National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 634a

Portland Cement

This Standard Reference Material (SRM) is intended primarily for evaluation of chemical and instrumental methods of analysis of cement and materials of similar matrix. A unit of SRM 634a consists of one bottle containing approximately 100 g of portland cement, ground to pass a 75 μm (No. 200) sieve, and sealed in a foil pouch.

Certified Mass Fraction Values: Certified values for constituents in SRM 634a 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.

Reference Mass Fraction Values: Reference values for constituents and loss on ignition in SRM 634a are reported in Table 2 as mass fractions on an as-received basis [1]. A NIST reference value is a non-certified 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 [2].

Information Mass Fraction Values: Information values for constituents of SRM 634a are reported in Table 3 as mass fractions on an as-received basis [1]. 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 634a** is valid, within the measurement uncertainty specified, until **01 March 2025**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for 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 certification, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

The coordination of the technical measurements for certification of this SRM 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 and by D. Broton of CTL Group, Inc., Skokie, IL. See "Preparation and Analysis" for additional information.

Statistical consultation for this SRM was provided by S.D. Leigh and 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: 28 April 2015
Certificate Revision History on Page 4

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

INSTRUCTIONS FOR USE

Cement powder is hygroscopic and will react slowly with moisture changing the chemical composition. Each unit of the SRM is shipped in a sealed foil pouch to prevent moisture uptake. The unit should be left in the sealed pouch until just before it is needed in the laboratory. After the pouch is removed, the material should be stored in its original container, recapped tightly, and stored in a desiccator immediately after use.

When a sample is used after storage in a previously opened bottle, 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 [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 °C. See Appendix A for more information about LOI of portland cement.

To relate analytical determinations to the values and uncertainty estimates in this certificate, a minimum sample quantity of 500 mg is recommended.

PREPARATION AND ANALYSIS[(1)]

The material for SRM 634a was obtained in the form of bagged product by the Cement and Concrete Reference Laboratory (CCRL), Frederick, MD. Homogeneity testing for within-unit and between-unit variability was performed at NIST using X-ray fluorescence spectrometry after borate fusion sample preparation of 0.5 g specimens.

Certification of the material was based on X-ray fluorescence measurements performed at NIST [4] in combination with the proficiency test results from CCRL material #155 (identical to the material that is SRM 634a), which were reviewed by the SRM project leader. Laboratories participating in the CCRL program perform test methods published in ASTM Standard C114 [3]. The average value from the acceptable CCRL results for each constituent was treated as a single test method for combination with the NIST XRF results. Loss on ignition was determined by NIST and CTL Group using the procedure in ASTM C114. The constituents listed in this certificate are expressed as the chemical forms and in the order given in ASTM C114, Section 3, Table 1.

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 SI unit of mass, expressed as a percent. Each certified value is an unweighted mean of the results from two analytical methods [5]. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor *k*, calculated by combining a between-method variance with a pooled, within-method variance following the ISO/JCGM Guide [6] for all constituents.

Table 1. Certified Mass Fraction Values for SRM 634a Portland Cement

Constituents	Value (%)	Expanded Uncertainty (%)	Coverage Factor (*k*)
SiO_2	20.493	0.068	2.4
Al_2O_3	5.015	0.023	2.4
Fe_2O_3	3.362	0.026	2.2
CaO	65.07	0.26	2.4
MgO	1.0057	0.0083	2.4
SO_3	2.780	0.077	2.0
K_2O	0.3572	0.0039	2.2
TiO_2	0.2463	0.0028	2.2
P_2O_5	0.1767	0.0030	2.4

[(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 measurands are the mass fractions of selected elements in cement, expressed as their corresponding oxide, and mass loss in air in the listed temperature range as determined by the indicated method or methods. The reference values are metrologically traceable to SI unit of mass, expressed as a percent. The assigned values for Na_2O and Mn_2O_3 are unweighted means of the results from two analytical methods [5]. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor *k*, calculated by combining a between-method variance with a pooled, within-method variance following the ISO/JCGM Guide [6]. The assigned values for Cr_2O_3, ZnO, and SrO were obtained using a single method performed at NIST. The assigned values for LOI in four temperature ranges are the weighted means of results from one test method performed by two laboratories [7,8]. The expanded uncertainty for each value was calculated as a 95 % confidence interval, where $U = ku_c$. The quantity u_c is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated following the ISO/JCGM Guide and its Supplement [6,9].

Table 2. Reference Mass Fraction Values for SRM 634a Portland Cement

Constituents	Mass Fraction (%)	Expanded Uncertainty (%)	Coverage Factor (*k*)
Na_2O	0.0842	0.0029	2.4
Cr_2O_3	0.0114	0.0013	2.0
ZnO	0.0222	0.0022	2.0
Mn_2O_3	0.0229	0.0011	2.4
SrO	0.0735	0.0052	2.0
LOI between 45 °C and 220 °C	0.580	0.039	2.2
LOI between 220 °C and 550 °C	0.749	0.018	2.1
LOI between 550 °C and 950 °C	0.340	0.017	2.1
LOI total at 950 °C	1.683	0.013	2.5

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 time of analysis were less than this value. The values for free lime (free CaO) and insoluble residue were determined by the CCRL participating laboratories using the procedure in ASTM International Standard C 114-03 [10].

Table 3. Information Mass Fraction Values for SRM 634a Portland Cement

Constituents	Value (%)
LOI between ambient temperature and 45 °C	< 0.02
Free CaO	1.86
Insoluble residue	0.21

REFERENCES

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[9] 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/utils/common/documents/jcgm/JCGM_101_2008_E.pdf (accessed Apr 2015).

[10] ASTM C114-03; *Standard Test Methods for Chemical Analysis of Hydraulic Cement*; Annu. Book ASTM Stand., Vol. 04.01, West Conshohocken, PA.

[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.

Certificate Revision History: 28 April 2015 (Revised reference value for LOI Total at 950 °C; added reference values for LOI at additional temperatures; added Appendix A; editorial changes); 05 December 2014 (Change of expiration date; editorial changes); 08 November 2006 (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; fax (301) 948-3730, email srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

APPENDIX A

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 are presented as reference values with limited validity after an SRM unit is removed from its foil pouch. The actual results obtained from a specimen of SRM 634a will depend on the age and storage history of the unit from which the sample is taken. Optimum LOI values are obtained when a unit is taken from a freshly opened foil pouch (see "Instructions for Use").

The values for LOI reported in the certificate for SRM 634a 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 [$CaSO_4 \cdot ½H_2O$], 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, respectively
- 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 634a.

ASTM International standard test methods 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 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 [12] 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, 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 X2 [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.