



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material® 1885b

#### Portland Cement

This Standard Reference Material (SRM) is a Type I-II portland cement [1] intended primarily for the evaluation of methods for analysis of cements and materials of similar matrix. A unit of SRM 1885b consists of five vials, each containing at least 5 g of portland cement ground to pass through a 75  $\mu\text{m}$  (No. 200) sieve, and each sealed in a foil pouch.

**Certified Mass Fraction Values:** Certified values for constituents of SRM 1885b are reported in Table 1 as mass fractions on an as-received basis [2]. 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 [3]. 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 Mass Fraction Values:** Reference values for constituents and loss on ignition (LOI) are reported in Table 2. A NIST reference value is a noncertified value that is the best estimate of the true value 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 reproducibility, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [3].

**Information Mass Fraction Values:** Information values for LOI between ambient temperature and 45 °C and total analyzed constituents are reported in Table 3. An information value is considered to be a value that may be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [3].

**Expiration of Certification:** The certification of **SRM 1885b** is valid, within the measurement uncertainty specified, until **01 November 2033**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see “Instructions for Handling, Storage, and Use”). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

**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) will facilitate notification.

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

Analyses leading to the certification of this SRM were performed at NIST by A.F. Marlow and J.R. Sieber of the NIST Chemical Sciences Division. Analytical determinations were also performed by D. Broton, G. Isono, R. Kelly, R. Naamane, S. Nettles, and C. Wedzicha of CTLGroup, Inc., Skokie, IL.

Statistical consultation for this SRM was provided by N.A. Heckert of the NIST Statistical Engineering Division.

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

Carlos A. Gonzalez, Chief  
Chemical Sciences Division

Gaithersburg, MD 20899  
Certificate Issue Date: 16 December 2013

Robert L. Watters, Jr., Director  
Office of Reference Materials

## INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Cement powder is hygroscopic. Samples should be used immediately after opening the vial. 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 and stored in a desiccator.

When a sample is used after storage in a previously opened vial, the total loss on ignition (LOI) at 950 °C for that sample should be determined in accordance with ASTM C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement [4] and the mass of the sample corrected for any additional moisture, combined water, or carbonate above the value reported in this certificate for total LOI at 950 °C. See Appendix B for more information about LOI of portland cement.

## PREPARATION AND ANALYSIS<sup>(1)</sup>

The material for SRM 1885b is a Type I-II portland cement [1] obtained in the form of powder prepared using a typical industrial process. Homogeneity testing was performed at NIST using X-ray fluorescence spectrometry (XRF). Quantitative determinations done at NIST included XRF [5] and thermogravimetric analysis. Methods employed by collaborating laboratories included XRF, inductively coupled plasma optical emission spectrometry (ICP-OES), and reference methods given in ASTM C114-11 [4]; see Appendix A for a complete list. The constituents listed in this Certificate of Analysis are expressed as the chemical forms and in the order given in ASTM C114-10, Section 3, Table 1, except for chlorine.

**Certified Mass Fraction Values:** The measurands are the mass fractions of selected elements in cement, expressed as their corresponding oxide. The certified values are metrologically traceable to the SI unit of mass. Each certified value is a weighted mean of the results from two to four methods [6]. The uncertainty listed with each certified value is an expanded uncertainty about the mean [7] with coverage factor,  $k = 2$ , (approximately 95 % confidence) calculated by combining a between-method variance incorporating inter-method bias with a pooled, within-method variance following the ISO/JCGM Guide [8] for all constituents.

Table 1. Certified Mass Fraction Values for SRM 1885b

Constituent	Mass Fraction (%)
SiO <sub>2</sub>	20.05 ± 0.40
Al <sub>2</sub> O <sub>3</sub>	4.70 ± 0.16
Fe <sub>2</sub> O <sub>3</sub>	3.044 ± 0.048
CaO	61.87 ± 0.11
MgO	3.86 ± 0.11
SO <sub>3</sub>	2.832 ± 0.048
Na <sub>2</sub> O	0.293 ± 0.030
K <sub>2</sub> O	0.497 ± 0.012
TiO <sub>2</sub>	0.2361 ± 0.0089
P <sub>2</sub> O <sub>5</sub>	0.0737 ± 0.0024
ZnO	0.0354 ± 0.0028
Mn <sub>2</sub> O <sub>3</sub>	0.1282 ± 0.0042
Cr <sub>2</sub> O <sub>3</sub>	0.02709 ± 0.00083
SrO	0.0795 ± 0.0036
BaO	0.0149 ± 0.0026

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<sup>(1)</sup>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.

**Reference Mass Fraction Values:** The measurands are the mass fractions of selected elements and chemical constituents in cement defined by the listed test methods in Appendix A. The reference values are metrologically traceable to the SI unit of mass. The reference values for sulfide sulfur, insoluble residue, free CaO, fluoride, chlorine, and LOI are the means of results obtained using one analytical technique found in ASTM C114 [4]. The associated uncertainty is calculated as  $U = ts/\sqrt{n}$  where  $s$  is the standard deviation and the coverage factor,  $t = 2.18$ , was determined from the Student's  $t$ -distribution corresponding to the 95 % confidence level and to  $(n - 1)$  degrees of freedom, where  $n = 12$  is the number of determinations on which each mean value is based.

Table 2. Reference Mass Fraction Values for SRM 1885b

Constituent	Mass Fraction (%)
Sulfide sulfur	0.042 ± 0.001
Insoluble residue	0.36 ± 0.03
Free CaO	0.27 ± 0.03
Fluoride (F <sup>-</sup> )	0.0524 ± 0.0002
Chlorine (Cl)	0.0021 ± 0.0003
Measurand	Mass Fraction (%)
LOI between 45 °C and 220 °C	0.821 ± 0.028
LOI between 220 °C and 550 °C	0.247 ± 0.015
LOI between 550 °C and 950 °C	1.237 ± 0.045
LOI total at 950 °C	2.310 ± 0.083

**Information Mass Fraction Values:** The information value reported for LOI between ambient temperature and 45 °C is the estimated limit of detection of the test method, which was performed at two laboratories. The mean values obtained by each analyst at the times of analysis were less than this value. For the calculated total of analyzed constituents plus LOI, three corrections have been made: (1) the amount of fluorine present, (2) the amount of chlorine present, and (3) the overestimation of oxygen by expressing total S as SO<sub>3</sub> when a quantifiable amount of sulfide sulfur is present. All three corrections were subtracted from the gross total. The correction for F<sup>-</sup> 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 of sulfide sulfur by the ratio of three times the atomic mass of oxygen to the atomic mass of sulfur (1.50).

Table 3. Information Mass Fraction Values for SRM 1885b

Measurand	Mass Fraction (%)
LOI between ambient temperature and 45 °C	< 0.2
Total analyzed constituents	100.02

## REFERENCES

- [1] ASTM C150-07; *Standard Specification for Portland Cement*; Annu. Book ASTM Stand., Vol. 04.01, West Conshohocken, PA.
- [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://www.nist.gov/pml/pubs/sp811/index.cfm> (accessed Dec 2013).
- [3] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definition 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: Washington, DC (2000); available at <http://www.nist.gov/srm/upload/SP260-136.PDF> (accessed Dec 2013).
- [4] ASTM C114-11; *Standard Test Methods for Chemical Analysis of Hydraulic Cement*; Annu. Book ASTM Stand., Vol. 04.01, West Conshohocken, PA.
- [5] 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 Issue 12, pp. 1899–1906 (2002).
- [6] DerSimonian, R.; Laird, N.; *Meta-analysis in Clinical Trials*; Control Clin. Trials, Vol. 7, pp. 177–188 (1986).
- [7] Horn, R.A.; Horn, S.A.; Duncan, D.B.; *Estimating Heteroscedastic Variance in Linear Models*; J. Am. Stat. Assoc., Vol. 70, pp. 380–385 (1975).
- [8] 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 (JCGM) (2008); available at [http://www.bipm.org/utis/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](http://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf) (accessed Dec 2013); 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://www.nist.gov/pml/pubs/index.cfm> (accessed Dec 2013).
- [9] Efron, B.; Tibshirani, R.J.; *An Introduction to the Bootstrap*; Chapman & Hall (1993).
- [10] 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 [http://www.bipm.org/utis/common/documents/jcgm/JCGM\\_101\\_2008\\_E.pdf](http://www.bipm.org/utis/common/documents/jcgm/JCGM_101_2008_E.pdf) (accessed Dec 2013).
- [11] ASTM C471M-01; *Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products (Metric)*; Annu. Book ASTM Stand., Vol. 04.01, West Conshohocken, PA.
- [12] ASTM C25-06; *Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime*; Annu. Book ASTM Stand., Vol. 04.01, West Conshohocken, PA.

*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; fax (301) 948-3730; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*

## APPENDIX A

### Analytical Methods

Constituent	Methods <sup>(a)</sup>
SiO <sub>2</sub>	Total Si determined using XRF, ICP-OES, and gravimetry
Al <sub>2</sub> O <sub>3</sub>	Total Al determined using XRF and ICP-OES
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>3</sub>	Total S determined using XRF, ICP-OES, and gravimetry
Na <sub>2</sub> O	Total Na determined using XRF and ICP-OES
K <sub>2</sub> O	Total K determined using XRF and ICP-OES
TiO <sub>2</sub>	Total Ti determined using XRF and ICP-OES
P <sub>2</sub> O <sub>5</sub>	Total P determined using XRF and ultraviolet absorbance
ZnO	Total Zn determined using XRF and ICP-OES
Mn <sub>2</sub> O <sub>3</sub>	Total Mn determined using XRF and ICP-OES
Cr <sub>2</sub> O <sub>3</sub>	Total Cr determined using XRF and ICP-OES
SrO	Total Sr determined using XRF and ICP-OES
BaO	Total Ba determined using XRF and ICP-OES
Sulfide S	KIO <sub>3</sub> titration after reaction with HCl
Insoluble Residue	ASTM C114-11 method performed by collaborating laboratory
Free CaO	ASTM C114-11 method performed by collaborating laboratory
Chlorine (Cl)	Total Cl determined using XRF <sup>(b)</sup> with standard additions at NIST
Flouride (F <sup>-</sup> )	Ion-selective electrode at collaborating laboratory
Loss on Ignition (LOI)	Thermogravimetric analysis performed at NIST and collaborating laboratory. See Appendix B for a discussion of test methods and relevance of values [3,10,11].

<sup>(a)</sup> Key to Methods:

XRF	X-ray fluorescence spectrometry after borate fusion at NIST [5] 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 114-10 performed by the collaborating laboratory

<sup>(b)</sup> Borate fusion was not used for Cl by the standard additions calibration.

## APPENDIX B

### Loss on Ignition (LOI) 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 as reference or information values with limited validity after an SRM vial is removed from its foil pouch. The actual results obtained from a specimen of SRM 1885b will depend on the age and storage history of the vial from which the sample is taken. Optimum LOI values are obtained when a vial is taken from a freshly opened foil pouch (see “Instructions for Handling, Storage, and Use”).

The values for LOI reported in the Certificate of Analysis for SRM 1885b came from a four-step thermogravimetric analysis program used for ordinary portland cement. Commercial, programmable thermogravimetric analyzers were employed for the measurements at NIST and CTLGroup. 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<sub>2</sub>O from gypsum [CaSO<sub>4</sub>·2H<sub>2</sub>O], plaster [CaSO<sub>4</sub>·½H<sub>2</sub>O], and syngenite [K<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O]
- 220 °C to 550 °C: Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> 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·Al<sub>2</sub>O<sub>3</sub>·2CaSO<sub>4</sub>·32H<sub>2</sub>O], calcium monosulfate aluminate [3CaO·Al<sub>2</sub>O<sub>3</sub>·CaSO<sub>4</sub>·12H<sub>2</sub>O], and hydrated forms of calcium silicates [Ca<sub>3</sub>SiO<sub>5</sub> and Ca<sub>2</sub>SiO<sub>4</sub>], calcium aluminate [4CaO·Al<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O], and calcium aluminoferrite [Ca<sub>2</sub>(Al<sub>1-x</sub>Fe<sub>1-x</sub>)<sub>2</sub>O<sub>5</sub>]. Crystal phase identification using X-ray diffraction was not performed to identify specific hydrates in SRM 1885b.

ASTM International standard test methods of 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 C471M Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products [11] identifies mass loss between ambient temperature and 45 °C as free moisture. Higher temperatures may decompose calcium sulfate forms and other hydrates. In addition, ASTM C471M utilizes the mass loss between 45 °C and 220 °C in the determination of the mass fraction of chemically combined H<sub>2</sub>O 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<sub>2</sub>O is completely removed by the time the temperature reaches 220 °C.

ASTM C25 Standard Test Methods for Chemical Analysis of Limestone, Quicklime and Hydrated Lime [12] assigns the mass loss between 110 °C and 550 °C as chemically combined water in Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> in the calculation of the total mass fraction of calcium and magnesium hydroxides. As stated in ASTM C471M, chemically bound water from gypsum and plaster is completely removed by the time the temperature reaches 220 °C. Therefore, mass loss between 220 °C and 550 °C is indicative of hydroxide compounds.

ASTM C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement, Appendix X2 [4] assigns the mass loss between 550 °C and 950 °C as loss of CO<sub>2</sub> 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)<sub>2</sub> may form as a result of removal of water bound to gypsum.