BUREAU OF ANALYSED SAMPLES LTD

BRITISH CHEMICAL STANDARD CERTIFIED REFERENCE MATERIAL

4004

CERTIFICATE OF ANALYSIS

BCS/SS-CRM No. 116

CALCIUM TREATED STEEL

Prepared under rigorous laboratory conditions and, AFTER CERTIFICATION ANALYSIS IN GREAT BRITAIN, AUSTRIA, HUNGARY, INDIA, THE NETHERLANDS, SPAIN, SWEDEN and, THE UNITED STATES OF AMERICA, issued by the Bureau of Analysed Samples Ltd.

ANALYSES

Mean of 4 values - mass content in %.

Analyst	C	Si	Mn	P	S	Cr	Ni	Al	N	Pb	Ti	Ca
1	0.6170	0.2012	0.6751	0.0094	0.00173	0.0139	0.0161	0.0576	0.0071	…	0.00160	0.0040
2	…	…	…	0.0094	…	0.0146	0.0159	0.0583	…	0.00006	0.00170	0.0037
3	0.6201	0.1937	0.6773	0.0099	0.00165	0.0158	0.0143	0.0574	0.0069	0.00008	0.00170	0.0035
4	…	…	0.6933	0.0085	…	0.0145	0.0165	0.0590	…	0.00010	0.00160	0.0030
5	0.6184	0.1960	0.6722	0.0094	0.00155	0.0142	0.0159	0.0593	0.0062	…	0.00168	0.0030
6	0.6181	…	…	…	0.00162	…	…	…	0.0068	…	…	…
7	0.6178	0.2058	0.6677	0.0095	0.00169	0.0131	0.0160	0.0589	0.0071	…	0.00178	0.0033
8	0.6190	0.2016	0.6743	…	0.00163	0.0143	0.0145	0.0587	0.0070	…	…	0.0042
9	…	0.2059	0.6784	0.0094	…	0.0142	0.0159	0.0598	…	…	0.00163	0.0037
10	0.6204	0.2070	…	…	…	0.0128	0.0145	0.0570	…	…	0.00168	…
11	…	0.2010	0.6768	0.0093	…	0.0144	0.0142	0.0585	…	0.00028	0.00170	0.0041
12	0.6021	0.1965	0.6708	0.0088	0.00220	0.0140	0.0141	0.0599	0.0070	0.00015	0.00200	0.0038
13	0.6113	0.1992	0.6773	0.0090	0.00169	0.0143	0.0154	0.0597	0.0072	0.00013	0.00187	0.0034
14	0.6085	…	…	…	0.00172	…	…	…	0.0072	…	…	…
15	0.6050	…	…	…	…	…	0.0161	…	…	0.00006	….	0.0032
16	…	…	0.6792	0.0088	0.00221	0.0138	0.0163	0.0588	…	…	0.00167	0.0040
17	0.6170	0.2034	0.6778	0.0091	0.00151	0.0135	0.0157	0.0593	0.0066	0.00009	0.00158	0.0029
18	0.6135	0.2089	0.6728	0.0100	0.00151	0.0133	0.0139	0.0559	0.0067	…	0.00180	0.0032
19	0.6179	…	…	…	0.00154	…	…	…	0.0067	…	…	…
20	0.6207	0.2105	0.6713	0.0094	0.00160	0.0147	0.0168	0.0615	0.0071	…	0.00184	…
21	…	0.1893	0.6650	0.0092	0.00185	0.0145	0.0144	0.0558	…	…	0.00185	0.0043
22	0.6245	0.2003	0.6777	0.0096	0.00160	0.0149	0.0173	0.0608	0.0069	…	0.00163	0.0030
23	…	…	…	0.0079	…	0.0137	0.0168	…	…	0.00006	0.00158	…
24	0.6262	…	…	…	0.00201	…	…	…	0.0067	…	…	…
25	0.6292	…	…	…	0.00189	…	…	…	0.0068	…	…	…
26	..	…	0.6752	…	0.00220	…	…	…	…	…	0.00172	0.0044
27	…	…	0.6784	0.0089	…	0.0130	0.0157	…	…	0.00014	0.00158	0.0031
28	…	…	…	0.0094	…	…	…	…	…	…	…	…
M_M	**0.6170**	**0.2014**	**0.6756**	**0.0092**	**0.00176**	**0.0141**	**0.0155**	**0.0587**	**0.0069**	**0.00012**	**0.00171**	**0.0036**
s_M	0.0070	0.0059	0.0060	0.0005	0.00024	0.0008	0.0011	0.0016	0.0003	0.00007	0.00012	0.0005
s_w	0.0024	0.0019	0.0032	0.0002	0.00010	0.0003	0.0003	0.0008	0.0002	0.00004	0.00005	0.0002

Additional Information: Lab 4 reported <0.001% Mg by ICP-OES and Lab 20 reported <0.001% Mo, 0.014% Cu and 0.005% Sn, all by ICP-OES.

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	Al	N	Pb	Ti	Ca
Cv	**0.617**	**0.201**	**0.6756**	**0.0092**	**0.00176**	**0.0141**	**0.0155**	**0.0587**	**0.0069**	**0.00012**	**0.00171**	**0.0036**
C(95%)	0.004	0.004	0.0030	0.0003	0.00012	0.0004	0.0005	0.0008	0.0002	0.00005	0.00006	0.0003
Minimum weight (g)	0.1	0.5	0.1	0.1	0.1	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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(The current edition is available at www.basrid.co.uk)

BCS/SS-CRM 116

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NOTES ON METHODS USED

CARBON

Analysts Nos. 1, 3, 6, 7, 8, 10, 19 and 20 determined carbon by combustion/infra-red methods calibrated with carefully selected CRMs (see below for details).

Analyst No. 12 used a gravimetric method following combustion in a stream of oxygen and No. 13 a non-aqueous titration following combustion in a stream of oxygen according to BS 6200.8.2: 1981.

The remaining Analysts used combustion infrared methods calibrated with pure chemicals or stoichiometric compounds. Analysts Nos. 15, 17, 18, 24 and 25 followed ISO 9556.

SILICON

Most Analysts determined silicon using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), No. 1 after acid dissolution, No. 3 after alkaline fusion and dissolution in HCl/HNO_3 and No. 20 after microwave assisted dissolution. No. 11 followed EN 10355:2013

Analysts Nos. 5, 12 and, 13 determined silicon gravimetrically after dehydration with perchloric acid whilst Nos. 8 and 18 also used a gravimetric method but dehydrated with sulphuric acid, No. 8 following ISO 439:1994 and No. 18 IS 228 (Part 8).

Analyst No. 17 determined silicon photometrically as molybdenum blue and without extraction.

MANGANESE

With the exception of Analyst No. 13 all Analysts determined manganese using ICP-OES, No. 1 after acid dissolution, No. 3 after alkali fusion and dissolution in HCl/HNO_3 No. 4 following ASTM E2594-09, No. 8 according to EN-ISO 10700, No. 11 following EN 10355:2013 , Nos. 16, 18 and 21 after digestion with HCl and HNO_3, No. 17 after fusion with $Na_2CO_3/Na_2B_4O_7$, No. 20 after microwave digestion and No 27 after digestion with $HClO_4/HF$.

Analyst No. 13 used a photometric method in which the manganese is oxidised with periodate.

PHOSPHORUS

Most Analysts determined phosphorus using ICP-OES, No. 1 after acid dissolution, No. 3 after alkali fusion and dissolution in HCl/HNO_3 No. 4 following ASTM E2594-09, No. 11 following EN 10355:2013, No. 16, 18, 21 and 23 digesting in HCl and HNO_3, No. 17 after fusion with $Na_2CO_3/Na_2B_4O_7$, No. 20 after microwave digestion and No 27 after digestion with $HClO_4/HF$.

Analysts Nos. 2, 23 and 28 used ICP-MS whilst Nos. 5, 12 and 13 used a photometric method, extracting the yellow phosphovanadomolybdate complex.

SULPHUR

Analysts Nos. 1, 3, 6, 7, 8, 19 and 20 determined sulphur by combustion/infra-red methods calibrated with carefully selected CRMs (see below for details).

Analyst No. 12 used an acid-base titration following combustion in a stream of oxygen; Nos. 13 and 16 used ICP-OES and No. 26 a gravimetric method, precipitating S as $BaSO_4$.

The other analysts all used combustion infrared methods calibrated with pure chemicals or stoichiometric compounds, Analysts Nos. 17, 18, 24 and 25 followed ISO 4935 and No. 22 IS 228 (Part 1).

CHROMIUM

With the exception of Analysts Nos.2 and 23, who used ICP-MS, all of the Analysts determined chromium using ICP-OES, No. 1 after acid digestion, No. 3 after alkali fusion and dissolution in HCl/HNO_3 No. 4 following ASTM E2594-09, No. 8 ISO 10318, No. 11 EN 10351:2011, Nos. 16, 18, 21 and 22 after digestion in HCl and HNO_3, No. 17 after fusion with $Na_2CO_3/Na_2B_4O_7$, No. 20 after microwave digestion and No 27 after digestion with $HClO_4/HF$.

NICKEL

With the exception of Analysts Nos.2 and 23, who both used ICP-MS, and No. 13 who used Flame Atomic Absorption Spectrometry (FAAS), all of the Analysts determined nickel using ICP-OES. No 1 used an acid digestion, No. 3 an alkali fusion and dissolution in HCl/HNO_3, No. 4 followed ASTM E2594-09 and No.8 followed ISO 4940. Analyst No. 11 followed EN 10355:2013, No. 15, after digestion with HCl/HNO_3 and fuming with $HClO_4$, bracketed with matrix matched standards and Analysts Nos. 16, 18, 21 and 22 digested with HCl/HNO_3. Analyst No. 17 used a digestion with $HClO_4/HF$, No. 20 a microwave digestion and No 27 a fusion with $Na_2CO_3/Na_2B_4O_7$.

ALUMINIUM

With the exception of Analyst No.2, who used ICP-MS, all of the Analysts determined aluminium using ICP-OES, No 1 after acid digestion, No. 3 after alkali fusion and dissolution in HCl/HNO_3 No. 4 following ASTM E2594-09, No.8 following ISO 9658, No. 11 following EN 10351:2011, Nos. 16, 18 and 21 after digestion with HCl/HNO_3, No. 17 after digestion with $HClO_4/HF$ and No. 20 after microwave digestion.

NITROGEN

Analysts Nos. 1, 3, 6, 7, 8, 19 and 20 determined nitrogen by thermal conductivity after decomposition in a graphite crucible and calibrated with carefully selected CRMs (see below for details).

Analysts Nos. 12 and 13 used an acid base titration following distillation.

The remaining Analysts used thermal conductivity after decomposition in a graphite crucible and calibrated with pure chemicals or stoichiometric compounds. Analysts Nos. 17, 18, 24 and 25 followed ISO 10720.

LEAD

Analysts Nos. 2, 15, 17 and 23 determined lead using ICP-MS, No.17 using a mixture of $HClO_4$ and HF and No. 23 using a mixture of HCl and HNO_3. Analyst No. 3 used Graphite Furnace Atomic Absorption Spectrometry (GFAAS) after dissolution in $HF/HCl/HNO_3$ and the remaining Analysts used ICP-OES, No. 4 following ASTM E2823-11 and using In as an internal standard, No. 11 following EN 10351:2011, No. 15 after digestion with HNO_3,and No 27 after fusion with $Na_2CO_3/Na_2B_4O_7$.

TITANIUM

Analysts Nos. 2 and 23 determined titanium by ICP-MS. The other Analysts all used ICP-OES, No. 1 after acid digestion, No. 3 dissolution in HF, HCl and HNO_3, No. 4 following ASTM E2594-09, No. 11 following EN 10351:2011, Nos. 16, 18, 21 and 23 after digestion with HCl and HNO_3, No. 17 after digestion with $HClO_4/HF$, No. 20 after microwave digestion and No 27 after fusion with $Na_2CO_3/Na_2B_4O_7$.

CALCIUM

With the exception of Analyst No. 2, who used ICP-MS, and Analyst No. 5 who used FAAS, all of the Analysts determined calcium by ICP-OES, No. 1 after acid digestion, No. 3 dissolution in HF, HCl and HNO_3, No. 4 following ASTM E2594-09, No. 8 following ISO 10697-2, No. 11 following EN 10351:2011, Nos. 15, 16, 18 and 21 after digestion with HCl and HNO_3, No. 17 after digestion with $HClO_4/HF$ and No 27 after fusion with $Na_2CO_3/Na_2B_4O_7$.

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CO-OPERATING ANALYSTS

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8, 24	GUSTAVSSON, I.,	Gustavsson Consulting, Stockholm, Sweden.
9	HENRICH, A.,	Höganäs AB, Höganäs, Sweden.
10	SCRIMSHIRE, P. J.,	IncoTest, Hereford.
11	KONDOROSI, G.,	Dunaferr Labor Nonprofit Ltd., Dunaújváros, Hungary.
12	CROCKER, F. H.,	Pattinson & Stead (2005) Ltd., Middlesbrough.
13, 26	JONES, S.J.,	Ridsdale & Co Ltd., Middlesbrough.
14	LINDKVIST, L.,	Sandvik Heating Technology AB, Hallstahammar, Sweden.
15	WICHARDT, C., & CARLSTROM-WANGELIN, A.,	AB Sandvik Materials Technology, Sandviken, Sweden.
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17, 27	VAN DER VEN-KONIJN, A.J.M.,	Tata Steel IJmuiden, The Netherlands.
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DESCRIPTION OF SAMPLE

British Chemical Standard BCS-CRM 116 is sold in the form of chips passing a nominal 1700µm aperture sieve from which the fines passing a nominal 250µm aperture sieve have been removed. It is supplied in bottles containing 100g.

Spectroscopic Standard SS-CRM 116 is sold in the form of 44mm diameter discs.

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/SS-CRM 116 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

BCS-CRM 116 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.

SS-CRM 116 is intended for establishing and checking the calibration of Optical Emission and X-Ray Spectrometers for the analysis of similar materials. The “as received” working surface of the sample should be linished before use to remove any protective coating. An area 6mm in diameter in the centre of the disc should be avoided for optical emission spectrometry.

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STABILITY

BCS-CRM 116 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.

SS-CRM 116 will remain stable provided that it is not subjected to excessive heat (e.g. during preparation of the working surface).

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, S 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/SS-CRM 116 and all of which demonstrate full unbroken traceability to the SI. Different Analysts used different combinations of CRMs. The CRMs used were as follows: BCS-CRMs 111, 112, 113, 114, and 115 and ECRMs 055-2, 056-2, 059-2, 192-1, 194-1 and 196-2.

MEASUREMENT UNCERTAINTY

The uncertainty of each of the certified values of BCS/SS-CRM 116 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 in accordance with ASTM E826 – 85 and found to be acceptable. Homogeneity 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 116 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.

In the case of SS-CRM 116 it has been established that, when using optical emission spectrometers, materials of similar composition from different sources may respond differently. The user should be aware that the metallurgical history of this SS-CRM may not accurately reflect the metallurgical history of the user's own materials.

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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For BUREAU OF ANALYSED SAMPLES LTD

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