



CERTIFICATE

SET OF CERTIFIED REFERENCE MATERIALS CZ 2001

LOW ALLOY STEEL FOR SOLID SAMPLE SPECTROMETRY CRM 180 – 189 A,B

Designed for the calibration and validation of methods of spectrometrical analysis on the planes of solid samples with an analyzed area of at least 4 mm in diameter: Atomic Emission Spectrometry with spark, glow discharge or laser excitation and X-ray Fluorescence Spectrometry.

The set covers the typical concentration ranges of the alloying elements and impurities of low alloy steels. The composition of the individual CRMs was balanced to avoid excessive matrix influence while sufficiently covering the above ranges. Consequently the CRMs may not correspond to any particular steel grade.

The CRMs can be used in sets of ten or individually.

Manufacture and Technical Parameters. The candidate materials were vacuum melted and cast, wrought and heat treated under the supervision of the producer except for type 180 - a carefully selected commercially available pure iron.

The samples are available as discs approximately 44mm in diameter and 13 or 25mm high.

Homogeneity was tested by spark Atomic Emission Spectrometry with an analytical area approximately 4 mm in diameter, supported by Combustion-IR Molecular Absorption Spectrometry and Thermoevolution with measurement based on temperature conductivity.

Tested were the random homogeneity, the axial trend homogeneity along successive bars and the radial trend homogeneity of the analytical surface.

Stability and storage. The CRM materials and certified constituents are stable over the entire period of validity. The CRM must be stored in a dry and non-corrosive environment.

Producer:

ČKD Technical Laboratories, Na Harfě 9, CZ - 190 02 Praha, Czech Republic

Fax: + 420 2 66036578, E-mail: standardy@quick.cz

Project Manager: Miroslav Gorný

Certified Quality Management System ISO 9001 is in force with the producer. Production and procurements, testing and certification were carried out in compliance with the ISO Guide 34 (2000).

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Deputy Director of CMI



VALUES AND UNCERTAINTIES OF CERTIFIED REFERENCE MATERIALS SET **CZ 2001** TEN TYPES **180 - 189 A, B**

N°	%m/m	C	Mn	Si	P	S	Cr	Ni	Mo	V	W	Cu	Al t	Al s*
180 A	value U _c	0.003	0.0001	0.0004 0.0001	0.0004 0.0002	0.0002 0.0001	0.004 0.001	0.0001 0.00005	0.004 0.001	0.0000	<0.0001	0.0000 0.00005	0.0001 0.00005	<0.0001
180 B	value U _c	0.003	0.047 0.002	0.001 0.001	0.004 0.001	0.0038 0.0003	0.013 0.001	0.018 0.001	0.001 0.001	0.000 0.001	0.0001	0.006 0.001	0.001	
181 A	value U _c	0.225 0.008	0.971 0.022	0.435 0.013	0.039 0.002	0.007 0.001	0.660 0.011	0.725 0.011	0.385 0.009	0.302 0.006	0.188 0.005	0.093 0.003	0.016 0.001	0.014 0.001
181 B	value U _c	0.240 0.008	0.988 0.022	0.445 0.013	0.042 0.002	0.008 0.001	0.669 0.011	0.737 0.011	0.395 0.009	0.307 0.006	0.188 0.005	0.095 0.003	0.016 0.001	0.014 0.001
182 A	value U _c	1.38 0.02	0.370 0.008	0.123 0.008	0.008 0.001	0.006 0.001	0.122 0.002	2.82 0.03	0.011 0.001	0.027 0.002	0.016 0.004	0.293 0.007	0.023 0.001	0.017 0.002
182 B	value U _c	1.39 0.02	0.370 0.008	0.126 0.008	0.008 0.001	0.006 0.001	0.122 0.002	2.82 0.03	0.011 0.001	0.027 0.002	0.016 0.004	0.293 0.007	0.023 0.001	0.017 0.002
183 A	value U _c	0.047 0.003	1.74 0.02	1.02 0.02	0.009 0.001	0.012 0.001	0.204 0.010	1.09 0.02	0.036 0.003	0.004 0.002	0.354 0.008	0.568 0.009	0.150 0.005	0.141 0.006
183 B	value U _c	0.050 0.003	1.76 0.02	1.03 0.02	0.010 0.001	0.012 0.001	0.204 0.010	1.10 0.02	0.036 0.003	0.004 0.002	0.347 0.008	0.575 0.009	0.150 0.005	0.141 0.006
184 A	value U _c	1.013 0.012	2.23 0.03	0.348 0.008	0.028 0.002	0.01	2.33 0.02	0.250 0.008	0.016 0.004	0.017 0.003	0.001	0.089 0.002	0.022 0.002	0.016 0.002
185 A	value U _c	0.566 0.009	0.715 0.004	0.230 0.005	0.024 0.001	0.02	0.032 0.003	3.84 0.04	0.123 0.006	0.178 0.006	0.001	0.179 0.003	0.060 0.002	0.054 0.004
186 A	value U _c	0.393 0.007	1.315 0.016	1.41 0.02	0.013 0.001	0.007 0.001	1.51 0.02	1.58 0.02	0.255 0.008	0.021 0.002	0.054 0.004	0.227 0.005	0.042 0.002	0.038 0.003
186 B	value U _c	0.382 0.010	1.299 0.016	1.41 0.02	0.012 0.001	0.007 0.001	1.50 0.02	1.57 0.02	0.251 0.008	0.020 0.002	0.054 0.004	0.227 0.005	0.042 0.002	0.038 0.003
187 A	value U _c	0.119 0.004	0.525 0.007	0.567 0.023	0.035 0.002	0.018 0.001	3.51 0.04	0.085 0.004	0.565 0.008	0.558 0.008	0.67 0.02	0.036 0.003	0.019 0.002	0.017 0.002
187 B	value U _c	0.119 0.004	0.529 0.007	0.577 0.023	0.035 0.002	0.014 0.001	3.51 0.04	0.085 0.004	0.565 0.008	0.558 0.008	0.67 0.02	0.036 0.003	0.027 0.002	0.025 0.002
188 A	value U _c	0.332 0.010	0.169 0.004	0.775 0.016	0.006 0.001	0.033 0.002	5.11 0.05	0.445 0.008	1.28 0.02	0.802 0.008	0.091 0.005	0.057 0.003	0.093 0.003	0.083 0.004
189 A	value U _c	0.175 0.006	0.262 0.004	0.286 0.007	0.032 0.002	0.051 0.002	1.065 0.014	5.34 0.02	0.837 0.009	0.054 0.006	1.30 0.02	0.060 0.003	0.041 0.002	0.039 0.003

Certified values: bold figures with uncertainty statement; figures in the last decimal are rounded.

Uncertainties: U_c - expanded combined uncertainty as the ± halfwidth interval except for certified zero values for which the + interval applies.

Non-certified values: thin figures without uncertainty statement. For information only, they must not be used for validation or calibration.

N°	%m/m	Ti	Zr	Co	B	Nb	Ta	Sn	As	Sb	Pb	Bi	N	Fe
180 A	value U _c	0.0000	0.0000 0.00001	0.0002	0.0000 0.00003	0.0000 0.00002	0.0000 0.00002	0.0000 0.00002	0.0000 0.00004	0.0000 0.00003	0.0000 0.00002	0.0000 0.00005	0.0004	99.98
180 B	value U _c	0.000 0.001	0.000 0.001	0.003 0.001	0.0000 0.0001	0.0001	0.0000	0.0011 0.0005	0.001 0.001	0.0004 0.0003	0.0002	0.0000	0.0028	99.9
181 A	value U _c	0.149 0.008	0.001 0.0005	0.050 0.003	0.0069 0.0005	0.058 0.003	0.039 0.003	0.113 0.004	0.027 0.001	0.016 0.001	0.0005 0.0002		0.005	95.48
181 B	value U _c	0.155 0.008	0.001 0.0005	0.050 0.003	0.0076 0.0005	0.062 0.003	0.042 0.003	0.122 0.004	0.029 0.001	0.017 0.001	0.0005 0.0002		0.005	95.37
182 A	value U _c	0.004 0.002	0.001 0.0004	0.171 0.004	0.0003 0.0001	0.001 0.0004	0.000 0.0002	0.004 0.001	0.005 0.0004	0.001 0.0006	0.000		0.0049 0.0003	94.60
182 B	value U _c	0.004 0.002	0.001 0.0004	0.171 0.004	0.0003 0.0001	0.001 0.0004	0.000 0.0002	0.004 0.001	0.005 0.0004	0.001 0.001	0.000		0.0049 0.0003	94.59
183 A	value U _c	0.003 0.001	0.078 0.004	0.119 0.003	0.0005 0.0001	0.006 0.001	0.000	0.051 0.002	0.005 0.001	0.001 0.0006	0.000	0.0000 0.00005	0.0036 0.0004	94.49
183 B	value U _c	0.003 0.001	0.082 0.004	0.119 0.003	0.0005 0.0001	0.006 0.001	0.000	0.054 0.002	0.004 0.001	0.001 0.0006	0.000	0.0000 0.00005	0.0036 0.0004	94.44
184 A	value U _c	0.010 0.002	0.002	0.007 0.002	0.0005 0.0002	0.013 0.001	0.000 0.0002	0.008 0.001	0.006 0.001	0.002 0.0007	0.000		0.0104 0.0005	93.58
185 A	value U _c	0.022 0.001	0.002 0.0006	0.032 0.001	0.0116 0.0014	0.20 0.01	0.085 0.005	0.003 0.001	0.022 0.002	0.011 0.001	0.002 0.0004		0.0051 0.0004	93.63
186 A	value U _c	0.047 0.004	0.002	0.006 0.002	0.0009 0.0001	0.004 0.001	0.009 0.001	0.018 0.001	0.007 0.001	0.002 0.0006	0.000		0.005	93.06
186 B	value U _c	0.044 0.004	0.002	0.006 0.002	0.0009 0.0002	0.004 0.001	0.009 0.002	0.018 0.002	0.007 0.001	0.002 0.0007	0.000		0.005	93.12
187 A	value U _c	0.087 0.005	0.013 0.001	0.071 0.003	0.0006 0.0002	0.028 0.003	0.015 0.002	0.013 0.001	0.007	0.023 0.002	0.003 0.0005	0.003 0.0004	0.0122 0.0007	93.01
187 B	value U _c	0.099 0.005	0.013 0.002	0.071 0.003	0.0006 0.0002	0.028 0.003	0.017 0.002	0.013 0.001	0.007	0.022 0.002	0.003 0.0005	0.003 0.0004	0.0122 0.0007	92.98
188 A	value U _c	0.034 0.003	0.052 0.003	0.006 0.001	0.0047 0.0004	0.122 0.003	0.022 0.002	0.005 0.001	0.005	0.006 0.002	0.001 0.0004		0.0076 0.0004	90.53
189 A	value U _c	0.326 0.010	0.005 0.001	0.007 0.002	0.0030 0.0003	0.017 0.002	0.005	0.029 0.002	0.080 0.003	0.003	0.002 0.0004		0.004	90.01

Further non-certified values are:

Se: 0.000% in 180A, 0.000% in 180B, 0.008% in 184A, 0.004% in 187A, 0.004% in 187B
Te: 0.000% in 180A, 0.000% in 180B, 0.005% in 185A, 0.001% in 188A

CERTIFICATION

Principle and Traceability. Certification based on an interlaboratory experiment performed by various independent analytical methods was carried out in compliance with the ISO Guide 35 (1989 and the final draft of the 2002 revision).

The results were traced to the primary substances and validated by other matrix-matching CRMs.

Methods. Atomic Emission Spectrometry with spark and glow discharge excitation, X-ray Fluorescence Spectrometry and Glow Discharge Mass Spectrometry were applied on a plane of the solid sample. Chips were analyzed by Combustion-IR Molecular Absorption Spectrometry, Thermoevolution with temperature conductivity measurement, Instrumental Neutron Activation Analysis and by solution methods which comprised: Atomic Emission Spectrometry and Mass Spectrometry with Inductively Coupled Plasma excitation-directly and with hydrides generation; Flame Atomic Absorption Spectrometry-directly and with hydrides generation, Electro-thermal Atomic Absorption Spectrometry-graphite furnace; Molecular Absorption Spectrometry (Spectrophotometry), Titrimetry and Gravimetry.

Participating laboratories (for both A and B types):

Analytika Company, Praha, Czech Republic (C.R.)
Applied Research Laboratories, Ecublens, Switzerland
Baird Europe, Zoeterwoude, the Netherlands
BIJO Company, Praha-Plzeň, C.R.
Brammer Standard Company, Houston, Texas, U.S.A.
CKD Technical Laboratories, Praha, C.R.
Hilger Analytical, Margate, United Kingdom
Hoesch Stahl, Dortmund, Germany
Institute CRM, Yekaterinburg, Russia
Institute of Chemical Technogy, Praha, C.R.
Jobin-Yvon, Longjumeau, France
Leco Instrumente Plzeň, Plzeň, C.R.
Nordstahl, Düsseldorf, Germany
Nová Hut', Ostrava, C.R.

Nuclear Physics Institute, Řež u Prahy, C.R.
Poldi Ocel, Kladno, C.R.
Shiva Technologies, Cicero, New York, U.S.A.
Shiva Technologies Europe, Ramonville, France
Škoda, Plzeň, C.R.
Spectro, Kleve, Germany
Třinecké železářny, Třinec, C.R.
Válcovny plechu, Frýdek-Místek, C.R.
Východoslovenské železiarne, Košice, Slovakia
VÚHŽ, Dobrá u Frýdku-Místku, C.R.
ŽDAS, Ždár nad Sázavou, C.R.
Železářny a drátovny Bohumín, Bohumín, C.R.
Železářny Hrádek, Hrádek u Rokycan, C.R.

Evaluation. First the values of laboratory means were assessed technically to justify the deletion of possible outliers. Next the normal distribution of the laboratory means in a set for each element/CRM was verified and the unrounded arithmetic averages and their standard deviations calculated.

Certified values are the averages of at least six accepted laboratory means the normal distributions of which were not rejected, rounded identically as their stated uncertainties except for a few minor values expressed by a single figure where one more decimal place for uncertainty is allowed. * The values of Al s. conventionally defined by dissolving the sample in a mixture of 3 parts of v/v HCl, 1 part of HNO₃ and 2 parts of water.

Uncertainty was estimated with respect to ISO Guide to the Expression of Uncertainty in Measurement, 1993 and ISO Guide 35 - Certification of Reference Materials: General and Statistical Principles as an expanded combined uncertainty with a coverage factor of 2-2,5 depending on the number of accepted laboratory means and a contribution of the standard uncertainty of homogeneity. It is expressed as the \pm halfwidth interval except for certified zero values for which only the + halfwidth interval applies. The sources of the estimates of uncertainty were the standard uncertainty of an average of the laboratory means and a contribution of the standard uncertainty of homogeneity when found to be statistically significant. The uncertainty statement is given by two significant figures at most and holds only for analytical areas 4 mm or more in diameter.

Non-certified values are given when less than six accepted laboratory means were available and serve only as supplementary matrix information. They must not be used for calibration and/or validation.

The non-certified values of the matrix element Fe were calculated by subtracting the sum of the certified and non-certified values and the 0,01% allowance for undetermined impurities from 100,0%.

Users instructions. Preparation of the analytical surfaces must be identical both for the CRMs and the analyzed samples in compliance with the instrument manual. When determining low contents of C, Si and Al special care must be taken to avoid the contamination of the analytical surface with residues of abrasives. Overheating of the disc during grinding should be avoided.