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Certification of Beryllium Mass Fraction in SRM 1877 Beryllium Oxide Powder Using High-Performance Inductively Coupled Plasma Optical Emission Spectrometry with Exact Matching

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High-performance inductively coupled plasma optical emission spectrometry (HP-ICP-OES) was used to certify the Be mass fraction in National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1877 Beryllium Oxide Powder. The certified value and expanded uncertainty expressed at a 95% confidence level is (0.3576 ± 0.0024) g/g. To obtain best results, the Be mass fractions, Mn (internal standard) mass fractions, and matrix compositions of the calibration solutions were carefully matched to those of the sample solutions for each individual HP-ICP-OES analysis. This "exact matching" approach was used because experience at NIST has shown that it often affords improved accuracy and precision in HP-ICP-OES analysis. NIST has never published these observations. Due to the toxicity of BeO and the difficulty of containing the very fine powder material, sets of solutions for HP-ICP-OES analysis were prepared by laboratories collaborating with NIST who have the experience and equipment needed to work with the material safely. Each laboratory utilized a unique digestion protocol(s). After preparing the sets of solutions, the collaborating laboratories shipped them to NIST for HP-ICP-OES analysis. NIST provided the collaborating laboratories with solution preparation kits and spreadsheets to help establish traceability of the HP-ICP-OES results to the International System of Units (SI) and to allow exact matching to be accomplished. The agreement observed among the four individual Be mass fraction values determined from the sets of solutions prepared by the collaborating laboratories was 0.074% relative (1*s* of mean). The excellent agreement provides a measure of confidence in the robustness of each of the digestion procedures, as well as in the certified Be mass fraction value. The analytical benefits of using exact matching for this particular certification were investigated. Results show that exactly matching the matrix compositions of the standards to the samples for each HP-ICP-OES analysis was critical to obtaining the excellent agreement observed among the individual Be mass fraction values and also helped to minimize bias and uncertainty in the certified value. Unlike previous NIST studies, exactly matching the Be and Mn mass fractions of the standards to the samples for this particular certification appears to have had little effect on the data.

Beryllium and compounds containing Be are used in the production of high-performance alloys and ceramics that are employed in the aerospace, nuclear, defense, telecommunications, biomedical, fire prevention, automotive, and other industries.[1,2] These chemicals pose a significant health risk for workers in these fields. This is because exposure to beryllium-containing materials through inhalation[3] or possibly dermal contact[4,5] can cause sensitization in susceptible individuals. According to a study by Newman et al.,[6] 30% of sensitized individuals developed chronic beryllium disease (CBD) within an average of 4 years (range: 1−10 years), which corresponded to a conversion rate of 8% per year. CBD is a potentially fatal progressive respiratory disease with no known cure.[7] CBD is characterized by the formation of granulomas which can appear decades after cessation of exposure.[1] Additionally, Be is listed as a carcinogen to humans by the National Toxicology Program[8] and the International Agency for

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Research on Cancer.[9] In 2004, the National Institute for Occupational Safety and Health (NIOSH) estimated that as many or more than 134 000 workers in the United States were potentially exposed to Be under a wide variety of circumstances.[10]

In order to help minimize worker exposure to beryllium, the environments in which they work must be monitored for contamination. Current exposure assessment approaches include determination of the mass concentration of airborne and/or surface-deposited particulate Be within the work environment. For aerosol materials, airborne particles are collected independent of chemical form by drawing air at a known flow rate through a sampler to capture the particles on a substrate. Contamination on surfaces is usually assessed by wiping a known surface area in a regular pattern with even pressure using a substrate (e.g., a water-moistened filter).[11] For both air filters and surface wipes, the filter or wipe and the particulate matter that has been collected are digested after sampling, and the mass of Be in the resulting solution is determined. Graphite furnace atomic absorption spectrophotometry (GFAAS) or inductively coupled plasma optical emission spectrometry (ICP-OES) are most often utilized for this determination, although inductively coupled plasma mass spectrometry (ICPMS) has also been employed in cases where the superior limit of detection is required.[12] Documentary standards that describe sampling and analysis procedures for Be workplace monitoring have been published.[13−16] The current action levels set by the U.S. Department of Energy (DOE) Chronic Beryllium Disease Prevention Program, also known as the DOE Beryllium Rule, are $0.2\ \mu g/m^3$ for air sampling and $0.2\ \mu g/(100\ cm^2)$ for surface sampling.[17]

Effective monitoring for Be contamination in the workplace depends upon the reliability of the analytical methodologies for determining the masses of Be collected on the air filters and surface wipes. Validation of these analytical methodologies has most often involved analysis of reference samples composed of easily digested forms of beryllium. For example, test samples employed for the Beryllium Proficiency Analytical Testing (BePAT) Program administered by the American Industrial Hygiene Association (AIHA, Fairfax, VA) consist of beryllium acetate deposited onto filters.[18] This approach to validation does not provide assurance of the reliability of the analytical methods for quantifying forms of Be that are difficult to digest (e.g., BeO) or having a range of particle sizes.[19] Validation based upon more difficult to digest forms of Be has not been possible, due to the lack of suitable reference materials.[11,19−21]

Working in collaboration with the U.S. Department of Energy, U.S. National Nuclear Security Administration, Brush Wellman, Inc. (Elmore, OH), the Savannah River Site (SRS, Aiken, SC), the Y-12 National Security Complex (Y-12, Oak Ridge, TN), Bureau Veritas North America, Inc., (BVNA, Novi, MI), and the National Institute for Occupational Safety and Health (NIOSH, Morgantown, WV), the National Institute of Standards and Technology (NIST, Gaithersburg, MD) recently issued Standard Reference Material (SRM) 1877 Beryllium Oxide Powder. This SRM consists of high-fired (i.e., calcined at a temperature greater than 1000 °C), crystalline, BeO, with an average primary particle diameter of approximately 200 nm, in aggregated clusters that have been size-separated to pass a 20 mesh screen. The mass fraction of Be is certified. Information values are provided for specific surface area, specific gravity, count median diameter, and mass median diameter. The geometric standard deviations associated with the count and mass median diameters are also given to help define the log−normal particle size distribution. Because BeO is very difficult to dissolve, SRM 1877 provides a means for validation of analytical methodologies used for workplace Be contamination monitoring, including the digestion of submicrometer size refractory forms of beryllium.[11] It is also expected to be used for toxicological research and to prepare test samples for the BePAT Program. The focus of this paper is the certification of the Be mass fraction in SRM 1877.

The Be mass fraction in SRM 1877 Beryllium Oxide Powder was certified using a methodology that we refer to as high-performance (HP)-ICP-OES. This methodology was developed at NIST nearly a decade ago and has been described in detail in several previous publications.[22−24] HP-ICP-OES has become one of the main techniques used at NIST for certification of chemical SRMs. Relative expanded uncertainties, expressed as 95% confidence intervals, are typically on the order of 0.1%. HP-ICP-OES is used routinely for the certification of elemental mass fraction in the 3100 series of elemental standard solution SRMs[22,25] and has also been used in other NIST measurements.[26−29] Measurements

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involving ICP-OES procedures that are similar to the high-performance protocol have been reported by other laboratories.[30−34]

It is important to emphasize that for the certification of Be mass fraction in SRM 1877, HP-ICP-OES was modified somewhat from the way it has been described previously. When HP-ICP-OES was first developed,[22,24] it was assumed that ICP-OES would be sufficiently immune to matrix effects and small variations in analyte and internal standard element concentrations to obviate any need for careful matching of standards to samples. Approximate matching was thought to be adequate. However, we have discovered through experience that this is not necessarily the case. For many combinations of analyte and internal standard, HP-ICP-OES precision and accuracy can be improved by carefully matching the matrix characteristics (e.g., acid fractions) and analyte and internal standard element concentrations of the standards to the samples. On the basis of these observations, this "exact matching" approach was employed here. This is the first time that NIST has published the implementation of exact matching with HP-ICP-OES. An assessment of the effectiveness of exact matching for this particular certification exercise is reported in this paper.

Other researchers have employed this sort of "exact matching" with ICP-OES methodologies that are similar to the HP-ICP-OES protocol. Merson and Evans[33] determined minor elements in steel with relative expanded uncertainties ($k = 2$) on the order of 1% by matching the analyte concentrations to within 5% relative and matrix Fe concentrations to within 3% relative between samples and calibration standards. They reported that matching the matrix Fe concentrations to better than 3% relative would likely be unprofitable, because the effect of a 3% change in the Fe concentration on the ratio of the analyte intensity to the internal standard element intensity was observed to be on the order of the 0.1% measurement precision for that ratio. Simpson, et al.,[34] applied the same approach to the determination of Ca in human serum, obtaining a relative expanded uncertainty ($k = 2$) of 1.2%.

More recently, Rabb and Olesik[32] investigated the implementation of HP-ICP-OES for high-precision, high-accuracy analyses of samples with complex matrixes. In attempts to mitigate matrix effects, they coupled the use of matrix matching, standard addition, and the common analyte internal standard (CAIS) technique[35−37] with HP-ICP-OES. As part of their studies, they found that even a small amount of an element that is present in samples but absent in calibration standards can induce an unacceptable bias in the analyte concentration determined with the methodology. Specifically, when considering the determination of Cu using Mn as the internal standard, they found that mass fractions of Zn as small as 25 μg/g resulted in a 0.56% change in the Cu/Mn intensity ratio. Although this matrix effect may seem small, it would induce a bias in the determined Cu concentration of approximately 0.5%, far exceeding the typical 0.1% relative expanded uncertainty associated with HP-ICP-OES. The need for careful matrix matching in this case is clear. The findings of Rabb and Olesik are consistent with our experience using HP-ICP-OES for high-precision, high-accuracy analyses.

For the certification of the Be mass fraction in SRM 1877, the HP-ICP-OES analyses were performed by NIST, but the preparations of the solutions for analysis were performed by three of the laboratories collaborating with NIST. This is the first time that an SRM has been certified based upon NIST analyses of candidate SRM samples digested by collaborating laboratories. To work safely with fine BeO powder, it is appropriate to have laboratory space and equipment demarcated for working with Be-containing materials. Contamination monitoring systems and specialized Be safety training for personnel are essential. This particular powder material is easily dispersed by ambient air currents and static charge. Opening and closing the SRM bottle can result in dispersal through generated air currents. The collaborating laboratories have the demarcated laboratory space and equipment, monitoring systems, and expertise needed to handle the material safely. This procedural model may be useful for future SRM certification exercises and may also be implemented by other reference material producers.

EXPERIMENTAL SECTION

Each of the three collaborating laboratories performed its own digestion protocol(s). Specifically, SRS and BVNA each prepared one set of solutions utilizing a digestion protocol based upon sulfuric acid and ammonium sulfate. Y-12 prepared two sets of solutions, one based upon a sulfuric acid/nitric acid method, and the other based upon the use of ammonium bifluoride. After performing the digestions, each collaborating laboratory shipped their solutions to NIST for HP-ICP-OES analysis. Although the two sulfuric acid/ammonium sulfate protocols are similar in principle, each is unique in application. Consequently, the four sets of solutions represent four independent digestion protocols performed by three different laboratories. Statistical agreement among the four resulting Be mass fraction values provides confidence in the robustness of the digestion protocols and in the certified value for SRM 1877.

A certified value assigned to a NIST SRM must have demonstrable traceability to the International System of Units (SI).[38] In order to help ensure the SI-traceability of the certified Be mass fraction in SRM 1877, NIST provided the collaborating laboratories with solution preparation kits and spreadsheets. Each kit included chemicals for use during the solution preparations, materials for shipping the solutions to NIST, and test masses to validate the

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analytical balances used by the laboratories. Each spreadsheet contained instructions for performing the preparations according to NIST protocol [not the digestion protocol(s), but other necessary details, as explained below] and provided a means for recording data and transferring it to NIST. Provision of the solution preparation kits and spreadsheets enabled NIST to maintain a sufficient level of oversight regarding the preparations of the solutions to ensure the validity of the certified Be mass fraction value assigned to the SRM.

Solution Preparation Kits. A separate kit was provided for each set of solutions to be prepared, meaning that Y-12 received two kits, whereas SRS and BVNA each received one. Each kit included four bottles of the candidate SRM 1877 material selected from the stock of packaged bottles by stratified random sampling, four nominally 72 mg pieces of high-purity Be metal assayed by NIST (assay mass fraction = 0.9946 ± 0.0014, with the uncertainty expressed at a level of confidence of 95%) for ICP-OES calibration, Mn internal standard stock solution, 2% volume fraction HNO_3 for making dilutions, the materials needed to ship the digested solutions to NIST, and two Au test masses (nominal masses of 250 mg and 750 mg) to validate the analytical balance used. In this way, each collaborating laboratory was equipped to prepare a nearly complete set of solutions for an HP-ICP-OES analysis. The only solution not provided by each collaborating laboratory was a quality control sample. Prior to running a set of solutions on the ICP-OES instrument, NIST only needed to prepare such a quality control sample and make final dilutions of the solutions received from the collaborating laboratory.

A key part of assuring SI-traceability of the HP-ICP-OES results involved the confirmation of the accuracy of each analytical balance used by a collaborating laboratory. The Au test masses were included in the solution preparation kits for this purpose. Before being sent to the collaborating laboratories, each test mass was cleaned by sonication in anhydrous methanol for 30 min and air-dried on a class 100 clean bench. The mass of each test mass was measured on a five-place balance, the accuracy of which had just been checked using NIST mass standards traceable to the SI. Each Au test mass was packaged in a separate clean glass vial for inclusion in the solution preparation kits. Each collaborating laboratory was asked to measure and report to NIST the masses of the two test masses received using the analytical balance to be used for the solution preparations. The collaborating laboratories then returned the Au test masses to NIST, where the masses were measured again to confirm that no changes had occurred.

At this point, it should be stated that accurate HP-ICP-OES analysis does not strictly require that the measurements made with the analytical balance used for solution preparation are *accurate*. It is sufficient that the response of the balance is *linear with an intercept near zero*, so long as the same balance is used to weigh both the calibration material and the unknown sample material. The deleterious effects of any multiplicative bias in the balance measurements on the HP-ICP-OES results are compensated through the ICP-OES calibration.

Solution Preparation Spreadsheets. The spreadsheet supplied to each collaborating laboratory contained instructions for the preparations of the solutions and shipment of those solutions to NIST, as well as cells for entering mass data needed to complete the HP-ICP-OES analyses. After the solutions had been prepared and shipped, each collaborating laboratory returned its completed spreadsheet to NIST.

Each spreadsheet included cells for entering the masses of Be metal, BeO, and internal standard stock solution added to the digestion vessels, as well as the masses of the digested solutions after dilution with the NIST-supplied diluent. It also included cells for recording the masses of the NIST-supplied shipping bottles containing the solutions just prior to shipment to NIST. The masses of the bottles upon receipt at NIST were checked as a means of detecting possible loss of solution during shipping. Additionally, each spreadsheet included cells for entering the masses of the Au test masses.

As directed by each spreadsheet, the nominal mass of BeO to be digested in each digestion vessel was 200 mg. This mass value was selected because it was small enough to ensure routine and complete digestion with each of the digestion protocols employed by the collaborating laboratories but large enough to minimize the effects of uncertainty in the analytical balance measurements on the HP-ICP-OES results. The nominal mass of Be metal calibration material to be digested in each digestion vessel was 72.4 mg. This mass value was selected so that the nominal masses of Be in the digested BeO and Be metal solutions would be equivalent. To accomplish the first step in exact matching, the target mass of internal standard stock solution to be added to a given digestion vessel was calculated based upon the actual, rather than the nominal, mass of Be metal or BeO added to that vessel. Note that the spreadsheet did not specify the digestion protocol(s) to be employed by the collaborating laboratories, giving each laboratory the freedom to use its own protocol(s).

Digestion Protocols. The specific digestion procedures employed by the three collaborating laboratories are described in the following subsections. The BeO was not dried prior to use.

BVNA. Beryllium metal, BeO, and internal standard stock solution were gravimetrically added to 250 mL Pyrex beakers. One gram of $(NH_4)_2SO_4$ (Mallinckrodt, reagent grade) was added to each vessel, followed by 7 mL of concentrated H_2SO_4 (J.T. Baker, Instra-Analyzed) and 5 mL of deionized water. The vessels were covered with Pyrex watch glasses and placed on a hotplate with a surface temperature of approximately 140 °C. The solutions were allowed to reflux until the more refractory solid component, BeO, had completely dissolved. The vessels were then removed from the hotplate and allowed to cool to room temperature. The digested solutions were quantitatively transferred to the NIST-supplied shipping bottles, diluted, and weighed. Strictly, HP-ICP-OES does not require the *quantitative* transfer, unless exact matching is being used. This is because the ratio of the mass fractions of the analyte to internal standard element in each digested solution is independent of the transfer. Two blanks were prepared in exactly the same way, except that no Be or BeO was added to the Pyrex beakers.

SRS. Two different procedures were used to digest the Be metal and the BeO. A consequence was that the matrix of the Be metal calibration solutions differed from that of the BeO solutions. Instead of preparing two identical blanks, SRS included one blank solution for each of the two digestion procedures.

For the Be metal, each portion of metal and the appropriate mass of internal standard stock solution were weighed into a separate polypropylene volumetric flask having a capacity of 50 mL. Five milliliters of concentrated HCl (Fisher, Optima grade) was added to each flask by drop over a period of 20 min. The reaction was allowed to continue for 2 h or until no evidence of reaction or solid pieces of Be were visible. The digested solutions were then quantitatively transferred, diluted, and weighed. A blank was prepared the same way, except that no Be or BeO was added to the flask.

For the BeO digestions, 0.5 g portions of $(NH_4)_2SO_4$ (Aldrich Chemical, ReagentPlus, 99.99+%) were weighed into separate 250 mL Pyrex Erlenmeyer flasks with screw cap closures. A Teflon-coated magnetic stirring bar was placed inside each flask. The appropriate masses of BeO and internal standard stock solution were weighed and added to each flask. Because the balance was not inside the hood, safely weighing a portion of BeO for addition to a given flask required an iterative process. Beryllium oxide was added to a separate tared bottle inside the hood, the bottle was capped and weighed on the balance, more BeO was added to the bottle inside the hood, the bottle was again capped and weighed, and so forth, until the appropriate mass of BeO had been added to the bottle. The BeO was then quantitatively transferred to the flask. Addition of the internal standard stock solution to the flask also required weighing the solution first into a separate bottle and then performing a quantitative transfer, because the flask containing the BeO could not be removed from the hood. Deionized water was utilized to assist the quantitative transfers.

After addition of the BeO and internal standard stock solution, 5 mL of concentrated H_2SO_4 (Fisher, Optima grade) was carefully added to each flask, resulting in a total volume of solution of approximately 150 mL. The Erlenmeyer flasks were stirred and heated at a medium temperature on a stirring hotplate until the volume of solution in each flask had been reduced to approximately 15 mL. The stirring rate and temperature were reduced and heating continued until the solutions evolved white fumes. Continued heating produced clear solutions as the volumes approached 10 mL. When the volumes had been reduced to approximately 5 mL, the flasks were removed from the hotplate and allowed to cool to room temperature. Ten milliliters of deionized water were added to each flask, by drop at first, and the solutions were again allowed to cool to room temperature. The digested solutions were quantitatively transferred, diluted, and weighed. A blank was prepared using the same protocol, but without the addition of Be or BeO.

Y-12 No. 1. Beryllium metal, BeO, and internal standard stock solution were gravimetrically added to 50 mL polypropylene digestion vials. Three milliliters of concentrated H_2SO_4 (J.T. Baker, Instra-Analyzed) were added to each vial, followed by 25 mL of 2% volume fraction HNO_3 (J.T. Baker, Ultrex II, diluted with deionized water). The vials were heated in a hotblock at 98 °C for 7 h, followed by sonication for 1 h. Two milliliters of concentrated H_2SO_4 and 25 mL of 10% volume fraction HNO_3 were added to each vial, and the vials were again sonicated for 1 h. The digested solutions were quantitatively transferred, diluted, and weighed. Two blanks were prepared in exactly the same way, except that no Be or BeO was added to the digestion vials.

Y-12 No. 2. Beryllium metal, BeO, and internal standard stock solution were gravimetrically added to polypropylene digestion vials. Twenty-five milliliters of 2% mass fraction NH_4HF_2 (J.T. Baker, reagent grade) in 10% volume fraction HNO_3 were added to each vial, and the vials were heated in a hotblock at 98 °C for 2 h. The digested solutions were quantitatively transferred, diluted, and weighed. Once again, two blanks were prepared using the same protocol, but without the addition of either Be or BeO.

Final Solution Preparations Performed at NIST. The first step in performing exact matching was accomplished through the use of the solution preparation spreadsheets sent to the collaborating laboratories. These spreadsheets calculated the target mass of internal standard stock solution to add to each digestion vessel on the basis of the actual mass of Be metal or BeO, rather than on the nominal mass. In this way, the ratios of Be mass to Mn mass among the solutions within a given solution set were closely matched. For the four sets of solutions, the average relative standard deviation (RSD) of the Be/Mn mass ratios was approximately 1%.

The remaining step in performing exact matching was undertaken at NIST prior to HP-ICP-OES analysis. The goal of this step was to match the Be mass fractions and the matrix compositions of the solutions within a given set. This was accomplished by diluting the solutions as received at NIST while adjusting the dilution factors for the actual masses of Be present in each solution. For the four sets of solutions, the average RSD of the Be mass fractions after these dilutions was approximately 0.006%.

The diluent used for the BVNA, Y-12 no. 1, and Y-12 no. 2 sets was 2% volume fraction HNO_3 (Fisher Scientific, trace metal grade, diluted with deionized water). The diluent used for the SRS set was 2% volume fraction H_2SO_4 (Fisher Scientific, trace metal grade, diluted with deionized water). The dilution factors employed with the SRS set were much larger than those applied with the other three solution sets. The SRS solutions were diluted as much as possible while still maintaining ICP-OES signal intensities that were sufficiently strong to avoid significant degradations in precision. As mentioned above, the solution set produced by SRS included calibration and sample solutions that were digested using different reactants. The large dilutions with 2% volume fraction H_2SO_4 enabled excellent matrix matching. Dilutions with H_2SO_4 rather than HNO_3 were chosen because some of the solutions as received at NIST contained significant amounts of H_2SO_4 and because H_2SO_4 causes more severe matrix effects than HNO_3. Estimates of the compositions of the final matrixes of the four sets of solutions are presented in Table 1, showing the very close matrix matching achieved.

Preparations of Control Solutions at NIST. Control solutions were prepared from SRM 3105a Beryllium Standard Solution, lot no. 892707, which has a certified Be mass fraction and expanded uncertainty expressed at a level of confidence of 95% of (10.83 ± 0.07) mg/g. The control solutions for the analyses of the SRS and Y-12 no. 2 sets were prepared by diluting appropriate masses of SRM 3105a with 2% volume fraction H_2SO_4 and 2% volume fraction HNO_3, respectively. However, preparation of matrix-matched control samples for the analyses of the BVNA and Y-12 no. 1 solution sets required a special approach. This

Table 1. Estimates of the Matrix Compositions, after Final Preparations at NIST, of the Solutions Comprising the (a) SRS, (b) BVNA, (c) Y-12 No. 1, and (d) Y-12 No. 2 Solution Sets

(a) SRS

solution type	H_2SO_4 (v/v)	$(NH_4)_2SO_4$ (m/m)	HNO_3 (v/v)	HCl (v/v)
calibration	2.0%		0.0019%	0.016%
SRM 1877	2.0%	0.0015%	0.0024%	
control	2.0%		0.0039%	

(b) BVNA

solution type	H_2SO_4 (v/v)	$(NH_4)_2SO_4$ (m/m)	HNO_3 (v/v)
calibration	0.21%	0.031%	2.0%
SRM 1877	0.21%	0.031%	2.0%
control	0.21%	0.031%	2.0%

(c) Y-12 No. 1

solution type	H_2SO_4 (v/v)	HNO_3 (v/v)
calibration	0.16%	2.1%
SRM 1877	0.16%	2.1%
control	0.14%	2.1%

(d) Y-12 No. 2

solution type	NH_4HF_2 (m/m)	HNO3 (v/v)
calibration	0.023−0.027%	2.1%
SRM 1877	0.024−0.029%	2.1%
control		2.0%

is because the solutions were not diluted with the NIST-supplied 2% volume fraction HNO_3 prior to shipment to NIST as much as was anticipated. To meet this challenge, the control samples for both the BVNA and Y-12 no. 1 analyses were prepared by spiking the blanks provided by the collaborating laboratories gravimetrically with SRM 3105a. As indicated in Table 1, the matrix matching of the control solution to the other solutions within each of the four sets was excellent.

HP-ICP-OES Analyses. Each set of solutions prepared by a collaborating laboratory was used to perform a separate HP-ICP-OES determination of the Be mass fraction in SRM 1877. The analyses were performed as described in detail in previous publications,[22−24,26] except that exact matching was employed. The HP-ICP-OES analyses were performed using an Optima 3300 DV instrument (Perkin-Elmer, Shelton, CT). Instrumental details and settings are presented in Table 2.

For each HP-ICP-OES analysis, the various solutions comprising a given set and two preparations of the control sample were run five times in a randomized complete block sequence, and the Be and Mn emission intensities were recorded. The Be/Mn intensity ratios were calculated and corrected for drift,[23] and the blank intensities were subtracted. The Be mass fractions in SRM 1877 and control SRM 3105a were calculated from the drift-corrected, blank-subtracted data. A full uncertainty budget accounting for all significant components of uncertainty was calculated in accordance with the statistical principles outlined in the ISO Guide to the Expression of Uncertainty in Measurement (GUM)[39] and NIST Technical Note 1297.[40]

Table 2. ICP-OES Instrument Details

parameter	setting
plasma Ar flow rate	15 L/min
auxiliary Ar flow rate	0.5 L/min
nebulizer Ar flow rate	0.8 L/min
rf power	1300 W
viewing	axial
sample uptake	1.5 mL/min
nebulizer	cross-flow
spray chamber (material)	Scott (ryton)
analyte wavelength	Be (I) 265.045 nm
internal standard wavelength	Mn (I) 279.482 nm
background correction	two-point interpolation
on-chip integration time	0.01 s
total read time	5 s

Evaluation of Moisture Behavior. The Be mass fraction in SRM 1877 was certified based upon analysis of samples of the material taken directly from the packaged bottles, without drying. This approach was taken because BeO is not appreciably hygroscopic. Although it contains a small amount of moisture, the moisture content is unlikely to change significantly under normal laboratory conditions, even with long-term storage. However, to ensure the validity of the certified value in different climates and over long periods of storage and use, it was necessary to include in the evaluation of the uncertainty of the certified value a component of uncertainty to account for possible changes in moisture content. Incorporation of such an uncertainty component required an evaluation of the amount of moisture mass that the BeO material might potentially gain or lose under different environmental conditions.

The moisture behavior of the material was evaluated at NIOSH according to NIST specifications. Triplicate 1 g samples from each of two SRM 1877 bottles were weighed into tared borosilicate glass scintillation vials. Three additional vials containing no BeO were used as blanks. The samples and blanks were dried in an oven at 110 °C to constant mass and then allowed to regain moisture while sitting open inside a laboratory hood. The samples and blanks were again dried in an oven at 110 °C to constant mass, and then allowed to regain moisture in the hood to constant mass. The moisture gain was followed for several days to ensure that constant mass had indeed been attained. The ambient laboratory temperature and relative humidity (RH) were recorded throughout this procedure.

RESULTS AND DISCUSSION

Gold Test Mass Data. The mass values for the Au test masses measured by NIST and the collaborating laboratories are given in Table 3. Comparison of the values in columns 3 and 4 indicates that no statistically significant changes in the masses of the Au pieces between the time of shipment from NIST and the time of return to NIST can be detected at the $P = 0.05$ significance level. This implies that the collaborating laboratories handled the test masses carefully and avoided compromising their metrological integrity.

As shown in the last column of Table 3, the analytical balance used by one of the collaborating laboratories (identity protected)

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(39) *Guide to the Expression of Uncertainty in Measurement*, 1st ed.; International Organization for Standardization (ISO): Geneva, Switzerland, 1993.

(40) 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 online at http://physics.nist.gov/Pubs/guidelines/TN1297/tn-1297s.pdf).

Table 3. Results of Mass Measurements Performed on the Au Test Masses by the Collaborating Laboratories (Identities Protected) and by NIST before and after Shipment to the Collaborating Laboratories (All Uncertainties Are 95% Confidence Intervals)

collaborating laboratory (CL)	Au wire	NIST value before sending to CL, g	NIST value after sending to CL, g	mean NIST value, g	value measured by CL, g	agreement?[a]
A	small	0.24768 ± 0.00002	0.24768 ± 0.00002	0.24768 ± 0.00001	0.24782 ± 0.00002	no
	large	0.73815 ± 0.00002	0.73816 ± 0.00002	0.73815 ± 0.00001	0.73834 ± 0.00002	no
B	small	0.25454 ± 0.00002	0.25451 ± 0.00002	0.25452 ± 0.00001	0.2546 ± 0.0002	yes
	large	0.82501 ± 0.00002	0.82499 ± 0.00002	0.82500 ± 0.00001	0.8250 ± 0.0002	yes
C	small	0.25452 ± 0.00002	0.25455 ± 0.00002	0.25454 ± 0.00001	0.2545 ± 0.0002	yes
	large	0.70670 ± 0.00002	0.70668 ± 0.00002	0.70669 ± 0.00001	0.7066 ± 0.0002	yes

[a] Refers to whether or not the interval defined by the mass measured by the CL and the associated uncertainty encompasses the average NIST value. Lack of agreement for results from laboratory A indicates that the balance of this CL was slightly out of calibration.

returned mass values for the test pieces that were statistically greater than those measured by NIST at the $P = 0.05$ level of significance. This implies that this particular balance was slightly out of calibration. The mean mass values for the smaller and larger test masses found by the collaborating laboratory were 0.057% and 0.025%, respectively, greater than the corresponding mean values measured by NIST (0.24768 and 0.73815 g, respectively). Assuming that the balance response is linear with true mass and that the mean NIST values represent true values, these data can be used to estimate the relative biases in the mass measurements made by the collaborating laboratory for the Be metal and BeO materials. The equation relating relative measurement bias expressed as a percentage to true mass is the equation of the line defined by the two points, (0.24768 g, 0.057%) and (0.73815 g, 0.025%), or relative bias $= (-0.065\%/\text{g})(\text{true mass}) + 0.073\%$. Therefore, the relative biases are estimated to be 0.068% and 0.060% for the nominal 72.4 mg Be metal and 200 mg BeO weighings, respectively. The similarity of the anticipated relative biases mitigates to the point of insignificance the effect of the balance miscalibration on the HP-ICP-OES analysis performed using the solution set prepared by this particular collaborating laboratory. Therefore, no corrections were made for this miscalibration.

HP-ICP-OES. The four values of the Be mass fraction in SRM 1877 determined using HP-ICP-OES analysis of the solution sets provided by the collaborating laboratories are compared graphically in Figure 1. The error bars represent expanded uncertainties at a level of confidence of 95% calculated by taking into account all known or suspected components of uncertainty. Uncertainty components included those associated with the assay value of the high-purity Be metal used for calibration, measurement replication for the calibration and SRM 1877 solutions, and mass measurements performed on the analytical balance. These uncertainties were calculated for the purpose of this graphical comparison and were not used in the evaluation of the uncertainty of the certified Be mass fraction in SRM 1877. The graph in Figure 1 shows clearly that all four Be mass fraction values are in statistical agreement at the 95% confidence level. This provides substantial assurance of the robustness of each of the four digestion protocols and confidence in the certified Be mass fraction in SRM 1877.

Moisture Behavior. The mass losses of the BeO material observed when the six vials of material were dried to constant mass ranged from 0.13% to 0.34% and averaged 0.24%. Upon equilibration with ambient atmosphere after the second heating cycle, these samples actually gained more mass than had been lost. The final masses of the samples were greater than their masses when taken out of the SRM 1877 bottles by values ranging from 0.04% to 0.14% and averaging 0.07%. Through the course of these experiments, the laboratory temperature was 19.5 ± 0.4 °C (1*s*). The more pertinent parameter is the RH, which ranged from 12.3% to 41.1% and averaged 27.7%. The RH averaged 35.3% during the final weighings after the second heating cycle when the material was in equilibrium with atmospheric humidity. The RH values during these experiments were generally low, because the studies were conducted in Morgantown, WV, in late autumn, when atmospheric conditions tend to be drier.

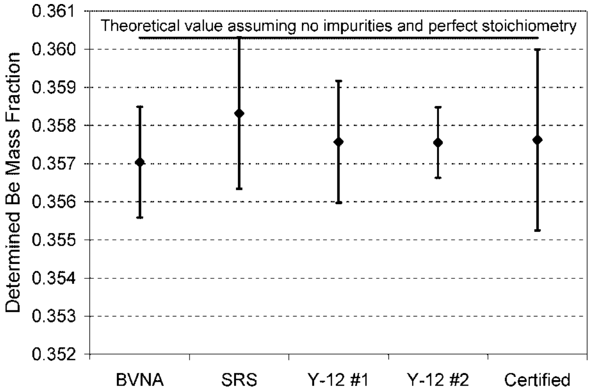
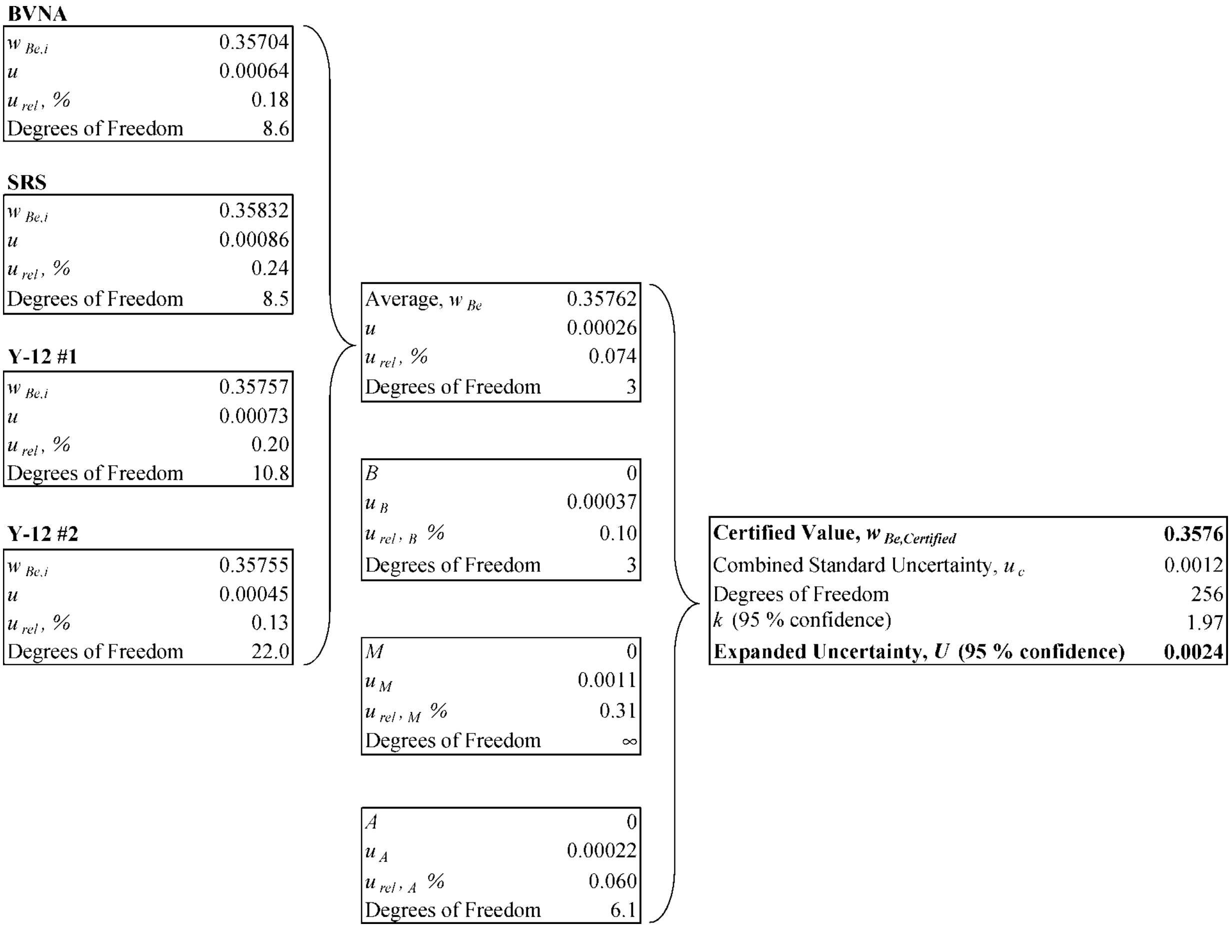


Figure 1. Graphical comparison of the results for the HP-ICP-OES analyses of the four solution sets provided by the collaborating laboratories, the certified value for SRM 1877, and the theoretical value calculated assuming no impurities or moisture and perfect BeO stoichiometry (error bars are 95% confidence intervals).

Calculation of the Certified Be Mass Fraction and Estimation of Uncertainty. The calculation of the certified value for the Be mass fraction in SRM 1877 and the evaluation of the uncertainty associated with the certified value are best understood by considering the following analytical equation:

$$w_{\text{Be,certified}} = \frac{\sum_{i=1}^{4} w_{\text{Be},i}}{4} + B + M + A \qquad (1)$$

In this equation, $w_{\text{Be,certified}}$ is the certified value for the Be mass fraction in SRM 1877, $w_{\text{Be},i}$ are the Be mass fraction values determined from the HP-ICP-OES analyses of the i solution sets prepared by the collaborating laboratories, and B, M, and A are terms employed to account for components of uncertainty associated with bias in the certified value, the effect of changes



BVNA

$w_{Be,i}$	0.35704
u	0.00064
u_{rel}, %	0.18
Degrees of Freedom	8.6

SRS

$w_{Be,i}$	0.35832
u	0.00086
u_{rel}, %	0.24
Degrees of Freedom	8.5

Y-12 #1

$w_{Be,i}$	0.35757
u	0.00073
u_{rel}, %	0.20
Degrees of Freedom	10.8

Y-12 #2

$w_{Be,i}$	0.35755
u	0.00045
u_{rel}, %	0.13
Degrees of Freedom	22.0

Average, w_{Be}	0.35762
u	0.00026
u_{rel}, %	0.074
Degrees of Freedom	3

B	0
u_B	0.00037
$u_{rel, B}$ %	0.10
Degrees of Freedom	3

M	0
u_M	0.0011
$u_{rel, M}$ %	0.31
Degrees of Freedom	∞

A	0
u_A	0.00022
$u_{rel, A}$ %	0.060
Degrees of Freedom	6.1

Certified Value, $w_{Be,Certified}$	**0.3576**
Combined Standard Uncertainty, u_c	0.0012
Degrees of Freedom	256
k (95 % confidence)	1.97
Expanded Uncertainty, U (95 % confidence)	**0.0024**

Figure 2. Graphical representation of the calculation of the certified Be mass fraction value and associated uncertainty for SRM 1877.

in moisture content of the material in different climates and over long-term storage and use, and the assay value of the Be metal calibration material, respectively. These three terms are taken to have mean values of zero with uncertainty. By means of the averaging of the $w_{\mathrm{Be},i}$ values, the experimental design represented by eq 1 inherently accounts for all components of random uncertainty associated with operations that were replicated, such as balance measurements, solution preparations, and ICP-OES signal intensity measurements.

The calculations of the certified Be mass fraction, $w_{\mathrm{Be,certified}}$, and the associated expanded uncertainty at a level of confidence of 95%, U, for SRM 1877 are summarized graphically in Figure 2. The means, the standard uncertainties, u, the relative standard uncertainties, u_{rel}, and the effective degrees of freedom associated with the various terms in eq 1 are given. The statistical parameters for the four $w_{\mathrm{Be},i}$ values in the left column of boxes are given for information only.

Referring to the second box in the middle column of Figure 2, the uncertainty component associated with bias in $w_{\mathrm{Be,certified}}$ was evaluated using the type B on bias (BOB) statistical method.[41] This method provides a meaningful way, consistent with the framework and approach of the ISO GUM,[39] to incorporate a component of uncertainty to account for bias in the combination of multiple results (the individual $w_{\mathrm{Be},i}$ values, in this case) when the number of results is small and it is not assumed that those results represent a random sample from a population of results that is centered at the true value of the measurand. As implied by the name, the BOB method evaluates this uncertainty component using a type B approach, in the vocabulary of the GUM.[39] With the use of the BOB method, a suitable probability distribution is used to quantify the component of uncertainty that is to account for bias. For the case at hand, bias was modeled as a uniform probability distribution centered at zero (i.e., $B = 0$) with width equal to the difference between the maximum and minimum values of $w_{\mathrm{Be},i}$. A uniform distribution was employed, because there is no reason to consider a particular value of B as being more likely than any other value within the limits of the distribution. The standard uncertainty, u_B, was found through normalization by dividing the half-width by the square root of three. Calculation of the effective degrees of freedom associated with u_B according to eq 20 in ref 41 resulted in a value less than 1. Such small degrees of freedom are caused by the small spread of mean $w_{\mathrm{Be},i}$ values relative to the uncertainties associated with those values (see Figure 1). In such cases, ref 41 suggests that the effective degrees of freedom not be allowed to drop below three. Therefore, the degrees of freedom associated with u_B in Figure 2 are set to three.

The third box in the middle column of Figure 2 concerns the effects of changes in the moisture content of SRM 1877 on the true Be mass fraction. Differences in moisture content are possible

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(41) Levenson, M. S.; Banks, D. L.; Eberhardt, K. R.; Gill, L. M.; Guthrie, W. F.; Liu, H. K.; Vangel, M. G.; Yen, J. H.; Zhang, N. F. *J. Res. Natl. Inst. Stand. Technol.* **2000**, *105*, 571–579.

when the material is stored and used in different climates and over long periods of time. A given percentage change in the mass of the material due to a change in moisture content would translate into an inverse change in true Be mass fraction by the same percentage. As described earlier, a study was performed to characterize the moisture behavior of the BeO material. The largest mass loss or gain was observed to be 0.34%. Potential changes in the true Be mass fraction caused by such changes in moisture content were conservatively modeled as a triangular probability distribution centered at zero (i.e., $M = 0$) with limits of ±0.75% of the average of the $w_{\mathrm{Be},i}$ values. A triangular distribution was employed, because smaller changes in moisture content are considered more likely than larger changes. The standard uncertainty, u_M, was calculated through normalization by dividing the half-width by the square root of six.

The final box in the middle column of Figure 2 is concerned with the effect of uncertainty in the NIST-assigned assay value for the high-purity Be metal used for HP-ICP-OES calibration on the value of $w_{\mathrm{Be,certified}}$. Because the same lot of high-purity Be metal was used to prepare calibration solutions for all four HP-ICP-OES analyses, this component of uncertainty is unaccounted for by the replication inherent within the experimental design. The effect of uncertainty in the assay value on the value of $w_{\mathrm{Be,certified}}$ was assumed to have a mean of zero (i.e., $A = 0$). The relative standard uncertainty, $u_{\mathrm{rel},A}$, and the effective degrees of freedom were taken to be numerically equivalent to the corresponding statistics associated with the assay value.

It is useful to compare the certified Be mass fraction value to the theoretical value calculated by assuming perfect BeO stoichiometry and no impurities or moisture. Given the atomic masses of Be and O, the theoretical value is 0.3603. The certified value is 99.25% of the theoretical value, and the interval defined by the certified value and expanded uncertainty does not overlap the theoretical value (see Figure 1). These results are reasonable, given the degrees of nonstoichiometry and contamination, including silicon[42] and moisture, which are known or anticipated for this particular BeO material.

The certified value for the Be mass fraction in SRM 1877 is based upon analyses using multiple preparations of nominally 200 mg samples of the BeO material. Therefore, the uncertainty associated with the certified value inherently accounts for heterogeneity in the Be content at the 200 mg sample mass. The heterogeneity of the material in terms of Be content has not been tested for sample sizes smaller than 200 mg. Additionally, it should be stated that since the Be mass fraction was certified without drying the material, SRM 1877 should not be dried prior to use, or else the certified value will not apply.

Analytical Benefits of Exact Matching. As stated earlier, NIST has found through experience with HP-ICP-OES that analytical precision and accuracy can often be improved by exactly matching the matrix compositions and analyte and internal standard element mass fractions among the calibration and sample solutions. NIST has never published these observations. A systematic investigation of the analytical benefits, and explanations for those benefits, afforded by exact matching and involving a large number of combinations of analyte and internal standard is currently underway and will be published in a future paper. As one example of results, analytical precisions observed for sets of solutions prepared with and without exact matching of analyte and internal standard element mass fractions have been compared for a number of elements of the periodic table. The results show precision improvements for some combinations of analyte and internal standard element that are larger than an order of magnitude when exact matching is employed, though there is little improvement for a small number of combinations. It was on the basis of such observations that the decision was made to implement exact matching for the determination of Be in SRM 1877.

The analytical benefits of employing exact matching for the certification reported in this paper have been investigated to gain an understanding of how the certified value and associated uncertainty might have been affected if exact matching had not been employed. Two aspects of exact matching were investigated separately. The first aspect involved exactly matching the analyte and internal standard element mass fractions among the unknown and calibration solutions, while approximately matching the matrix compositions. The second aspect was concerned with the effect of only approximately matching the analyte and internal standard element mass fractions, while keeping the matrix compositions identical.

To investigate the first aspect, the solution set prepared by SRS was chosen as a test case, because the Be metal calibration and BeO unknown solutions were prepared using different digestion protocols, as explained earlier. As a result, the BeO solutions, as received at NIST from SRS, contained 18% volume fraction H_2SO_4, whereas the Be metal solutions contained no H_2SO_4. Sulfuric acid is known to cause severe matrix effects in ICP analyses.[43] Consequently, the SRS solution set represents the worst-case scenario for this evaluation. A set of eight solutions were prepared having exactly matched Be and Mn mass fractions, but with four solutions having a matrix composition of 2.0% volume fraction H_2SO_4 and 0.07% volume fraction HCl, and the other four solutions having a matrix of 2.1% volume fraction H_2SO_4. These matrix compositions represent the compositions of the calibration and unknown solutions, respectively, which would have resulted if NIST had matched the matrixes slightly less carefully. These eight solutions were run according to the HP-ICP-OES protocol, and the instrumental sensitivity values (defined as the Be/Mn intensity ratio divided by the Be/Mn mass fraction ratio) observed for the individual solutions were plotted on a relative scale. As shown in Figure 3, there is a distinct 2.3% difference between the sensitivity values for the two matrixes. This clearly indicates that if the matrixes had not been exactly matched, the Be mass fraction value obtained using the solution set provided by SRS would likely have been biased. These data indicate that exactly matching the matrix compositions among the calibration and unknown solutions for each HP-ICP-OES analysis was essential for obtaining the very close agreement observed among the individual Be mass fraction values and also helped to minimize bias and uncertainty in the certified Be mass fraction in SRM 1877. These results support the use of exact matching for this certification.

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(42) Stefaniak, A. B.; Hoover, M. D.; Day, G. A.; Dickerson, R. M.; Peterson, E. J.; Kent, M. S.; Schuler, C. R.; Breysse, P. N.; Scripsick, R. C. *J. Environ. Monit.* **2004**, *6*, 523–532.

(43) Todolí, J.-L.; Mermet, J.-M. *Spectrochim. Acta, Part B* **1999**, *54*, 895–929.

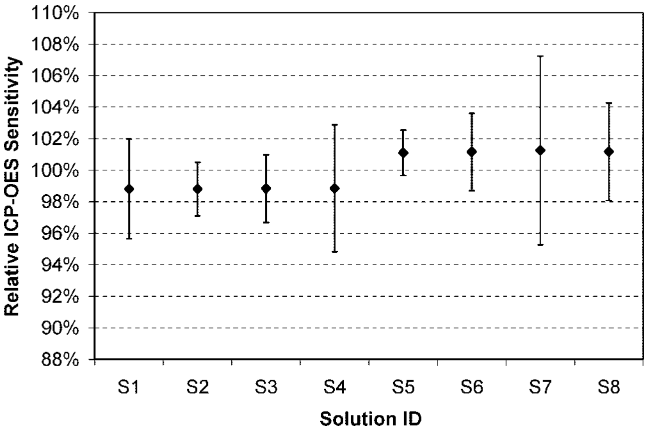

Figure 3. Graphical comparison of the relative ICP-OES sensitivity values (defined as Be/Mn intensity ratio divided by Be/Mn mass fraction ratio) observed for solutions containing exactly matched Be and Mn mass fractions but two different matrix compositions. The four points on the left represent a matrix composition of 2.1% volume fraction H_2SO_4, while the four points on the right represent a matrix consisting of 2.0% volume fraction H_2SO_4 and 0.07% volume fraction HCl (error bars are 95% confidence intervals).

To investigate the second aspect, sets of eight solutions were prepared with and without exact matching of the Be and Mn mass fractions. The matrix compositions of all solutions were held constant at 2.0% volume fraction HNO_3. The RSDs of the nominal Be and Mn mass fractions, as well as the RSDs of the ratios of the mass fractions, calculated across a set of approximately matched solutions averaged 6%. This is about the degree of matching that was typically used at NIST in HP-ICP-OES analyses prior to the implementation of the exact matching concept. The exactly matched and approximately matched solution sets were run in separate experiments according to the HP-ICP-OES protocol, and the instrumental sensitivity values (as defined above) observed for the individual solutions were calculated. For replicate experiments, there was little difference between the RSDs of the sensitivity values obtained with and without exact matching. These results indicate that, for this specific certification, exactly matching the Be and Mn mass fractions among the sample and calibration solutions provided little improvement in the overall uncertainty associated with the certified Be mass fraction in SRM 1877. This result stands in contrast with other combinations of analyte and internal standard element previously investigated by NIST.

CONCLUSIONS

HP-ICP-OES with exact matching has been used successfully for the certification of Be mass fraction in SRM 1877 Beryllium Oxide Powder. Sets of solutions for analysis were prepared by laboratories collaborating with NIST. The sets of solutions were shipped to NIST for HP-ICP-OES analysis. To accomplish exact matching and to help establish traceability of the results to the SI, NIST provided the collaborating laboratories with solution preparation kits containing NIST-supplied chemicals, shipping materials, and Au test masses for validation of the analytical balances used, and with solution preparation spreadsheets to assist with the preparations and for data entry. This procedural model worked well and may serve as an alternative for future certification of SRMs of a hazardous nature. It may also be used by other reference material producers.

It should be emphasized that the certified Be mass fraction for SRM 1877 is based upon analyses of four sets of solutions prepared by three collaborating laboratories using four different digestion protocols. The very close agreement among the Be mass fraction values determined from the four sets of solutions (1*s* of mean = 0.074% relative) provides a measure of confidence in the robustness of each of the digestion protocols, as well as in the certified Be mass fraction.

Research results presented here show that exactly matching the matrix compositions among the calibration and unknown solutions for each HP-ICP-OES analysis was critical to the attainment of the very close agreement among the individual Be mass fraction values. It also helped to minimize bias and uncertainty in the certified value. In unpublished work, NIST has found that exact matching of analyte and internal standard element mass fractions among calibration and unknown solutions is beneficial in HP-ICP-OES analysis for many combinations of analyte and internal standard. Research results presented here show that, for this particular certification, exactly matching the Be and Mn mass fractions provided little analytical benefit.

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