National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2066

K-411 Glass Microspheres

This Standard Reference Material (SRM) is intended for use as a standard for the quantitative microanalysis of particles and for the development of particle matrix correction procedures. The elements present in these microspheres, common to many classes of particles, are silicon, calcium, magnesium, iron, and oxygen. The bulk material used to produce SRM 2066 is the same K-411 glass certified in SRM 470 Glasses for Mineral Analysis [1]. SRM 2066 consists of approximately 50 mg of glass microspheres of known composition and size (1 μm to 40 μm) with minimal microheterogeneity.

Certified Values and Uncertainties: The certified compositions and uncertainties for silicon, calcium, magnesium, and iron, as well as the reference value for oxygen, are listed in Table 1. Certification is based on comparative analysis of SRM 2066 microspheres to the bulk K-411 glass (see Figure 1). The reference value for oxygen was calculated from stoichiometry. The certified values are weighted means of values from 13 samples selected by random stratified sampling. The mathematical weighting scheme, described in References [2-4], combines an estimate of within-vial variation with an estimate of between-vial variation, combined in quadrature, and expanded to an overall uncertainty (95 %) by a coverage factor of 2 [5,6]. These certified values apply only to microspheres that are 2 μm or larger in diameter.

Table 1. Certified Concentration in Mass Fraction (kg/kg) of Microspheres Larger Than 2 μm

Element	Concentration
Silicon	0.256 ± 0.017
Calcium	0.112 ± 0.023
Magnesium	0.092 ± 0.014
Iron	0.112 ± 0.023
Oxygen*	0.429 ± 0.012

***NOTE:** The oxygen value is a reference value [7].

Glass furnace design and glass microsphere production were provided by D.H. Blackburn and D.A. Kaufman of the NIST Ceramics Division.

Electron probe quantitative microanalysis, sample preparation, and bottling were provided by S.V. Roberson of the NIST Surface and Microanalysis Science Division.

The technical and support aspects concerning the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by R.J. Gettings and N.M. Trahey.

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Statistical evaluation of the data was provided by S.D. Leigh of the NIST Statistical Engineering Division.

Coordination of the technical measurements leading to certification of this SRM was provided by R.B. Marinenko and J.A. Small of the NIST Surface and Microanalysis Science Division.

Material Processing: The bulk K-411 glass used to make SRM 2066 was one of the glasses issued in the discontinued SRM 470. Glass microspheres were formed from the bulk material in a special furnace developed at NIST [8,9]. Micrometer-size K-411 ground glass shards were dispersed and transported with a low velocity air stream (10 L/min) through a tube heated to 1350 °C, that was above the softening point of the glass [10]. The shards formed spheres from the combined effects of lowered viscosity and surface tension forces. Crystalline silica, 425 µm to 300 µm in diameter (No. 40 screen to No. 50 screen), was mixed with the finely powdered K-411 glass shards to prevent agglomeration of the glass powder and stabilize the fluidization process. A 2:1 ratio (by volume) of silica to powdered glass was used in the process. **NOTE:** Most of the silica particles were too large to be transported in the arc stream and remained in the fluidizing chamber. Seven grams of microspheres ranging from approximately 1 µm to 40 µm were collected and homogeneously divided into units.

Preparation and Certification Procedure: Microspheres were dispersed onto conductive carbon tape for analysis and coated with about 10 nm of carbon. To avoid agglomeration of microspheres, a dispersion technique was developed at NIST [8,9] and is outlined in the section on Instructions for Sample Preparation. Particle analysis was done at an excitation potential of 15 kV with an electron microprobe using an automated particle analysis procedure developed at NIST [11]. Energy dispersive spectra (EDS) were processed with the sequential simplex curve-fitting procedure and quantitated with the ZAF matrix correction procedure in the Desktop Spectral Analyzer (DTSA) program that was developed by the National Institutes of Health (NIH) and NIST [12]. Thirteen different microsphere samples were analyzed. Eleven were from vials randomly selected from the SRM unit population, each containing about 50 mg of the microspheres, while two were duplicate samples taken from two of the 11 selected vials. From each of the 13 samples, 100 to 200 microspheres, ranging in size from less than 1 µm to about 40 µm, were analyzed. The bulk K-411 glass was used as a quantitative standard. In addition to the certified elements, trace levels (< 0.1 %) of Al_2O_3 and approximately 0.1 % of MnO were observed in the bulk K-411 glass.

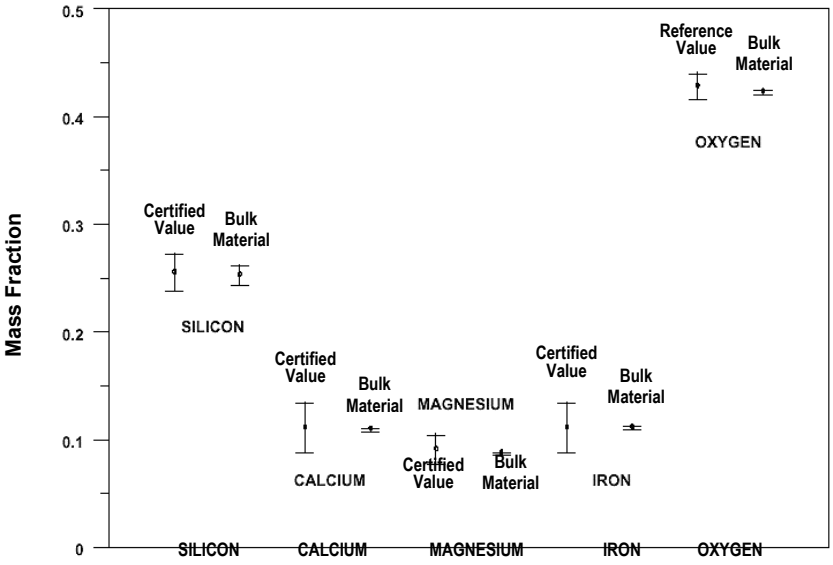
Discussion: Two effects must be considered in the electron microprobe quantitative analysis of microspheres since quantitative matrix correction procedures are written for flat, polished specimens. First, there is the mass/size effect [13,14] of a microsphere. Fewer x-rays are emitted from a microsphere than from a bulk specimen. Therefore, NIST data were normalized to enable a comparison of concentrations from each microsphere with the bulk K-411 glass. In addition, unnormalized data that totaled 0.5 or less (the sum of concentrations Mg + Si + Ca + Fe + O) were removed from the data set. This analysis excluded data from microspheres that were less than 2 µm in diameter. For larger diameter spheres, very few or no electrons escape without the opportunity to produce x-rays. However, at an excitation potential of 15 kV, several electrons entering a sphere **smaller than 2 µm** diameter will pass through the sphere without generating x-rays. Inclusion of such small spheres would negatively bias the certified values.

The second effect, resulting from the particle geometry, shortens the path length of the x-rays exiting a sphere. The absorption by the matrix of low energy x-ray lines exiting the specimen will be reduced. For SRM 2066, the low-energy lines for Mg Kα and Si Kα x-rays can be effected. This may be the reason why the certified value for magnesium in SRM 2066 is greater than for the bulk K-411 glass (see Figure 1).

Instructions for Sample Preparation: To minimize agglomeration, the following specimen preparation technique [8,9] should be used.

1. Cover a 2.54 cm carbon planchette with a strip of double-sided, conductive, carbon sticky tape.
2. Obtain a 500 mL wide-mouth jar and punch two holes in the lid, each about 30 cm apart and 20 cm from the edge.
3. Place the carbon planchette on one side of the bottom of the jar and approximately 2 mg to 5 mg of microspheres on the other side.

4. With the lid screwed onto the jar, direct a low-pressure burst of gas from a hand-held duster nozzle at the microspheres through one of the holes in the lid. Several thousand microspheres will now be distributed onto the planchette with little or no agglomeration.
5. Coat microspheres with approximately 10 nm of carbon.



	SRM 2066 Value	Bulk Glass Value
Silicon	0.256 ± 0.017	0.2538 ± 0.0090
Calcium	0.112 ± 0.023	0.1106 ± 0.0014
Magnesium	0.092 ± 0.014	0.0885 ± 0.0012
Iron	0.112 ± 0.023	0.1121 ± 0.0016
Oxygen	0.429 ± 0.012	0.4236 ± 0.0024

Figure 1. Comparison of SRM 2066 certified and reference values versus bulk K-411 glass values.

REFERENCES

[1] Marinenko, R.B., "Preparation and Characterization of K-411 and K-412 Mineral Glasses for Microanalysis: SRM 470," NBS Special Publication 260-74, (1982).

[2] Mandel, J. and Paule, R., "Interlaboratory Evaluation of a Material with Unequal Number of Replicates," Anal. Chem. **42**, p. 1194, (1970).

[3] Mandel, J., "Evaluation and Control of Measurements," New York: Marcel-Dekker, (1991).

[4] Schiller, S.B. and Eberhardt, K.R., "Combining Data from Independent Chemical Analysis Methods," Spectro. Acta, **46B,** p. 1607, (1991).

[5] Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluation and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, Gaithersburg, MD, (1994).

[6] ISO U.S. Guide to the Expression of Uncertainty in Measurement, Internat. Stand. Org (1995) or U.S. Guide to the Expression of Uncertainty in Measurement, (1997), Doc. No. ANSI/NCSL Z540.2.

[7] May, W.E., Parris, R.M., Beck, C.M., Fassett, J.D., Greenberg, R.R., Guenther, F.R., Kramer, G.W., Wise, S.A., Gills, T.E., Colbert, J.C., Gettings, R.J., and MacDonald, B.S., "Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements," NIST Special Publication 260-136, (2000).

[8] Roberson, S., Marinenko, R.B., Small, J.S., Blackburn, D., Kauffman, D., and Leigh, S., "Certification of K-411 Glass Microspheres with Electron Probe Microanalysis," Microbeam Analysis-1995 Proc. 29th Ann. Conf. Micro. Beam. Anal. Soc., Breckenridge, CO, August 6-11, p. 225, (1995).

[9] Marinenko, R.B., Roberson, S., Small, J.S., Thorne, B.B., Blackburn, D., Kauffman, D., and Leigh, S., "Preparation and Certification of K-411 Glass Microspheres," Microscopy and Microanalysis Journal, (in press).
[10] ASTM Standard C-338-93, "Standard Test Method for Softening Point of Glass," 1998 Annl. Book of ASTM Standards, **15.02**, p. 101, (1998).
[11] Bright, D.S., "A LISP-Based Image Analysis System with Applications to Microscopy," J. Microsc. **148**, p. 51, (1987).
[12] Fiori, C.E. and Swyt, C.R., "Desk Top Spectrum Analyzer (DTSA)," U.S. Patent 5,299,138, (1994).
[13] Small, J.A., "Quantitative Particle Analysis in Electron Beam Instruments," Scan. Elect. Microsc., **I**, p. 447, (1981).
[14] Armstrong, J.T., "Quantitative Elemental Analysis of Individual Microparticles with Electron Beam Instrument," *Electron Probe Quantitation,* Heinrich, J.F.K., Newbury, D.E. (eds), New York: Plenum Press, p. 261, (1991).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.