

Determination of Si in Standard Reference Material SRM 295x Silica-on-Filter

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Respirable crystalline silica is an occupational hazard whose presence in the workplace is strictly regulated. A new series of Standard Reference Materials (SRMs) is being developed to assure the quality of silica measurements and to provide for accurate instrument calibration. SRMs 295x (the value x will designate a specific level of silica loading), Silica-on-Filter, have been prepared by gravimetric delivery of SRM 1878a Respirable Alpha Quartz onto individual filters. The silica on the filter has been verified indirectly by the measurement of the elemental silicon, taking advantage of the knowledge in the filter preparation. An HF acid digestion method has been developed for sample digestion, and a high-resolution inductively coupled plasma mass spectrometric method for the determination of silicon has been developed and validated.

Nearly 2 million US workers (and millions more worldwide) are potentially exposed to crystalline silica, which causes the debilitating and incurable but entirely preventable lung disease called silicosis.¹ There is also substantial evidence that the exposure may also cause cancer.¹ The costs to the construction, mining and other industries are significant. As a result, respirable crystalline silica is regulated by the Occupational Safety and Health Administration (OSHA).

Crystalline silica is difficult to measure accurately by using the standard industrial techniques X-ray diffraction (XRD), infrared spectrometry (IR), and visible absorption spectrophotometry (UV/VIS).² The lack of an appropriate reference material exacerbates the problem of validating the determination of crystalline silica, and consequently the results from interlaboratory comparison exercises have shown poor agreement.³ The metrological challenges frustrate the effective enforcement of the existing regulations on respirable crystalline silica. 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) in collaboration with OSHA, Mine Safety and Health Administration (MSHA), and industry representatives have sponsored the development of a suite of silica-on-filter calibration materials with distinct silica loadings between 5 μg and 1000 μg by the National Institute of Standards and Technology (NIST). These materials will serve many laboratories that perform airborne crystalline silica analyses and allow accurate measurements around the regulatory limits that are enforced by OSHA.

The new Standard Reference Materials (SRM[®]) are prepared by depositing SRM 1878a, which is certified 100.00% \pm 0.21% crystalline α -quartz, on PVC filters. Since the only source of Si on the filters is α -quartz of known purity, the mass of Si on the filters can be used as a substitute for the quantification of the crystalline silica on the filters. Consequently, the techniques capable of accurately determining Si can be used for the certification analysis of silica on the filter.

We have considered several options for the determination of Si including X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA). The low levels of Si on

the filters eliminate direct XRF analysis. The chlorine-containing filters preclude direct analysis by INAA. We have concluded that high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) are the appropriate techniques for the certification analysis. Sample preparation for the mass spectrometric determination of Si is a challenge. We show a new sample preparation technique for the quantitative digestion of silica that minimizes the mass spectrometric measurement uncertainties, and we validate the HR-ICP-MS measurement by comparative ICP-OES measurement of SRM 295x (the value x will designate a specific level of silica loading) Silica-on-Filter.

Experimental

Instrumentation†

The HR-ICP-MS measurements were made using an Element (Finnigan-MAT, Bremen, Germany) double focusing sector field high-resolution mass spectrometer equipped with a demountable Fassel Torch and an alumina injector (Glass Expansion, Hawthorn, Australia). A sapphire injector (Elemental Scientific, Omaha, NE) was compared with the alumina injector. The medium resolution setting ($m/\Delta m \approx 3000$) of the instrument was used for this work. Aerosols of the solutions were generated by using a perfluoralkohol (PFA) Microflow Nebulizer fitted with a PFA spray chamber (Elemental Scientific, Omaha, Nebraska). The optical emission measurements were made with an Optima 3300DV ICP-OES equipped with a Rytan spray chamber, a gem-tipped cross-flow nebulizer, and a demountable torch with an alumina injector (Perkin-Elmer, Norwalk, CT). An MLS 1200 Mega microwave system from Milestone (Monroe, CT) was used to digest the filter substrates.

†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, nor does it imply that the equipment identified is necessarily the best for the purpose.

Procedure

SRMs 295x Silica-on-Filter are prepared by High Purity Standards, Charleston, SC. For the 100 µg loading filters, a 0.2000 g portion of SRM 1878a Respirable Alpha Quartz was transferred to a beaker and diluted to 50.00 g with a proprietary solution containing a mass fraction of 10% glycerol and a wetting agent. The mixture was sonicated for 30 min. A 24.5 µL aliquot of the slurry, which produces the desired mass of 0.0250 g, was transferred to a 25 mm, 5.0 µm PH-PVC Filter from Omega Specialty Instrument (Chelmsford MA). The filter was air-dried for 15 min in class 100 clean area before a thin coat of proprietary polymer spray was applied to enhance the filter stability. After drying under an infrared heat lamp for 30 min, the filter was placed between the light blue spacers provided by Omega Specialty Instrument and stored in a 37 mm petri dish.

For the determination of the silica loading on filter, each filter sample was digested with HF in a 60 mL polyethylene bottle at room temperature. After the filter sample was deposited into the bottle, 1 mL of deionized water and 1 mL of Optima grade HF (Fisher Scientific, Pittsburgh, PA) were added. The bottle was capped and the contents agitated in an ultrasonic bath for 15 s to ensure complete wetting of the filter. The sample was held at room temperature for about 16 h before 10 mL of 25% by mass fraction of tetramethyl ammonium hydroxide (TMAH) (Alfa Aesar, Ward Hill, MA) was added to neutralize the solution as will be explained later. After 1 g of a 20 µg g⁻¹ Al solution was added as an internal standard for the HR-ICP-MS measurement, the digest was diluted to approximately 50 g. The mass of the analyte found on the filter is calculated by the following equation:

$$M_{\text{Si}} = \frac{M_{\text{Al}} \times I_{\text{Si}} \times I_{\text{Al}}^{\text{s}} \times M_{\text{Si}}^{\text{s}}}{I_{\text{Si}}^{\text{s}} \times I_{\text{Al}} \times M_{\text{Al}}^{\text{s}}} \quad (1)$$

where M_{Si} , M_{Si}^{s} , M_{Al} , M_{Al}^{s} are masses of Si in the sample, Si in the standard, Al in the sample, and Al in the standard, respectively, and I_{Si} , I_{Si}^{s} , I_{Al} , I_{Al}^{s} are intensities of Si of the sample, Si of the standard, Al of the sample, and Al of the standard, respectively. All calibration standards were prepared from SRM 3150 Spectrometric Solution of Si, and were spiked with the same 20 µg g⁻¹ Al solution. They contained a similar amount of HF and TMAH to match that in the samples.

To determine whether a loss of Si had occurred during the HF digestion, four solution samples were prepared each containing about 1 g of 197 µg g⁻¹ Si. Each sample was digested in 1 mL HF for 16 h in a capped polyethylene bottle and the resulting solution was treated with TMAH in the same way as a filter sample. The Si in each digest was measured to calculate the recovery of the procedure.

To determine if Silica-on-Filter digests completely, the presence or the absence of Si on the filter was investigated after the HF digestion. Four filters with a nominal 100 µg loading of silica on each and two blank filters were digested with the method described previously. Then, each filter was deposited into a microwave cell after the filter was rinsed with about 40 mL of deionized water. The rinsate was combined with the digest, and after the addition of 10 mL of 25% by mass fraction of TMAH the digest was analyzed for Si. The four filter substrates and two procedure blanks were digested in the microwave with 2.5 mL of nitric acid using the parameters listed in Table 1. After the digestion, the cap of the microwave

vessel was removed and the remaining nitric acid in the digest was evaporated on a hotplate. The microwave vessel was cooled to room temperature before 1 mL of deionized water and 1 mL of HF was added. The vessel was then covered airtight with Parafilm and was allowed to stand for about 16 h. The solution in each microwave cell was transferred to a 60 mL polyethylene bottle and diluted to about 50 g with deionized water after 10 mL of 25% by mass fraction of TMAH was added. The Si content in the solution was determined.

The detection limit was determined as the concentration giving a signal equivalent to 3 times the noise, calculated from the standard deviation of 11 repetitive measurements of a blank solution. All reported uncertainties are at 95% confidence interval unless otherwise stated.

Results and discussion

Mass spectrometric measurements

Silicon has three isotopes, ²⁸Si, ²⁹Si, and ³⁰Si with nominal abundances of 92.23%, 4.67%, and 3.01%, respectively. Each silicon isotope is interfered with by isobars: ¹⁴N₂⁺ and ¹²C¹⁶O⁺ at mass 28, ¹⁴N¹⁵N⁺ and ¹³C¹⁶O⁺ at mass 29, and ¹⁴N¹⁶O⁺ at mass 30. A quadrupole based ICP-MS with a unit mass resolution cannot resolve the isobaric interferences; therefore, a HR-ICP-MS must be used for the determination of Si. The interferences at the Si masses are resolved at the medium resolution setting of the HR-ICP-MS ($m/\Delta m = 3000$); therefore, quantitative measurements of Si can be made at all three masses. The determination of Si by isotope dilution mass spectrometry becomes possible as it has been demonstrated by Kliemens and Heumann for the determination of traces of Si in biological and clinical samples.⁴ The overall uncertainty of the silica loading on the filter is determined by the repeatability in the preparation of the filter (discussed later), therefore the simpler external calibration technique was chosen over the more precise but time consuming isotope dilution technique. The calibration was based on the measurement of the most abundant silicon isotope ²⁸Si and the added internal standard ²⁷Al. Aluminium is a good internal standard because of the one mass difference between the analyte and the internal standard, which makes electronic scanning possible, minimizing the delay between their measurements. The Silica-on-Filter SRMs were prepared in a clean environment, and they have very low Al content. The baseline intensity at mass 27, equivalent to about 2 ng Al g⁻¹, is primarily from the instrument since this intensity was observed for the standard torch with quartz injector, as well as for the demountable torch with alumina or sapphire injectors. This constant baseline did not adversely affect the repeatability of the measurement because it can be subtracted, and because it was much smaller compared to the concentration of the internal standard at about 400 ng Al g⁻¹. The detection limit of Si was determined to be 3 ng g⁻¹ measured at mass 28.

Contamination and memory effects

Contamination and memory effects are major challenges in Si determination because of its ubiquity. The standard Finnigan glass nebulizer-sample introduction system was replaced with PFA Microflow nebulizer, PFA spray chamber and a demountable torch with an alumina injector; still, a direct determination of the sample after an HF digestion was impossible because of a high and erratic baseline intensity and an extremely long memory. The source of the high Si baseline was determined to be the alumina injector that comes with the demountable torch. Classified as HF resistant, the alumina injector is made with a sintering process using between 0.2% and 5% silica as a binder. The interaction of the HF in the digest with the alumina injector releases Si, probably as SiF₄,

Table 1 Parameters for microwave digestion of PVC filter

Program step	Power/W	Time/min
1	250	6
2	600	12
3	500	6

and hence, the high Si blank and a long memory between measurements. Replacing the alumina injector with a sapphire injector significantly reduced the baseline intensity (to about 3000 c s^{-1}); however, the memory effect persisted. The source of the memory effect was believed to be the sample droplets deposited on the inner wall of the injector. As the injector was conductively and radiatively heated by the plasma, gaseous SiF_4 was released.

Since the reaction of HF with silica and the release of the gaseous SiF_4 are driven by the acidity of the solution, neutralizing the acid in the digest quenches the reactivity of the HF in the sample matrix and prevents the release of the gaseous SiF_4 . If an alkali or alkaline earth hydroxide is used to neutralize the HF, a large amount of metal ion will be introduced, which defeats the very purpose of the HF digestion (discussed later); therefore a metal-free base is sought. The CFA-C reagent (a proprietary mixture of tertiary amines) was reported effective for neutralizing the acid.⁵ The reagent was not used for this work because the composition of the reagent is unknown and thus the pH of the neutralized sample is not readily predicted. Electronic-grade TMAH is a high-purity strong base that meets the requirement. The baseline intensity of Si was reduced (to about 2000 c s^{-1}) and the memory effect was eliminated after neutralizing the digest with TMAH.

The remaining baseline intensity of about 2000 c s^{-1} , comparable to those reported in the literature,⁴ originates from the mass spectrometer behind the sampler cone since this intensity was observed even without sample nebulization. It has been reported that the signal to background ratio of $^{28}\text{Si}^+$ decreases with the increase of the extraction lens potential.⁶ These observations suggest that the release of contaminants from the extraction lens is responsible for this baseline intensity; therefore, this baseline intensity can be minimized by replacing the extraction lens.⁷ Replacing the extraction lens was not attempted here because of the practical consideration that the accuracy of measuring the silica loading on the filter is not limited by the baseline intensity but by the repeatability of the filter production, which is discussed later.

Fusion versus HF digestion

Silica can be digested by fusion with Na_2CO_3 or by wet ashing using HF. Fusion invariably introduces large amounts of metal ions into the sample matrix that not only contaminate the instrument but also adversely affect its performance; therefore, fusion was rejected as a choice of sample digestion for this work. The HF wet digestion results in a simpler matrix relative to that by fusion; however, the technique is susceptible to a loss of Si as SiF_4 during the digestion,⁸ since HF in combination with a strong acid like HClO_4 is known to quantitatively remove silicon in a solution at high temperatures. On the other hand, SiF_4 is highly soluble in aqueous solution to form fluorosilicic acid, and this property of SiF_4 has been used to scrub the substance in the gas phase.⁹ We considered the digestion of the Silica-on-Filter sample at room temperature in a closed polyethylene bottle. Only HF was used for the digestion since the combination of HF with strong acids destabilizes the SiF_6^{2-} and releases SiF_4 .¹⁰

We determined the presence or the absence of a loss of Si during an HF digest by using four samples each with known amount of Si as described in the procedure section. The analyte found after the digestion was compared to the analyte prepared in the solution to calculate the recovery. Table 2 lists the results of the recovery study. The Si content in the four standards prepared for the digestion is listed in the second column, and the Si determined in the four digests is listed in the third column. If analyte loss occurs during the digestion, less than 100% recovery will be indicated. The obtained recovery was $100.6 \pm 1.4\%$, overlapping the target recovery of 100%. The uncertainty is based on replication at the 95% confidence level

Table 2 Analyte recovery from HF digestion (μg)

ID	Prepared	Found	Recovery (%)
STD1	197.6	199.7	101.1
STD2	197.2	200.4	101.6
STD3	197.4	196.7	99.7
STD4	197.6	197.8	100.1
Average			100.6
U			1.4

(a coverage factor of 3.18). Therefore, no loss of Si is observed under the experimental parameters of the established wet digestion method.

Developing and evaluating the HF digestion technique

The optimum length of time for the HF digestion was determined by digesting 4 filters each with nominal silica loading of $100 \mu\text{g}$. The duration of the digestion was 1 h, 2 h, 19 h, and 20 h, respectively. The Si in the four digests was determined to contain $92.6 \mu\text{g}$, $95.4 \mu\text{g}$, $95.1 \mu\text{g}$, and $95.2 \mu\text{g}$ silica, respectively. The $92.6 \mu\text{g}$ silica found for the filter subjected to 1 h digestion is statistically different at a 95% confidence level relative to the other three values based on the Dixon's Q test, suggesting that the 1 h digestion time is insufficient. There is little difference between the values from a 2 h digestion and a 20 h digestion, suggesting that the digestion is complete after 2 h. Samples are typically digested overnight for 16 h in our laboratory.

The HF digestion method developed here selectively digests the silica on the loaded filter, and the filter substrate is not digested in the process. Whether this method completely digests the silica on the filter was investigated with the procedure described earlier and the results are shown in Table 3. The silica found on the filters ranges from $97.7 \mu\text{g}$ to $103.3 \mu\text{g}$ with a relative standard deviation of about 2.4%. The average of the four filters, $101.1 \mu\text{g}$, is consistent with the nominal $100 \mu\text{g}$ loading of these filters. The relative standard deviations of the four filter samples measured by HR-ICP-MS, 2%, compare favorably to the 2–4% obtainable by isotope dilution HR-ICP-MS.⁴

The Si found in the filter samples after the microwave digestion, listed in the "residual" column in Table 3, and that in the procedure blanks was at or below the instrument detection limit of $0.3 \mu\text{g}$ silica per filter. These results suggest that all silica on the loaded filters was digested before the microwave digestion; therefore, the HF digestion method described here digests the silica on the PVC filters completely. A robust sample digestion method for the Silica-on-Filter reference material was established.

Validating HR-ICP-MS method

At NIST, Certified Reference Materials (CRMs) or SRMs of matrices similar to the sample are used as quality controls to assess systematic errors of the measurement technique.¹¹ SRMs

Table 3 Silica \pm expanded uncertainty on nominal $100 \mu\text{g}$ filter and silica in filter residue

	Silica found/ μg	Residual Si/ μg^a
Filter 1	101.4 ± 2.5	<0.3
Filter 2	103.3 ± 2.6	0.3
Filter 3	97.7 ± 1.7	<0.3
Filter 4	101.9 ± 1.7	<0.3
Blank 1		<0.3
Blank 2		<0.3
Filter average	101.1 ± 2.1	
Filter standard deviation	2.4	

^aThe instrument detection limit is $0.3 \mu\text{g}$ silica on filter.

295x form a novel series of Silica-on-Filter reference materials; other SRMs or CRMs of similar matrix are unavailable as quality controls. Consequently, the validity of the HR-ICP-MS method was assessed by comparing the HR-ICP-MS results to those obtained by ICP-OES, and the HR-ICP-MS results were confirmed by establishing the statistical equivalence of the HR-ICP-MS results and the ICP-OES results.¹¹ Of the three commonly used silicon lines at 212.412 nm, 251.611 nm, and 288.158 nm, the 251.611 nm line was chosen for its low baseline intensity and high sensitivity. Manganese was added to each solution at about 0.1 $\mu\text{g g}^{-1}$ as an internal standard to correct for a drift of the analyte signal during the ICP-OES measurements, and the internal standard was measured at the 257.610 nm line. A detection limit of 8 ng Si g^{-1} was obtained with the plasma viewed at the axial position.

The four filter samples of 100 μg nominal silica loading that had been analyzed by HR-ICP-MS previously (see Table 3) were analyzed again using ICP-OES. The amount of silica found on each filter sample was 102.1 $\mu\text{g} \pm 2.5 \mu\text{g}$, 103.1 $\mu\text{g} \pm 2.5 \mu\text{g}$, 101.4 $\mu\text{g} \pm 2.5 \mu\text{g}$, and 102.3 $\pm 2.7 \mu\text{g}$ for Filter 1, Filter 2, Filter 3, and Filter 4, respectively. Paired *t*-tests performed on the four filters show that the HR-ICP-MS results are statistically identical to those by ICP-OES, confirming the HR-ICP-MS results.

The reproducibility of the externally calibrated HR-ICP-MS method was evaluated with respect to the reproducibility of silica loading of the filters. The reproducibility of the silica loading on filters is determined by the repeatability of depositing a 25 μL aliquot of SRM 1878a slurry onto each filter. Based on the 402 samples of quality control and quality assurance data points from the producer, the relative standard uncertainty for the loading of the 100 μg level filters is 3.7%, which is greater than the 2% relative standard uncertainty of measurements by HR-ICP-MS.¹² The overall uncertainty of the measurement, which combines the loading uncertainty and the measurement uncertainty, is dominated by the loading uncertainty. A more precise analytical technique will not improve the reproducibility of the measured silica loading of the filters and, therefore, is not warranted for the confirmation measurement.

Conclusion

Respirable crystalline silica is an environmental and occupational hazard, and the occupational exposure to the substance is regulated by OSHA. SRMs 295x Silica-on-Filter are being developed to address the interlaboratory comparability issue that handicaps the effective enforcement of the regulation. In contrast to the commonly used techniques for silica determination, the HR-ICP-MS method described here determines the Si on the filter, which indirectly determines the silica loading of

the filter. The method has the precision and accuracy required of the certification analysis. HF is used to digest the filter samples at room temperature to prevent the loss of the analyte, and the Si baseline intensity resulting from the matrix of the digest has been minimized. The new SRMs are scheduled to be completed in early 2003. Production of a series of Crystallite-on-Filter Standard Reference Materials has also been planned.

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