AMIS0224

Certified Reference Material

Gold and copper concentrate, greenstone Bulyanhulu Mine, Tanzania

Certificate of Analysis

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Certified Concentrations

Analyte	Method	[8]Certified(μ)	[10]Two Standard deviation (2s) ±	Unit
Au	Pb collection[1]	113.4	6.8	g/t
Ag	4A-MICP[2]	131	11.4	ppm
Cu	4A-MICP[2]	11.63	0.635	%
LOI	LOI[4]	27.1	0.82	%
S	Comb/LECO[5]	33.5	1.29	%
SG	SG[6]	3.88	0.21	Dimensionless

Major Oxides

Certified Concentrations (at two Standard Deviations)

Analyte	Method	[8]Certified(μ)	[10]Two Standard deviation (2s) ±	Unit
Al_2O_3	XRF[3]	1.48	0.046	%
CaO	XRF[3]	0.68	0.05	%
Fe_2O_3	XRF[3]	43.28	1.13	%
K_2O	XRF[3]	0.39	0.04	%
MnO	XRF[3]	0.03	0.01	%
SiO_2	FUS[7]	10.65	0.263	%
SiO_2	XRF[3]	10.48	1.08	%
TiO_2	XRF[3]	0.12	0.02	%

1. Certified Concentrations and Uncertainties

AMIS0224 is a new standard material, developed and certified in August, 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)	N	n	k	% RSD	[8]Combined uncertainty (u_c)	[9]Two Standard deviation (2s) ±	[10]Expanded uncertainty (U) ±	Unit
Au	Pb collection[1]	113.4	15	117	2.14	3.0	3.4	6.8	7	g/t
Ag	4A-MICP[2]	131	4	32	3.18	4.4	5.7	11.4	18	ppm
Cu	4A-MICP[2]	11.63	5	38	2.78	2.7	0.32	0.635	0.9	%
LOI	LOI[4]	27.1	6	47	2.57	1.5	0.41	0.82	1	%
S	Comb/LECO[5]	33.5	8	61	2.36	1.9	0.64	1.29	2	%
SG	SG[6]	3.88	3	23	4.30	2.7	0.10	0.21	0.4	Dimensionless

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

Analyte	Method	[7]Certified(µ)	N	n	k	% RSD	[8]Combined uncertainty (u_c)	[9]Two Standard deviation (2s) ±	[10]Expanded uncertainty (U) ±	Unit
Al_2O_3	XRF[3]	1.48	4	32	3.18	1.6	0.023	0.046	0.1	%
CaO	XRF[3]	0.68	4	32	3.18	3.4	0.02	0.05	0.1	%
Fe_2O_3	XRF[3]	43.28	5	39	2.78	1.3	0.567	1.13	2	%
K_2O	XRF[3]	0.39	4	31	3.18	5.4	0.02	0.04	0.1	%
MnO	XRF[3]	0.03	4	29	3.18	14.8	0.005	0.01	0.02	%
SiO_2	FUS[7]	10.65	3	22	4.30	1.2	0.132	0.263	0.6	%
SiO_2	XRF[3]	10.48	4	30	3.18	5.2	0.541	1.08	2	%
TiO_2	XRF[3]	0.12	5	37	2.78	7.9	0.01	0.02	0.03	%

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. *Comb/LECO is combustion infra-red analysis*
6. *SG is Specific Gravity*
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: uc x 2 = 0.23 x 2=0.46%. See section 24, page 15 for recommended use in quality control.*
10. *Expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (uc) with a coverage factor (k) found from N-1 degrees of freedom (see Appendix 7 for t-distribution table). Example: U = 2.36 x 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-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-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
Fe_2O_3 Fus	44.66%	Fe_2O_3 XRF	43.28%	0.021	*Reject* H_0; certified values are not 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
SiO_2 XRF	10.48%	SiO_2 Fus	10.65%	0.60	Accept H_0; certified values are equal

3. Intended Use

AMIS0224 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

The material originates from the Bulyanhulu Gold Mine, which is wholly owned and operated by the Barrick Gold Corporation.Bulanyhulu is an Archaen orogenic lode gold deposit located SE of Lake Victoria in the Lake Victoria Greenstone Belt in Tanzania, East Africa. It is a narrow-vein underground gold mine containing gold, silver and copper mineralisation in sulphides.The geology consists of mafic volcanic flows overlain by a series of pyroclastics and ash tuffs. Argillite is present at the contact between the mafic and felsic rocks. Gold, silver and copper mineralization on the property occurs in mineralized "reefs" or quartz veins localized along steeply dipping NW-striking structures, generally localized in the argillite units. Mineralization has been defined over a strike length of 5 km and averages 2m to 3m wide. The most significant structure discovered on the property to date is Reef 1 and it contains the bulk of the mineral reserves defined to date.

9. Approximate Mineral and Chemical Composition

Bulyanhulu ore is quite simple with gold occurring as free gold with grain sizes up to 850 microns or possibly in electrum, in close association with chalcopyrite, pyrite and pyrrhotite. The free gold is collected in a gravity circuit, while the sulphide-associated gold is recovered in a flotation circuit in the form of a copper concentrate. Gold mineralisation is preferentially localized in the Reef 1 quartz veins and the wall rocks are barren of economic gold mineralisation except where quartz veins and sulphide stringers are present. The dominant wallrock alteration minerals are quartz, chlorite and calcite.

10. Health and Safety

The material is a very fine powder coloured Dark grey 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 by Pb collection with ICP-OES or ICP-MS finish (If finish is different, please specify)
2. Multi element scan to include Ag and Cu. Multi-acid total digestion, including HF, ICP-OES or ICP-MS **or** fusion finished with ICP-OES or ICP-MS or AAS
3. Ag and Cu by XRF analysis
4. Majors (Al_2O_3, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, SiO_2, TiO_2, U_3O_8, P_2O_5,LOI) XRF fusion **or** fusion/4 acid digest finished with ICP/AAS finish
5. SG – gas pycnometer
6. S Combustion/LECO

14. Information Requested of Participating Laboratories

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

1. State aliquots used for all determinations.
2. All results for Gold to be reported as ppm.
3. All results for major elements to be reported as oxides in percentages.
4. All results for multi-element scans to be reported in ppm.
5. Report all QC data, to include replicates, blanks and certified reference materials used.
6. All results to include more than three decimal places, if possible.
7. State and provide brief description of analytical techniques used.
8. Send a PDF and excel of the results. (Excel template format was sent to the labs. If you have not received it, please email Melesha and she will send it through)

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

Nineteen laboratories were each given eight randomly selected packages of the CRM. Seventeen laboratories of the Nighnteen laboratories submitted results in time for certification, with the data for two of these laboratories not being included in the certification.

The 17 laboratories that provided results timeously are:

1. ALS OMAC (Ireland)
2. ALS Chemex Laboratory Group Lima (Peru)
3. ALS Chemex Laboratory Group Johannesburg SA
4. ALS (Vancouver) - Analytical Laboratory Services - Vancouver, Canada
5. Antech Zimbabwe
6. Chromatech Services
7. Genalysis Laboratory Services (W Australia P)
8. Gumustas Mad. Ve Tic. A.S Testing Laboratory (Turkey)
9. Koza Altin Isletmeleri
10. Quality Labs Tanzania
11. Ready Lead Assay Laboratory
12. SGS Ankara (Turkey)
13. SGS Mineral Services Lakefield (Canada)
14. SGS South Africa
15. SGS Welkom
16. Shiva Analyticals India
17. Super Laboratory Services (Pty) Ltd. Springs
18. UIS Analytical Services (pty) Ltd
19. Bureau Veritas Minerals Ultra Trace Pty Ltd
20. SGS Barbeton

17. Accepted Assay Data

Data from the 20 laboratories used for certification are set out in Table 6.

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

Pb Collection Au %	Pb Collection Au %	4A-MICP Ag ppm	4A-MICP Cu ppm	SG Dimensionless
107.04	115.42	136	116000	3.81
107.30	112.45	135	115000	3.81
107.23	114.87	135	118000	3.81
107.28	116.00	134	115000	3.85
107.24	111.00	140	118000	3.88
106.75	113.00	138	117000	3.84
107.51	114.00	137	117000	3.84
106.85	112.00	141	118000	3.88
108.14	108.00	137	118082	3.81
111.60	110.00	132	115388	3.83
109.96	113.00	129	115150	3.79
108.30	116.00	128	115750	3.81
111.70	117.00	134	115154	3.81
107.00	117.00	133	117207	3.79
113.64	118.00	133	115733	3.83
111.52	119.00	131	115827	3.81
112.96	119.00	130	117559	4.00
112.00	116.00	127	116335	3.98
111.36	115.00	125	115504	4.01
112.32	115.00	135	116156	3.97
112.64	114.00	132	120855	3.98
112.96	116.00	130	116900	4.02
111.04	115.00	131	118763	4.05
112.00	116.00	127	119697	
112.00	114.00	121	120900	
107.00	111.85	123	118500	
110.00	113.57	125	117000	
111.00	112.27	124	121500	
112.00	113.81	127	119800	
111.00	113.32	125	120300	
111.00	113.22	127	120800	
108.00	111.63	125	117400	
113.98	113.38		111000	
113.97	117.00		111000	
113.94	118.00		111000	
113.52	118.00		110000	
113.54	119.00		111000	
113.52	118.00		114000	
113.54	117.00			
113.92	120.00			
113.00	114.00			
113.00	115.00			
113.00	116.00			
113.00	115.00			
114.00	116.00			
116.00	115.00			
116.00	117.00			
112.00	116.00			
115.95	114.00			
116.65	111.00			
117.55	114.00			
118.75	111.00			
119.20	110.00			
118.45	112.00			
119.51	111.00			
118.80	111.00			
111.96				
107.03				
116.27				
116.53				
117.93				

Assay Data (Cont)

Comb/LECO S %	LOI %	XRF Al₂O₃ %	XRF CaO %	XRF Fe₂O₃ %	XRF K₂O %	FUS SiO₂ %	XRF SiO₂ %	XRF TiO₂ %
34.30	27.36	1.52	0.70	43.22	0.42	10.80	11.39	0.13
33.80	27.50	1.48	0.71	43.19	0.41	10.75	11.24	0.13
34.00	26.94	1.46	0.70	44.09	0.41	10.70	11.25	0.12
34.00	27.47	1.48	0.70	43.62	0.42	10.68	11.21	0.12
33.90	27.50	1.48	0.70	43.05	0.42	10.65	11.40	0.13
34.00	27.18	1.46	0.71	43.34	0.42	10.70	11.43	0.13
33.80	27.22	1.44	0.71	43.18	0.41	10.78	10.30	0.12
33.80	27.23	1.47	0.71	43.33	0.40	10.60	10.27	0.13
33.20	26.66	1.50	0.67	43.58	0.40	10.40	10.24	0.12
33.40	27.03	1.51	0.66	42.84	0.40	10.40	10.24	0.12
33.40	26.81	1.48	0.66	42.72	0.40	10.50	10.32	0.13
33.20	26.63	1.50	0.67	42.56	0.40	10.70	10.26	0.12
33.10	26.69	1.49	0.67	43.61	0.40	10.70	10.35	0.12
33.10	26.74	1.48	0.66	42.57	0.40	10.70	10.32	0.12
33.40	27.03	1.50	0.68	42.28	0.40	10.50	10.00	0.11
33.50	26.59	1.48	0.67	43.61	0.38	10.70	10.10	0.13
33.60	26.95	1.49	0.68	43.82	0.38	10.70	10.00	0.12
33.40	26.97	1.51	0.69	43.92	0.37	10.80	10.00	0.11
33.30	26.99	1.48	0.67	43.87	0.38	10.60	10.00	0.11
33.80	26.95	1.50	0.69	44.03	0.37	10.70	10.00	0.12
34.20	26.91	1.49	0.69	43.92	0.36	10.70	10.00	0.11
34.30	26.90	1.50	0.69	44.01	0.38	10.40	10.00	0.11
33.80	26.95	1.48	0.69	43.92	0.38		10.30	0.12
33.90	26.88	1.50	0.69	44.01	0.37		10.42	0.12
33.21	27.81	1.45	0.66	42.80	0.38		10.32	0.13
33.38	27.72	1.49	0.66	43.00	0.37		10.10	0.13
32.43	27.82	1.46	0.66	42.80	0.37		10.29	0.12
33.18	27.83	1.44	0.64	42.80	0.38		10.32	0.13
32.89	27.70	1.47	0.66	42.90	0.37		10.22	0.13
33.50	27.80	1.44	0.65	42.80	0.37		10.27	0.13
32.75	27.82	1.45	0.65	42.70	0.37			0.13
33.23	27.81	1.46	0.65	42.90				0.13
33.10	26.80			43.40				0.10
33.20	26.90			43.81				0.11
33.40	26.90			43.51				0.10
33.40	26.70			42.36				0.13
33.20	26.50			44.00				0.11
33.90	26.90			42.54				
33.80	26.90			43.22				
33.80	27.35							
32.30	26.97							
32.40	27.28							
32.40	27.12							
32.60	27.38							
32.40	27.23							
32.30	27.31							
32.60	27.40							
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33.60								
33.40								
33.50								
33.40								
33.70								
33.60								
33.60								

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.
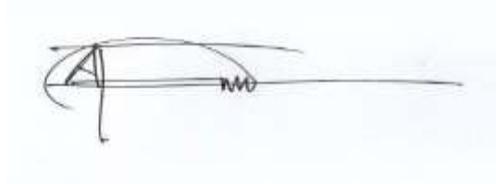
02 August 2017

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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	Element	Gen Method	N	Mean	s	RSD %	Unit
Ag	2A_MICP	16	127.438	2.308	1.811	ppm	MnO	CALC	8	0.035	0.001	2.433	%
Ag	Pb Collection	8	191.119	4.683	2.450	ppm	MnO	FUS	16	0.033	0.003	8.179	%
Al	4A_MICP	32	5865.852	3443.025	58.696	ppm	Mo	4A_MICP	32	8.953	1.608	17.963	ppm
Al_2O_3	CALC	7	1.500	<0.001	<0.001	%	Na	4A_MICP	32	350.000	50.800	14.514	ppm
Al_2O_3	FUS	15	1.441	0.062	4.276	%	Na_2O	4A_MICP	8	0.047	0.002	3.217	%
Ars	4A_MICP	31	837.323	57.615	6.881	ppm	Na_2O	CALC	8	0.048	0.005	9.745	%
Ba	4A_MICP	29	47.069	6.595	14.012	ppm	Na_2O	FUS	3	0.093	0.015	16.366	%
BaO	CALC	7	0.006	<0.001	2.525	%	Na_2O	XRF	24	0.122	0.057	47.084	%
BaO	XRF	9	0.010	<0.001	<0.001	%	Nb	4A_MICP	15	0.887	0.125	14.052	ppm
Be	4A_MICP	7	0.100	<0.001	<0.001	ppm	Nd	4A_MICP	14	8.125	0.112	1.381	ppm
Bi	4A_MICP	24	115.783	20.582	17.776	ppm	Ni	4A_MICP	32	663.719	77.338	11.652	ppm
Ca	4A_MICP	30	4796.667	103.335	2.154	ppm	P	4A_MICP	30	303.333	357.658	117.909	ppm
CaO	CALC	8	0.688	0.016	2.300	%	P	XRF	8	200.000	<0.001	<0.001	ppm
CaO	FUS	15	0.614	0.018	2.939	%	P_2O_5	4A_MICP	8	0.026	0.005	19.716	%
Cd	4A_MICP	32	11.653	2.642	22.673	ppm	P_2O_5	CALC	1	0.030	<0.001	<0.001	%
Ce	4A_MICP	14	19.379	0.269	1.390	ppm	P_2O_5	XRF	31	0.033	0.004	12.438	%
Co	4A_ICPES	8	319.875	8.008	2.503	ppm	Pb	4A_MICP	31	737.045	56.881	7.717	ppm
Co	4A_MICP	40	299.400	22.441	7.495	ppm	PbO	XRF	7	0.060	<0.001	<0.001	%
Cr	4A_MICP	31	398.742	88.624	22.226	ppm	Pd	Pb Collection	7	0.400	<0.001	<0.001	g/t
Cr_2O_3	CALC	8	0.062	0.002	2.910	%	Pr	4A_MICP	16	2.271	0.066	2.910	ppm
Cr_2O_3	FUS	8	0.070	<0.001	<0.001	%	Pt	Pb Collection	7	0.400	<0.001	<0.001	g/t
Cr_2O_3	XRF	40	0.093	0.015	15.647	%	Rb	4A_MICP	16	11.475	0.634	5.525	ppm
Cs	4A_MICP	13	0.454	0.078	17.104	ppm	Re	4A_MICP	2	0.025	0.007	28.284	ppm
Cu	2A_MICP	8	114875.000	2232.071	1.943	ppm	S	4A_MICP	16	32.301	0.918	2.843	%
Cu	XRF	16	116062.500	1611.159	1.388	ppm	Sb	4A_MICP	31	25.594	5.841	22.823	ppm
CuO	XRF	7	14.769	0.034	0.233	%	Sc	4A_MICP	22	1.041	0.232	22.317	ppm
Dy	4A_MICP	16	0.916	0.114	12.407	ppm	Se	4A_MICP	15	15.467	0.915	5.919	ppm
Er	4A_MICP	16	0.556	0.051	9.211	ppm	Sm	4A_MICP	14	1.325	0.051	3.845	ppm
Eu	4A_MICP	16	0.269	0.036	13.373	ppm	Sn	4A_MICP	24	18.292	12.736	69.629	ppm
Fe	4A_MICP	16	317225.000	7414.535	2.337	ppm	SO_3	CALC	8	78.789	1.746	2.217	%
Fe	XRF	7	302700.000	1274.101	0.421	ppm	SO_3	XRF	14	11.252	1.324	11.770	%
Fe_2O_3	CALC	8	46.226	0.724	1.566	%	Sr	4A_MICP	31	17.787	0.985	5.537	ppm
Fe2O3	FUS	24	44.66	0.969	2.20	%	Ta	4A_MICP	2	0.100	<0.001	<0.001	ppm
Ga	4A_MICP	14	2.586	0.183	7.092	ppm	Tb	4A_MICP	15	0.119	0.018	15.013	ppm
Gd	4A_MICP	16	0.981	0.091	9.280	ppm	Te	4A_MICP	16	5.438	0.228	4.187	ppm
Ge	4A_MICP	1	0.500	<0.001	<0.001	ppm	Th	4A_MICP	16	2.025	0.106	5.257	ppm
Hf	4A_MICP	15	1.720	0.077	4.503	ppm	Ti	4A_MICP	32	0.038	0.011	28.455	%
Ho	4A_MICP	15	0.201	0.005	2.565	ppm	TiO_2	CALC	8	0.067	0.004	6.306	%
Ind	4A_MICP	16	5.447	0.169	3.110	ppm	TiO_2	FUS	16	0.120	0.005	4.303	%
K	4A_MICP	31	3396.774	111.007	3.268	ppm	Tl	4A_MICP	16	0.569	0.079	13.946	ppm
K_2O	CALC	8	0.390	0.011	2.741	%	Tm	4A_MICP	10	0.084	0.008	10.039	ppm
K_2O	FUS	16	0.377	0.031	8.262	%	U	4A_MICP	16	5.631	0.444	7.881	ppm
La	4A_MICP	30	10.057	0.678	6.743	ppm	V	4A_MICP	25	22.760	15.265	67.070	ppm
Li	4A_MICP	30	2.200	0.407	18.493	ppm	W	4A_MICP	24	19.104	3.508	18.361	ppm
Lu	4A_MICP	8	0.080	<0.001	<0.001	ppm	Y	4A_MICP	30	4.613	0.680	14.743	ppm
Mg	4A_MICP	32	3378.125	112.836	3.340	ppm	Yb	4A_MICP	14	0.561	0.045	7.959	ppm
MgO	CALC	8	0.544	0.012	2.184	%	Zn	4A_MICP	31	1708.484	45.000	2.634	ppm
MgO	FUS	16	0.532	0.034	6.412	%	ZnO	XRF	8	0.195	0.005	2.741	%
MgO	XRF	39	0.579	0.054	9.318	%	Zr	4A_MICP	32	61.013	10.434	17.101	ppm
Mn	4A_MICP	32	254.344	22.372	8.796	ppm	ZrO_2	XRF	8	0.010	<0.001	<0.001	%
Mn	XRF	8	300.000	<0.001	<0.001	ppm							
Mn_3O_4	XRF	8	0.040	<0.001	<0.001	%							

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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]:

$$z = \frac{x - x_a}{s_p}$$

[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:

$$C_{calc} = \frac{s_{max}^2}{\sum_{i=1}^{l} s_i^2}$$

[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

$$G_{1\ calc} = \frac{|Suspect\ value - \bar{x}|}{s}$$ [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%. 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 $G_{2\ calc}$

$$G_{2\ calc} = \frac{|x_n - x_1|}{s}$$ [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 $G_{3\ calc}$ given by:

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

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

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

$$Observed\ \%RSD = \frac{s}{Mean} x100$$ [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):

$$HorRat = \frac{\%RSD\ Observed}{\%RSD\ Calculated}$$ [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*) :

$$\bar{\bar{x}} = \sum \frac{x}{n}$$
[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):

$$s_r \leq 0.3 u_c$$
[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.

$$SST = \sum (x - \bar{\bar{x}})^2$$
[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.

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

$$MS = \frac{SSB}{n - 1}$$
[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.

$$SSW = \sum df \cdot s^2$$
[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:

$$MSW = \frac{SSW}{P - n}$$ [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:

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

Within laboratory repeatability is determined as

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

and, the between laboratory precision as

$$s_s = \sqrt{\frac{(MSW - MSB)}{n}}$$ [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.

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

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

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 Al_2O_3 concentration by XRF analysis, *i.e.* 9 individual fused glass beads were prepared. The observed mean and standard deviation of the replicate data are shown with the certified value and expanded uncertainty in Table 9. In validation of accuracy, the hypothesis question is: Is the difference between the observed mean and the certified value statistically significant at a level of confidence of 95%? Alternatively put, is there sufficient evidence to conclude that the data *i.e.* replicates generated, are inaccurate?

The relevant hypotheses are:

Null hypothesis: 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:

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

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 ±2s and ±3s, where *s* is the standard deviation calculated from [21].
8. Construct the Shewhart control chart around the mean of *n* replicates;
9. Use ±2s as the warning limits;
10. Use ±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 105ºC 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:

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

$$Air\ dry\ basis\ concentration = MCF\ x\ certified\ value\ on\ a\ dry\ basis \qquad [23]$$

Example

The moisture content determined at 105ºC 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:

$$Moisture\ correction\ factor = \frac{100 - 0.500}{100} = 0.995$$

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:

$$0.995\ x\ 12.62\% = 12.56\%$$

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 1µg or 0.001mg. Even with a microscope it may be difficult to locate and pick up a prill weighing ten times that amount (*i.e.* 0.01mg or 10µg) and weigh it. Assuming that an analyst can weigh a prill of 1µg then the LOD becomes 1µg. However, the concentration factor would be 50 times for a 50 gram assay sample and therefore the LOD in g/t becomes 1µg divided by the original mass of the sample in grams taken for fire assay [24]. Therefore, the LOD in fire assay is computed as:

$$LOD = \frac{m\ (\mu g)}{Mass_{assay}\ (g)}\ (g/t)$$

[24]

And, the limit of quantitation (LOQ), is simply the LOD multiplied by 10 (Long & Winefordner, 1983):

$$LOQ = 10 \cdot \frac{m\ (\mu g)}{Mass_{assay}\ (g)}\ (g/t)$$

[25]

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be 0.02g/t. *i.e.* 1µg = 1g/t, therefore 1µg/50g = 0.02g/t. If no prill was found to be weighed then the LOD result would be <0.02 g/t or "not detected". Table 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 1µg or 0.001mg.

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

Table 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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