National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 635a

Portland Cement
(Blended with Slag)

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 contents. It can be used to validate value assignment of in-house reference materials. A unit of SRM 635a consists of five vials, each containing about 5 g of cement ground to pass through a 75 µm (No. 200) sieve, and each sealed in a foil pouch.

Certified Mass Fraction Values: Certified values for constituents of SRM 635a 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 repeatability, 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 individual constituents and for the total of 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 635a** is valid, within the measurement uncertainty specified, until **15 November 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 J. Bass, D. Broton, E. Engstrom, J. John, R. Naamane, S. Nettles, and M. Schroeder 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: 15 March 2017

Steven J. Choquette, Director
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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. A vial containing unused material 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.

PREPARATION AND ANALYSIS[(1)]

The material for SRM 635a consists of a type 1S-40 blend of portland cement clinker, blast furnace slag (cement/slag intergrind 60/40 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.

[(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.

Certified Mass Fraction Values: The measurands are the total mass fractions of the elements in cement listed in Table 1. 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. The certified values are metrologically traceable to the SI derived unit for mass fraction (expressed as 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 635a Portland Cement (Blended with Slag)

Constituent	Mass Fraction (%)		
Silicon Dioxide (SiO_2)	23.13	±	0.13
Aluminum Trioxide (Al_2O_3)	7.867	±	0.049
Iron (III) Oxide (Fe_2O_3)	3.175	±	0.025
Calcium Oxide (CaO)	54.85	±	0.36
Magnesium Oxide (MgO)	3.817	±	0.065
Sulfur Trioxide (SO_3)	3.222	±	0.045
Sodium Oxide (Na_2O)	0.2477	±	0.0037
Potassium Oxide (K_2O)	0.725	±	0.019
Titanium Dioxide (TiO_2)	0.353	±	0.010
Phosphorus Pentoxide (P_2O_5)	0.0949	±	0.0046
Manganese Trioxide (Mn_2O_3)	0.1279	±	0.0027
Chromium Trioxide (Cr_2O_3)	0.01012	±	0.00063
Zinc Oxide (ZnO)	0.02619	±	0.00087
Strontium Oxide (SrO)	0.1754	±	0.0088
Barium Oxide (BaO)	0.0315	±	0.0043
Chlorine (Cl)	0.0146	±	0.0028

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. The reference values are metrologically traceable to the SI derived units of mass fraction (expressed as 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, within-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 $U = ks/\sqrt{n}$, where s is the standard deviation and the coverage factor, $k = 2.18$, 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 635a Portland Cement (Blended with Slag)

Constituent	Mass Fraction (%)		
Insoluble residue	0.559	±	0.028
Free CaO	0.527	±	0.023
Sulfide Sulfur	0.242	±	0.021
Fluorine (F)	0.0553	±	0.0002

Measurand	Mass Fraction (%)		
LOI between 45 ºC and 220 ºC	0.857	±	0.002
LOI between 220 ºC and 550 ºC	0.35	±	0.03
LOI between 550 ºC and 950 ºC	1.20	±	0.02
LOI total at 950 ºC	2.45	±	0.06

Information Mass Fraction Values: The information value reported for loss on drying between ambient temperature and 45 °C is the estimated limit of detection of the test method. For the calculated total of analyzed constituents plus LOI total at 950 ºC, 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^- 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 635a Portland Cement (Blended with Slag)

Measurand	Mass Fraction (%)
Loss on drying between ambient temperature and 45 ºC	< 0.1
Total analyzed constituents	100.34

Table 4. Analytical Methods Used on SRM 635a Portland Cement (Blended with Slag)

Constituent	Methods[(a)]
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, ICP-OES and spectrophotometry
ZnO	Total Zn determined using XRF and ICP-OES
Mn_2O_3	Total Mn determined using XRF and ICP-OES
Cr_2O_3	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_3 titration after reaction with HCl performed by collaborating laboratory
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[(b)] with standard additions at NIST, and an ion-selective electrode method at the collaborating laboratory
Fluorine (F)	Ion-selective electrode and XRF at the collaborating laboratory
Loss on Ignition (LOI)	Thermogravimetric analysis performed at NIST and the collaborating laboratory. See Appendix A for a discussion of test methods and relevance of values [3,9,10].

[(a)] 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

[(b)] 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 Mar 2017).

[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 Mar 2017).

[3] ASTM C114-15; *Standard Test Methods for Chemical Analysis of Hydraulic Cement*; Annu. Book ASTM Stand., Vol. 04.01, West Conshohocken, PA.

[4] ASTM C595/C595M – 16; *Standard Specification for Blended Hydraulic Cements*; 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 (12), pp. 1899–1906 (2002).

[6] DerSimonian, R. and 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*; (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 Mar 2017); 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 Mar 2017).

[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; 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 635a 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 635a 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 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,
- 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 635a.

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 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 [10] 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.