BUREAU OF ANALYSED SAMPLES LTD

BRITISH CHEMICAL STANDARD CERTIFIED REFERENCE MATERIAL

4004

CERTIFICATE OF ANALYSIS

BCS-CRM No. 203/6

LOW CARBON FERRO-CHROMIUM

Prepared under rigorous laboratory conditions and, AFTER CERTIFICATION ANALYSIS IN GREAT BRITAIN, BELGIUM, CANADA, CHINA, ESTONIA, HUNGARY, INDIA, THE NETHERLANDS, SWEDEN and SPAIN issued by the Bureau of Analysed Samples Ltd.

ANALYSES

Mean of 4 values - mass content in %.

Analyst	C	Si	Mn	P	S	Cr	Ni	Co	V	*N*	*Ti*
1	0.0256	0.3686	0.1437	0.0193	0.0033	70.868	0.1929	0.0406	0.0659	*0.0231*	*0.0024*
2	0.0249	0.3982	0.1603	0.0201	0.0034	71.100	0.2062	0.0494	0.0741	*0.0297*	*0.0031*
3	0.0261	0.4209	…	…	0.0042	…	…	…	…	*0.0294*	…
4	…	…	…	…	…	70.858	…	…	…	…	…
5	…	…	0.1575	0.0198	…	71.158	0.2150	…	0.0708	…	*0.0050*
6	0.0293	…	…	…	0.0044	…	…	…	…	…	…
7	0.0293	0.3417	0.1410	0.0196	0.0045	71.055	0.2088	0.0454	0.0740	*0.0348*	*0.0029*
8	0.0250	0.3857	0.1472	0.0184	0.0043	70.841	0.2344	0.0462	0.0667	*0.0308*	*0.0030*
9	0.0260	…	…	…	0.0040	…	…	…	…	…	…
10	…	0.3745	0.1453	0.0205	…	…	0.2138	0.0424	0.0707	…	*<0.0005*
11	…	0.3869	0.1504	0.0206	…	71.155	0.2189	0.0433	0.0765	*0.0225*	*<0.005*
12	0.0254	…	…	…	…	…	…	…	…	*0.0298*	…
13	0.0266	0.3735	0.1588	0.0191	0.0034	70.786	0.2189	0.0423	0.0761	…	…
14	0.0256	…	0.1534	0.0189	0.0034	70.944	0.2150	0.0435	0.0747	…	*<0.003*
15	0.0270	0.3834	0.1623	0.0192	0.0038	70.850	0.2045	…	0.0769	*0.0266*	…
16	…	…	0.1613	…	…	71.215	0.2343	…	0.0800	…	*0.0038*
17	….	0.4111	0.1547	0.0184	…	…	0.2165	0.0436	…	…	*<0.001*
18	0.0276	0.3885	0.1593	0.0197	0.0049	71.063	0.2158	0.0407	0.0723	…	*<0.0005*
19	0.0295	0.3558	0.1455	0.0185	0.0057	71.106	0.2359	0.0436	0.0663	…	*0.0022*
20	0.0303	0.3515	…	0.0207	0.0046	71.058	0.2259	0.0478	0.0752	…	*0.0026*
21	…	…	…	…	…	71.150	0.2140	0.0498	0.0741	…	…
22	…	…	…	…	…	71.125	…	…	…	*0.0268*	*<0.0005*
23	…	0.3900	0.1600	0.0200	…	70.840	0.2300	0.0400	…	*0.0325*	*0.0033*
24	…	…	…	…	…	…	0.2150	0.0438	0.0720	…	*0.0028*
25	…	…	…	…	0.0048	…	…	…	…	…	…
26	…	…	…	…	0.0048	…	…	…	…		
27	…	…	…	…	0.0043	…	…	…	…	…	…
M_M	**0.0270**	**0.3807**	**0.1534**	**0.0195**	**0.0042**	**71.010**	**0.2175**	**0.0442**	**0.0729**	*0.029*	*0.003*
s_M	0.0019	0.0221	0.0073	0.0008	0.0007	0.143	0.0113	0.0031	0.0041		
s_w	0.0008	0.0058	0.0032	0.0004	0.0003	0.092	0.0031	0.0005	0.0010		

Values given in italics are for information only.

Additional Information: Analyst Nos. 2 & 16 reported values of 27.8 % and 27.5% for Fe by ICP-OES and XRF respectively. No. 16 also reported a value of 0.02% Cu by XRF

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 %

	C	Si	Mn	P	S	Cr	Ni	Co	V
Cv	**0.0270**	**0.381**	**0.153**	**0.0195**	**0.004**	**71.01**	**0.218**	**0.0442**	**0.0729**
C(95%)	0.0011	0.013	0.005	0.0005	0.001	0.08	0.006	0.0017	0.0022
Minimum weight (g)	0.15	0.25	0.1	0.1	0.1	0.1	0.1	0.1	0.1

The half width confidence interval, C(95%), is an expression of the uncertainty of the certified value. 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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CO-OPERATING ANALYSTS

1	BLUNDELL, P.,	ALS Inspection UK Ltd., Prescot.
2	HURDITCH, P.,	AMG Analytical Services Ltd, Rotherham.
3	SCRIMSHIRE, P. J.,	IncoTest, Hereford.
4	HARGREAVES, C.,	Inspectorate International Ltd., Witham.
5	SIMPSON, P.,	Alfred Knight International Ltd., St Helens.
6	JAMIESON, S. N.,	NSG European Technical Centre, Lathom.
7, 26	CROCKER, F. H.,	Pattinson & Stead (2005) Ltd., Middlesbrough.
8, 27	JONES, S. J.,	Ridsdale & Co. Ltd., Middlesbrough.
9	SNOWDEN, Y.,	British Steel Testing Solutions, Scunthorpe.
10	RODUSHKIN, I.,	ALS Scandinavia AB, Luleå, Sweden.
11	HENRICH, A.,	Höganäs Sweden AB, Höganäs, Sweden.
12	LINDKVIST, L.,	Sandvik Heating Technology, Hallstahammar, Sweden.
13	WICHARDT, C.,	AB Sandvik Materials Technology, Sandviken, Sweden.
14, 25	GRANFORS, M.,	Swerea-Kimab, Kista, Sweden.
15	QUIRÓS, E. & PEREZ, D.,	Acerinox Europa SAU, Cadiz, Spain.
16	BOUCHARD, M.,	Claisse, Quebec, Canada.
17	KICQ, P.,	CTP, Tournai, Belgium.
18	JIANG, J.,	Inspectorate (Shanghai) Ltd., Shanghai, China.
19	YARUSHKINA, M.,	Inspectorate Estonia AS, Tallinn, Estonia.
20	CHATTOPADHYAY, S.,	Inspectorate Griffith India PVT. Ltd., Bhubaneswar, India.
21	KONDOROSI, G.,	Dunaferr Labor Nonprofit Ltd., Dunaújváros, Hungary.
22	CULLEY, N.,	LMA CV, Sleeuwijk, The Netherlands.
23	BIJL, G., P.,	SGS Netherland BV, LA Spijkenisse, The Netherlands.
24	COLLINS, P.,	Tata Steel Technical, Swinden Laboratories, Rotherham.

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NOTES ON METHODS USED

CARBON

With the exception of Analysts Nos. 7 and 8 all of the Analysts determined carbon using combustion/infra-red methods, Nos.1, 2, 3, 6, 9 and 15 calibrating with carefully selected CRMs (see below for details) and the rest with pure chemicals or stoichiometric compounds, Nos. 13, 14 and 19 by following ISO 9556 whilst No 18 used the method GB/T 4699-4-2008. Nos. 7 and 8 used a non-aqueous titration following combustion in a stream of oxygen

SILICON

Most of the Analysts determined silicon with Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). No. 2 dissolved the sample in HCl/HNO_3 after an alkaline fusion and used standard addition, Nos. 11 and 18 used microwave dissolution (No. 18 following SN/T 3708-2013), No 15 fused the sample and dissolved the melt in acid, No. 17 used an aqua-regia digestion combined with an alkaline fusion of the residue and No. 23 fused the sample with peroxide.

Analysts Nos. 7, 8, 19 and 20 used a gravimetric method, dehydrating with perchloric acid, No. 19 according to ISO 4158-1978 and No. 20 according to IS 13452 (Part 2) 1992. No 10 used Inductively-Coupled Plasma – Mass Spectrometry (ICP-MS) and No.13 used a molybdenum blue spectrophotometric method without extraction, as described in EN 24829-1.

MANGANESE

With the exception of Analyst No. 10, who used ICP-MS, and Lab 16, who used X-ray fluorescence spectrometry (XRF), all of the Analysts determined manganese using ICP-OES. No. 2 dissolved the sample in HCl/HNO_3 after an alkaline fusion and used standard addition, No. 11 used a microwave digestion, No. 13 used matrix matched bracketing standards, No. 14 a combination of HCl, HNO_3 and HF, No. 15 fused the sample and dissolved in acid, No. 17 dissolved with aqua regia before using an alkaline fusion, No. 19 followed GOST R 53659-2009 and No. 23 used a peroxide fusion.

PHOSPHORUS

Most Analysts determined phosphorus using ICP-OES, No. 2 dissolved the sample in HCl/HNO_3 after an alkaline fusion and used standard addition, No. 11 used a microwave digestion, No. 14 a combination of HCl, HNO_3 and HF, No. 15 fused the sample and dissolved in acid, No. 17 dissolved with aqua regia before using an alkaline fusion, No. 18 followed SN/T 3708-2013 after microwave digestion and No. 23 used a peroxide fusion.

Nos, 7, 8 and 13 determined phosphorus spectrophotometrically as phosphovanadomolybdate after solvent extraction. No. 10 used ICP-MS whilst Analyst No 20 determined phosphorus by acidimetric titration of ammonium phosphomolybdate according to IS 1559-1961 and after fusion with Na_2O_2.

SULPHUR

Most Analysts determined sulphur by combustion/infra-red methods, Nos. 1,2, 3, 6, 9 and 15 calibrating with carefully selected CRMs (see below for details) and Nos. 13, 18, 19, 20 and 25 calibrating with pure chemicals or stoichiometric compounds. Analysts Nos. 13, 19 and 25 used ISO 4935 and No. 18 GB/T 4699.6-2008. No. 7 used an acid/base titration following combustion in a stream of oxygen. Nos. 8, 14 and 26 used ICP-OES, No. 14 digesting with a mixture of $HCl/HNO_3/HF$. No 27 determined sulphur gravimetrically as $BaSO_4$.

CHROMIUM

Analysts Nos. 1, 5, 18, 20, 21, 22 and 23 determined chromium by titration with Fe (II) after oxidation with persulphate. No. 1 used a potentiometric titration, No. 18 GB/T 4699.2-2009, No. 20 IS 13452 (part 6) 1997 and Nos. 21, 22 and 23 ISO 4140.

Analysts Nos. 2, 11, 14 and 15 used ICP-OES, No. 2 dissolving the sample in HCl/HNO_3 after an alkaline fusion and using standard addition, No. 11 after a microwave digestion, No. 14 after treating with a combination of HCl, HNO_3 and HF and No. 15 after fusing the sample and dissolving in acid.

Analysts Nos. 4, 7, 8, 13 and 19 oxidised chromium with persulphate, added excess Fe(II) and back titrated the excess Fe(II) with $K_2Cr_2O_7$ in the case of Analysts Nos. 7, 8 and 13 (No. 13 following ISO 15355), and $KMnO_4$ in the case of Lab 19 who followed GOST 21600.17-83.

Analyst No. 16 determined chromium by XRF.

NICKEL

With the exception of Analyst Nos. 10 and 24, who used ICP-MS (No. 24 after microwave dissolution with aqua regia) and No. 16, who used XRF, all of the Analysts determined nickel using ICP-OES. No. 2 dissolved the sample in HCl/HNO_3 after an alkaline fusion and used standard addition, No. 11 used microwave digestion, No. 13 used matrix matched bracketing standards, No. 14 a combination of HCl, HNO_3 and HF, No. 15 fused the sample and dissolved in acid, No 16 used XRF. No. 17 dissolved with aqua regia before using an alkaline fusion. No. 18 followed TOP-04 after an acid dissolution and No. 19 followed GOST R 53659-2009 after an alkaline fusion and No. 23 used a peroxide fusion.

COBALT

With the exception of Analyst Nos. 10 and 24, who used ICP-MS (No. 24 after microwave dissolution with aqua regia), all of the Analysts determined cobalt using ICP-OES. No. 2 dissolved the sample in HCl/HNO_3 after an alkaline fusion and used standard addition, No. 11 used a microwave digestion, No. 13 used matrix matched bracketing standards, No. 14 a combination of HCl, HNO_3 and HF, No. 17 dissolved with aqua regia before using an alkaline fusion. Analyst No. 18 used the method TOP-04 after an acid dissolution and No. 19 GOST R 53659-2009 after an alkaline fusion. No. 23 used a peroxide fusion.

VANADIUM

With the exception of Analyst Nos. 10 and 24, who used ICP-MS (No. 24 after microwave dissolution with aqua regia) and No. 16, who used XRF, all of the Analysts determined vanadium using ICP-OES, No. 2 dissolved the sample in HCl/HNO_3 after an alkaline fusion and used standard addition, No. 11 used a microwave digestion, Nos. 13 and 14 dissolved the sample in a mixture of HCl, HNO_3 and HF, No. 13 also using matrix matched bracketing standards, No. 15 fused the sample and dissolved in acid and Analyst No. 19 used GOST R 53659-2009 after an alkaline fusion.

NITROGEN

With the exception of Analysts Nos. 7 and 8 all of the Analysts determined nitrogen using thermal conductivity, Nos.1, 2, 3, and 15 calibrating with carefully selected CRMs (see below for details) and the rest with pure chemicals or stoichiometric compounds, No. 11 following ISO 15351.

Analyst No. 7 used a Kjeldahl digestion and steam distilled the ammonia into Nessler's reagent before completing spectrophotometrically. No. 8 also used a Kjeldahl digestion but followed the steam distillation by titration of the distillate with hydrochloric acid.

TITANIUM

With the exception of Analyst Nos. 10 and 24, who used ICP-MS (No. 24 after microwave dissolution with aqua regia) and No. 16, who used XRF, , all of the Analysts determined titanium using ICP-OES,. No. 2 dissolved the sample in HCl/HNO3 after an alkaline fusion and used standard addition, No. 11 used a microwave digestion, No. 14 a combination of HCl, HNO_3 and HF. Analyst No. 18 followed TOP-04 after an acid dissolution, No.19 followed GOST R 53659-2009 after an alkaline fusion and No. 23 used a peroxide fusion

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DESCRIPTION OF SAMPLE

BCS-CRM 203/6 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 203/6 as defined in BS EN ISO 17034:2016, is fully responsible for assigning the certified values and their uncertainties.

INTENDED USE

BCS-CRM 203/6 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 not less than the minimum weight stated on the certificate for that element, this being the lowest sample mass used by any of the Co-operating Analysts contributing to the certified value. Users of this material should be aware that the use of a smaller sub-sample size may invalidate the certified values and the associated 95% confidence limits.

The sample should be mixed thoroughly before each use.

STABILITY

BCS-CRM 203/6 will remain stable provided that the bottle remains sealed and is stored in a dry atmosphere. Once 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. With the exception of C and N 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.

For C, S and N results have been obtained using stoichiometric analytical techniques, methods which were calibrated against pure metals or stoichiometric compounds or by calibration using 5 certified reference materials carefully selected to be similar in composition to BCS-CRM 203/6 and all of which demonstrate full unbroken traceability to the SI. Different Analysts used different combinations of CRMs. The CRMs used were as follows: DFS 1, DFS2, ECRM 509-1, ECRM 580-1, ECRM 585-2, ICRM F 15/2, ICRM F 35/2, ICRM F 45, ICRM F 47, IPT 65, NCS 25644, NCS 37608 and NCS 93604.

MEASUREMENT UNCERTAINTY

The uncertainty of each of the certified values of BCS-CRM 203/6 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 203/6 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.

NEWHAM HALL, NEWBY
MIDDLESBROUGH
ENGLAND
TS8 9EA
Email: enquiries@basrid.co.uk
Website: www.basrid.co.uk

For BUREAU OF ANALYSED SAMPLES LTD

R P MEERES,
Managing Director
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First published September 2017 with certified value for sulphur.
Revised July 2018 with sulphur reduced to uncertified status following concern over the accuracy of the value.
Revised February 2019 with sulphur reinstated as a certified constituent but with a lower precision.