

AMIS0295

Certified Reference Material

**Copper cobalt oxide ore
Tenke Fungurume, DRC**

Certificate of Analysis

AMIS

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SUMMARY STATISTICS

Recommended Concentrations and Limits (at two Standard Deviations)

Certified Concentrations

Analyte	Method	⁷ Certified(μ)	⁹ Two Standard deviation (2s) \pm	Unit
Au	Pb collection ¹	0.018	0.01	g/t
Co	FUS ⁶	413	34	ppm
Co	4A-MICP ²	410	19	ppm
Cu	FUS ⁶	5.21	0.28	%
Cu	4A_MICP ²	5.28	0.11	%
U	4A_MICP ²	8.4	0.9	ppm
LOI	LOI ⁴	4.45	0.23	%
SG	SG ⁵	2.8	0.1	Dimensionless

Major Oxides

Certified Concentrations (at two Standard Deviations)

Analyte	Method	⁷ Certified(μ)	⁹ Two Standard deviation (2s) \pm	Unit
Al ₂ O ₃	XRF ³	5.47	0.12	%
Fe ₂ O ₃	XRF ³	1.64	0.058	%
K ₂ O	XRF ³	0.73	0.05	%
MgO	XRF ³	2.99	0.11	%
Na ₂ O	XRF ³	0.17	0.03	%
P ₂ O ₅	XRF ³	0.11	0.02	%
SiO ₂	XRF ³	77.08	0.884	%
TiO ₂	XRF ³	0.34	0.02	%

1. Certified Concentrations and Uncertainties

AMIS0295 is a new standard material, developed and certified in September, 2017. Table 1 gives the certified concentrations, combined and expanded uncertainty for certified reference material. Table 2 shows the certified major oxides concentrations, two standard deviations, combined and expanded uncertainty.

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

Analyte	Method	⁷ Certified(μ)	<i>N</i>	<i>n</i>	<i>k</i>	% RSD	⁸ Combined uncertainty (u_c)	⁹ Two Standard deviation (2s) \pm	¹⁰ Expanded uncertainty (U) \pm	Unit
Au	Pb collection ¹	0.018	9	70	2.31	16.9	0.003	0.01	0.01	g/t
Co	FUS ⁶	413	5	40	2.78	4.1	17	34	47	ppm
Co	4A_MICP ²	410	8	63	2.36	2.3	10	19	23	ppm
Cu	FUS ⁶	5.21	5	40	2.78	2.7	0.14	0.28	0.4	%
Cu	4A_MICP ²	5.28	5	43	2.78	1.0	0.053	0.11	0.1	%
U	4A_MICP ²	8.4	5	40	2.78	5.3	0.4	0.9	1	ppm
LOI	LOI ⁴	4.45	9	70	2.31	2.6	0.11	0.23	0.3	%
SG	SG ⁵	2.8	4	30	3.18	1.5	0.04	0.1	0.1	Dimensionless

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

Analyte	Method	⁷ Certified(μ)	<i>N</i>	<i>n</i>	<i>k</i>	% RSD	⁸ Combined uncertainty (u_c)	⁹ Two Standard deviation (2s) \pm	¹⁰ Expanded uncertainty (U) \pm	Unit
Al ₂ O ₃	XRF ³	5.47	7	56	2.45	1.1	0.062	0.12	0.2	%
Fe ₂ O ₃	XRF ³	1.64	8	62	2.36	1.8	0.029	0.058	0.1	%
K ₂ O	XRF ³	0.73	8	63	2.36	3.5	0.03	0.05	0.1	%
MgO	XRF ³	2.99	7	56	2.45	1.8	0.054	0.11	0.1	%
Na ₂ O	XRF ³	0.17	6	48	2.57	8.7	0.01	0.03	0.04	%
P ₂ O ₅	XRF ³	0.11	7	56	2.45	6.6	0.01	0.02	0.02	%
SiO ₂	XRF ³	77.08	7	55	2.45	0.6	0.442	0.884	1	%
TiO ₂	XRF ³	0.34	8	62	2.36	1.9	0.01	0.02	0.02	%

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. LOI is Loss On Ignition
5. SG is Specific Gravity
6. FUS-Sodium peroxide/ Lithium tetraborate fusion
7. 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.
8. 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.
9. The two standard deviations (2s) is calculated as for example: $u_c \times 2 = 0.23 \times 2 = 0.46\%$. See section 25, page 14 for recommended use in quality control.
10. Expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (u_c) with a coverage factor (k) found from *N*-1 degrees of freedom (see Appendix 7 for *t*-distribution table). Example: $U = 2.36 \times 0.23 = 0.54\%$.

2. Statistical Comparison of Means

Comparison of means for the same element between different analytical methods was done by first comparing the variances between the two data sets; if the variances were found to be equal (F-test, $p\text{-value} > 0.05$), then an equal variance t-test was applied. Should the variances be statistically significant, then an unequal variance t-test was performed on the data. With a $p\text{-value} > 0.05$, the null hypothesis that the means (certified values) are equal is accepted (Table 3 and Table 4).

Table 3. The results of a two sample equal variance t-test (two-tailed) those data sets demonstrating equal variances.

Method	Certified value	Method	Certified value	p-value (t-test)	t-test outcome
Co 4A_MICP	410 ppm	Co Fus	413 ppm	0.68	Accept H_0 ; certified values are equal

Table 4. The results of a two sample unequal variance t-test (two-tailed) for those data sets demonstrating unequal variances.

Method	Certified value	Method	Certified value	p-value (t-test)	t-test outcome
Cu 4A_MICP	52751 ppm	Cu Fus	52134 ppm	0.34	Accept H_0 ; certified values are equal

3. Intended Use

AMIS0295 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.

4. Abbreviations and Symbols

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

Table 5. Abbreviations, symbols and descriptions.

Abbreviation/Symbol	Description
Alpha (α)	Significance level (denoted by alpha, ' α ') of 0.05 or 5%
ANOVA	Analysis of variance by statistical means
BIF	Banded iron formation
CRM	Certified reference material
df	Degrees of freedom, typically, $n-1$, or $N-1$
F_{calc}	Calculated F statistic from ANOVA or Fisher's test
F-critical or F_{crit}	F-critical value from F-distribution table
GOI	Gain on ignition
H_0	Null hypothesis
H_1	Alternate hypothesis
g/t	Grams per tonne
k	Coverage factor, e.g. $k=2$ for 95% level of confidence
LOC	Level of confidence or confidence level
LOD	Limit of detection
LOQ	Limit of quantitation
LOI	Loss on ignition
MS	Mean squares (ANOVA)
MSb	Mean squares between(ANOVA)
MSw	Mean squares within (ANOVA)
N	Number of labs
n	Number of replicates
μ	Property or certified value of a CRM

Table 5 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 $k=1$
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 CRM is made from run-of-mine oxide Cobalt-Copper ore from the Tenke Fungurume (Tenke) mine operated by Freeport- McMoRan Copper & Gold Inc. The mine is situated in Katanga Province of the Democratic Republic of Congo. The Tenke-Fungurume deposits are sedimentary copper deposits located in the Lufilian arc, an 800 km fold belt formed between the Angolan Plate to the southeast and Congo Plate to the northwest during the late Neoproterozoic approximately 650 to 600 million years before present (Ma). Copper mineralization at Tenke-Fungurume is stratabound and generally restricted to two dolomitic shale horizons (RSF and SDB respectively) each ranging in thickness from 5 to 15 m, separated by 20 m of cellular silicified dolomite (RSC).

9. Approximate Mineral and Chemical Composition

The main economic minerals present at Tenke and Fungurume are malachite, chrysocolla, bornite, and heterogenite; the primary copper and cobalt mineralogy is predominately chalcocite (Cu_2S), digenite (Cu_9S_5), bornite (Cu_5FeS_4), and carrollite (CuCo_2S_4); however oxidation has resulted in widespread alteration producing malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), pseudomalachite ($\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$), chrysocolla (hydrated copper silicate) and heterogenite ($\text{Co}_3\text{O}(\text{OH})$).

The primary copper-cobalt mineral associations are homogeneous in both mineralized zones and any variations are due to the effect of oxidation and supergene enrichment. Consequently the mineral assemblages can be grouped into three main categories dependent upon the degree of alteration – oxide, mixed and sulfide zone. Dolomite and quartz are the main gangue minerals present. Dolomite or dolomitic rocks make up the bulk of the host strata. Weathering of the host rocks is normally depth related, intensity decreasing with increasing depth, producing hydrated iron oxides and silica at the expense of dolomite, which is leached and removed.

For a detailed description please refer to the Technical Report prepared for Tenke Mining Corp by GRD Minproc Limited available at:

<http://www.lundinmining.com/i/pdf/TenkeFungurumeFeasibilityStudy.pdf>

10. Health and Safety

The material is a very fine powder coloured Yellowish Gray (5Y 8/2). Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

11. Method of Preparation

The particle size distribution for this material was shown to have a nominal top size of 54µm (95% passing 54µm). The procedure of preparation in brief is as follows: the material was crushed, dry-milled and air-classified to <54µm. It was then blended in a bi-conical mixer, systematically divided and sealed into 1kg Laboratory Packs. Explorer Packs are then subdivided from the Laboratory Packs as required. Final packaged units were then selected on a random basis and submitted for analysis to an independent laboratory accredited with the ISO17025:2005 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.

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 finished with gravimetric or AAS or ICP-OES/ICP-MS.
2. Cu and Co Fusion finished with AAS or ICP-OES/MS
3. 4-acid digest multi-element scan - (to include Cu and Co) finished with AAS or ICP-OES/MS
4. Majors (Al₂O₃, CaO, Cr₂O₃, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, TiO₂, LOI) XRF fusion
5. S Combustion/LECO
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 base metals to be reported in ppm, oxides to be reported in % and Gold to be reported in ppb.
5. Report all QC data, to include replicates, blanks and certified reference materials used

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 12, Appendix 7 for a t-critical table). N is the number of laboratory means used in the establishment of the certified value. Since the estimated values of the CRM approximate a normal distribution with combined uncertainty, u_c , the certified value of the CRM is understood to lie in the interval defined by U with a level of confidence of 95 % (Thompson & Lowthian, 2011).

Appendix 2 gives detail on the principles used for certification of the reported assay values and estimation of measurement uncertainty.

16. Participating Laboratories

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

The 15 laboratories that provided results timeously are:

1. UIS Analytical Services (pty) Ltd
2. Shiva Analyticals India
3. SGS South Africa
4. SGS Mineral Services Lakefield (Canada)
5. SGS Ankara (Turkey)
6. SGS Ahafo Ghana
7. Mimosa Mine Laboratory Zimbabwe
8. Intertek Utama Services (Indonesia)
9. Genalysis Laboratory Services (W Australia P)
10. Bureau Veritas Minerals Ultra Trace Pty Ltd
11. ARGETEST
12. ALS (Vancouver) - Analytical Laboratory Services - Vancouver, Canada
13. ALS Chemex Laboratory Group Johannesburg SA
14. ALS Chemex Laboratory Group Lima (Peru)
15. ALS OMAC (Ireland)

Assay Data (Cont)

LOI %	XRF Al ₂ O ₃ %	XRF Fe ₂ O ₃ %	XRF K ₂ O %	XRF MgO %	XRF Na ₂ O %	XRF P ₂ O ₅ %	XRF SiO ₂ %	XRF TiO ₂ %
4.62	5.51	1.58	0.73	2.92	0.19	0.12	77.34	0.34
4.64	5.57	1.58	0.74	2.92	0.18	0.12	77.57	0.34
4.66	5.43	1.61	0.74	2.91	0.20	0.12	77.49	0.34
4.64	5.51	1.59	0.74	2.91	0.18	0.12	77.32	0.33
4.63	5.48	1.60	0.74	2.92	0.20	0.12	77.30	0.33
4.64	5.47	1.59	0.74	2.90	0.18	0.12	77.33	0.34
4.54	5.52	1.60	0.74	2.93	0.18	0.12	77.61	0.34
4.50	5.51	1.59	0.73	2.92	0.18	0.12	77.48	0.34
4.29	5.46	1.64	0.72	2.98	0.18	0.12	77.00	0.34
4.19	5.45	1.64	0.72	2.99	0.19	0.12	76.95	0.35
4.27	5.46	1.63	0.72	2.97	0.19	0.12	76.96	0.35
4.38	5.46	1.63	0.72	2.97	0.19	0.12	77.07	0.33
4.39	5.45	1.62	0.72	2.97	0.18	0.12	76.87	0.34
4.28	5.45	1.63	0.72	2.98	0.18	0.12	77.04	0.33
4.28	5.44	1.64	0.72	2.98	0.18	0.12	76.78	0.34
4.28	5.45	1.64	0.71	2.99	0.18	0.12	76.97	0.33
4.60	5.44	1.65	0.71	2.98	0.18	0.11	77.14	0.33
4.50	5.45	1.66	0.71	2.99	0.16	0.11	77.24	0.33
4.50	5.44	1.63	0.72	2.98	0.16	0.11	77.18	0.34
4.60	5.46	1.65	0.71	2.99	0.16	0.11	77.17	0.33
4.50	5.44	1.65	0.70	2.98	0.16	0.11	77.11	0.33
4.50	5.45	1.65	0.71	2.99	0.16	0.11	77.21	0.34
4.60	5.45	1.63	0.71	2.98	0.18	0.11	77.21	0.34
4.70	5.43	1.63	0.72	2.98	0.18	0.11	77.06	0.34
4.43	5.49	1.66	0.72	2.98	0.19	0.11	76.92	0.34
4.45	5.61	1.69	0.74	3.05	0.17	0.10	77.95	0.35
4.45	5.57	1.69	0.73	3.03	0.16	0.10	76.06	0.35
4.45	5.41	1.63	0.71	2.96	0.19	0.11	76.84	0.34
4.46	5.50	1.65	0.72	2.97	0.18	0.10	77.34	0.34
4.44	5.51	1.68	0.73	2.98	0.16	0.10	77.55	0.34
4.44	5.51	1.68	0.74	3.00	0.18	0.11	78.21	0.34
4.47	5.56	1.70	0.74	3.03	0.17	0.11	77.07	0.35
4.29	5.52	1.65	0.69	3.05	0.15	0.11	77.56	0.35
4.29	5.55	1.64	0.75	3.09	0.15	0.12	77.29	0.34
4.33	5.52	1.65	0.73	3.09	0.15	0.11	77.60	0.35
4.33	5.53	1.66	0.72	3.09	0.15	0.11	77.38	0.34
4.36	5.52	1.64	0.72	3.09	0.15	0.11	77.38	0.33
4.31	5.55	1.63	0.72	3.08	0.15	0.12	75.79	0.33
4.46	5.60	1.59	0.69	3.10	0.15	0.12	77.09	0.34
4.41	5.51	1.62	0.68	3.06	0.15	0.11	76.50	0.34
4.45	5.43	1.61	0.69	3.03	0.17	0.10	76.40	0.35
4.40	5.34	1.61	0.69	2.94	0.17	0.10	76.60	0.34
4.45	5.34	1.61	0.72	2.94	0.17	0.10	76.50	0.34
4.42	5.42	1.62	0.70	2.95	0.17	0.10	76.40	0.35
4.48	5.38	1.64	0.73	2.98	0.17	0.10	76.60	0.35
4.44	5.38	1.62	0.70	2.91	0.17	0.10	76.60	0.34
4.38	5.41	1.67	0.72	2.98	0.17	0.10	76.60	0.34
4.38	5.36	1.67	0.78	2.95	0.17	0.10	77.18	0.34
4.51	5.50	1.65	0.78	3.01		0.11	77.36	0.33
4.47	5.51	1.66	0.78	3.01		0.11	76.67	0.35
4.51	5.45	1.65	0.78	2.98		0.11	76.94	0.33
4.49	5.46	1.64	0.78	2.99		0.11	77.07	0.34
4.47	5.48	1.66	0.77	3.00		0.11	76.90	0.35
4.46	5.47	1.68	0.77	3.00		0.11	77.26	0.35
4.48	5.51	1.66	0.78	3.00		0.11	77.27	0.34
4.55	5.50	1.66	0.72	3.01		0.11		0.34
4.50		1.65	0.72					0.34
4.53		1.65	0.72					0.34
4.49		1.66	0.72					0.34
4.54		1.65	0.72					0.34
4.56		1.66	0.72					0.34
4.57		1.66	0.72					0.34
4.39			0.72					
4.38								
4.24								
4.43								
4.41								
4.54								
4.47								
4.42								

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. Limit of Detection and Limit of Quantitation in Gravimetric Fire Assay

In the determination of limit of detection (LOD) and limit of quantitation (LOQ) in gravimetric fire assay (*i.e.* lead collection and weighing of resulting gold prill), the minimum mass that an assay microbalance is capable of weighing and the original test sample mass determines the LOD and the LOQ in the assay (Fraser, 2015), (see Appendix 6 for an example of the calculation LOD and LOQ and Table 11 for a recommend reporting scheme for LOD and LOQ values).

21. 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.

22. 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.

23. 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.

24. 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.

25. Recommended use in Quality Control

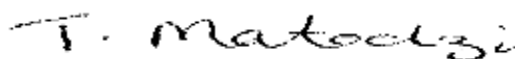
Users should set their own limits *i.e.* 1, 2 and 3 standard deviations from an obtained mean value based on at least 10 replicate analyses using this CRM (see Appendix 4 for detail on the use of this CRM in quality control).

26. 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.

07 September 2017

Certifying Officers:



African Mineral Standards: _____

Thivhafuni Matodzi



Geochemist: _____

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

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APPENDICES

Appendix 1: Uncertified Element Statistics

Uncertified element statistics are shown in Table 7.

Table 7. Uncertified element concentrations statistics.

Element	Gen Method	N	Mean	s	RSD %	Unit
Ag	2A_MICP	8	0.219	0.015	6.664	ppm
Ag	4A_MICP	24	1.396	1.223	87.602	ppm
Al	2A_MICP	8	13250.000	200.000	1.509	ppm
Al	4A_MICP	48	27979.167	1542.029	5.511	ppm
Al ₂ O ₃	FUS	16	2.587	2.672	103.292	%
As	2A_MICP	8	1.163	0.092	7.881	ppm
As	4A_MICP	19	2.895	3.125	107.957	ppm
Ba	2A_MICP	8	32.250	0.707	2.193	ppm
Ba	4A_ICPES	8	64.500	2.563	3.974	ppm
Ba	4A_MICP	48	70.625	4.441	6.289	ppm
BaO	XRF	21	0.010	<0.001	<0.001	%
Be	2A_MICP	8	0.763	0.052	6.788	ppm
Be	4A_MICP	36	1306.645	3747.519	286.805	ppm
Bi	2A_MICP	8	11.288	0.210	1.861	ppm
Bi	4A_MICP	24	11.363	0.521	4.583	ppm
Ca	2A_MICP	8	300.000	<0.001	<0.001	ppm
Ca	4A_MICP	47	510.383	108.280	21.215	ppm
CaO	FUS	7	0.053	0.015	28.303	%
CaO	XRF	60	0.065	0.016	24.481	%
Ce	2A_MICP	8	17.400	0.812	4.669	ppm
Ce	4A_MICP	24	23.425	6.576	28.071	ppm
Co	2A_MICP	14	405.214	4.577	1.130	ppm
Co	4A_ICPES	8	422.750	5.036	1.191	ppm
Cr	2A_MICP	8	158.875	2.031	1.278	ppm
Cr	4A_MICP	40	213.338	64.195	30.091	ppm
Cr ₂ O ₃	FUS	8	0.034	0.005	15.335	%
Cr ₂ O ₃	XRF	60	0.043	0.008	18.547	%
Cs	2A_MICP	8	0.239	0.017	7.233	ppm
Cs	4A_MICP	21	0.600	<0.001	<0.001	ppm
Cu	2A_MICP	16	5.286	0.112	2.123	ppm
Cu	4A_ICPES	8	53354.875	687.406	1.288	ppm
CuO	XRF	8	6.839	0.025	0.362	%
Dy	4A_MICP	14	2.736	0.069	2.527	ppm
Er	4A_MICP	15	1.497	0.064	4.276	ppm
Eu	4A_MICP	15	0.500	<0.001	<0.001	ppm
Fe	2A_MICP	8	10137.500	51.755	0.511	ppm
Fe	4A_MICP	55	11641.818	336.480	2.890	ppm
Fe	XRF	8	11150.000	75.593	0.678	ppm
Fe ₂ O ₃	FUS	8	1.470	0.162	11.047	%
Ga	2A_MICP	8	3.625	0.116	3.214	ppm
Ga	4A_MICP	24	6.663	0.634	9.522	ppm
Gd	4A_MICP	16	3.094	0.106	3.435	ppm
Ge	4A_MICP	8	0.963	0.052	5.377	ppm
Hf	2A_MICP	8	0.485	0.024	4.929	ppm
Hf	4A_MICP	24	2.108	0.477	22.636	ppm
Ho	4A_MICP	15	0.497	0.007	1.415	ppm
In	2A_MICP	8	0.121	0.008	6.883	ppm
In	4A_MICP	24	0.168	0.027	15.831	ppm
K	2A_MICP	8	2457.500	30.119	1.226	ppm
K	4A_MICP	48	6023.958	199.251	3.308	ppm
K ₂ O	FUS	8	0.673	0.133	19.819	%
La	2A_MICP	8	8.609	0.083	0.969	ppm
La	4A_MICP	37	10.870	3.147	28.952	ppm
Li	2A_MICP	8	79.238	1.344	1.696	ppm
Li	4A_MICP	48	87.867	3.929	4.471	ppm
Lu	4A_MICP	16	0.211	0.010	4.738	ppm
Mg	2A_MICP	8	14937.500	91.613	0.613	ppm
Mg	4A_MICP	48	18087.500	825.556	4.564	ppm
MgO	FUS	8	2.784	0.299	10.732	%
Mn	2A_MICP	8	186.375	1.302	0.699	ppm
Mn	4A_MICP	55	200.775	9.558	4.760	ppm
Mn	XRF	8	287.500	64.087	22.291	ppm
Mn ₂ O ₄	XRF	8	0.039	0.011	29.058	%
MnO	FUS	8	0.024	0.005	21.792	%
MnO	XRF	54	0.026	0.007	25.206	%

Element	Gen Method	N	Mean	s	RSD %	Unit
Mo	2A_MICP	7	9.871	0.095	0.964	ppm
Mo	4A_MICP	48	10.104	1.167	11.549	ppm
Na	2A_MICP	8	100.000	<0.001	<0.001	ppm
Na	4A_MICP	48	674.432	322.137	47.764	ppm
Na ₂ O	FUS	8	0.160	0.095	59.574	%
Nb	4A_MICP	24	5.958	1.705	28.623	ppm
Nd	4A_MICP	15	9.040	0.169	1.872	ppm
Ni	2A_MICP	8	11.538	0.169	1.460	ppm
Ni	4A_ICPES	6	21.833	5.636	25.815	ppm
Ni	4A_MICP	40	14.305	1.277	8.926	ppm
P	2A_MICP	8	742.500	30.119	4.056	ppm
P	4A_MICP	48	460.576	242.187	52.583	ppm
P	XRF	8	537.500	51.755	9.629	ppm
Pb	2A_MICP	8	3.263	0.130	3.992	ppm
Pb	4A_MICP	40	5.575	2.582	46.317	ppm
PbO	XRF	8	0.010	<0.001	<0.001	%
Pd	Pb Collection	4	0.003	0.002	83.616	g/t
Pr	4A_MICP	15	2.251	0.057	2.522	ppm
Pt	Pb Collection	9	0.002	0.001	75.966	g/t
Rb	2A_MICP	8	9.775	0.142	1.453	ppm
Rb	4A_MICP	24	23.279	0.724	3.108	ppm
S	2A_MICP	8	0.020	<0.001	<0.001	%
S	4A_MICP	22	0.020	0.001	5.588	%
S	Combustion/LECO	66	0.019	0.009	48.857	%
S	XRF	7	0.008	<0.001	4.642	%
Sb	4A_MICP	15	0.207	0.128	61.930	ppm
Sc	2A_MICP	8	5.000	<0.001	<0.001	ppm
Sc	4A_MICP	32	6.528	0.415	6.361	ppm
Se	4A_MICP	8	1.000	<0.001	<0.001	ppm
SiO ₂	FUS	8	77.075	0.191	0.248	%
Sm	4A_MICP	15	2.870	0.092	3.212	ppm
Sn	4A_MICP	24	1.217	0.530	43.537	ppm
SO ₃	XRF	22	0.050	0.012	24.689	%
Sr	2A_MICP	8	5.575	0.089	1.590	ppm
Sr	4A_ICPES	8	16.375	0.744	4.544	ppm
Sr	4A_MICP	40	19.345	2.425	12.536	ppm
SrO	XRF	15	0.010	<0.001	<0.001	%
Ta	4A_MICP	24	0.629	0.205	32.633	ppm
Tb	4A_MICP	16	0.444	0.031	7.019	ppm
Th	2A_MICP	8	2.393	0.051	2.140	ppm
Th	4A_MICP	31	5.458	0.331	6.072	ppm
Ti	2A_MICP	8	0.006	<0.001	4.461	%
Ti	4A_MICP	56	0.118	0.062	52.269	%
TiO ₂	FUS	8	0.325	0.035	10.910	%
Tl	2A_MICP	8	0.171	0.011	6.575	ppm
Tl	4A_MICP	21	0.300	<0.001	<0.001	ppm
Tm	4A_MICP	16	0.209	0.010	4.909	ppm
U	2A_MICP	8	4.278	0.082	1.915	ppm
V	2A_MICP	8	35.750	0.463	1.295	ppm
V	4A_MICP	48	71.713	4.848	6.761	ppm
V ₂ O ₅	XRF	16	0.014	0.005	35.642	%
W	2A_MICP	8	0.150	0.053	35.635	ppm
W	4A_MICP	17	1.135	0.177	15.553	ppm
Y	2A_MICP	8	8.456	0.214	2.532	ppm
Y	4A_MICP	40	13.765	0.864	6.279	ppm
Yb	4A_MICP	16	1.413	0.106	7.481	ppm
Zn	2A_MICP	8	76.500	0.926	1.210	ppm
Zn	4A_ICPES	8	125.375	49.733	39.668	ppm
Zn	4A_MICP	46	33.783	30.596	90.567	ppm
ZnO	XRF	8	0.010	<0.001	<0.001	%
Zr	2A_MICP	8	17.300	0.151	0.874	ppm
Zr	4A_ICPES	7	83.857	6.067	7.235	ppm
Zr	4A_MICP	40	70.738	14.397	20.352	ppm
ZrO ₂	XRF	8	0.030	<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
 $|z| > 2$ 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.

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

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 8 is developed.

Table 8. A single-factor ANOVA table showing key elements. Where P is the total number of groups, or laboratories. P-1 is 1 less than number of laboratories, P (n-1) is the number of data values minus number of groups (equals degrees of freedom for each group added together), and P-1 + P(n-1) is 1 less than 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 :

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

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 Appendix 7, or from MS Excel as =TINV (5%, df)).

Uncertainty Statement

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

Appendix 3. Example: Comparison of Mean and Certified Value for Validation of Accuracy (Prepared by Allan Fraser)

According to ERM (2005); Eurolab (2007); Abzalov (2011) and Carr (2011), the validation of accuracy for a given mean and certified value requires the inclusion of the measurement uncertainty of the CRM in a t-test for statistical significance. The classical Student's t-test as shown in [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 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 | | 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 Al₂O₃ concentration by XRF analysis, *i.e.* 9 individual fused glass beads were prepared. The observed mean and standard deviation of the replicate data are shown with the certified value and expanded uncertainty in Table 9. In validation of accuracy, the hypothesis question is: Is the difference between the observed mean and the certified value statistically significant at a level of confidence of 95%? Alternatively put, is there sufficient evidence to conclude that the data *i.e.* replicates generated, are inaccurate?

The relevant hypotheses are:

Null hypothesis: H₀: Mean = Certified value of CRM with stated measurement uncertainty. The acceptance of H₀ means that accuracy is demonstrated; *i.e.* insufficient evidence to reject H₀;

Alternate hypothesis: H₁: Mean ≠ Certified value of CRM with stated measurement uncertainty. The acceptance of H₁ means that accuracy is not demonstrated, *i.e.* there is sufficient evidence to accept H₁;

Table 9. CRM certified value, quoted expanded uncertainty U , the coverage factor for the CRM, $k=2.25$ and mean for $n=9$ replicates and corresponding standard deviation for the replicate data.

CRM Certified Value	Expanded 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 7, page 25) which is >0.84 . Similarly, the p -value=0.43 which is >0.05 . This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

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Appendix 4. Using the CRM in Quality Control
(Prepared by Allan Fraser)

QC chart control limits should not be determined by the certified value and stated measurement uncertainty of the certified reference material used. These parameters although “certified” will never be known; it is only the corresponding statistical estimates, *i.e.* standard deviation and the mean calculated from replicated results that are known and these should be used in quality control charts. However, should the laboratory 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 to15 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].

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Appendix 5. Conversion to Air-dry Basis
(Prepared by Allan Fraser)

Since AMIS certified analyte values are reported on a dry-basis, the user laboratory is required to dry a portion (accurately weigh out 1.0 grams in duplicate) of the CRM material in air at 105°C in a drying oven to constant mass to determine the moisture content. Use a crucible with a flat inner surface with a surface area not smaller than 10 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 x 0.52 = 0.51(7), rounded to 0.52%. The air-dry basis concentration *i.e.* 12.56±0.52% is to be used as the certified value with its corresponding measurement of uncertainty.

Appendix 6. Example of Determination of LOD and LOQ in Fire Assay
Prepared by Allan Fraser

The limit of detection (LOD) is the minimum detectable quantity of the analyte of interest (Skoog & West, 1985). In order to determine the LOD in fire assay by lead collection, the minimum mass that an assay microbalance is capable of weighing (m in micrograms, and the original test sample mass, $Mass_{assay}$ 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. Assuming that 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:

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

And, 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 to be weighed then the LOD result would be $<0.02\text{g/t}$ or “not detected”. Table 11 gives a recommended reporting scheme for LOD and LOQ.

Table 10. Mass of assay sample and corresponding limit of detection and limit of quantitation for an assay microbalance capability of smallest prill mass of $1\mu\text{g}$ or 0.001mg .

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 11. Recommended reporting scheme for LOD and LOQ in fire assay.

Data	Report as
<LOD	Not detected
<LOQ	Detected
≥LOQ	Report assay result

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Appendix 7. T-distribution table

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

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

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