

**AMIS0515**

**Certified Reference Material**

**Gold and Uranium Ore  
Witwatersrand, South Africa**

***Certificate of Analysis***

---

**AMIS**

(A Division of Torre Analytical Services (Pty) Limited)  
(Reg. No. 1989/000201/07)

**A:** 11 Avalon Road, West Lake View Ext 11, Modderfontein, South Africa

**P:** PO Box 856, Isando, 1600, Gauteng, South Africa

**T:** +27 (0) 11 923-0800

**W:** [www.amis.co.za](http://www.amis.co.za)

**Directors:** JT Botes, R Naidoo, NN Robinson, M Padayachee

# TABLE OF CONTENTS

TABLE OF CONTENTS .....	1
LIST OF TABLES .....	2
LIST OF APPENDICES .....	2
SUMMARY STATISTICS .....	3
<b>1. Certified Concentrations and Uncertainties .....</b>	<b>4</b>
<b>2. Intended Use .....</b>	<b>5</b>
<b>3. Abbreviations and Symbols .....</b>	<b>5</b>
<b>4. Uncertified Concentration Values .....</b>	<b>7</b>
<b>5. Units .....</b>	<b>7</b>
<b>6. Analytical and Physical Methods .....</b>	<b>7</b>
<b>7. Origin of Material .....</b>	<b>7</b>
<b>8. Approximate Mineral and Chemical Composition .....</b>	<b>7</b>
<b>9. Health and Safety .....</b>	<b>7</b>
<b>10. Method of Preparation .....</b>	<b>7</b>
11. Radioactivity .....	7
<b>12. Handling .....</b>	<b>8</b>
<b>13. Methods of Analysis Requested .....</b>	<b>8</b>
<b>14. Information Requested of Participating Laboratories .....</b>	<b>8</b>
<b>15. Certification of Mean and Estimation of Measurement Uncertainty .....</b>	<b>8</b>
<b>16. Participating Laboratories .....</b>	<b>9</b>
<b>17. Accepted Assay Data .....</b>	<b>10</b>
<b>18. Reported Values .....</b>	<b>11</b>
<b>19. Validation of Accuracy (Trueness) .....</b>	<b>11</b>
<b>20. Metrological Traceability .....</b>	<b>11</b>
<b>21. Period of Validity .....</b>	<b>11</b>
<b>22. Minimum Sample Size .....</b>	<b>11</b>
<b>23. Availability .....</b>	<b>11</b>
<b>24. Recommended use in Quality Control .....</b>	<b>11</b>
<b>25. Legal Notice .....</b>	<b>11</b>
REFERENCES .....	13
APPENDICES .....	14

## LIST OF TABLES

<b>Table 1.</b> Certified concentrations, two standard deviations, combined and expanded uncertainty. ....	4
<b>Table 2.</b> Certified major oxides concentrations, two standard deviations, combined and expanded uncertainty.....	4
<b>Table 3.</b> Provisional major oxides concentrations, two standard deviations, combined and expanded uncertainty.....	4
<b>Table 3.</b> Abbreviations, symbols and descriptions. ....	5
<b>Table 4.</b> Data used to calculate the certified values after removal of outliers. ....	10
<b>Table 5.</b> Uncertified element concentrations statistics. ....	14
<b>Table 6.</b> 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 <i>et al.</i> , (2009), Table 6.2, page 61.....	18
<b>Table 7.</b> 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. ....	19
<b>Table 8.</b> T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence. ....	22

## LIST OF APPENDICES

<b>Appendix 1:</b> Uncertified Element Statistics.....	14
<b>Appendix 2.</b> Certification of Reference Material and Estimation of Measurement Uncertainty.....	14
<b>Appendix 3.</b> Example: Comparison of Mean and Certified Value for Validation of Accuracy .....	19
<b>Appendix 4.</b> Using the CRM in Quality Control.....	20
<b>Appendix 5.</b> Conversion to Air-dry Basis .....	21
<b>Appendix 6.</b> T-distribution table .....	22

## SUMMARY STATISTICS

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

#### ***Certified Concentrations***

Analyte	Method	<sup>6</sup> Certified( $\mu$ )	<sup>8</sup> Two Standard deviation (2s) $\pm$	Unit
Au	Pb collection <sup>1</sup>	0.51	0.05	g/t
U	4A-MICP <sup>2</sup>	14.2	1.4	ppm
U	XRF <sup>3</sup>	13.9	2.3	ppm
U <sub>3</sub> O <sub>8</sub>	XRF <sup>3</sup>	16.4	2.8	ppm
LOI	LOI <sup>4</sup>	2.55	0.34	%
S	Comb/LECO <sup>5</sup>	0.530	0.030	%

#### **Major Oxides**

#### ***Certified Concentrations***

Analyte	Method	<sup>6</sup> Certified( $\mu$ )	<sup>8</sup> Two Standard deviation (2s) $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>3</sup>	3.99	0.048	%
CaO	XRF <sup>3</sup>	0.33	0.02	%
Cr <sub>2</sub> O <sub>3</sub>	XRF <sup>3</sup>	0.11	0.02	%
Fe <sub>2</sub> O <sub>3</sub>	XRF <sup>3</sup>	3.09	0.11	%
K <sub>2</sub> O	XRF <sup>3</sup>	0.66	0.02	%
SiO <sub>2</sub>	XRF <sup>3</sup>	88.73	0.53	%
TiO <sub>2</sub>	XRF <sup>3</sup>	0.18	0.02	%

#### ***Provisional Concentrations***

Analyte	Method	<sup>6</sup> Certified( $\mu$ )	<sup>8</sup> Two Standard deviation (2s) $\pm$	Unit
MgO	XRF <sup>3</sup>	0.09	0.02	%
Na <sub>2</sub> O	XRF <sup>3</sup>	0.13	0.02	%

# 1. Certified Concentrations and Uncertainties

AMIS0515 is a new standard material, developed and certified in July, 2017. Table 1 gives the certified major oxides concentrations, combined and expanded uncertainty for certified reference material. Table shows the provisional major oxides concentrations, two standard deviations, combined and expanded uncertainty.

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

Analyte	Method	<sup>6</sup> Certified( $\mu$ )	<i>N</i>	<i>n</i>	<i>k</i>	% RSD	<sup>7</sup> Combined uncertainty ( $u_c$ )	<sup>8</sup> Two Standard deviation (2s) $\pm$	<sup>9</sup> Expanded uncertainty ( <i>U</i> ) $\pm$	Unit
Au	Pb collection <sup>1</sup>	0.51	9	71	2.31	4.7	0.02	0.05	0.1	g/t
U	4A-MICP <sup>2</sup>	14.2	4	32	3.18	5.1	0.72	1.4	2	ppm
U	XRF <sup>3</sup>	13.9	5	36	2.78	8.4	1.2	2.3	3	ppm
U <sub>3</sub> O <sub>8</sub>	XRF <sup>3</sup>	16.4	5	36	2.78	8.4	1.38	2.8	4	ppm
LOI	LOI <sup>4</sup>	2.55	7	63	2.45	6.7	0.17	0.34	0.4	%
S	Comb/LECO <sup>5</sup>	0.53	5	36	2.78	2.8	0.015	0.030	0.04	%

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

Analyte	Method	<sup>6</sup> Certified( $\mu$ )	<i>N</i>	<i>n</i>	<i>k</i>	% RSD	<sup>7</sup> Combined uncertainty ( $u_c$ )	<sup>8</sup> Two Standard deviation (2s) $\pm$	<sup>9</sup> Expanded uncertainty ( <i>U</i> ) $\pm$	Unit
Al <sub>2</sub> O <sub>3</sub>	XRF <sup>3</sup>	3.99	8	63	2.36	0.6	0.024	0.048	0.1	%
CaO	XRF <sup>3</sup>	0.33	6	48	2.57	2.5	0.01	0.02	0.02	%
Cr <sub>2</sub> O <sub>3</sub>	XRF <sup>3</sup>	0.11	8	59	2.36	8.8	0.01	0.02	0.02	%
Fe <sub>2</sub> O <sub>3</sub>	XRF <sup>3</sup>	3.09	8	61	2.36	1.8	0.055	0.11	0.1	%
K <sub>2</sub> O	XRF <sup>3</sup>	0.66	6	48	2.57	1.0	0.01	0.02	0.02	%
SiO <sub>2</sub>	XRF <sup>3</sup>	88.73	8	60	2.36	0.3	0.265	0.530	0.6	%
TiO <sub>2</sub>	XRF <sup>3</sup>	0.18	8	61	2.36	4.5	0.01	0.02	0.02	%

**Table 3.** Provisional major oxides concentrations, two standard deviations, combined and expanded uncertainty.

Analyte	Method	<sup>6</sup> Certified( $\mu$ )	<i>N</i>	<i>n</i>	<i>k</i>	% RSD	<sup>7</sup> Combined uncertainty ( $u_c$ )	<sup>8</sup> Two Standard deviation (2s) $\pm$	<sup>9</sup> Expanded uncertainty ( <i>U</i> ) $\pm$	Unit
MgO	XRF <sup>3</sup>	0.09	7	56	2.45	11.5	0.01	0.02	0.03	%
Na <sub>2</sub> O	XRF <sup>3</sup>	0.13	7	55	2.45	21.7	0.03	0.02	0.07	%

1. Pb Collection is fire assay by lead collection
2. 4A\_MICP is a Multi-acid digestion with ICP finish
3. XRF is X-ray Fluorescence
4. FUS is Fusion by ICP finish
5. Comb/LECO is combustion infra-red analysis
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.
8. The two standard deviations (2s) is calculated as for example:  $u_c \times 2 = 0.23 \times 2 = 0.46\%$ . See section 24, page 11 for recommended use in quality control.
9. 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 6 for *t*-distribution table). Example:  $U = 2.36 \times 0.23 = 0.54\%$ .
10. Provisional: the reported provisional concentrations are to be used as indicative values only.

## 2. Intended Use

AMIS0515 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.

## 3. 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
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, <i>e.g.</i> $k=2$ 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 3:** Continued

Abbreviation/Symbol	Description
$p$	' $p$ -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

#### **4. Uncertified Concentration Values**

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

#### **5. Units**

All results for major oxides are reported as oxides in percentages.

#### **6. 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)

#### **7. Origin of Material**

This standard is a blend of Ventersdorp Contact Reef, Carbon Leader Reef and Vaal Reef material provided by Harmony Gold in South Africa.

#### **8. Approximate Mineral and Chemical Composition**

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

#### **9. Health and Safety**

The material is a very fine powder coloured Very light grey (5Y 8/1). Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

#### **10. 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.

#### **11. Radioactivity**

Shipments of this material require special labelling and placarding. AMIS0514 contains U (0.18 Bq/g) and Th 0.02 Bq/g) and is classified as EXEMPT MATERIAL in terms of "Safety Standards Series No. TS-R-1: Regulations for the Safe Transport of Radioactive Material, International Atomic Energy Agency, 2005, para 403, Table 1".



## 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 in order to convert any obtained assay values to an air-dry basis (see Appendix 5 for an example calculation).

## 13. Methods of Analysis Requested

1. Au – Pb collection ICP-OES or ICP-MS or AA or Gravimetry finish
2. Multi-acid digest, including HF, ICP- OES or ICP-MS. Multi element scan to include U
3. U – XRF
4. Majors (Al<sub>2</sub>O<sub>3</sub>, CaO, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MgO, MnO, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>, LOI) XRF fusion
5. S – Combustion analysis
6. SG – Gas Pycnometer

## 14. Information Requested of Participating Laboratories

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

1. State and provide brief description of analytical techniques used
2. State aliquots used for all determinations
3. Results for individual analyses to be reported
4. All results for Gold and Uranium to be reported in ppm
5. All oxides to reported in percentage
6. All other elements to be reported in ppm
7. Report all QC data, to include replicates, blanks and certified reference materials used
8. Please use the excel template provided by AMIS. If you require a copy, please email any of the email addresses below

## 15. 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], [3], [4] and [5]. 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, [10],[11],[12],[13] and [14] 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 [15], [16] and [17]. The Horwitz function is applied to assess the performance of the data under consideration with respect to precision as relative standard deviation (equations [6], [7] and [8]). Should the ratio of the observed %RSD and a calculated %RSD be <2, the observed %RSD is accepted (Horwitz & Albert, 2006). A final certified value is then found by calculating a grand mean of equally weighted individual laboratory means [9] (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 8, Appendix 6 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.

## 16. Participating Laboratories

Twenty three laboratories were each given eight randomly selected packages of the CRM. Twenty one laboratories of the twenty three laboratories submitted results in time for certification.

The 21 laboratories that provided results timeously are:

1. UIS Analytical Services (pty) Ltd
2. Super Laboratory Services (Pty) Ltd. Springs
3. Shiva Analyticals India
4. Set Point Laboratories Husab Namibia
5. Rossing Uranium Limited
6. Ready Lead Assay Laboratory
7. Quality Labs Tanzania
8. Performance Laboratories Zimbabwe
9. Koza Altin Isletmeleri
10. Genalysis Laboratory Services (W Australia P)
11. Chromatech Services
12. Bureau Veritas Minerals Ultra Trace Pty Ltd
13. ARGETEST
14. ALS (Vancouver) - Analytical Laboratory Services - Vancouver, Canada
15. ALS Chemex Laboratory Group Johannesburg SA
16. ALS Chemex Laboratory Group Lima (Peru)
17. ALS OMAC (Ireland)
18. Anglo Gold Ashanti - Vaal River Laboratory SA
19. Laboratory of Analytical Chemistry-INGEMMET
20. SGS South Africa (Pty) Ltd – Barberton
21. SGS\_South Africa

## 17. Accepted Assay Data

Data from the 21 laboratories used for certification are set out in Table 5.

**Table 5.** Data used to calculate the certified values after removal of outliers.

Pb Collection Au %	4A-MICP U ppm	XRF U ppm	XRF U <sub>3</sub> O <sub>8</sub> ppm	Comb/LECO S %	LOI %	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 Na <sub>2</sub> O %	XRF SiO <sub>2</sub> %	XRF TiO <sub>2</sub> %
0.50	15.10	12.00	14.15	0.54	2.68	3.99	0.33	0.11	3.00	0.66	0.08	0.14	88.40	0.18
0.48	15.10	13.00	15.33	0.53	2.66	3.97	0.33	0.11	3.03	0.66	0.09	0.13	88.75	0.18
0.49	15.00	15.00	17.69	0.54	2.66	3.97	0.33	0.11	3.00	0.66	0.08	0.13	88.83	0.18
0.47	15.30	14.00	16.51	0.52	2.68	4.01	0.33	0.12	3.00	0.67	0.08	0.13	88.64	0.18
0.48	15.30	14.00	16.51	0.53	2.66	4.00	0.33	0.11	3.02	0.67	0.09	0.14	88.55	0.18
0.48	15.10	13.00	15.33	0.52	2.67	3.95	0.33	0.11	3.02	0.67	0.08	0.13	88.45	0.18
0.45	15.00	15.00	17.69	0.54	2.66	3.96	0.33	0.11	3.00	0.66	0.08	0.14	88.66	0.18
0.48	15.10	15.00	17.69	0.53	2.66	3.98	0.33	0.11	3.05	0.67	0.08	0.14	88.75	0.18
0.50	13.61	12.29	14.49	0.56	2.45	4.01	0.33	0.11	3.10	0.66	0.10	0.12	88.91	0.18
0.50	13.79	13.17	15.53	0.54	2.38	4.00	0.33	0.11	3.10	0.65	0.11	0.13	88.71	0.18
0.50	13.40	12.29	14.49	0.55	2.53	4.01	0.33	0.11	3.12	0.66	0.11	0.13	88.90	0.18
0.50	14.19	12.29	14.49	0.56	2.39	4.02	0.33	0.11	3.14	0.65	0.11	0.12	88.68	0.18
0.49	14.06	14.04	16.56	0.56	2.38	4.04	0.33	0.11	3.14	0.66	0.11	0.13	88.77	0.18
0.49	13.58	11.41	13.46	0.53	2.37	4.02	0.33	0.11	3.13	0.65	0.10	0.14	88.81	0.18
0.49	13.37	13.90	16.40	0.51	2.37	4.02	0.33	0.11	3.10	0.66	0.11	0.13	88.90	0.18
0.50	14.04	13.80	16.30	0.53	2.42	4.00	0.33	0.11	3.10	0.65	0.10	0.12	88.77	0.18
0.49	13.40	13.90	16.40	0.53	2.40	4.00	0.34	0.11	3.10	0.66	0.10	0.18	88.74	0.20
0.46	13.10	13.90	16.40	0.52	2.40	3.99	0.33	0.11	3.08	0.65	0.10	0.18	88.70	0.19
0.51	13.30	13.90	16.40	0.53	2.39	3.99	0.33	0.11	3.09	0.66	0.10	0.18	88.76	0.19
0.51	13.90	13.80	16.30	0.51	2.38	3.99	0.33	0.11	3.08	0.65	0.11	0.18	88.76	0.19
0.50	13.90	13.90	16.40	0.54	2.39	4.02	0.34	0.12	3.11	0.66	0.11	0.18	88.80	0.19
0.49	13.60	13.80	16.30	0.53	2.38	4.00	0.34	0.12	3.10	0.66	0.10	0.18	88.84	0.19
0.48	13.60	15.00	17.69	0.52	2.41	4.01	0.33	0.12	3.09	0.66	0.11	0.17	88.81	0.20
0.50	13.80	15.00	17.69	0.53	2.38	3.99	0.33	0.12	3.09	0.66	0.10	0.10	88.71	0.19
0.50	14.20	16.00	18.87	0.52	2.81	3.95	0.32	0.12	3.21	0.67	0.09	0.10	88.82	0.20
0.49	14.10	16.00	18.87	0.54	2.83	3.95	0.32	0.12	3.19	0.67	0.11	0.10	88.94	0.20
0.50	14.20	16.00	18.87	0.52	2.84	3.97	0.32	0.12	3.19	0.66	0.09	0.10	88.72	0.20
0.49	14.20	15.00	17.69	0.51	2.80	3.98	0.32	0.12	3.20	0.67	0.09	0.10	88.81	0.20
0.50	14.20	13.60	16.00	0.52	2.85	3.96	0.32	0.12	3.21	0.67	0.10	0.10	88.70	0.20
0.50	14.10	13.60	16.00	0.52	2.82	3.99	0.33	0.12	3.11	0.67	0.09	0.10	88.73	0.20
0.49	14.10	12.60	14.90	0.52	2.82	4.00	0.32	0.12	3.11	0.65	0.08	0.10	88.81	0.20
0.53	14.10	14.50	17.10	0.52	2.81	3.96	0.32	0.12	3.08	0.67	0.09	0.10	88.73	0.20
0.54		13.90	16.40	0.52	2.39	3.99	0.33	0.12	3.12	0.66	0.09	0.10	88.63	0.18
0.53		13.80	16.30	0.53	2.33	3.99	0.33	0.12	3.12	0.66	0.08	0.10	88.58	0.18
0.49		13.30	15.70	0.52	2.40	3.96	0.33	0.11	3.11	0.66	0.09	0.09	88.10	0.18
0.52		14.00	16.50	0.50	2.46	4.01	0.33	0.12	3.06	0.66	0.08	0.10	89.25	0.18
0.51					2.40	3.99	0.33	0.11	3.11	0.66	0.08	0.10	89.03	0.18
0.51					2.39	3.99	0.33	0.11	3.09	0.66	0.08	0.10	88.84	0.18
0.50					2.34	3.96	0.33	0.11	3.07	0.66	0.09	0.10	88.88	0.18
0.53					2.37	4.00	0.33	0.11	3.06	0.66	0.08	0.12	89.32	0.18
0.49					2.64	4.02	0.31	0.11	3.06	0.65	0.10	0.15	88.97	0.19
0.52					2.63	4.01	0.32	0.11	3.07	0.66	0.09	0.13	89.05	0.18
0.51					2.70	4.02	0.31	0.12	3.06	0.66	0.10	0.15	88.94	0.19
0.53					2.46	4.01	0.32	0.11	3.07	0.66	0.09	0.14	88.96	0.18
0.52					2.53	4.02	0.31	0.11	3.06	0.65	0.08	0.15	88.85	0.18
0.51					2.73	4.02	0.31	0.11	3.01	0.66	0.09	0.16	89.26	0.18
0.51					2.69	4.03	0.31	0.11	3.17	0.66	0.09	0.13	88.79	0.19
0.51					2.86	4.01	0.32	0.11	3.10	0.66	0.10	0.11	87.96	0.18
0.51					2.59	3.97		0.11	3.09		0.09	0.12	88.51	0.17
0.50					2.64	4.01		0.11	3.07		0.09	0.11	88.69	0.18
0.50					2.75	3.98		0.11	3.13		0.09	0.12	88.87	0.19
0.51					2.61	3.98		0.12	3.08		0.09	0.11	88.63	0.18
0.50					2.57	3.97		0.11	3.18		0.08	0.12	88.90	0.18
0.51					2.60	4.03		0.12	3.02		0.09	0.11	87.98	0.18
0.50					2.56	4.04		0.12	3.05		0.09	0.11	88.76	0.18
0.52					2.40	4.02		0.11	3.10		0.09		88.37	0.18
0.51					2.65	3.95		0.11	3.06				89.01	0.18
0.49					2.48	4.00		0.11	3.03				88.49	0.18
0.53					2.54	3.99		0.11	3.04				88.19	0.18
0.54					2.54	4.02			3.03				88.54	0.18
0.55					2.60	3.97			3.05					0.18
0.57					2.65	3.97								
0.54					2.52	4.00								
0.55					2.62									
0.55														
0.55														
0.54														
0.54														
0.53														
0.55														
0.53														

## **18. Reported Values**

The certified values listed in this certificate fulfil the AMIS statistical criteria (see section 15) regarding agreement for certification and have been independently validated by Allan Fraser.

## **19. 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.

## **20. 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.

## **21. 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.

## **22. 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.

## **23. 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.

## **24. 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).

## **25. 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.

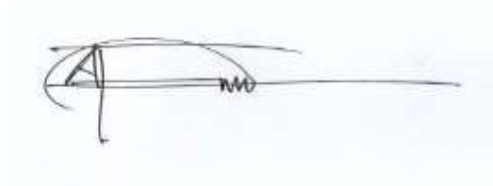
10 July 2017

Certifying Officers:

*T. Matodzi*

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

**Thivhafuni Matodzi**



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

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

## REFERENCES

- Abzalov, M. (2011). Sampling Errors and Control of Assay Data Quality in Exploration and Mining Geology, Applications and Experiences of Quality Control. Ivanov, O., (Ed.), InTech, DOI: 10.5772/14965. Available from: <http://www.intechopen.com/books/applications-and-experiences-of-quality-control/sampling-errors-and-control-of-assay-data-quality-in-exploration-and-mining-geology>. Accessed 25<sup>th</sup> September, 2016.
- ASTM E122-09e1, Standard Practice for Calculating Sample Size to Estimate, With Specified Precision, the Average for a Characteristic of a Lot or Process, ASTM International, West Conshohocken, PA, 2011, [www.astm.org](http://www.astm.org)
- Barwick V.J., Pritchard E. (Eds). (2011). Eurachem Guide; Terminology in Analytical Measurement – Introduction to VIM 3 (2011). ISBN 978-0-948926-29-7.
- Carr R.H. (2011). Estimating errors using graphs and taking good data. California State University Los Angeles. March 2011. 14. <http://web.calstatela.edu/faculty/kaniol/Err-Gph-Meas-IBooklet.pdf>. Retrieved: 29 August, 2016.
- Cochran, W.G. (1950). The Comparison of Percentages in Matched Samples. *Biometrika*, 37, 256-66.
- Ellison, S., Barwick, V., Duguid Farrant, T. (2009). *Practical statistics for the analytical scientist, a bench guide. 2<sup>nd</sup> Edition*. RSC Publishing. 25-172.
- ERM Application Note 1. (2005). Comparison of a measurement value with a certified value. European Commission – Joint Research Centre Institute for Reference Materials and Measurements (IRMM). 1-2.
- EURACHEM / CITAC Guide CG 4. (2012). Quantifying uncertainty in analytical measurement. 3<sup>rd</sup> Edition. Editors: Ellison, S. L. R., Williams, A. 4-121.
- Eurolab Technical Report No.1/2007. (2007). Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation. European Federation of National Associations of Measurement, Testing and Laboratories. 43-46.
- Fraser, A.W. (2015). Minimising uncertainty in measurement and improving limit of detection in gold bearing ores from concentrations predicted by linear regression in atomic absorption spectrometry. M.Sc. thesis (unpublished), University of Johannesburg: 199 pages.
- Grubbs, F.E. (1969). Procedures for detecting outlying observations in samples. *Technometrics*, 11, 1969. 1-21.
- Horwitz, W., Albert, R. (2006). The Horwitz Ratio (HorRat): A useful index of method performance with respect to precision, *Journal of Association of Official Analytical Chemists International*, 89: 1095-1109.
- ISO/IEC 17025:2005(E). (2005). *General requirements for the competence of testing and calibration laboratories*. 2<sup>nd</sup> Edition: 14-59.
- ISO Guide 35 (2003). Certification of reference materials — General and Statistical principles, 3<sup>rd</sup> edition. ISO/REMCO WG 1.
- ISO 5725-2:1994. Accuracy (trueness and precision) of measurement methods and results -- Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.
- Long, J., Winefordner, J. (1983). Limit of detection - a closer look at the IUPAC definition. *Analytical Chemistry* 55: 712A - 724A.
- Miller, J., Miller, J. (2010). *Statistics for analytical chemistry*. 6<sup>th</sup> Edition. New York: Ellis Horwood. 36-126.
- Nelsen T.C., Wehling P. (2008). Collaborative studies for quantitative chemical analytical methods. AACC International Report. *Cereal Foods World*. September – October 2008, Vol. 53, No. 5. 285-288.
- Skoog, D., West, D. (1982). *Fundamentals of analytical chemistry*. 4th Edition. CBS College Publishing. Holt Saunders International Editions: 39-73.
- Thompson, M. (Ed.) (2008). Test for 'sufficient homogeneity' in a reference material. Analytical Methods Committee, AMCTB 17A, ISSN 1757-5958.
- Thompson, M. (Ed.) (2010). Internal quality control in routine analysis. AMC Technical Brief. Analytical Methods Committee. AMCTB No.46. 2010. Issn 1757-5958.
- Thompson, M., Lowthian, P. (2011). *Notes on statistics and data quality for analytical chemists*. Imperial College Press: 15-115.
- Vermeulen N.J (2001). Literature review. University of Pretoria. 2.1-2.99

## APPENDICES

### Appendix 1: Uncertified Element Statistics

Uncertified element statistics are shown in Table 6.

**Table 6.** Uncertified element concentrations statistics.

Element	Gen Method	N	Mean	s	RSD %	Unit
Ag	4A_MICP	8	0.18	0.05	26.45	ppm
Al	4A_MICP	23	21003.48	407.05	1.94	ppm
Al <sub>2</sub> O <sub>3</sub>	FUS	8	3.80	0.03	0.91	%
As	4A_MICP	23	121.41	7.32	6.03	ppm
Au	FA_AAS	8	0.58	0.02	2.92	g/t
Au	FA_ICPES	8	0.60	0	1.65	g/t
Ba	4A_MICP	24	152.17	21.60	14.19	ppm
BaO	XRF	32	0.01	0.00	35.91	%
Be	4A_MICP	16	0.56	0.05	9.21	ppm
Bi	4A_MICP	16	0.44	0.04	8.52	ppm
Ca	4A_MICP	23	2533.87	142.24	5.61	ppm
Cd	4A_MICP	8	1.50	<0.001	<0.001	ppm
Ce	4A_MICP	16	46.825	3.558	7.60	ppm
Co	4A_MICP	32	9.36	0.58	6.24	ppm
Cr	4A_MICP	24	553.10	102.33	18.50	ppm
Cs	4A_MICP	16	0.87	0.07	8.11	ppm
Cu	2A_MICP	7	17.96	1.09	6.09	ppm
Cu	4A_MICP	39	20.70	0.77	3.71	ppm
CuO	XRF	8	0.07	0.04	61.13	%
Dy	4A_MICP	8	1.31	0.03	2.45	ppm
Er	4A_MICP	8	0.74	0.02	3.14	ppm
Eu	4A_MICP	7	0.45	<0.001	<0.001	ppm
Fe	4A_MICP	24	22520.83	1226.51	5.45	ppm
Fe	XRF	8	21087.50	112.60	0.53	ppm
Ga	4A_MICP	15	4.71	0.24	5.17	ppm
Gd	4A_MICP	8	1.68	0.10	6.18	ppm
Ge	4A_MICP	8	0.91	0.06	7.02	ppm
Hf	4A_MICP	16	2.71	0.09	3.26	ppm
Ho	4A_MICP	8	0.26	0.01	3.63	ppm
K	4A_MICP	24	5548.42	110.95	2.00	ppm
La	4A_MICP	16	22.10	0.25	1.13	ppm
Li	4A_MICP	16	3.18	0.19	5.99	ppm
Lu	4A_MICP	8	0.11	0.01	8.82	ppm
Mg	4A_MICP	24	583.67	24.01	4.11	ppm
Mn	4A_MICP	24	156.23	20.55	13.16	ppm
Mn	XRF	8	200.00	<0.001	<0.001	ppm
Mn <sub>3</sub> O <sub>4</sub>	XRF	8	0.03	0.00	16.83	%
MnO	XRF	39	0.02	<0.001	<0.001	%

Element	Gen Method	N	Mean	s	RSD %	Unit
Mo	4A_MICP	16	1.83	0.23	12.73	ppm
Na	4A_MICP	24	1065.50	241.70	22.68	ppm
Nb	4A_MICP	16	2.89	1.03	35.48	ppm
Nd	4A_MICP	8	15.65	0.23	1.49	ppm
Ni	4A_MICP	24	24.03	2.93	12.18	ppm
P	4A_MICP	16	102.56	34.52	33.65	ppm
P	XRF	8	100.00	<0.001	<0.001	ppm
P <sub>2</sub> O <sub>5</sub>	XRF	53	0.02	<0.001	3.30	%
Pb	4A_MICP	24	136.88	23.40	17.10	ppm
PbO	XRF	8	0.03	<0.001	<0.001	%
Pd	Pb Collection	7	0.01	<0.001	<0.001	g/t
Pr	4A_MICP	8	4.61	0.05	1.08	ppm
Pt	Pb Collection	8	0.01	0.00	21.38	g/t
Rb	4A_MICP	16	23.08	1.59	6.89	ppm
S	4A_MICP	16	0.53	0.01	1.15	%
Sb	4A_MICP	16	2.33	0.13	5.36	ppm
Sc	4A_MICP	16	3.38	0.50	14.81	ppm
SG	SG	8	2.77	0.02	0.90	Dimensionless
Sm	4A_MICP	8	2.66	0.06	2.19	ppm
Sn	4A_MICP	14	1.97	0.05	2.38	ppm
SO <sub>3</sub>	XRF	40	1.36	0.12	9.15	%
Sr	4A_MICP	16	24.24	1.04	4.30	ppm
SrO	XRF	8	0.01	<0.001	<0.001	%
Ta	4A_MICP	16	0.52	0.04	8.29	ppm
Tb	4A_MICP	8	0.21	0.01	4.99	ppm
Th	4A_MICP	24	5.64	2.52	44.72	ppm
Ti	4A_MICP	24	0.06	0.01	22.65	%
Tl	4A_MICP	15	0.30	0.01	3.03	ppm
Tm	4A_MICP	7	0.10	<0.001	<0.001	ppm
V	4A_MICP	21	24.33	1.22	5.02	ppm
W	4A_MICP	16	0.76	0.19	24.36	ppm
Y	4A_MICP	16	5.48	0.97	17.65	ppm
Yb	4A_MICP	8	0.77	0.03	3.37	ppm
Zn	4A_MICP	24	22.16	6.60	29.78	ppm
ZnO	XRF	8	0.01	<0.001	<0.001	%
Zr	4A_MICP	24	112.36	20.12	17.91	ppm
ZrO <sub>2</sub>	XRF	8	0.03	<0.001	<0.001	%

.....

### 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%. If the data set contains two or more suspect values at either the high end of the dataset or at the low end, or at both ends of the data range, the Grubbs test is adapted to detect such outliers by the calculation of  $G_{2\text{ calc}}$

$$G_{2\text{ calc}} = \frac{|x_n - x_1|}{s} \quad [4]$$

where,  $x_n$  and  $x_1$  are the suspect values that occur at the opposite ends of the dataset.

When there are two suspect values at the at the same end of the dataset two separate standard deviations of all of the data,  $s^*$  is the standard deviation of the data with the two suspect values excluded with  $G_{3\text{ calc}}$  given by:

$$G_{3\text{ calc}} = \frac{(n-3)s^*}{(n-1)s^2} \quad [5]$$

### 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

$$\%RSD = \pm 2^{(1-0.5\log C)} \quad [6]$$

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

$$\text{Observed \%RSD} = \frac{s}{\text{Mean}} \times 100 \quad [7]$$

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

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

$$\text{HorRat} = \frac{\%RSD \text{ Observed}}{\%RSD \text{ Calculated}} \quad [8]$$

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 ( $n$ ):

$$\bar{\bar{x}} = \sum \frac{x}{n} \quad [9]$$

## Certified Value

From ANOVA as per the description in section 15, an 'appropriate precision' as shown in [10] is calculated for sufficient homogeneity (Thompson, 2008):

$$s_r \leq 0.3u_c \quad [10]$$

Where,  $s_r$  is the within laboratory repeatability, as determined from [16]. Once [10] is satisfied, a grand mean [9] 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.

$$SST = \sum (x - \bar{x})^2 \quad [11]$$

## 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 [12]. 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.

$$SSB = \sum n(\bar{x} - \bar{\bar{x}})^2 \quad [12]$$

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.

$$MS = \frac{SSB}{n - 1} \quad [13]$$

## 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:  $df = n - P$ .

$$SSW = \sum df \cdot s^2 \quad [14]$$

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:

$$MSW = \frac{SSW}{P - n} \quad [15]$$

From equations [9] through [15], the ANOVA table as shown in Table 7 is developed.

**Table 7.** 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,  $s_s$ :

$$u_c = \sqrt{s_r^2 + s_s^2} \quad [16]$$

Within laboratory repeatability is determined as

$$s_r = \sqrt{MSB} \quad [17]$$

and, the between laboratory precision as

$$s_s = \sqrt{\frac{(MSW - MSB)}{n}} \quad [18]$$

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 **Error! Reference source not found.**, or from S 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 [19], does not take into account the measurement uncertainty of the CRM. To compensate for this, Eurolab Technical Report No.1/2007 recommends equation [20] for the validation of CRMs with stated measurement uncertainties.

$$t_{calc} = \frac{|\bar{x} - \mu|}{\frac{s}{\sqrt{n}}} \quad [19]$$

$$t_{calc} = \frac{|\bar{x} - \mu|}{\sqrt{(u_{\mu})^2 + \frac{s^2}{n}}} \quad [20]$$

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 [20] 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 8. 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 8.** 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 [20]:

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

Therefore,  $t_{calc} = 0.84$  and  $t_{crit}(5\%, 8) = 2.31$  ( $df$  is 8, therefore,  $t_{crit}=2.31$ , see Appendix 6, page 22) 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. 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 chose 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 [21], of the replicates;
5. Calculate the standard deviation,  $s$  from:

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

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 [20];
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 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 recommend 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 [20].

.....

**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:

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

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

**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 x 0.52 = 0.51<sub>(7)</sub>, 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.** T-distribution table

Table 9. 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		

.....