

## QOTHO CERTIFIED REFERENCE MATERIAL (QCRM)

### QCRM-2-168

MANGANESE ORE - HIGH GRADE

### CERTIFICATE OF ANALYSIS

CERTIFIED VALUES			
ANALYTES	UNITS	CONCENTRATIONS	EXPANDED UNCERTAINTY
Mn	%	42.32	±0.25
ASSIGNED VALUES (FOR INFORMATION ONLY)			
ANALYTES	UNITS	CONCENTRATIONS	EXPANDED UNCERTAINTY
Al <sub>2</sub> O <sub>3</sub>	%	0.30	±0.02
BaO	%	0.53	±0.03
CaO	%	5.10	±0.12
FeO	%	23.58	±0.20
MgO	%	0.29	±0.03
P	%	0.031	±0.005
S	%	0.117	±0.008
SiO <sub>2</sub>	%	3.96	±0.11

**1. Use:**

QCRM-2-168 is a certified reference material which is suitable for use as random control samples in routine analytical laboratory quality control, when inserted within a batch of samples and measured in parallel to the unknown. The QCRM can also be used as a control sample in the analysis of samples of a similar type, verification of analytical methods for Manganese Ore and as a calibration standard for the calibration of equipment used for analysing similar materials.

**2. Origin of Material:**

This standard was sponsored by Assmang Blackrock Manganese Mine, located approximately 14 km north west of Hotazel, in the Northern Cape Province, South Africa.

**3. Mineral and Chemical Composition:**

The manganese ores of the Kalahari Manganese field are contained within sediments of the Hotazel Formation of the Griqualand West Sequence, a subdivision of the Proterozoic Transvaal Supergroup. The average thickness of the Hotazel Formation is approximately 40 meters. The manganese ore bodies exhibit a complex mineralogy and more than 200 mineral species have been identified to date. The hydrothermal upgrading has resulted in a zoning of the orebody with regard to fault positions. The ore is rich in Hausmannite, Bixbyite and Braunite II. It consists of shales, siltstones, quartzites, subordinate carbonates and basaltic to amygdaloidal lavas.

**4. Date of Initial Issue:**

6 February 2023.

**5. Packaging & Handling instructions:**

The material was packaged as 100g unit sizes, placed in geo-envelopes, within a vacuum sealed aluminum foil bag. Open the seal of the foil with care and shake or otherwise agitate prior to use. Normal safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves, and a laboratory coat. Once opened, material must be stored in a cool, dry environment. Results on page 1 is presented on dry basis. Analysis should therefore be done on dry basis, after drying to constant mass, at 105 degrees Celsius.

**6. Method of Preparation:**

The material was sieved through a 75-micron screen and the oversize was re-milled to ensure 100% passing through the screen. It was then blended, systematically divided, and packaged into 100-gram zip-lock bags. Randomly selected samples, from the bags, were tested in-house via XRF, to confirm homogeneity. Once confirmed and certification completed, the items were placed in geo-envelopes and vacuum sealed in aluminium foil bags.

**7. Methods of Analysis used:**

- Sodium peroxide fusion with ICP-OES or AAS finish
- Multi-acid digestion with ICP-OES finish
- Fused beads with XRF finish.
- Pressed pellets with XRF finish
- Manganese and Iron by multi-acid digestion and Potentiometric titration
- Manganese and Iron by sodium peroxide fusion with Potentiometric titration
- Silica by multi-acid digestion and gravimetric finish
- Sulphur by combustion analysis.

**8. Analysis required:**

An instruction letter was sent to all participants. The analysis required was noted in the instruction letter and reporting template, including but not limited to  $Al_2O_3$ , BaO, CaO, FeO,  $K_2O$ , MgO, Mn, P, S and  $SiO_2$ .

**9. Participating Laboratories:**

NO	LABORATORY	COUNTRY
1.	AHK Richards Bay	South Africa
2.	ALS Geochemistry Kempton Park	South Africa
3.	ARM Machadodorp	South Africa
4.	Assmang Blackrock	South Africa
5.	Intertek Kathu	South Africa
6.	Manganese Metal Company	South Africa
7.	Mitra SK South Africa	South Africa
8.	UIS Analytical Services	South Africa

**10. Assay Data:**

Data used for Assigning Values and Certification.

LABORATORY	Al <sub>2</sub> O <sub>3</sub>	BaO	CaO	FeO	K <sub>2</sub> O	MgO	Mn	P	S	SiO <sub>2</sub>
UNIT	%	%	%	%	%	%	%	%	%	%
LAB001	0.259	0.527	5.293	23.677		0.334	42.141	0.028		4.007
LAB002	0.293	0.52	4.986	23.106		0.312	42.165		0.122	3.905
LAB003							41.953			
LAB004	0.305	0.516	5.13	23.86	< 0.050	0.299	42.1	0.029	0.31	3.915
LAB005	0.32		5	23.665		0.29	42.49	0.029	0.12	4
LAB006	0.315		4.98	23.695	0.019	0.3	42.675	0.035	0.116	3.845
LAB007							42.275			
LAB008	0.29		5.24	23.78		0.295	42.38	0.033	0.117	3.955
LAB009	0.315	0.578	4.975	23.17	0.009	0.27			0.118	
LAB010	0.3	0.51	5.105	23.62	0.01	0.285	42.62	0.03	0.11	4
LAB011							42.535			
LAB012	0.32		5.185	14.56		0.24	42.155	0.033		4.065

## 11. Method of Certification:

### QM is a SANAS Accredited Proficiency Testing Scheme Provider, No. PTS0012

This material was distributed as test items, in the Qotho Manganese PT Round 5 of 2021. The participating laboratories were each given 1 randomly selected sample from the batch, to analyse and report on in duplicate. Some laboratories reported results via more than one analytical method. Obvious blunders were resolved with the laboratories (if any), after which the data was processed using Robust Statistics, through PROLab Plus.

Not all the participating laboratories were accredited. Historical performance in Qotho PT Schemes, as well as an evaluation of the CRM QA/QC data generated by the laboratories, during the analysis of this QRM, were considered, to evaluate the competence of laboratories. Where competence could not be confirmed, the affected data was deselected from the dataset. Certification of analytes was then done, provided that a minimum of 10 qualifying datapoints remained available.

Where analytes could not be certified, estimate concentrations were assigned, using all the data in the dataset.

## 12. Measurement of Uncertainty:

Standard uncertainty,  $u_{CRM}$ , was calculated according to ISO 13528:2015 (equation 6), and it includes the effects of uncertainty due to inhomogeneity, transport, potential instability, and laboratory uncertainty. Because of all the uncertainties under consideration, QM further applies an expanded uncertainty, for certification purposes. The measurement uncertainty of the certified value is therefore calculated as follows:  $U_{CRM} = k u_{CRM}$ , where  $k$  is a coverage factor, which is determined from the Student's  $t$ -distribution, based on the degrees of freedom, per analyte. This presents a certified value, as follows:  $x_{CRM} \pm U_{CRM}$ .

Measurement uncertainty for Assigned values, are calculated in the same manner.

Laboratories which prefer to use the 95% measurement uncertainty, rather than the expanded uncertainty, all available information relating to measurement uncertainty of the certified/assigned values, are given below:

Analyte	Unit of measure	$s$ (Standard Deviation of Dataset)	$\nu$ (Degrees of Freedom)	$k$ (Coverage Factor)	$u$ (Standard Uncertainty)	95% Measurement Uncertainty	Expanded Uncertainty
Al <sub>2</sub> O <sub>3</sub>	%	0.020	8	2.306	0.008	± 0.02	± 0.02
BaO	%	0.024	4	2.776	0.009	± 0.02	± 0.03
CaO	%	0.145	8	2.306	0.051	± 0.10	± 0.12
FeO	%	0.274	8	2.306	0.087	± 0.17	± 0.20
MgO	%	0.04	8	2.306	0.011	± 0.02	± 0.03
Mn	%	0.302	10	2.228	0.11	± 0.22	± 0.25
P	%	0.004	6	2.447	0.002	± 0.004	± 0.005
S	%	0.011	6	2.447	0.003	± 0.006	± 0.008
SiO <sub>2</sub>	%	0.106	7	2.365	0.044	± 0.09	± 0.11

**13. 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 accredited laboratories, as ISO 17025 requires laboratories to use CRM's traceable to the SI units, during the calibration of their equipment. Not all laboratories were accredited.

Fortunately, most laboratories reported on the QA/QC CRMs used during the analysis of this QRM and reported the values obtained during the sample run. Evaluation of their QA/QC performance serves as further evidence of metrological traceability.

Equivalence tests were performed on all analytes to determine whether the metrologically traceable data and those for which traceability evidence was not available, could be treated as equal (at a level of significance of  $\alpha = 0.05$ ). Where equivalent, all the data was used. Where not equivalent, only the metrologically traceable data was considered.

**14. Minimum sample size:**

The recommended minimum sample size for the use of this material is as per the participants method validation criteria.

**15. Period of validity:**

The certified values are valid for this product, while still sealed in its original packaging, for a minimum period of 5 years from date of Initial Certification. Stability monitoring of inventory will be done at regular intervals. Any concerns regarding potential instability of the material, will immediately be communicated to all consumers.

**16. Legal:**

This certificate and the reference material described in it were prepared with due care and attention. The requirements of ISO Guide 31, ISO 17043 and ISO 17034 were followed in the preparation of this reference material and certificate of analysis.

Qotho Minerals, however, accepts no liability for any decisions or actions taken following the use of the reference material. The company has a complaints procedure, which will be made available upon request, should there be any dissatisfaction with either the product or the COA.

Certifying & Technical Signatories	
<i>Dr Hannelie de Beer (Pr. Sci. Nat.)</i>	<i>Takudzwa Tsapayi (Pr. Sci. Nat.)</i>
6 February 2023	

*This Certificate of Analysis (CoA) has been electronically signed using an Advanced Electronic Signature (AES) in terms of the Electronic Communications and Transactions Act No. 15, 2002 (ECT Act). Any amendments to the CoA can be detected by reference to the Signature Panel displayed in the electronic pdf version of the CoA.*

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