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Certificate

AMIS0390

Certified Reference Material

Chrome, LG6 Foundry Grade,
Kroondal Mine, Bushveld, South Africa

Certificate of Analysis

AMIS

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Summary Statistics

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

Analyte	Method	Certified (μ) ⁵	(2s) ⁷ \pm	Unit
Cr	FUS ¹	30.98	2.4	%
Cr	XRF ²	31.31	0.31	%
SG	SG ³	4.51	0.35	Dimensionless
Al	FUS	7.96	0.32	%
Al	4A_MICP ⁴	7.63	0.70	%
Ce	4A_MICP	0.3	0.07	ppm
Co	FUS	279	49	ppm
Co	4A_MICP	271	63	ppm
Fe	FUS	19.95	0.95	%
Mg	FUS	5.79	0.23	%
Mg	4A_MICP	5.32	0.56	%
Mn	FUS	1856	195	ppm
Mn	4A_MICP	1679	200	ppm
Ni	FUS	943	203	ppm
Ni	4A_MICP	837	172	ppm
Sn	4A_MICP	0.8	0.2	ppm
Sr	4A_MICP	1	0.7	ppm
Ti	FUS	4158	355	ppm
V	FUS	2145	261	ppm
Y	4A_MICP	0.2	0.1	ppm
Zn	4A_MICP	661	125	ppm

Major Oxides
Certified Concentrations (at two Standard Deviations)

Analyte	Method	Certified (μ) ⁵	(2s) ⁷ \pm	Unit
Cr ₂ O ₃	XRF	45.76	0.46	%
Al ₂ O ₃	XRF	15.04	0.30	%
Al ₂ O ₃	FUS	14.63	1.3	%
Fe ₂ O ₃	XRF	28.90	0.23	%
Fe ₂ O ₃	FUS	28.17	1.4	%
MgO	XRF	9.59	0.33	%
MgO	FUS	9.68	0.51	%
MnO	XRF	0.23	0.02	%
SiO ₂	XRF	1.27	0.18	%
TiO ₂	XRF	0.71	0.03	%

1. Certified Concentrations and Uncertainties

AMIS0390 was certified in April 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 (μ) ⁵	N	n	k	% RSD	(u_c) ⁶	(2s) ⁷ \pm	(U) ⁸ \pm	Unit
Cr	FUS ¹	30.98	8	61	2.365	4	1.2	2.4	3	%
Cr	XRF ²	31.31	8	64	2.365	0.5	0.16	0.31	0.4	%
SG	SG ³	4.51	9	61	2.306	4	0.18	0.35	0.4	Dimensionless
Al	FUS	7.96	8	57	2.365	2	0.16	0.32	0.4	%
Al	4A_MICP ⁴	7.63	5	40	2.776	5	0.35	0.70	1	%
Ce	4A_MICP	0.3	3	24	4.303	10	0.03	0.07	0.1	ppm
Co	FUS	279	5	40	2.776	9	24	49	67	ppm
Co	4A_MICP	271	6	48	2.571	12	31	63	81	ppm
Fe	FUS	19.95	10	76	2.262	2	0.47	0.95	1	%
Mg	FUS	5.79	7	52	2.447	2	0.12	0.23	0.3	%
Mg	4A_MICP	5.32	5	40	2.776	5	0.28	0.56	0.8	%
Mn	FUS	1856	5	37	2.776	5	97	195	271	ppm
Mn	4A_MICP	1679	6	48	2.571	6	100	200	256	ppm
Ni	FUS	943	6	45	2.571	11	101	203	261	ppm
Ni	4A_MICP	837	6	48	2.571	10	86	172	221	ppm
Sn	4A_MICP	0.8	3	23	4.303	14	0.1	0.2	0.5	ppm
Sr	4A_MICP	1	5	37	2.776	25	0.3	0.7	0.9	ppm
Ti	FUS	4158	7	55	2.447	4	178	355	435	ppm
V	FUS	2145	8	60	2.365	6	130	261	308	ppm
Y	4A_MICP	0.2	4	31	3.182	28	0.05	0.1	0.2	ppm
Zn	4A_MICP	661	6	48	2.571	9	63	125	161	ppm

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

Analyte	Method	Certified (μ) ⁵	N	n	k	% RSD	(u_c) ⁶	(2s) ⁷ \pm	(U) ⁸ \pm	Unit
Cr ₂ O ₃	XRF	45.76	8	64	2.365	0.5	0.23	0.46	0.5	%
Al ₂ O ₃	XRF	15.04	8	64	2.365	1	0.15	0.30	0.4	%
Al ₂ O ₃	FUS	14.63	4	31	3.182	4	0.63	1.3	2	%
Fe ₂ O ₃	XRF	28.90	7	54	2.447	0.4	0.11	0.23	0.3	%
Fe ₂ O ₃	FUS	28.17	4	29	3.182	3	0.72	1.4	2	%
MgO	XRF	9.59	9	69	2.306	2	0.16	0.33	0.4	%
MgO	FUS	9.68	4	30	3.182	3	0.26	0.51	0.8	%
MnO	XRF	0.23	7	56	2.447	4	0.008	0.02	0.02	%
SiO ₂	XRF	1.27	7	56	2.447	7	0.089	0.18	0.2	%
TiO ₂	XRF	0.71	8	60	2.365	2	0.01	0.03	0.03	%

1. FUS is Fusion digestion with ICP finish

2. XRF is X-ray Fluorescence

3. SG is Specific Gravity

4. 4A_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish

5. The certified value μ , is an unweighted grand mean of the means of N accepted sets of data from different laboratories and n number of test sample replicates. The certified value is traceable to SI units and is reported on a dry basis.

6. 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)

7. Two standard deviations (2s)

8. 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 ≥ 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
Al 4A_MICP	7.63 %	Al Fus	7.96 %	Unequal Variance ($p=0.021$)	0.041	Reject H_0 ; certified values are <i>not</i> equal
Co 4A_MICP	271 ppm	Co Fus	279 ppm	Equal Variance ($p=0.29$)	0.67	Accept H_0 ; certified values are equal
Mg 4A_MICP	5.32 %	Mg Fus	5.79 %	Unequal Variance ($p=0.003$)	0.001	Reject H_0 ; certified values are not equal
Mn 4A_MICP	0.167 %	Mn Fus	0.186 %	Equal Variance ($p=0.49$)	0.008	Reject H_0 ; certified values are <i>not</i> equal
Ni 4A_MICP	0.084 %	Ni Fus	0.094 %	Equal Variance ($p=0.48$)	0.052	Accept H_0 ; certified values are equal
Cr Fus	30.98 %	Cr XRF	31.31 %	Unequal Variance ($p<0.001$)	0.45	Accept H_0 ; certified values are equal
Al ₂ O ₃ Fus	14.60 %	Al ₂ O ₃ XRF	15.04 %	Unequal Variance ($p=0.002$)	0.16	Accept H_0 ; certified values are equal
Fe ₂ O ₃ Fus	28.17 %	Fe ₂ O ₃ XRF	28.90 %	Unequal Variance ($p<0.001$)	0.033	Reject H_0 ; certified values are <i>not</i> equal
MgO Fus	9.68 %	MgO XRF	9.50%	Equal Variance ($p=0.26$)	0.33	Accept H_0 ; certified values are equal
Al 4A_MICP	7.63 %	Al Fus	7.96 %	Unequal Variance ($p=0.021$)	0.041	Reject H_0 ; certified values are <i>not</i> equal
Co 4A_MICP	271 ppm	Co Fus	279 ppm	Equal Variance ($p=0.29$)	0.67	Accept H_0 ; certified values are equal
Mg 4A_MICP	5.32 %	Mg Fus	5.79 %	Unequal Variance ($p=0.003$)	0.001	Reject H_0 ; certified values are not equal

3. Intended Use

AMIS0390 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 (α)	Significance level (denoted by alpha, ' α ') of 0.05 or 5%
ANOVA	Analysis of variance by statistical means
Bq	The becquerel is the SI derived unit of radioactivity.
BIF	Banded iron formation
CRM	Certified reference material
df	Degrees of freedom, typically, $n-1$, or $N-1$
F_{calc}	Calculated F statistic from ANOVA or Fisher's test
F-critical or F_{crit}	F-critical value from F-distribution table
GOI	Gain on ignition
H_0	Null hypothesis
H_1	Alternate hypothesis
g/t	Grams per tonne
k	Coverage factor, e.g. $k=2$ for 95% level of confidence
LOC	Level of confidence or confidence level
LOD	Limit of detection
LOQ	Limit of quantitation
LOI	Loss on ignition
MS	Mean squares (ANOVA)
MSb	Mean squares between(ANOVA)
MSw	Mean squares within (ANOVA)
N	Number of labs
n	Number of replicates
μ	Property or certified value of a CRM
p	' p -value' a measure of the strength of evidence against H_0
P	Total number of data points in ANOVA
ppm	Parts per million. Equivalent to g/t
RSD	Relative standard deviation usually expressed as % at a 68% LOC
Replicates	Replication is the repetition of an experimental condition so that the variability associated with an analysis can be estimated (ASTM E1847)
s	Standard deviation
s_r	Within laboratory repeatability as derived from ANOVA
s_s	Between laboratory standard deviation as derived from ANOVA
SS	Sum of squares in ANOVA
SST	Total variation in ANOVA
SSB	Between group (laboratory) variance
SSW	Within group (laboratory) variance

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
μm	Micron, is an SI derived unit of length equaling 1×10^{-6} of a meter

5. Uncertified Concentration Values

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

6. Units

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

7. Analytical and Physical Methods

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

8. Origin of Material

This standard was made using LG6 foundry grade material supplied by Glencore Xstrata plc from the Kroondal Chrome Mine. The mine is situated on the Western Limb of the Bushveld Complex 12km south east of Rustenburg in the North West Province of South Africa. The standard comprises of LG6 foundry grade. The foundry is a concentrated product derived from mining the LG6 chromitite layer, the LG6 middling pyroxenite and the LG6A chromitite layer which occurs in the lower portion of the Critical Zone.

9. Approximate Mineral and Chemical Composition

The LG6 foundry consists of chromite concentrate derived from the mining of the LG6 and LG6A chromitite layers. The LG6 foundry consist mainly of fine to medium size liberated chromite grains with minor liberated pyroxene and plagioclase grains. Major element chemistry data from eleven of the labs has been compiled and certified. Uncertified summary statistics for trace element data are set out in the appendix.

10. Health and Safety

The material is a very fine powder coloured Dark Greenish Grey (Corstor 10Y 6/1). 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) Multi element scan. Multi-acid total digestion, including HF, ICP-OES or ICP-MS.
- b) Sodium Peroxide Fusion, Cr, Si, Fe, Al, Mg, Ti, P, V - ICP-OES or ICP-MS.
- c) Majors (Al_2O_3 , CaO , Cr_2O_3 , Fe_2O_3 , K_2O , MgO , MnO , Na_2O , P_2O_5 , SiO_2 , TiO_2 . LOI.) XRF fusion.
- d) 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.
- d) All results for base metals to be reported in ppm.
- e) 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 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. Antech Activation Laboratories Pty Ltd (ActLabs) CA
2. Alfred H Knight (SA)
3. ALS Chemex Laboratory Group Johannesburg SA
4. ALS Chemex Laboratory Group Perth WA
5. BV Rustenburg (South Africa)
6. Genalysis Laboratory Services (W Australia P)
7. Intertek Utama Services (Indonesia)
8. Labtium Inc Finland
9. Lanxess Chrome Mine
10. Nkomati JV Laboratory SA
11. Set Point Laboratories (Isando) SA
12. SGS Australia Pty Ltd (Newburn) WA
13. SGS Geosol Laboratories Ltda (Brazil)
14. SGS Mineral Services Lakefield (Canada)
15. SGS South Africa (Pty) Ltd - Booysens JHB
16. Suntech Geometallurgical SA
17. Ultra-Trace (Pty) Ltd WA
18. Xstrata Eland Mine

22. Accepted Assay Data

Data from the 18 laboratories used for certification are set out in Table 5.

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

XRF	XRF	FUS	XRF	FUS	XRF	FUS	XRF	XRF	XRF
Cr ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	Fe ₂ O ₃	MgO	MgO	MnO	SiO ₂	TiO ₂
%	%	%	%	%	%	%	%	%	%
45.65	15.07	15.00	28.95	28.40	9.88	9.61	0.24	1.36	0.72
45.83	14.59	14.60	29.11	27.80	9.88	9.34	0.24	1.29	0.73
45.15	15.19	15.10	28.99	28.60	9.77	9.66	0.24	1.27	0.72
45.29	15.14	15.00	28.86	27.70	9.86	9.53	0.24	1.27	0.72
45.61	14.88	14.80	29.05	28.00	9.85	9.51	0.24	1.31	0.73
45.72	14.74	15.30	29.13	28.90	9.81	9.76	0.24	1.29	0.73
45.50	15.06	15.00	28.94	28.30	9.86	9.62	0.23	1.31	0.72
45.33	14.83	14.40	28.78	27.30	9.83	9.24	0.24	1.38	0.72
45.74	14.88	14.25	28.63	28.14	9.25	9.58	0.23	1.32	0.70
45.86	15.00	13.99	29.23	28.19	9.26	9.64	0.24	1.32	0.73
45.92	14.82	14.08	28.79	28.29	9.28	9.70	0.24	1.34	0.73
45.78	14.72	14.09	28.89	27.84	9.30	9.74	0.23	1.26	0.74
45.92	14.66	14.19	28.74	27.65	9.25	9.78	0.23	1.31	0.71
46.16	14.83	14.14	28.90	28.26	9.64	9.90	0.24	1.38	0.70
45.79	14.83	14.06	28.90	28.00	9.79	9.79	0.24	1.30	0.70
45.62	14.88	14.39	28.90	28.47	9.56	9.77	0.25	1.33	0.71
46.34	15.18	13.72	29.00	26.46	9.62	9.66	0.23	1.29	0.70
45.62	15.22	13.68	29.00	27.16	9.62	9.64	0.23	1.28	0.70
45.89	14.94	14.03	29.00	27.20	9.73	9.79	0.23	1.27	0.71
45.70	14.90	15.12	28.90	28.99	9.69	9.79	0.23	1.28	0.70
46.16	14.99	14.23	28.90	27.63	9.59	10.40	0.23	1.29	0.72
46.12	14.97	15.43	29.00	29.16	9.59	9.44	0.23	1.30	0.71
46.03	14.83	13.51	28.80	28.50	9.55	9.51	0.23	1.28	0.72
46.27	15.01	15.55	29.00	28.80	9.58	10.25	0.23	1.28	0.71
45.60	15.00	14.85	28.90	27.90	9.61	9.58	0.24	1.10	0.72
45.50	15.10	15.10	28.60	30.00	9.61	9.35	0.25	1.10	0.72
45.60	14.90	14.65	28.90	28.10	9.56	10.15	0.25	1.10	0.72
45.60	15.00	15.90	28.90	28.80	9.60	9.37	0.23	1.10	0.72
45.60	15.10	14.70	28.90	28.80	9.56	9.67	0.24	1.20	0.71
45.50	15.10	15.20	29.10		9.50	9.57	0.22	1.10	0.69
45.60	15.00	15.10	28.90		9.30		0.23	1.20	0.71
45.60	15.10		28.90		9.40		0.25	1.10	0.71
46.00	15.20		28.90		9.40		0.23	1.23	0.69
46.00	15.20		28.90		9.50		0.22	1.25	0.70
45.80	15.20		28.90		9.40		0.22	1.24	0.69
45.70	15.30		29.00		9.50		0.22	1.25	0.69
45.90	15.10		28.90		9.50		0.22	1.24	0.69
46.10	15.10		29.00		9.80		0.23	1.24	0.69
45.60	15.10		28.93		9.60		0.22	1.29	0.69
46.10	15.10		28.89		9.87		0.22	1.25	0.69
45.80	15.10		28.87		9.62		0.23	1.25	0.68
45.70	15.10		28.79		9.58		0.23	1.24	0.69
45.90	15.20		28.93		9.75		0.23	1.26	0.71
45.80	15.20		28.80		9.76		0.23	1.26	0.69
45.70	15.10		28.83		9.86		0.23	1.28	0.71
45.80	15.10		28.85		9.60		0.23	1.25	0.72
45.70	15.20		28.86		9.59		0.23	1.25	0.71
45.80	15.20		28.91		9.64		0.23	1.24	0.71
45.72	15.06		28.92		9.64		0.24	1.26	0.71
45.82	15.09		28.95		9.59		0.24	1.50	0.71
45.75	15.12		28.92		9.59		0.24	1.42	0.71
45.69	15.12		28.73		9.68		0.24	1.27	0.71
45.79	15.02		28.71		9.62		0.24	1.42	0.69
45.61	15.16		28.81		9.56		0.24	1.39	0.71
45.70	15.14				9.54		0.24	1.38	0.71
45.64	15.15				9.55		0.24	1.43	0.69
45.65	14.98				9.45				0.72
45.69	15.06				9.54				0.71
45.91	15.16				9.60				0.70
45.93	15.03				9.59				0.71
45.79	15.16				9.53				
45.49	15.05				9.69				
45.49	15.08				9.62				
45.78	15.10				9.64				
					9.63				
					9.66				
					9.59				

Assay Data (Cont.)

SG	FUS	XRF	FUS	4A_MICP	4A_MICP	FUS	4A_MICP	FUS	FUS	4A_MICP
SG	Cr	Cr	Al	Al	Ce	Co	Co	Fe	Mg	Mg
Dimensionless	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
4.5	302000	312337.3	81300	73700	0.4	304	292	207000	59500	54100
4.52	300000	313568.86	80100	73900	0.3	295	294	204000	58500	54200
4.5	304000	308916.3	78500	74400	0.3	286	296	204000	57800	54600
4.54	303000	309874.18	80100	75000	0.3	292	297	205000	58700	54700
4.55	289000	312063.62	79700	74300	0.3	292	293	200000	58400	54300
4.51	288000	312816.24	80000	70500	0.3	295	285	195000	57700	52000
4.52	286000	311311	78500	73700	0.3	298	292	196000	57500	53700
4.54	293000	310147.86	78000	74900	0.4	310	300	196000	56700	55100
4.71	304000	312935.975	80100	75600	0.39	281	290	200000	57300	48000
4.89	305000	313780.962	80500	70500	0.34	284	290	202000	58000	49400
4.91	303000	314177.798	79800	78200	0.38	282	285	201000	57800	54100
4.93	304000	313199.392	80000	77800	0.38	283	290	200000	58100	54200
4.83	301000	314167.535	79200	80000	0.32	281	285	198000	57300	55100
4.87	303000	315819.878	79800	77000	0.35	293	280	199000	57500	53300
4.73	305000	313315.706	80300	69900	0.32	285	290	200000	58000	49400
4.36	302000	312118.356	79500	75700	0.31	283	280	199000	57400	52900
4.28	315000	317024.07	79300	81800	0.35	265	199	203000	57800	51600
4.03	315000	312145.724	78800	79200	0.32	265	203	203000	58000	53600
4.01	309000	313993.064	78800	76900	0.32	250	224	202000	57700	53200
4.56	314000	312686.242	79100	79900	0.34	275	225	203000	57700	51100
4.52	309000	315854.088	80500	78900	0.34	280	228	205000	58300	53900
4.56	314000	315546.198	79900	80000	0.31	250	223	202000	57500	55300
4.5	311000	314916.734	79900	79300	0.34	240	201	201000	57400	55200
4.52	314000	316599.866	79200	83800	0.36	235	217	202000	57700	50300
4.54	317000	311995.2	81900	77500		250	268	208000	59800	52100
4.54	314000	311311	81200	71000		270	243	205000	57900	48800
4.52	313000	311995.2	81000	75700		250	253	203000	57900	51200
4.58	311000	311995.2	80700	77200		260	262	202000	57400	51900
4.53	314000	311995.2	81400	77700		250	286	205000	59500	52400
4.56	312000	311311	81500	76000		230	285	205000	59700	51300
4.59	310000	311995.2	81600	68700		250	290	204000	58200	46900
4.53	315000	311995.2	82300	71800		270	272	206000	58400	49100
4.55	325000	314732	81300	77915		300	280	205000	58270	56205
4.6	318000	314732	81400	78252		305	260	199000	58120	57159
4.53	321000	313363.6	81100	76737		310	270	199000	59010	54339
4.55	323000	312679.4	81400	77458		309	280	200000	59000	56281
4.55	323000	314047.8	79800	77367		301	280	201000	56900	56559
4.54	322000	315416.2	80500	78717		282	270	196000	60400	57429
4.56	323000	311995.2	80900	77933		298	250	202000	54600	56772
4.54	312000	315416.2	79600	78721		308	260	202000	57200	56393
4.55	312700	313363.6	74250				295.6	196800	58400	
4.56	311700	312679.4	80040				289.1	197200	58900	
4.54	314100	314047.8	75300				292.6	197900	61800	
4.325	310600	313363.6	81640				291.1	194700	56600	
4.339	310300	312679.4	82300				292.1	193400	56100	
4.62	311900	313363.6	80400				298.8	197700	56800	
4.59	312400	312679.4	77800				297.2	195800	56700	
4.66	312800	313363.6	78600				307.1	199100	57300	
4.65	325400	312782.03	77400					189940	56300	
4.63	330600	313493.598	77800					190230	57100	
4.62	329750	313000.974	79000					202770	57400	
4.61	336600	312576.77	79000					193230	56600	
4.65	312200	313302.022	79900					203930		
4.54	292999	312049.936	78200					195000		
4.57	292272	312652.032	79200					193000		
4.57	290482	312282.564	76700					204000		
4.54	297493	312337.3	79100					207000		
4.22	291554	312610.98						207000		
4.57	292981	314116.22						199000		
4.57	289279	314253.06						196000		
4.16	300136	313295.18						190000		
		311242.58						199000		
		311242.58						202000		
		313226.76						195500		
								210000		
								196500		
								201000		
								201000		
								196900		
								192100		
								193500		
								194700		
								193700		
								195000		

Assay Data (Cont.)

FUS	4A_MICP	FUS	4A_MICP	4A_MICP	4A_MICP	FUS	FUS	4A_MICP	4A_MICP
Mn	Mn	Ni	Ni	Sn	Sr	Ti	V	Y	Zn
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1876	1710	886	813	0.70	1.00	4500	2000	0.20	649
1912	1710	864	819	0.70	1.00	4400	2000	0.20	660
1887	1740	850	818	0.70	1.00	4300	2000	0.20	660
1893	1740	837	826	0.70	1.00	4300	2000	0.20	663
1887	1690	920	816	0.60	1.00	4300	2000	0.20	658
1883	1660	891	815	0.60	1.00	4300	1900	0.20	635
1867	1680	873	808	0.80	1.00	4200	1900	0.20	654
1900	1740	874	836	0.70	1.00	4200	1900	0.20	672
1787	1750	896	905	0.90	2.00	4040	2090	0.20	700
1773	1750	865	920	0.80	2.00	4060	2120	0.20	705
1768	1770	865	915	0.80	1.50	4050	2110	0.10	715
1767	1770	870	920	0.80	1.50	4020	2100	0.20	710
1739	1790	889	910	0.90	1.50	3960	2080	0.10	700
1731	1760	884	925	0.80	1.50	4000	2090	0.10	710
1782	1740	892	920	0.90	1.50	4020	2100	0.10	715
1783	1760	873	915	0.80	1.50	4010	2100	0.10	695
1850	1454	1100	630	0.70	1.30	4200	2200	0.23	522
1850	1508	1100	649	0.90	1.40	4300	2200	0.24	546
1900	1648	1170	715	0.60	1.30	4300	2200	0.23	591
1840	1655	1150	720	0.90	1.40	4300	2200	0.23	593
2070	1666	840	734	0.90	1.30	4300	2200	0.22	606
1810	1608	990	707	0.70	1.30	4300	2250	0.20	582
2010	1479	995	648	0.70	1.20	4200	2200	0.23	531
2050	1601	965	694		1.20	4300	2250	0.24	575
2000	1700	1010	873		1.00	4428	2177	0.20	689
1980	1740	1070	896		2.00	4353	2181	0.20	732
1970	1720	990	909		2.00	4347	2141	0.10	851
1870	1640	890	873		2.00	4340	2142	0.10	781
1840	1720	865	927		1.00	4389	2154	0.20	668
1744	1800	870	928		1.40	4346	2153	0.20	659
1780	1780	1150	934		1.20	4372	2152	0.20	734
1779	1600	920	870		1.80	4397	2174		620
1788	1600	930	870		1.20	4100	2017		700
1765	1500	960	820		1.50	3800	2017		630
1785	1600	1010	870		1.30	3900	2028		670
1732	1600	970	890		1.40	4000	1964		680
1775	1600	1160	870		1.40	4000	1984		690
	1600	869	860			4000	2089		670
	1500	845	770			4100	2120		610
	1500	865	820			4000	2111		640
	1785	876	830			4100	2450		665
	1746	873	832			4100	2380		675
	1768	873	868			4000	2460		619
	1727	847	827			4300	2300		659
	1728	859	849			4300	2270		666
	1740		896			4100	2250		655
	1726		865			3900	2190		670
	1794		859			4000	2350		654
						4000	2380		
						4100	2230		
						4100	2090		
						4000	2010		
						4100	2052		
						3900	2067		
						4000	2069		
							2098		
							2083		
							2074		
							2032		
							2088		

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 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 v1.00: 05 April 2019

Version: v1.00

Reason for Version v1.00: Rectification of all elements.

Version v1.00 replaces the original report of AMIS0390 Certification

Date of Version 000: 18 November 2014


Version: 000

Approving Officer:

African Mineral Standards: _____

Makhosi Khoza (Quality Specialist)

Certifying Officer:

A handwritten signature in black ink, appearing to be 'AF' followed by a stylized flourish.

Geochemist: _____

Allan Fraser

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

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 25th 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
- 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. 2nd 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. 3rd 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*. 2nd Edition: 14-59.
- ISO Guide 35 (2003). Certification of reference materials — General and Statistical principles, 3rd 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*. 6th 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.

Appendices

Appendix 1: Uncertified Element Statistics

Uncertified element statistics are shown in **Table 6**.

Table 6. Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	4A_MICP	11	2.2	1.2	56	ppm
As	4A_MICP	31	14.4	14.2	99	ppm
As	FUS	8	85.8	2.6	3	ppm
B	FUS	2	20.0	*	*	ppm
Ba	4A_MICP	40	5.7	3.2	56	ppm
Ba	FUS	31	10.3	8.7	85	ppm
BaO	XRF	8	0.01	*	*	%
Bi	4A_MICP	11	50.0	32.2	64	ppm
Bi	FUS	8	0.1	0.05	37	ppm
Ca	4A_MICP	56	583.6	83.8	14	ppm
Ca	FUS	15	1173.3	311.9	27	ppm
CaO	FUS	24	0.7	1.0	143	%
CaO	XRF	71	0.1	0.02	24	%
Cd	4A_MICP	9	0.4	0.2	59	ppm
Cd	FUS	8	366.3	5.2	1	ppm
Cr	4A_MICP	8	254375.0	10582.2	4	ppm
Cr	Titration	14	314121.4	520.6	0.2	ppm
Cu	4A_MICP	51	14.5	4.2	29	ppm
Cu	FUS	24	70.2	104.9	149	ppm
Fe	4A_MICP	40	180742.5	36109.0	20	ppm
Fe	Titration	8	199525.0	587.4	0.3	ppm
FeO	XRF	8	26.0	0.1	0.2	%
Ga	4A_MICP	38	62.1	34.7	56	ppm
Ga	FUS	7	54.1	0.7	1	ppm
Hf	4A_MICP	22	0.1	0.01	15	ppm
Hg	4A_MICP	8	6.9	1.1	16	ppm
In	4A_MICP	10	0.02	*	*	ppm
K	4A_MICP	24	100.0	69.2	69	ppm
K	FUS	16	1712.5	1478.7	86	ppm
K ₂ O	FUS	3	0.1	0.01	11	%
K ₂ O	XRF	21	0.03	0.01	45	%
La	4A_MICP	24	0.3	0.1	50	ppm
Li	4A_MICP	29	1.3	0.4	31	ppm
Li	FUS	8	2.1	0.6	30	ppm
Lu	4A_MICP	8	0.02	0.01	32	ppm
Mo	4A_MICP	44	5.2	3.5	68	ppm
Mo	FUS	16	9.4	6.3	67	ppm
Na	4A_MICP	26	166.4	108.4	65	ppm
Na ₂ O	4A_MICP	7	0.01	0.002	17	%

Element	Generic Method	n	Mean	SD	RSD %	Unit
Na ₂ O	XRF	18	0.1	0.03	45	%
Nb	4A_MICP	22	0.4	0.2	50	ppm
Nb	FUS	5	2.6	0.9	34	ppm
P	4A_MICP	8	43.1	5.3	12	ppm
P ₂ O ₅	XRF	24	0.004	0.001	28	%
Pb	4A_MICP	26	2.8	2.1	76	ppm
Pb	FUS	17	232.9	195.3	84	ppm
PbO	FUS	8	0.05	0.01	13	%
Pr	4A_MICP	8	0.04	*	*	ppm
Rb	4A_MICP	32	2.1	1.4	64	ppm
Rb	FUS	2	0.6	0.1	13	ppm
S	4A_MICP	17	0.01	0.01	60	%
S	Combustion/LECO	8	0.02	0.01	32	%
S	FUS	8	0.03	0.01	41	%
Sb	4A_MICP	29	0.3	0.2	53	ppm
Sb	FUS	15	462.4	447.3	97	ppm
Sc	4A_MICP	48	6.2	2.3	38	ppm
Sc	FUS	8	6.5	0.5	8	ppm
Se	4A_MICP	7	40.0	*	*	ppm
Si	FUS	60	6208.2	537.8	9	ppm
Sm	4A_MICP	1	0.1	*	*	ppm
SO ₃	XRF	15	0.01	0.005	33	%
Sr	FUS	8	100.0	*	*	ppm
Ta	FUS	2	0.2	0.1	47	ppm
Te	4A_MICP	6	0.1	0.1	60	ppm
Th	4A_MICP	17	0.1	0.2	144	ppm
Th	FUS	3	0.1	*	*	ppm
Ti	4A_MICP	32	3548.3	849.6	24	ppm
TiO ₂	FUS	16	0.7	0.04	5	%
Tl	4A_MICP	8	179.1	4.1	2	ppm
Tm	4A_MICP	5	0.02	*	*	ppm
U	4A_MICP	17	67.1	73.3	109	ppm
U	FUS	2	0.1	*	*	ppm
V	4A_MICP	47	1790.0	385.8	22	ppm
V ₂ O ₅	FUS	8	0.4	0.01	2	%
W	4A_MICP	28	3.5	4.8	138	ppm
W	FUS	1	6.0	*	*	ppm
Zn	FUS	32	524.3	268.1	51	ppm
Zr	4A_MICP	36	4.2	2.7	65	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 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 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 _{crit}
Between Laboratories	SSB	P-1	MSB=SSB/df	MSB/MSW	=FDIST(x,df,df)	F-table
Within Laboratories	SSW	P(n-1)	MSW=SSW/df	–	–	–
Total	SSB+SSW	P-1 + P(n-1)	–	–	–	–

Combined Standard Uncertainty

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

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

Within laboratory repeatability is determined as

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

and, the between laboratory precision as

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

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

Expanded Uncertainty

The expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (u_c) by a coverage factor (k) found from $N-1$ degrees of freedom (df), where N is the number of laboratory means accepted in the establishment of the certified value. The t-critical value for 5% significance can be found in a t-critical table (see Appendix 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 μ certified value. The standard uncertainty u is the stated expanded uncertainty (U) of the CRM divided by the coverage factor (k) as stated on the certificate of analysis. Note that the $| \quad |$ bars indicate that the absolute value between the mean and the certified value is to be used, *i.e.* ignore the sign.

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

Example

A CRM is independently replicated nine times for Al_2O_3 concentration by XRF analysis, *i.e.* 9 individual fused glass beads were prepared. The observed mean and standard deviation of the replicate data are shown with the certified value and expanded uncertainty in Table 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 % (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 cm² with the CRM material spread evenly over same; this represents a 0.1 gram spread per cm². In correcting the certified value for moisture content, a moisture correction factor is calculated:

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

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

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 0.001mg . Even with a microscope it may be difficult to locate and pick up a prill weighing ten times that amount (*i.e.* 0.01mg or $10\mu\text{g}$) 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 0.02g/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 8). Table 10 gives a recommended reporting scheme for LOD and LOQ.

Table 9. 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 0.001mg .

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

Table 10. 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 11. 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