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Effect of Valence State on ICP-OES Value Assignment of SRM 3103a Arsenic Spectrometric Solution

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The certification of Standard Reference Material (SRM is a registered trademark of NIST) 3103a As Spectrometric Solution is based on the gravimetric preparation value that is verified by inductively coupled plasma optical emission spectrometry (ICP-OES) measurements. A disagreement between the gravimetric and the spectrometric values for a batch of As calibration solutions led to the discovery that the solutions contained a mixture of trivalent and pentavalent As species and that the pentavalent species was ~8% more sensitive than the trivalent species with ICP-OES determination. The kinetics of the reaction between As metal and nitric acid were studied, and the results were applied to develop a procedure that would consistently produce single-species pentavalent As standards, which eliminates As speciation as a source of measurement bias in the SRM certification process.

The 3100 series Standard Reference Materials (SRM) Single-Element Spectrometric Solutions are developed as primary calibration standards that provide a basis for traceability to International System of Units (SI) in instrumental calibration and in the production of secondary commercial calibration standards. The SI traceability of the Spectrometric Solutions is realized by gravimetric preparation using NIST primary materials—high-purity metals or compounds that have been well characterized for impurities and for which a history of comparison against other materials is kept. Because of the ease with which metals of higher purities are characterized relative to the compounds, metals are the preferred source of primary materials for the preparation of SRM 3100 series Single-Element Spectrometric Solutions.[1]

SRM 3103a As Spectrometric Solution, for example, was prepared by dissolving on a hot plate NIST primary As metal in 50% (volume fraction) concentrated nitric acid in water. The resulting solution was gravimetrically diluted to produce a solution containing ~10.00 mg/g of As. The mass fraction of As in the solution based on the gravimetric preparation was verified with inductively coupled plasma optical emission spectrometry (ICP-OES) measurements using calibrants prepared from a separate digestion of high-purity NIST primary As metal.[2,3] Although the spectrometric measurement values for most elements have agreed with the gravimetric preparation values to well within 0.3 %, As was an exception. A deviation of as much as 3% between the spectrometric measurement value and the gravimetric preparation value was observed sometimes, and the deviation could not be accounted for by preparation or measurement uncertainties of the two techniques. Not only did this unexpected disagreement between gravimetric preparation and ICP-OES measurement values result in large uncertainties in the certified value of the SRM, but a greater concern was whether systematic errors existed in the ICP-OES measurement or the production of SRM 3103a As Spectrometric Solution.

We have investigated the apparent deviation between the gravimetric preparation and the ICP-OES measurement values, and we have traced the problem to differences in As speciation in standards coupled with a systematic error in ICP-OES measurements of different As species. Guidelines have been established to circumvent the systematic error in the measurement of As in general and to produce a more accurate and precise As calibration standards in specific.

EXPERIMENTAL SECTION

Instrumentation. (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.) The optical emission measurements were made by using a PerkinElmer (Shelton, CT) model Optima 3300 DV ICP-OES equipped with a standard quartz torch, an alumina injector, a cross-flow nebulizer, and a Ryton spray chamber. Sample introduction for the speciation measurements was accomplished by using a PerkinElmer series 200 autosampler equipped with a stainless steel needle and a Peltier chilled sample tray. Arsenic species were separated with a biocompatible PerkinElmer series 200 high-performance liquid chromatography system (HPLC) using a PerkinElmer Brownlee model 3CR C8 column and were detected with a PerkinElmer Sciex (Thornton, ON, Canada) model Elan DRC II inductively coupled plasma mass spectrometry (ICPMS). A PerkinElmer Sciex model Elan 5000 ICPMS equipped with a standard quartz torch, an alumina injector,

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Table 1. Instrument Parameters

ICP-OES	
plasma flow	15 L/min
auxiliary flow	0.5 L/min
nebulizer flow	0.8 L/min
rf power	1300 W
signal measurement mode	peak integration, low-resolution readout
background correction	manually selected 2-point interpolation
measurement time	40 s
replicate measurement	6
auxiliary flow	0.5 L/min
HPLC−ICPMS	
plasma flow	15 L/min
auxiliary flow	1 L/min
nebulizer flow	1.2 L/min
rf power	1100 W
dwell time	1 s
readings per replicate	300
number of replicate	1
mobile phase	5% methanol 95% buffer solution at pH 5.8 containing 1 mM phosphate and 1 mM TBAH
mobile phase flow rate	1.5 mL/min
ICPMS	
plasma flow	15 L/min
auxiliary flow	0.8 L/min
nebulizer flow	1 L/min
rf power	1000 W
replicate time	4 s
number of replicate	6

a cross-flow nebulizer, and a Ryton spray chamber was used to measure As at mass 75. The operating conditions for ICP-OES, HPLC−ICPMS, and ICPMS are listed in Table 1.

Reagents. HPLC reagent grade tetrabutylammonium hydroxide (TBAH) and Ultrex grade ammonium hydroxide from Baker (Phillipsburg, NJ) and reagent grade potassium dihydrogen phosphate from GFS Chemicals (Columbus, OH) were used to prepare HPLC mobile phase containing 1 mmol /L TBAH in 1 mmol/L phosphate buffer at pH 5.8. Puratronic grade iodine and Puratronic grade sodium hydrogen carbonate were purchased from Alpha Aesar (Ward Hill, MA). Reagent grade potassium iodide was obtained from Baker (Phillipsburg, NJ). Trivalent and pentavalent As standards were obtained from SPEX CertiPrep (Metuchen, NJ). Optima grade nitric acid was purchased from Fisher Scientific (Bedford, MA). All solutions were prepared in sub-boiling distilled water produced locally.

Procedure. For HPLC−ICPMS measurements, all samples were prepared in the pH 5.8 mobile phase. Arsenic was detected at mass 75 with the ICPMS operating in the normal mode. For ICP-OES measurements, the experimental design was modeled after the drift correction procedure described by Salit and Turk[3] with each solution being measured six times during an analysis campaign. All uncertainties reported in this work are expanded uncertainties calculated according to ISO Guide at a 95% confidence interval.[4]

For the oxidation of As^{3+} to As^{5+}, a solution of iodine as the oxidizer was prepared by first dissolving 0.43 g of KI in 1.7 mL of water, then adding and dissolving 0.24 g of iodine in the KI solution, and finally diluting the solution with water to ~60 g. A solution that contained 3 g of $NaHCO_3$ in 47 g of water was used to keep the reaction at pH close to 7 to control the oxidative power of I_2 relative to that of As^{3+}. Oxidation of As^{3+} to As^{5+} was accomplished by adding 5 mL of the iodine solution and 5 mL of the $NaHCO_3$ to 7 mL of 1000 μg/g As^{3+} standard before diluting the solution with water to ~100 g.

The reaction kinetics of As and nitric acid were studied by digesting ~1 g of As metal in 50% (volume fraction) of concentrated nitric acid in water on a hot plate at 177 °C surface temperature to keep the solution from boiling. A sample of 0.2 mL of digest was withdrawn every 1−2 h until 25 h after the As metal was completely digested. The samples were measured for As^{3+} and As^{5+} ratio by using the HPLC−ICPMS method described previously.

Table 2. Relative ICP-OES Sensitivity and As^{3+} Mass Fraction of As Standards

standard ID	C1S1	C1S2	C2S1	C2S2
sensitivity[a]	100.03 ± 0.15	99.98 ± 0.03	99.69 ± 0.11	97.54 ± 0.08
As^{3+}, %	0.7 ± 0.4	0.0 ± 0.4	0.0 ± 0.4	21.1 ± 3.2

[a] Sensitivity is calculated as emission intensity divided by analyte mass fraction in the solution.

RESULTS AND DISCUSSION

Preparation and Measurement of As Standard. For the production and certification measurements of SRM 3103a by ICP-OES, the instrument was calibrated with standards prepared from metallic As primary material. To prevent error in the preparation of the calibration standards, the experimental design called for two chemists each digesting two samples of the identical source primary As metal to produce a total of four standards. Each standard solution was prepared by digesting on a hot plate ~1 g of As metal in a Teflon beaker containing 50% (volume fraction) of concentrated nitric acid in water. After the As metal was digested, the solution was diluted with water to contain 10 mg/g As and 10 vol % concentrated nitric acid. The four As standards were measured by using ICP-OES for comparability before being qualified as calibration standards for the certification measurements.[5] The relative sensitivity of each standard, defined as the emission intensity divided by the mass fraction of As in the solution, was used as a criterion to determine the comparability of the four standards.

The second row of Table 2 lists the values and the uncertainties of four standards produced in one certification campaign. The two standards prepared by the first chemist are labeled C1S1 and C1S2, and those by the second chemist C2S1 and C2S2. Standards C1S1 and C1S2 are in good agreement as suggested by the overlap of their confidence intervals. Standard C2S1 is lower than C1S1 and C1S2 by a small yet statistically significant 0.3% that might be attributed to small differences in the execution of the sample preparation by the two chemists. A standout is C2S2. At more than 2% lower than the other standards, the inconsistency of C2S2 with the other three standards is too big to be attributed to

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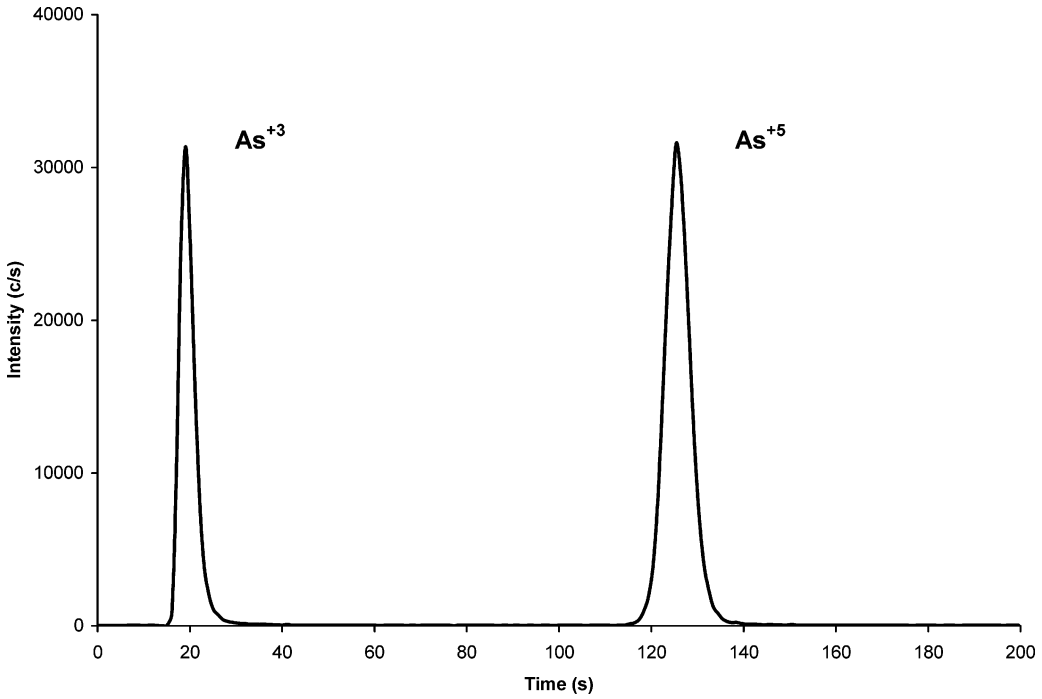

Figure 1. Chromatogram of a standard containing 10 ng/g each of As^{3+} and As^{5+}.

preparation errors since C2S1 and C2S2 were prepared in identical conditions without any incident. Provided that the gravimetric preparation values of the standards were correct, then the ICP-OES measurement of As was in error.

The instrument-related factors such as optimization parameters and instrument calibration were discounted as sources of the error because the four standards were measured at the same time under the same condition with drift correction[3] and because the measurement of relative sensitivity required no instrument calibration; therefore, the answer to the disagreement among the standards existed within the four standards. The matrix was excluded as a source of the error because, other than the analyte, each stock solution of the standards contained only 10% (volume fraction) nitric acid, and the analytical samples of the stocks were prepared with identical dilution procedure to contain 2% (volume fraction) nitric acid. The analyte, being the sole remaining component of the standard solutions, became the suspect; consequently, the only possible explanation for the differing instrument response was somehow that the analyte(s) in the standards were different.

Based on the electrochemical series shown by eqs 1−3, two arsenic species, arsenious acid and arsenic acid, are possible products of reactions between As metal and nitric acid.

$$HAsO_2 + 3H^+ + 2e^- = 2As + 2\,H_2O \qquad 0.248\ V \quad (1)$$

$$H_3AsO_4 + 2H^+ + 2e^- = HAsO_2 + 2H_2O \qquad 0.560\ V \quad (2)$$

$$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O \qquad 0.957\ V \quad (3)$$

The two species of As in the standards were measured to determine whether they might account for the differing relative sensitivity of the standards. Arsenic species in aqueous solutions were typically separated by anion exchange chromatography or ion-pair reversed-phase chromatography.[6,7] The matrix of the sample was very simple and consistent in this work; therefore, either approach would be sufficient to separate the two species. We adopted the ion-pair reversed-phase chromatographic method developed by Neubauer et al. because of its speed.[8] Analytes were eluted in less than 3 min and baseline separation of As^{3+} and As^{5+} was achieved, as shown in Figure 1 for a standard containing 10 ng/g each of As^{3+} and As^{5+}. Arsenic species in the four standards were measured by using the HPLC−ICPMS method, and the mass fraction of As^{3+} as a percent of total As for each standard is listed in the third row of Table 2. All standards contained less than 1% As^{3+} except for C2S2, in which over 21% of As was at the trivalent state. It appeared that the low relative sensitivity of the standard correlated with the high mass fraction of As^{3+} in the solution.

Effect of As Speciation. To determine whether As^{3+} was less sensitive relative to As^{5+}, we measured an As^{3+} standard with the ICP-OES instrument calibrated against an As^{5+} standard. Mindful that a low ICP-OES reading of the As^{3+} standard can also result from a disagreement of the total As between this and the As^{5+} calibrant, we checked the comparability of the total As in the As^{3+} and the As^{5+} standards with respect to their nominal values to eliminate this possibility. The As^{3+} standard was measured against the As^{5+} standard by using ICP-OES after all arsenic was oxidized to the pentavalent state to eliminate the valence state as a variable in the comparison; moreover, the same amount of the oxidant was added to the As^{3+} and the As^{5+} standard to ensure matching matrixes.

Two criteria were used in selecting the oxidant: it must oxidize As^{3+} to As^{5+} quantitatively and it must do so at about pH 6 so

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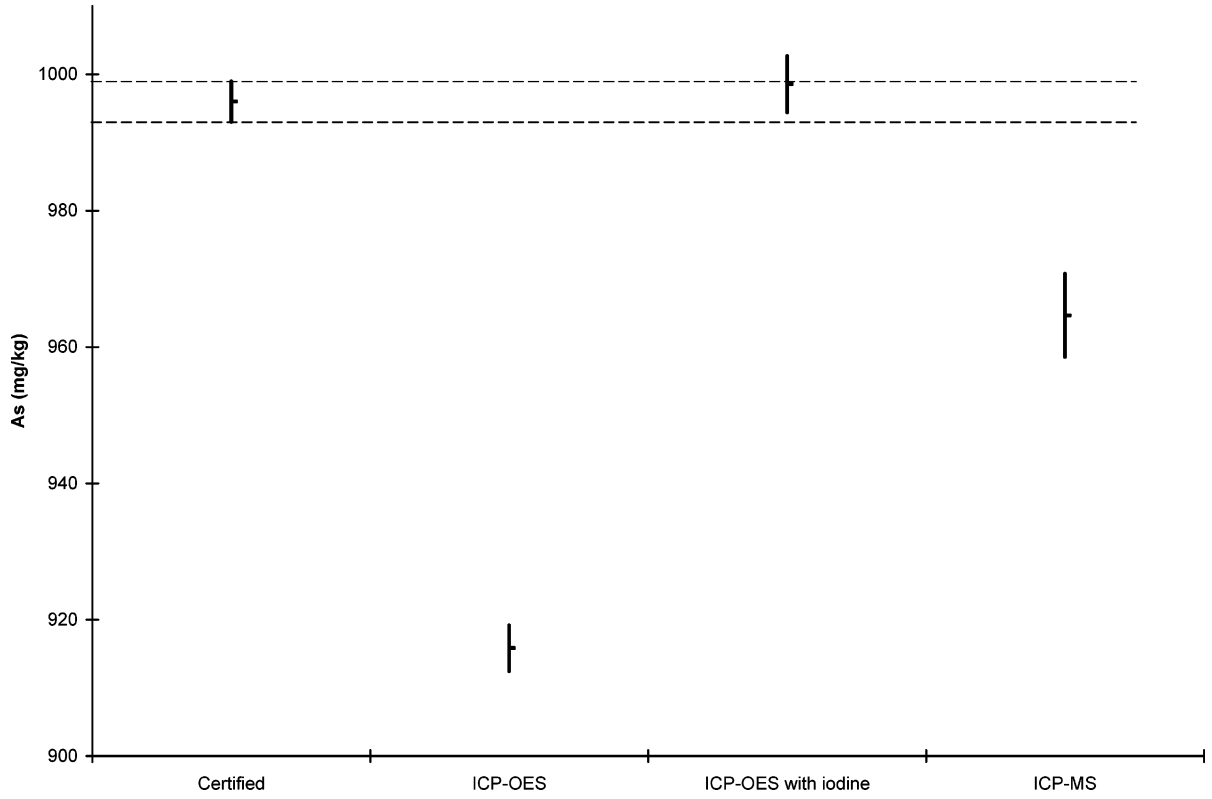

Figure 2. ICP-OES and ICPMS measurement values of an As^{3+} standard.

that the aforementioned HPLC method can be used to verify the speciation of the standards before and after the oxidation. Some well-characterized oxidants were excluded either because they favor a low pH, i.e., $K_2Cr_2O_7$, or because they form precipitate at the targeted neutral pH, i.e., $KMnO_4$. We chose iodine, a mild oxidant that is gentler to the column and the HPLC system than the alternatives. The reaction between iodine and As^{3+} is well characterized, as evidenced by the fact that As^{3+} is used to standardize iodine in iodimetry.[9]

The As mass fraction of the trivalent standard was determined to be 915.8 ± 3.4 and 998.6 ± 4.1 mg/kg before and after the reaction with iodine, respectively, relative to the certified value of 996.0 ± 3.0 mg/kg. As shown in Figure 2, the ICP-OES measurement value of the oxidized standard agrees with the certified value of the As^{3+} standard as indicated by the overlap between the confidence intervals of the two; therefore, the total As in the trivalent and the pentavalent standards agree with each other. Finally, the more than 8% lower reading of the trivalent standard before oxidation is a result of As^{3+} being less sensitive relative to As^{5+} with ICP-OES determination. We refer to the phenomenon of As^{3+} exhibiting a lower sensitivity than As^{5+} as "speciation effect" and the consequent measurement bias from the speciation effect as "speciation bias" in the discussion that follows.

The effect of the speciation bias on the certification of SRM 3103a was evaluated. The certified value of As in SRM 3103a is derived by combining the gravimetric preparation value with the ICP-OES measurement value whereby the certified mean is the average of the two method means, and the certified uncertainty is the combined uncertainty of both methods and the uncertainty from the bias between the method means.[10] The speciation bias, if present, does not invalidate the accuracy of the certified value because the uncertainty interval of the certified value is proportionally increased by the resulting between-method bias term;[10] nevertheless, the presence of the speciation bias degrades the precision of the certified value by enlarging the uncertainty interval. To ensure highest accuracy and precision expected of a primary standard such as SRM 3103a, any measurement bias, including speciation bias, must be eliminated from the certification process.

Digestion Kinetics of As Metal. The speciation bias is a result of the disparate composition of As species in the sample and the calibrant. One solution to the problem is to bring the As species in the sample and the calibrant to the same oxidative state by either reducing or oxidizing the analyte to As^{3+} or As^{5+}, respectively. Oxidizing As to the terminal pentavalent state is preferred because it allows a wide selection of oxidants to suit various conditions of the sample matrix and needs of the instrument in the subsequent measurement, as we demonstrated previously in choosing iodine as the oxidant in this work. For the purpose of preparing and certifying SRM 3103a, the best solution to the speciation bias is to avoid it completely by consistently producing a single-species As solution.

The reduction potential for nitric acid is greater than that for As^{5+} being reduced to As^{3+} as shown in eqs 2 and 3, indicating that the production of As^{5+} is favored thermodynamically when As metal digests in nitric acid. The fact that various As species

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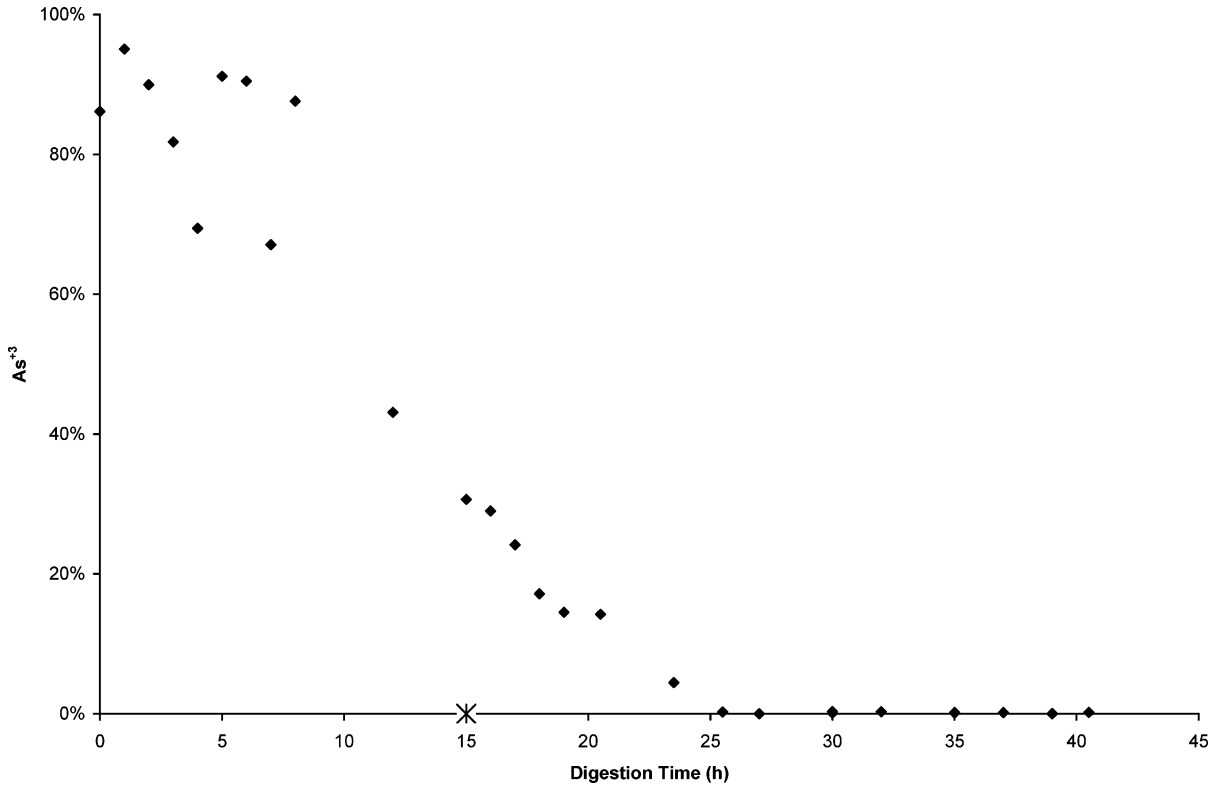

Figure 3. Mass fraction of As^{3+} relative to total As in solution as a function of time.

were found in the standards listed in Table 2 suggested that the reaction kinetics was a factor in the production of the standards. To find conditions that can consistently produce standards of As^{5+} species, we studied the kinetics of the digestion by periodically sampling the digest of an ongoing reaction between As metal and nitric acid, as described in detail in the Procedure section. The ratio of As^{3+} and As^{5+} was measured, and as shown in Figure 3, the fraction of As^{3+} relative to the total As in solution was plotted as a function of digestion time.

When the arsenic metal reacted with the nitric acid, elemental As was oxidized to form arsenious acid in accordance with eq 1. As the digestion progressed, the trivalent state As of the arsenious acid was further oxidized to the pentavalent state to form arsenic acid in accordance with eq 2. The fact that both As^{3+} and As^{5+} were found in the digest up to the 25th hour suggested that the oxidation of As^{3+} to As^{5+} was the rate-limiting step in producing As^{5+} from As metal. At the onset of the reaction, the digest was composed primarily of As^{3+} as shown in Figure 3. With the passing of time, the As^{3+} in the digest was gradually oxidized to As^{5+}, resulting in a gradual decrease of the fraction of As^{3+} relative to total As in the digest. The oscillation of the As^{3+} fraction relative to the total As in solution for the first 10 h probably reflected the digestion rate fluctuation of the As metal. As the fraction of As^{5+} in the digest increased with time, the effect of the digestion rate fluctuation on the fraction of As^{3+} decreased, resulting in a smoother curve beyond the 10th hour. When As metal was completely digested upon visual inspection, as marked by the "*" on the Time axis in Figure 3, ~31% of As in the digest was still at trivalent state. The remaining As^{3+} was not fully oxidized to As^{5+} until 12 h after the As metal was completely digested. Any digestion stopped within the 12-h window after the disappearance of the As metal would result in a As^{3+} and As^{5+} mixture under the experimental condition. The reason some of the As calibration standards shown in Table 2 contained both As^{3+} and As^{5+} species was easily understood since the protocol for preparing the As standards regarded the digestion complete once the metal disappeared. Preparing a solution of pure As^{3+} species by digesting As metal in nitric acid may be very difficult if not impossible according to Figure 3; however, a pure As^{5+} solution can be prepared simply by keeping the solution under the same conditions for 12 h or more after the As metal is completely digested. A modified digestion procedure that takes into account of the extra 12 h needed to oxidize As^{3+} to As^{5+} after the dissolution of the As metal should yield the analyte as arsenic acid. The possibility of speciation bias is eliminated from the certification process when both the calibrant and candidate SRMs are produced with the modified digestion procedure.

ICPMS Measurement of As Species. ICPMS was used to verify the ICP-OES results after the discovery of a disagreement between the candidate calibrants C1S1, C1S2, C2S1, and C2S2 as discussed previously. A relative sensitivity pattern similar to that of ICP-OES was observed, with C2S2 being the lowest and obvious outlier of the four. In the subsequent measurements using the As^{5+} standard solution as a calibrant, the As^{3+} stock solution with a certified value of 996.0 ± 3.0 mg/kg yielded an apparent content of 964.6 ± 6.1 mg/kg As. The measured value was lower than and was statistically different from the certified value as shown in Figure 2, confirming the presence of a speciation effect akin to what was observed with ICP-OES.

Unlike the observations by ICP-OES discussed here, the dissimilar sensitivity of As species to ICPMS determination has been reported in the literature. Using As solutions prepared from hydrogen arsenate disodium salt and arsenite sodium salt, respectively, Larson and Sturup found that the sensitivity of the

As^{5+} solution was 93% that of the As^{3+} as measured by ICPMS.[11] The report of As^{3+} being more sensitive than As^{5+} was to the contrary of the observations made in this work; however, it was not clear whether and how the purity of the arsenate and arsenite was accessed independent of nominal or the gravimetric preparation values. A "zone model", which describes the mass dependency of the zone of optimum ion extraction from the plasma to the mass spectrometer, was used by Larson et al. to rationalize the differing responses of the As species.[11,12] Although the zone model appears to explain the observations by ICPMS that has a finite sampling depth, it has difficulty interpreting what was observed by the axial-viewing optics of the ICP-OES of this work since the sampling depth of the technique is much greater than ICPMS. Creed and co-workers found that As^{3+} response was "suppressed" by ~20% relative to that of As^{5+} when determined by using ICPMS equipped with an ultrasonic nebulizer (USN).[13] They attributed the lower response of As^{3+} to a preferential loss of As^{3+} relative to As^{5+} in the condenser of the USN as a result of a "desolvation effect", whereby the analyte-containing compound is lost to the condensate when the melting point or the boiling point of the compound approximates the temperature of the heating chamber or the condenser of the USN, respectively.[14] The theory does not quite explain the ICP-OES and ICPMS results of this work, which were obtained with pneumatic nebulization whose desolvation effect was not evident.[12]

As shown in the Instrumentation section, the nebulizer spray chamber, injector, and torch in the ICP-OES and the ICPMS instruments used in this work were practically identical. The only functional difference between the two instruments in this work was that ICP-OES and ICPMS served as atom and ion detectors, respectively. The fact that both the atom detector and the ion detector were similarly impacted by the As speciation effect suggests that the cause of the speciation effect must have occurred before the atomization step. It follows that the speciation effect was induced in the same apparatus that both ICP-OES and ICPMS shared since the apparatus of the two instruments were identical upstream of the atomization source; consequently, the cause for the speciation effect observed by ICP-OES and ICPMS was identical. The speciation effect was unlikely to result from the pneumatic nebulizer as discussed previously; therefore, it must have occurred between steps of aerosol transportation from the spray chamber to the plasma, droplet desolvation and vaporization near or within the plasma, and analyte atomization in the plasma. Unfortunately, following changes of the analyte in these steps is difficult because there is no easy ways to precisely determine the analyte existing in various associated forms through desolvation, dissociation, and atomization. It is beyond the scope of this work to delineate the fate of the analyte in these steps, and the mechanism that is responsible for the speciation effect merits dedicated study. Until the speciation effect is better understood and a better solution to the speciation bias problem is found, the best practice to prevent the bias from occurring is to ensure that the analyte in the sample and the calibrant is at the same valence state.

CONCLUSION

The disagreement between the gravimetric and ICP-OES measurement values of candidate As calibrants was a result of As^{3+} being less sensitive relative to As^{5+} by ICP-OES determination. A preparation procedure that consistently produces As^{5+} standards eliminates the potential for the ICP-OES measurement bias. As a guideline for accurate ICP-OES and ICPMS measurements, the consistency of As species in the sample and the calibrant must be assured. In practice, a pentavalent state As should be used for calibration and analyte in the sample must be oxidized to the pentavalent state during sample digestion. A longer digestion time and a higher digestion temperature facilitate the conversion of As^{3+} to As^{5+}. The mechanism resulting in the speciation effect is yet to be investigated.

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