BUREAU OF ANALYSED SAMPLES LTD

BRITISH CHEMICAL STANDARD CERTIFIED REFERENCE MATERIAL

4004

CERTIFICATE OF ANALYSIS

BCS/SS-CRM No. 115

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	Ti	Ca
1	…	0.2164	0.6786	0.0122	…	0.0199	0.0204	0.0543	...	...	0.0064
2	…	0.2083	…	0.0124	0.00089	0.0207	0.0192	0.0517	...	0.0030	0.0060
3	0.6228	0.2006	0.6785	0.0121	0.00092	0.0200	0.0187	0.0521	0.0070	0.0028	0.0060
4	…	…	0.6898	0.0130	…	0.0193	0.0209	0.0558	...	0.0026	0.0057
5	0.6234	0.2056	0.6891	0.0130	0.00085	0.0191	0.0199	0.0525	0.0062	0.0024	0.0056
6	0.6202	…	…	...	0.00096	…	…	…	0.0066	...	…
7	0.6254	0.2100	0.6828	0.0124	0.00106	0.0198	0.0200	0.0531	0.0069	0.0024	0.0059
8	0.6238	0.2074	0.6759	0.0131	0.00092	0.0186	0.0193	0.0563	0.0072	0.0034	0.0049
9	0.6136	…	0.6763	...	0.00091	0.0196	0.0182	0.0513	0.0066	...	0.0055
10	…	0.2068	0.6693	0.0128	…	0.0186	0.0204	0.0509	...	0.0024	0.0057
11	0.6203	0.2118	0.6787	0.0119	0.00070	0.0217	0.0191	0.0514	...	0.0030	0.0050
12	…	0.2055	0.6773	0.0119	…	0.0207	0.0183	0.0536	...	0.0026	0.0068
13	0.6168	0.2013	0.6766	0.0109	0.00115	0.0195	0.0190	0.0531	…	0.0035	0.0059
14	0.6303	0.2034	0.6823	0.0133	0.00106	0.0203	0.0192	0.0534	0.0065	0.0026	…
15	0.6233	…	…	...	0.00097	…	…	…	0.0069	...	…
16	0.6121	0.2048	0.6713	0.0123	0.00050	0.0185	0.0201	0.0509	0.0064	0.0028	0.0055
17	…	0.2082	0.6856	0.0120	…	0.0224	0.0202	0.0528	...	0.0027	0.0062
18	0.6249	0.2134	0.6831	0.0128	0.00090	0.0186	0.0192	0.0526	0.0067	0.0026	0.0063
19	0.6263	0.2067	0.6820	0.0120	0.00128	0.0203	0.0195	0.0512	0.0066	0.0029	0.0059
20	0.6253	0.2192	0.6890	0.0122	0.00091	0.0190	…	0.0534	0.0069	0.0023	…
21	0.6217	0.1987	0.6895	0.0121	0.00083	0.0194	0.0201	…	0.0067	0.0022	…
22	0.6234	0.2130	0.6960	0.0120	0.00124	0.0204	0.0209	0.0517	0.0067	0.0021	0.0060
23	…	…	…	...	…	…	…	…	...	0.0023	…
24	0.6210	…	…	...	0.00095	…	…	…	0.0064	...	…
25	…	…	0.6947	...	…	0.0186	0.0192	…	...	...	…
26	…	…	0.6833	...	…	…	0.0208	…	...	...	…
27	0.6282	…	…	...	0.00058	…	…	…	0.0068	...	…
M_M	**0.6224**	**0.2078**	**0.6824**	**0.0123**	**0.00093**	**0.0198**	**0.0196**	**0.0527**	**0.0067**	**0.0027**	**0.0058**
s_M	0.0047	0.0055	0.0072	0.0006	0.00019	0.0011	0.0009	0.0016	0.0003	0.0004	0.0005
s_w	0.0026	0.0031	0.0033	0.0004	0.00009	0.0004	0.0003	0.0006	0.0002	0.0002	0.0003

Co	*Cu*	*Pb*	*Sn*	*V*
...	...	*0.000195*	...	...
0.0069	*0.0095*	*0.000125*	*0.0012*	*0.0014*
...	...	*0.000300*	...	...
...	...	*0.000140*	...	...
...	...	*0.000168*	...	...
...	...	...	...	...
...	...	*0.000368*	...	...
...	...	*<0.0010*	...	...
...	...	...	...	...
0.0062	*0.0086*	...	*0.0013*	*0.0012*
...	...	...	...	...
...	...	*0.000400*	...	...
0.0068	*0.0090*	*<0.0005*	*0.0027*	*0.0013*
...	...	*<0.001*	...	...
...	...	...	...	...
...	...	*0.000173*	...	...
0.0058	*0.0102*	*0.000143*	*0.0012*	*0.0017*
...	...	*0.000168*	...	...
...	...	*0.000675*	...	...
...	*0.0088*	...	*0.0025*	...
...	...	...	...	...
...	...	*0.000175*	...	...
...	...	...	...	...
...	...	...	...	...
...	...	...	...	...
...	...	...	...	...
...	...	...	...	...
0.006	*0.009*	*0.0002*	*0.002*	*0.001*

Values given in italics are for information only

Additional Information: B: 0.0001% and <0.0001%, Zn: 0.0006%, Mo: 0.003%.

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	Ti	Ca
Cv	**0.6224**	**0.2078**	**0.682**	**0.0123**	**0.00093**	**0.0198**	**0.0196**	**0.0527**	**0.0067**	**0.0027**	**0.0058**
C(95%)	0.0024	0.0027	0.004	0.0003	0.00010	0.0005	0.0004	0.0008	0.0002	0.0002	0.0003
Minimum weight (g)	0.3	0.1	0.1	0.1	0.3	0.1	0.1	0.1	0.3	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 115

CALCIUM TREATED STEEL

NOTES ON METHODS USED

CARBON

Analysts Nos. 3, 6, 7, 8, 9, 11, 20, 21 and 27 determined carbon by combustion/infra-red methods calibrated with carefully selected CRMs (see below for details). Analysts Nos. 13 and 14 used a gravimetric method following combustion in a stream of oxygen and the remaining Analysts used combustion infrared methods calibrated with pure chemicals or stoichiometric compounds, No. 4 according to ASTM E1019-11 and Nos. 16, 18, 19 and 24 to ISO 9556.

SILICON

Analyst No 2 determined silicon using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Analyst Nos. 5, 13, 14 and 19 determined silicon gravimetrically, Nos. 5, 13 and 14 dehydrating with perchloric acid and No 19 with sulphuric acid. Nos. 7, 16 and 18 used a molybdenum blue photometric method without extraction. The remaining Analysts used Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), No. 3 after an alkali fusion and dissolution in HCl and HNO_3 and Nos. 10 and 20 after microwave digestion.

MANGANESE

With the exception of Analysts Nos. 7, 14 16 and 26, all Analysts determined manganese using ICP-OES, Nos. 10 and 21 after microwave digestion. Nos. 7, 14 and 16 used a photometric method in which the manganese is oxidised with periodate and No 26 used Flame Atomic Absorption Spectrometry (FAAS).

PHOSPHORUS

Most Analysts determined phosphorus using ICP-OES, No. 3 after an alkali fusion and dissolution in HCl and HNO_3 and No. 10 after microwave digestion. Analysts Nos. 2 and 5 used ICP-MS, and Nos. 7, 13, 14, 16 and 22 used photometric methods, Nos. 7 and 22 using the molybdenum blue complex without extraction and Nos. 13, 14 and 16 extracting the yellow phosphovanadomolybdate complex.

SULPHUR

Analyst No. 2 determined sulphur using ICP-MS. Analysts Nos. 3, 6, 7, 8, 9, 11, 20, 21 and 27 determined sulphur by combustion/infra-red methods calibrated with carefully selected CRMs (see below for details). No. 13 used an acid-base titration following combustion in a stream of oxygen and No. 14 used ICP-OES. The other analysts all used combustion infrared methods calibrated with pure chemicals or stoichiometric compounds, No. 4 according to ASTM E1019-11 and Nos. 16, 18, 19 and 24 according to ISO 4935.

CHROMIUM

With the exception of Analyst No.2, who used ICP-MS, all of the Analysts determined chromium using ICP-OES, Nos. 10 and 20 after microwave digestion.

NICKEL

With the exception of Analyst No.2, who used ICP-MS and No. 26, who used FAAS, all of the Analysts determined nickel using ICP-OES, No. 3 after an alkali fusion and dissolution in HCl and HNO_3 and No. 10 after microwave digestion.

ALUMINIUM

With the exception of Analyst No.2, who used ICP-MS, all of the Analysts determined aluminium using ICP-OES, No. 3 after an alkali fusion and dissolution in HCl and HNO_3 and Nos. 10 and 20 after microwave digestion.

NITROGEN

Analysts Nos. 3, 6, 7, 8, 19, 20, 21 and 27 determined nitrogen by thermal conductivity after decomposition in a graphite crucible and calibrated with carefully selected CRMs (see below for details). Analyst No. 14 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, No. 4 according to ASTM E1019-11 and Nos. 16, 18, 19 and 24 according to ISO 10720.

TITANIUM

Analysts Nos. 2 and 23 determined titanium by ICP-MS. The other Analysts all used ICP-OES, No. 3 after an alkali fusion and dissolution in HCl and HNO_3 and Nos. 10 and 20 after microwave digestion.

CALCIUM

With the exception of Analysts Nos. 2 and 5 all of the Analysts used ICP-OES, No. 10 after microwave digestion. Analyst No. 2 used ICP-MS whilst No. 5 used FAAS.

COBALT

Analyst No. 2 determined cobalt using ICP-MS; the other Analysts used ICP-OES, No. 10 after microwave digestion.

COPPER

Analyst No. 2 determined copper using ICP-MS. Analyst No. 13 used FAAS and the remaining Analysts used ICP-OES, No. 10 after microwave digestion.

LEAD

Analysts Nos. 1, 8, 13, 18 and 19 determined lead by ICP-OES, No. 1 using selective extraction with xylene whilst Nos. 2, 4, 5, 16 and 17 used ICP-MS, No. 4 according to ASTM E2823-11. Analysts Nos. 3 and 22 used Electrothermal Atomic Absorption Spectrometry (EAAS) and No. 7 a photometric method with dithizone.

TIN

Analyst Nos. 2 and 17 determined tin using ICP-MS; the other Analysts used ICP-OES, Nos. 10 and 20 after microwave digestion.

VANADIUM

Analyst No. 2 determined vanadium using ICP-MS; the other Analysts used ICP-OES, No. 10 after microwave digestion.

BCS/SS-CRM 115

CALCIUM TREATED STEEL
CO-OPERATING ANALYSTS

1	QUIRÓS, E.,	Acerinox Europa S.A.U., Cadiz, Spain.
2	RODUSHKIN, I.,	ALS Environmental, Lulea, Sweden.
3	HURDITCH, P.,	AMG Analytical Services, Rotherham.
4	COLE, P. & WILSON B.,	ATI Specialty Materials, Monroe, USA.
5	PRATTES, K.,	Böhler Edelstahl GmbH & Co KG, Kapfenberg, Austria.
6	LIND, A.,	Chemal, Hofors, Sweden.
7	HASTINGS, J.,	Element Materials Testing, Sheffield.
8	COFFEY, R, N., *BSc, (Hons),*	Exova Teesside, Middlesbrough.
9, 24	GUSTAVSSON, I., *PhD,*	Gustavsson Consulting, Stockholm, Sweden.
10	HENRICH, A, *PhD,*	Höganäs AB, Höganäs, Sweden.
11	SCRIMSHIRE, P. J., *BSc,*	IncoTest, Hereford.
12, 26	KONDOROSI G.,	ISD Dunaferr, Dunaújváros, Hungary.
13	CROCKER, F. H.,	Pattinson & Stead (2005) Ltd., Middlesbrough.
14	JONES, S.J., *BSc, CChem, MRSC,*	Ridsdale & Co Ltd., Middlesbrough.
15	LINDKVIST, L.,	Sandvik Heating Technology AB, Hallstahammar, Sweden.
16, 27	WICHARDT, C., & CARLSTROM-WANGELIN, A.,	AB Sandvik Materials Technology, Sandviken, Sweden.
17, 23	GRANFORS, M.,	Swerea-Kimab, Stockholm, Sweden.
18, 25	DE WEERDT, J. A.,	Tata Steel IJmuiden, The Netherlands.
19	UDPA, K.N., *PhD,*	Tata Steel, Jamshedpur, India.
20	RUGG, P.,	Tata Steel, Rotherham.
21	SNOWDEN, Y.,	Tata Steel Testing Solutions, Scunthorpe.
22	GRIENBERGER, S.,	voestalpine, Linz, Austria.

DESCRIPTION OF SAMPLE

British Chemical Standard BCS-CRM 115 is sold in the form of chips passing a nominal 1700µm aperture sieve from which the fines passing a nominal 250µm sieve have been removed. It is supplied in bottles containing 100g.

Spectroscopic Standard SS-CRM 115 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-CRM 115 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 115 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 will invalidate the certified values and the associated 95% confidence limits.

The sample should be mixed thoroughly before each use.

SS-CRM 115 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.

STABILITY

BCS-CRM 115 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 115 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.

With the exception of C, S and N 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.

For C, S and N at least half of the results have been obtained using either stoichiometric analytical techniques or methods which were calibrated against pure metals or stoichiometric compounds. The remaining results have been obtained using calibrations based on 5 certified reference materials carefully selected to be similar in composition to BCS-CRM 115 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-CRM 111, BCS-CRM 112, BCS-CRM 113, BCS-CRM 114, BCS-CRM 404/2, ECRM 055-2, ECRM 056-2 (C and S only) ECRM 059-2, ECRM 192-1, ECRM 194-1 and ECRM 196-2.

MEASUREMENT UNCERTAINTY

The uncertainty of each of the certified values of BCS/SS-CRM 115 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 115 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 115 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

R P MEERES,
Managing Director
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