BUREAU OF ANALYSED SAMPLES LTD

BRITISH CHEMICAL STANDARD CERTIFIED REFERENCE MATERIAL

UKAS REFERENCE MATERIALS

4004

CERTIFICATE OF ANALYSIS

BCS/SS-CRM No. 476

MOLYBDENUM STABILISED STAINLESS STEEL

Prepared under rigorous laboratory conditions and, AFTER CERTIFICATION ANALYSIS IN GREAT BRITAIN, AUSTRIA, HUNGARY, INDIA, ITALY, RUSSIA, SPAIN and SWEDEN issued by the Bureau of Analysed Samples Ltd.

ANALYSES

Mean of 4 values - mass content in %

Analyst	C	Si	Mn	P	S	Cr	Mo	Ni	As	Co	Cu	N	Nb	Sn	V	W	Ca
1	0.0166	0.3263	1.7653	0.0300	0.0240	16.9475	2.0488	10.1825	…	0.1608	0.3090	0.0786	…	…	0.0705	0.0445	0.00225
2	...	0.3200	…	0.0285	0.0216	…	…	…	0.00524	0.1536	0.2975	…	0.0105	0.00582	0.0671	0.0404	0.00275
3	0.0169	0.3309	1.7366	0.0289	0.0236	16.8853	2.0339	10.1925	0.00478	0.1594	0.2980	0.0793	0.0119	0.00578	0.0693	…	…
4	0.0167	0.3152	1.7683	0.0302	0.0208	16.9135	2.0158	10.1408	0.00568	0.1623	0.3063	0.0777	0.0110	0.00583	0.0655	0.0443	0.00240
5	0.0164	…	…	…	0.0233	…	…	…	…	…	…	0.0794	…	…	…	…	..
6	0.0173	…	…	…	0.0226	…	…	…	…	…	…	0.0794	…	…	…	…	...
7	…	0.3223	1.7686	…	…	16.8298	2.0198	10.0858	…	0.1659	0.3047	…	…	…	0.0666	0.0405	…
8	0.0178	0.3356	1.7500	0.0310	0.0243	16.9425	2.0248	…	…	0.1659	0.3023	0.0810	…	0.00580	0.0657	0.0401	…
9	…	0.3192	1.7605	0.0301	…	16.7889	2.0178	10.1481	0.00580	0.16357	0.3017	…	0.0109	0.00663	0.0665	0.0415	0.00268
10	0.0186	0.3123	1.7638	0.0303	0.0254	16.7850	2.0740	10.2400	…	…	0.3025	0.0798	…	…	…	…	…
11	0.0162	0.3287	1.7728	0.0317	0.0242	…	2.0834	10.1081	…	0.1653	0.3077	0.0805	0.0114	0.00553	0.0664	0.0422	0.00235
12	…	0.3181	1.7387	0.0305	…	…	2.0484	10.1032	0.00508	0.1595	0.3050	…	…	0.00525	0.0664	…	0.00302
13	0.0170	…	…	…	0.0236	…	…	…	…	…	…	0.0797	…	…	…	…	…
14	0.0160	…	…	…	0.0230	…	…	…	…	…	…	…	…	…	…	…	…
15	0.0174	0.3305	1.7342	0.0322	0.0214	16.9867	2.0393	10.0717	0.00475	0.1636	0.3001	0.0782	0.0104	0.00565	0.0645	0.0400	0.00333
16	…	0.3220	1.7308	0.0302	0.0256	16.8558	2.0904	10.2625	0.00503	0.1586	0.3052	…	0.0102	0.00593	0.0604	…	0.00310
17	0.0172	0.3286	1.7687	0.0303	0.0229	16.8909	2.0901	10.0828	0.00553	0.1655	0.2939	0.0791	0.0106	0.00525	0.0640	0.0425	0.00263
18	0.0157	…	…	…	0.0237	…	…	…	…	…	…	0.0796	…	…	…	…	…
19	0.0172	…	…	…	0.0244	16.9226	…	…	0.00528	…	…	0.0766	0.0111	0.00559	..	0.0425	…
20	0.0173	…	1.7678	0.0304	…	16.9266	2.0386	10.2625	…	0.1653	0.3092	0.0805	0.0116	0.00532	0.0637	0.0398	0.00253
21	…	0.3185	1.7456	0.0304	0.0225	16.7934	2.0583	10.2173	…	0.1690	0.2943	0.0805	0.0101	…	0.0706	…	0.00308
22	0.0193	0.3216	1.7440	0.0283	0.0250	16.9213	2.0023	10.1965	0.00640	0.16405	0.3003	0.0787	0.0104	0.00700	0.0659	0.0433	0.00275
23	…	…	…	…	…	…	…	…	0.00582	…	0.3075	…	0.0103	0.00605	0.0670	0.0425	…
24	0.0174	…	1.7550	…	0.0224	…	…	…	0.00496	…	…	…	…	…	…	0.0426	0.00320
25	0.0166	…	…	…	0.0242	…	…	…	…	…	…	0.0815	…	…	…	…	…
26	…	…	…	…	…	…	2.0531	10.0963	…	…	…	…	…	…	…	…	…
27	…	0.3193	1.7603	0.0305	…	16.8250	2.0908	10.2875	0.00508	…	0.3015	0.0791	0.0099	0.00650	…	…	…
28	…	…	…	…	…	…	…	…	0.00498	…	…	…	…	…	…	…	0.00255
M_M	**0.0171**	**0.3231**	**1.7548**	**0.0302**	**0.0234**	**16.8810**	**2.0488**	**10.1674**	**0.00532**	**0.1628**	**0.3026**	**0.0794**	**0.0107**	**0.00586**	**0.0663**	**0.0419**	**0.00276**
s_M	0.0009	0.0064	0.0140	0.0011	0.0013	0.0643	0.0288	0.0724	0.00048	0.0039	0.0047	0.0012	0.0006	0.00051	0.0026	0.0016	0.00034
s_w	0.0005	0.0035	0.0072	0.0006	0.0004	0.0006	0.0148	0.0414	0.00027	0.0022	0.0024	0.0006	0.0004	0.00028	0.0014	0.0010	0.0020

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	Mo	Ni	As	Co	Cu	N	Nb	Sn	V	W	Ca
Cv	**0.0171**	**0.323**	**1.755**	**0.0302**	**0.0234**	**16.88**	**2.049**	**10.17**	**0.0053**	**0.1628**	**0.3026**	**0.0794**	**0.0107**	**0.0059**	**0.0663**	**0.0419**	**0.0028**
C(95%)	0.0005	0.004	0.008	0.0006	0.0007	0.04	0.015	0.04	0.0003	0.0022	0.0024	0.0006	0.0004	0.0003	0.0014	0.0010	0.0002
Minimum weight (g)	0.3	0.05	0.2	0.05	0.05	0.1	0.1	0.1	0.05	0.05	0.05	0.15	0.05	0.05	0.05	0.05	0.05

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.

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.

Date of this edition: July 2019
(The current edition is available at www.basrid.co.uk)

Additional Values Given For Information

Analyst	*Al*	*Pb*	*Ti*	*Zr*	*Ta*
1	…	<0.001	…	…	…
2	0.0010	0.00003	0.0004	0.00002	0.00001
3	0.0040	<0.005	0.0025	…	…
4	<0.005	<0.0003	<0.001	<0.001	<0.001
8	0.0026	…	<0.005	<0.005	<0.005
9	0.0011	…	0.0003	…	…
11	0.0061	<0.005	0.0002	0.0002	…
12	…	…	0.0025	0.0018	…
15	0.0063	<0.005	0.0024	0.0027	<0.0001
16	0.0006	<0.0005	0.0020	<0.0005	<0.0005
17	<0.0005	<0.005	0.0017	0.0033	<0.0001
19	…	0.00003	0.0002	…	…
21	0.0081	…	0.0033	…	…
22	0.0012	<0.0001	0.0008	<0.0001	<0.001
23	0.0014	0.00003	0.0004	0.00003	0.00003

Laboratories Nos. 2 and 11 also determined Ga and Sb (No. 2 by ICP-MS and No. 11 by both GD-MS and Hollow Cathode Emission) and each reported 0.003% Ga and 0.001% Sb.

CO-OPERATING ANALYSTS

1	QUIRÓS, E. & PEREZ, D.,	Acerinox, Cadiz, Spain.
2	RODUSHKIN, I.,	ALS Scandinavia, Luleå, Sweden.
3	HURDITCH, P.,	AMG Analytical Services Ltd., Rotherham.
4	TOMISSER, M.,	voestalpine BÖHLER Edelstahl GmbH & Co KG, Kapfenberg, Austria.
5	CARDY, J.,	Testing Solutions, British Steel, Scunthorpe.
6	LIND, A.,	Chemal, Hofors, Sweden.
7	ROLLET, S.,	Cogne Acciai Speciali S.p.A., Aosta, Italy.
8	COFFEY, R. N.,	Exova Teesside, Middlesbrough.
9	HENRICH, A.,	Höganäs Sweden AB, Höganäs, Sweden.
10 & 27	STEPANOVSKIKH, V.,	ICRM, Yekaterinburg, Russia.
11	SCRIMSHIRE, P.J.,	IncoTest, Hereford.
12 & 26	KONDOROSI, G.,	Dunaferr Labor Nonprofit Kft, Dunaújváros, Hungary.
13	RUGG, P.,	Liberty Speciality Steels, Stocksbridge.
14	JAMIESON S.N., CLARK, J & BARTON J.,	NSG European Technical Centre, Lathom.
15 & 28	CROCKER, F. H. & ATKINSON, M. J.,	Pattinson & Stead (2005) Ltd., Middlesbrough.
16	MUTGI, R.,	Raghavendra Spectro Metallurgical Laboratory, Bangalore, India.
17 & 24	JONES, S.J,	Ridsdale & Co Ltd., Middlesbrough.
18	LINDKVIST, L.,	Sandvik Heating Technology AB, Hallstahammar, Sweden.
19 & 25	WICHARDT, C.,	Sandvik Materials Technology AB, Sandviken, Sweden.
20 & 23	GRANFORS, M.,	Swerim, Kista, Sweden.
21	MOHAPTRA, J. K.,	Tata Steel Ltd., Jamshedpur, India.
22	GRIENBERGER, S.,	voestalpine Stahl GmbH, Linz, Austria.

BCS/SS-CRM 476
MOLYBDENUM STABILISED STAINLESS STEEL
METHODS USED

CARBON
Analysts Nos. 1, 3, 5, 6, 8, 11 13, 14 and 19 determined carbon using combustion/infra-red methods calibrated with carefully selected CRMs (see below for details). Analysts Nos. 4, 10, 18, 20, 22 and 25 used combustion/infrared methods calibrating with pure chemicals or stoichiometric compounds. Nos. 15 and 17 used a non-aqueous titration following combustion in a stream of oxygen according to BS 6200.8.2: 1981 and No. 24 determined carbon gravimetrically as CO_2 after combustion in a stream of oxygen and according to BS EN 10036:1991.

SILICON
Analysts Nos. 1, 3, 4, 8, 9, 11, 12, 21, 22 and 27 determined silicon using used Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), No.9 after microwave digestion, No. 12 treating with HNO_3/HCl/HF and H_2BO_3, fusing the residue with K_2CO_3 and extracting with HCl in accordance with EN 10351:2011 and No. 21 digesting with aqua regia. Analyst No. 2 used Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) after a microwave digestion with aqua regia and HF. Analysts Nos. 7, 10, 15, 16 and 17 determined silicon gravimetrically, dehydrating with perchloric acid; No. 7 following ASTM E353, Nos. 15 and 17 BS 6200-3.26.1:1995 and No. 16 IS 228 Part 8.

MANGANESE
Other than Analyst Nos. 10, 16 and 17, all Analysts determined manganese using ICP-OES, No. 9 after microwave digestion, No. 20 after digestion with HCl, HNO_3 and HF and No. 21 digesting with aqua regia. Analysts Nos. 10 and 17 used a photometric method in which the manganese is oxidised with periodate, No. 17 in accordance with BS 6200:3.18.2:1985. No. 16 titrated manganese with arsenite, after oxidation with persulphate, according to IS 228 Part 2.

PHOSPHORUS
With the exception of Analyst Nos. 2, 4, 10, 15, 16 and 17 all Analysts determined phosphorus using ICP-OES, No. 9 after microwave digestion, No. 12 treating with HNO_3/HCl/HF and H_2BO_3, fusing the residue with K_2CO_3 and extracting with HCl in accordance with EN 10351:2011, No. 20 after digestion with HCl, HNO_3 and HF and No. 21 digesting with aqua regia. Analysts Nos. 2 and 4 used ICP-MS, No. 2 after microwave digestion with aqua regia and HF. Analyst No. 10 used a molybdenum blue photometric method without extraction and Nos. 15 and 17 also used a photometric method, extracting the yellow phosphovanadomolybdate complex. Analyst No. 16 carried out an acidimetric titration of ammonium phosphomolybdate, according to IS 228 Part 3.

SULPHUR
Analysts Nos. 1, 3, 5, 6, 8, 11 13, 14 and 19 determined sulphur using combustion/infra-red methods calibrated with carefully selected CRMs (see below for details). Analyst No. 2 used ICP-MS after a microwave digestion with aqua regia and HF. Analysts Nos. 4, 10, 18, 21, 22 and 25 used combustion/infrared methods calibrating with pure chemicals or stoichiometric compounds. Analyst No. 15 used an acid-base titration following combustion in a stream of oxygen; No. 16 used a methylene blue photometric method, having evolved sulphur as H_2S using hypophosphoric and formic acids following IS 228 Part 2. No. 17 determined sulphur gravimetrically. Analyst No. 24 determined S using ICP-OES

CHROMIUM
Analysts Nos. 1, 3, 4, 8, 9, 20, 21, 22 and 27 determined chromium by ICP-OES, No. 9 after microwave digestion, No. 20 after digestion with HCl, HNO3 and HF and No. 21 digesting with aqua regia. The remaining analysts used a titrimetric method in which Cr(VII) is titrated with Fe(II) after oxidation with persulphate, No. 16 following IS 228 Part 6 and No. 19 ISO 15355.

MOLYBDENUM
With the exception of Nos.10, 16 and 17 all Analysts determined molybdenum using ICP-OES, No. 9 after microwave digestion, No. 20 after digestion with HCl, HNO_3 and HF and No. 21 digesting with aqua regia. Analysts Nos 10 and 17 used photometric methods in which the thiocyanate complex is reduced with Sn(II), No, 10 using a hydroxide separation and No. 17 after extraction. Analyst No. 16 used a gravimetric method, precipitating molybdenum with benzoin oxime as in IS 228 Part 5.

NICKEL
Apart from Analysts Nos. 7, 10, 15, 16 and 17 all Analysts determined nickel using ICP-OES. Analysts Nos. 7 and 16 determined nickel gravimetrically after precipitation with dimethylglyoxime (DMG), No 16 following IS 228 Part 5. Nos. 10, 15 and 17 used titrimetric methods after separation with DMG, No 15 titrating with EDTA and No. 17 with Cr(VII).

ARSENIC
With the exception of Analyst Nos. 2, 4, 15, 17, 19 and 23 all Analysts determined arsenic using ICP-OES.. Nos. 2, 4, 19 and 23 used ICP-MS, Nos. 2 and 23 after digestion with aqua regia and HF. Analysts Nos. 15 and 17 used a photometric method in which AsH_3 is bubbled through a solution of silver diethyldithiocarbamate.

COBALT
Analyst No. 2 determined cobalt using ICP-MS after microwave digestion with aqua regia and HF. The other Analysts used ICP-OES, No. 3 after acid dissolution and using standard addition.

COPPER
Analysts Nos. 2 and 23 determined copper by ICP-MS after digestion with aqua regia and HF, No10 used a photometric method with diethyldithiocarbamate, No.15 used Flame Atomic Absorption Spectrometry (FAAS) and all of the other Analysts determined copper using ICP-OES, No. 3 after acid dissolution and using standard addition.

NITROGEN
Analysts Nos. 1, 3, 5, 6, 8, 11, 13 and 19 determined nitrogen using thermal conductivity methods calibrated with carefully selected CRMs (see below for details). Nos. 4, 18, 20, 21, 22, 25 and 27 also used thermal conductivity methods but calibrating with pure chemicals or stoichiometric compounds. Nos. 10, 15 and 17 used a Kjeldahl type digestion followed by distillation and an acid-base titration.

NIOBIUM
Other than Analysts Nos. 2 and 23, who used ICP-MS, No. 2 after microwave digestion with aqua regia and HF, all analysts determined niobium using ICP-OES, No. 9 after microwave digestion and No. 19 after dissolution in aqua-regia and HF, fuming with $HClO_4$/H_3PO_4 and using a closely bracketed calibration. No. 20 digested the sample with HCl, HNO_3 and HF and No. 21 with aqua regia.

TIN
Analysts Nos. 2, 4, 19 and 23 determined tin using ICP-MS, Nos. 2 and 23 after digestion with aqua regia and HF. The other Analysts used ICP-OES, No. 3 after acid dissolution and using standard addition.

VANADIUM
Analysts Nos. 2 and 23 determined vanadium by ICP-MS, No. 2 after microwave digestion with aqua regia and HF. The others used ICP-OES, No. 9 after microwave digestion, No. 12 treating with HNO_3/HCl/HF and H_2BO_3, fusing the residue with K_2CO_3 and extracting with HCl in accordance with EN 10351:2011, No. 20 after digestion with HCl, HNO_3 and HF and No. 21 digesting with aqua regia.

TUNGSTEN
Analysts Nos. 2 and 23 determined tungsten by ICP-MS, No. 2 after digestion with aqua regia and HF. The others used ICP-OES, No. 9 after microwave digestion, and No. 19 after dissolution in aqua-regia and HF, fuming with $HClO_4$/H_3PO_4 and using a closely bracketed calibration. No. 20 digested the sample with HCl, HNO_3 and HF.

CALCIUM
Most Analysts determined calcium by ICP-OES, No. 9 after microwave digestion, No. 12 treating with HNO_3/HCl/HF and H_2BO_3, fusing the residue with K_2CO_3 and extracting with HCl in accordance with EN 10351:2011, No. 20 after digestion with HCl, HNO_3 and HF and No. 21 digesting with aqua regia. No. 2 used ICP-MS after microwave digestion with aqua regia and HF. Nos. 4, 24 and 28 used FAAS.

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MOLYBDENUM STABILISED STAINLESS STEEL
METHODS USED

ALUMINIUM

With the exception of Analysts Nos. 2 and 23, who used ICP-MS after digestion with aqua regia and HF, all Analysts determined aluminium using ICP-OES, No. 9 after microwave digestion and No. 21 digesting with aqua regia.

LEAD

Except for Nos. 2, 4, 19 and 23 who used ICP-MS, Nos. 2 and 23 after digestion with aqua regia and HF, all of the Analysts determined lead using ICP-OES.

TITANIUM

Analysts Nos. 2, 19 and 23 determined titanium using ICP-MS. All the other Analysts determined titanium using ICP-OES, No. 3 after acid dissolution and using standard addition.

ZIRCONIUM

Analysts Nos. 2, 4 and 23 determined zirconium using ICP-MS, No. 2 after microwave digestion with aqua regia and HF. The remaining analysts used ICP-OES, No. 12 treating with HNO_3/HCl/HF and H_2BO_3 fusing the residue with K_2CO_3 and extracting with HCl in accordance with EN 10351:2011.

TANTALUM

Analysts Nos. 2 and 23 determined tantalum using ICP-MS after digestion with aqua regia and HF. The other Analysts all used ICP-OES.

DESCRIPTION OF SAMPLE

British Chemical Standard BCS-CRM 476 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 476 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 476 as defined in BS EN ISO 17034, is fully responsible for assigning the certified values and their uncertainties in accordance with BS EN ISO 17034 and ISO Guide 35.

INTENDED USE

BCS-CRM 476 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 476 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. Users of optical emission spectrometry should also be aware that a minimum of three sparks, made on separate, clean locations across the face of the disc, should be made in order to establish a reliable mean value.

STABILITY

BCS-CRM 476 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 476 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 stoichiometric compounds or by calibration using 5 certified reference materials carefully selected to be similar in composition to BCS/SS-CRM 476 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 462/1, 463/1, 464/1, 465/1, 466/2, 468/1, 470, 472, 473, 474 and 479 and ECRMs 274-1, 276-1, 281-1, 285-2, 287-1, 291-1, 292-1, 294-1, 295-1, 296-1 and 298-1.

MEASUREMENT UNCERTAINTY

The uncertainty of each of the certified values of BCS/SS-CRM 476 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 476 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 476 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
July 2019

First published February 2019.
Revised July 2019 with all ICP-OES values for Pb reported as “less than” values and with corrections to some method details