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Certificate

# AMIS0373

## Certified Reference Material

Fe 56.59% Hamersley AU

### *Certificate of Analysis*

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#### AMIS

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## SUMMARY STATISTICS

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

#### *Certified Concentrations including oxides*

Analyte	Method	<sup>8</sup> Certified (μ)	<sup>10</sup> Two Standard Deviation (2s) ±	Unit
LOI	LOI405 <sup>6</sup>	2.84	0.24	%
LOI	LOI <sup>7</sup>	3.73	0.39	%
Fe	Titration <sup>5</sup>	56.048	3.170	%
Fe	XRF <sup>1</sup>	56.516	0.475	%
Fe	FUS <sup>2</sup>	56.000	2.536	%
Al	FUS <sup>2</sup>	14039	1597	ppm
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>1</sup>	2.72	0.06	%
As	FUS <sup>2</sup>	92	25	ppm
As	XRF <sup>1</sup>	98	22	ppm
Fe <sub>2</sub> O <sub>3</sub>	XRF <sup>1</sup>	80.977	1.07	%
K <sub>2</sub> O	XRF <sup>1</sup>	0.031	0.00	%
Mn	FUS <sup>2</sup>	1106	122	ppm
Mn	XRF <sup>1</sup>	1123	48	ppm
MnO	XRF <sup>1</sup>	0.14	0.01	%
P	XRF <sup>1</sup>	394.3	25	ppm
P <sub>2</sub> O <sub>5</sub>	XRF <sup>1</sup>	0.090	0.005	%
S	XRF <sup>1</sup>	0.020	0.00	%
SG	SG <sup>3</sup>	4.05	0.38	Dimensionless
Si	FUS <sup>2</sup>	5.38	0.39	%
SiO <sub>2</sub>	FUS <sup>2</sup>	11.8	0.59	%
SiO <sub>2</sub>	XRF <sup>1</sup>	11.9	0.23	%
Ti	FUS <sup>2</sup>	0.11	0.02	%
TiO <sub>2</sub>	XRF <sup>1</sup>	0.19	0.02	%
V	XRF <sup>1</sup>	56	10	ppm
V <sub>2</sub> O <sub>5</sub>	XRF <sup>1</sup>	0.009	0.003	%

### *Certified Elements Concentrations (at two Standard Deviations)*

Analyte	Method	<sup>8</sup> Certified (μ)	<sup>10</sup> Two Standard Deviation (2s) ±	Unit
Al	4A_MICP <sup>4</sup>	1.437	0.197	%
As	4A_MICP <sup>4</sup>	84	15	ppm
Ba	4A_MICP <sup>4</sup>	21	6	ppm
Be	4A_MICP <sup>4</sup>	1	0.4	ppm
Bi	4A_MICP <sup>4</sup>	1	0.1	ppm
Cd	4A_MICP <sup>4</sup>	0.1	0.04	ppm
Ce	4A_MICP <sup>4</sup>	12	1	ppm
Co	4A_MICP <sup>4</sup>	9	4	ppm
Cr	4A_MICP <sup>4</sup>	108	30	ppm
Cs	4A_MICP <sup>4</sup>	0.1	0.1	ppm
Dy	4A_MICP <sup>4</sup>	1	0.2	ppm

Analyte	Method	<sup>8</sup> Certified (μ)	<sup>10</sup> Two Standard Deviation (2s) ±	Unit
Al	4A_MICP <sup>4</sup>	1.437	0.197	%
As	4A_MICP <sup>4</sup>	84	15	ppm
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Be	4A_MICP <sup>4</sup>	1	0.4	ppm
Bi	4A_MICP <sup>4</sup>	1	0.1	ppm
Cd	4A_MICP <sup>4</sup>	0.1	0.04	ppm
Ce	4A_MICP <sup>4</sup>	12	1	ppm
Co	4A_MICP <sup>4</sup>	9	4	ppm
Cr	4A_MICP <sup>4</sup>	108	30	ppm
Cs	4A_MICP <sup>4</sup>	0.1	0.1	ppm
Dy	4A_MICP <sup>4</sup>	1	0.2	ppm
Er	4A_MICP <sup>4</sup>	1	0.1	ppm
Eu	4A_MICP <sup>4</sup>	0.2	0.04	ppm
Ga	4A_MICP <sup>4</sup>	5	1	ppm
Gd	4A_MICP <sup>4</sup>	1	0.2	ppm
Hf	4A_MICP <sup>4</sup>	1	0.3	ppm
Ho	4A_MICP <sup>4</sup>	0.2	0.04	ppm
Ind	4A_MICP <sup>4</sup>	0.04	0.02	ppm
La	4A_MICP <sup>4</sup>	4.8	1	ppm
Li	4A_MICP <sup>4</sup>	2.1	1	ppm
Lu	4A_MICP <sup>4</sup>	0.1	0.04	ppm
Mn	4A_MICP <sup>4</sup>	1059	158	ppm
Mo	4A_MICP <sup>4</sup>	1.3	0.3	ppm
Nb	4A_MICP <sup>4</sup>	3.1	1	ppm
Nd	4A_MICP <sup>4</sup>	4.1	1	ppm
Ni	4A_MICP <sup>4</sup>	16.5	5	ppm
P	4A_MICP <sup>4</sup>	358.2	65	ppm
Pb	4A_MICP <sup>4</sup>	20.7	4	ppm
Pr	4A_MICP <sup>4</sup>	1.1	0.2	ppm
Rb	4A_MICP <sup>4</sup>	1.2	0.4	ppm
Re	4A_MICP <sup>4</sup>	0.0	0.01	ppm
Sb	4A_MICP <sup>4</sup>	4.6	1	ppm
Sc	4A_MICP <sup>4</sup>	3.9	1	ppm
Sm	4A_MICP <sup>4</sup>	0.9	0.1	ppm
Sn	4A_MICP <sup>4</sup>	0.8	0.2	ppm
Sr	4A_MICP <sup>4</sup>	3.5	1	ppm
Ta	4A_MICP <sup>4</sup>	0.7	0.4	ppm
Tb	4A_MICP <sup>4</sup>	0.2	0.03	ppm
Th	4A_MICP <sup>4</sup>	4.1	1	ppm
Ti	4A_MICP <sup>4</sup>	0.10	0.02	%
Tl	4A_MICP <sup>4</sup>	0.02	0.01	ppm
Tm	4A_MICP <sup>4</sup>	0.1	0.03	ppm
U	4A_MICP <sup>4</sup>	3	0.40	ppm
W	4A_MICP <sup>4</sup>	23	8	ppm
Y	4A_MICP <sup>4</sup>	7	1	ppm
Yb	4A_MICP <sup>4</sup>	1	0.1	ppm
Zr	4A_MICP <sup>4</sup>	39	10	ppm

## 1. Certified Concentrations and Uncertainties

AMIS0373 is a standard material, re-certified in January 2018. Table 1 gives the certified concentrations, including oxides, combined and expanded uncertainty for certified reference material. Table 2 shows the certified elements concentrations, two standard deviations, combined and expanded uncertainty.

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

Analyte	Method	<sup>8</sup> Certified ( $\mu$ )	N	n	k	% RSD	<sup>9</sup> Combined uncertainty ( $u_c$ )	<sup>10</sup> Two Standard Deviation (2s) $\pm$	<sup>11</sup> Expanded uncertainty (U) $\pm$	Unit
LOI	LOI405 <sup>6</sup>	2.84	3	24	4.30	4	0.1	0.24	0.51	%
LOI	LOI1000 <sup>7</sup>	3.73	17	136	2.12	5	0.20	0.39	0.42	%
Fe	Titration <sup>5</sup>	56.048	3	24	4.30	3	1.585	3.170	7	%
Fe	XRF <sup>1</sup>	56.516	11	82	2.23	0	0.238	0.475	1	%
Fe	FUS <sup>2</sup>	56.000	8	64	2.36	2	1.268	2.536	3	%
Al	FUS <sup>2</sup>	14039	7	56	2.45	6	799	1597	1954	ppm
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>1</sup>	2.72	16	128	2.13	1	0.030	0.060	0.06	%
As	FUS <sup>2</sup>	92	5	37	2.78	13	12	25	34	ppm
As	XRF <sup>1</sup>	98	6	42	2.57	11	11	22	28	ppm
Fe <sub>2</sub> O <sub>3</sub>	XRF <sup>1</sup>	80.977	8	62	2.36	1	0.537	1.07	1	%
K <sub>2</sub> O	XRF <sup>1</sup>	0.031	17	131	2.12	4	0.001	0.002	0.002	%
Mn	FUS <sup>2</sup>	1106	5	38	2.78	5	61	122	169	ppm
Mn	XRF <sup>1</sup>	1123	7	54	2.45	2	24	48	59	ppm
MnO	XRF <sup>1</sup>	0.14	11	88	2.23	3	0.004	0.01	0.01	%
P	XRF <sup>1</sup>	394.3	10	80	2.26	3	12	25	28	ppm
P <sub>2</sub> O <sub>5</sub>	XRF <sup>1</sup>	0.090	8	60	2.36	3	0.002	0.005	0.01	%
S	XRF <sup>1</sup>	0.020	8	63	2.36	6	0.001	0.002	0.002	%
SG	SG <sup>3</sup>	4.05	18	142	2.11	5	0.19	0.38	0.4	Dimensionless
Si	FUS <sup>2</sup>	5.38	5	38	2.78	4	0.19	0.39	0.5	%
SiO <sub>2</sub>	FUS <sup>2</sup>	11.8	3	24	4.30	3	0.30	0.59	1	%
SiO <sub>2</sub>	XRF <sup>1</sup>	11.9	17	133	2.12	1	0.11	0.23	0.2	%
Ti	FUS <sup>2</sup>	0.11	5	39	2.78	10	0.01	0.02	0.03	%
TiO <sub>2</sub>	XRF <sup>1</sup>	0.19	17	132	2.12	4	0.008	0.02	0.02	%
V	XRF <sup>1</sup>	56	4	29	3.18	9	5	10	16	ppm
V <sub>2</sub> O <sub>5</sub>	XRF <sup>1</sup>	0.009	9	68	2.31	15	0.001	0.003	0.003	%

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

Analyte	Method	<sup>8</sup> Certified ( $\mu$ )	N	n	k	% RSD	<sup>9</sup> Combined uncertainty ( $u_c$ )	<sup>10</sup> Two Standard Deviation (2s) $\pm$	<sup>11</sup> Expanded uncertainty (U) $\pm$	Unit
Al	4A_MICP <sup>4</sup>	1.44	15	120	2.14	7	0.098	0.12	0.2	%
As	4A_MICP <sup>4</sup>	84	14	112	2.16	9	8	15	16	ppm
Ba	4A_MICP <sup>4</sup>	21	14	111	2.16	14	3	6	6	ppm
Be	4A_MICP <sup>4</sup>	1	12	91	2.20	15	0.2	0.4	0.4	ppm
Bi	4A_MICP <sup>4</sup>	1	12	93	2.20	10	0.1	0.1	0.1	ppm
Cd	4A_MICP <sup>4</sup>	0.1	6	44	2.57	36	0.02	0.04	0.1	ppm
Ce	4A_MICP <sup>4</sup>	12	9	71	2.31	4	0.5	1	1	ppm
Co	4A_MICP <sup>4</sup>	9	13	104	2.18	21	2	4	4	ppm
Cr	4A_MICP <sup>4</sup>	108	14	112	2.16	14	15	30	32	ppm
Cs	4A_MICP <sup>4</sup>	0.1	10	71	2.26	35	0.04	0.1	0.1	ppm
Dy	4A_MICP <sup>4</sup>	1	6	47	2.57	8	0.1	0.2	0.2	ppm
Er	4A_MICP <sup>4</sup>	1	6	45	2.57	6	0.05	0.1	0.1	ppm
Eu	4A_MICP <sup>4</sup>	0.2	6	47	2.57	8	0.02	0.04	0.05	ppm
Ga	4A_MICP <sup>4</sup>	5	12	96	2.20	7	0.4	1	1	ppm
Gd	4A_MICP <sup>4</sup>	1	6	47	2.57	9	0.1	0.2	0.2	ppm
Hf	4A_MICP <sup>4</sup>	1	10	78	2.26	17	0.2	0.3	0.4	ppm
Ho	4A_MICP <sup>4</sup>	0.2	6	47	2.57	10	0.02	0.04	0.1	ppm
In	4A_MICP <sup>4</sup>	0.04	9	68	2.31	19	0.01	0.02	0.02	ppm
La	4A_MICP <sup>4</sup>	4.8	11	88	2.23	11	1	1	1	ppm
Li	4A_MICP <sup>4</sup>	2.1	12	96	2.20	14	0.3	1	1	ppm
Lu	4A_MICP <sup>4</sup>	0.1	7	53	2.45	16	0.02	0.04	0.1	ppm
Mn	4A_MICP <sup>4</sup>	1059	16	124	2.13	7	79	158	168	ppm
Mo	4A_MICP <sup>4</sup>	1.3	10	80	2.26	13	0.2	0.3	0.4	ppm
Nb	4A_MICP <sup>4</sup>	3.1	12	94	2.20	18	1	1	1	ppm

Analyte	Method	<sup>8</sup> Certified ( $\mu$ )	N	n	k	% RSD	<sup>9</sup> Combined uncertainty ( $u_c$ )	<sup>10</sup> Two Standard Deviation (2s) $\pm$	<sup>11</sup> Expanded uncertainty (U) $\pm$	Unit
Nd	4A_MICP <sup>4</sup>	4.1	6	48	2.57	11	0.4	1	1	ppm
Ni	4A_MICP <sup>4</sup>	17	16	123	2.13	16	3	5	6	ppm
P	4A_MICP <sup>4</sup>	358	14	107	2.16	9	32	65	70	ppm
Pb	4A_MICP <sup>4</sup>	21	14	112	2.16	10	2	4	5	ppm
Pr	4A_MICP <sup>4</sup>	1	6	45	2.57	8	0.1	0.2	0.2	ppm
Rb	4A_MICP <sup>4</sup>	1	12	93	2.20	16	0.2	0.4	0.4	ppm
Re	4A_MICP <sup>4</sup>	0.004	3	24	4.30	73	0.003	0.01	0.01	ppm
Sb	4A_MICP <sup>4</sup>	5	12	96	2.20	13	1	1	1	ppm
Sc	4A_MICP <sup>4</sup>	4	11	88	2.23	15	1	1	1	ppm
Sm	4A_MICP <sup>4</sup>	0.9	6	47	2.57	7	0.1	0.1	0.2	ppm
Sn	4A_MICP <sup>4</sup>	0.8	10	80	2.26	14	0.1	0.2	0.3	ppm
Sr	4A_MICP <sup>4</sup>	4	13	104	2.18	18	1	1	1	ppm
Ta	4A_MICP <sup>4</sup>	0.7	11	84	2.23	29	0.2	0.4	0.5	ppm
Tb	4A_MICP <sup>4</sup>	0.2	7	56	2.45	10	0.02	0.03	0.04	ppm
Th	4A_MICP <sup>4</sup>	4	12	91	2.20	6	0.3	1	1	ppm
Ti	4A_MICP <sup>4</sup>	0.1	11	84	2.23	11	0.01	0.02	0.02	%
Tl	4A_MICP <sup>4</sup>	0.02	5	34	2.78	22	0.005	0.01	0.01	ppm
Tm	4A_MICP <sup>4</sup>	0.1	5	40	2.78	14	0.02	0.03	0.04	ppm
U	4A_MICP <sup>4</sup>	3	12	91	2.20	6	0.2	0.4	0.5	ppm
W	4A_MICP <sup>4</sup>	23	15	115	2.14	16	4	8	8	ppm
Y	4A_MICP <sup>4</sup>	7	13	102	2.18	7	0.4	1	1	ppm
Yb	4A_MICP <sup>4</sup>	1	7	53	2.45	6	0.05	0.1	0.1	ppm
Zr	4A_MICP <sup>4</sup>	39	11	88	2.23	13	5	10	11	ppm

1. XRF is X-ray Fluorescence
2. FUS is Fusion by ICP finish
3. SG is Specific Gravity
4. 4A\_MICP is a Multi-acid digestion with ICP finish
5. Titration is titrimetry
6. LOI 405 is Loss on Ignition at 405°C
7. LOI 1000 is Loss on Ignition at 1000°C
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.
10. The two standard deviations (2s) is calculated as for example:  $u_c \times 2 = 0.23 \times 2 = 0.46\%$ . See section 28, page 19, 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, page 31 for t-distribution table). Example:  $U = 2.36 \times 0.23 = 0.54$

## 2. Statistical Comparison of Means

Iron (Fe) was determined by titrimetry, XRF, ICP Fusion and by 4A\_MICP. The data generated by 4A\_MICP are not considered here as they failed certification. In order to establish if the remaining three mean values are statistically equal, an ANOVA was conducted. The F-ANOVA gave a  $p$ -value of 0.28, which suggests that all of the mean values are equal and belong to the same population (Table 3). The comparison of the means for three different methods for the determination of As shows that at least one of the As means is statistically different (F-ANOVA  $p$ -value is 0.005) from the other means. For Mn, the converse is applicable, *i.e.*, the F-ANOVA  $p$ -value of 0.083 suggests that the three-different means are equal and belong to the same population.

**Table 3.** The results of a single factor ANOVA showing the means obtained from N laboratories on three different analytical methods for Fe, As and Mn determination.

Methods	N	Mean %Fe	s			
Fe XRF	11	56.516	0.20			
Fe Fus	8	56.000	0.82			
Fe Titration	3	56.048	1.5			
Source of Variation	SS	df	MS	F	p	F crit
Between Methods	13949	2	6975	1.37	0.28	3.52
Within Methods	96518	19	5080			
Methods	N	Mean As (ppm)	s			
As Fus	5	91	10			
As XRF	6	98	8			
As 4A_MICP	14	84	7			
Source of Variation	SS	df	MS	F	p	F crit
Between Methods	913	2	456	6.86	0.005	3.44
Within Methods	1464	22	67			
Methods	N	Mean Mn (ppm)	s			
Mn Fus	5	1106	56			
Mn XRF	7	1123	22			
Mn 4A_MICP	16	1059	78			
Source of Variation	SS	df	MS	F	p	F crit
Between Methods	23366	2	11683	2.74	0.083	3.39
Within Methods	106406	25	4256			

In the comparison of means for the same element between two different analytical methods firstly the variances between the two data sets are compared. If the variances are found to be equal (F-test,  $p$ -value $\geq$ 0.05), then an equal variance t-test is applied. Should the variances be statistically significant, then an unequal variance t-test is performed on the data. With a  $p$ -value $>$ 0.05, the null hypothesis that the means (certified values) are equal is accepted (Table 4 and 5).



**Table 4.** The 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 Fus	1.40%	Al 4A_MICP	1.43%	0.41	Accept H <sub>0</sub> , means are equal
Ti Fus	0.11%	Ti 4A_MICP	0.10%	0.030	Reject H <sub>0</sub> , means are <i>not</i> equal

**Table 5.** The results of a two-sample unequal variance t-test (two-tailed) on data sets for P demonstrating unequal variances. There is a highly significant difference between the means, *i.e.*, they are not equal ( $p < 0.001$ )

Method	Certified value	Method	Certified value	p-value (t-test)	t-test outcome
P XRF	394ppm	P 4A_MICP	358ppm	<0.001	Reject H <sub>0</sub> , means are <i>not</i> equal
SiO <sub>2</sub> Fus	11.8%	SiO <sub>2</sub> XRF	11.9%	0.56	Accept H <sub>0</sub> , means are equal

### 3. Loss on Ignition

Loss on ignition was determined to constant mass at temperatures of 105, 371, 650, 850 and 1000°C. From the data shown Figure 1 it is apparent that the loss on ignition reaches a constant value from about 650°C.

Temp °C	%LOI
105	1.0
371	8.8
650	10.4
850	11.5
1000	10.8

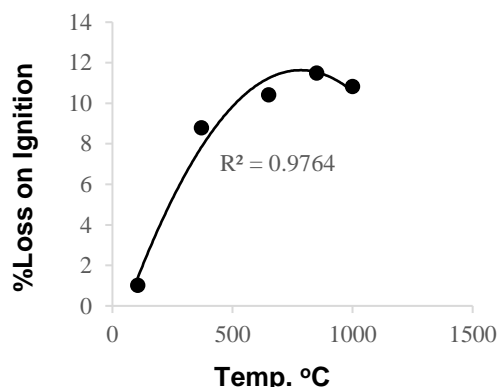


Figure 1. Loss on ignition profile at different temperatures.

### 4. Intended Use

AMIS0373 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 participated in the exercise.

## 5. Abbreviations and Symbols

Abbreviations and symbols used in this document are shown in Table 6.

**Table 6.** 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
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

**Table 6** Continued.

<b>Abbreviation/Symbol</b>	<b>Description</b>
$p$	' $p$ -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 $k=1$
$\mu m$	Micron, is an SI derived unit of length equaling $1 \times 10^{-6}$ of a meter

## 6. Uncertified Concentration Values

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

## 7. 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.

## 8. 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)

## 9. Origin of Material

The Hamersley iron resources, contained in banded iron formations of Precambrian age, cover extensive areas of the Pilbara region. Haematite is the principal iron mineral. The Hamersley Province of western Australia contains numerous economic deposits of iron ore where Proterozoic banded iron formations (BIF) composed predominantly of magnetite and chert layers has been converted to oxidised iron minerals. Many of these bedded orebodies consist of martite and goethite formed from the Marra Mamba and Brockman Iron formations.

## 10. Approximate Mineral and Chemical Composition

Iron ore deposits of the Hamersley Province are mostly hosted within banded iron formation (BIF) sequences of the Brockman and Marra Mamba Iron Formations of the Hamersley Group and consist of two types: martite-microplaty hematite containing between 60 and 68 wt. % Fe, and martite-goethite containing between 56 and 63 wt. % Fe.

## 11. 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.

## 11.1 Sample preparation for X-Ray Diffraction

The material submitted was prepared for XRD analysis using a backloading preparation method. The relative phase amounts (weight %) were estimated using the Rietveld method.

## 11.2 XRD Results

The obtained diffractogram is shown in Figure 2 gives the identified and quantified mineral species using Rietveld Refinement. Table 9 presents the % mineral composition of AMIS0373.

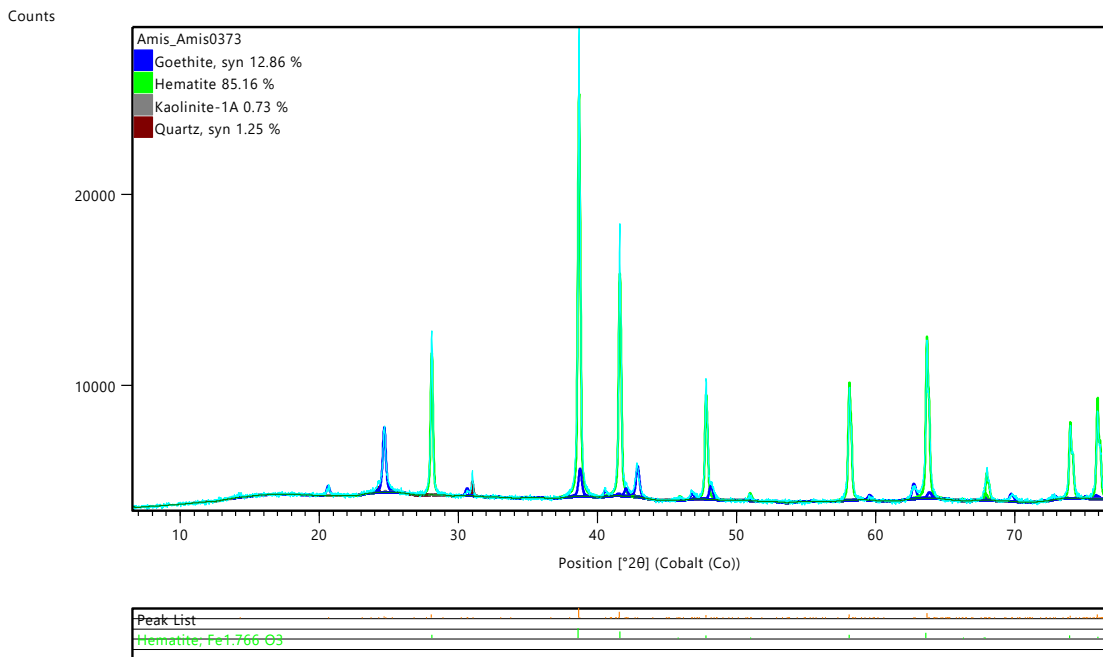


Figure 2. Diffractogram for AMIS0373 showing presence of different mineral phases.

**Table 7.** Mineral species identified and quantified on AMIS0373.

Sample ID	%Goethite	%Hematite	% Kaolinite	% Quartz	% Muscovite
AMIS0373	12.86	85.16	0.73	1.25	Not detected

## 12. Health and Safety

The material is a very fine powder coloured strong brown (5YR 4/6). Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

## 13. 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.

## **14. Handling**

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

## **15. Storage information**

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

## **16. Methods of Analysis Requested**

### **16.1 Initial Certification**

- Multi element scan to include Fe. Fusion ICP.
- Multi-acid digest, including HF, ICP- OES or ICP-MS. Multi element scan.
- Iron Ore package. XRF fusion.
- S, IR.
- LOI (TGA) – 105°C, 1000°C.
- SG, gas pycnometer.

### **16.2 Certification for additional elements**

- Fe- Titration
- LOI at LOI at 371°C, 405°C, 650°C and 850°C
- Major oxides by XRF (it must have BaO, if not, please do not analyse)

## **17. Information Requested of Participating Laboratories**

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

### **17.1 Initial Certification**

State and provide brief description of analytical techniques used.  
State aliquots used for all determinations.  
Results for individual analyses to be reported.  
Report all QC data, to include replicates, blanks and certified reference materials used.

### **17.2 Certification of additional elements**

- State aliquots used for all determinations.
- Fe titration ppm
- Oxides to be reported in %
- Report all QC data, to include replicates, blanks and certified reference materials used.

- All Round robin samples must be treated the same as routine test samples.
- All results must be reported to maximum decimal places i.e. dependent on laboratories capabilities.
- 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.
- Please use the excel template provided by AMIS. If you require a copy, please email any of the email addresses below and ensure all uncertainties are added to the results.
- Please send PDF of all results.
- Ensure correct PPE is used i.e. gloves, dust masks and protective clothing.
- Analysis should be done under controlled environmental conditions.

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

The samples used in this certification process have been selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore, all possible 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 Grubbs tests 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  $\leq 2$ , 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.

## 19. Participating Laboratories

Twenty-four laboratories were each given eight randomly selected packages of the CRM. Twenty-one laboratories of the twenty-four laboratories submitted results in time for certification. For certification of additional elements, five laboratories were each given eight randomly selected packages of the CRM and four of the laboratories submitted results in time for certification.

The laboratories that provided results timeously are:

1. ACME Analytical Laboratories Ltd CA
2. Activation Laboratories Pty Ltd (ActLabs) CA
3. ALS Ammtec (Australia)
4. ALS Chemex Laboratory Group Brisbane Australia
5. ALS Chemex Laboratory Group Johannesburg SA
6. ALS Chemex Laboratory Group Perth WA
7. ALS Chemex Laboratory Group Vancouver CA
8. ALS OMAC (Ireland)
9. Anglo American Technical Solutions
10. BV Amdel (Australia)
11. Genalysis Laboratory Services (South Africa) Pty
12. Genalysis Laboratory Services (W Australia P)
13. Intertek Utama Services (Indonesia)
14. Scrooby's Lab
15. Set Point Laboratories (Isando) SA
16. SGS Australia Pty Ltd (Newburn) WA
17. SGS Geosol Laboratories Ltda (Brazil)
18. SGS Mineral Services Callao (Peru)
19. SGS Mineral Services Lakefield (Canada)
20. SGS South Africa
21. SGS Townsville (Australia)
22. SGS Vancouver (Canada)
23. Shiva Analyticals India
24. Ultra Trace (Pty) Ltd WA



## 20. Accepted Assay Data

Data from the 24 laboratories used for certification are set out in Table 8.

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

LOI405 LOI %	LOI LOI %	LOI LOI %	Titration Fe ppm	XRF Fe ppm	XRF Fe ppm	FUS Fe ppm	XRF S %	SG SG Dimensionless	SG SG Dimensionless	SG SG Dimensionless	FUS Si %	XRF Al <sub>2</sub> O <sub>3</sub> %
2.83	3.58	3.50	543400	567000	564900	579000	0.02	4.28	4.08	3.85	5.57	2.70
2.95	3.57	3.80	546900	568300	565400	573000	0.02	4.30	4.04	3.75	5.64	2.74
2.70	3.56	3.60	542800	568200	564000	566000	0.02	4.27	4.07	4.26	5.67	2.71
2.69	3.59	3.80	554800	568800	563700	575000	0.02	4.29	4.07	4.34	5.72	2.71
2.65	3.60	3.91	564200	568300	565100	572000	0.02	4.29	4.06	4.33	5.63	2.74
2.83	3.64	4.02	550000	567100	567400	567000	0.02	4.30	3.79	4.25	5.63	2.74
2.72	3.59	4.08	535300	567600	566300	575000	0.02	4.30	3.78	4.22	5.65	2.75
2.94	3.59	4.17	548800	568000	565800	578000	0.02	4.29	3.85	4.17	5.61	2.74
3.03	3.74	4.20	578000	561700	565900	576000	0.02	4.06	3.86	4.10	5.30	2.72
2.96	4.04	4.08	579000	566000	566500	576000	0.02	4.06	3.82	4.22	5.00	2.68
2.94	3.81	3.91	575000	559600	566100	565000	0.02	4.07	3.87		5.20	2.75
2.97	3.71	3.96	575000	562900	566900	563000	0.02	4.06	3.82		5.30	2.74
2.89	3.75	3.69	578000	564800	565700	565000	0.02	4.06	3.78		5.20	2.72
2.97	3.78	3.60	578000	560500	566800	570000	0.02	4.05	4.06		5.30	2.72
2.94	3.95	4.02	578000	563700	566300	562000	0.02	4.06	4.06		5.40	2.77
2.97	3.82	3.99	578000	559700	566000	580000	0.02	4.06	4.05		5.30	2.72
2.79	3.76	3.99	554700	562100		551000	0.02	3.87	4.00		5.20	2.69
2.79	3.76	3.61	555800	564700		553000	0.02	3.90	4.07		5.20	2.68
2.79	3.71	4.10	557700	560200		549000	0.02	3.85	4.07		5.20	2.67
2.79	3.74	4.02	553000	568000		555000	0.02	3.87	4.04		5.30	2.74
2.78	3.75	3.40	556400	568000		554000	0.02	3.87	4.04		5.20	2.73
2.79	3.76	3.39	556000	568000		535000	0.02	3.87	4.18		5.60	2.71
2.78	3.71	3.41	556200	567000		556000	0.02	3.89	4.13		5.20	2.72
2.78	3.74	3.37	556600	567000		545000	0.02	3.88	4.14		5.33	2.68
	3.79	3.40		567000		559000	0.02	3.99	4.21		5.14	2.70
	3.68	3.41		568000		561000	0.02	3.95	4.17		5.23	2.73
	3.70	3.47		568000		565000	0.02	3.96	4.20		5.46	2.73
	3.72	3.41		567700		560000	0.02	4.00	4.14		5.55	2.71
	3.74	3.60		562100		562000	0.02	4.04	4.17		5.45	2.72
	3.79	3.60		560800		559000	0.02	4.01	4.15		5.17	2.74
	3.82	3.70		560700		568000	0.02	3.99	4.14		5.31	2.73
	3.75	3.60		562600		560000	0.02	4.04	4.17		5.50	2.72
	4.12	3.70		562600		556200	0.02	3.75	4.14		5.30	2.74
	4.10	3.60		564900		500800	0.02	3.78	4.15		5.50	2.73
	4.04	3.70		565900		558600	0.02	3.80	4.17		5.50	2.70
	4.10	3.70		564400		580900	0.02	3.72	4.14		5.40	2.75
	4.07	3.63		566800		559100	0.02	3.77	4.14		5.40	2.69
	4.08	3.61		565000		552600	0.02	3.77	3.91		5.30	2.71
	4.16	3.62		565200		550100	0.02	3.82	3.90			2.73
	4.22	3.66		566000		557300	0.02	3.81	3.89			2.80
	3.68	3.66		564000		557000	0.02	4.34	3.87			2.71
	3.68	3.66		564600		556000	0.02	4.34	3.90			2.71
	3.69	3.64		563700		551000	0.02	4.32	3.88			2.71
	3.67	3.63		567400		559000	0.02	4.32	3.89			2.72
	3.68	3.62		566400		554000	0.02	4.30	3.91			2.71
	3.67	3.62		562500		559000	0.02	4.33	3.75			2.71
	3.65	3.64		564500		557000	0.02	4.33	3.74			2.71
	3.62	3.61		568600		553000	0.02	4.32	3.69			2.69
	3.94	3.60		563900		554000	0.02	4.20	3.74			2.70
	3.90	3.60		561200		561000	0.02	4.23	3.70			2.66
	3.81	3.62		567900		560000	0.02	4.28	3.71			2.68
	3.86	3.56		566400		549000	0.02	4.22	4.14			2.73
	3.87	3.74		566300		554000	0.02	4.22	4.15			2.69
	4.04	3.74		566400		557000	0.02	4.21	4.14			2.68
	3.92	3.74		567300		559000	0.02	4.12	4.15			2.66
	3.90	3.73		567500		558000	0.02	4.16	4.15			2.66
	3.81	3.72		568900		576000	0.02	4.26	4.15			2.69
	3.79	3.75		566200		559600	0.02	4.28	4.14			2.74
	3.81	3.74		564700		586900	0.02	4.25	4.15			2.73
	3.82	3.73		563500		552300	0.02	4.30	3.88			2.64
	3.81	3.63		563200		544800	0.02	4.25	3.84			2.72
	3.77	3.56		565400		553900	0.02	4.21	3.86			2.70
	3.81	3.41		564900		563400	0.02	4.25	3.90			2.77
	3.82	3.45		563700		555400		4.28	3.78			2.68
	3.50	3.45		564400				4.07	3.78			2.69
	3.50	3.58		565100				4.09				2.71
	3.50	3.52						4.07				
	3.50	3.52										

Assay Data (Cont.)

XRF Al <sub>2</sub> O <sub>3</sub> %	XRF Fe <sub>2</sub> O <sub>3</sub> %	XRF K <sub>2</sub> O %	XRF K <sub>2</sub> O %	XRF MnO %	XRF MnO %	XRF P <sub>2</sub> O <sub>5</sub> %	FUS SiO <sub>2</sub> %	XRF SiO <sub>2</sub> %	XRF SiO <sub>2</sub> %	XRF TiO <sub>2</sub> %	XRF TiO <sub>2</sub> %	XRF V <sub>2</sub> O <sub>5</sub> %
2.71	80.90	0.03	0.03	0.14	0.14	0.09	12.00	11.82	11.80	0.19	0.17	0.01
2.74	80.90	0.03	0.03	0.14	0.14	0.09	12.00	11.93	11.80	0.19	0.19	0.01
2.71	80.60	0.03	0.03	0.15	0.14	0.09	12.00	11.84	11.80	0.19	0.19	0.01
2.71	80.50	0.03	0.03	0.15	0.14	0.09	11.80	11.86	11.92	0.19	0.19	0.01
2.71	80.80	0.03	0.03	0.15	0.14	0.10	12.00	11.88	11.90	0.19	0.19	0.01
2.70	80.80	0.03	0.03	0.14	0.14	0.09	12.00	11.92	11.91	0.19	0.19	0.01
2.72	80.60	0.03	0.03	0.14	0.14	0.09	11.80	11.91	11.90	0.19	0.18	0.01
2.70	80.80	0.03	0.03	0.14	0.14	0.09	12.20	11.87	11.94	0.19	0.18	0.01
2.69	81.57	0.03	0.03	0.14	0.15	0.09	11.50	11.80	11.86	0.19	0.18	0.01
2.70	81.70	0.03	0.03	0.14	0.14	0.10	11.85	11.80	11.92	0.18	0.19	0.01
2.71	80.53	0.03	0.03	0.14	0.14	0.09	11.39	11.90	11.89	0.19	0.19	0.01
2.68	81.17	0.03	0.03	0.14	0.15	0.09	11.48	12.00	11.90	0.19	0.19	0.01
2.70	80.72	0.03	0.03	0.14	0.14	0.10	11.56	12.00	11.90	0.19	0.19	0.01
2.70	81.44	0.03	0.03	0.14	0.15	0.09	11.25	12.00	11.95	0.19	0.19	0.01
2.74	81.50	0.03	0.03	0.15	0.14	0.09	11.27	12.10	12.00	0.19	0.19	0.01
2.74	81.19	0.03	0.03	0.14	0.15	0.09	11.47	11.90	12.00	0.19	0.19	0.01
2.77	81.07	0.03	0.03	0.15	0.15	0.09	11.90	11.91	11.95	0.18	0.19	0.01
2.76	81.04	0.03	0.03	0.14	0.15	0.09	12.00	11.83	11.90	0.17	0.19	0.01
2.77	80.82	0.03	0.03	0.14	0.15	0.09	11.90	11.81	11.85	0.18	0.19	0.01
2.74	81.24	0.03	0.03	0.15	0.14	0.09	11.70	12.01	11.80	0.18	0.19	0.01
2.74	80.81	0.03	0.03	0.14	0.15	0.09	11.80	11.96	11.80	0.18	0.19	0.01
2.74	81.02	0.03	0.03	0.15	0.14	0.09	11.60	11.98	11.90	0.18	0.19	0.01
2.72	80.03	0.03	0.03	0.15		0.09	11.90	11.93	11.80	0.18	0.19	0.01
2.70	80.61	0.03	0.03	0.14		0.09	11.80	11.88	11.80	0.18	0.20	0.01
2.76	80.53	0.03	0.03	0.14		0.09		11.90	11.80	0.18	0.20	0.01
2.71	80.55	0.03	0.03	0.15		0.09		12.00	11.80	0.18	0.19	0.01
2.73	80.28	0.03	0.03	0.15		0.09		12.00	11.80	0.18	0.19	0.01
2.75	81.18	0.03	0.03	0.15		0.09		11.95	11.76	0.18	0.20	0.01
2.73	80.20	0.03	0.03	0.14		0.09		12.00	11.81	0.18	0.20	0.01
2.71	80.50	0.03	0.03	0.15		0.09		12.00	11.82	0.18	0.20	0.01
2.67	80.79	0.03	0.03	0.14		0.09		11.90	11.79	0.18	0.20	0.01
2.66	80.36	0.03	0.03	0.14		0.09		12.10	11.79	0.18	0.19	0.01
2.67	80.71	0.03	0.03	0.14		0.09		12.04	11.77	0.21	0.19	0.01
2.65	81.05	0.03	0.03	0.14		0.09		11.63	11.79	0.20	0.19	0.01
2.67	80.79	0.03	0.03	0.14		0.09		12.02	11.73	0.20	0.19	0.01
2.68	80.82	0.03	0.03	0.14		0.09		11.96	11.83	0.21	0.18	0.01
2.66	80.94	0.03	0.03	0.14		0.09		11.93	11.70	0.20	0.18	0.01
2.65	80.65	0.03	0.03	0.14		0.09		11.93	11.69	0.21	0.19	0.01
2.74	80.74	0.04	0.03	0.14		0.09		12.03	11.76	0.20	0.19	0.01
2.74	80.61	0.03	0.03	0.14		0.09		11.90	11.65	0.19	0.18	0.01
2.74	80.40	0.03	0.03	0.14		0.09		11.90	11.73	0.19	0.19	0.01
2.74	79.90	0.03	0.03	0.14		0.09		12.00	11.77	0.19	0.19	0.01
2.74	80.40	0.03	0.03	0.14		0.09		12.00	11.71	0.19	0.19	0.01
2.75	80.40	0.03	0.03	0.14		0.09		11.90	11.90	0.19	0.19	0.01
2.75	80.60	0.03	0.03	0.14		0.09		11.90	11.85	0.19	0.19	0.01
2.75	80.40	0.03	0.03	0.14		0.09		11.90	11.90	0.19	0.18	0.01
2.72	80.40	0.03	0.03	0.14		0.09		11.90	11.85	0.19	0.19	0.01
2.70	80.40	0.03	0.03	0.14		0.09		11.75	11.90	0.19	0.19	0.01
2.76	82.01	0.03	0.03	0.15		0.09		11.65	12.00	0.18	0.19	0.01
2.73	81.71	0.03	0.03	0.14		0.09		11.70	11.95	0.18	0.18	0.01
2.75	81.85	0.03	0.03	0.15		0.09		11.85	11.85	0.19	0.18	0.01
2.75	81.72	0.03	0.03	0.15		0.09		11.75	11.94	0.19	0.19	0.01
2.76	82.00	0.03	0.03	0.15		0.09		11.70	11.95	0.19	0.19	0.01
2.73	81.95	0.03	0.03	0.15		0.09		11.70	11.90	0.19	0.18	0.01
2.72	81.60	0.03	0.03	0.15		0.09		11.65	11.98	0.19	0.19	0.01
2.76	81.50	0.03	0.03	0.15		0.09		11.63	11.91	0.19	0.18	0.01
2.75	81.60	0.03	0.03	0.15		0.09		11.71	11.96	0.20	0.19	0.01
2.72	81.40	0.03	0.03	0.15		0.09		11.60	11.93	0.19	0.19	0.01
2.71	81.50	0.03	0.03	0.15		0.09		11.58	11.95	0.19	0.20	0.01
2.71	81.40	0.03	0.03	0.15		0.09		11.59	12.00	0.19	0.20	0.01
2.73	81.30	0.03	0.03	0.15				11.60	12.00	0.19	0.19	0.01
2.73	81.30	0.03	0.03	0.15				11.70	12.00	0.19	0.19	0.01
		0.03	0.03	0.15				11.80	11.90	0.19	0.19	0.01
		0.03	0.03	0.15				11.90	11.90	0.17	0.19	0.01
		0.03	0.03	0.14				11.90	11.90	0.17	0.20	0.01
		0.03		0.14				11.80	11.80	0.17		0.01
								12.00	0.17			0.01
												0.01

Assay Data (Cont.)

FUS Al ppm	FUS As ppm	XRF Mn ppm	FUS Mn ppm	4A_MICP Mn ppm	4A_MICP Mn ppm	XRF P ppm	XRF P ppm	4A_MICP P ppm	4A_MICP P ppm	FUS Ti %	XRF V ppm
14800	70.00	1120	1100	1100	922	400	370	400	400	0.12	50.00
14300	80.00	1130	1100	1120	916	400	370	400	350	0.11	50.00
14300	70.00	1130	1100	1120	1200	400	370	400	350	0.11	60.00
14200	80.00	1120	1200	1120	1200	400	370	350	350	0.12	50.00
14500	75.00	1120	1100	1100	1200	400	370	400	350	0.12	50.00
14300	65.00	1130	1100	1100	1200	400	370	400	360	0.12	60.00
14100	96.00	1130	1100	1100	1100	400	400	350	350	0.12	60.00
14500	99.00	1120	1100	1100	1100	390	400	400	350	0.12	60.00
14800	93.00	1100	1090	1200	1100	390	400	400	360	0.10	60.00
14800	95.00	1100	1020	1150	1100	380	410	400	326	0.10	60.00
14800	98.00	1100	1060	1200	1030	390	400	400	326	0.10	60.00
14800	94.00	1100	1090	1150	1040	390	400	400	315	0.12	60.00
14800	95.00	1100	1080	1100	1060	380	410	380	315	0.12	60.00
14400	89.00	1100	1090	1150	1050	390	400	370	317	0.12	60.00
14400	110.00	1140	1100	1150	1040	400		360	331	0.12	50.00
14800	100.00	1100	1170	1150	1020	390		360	322	0.12	50.00
12800	90.00	1120	1060	1080	1040	400		380	343	0.11	50.00
12200	70.00	1130	1050	1070	1010	410		360	381	0.11	50.00
12600	80.00	1130	1070	1060	1030	410		370	338	0.11	60.00
13000	80.00	1130	1070	1010	974	410		380	396	0.11	50.00
13100	100.00	1120	1060	1080	995	400		371	320	0.11	60.00
13200	95.00	1120	1130	1050	1010	390		382	431	0.12	60.00
13200	103.00	1100	1040	1060	1020	410		363	372	0.11	60.00
12600	91.00	1100	1050	1090	992	390		353	430	0.10	60.00
14500	102.00	1080	1080	935.7	984	380		363	328	0.10	60.00
14700	109.00	1100	990	948.6	980	380		368	362	0.09	60.00
13700	103.00	1100	1050	980.9	1035	380		351	369	0.10	60.00
14200	102.00	1090	1110	959	1039	380		361	364	0.11	60.00
14500	97.00	1100	1070	967.5	972	390		300	363	0.10	60.00
15700	97.00	1100	1040	986.6	975	390		320	354	0.10	
13700	99.00	1170	1090	974.1	1007	380		310	360	0.10	
13900	99.00	1180	1080	964.9	1024	380		320	366	0.11	
14600	99.00	1130	1170	1150	1058	390		310	354	0.13	
13000	98.00	1140	1217	1220	1079	400		310	357	0.13	
14100	101.00	1140	1236	1200	1112	400		310	363	0.13	
15100	100.00	1180	1175	1220	1131	400		310	358	0.13	
14600	101.00	1160	1191	1220	1145	400		330	392	0.13	
14600		1170	1205	1080	1118	390		330	375	0.13	
14500		1100		1080	1130	400		320	383	0.13	
14700		1110		1090	1146	400		350	401		
13200		1110		1140	1120	400		330	366		
13200		1130		1110	1113	410		355			
13000		1120		1090	1000	390		340			
13400		1110		1090	990	390		335			
13600		1130		1120	990	400		370			
13600		1130		1030	1000	400		360			
13000		1150		1000	1000	390		360			
13300		1130		1020	1000	400		370			
14700		1140		1050	1000	410		380			
14000		1140		1060	980	390		360			
15200		1140		1150	954	410		360			
13900		1150		1040	1006	390		370			
14200		1150		1030	949	410		320			
14200		1140		1020	1007	400		310			
14200				1110	996	400		320			
14100				1040	985	410		320			
				1080	991	400		300			
				1070	989	390		300			
				1060		410		300			
				1090		390		400			
				1080		400		300			
				913		390		400			
				914		410		400			
				911		410		400			
				927		370		400			
				920		370		400			

## 21. Reported Values

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

## 22. 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.

## 23. 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).

## 24. 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.

## 25. 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.

## 26. 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.

## 27. 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.

## 28. 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).

## 29. 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.

**Revision: 001**

**Date of revision: 14 February 2018**

**Reason for new report:** Recertification of all elements and methods, format updated

**Revision: 002**

**Date of revision: 27 January 2020**

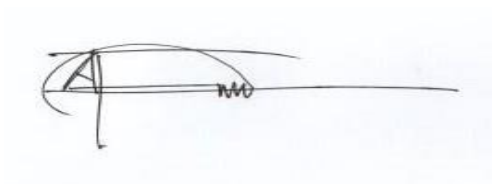
**Reason for new report: Amendment of COA name**

**Certifying Officers:**

*T. Matodzi*

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

**Thivhafuni Matodzi (Quality Specialist)**



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

**Allan Fraser**

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

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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	Mean	n	% RSD	SD	Unit
Moisture	MOIST	1.11	71	21.935	0.243	%
LOI	LOI371	2.94	24	16.559	0.487	%
LOI	LOI650	3.75	24	16	0.595	%
Fe	4A_MICP	501511	77	8	39887	ppm
S	4A_MICP	0.020	92	24	0.005	%
S	Combustion/LECO	0.021	97	44	0.009	%
CaO	XRF	0.024	127	22	0.005	%
Cl	XRF	167	53	20	33	ppm
Cr <sub>2</sub> O <sub>3</sub>	XRF	0.018	123	30	0.005	%
MgO	XRF	0.066	121	18	0.012	%
Na <sub>2</sub> O	XRF	0.019	83	44	0.008	%
Ag	4A_MICP	0.2	74	44	0.071	ppm
Ba	FUS	47	32	115	54	ppm
Ca	FUS	685	28	133	914	ppm
Ca	4A_MICP	192	116	29	55	ppm
Ce	FUS	15	22	24	4	ppm
Co	XRF	16	24	35	6	ppm
Co	FUS	16	23	81	13	ppm
Cr	FUS	139	64	30	41	ppm
Cu	XRF	24	38	41	10	ppm
Cu	FUS	23	31	21	5	ppm
Cu	4A_MICP	20	136	21	4	ppm
Ge	4A_MICP	2	52	79	1	ppm
K	FUS	1075	27	78	842	ppm
K	4A_MICP	258	122	25	65	ppm
Mg	FUS	385	42	21	82	ppm
Mg	4A_MICP	335	103	25	84	ppm
Na	4A_MICP	140.1	91	58	81	ppm
Pb	XRF	35.1	30	59	21	ppm
Se	4A_MICP	1.0	27	32	0.3	ppm
Te	4A_MICP	0.1	53	75	0.1	ppm
V	FUS	66	32	26	17	ppm
V	4A_MICP	47	103	22	10	ppm
Y	FUS	6	23	50	3	ppm
Zn	XRF	16	29	33	5	ppm
Zn	4A_MICP	19	104	37	7	ppm
Zr	XRF	62	37	68	42	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

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

where the sample mean and standard deviation,  $\bar{x}$  and  $s$ , are calculated with the suspect value included. The  $G_{1\text{ calc}}$  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

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

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

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

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

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

### Grand Mean

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

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

### Certified Value

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

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

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

### Total Variation (SST)

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

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

### Between Group Variation (SSB)

The *variation* due to the 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 <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 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  $\mu$  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 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 31) 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:

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

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 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:

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

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

**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 [21] 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<sub>assay</sub>* 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

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**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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