



African Mineral Standards

MATRIX REFERENCE MATERIALS

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AMIS0402

Certified Reference Material

**Manganese Ore, Wessels Mine, Kalahari Manganese
Field, South Africa**

Certificate of Analysis

**Recommended Concentrations and Limits¹
(at two Standard Deviations)**

Certified Concentrations²

Mn Fusion	43.01	±	4.00	%
Mn XRF	43.97	±	0.36	%
Fe M/ICP	14.53	±	1.22	%
Fe Fusion	15.38	±	1.18	%
Ca M/ICP	3.94	±	0.34	%
Ca Fusion	3.88	±	0.34	%
Specific Gravity	4.62	±	0.18	

1. Manufacturers recommended limits for use of the material as control samples, based on two standard deviations, calculated using "Between Laboratory" statistics for treatment of the data for trivial, non-trivial and technically invalid results. See sections 1, 9 and 12.

2. There is additional certified major element data presented on p2 and uncertified trace element data presented as an appendix.

Major Element Recommended Concentrations and Limits (at two Standard Deviations)

Certified Concentrations

Al ₂ O ₃	0.38	±	0.04	%
CaO	5.70	±	0.16	%
Fe ₂ O ₃	22.12	±	0.26	%
MgO	0.54	±	0.06	%
MnO	56.77	±	0.40	%
P ₂ O ₅	0.10	±	0.01	%
SiO ₂	4.31	±	0.16	%
LOI	4.97	±	0.28	%

Provisional Concentrations

Cr ₂ O ₃	0.05	±	0.01	%
Na ₂ O	0.11	±	0.03	%

Indicated Means

K ₂ O	0.02	%
TiO ₂	0.024	%

1. **Intended Use:** AMIS0402 can be used to check analysis of samples of manganese ores hosted by banded manganese formation sequences with a similar grade and matrix.

It is a matrix matched Certified Reference Material, fit for use as control samples in routine assay laboratory quality control when inserted within runs of samples and measured in parallel to the unknown. Its purpose is to monitor inter-laboratory or instrument bias and within lab precision. It can be used, indirectly, to establish the traceability of results to an SI system of units.

The recommended concentrations and limits for this material are property values based on a measurement campaign (round robin) and reflect consensus results from the laboratories that participated in the round robin.

Slight variations in analytical procedures between laboratories will reflect as slight biases to the recommended concentrations (see 19). Good laboratories will report results within the two standard deviation levels with a failure rate of <10 %.

The material can also be used for method development and for the calibration of equipment.

2. **Origin of Material:** The raw material for AMIS0402 was supplied by BHP Billiton from the Wessels Manganese Mine situated in the Kalahari manganese field, 14 km north west of Hotazel, in the Northern Cape Province, South Africa. The ore is a diagenetic to very low grade metamorphic, carbonate-bearing braunitic manganolite, preserved in the Griqualand West Basin of the 2500 Ma old Neoproterozoic Transvaal Supergroup.

3. **Mineral and Chemical Composition:** The main manganese mineral is braunite. It is often intergrown with kutnahorite and other minerals (hematite, hausmannite, Mg-calcite, calcite, jacobsonite, serpentine and garnet), which are present in variable amounts.

- 4. Appearance:** The material is a very fine Dusky brown powder (Corstor 5YR 2.5/2).
- 5. Handling instructions:** The material is packaged in Laboratory Packs and Explorer Packs that must be shaken or otherwise agitated before use. Normal safety precautions for handling fine particulate matter are suggested, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.
- 6. Method of Preparation:** The material was crushed, dry-milled and air-classified to <54um. Wet sieve particle size analysis of random samples confirmed the material was 98.5% <54um. It was then blended in a bi-conical mixer, systematically divided and then sealed into 1kg Laboratory Packs. Explorer Packs are subdivided from the Laboratory packs as required. Samples were randomly selected for homogeneity testing and third party analysis. Statistical analysis of both homogeneity and consensus test results were carried out by an independent statistician.
- 7. Methods of Analysis requested:**
1. Mn. Fusion, ICP-OES.
 2. Multi element scan to include Mn. Multi-acid digest, ICP-OES or ICP-MS.
 3. Majors (Al₂O₃, CaO, Cr₂O₃, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, TiO₂, V₂O₅. LOI.) XRF fusion.
 4. SG, gas pycnometer.
- 8. Information requested:**
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. Report all QC data, to include replicates, blanks and certified reference materials used.
- 9. Method of Certification:** Twenty two laboratories were each given eight randomly selected packages of sample. Twenty one of the laboratories submitted results in time for certification.
- Final limits were calculated after first determining if all data was compatible within a spread normally expected for similar analytical methods done by reputable laboratories. Data from any one laboratory was then removed from further calculations when the mean of all analyses from that laboratory failed a "t test" of the global means of the other laboratories. The means and standard deviations were then re-calculated using all remaining data. Any analysis that fell outside of the new two standard deviations was removed from the ensuing data base. The mean and standard deviations were again calculated using the remaining data.
- The "between-laboratory" standard deviation is used in the calculation to eliminate technically and statistically invalid data. Upper and lower limits are based on the standard deviation of the remaining data, which reflect individual analyses and can be used to monitor accuracy in routine laboratory quality control. This is different to limits based on standard deviations derived from grouped set of analyses (see 12), which provide important measures for precision and trueness, but which are less useful for routine QC.
- Standards with an RSD of near or less than 5 % are termed "Certified", RSD's of between near 5 % and 15 % are termed "Provisional", and RSD's over 15 % are termed "Informational".
- 10. Participating Laboratories:** The 21 out of 22 laboratories that provided results timeously were (not in same order as in the table of assays):
1. ACME Analytical Laboratories Ltd CA
 2. Activation Laboratories Pty Ltd (ActLabs) CA
 3. ALS Ammtec (Australia)
 4. ALS Chemex Laboratory Group Brisbane Australia

5. ALS Chemex Laboratory Group Johannesburg SA
6. ALS Chemex Laboratory Group Perth WA
7. ALS Chemex Laboratory Group Vancouver CA
8. ALS OMAC (Ireland)
9. BHP Billiton Mamatwan Mine (South Africa)
10. BHP Billiton Wessells (South Africa)
11. BV Amdel (Australia)
12. Genalysis Laboratory Services (South Africa) Pty
13. Genalysis Laboratory Services (W Australia P)
14. Intertek Utama Services (Indonesia)
15. Set Point Laboratories (Isando) SA
16. SGS Australia Pty Ltd (Newburn) WA
17. SGS Geosol Laboratories Ltda (Brazil)
18. SGS Mineral Services Lakefield (Canada)
19. SGS South Africa (Pty) Ltd - Booyens JHB
20. SGS Vancouver (Canada)
21. Ultra Trace (Pty) Ltd WA

11. Assay Data: Data as received from the laboratories for the important certified elements listed on p1 is set out below.

Lab Code	Mn Fusion %	Mn XRF %	Fe M/ICP %	Fe Fusion %	Ca M/ICP %	Ca Fusion %	Al ₂ O ₃ XRF %	CaO XRF %	Cr ₂ O ₃ XRF %	Fe ₂ O ₃ XRF %	K ₂ O XRF %	MgO XRF %	MnO XRF %	Na ₂ O XRF %	P ₂ O ₅ XRF %	SiO ₂ XRF %	TiO ₂ XRF %	LOI %	SG pyc
A		44.5					0.32			21.5	0.02	0.18	57.4	0.09	0.10	4.02			
A		44.7					0.32			21.6	0.02	0.19	57.7	0.07	0.10	4.02			
A		44.5					0.32			21.4	0.02	0.19	57.5	0.09	0.10	4.01			
A		44.6					0.32			21.4	0.02	0.19	57.5	0.09	0.10	4.02			
A		44.5					0.32			21.7	0.02	0.20	57.4	0.09	0.10	4.01			
A		44.6					0.32			21.6	0.02	0.19	57.5	0.09	0.10	4.02			
A		44.6					0.33			21.7	0.02	0.20	57.5	0.07	0.10	4.02			
A		44.5					0.32			21.4	0.02	0.19	57.4	0.09	0.10	4.00			
B		44.6					0.35	5.58		22.2	0.02	0.35	57.9	0.06	0.10	4.17			
B		44.5					0.35	5.58		22.2	0.02	0.35	57.8	0.05	0.10	4.16			
B		44.6					0.35	5.58		22.2	0.02	0.35	57.9	0.06	0.10	4.15			
B		44.6					0.35	5.58		22.2	0.02	0.36	57.9	0.05	0.10	4.16			
B		44.8					0.36	5.60		22.3	0.02	0.36	58.2	0.05	0.10	4.17			
B		44.7					0.35	5.59		22.2	0.02	0.36	58.0	0.06	0.10	4.15			
B		44.7					0.35	5.58		22.2	0.02	0.35	58.0	0.05	0.10	4.17			
B		44.7					0.36	5.58		22.2	0.02	0.36	58.0	0.06	0.10	4.16			
C	41.1	44.1	14.9		4.05		0.38	5.70	0.04	22.2	0.01	0.53	56.9	0.10	0.10	4.30		5.06	4.48
C	43.3	44.1	14.8		4.03		0.39	5.73	0.05	22.2	0.01	0.54	56.8	0.10	0.10	4.30		5.06	4.42
C	42.1	44.0	14.8		4.02		0.39	5.69	0.04	22.2	0.02	0.53	56.8	0.11	0.10	4.30		5.01	4.43
C	42.5	44.1	14.9		4.07		0.39	5.70	0.05	22.2	0.01	0.54	57.0	0.10	0.10	4.30		5.02	4.44
C	40.8	44.1	14.8		4.07		0.39	5.69	0.05	22.2	0.01	0.54	57.0	0.10	0.10	4.40		4.98	4.45
C	42.6	44.3	14.7		3.98		0.39	5.73	0.05	22.2	0.01	0.52	57.1	0.10	0.10	4.30		5.03	4.42
C	43.1	44.6	14.6		4.00		0.39	5.74	0.05	22.4	0.02	0.55	57.6	0.11	0.10	4.30		4.99	4.44
C	41.3	44.2	14.8		4.04		0.39	5.72	0.05	22.2	0.02	0.53	57.0	0.09	0.10	4.30		4.96	4.44
D		44.1	15.5		4.21		0.39	5.72	0.05	22.1	0.02	0.58	56.8		0.11	4.41	0.03	4.94	4.55
D		44.0	15.5		4.21		0.40	5.70	0.05	22.1	0.02	0.59	56.8		0.11	4.42	0.03	5.00	4.65
D		44.0	15.5		4.22		0.40	5.72	0.05	22.1	0.02	0.58	56.8		0.11	4.38	0.03	5.02	4.56
D		44.1	15.7		4.21		0.40	5.72	0.04	22.1	0.02	0.59	56.8		0.11	4.40	0.03	4.99	4.55
D		44.0	15.7		4.21		0.39	5.71	0.05	22.1	0.02	0.58	56.7		0.11	4.39	0.03	4.96	4.65
D		44.1	15.8		4.21		0.40	5.72	0.04	22.2	0.02	0.59	56.9		0.11	4.39	0.03	4.97	4.69
D		44.0	15.7		4.18		0.39	5.73	0.04	22.1	0.02	0.59	56.8		0.11	4.41	0.03	4.95	4.58
D		44.1	15.6		4.19		0.41	5.72	0.04	22.1	0.02	0.59	56.9		0.11	4.38	0.03	4.95	4.60
E			13.5	15.0	3.89	3.70													4.64
E			13.6	14.4	3.94	3.70													4.64
E			13.3	14.3	3.80	3.70													4.65
E			13.6	14.9	3.91	3.70													4.64
E			13.4	15.4	3.92	3.70													4.63
E			13.7	15.3	4.00	3.70													4.63
E			14.0	15.3	4.07	3.70													4.64
E			13.8	15.2	3.98	3.70													4.65
G		43.9	16.0	15.5	3.94	3.80	0.37	5.59	0.05	21.8	0.01	0.55	56.7	0.13	0.10	4.34	0.03	5.50	
G		44.0	16.3	14.8	3.94	3.70	0.37	5.62	0.05	21.8	0.01	0.55	56.8	0.12	0.11	4.34	0.03	5.37	
G		43.9	16.4	14.5	4.02	3.60	0.37	5.59	0.04	21.8	0.01	0.54	56.6	0.12	0.11	4.30	0.03	5.45	
G		43.9	16.4	15.0	4.17	3.70	0.37	5.57	0.04	21.7	0.01	0.54	56.6	0.12	0.11	4.32	0.03	5.38	
G		43.9	16.9	14.6	4.10	3.60	0.38	5.60	0.04	21.8	0.02	0.55	56.7	0.12	0.11	4.31	0.03	5.50	
G		43.9	16.3	14.9	4.04	3.70	0.37	5.60	0.04	21.8	0.01	0.54	56.6	0.13	0.11	4.30	0.03	5.42	
G		43.9	17.1	15.3	4.17	3.70	0.38	5.61	0.04	21.8	0.02	0.55	56.6	0.12	0.11	4.35	0.03	5.33	
G		43.9	16.4	14.9	3.98	3.60	0.37	5.62	0.05	21.8	0.02	0.54	56.7	0.11	0.11	4.33	0.03	5.34	
H		43.5					0.37	5.80	0.04	21.7	0.02	0.51	56.1	0.11	0.11	4.19	0.03	4.95	
H		43.4					0.39	5.82	0.05	21.7	0.02	0.52	56.0	0.13	0.11	4.23	0.03	4.89	
H		43.3					0.38	5.79	0.05	21.7	0.02	0.52	55.9	0.12	0.10	4.24	0.03	4.98	
H		43.4					0.37	5.80	0.05	21.7	0.02	0.51	56.0	0.12	0.10	4.19	0.03	4.99	
H		43.8					0.39	5.85	0.04	21.9	0.02	0.51	56.5	0.11	0.11	4.21	0.03	4.96	
H		43.4					0.39	5.82	0.05	21.7	0.01	0.51	56.0	0.10	0.10	4.24	0.03	4.95	
H		43.4					0.39	5.83	0.04	21.7	0.02	0.50	56.0	0.12	0.10	4.20	0.02	5.04	
H		43.4					0.38	5.80	0.05	21.8	0.02	0.50	56.0	0.13	0.10	4.21	0.03	4.90	

12. Measurement of Uncertainty :(ref Dr Hugh Bartlett, Hugh Bartlett Consulting CC.)

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 (sample uncertainty and measurement uncertainty) are included in the final combined standard uncertainty determination.

The uncertainty measurement takes into consideration the between lab and the within lab variances and is calculated from the square roots of the variances of these components using the formula:

$$\text{Combined standard uncertainty} = \sqrt{(\text{between lab.var/no of labs}) + (\text{mean square within lab.var /no of assays})}$$

These uncertainty measurements may be used, by laboratories, as a component for calculating the total uncertainty for method validation according to the relevant ISO guidelines.

Analyte	Method	Unit	S ¹	σ_L ²	S _w ³	CSU ⁴
Mn	Fusion	%	2.004	2.175	0.581	0.826
Mn	XRF	%	0.179	0.127	0.092	0.038
Fe	M/ICP	%	0.608	0.472	0.188	0.138
Fe	Fusion	%	0.589	0.657	0.257	0.271
Ca	M/ICP	%	0.171	0.127	0.061	0.036
Ca	Fusion	%	0.166	0.190	0.063	0.078
Al ₂ O ₃	XRF	%	0.021	0.014	0.010	0.004
CaO	XRF	%	0.078	0.051	0.027	0.013
Cr ₂ O ₃	XRF	%	0.005	0.002	0.004	0.001
Fe ₂ O ₃	XRF	%	0.131	0.076	0.073	0.020
K ₂ O	XRF	%	0.004	0.002	0.003	0.001
LOI		%	0.136	0.093	0.070	0.027
MgO	XRF	%	0.027	0.017	0.014	0.004
MnO	XRF	%	0.198	0.131	0.118	0.040
Na ₂ O	XRF	%	0.013	0.010	0.007	0.003
P ₂ O ₅	XRF	%	0.006	0.003	0.003	0.001
SiO ₂	XRF	%	0.083	0.052	0.036	0.013
TiO ₂	XRF	%	0.007	0.004	0.004	0.001
SG	pyc		0.088	0.063	0.038	0.018

1 S - Std Dev for use on control charts.

2 σ_L - Betw Lab Std Dev, for use to calculate a measure of accuracy.

3 S_w - Within Lab Stc Dev, for use to calculate a measure of precision.

4 CSU - Combined Standard Uncertainty, a component for use to calculate the total uncertainty in method validation.

13. Uncertified values: The Certified, Provisional and Informational values listed on p1 and p2 of this certificate fulfill the AMIS statistical criteria regarding agreement for certification and have been independently validated by Dr Barry Smees.

14. 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, who have maintained measurement traceability during the analytical process.

15. Certification: AMIS0402 is a new material.

16. 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.

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


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

19. Recommended use: The data used to characterize this CRM has been scrutinized using outlier treatment techniques. This, together with the number of participating laboratories, should overcome any "inter-laboratory issues" and should lead to a very accurate measure for the given methods, notwithstanding the underlying assumption that what the good inter-laboratory labs reported was accurate. However an amount of bad data might have had an effect, resulting in limits which in some situations might be too broad for the effective monitoring of a single analytical method, laboratory or production process. Users should set their own limits based on their own data quality objectives and control measurements, after determining the performance characteristics of their own particular method, using a minimum of 20 analyses using this CRM. User set limits should normally be within the limits recommended on p1 and 2 of this certificate.

20. Legal Notice: This certificate and the reference material described in it have been prepared with due care and attention. However AMIS, Set Point Technology (Pty) Ltd, Mike McWha, Dr Barry Smee and Smee and Associates Ltd; accept no liability for any decisions or actions taken following the use of the reference material.

18 June 2013

Certifying Officers:



African Mineral Standards: _____

Mike McWha
BSc (Hons), FGSSA, MAusIMM, Pr.Sci.Nat



Geochemist: _____

Barry W. Smee
BSc, PhD, P.Geo, (B.C.)

Appendix - uncertified trace element statistics

Analyte	Method	Unit	Mean	2SD	RSD%	n
Ag	M/ICP	ppm	0.24	1.4	293	33
Al	M/ICP	%	0.22	0.07	16.6	96
As	M/ICP	ppm	25.1	7.8	15.6	80
Ba	M/ICP	ppm	4910	370	3.8	90
Be	M/ICP	ppm	0.98	0.27	13.7	72
Bi	M/ICP	ppm	2.5	12.1	242	56
Cd	M/ICP	ppm	0.84	2.1	125	72
Ce	M/ICP	ppm	7.8	0.85	5.5	55
Co	M/ICP	ppm	83.8	19.8	11.8	121
Cr	M/ICP	ppm	266	65.4	12.3	96
Cs	M/ICP	ppm	0.16	0.10	29.6	56
Cu	M/ICP	ppm	139	21.1	7.6	112
Dy	M/ICP	ppm	1.7	0.37	11.2	16
Er	M/ICP	ppm	1.2	0.22	9.0	16
Eu	M/ICP	ppm	0.29	0.03	4.4	8
Ga	M/ICP	ppm	7.1	2.0	13.9	56
Gd	M/ICP	ppm	1.6	0.47	14.9	16
Ge	M/ICP	ppm	0.25	0.89	175	42
Hf	M/ICP	ppm	0.10	0.00	0.00	34
Ho	M/ICP	ppm	0.44	0.08	9.2	14
In	M/ICP	ppm	0.01	0.01	33.1	25
K	M/ICP	%	0.02	0.01	30.9	94
La	M/ICP	ppm	7.1	1.0	6.9	72
Li	M/ICP	ppm	40.6	11.8	14.6	104
Lu	M/ICP	ppm	0.17	0.14	41.4	16
Mg	M/ICP	%	0.29	0.05	9.4	96
Mn	M/ICP	%	44.1	1.2	1.3	37
Mo	M/ICP	ppm	3.4	4.5	65.6	56
Na	M/ICP	%	0.10	0.03	14.2	104
Nb	M/ICP	ppm	0.68	0.10	7.2	48
Nd	M/ICP	ppm	5.5	1.5	13.9	16
Ni	M/ICP	ppm	26.6	18.4	34.5	112
P	M/ICP	ppm	463	84.3	9.1	80
Pb	M/ICP	ppm	89.3	39.7	22.3	104
Pr	M/ICP	ppm	1.3	0.3	13.0	16
Rb	M/ICP	ppm	0.60	0.21	17.2	63
S	M/ICP	%	0.13	0.07	25.6	79
Sb	M/ICP	ppm	1.1	1.6	72.2	66
Sc	M/ICP	ppm	1.6	0.69	21.1	83
Si	M/ICP	%	2.1	0.04	0.92	8
Si	Fusion	%	2.2	0.30	6.7	40
Sm	M/ICP	ppm	1.1	0.39	17.9	16
Sn	M/ICP	ppm	0.52	0.19	18.0	46
Sr	M/ICP	ppm	1761	220	6.2	96
Ta	M/ICP	ppm	0.05	0.00	0.00	26
Tb	M/ICP	ppm	0.22	0.05	10.8	16
Te	M/ICP	ppm	0.22	0.37	82.3	34
Th	M/ICP	ppm	0.77	0.09	6.0	62
Ti	M/ICP	%	0.01	0.01	22.7	96
Tl	M/ICP	ppm	0.57	0.10	9.0	57
Tm	M/ICP	ppm	0.20	0.00	0.00	14
U	M/ICP	ppm	0.34	0.09	13.7	62
V	M/ICP	ppm	18.1	14.2	39.1	95
W	M/ICP	ppm	2.0	0.43	10.6	56
Y	M/ICP	ppm	15.0	1.6	5.3	80
Yb	M/ICP	ppm	1.2	0.55	23.5	16
Zn	M/ICP	ppm	212	43.1	10.2	112
Zr	M/ICP	ppm	8.9	4.4	24.7	88