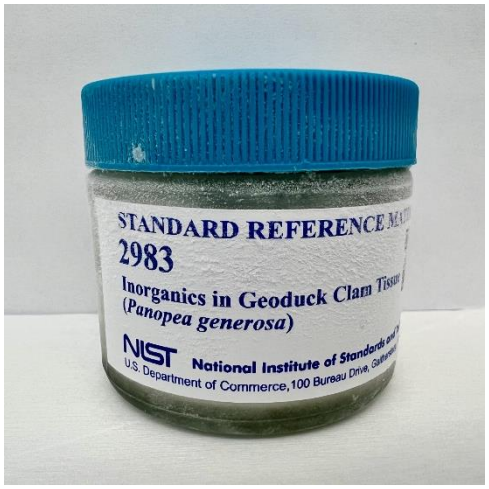
NIST Special Publication 260
NIST SP 260-246

# Certification of Standard Reference Material® 2983

*Inorganics in Geoduck Clam Tissue (Panopea generosa)*

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## *Inorganics in Geoduck Clam Tissue (Panopea generosa)*

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## Abstract

Standard Reference Material (SRM) 2983 Inorganics in Geoduck Clam Tissue (*Panopea generosa*) is intended to be used for the evaluation of methods for the determination of elements, arsenic species, and proximates in this and similar matrices. A unit of SRM 2983 consists of one jar containing approximately 12 g of cryogenically homogenized frozen material. This publication documents the production, analytical methods, and statistical evaluations involved in characterizing this material.

## Keywords

Arsenic; Geoduck Clam; Inorganic Arsenic (iAs); Proximates; Trace elements.

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# 1. Introduction

The National Institute of Standards and Technology (NIST) has developed many environmentally relevant Standard Reference Materials (SRMs) over the years, including whale blubber, fish and mussel tissues, human blood, house dust, and a variety of sediments, with a broad range of individual organic and inorganic contaminants characterized to suit the needs of the environmental community. However, a higher order reference material is needed for quality assurance of measurements conducted for arsenic species assessment in matrix-rich shellfish.

Several agencies, including the National Oceanic and Atmospheric Administration (NOAA) Fisheries, Washington Department of Health (WA DOH), and the Southeast Alaska Regional Dive Fisheries Association (SARDFA) have requested the production of a geoduck clam reference material containing naturally representative levels of inorganic arsenic (iAs). In compliance with the recent trade agreement between the US and the People's Republic of China, individual states are now required to routinely monitor iAs contamination in geoduck clams as part of NOAA Fisheries' Seafood Inspection Program [1]. SRM 2983 fulfills this requirement, providing quality assurance and traceability in measurements for assessing potential health risks associated with shellfish. In addition to the mandated monitoring in geoduck clams, the SRM material may be used worldwide for environmental and foodstuff assessments.

# 2. Production

## 2.1. Materials

Twenty (20) geoduck clams were harvested from Vegas Hot Spur, Alaska (Lat. 54°57.297, Long. 131° 29.172) and shipped live on ice overnight to NIST-Charleston, yielding ≈ 6.8 kg of tissue. Additionally, ≈ 10.0 kg of fresh frozen homogenate from 21 geoduck clams harvested from seven sites in southeastern Alaska had been previously cryogenically homogenized using polytetrafluoroethylene (PTFE) disk mills and stored at liquid nitrogen ($LN_2$) vapor-phase temperatures (≤ -150 °C) for inclusion in SRM 2983. Before homogenization, the total geoduck mass was 16.8 kg; after homogenization and blending it was 15.1 kg for a net loss of ≈ 10 %.

Pre-cleaned and certified 2 oz. glass jars with PTFE-lined lids were obtained from Scientific Specialties Services (Hanover, MD) and used for the bottling of the SRM material.

## 2.2. Sample Preparation

The homogenization and cleaning procedures used to produce frozen tissue homogenates using the Palla VM-KT Vibrating Cryomill are detailed in [2]. These procedures were used with little modification to produce the SRM 2983 material. In brief, twenty geoduck clams were received live in plastic bags on ice from SARDFA on April 21, 2015. Upon arrival, each clam was rinsed with Milli-Q (minimum resistivity 18.2 MΩ $cm^{-1}$) water to remove extraneous debris (e.g., sand, shell, etc.). Samples were then shucked by sliding a gloved thumb or finger between the mantle and the shell, then prying the shell open. The tissue contents (siphon, gastric sack, skin, and mantle) were then removed from the shell and rinsed again with Milli-Q water to remove any remaining debris. The shells were placed in a large plastic bag and sent to the Alaska Department

of Fish and Game Age Determination Unit for future age determinations. Tissue contents were then cut into ≈ 1.5 $cm^3$ pieces with a titanium knife, rinsed again with Milli-Q water, placed on a fluorinated ethylene propylene (FEP)-lined tray, and frozen in $LN_2$ vapor-phase (≤ -150 °C) until homogenization. The process is pictorially described in Fig. 1.

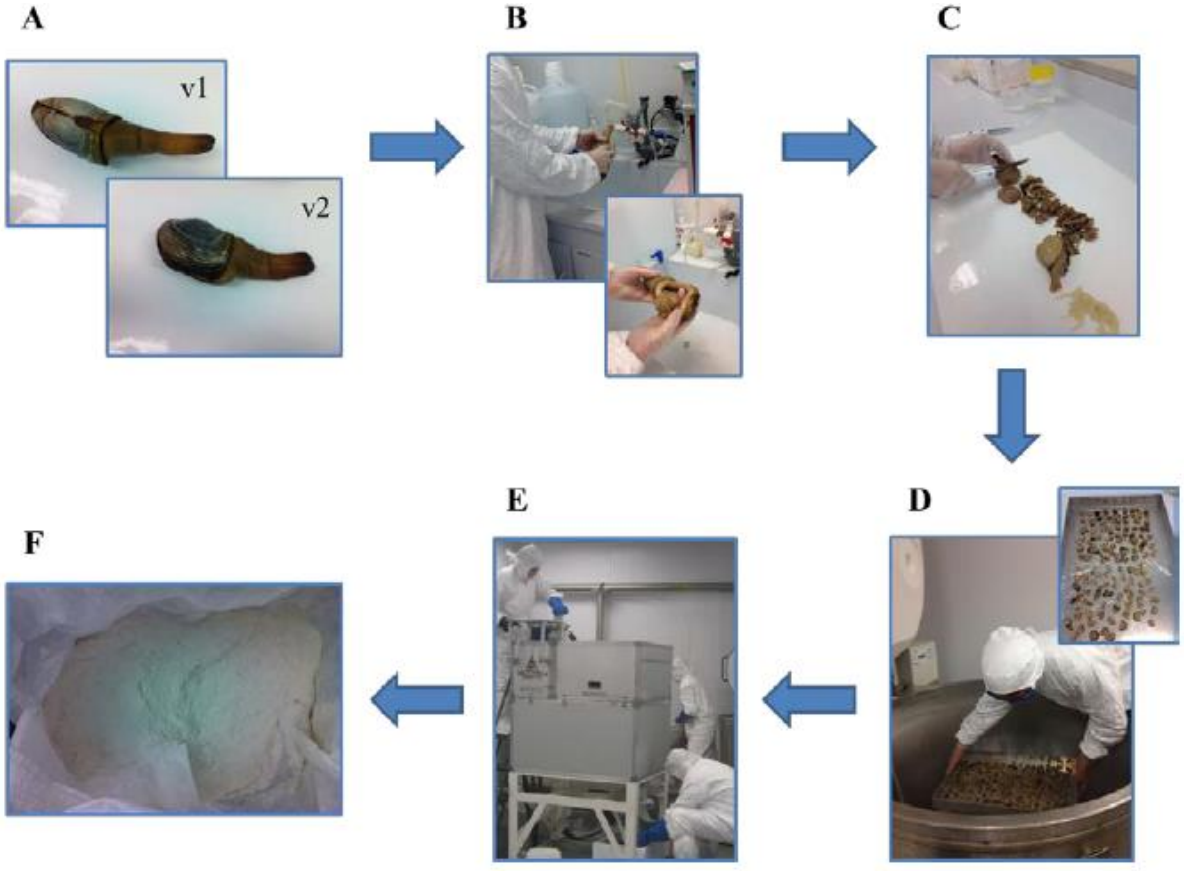



**Fig. 1.** Homogenization Procedure.

Prior to cryohomogenization, geoduck clams (A – v1 top view; v2 side view) were rinsed to remove any extraneous debris (B). After samples were shucked, the tissue (skin, viscera, and meat) was rinsed a second time and then cut into ≈1.5 cm wide sections, rinsed a third time, and then cut into smaller ≈1.5 $cm^3$ pieces (C) with a titanium knife. The pieces were transferred to a FEP-lined tray and frozen in an $LN_2$ vapor-phase freezer (D). The frozen material was then combined with additional material that had been previously homogenized and was milled and blended into a consistent fine frozen powder (F) following four rounds of cryohomogenization. The homogenate was bottled and stored at -80 °C until further analysis.

## 2.3. Homogenization and Blending

Prior to cryohomogenization, all homogenization equipment (scoops and FEP-lined collection baskets and buckets) were placed in an $LN_2$ vapor-phase freezer and allowed to equilibrate overnight to ≈ -150 °C. In addition to the frozen ≈1.5 $cm^3$ samples described above, approximately 10 kg of fresh frozen powder from twenty-one (21) additional geoduck clams that had been previously processed and cryohomogenized during the summer of 2014 using methods described in NIST IR 7389 [3] and stored in $LN_2$ vapor were incorporated into the production of the SRM material.

The Palla VM-KT Vibrating cryomill was allowed to cool to approximately -180 °C prior to homogenization. The temperature of the Palla cryomill was monitored throughout the cryohomogenization process. Once the internal temperature of the cryomill reached -110 °C, the instrument was stopped and cooled again to approximately -180 °C. During the cryomilling process, frozen geoduck material was added to the cryomill at a ratio of approximately 2:1 of previously homogenized geoduck powder to ≈1.5 $cm^3$ frozen geoduck tissue. The milled frozen geoduck powder was collected in pre-cooled FEP-lined stainless steel receptacles over a container of $LN_2$ in order to keep the material frozen during the collection process. Once the collection receptacle was near capacity, it was exchanged with a second pre-cooled collection receptacle and the contents of the first collection receptacle were transferred into one of two large FEP-lined collection baskets stored inside a $LN_2$ vapor-phase freezer, alternating between the two baskets with every other transfer in order to aid in the blending of the material. During the initial round of cryomilling (Round 1) the internal temperature of the cryomill reached -110 °C, at which point the milling process was stopped and the cryomill was cooled again with $LN_2$ to an internal temperature of -180 °C. Once cooled, the cryomilling process was continued until all of the starting material had undergone an initial round of homogenization through the cryomill.

To ensure complete homogenization and blending of the material, three additional rounds of cryomilling were conducted. The resulting material collected in the two FEP-lined baskets during the previous round of homogenization was added to the cryomill at a 1:1 ratio. The resulting material from the current round of homogenization was collected as before and transferred once again to two FEP-lined collection baskets, alternating between the two baskets with every transfer.

At the end of the third round, the internal temperature of the cryomill reached -110 °C. Attempts to recharge the mill were unsuccessful as a result of a clog in the outlet tube. The cryomill was thawed, dismantled, cleaned, and reassembled following the procedure detailed in [2]. The following morning the cryomill was again cooled to approximately -180 °C prior to the fourth and final round of homogenization. The final round of cryomilling was conducted as described above; however, the final frozen homogenized powder was transferred sequentially to the two FEP-lined collection baskets. A schematic workflow of the homogenization and bottling process is provided in Fig. 2.

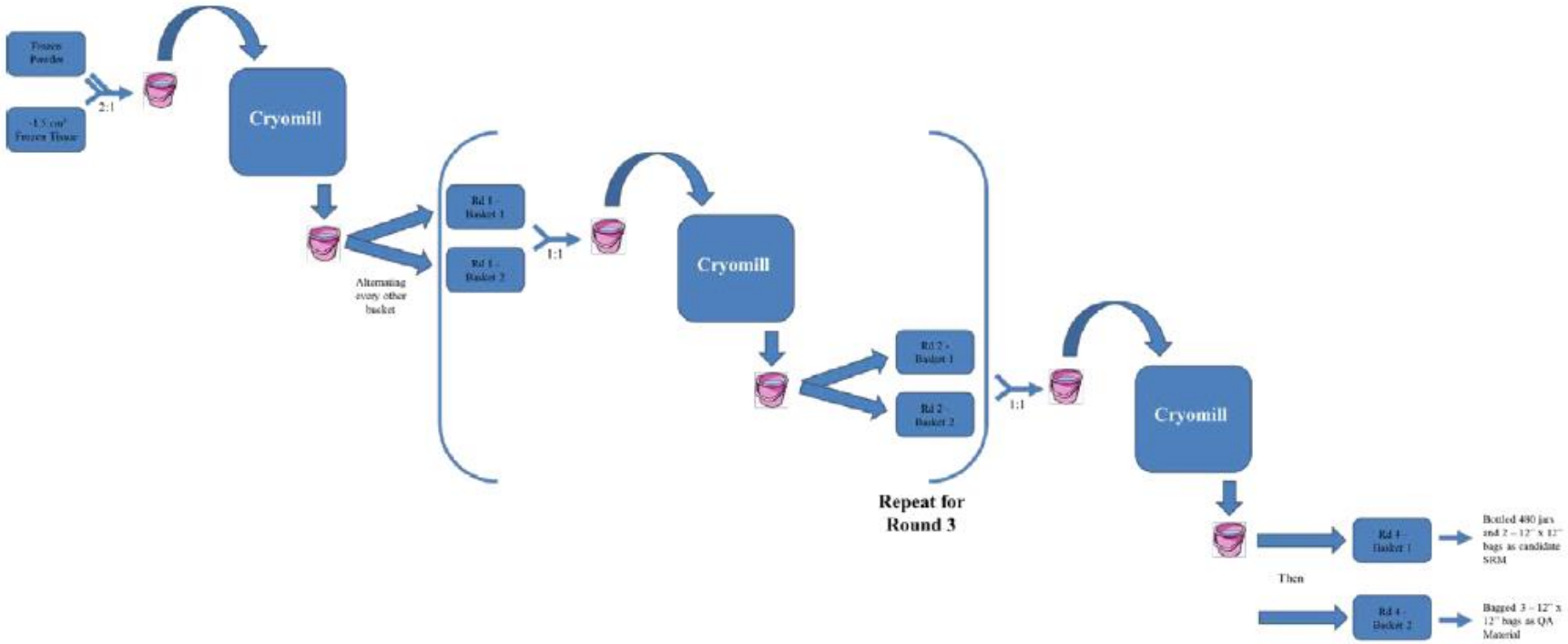



**Fig. 2.** Cryomilling Workflow.

During the initial round of homogenization, the material from two sources of fresh frozen geoduck clam tissue was added at a ratio of 2:1 of previously homogenized powder to ≈1.5 $cm^3$ frozen tissue, respectively. The material was collected and transferred to two collection baskets, alternating baskets between every other transfer. The material resulting from round 1 (Rd 1) was then combined at a 1:1 ratio and cryomilled for a second time, once again alternating baskets between every other transfer during the collection process. The material resulting from round 2 (Rd 2) was processed once again in the same manner for a third round of cryomilling. During the fourth and final round of cryomilling, the material resulting from round 3 (Rd 3) was processed similar to the previous round with the exception that the frozen homogenized powder collected was transferred sequentially to the two collection baskets.

## 2.4. Packaging, Jars 1 to 480

The frozen homogenized material was bottled in pre-cleaned and certified 2 oz. glass jars with PTFE-lined caps that had been labeled and pre-cooled to -80 °C. Approximately 12 g of homogenized material was transferred to each jar with a large pre-cooled PTFE scoop, weighing every third or fourth jar to ensure consistency during the bottling process. All jars were bottled from the geoduck material in the first collection basket from the final round of homogenization (Fig. 2). After filling the first 480 jars, the remaining material was bagged in two 12 in. × 12 in. FEP bags, heat sealed, labeled as extra source material, and stored at -80 °C.

The first 456 jars produced were labeled as SRM 2983. Jars 457 to 480, while containing the same source material as those labeled as SRM, were labeled for use in a NIST interlaboratory comparison exercise. The two labels are shown in Fig. 3. The interlaboratory comparison jars are independent of the SRM 2983 jars since final packaging and storage where not done the same, therefore future measurements of interlaboratory comparison jars are not necessarily representative of SRM 2983.

A


B


**Fig. 3.** Labels.

All 480 jars of SRM 2983 contain ≈ 12 g of the same frozen homogenate, however, jars 1 to 456 are the SRM (A) whereas jars 457 to 480 contain the same source material with an alternate label (B) for use in a NIST interlaboratory comparison exercise.

## 2.5. Packaging, Jars 481 to 568

An additional 88 jars of material were bottled three years after the material was homogenized and blended. These jars were filled from the material from the first collection basket that had been stored in heat sealed 12 in. × 12 in. FEP bags at -80 °C. The bottling process described above was followed. These additional units were produced to expand the number available for sales.

## 2.6. Summary

Approximately 16.8 kg of geoduck clam tissue was cryogenically homogenized and blended during four rounds of homogenizations using a Palla VM-KT Vibrating cryomill, yielding 15.1 kg of fresh frozen powder (Fig. **1** panel F). There was only a ≈ 10 % loss of material throughout the homogenization and blending process. The majority of the loss was a result of having to shut down the cryomill between the third and fourth rounds of cryomilling.

Initially, 480 jars were filled with ≈ 12 g each of the frozen geoduck powder and stored at -80 °C. Three years after the initial bottling, 88 additional jars were filled with ≈ 12 g each of the same source material that had been stored in FEP bags at -80 °C.

A total of 568 jars of SRM 2983 were produced and stored in 24 cases, each case having 24 positions. Once jars were removed from the cases for homogeneity assessment and value assessment, each case was placed in a large aluminized polyester bag and vacuum sealed for long term storage at -80 °C. When a case is opened for sale of the SRM, each bottle from that open case will be placed in a aluminized polyester bag and vacuum sealed for continued storage at -80 °C until sold.

## 3. Homogeneity Assessment and Value Assessment, NIST Charleston

A total of 568 jars of SRM 2983 were produced and a representative set of jars was selected for trace element homogeneity assessment and value assessment. Total arsenic, selenium, cadmium, and lead were determined at NIST Charleston using an inductively coupled plasma tandem mass spectrometric (ICP-MS/MS) method. Total mercury was determined at NIST Charleston using direct combustion atomic absorption spectrometry (DC AAS).

### 3.1. Materials

Ten jars were used for homogeneity assessment: the first and last jars of the first bottling, six randomly selected jars from the first bottling, and two randomly selected jars from the second bottling. One jar at a randomly selected position within a case was chosen from six different randomly selected cases containing the original bottling. One jar at a randomly selected position within a case was chosen from two of the three cases containing the second bottling.

One unit of each SRM 3100 series single-element standard solution listed in Table 1 was obtained from the Office of Reference Materials (ORM). Bismuth (Bi) (1000 mg/kg; Lot 1129902) single element standard solution was obtained from High Purity Standards, North Charleston, South Carolina.

**Table 1.** SRM Single-Element Standard Solutions.

Materials used to make custom spike, calibration, and internal standard stock solutions.

| SRM | Description | Lot No. | Mass Fraction ± $U_{95}$ mg/kg |
|---|---|---|---|
| 3103a | Arsenic (As) Standard Solution | 100818 | 9999 ± 15 |
| 3108 | Cadmium (Cd) Standard Solution | 130116 | 10007 ± 27 |
| 3124a | Indium (In) Standard Solution | 110516 | 10009 ± 23 |
| 3128 | Lead (Pb) Standard Solution | 101026 | 9995 ± 14 |
| 3133 | Mercury (Hg) Standard Solution | 160921 | 10004 ± 40 |
| 3149 | Selenium (Se) Standard Solution | 100901 | 10042 ± 51 |
| 3167 | Yttrium (Y) Standard Solution | 120314 | 9993 ± 25 |

### 3.2. Control Material

One unit of SRM 1566b Oyster Tissue, obtained from ORM, was used as the control material. The calculated measured trace element mass fractions for SRM 1566b were converted to a dry mass basis using 4.8 % water content ($n$ = 4, RSD = 3.34 %) dried by vacuum desiccation.

### 3.3. Blanks

The procedural blanks for the analysis of SRM 2983 were processed and measured concurrently with the samples. The mass fractions of the analytes in SRM 2983 and control samples were blank corrected by subtracting the mean of the procedural blank measurements.

## 3.4. Analytical Analysis

### 3.4.1. Arsenic, Cadmium, Lead, and Selenium

#### 3.4.1.1. Sample Preparation

All SRM 2983 material, control material, and procedural blank preparations were weighed by difference using a four-place balance that had been internally calibrated and checked using external weights prior to use. A mixed internal standard (IS) stock solution was made with Y (0.9126 mg/kg), In (0.9173 mg/kg), and Bi (0.8148 mg/kg). Samples (≈ 0.35 g SRM 2983 and 0.25 g SRM 1566b) and IS stock solution (≈ 0.25 g for SRM 2983 and procedural blanks; 0.5 g for SRM 1566b) were digested in acid-cleaned quartz microwave vessels with 5 mL of high purity nitric acid ($HNO_3$, Fisher Scientific, Suwanee, GA) and 1 mL of high purity hydrogen peroxide ($H_2O_2$, 30 % mass fraction in water, Fluka, Sigma-Aldrich, St. Louis, MO). Microwave digestion was carried out in an Anton Paar (Ashland, VA) Multiwave 3000 microwave, using the following program: 600 watts of power, 10 min ramp and 5 min hold; and 1400 watts of power, 5 min ramp and 20 min hold.

After microwave digestion and cooling, the digests were handled quantitatively and gravimetrically transferred. SRM 2983 and procedural blank samples were transferred to 50 mL acid-cleaned polypropylene centrifuge tubes, diluted to ≈ 50 g using high-purity deionized water, and weighed. Half of each sample solution was then transferred into another acid-cleaned 50 mL polypropylene centrifuge tube and weighed; spiked (approximately 0.1 g for procedural blanks and 0.44 g for SRM 2983) with the multi-element custom spike solution described in Table 2 and weighed. Each tube was diluted back to approximately 50 g with high-purity deionized water and weighed.

**Table 2.** Nominal Mass Fractions (µg/kg) of Custom Multi-element Spikes.

| Element | Procedural Blanks and SRM 2983 µg/kg | SRM 1566b µg/kg |
|---|---|---|
| Arsenic | 2563.12 | 5356.24 |
| Selenium | 1009.53 | 1710.62 |
| Cadmium | 669.68 | 1992.53 |
| Lead | 124.73 | 259.89 |

SRM 1566b samples were transferred to 125 mL acid-cleaned low-density polyethylene (LDPE) bottles, approximately 5 g of $HNO_3$ was added to maintain 5 % (*v*/*v*) final acid concentration for analysis, diluted to approximately 100 g using high purity deionized water, and weighed. Half of each sample solution was then transferred into another acid-cleaned 125 mL LDPE bottle and weighed, spiked with approximately 0.44 g multi-element custom spike solution described in Table 2 and weighed. Each tube was diluted back to approximately 100 g with high-purity deionized water and weighed. A portion of the unspiked and spiked SRM 1566b samples was transferred to acid-cleaned 50 mL polypropylene centrifuge tubes prior to analysis to fit in the instrument auto-sampler racks.

### 3.4.1.2. ICP-MS/MS Measurements with Single-Point Standard Additions

An analytical quantification and validation scheme using the method of single-point standard additions was employed for trace element mass fraction measurements in SRM 2983, SRM 1566b, and procedural blank samples. Single-point standard additions methods mitigate matrix effects by splitting a single sample and spiking one of the sample splits, to maintain matrix matching. The custom multi-element spike solutions were prepared from SRM 3100 series single element standard solutions to spike samples at approximately 3 to 4 times that of the native mass fraction of the trace element in the unspiked sample.

An Agilent 8800 QQQ-ICP-MS system (Agilent, Santa Clara, CA) was used for measuring the analytical samples and blanks. The instrument working conditions were optimized prior to data collection by running a plasma condition performance test followed by tuning with 1 ng/g As, Se, Cd, and Pb, and 1 ng/g Y, In, and Bi solutions. The signals were monitored in no gas mode, oxygen mass shift mode, and helium reaction gas mode for the isotopes of interest listed in Table 3. The specific MS/MS chemical transitions using oxygen mass shift mode listed reflect measurement of the trace element isotopes and the internal standards as the corresponding oxides,+16 *m*/*z* units higher than their native *m*/*z* state.

**Table 3.** Tandem MS Chemical Transitions for Measured Analyte Isotopes.

| Element | Mode | Q1 *m*/*z* | Q2 *m*/*z* |
|---|---|---|---|
| As | He Gas | 75 | 75 |
| | $O_2$ Gas | 75 | 91 |
| Se | He Gas | 78, 80 | 78, 80 |
| | $O_2$ Gas | 78, 80 | 94, 96 |
| Y | No gas, He gas | 89 | 89 |
| | $O_2$ Gas | 89 | 105 |
| Cd | No gas, He and $O_2$ gas | 111, 112, 113, 114 | 111, 112, 113, 114 |
| In | No gas, He and $O_2$ gas | 115 | 115 |
| Pb | No gas, He and $O_2$ gas | 206, 207, 208 | 206, 207, 208 |
| Bi | No gas, He and $O_2$ gas | 209 | 209 |

### 3.4.1.3. Results and Discussion

All mass fraction results in tables, figures, and uncertainty budgets are presented in units of dry mass fraction (μg/kg) for SRM 1566b and wet mass fraction (μg/kg) for SRM 2983. The elements of interest were run in multiple ICP-MS/MS modes as an internal quality check on the data generated for each mode of operation. Reported results for each element were selected by which isotope and instrument mode optimized reducing interferences and offered the greatest sensitivity. Oxygen mass shift mode was utilized to mitigate interferences such as $ArCl^+$ and rare earth element dimers ($^{150}Nd^{++}$ and $^{150}Sm^{++}$) on $^{75}As$; and $^{40}Ar_2^+$ on the native $^{78,80}Se$ envelope. Helium collision mode was utilized for Cd isotopes to remove potential interferences by $MoO^+$. Yttrium was chosen as the IS for As and Se calculations due to its proximity in atomic mass to these elements and high oxide ($YO^+$) formation efficiency. Indium was chosen as the IS for Cd and Bi was chosen as the IS for Pb due to their close proximity in atomic mass. The mass fractions of trace elements in SRM 2983 samples, control material, and procedural blanks were calculated using the following measurement function:

$$F_{\text{sample}} = R_{\text{u}}\left(\frac{\left({}^{m_{\text{sp}}F_{\text{sp}}}\!/_{m_{\text{spsolu}}}\right)}{R_{\text{sp}}-R_{\text{u}}}\right)\left(\frac{m_{\text{solu}}}{m_{\text{sample}}}\right) \quad (1)$$

where: $F_{\text{sample}}$ is the mass fraction,
$m_{\text{sample}}$ is the mass of the sample,
$m_{\text{solu}}$ is the mass of the solution after digestion and dilution,
$m_{\text{spsolu}}$ is the mass of the solution transferred for spiking,
$F_{\text{sp}}$ is the mass fraction of the spike,
$m_{\text{sp}}$ is the mass of the spike,
$R_{\text{sp}}$ is analyte/IS signal ratio for spiked solution, and
$R_{\text{u}}$ is analyte/IS signal ratio for unspiked solution.

Measurement uncertainties were estimated according to ISO/JCGM guidelines [4]. The standard uncertainty expressed as a 95 % confidence interval was calculated for each element by:

$$u = \sqrt{\frac{A_1^2}{n_1} + \frac{A_2^2}{n_2} + B_1^2 + B_2^2};\ U_{95} = ku \quad (2)$$

where: $u$ is the combined standard uncertainty,
$A_1$ is the uncertainty for $n_1$ replicate measurements of control and SRM material,
$A_2$ is the uncertainty for $n_2$ blank measurements,
$B_1$ is the standard uncertainty of the weighing measurements,
$B_2$ is the standard uncertainty of the SRM 3100 series elemental standard, and
$k$ is the coverage factor.

Table 4 outlines the components of uncertainty considered.

**Table 4.** Summary of Components of Uncertainty for Trace Elements.

| Source | Basis | Type | Degrees of Freedom |
|---|---|---|---|
| Replication | Standard uncertainty of sample measurement based on replicate measurements | A | 5, 9, or 12 |
| Blank correction | Standard uncertainty of blank correction | A | 7 |
| Weighing | Standard uncertainty of calibration, drift (temporal and electrostatic) and relative impact on weighing measurements: estimated at 0.1 % relative | B | large |
| SRM 3100 series | Standard uncertainty of SRM 3100 standard | B | 12 to 1298 |

Data for the eight procedural blanks is summarized in Table 5. The mass fractions of the analytes in SRM 2983 and control samples were blank corrected by subtracting the mean of the procedural blank measurements. The standard uncertainty of the mean, $u$(Mean), is estimated as the standard deviation (SD) divided by the square root of the number of replicates: $u = \text{SD}/\sqrt{8}$.

**Table 5.** Trace Element Mass Fractions (µg/kg, wet mass) in Procedural Blanks.

| Blank | $^{75}$As | $^{78}$Se | $^{111}$Cd | $^{206+207+208}$Pb |
|---|---|---|---|---|
| 1 | 0.93 | 1.76 | 0.03 | 0.05 |
| 2 | 2.79 | 1.81 | 0.06 | 0.14 |
| 3 | 2.51 | 0.36 | 0.05 | 0.09 |
| 4 | 2.21 | 1.62 | 0.01 | 0.20 |
| 5 | 3.01 | 0.62 | 0.01 | 0.20 |
| 6 | 2.82 | 1.93 | 0.08 | 0.15 |
| 7 | 3.13 | 3.82 | 0.10 | 0.07 |
| 8 | 2.44 | 1.33 | 0.05 | 0.06 |
| Mean | 2.48 | 1.65 | 0.05 | 0.12 |
| SD | 0.70 | 1.04 | 0.03 | 0.06 |
| *u*(Mean) | 0.25 | 0.37 | 0.01 | 0.02 |

Measurement results and the uncertainty budget for each element measured in the SRM 1566b control material are outlined in Table 6. The measured mass fraction results and the certified values for the elements measured are compared in Fig. 4. The measured and certified values for the control material are in excellent agreement. This suggests that the analysis procedure is providing accurate results for these elements.

**Table 6.** Summary of Trace Element Results (µg/kg, dry mass) for SRM 1566b.

| SRM1566b | $^{75}$As | $^{78}$Se | $^{111}$Cd | $^{206+207+208}$Pb |
|---|---|---|---|---|
| Replicate 1 | 7682 | 1973 | 2522 | 305 |
| Replicate 2 | 7587 | 1901 | 2494 | 304 |
| Replicate 3 | 7590 | 1954 | 2495 | 312 |
| Replicate 4 | 7610 | 2183 | 2474 | 300 |
| Replicate 5 | 7680 | 1991 | 2489 | 304 |
| Replicate 6 | 7605 | 1970 | 2510 | 305 |
| Determined Value | 7626 | 1995 | 2497 | 305 |
| Standard Deviation | 44 | 97 | 17 | 4 |
| RSD | 0.6 % | 4.9 % | 0.7 % | 1.4 % |
| Uncertainty Budget, µg/kg | | | | |
| Replication (Type A) | 18 | 40 | 6.8 | 1.7 |
| Blank (Type A) | 0.25 | 0.37 | 0.010 | 0.020 |
| Weighing (Type B) | 7.6 | 2.0 | 2.5 | 0.3 |
| SRM 3100 Series (Type B) | 5.7 | 5.0 | 3.4 | 0.2 |
| *u* | 20 | 40 | 8.1 | 1.7 |
| Effective Degrees of Freedom | 8.3 | 5.2 | 9.6 | 5.5 |
| Coverage Factor | 2.3 | 2.6 | 2.3 | 2.6 |
| $U_{95}$ | 47 | 103 | 18 | 4.4 |
| Certified Value ± $U_{95}$ | 7650 ± 650 | 2060 ± 150 | 2480 ± 80 | 308 ± 9 |

The individual sample mass fractions determined for the elements measured in SRM 2983 are displayed in Fig. 5 as functions of Jar-order. There is little or no indication of Jar-order trends, nor of systematic differences between material from the two bottling sessions.

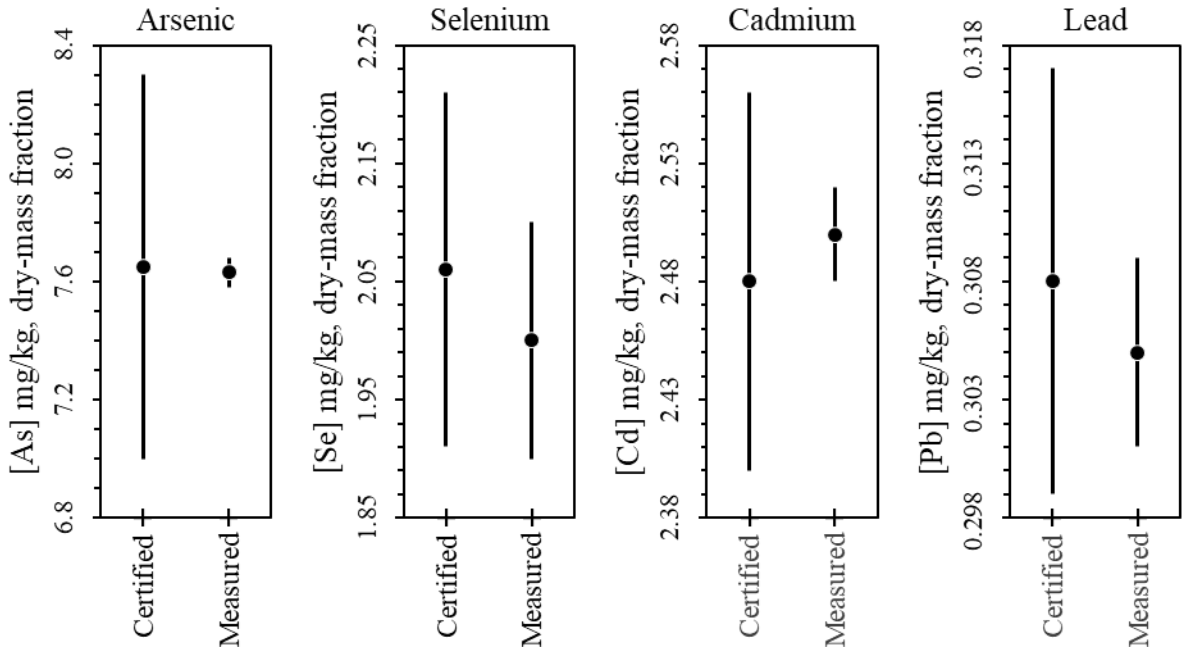



**Fig. 4.** Comparison of Certified and Measured Mass Fraction Values for SRM 1566b.

Dots represent the certified values and the means of the measured values. Bars represent approximate 95 % level of confidence intervals.

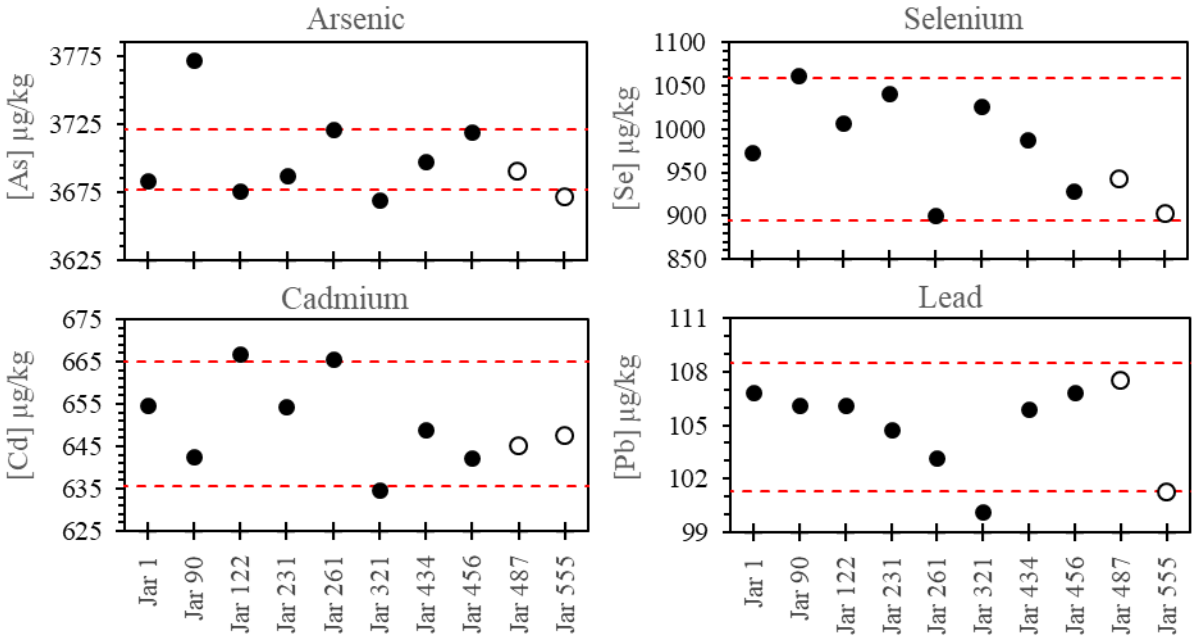



**Fig. 5.** Measured Mass Fraction Values for the individual Jars of SRM 2983.

Solid circles represent measurements of the material in jars from the initial bottling. Open circles represent measurements of the materials in jars from the second bottling. Dashed horizontal lines bound an approximate 95 % level of confidence interval about the mean measured value.

The measurement results and summary statistics for As, Se, Cd, and Pb in SRM 2983 are shown in Table 7. The between-jar relative precision, 100·SD/Mean, for the ten replicate measurements was 0.9 %, 5.9 %, 1.6 %, and 2.4 % for these four elements; the relative 95 % level of confidence uncertainties, $100 \cdot U_{95}$/Mean, are 0.6 %, 4.3 %, 1.2 %, and 1.7 %. These values suggest that the As, Se, Cd, and Pb mass fractions in the SRM 2983 material are acceptably homogenous.

**Table 7.** Summary of Trace Element Results (µg/kg, dry mass) for SRM 2983.

| SRM 2983 | $^{75}$As | $^{78}$Se | $^{111}$Cd | $^{206+207+208}$Pb |
|---|---|---|---|---|
| Jar 1 | 3683 | 973 | 655 | 107 |
| Jar 90 | 3772 | 1063 | 642 | 106 |
| Jar 122 | 3676 | 1007 | 667 | 106 |
| Jar 231 | 3687 | 1041 | 655 | 105 |
| Jar 261 | 3721 | 901 | 666 | 103 |
| Jar 321 | 3669 | 1027 | 635 | 100 |
| Jar 434 | 3698 | 987 | 649 | 106 |
| Jar 456 | 3719 | 929 | 642 | 107 |
| Jar 487 | 3691 | 943 | 645 | 108 |
| Jar 555 | 3672 | 902 | 648 | 101 |
| Determined Value | 3699 | 977 | 650 | 105 |
| Standard Deviation | 31 | 58 | 10 | 2.5 |

Uncertainty Budget, µg/kg

| | | | | |
|---|---|---|---|---|
| Replication (Type A) | 9.89 | 18.19 | 3.26 | 0.80 |
| Blank (Type A) | 0.25 | 0.37 | 0.01 | 0.02 |
| Weighing (Type B) | 3.70 | 0.98 | 0.65 | 0.10 |
| SRM 3100 Series (Type B) | 2.76 | 2.46 | 0.89 | 0.07 |
| $u$ | 10.92 | 18.39 | 3.44 | 0.81 |
| Effective Degrees of Freedom | 13.35 | 9.39 | 11.19 | 9.48 |
| Coverage Factor | 2.16 | 2.26 | 2.20 | 2.26 |
| $U_{95}$ | 23.59 | 41.59 | 7.57 | 1.83 |

### 3.4.2. Mercury

#### 3.4.2.1. Direct Combustion Atomic Absorption Spectrometry

The mass fraction of total Hg was determined with a direct Hg analyzer DMA 80 (Milestone Scientific, Shelton, CT) by external calibration. The external calibration curve was prepared on 22 February 2018 by gravimetrically aliquoting different masses of aqueous dilutions of SRM 3133 Mercury Standard Solution into quartz sample boats. Mercury was measured in SRM 2983 and SRM 1566b samples by weighing approximately 100 mg of material into pre-cleaned nickel weigh boats and placing them into the instrument auto-sampler rotor. SRM 1566b and procedural blanks (empty nickel weigh boat) were bracketed between blocks of two to four unknown Hg mass fraction SRM 2983 samples to verify instrument calibration and monitor instrumental drift. The following outlines the method parameters used for the sample analysis:

Aqueous Solution (SRM 3133 calibration curve)
90 s ramp to 200 °C; 30 s hold
90 s ramp to 650 °C; 180 s hold

Mollusc Material (SRM 1566b, SRM 2983, and procedural blanks)
30 s ramp to 200 °C, 30 s hold
60 s ramp to 300 °C; 60 s hold
60 s ramp to 450 °C; 30 s hold
60 s ramp to 650 °C; 240 s hold

#### 3.4.2.2. Results and Discussion

External calibration curves (peak area versus Hg ng) were constructed using SRM 3133. A second order fit was applied to the long path cell (cell 1) and short path cell (cell 2) data to account for an asymptotic or slight rollover effect due to non-ideal Beer-Lambert Law behavior. Coefficients resulting from the second order fit and the instrument signal (peak area) were used to solve the quadratic equation to calculate the mass of Hg in SRM 2983, SRM 1566b, and procedural blank samples.

The following functional relationship was used to calculate each of the individual DC AAS mass fraction results:

$$C_S = \left[\left(\left(\frac{-b \pm \sqrt{b^2 - 4a(c-y)}}{2a}\right)/W\right) - B_C\right] / D_C \qquad (3)$$

where: $C_S$ is the dry mass fraction of mercury in the sample (µg/kg).
$a, b, c$ are the coefficient constants of the calibration curve quadratic fit.
$y$ is the peak area of the DC AAS absorbance (AU).
$W$ is the mass of sample aliquot taken (g).
$B_C$ is the mean measured blank (µg/kg).
$D_C$ is the wet-dry mass correction factor (unitless) (SRM 1566b only).

Measurement uncertainties were estimated according to ISO/JCGM guidelines [4]. The standard uncertainty expressed as a 95 % confidence interval was calculated for each element by:

$$u = \sqrt{\frac{A_1^2}{n_1} + \frac{A_2^2}{n_2} + B_1^2 + B_2^2};\ U_{95} = ku \qquad (4)$$

where: $u$ is the combined standard uncertainty,
$A_1$ is the uncertainty for $n_1$ replicate measurements of control and SRM material,
$A_2$ is the uncertainty for $n_2$ blank measurements,
$B_1$ is the standard uncertainty of the weighing measurements,
$B_2$ is the standard uncertainty of SRM 3133 Hg elemental standard, and
$k$ is the coverage factor.

Table 4 outlines the components of uncertainty considered.

The mass fractions of Hg in procedural blanks were very low with a mean of 0.03 µg/kg. Data for the eight procedural blanks is summarized in Table 8. The mass fractions of the analytes in SRM 2983 and control samples were blank corrected by subtracting the mean of the procedural blank measurements. The standard uncertainty of the mean, *u*(Mean), is estimated as the standard deviation (SD) divided by the square root of the number of replicates: $u = \mathrm{SD}/\sqrt{8}$.

**Table 8.** Trace Element Mass Fractions (µg/kg, wet mass) in Procedural Blanks.

| Blank | Hg |
|---|---|
| 1 | 0.055 |
| 2 | 0.050 |
| 3 | 0.033 |
| 4 | 0.025 |
| 5 | 0.018 |
| 6 | 0.020 |
| 7 | 0.014 |
| 8 | 0.004 |
| Mean | 0.027 |
| SD | 0.017 |
| *u*(Mean) | 0.006 |

Measurement results and the uncertainty budget for Hg measured in the SRM 1566b control material are outlined in Table 9. The measured mass fraction results are compared with the certified value for Hg in SRM 1566b. As shown in Fig. 6, the measured and certified values for the control material are in good agreement. This suggests that the analysis procedure is providing accurate results for Hg.

**Table 9.** Summary of Mercury Results for SRM 1566b.

| SRM1566b | Hg (µg/kg, dry mass) |
|---|---|
| Replicate 1 | 37.6 |
| Replicate 2 | 38.0 |
| Replicate 3 | 37.4 |
| Replicate 4 | 37.4 |
| Replicate 5 | 36.3 |
| Replicate 6 | 37.8 |
| Replicate 7 | 36.4 |
| Replicate 8 | 36.9 |
| Replicate 9 | 36.0 |
| Replicate 10 | 36.9 |
| Replicate 11 | 36.4 |
| Replicate 12 | 36.3 |
| Replicate 13 | 36.6 |
| Determined Value | 36.9 |
| Standard Deviation | 0.7 |
| RSD | 1.8 % |

Uncertainty Budget, µg/kg

| | |
|---|---|
| Replication (Type A) | 0.18 |
| Blank (Type A) | 0.01 |
| Weighing (Type B) | 0.04 |
| SRM 3133 (Type B) | 0.07 |
| $u$ | 0.20 |
| Effective Degrees of Freedom | 16.69 |
| Coverage Factor | 2.12 |
| $U_{95}$ | 0.42 |

| | |
|---|---|
| Certified Value ± $U_{95}$ | 37.1 ± 1.3 |

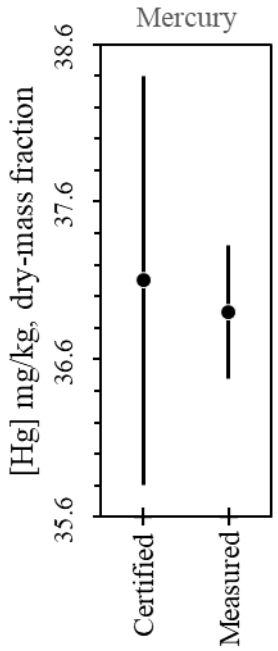



**Fig. 6.** Comparison of Certified and Measured Mercury Mass Fraction Values for SRM 1566b.

Dots represent the certified values and the means of the measured values. Bars represent approximate 95 % level of confidence intervals.

The individual sample mass fractions determined for Hg measured in SRM 2983 are displayed in Fig. 7 as a function of jar order.

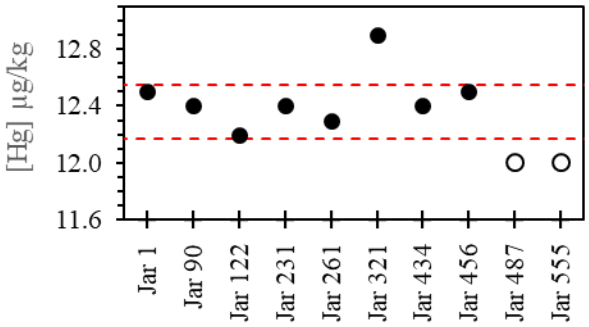



**Fig. 7.** Measured Mass Fraction Values for the individual Jars of SRM 2983.

Solid circles represent measurements of the material in jars from the initial bottling. Open circles represent measurements of the materials in jars from the second bottling. Dashed horizontal lines bound an approximate 95 % level of confidence interval about the mean measured value.

The measurement results and summary statistics for Hg in SRM 2983 are shown in Table 10. The between-jar relative precision, 100·SD/Mean, for the ten replicate measurements was 2.1 % for Hg; the relative 95 % level of confidence uncertainties, 100·$U_{95}$/Mean, is 1.5 %. These values suggest that the Hg mass fraction in the SRM 2983 material is acceptably homogenous.

**Table 10.** Summary of Mercury Results for SRM 2983.

Measurements, µg/kg, wet mass fraction

| SRM 2983 | Hg |
|---|---|
| Jar 1 | 12.5 |
| Jar 90 | 12.4 |
| Jar 122 | 12.2 |
| Jar 231 | 12.4 |
| Jar 261 | 12.3 |
| Jar 321 | 12.9 |
| Jar 434 | 12.4 |
| Jar 456 | 12.5 |
| Jar 487 | 12.0 |
| Jar 555 | 12.0 |
| Determined Value | 12.4 |
| Standard Deviation | 0.3 |

Uncertainty Budget, µg/kg

| | |
|---|---|
| Replication (Type A) | 0.08 |
| Blank (Type A) | 0.01 |
| Weighing (Type B) | 0.01 |
| SRM 3133 (Type B) | 0.02 |
| $u$ | 0.08 |
| Effective Degrees of Freedom | 11.08 |
| Coverage Factor | 2.20 |
| $U_{95}$ | 0.19 |

## 3.5. Metrological Traceability

Traceability to the International System of Units (SI) derived unit of mass fraction for the measured trace element content was achieved through calibration with gravimetric preparations of SRM 3100 series single-element primary standard solutions and validation with SRM 1566b Oyster Tissue.

# 4. Arsenic, NIST Gaithersburg

Total arsenic in SRM 2983 was determined at NIST Gaithersburg using an inductively coupled plasma mass spectrometric (ICP-MS) method.

## 4.1. Materials

Six jars of SRM 2983 were obtained from the NIST Biorepository in Charleston, South Carolina and stored in a -80°C freezer. One bottle of SRM 1566b Oyster Tissue obtained from ORM was used for quality assurance.

Optima grade nitric acid ($HNO_3$) and Fisher brand ACS Reagent grade hydrogen peroxide ($H_2O_2$, Fisher Scientific, Suwanee, GA) were used for sample preparation. Locally prepared sub-boiling distilled water was used as a solvent in the preparation of samples, standards, and dilute acids. The concentration of a dilute acid is expressed as the volume fraction of the acid relative to the solution. The following reference materials were used as calibrants:

As: SRM 3103a Arsenic (As) Standard Solution, Lot 100818
Rh: SRM 3144 Rhodium (Rh) Standard Solution, Lot 070619

## 4.2. Equipment

An Agilent model 8800 triple quadrupole (QQQ) ICP-MS was used for elemental measurements. A Mettler model AT261 Delta Range analytical balance (Mettler-Toledo, LLC, Columbus, OH) was used for weighing during the preparation of samples and standards. The balance is serviced and calibrated annually by Mettler. Prior to use, calibration of the balance was verified using standard masses ranging from 0.5 g to 20 g that are traceable to the SI through the standard mass set maintained by the Chemical Sciences Division. A Fisher Scientific Isotemp oven, model number 737F, was used to carry out drying studies. A CEM (Matthews, NC) model MARS5 microwave system equipped with EasyPrep TFM™ microwave vessels was used to digest the geoduck and control samples.

## 4.3. Sample Preparation

Six jars of SRM 2983 were transferred from the freezer onto a bench in the laboratory for equilibration with the room temperature at 21 °C. After 5 h of thawing, approximately 1 g sample from each jar was weighed into a pre-cleaned EasyPrep microwave vessel. Three SRM 1566b samples each weighing approximately 1 g were transferred into three pre-cleaned EasyPrep microwave vessels. After 8 mL of $HNO_3$ was added, each vessel was loosely capped, and the contents were allowed to react overnight at room temperature. Three procedure blanks were prepared similarly.

The vessel was capped the next day after 1 mL of $H_2O_2$ was added. The samples were microwaved using a power of 1600 W, 25 min ramp time to 220 °C, and held for 15 min. The contents were quantitatively transferred to 60 mL LDPE bottles and diluted to 50 g with water. A 5 g aliquot of the digest and 0.5 g of a solution containing 0.5 mg/kg Rh as an internal standard were transferred to a 60 mL LDPE bottle, and the contents were diluted to 50 g with water to constitute an unspiked sample. A spiked sample was prepared by weighing 25 g of the unspiked

sample and 0.5 g of a standard containing 0.75 mg/kg As into a 30 mL LDPE bottle. The unspiked and spiked samples and controls were used for the quantification of As by the method of standard addition.

Separately, four 1 g portions from the bottle of SRM 1566b were transferred into four pre-weighed glass weighing vessels of 20 mm internal diameter. The samples in the weighing vessels were weighed and then dried over magnesium perchlorate in a desiccator. After 5 d, the weighing vessels were capped and the masses of their contents were weighed. The difference of the masses before and after drying was used to determine the moisture content of the sample.

## 4.4. Measurements

All measurements were made in tandem mass spectrometry (MS/MS) mode using the Spectrum setting of the Agilent 8800 QQQ-ICP-MS. Arsenic was measured at 91 *m*/*z* as $AsO^+$ while the internal standard Rh was measured on-mass at 103 *m*/*z*.

## 4.5. Results and Discussion

Table 11 lists the results and measurement uncertainty of arsenic in SRM 2983.

**Table 11.** Results and Measurement Uncertainty of As in SRM 2983.

| | Total Arsenic, µg/g |
|---|---|
| Jars 1 to 6 | 3.51, 3.62, 3.65, 3.88, 3.77, 3.50 |
| Average | 3.66 |
| SD | 0.15 |
| RSD | 4.1 % |

| Uncertainty Budget | |
|---|---|
| $u_{reps}$ | 0.061 |
| $u_{repb}$ | 0.0022 |
| Calibrant ($B_1$) | 0.0027 |
| Weighing ($B_2$) | 0.00049 |
| $u$ | 0.061 |
| $V_{eff}$ | 5 |
| $k$ | 2.57 |
| $U$ | 0.16 |

The mass fraction of the analyte was calculated according to the method of standard addition:

$$x = \frac{usp}{sp - usp} \times \frac{w_{sp}}{w_{sa}} \times C \times dil \qquad (5)$$

where $x$ is the mass fraction of the analyte in the sample; *sp* and *usp* are the internal-standard corrected count rate of the spiked and the unspiked measurement samples; $w_{sa}$ and $w_{sp}$ are the mass of the sample and the mass of the spike solution; $C$ and *dil* are the mass fraction of the analyte in the spike solution and the dilution factor of the sample.

The uncertainty of the measurement is calculated using the following:

$$U_{95} = k\sqrt{u_{\text{reps}}^2 + u_{\text{repb}}^2 + B_1^2 + B_2^2} \quad (6)$$

where *k* is the coverage factor from Student's *t* table for a 95 % level of confidence with the associated degrees of freedom.

Table 12 summarizes the sources of measurement uncertainty for As in SRM 2983. Table 13 lists the mass of As found in the procedure blanks. Table 14 lists the results for the determination of moisture in samples of SRMs 1566b.

**Table 12.** Summary of Components of Uncertainty for Arsenic in SRM 2983.

| Source | Basis | Type | Degrees of Freedom |
|---|---|---|---|
| Replication of Samples, $u_{\text{reps}}$ | Standard uncertainty of replicate ICP-MS measurements of SRM 2983 samples | A | 5 |
| Replication of Blanks, $u_{\text{repb}}$ | Standard uncertainty of replicate ICP-MS measurements of procedural blanks | A | 2 |
| Calibrant, $B_1$ | Expanded uncertainty of the primary standard converted to standard uncertainty. | B | large |
| Weighing, $B_2$ | Estimated 0.08 mg weighing uncertainty due to the calibration of the balance used for weighing mass of the samples [5], assuming uniform distribution, normalized by dividing by √3. | B | large |

**Table 13.** Mass of Arsenic in Procedural Blanks.

| | Arsenic, ng |
|---|---|
| Blanks 1 to 3 | 2.08, 9.09, 9.64 |
| Average | 6.93 |
| SD | 4.21 |
| RSD | 61 % |

**Table 14.** Dry Mass Fraction in As-received Samples of SRM 1566b.

| Sample | As received g | Moisture g | Dry Mass % |
|---|---|---|---|
| 1 | 1.0246 | 0.0564 | 94.50 |
| 2 | 1.1857 | 0.0592 | 95.01 |
| 3 | 1.0044 | 0.0505 | 94.97 |
| 4 | 0.9949 | 0.0523 | 94.74 |
| | | Average | 94.80 |
| | | SD | 0.24 |

Arsenosugars were found to be the primary species of As in geoduck samples. Arsenosugars would not decompose to arsenate at mild microwave conditions that were sufficient to digest the geoduck sample [6], which can result in measurement bias when SRM 3103a was used as the calibrant [7]. Therefore, a vigorous microwave digestion method was used primarily to facilitate the conversion of arsenic species.

## 4.6. Quality Assurance

Table 15 lists the results for SRM 1566b used as a control for the measurement.

**Table 15.** Measured Results and Certified Values of As in SRM 1566b.

| | Arsenic, ng |
|---|---|
| Samples 1 to 3 | 7.44, 7.65, 7.46 |
| Average | 7.52 |
| SD | 0.12 |
| $U_{95}$ | 0.29 |
| RSD | 1.6 % |

The measured values are compared to the certified value, (7.65, $U_{95}$ = 0.65) mg/kg, in Fig. 8. The uncertainty interval of the measured values overlaps the target values, suggesting that there is no detectable bias in the measurement of the analyte.

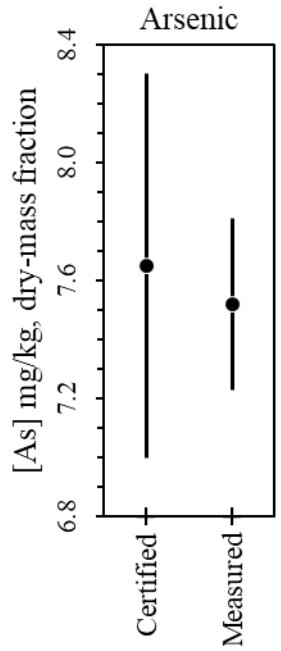



**Fig. 8.** Comparison of Certified and Measured Mass Fraction Values for SRM 1566b.

Dots represent the certified values and the means of the measured values. Bars represent approximate 95 % level of confidence intervals.

## 4.7. Metrological Traceability

Traceability to the SI derived unit of mass fraction for the measured trace element content was achieved through calibration with gravimetric preparations of SRM 3100 series single-element primary standard solutions and validation with SRM 1566b Oyster Tissue.

# 5. Inorganic Arsenic (iAs), NIST Gaithersburg

Inorganic arsenic (iAs) in SRM 2983 was determined at NIST Gaithersburg using a liquid chromatography inductively coupled plasma mass spectrometric (LC-ICP-MS) method.

## 5.1. Materials

Six jars of SRM 2983 and one bottle of SRM 1568b Rice Flour were obtained from ORM. Jars of SRM 2983 were stored in a -80 °C freezer until use.

Optima grade $HNO_3$, Fisher brand ACS Reagent grade $H_2O_2$, and Puratronic grade ammonium carbonate were purchased from Fisher Scientific. Locally prepared sub-boiling distilled water was used as a solvent in the preparation of samples, standards, and dilute acids. The concentration of a dilute acid is expressed as the volume fraction of the acid relative to the solution. The following reference materials were used as calibrants:

SRM 3036 Arsenic Acid (AsV) Standard Solution
SRM 3030 Monomethylarsonic Acid Standard Solution

## 5.2. Equipment

A PerkinElmer LC system (PerkinElmer, Shelton, CT) coupled to a PerkinElmer model Elan DRC II ICP-MS was used. Set up and optimization of the ICP-MS was performed daily. The LC system consisted of a Peltier-cooled Series 200 autosampler and a Series 200 quaternary pump. Separation of As species was performed using a PRP-X100 anion exchange column from Hamilton (Hamilton Company, Reno, NV). A Mettler model AT261 Delta Range analytical balance was used for weighing during the preparation of samples and standard. The balance is serviced and calibrated annually by Mettler. Prior to use, calibration of the balance was verified using standard masses ranging from 0.5 g to 50 g that are traceable to the SI through the standard mass set maintained by the Chemical Sciences Division. A Fisher Scientific Isotemp oven, model number 737F, was used to carry out drying studies.

## 5.3. Sample Preparation

Jars of SRM 2983 were transferred from the freezer into a Styrofoam box containing dry ice. Approximately 1 g sample from each jar was weighed into a 50 mL tube while frozen. Four 0.5 g portions of SRM 1566b were weighed into four 50 mL tubes. A 5 mL solution containing 0.2 mol/L $HNO_3$ and 6 % volume fraction $H_2O_2$ in water was added to each tube, and water was used to bring the overall added solution to 10 g. Four procedural blanks were prepared similarly. The samples and the blanks were loosely capped and transferred to an oven preheated to 90 °C.

The samples and blanks were removed from the oven after 3 h. After the temperature was equilibrated to room temperature (21 °C), the samples were centrifuged at 419 rad/s (4000 RPM) in a Jouan model C312 centrifuge (ThermoFisher Scientific, Waltham, MA) for 30 min. The supernatant of a sample was transferred to a 15 mL tube. An unspiked sample was prepared by weighing 4 g of the supernatant into a 4 mL polypropylene tube containing 0.1 g of 1 mg/kg monomethylarsonic acid (MMA) serving as the internal standard. A spiked sample was prepared by weighing 0.5 g of the unspiked sample into a 0.75 mL polypropylene autosampler vial

containing 0.1 g of 0.08 mg/kg arsenate (AsV) for the purpose of calibration by the method of standard addition.

## 5.4. Measurements

Arsenic species were separated by using a PRP X-100 anion exchange column, and arsenic from each species was determined at 75 *m/z* by ICP-MS in normal mode. To separate MMA and AsV in the SRM 2983 sample material, a PRP X-100 (4.6 mm × 250 mm, 10 µm) analytical column was used with a PEEK X-100 guard column. The mobile phase was 50 mmol/L ammonium carbonate in water, pH 10, at a 1.0 mL/min flow rate [6].

## 5.5. Results and Discussion

European Standard EN 16802:2016 [8] was applied to the measurement of inorganic arsenic in the SRM 2983 material. The standard describes the determination of inorganic arsenic in seafood as AsV. A mixture of dilute nitric acid and hydrogen peroxide was employed in the standard to convert and extract inorganic arsenic in the seafood. The mixture can potentially oxidize and decompose arsenicals in the sample, which makes the quantification of species other than AsV unfavorable.

A typical chromatogram of a SRM 2983 sample spiked with MMA as an internal standard is shown in Fig. 9. The peaks of MMA and AsV are baseline resolved, but the peak of DMA is overlapped by the arsenosugar peak to the right. Arsenite (AsIII) is not observed because EN 16802:2016 protocol converts AsIII to AsV in the extraction process, and because AsIII was not detected in this work when water was used as an extraction solvent. Therefore, the AsV found in this work is the iAs in the sample. The iAs in the procedural blanks is below detection.

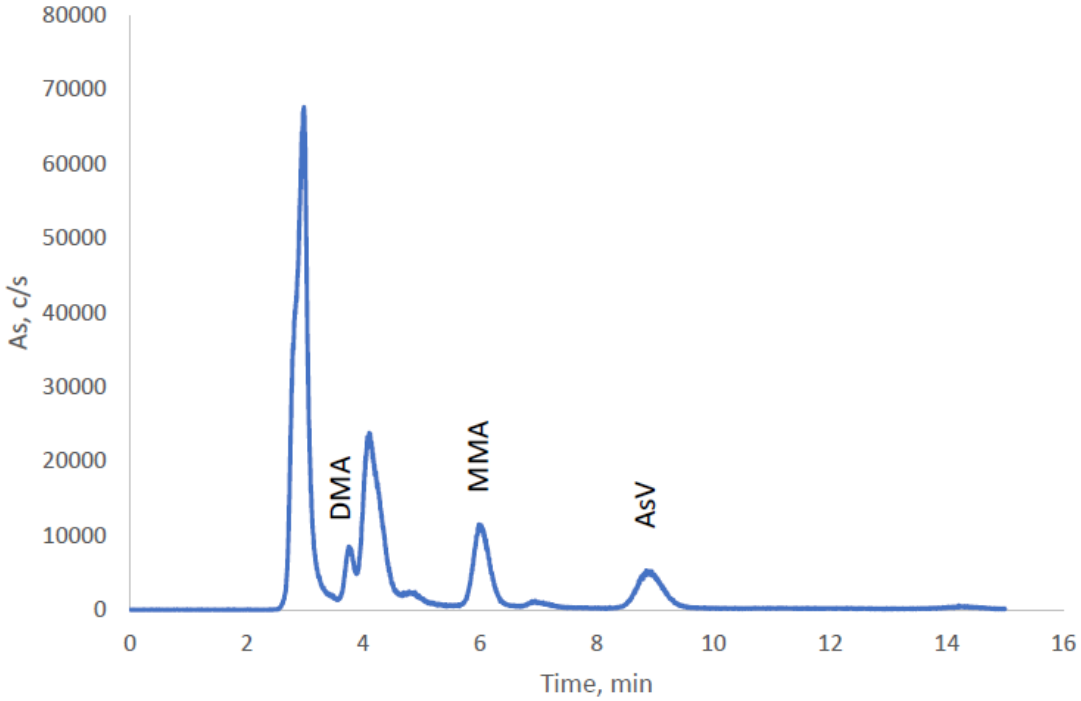



**Fig. 9.** Typical Chromatogram of a SRM 2983 Sample Spiked with MMA.

Table 16 lists the results and measurement uncertainty of AsV in SRM 2983.

**Table 16.** Results and Measurement Uncertainty of iAs in SRM 2983.

| Jar ID | iAs (mg/kg) |
|---|---|
| 1 | 0.214 |
| 2 | 0.200 |
| 3 | 0.208 |
| 4 | 0.210 |
| 5 | 0.185 |
| 6 | 0.173 |
| Average | 0.198 |
| SD | 0.016 |
| RSD | 8.3 % |

| Uncertainty Budget | |
|---|---|
| $u_{reps}$ | 0.0066 |
| Calibrant ($B_1$) | 0.00045 |
| Weighing ($B_2$) | 0.00013 |
| $u$ | 0.0067 |
| $V_{eff}$ | 5 |
| $k$ | 2.57 |
| $U_{95}$ | 0.017 |

The mass fraction of the analyte was calculated according to the method of standard addition:

$$x = \frac{usp}{sp-usp} \times \frac{w_{sp}}{w_{sa}} \times C \times dil \quad (7)$$

where $x$ is the mass fraction of the analyte in the sample; *sp* and *usp* are the internal-standard corrected count rate of the spiked and the unspiked measurement samples; $w_{sa}$ and $w_{sp}$ are the mass of the sample and the mass of the spike solution; $C$ and *dil* are the mass fraction of the analyte in the spike solution and the dilution factor of the sample.

Table 17 summarizes the sources of measurement uncertainty for iAs in SRM 2983.

**Table 17.** Summary of Components of Uncertainty for Arsenic in SRM 2983.

| Source | Basis | Type | Degrees of Freedom |
|---|---|---|---|
| Replication of Samples, $u_{reps}$ | Standard uncertainty of replicate LC-ICP-MS measurements of 6 SRM 2983 samples | A | 5 |
| Calibrant, $B_1$ | Expanded uncertainty of the primary standard converted to standard uncertainty. | B | large |
| Weighing, $B_2$ | Estimated 0.08 mg weighing uncertainty due to the calibration of the balance used for weighing mass of the samples [5], assuming uniform distribution, normalized by dividing by √3. | B | large |

The uncertainty of the measurement is calculated using the following:

$$U_{95} = k\sqrt{u_{\text{reps}}^2 + B_1^2 + B_2^2} \quad (8)$$

where *k* is the coverage factor from Student's *t* table for a 95 % level of confidence with the associated degrees of freedom.

## 5.6. Quality Assurance

Table 18 lists the results for SRM 1568b used as a control for the measurement. The certified and measured values are compared in Fig. 10. The uncertainty interval of the measured values overlaps the certified values, suggesting that there is no detectable bias in the measurement of iAs.

**Table 18.** Measured Results and Certified Values of Inorganic Arsenic in SRM 1568b.

| Sample ID | iAs (µg/kg) |
|---|---|
| Sample 1 | 99.3 |
| Sample 2 | 97.5 |
| Sample 3 | 95.8 |
| Sample 4 | 91.4 |
| Average | 96.0 |
| SD | 3.4 |
| $U_{95}$ | 5.5 |
| RSD | 3.5 % |

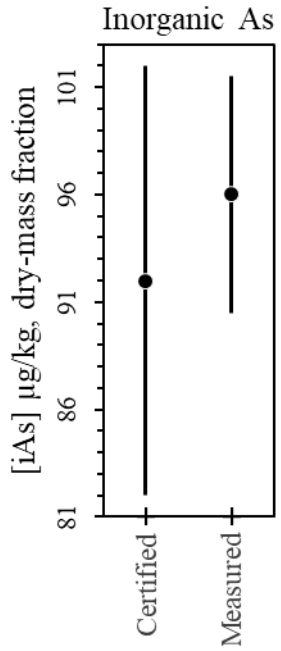



**Fig. 10.** Comparison of Certified and Measured Mass Fraction Values for SRM 1568b.

Dots represent the certified values and the means of the measured values. Bars represent approximate 95 % level of confidence intervals.

## 5.7. Metrological Traceability

Results for iAs are traceable to the SI through the SRM 3036 calibrant, validated with SRM 1568b.

# 6. Inorganic Arsenic (iAs), NMIJ

In order for inorganic arsenic (iAs) to be a certified value in SRM 2983, measurements are needed from at least two independent methods since there is not a primary method. Arsenic species analysis was done at NIST Gaithersburg and by an external collaboration with Tomohiro Narukawa at the National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Six jars of SRM 2983 were obtained from the NIST Biorepository in Charleston, SC and shipped by ORM to the NMIJ. The following is derived from the report of analysis submitted to NIST by NMIJ.

## 6.1. Materials

The Japan Calibration Service System (JCSS) arsenic standard solution (ca. 1000 mg $L^{-1}$, Kanto Chemical Co., Inc., Tokyo, Japan) was used as the source of the calibration standard solution for AsIII. The certified reference materials of AsV (NMIJ CRM 7912-a), the dimethylarsinic acid (DMA) (NMIJ CRM 7913-a) and the arsenobetaine (AsB) (NMIJ CRM 7901-a) supplied by the National Metrology Institute of Japan/National Institute of Advanced Industrial Science and Technology (NMIJ/AIST, Tsukuba, Japan) were used as source standard solutions. Working mixed standard solutions (calibration range: 1 to 30 ng $g^{-1}$ as As) were prepared daily by mixing the stock solutions and diluting with water.

The nitric acid used was of ultrapur® grade (Kanto). Sodium 1-butanesulfonate (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), malonic acid (Wako Pure Chemical Industries, Ltd., Osaka, Japan), and tetramethylammonium hydroxide (TMAH, Tama Chemicals Co., Ltd., Kanagawa, Japan) were obtained as indicated. Ultra-purewater was generated with a Milli Q-Labo filter (Nippon Millipore Ltd, Tokyo, Japan) and was used throughout.

In-house standard solutions of monomethyarsonic acid (MMA), trimethylarsine oxide (TMAO), tetramethylarsonium ion (TeMA) and arsenocholine (AsC) were used to confirm their peak positions. An extract of NMIJ CRM 7405-a hijiki seaweed powder was used to confirm peak positions of arsenosugar compounds.

## 6.2. Equipment

An ICP-MS (7500c, Agilent, Tokyo, Japan) equipped with a micromist nebulizer (0.1 mL $min^{-1}$ type) and a Scott spray chamber (2 °C) was used. Typical operating parameters for the ICP-MS were as follows: incident RF power was 1600 W, outer Ar gas flow rate 15 L $min^{-1}$, intermediate Ar gas flow rate 0.9 L $min^{-1}$, carrier Ar gas flow rate 0.8 L $min^{-1}$ and make-up Ar gas flow rate 0.4 mL $min^{-1}$. The ICP-MS was usually operated using He as the collision cell gas (3 mL $min^{-1}$) to reduce some polyatomic molecular interferences. The signal at *m*/*z* 75 was monitored, and the data evaluation was carried out with chromatographic software Chemstation.

An HPLC (NANOSPACE SI-2, Shiseido Co. Ltd., Tokyo, Japan) was used for separation of arsenic species. The exit of the HPLC column was directly connected to the nebulizer of the ICP-MS with PEEK tubing (LC-ICP-MS).

The mobile phase containing 10 mmol $L^{-1}$ sodium 1-butanesulfonate / 4 mmol L-1 malonic acid / 4 mmol L-1 tetramethylammonium hydroxide / 0.05 % methanol (pH 3.0) at a flow rate of 0.5 mL $min^{-1}$ was used for the reversed phase type columns. Typical injection volume was 20 μL. A CAPCELL PAK C18 MG column (particle size of the filler 3 μm, ID 4.6 mm×150 mm, polymer-coated type, Osaka Soda Co., Ltd., Osaka, Japan) was used.

## 6.3. Sample Preparation

Water-soluble arsenic species in the SRM material were extracted by two independent conditions. A gravimetric method was employed in all preparations in this study. Blank tests were performed to investigate possible As contamination.

### 6.3.1. Method 1: Water, Ultrasonic Extraction

A portion of the SRM material (ca. 0.5 g) was accurately weighed into a 50 mL-polypropylene tube and 10 g of water was added. The tube was capped and placed in an ultrasonic bath for 1 h. The tube was centrifuged at 419 rad/s (4000 rpm) for 10 min, and the liquid phase was then passed through a 0.45 μm syringe-type polyvinylidene difluoride (PVDF) membrane filter. The filtrate was analyzed by HPLC-ICP-MS, immediately. The top panel of Fig. 11 displays a typical chromatogram for this method.

### 6.3.2. Method 2: Acid, Heat Extraction (Adapted from WA DOH Method)

A portion of sample (ca. 0.5 g) was accurately weighed into a 50 mL-polypropylene tube and 10 g of 0.28 mol $L^{-1}$ $HNO_3$ was added. The tube was capped and placed in a dry heating block system at 95 °C for 90 min. The tube was centrifuged at 419 rad/s (4000 rpm) for 10 min, and the liquid phase was then passed through a 0.45 μm syringe-type polyvinylidene difluoride (PVDF) membrane filter, and the 1 g of the filtrate was diluted with water to be 2 g (2-fold), then the measurement solution was analyzed by HPLC-ICP-MS. The bottom panel of Fig. 11 displays a typical chromatogram for this method [9].

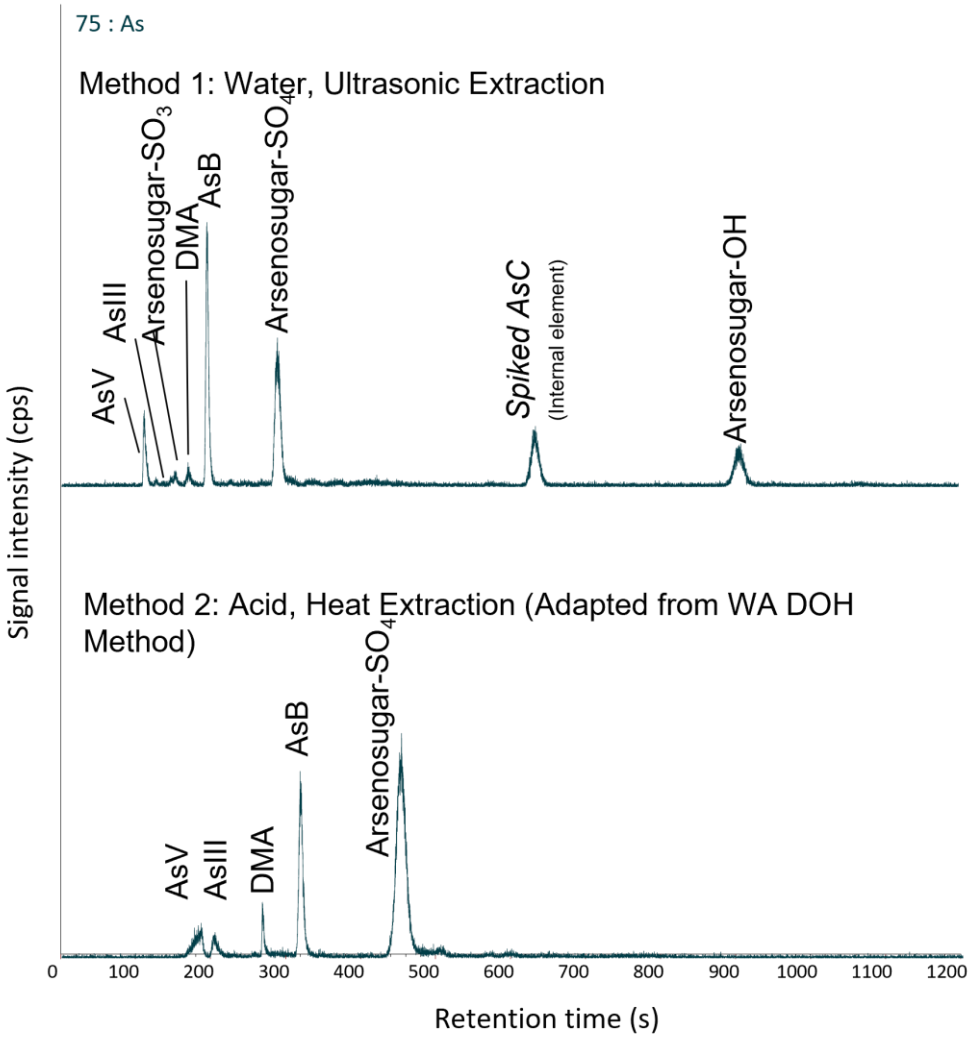



**Fig. 11.** Typical Reversed Phase HPLC-ICP-MS Chromatograms of SRM 2983.

## 6.4. Results and Discussion

Table 19 lists the results for iAs, DMA, and AsB in the six jars for both extraction methods along with their summary statistics. Table 20 lists the uncertainty components related to the standard solution (*u_std*) and measurement results (*u_anal*) for iAs, DMA, and AsB. The DMA results from Method 2 using acid extraction has contributions from the decomposition products of arsenosugars and therefore should not be used as information values.

**Table 19.** Results and Summary Statistics for iAs, DMA, and AsB.

Method 1: Water, Ultrasonic Extraction (mg kg$^{-1}$, wet mass fraction)

| Jar | Peak 1 AsV | Peak 2 AsIII | Peaks 1+2 iAs | Peak 4 DMA | Peak 5 AsB |
|---|---|---|---|---|---|
| 1 | 0.1636 ± 0.0001 | 0.0214 ± 0.0017 | 0.1850 ± 0.0016 | 0.0459 ± 0.0001 | 0.4822 ± 0.0004 |
| 2 | 0.1630 ± 0.0013 | 0.0194 ± 0.0001 | 0.1824 ± 0.0013 | 0.0456 ± 0.0009 | 0.4878 ± 0.0009 |
| 3 | 0.1661 ± 0.0021 | 0.0195 ± 0.0001 | 0.1856 ± 0.0021 | 0.0461 ± 0.0005 | 0.4878 ± 0.0001 |
| 4 | 0.1650 ± 0.0003 | 0.0212 ± 0.0011 | 0.1862 ± 0.0013 | 0.0456 ± 0.0002 | 0.4868 ± 0.0013 |
| 5 | 0.1642 ± 0.0001 | 0.0195 ± 0.0001 | 0.1837 ± 0.0001 | 0.0462 ± 0.0001 | 0.4843 ± 0.0007 |
| 6 | 0.1658 ± 0.0005 | 0.0204 ± 0.0003 | 0.1862 ± 0.0009 | 0.0456 ± 0.0004 | 0.4840 ± 0.0006 |
| Mean | 0.1646 | 0.0202 | 0.1849 | 0.0458 | 0.486 |
| SD | 0.0012 | 0.0009 | 0.0015 | 0.0003 | 0.002 |
| RSD | 0.70% | 4.60% | 0.80% | 0.60% | 0.50% |

Method 2: Acid, Heat Extraction (mg kg$^{-1}$, wet mass fraction)

| Jar | AsV | AsIII | iAs | DMA | AsB |
|---|---|---|---|---|---|
| 1 | 0.1256 ± 0.0016 | 0.0623 ± 0.0024 | 0.1879 ± 0.0063 | 0.0837 ± 0.0022 | 0.4816 ± 0.0077 |
| 2 | 0.1059 ± 0.0021 | 0.0826 ± 0.0035 | 0.1885 ± 0.0039 | 0.0811 ± 0.0024 | 0.4837 ± 0.0112 |
| 3 | 0.1288 ± 0.0023 | 0.0594 ± 0.0032 | 0.1882 ± 0.0022 | 0.0861 ± 0.0031 | 0.4872 ± 0.0107 |
| 4 | 0.1305 ± 0.0005 | 0.0811 ± 0.0001 | 0.1843 ± 0.0004 | 0.0827 ± 0.0002 | 0.4827 ± 0.0003 |
| 5 | 0.1305 ± 0.1186 | 0.0573 ± 0.0017 | 0.1878 ± 0.0045 | 0.0812 ± 0.0016 | 0.4852 ± 0.0059 |
| 6 | 0.1186 ± 0.0024 | 0.0710 ± 0.0026 | 0.1896 ± 0.0048 | 0.0831 ± 0.0013 | 0.4832 ± 0.0011 |
| Mean | 0.119 | 0.069 | 0.1877 | 0.083 | 0.484 |
| SD | 0.012 | 0.011 | 0.0018 | 0.0018 | 0.002 |
| RSD | 9.90% | 16.00% | 1.00% | 2.20% | 0.40% |

**Table 20.** Uncertainty Estimates for iAs, DMA, and AsB.

| | | Method 1 | | | Method 2 | | |
|---|---|---|---|---|---|---|---|
| Parameter | Unit | iAs | DMA | AsB | iAs | DMA | AsB |
| *u_anal* Rel. | % | 1.70 | 2.64 | 1.10 | 1.70 | 2.64 | 1.10 |
| *u_std* Rel. | % | 0.70 | 2.68 | 0.56 | 0.84 | 1.39 | 1.27 |
| combined *u* Rel. | % | 1.84 | 3.76 | 1.24 | 1.89 | 2.98 | 1.68 |
| *u* | mg kg$^{-1}$ | 0.003 | 0.002 | 0.006 | 0.004 | 0.002 | 0.008 |

## 6.5. Metrological Traceability

Results for iAs are traceable to the SI through the JCSS AsIII calibration solution and NMIJ CRM 7912-a CRM for AsV.

# 7. Proximate Analysis

Six jars of SRM 2983 Inorganics in Geoduck Clam Tissue (*Panopea generosa*) were sent to Covance Laboratories, Madison WI, for determination of ash, calories, calories from fat, carbohydrates, moisture, protein, and total fat.

## 7.1. Methods Used

### 7.1.1. Ash

Official Methods of Analysis of AOAC INTERNATIONAL (2005) 18th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, USA, Official Method 923.03 Ash of Flour. Approximately 1 g of SRM 2983 was used for each replicate measurement.

### 7.1.2. Calories

Calories were determined by calculation using the measured total fat and protein content along with the calculated carbohydrate content:

$$\text{Calories} = 9\ (\text{total fat}) + 4\ (\text{protein}) + 4\ (\text{carbohydrate}) \quad (9)$$

### 7.1.3. Calories from Fat

Calories from were determined by calculation using the measured total fat content.

$$\text{Calories from fat} = 9\ (\text{total fat}) \quad (10)$$

### 7.1.4. Carbohydrates

Carbohydrates were determined by calculation using the measured moisture, protein, total fat, and ash content.

$$\%\ \text{carbohydrates} = 100 - (\%\ \text{moisture}) - (\%\ \text{protein}) - (\%\ \text{total fat}) - (\%\ \text{ash}) \quad (11)$$

### 7.1.5. Moisture

Official Methods of Analysis of AOAC INTERNATIONAL (2005) 18th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, USA, Official Method 925.09 Solids (Total) and Moisture in Flour and 926.08 Moisture in Cheese. Approximately 2 g of SRM 2983 was used for each replicate measurement.

### 7.1.6. Protein

Official Methods of Analysis of AOAC INTERNATIONAL (2005) 18th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, USA, Official Method 968.06 Protein (Crude) in Animal Feed and 992.15 Crude Protein in Meat and Meat Products Including Pet Foods. Approximately 2 g of SRM 2983 was used for each replicate measurement.

### 7.1.7. Total Fat

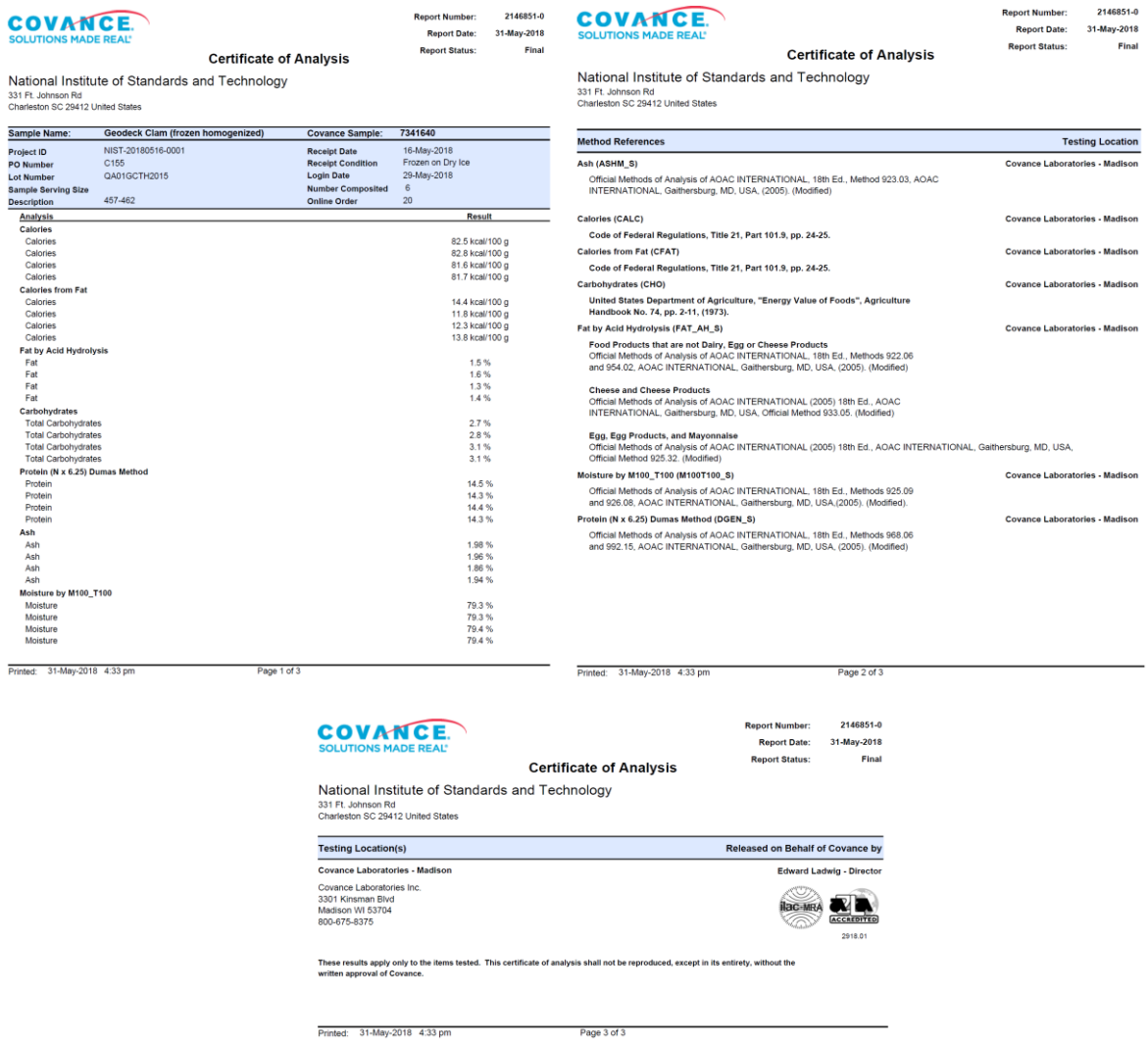
Official Methods of Analysis of AOAC INTERNATIONAL (2005) 18th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, USA, Official Method 922.06 Fat in Flour and 954.02 Fat (Crude) or Ether Extract in Pet Food. Approximately 10 g of SRM 2983 was used for each replicate measurement.

## 7.2. Results

Table 21 summarizes the results returned by Covance Laboratories – Madison. Their Certificate of Analysis is reproduced in Fig. 12.

**Table 21.** Results for Proximates Provided by Covance Laboratories – Madison.

| Sample | Ash % | Calories kcal/100 g | Calories from Fat kcal/100 g | Carbohydrates % | Moisture % | Protein % | Total Fat % |
|---|---|---|---|---|---|---|---|
| 1 | 1.98 | 82.5 | 14.4 | 2.7 | 79.3 | 14.5 | 1.5 |
| 2 | 1.96 | 82.8 | 11.8 | 2.8 | 79.3 | 14.3 | 1.6 |
| 3 | 1.86 | 81.6 | 12.3 | 3.1 | 79.4 | 14.4 | 1.3 |
| 4 | 1.94 | 81.7 | 13.8 | 3.1 | 79.4 | 14.3 | 1.4 |
| Mean | 1.94 | 82.2 | 13.1 | 2.9 | 79.4 | 14.4 | 1.5 |
| SD | 0.05 | 0.6 | 1.2 | 0.2 | 0.1 | 0.1 | 0.1 |



COVANCE
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Report Number: 2146851-0
Report Date: 31-May-2018
Report Status: Final

**Certificate of Analysis**

National Institute of Standards and Technology
331 Ft. Johnson Rd
Charleston SC 29412 United States

| Sample Name: | Geodeck Clam (frozen homogenized) | Covance Sample: | 7341640 |
|---|---|---|---|
| Project ID | NIST-20180516-0001 | Receipt Date | 16-May-2018 |
| PO Number | C155 | Receipt Condition | Frozen on Dry Ice |
| Lot Number | QA01GCTH2015 | Login Date | 29-May-2018 |
| Sample Serving Size | | Number Composited | 6 |
| Description | 457-462 | Online Order | 20 |

| Analysis | Result |
|---|---|
| **Calories** | |
| Calories | 82.5 kcal/100 g |
| Calories | 82.8 kcal/100 g |
| Calories | 81.6 kcal/100 g |
| Calories | 81.7 kcal/100 g |
| **Calories from Fat** | |
| Calories | 14.4 kcal/100 g |
| Calories | 11.8 kcal/100 g |
| Calories | 12.3 kcal/100 g |
| Calories | 13.8 kcal/100 g |
| **Fat by Acid Hydrolysis** | |
| Fat | 1.5 % |
| Fat | 1.6 % |
| Fat | 1.3 % |
| Fat | 1.4 % |
| **Carbohydrates** | |
| Total Carbohydrates | 2.7 % |
| Total Carbohydrates | 2.8 % |
| Total Carbohydrates | 3.1 % |
| Total Carbohydrates | 3.1 % |
| **Protein (N x 6.25) Dumas Method** | |
| Protein | 14.5 % |
| Protein | 14.3 % |
| Protein | 14.4 % |
| Protein | 14.3 % |
| **Ash** | |
| Ash | 1.98 % |
| Ash | 1.96 % |
| Ash | 1.86 % |
| Ash | 1.94 % |
| **Moisture by M100_T100** | |
| Moisture | 79.3 % |
| Moisture | 79.3 % |
| Moisture | 79.4 % |
| Moisture | 79.4 % |

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Report Number: 2146851-0
Report Date: 31-May-2018
Report Status: Final

**Certificate of Analysis**

National Institute of Standards and Technology
331 Ft. Johnson Rd
Charleston SC 29412 United States

| Method References | Testing Location |
|---|---|
| **Ash (ASHM_S)** | **Covance Laboratories - Madison** |
| Official Methods of Analysis of AOAC INTERNATIONAL, 18th Ed., Method 923.03, AOAC INTERNATIONAL, Gaithersburg, MD, USA, (2005). (Modified) | |
| **Calories (CALC)** | **Covance Laboratories - Madison** |
| **Code of Federal Regulations, Title 21, Part 101.9, pp. 24-25.** | |
| **Calories from Fat (CFAT)** | **Covance Laboratories - Madison** |
| **Code of Federal Regulations, Title 21, Part 101.9, pp. 24-25.** | |
| **Carbohydrates (CHO)** | **Covance Laboratories - Madison** |
| **United States Department of Agriculture, "Energy Value of Foods", Agriculture Handbook No. 74, pp. 2-11, (1973).** | |
| **Fat by Acid Hydrolysis (FAT_AH_S)** | **Covance Laboratories - Madison** |
| **Food Products that are not Dairy, Egg or Cheese Products** Official Methods of Analysis of AOAC INTERNATIONAL, 18th Ed., Methods 922.06 and 954.02, AOAC INTERNATIONAL, Gaithersburg, MD, USA, (2005). (Modified) | |
| **Cheese and Cheese Products** Official Methods of Analysis of AOAC INTERNATIONAL (2005) 18th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, USA, Official Method 933.05. (Modified) | |
| **Egg, Egg Products, and Mayonnaise** Official Methods of Analysis of AOAC INTERNATIONAL (2005) 18th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, USA, Official Method 925.32. (Modified) | |
| **Moisture by M100_T100 (M100T100_S)** | **Covance Laboratories - Madison** |
| Official Methods of Analysis of AOAC INTERNATIONAL, 18th Ed., Methods 925.09 and 926.08, AOAC INTERNATIONAL, Gaithersburg, MD, USA,(2005). (Modified). | |
| **Protein (N x 6.25) Dumas Method (DGEN_S)** | **Covance Laboratories - Madison** |
| Official Methods of Analysis of AOAC INTERNATIONAL, 18th Ed., Methods 968.06 and 992.15, AOAC INTERNATIONAL, Gaithersburg, MD, USA, (2005). (Modified) | |

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Report Number: 2146851-0
Report Date: 31-May-2018
Report Status: Final

**Certificate of Analysis**

National Institute of Standards and Technology
331 Ft. Johnson Rd
Charleston SC 29412 United States

| Testing Location(s) | Released on Behalf of Covance by |
|---|---|
| **Covance Laboratories - Madison** | **Edward Ladwig - Director** |

Covance Laboratories Inc.
3301 Kinsman Blvd
Madison WI 53704
800-675-8375

ILAC-MRA ACCREDITED
2918.01

**These results apply only to the items tested. This certificate of analysis shall not be reproduced, except in its entirety, without the written approval of Covance.**

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**Fig. 12.** Covance Laboratories Certificate of Analysis for Proximates.

# 8. Value Assignment

## 8.1. Statistical Approaches

Statistical analysis of the data collected for the characterization of SRM 2983 was provided by the NIST Statistical Engineering Division.

## 8.2. Assignment of Values and Uncertainties

For each analyte, the estimated value is the mean of the method estimates available for that analyte. The uncertainty of the combined mean is estimated using a bootstrap procedure based on a Gaussian random effects model for the between-method effects [4,10,11,12].

The method estimate for an analyte is the mean of the measurements for that analyte using that method. The combined standard uncertainty [4] of each method mean is taken from the information provided in the preceding sections of this document.

## 8.3. Measurements Used

Table 22 and Table 23 list the results used to estimate the mass fraction of total and inorganic arsenic in SRM 2983.

**Table 22.** Results (mg/kg, wet mass fraction) for Total Arsenic in SRM 2983.

| Sample | NIST Charleston | NIST Gaithersburg |
|---|---|---|
| 1 | 3.683 | 3.51 |
| 2 | 3.772 | 3.62 |
| 3 | 3.676 | 3.65 |
| 4 | 3.687 | 3.88 |
| 5 | 3.721 | 3.77 |
| 6 | 3.669 | 3.50 |
| 7 | 3.698 | |
| 8 | 3.719 | |
| 9 | 3.691 | |
| 10 | 3.672 | |

[a] Results stated in units of mg/kg, wet mass fraction

**Table 23.** Results (mg/kg, wet mass fraction) for Inorganic Arsenic in SRM 2983.

| | NIST Gaithersburg | NMIJ Method 2 | |
|---|---|---|---|
| Sample | Value | Value | *u*(Value) |
| 1 | 0.214 | 0.1879 | 0.0063 |
| 2 | 0.200 | 0.1885 | 0.0039 |
| 3 | 0.208 | 0.1882 | 0.0022 |
| 4 | 0.210 | 0.1843 | 0.0004 |
| 5 | 0.185 | 0.1878 | 0.0045 |
| 6 | 0.173 | 0.1896 | 0.0048 |

## 8.4. Combined Values

Table 24 lists the results of the statistical analysis. The data and the summary results are displayed in Fig. 13.

**Table 24.** Combined Values.

| Analyte | Units | Value | $U_{95}$ | $k$ |
|---|---|---|---|---|
| Total As | mg/kg | 3.677 | 0.063 | 2.0 |
| Inorganic As | mg/kg | 0.193 | 0.011 | 2.0 |

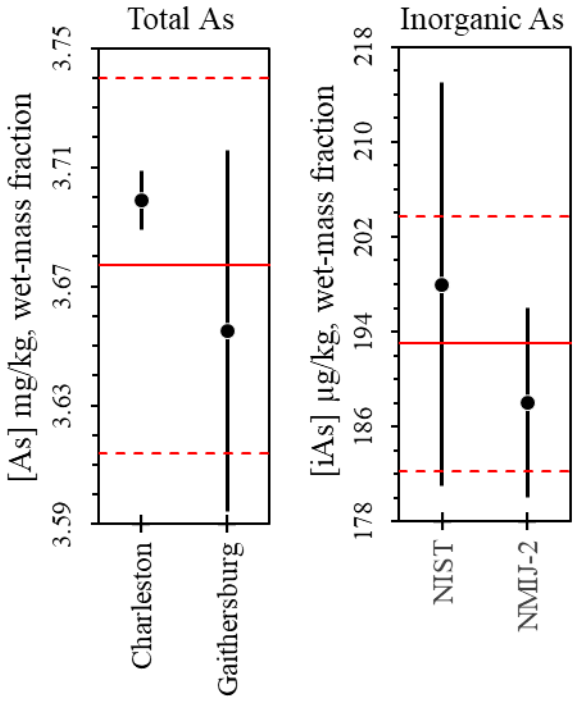


**Fig. 13.** Results and Assigned Values.

Dots represent the means of measured values. Bars represent approximate 95 % level of confidence intervals on those means. The solid horizontal line ion each panel represents the estimated value. The dashed lines represent the approximate 95 % level of confidence interval centered on the estimated value.

## 9. Acknowledgements

The authors thank Dave Duewer of the NIST Chemical Sciences Division for assistance in preparation of this report.

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## Appendix A. Acronyms

| | |
|---|---|
| AsB | arsenobetaine |
| AsC | arsenocholine |
| AsIII | arsenite |
| AsV | arsenate |
| CRM | certified reference material |
| DC AAS | direct combustion atomic absorption spectrometry |
| DMA | dimethylarsinic acid |
| FEP | fluorinated ethylene propylene |
| $H_2O_2$ | hydrogen peroxide |
| iAs | inorganic arsenic (AsIII plus AsV) |
| ICP-MS | inductively coupled plasma mass spectrometry |
| ICP-MS/MS | inductively coupled plasma tandem mass spectrometry |
| IS | internal standard |
| JCSS | Japan Calibration Service System |
| LC-ICP-MS | liquid chromatography inductively coupled plasma mass spectrometry |
| LDPE | low density polyethylene |
| $LN_2$ | liquid nitrogen |
| MMA | monomethylarsonic acid |
| MS/MS | tandem mass spectrometry |
| NIST | National Institute of Standards and Technology |
| NMIJ | National Metrology Institute of Japan |
| NOAA | National Oceanic and Atmospheric Administration |
| ORM | NIST Office of Reference Materials |
| $HNO_3$ | nitric acid |
| PTFE | polytetrafluoroethylene |
| PVDF | polyvinylidene difluoride |
| QQQ-ICP-MS | triple quadrupole inductively coupled plasma mass spectrometry |
| RPM | revolutions per minute |
| RSD | relative standard deviation |
| SARDFA | Southeast Alaska Regional Dive Fisheries Association |
| SD | standard deviation |
| SI | International System of Units |
| SRM | Standard Reference Material |
| TeMA | tetramethylarsonium ion |
| TMAH | tetramethylammonium hydroxide |
| TMAO | trimethylarsine oxide |
| WA DOH | Washington State Department of Health |