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UKAS REFERENCE MATERIALS
4004

BRITISH CHEMICAL STANDARD CERTIFIED REFERENCE MATERIAL

CERTIFICATE OF ANALYSIS
BCS-CRM No. 176/3
MANGANESE ORE

Prepared under rigorous laboratory conditions and, AFTER CERTIFICATION ANALYSIS IN GREAT BRITAIN, CANADA, CHINA, The CZECH REPUBLIC, GHANA, HUNGARY, INDIA, The NETHERLANDS and The REPUBLIC OF SOUTH AFRICA
issued by the Bureau of Analysed Samples Ltd.

ANALYSES

Mean of 4 values - mass content in %.

Analyst	Mn	Fe	SiO_2	Al_2O_3	TiO_2	CaO	MgO	P	Na_2O	K_2O	BaO	Co	Cu	*S*	*As_2O_3*	*B*
1	27.6221	1.0338	14.0843	2.5041	0.0968	6.8615	…	0.0602	…	…	0.0159	0.0057	0.0051	*0.2464*	*0.0457*	*0.0116*
2	27.6474	1.0299	14.3120	2.4523	0.0876	6.7125	4.7184	0.0626	0.2805	0.3533	0.0146	0.0056	0.0061	*0.2213*	*0.0519*	*0.0082*
3	27.7100	0.9950	14.5300	2.5303	0.0963	6.9548	4.7473	0.0605	0.2975	0.3700	0.0160	0.0050	0.0060	*0.2427*	*0.0455*	*0.0110*
4	27.6688	0.9498	14.3828	2.5300	0.1045	6.8098	4.6768	0.0578	0.2878	0.3888	0.0159	0.0053	0.0042	…	*0.0473*	…
5	27.6538	0.9353	14.2750	2.4350	0.0963	7.0550	4.8475	0.0593	…	0.3593	…	…	…	*0.2445*	…	…
6	27.7340	0.9580	14.2590	2.5598	0.0945	6.8853	4.6445	0.0577	0.2790	0.3825	0.0148	0.0058	0.0057	*0.2298*	*0.0493*	*0.0074*
7	27.6675	0.9425	14.5150	2.4275	0.0938	6.8050	4.6825	0.0583	0.3025	0.3575	0.0158	0.0055	0.0048	*0.2240*	*0.0495*	*0.0040*
8	27.7733	1.0020	14.2373	2.5358	0.0988	…	4.7198	0.0600	0.2838	0.3665	0.0163	0.0061	0.0052	*0.2205*	*0.0493*	*0.0094*
9	27.6494	0.9956	14.2675	2.5919	0.1069	6.9725	4.8194	0.0590	…	…	…	…	…	*0.2556*	…	…
10	27.5750	0.9950	14.3050	2.4989	0.1009	6.6890	4.6898	0.0613	0.2802	0.3503	0.0154	0.0052	0.0051	…	…	…
11	27.7030	0.9758	14.3139	2.5401	0.1011	6.7652	4.7981	0.0604	0.2773	0.3502	0.0158	0.0057	0.0059	*0.2323*	*0.0475*	*0.0074*
12	…	0.9443	14.3450	2.4500	…	6.7455	4.5932	0.0599	…	…	…	…	…	…	…	…
13	27.6066	1.0019	14.2412	2.4990	0.0975	6.6778	4.7304	0.0627	0.2803	0.3469	0.0162	0.0062	0.0057	*0.2284*	*0.0531*	*0.0085*
14	27.6500	0.9788	14.4375	2.4770	0.0929	6.7815	4.6859	0.0585	….	0.3680	…	…	…	*0.2349*	…	…
15	27.7129	0.9730	14.2571	2.5277	…	…	…	0.0628	…	…	…	…	…	*0.2319*	…	…
16	27.8001	…	…	2.4887	…	…	…	0.0626	…	…	…	…	…	…	…	….
17	27.8475	0.9175	14.0600	2.5000	0.0900	6.7985	4.6475	….	…	0.3650	…	…	…	*0.2325*	*0.0523*	*0.0132*
18	…	0.9713	14.5129	2.5162	0.1008	6.9750	4.7765	0.0609	…	…	…	…	…	*0.2436*	…	…
19	…	…	…	…	…	…	…	0.0589	…	…	…	…	…	…	…	…
20	27.7250	…	…	…	…	…	…	….	…	…	…	…	…	…	…	…
M_M	**27.6910**	**0.9764**	**14.3139**	**2.5036**	**0.0972**	**6.8326**	**4.7185**	**0.0602**	**0.2854**	**0.3632**	**0.0157**	**0.0056**	**0.0054**	*0.235*	*0.049*	*0.009*
s_M	0.0709	0.0326	0.1338	0.0437	0.0052	0.1147	0.0701	0.0017	0.0089	0.0130	0.0006	0.0004	0.0007			
s_W	0.0512	0.0135	0.0688	0.0269	0.0028	0.0408	0.0341	0.0010	0.0074	0.0041	0.0013	0.0003	0.0005			

Values given in italics are for information only

Additional Information: Analyst No.4 determined Cr and Sr by ICP and reported values of 0.003% and 0.021% respectively. The same Analyst determined Zn and Ni by XRF and reported values of 0.013% and 0.032% respectively along with a Loss On Ignition of 29.7%.

M_M: Mean of the laboratory mean values. **s_M**: standard deviation of the laboratory mean values.. **s_W**: average within laboratory standard deviation.

CERTIFIED VALUES (Cv)

mass content in %

	Mn	Fe	SiO_2	Al_2O_3	TiO_2	CaO	MgO	P	Na_2O	K_2O	BaO	Co	Cu
Cv	**27.69**	**0.976**	**14.31**	**2.504**	**0.0972**	**6.83**	**4.72**	**0.0602**	**0.285**	**0.363**	**0.0157**	**0.0056**	**0.0054**
C(95%)	0.04	0.017	0.07	0.022	0.0029	0.07	0.04	0.0009	0.007	0.009	0.0005	0.0003	0.0005

The half width confidence interval **C**(95%) = $\frac{t \times s_M}{\sqrt{n}}$ where "t" is the appropriate two sided Student's t value at the 95% confidence level for "n" acceptable mean values

For further information regarding the confidence interval for the certified value see ISO Guide 35:2006 sections 6.1 and 10.5.2

NB: Although widely accepted within the industry "mass content in %" is neither an SI nor an IUPAC supported quantity. Multiplication of the certified value (Cv) by 10^4 will yield the value in µg/g.

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NOTES ON METHODS USED

MANGANESE

Analysts Nos. 1, 2, 3, 7, 8, 10, 14, 17 and 20 determined manganese titrimetrically. Nos. 1, 2, 3, 7, 8, 10 and 17 titrated with Mn(VII), Nos. 1, 2 and 3 finishing with a potentiometric titration and No 10 after a zinc oxide separation. No. 14 titrated with Fe(II). Analysts Nos. 4, 5, 6 and 9 used X-Ray Fluorescence Spectrometry (XRF), No. 4 according to BS EN ISO 12677, whilst Nos. 11 and 13 used Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Analyst No.15 followed IS-1473:2004 and No. 16 IS: 1673 1960-1991.

IRON

Analysts Nos. 1 and 12 determined iron by Flame Atomic Absorption Spectrometry (FAAS). Nos. 2 and 10 titrated with Cr(VI) after reduction with Sn(II). Analysts Nos. 3, 7, 8, 11 and 13 used ICP-OES. Analyst No 15 followed IS-1473:2004. The remaining Analysts used XRF, No. 3 according to BS EN ISO 12677 and No 18 according to ISO 9516.

SILICA

Analysts Nos. 1, 2, 3, 7, 10, 12 and 13 determined silica gravimetrically, No. 1 after dehydration with hydrochloric acid, No. 2 after dehydration with sulphuric acid and No. 3 after dehydration with perchloric acid. No. 10 followed ISO 2598:1993, No 12 ISO 311 and No.13 ISO 5890:1981. Nos. 4, 5, 6, 9, 14 and 18 used XRF, No. 4 following BS EN ISO 12677 and No 18 ISO 9516. Analysts Nos. 8 and 11 used ICP-OES. No 15 followed IS-1473:2004.

ALUMINA

Analysts Nos. 1 and 2 determined alumina by FAAS. Analysts Nos. 3, 7, 8, 10, 11 and 13 used ICP-OES. Nos. 4, 5, 6, 9 14, 17 and 18 used XRF, No. 4 following BS EN ISO 12677 and No 18 ISO 9516. Analyst No. 12 used the gravimetric method in ISO 318. No. 15 used IS-1473:2004.

TITANIA

With the exception of Analysts Nos. 4, 5, 6, 9, 14, 17 & 18 all Analysts determined titania by ICP-OES. The remaining Analysts used XRF, No 4 according to BS EN ISO 12677 and No. 18 according to ISO 9516.

LIME

Analysts Nos. 1, 2, 3, 7, 8, 11 and 13 determined lime by ICP-OES. Analysts Nos. 4, 5, 6, 9, 14, 17 & 18 used XRF, No 4 according to BS EN ISO 12677 and No. 18 according to ISO 9516. Analyst No.10 used a complexometric titration with a visual endpoint.

MAGNESIA

Analysts Nos. 2, 3, 7, 8, 11 and 13 determined magnesia using ICP-OES. Nos. 4, 5, 6, 9, 14, 17 and 18 used XRF, No 4 according to BS EN ISO 12677 and No. 18 according to ISO 9516. Analyst No. 10 used a complexometric titration with a visual endpoint and No. 12 used FAAS.

PHOSPHORUS

Analyst Nos.1 and 2 determined phosphorus as phosphovanadomolybdate using a spectrophotometric method. Both Analysts extracted the yellow complex with 4-metyl-penatan-2-one. Analysts Nos. 3, 4, 8, 10, 11, 13 and 19 used ICP-OES. Analyst No 12 titrated ammonium phosphovanadomolybdate according to ISO 321 and No 15 followed IS-1473:2004. The remaining Analysts used XRF; No 4 according to BS EN ISO 12677 and No. 18 according to ISO 9516.

SODIUM OXIDE

Analysts Nos. 2 and 10 determined sodium oxide by FAAS. With the exception of Analyst No 6, who used XRF, all of the other Analysts used ICP-OES.

POTASSIUM OXIDE

Analysts Nos. 2 and 10 determined potassium oxide by FAAS. With the exception of Analysts Nos. 6, 14 & 17, who used XRF, all of the other Analysts used ICP-OES.

BARIUM OXIDE

All of the Analysts determined barium oxide using ICP-OES.

COBALT

Analyst No. 1 determined cobalt by FAAS. The remaining Analysts used ICP-OES.

COPPER

Analysts Nos. 1 and 2 determined copper by FAAS. The remaining Analysts used ICP-OES.

SULPHUR

Analyst No. 1 determined sulphur gravimetrically as barium sulphate. No. 2 used an acidimetric titration following combustion, Analysts Nos. 9 and 18 used XRF, No. 18 according to ISO 9516. Analyst No. 11 used ICP-OES, Analyst No 15 followed IS-1473:2004 and the remaining Analysts used infrared absorption following combustion.

ARSENIC OXIDE

Analysts Nos. 1 and 2 determined arsenic oxide spectrophotometrically as the diethyldithiocarbamate complex following evolution as arsine. With the exception of Analysts No. 17, who used XRF, the remaining Analysts used ICP-OES

BORON

Analysts Nos. 1 and 2 determined boron spectrophotometrically as the curcumin complex. The other Analysts used ICP-OES.

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CO-OPERATING ANALYSTS

1	JONES, S.J., *BSc, CChem, MRSC,*	Ridsdale & Co. Ltd., Middlesbrough.
2	CROCKER, F.H.,	Pattinson & Stead (2005) Ltd., Middlesbrough.
3	BLUNDELL, P.,	ALS Minerals Division, Prescot.
4	SHAW, D.,	Lucideon, Stoke-on-Trent.
5, 20	HARGREAVES, C.,	Inspectorate International Ltd, Witham.
6, 19	HURDITCH, P.,	AMG Superalloys UK. Ltd., Rotherham.
7	OOSTERHOFF, A.,	Laboratory Services International, Rotterdam, The Netherlands.
8	VAN CROONENBURG, F.,	SGS Nederland B.V, Spijkenisse, The Netherlands.
9	CULLEY, N.,	LMA, Sleeuwijk, The Netherlands.
10	KONDOROSI, G.,	ISD Dunaferr, Dunaujvaros, Hungary.
11	BULKA, V.,	Lithea Ltd., Brno, Czech Republic.
12	BLEWUSI, G.,	Ghana Manganese Co. Ltd., Nsuta-Wassa, Ghana.
13	CHATTOPADHYAY, S.,	Inspectorate Griffith India Pvt Ltd., Bhubaneswar, India
14	WU, D.,	Inspectorate (Shanghai) Ltd., Shanghai, China
15	HATI, K., C.,	Inspectorate Griffith India Pvt Ltd., Visakhapatnam, India
16	MONDAL, S.,	Inspectorate Griffith India Pvt Ltd., Keonjhar, India
17	NAIDOO, V.,	Bureau Veritas Inspectorate Laboratories (Pty) Ltd., Rustenburg, Republic of South Africa
18	BOUCHARD M.,	Claisse (Corporation Scientifique) Quebec, Canada

DESCRIPTION OF SAMPLE

BCS-CRM 176/3 is sold in the form of finely divided material passing a nominal 150 micron aperture and packed into bottles of 100g.

The preparation of representative samples for chemical analysis and the certification by co-operative analysis was undertaken by Bureau of Analysed Samples Ltd.

Bureau of Analysed Samples Ltd is a United Kingdom Accreditation Service (UKAS) Accredited Reference Material Producer, No 4004, and, as the Producer of BCS-CRM 176/3 as defined in ISO Guide 34:2009 section 3.1, is fully responsible for assigning the certified values and their uncertainties in accordance with ISO Guides 34:2009 and 35:2006.

INTENDED USE

This sample is intended for the verification of analytical methods, such as those used by the participating laboratories, for the calibration of analytical instruments, for establishing values for secondary reference materials and for training purposes.

In order to ensure that a fully representative sample is taken users should take a minimum sub-sample size of 1.0g. Users of this material should be aware that the use of a smaller sub-sample size will invalidate the certified values and the associated 95% confidence limits.

The sample should be mixed thoroughly before each use.

STABILITY

BCS-CRM 176/3 will remain stable provided that the bottle remains sealed and is stored in a dry atmosphere. When the bottle has been opened the lid should be secured immediately after use.

TRACEABILITY

The characterisation of this material has been achieved by chemical analysis involving inter-laboratory study, each laboratory using the method of their choice, details of which are given above.

Most of the analytical methods used in the characterisation of this CRM were either international or national standard methods or methods which are technically equivalent. All laboratories used either stoichiometric analytical techniques or methods which were calibrated predominantly against pure metals or stoichiometric compounds, ensuring traceability of the individual results to the SI.

MEASUREMENT UNCERTAINTY

The uncertainty of each of the certified values of BCS-CRM 176/3 has been established by multiplying the standard error arising from the chemical analysis by the appropriate two sided Student's t value at the 95% confidence level for the number of results. Homogeneity has been assessed on the bulk material using one way ANOVA and has been found to be acceptable. It has not, therefore, been included in the calculated measurement uncertainty. The stability of this CRM and its transportation also make negligible contributions to the overall uncertainty of the certified values.

COMMUTABILTY

BCS-CRM 176/3 is intended to be used in the same physical form as that used by the participating analysts and therefore commutability is not of relevance in respect of this CRM.

Further information and advice on this or other Certified Reference Materials or Reference Materials produced by Bureau of Analysed Samples Ltd may be obtained from the address below.

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