



# Certificate of Analysis

## Standard Reference Material® 1881b

### Portland Cement (Blended with Fly Ash)

This Standard Reference Material (SRM) is intended primarily for use in validation of chemical and instrumental methods of analysis of cements and materials of similar matrix for elemental content. It can be used to validate value assignment of in-house reference materials. A unit of SRM 1881b consists of five vials, each containing approximately 5 g of 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 1881b are reported in Table 1 as mass fractions [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.

**Reference Mass Fraction Values:** Reference values for constituents and loss on ignition (LOI) are reported in Table 2 as mass fractions. A NIST reference value is a noncertified value that is the present 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 associated uncertainties 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 [2].

**Information Mass Fraction Values:** Information values for constituents, for LOI between ambient temperature and 45 °C, and for total analyzed constituents are reported in Table 3 as mass fractions. 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 [2]. Information values cannot be used to establish metrological traceability.

**Expiration of Certification:** The certification of **SRM 1881b** is valid, within the measurement uncertainty specified, until **01 February 2036**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see “Instructions for Handling, Storage, and Use”). Periodic recalibration or recertification of this SRM is not required. 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 or register online) will facilitate notification.

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.

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Certificate Issue Date: 16 June 2016

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## **INSTRUCTIONS FOR HANDLING, STORAGE, AND USE**

Cement powder is hygroscopic. Samples should be used immediately after opening the vial to minimize changes from reaction with moisture and carbon dioxide in air. 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, placed back in the labeled foil pouch, and stored in a desiccator.

When a sample is used after storage in a previously opened vial, the loss on ignition (LOI) at 950 °C value for that sample should be determined in accordance with ASTM C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement [3] and the mass of the sample corrected for any increase above the value reported in Table 2 for LOI total at 950 °C. See Appendix A for more information about LOI of portland cement.

## **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](mailto:srms@nist.gov).

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

The material for SRM 1881b consists of a blend of portland cement clinker, class F fly ash (cement/fly ash intergrind 70/30 nominal ratio) and gypsum [4] obtained as a finished product from a commercial cement producer. Homogeneity testing was performed at NIST using X-ray fluorescence spectrometry (XRF). Material heterogeneity was low and fit for the purpose of value assignment. 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 C114-15 [3]; see Table 4 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 C114-15, Section 3, Table 1, except for chlorine.

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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.

**Certified Mass Fraction Values:** The measurands are the mass fractions of the elements in cement listed in Table 1. Metrological traceability is to the SI derived unit for mass fraction (expressed as a percent). 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,  $k = 2$ , calculated by combining a between-method variance incorporating inter-method bias with a pooled, intra-method variance following the ISO/JCGM Guide [8] for all constituents.

Table 1. Certified Mass Fraction Values for SRM 1881b Portland Cement (Blended with Fly Ash)

Constituent	Mass Fraction (%)		
SiO <sub>2</sub>	29.045	±	0.066
Al <sub>2</sub> O <sub>3</sub>	8.812	±	0.086
Fe <sub>2</sub> O <sub>3</sub>	3.365	±	0.023
CaO	49.27	±	0.11
MgO	2.741	±	0.043
SO <sub>3</sub>	2.72	±	0.12
Na <sub>2</sub> O	0.790	±	0.044
K <sub>2</sub> O	0.721	±	0.021
TiO <sub>2</sub>	0.3011	±	0.0073
P <sub>2</sub> O <sub>5</sub>	0.0510	±	0.0022
Mn <sub>2</sub> O <sub>3</sub>	0.1175	±	0.0029
Cr <sub>2</sub> O <sub>3</sub>	0.00949	±	0.00097
ZnO	0.1198	±	0.0067
SrO	0.0836	±	0.0026
BaO	0.191	±	0.021
Chlorine (Cl)	0.0081	±	0.0014

**Reference Mass Fraction Values:** The measurands are the mass fractions of the chemical constituents in cement listed in Table 2 as determined by the methods indicated in Table 4. Metrological traceability is to the SI derived unit for mass fraction (expressed as a percent). For Loss on Ignition (LOI), each reference value is a weighted mean of the results from one method performed at two laboratories [6]. The uncertainty listed with each reference value is an expanded uncertainty about the mean [7] with coverage factor,  $k = 2$ , calculated by combining a between-method variance incorporating inter-laboratory bias with a pooled, intra-method variance following the ISO/JCGM Guide [8] for all constituents. The reference values for insoluble residue and free CaO are the means of results obtained using one analytical technique found in ASTM C114 [3]. 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 1881b Portland Cement (Blended with Fly Ash)

Constituent	Mass Fraction (%)		
Insoluble residue	16.4	±	0.4
Free CaO	1.16	±	0.02
Measurand	Mass Fraction (%)		
LOI between 45 °C and 220 °C	0.589	±	0.038
LOI between 220 °C and 550 °C	0.196	±	0.018
LOI between 550 °C and 950 °C	0.930	±	0.060
LOI total at 950 °C	1.699	±	0.027

**Information Mass Fraction Values:** The information value for fluoride is the mean of results from a single test method. The information values reported for sulfide sulfur and loss on drying between ambient temperature and 45 °C are the estimated limits of detection of the test methods. For mercury, the reported value in units of micrograms per kilogram was obtained using a single test method. For the calculated total of analyzed constituents plus LOI, two corrections have been made: (1) the amount of fluorine present, and (2) the amount of chlorine present. Both 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).

Table 3. Information Mass Fraction Values for SRM 1881b Portland Cement (Blended with Fly Ash)

Measurand	Mass Fraction
Fluoride (F <sup>-</sup> )	0.09 %
Sulfide Sulfur	< 0.008 %
Loss on drying between ambient temperature and 45 °C	< 0.06 %
Mercury (Hg)	58 µg/kg
Total analyzed constituents	100.09 %

Table 4. Analytical Methods Used on SRM 1881b Portland Cement (Blended with Fly Ash)

Constituent	Methods <sup>(a)</sup>
SiO <sub>2</sub>	Total Si determined using XRF and ICP-OES
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 and ICP-OES
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, ICP-OES and spectrophotometry
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
Hg	Direct mercury analyzer at collaborating laboratory
Sulfide S	KIO <sub>3</sub> titration after reaction with HCl
Insoluble Residue	ASTM C114-15 method performed by collaborating laboratory
Free CaO	ASTM C114-15 method performed by collaborating laboratory
Chlorine (Cl)	Total Cl determined using XRF <sup>(b)</sup> with standard additions at NIST, and an ion-selective electrode method at the collaborating laboratory
Fluoride (F <sup>-</sup> )	Ion-selective electrode at collaborating laboratory
Loss on Ignition (LOI)	Thermogravimetric analysis performed at NIST and collaborating laboratory. See Appendix A for a discussion of test methods and relevance of values [3,9,10].

<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 114-15 performed by the collaborating laboratory

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

## 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 <http://www.nist.gov/pml/pubs/sp811/index.cfm> (accessed June 2016).
- [2] 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 June 2016).
- [3] ASTM C114-15; *Standard Test Methods for Chemical Analysis of Hydraulic Cement*; Annu. Book ASTM Stand., Vol. 04.01, West Conshohocken, PA.
- [4] CSA A3000-13; *Cementitious Materials Compendium*; ISBN: 9781771393218; 264 pp; CSA Group; October 2013.
- [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 (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 June 2016); 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 June 2016).
- [9] 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.
- [10] 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

### 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 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 1881b will depend on the age and storage history of the vial from which the specimen was obtained. The optimum situation for validity of LOI values involves the use of a vial taken from a freshly opened pouch (see “Instructions for Handling, Storage, and Use”).

The values for LOI reported in the Certificate of Analysis for SRM 1881b came from a four-step thermogravimetric analysis program used for portland cement. Commercial, programmable thermogravimetric analyzers were employed for the measurements at NIST and CTL Group. 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>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 1881b.

ASTM International standard test methods include the compounds listed above and the analytical test conditions. 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 [9] 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 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 [10] 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 [3] 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.