National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 691

Reduced Iron Oxide

This Standard Reference Material (SRM) is intended primarily for use in validation of chemical and instrumental methods of analysis for elemental contents of reduced iron oxide and materials of similar matrix. It can be used to validate value assignment of in-house reference materials. A unit of SRM 691 consists of one bottle containing approximately 100 g of powder with < 74 μm (200 mesh) particle sizes.

Certified Mass Fraction Values: Certified values for constituents of SRM 691 are reported in Table 1 as mass fractions of the constituents in an iron matrix [1]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been taken into account [2]. A certified value is the present best estimate of the true value. The certified values are metrologically traceable to the International System of Units (SI) derived unit for mass fraction (expressed as percent). The expanded uncertainty estimates are expressed at a confidence level of approximately 95 %. Constituents listed as compounds are given according to industry convention, assuming perfect stoichiometry.

Table 1. Certified Mass Fraction Values for SRM 691 Reduced Iron Oxide

Constituent	Mass Fraction (%)	Expanded Uncertainty (%)
Aluminum Oxide (Al_2O_3)	1.215	0.073
Calcium Oxide (CaO)	0.640	0.025
Chromium (Cr)	0.0256	0.0016
Cobalt (Co)	0.0317	0.0046
Copper (Cu)	0.0309	0.0029
Iron (Total Fe)	90.55	0.60
Magnesium Oxide (MgO)	0.517	0.018
Manganese(II) Oxide (MnO)	0.0428	0.0012
Phosphorus (P)	0.0052	0.0011
Potassium (K)	0.0656	0.0071
Silicon Dioxide (SiO_2)	3.66	0.11
Sodium Oxide (Na_2O)	0.1775	0.0037
Titanium Dioxide (TiO_2)	0.275	0.024
Vanadium (V)	0.0154	0.0033

Expiration of Certification: The certification of **SRM 691** is valid indefinitely, within the measurement uncertainty specified, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). Periodic recertification of this SRM is not required. The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

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Gaithersburg, MD 20899
Certificate Issue Date: 21 April 2021
Certificate Revision History on Last Page

Steven J. Choquette, Director
Office of Reference Materials

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Coordination of technical measurements for certification was performed by J.I. Schultz, formerly of NIST. Review and revision of values and uncertainty estimates were coordinated by J.R. Sieber of the NIST Chemical Sciences Division.

Measurements for value assignment of SRM 691 were performed by M.S. Epstein, R.M. Lindstrom, A.F. Marlow, and J.R. Sieber of the NIST Chemical Sciences Division and C.G. Blundell, T.A. Butler, M. Dadjadi, E.R. Deardorff, T.C. Rains, and R.M. Stone, formerly of NIST. Additional measurements were performed by Allis-Chalmers (Milwaukee, WI); Andrew S. McCreath & Son, Inc. (Harrisburg, PA); Inland Steel Co. (East Chicago, IN); Institut de Recherches de la Siderurgie (Maizieres-Les-Metz, France); Ledoux and Company (Teaneck, NJ); and United States Steel Corp. (Monroeville, PA).

Statistical consultation for this SRM was provided by A.M. Possolo of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

To dry samples, heat in an oven at 105 °C for 1 h. To relate analytical determinations to the certified values in this Certificate of Analysis, a minimum test portion of 0.5 g should be used. Before sampling, it is recommended to mix the powder by inverting and rotating the bottle by hand for at least one minute. A bottle containing unused material should be recapped immediately and stored at room temperature away from light.

To use the uncertainty estimates given in this certificate, divide the expanded uncertainty by $k = 2$ to obtain the combined standard uncertainty.

PREPARATION AND ANALYSIS[(1)]

The reduced iron oxide material for this SRM was produced by Allis-Chalmers (Milwaukee, WI). It was crushed, ground, sieved to pass a 74 µm sieve (200 mesh), and mixed at the Colorado School of Mines Research Institute (Golden, CO). At NIST, the material was sieved again and blended, then bottled under a dry nitrogen atmosphere to inhibit oxidation. Homogeneity testing of total iron content was performed at NIST, and the results indicated the material variability for 0.5 g samples was less than the test method repeatability. Additional testing for all elements, except sulfur, by borate fusion of 1.0 g samples and X-ray fluorescence spectrometry showed all tested elements, except chromium, are sufficiently homogeneous within and among units for quantitative determinations.

Each certified value is a weighted average of the results from the methods listed in Table 4. The uncertainty listed with each certified value is an expanded uncertainty about the mean, with coverage factor, $k = 2$, calculated in accordance with the ISO/JCGM Guide [3–8].

ADDITIONAL CONSTITUENTS

Non-certified values are provided for the following additional constituents in SRM 691. These values are not certified, because NIST cannot vouch fully for the calibrations of the test methods and other details.

Reference Mass Fraction Values: Reference values for SRM 691 are reported in Table 2 as the mass fraction of the elements in an iron oxide matrix, expressed as percent. A NIST reference value is a non-certified value that is the present best estimate based on available data; however, the value does not meet the NIST criteria for certification and is provided with an associated uncertainty that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [2]. The value is the unweighted mean of results obtained at collaborating laboratories. The expanded uncertainty, U, is an expanded uncertainty about the mean, with coverage factor, $k = 2$ [3–8]. Results derived from the use of this value are considered by NIST to be traceable only to the value itself.

[(1)] Certain commercial equipment, instruments or materials are identified in this certificate 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.

Table 2. Reference Mass Fraction Values for SRM 691 Reduced Iron Oxide

Constituent	Mass Fraction (%)	Expanded Uncertainty (%)
Carbon (Total C)	0.12	0.03
Metallic Iron (Fe^0)	84.73	0.47
Nickel (Ni)	0.269	0.003
Sulfur (S)	0.009	0.002
Tungsten (W)	0.059	0.008
Zirconium (Zr)	0.0015	0.0003

Information Mass Fraction Values: Information values for constituents in SRM 691 are reported as mass fractions in Table 3. A NIST Information value is a value that may be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [2]. Information values cannot be used to establish metrological traceability.

Table 3. Information Mass Fraction Values for SRM 691 Reduced Iron Oxide

Constituent	Mass Fraction (%)
Arsenic (As)	0.0014
Cadmium (Cd)	< 0.0005
Lead (Pb)	< 0.002
Molybdenum (Mo)	< 0.002
Nitrogen (N)	0.005
Tin (Sn)	< 0.001
Zinc (Zn)	0.004

NOTICE TO USERS

NIST strives to maintain the SRM inventory supply, but NIST cannot guarantee the continued or continuous supply of any specific SRM. Accordingly, NIST encourages the use of this SRM as a primary benchmark for the quality and accuracy of the user's in-house reference materials and working standards. As such, the SRM should be used to validate the more routinely used reference materials in a laboratory. Comparisons between the SRM and in-house reference materials or working measurement standards should take place at intervals appropriate to the conservation of the SRM and the stability of relevant in-house materials. For further guidance on how this approach can be implemented, contact NIST by email at srms@nist.gov.

Table 4. Analytical Methods

Constituent	Method
Al_2O_3	Chromeazurol S photometric method
	Flame atomic absorption spectrometry
	Flame atomic emission spectrometry
	X-ray fluorescence spectrometry after borate fusion
CaO	Flame atomic absorption spectrometry
	Flame atomic emission spectrometry
	Spectrographic method
	X-ray fluorescence spectrometry after borate fusion
Chromium (Cr)	X-ray fluorescence spectrometry after borate fusion
Metallic Fe	ISO 5416 Direct reduced iron — Determination of metallic iron — Bromine-methanol titrimetric method [9]
Total Fe	$K_2Cr_2O_7$ titration after dissolution with reduction by $SnCl_2$
	$K_2Cr_2O_7$ titration after dissolution with reduction by H_2S
	Silver reductor method
K_2O	Flame atomic absorption spectrometry
	Flame atomic emission spectrometry
	Spectrographic method
	X-ray fluorescence spectrometry after borate fusion
MgO	Flame atomic absorption spectrometry
	Spectrographic method
	X-ray fluorescence spectrometry after borate fusion
MnO	Flame atomic absorption spectrometry
	Photometric method
	X-ray fluorescence spectrometry after borate fusion
Na_2O	Flame atomic absorption spectrometry
	Flame atomic emission spectrometry
	Spectrographic method
Nickel (Ni)	X-ray fluorescence spectrometry after borate fusion
Phosphorus (P)	Alkali-molybdate method
	Photometric method
	X-ray fluorescence spectrometry after borate fusion
SiO_2	Gravimetry after $HClO_4$ dehydration
	Fusion with Na_2CO_3
	X-ray fluorescence spectrometry after borate fusion
Sulfur (S)	Combustion and titration
TiO_2	Chromotropic acid photometric method
	Flame atomic absorption spectrometry
	Flame atomic emission spectrometry
	H_2O_2 photometric method
	4,4′-Methylenediantipyrine photometric method
	X-ray fluorescence spectrometry after borate fusion
Tungsten (W)	X-ray fluorescence spectrometry after borate fusion
Vanadium (V)	X-ray fluorescence spectrometry after borate fusion
Zirconium (Zr)	X-ray fluorescence spectrometry after borate fusion

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 Apr 2021).

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[9] ISO 5416:2006(E); *Direct Reduced Iron — Determination of Metallic Iron — Bromine-Methanol Titrimetric Method*, 3rd ed. (2006).

Certificate Revision History: 21 April 2021 (Revised values and uncertainties for all constituents; metallic iron, potassium, vanadium and chromium changed from information values to certified values; carbon and sulfur changed from certified values to reference values; nickel changed from information value to reference value; tungsten and zirconium added as reference values; title updated; editorial changes); 10 October 1991 (editorial changes); 12 April 1982 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; e-mail srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.