.20	13.10
16252	17900	18000	9628	9670	9480	0.03	0.13	0.03	3.19	12.90
16260	18300	17800	9605	9780	9430	0.03	0.11	0.03	3.19	12.90
16150	17721	17750	9722	9660	9420	0.03	0.12	0.04	3.21	13.08
17950	17852	17400	9490	9400	9540	0.03	0.11	0.04	3.41	12.94
17900	17872	17300	9630	9400	9620	0.03	0.11	0.03	3.40	13.10
18150	17757	17400	9600	9300	9460	0.03	0.11	0.03	3.41	13.12
17950	17835	17300	9810	9500	9510	0.03	0.12	0.03	3.41	12.97
17900	17862	17500	9790	9400	9670	0.03	0.12	0.03	3.41	13.09
18050	17908	17200	9750	9300	9620	0.03	0.11	0.04	3.41	13.08
17750	17700	17600	9700	9400	9690	0.03	0.12	0.04	3.40	13.09
18000	17800	17500	9740	9445	9510	0.03	0.13	0.03	3.41	12.90
16700	17700	18600	9730	9459	9800	0.04	0.12	0.03	3.22	12.90
16850	17700	18500	10000	9550	9750	0.04	0.13	0.03	3.25	12.90
16950	17700	17900	9740	9532	9700	0.04	0.13	0.03	3.28	12.90
16800	17600	18000	9650	9471	9750	0.03	0.13	0.03	3.23	13.00
16600	17800	18200	9740	9565	9750	0.04	0.12	0.03	3.26	12.90
16950	17700	18000	9690	9552	9700	0.04	0.12	0.03	3.29	12.80
17100	17600	17900	9660	9517	9700	0.04	0.13	0.03	3.27	12.90
16650	18080	17900	9110.3	9570	9900	0.03	0.12	0.02	3.23	13.15
17350	17960	17600	9292.3	9400	9700	0.03	0.10	0.02	3.23	13.35
17100	18080	17600	9076.1	9440	9900	0.03	0.11	0.02	3.25	13.00
17100	17780	18100	9214.3	9470	9800	0.03	0.10	0.02	3.28	13.35
17250	18030	17600	9176	9730	9900	0.03	0.11	0.02	3.25	13.10
17100	17910	17800	9267.3	9500	9900	0.02	0.11	0.03	3.28	13.20
17450	17850	17800	9133.7	9440	9800	0.03	0.11	0.02	3.29	12.85
17050	18080	17900	9503.2	9460	9800	0.03	0.12	0.03	3.26	13.50
17300	17550	17700	9488	9780	9800	0.04	0.13	0.02	3.25	13.39



**Assay Data (Cont.)**

2A_MICP	4A_MICP	2A_MICP	4A_MICP	Pb Collection	Pb Collection	Pb Collection	SG	Combustion/LECO
S	Ni	Cu	Cu	Au	Pd	Pt	SG	S
%	ppm	ppm	ppm	g/t	g/t	g/t	Dimensionless	%
12.46	17800.00	9539.00	9750.00	0.04	0.12	0.04	3.26	13.53
12.35	17600.00	9604.00	9770.00	0.04	0.13	0.03	3.25	13.48
12.41	17850.00	9545.00	9570.00	0.04	0.13	0.04	3.36	13.46
12.09	17800.00	9214.00	9740.00	0.03	0.13	0.03	3.28	13.41
12.52	17700.00	9330.00	9670.00	0.03	0.13	0.04	3.35	13.50
12.05	17550.00	9574.00	9570.00	0.04	0.13	0.03	3.32	13.50
12.46	17350.00	9359.00	9650.00	0.04	0.13	0.04	3.27	13.39
12.35	17450.00	9876.70	9670.00	0.02	0.12	0.03	3.37	13.00
12.95	17500.00	9708.40	9880.00	0.03	0.13	0.03	3.31	12.90
12.80	17700.00	9674.70	9960.00	0.03	0.13	0.03	3.33	12.90
12.75	17750.00	9312.10	9750.00	0.03	0.12	0.03	3.33	12.90
12.90	17650.00	9716.10	9950.00	0.03	0.13	0.03	3.32	13.00
12.75	17650.00	9645.60	9770.00	0.03	0.12	0.03	3.31	13.00
13.00	17550.00	9750.20	9800.00	0.03	0.12	0.02	3.31	13.00
12.80	17300.00	9636.90	9560.00	0.03	0.11	0.02	3.31	12.90
13.00	16700.00	9020.00	9730.00	0.03	0.11	0.02	3.31	12.84
	16700.00	9140.00	9860.00	0.03	0.11	0.02	3.33	12.76
	16700.00	9120.00	9630.00	0.04	0.11	0.03	3.29	12.79
	16700.00	9110.00	9790.00	0.03	0.11	0.02	3.30	12.97
	16800.00	9000.00	9760.00	0.03	0.12	0.03	3.32	13.13
	16700.00	9150.00	9710.00	0.03	0.11	0.02	3.29	12.75
	16700.00	9170.00	9670.00	0.03	0.11	0.03	3.31	12.72
	17600.00	8920.00	9440.00	0.03	0.11	0.03	3.32	12.82
	17300.00	9560.00	9760.00		0.11	0.03	3.29	12.50
	17600.00	9490.00	9670.00		0.11	0.03	3.36	12.40
	17600.00	9430.00	9930.00		0.11	0.03	3.38	12.60
	17300.00	9410.00	9880.00		0.10	0.03	3.31	12.60
	17200.00	9420.00	9840.00		0.10	0.03	3.27	12.70
	17200.00	9560.00	9800.00		0.12	0.03	3.32	12.70
	17400.00	9480.00	9730.00		0.12	0.04	3.29	12.50
	17200.00	9620.00	9600.00		0.12	0.04	3.38	12.60
	17200.00	9550.00	9700.00		0.12	0.04	3.28	13.60
	17200.00	9660.00	9700.00		0.13	0.04	3.21	13.50
	17100.00	9700.00	9700.00		0.12	0.04	3.21	13.50
	17100.00	9560.00	9700.00		0.13	0.04	3.24	13.40
	17200.00	9570.00	9700.00		0.12	0.04	3.23	13.40
	17300.00	9700.00	9400.00				3.28	13.30
	17500.00	9570.00	9400.00				3.27	13.30
		9570.00	9960.00				3.26	13.40
			9770.00				3.25	13.35
			9810.00				3.32	13.45
			9760.00				3.36	13.65
			9730.00				3.36	13.65
			9730.00				3.32	13.45
			9750.00				3.35	13.45
			9790.00				3.35	13.40
			9360.00				3.34	13.35
			9360.00				3.36	12.60
			9280.00				3.37	12.80

Assay Data (Cont.)

FUS	XRF	XRF	FUS	FUS	XRF	XRF	FUS	XRF	XRF	XRF	FUS	XRF	FUS	XRF
Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MgO	MnO	Na <sub>2</sub> O	SiO <sub>2</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	TiO <sub>2</sub>
%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
8.52	8.77	3.28	0.25	36.74	35.30	0.97	3.22	3.18	0.13	0.90	34.66	33.07	0.35	0.38
8.33	8.69	3.24	0.23	35.17	35.00	0.97	3.15	3.15	0.12	0.89	34.23	32.80	0.37	0.38
8.52	8.82	3.26	0.23	36.89	35.30	0.99	3.22	3.19	0.12	0.91	33.80	32.75	0.35	0.38
8.43	8.70	3.24	0.23	36.89	35.00	0.97	3.25	3.18	0.12	0.91	34.02	32.83	0.35	0.38
8.48	8.77	3.27	0.25	36.17	35.10	0.96	3.22	3.16	0.13	0.89	34.44	33.01	0.35	0.37
8.54	8.77	3.28	0.23	38.03	35.40	0.95	3.17	3.19	0.12	0.90	34.23	33.18	0.37	0.37
8.31	8.75	3.28	0.25	37.03	35.20	0.98	3.15	3.20	0.13	0.92	33.80	32.84	0.35	0.38
8.26	8.85	3.26	0.25	36.03	35.84	0.97	3.17	3.23	0.12	0.92	33.37	32.78	0.37	0.38
8.65	8.98	3.13	0.26	34.88	36.15	1.03	3.19	3.36	0.13	0.82	31.80	30.70	0.38	0.37
8.77	8.93	3.15	0.24	35.89	36.04	1.02	3.13	3.30	0.12	0.81	32.10	30.80	0.37	0.36
8.56	8.92	3.14	0.24	36.17	36.03	1.02	3.13	3.31	0.12	0.80	31.10	30.70	0.37	0.36
8.59	8.93	3.12	0.26	35.31	36.17	1.03	3.19	3.31	0.12	0.82	31.30	30.80	0.37	0.37
8.78	8.98	3.14	0.25	35.89	36.13	1.04	3.18	3.33	0.13	0.83	31.80	30.80	0.40	0.37
8.69	9.03	3.13	0.25	35.60	35.80	1.05	3.22	3.35	0.13	0.83	31.40	32.00	0.38	0.37
8.85	8.95	3.15	0.25	35.31	36.34	1.02	3.16	3.31	0.12	0.81	31.90	32.20	0.37	0.37
8.64	8.90	3.19	0.25	35.17	35.80	1.02	3.23	3.32	0.12	0.82	31.30	32.20	0.36	0.37
8.50	3.20	0.25		32.45	35.80	0.94	3.32	3.24	0.11	0.86	32.52	32.30	0.36	0.36
8.50	3.20	0.25		34.60	35.80	0.95	3.30	3.28	0.11	0.86	32.73	32.20	0.36	0.36
8.50	3.20	0.25		33.03	35.90	0.95	3.30	3.27	0.11	0.86	32.73	32.10	0.36	0.36
8.50	3.21	0.25		33.45	35.80	0.94	3.33	3.26	0.11	0.86	32.52	32.10	0.36	0.36
8.60	3.18	0.25		32.45	35.80	0.94	3.30	3.25	0.11	0.86	32.52	32.00	0.36	0.36
8.50	3.20	0.25		35.80	35.80	0.94	3.32	3.26	0.11	0.86	32.09	33.10	0.36	0.36
8.60	3.20	0.23		35.80	35.80	0.94	3.28	3.25	0.11	0.86	32.73	32.60		0.36
8.79	3.24	0.23		35.60	36.22	0.96		3.25	0.11	0.85	32.73	32.90		0.36
8.93	3.24	0.23		35.30	36.19	1.00		3.38	0.13			32.80		0.39
8.90	3.22	0.23		35.90	36.13	1.01		3.32	0.12			33.00		0.39
8.87	3.22	0.23		35.70	36.18	1.01		3.34	0.13			32.90		0.39
8.89	3.23	0.23		35.70	36.20	1.00		3.35	0.13			33.10		0.39
8.87	3.26	0.23		35.30	36.22	1.01		3.36	0.13			32.80		0.39
8.86	3.25	0.23		36.46	36.24	1.01		3.35	0.12			32.96		0.39
8.81	3.22			36.46	36.27	1.00		3.39	0.12			32.94		0.39
9.03	3.28			36.46		1.00		3.33	0.13			32.89		0.39
8.96	3.28			36.03		1.02		3.37	0.13			32.81		0.40
8.98	3.30			36.03		1.02		3.36	0.13			32.85		0.40
8.98	3.26			36.03		1.02		3.38	0.13			32.91		0.40
9.01	3.28			36.17		1.02		3.36	0.13			32.90		0.39
9.00	3.27			36.03		1.02		3.34	0.13			32.90		0.40
9.04	3.27					1.02		3.34	0.13					0.40
8.96	3.27					1.02		3.38	0.13					0.40
9.01						1.01		3.36	0.13					0.40
9.04						1.03								
8.98						1.02								
8.98						1.02								
9.01						1.02								
9.03						1.03								
9.03						1.03								
9.01						1.03								
						1.03								

**Assay Data (Cont.)**

2A MICP	4A MICP	4A MICP	FUS	4A MICP	4A MICP	FUS	2A MICP	4A MICP	2A MICP	4A MICP
Ag	Ag	Al	Al	Bi	Ca	Ca	Co	Co	Co	Co
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
3.00	3.00	45200	45100	2.54	23100	25900	940	950	876	886
2.00	3.00	49200	44100	2.48	24300	25100	940	960	963	924
3.00	3.00	49000	45100	2.42	24400	25500	920	950	951	909
3.00	2.00	48400	44600	2.23	24100	25600	930	950	956	911
2.00	3.00	48500	44900	2.31	23600	25300	930	950	936	921
3.00	3.00	48800	45200	2.31	24000	26000	930	950	939	901
3.00	3.00	48300	44000	2.43	24400	25200	950	940	929	903
3.00	3.00	47900	43700	2.27	23900	25400	930	940	927	955
2.80	3.00	42626	45845	2.90	21934	22809	982	950	940	945
2.90	2.00	43621	46481	3.00	21888	23238	968	950	752	970
2.90	3.00	42805	45368	3.00	21612	22666	960	947	772	955
2.90	3.00	43723	45527	2.90	21527	23023	935	946	751	985
2.90	3.00	43449	46534	2.80	21729	23810	960	953	747	945
2.70	3.00	44134	46057	2.80	22051	23810	960	920	760	940
2.50	3.00	43170	46905	2.80	21800	23524	951	956	880	965
2.80	2.80	43657	45792	2.80	21922	22809	995	971	880	920
3.00	2.70	45900		2.10	20500		980	920	870	940
3.00	2.70	45500		2.00	20300		980	960	880	930
3.00	2.70	45600		2.10	20100		980	980	870	940
3.00	2.80	45800		2.00	20200		960	960	880	950
2.00	2.70	45500		2.10	20100		970	960	890	940
3.00	2.70	45600		2.00	20300		970	980	870	930
3.00	2.80	45500		2.00	20100		980	970	863	920
2.00	3.20	45700		2.10	23100		980	960	877	940
3.00	3.10	50600			23600		832	906	871	940
3.00	3.20	50600			24300		842	894	880	970
3.00	3.30	51500			24100		838	912	874	960
2.00	3.30	51000			23700		843	916	889	960
2.00	3.30	50300			23600		826	940	857	950
	3.30	51000			23500		851	908	862	950
	3.40	51500			24000		848	920		940
	2.00	45900			22300		832	913		901
	2.00	47100			22400		822	950		889
	2.00	43900			21800		830	950		886
	2.00	44400			22100		815	960		894
	2.00	44600			22300		819	960		905
	2.00	44800			22000		807	960		893
	2.00	43900			21700		804	950		891
	2.00	43500			21400		793	960		895
	3.00	43600			23100		815	960		925
	3.00	42200			22600		970	900		925
	3.00	40800			23600		960	900		920
	3.00	45100			23200		960	900		910
	3.00	42100			23500		950	900		900
	3.00	43200			23000		950	900		915
	3.00	47112			23100		970	900		910
	3.00	48192			23000		960	900		910
		47931			21590		960	900		898
		48239			22139		832.88	988.1		895

Assay Data (Cont.)

FUS	4A_MICP	FUS	2A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP
Co	Cr	Cr	Fe	Fe	Fe	Hf	In	Mg	Mg	Mn	Na	Nb
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
985	1390	1700	223000	247000	257000	0.70	0.25	18800	19400	900	6200	4.40
987	1420	1600	224000	255000	246000	0.60	0.25	19400	18500	1000	6300	4.40
954	1420	1600	222000	256000	258000	0.70	0.23	19500	19000	1000	6300	4.40
965	1440	1600	218000	252000	258000	0.60	0.22	19200	19400	1000	6200	4.50
961	1390	1700	222000	252000	253000	0.60	0.24	19200	19600	900	6300	4.40
989	1410	1600	219000	254000	266000	0.60	0.24	19300	19400	1000	6200	4.30
951	1470	1700	222000	260000	259000	0.60	0.24	19900	19100	1000	6500	4.50
973	1400	1700	222000	252000	252000	0.70	0.22	19200	19000	1000	6200	4.30
962	1481	1780	211200	250000	244000	0.80	0.28	18306	19020	900	6139	4.50
964	1441	1650	209400	251000	251000	0.80	0.26	18855	19140	1000	6105	4.50
960	1465	1650	211300	254000	253000	0.70	0.25	18578	18780	1000	6030	4.50
962	1503	1800	212800	249000	247000	0.80	0.28	18838	18780	1000	6031	4.50
950	1469	1720	212200	252000	251000	0.70	0.31	18740	19140	1000	6047	4.50
952	1440	1720	207300	252000	249000	0.70	0.29	18997	19080	1000	6035	4.50
965	1476	1700	210400	254000	247000	0.80	0.24	18602	19320	1000	6038	4.50
963	1492	1700	208400	251000	246000	0.70	0.24	18738	18960	1000	6125	4.50
1030	1360	1700	223000	264100	227000	0.80	0.20	19600	19500	878	6500	
965	1370	1700	219000	265200	242000	0.80	0.26	19400	20000	905	6400	
970	1350	1700	225000	261300	231000	0.60	0.24	19300	19900	892	6400	
1020	1370	1700	222000	263100	234000	0.60	0.24	19400	19900	908	6500	
985	1380	1700	222000	263100	227000	0.60	0.24	19400	20100	900	6300	
990	1340	1700	223000	263600	250000	0.60	0.22	19500	19900	914	6400	
990	1350	1600	220000	259800	250000	0.60		19300	20000	888	6400	
990	1330	1600	220000	262200	249000			19200	19800	903	6500	
920	1410	1600	210300	250000	247000			20400		888	6200	
940	1400	1600	209700	244000	251000			20200		883	6300	
1000	1480	1600	204100	248000	249000			20700		878	6100	
1000	1450	1600	201200	253000	250000			20800		881	6200	
920	1430	1600	206600	245000	247000			20600		878	6200	
890	1430	1600	208300	249000	255000			20100		883	6200	
920	1420		208200	250000	255000			20500		895	6100	
920	1420		201000	255000	255000			20400		884	6100	
940			207000	254900	252000			17800		1018	5900	
920			215000	257800	252000			18000		1010	5900	
920			214000	266300	252000			17200		1036	6100	
920			207000	261900	253000			17600		1034	6000	
940			211000	256700	252000			17500		1022	6000	
920			214000	256200				17600		1001	6000	
967			217000	259100				17100		1020	6000	
969			211000	264300				16900		1013	5900	
949			212000	240000				17300		900	6100	
954			210000	244000				16600		900	6100	
975			209000	241000				17100		900	6000	
944			211000	243000				16800		900	5900	
945			209000	244000				17700		900	6200	
933			212000	242000				16900		900	6000	
921			210000	241000				17200		900	6200	
928			213000	237000				18506		900	5900	
945				241000				18355		1000		

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	2A_MICP	4A_MICP
P	Sc	Se	Si	Sr	Te	Ti	Ti	V	W	Y	Zn	Zn
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
250	13.00	23.00	162000	100	1.00	2046	2100	100	1.10	11.10	50.00	120
240	14.00	23.00	160000	100	0.90	2090	2200	100	0.90	11.70	60.00	120
240	14.00	22.00	158000	100	1.10	2053	2100	100	0.80	11.40	50.00	120
230	14.00	22.00	159000	100	1.00	2092	2100	100	0.80	11.00	50.00	120
230	14.00	22.00	161000	100	1.10	2088	2100	100	0.90	11.00	50.00	110
200	14.00	23.00	160000	100	1.00	2106	2200	100	1.00	11.10	50.00	110
240	13.00	22.00	158000	100	1.10	2065	2100	100	0.80	11.00	50.00	110
205	14.00	22.00	156000	100	1.10	2092	2200	100	0.80	11.20	60.00	120
219	13.00	20.00	149460	104	1.20	2440	2300	119	0.90	11.00	50.00	130
220	13.00	20.00	150870	104	1.30	2430	2200	117	0.90	10.00	60.00	130
220	13.00	20.00	146170	103	1.20	2420	2200	119	0.90	10.00	50.00	120
233	13.00	20.00	147110	102	1.40	2510	2200	117	1.00	10.00	40.00	120
205	13.00	20.00	149460	100	1.10	2490	2400	123	1.00	10.00	60.00	120
215	14.00	20.00	147580	101	1.30	2510	2300	123	1.10	10.00	50.00	100
226	13.00	20.00	149930	102	1.50	2490	2220	121	0.90	10.00	50.00	120
250	14.00		147110	101	1.00	2520	2160	118	1.00	10.00	69.10	110
250	14.00		152000	98	1.00	2300	2160	124	1.00	12.60	68.80	110
250	13.00		153000	96	1.20	2300	2160	123	1.00	12.30	69.50	100
270	13.00		153000	95	1.20	2300	2160	122	1.00	12.30	68.40	110
260	13.00		152000	95	1.20	2300	2160	123	1.00	12.50	67.70	100
250	13.00		152000	96	1.20	2300	2160	123	1.00	12.50	66.80	100
250	13.00		150000	97	1.20	2300	2160	127	1.00	12.40	67.80	100
240	13.00		153000	95	1.40	2400		122	1.00	13.00	68.20	100
230	13.00		153000	96		2400		123		12.90	55.00	111
250	15.00			100				143		12.50	58.00	113
240	15.00			100				141		12.80	53.00	110
230	14.00			100				144		12.70	56.00	112
240	14.00			100				141		13.00	57.00	111
250	14.00			100				144		12.80	59.00	114
220	14.00			100				144		12.70	57.00	112
230	14.00			100				100		12.50	56.00	113
230	14.00			100				100		12.50	60.00	122
260	13.00			100				100			60.00	120
250	12.00			100				100			70.00	122
250	13.00			100				100			60.00	125
250	13.00			100				100			60.00	125
260	14.00			100				100			60.00	119
240	12.00			100				100			60.00	122
240	13.00			100				100			70.00	123
	13.00			100				100				120
	13.00			101				100				120
	13.00			103				100				110
	13.00			102				100				120
	13.00			104				100				110
	13.00			103				100				130
	12.00			103				100				120
	13.00			101				122				110
	12.00			101				121				140
								120				150

## **24. Reported Values**

The certified values listed in this certificate fulfil the AMIS statistical criteria (see section 17) regarding agreement for certification and have been independently validated by Allan Fraser.

## **25. 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.

## **26. 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.

## **27. Period of Validity**

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

## **28. 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.

## **29. 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.

## **30. 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).

### 31. 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:** 15 January 2014

**Version:** 000

**Date of Version v1.00:** 21 June 2019

**Version:** v1.00

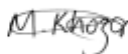
**Reason for Version v1.00:** Rectification of everything due to customer request

**Date of Version v2.00:** 27 January 2020

**Version:** v2.00

**Reason for Version v2.00:** Amendment of COA name

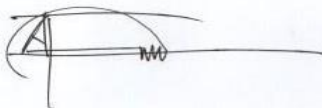
**Approving Officer:**



**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

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# Appendices

## Appendix 1: Uncertified Element Statistics

Uncertified element statistics are shown in **Table 8**.

**Table 8.** Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
Al	2A_MICP	16	28662.5	386.2	1	ppm
As	2A_MICP	5	3.8	1.2	33	ppm
Au	2A_MICP	8	0.04	0.01	29	g/t
B	FUS	3	20.0	*	*	ppm
Ba	2A_MICP	16	57.8	40.3	70	ppm
Ba	4A_MICP	16	110.3	117.4	106	ppm
Ba	FUS	24	185.6	55.6	30	ppm
BaO	FUS	24	0.02	0.01	30	%
Be	4A_MICP	17	0.7	0.1	13	ppm
Bi	2A_MICP	8	2.5	0.1	5	ppm
Bi	FUS	1	22.0	*	*	ppm
Ca	2A_MICP	16	15087.5	309.6	2	ppm
CaO	FUS	16	3.4	0.2	7	%
Cd	2A_MICP	8	1.8	0.2	10	ppm
Cd	4A_MICP	13	1.9	0.1	6	ppm
Ce	4A_MICP	8	44.8	1.0	2	ppm
Ce	FUS	16	35.1	6.9	20	ppm
Co	4A_ICPES	8	938.8	6.4	1	ppm
Cr	2A_MICP	16	358.4	15.9	4	ppm
Cr	XRF	8	1662.5	74.4	4	ppm
Cr <sub>2</sub> O <sub>3</sub>	XRF	31	0.2	0.03	15	%
Cs	4A_MICP	16	1.6	0.1	3	ppm
Cu	XRF	8	9600.0	*	*	ppm
Dy	FUS	8	2.8	0.3	9	ppm
Er	FUS	8	1.5	*	*	ppm
Eu	FUS	8	0.7	0.1	15	ppm
Fe	XRF	8	250500.0	1069.0	0.4	ppm
Fe <sub>2</sub> O <sub>3</sub>	4A_MICP	8	37.0	0.3	1	%
Ga	2A_MICP	7	8.0	*	*	ppm
Ga	4A_MICP	14	11.4	0.1	1	ppm
Gd	FUS	8	3.3	1.0	32	ppm
Ge	4A_MICP	8	0.6	0.2	33	ppm
Hg	2A_MICP	3	0.01	*	*	ppm
Ho	FUS	8	0.6	0.1	17	ppm
K	2A_MICP	16	4787.5	328.4	7	ppm
K	4A_MICP	53	8021.6	801.2	10	ppm
K	FUS	24	8520.8	821.4	10	ppm
K <sub>2</sub> O	FUS	24	1.0	0.1	10	%
La	2A_MICP	16	8.1	1.0	12	ppm
La	4A_MICP	16	20.7	2.9	14	ppm
La	FUS	24	24.3	8.5	35	ppm
Li	2A_MICP	8	8.5	0.5	6	ppm
Li	4A_MICP	36	10.5	2.8	27	ppm
Li	FUS	11	15.8	4.0	25	ppm
LOI	LOI	32	9.3	0.6	6	%
Lu	FUS	6	0.2	*	*	ppm
Mg	2A_MICP	16	6268.8	94.6	2	ppm
Mn	2A_MICP	40	335.9	59.1	18	ppm
Mn	FUS	8	960.0	10.8	1	ppm
Mn	XRF	7	1000.0	*	*	ppm
MnO	FUS	8	0.1	*	*	%
Mo	2A_MICP	16	3.8	1.0	25	ppm
Mo	4A_MICP	24	6.4	1.5	24	ppm

Element	Generic Method	n	Mean	SD	RSD %	Unit
Na	2A_MICP	16	2538.8	84.5	3	ppm
Na <sub>2</sub> O	4A_MICP	8	0.8	0.01	1	%
NAE	XRF	8	99.9	0.5	1	%
Nd	FUS	8	16.6	0.4	3	ppm
Ni	XRF	8	17675.0	88.6	1	ppm
P	2A_MICP	8	193.8	7.4	4	ppm
P	FUS	8	237.5	51.8	22	ppm
P <sub>2</sub> O <sub>5</sub>	XRF	8	0.1	*	*	%
Pb	2A_MICP	33	12.6	4.4	35	ppm
Pb	4A_MICP	70	21.2	5.3	25	ppm
Pb	FUS	10	71.2	16.6	23	ppm
Pr	FUS	8	4.9	0.1	1	ppm
Rb	4A_MICP	16	42.4	5.4	13	ppm
Rb	FUS	8	49.8	1.3	3	ppm
Re	4A_MICP	16	0.1	0.01	17	ppm
S	4A_MICP	32	12.2	0.7	6	%
S	FUS	7	12.8	0.1	1	%
S	XRF	8	12.4	0.1	1	%
Sb	2A_MICP	1	0.1	*	*	ppm
Sb	4A_MICP	29	5.2	8.6	165	ppm
Sb	FUS	1	77.0	*	*	ppm
Sc	2A_MICP	15	4.0	0.1	3	ppm
Sc	FUS	8	11.6	0.5	4	ppm
Se	2A_MICP	14	22.5	1.1	5	ppm
Sm	FUS	8	3.6	0.4	12	ppm
Sn	4A_MICP	14	1.9	0.1	6	ppm
Sr	2A_MICP	16	61.4	2.9	5	ppm
Sr	FUS	16	85.5	29.6	35	ppm
Ta	4A_MICP	16	0.5	0.2	51	ppm
Tb	FUS	7	0.4	*	*	ppm
Te	2A_MICP	8	1.2	0.2	13	ppm
Th	2A_MICP	8	2.4	0.1	4	ppm
Th	4A_MICP	16	8.6	1.1	13	ppm
Th	FUS	8	6.2	0.4	6	ppm
Ti	2A_MICP	16	940.6	119.7	13	ppm
Tl	2A_MICP	7	0.2	*	*	ppm
Tl	4A_MICP	16	0.3	0.04	14	ppm
Tm	FUS	8	0.2	*	*	ppm
U	4A_MICP	16	1.4	0.3	19	ppm
U	FUS	8	1.5	0.3	18	ppm
V	2A_MICP	16	82.1	6.3	8	ppm
V	FUS	16	119.0	5.9	5	ppm
V <sub>2</sub> O <sub>5</sub>	XRF	8	0.01	0.001	8	%
W	2A_MICP	8	0.4	0.05	12	ppm
W	FUS	7	71.6	3.2	4	ppm
Y	2A_MICP	8	3.6	0.1	3	ppm
Y	FUS	15	12.1	0.8	7	ppm
Yb	FUS	7	1.5	*	*	ppm
Zn	FUS	26	144.2	52.5	36	ppm
Zr	2A_MICP	8	7.5	0.2	3	ppm
Zr	4A_MICP	16	21.2	1.0	5	ppm
Zr	FUS	8	50.0	*	*	ppm

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

Appendix 2 through 9, prepared by Allan Fraser.

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

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

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

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

### Z-Score

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

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

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

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

(Thompson & Lowthian, 2011)

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

### Cochran's Test

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

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

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

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

### Grubbs Test

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

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

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

### Method Performance

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

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

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

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

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

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

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

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

### Grand Mean

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

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

### Certified Value

From ANOVA as per the description in section 17, an 'appropriate precision' as shown in [8] is calculated for sufficient homogeneity (Thompson, 2008):

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

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

### Total Variation (SST)

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

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

### Between Group Variation (SSB)

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

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

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

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

### Within Group Variation (SSW)

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

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

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

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

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

**Table 9.** A single-factor ANOVA table showing key elements. Where P is the total number of groups, or laboratories. P-1 is 1 less than number of laboratories, P (n-1) is the number of data values minus number of groups (equals degrees of freedom for each group added together), and P-1 + P(n-1) is 1 less than the number of data points. MS is the mean squares of between laboratories and within laboratories. After Ellison *et al.*, (2009), Table 6.2, page 61.

Source	Sum of Squares	df	Mean Sum of Squares	F	p	F <sub>crit</sub>
Between Laboratories	SSB	P-1	MSB=SSB/df	MSB/MSW	=FDIST(x,df,df)	F-table
Within Laboratories	SSW	P(n-1)	MSW=SSW/df	–	–	–
Total	SSB+SSW	P-1 + P(n-1)	–	–	–	–

### Combined Standard Uncertainty

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

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

Within laboratory repeatability is determined as

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

and, the between laboratory precision as

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

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

### Expanded Uncertainty

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

### Uncertainty Statement

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

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

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

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

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

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

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

#### Example

A CRM is independently replicated nine times for  $Al_2O_3$  concentration by XRF analysis, *i.e.* 9 individual fused glass beads were prepared. The observed mean and standard deviation of the replicate data are shown with the certified value and expanded uncertainty in Table 10. 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 10.** CRM certified value, quoted expanded uncertainty  $U$ , the coverage factor for the CRM,  $k=2.25$  and mean for  $n=9$  replicates and corresponding standard deviation for the replicate data.

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

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

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

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

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

Therefore,  $t_{calc} = 0.84$  and  $t_{crit}(5\%, 8) = 2.31$  ( $df$  is 8, therefore,  $t_{crit}=2.31$ , see Appendix 9, page 34) which is  $>0.84$ . Similarly, the  $p$ -value=0.43 which is  $>0.05$ . This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known, the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

#### Appendix 4. Two-standard Deviations

Two-standard deviations are calculated using the expression:

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

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

#### Appendix 5. Confidence Interval

Confidence interval is calculated as:

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

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

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

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

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

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

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

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

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

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

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

Since AMIS certified analyte values are reported on a dry-basis, the user laboratory is required to dry a portion (accurately weigh out 1.0 grams in duplicate) of the CRM material in air at 105°C in a drying oven to constant mass to determine the moisture content. Use a crucible with a flat inner surface with a surface area not smaller than 10 cm<sup>2</sup> with the CRM material spread evenly over same; this represents a 0.1 gram spread per cm<sup>2</sup>. In correcting the certified value for moisture content, a moisture correction factor is calculated:

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

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

#### **Example**

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

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

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

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



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

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

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

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

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

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

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be  $0.02\text{g/t}$ . *i.e.*  $1\mu\text{g} = 1\text{g/t}$ , therefore  $1\mu\text{g}/50\text{g} = 0.02\text{g/t}$ . If no prill was found, then the LOD result would be  $<0.02\text{g/t}$  or "not detected". Using a larger assay sample mass improves the LOD and LOQ (Table 10). Table 12 gives a recommended reporting scheme for LOD and LOQ.

**Table 11.** Mass of assay sample and corresponding limit of detection and limit of quantitation for an assay microbalance capability of smallest prill mass of  $1\mu\text{g}$  or  $0.001\text{mg}$ .

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

**Table 12.** Recommended reporting scheme for LOD and LOQ in fire assay.

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

**Appendix 9.** T-distribution table

**Table 13.** T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence.

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

**End of certificate**