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Certificate

# AMIS0454

## Certified Reference Material

Ilmenite, Mineral Sand Concentrate,  
Tronox Mineral Sands (Namakwa Sands) Mine,  
South Africa

### *Certificate of Analysis*

#### AMIS

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## Summary Statistics

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

<b>Analyte</b>	<b>Method</b>	<b>Certified (<math>\mu</math>)<sup>6</sup></b>	<b>(2s)<sup>8</sup> <math>\pm</math></b>	<b>Unit</b>
GOI	GOI <sup>1</sup>	3.00	0.13	%
SG	SG <sup>2</sup>	4.67	0.13	Dimensionless
Fe	Titration <sup>3</sup>	37.41	0.97	%
Fe	XRF <sup>4</sup>	36.41	0.77	%
Ba	4A_MICP <sup>5</sup>	22	7	ppm
Co	4A_MICP	62	20	ppm
K	4A_MICP	384	93	ppm
La	4A_MICP	16	2	ppm
Mn	4A_MICP	8965	1276	ppm
Ni	4A_MICP	69	17	ppm
Sc	4A_MICP	59	9	ppm
Sr	4A_MICP	10	3	ppm
Ti	XRF	26.53	1.0	%
Y	4A_MICP	12	4	ppm
Zn	4A_MICP	450	87	ppm

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

Analyte	Method	Certified ( $\mu$ ) <sup>6</sup>	(2s) <sup>8</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	XRF	0.74	0.05	%
CaO	XRF	0.22	0.01	%
Cr <sub>2</sub> O <sub>3</sub>	XRF	0.12	0.01	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	52.25	1.1	%
K <sub>2</sub> O	XRF	0.045	0.01	%
MgO	XRF	0.75	0.06	%
MnO	XRF	1.19	0.04	%
Nb <sub>2</sub> O <sub>5</sub>	XRF	0.091	0.01	%
SiO <sub>2</sub>	XRF	2.23	0.12	%
TiO <sub>2</sub>	XRF	44.84	0.90	%
V <sub>2</sub> O <sub>5</sub>	XRF	0.25	0.03	%
ZrO <sub>2</sub>	XRF	0.12	0.004	%

## 1. Certified Concentrations and Uncertainties

AMIS0454 is a new standard material, developed and certified in March 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>6</sup>	N	n	k	% RSD	( $u_c$ ) <sup>7</sup>	(2s) <sup>8</sup> $\pm$	(CI) <sup>9</sup> 95%	(U) <sup>10</sup> $\pm$	Unit
GOI	GOI <sup>1</sup>	3.00	10	78	2.262	2	0.066	0.13	0.044	0.2	%
SG	SG <sup>2</sup>	4.67	7	56	2.447	1	0.067	0.13	0.059	0.2	Dimensionless
Fe	Titration <sup>3</sup>	37.41	3	24	4.303	1	0.48	0.97	1.0	2	%
Fe	XRF <sup>4</sup>	36.41	6	45	2.571	1	0.38	0.77	0.42	1.0	%
Ba	4A_MICP <sup>5</sup>	22	4	32	3.182	16	4	7	5	11	ppm
Co	4A_MICP	62	5	40	2.776	16	10	20	13	28	ppm
K	4A_MICP	384	5	40	2.776	12	46	93	54	129	ppm
La	4A_MICP	16	3	24	4.303	6	1	2	2	4	ppm
Mn	4A_MICP	8965	5	39	2.776	7	638	1276	799	1771	ppm
Ni	4A_MICP	69	6	48	2.571	12	8	17	8	22	ppm
Sc	4A_MICP	59	5	40	2.776	8	5	9	6	13	ppm
Sr	4A_MICP	10	6	44	2.571	15	1	3	2	4	ppm
Ti	XRF	26.53	5	36	2.776	2	0.52	1.0	0.81	1	%
Y	4A_MICP	12	4	32	3.182	15	2	4	3	6	ppm
Zn	4A_MICP	450	5	39	2.776	10	44	87	54	121	ppm

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

Analyte	Method	Certified ( $\mu$ ) <sup>6</sup>	N	n	k	% RSD	( $u_c$ ) <sup>7</sup>	(2s) <sup>8</sup> $\pm$	(CI) <sup>9</sup> 95%	(U) <sup>10</sup> $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	XRF	0.74	12	91	2.201	3	0.02	0.05	0.01	0.05	%
CaO	XRF	0.22	12	92	2.201	3	0.007	0.01	0.004	0.02	%
Cr <sub>2</sub> O <sub>3</sub>	XRF	0.12	10	80	2.262	6	0.007	0.01	0.004	0.02	%
Fe <sub>2</sub> O <sub>3</sub>	XRF	52.25	11	85	2.228	1	0.57	1.1	0.40	1	%
K <sub>2</sub> O	XRF	0.045	9	67	2.306	11	0.005	0.01	0.003	0.01	%
MgO	XRF	0.75	11	83	2.228	4	0.03	0.06	0.02	0.07	%
MnO	XRF	1.19	11	88	2.228	2	0.021	0.04	0.013	0.05	%
Nb <sub>2</sub> O <sub>5</sub>	XRF	0.091	7	56	2.447	6	0.005	0.01	0.003	0.01	%
SiO <sub>2</sub>	XRF	2.23	11	86	2.228	3	0.059	0.12	0.036	0.1	%
TiO <sub>2</sub>	XRF	44.84	10	80	2.262	1	0.45	0.90	0.31	1	%
V <sub>2</sub> O <sub>5</sub>	XRF	0.25	12	95	2.201	7	0.02	0.03	0.01	0.04	%
ZrO <sub>2</sub>	XRF	0.12	6	48	2.571	2	0.002	0.004	0.001	0.01	%

1. GOI is Gain on Ignition
2. SG is Specific Gravity
3. Titration
4. XRF is X-ray Fluorescence
5. 4A\_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
6. 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.
7. 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. ( $u_c$ )
8. Two standard deviations (2s)
9. Confidence interval at 95% level of confidence.
10. 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
Fe Titration	37.41 %	Fe XRF	36.41 %	Equal Variance ( $p=0.429$ )	0.010	Reject $H_0$ ; certified values are <i>not</i> equal

## 3. Intended Use

AMIS0454 is a matrix matched Certified Reference Material, fit for use as a control sample in routine assay laboratory quality control when inserted within runs of test samples and measured in parallel to test samples. This material can also be used for method development, use as independent calibration verification check standard (i.e. if not used as a calibration standard in an instrument calibration), or for validation of accuracy in a method validation exercise (see Appendix 3). The recommend procedure for the use of this CRM as a control standard in laboratory quality control is to develop a Shewhart chart, where a mean value and corresponding 1, 2 and 3 standard deviations are derived from replicate measurements of the CRM (see Appendix 6). This CRM can also be used to assess inter-laboratory or instrument bias and establish within-laboratory precision and within-laboratory reproducibility. The certified concentrations and expanded uncertainty for this material are property values based on an inter-laboratory measurement campaign and reflect consensus results from the laboratories that took part in the exercise

#### 4. Abbreviations and Symbols

Abbreviations and symbols used in this document are shown in **Table 4**.

**Table 4.** Abbreviations, symbols and descriptions.

Abbreviation/Symbol	Description
Alpha ( $\alpha$ )	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
$t_{calc}$	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%, <i>df</i> )	MS Excel function for t-critical value at LOC 95% and <i>df</i>
<i>U</i>	Expanded uncertainty at a given k
<i>u</i>	Standard uncertainty at k=1
$u_c$	Combined standard uncertainty at $k=1$
$\mu\text{m}$	Micron, is an SI derived unit of length equaling $1 \times 10^{-6}$ of a meter

## 5. Uncertified Concentration Values

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

## 6. Units

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

## 7. Analytical and Physical Methods

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

## 8. Origin of Material

The raw material for AMIS0454 is ilmenite from the Tronox Mineral Sands (Namakwa Sands) Mine, situated at Brand-se-Baai, 385 km north of Cape Town in the Northern Cape Province, South Africa. The ore is mined and processed at primary concentration plants to produce a mineral concentrate. It undergoes further processing at the secondary concentration plant to yield a magnetic and non-magnetic stream. These concentrates are then put through a Mineral Separation Plant where the minerals in the streams are separated to produce zircon, rutile and ilmenite.

## 9. Approximate Mineral and Chemical Composition

Ilmenite is the titanium-iron oxide mineral with the idealized formula  $\text{FeTiO}_3$ . Ilmenite is mined primarily for the production of titanium dioxide.

## 10. Health and Safety

The material is a very fine powder coloured Dusky brown powder (Corstor 5YR 2.5/2). Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

## 11. 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.

## 12. 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).

## 13. 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.

## 14. Methods of Analysis Requested

The following methods of analysis were requested:

- a) Fe, Ti by XRF
- b) Fe, Ti by Titration
- c) Multi-acid digest, multi element scan, to include Fe, Ti, Ca, Al, Mg, Si, Mn, V, Zr, Cr, Nb, Ta: ICP-OES
- d) Major elements by XRF fusion ( $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ , LOI)
- e) SG – Gas Pycnometer

## 15. 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, with units of measure clearly marked
- d) Report all QC data, to include replicates, blanks and certified reference materials used

## 16. 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)

## 17. 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]).

## 18. 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%,  $df$ ).

## 19. 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]).

## 20. 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 5 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 5.** Example of replicate assay data in which the *CI*, *2s* and *U* are shown.

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

## 21. Participating Laboratories

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

1. ACME Vancouver
2. ALS (Vancouver) - Analytical Laboratory Services - Vancouver, Canada
3. ALS Ammtec Australia
4. ALS Brisbane
5. Bureau Veritas Minerals Ultra Trace Pty Ltd
6. Labtium - Finland
7. Set Point Laboratories (Isando) SA
8. SGS Callao Peru
9. SGS Geosol Laboratories Ltd. (Brazil)
10. SGS Mineral Services Lakefield (Canada)
11. SGS Newburn
12. SGS South Africa (Pty) Ltd. - Barberton
13. SGS Vancouver (Canada)
14. Tronox Chandala Aus
15. Tronox Mineral Sands Mine - KZN

## 22. Accepted Assay Data

Data from the 15 laboratories used for certification are set out in Table 6.

**Table 6.** Data used to calculate the certified values after removal of outliers.

GOI	SG	Titration	XRF	4A_MICP	4A_MICP	4A_MICP
GOI	SG	Fe	Fe	Ba	Co	K
%	Dimensionless	ppm	ppm	ppm	ppm	ppm
3.02	4.65	379000	360200	22	64.7	400
3.01	4.68	379000	360900	22	64.2	400
3.01	4.66	377000	360200	23	65.5	400
3.02	4.67	373000	360900	23	65.7	400
3.02	4.68	373000	360200	21	66.1	400
3.02	4.66	374000	360900	21	64.2	400
3.02	4.67	372000	360200	21	65.2	400
3.01	4.68	372000	360900	20	67.9	400
3	4.66	369900	368000	23	60	300
2.95	4.66	369900	369000	25	65	300
2.96	4.66	369200	369000	26	65	300
2.92	4.66	368700	368000	24	65	300
2.97	4.67	370500	369000	25	65	300
3	4.67	368700	369000	26	65	300
3.01	4.66	370600	369000	26	60	300
2.94	4.67	370600	369000	24	60	400
2.96	4.71	380000	366000	18	47	380
2.96	4.7	377000	366100	17	48	370
2.97	4.64	378000	366100	18	50	380
2.96	4.66	378000	366300	17	51	380
2.95	4.69	379000	366000	18	51	380
2.96	4.64	380000	367400	17	48	370
2.96	4.68	381000	366300	18	49	400
2.97	4.65	369000	366600	17	47	390
2.96	4.62		366000	25	57	400
2.93	4.63		364000	25	58	400
2.93	4.52		365000	25	58	400
2.95	4.6		364000	25	58	400
2.96	4.52		366000	24	58	400
2.94	4.57		365000	25	56	400
2.98	4.53		366000	24	60	400
2.97	4.62		365000	24	59	400
3.1	4.759		357000		78	442
3.05	4.755		358000		74	429
3.09	4.773		358000		78	435
3.05	4.786		360000		78	412
3.08	4.763		357000		78	409
3.03	4.782		364000		77	431
3.08	4.755		365000		73	422
3.04	4.785		364000		75	440
2.94	4.61		366000			
2.93	4.62		367000			
2.93	4.59		368000			
2.94	4.59		367000			
2.93	4.61		367000			
2.93	4.63					
2.92	4.62					
2.91	4.56					
3.13	4.71					
3.1	4.7					
3.06	4.71					
3.07	4.7					
3.1	4.69					
3.15	4.71					
3.11	4.71					
3.12	4.69					
3.018						
3.028						
3.021						
3.016						
3.011						
3.015						
3.023						
3.016						
2.99						
3.12						
3.04						
3.03						
3.04						
2.97						
2.92						
2.93						
2.91						
2.84						
2.9						
2.93						
2.93						
2.93						

Assay Data (Cont.)

XRF Al <sub>2</sub> O <sub>3</sub>	XRF CaO	XRF Cr <sub>2</sub> O <sub>3</sub>	XRF Fe <sub>2</sub> O <sub>3</sub>	XRF K <sub>2</sub> O	XRF MgO	XRF MnO	XRF Nb <sub>2</sub> O <sub>5</sub>	XRF SiO <sub>2</sub>	XRF TiO <sub>2</sub>	XRF V <sub>2</sub> O <sub>5</sub>	XRF ZrO <sub>2</sub>
%	%	%	%	%	%	%	%	%	%	%	%
0.76	0.22	0.11	51.7	0.04	0.68	1.17	0.08	2.32	44.4	0.28	0.12
0.75	0.21	0.11	51.7	0.04	0.68	1.17	0.09	2.35	44.4	0.28	0.12
0.73	0.21	0.11	51.4	0.04	0.69	1.16	0.08	2.2	44.6	0.28	0.12
0.76	0.21	0.11	51.5	0.04	0.69	1.16	0.09	2.2	44.3	0.28	0.12
0.73	0.21	0.1	51.4	0.04	0.68	1.16	0.09	2.27	44	0.27	0.12
0.73	0.21	0.11	51.6	0.04	0.68	1.17	0.08	2.34	44.2	0.28	0.12
0.75	0.21	0.11	51.7	0.04	0.77	1.17	0.09	2.24	44.3	0.28	0.12
0.76	0.22	0.11	51.5	0.04	0.77	1.17	0.08	2.24	44.5	0.23	0.12
0.74	0.22	0.12	52.2	0.04	0.77	1.18	0.09	2.26	45.46	0.24	0.12
0.75	0.22	0.11	52.3	0.05	0.76	1.18	0.1	2.23	45.38	0.23	0.12
0.72	0.22	0.11	52.4	0.04	0.76	1.19	0.1	2.23	45.55	0.24	0.12
0.77	0.23	0.12	52.1	0.05	0.76	1.17	0.09	2.25	45.31	0.23	0.12
0.75	0.23	0.12	52	0.04	0.77	1.18	0.09	2.27	45.43	0.23	0.12
0.75	0.22	0.11	52.1	0.04	0.76	1.17	0.09	2.29	45.42	0.23	0.12
0.74	0.22	0.11	52.2	0.05	0.73	1.17	0.1	2.25	45.58	0.23	0.13
0.75	0.22	0.11	52.4	0.04	0.73	1.19	0.09	2.23	45.37	0.25	0.12
0.75	0.22	0.112	53.17	0.05	0.72	1.21	0.09	2.26	44.8	0.249	0.12
0.75	0.23	0.114	53.09	0.04	0.72	1.22	0.09	2.23	44.7	0.247	0.12
0.75	0.22	0.112	53.17	0.04	0.73	1.22	0.09	2.25	44.6	0.252	0.12
0.74	0.22	0.115	53.04	0.04	0.72	1.21	0.09	2.22	44.7	0.248	0.12
0.7	0.22	0.116	53.12	0.05	0.72	1.21	0.09	2.26	44.7	0.251	0.12
0.72	0.22	0.111	53.11	0.05	0.73	1.2	0.09	2.23	44.7	0.248	0.12
0.7	0.23	0.114	53.31	0.05	0.78	1.22	0.09	2.22	44.7	0.251	0.12
0.7	0.21	0.112	53.14	0.05	0.78	1.22	0.09	2.22	44.6	0.22	0.13
0.7	0.21	0.12	52.6	0.05	0.77	1.18	0.09	2.23	44.91	0.22	0.12
0.7	0.21	0.12	52.7	0.05	0.77	1.18	0.09	2.23	45.15	0.22	0.12
0.71	0.22	0.12	52.7	0.05	0.77	1.18	0.09	2.23	44.74	0.23	0.12
0.72	0.21	0.12	52.6	0.05	0.78	1.17	0.1	2.23	44.73	0.22	0.12
0.75	0.21	0.12	52.7	0.05	0.77	1.18	0.09	2.23	44.61	0.22	0.12
0.74	0.21	0.12	52.7	0.05	0.78	1.18	0.1	2.22	44.9	0.22	0.12
0.74	0.22	0.12	52.7	0.04	0.78	1.19	0.09	2.09	44.78	0.22	0.12
0.73	0.21	0.12	52.7	0.04	0.76	1.17	0.1	2.11	44.9	0.26	0.12
0.74	0.21	0.11	51.3	0.04	0.75	1.24	0.09	2.08	45.9	0.26	0.12
0.74	0.21	0.11	51.2	0.04	0.74	1.24	0.09	2.08	45.7	0.26	0.12
0.74	0.21	0.1	51.1	0.04	0.76	1.22	0.09	2.07	45.8	0.26	0.12
0.73	0.21	0.11	51.3	0.05	0.77	1.23	0.09	2.07	45.7	0.25	0.12
0.78	0.21	0.11	51.3	0.05	0.74	1.23	0.1	2.07	45.7	0.26	0.12
0.78	0.21	0.11	52.3	0.05	0.76	1.23	0.09	2.07	45.9	0.26	0.12
0.76	0.21	0.1	52.1	0.05	0.77	1.22	0.09	2.24	45.6	0.26	0.12
0.75	0.21	0.11	52.2	0.05	0.77	1.22	0.1	2.24	45.8	0.26	0.12
0.76	0.23	0.12	52.1	0.05	0.76	1.19	0.09	2.21	44.8	0.26	0.12
0.77	0.23	0.13	52.3	0.05	0.75	1.18	0.09	2.26	44.8	0.26	0.12
0.75	0.22	0.13	52.2	0.05	0.76	1.17	0.09	2.21	44.7	0.26	0.12
0.78	0.22	0.13	52.3	0.05	0.76	1.17	0.09	2.26	44.7	0.26	0.12
0.76	0.22	0.12	52.3	0.04	0.76	1.17	0.09	2.18	44.7	0.26	0.12
0.76	0.23	0.12	52.4	0.04	0.76	1.18	0.09	2.24	44.8	0.27	0.12
0.76	0.22	0.12	52.4	0.04	0.73	1.17	0.09	2.22	44.8	0.27	0.12
0.76	0.23	0.13	52.2	0.04	0.74	1.18	0.09	2.23	44.6	0.24	0.12
0.75	0.22	0.13	52.6	0.04	0.74	1.19	0.1	2.25	44.5	0.24	
0.76	0.23	0.12	52.4	0.04	0.74	1.2	0.09	2.24	44.5	0.24	
0.76	0.23	0.12	52.5	0.04	0.74	1.19	0.1	2.23	44.5	0.24	
0.76	0.22	0.12	52.3	0.046	0.72	1.2	0.1	2.24	44.6	0.24	
0.72	0.22	0.12	52.3	0.047	0.73	1.2	0.09	2.23	44.5	0.25	
0.71	0.23	0.12	52	0.048	0.77	1.19	0.1	2.24	44.6	0.24	
0.71	0.22	0.12	52	0.047	0.77	1.19	0.09	2.21	44.5	0.24	
0.73	0.22	0.12	52.2	0.046	0.77	1.2	0.09	2.2	44.5	0.23	
0.73	0.23	0.11	52.2	0.047	0.79	1.18		2.24	44.3	0.23	
0.72	0.23	0.12	52	0.048	0.78	1.17		2.23	44.4	0.23	
0.72	0.22	0.12	52.3	0.047	0.77	1.17		2.23	44.6	0.23	
0.72	0.23	0.12	52.1	0.05	0.78	1.2		2.24	44.5	0.24	
0.73	0.23	0.12	52.1	0.04	0.77	1.19		2.26	44.3	0.24	
0.74	0.22	0.12	51.8	0.04	0.78	1.18		2.23	44.6	0.23	
0.73	0.22	0.12	51.9	0.04	0.77	1.18		2.24	44.5	0.24	
0.73	0.22	0.12	51.9	0.05	0.77	1.18		2.24	44.5	0.25	
0.73	0.21	0.11	51.8	0.04	0.8	1.21		2.26	44.7	0.25	
0.74	0.22	0.12	51.9	0.05	0.79	1.21		2.27	44.7	0.25	
0.74	0.22	0.12	51.6	0.05	0.78	1.22		2.24	44.7	0.24	
0.75	0.21	0.12	51.7		0.77	1.21		2.26	44.9	0.25	
0.74	0.21	0.12	51.7		0.76	1.21		2.26	44.9	0.24	
0.77	0.22	0.12	52.1		0.81	1.22		2.21	45	0.24	
0.77	0.22	0.12	52.2		0.8	1.21		2.25	44.8	0.25	
0.74	0.22	0.11	52.1		0.8	1.21		2.24	45	0.26	
0.78	0.23	0.12	52.3		0.8	1.22		2.28	44.8	0.27	
0.77	0.22	0.11	52.4		0.8	1.2		2.27	44.8	0.27	
0.75	0.23	0.12	52.6		0.8	1.21		2.3	45	0.27	
0.76	0.22	0.12	52.4		0.8	1.2		2.26	44.9	0.27	
0.7	0.22	0.12	52.5		0.72	1.2		2.28	44.8	0.27	
0.7	0.22	0.12	53.2		0.75	1.2		2.27	44.7	0.27	
0.7	0.22	0.12	53.2		0.75	1.2		2.2	44.7	0.28	
0.7	0.22	0.11	53.2		0.74	1.21		2.09	44.8	0.26	
0.7	0.21		53.2		0.73	1.2		2.21		0.26	
0.7	0.2		53.1		0.79	1.2		2.21		0.25	
0.7	0.21		52.9		0.71	1.2		2.2		0.26	
0.75	0.21		53.1			1.2		2.2		0.26	
0.75	0.22		53			1.19		2.21		0.26	

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	XRF	4A_MICP	4A_MICP
La	Mn	Ni	Sc	Sr	Ti	Y	Zn
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
16.1	9401	76.4	64	10	253600	11.7	424
16.2	9502	75.6	64	10	253600	11.6	443
17.1	9603	78.8	64	10	253600	11.7	450
16.8	9758	75	65	10	253600	11.8	446
17.1	9590	79.6	64	10	268600	12	442
15.8	9399	73.1	63	10	268000	11.3	432
16.2	9750	76.5	65	10	267400	11.8	453
16.9	9580	80.7	63	11	268000	11.6	480
15.7	9541	80	61	9.5	268000	12.6	440
15.2	9558	75	62	9	268000	12.4	432.3
15.8	9560	70	61	9	268000	13	448
15.8	9527	75	62	9	267400	12.8	433.3
15.4	9546	75	62	9	268000	13	451.6
15.3	9528	80	62	9	268000	13.1	442.5
15.5	9519	75	61	9	268000	13	442.3
15.5	9521	70	61	9	268000	12.8	452.3
14.6	8730	59	51.7	12.1	268000	14	494
14.9	8690	61	53.3	12	267000	14	493
14.6	8700	58	52.4	11.7	268000	14	494
14.2	8580	60	52.3	12.3	267000	14	477
15	8540	59	53.7	11.7	268000	14	468
15	8530	57	52.1	11.6	269000	14	459
14.4	8840	59	52.3	12.1	268000	14	472
14.4	8590	59	51.9	11.9	268000	14	503
	7910	74	55.4	7	268000	10	377
	7890	75	56.6	7	269000	9.7	374
	8050	75	58.5	7	269000	9.3	398
	8280	75	57.5	7	268000	9.3	388
	8160	75	57.5	9.7	268000	9.8	388
	8130	75	55.6	9.8	268000	9.9	375
	7860	78	56.9	10.1	268000	10	386
	9017	83	54.2	10.2	269000	10	496
	9094	60	60	9.9	269000		499
	9084	59	61	10	270000		502
	9102	62	61	10	269000		495
	8956	61	60	9.5	270000		490
	8927	62	60	10			493
	9068	60	60	9.8			490
	8948	60	60	9.7			494
		58	60	9.6			
		72		9.5			
		68		9.7			
		67		9.6			
		72		9.8			
		66					
		67					
		68					
		70					

## **23. Reported Values**

The certified values listed in this certificate fulfil the AMIS statistical criteria (see section 16) regarding agreement for certification and have been independently validated by Allan Fraser.

## **24. 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.

## **25. Metrological Traceability**

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

## **26. Period of Validity**

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

## **27. Minimum Sample Size**

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

## **28. Availability**

This product is available in Laboratory Packs containing 1kg of material and Explorer Packs containing custom weights (from 50 to 250g) of material. The Laboratory Packs are sealed bottles delivered in sealed foil pouches. The Explorer Packs contain material in standard geochem envelopes, nitrogen flushed, and vacuum sealed in foil pouches.

## **29. Recommended use in Quality Control**

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

### 30. Legal Notice

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

**Date of Version 000:** 07 March 2019

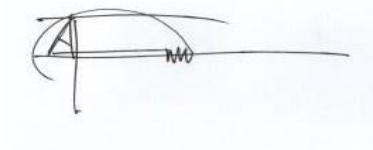
**Version:** 000

**Approving Officer:**

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

**Makhosi Khoza (Quality Specialist)**

**Certifying Officer:**

A handwritten signature in black ink, appearing to be 'AF', is written over a horizontal line. The signature is stylized and somewhat abstract.

**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 7**.

**Table 7.** Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	4A_MICP	8	0.3	0.1	31	ppm
Ag	FUS	8	5.1	0.8	16	ppm
Al	4A_MICP	37	4049.7	599.6	15	ppm
Al	FUS	16	4393.8	653.7	15	ppm
As	4A_MICP	32	3.5	1.5	44	ppm
As	FUS	8	19.8	2.4	12	ppm
B	FUS	2	20.0	*	*	ppm
Ba	FUS	8	43.0	1.9	4	ppm
Ba	XRF	1	100.0	*	*	ppm
Be	4A_MICP	16	1.8	1.6	92	ppm
Bi	4A_MICP	16	0.3	0.1	18	ppm
Bi	FUS	8	3.6	0.6	18	ppm
Ca	4A_MICP	40	1549.5	237.8	15	ppm
Ca	FUS	8	3525.0	70.7	2	ppm
Cd	4A_MICP	17	1.9	1.7	91	ppm
Cd	FUS	1	0.3	*	*	ppm
Ce	4A_MICP	16	32.8	0.9	3	ppm
Ce	FUS	8	28.0	1.1	4	ppm
Co	FUS	8	42.1	2.8	7	ppm
Cr	4A_MICP	32	593.0	249.5	42	ppm
Cr	FUS	16	844.1	61.6	7	ppm
Cs	4A_MICP	8	0.2	*	*	ppm
Cs	FUS	8	0.2	0.04	17	ppm
Cu	4A_MICP	40	37.1	10.7	29	ppm
Cu	FUS	8	44.3	2.0	4	ppm
Cu	XRF	6	35.0	8.4	24	ppm
Dy	4A_MICP	8	2.2	0.1	3	ppm
Dy	FUS	8	3.3	0.2	7	ppm
Er	4A_MICP	8	1.6	0.1	3	ppm
Er	FUS	8	2.7	0.2	9	ppm
Eu	4A_MICP	8	0.2	*	*	ppm
Eu	FUS	8	0.7	0.2	33	ppm
Fe	4A_MICP	24	332812.5	22325.3	7	ppm
Fe	FUS	8	367875.0	1126.0	0.3	ppm
Fe <sup>2+</sup>	Titration	8	23.7	0.1	0.4	%
Fe <sup>3+</sup>	Titration	8	13.4	0.2	1	%
FeO	VOL	8	30.8	0.1	0.3	%
FeO	XRF	8	0.1	0.001	1	%
Ga	4A_MICP	8	6.5	0.1	2	ppm
Ga	FUS	8	4.1	0.4	9	ppm
Gd	4A_MICP	8	2.4	0.1	4	ppm
Gd	FUS	8	3.6	0.3	8	ppm
Hf	4A_MICP	16	5.6	1.3	23	ppm
Hf	FUS	8	26.3	1.5	6	ppm
Ho	4A_MICP	8	0.5	0.01	2	ppm
Ho	FUS	8	0.6	0.05	8	ppm
In	4A_MICP	16	0.5	0.05	9	ppm
In	FUS	8	0.6	0.1	13	ppm
K	FUS	8	1387.5	112.6	8	ppm
La	FUS	8	13.9	1.0	7	ppm
Li	4A_MICP	40	3.2	1.0	30	ppm
Lu	4A_MICP	8	0.5	0.03	5	ppm
Lu	FUS	8	0.5	0.1	22	ppm
Mg	4A_MICP	39	4155.9	495.5	12	ppm
Mg	FUS	16	4637.5	359.4	8	ppm
Mn	FUS	16	9568.8	499.8	5	ppm
Mo	4A_MICP	32	6.0	5.4	90	ppm
Mo	FUS	8	11.0	0.9	8	ppm
Na	4A_MICP	32	264.8	41.5	16	ppm
Na <sub>2</sub> O	XRF	32	0.1	0.03	53	%
Nb	4A_MICP	24	436.8	262.9	60	ppm
Nb	FUS	16	563.6	36.7	7	ppm
Nd	4A_MICP	8	14.5	0.4	2	ppm
Nd	FUS	8	13.1	0.8	6	ppm
Ni	FUS	8	43.4	2.1	5	ppm
Ni	XRF	8	36.3	16.9	46	ppm
P	4A_MICP	32	83.3	20.6	25	ppm
P	FUS	8	237.5	51.8	22	ppm
P <sub>2</sub> O <sub>5</sub>	XRF	40	0.04	0.01	25	%
Pb	4A_MICP	39	21.1	9.0	42	ppm
Pb	FUS	8	20.0	1.4	7	ppm
Pb	XRF	8	48.8	23.0	47	ppm
PbO <sub>2</sub>	XRF	7	0.002	0.001	50	%
Pr	4A_MICP	8	4.0	0.1	1	ppm
Pr	FUS	8	3.7	0.2	4	ppm
Rb	4A_MICP	16	2.7	0.2	8	ppm
Rb	FUS	8	2.5	0.2	6	ppm
S	4A_MICP	28	0.01	0.003	33	%
S	Combustion/LECO	8	0.01	*	*	%
Sb	4A_MICP	16	20.2	20.1	100	ppm
Sb	FUS	8	1.5	0.3	22	ppm
Sc	FUS	8	12.0	1.3	11	ppm
Se	4A_MICP	2	1.0	*	*	ppm
Si	FUS	24	11262.5	996.4	9	ppm
Sm	4A_MICP	8	2.8	0.1	2	ppm
Sm	FUS	8	2.6	0.2	7	ppm
Sn	4A_MICP	16	9.3	9.5	102	ppm
Sn	FUS	8	17.9	1.4	8	ppm
SnO <sub>2</sub>	XRF	5	0.003	0.001	33	%
Sr	FUS	8	20.6	2.4	12	ppm
Sr	XRF	2	35.0	7.1	20	ppm
Ta	4A_MICP	16	25.5	11.7	46	ppm
Ta	FUS	16	25.2	4.4	17	ppm
Ta <sub>2</sub> O <sub>5</sub>	XRF	5	0.02	0.004	25	%
Tb	4A_MICP	8	0.4	0.01	3	ppm
Tb	FUS	8	0.5	0.2	32	ppm
Th	4A_MICP	16	10.9	0.9	9	ppm
Th	FUS	8	14.6	1.8	12	ppm
Th	XRF	7	11.4	3.8	33	ppm
Ti	4A_MICP	16	99902.5	15735.2	16	ppm
Ti	FUS	8	267500.0	1511.9	1	ppm
Ti	Titration	8	266625.0	517.5	0.2	ppm
Tm	4A_MICP	8	0.3	0.01	3	ppm
Tm	FUS	8	0.4	0.1	18	ppm
U	4A_MICP	16	1.5	0.04	2	ppm
U	FUS	8	1.7	0.1	3	ppm
U	XRF	1	10.0	*	*	ppm
V	FUS	16	1481.0	182.5	12	ppm
W	4A_MICP	8	3.6	0.4	13	ppm
W	FUS	16	5.7	3.6	62	ppm
Y	FUS	8	12.4	0.6	5	ppm
Yb	4A_MICP	8	2.6	0.1	4	ppm
Yb	FUS	8	2.6	0.2	6	ppm
Zn	FUS	16	499.9	22.5	4	ppm
Zn	XRF	8	471.3	12.5	3	ppm
Zr	XRF	8	875.0	24.5	3	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 16, 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 8 is developed.

**Table 8.** 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 9. 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 9.** 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 29) 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 9). Table 11 gives a recommended reporting scheme for LOD and LOQ.

**Table 10.** 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 11.** 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 12.** T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence.

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

**End of certificate**