

Lee L. Yu,¹ John D. Fassett,¹ Bruce S. MacDonald,¹ Therese A. Butler,¹ Dawn M. Ramsey,² Rosa J. Key-Schwartz,² and Theodore C. Rains³

Development of SRMs 295x and 296x, Respirable Crystalline Silica on Filter

ABSTRACT: Standard Reference Material (SRM[®]) series 2951 to 2958 (5 µg to 1000 µg) Respirable Alpha Quartz on Filter and SRM series 2961 to 2967 (5 µg to 1000 µg) Respirable Cristobalite on Filter were prepared gravimetrically by depositing SRM 1878a Respirable Alpha Quartz and SRM 1879a Respirable Cristobalite on filters, respectively. These new SRMs are developed to assure the quality of respirable crystalline silica measurements using x-ray diffraction and infrared spectrometry around the regulatory limits that are enforced by the Occupational Safety and Health Administration (OSHA). The mass of silica determined by highly sensitive, but non-polymorph-specific, inductively coupled plasma optical emission spectrometry (ICP-OES) was successfully used to calculate the mass of polymorph-specific crystalline silica on filter after all sources of Si on the new SRMs were carefully analyzed. The certified values of alpha quartz in SRMs 2951 to 2958 and cristobalite in SRMs 2961 to 2967, respectively, were established from the gravimetric preparation values and the spectrometric measurement values.

KEYWORDS: respirable, alpha quartz, cristobalite, ICP-OES, Standard Reference Material, SRM, uncertainty budget, combining results

Occupational exposures to respirable crystalline silica are associated with the development of silicosis, lung cancer, pulmonary tuberculosis, and other airway diseases [1]. The Occupational Safety and Health Administration (OSHA) has developed strict limits that regulate the emission of respirable crystalline silica in the work place. Unfortunately, crystalline silica is difficult to measure accurately by using the standard industrial techniques, X-ray diffraction (XRD), infrared spectrometry (IR), or spectrophotometry (UV/VIS), which hampers the enforcement of the regulations [2].

To improve the robustness of the measurement protocol and to establish a basis for the comparability of results from various laboratories, the National Institute of Occupational Safety and Health (NIOSH) has sponsored the development of a suite of respirable crystalline silica-on-filter calibration Standard Reference Materials (SRM[®]s) by the National Institute of Standards and Technology (NIST) with distinct cristobalite loadings between 5 µg and 500 µg and alpha quartz loadings between 5 µg and 1000 µg. The relative expanded uncertainty of the certified value for each filter was targeted to be less than 15 %. These materials will serve the many laboratories that perform airborne crystalline silica analyses using XRD and IR and allow accurate measurements around the regulatory limits that are enforced by OSHA [2].

A critical challenge for the development of these SRMs is a lack of analytical techniques capable of quantifying crystalline silica as low as 5 µg. The detection limit of XRD, the only

Manuscript received 28 April 2004; accepted for publication 29 September 2004; published May 2005. Presented at ASTM Symposium on Silica: Sampling and Analysis on 22-23 April 2004 in Salt Lake City, UT.

¹ National Institute of Standards and Technology, Gaithersburg, MD, USA.

² National Institute for Occupational Safety and Health, Cincinnati, OH, USA.

³ High Purity Standards, Charleston, SC, USA.

technique that can distinguish the various polymorphs of silica, is about 5 µg for crystalline silica; however, the limit of quantification is much higher [2]. We employed a novel approach in the development of the suite of respirable crystalline silica on filter SRMs, which allowed us to certify as low as 5 µg alpha quartz or cristobalite on filter. Crystalline silica of certified purity and polymorph, SRM 1878a Respirable Alpha Quartz and SRM 1879a Respirable Cristobalite, were used as the source of respirable crystalline silica to prepare SRM series 2951 to 2958 (5 µg to 1000 µg) Respirable Alpha Quartz on Filter and SRM series 2961 to 2967 (5 µg to 1000 µg) Respirable Cristobalite on Filter. Since the source of crystalline silica is of known purity, the mass of Si becomes an alternative measure to quantify the crystalline silica on the filter. Consequently, elemental analysis techniques with ng/g detection capabilities for Si, i.e., inductively coupled plasma optical emission (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS), can be used for the certification analysis [3]. We determined the mass of silicon on the filters by using ICP-OES. We derived the average values of crystalline silica on the filters from the gravimetric preparation values, the spectrometric measurement values, and the certified values of the crystalline component of SRMs 1878a and 1879a.

Experimental

Instrumentation⁴

A model 776 DOSIMAT Automatic Pipette from Brinkmann Metrohm (Westbury, NY) was used to deposit SRM 1878a and SRM 1879a onto filters. The optical emission measurements were made with an Optima 3300 DV ICP-OES equipped with a Ryton spray chamber, a gem-tipped cross-flow nebulizer, and a demountable torch with an alumina injector (Perkin-Elmer, Norwalk, CT).

Procedure

The preparation, measurement, and certification of alpha quartz on filters and cristobalite on filters are identical. We use the development of alpha quartz on filters as an example to simplify the descriptions and arguments in the following. All procedures and discussions pertaining to Respirable Alpha Quartz on Filters are applicable to Respirable Cristobalite on Filters unless otherwise noted.

Preparation and gravimetric measurements: A known mass of SRM 1878a (SRM 1879a for Cristobalite on Filter) was dispersed in a 10 % (volume fraction) glycerol solution in water to form a slurry under sonication. A desired aliquot of the slurry was deposited onto a 25 mm diameter, 5.0 µm pore PH-PVC Filter (Omega Specialty Instrument, Chelmsford, MA). A blank filter was prepared similarly by depositing on the filter an aliquot of a 10 % (volume fraction) glycerol solution in water. A thin, polymer protective coating was applied on the filter after the slurry was dried in class-100 clean environment. The finished filter was placed between light blue spacers and stored in a 37 mm petri dish. The gravimetric-preparation mass of the alpha

⁴ Certain commercial instruments are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology or the National Institute for Occupational Safety and Health, nor does it imply that the equipment identified is necessarily the best for the purpose.

quartz on filters was determined based on the mass of aliquots of the slurry randomly sampled during the preparation of the filters.

ICP-OES Measurements—Eight petri dishes of loaded filters and eight petri dishes of blank filters at each level of alpha quartz loading were randomly selected from the finished SRM products. One filter from each petri dish was transferred into a 60 mL polyethylene bottle. The bottle was capped after 1 mL of deionized water and 1 mL of Optima grade hydrofluoric acid (HF, Fisher Scientific, Pittsburgh, PA) were added. The bottle was gently swirled to ensure complete wetting of the filter and then left for 16 h at room temperature. The HF in the bottle was neutralized with 10 mL of 25 % (mass fraction) of tetramethyl ammonium hydroxide (TMAH) (Alfa Aesar, Ward Hill, MA) in water, and the digest was diluted to approximately 50 g. All calibration standards were prepared from SRM 3150 Spectrometric Solution of Si, and they contained a similar amount of HF and TMAH to match that in the samples. Silicon emission was measured at 251.611 nm with the axial-view mode of the spectrometer. The mass of Si on filter is obtained by using the calibration curve function [3].

Results and Discussion

Certification Strategy

At NIST, a certified value can be established by using a single primary method with confirmation by other method(s), or two independent critically-evaluated methods [4]. A measurement method based solely on gravimetric dilution of a homogeneous solution of an SRM is considered a primary direct method because it “measures the value of an unknown without reference to a standard of the same quantity” [4]. However, SRMs 2951 to 2958 are prepared by dispensing onto filters a slurry of SRM 1878a that is microscopically inhomogeneous. Furthermore, the stability of the slurry is susceptible to a gravitational separation force whose effect on measurement uncertainty is not easily described in terms of SI units. Therefore, for this work, the gravimetric preparation of SRMs 2951 to 2958 is considered an *independent method* rather than a primary method [4]. Consequently, the two independent methods of certification have been adopted [4]. Values from both the gravimetric preparation and the ICP-OES measurement of total Si have been used to establish an average value, and the crystalline silica value calculated from ICP-OES measurement of Si becomes a critical part of value assignment in the certification of SRMs 2951 to 2958.

Gravimetric Preparation Value

Alpha quartz was delivered onto the filter in the form of SRM 1878a slurry by using a calibrated pipette. The mass of alpha quartz (Q) in the aliquot of slurry is given by:

$$Q = \frac{A \cdot C}{W} \cdot M \quad (1)$$

where M is the mass of the slurry deposited onto the filter, C is the certified mass fraction of alpha quartz in SRM 1878a, and W is the mass of the slurry that contains A grams of SRM 1878a.

The uncertainty of the gravimetric-preparation value is determined according to the ISO Guide to the Expression of Uncertainty in Measurement [5]. The Type A measurement uncertainty is calculated from the repeatability of M found in the producer's report of analysis.

There are four sources of Type B uncertainty: the measurement uncertainty for A and W , the uncertainty of the certified value of alpha quartz in SRM 1878a, and the uncertainty resulting from the heterogeneity of the slurry. The measurement uncertainty of A and C are estimated to be the readability of the balances used to weigh the materials at 0.0001 g and 0.01 g, respectively. These uncertainties are normalized by division by $\sqrt{3}$ assuming uniform distribution for the two variables. The uncertainty of the alpha quartz mass fraction is taken from the certificate of SRM 1878a. Assuming a normal distribution, this uncertainty is normalized by division by 2. The uncertainty from the heterogeneity of the slurry is estimated to be 2 % of the measured value, and it is normalized by division by $\sqrt{3}$ assuming uniform distribution.

The combined uncertainty is the square root of the sum of squared Type A and Type B uncertainties, and the degrees of freedom (DF) of the combined uncertainty is given by the Welch-Satterthwaite formula [6]. The expanded measurement uncertainty is the combined uncertainty multiplied by a coverage factor that equals the t -distribution value of the calculated DF at the 95 % confidence level. The third columns of Tables 1 and 2 list the mean and the expanded uncertainty of gravimetric preparation values of SRMs 2951 to 2958 and SRMs 2961 to 2967, respectively.

Spectrometric Measurement Value

The mass of silicon on each filter was determined by using ICP-OES, and the mass of silicon was converted to the mass of silica with a multiplication factor of 2.14 (molar mass of silica divided by molar mass of silicon). The mass of alpha quartz on each filter was calculated using the following formula:

$$Q = (S - B) \cdot \frac{C}{P} \quad (2)$$

where S and B are the silica on the loaded filter and the blank filter, respectively; C is the certified mass fraction of alpha quartz in SRM 1878a; and P is the mass fraction of silica in SRM 1878a.

ICP-OES is an elemental analysis technique that gives the value of total Si regardless of the polymorphic form. To accurately assign the value of the Si from crystalline silica, experiments were conducted to ensure that: 1) Si from SRM 1878a on filter is completely digested without loss so that the alpha quartz value determined by using ICP-OES is not negatively biased, and 2) Si from sources other than SRM 1878a is accounted for and corrected. A method that completely digests SRM 1878a on filter without loss of Si has been described [3]. Here we address the second issue by identifying, minimizing, and correcting the Si other than that from SRM 1878a.

There are five possible sources of extraneous Si that may bias the true alpha quartz value as a result of ICP-OES measurement. They are: (i) Si in the filter substrate, (ii) Si in the deposited solvent, (iii) Si in the added protective coating, (iv) Si added by the reagents and handling during sample preparation for ICP-OES measurement, and (v) Si in SRM 1878a that is not of alpha quartz polymorph origin. The overall Si from slurry reagents (the second potential source) and Si from sample preparation for ICP-OES measurement (the fourth potential source) is below the 8 ng/g Si solution detection limit of ICP-OES technique [3]. Furthermore, the trace amount of Si in the homogeneous reagents and solutions used in the sample preparation is not in a form of crystalline silica. These sources of Si are corrected when the blank is subtracted, and they do not result in systematic errors in the alpha quartz values calculated from ICP-OES measurements.

The filter substrate (the first potential source of Si) and the protective coating (the third potential source of Si) were examined experimentally. Five base filters and five coated filters were digested with the procedure described previously, and the digests were analyzed for Si. The silicon found in the base and the coated filters was the equivalent of $0.2 \mu\text{g} \pm 0.4 \mu\text{g}$ per filter and $1.7 \mu\text{g} \pm 0.4 \mu\text{g}$ silica per filter, respectively. It suggests that the filter base contains little Si, while the protective coating is a significant source of Si.

Whether or not the Si from the protective coating is a form of crystalline silica is of particular interest. If this source of Si is alpha quartz (or cristobalite in the case of SRM 296x), the crystalline silica value of a loaded filter will be negatively biased after subtraction of the blank. To prevent the potential incorrect blank corrections, XRD was employed to determine the polymorph of this source Si. A filter layered with 100 times the normal amount of coating material was used for the measurement to enhance the signal intensity, yet the crystalline silica intensity of the filter was below the detection limit of the XRD method. The total crystalline silica in a single layer of the protective coating is estimated to be below $0.1 \mu\text{g}$, which is below the ICP-OES measurement uncertainty of $0.4 \mu\text{g}$. Therefore, the amount of crystalline silica from the protective coating is negligible, and correction of this source of Si by blank subtraction does not adversely affect the accuracy of the spectrometric measurement of alpha quartz on filter. In summary, Si of all aforementioned sources is accurately correctible by blank subtraction, and what remains after the correction is the silica from SRM 1878a.

To convert the aforementioned silica on filter to the amount of alpha quartz on filter, alpha quartz to total silica ratio (C/P) of SRM 1878a must be determined. Alternatively, the mass fraction of silica in SRM 1878a (P) was determined since C is known. Six samples of SRM 1878a were digested, and Si in each solution was determined by using ICP-OES. The mass fraction (P) and measurement uncertainty (u_p) calculated from the six measurements is $99.65 \% \pm 1.36 \%$, respectively. With P as a known quantity, alpha quartz on filter is readily calculated from the spectrometric value of silicon by using Eq 2.

The uncertainty of the spectrometric measurement of alpha quartz is estimated according to the ISO Guide to the Expression of Uncertainty in Measurement [5]. The Type A measurement uncertainty of alpha quartz on filter is derived from Eq 2:

$$u_a = \sqrt{\left(\frac{C}{P}\right)^2 u_s^2 + \left(\frac{C}{P}\right)^2 u_B^2 + \left(\frac{Q}{P}\right)^2 u_P^2} \quad (3)$$

where u_s , u_B , and u_P , are the repeatability for S , B , and P , respectively. The repeatability of ICP-OES measurements, u_s , is determined primarily by the repeatability of the amount of alpha quartz deposited on each filter, which will be discussed later. Therefore, the expression of Eq 3 is modified to report the uncertainty as 95 % prediction intervals:

$$u_a = \sqrt{\left(\frac{C}{P}\right)^2 (1+N) \cdot u_s^2 + \left(\frac{C}{P}\right)^2 u_B^2 + \left(\frac{Q}{P}\right)^2 u_P^2} \quad (4)$$

where N is the number of loaded filters analyzed. The three sources of Type A uncertainty for the spectrometric measurement of alpha quartz on filter are the repeatability of sample measurement, the repeatability of blank measurement, and the repeatability of the mass fraction of silica measurement, as they are shown in Eq 4.

There are five sources of Type B uncertainty: dilution, calibrant certification, measurement, alpha quartz certification, and crystalline silica detection by XRD. Dilution uncertainty refers to

the uncertainty from the balance used for weighing in serial dilution. The readability of the balance (0.00001 g) is taken as the measurement uncertainty, and it is converted to standard uncertainty by division by $\sqrt{3}$ assuming uniform distribution. The calibration of the Si is based on the single-element Spectrometric Solution SRM 3150 containing Si, the solution used to prepare the calibration standards. Calibrant certification uncertainty is derived from the expanded uncertainties reported on the certificate of SRM 3150. The reported expanded uncertainty is converted to a standard uncertainty by division by 2, assuming a normal distribution. The measurement uncertainty refers to the uncertainty resulting from the measurement of the intensity of the analyte signal and the conversion of the intensity signal to mass fraction by using the calibration curve function. It is the uncertainty of the instrument drift occurring between the measurement of the standard and the measurement of the unknown combined with the uncertainty of the linearity of the calibration curve. This uncertainty is estimated to be 2 % of the measured value, and it is converted to standard uncertainty by division by $\sqrt{3}$, assuming uniform distribution. The alpha quartz certification uncertainty has been discussed above, and here the same treatment applies. The crystalline silica detection uncertainty refers to the uncertainty in the determination of crystalline silica on the blank filter by XRD. This source of uncertainty is estimated to be the detection limit of the XRD method, and it is normalized by division by $\sqrt{3}$, assuming uniform distribution.

The combined and the expanded spectrometric measurement uncertainty for alpha quartz and cristobalite on filter are calculated similarly as described above, and the mean and the expanded uncertainty for SRMs 2951 to 2958 and SRMs 2961 to 2967 are shown in the fourth columns of Tables 1 and 2, respectively.

Evaluating and Combining the Data

The relative expanded uncertainty, defined as the expanded uncertainty divided by the mean, of the spectrometric values in Tables 1 and 2 is from 4 % to 16 %. This uncertainty reflects the filter-to-filter variability resulting from the gravimetric deposition of SRM 1878a or SRM 1879a on the filter, because the relative uncertainty of the ICP-OES method is negligible at 1.4 % [3]. A more rigorous quality control in the filter production is required if a better homogeneity of the filters is desired.

The average and the uncertainty intervals of the gravimetric value and the spectrometric value are compared. The uncertainty intervals of the two methods overlap for each SRM, suggesting good agreement between the two methods. The means of the two methods are evaluated by using the sign test [7]. No significant difference is found between the means of the two methods, suggesting no systematic bias between the two methods.

The gravimetric-preparation values and the spectrometric-measurement values of alpha quartz on filter are combined by using the “Type B on Bias” model [8]. The average value is the average of the gravimetric-preparation mean and the spectrometric-measurement mean. Accordingly, the Type A uncertainty of the average value results from the combined Type A variance of the two methods [5,8]. The Type B uncertainty of the average value is the combined Type B variance of the two methods plus the Type B variance resulting from the difference between the means of the two methods [8]. The preliminary average values for SRMs 2951 to 2958 and SRMs 2961 to 2967 are listed in the fifth columns of Tables 1 and 2, respectively. The relative expanded uncertainty of the average values are listed in the sixth columns of Tables 1 and 2, and they are within the target relative expanded uncertainty level of 15 %.

TABLE 1—*Summary of gravimetric-preparation values, spectrometric-measurement values, and average values of SRMs 2951 to 2958 Alpha Quartz on Filter, in µg per filter**.

SRM #	Nominal	Gravimetry	Spectrometry	Average [†]	U %
2951	5	4.8 ± 0.1	5.0 ± 0.5	4.9 ± 0.5	10 %
2952	10	9.7 ± 0.2	9.9 ± 1.2	9.8 ± 1.2	12 %
2953	20	19.7 ± 0.5	19.7 ± 1.4	19.7 ± 1.3	7 %
2954	50	48.7 ± 1.1	50.1 ± 5.0	49.4 ± 4.8	10 %
2955	100	98 ± 2	98 ± 5	98 ± 5	5 %
2956	250	245 ± 6	254 ± 21	250 ± 19	8 %
2957	500	485 ± 11	497 ± 33	491 ± 32	7 %
2958	1000	941 ± 22	978 ± 56	959 ± 55	6 %

* Values are expressed as mean ± expanded uncertainty at 95 % confidence level.

†The values are based on the alpha quartz in SRM 1878a mass fraction of 97.0 % ± 0.2 % that is currently under revision.

TABLE 2—*Summary of gravimetric-preparation values, spectrometric-measurement values, and average values of SRMs 2961 to 2967 Cristobalite on Filter, in µg per filter**.

SRM #	Nominal	Gravimetry	Spectrometry	Average [†]	U %
2961	5	5.0 ± 0.1	5.5 ± 0.9	5.2 ± 0.8	15 %
2962	10	10.0 ± 0.2	10.5 ± 1.3	10.3 ± 1.2	12 %
2963	20	20.1 ± 0.5	20.0 ± 1.7	20.0 ± 1.6	8 %
2964	50	49.8 ± 1.2	49.4 ± 2.5	49.6 ± 2.3	5 %
2965	100	100 ± 2	102 ± 7	101 ± 7	7 %
2966	250	251 ± 6	257 ± 9	254 ± 8	3 %
2967	500	501 ± 12	475 ± 28	488 ± 29	6 %

* Values are expressed as mean ± expanded uncertainty at 95 % confidence level.

†The cristobalite values are based on the cristobalite in SRM 1879a mass fraction of 95.6 % ± 0.4 % that is currently under revision.

Conclusion

We have developed SRMs 2951 to 2958 Respirable Alpha Quartz on Filter and SRMs 2961 to 2967 Respirable Cristobalite on Filter by using an approach that allowed us to determine indirectly the alpha quartz or the cristobalite on filter. With a careful regime for preparing SRM 1878a or SRM 1879a on filter, we were able to evaluate all sources of Si on filter and, subsequently, to determine the desired polymorph of crystalline silica by using ICP-OES. Average values for SRMs 2951 to 2958 and SRMs 2961 to 2967 were established by combining the gravimetric preparation values and the spectrometric measurement values based on the “Type B on Bias” model [8]. The specification and the quality, defined by the mass and the uncertainty, of the new alpha quartz and cristobalite on filter SRMs fit the purpose of instrument calibration and quality assurance for the measurements of airborne crystalline silica around the regulatory limits.

References

- [1] "NIOSH Hazard Review: Health Effects of Occupational Exposure to Respirable Crystalline Silica," DHHS (NIOSH) Publication No. 2002-129, April 2002.
- [2] "NIOSH Manual of Analytical Methods (NMAM®)," M. E. Cassinelli and P. F. O'Connor, Eds., DHHS (NIOSH) Publication 94-113, 4th ed., August 1994.
- [3] Yu, L. L., Fassett, J. D., and Lindstrom A. P., *J. Anal. At. Spectrom.*, 18, 2003, p. 738. [[CrossRef](#)]
- [4] May, W., Parris, R., Beck, C., Fassett, J., Greenberg, R., Guenther, F., et al., "Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements," *NIST special publication 260-136*, US Government Printing Office, Washington, DC, USA, 2000.
- [5] "Guide to the Expression of Uncertainty in Measurement," ISBN 92-67-10188-9, 1st ed., ISO, Geneva, Switzerland, 1993.
- [6] Taylor, B. N. and Kuyatt, C. E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," *NIST Technical Note 1297*, US Government Printing Office, Washington, 1994.
- [7] Miller, J. C. and Miller, J. N., "Statistics for Analytical Chemistry," Wiley, New York, 1984.
- [8] Levenson, M. S., Banks, D. L., Eberhardt, K. R., Gills, L. M., Guthrie, W. F., Liu, H. K., et al., *J. Res. Natl. Inst. Stand. Technol.*, 105, 2000, p. 571.