Determination of Arsenic in Food and Dietary Supplement Standard Reference Materials by Neutron Activation Analysis

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Arsenic was measured in food and dietary supplement Standard Reference Materials by neutron activation analysis for the purpose of assigning certified or reference As mass fractions and to assess material homogeneity. Instrumental neutron activation analysis (INAA) was used to value assign As in candidate SRM 3532 Calcium Dietary Supplement and candidate SRM 3262 *Hypericum perforatum* (St. John's Wort) Aerial Parts down to about 100 µg/kg. Values were also determined for two additional candidate St. John's Wort SRMs with As mass fractions < 100 µg/kg. The presence of significant amounts of ^{24}Na and ^{82}Br limited the reproducibility of the method below 100 µg/kg. For measurement of lower As mass fractions, a radiochemical neutron activation analysis method (RNAA) with extraction of As^{3+} into diethyl-dithiocarbamate in chloroform and detection limits down to 0.1 µg/kg As was used to value-assign As mass fractions for SRM 3280 Multivitamin/Multielement Tablets and for candidate SRM 3233 Fortified Breakfast Cereal, and at < 10 µg/kg in candidate SRM 1845a Whole Egg Powder.

Introduction

Exposure of humans to arsenic, even at low levels, has been linked to a variety of health problems, including heart disease, skin damage, and lung, bladder, and kidney cancers. The U.S. Environmental Protection Agency currently sets the arsenic standard for drinking water at 10 µg/kg.[1] Monitoring of arsenic levels in water, biological tissues, and especially foods is therefore vital to the public health; however, this monitoring requires reliable methods for determination of arsenic at these levels as well as certified reference materials for method validation. In response to the latter need, the National Institute of Standards and Technology (NIST) has established a continually expanding portfolio of biological Standard Reference Materials (SRMs) certified for arsenic content.[2]

One of the modes of certification used at NIST requires measurement by two or more independent methods.[3] Neutron activation analysis (NAA), which has few sources of bias in common with non-nuclear techniques, continues to play a key role in the certification of arsenic and other elements in biological reference materials. Arsenic is quantified by counting of the principal gamma-ray line (559 keV) emitted from ^{76}As, $t_{1/2}$ = 1.09379 d ± 0.00045 d, formed upon neutron capture of ^{75}As.[4] Instrumental neutron

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activation analysis (INAA) is typically used to determine As mass fractions ≥100 μg/kg in biological materials, and at lower levels in the absence of significant amounts of ^{24}Na ($t_{1/2}$ = 15 h), ^{82}Br ($t_{1/2}$ = 35.3 h), or ^{32}P ($t_{1/2}$ = 14.3 d), which can result in high count-rates, decreased signal-to-noise ratio, and poorer detection limits. At lower levels and/or in the presence of interfering nuclides, radiochemical neutron activation analysis (RNAA) gives best results. RNAA with retention of arsenic and other elements on hydrated manganese dioxide (HMD) has been used to value-assign arsenic mass fractions in SRM 1548a Typical Diet, SRM 1570a Trace Elements in Spinach Leaves; SRM 1573a Tomato Leaves, and SRM 1577c Bovine Liver at levels below 100 μg/kg.[2] More recently separation of arsenic by solvent extraction into chloroform containing zinc diethyldithiocarbamate, ($ZnDDC_2$) with addition of ^{77}As tracer to monitor recovery yield, yielding limits of detection down to ≈ 0.1 μg/kg (a three-fold improvement over the HMD procedure)[5] has been used in the certification of arsenic mass fractions in SRM 2668 Toxic Elements in Frozen Human Urine (at 10 μg/kg and 200 μg/kg) and in SRM 955c Toxic Elements in Caprine Blood (at 80 μg/kg, 50 μg/kg, 20 μg/kg, and < 5 μg/kg).

This investigation reports recent measurements of arsenic in foods and dietary supplements using INAA and the RNAA solvent extraction procedure. INAA is used to value-assign arsenic mass fractions in dietary supplements; RNAA to value assign arsenic mass fractions in vitamin tablets and in foods.

Experimental

Preparation and irradiation of samples, standards, and quality assurance SRMs

Dietary supplement materials analyzed for arsenic were candidate Standard Reference Materials (cSRMs), except for SRM 3280, an established SRM that is certified for arsenic content. These included the St. John's Wort SRM suite, a set of dietary supplement materials consisting of cSRM 3262 *Hypericum perforatum* (St. John's Wort) Aerial Parts, cSRM 3264 *Hypericum perforatum* (St. John's Wort) Methanol Extract, and cSRM 3265 *Hypericum perforatum* (St. John's Wort) Solid Oral Dosage. The fourth material in the series, cSRM 3263 *Hypericum perforatum* (St. Johns's Wort) CO_2 Extract, a low boiling point wax, was deemed unsuitable for NAA due to its volatility at temperatures reached during neutron irradiation. cSRM 3262 was received as a powder in sealed envelopes; two aliquots from each of ten envelopes were

sampled for analysis. cSRM 3264, also a powder was sampled directly from sealed envelopes; cSRM 3265, in the form of tablets, was sampled after grinding tablets into a powder using an electric blade coffee grinder. Preliminary analyses indicated that arsenic in cSRMs 3264 and 3265 was near the detection limit for INAA, therefore only three portions of each were analyzed to provide information values. cSRM 3532 Calcium Dietary Supplement was received as a powder (prepared by grinding tablets) in sealed envelopes. Two aliquots from each of six envelopes were sampled. SRM 3280 Multielement/Multivitamin Tablets was prepared for analysis by grinding the SRM tablets in the same manner as cSRM 3265, with aliquots of the powder distributed for analysis in capped tubes. One aliquot from each of five tubes was sampled. All powders analyzed were mixed thoroughly before sampling.

Food SRMs analyzed included cSRMs 1845a Whole Egg Powder and 3233 Fortified Breakfast Cereal. These were received as powders in sealed envelopes and glass jars, respectively, and were analyzed as received, with one aliquot per package.

All powder samples were pressed into 12.7 mm diameter disks using a stainless steel die and hydraulic press. Table 1 gives average sample masses and number of samples analyzed for each material. Disks were sealed into bags prepared by heat-sealing acid-washed polyethylene film. In order to ensure containment, each bag was then heat-sealed inside a second polyethylene film bag.

A solution containing (52.02 ± 0.08) µg/g of arsenic, prepared by gravimetric dilution of SRM 3103a Arsenic Standard Solution was used to prepare comparator element standards for analysis. A disposable pipet was used deposit two to three drops of the solution onto a series of Whatman 41 filter papers. The pipet was weighed before and after dispensing in order to determine the mass of solution deposited. Filter papers were allowed to dry for several days in a clean hood, then each paper was formed into a disk using a stainless steel die and hydraulic press. Filter paper standards were doubly-encapsulated in polyethylene film, with three to four standards used in the analysis of each material.

SRMs included for quality assurance were prepared by pressing the materials into disks and encapsulating the disks in the same manner as the samples. Table 1 gives SRMs included with the analysis of each sample set.

Sample cSRMs, element standards, and quality assurance SRMs were packaged into polyethylene irradiation vessels (rabbits) along with flux monitors (6 mg iron foils) included to monitor differences in

neutron fluence within a rabbit and between rabbits. Empty polyethylene bags were also included as blanks. Rabbits were irradiated at the NIST Center for Neutron Research (NCNR) at a reactor power of 20 MW. Two irradiation facilities were utilized: RT1, with a neutron flux of approximately 1 x 10^{14} $cm^{-2}s^{-1}$, and RT2, with a neutron flux of approximately 3 x 10^{13} $cm^{-2}s^{-1}$. Table 1 gives the facility used for the irradiation of each material, along with irradiation time. Each rabbit was flipped (rotated 180° end over end) at the midpoint of the irradiation to ensure that the entire rabbit received a uniform neutron exposure.

INAA

Arsenic in the St. John's Wort suite and Calcium Dietary Supplement cSRMs was determined by INAA. St. John's Wort cSRMs were allowed to decay for 5 to 7 days to allow decay of ^{24}Na, and Calcium Dietary Supplement was allowed to decay for two to three days to allow decay of ^{49}Ca, and ^{56}Mn. Sample cSRMs, standards, and quality assurance SRMs were removed from rabbits and transferred to plastic 20-mL counting vials. Each was positioned flat in the bottom of the vial, held in place with a polystyrene plug placed between the sample and vial cap. Gamma-ray spectroscopy was performed using a high-purity intrinsic germanium detector with pileup rejection and associated electronics in conjunction with an automatic sample changer. A second germanium detector system with software pileup correction was used to count quality assurance SRMs to ensure that all materials and standards were measured before ^{76}As decayed away. cSRM 3262 samples were counted for 5 h, cSRMs 3264 and 3265 for 10 h, cSRM 3532 for 3 h, and standards for at least 30 minutes, all at a distance of 2 cm from the detector.

The 559 keV ^{76}As peak was integrated using both a standard peak search program and an interactive peak fit program. The interactive peak fit helped to resolve the ^{76}As peak from ^{82}Br at 554.3 keV and ^{122}Sb at 564.1 keV. Results from the interactive fit were used to calculate As mass fractions; results from both methods were used to estimate peak fit uncertainties. Observed count rates were corrected for radioactive decay and pulse pileup (where necessary). Neutron absorption and gamma-ray attenuation effects were minimal in these materials because all targets measured were relatively thin. Arsenic mass fractions were calculated on an "as-received" mass basis.

RNAA

Arsenic in the food cSRMs and in the multivitamin/multielement tablet SRM (3280) was measured by RNAA. The cSRM samples, standards, and quality assurance SRMs were allowed to decay for 4 to 6 days. A series of Teflon beakers were prepared to contain the following: 0.1 mL of an arsenic carrier solution containing ≈1 g/mL of arsenic, and 1 mL of a tracer solution containing ^{77}As, delivered from a calibrated pipet. The preparation of the ^{77}As tracer is described elsewhere.[5,6] cSRM 3280 samples and quality assurance SRMs were removed from bags, weighed and transferred to Teflon beakers. Removal of Fortified Breakfast Cereal (cSRM 3233) and Whole Egg powder (cSRM 1845a) samples from bags was difficult because disks had disintegrated during irradiation. These were transferred to beakers without removal from bags and the bags slit open with a knife after addition of a few milliliters of water to the beakers. Filter paper element standards were removed from bags and transferred to beakers without weighing.

Samples, quality assurance SRMs, and standards were digested, using in sequence: 10 mL H_2O/10 mL concentrated nitric acid, 10 mL concentrated nitric acid/10 mL concentrated perchloric acid, 10 mL concentrated nitric acid/10 mL concentrated perchloric acid, heating to near dryness after each digestion. The digestion procedure is described elsewhere.[5] During the initial nitric acid digestion, cereal and whole egg powder samples were leached out of the bags by the nitric acid and the bags rinsed with water and removed for counting.

Arsenic in the digests was separated by solvent extraction.[5, 7] Five milliliters of concentrated H_2SO_4 were added to each digest followed by heating at 250 °C to 275 °C for 30 min to evaporate traces of $HClO_4$. After cooling to room temperature, followed by dropwise addition of 15 mL H_2O and 1.5 mL of 0.2 mol/L KI solution, As^{5+} was reduced to As^{3+} by boiling the solution for 10 min to 15 min. Conversion to As^{3+} was completed by addition of 1.5 mL of 0.8 mol/L ascorbic acid and cooling to room temperature. Each solution was transferred to a 60 mL separatory funnel and extracted with 10 mL and 5 mL portions of 0.025 mol/L $Zn(DDC)_2$ in chloroform. The combined 15 mL chloroform phase was washed with 5 mL of 2 mol/L H_2SO_4 containing 100 mg of $ZnSO_4$, and the chloroform layer drained into a 20 mL plastic liquid scintillation counting vial for gamma-ray spectrometry of ^{76}As and ^{77}As.

Samples in vials were counted for 5 h at the face of the detector, except for SRM 3280 samples,

which were counted at a distance of 2 cm. Screening of residue in leached polyethylene bags from cereal and whole egg powder samples indicated no residual As activity. The ^{76}As peak at 559 keV and ^{77}As peak at 239 keV were integrated using both a standard peak search program and an interactive peak fit program. Results from the interactive fit were used in the calculation of arsenic mass fractions; results from both methods were used to estimate peak fit uncertainties. Observed count rates were corrected for radioactive decay and pulse pileup (where necessary). The corrected ^{77}As count rate was used as a measure of differences in recovery yields and counting geometries between samples and standards and from sample to sample. Yield/geometry corrections for samples were determined relative to standards as the ratio of the ^{77}As count rate for each sample to the average ^{77}As count rate of the processed standards. Correction factors ranged from about 0.9 to 1.1. SRM 3280 mass fractions were reported on a dry mass basis using a drying factor of 0.9874 determined by desiccator drying over magnesium perchlorate for 12 d, the procedure outlined in the Certificate of Analysis. Arsenic mass fractions in the food cSRMs were calculated on an "as-received" mass basis.

Results and Discussion

Results

Arsenic results for samples measured by NAA are given in Table 2. Expanded uncertainties (*U)* were calculated by combining uncertainties from individual sources in quadrature to obtain a combined standard uncertainty (u_c), which was then multiplied by a coverage factor of 2 to obtain the expanded uncertainty (U).[8] A complete discussion of evaluation of uncertainties in NAA may be found elsewhere.[9-11] Sources of uncertainty evaluated for INAA, with typical associated relative 1s uncertainties, include the following: measurement replication for samples (s/√n, varies greatly with material), measurement replication for standards (s/√n, 0.5 % to 1 %), and uncertainties associated with counting geometry (0.2 %), irradiation geometry (0.2 %), sample mass determination (0.003 %), corrections for neutron self shielding and gamma-ray attenuation (< 0.1 %), mass fraction of standard solution (0.29 %), delivery of standard solution (0.15 %) and peak integration (0.2 % to 2 %). Peak integration uncertainties were determined by comparing peak areas obtained by two different integration methods and assuming a rectangular distribution. Uncertainties evaluated for RNAA included those listed above, with the following corrections

and additions. The counting geometry uncertainty was replaced by the uncertainty in the yield/counting geometry correction factor, evaluated at 0.3 % based on ^{77}As counting statistics and calibration of the pipet used to delivery the tracer solution. An additional uncertainty of $\leq$ 1 % was added to Whole Egg Powder and Breakfast Cereal results to account for the possibility of incomplete dissolution of sample from the bag, and was evaluated from the detection limit of As in the leached bags.

Table 3 gives results for quality assurance materials analyzed by INAA and RNAA with expanded uncertainties (*U*). Mass fractions for all quality assurance materials are reported on a dry mass basis using drying factors determined by desiccator drying over magnesium perchlorate, the procedure outlined in the Certificate of Analysis. NAA values are in agreement with certified values within the stated uncertainties.

Arsenic NAA results for the various materials are discussed below. Certified values for SRM 3280 were assigned by combining NAA data with inductively coupled plasma-mass spectrometry (ICP-MS) data. NAA values for other materials were submitted for determination of certified, reference, or information values for arsenic mass fractions in the cSRMs and, in some cases, for assessment of material homogeneity. Certified values will be assigned only after combining NAA data with values from other methods if available.

St John's Wort

The presence of significant amounts of ^{24}Na and ^{82}Br in the spectra hindered the measurement of arsenic at low levels in these materials. The large ^{82}Br peak at 554 keV (Br/As peak ratios > 50 for cSRM 3262, > 100 for cSRMs c3264 and 3265) resulted in significant peak fitting uncertainties for the ^{76}As 559 keV peak. cSRM 3262 was determined with about 3 % counting statistics, relative at the 1s level. The standard deviation of the 20 values was comparable to the total uncertainty from measurement replication and peak fitting, giving no reason to suspect material heterogeneity. Counting statistics and reproducibility for cSRM 3264 were poor, thus INAA values should be used only for information or for confirmation of a second method. Arsenic in cSRM 3265 was below the limit of detection, as no statistically significant peak was observed. A detection limit was calculated for the three samples analyzed using an equation derived from the works of Jaklevic and Walter[12] and Currie[13] :

$$LOD = 4.65 (R_b/t)_{1/2}/S$$

where R_b is the background counting rate (counts per seconds squared), t is the duration of the count (s), and S is the As sensitivity in counts per second per nanogram. From these results an upper limit of $\leq$ 30 µg/kg was determined.

Calcium Dietary Supplement

INAA arsenic values for cSRM 3532 ranged from 270 µg/kg to 645 µg/kg, with an RSD of 32 %, far more uncertainty than can be explained by counting statistics and peak fitting. If samples were contaminated by arsenic (possibly from standards) during pre-irradiation preparation, we might expect to see such results. However, arsenic mass fractions measured in quality assurance materials SRM 1566b and SRM 1575a, prepared and irradiated alongside the samples using the same equipment, are in agreement with certified values. If arsenic contamination were present, the low level SRM 1575a would be expected to show greatly elevated values. Furthermore it does not appear that the Calcium Dietary Supplement is heterogeneous with respect to all elements. Prompt gamma activation analysis (PGAA) measurements of boron in 6 samples of the same material yielded a value (mean ± SD) of 87.03 mg/kg ± 1.31 mg/kg (RSD = 1.5 %), albeit PGAA used a sample size of about twice that used in the arsenic measurements. Therefore the heterogeneity of the material may be limited to arsenic and other selected elements.

Food cSRMs

Arsenic was determined with good precision in the Whole Egg Powder and Fortified Breakfast Cereal cSRMs. For cSRM 3233 Fortified Breakfast Cereal, the standard deviation of 3.84 % is larger than the variation given by the sum of counting statistics, yield/geometry correction uncertainties, peak fitting uncertainties, and correction for loss during dissolution (about 1.2 %). An additional 3.6 % uncertainty from heterogeneity is necessary to account for the additional variation. The standard deviation of 2.27 % for the 5 values for cSRM 1845a Whole Egg Powder is smaller than the above-mentioned uncertainties, giving no reason to suspect additional uncertainty from heterogeneity. The results show that As may be determined in foods by the RNAA method with good precision at mass fractions below 10 µg/kg.

Multivitamin

The standard deviation of the five values for SRM 3280 is smaller than the uncertainty from counting statistics, giving no reason to suspect arsenic heterogeneity. Measurement of arsenic in 21 samples by ICP-MS yielded a value of 152.5 µg/kg ± 6 µg/kg (mean ± *U*) compared with the RNAA value of 110 µg/kg ± 2 µg/kg. The reason for the discrepancy is unknown. Although the samples appeared to dissolve completely as evidenced by a clear solution, it is possible that the nitric/perchloric acid dissolution used for RNAA, though effective on biological materials, may not give complete dissolution of the multivitamin SRM which contains a large amount of inorganic matter. The ICP-MS procedure used a mixture of nitric and hydrofluoric acids with a microwave digestion. However, an attempt to add hydrofluoric acid to the RNAA dissolution resulted only in decreased reproducibility, most likely due to loss of arsenic as volatile AsF_3. Since it could not be ascertained which data set was biased, a certified value of 132 µg/kg ± 44 µg/kg was determined from the equally weighted means of the two data sets.

Conclusions

NAA methods were used to value assign arsenic mass fractions and assess homogeneity of food and dietary supplement reference materials. Arsenic was determined with good precision down to about 100 µg/kg in dietary supplements by INAA, and below 10 µg/kg in foods by RNAA. Values will be used to determine certified, reference, or information values for the SRMs. Analyses of additional food SRMs are underway. As more becomes known about the health effects of arsenic, it is likely that stricter regulations for arsenic contents in foods will be enacted, increasing the need for food SRMs certified for As at low levels.

Because the toxicity of arsenic is dependent upon the chemical species (inorganic arsenic being more toxic than organic arsenic), certification of arsenic species in reference materials is also of paramount important. NIST currently has one SRM certified for arsenic species (SRM 2669 Arsenic Species in Human Urine, with As species concentrations certified by ion exchange chromatography coupled with ICP-MS)

and is currently in the process of certifying As species in several food SRMs using the same methods. Arsenic speciation by NAA with pre-irradiation chemistry has been performed elsewhere[14-18] and could be developed at NIST to complement the ion exchange - ICP-MS methods. The potential role of NAA in the certification of arsenic species should be investigated.

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The identification of certain commercial equipment, instruments, or materials does not imply recommendation or endorsement by the National Institute of Standards and Technology. These identifications are made only in order to specify the experimental procedures in adequate detail.

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Table 1. Material and irradiation information for NAA determinations.

Candidate SRM#	Approx. sample size (mg)	n	Facility/ Irradiation time	Method	SRMs Included for Quality assurance
Dietary supplements					
3262 *Hypericum perforatum* (St. John's Wort) Aerial Parts	325	20	RT1 2 h	INAA	SRM 3240 Ephedra Aerial Parts SRM 3242 Ephedra Commercial Extract
3264 *Hypericum perforatum* (St. John's Wort) Methanol Extract	300	3	RT1 2 h	INAA	
3265 *Hypericum perforatum* (St. John's Wort) Solid Oral Dosage	300	3	RT1 2 h	INAA	
3280 Multivitamin/Multielement Tablets	200	5	RT2 8h	RNAA	SRM 1547 Peach Leaves
3532 Calcium Dietary Supplement	325	12	RT2 1 h	INAA	SRM 1566b Oyster Tissue SRM 1575a Trace Elements in Pine Needles
Foods					
3233 Fortified Breakfast Cereal	225	6	RT2 5 h	RNAA	SRM 1575a Trace Elements in Pine Needles
1845a Whole Egg Powder	225	5	RT1 5h	RNAA	SRM 1575a Trace Elements in Pine Needles SRM 1577c Bovine Liver

Table 2. Arsenic results for materials analyzed by NAA. Expanded uncertainties (U) were calculated using a coverage factor of 2.

SRM or Candidate SRM	**As (µg/kg) Mean ± 1s (n)**	**Average 1s counting statistics uncertainty**	**As (µg/kg) Recommended NAA Value (mean ± *U*)**
INAA			
3262 *Hypericum perforatum* (St. John's Wort) Aerial Parts	138 ± 6 (20)	3.2 %	138 ± 7
3264 *Hypericum perforatum* (St. John's Wort) Methanol Extract	71.5 ± 11.8 (3)	8.2 %	70
3265 *Hypericum perforatum* (St. John's Wort) Solid Oral Dosage	< 30 (3)	No peak	< 30
3532 Calcium Dietary Supplement	352.6 ± 111.4 (12)	2.0 %	352.6 ± 91.1
RNAA			
3280 Multivitamin/Multielement Tablets	110 ± 2 (5)	3.5 %	110 ± 4.4
3233 Fortified Breakfast Cereal	89.34 ± 3.15 (6)	1.2 %	89.34 ± 2.96
1845a Whole Egg Powder	6.35 ± 0.14 (5)	4.0 %	6.35 ± 0.28

Table 3. Arsenic measured by NAA in SRMs included for quality assurance.

SRMs Included for Quality assurance	**INAA As (µg/kg) Mean ± *U* (n)**	**RNAA As (µg/kg) Mean ± *U* (n)**	**Certified value**
SRM 3240 Ephedra Aerial Parts	257 ± 11 (8)	n.d.	265 ± 16
SRM 3242 Ephedra Commercial Extract	1045 ± 45 (3)	n.d.	1040 ± 33
SRM 1566b Oyster Tissue	7670 ± 190 (2)	n.d.	7650 ± 650
SRM 1575a Trace Elements in Pine Needles	38.6 ± 3.8 (2)	37.9 ± 1.7 (3)	39 ± 2
SRM 1547 Peach Leaves	n.d.	67.2 ± 2.6 (2)	60 ± 18
SRM 1577c Bovine Liver	n.d.	19.6 ± 1.5 (2)	19.6 ± 1.6

n.d. = not determined