

# Determination of Be in alumina by ICP-OES after Carius tube digestion†

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Standard Reference Material (SRM<sup>®</sup>) 699 Alumina (Reduction Grade) was digested in HCl at 240 °C inside Carius tubes. Beryllium was measured with inductively coupled plasma optical emission spectrometry at the 313.107 nm line and quantified to be  $2.90 \pm 0.24 \mu\text{g g}^{-1}$  by the method of standard addition. The uncertainty of the measurement was evaluated by taking into account the often-neglected contribution from the correlation between the intercept and the slope of the regression curve.

## Introduction

Beryllium is responsible for berylliosis. The element is present as an impurity in smelting grade alumina (SGA) which is used in the commercial production of aluminium. The aluminium industry has been determining Be at various stages of SGA production for the purpose of reducing Be in SGA and eliminating the potential occupational risk of over exposure to Be in the production of aluminium.<sup>1</sup> Validation of the measurements requires a certified reference material (CRM) of alumina with a certified Be value, which is not available. The National Institute of Standards and Technology (NIST) has been asked by the aluminium industry to add a certified value of Be to the existing Standard Reference Material (SRM<sup>®</sup>) 699 Alumina (Reduction Grade).

Alumina is considered to be one of the most refractory ceramic materials. Several publications have been devoted to the digestion of this material<sup>2–7</sup> for trace element analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). Alkali fusion, open beaker digestion with a mixture of phosphoric and sulfuric acids, high-pressure HCl dissolution, and microwave digestion have all been reported; however, no Carius tube digestion of alumina has been found in the literature. The matrices of alkali fusion and open beaker phosphoric–sulfuric acid digestion resulted in poor measurement precision and high limits of detection in the subsequent ICP-OES measurements.<sup>2</sup> High-pressure HCl dissolution resulted in a matrix that was more compatible with ICP-OES analysis, although Be was not measured.<sup>2,3</sup> Microwave digestion of alumina has been extensively studied with various acids and acid mixtures.<sup>4–7</sup> Sulfuric acid was frequently used to achieve the high temperatures required to digest alumina;<sup>4,5</sup> however, the presence of sulfuric acid in the sample matrix was detrimental to the determination of Be (see below). Phosphoric acid decreased nebulization efficiency and suppressed the emission intensity of trace elements.<sup>6</sup>

Alternatively, alumina was digested in an HF, HCl and HNO<sub>3</sub> acid mixture with a multi-stage microwave digestion procedure.<sup>7</sup> The capability of digesting up to 0.2 g of alumina in each vessel precludes the use of microwave methods for this work since the minimum sample size recommended for SRM 699 is 0.5 g.<sup>8</sup> Even if the microwave methods were capable of digesting more sample, the H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> needed in the acid mixture make the subsequent ICP-OES determination of Be very difficult, if not impossible.

The objective of this work is the determination of Be in SRM 699 by using ICP-OES as part of the effort to establish a certified value of Be. Calibration of the measurement is accomplished by the method of standard addition.<sup>9</sup> While it is well known that the slope and the intercept of a regression line are correlated and the covariance term in the uncertainty estimate can be significant, this term has been typically neglected in standard addition analysis. We show that the measurement uncertainty by the method of standard addition has a relatively large covariance component that, if neglected, can result in significant underestimation of the uncertainty.

## Experimental

### Instrument and reagents‡

A PerkinElmer (Shelton, CT, USA) Optima 3300 DV ICP-OES was used. Table 1 lists the measurement parameters. Be and Y solutions were prepared from SRMs 3105a and 3167a Single Element Standards (NIST, Gaithersburg, MD, USA). CRM ST1-5000A Aluminum Disk was purchased from ALCOA (Alcoa Center, PA, USA). Optima grade HCl was obtained from Fisher Scientific (Pittsburgh, PA, USA). Acid concentrations are reported as the volume fraction of the concentrated acid in water.

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† Electronic supplementary information (ESI) available: internal standard adjusted spike concentration and Be emission intensity and definition of terms in eqns 1 and 2. See DOI: 10.1039/b700486a

‡ Certain commercial items 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.

**Table 1** ICP-OES instrument parameters

Rf power/W	1300
Rf frequency/MHz	40
Bandwidth FWHM/nm	<0.01
Plasma flow/L min <sup>-1</sup>	15
Auxiliary flow/L min <sup>-1</sup>	0.5
Nebulizer flow/L min <sup>-1</sup>	0.8
Observation height/mm above load coil	15
Sample uptake rate/mL min <sup>-1</sup>	1.4
Integration time/s	0.100
Read time/s	2.000

## Procedure

Samples of nominally 0.5 g were transferred from each of six different bottles of SRM 699 to Carius tubes. Two samples were taken from bottle 1. One sample each was taken from bottles 2 through 6 and an increasing mass of 10.006 mg L<sup>-1</sup> Be standard solution was added to each tube. Approximately 0.2 g of a solution containing 85 mg L<sup>-1</sup> of Y was added to each tube as an internal standard. A solution containing the same amount of acid as in the Be standard was added to each sample to compensate for the different amounts of acid introduced *via* the addition of the Be standard. Eight g of HCl was added to all tubes before the tubes were sealed. Four blank samples were prepared similarly. Two 0.25 g samples of ST1-5000A as quality controls were treated similarly to the SRM 699 samples with the exception that the 8 g of HCl was added in 2 g increments and allowed to react completely with the sample before the next addition. This procedure permitted the escape of hydrogen gas from each tube before it was sealed. All 13 tubes were placed in steel shells along with 10 g of solid CO<sub>2</sub>, then capped and placed in a laboratory oven where they were heated at 240 °C for 24 hours.

The tubes were allowed to cool to room temperature, and were removed from the steel shells. The neck of each tube was heated with a torch flame until a small hole was formed from the bursting of gas to relieve the pressure. Next, the tubes were scored and fire-opened. The digests were transferred to beakers and evaporated to near dryness. The solutions were then transferred to 30 mL polyethylene bottles and diluted to 30 g with 5% HCl.

The moisture content in SRM 699 was measured (3.17%,  $s = 0.094\%$ ,  $n = 6$ ) with approximately 2 g of sample from each bottle using the procedure described in the Certificate of Analysis.<sup>8</sup> The linearity of the Be calibration curve was verified by measuring solutions containing (0, 0.01, 0.05, 0.1, 0.3, and 1) µg g<sup>-1</sup> Be in 5% HCl before all analytical samples were measured in random order. Be and Y were determined at the 313.107 nm line and the 371.030 nm line, respectively, by using the radial-view mode of the ICP-OES. The measurement uncertainties are reported as 95% confidence intervals.

## Results and discussion

### Carius tube digestion

Efforts were made to digest alumina in HCl since that is more amenable to ICP-OES determination of Be relative to sulfuric or phosphoric acid. Alumina can be digested in HCl at temperatures above 215 °C,<sup>2,3</sup> and the Carius tube digestion

technique can easily achieve these temperatures.<sup>10</sup> Two temperature settings that bracketed the 215 °C to 240 °C found in the literature<sup>2,3</sup> were used in this work since SRM 699 contains about 17.1% of the more refractory  $\alpha$ -alumina crystalline form.<sup>4</sup> The alumina samples were digested at 240 °C, but the digestion was incomplete at 200 °C based on visual inspection.

Clear hexagonal crystals, presumably AlCl<sub>3</sub>, were formed after the digests in Carius tubes were cooled. The solubility of AlCl<sub>3</sub> in water is 45.1 g per 100 g H<sub>2</sub>O. A sample of 0.5 g of alumina yields 1.3 g of AlCl<sub>3</sub>, which should dissolve in 5 g of water contained in the 8 g of concentrated HCl for the digestion. The crystals may have formed as a result of the common ion effect due to the excess HCl in the Carius tube. Unlike the sample preparation for isotope dilution measurements, where the precipitates can be disregarded after the equilibration of the digest, the analyte-to-internal standard ratio in the digest and the AlCl<sub>3</sub> crystals may not be the same. To maintain the integrity of the analyte-to-internal standard ratio for the sample, the crystals cannot be discarded. The crystals were readily dissolved by addition of water to the Carius tubes. Once all had been dissolved, the solution was transferred from the Carius tube into a beaker.

### ICP-OES determination

Beryllium can be measured at 313.107 nm, 313.042 nm, 234.861 nm, and 265.045 nm with Optima 3300 DV ICP-OES. The 234.861 nm line that reportedly gave the most precise results was interfered by the emission of Fe<sup>+</sup> at 234.830 nm.<sup>1,11</sup> We studied the spectra of SRM 699 samples and blanks in the vicinity of the 234.861 nm line and found that the presence of Fe at a mass fraction of 91 µg g<sup>-1</sup> ± 7 µg g<sup>-1</sup> in SRM 699 (≈1.5 µg g<sup>-1</sup> in samples for the measurement) made accurate correction for the interference impossible.<sup>8</sup> No signal from Be in an SRM 699 sample was observed at the 265.045 line as the line is the least sensitive of the four. The 313.042 nm line was located between two peaks, probably from OH molecular bands, making measurements of Be in SRM 699 samples impossible.<sup>11</sup> Fortunately, the 313.107 nm line was adequately strong and free of interferences. The absence of spectral interference from Fe was confirmed by using a 1.5 µg g<sup>-1</sup> Fe solution. The absence of interference from Ti<sup>+</sup>, which has a weak emission line at 313.080 nm, was confirmed by using a 0.1 µg g<sup>-1</sup> Ti solution whose concentration equals that in the measurement samples of SRM 699.<sup>8</sup> The signal-to-noise ratio at the 313.107 nm line was higher with radial-view relative to axial-view, probably as a result of the high Al salt content in the sample. Consequently, all measurements were made with radial-view mode.

The use of HCl rather than sulfuric acid in sample digestion has several advantages. The detection limit (DL) of Be, calculated as three times the standard deviation of 10 replicate measurements of a blank, is an order of magnitude better in 5% HCl (DL = 0.7 ng g<sup>-1</sup>) than in 5% sulfuric acid (DL = 11 ng g<sup>-1</sup>). At about 48 ng g<sup>-1</sup> (calculated from Be mass fraction of 2.90 µg g<sup>-1</sup> in SRM 699, see below), Be mass fraction in the unspiked sample is near the detection limit of the element in 5% sulfuric acid. The improved detection limit of Be in an HCl matrix was a deciding factor for choosing HCl

for sample digestion. In addition, HCl was much easier to evaporate than sulfuric acid; the digests must be evaporated to concentrate the analyte and to reduce the acid content to about 5% to facilitate the ICP-OES measurements.

The linear range of Be optical emission was verified with a calibration curve of Be standards. The correlation coefficient  $r^2$  for the curve equals 0.999993, suggesting that the optical emission of Be at the 313.107 nm line was linear up to the highest point of the curve at 153 000 cps for the 1  $\mu\text{g g}^{-1}$  Be solution. The highest point for the multi-point standard addition curve at 30 000 cps was well within the linear range.

### Mass fraction of Be in SRM 699

In a typical standard addition scheme for an aqueous sample, equal aliquots of the sample are taken. Increasing amounts of analyte spikes are added into each aliquot of the sample for the purpose of calibration by the method of standard addition. Weighing exactly the same amount of SRM 699 into each Carius tube for spiking is extremely difficult, if not impossible, and it is not necessary. The mass of the spiked analyte,  $x$ , and the Be/Y intensity ratio,  $y$ , used to construct the standard addition curve are normalized against the mass of the sample. Consequently, the slope, the intercept, and the  $x$ -intercept of the standard addition curve are not affected by the differences in the amount of SRM 699 in each Carius tube.<sup>9</sup> The regression curve for the standard addition calibration is described by:

$$y = mx + b \quad (1)$$

where  $m$  and  $b$  are the slope and the intercept of the regression curve, respectively. The mass fraction of Be in SRM 699 equals  $b$  divided by  $m$  and it is calculated to be 2.90  $\mu\text{g g}^{-1}$ .

The measurement uncertainty of Be in SRM 699 is derived in accordance with the ISO and NIST guides.<sup>12</sup> The uncertainty due to regression,  $u(c)$ , is calculated by using eqn (2), where  $s_m$ ,  $s_b$ , and  $s_y$ , are standard uncertainties of  $m$ ,  $b$ , and  $y$  estimates, respectively, and  $\bar{x}$  is the average of the  $x$  values. The  $s_{xx}$  term is calculated as  $N - 1$  multiplied by the square of the standard deviation of the  $x$  values.

$$u(c) = \sqrt{c^2 \left(\frac{s_m}{m}\right)^2 + c^2 \left(\frac{s_b}{b}\right)^2 + \frac{2b\bar{x}s_y^2}{m^3 s_{xx}}} \quad (2)$$

Eqn (2) includes variance from the correlation between the slope and the intercept,<sup>13</sup> which is a significant contributor to the overall variance of the regression analysis (see below). The value for each term in eqns (1) and (2) is calculated directly from the LINEST function of a Microsoft EXCEL spreadsheet except  $c$ ,  $s_{xx}$ , and  $\bar{x}$  terms whose calculation has been discussed previously. The uncertainty for Be in SRM 699 is based solely on that due to regression since the uncertainties due to drift, spike calibrant, blank, and internal precision of measurements are small.<sup>9</sup> The expanded uncertainty for Be in SRM 699 equals the standard uncertainty multiplied by a coverage factor of 2. The recommended value and the expanded uncertainty of Be in SRM 699 are 2.90  $\mu\text{g g}^{-1} \pm 0.24 \mu\text{g g}^{-1}$ .

The analyte concentration and the expanded uncertainty of Be in ST1-5000A are 10.33  $\mu\text{g g}^{-1} \pm 0.41 \mu\text{g g}^{-1}$  and 10.58  $\mu\text{g g}^{-1} \pm 0.42 \mu\text{g g}^{-1}$  for Control 1 and Control 2, respectively, calculated with the method described by Christopher *et al.*<sup>9</sup> The performance of the measurements based on the difference between the measured values and the certified value of 10  $\mu\text{g g}^{-1} \pm 4 \mu\text{g g}^{-1}$  Be in ST1-5000A is evaluated by using the method proposed by Linsinger.<sup>14</sup> The measured values of both ST1-5000A samples are found to be not significantly different from the certified value.

To demonstrate the significance of the covariance term in the uncertainty estimate of the regression analysis of this work, the magnitude of the relative uncertainty resulting from slope, intercept, and covariance corresponding to the first, second, and the third terms in eqn (2) is calculated to be 1.5%, 2.9%, and 2.5%, respectively. Note that the uncertainty from the covariance component is larger than that for the slope,  $m$ , and is almost as large as that for the intercept,  $b$ . The combined uncertainty of the three terms is 4.1% relative, which yields an expanded uncertainty of 8.2% ( $k = 2$ ) relative. If the covariance term were omitted, the combined uncertainty of this work would have been 6.4% relative rather the more realistic estimate of 8.2%.

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