National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1884b

Portland Cement

This Standard Reference Material (SRM) is intended primarily for the evaluation or calibration of methods for analysis of cements and materials of similar matrix. A unit of SRM 1884b consists of five sealed vials, each containing approximately 4.5 g of portland cement ground to pass through a 75 µm (No. 200) sieve.

Certified Values: Certified values for 13 constituents in SRM 1884b are reported in Table 1 as mass fractions on an as-received basis [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 investigated or taken into account [2]. A certified value is the present best estimate of the true value based on the results of analyses performed at NIST and collaborating laboratories using the instrumental and classical test methods listed in Appendix A.

Reference Values: Reference values for nine constituents are reported in Table 2. Reference values are non-certified values that are the present best estimates of the true values. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [2].

Information Values: A calculated Total value accounting for all determined constituents is reported as an information value in Table 3. An information value is considered to be a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [2].

Expiration of Certification: The certification of **SRM 1884b** is valid, within the measurement uncertainty specified, until **01 May 2024**, provided the SRM is handled in accordance with instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of 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 certification, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The coordination of technical measurements for certification was performed by J.R. Sieber of the NIST Analytical Chemistry Division.

Analyses leading to the certification of this SRM were performed at NIST by A.F. Marlow and J.R. Sieber of the NIST Analytical Chemistry Division and M. Stair of the Cement and Concrete Reference Laboratory. Analytical determinations were also performed by D. Broton, M. Bharucha, S. Markovic, R. Naamane, and C. Wedzicha of Construction Technology Laboratories, Inc., Skokie, IL.

Statistical consultation for this SRM was provided by S.D. Leigh of the NIST Statistical Engineering Division.

Support aspects involved with the certification and issuance of this SRM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 02 November 2009

Robert. L Watters, Jr., Chief
Measurement Services Division

INSTRUCTIONS FOR USE

Cement powder is hygroscopic and the following procedure is recommended. Samples should be used immediately after opening. To relate analytical determinations to the certified values in this Certificate of Analysis, a minimum test portion of 500 mg should be used. The vial should be recapped immediately after removal of a test portion and stored in a desiccator. When a sample is used after storage in a previously opened vial, the Loss on Ignition (LOI) at 950 ºC for that sample should be determined in accordance with ASTM C 114-07 Standard Test Methods for Chemical Analysis of Hydraulic Cement [3] and the mass of the sample corrected for any additional moisture, combined water, or carbonate above the value reported in this certificate for LOI at 950 ºC. See Appendix B for additional information.

Preparation and Analysis[1]: The material for SRM 1884b was obtained in the form of powder prepared using a typical industrial process. The material was blended and bottled at NIST under the direction of M.P. Cronise of the NIST Measurement Services Division. Homogeneity testing was performed at NIST using X-ray fluorescence spectrometry. For most constituents, material heterogeneity was low and fit for the purpose of value assignment. Quantitative determinations done at NIST included X-ray fluorescence spectrometry [4] and thermogravimetric analysis. Methods employed by collaborating laboratories included X-ray fluorescence spectrometry, inductively coupled plasma optical emission spectrometry, and reference methods given in ASTM C 114-07.

Reporting: The constituents listed in this Certificate of Analysis are expressed as the chemical forms and in the order given in ASTM C 114-07, Section 3, Table 1.

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Table 1. Certified Values for SRM 1884b

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Constituent	Mass Fraction[a] (%)		
SiO_2	19.30	±	0.18
Al_2O_3	4.851	±	0.021
Fe_2O_3	2.937	±	0.020
CaO	61.31	±	0.36
MgO	4.74	±	0.13
SO_3	4.034	±	0.067
Na_2O	0.278	±	0.010
K_2O	0.957	±	0.018
TiO_2	0.2651	±	0.0084
P_2O_5	0.0965	±	0.0033
Mn_2O_3	0.0750	±	0.0013
Cr_2O_3	0.00791	±	0.00070
SrO	0.0258	±	0.0038

[a] Each certified value is the unweighted mean of the results from two to four methods. The uncertainty of a certified value is expressed as an expanded uncertainty, U, and is calculated according to the method described in the ISO Guide [5]. The expanded uncertainty is $U = ku_c$, where u_c is calculated, at the level of one standard deviation, by combining a between-method variance with a pooled, within-method variance [6]. The coverage factor, $k = 2$, was used, corresponding to approximately 95 % confidence.

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[1]Certain commercial organizations, services, equipment, or materials are identified in this certificate in order 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 organizations, services, materials, or equipment identified are necessarily the best available for the purpose.

Table 2. Reference Values for SRM 1884b

Constituent	Mass Fraction (%)		
LOI between 45 °C and 220 °C[a]	0.590	±	0.029
LOI between 220 °C and 550 °C[a]	0.261	±	0.024
LOI between 550 °C and 950 °C[a]	0.597	±	0.031
ZnO[a]	0.0042	±	0.0011
Cl[a]	0.0065	±	0.0010
Sulfide Sulfur[b]	0.0072	±	0.0006
Insoluble Residue[b]	0.159	±	0.009
Free CaO[b]	0.418	±	0.001
Fluoride (F⁻)[b]	0.0394	±	0.0009

[a] Each reference value is the unweighted mean of the results from two to four methods. The uncertainty of the reference value is expressed as an expanded uncertainty, U, and is calculated according to the method described in the ISO Guide [5]. The expanded uncertainty is $U = ku_c$, where u_c is calculated, at the level of one standard deviation, by combining a between-method variance with a pooled, within-method variance [6]. The coverage factor, $k = 2$, was used, corresponding to approximately 95 % confidence.

[b] Each reference value is the mean of results obtained by a single laboratory using one analytical technique. The expanded uncertainty is calculated as $U = ts$ where s is the standard deviation of the mean, and the coverage factor, t, was determined from the Student's t-distribution corresponding to the associated degrees of freedom and 95% confidence level for each analyte.

Table 3. Information Value for SRM 1884b

Constituent	Mass Fraction (%)
Total[a]	100.54

[a] Three corrections have been made to the calculated Total of analyzed constituents: 1) the amount of fluorine present, 2) the amount of chlorine present, and 3) the overestimation of oxygen by expressing total S as SO_3 when a quantifiable amount of sulfide sulfur is present. All three corrections were subtracted from the gross total. The correction for fluorine was determined by multiplying the mass fraction of fluorine by the ratio of the atomic mass of oxygen to two times the atomic mass of fluorine (0.421). The correction for chlorine was determined by multiplying the mass fraction of chlorine by the ratio of the atomic mass of oxygen to two times the atomic mass of chlorine (0.226). The correction for sulfide sulfur was determined by multiplying the mass fraction sulfide sulfur by the ratio of three times the atomic mass of oxygen to the atomic mass of sulfur (1.50).

REFERENCES

[1] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements;* NIST Special Publication 260-136, U.S. Government Printing Office, Gaithersburg, MD (2000); available at
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[2] 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: http://ts.nist.gov/WeightsAndMeasures/Metric/mpo_pubs.cfm.

[3] ASTM C 114-07, Standard Test Methods for Chemical Analysis of Hydraulic Cement, *Annu. Book ASTM Stand.*, Vol. 04.01, West Conshohocken, PA.

[4] Sieber, J.; Broton, D.; Fales, C.; Leigh, S.; MacDonald, B.; Marlow, A.; Nettles, S.; Yen, J.; *Standard Reference Materials for Cement*; Cement and Concrete Res., Vol. 32 (12), pp 1899–1906 (2002).

[5] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (ISO GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf; 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 http://physics.nist.gov/Pubs/.

[6] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.K.; Vangel, M.G.; Yen, J.H.; Zhang, N.F.; *An Approach to Combining Results from Multiple Methods Motivated by the ISO GUM*; J. Res. Natl. Inst. Stand. Technol., Vol. 105, pp 571–579 (2000).

[7] ASTM C 471M-01; *Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products (Metric)*, Annu. Book ASTM Stand., Vol. 04.01 (2006).

[8] ASTM C 25-06; *Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime*; Annu. Book ASTM Stand., Vol. 04.01 (2006).

APPENDIX A

Analytical Methods

Constituent	Methods
SiO_2	Total Si determined using XRF, ICP-OES, and gravimetry
Al_2O_3	Total Al determined using XRF and ICP-OES
Fe_2O_3	Total Fe determined using XRF and ICP-OES
CaO	Total Ca determined using XRF, ICP-OES, and gravimetry
MgO	Total Mg determined using XRF and ICP-OES
SO_3	Total S determined using XRF, ICP-OES, and gravimetry
Na_2O	Total Na determined using XRF and ICP-OES
K_2O	Total K determined using XRF and ICP-OES
TiO_2	Total Ti determined using XRF and ICP-OES
P_2O_5	Total P determined using XRF and ICP-OES
Mn_2O_3	Total Mn determined using XRF and ICP-OES
Cl	Total Cl determined using XRF[e] with standard additions at NIST and ion-selective electrode at the collaborating laboratory
Cr_2O_3	Total Cr determined using XRF and ICP-OES
SrO	Total Sr determined using HP-BF-XRF, XRF, ICP-OES
ZnO	Total Zn determined using XRF and ICP-OES
Sulfide S	KIO_3 titration after reaction with HCl
Insoluble Residue	Gravimetry
Free CaO	ASTM C 114-07 method performed by the collaborating laboratory
F	Ion-selective electrode at collaborating laboratory
Loss on Ignition (LOI)	Thermogravimetric analysis performed by both NIST and the collaborating laboratory. See the Appendix for a discussion of the test method and relevance of values [2, 3, 7, 8].

[e] Borate fusion was not used for Cl.

Key to Methods:

XRF	X-ray fluorescence spectrometry after borate fusion at NIST and the collaborating laboratory
ICP-OES	Inductively coupled plasma optical emission spectrometry at the collaborating laboratory
Gravimetry	Indicates the specific gravimetric method found in ASTM C 114-07 performed by the collaborating laboratory

APPENDIX B

Loss on Ignition of Portland Cement

In conjunction with other analyses, thermal analysis of cement is helpful in investigation of performance issues and in resolution of disputes. Mass losses listed in the certificate of analysis are presented for information purposes only and can be used as a guide for analyzing cement. The actual results obtained from a specimen of SRM 1884b will depend on the age and storage history of the vial from which the specimen was obtained. The optimum situation involves the use of a vial taken from a freshly opened pouch. See Instructions for Use.

The values reported in the Certificate of Analysis for SRM 1884b came from a four-step thermogravimetric analysis program used for ordinary portland cement. Commercial, programmable thermogravimetric analyzers were employed for the measurements at the laboratories of NIST and Construction Technologies Laboratories. After constant mass was attained at the specified temperature, the temperature was increased to the next programmed step. The mass losses at these temperatures may be indicative of the following:

- Ambient to 45 °C: Free moisture in the specimen,
- 45 °C to 220 °C: Combined H_2O from gypsum [$CaSO_4 \cdot 2H_2O$], plaster [$CaSO_4 \cdot \frac{1}{2}H_2O$], and syngenite [$K_2Ca(SO_4)_2 \cdot H_2O$],
- 220 °C to 550 °C: $Ca(OH)_2$ and $Mg(OH)_2$ converted to CaO and MgO,
- 550 °C to 950 °C: Carbonate compounds converted to oxide compounds.

The compounds listed above may be present in portland cement. Additional compounds may be present in pre-hydrated cement. The hydrate compounds may include ettringite [$3CaO \cdot Al_2O_3 \cdot 2CaSO_4 \cdot 32H_2O$], calcium monosulfate aluminate [$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$], and hydrated forms of calcium silicates [Ca_3SiO_5 and Ca_2SiO_4], calcium aluminate [$4CaO \cdot Al_2O_3 \cdot nH_2O$], and calcium aluminoferrite [$Ca_2(Al_xFe_{1-x})_2O_5$]. Crystal phase identification using X-ray diffraction was not performed to identify specific hydrates in SRM 1884b.

ASTM International standard methods of test include the compounds listed above and the analytical conditions of the test. These industry standards contain assignments of compounds and processes associated with mass loss as a function of temperature from hydraulic cement and its chemical constituents.

ASTM C 471M Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products identifies mass loss between ambient temperature and 45 °C as free moisture. Higher temperatures may decompose calcium sulfate forms and other hydrates. In addition, C 471M utilizes the mass loss between 45 °C and 220 °C in the determination of the mass fraction of chemically combined H_2O and in the calculation of the amount of gypsum or gypsum and plaster in gypsum-containing products. Although gypsum and plaster decompose at specific temperatures, the chemically bound H_2O is completely removed by 220 °C.

ASTM C 25 Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime assigns the mass loss between 110 °C and 550 °C as chemically combined water in $Ca(OH)_2$ and $Mg(OH)_2$ in the calculation of the total mass fraction of Ca and Mg hydroxides. As stated in ASTM C471M, chemically bound water from gypsum and plaster is completely removed by 220 °C. Therefore, mass loss between 220 °C and 550 °C is indicative of hydroxide compounds.

ASTM C114 Standard Test Method for Chemical Analysis of Hydraulic Cement, Appendix X2 assigns the mass loss between 550 °C and 950 °C as loss of CO_2 from hydraulic cement, which is primarily the result of decomposition of carbonate compounds.

Decomposition of compounds at lower temperatures may influence the amounts of compounds that decompose at higher temperatures. For example, $Ca(OH)_2$ may form as a result of removal of water bound to gypsum.