National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 633a

Portland Cement

This Standard Reference Material (SRM) is intended primarily for the evaluation of methods for analysis of cements and materials of similar matrix. A unit of SRM 633a consists of four vials, each containing approximately 5 g of portland cement ground to pass through a 75 µm (No. 200) sieve, and each sealed into a foil pouch.

Certified Mass Fraction Values: Certified values for 15 constituents of SRM 633a 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 Mass Fraction Values: Reference mass fraction values for ten constituents are reported in Table 2 on an as-received basis. A reference value is a non-certified value that is the best estimate of the true value based on available data. These values do not meet NIST criteria for certification and are 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: Two mass fraction information values are reported in Table 3 on an as-received basis. 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].

Expiration of Certification: The certification of **SRM 633a** is valid, within the measurement uncertainty specified, until **01 May 2027**, provided the SRM is handled 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 Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before expiration, 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 S.E. Long, A.F. Marlow, and J.R. Sieber of the NIST Analytical Chemistry 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 in the 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: 26 October 2012

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

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 ºC for that sample should be determined in accordance with ASTM C114 [3], 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 ºC (i.e., the sum of the individual LOI values reported in the tables). See Appendix B for more information about loss on ignition of portland cement.

Users should be aware that during homogeneity testing, a high repeatability variance was observed for Cr. The source was determined to be a very high measured result for approximately one sample in 20.

PREPARATION AND ANALYSIS(1)

The material for SRM 633a is a Type V cement [4] 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. Material heterogeneity was low and fit for the purpose of value assignment. Quantitative determinations done at NIST included X-ray fluorescence spectrometry [5] and thermogravimetric analysis. 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. Methods employed by collaborating laboratories included X-ray fluorescence spectrometry, inductively coupled plasma optical emission spectrometry (ICP-OES), and reference methods given in ASTM C114-10 Standard Test Methods for Chemical Analysis of Hydraulic Cement [3]. See Appendix A for a complete list.

Certified Mass Fraction Values: Each certified value (except for mercury) 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 2 (approximately 95 % confidence) calculated by combining a between-method variance incorporating inter-method bias with a pooled, within-method variance following the ISO Guide [8]. The certified value for mercury was obtained using a single NIST method [9]. The uncertainty is an expanded uncertainty about the mean with coverage factor 2 (approximately 95 % confidence) calculated by combining the effects of measurement variability and mercury inhomogeneity following the ISO Guide [8].

Table 1. Certified Mass Fraction Values for SRM 633a

Constituent	Mass Fraction (%)		
SiO_2	22.38	±	0.27
Al_2O_3	2.911	±	0.015
Fe_2O_3	3.738	±	0.060
CaO	64.129	±	0.096
MgO	1.1532	±	0.0059
SO_3	2.178	±	0.034
Na_2O	0.203	±	0.022
K_2O	0.391	±	0.010
TiO_2	0.2157	±	0.0032
P_2O_5	0.14263	±	0.00080
ZnO	0.123	±	0.012
Mn_2O_3	0.1176	±	0.0011
Cl	0.0087	±	0.0011
SrO	0.0507	±	0.0036
Constituent	Mass Fraction (ng/g)		
Hg	24.70	±	0.81

(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.

Reference Mass Fraction Values: The reference values for Cr_2O_3 and BaO are weighted means of the results from two to four methods [6]. The uncertainty listed with each reference value is an expanded uncertainty about the mean [7] with coverage factor 2 (approximately 95 % confidence) calculated by combining a between-method variance incorporating inter-method bias with a pooled, within-method variance following the ISO Guide [8]. The reference values for sulfide sulfur, insoluble residue, free CaO, fluoride, and loss on ignition (LOI) are the means of results obtained using one analytical technique. The associated uncertainty is calculated as $U = ts/\sqrt{n}$ where s is the standard deviation and the coverage factor, t, was determined from the Student's t-distribution corresponding to 11 degrees of freedom and to the 95 % confidence level.

Table 2. Reference Mass Fraction Values for SRM 633a

Constituent	Mass Fraction (%)		
Cr_2O_3	0.0124	±	0.0016
Sulfide Sulfur	0.049	±	0.003
Insoluble Residue	0.23	±	0.03
Free CaO	1.60	±	0.02
Fluoride (F^-)	0.038	±	0.005
BaO	0.256	±	0.020

Measurand	Mass Fraction (%)		
LOI between 45 ºC and 220 ºC	0.264	±	0.049
LOI between 220 ºC and 550 ºC	0.381	±	0.036
LOI between 550 ºC and 950 ºC	1.805	±	0.037
LOI total at 950 °C	2.460	±	0.084

Information Mass Fraction Values: The information value reported for loss on ignition (LOI) 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 analyses were less than this value. For the calculated total of analyzed constituents plus loss on ignition, 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_3 when a quantifiable amount of sulfide sulfur is present. All three corrections were subtracted from the gross total. The correction for F 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).

Table 3. Information Mass Fraction Value for SRM 633a

Measurand	Mass Fraction (%)
LOI between ambient temperature and 45 ºC	< 0.05
Total analyzed constituents	100.41

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 Print Office, Washington, DC (2008); available at http://www.nist.gov/pml/pubs/index.cfm/ (accessed Oct 2012).

[2] 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 (2000); available at http://www.nist.gov/srm/upload/SP260-136.PDF (accessed Oct 2012).

[3] ASTM C114-10; *Standard Test Methods for Chemical Analysis of Hydraulic Cement*; Annu. Book ASTM Stand., Vol. 04.01.

[4] ASTM C150-07; *Standard Specification for Portland Cement*; Annu. Book ASTM Stand., Vol. 04.01.

[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, 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;* (ISO GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Oct 2012); 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 Oct 2012).

[9] Christopher, S.J.; Long, S.E.; Rearick, M.S.; Fassett, J.D.; *Development of High Accuracy Vapor Generation Inductively Coupled Plasma Mass Spectrometry and its Application to the Certification of Mercury in Standard Reference Materials*; Anal. Chem., Vol. 73, pp 2190-2199 (2001).

[10] ASTM C471M-01; *Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products (Metric)*; Annu. Book ASTM Stand., Vol. 04.01 (2006).

[11] ASTM C25-06; *Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime*; Annu. Book ASTM Stand., Vol. 04.01.

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; or via the Internet at http://www.nist.gov/srm.

APPENDIX A

Analytical Methods

Constituent	Methods
SiO_2	Total Si determined using XRF, ICPOES 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 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[a] with standard additions at NIST and ion-selective electrode at collaborating laboratory
Cr_2O_3	Total Cr determined using XRF and ICP-OES
SrO	Total Sr determined using XRF and ICP-OES
ZnO	Total Zn determined using XRF and ICP-OES
Hg	Total Hg determined using ID-CV-ICPMS
BaO	Total Ba determined using XRF[a] with standard additions at NIST and XRF at collaborating laboratory
Sulfide S	KIO_3 titration after reaction with HCl
Insoluble Residue	Gravimetry
Free CaO	ASTM C114-10 method performed by collaborating laboratory
F	Ion-selective electrode at collaborating laboratory
Loss on Ignition (LOI)	Thermogravimetric analysis performed at NIST and by collaborating laboratory. See Appendix B for a discussion of test methods and relevance of values [3, 10, 11].

[a] Borate fusion was not used for Cl and Ba by the standard additions calibration.

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 C114-10 performed by the collaborating laboratory,
ID-CV-ICPMS	Isotope dilution cold vapor inductively coupled plasma mass spectrometry performed at NIST and confirmed using direct mercury analysis at 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 as reference or information values with limited validity after an SRM vial is removed from its foil pouch. The actual results obtained from analysis of a specimen of SRM 633a 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 Handling, Storage, and Use."

The values for LOI reported in the Certificate of Analysis for SRM 633a 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 ºC: Free moisture in the specimen,
- 45 ºC to 220 ºC: 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 ºC to 550 ºC: $Ca(OH)_2$ and $Mg(OH)_2$ converted to CaO and MgO,
- 550 ºC to 950 ºC: 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 633a.

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 C471M Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products [10] identifies mass loss between ambient temperature and 45 ºC as free moisture. Higher temperatures may decompose calcium sulfate forms and other hydrates. In addition, ASTM C471M utilizes the mass loss between 45 ºC and 220 ºC 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 the time the temperature reaches 220 ºC.

ASTM C25 Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime [11] assigns the mass loss between 110 ºC and 550 ºC as chemically combined water in $Ca(OH)_2$ and $Mg(OH)_2$ 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 ºC. Therefore, a mass loss between 220 ºC and 550 ºC is indicative of hydroxide compounds.

ASTM C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement, Appendix 2 [3] assigns the mass loss between 550 ºC and 950 ºC 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.