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Reference Material® 8499

Trace Elements in Coal

(Bituminous)

REFERENCE MATERIAL INFORMATION SHEET

Purpose: This reference material is intended primarily for use in process control in the analysis of coals and materials of a similar matrix.

Description: A unit of RM 8499 consists of 50 g of bituminous coal that was ground to pass a 250 µm (60 mesh) sieve, homogenized, bottled under an argon atmosphere, and sealed in an aluminized bag.

Non-Certified Values: Non-certified values are suitable for use in method development, method harmonization, and process control but do not provide metrological traceability to the International System of Units (SI) or other higher-order reference system [1]. Non-certified mass fraction values are provided below. These non-certified values are metrologically traceable to the materials and procedures used in their determination.

Table 1. Non-Certified Mass Fraction Values for Major and Minor Elements (Dry-Mass Basis) in RM 8499[(a)]

Element	Major Constituents Mass Fraction (%)	*k*	Element	Minor Constituents Mass Fraction (%)	*k*
Hydrogen (H)	4.97 ± 0.16	2	Aluminum (Al)	0.960 ± 0.049	2.15
Iron (Fe)	1.42 ± 0.13	2.20	Calcium (Ca)	0.1714 ± 0.0084	2.08
Silicon (Si)	1.81 ± 0.13	2.13	Potassium (K)	0.1248 ± 0.0052	2.20
Sulfur (S)	2.738 ± 0.057	2			

[(a)] Values are expressed as $x \pm U_{95\%}(x)$, where x is the non-certified value and $U_{95\%}(x)$ is the expanded uncertainty of the non-certified value. The value of the analyte is believed to lie within the interval $x \pm U_{95\%}(x)$ with 95 % confidence, although some components of bias or uncertainty might remain unaccounted for. To propagate the stated uncertainty, treat the value as a normally distributed random variable with mean x and standard deviation $U_{95\%}(x)/2$ [2–4].

Additional Information: Information of potential interest to users is provided in Appendix A.

Period of Validity: The non-certified values are valid within the measurement uncertainty specified until **30 September 2027**. The value assignments are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

Maintenance of Non-Certified Value: NIST will monitor this material to the end of its period of validity. If substantive technical changes occur that affect the non-certified values during this period, NIST will update this Reference Material Information Sheet and notify registered users. RM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the RM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (https://www.nist.gov/srm).

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Table 2. Non-Certified Mass Fraction Values for Trace Elements (Dry Mass Basis) in RM 8499[(a)]

Element	Major Constituents Mass Fraction (mg/kg)			*k*	Element	Minor Constituents Mass Fraction (mg/kg)			*k*
Antimony (Sb)	0.428	±	0.040	2.05	Manganese (Mn)	18.4	±	1.1	1.81
Arsenic (As)	8.55	±	0.49	2	Mercury (Hg)	0.1351	±	0.0035	2
Barium (Ba)	62.8	±	3.5	2	Nickel (Ni)	11.08	±	0.35	2
Boron (B)	75.7	±	4.1	2.05	Rubidium (Rb)	8.49	±	0.87	2.13
Bromine (Br)	11.9	±	1.0	2.11	Scandium (Sc)	3.583	±	0.088	2
Cerium (Ce)	12.24	±	0.27	2	Selenium (Se)	1.525	±	0.078	2
Cesium (Cs)	0.648	±	0.021	2	Sodium (Na)	374	±	16	2.10
Chlorine (Cl)	963	±	23	2.09	Strontium (Sr)	84.1	±	5.3	2.32
Chromium (Cr)	16.57	±	0.34	2	Titanium (Ti)	519	±	19	2.05
Cobalt (Co)	3.622	±	0.090	2	Uranium (U)	0.636	±	0.032	2.06
Copper (Cu)	5.70	±	0.14	2	Vanadium (V)	29.2	±	1.5	1.72
Europium (Eu)	0.2457	±	0.0063	2	Zinc (Zn)	13.0	±	1.3	2.17
Magnesium (Mg)	391	±	32	2					

[(a)] Values are expressed as $x \pm U_{95\%}(x)$, where x is the non-certified value and $U_{95\%}(x)$ is the expanded uncertainty of the non-certified value. The value of the analyte is believed to lie within the interval $x \pm U_{95\%}(x)$ with 95 % confidence, although some components of bias and uncertainty might remain unaccounted for. To propagate this uncertainty, treat the value as a normally distributed random variable with mean x and standard deviation $U_{95\%}(x)/2$ [2–4].

Safety: RM 8499 is intended for research use. Please consult the Safety Data Sheet for this product.

Storage: The original unopened bottles of RM 8499 should be stored tightly sealed and away from sunlight and intense sources of radiation at room temperature (20 °C ± 5 °C). An open bottle can be reused until the material reaches its expiration date, provided that the open bottle is resealed and stored at room temperature (20 °C ± 5 °C).

Use: Before it is sampled, the unit should be thoroughly mixed by carefully inverting and rotating the tightly sealed bottle. For analytical determinations use a minimum test portion mass of 30 mg for aluminum, calcium, chlorine, chromium, copper, iron, magnesium, manganese, potassium, silicon, sodium, strontium, sulfur, titanium, vanadium, and zinc; 100 mg for barium and scandium; 200 mg for antimony, arsenic, boron, bromine, cerium, cesium, cobalt, europium, rubidium, selenium, and uranium; 250 mg for mercury; 400 mg for nickel; and 750 mg for hydrogen.

Drying Instructions: To relate measurements directly to the certified and reference values, which are expressed on a dry-mass basis, users should determine a drying correction at the time of the analysis. The correction is determined by oven-drying a separate 1 g sample in a nitrogen atmosphere at 107 °C ± 3 °C to a constant mass [5] or equivalent technique. Attainment of constant mass is defined according to the ASTM thermogravimetric (TG) method as either a mass loss of ≤ 0.05 %, relative, over a nine-minute period or the mass loss after one hour of heating [5]. At NIST, the mass losses determined in both manners, and in both nitrogen and air, were similar.

The mass loss determined in both a nitrogen and air atmosphere, which is reported ***for information purposes only***, was nominally 2 %. The mass loss determined by the user may be different, depending on ambient conditions when the bottle is sampled.

SOURCE, PREPARATION, AND HOMOGENEITY ASSESSMENT

Source and Preparation of Material: The coal for this RM was obtained from the Bailey Mine of CONSOL Energy Inc. in southwestern Green County, PA. This mine produces bituminous coal obtained from the Pittsburgh seam. The collection of the approximately 450 kg of coal was performed under the direction of D. Wilson. The coal was air-dried and subsequently pulverized to pass a 250 µm (60 mesh) sieve by a company under contract to NIST. The entire lot was divided into two portions using the spinning riffler technique. One portion of the lot was sealed in Mylar bags filled under an argon atmosphere for long-term storage. The other portion was further divided by the spinning riffler technique, bottled under an argon atmosphere, and sealed in Mylar bags to prepare RM 8499.

Heterogeneity Assessment: Heterogeneity was assessed for selected elements in the bottled material using wavelength dispersive X-ray fluorescence spectrometry (WDXRF), instrumental neutron activation analysis (INAA), prompt gamma-ray activation analysis (PGAA), and isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS).

Values Assignment: Measurements were modeled using linear mixed effects statistical models, the parameters of which were estimated using the Bayesian inference paradigm [6]. The Monte Carlo method [3] was used to propagate all components of uncertainty. Values are given with an expanded uncertainty, U, which can be expressed in a manner that is consistent with the ISO/JCGM Guide [4] as $U = ku_c$. The quantity, k, is the effective coverage factor used to obtain an expanded uncertainty that provides a symmetric, approximately 95 % coverage interval. An effective value of k was calculated as the ratio U/u_c, which resulted in a value of $k < 1.96$ for two elements, manganese and vanadium. A value of $k < 1.96$ can occur when the distribution of Monte Carlo samples deviates substantially from a Gaussian distribution. For all elements, except bromine, hydrogen, nickel, and rubidium, the quantity u_c represents, at the level of one standard deviation, the estimated uncertainty in the mass fraction for the mean of all bottles of RM 8499, because the underlying mass fraction is assumed to be the same for each bottle. For bromine, hydrogen, nickel, and rubidium, the quantity u_c represents, at the level of one standard deviation, the estimated uncertainty for the mean of a single randomly chosen bottle of RM 8499, which accounts for possible material heterogeneity. The analytical techniques used for each element are listed in Table A2.

REFERENCES

[1] Thompson, A.; Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*; NIST Special Publication 811; U.S. Government Printing Office: Washington, DC (2008); available at https://www.nist.gov/pml/special-publication-811 (accessed Aug 2022).

[2] Beauchamp, C.R.; Camara, J.E.; Carney, J.; Choquette, S.J.; Cole, K.D.; DeRose, P.C.; Duewer, D.L.; Epstein, M.S.; Kline, M.C.; Lippa, K.A.; Lucon, E.; Molloy, J.; Nelson, M.A.; Phinney, K.W.; Polakoski, M.; Possolo, A.; Sander, L.C.; Schiel, J.E.; Sharpless, K.E.; Toman, B.; Winchester, M.R.; Windover, D.; *Metrological Tools for the Reference Materials and Reference Instruments of the NIST Material Measurement Laboratory*; NIST Special Publication (NIST SP) 260-136, 2021 edition; U.S. Government Printing Office: Washington, DC (2021); available at https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-136-2021.pdf (accessed Aug 2022).

[3] JCGM 101:2008; *Evaluation of Measurement Data — Supplement 1 to the "Guide to the Expression of Uncertainty in Measurement" — Propagation of Distributions Using a Monte Carlo Method*; JCGM (2008); available at https://www.bipm.org/en/publications/guides (accessed Aug 2022).

[4] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at https://www.bipm.org/en/publications/guides (accessed Aug 2022); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at https://www.nist.gov/pml/nist-technical-note-1297 (accessed Aug 2022).

[5] ASTM D7582-15; *Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis*; Annu. Book ASTM Stand., Vol 05.06, pp. 965–973 (2021).

[6] Gelman, A.; Carlin, J.B.; Stern, H.S.; Rubin, D.B.; *Bayesian Data Analysis*; Chapman & Hall (2004).

Certain commercial equipment, instruments, or materials may be identified in this Reference Material Information Sheet to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Users of this RM should ensure that the Reference Material Information Sheet in their possession is current. This can be accomplished by contacting the Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at https://www.nist.gov/srm.

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APPENDIX A

Table A1. Mass Fraction Values (Dry Mass Basis) of Potential Interest to Users for Elements in RM 8499[a]

Major Constituents

Element	Mass Fraction (%)	Element	Mass Fraction (%)
Carbon (C)	76	Oxygen (O)	7
Nitrogen (N)	1.4		

Trace Elements

Element	Mass Fraction (mg/kg)	Element	Mass Fraction (mg/kg)
Silver (Ag)	0.02	Neodymium (Nd)	6
Beryllium (Be)	1	Niobium (Nb)	2
Bismuth (Bi)	<1	Osmium (Os)	<1
Cadmium (Cd)	0.1	Palladium (Pd)	<1
Dysprosium (Dy)	1	Phosphorus (P)	150
Erbium (Er)	0.7	Platinum (Pt)	<1
Fluorine (F)	60	Praseodymium (Pr)	1.5
Gadolinium (Gd)	1	Rhenium (Re)	<10
Gallium (Ga)	5	Rhodium (Rh)	<1
Germanium (Ge)	3	Ruthenium (Ru)	<1
Gold (Au)	<1	Samarium (Sm)	1
Hafnium (Hf)	0.6	Tantalum (Ta)	0.1
Holmium (Ho)	0.2	Tellurium (Te)	<1
Indium (In)	0.01	Terbium (Tb)	0.2
Iodine (I)	1	Thallium (Tl)	0.4
Iridium (Ir)	<1	Thorium (Th)	1
Lanthanum (La)	7	Thulium (Tm)	0.1
Lead (Pb)	5	Tin (Sn)	0.8
Lithium (Li)	8	Tungsten (W)	<10
Lutetium (Lu)	0.1	Ytterbium (Yb)	0.6
Molybdenum (Mo)	1	Yttrium (Y)	6
		Zirconium (Zr)	20

[a] The non-certified mass fraction values given in Table A1 are provided without uncertainty estimates and are given as additional information on the matrix. These values cannot be used to establish metrological traceability.

Table A2. Methods of Analysis

Methods	Element
CANSPEX Interlaboratory Study	S
Isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) at NIST	Hg
Isotope dilution sector field inductively coupled plasma mass spectrometry (ID-SF-ICP-MS) at NIST	S
Instrumental neutron activation analysis (INAA) at NIST	Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Cu, Eu, Fe, Mg, Mn, Na, Rb, Sb, Sc, Se, Sr, Ti, U, V, Zn
Prompt gamma-ray activation analysis (PGAA) at NIST	Al, B, Cl, Fe, H, K, Si, Ti
Wavelength dispersive X-ray fluorescence spectrometry (WDXRF) at NIST	Al, Ca, Fe, K, Na, Ni, Rb, Si, Sr, Ti, Zn

Values of Potential Interest to Users: Particle size measurements were made using a laser-based light scattering system. Approximately 0.5 g of material (refractive index: 1.746, absorption index: 1.0) was measured using water as the dispersant, (refractive index: 1.33) and 0.01 % Triton X-100 as a pre-wetting surfactant. Calculated 10th percentile ($d_{0.1}$), 50th percentile ($d_{0.5}$), and 90th percentile ($d_{0.9}$) particle sizes (volume fraction of particles smaller than the value) are $d_{0.1}$ = 10.4 µm, $d_{0.5}$ = 67.7 µm, and $d_{0.9}$ = 179 µm. The volume fraction of material smaller than 10 µm in diameter is 10 %. The particle size distribution is shown in Figure A1.

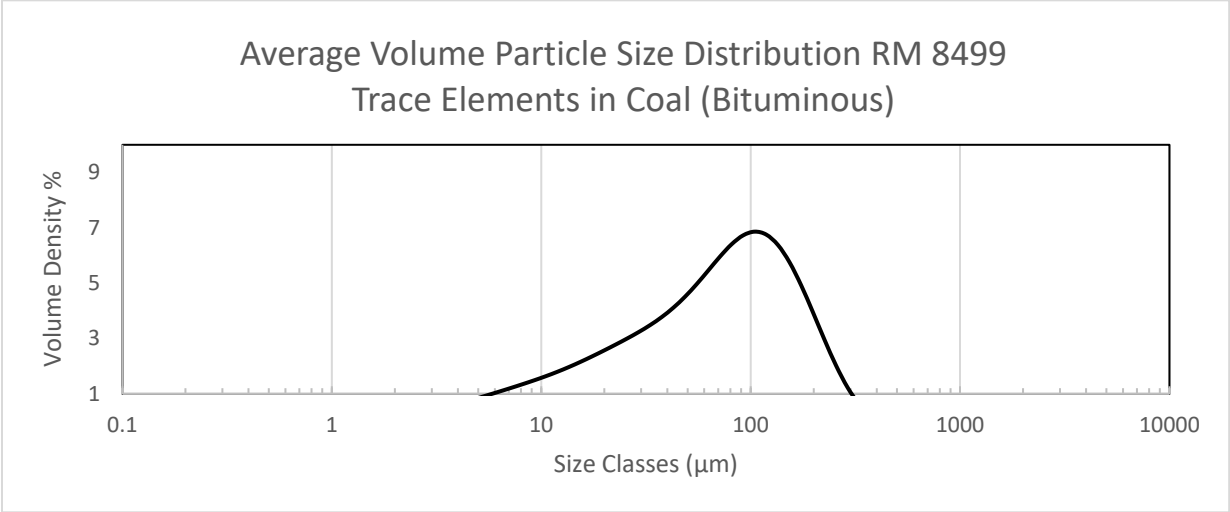


Figure A1. Average Volume Particle Size Distribution for RM 8499 as measured by a laser-based light scattering system.

Additional Values of Potential Interest to Users: Portions of RM 8499 were analyzed as unknown samples in the round robin study CANSPEX 2015-3, conducted by Quality Associates International, Ltd. Summary results shown in Table A1 were provided by Quality Associates International, Ltd. These results are included as an Appendix to the Reference Material Information Sheet for RM 8499 to demonstrate user experience with this material using conventional methods and to better characterized the matrix. Results from this study should **NOT** be used as substitutes for the NIST values.

Table A3. RM 8499 CANSPEX Interlaboratory Study Results

Parameter	Most Likely Value [(a)]	Unit	95 % Coverage Interval of Most Likely Value	Pooled Within Lab Standard Deviation (s_w)	Pooled Between Lab Standard Deviation (s_B)	Total Number of Labs
Moisture	1.664	%	0.033	0.033	0.158	127
Ash	8.488	%	0.013	0.034	0.053	125
Volatile	38.19	%	0.19	0.12	0.81	101
Btu	13 678	per lb	10	16	46	116
Carbon	75.85	%	0.19	0.13	0.66	66
Hydrogen	5.130	%	0.037	0.032	0.119	61
Nitrogen	1.444	%	0.014	0.018	0.039	58
Total Sulfur	2.761	%	0.023	0.021	0.106	121
Pyritic Sulfur	1.291	%	0.049	0.023	0.080	19
Sulfate Sulfur	0.049	%	0.009	0.004	0.015	20
Chlorine	942	µg/g	25	18	73	52
Fluorine	65	µg/g	5	2	14	39
Mercury	135	ng/g	3	4	8	46
Selenium	1.40	µg/g	0.24	0.10	0.33	13
FSI[(b)]	8.0		0.2	0.3	0.4	58

[(a)] Values are expressed on a dry-mass basis for all parameters except moisture. The moisture value is expressed on an "as received" basis.
[(b)] Free Swelling Index

Table A4. Derived Standard Deviations (in %) of Repeatability (s_r) and Reproducibility (s_R), and Tally of Published Methods Used in CANSPEX Interlaboratory Study[a]

Parameter	Total Number of Labs	Standards Australia (AS)				ASTM International				British Standards Institution (BSI)				Deutsches Institut für Normung (DIN)				China National Standards (GB)				International Organization for Standardization (ISO)				Association Francaise de Normalisation (NF)				South African Bureau of Standards (SABS)				In-house[b]
		AS	s_r	s_R	No.	ASTM	s_r	s_R	No.	BSI	s_r	s_R	No.	DIN	s_r	s_R	No.	GB	s_r	s_R	No.	ISO	s_r	s_R	No.	NF	s_r	s_R	No.	SABS	s_r	s_R	No.	No.
Moisture %	127	**1038.3**	0.04	-	2	**D2013**	0.04	0.09	0	**1016**	0.04	-	1	**51718**	0.07	-	2	**212**	0.07	-	1	**589**	0.11	-	1	**3-037**	-	-		**925**	-	-	0	18
						D3173	0.04	0.09	56													**11722**	0.04	-	12									
						D3302	0.04	0.09	0													**5068**	0.07	-	1									
						D5142	0.08	0.11	11																									
						D7582	0.09	0.28	22																									
Ash % dry basis	127	**1038.3**	0.04	0.05	2	**D3174**	0.08	0.11	53	**1016**	0.05	0.11	1	**51719**	0.07	0.11	3	**212**	0.07	0.11	1	**1171**	0.07	0.11	16	**3-003**	-	-			-	-		16
						D5142	0.09	0.12	12																									
						D7582	0.07	0.11	23																									
Volatile % dry basis	101	**1038.3**	0.07	0.35	2	**D3175**	0.18	0.35	40	**1016**	0.11	0.35	1	**51720**	0.41	0.54	2	**212**	0.18	0.35	1	**562**	0.41	0.54	19									13
						D5142	0.29	0.86	15																									
						D7582	0.13	0.47	8																									
Btu/lb dry basis	116	**1038.5**	20	46	1	**D1989**	23	39	2	**1016**	18	43	0	**51900**	18	46	4	**213**	18	46	1	**1928**	43	106	19									11
						D2015	24	38	0																									
						D3286	18	35	3																									
						D5865	24	38	75																									
Carbon % dry basis	66	**1038.6.4**	0.11	0.21	3	**D3178**	0.11	-	0					**51732**	-	-	2	**476**	0.18	0.35	1	**609**	0.09	0.18	2									8
						D5373	0.16	0.35	44													**29541**	0.18	0.46	6									
Hydrogen % dry basis	61	**1038.6.4**	0.04	0.07	3	**D3178**	0.02	-	0					**51732**	-	-	2	**476**	0.05	0.09	1	**609**	0.04	0.09	2									5
						D5373	0.04	0.09	42													**29541**	0.04	0.14	6									
Nitrogen % dry basis	58	**1038.6.4**	0.01	0.03	3	**D3179**	0.07	0.12	0					**51732**	-	-	2	**476**	0.03	0.05	1	**333**	0.02	0.04	1									8
						D5373	0.02	0.05	39													**29541**	0.01	0.05	4									
Total Sulfur % dry basis	121	**1038.6.3.3**	0.02	0.08	2	**D3177**	0.02	0.04	1	**1016**	0.02	0.04	1	**51724-3**	0.01	0.02	2	**214**	0.04	0.09	1	**351**	0.02	0.04	3	**3-038**	-	-	0		-	-		17
						D4239	0.04	0.10	83													**19579**	0.04	0.10	7									
						D5016	0.08	0.27	4																									
Pyritic Sulfur % dry basis	19	**1038.11**	0.02	0.05	1	**D2492**	0.07	0.18	15									**215**	0.02	0.04	1													2
Sulfate Sulfur % dry basis	20	**1038.11**	0.007	0.011	1	**D2492**	0.007	0.014	16									**215**	0.01	0.04	1													2
Chlorine µg/g dry basis	52	**1038.8.2**	35	71	1	**D2361**	106	213	1	**1016**	177	177		**51727**	71	106	1	**3558**	35	71	1	**587**	-	-	0	**3-009**	-	-	1		-	-		21
						D4208	61	148	19																									
						D6721	21	26	8																									
Fluorine µg/g dry basis	39					**D3761**	5	5	16					**51723**	8	14	0	**4663**	6	7	1	**11724**	4	7	2	**03-009**	-	-						18
						D5987	4	7	2																									
Mercury ng/g dry basis	46					**D6414**	10	13	2					**22022**	-	-																		7
						D6722	3	9	37																									
Selenium µg/g dry basis	12					**D4606**	0.210	0.18	2	**5.000**																								10
FSI	58	**1038.17**	0.18	0.35	1	**D720**	0.35	0.71	40	**1016**	-	-	0	**51741**	-	-	0	**5448**	0.35	0.53	1	**501**	0.35	0.18	9									7

[a] The above precision standard deviations are derived from the division of each method's published precision values by an estimate of the coverage factor used.

[b] Method is designated "In-house" if lab reports method as In-house; lab reports methods as modified; or does not report a method. CANSPEX does not provide repeatability or reproducibility information for In-house methods.

[c] "-" indicates documentation confirming the repeatability or reproducibility is not available.

The above referenced methods are available through the following websites:

AS https://www.standards.org.au (accessed Aug 2022)
ASTM https://www.astm.org/ (accessed Aug 2022)
BSI https://www.bsigroup.com/ (accessed Aug 2022))
DIN https://www.din.de/en (accessed Aug 2022)
GB https://www.gbstandards.org/ (accessed Aug 2022)
ISO https://www.iso.org/standards.html (accessed Aug 2022)
NF https://www.afnor.org/en/ (accessed Aug 2022)
SABS https://www.sabs.co.za/ (accessed Aug 2022)

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