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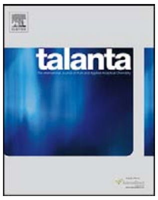

Accurate determination of arsenic in arsenobetaine standard solutions of BCR-626 and NMIJ CRM 7901-a by neutron activation analysis coupled with internal standard method

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ABSTRACT

Neutron activation analysis (NAA) coupled with an internal standard method was applied for the determination of As in the certified reference material (CRM) of arsenobetaine (AB) standard solutions to verify their certified values. Gold was used as an internal standard to compensate for the difference of the neutron exposure in an irradiation capsule and to improve the sample-to-sample repeatability. Application of the internal standard method significantly improved linearity of the calibration curve up to 1 μg of As, too. The analytical reliability of the proposed method was evaluated by k_0-standardization NAA. The analytical results of As in AB standard solutions of BCR-626 and NMIJ CRM 7901-a were (499 ± 55) mg kg^{-1} ($k = 2$) and (10.16 ± 0.15) mg kg^{-1} ($k = 2$), respectively. These values were found to be 15–20% higher than the certified values. The between-bottle variation of BCR-626 was much larger than the expanded uncertainty of the certified value, although that of NMIJ CRM 7901-a was almost negligible.

1. Introduction

Arsenic is one of the most interesting elements for analytical chemists scientifically and epidemiologically because of its toxic nature. Arsenic widely exists in various chemical forms in the environment and its toxic nature is significantly dependent on As species. For example, inorganic As such as As(III) is extremely toxic for the human body, although organic As such as arsenobetaine (AB) is almost non-toxic. Arsenic speciation analysis as well as total analysis is very important for As chemistry, but very difficult. Under the above common understanding, an international comparison relating to analytical capability of As and AB in fish tissue sample was carried out among the national metrology institutes in Consultative Committee for Amount of Substance-Metrology in Chemistry/the International Committee of Weights and Measures (CCQM/CIPM) under the Meter Convention in 2007. The analytical results of As reported by the institutes participated were in good agreement with each other, and it demonstrated their excellent measurement capabilities of As. However, a significant discrepancy in the measurement results of AB was found in the international comparison, when two different standard solutions of AB, that is, Institute for Reference Materials and Measurements (IRMM) BCR-626 [1] and National Metrology Institute of Japan (NMIJ) CRM 7901-a [2] were used as calibration standards. The committee concluded that the certified values of both the CRMs should be verified again by using an analytical method whose principle was different from those used in their certification procedures.

Neutron activation analysis (NAA) is one of the most useful measurement methods with multielement determination capability. It is widely applied to multielement analysis in geochemistry, geology, meteoritics, archaeology, and so on [3–5]. In recent years, NAA has been recognized as a potential primary method of measurement in CCQM/CIPM, since the principle of NAA is well defined as the following equation and all the parameters are strictly understood [6,7]

$$m_{unk} = m_{std}\frac{A_{0,unk}}{A_{0,std}}R_\theta R_\phi R_\sigma R_\varepsilon$$

where m_{unk} and m_{std} are masses of the element in a sample and a comparator standard, $A_{0,unk}$ and $A_{0,std}$ the count rates of an induced radionuclide in the sample and the comparator standard (which are corrected based on the radioactive decay), and R_θ, R_φ, R_σ, and R_ε the ratio of isotopic abundance between the sample and the

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comparator standard, the ratio of neutron fluence, the ratio of effective cross-section, and the ratio of counting efficiency. Moreover, NAA is well known as a non-destructive analytical method, which can determine most elements without any chemical pretreatments, that is, NAA is basically free from a potential risk of loss and contamination during the sample preparation and measurement procedures. Therefore, NAA has a potentially high ability to derive accurate measurement results. Greenberg and his colleagues successfully applied NAA to the accurate determination of minor and trace elements in various types of samples when they developed CRMs, and they demonstrated NAA could establish the metrological traceability as a primary method of measurement [8,9]. In particular, NAA is very useful to determine mono-isotopic elements such as As and Co in environmental and biological samples, since the isotope dilution analysis that is one of the primary ratio methods of measurement cannot be applied to those elements. However, NAA sometimes shows a large measurement uncertainty compared with other analytical methods such as inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The main components of measurement uncertainty of NAA are those associated with corrections for the differences of neutron flux among samples and comparator standards and the sample-to-sample repeatability. The most practical way to eliminate the above uncertainty sources is to apply an internal standard method to NAA [10–13]. The present authors determined Cr and Co in ceramics by NAA with the internal standard method and reported significant improvement of the measurement uncertainty of NAA [10].

In this study, NAA coupled with an internal standard method was applied to the determination of total As in AB standard solutions of BCR-626 and NMIJ CRM 7901-a to evaluate the certified values.

The calibration standards assayed by National Institute for Standards and Technology (NIST) were used to establish the accurate and traceable determination. The NIST's standards, neither the NMIJ's nor IRMM's ones, were intentionally used to avoid the systematic errors based on the standards. The uncertainties of each analytical process were carefully estimated and the total uncertainty of measurement was calculated. In addition, the measurement results obtained by this method were evaluated with k_0-standardization NAA (k_0-NAA) [14].

2. Experimental

2.1. Samples

Two AB certified reference materials of IRMM BCR-626 and NMIJ CRM 7901-a were measured. The former certified value was $(1031 \pm 6)\,\mathrm{mg\,kg^{-1}}$ ($k = 2$), that is, As concentration was $(433.8 \pm 2.5)\,\mathrm{mg\,kg^{-1}}$ ($k = 2$). The total amount of the As impurities of BCR-626 was deduced to be lower than 0.15% by high performance liquid chromatography–ICP-MS (LC–ICP-MS) analysis [1]. The later certified value was $(19.98 \pm 0.47)\,\mathrm{mg\,kg^{-1}}$ ($k = 2$), at the same time, As concentration was $(8.43 \pm 0.20)\,\mathrm{mg\,kg^{-1}}$ ($k = 2$). From the analytical results of LC–ICP-MS analysis, NMIJ CRM 7901-a contains 99.7% of AB and 0.3% of trimethylarsine oxide (TMAO) [2]. Therefore, As concentration of NMIJ CRM 7901-a is the sum of As contained in AB and TMAO.

2.2. Reagents

Pure water used throughout the experiment was prepared with Milli-Q SP RFG40 ICP-MS system (Japan Millipore Ltd, Shinagawa, Japan). Ultrapure grade HCl and HNO_3 used were purchased from Kanto Chemicals Ltd. (Tokyo, Japan).

Two kinds of inorganic As standard solutions were used. One was NIST SRM 3103a As standard solution ($[\mathrm{As}] = (9.933 \pm 0.055)\,\mathrm{mg\,g^{-1}}$, $k = 2.26$) and the other was the trivalent As standard solution [As(III)] which was prepared by dissolving NIST SRM 83d As_2O_3 (reductometric assay; 99.9926 ± 0.0030%) in our laboratory. The former must be the pentavalent As standard solution [As(V)] although its chemical form is not guaranteed, because As is intentionally oxidized to As(V) during the producing process and the solution contains 10% HNO_3 to avoid the reduction of As(V) [15]. The Au internal standard solution was prepared from the high purity Au metal (informative purity value; 99.999%, Osaka Asahi Metal MFG. Co., Ltd., Osaka, Japan). The concentration of As impurity in the Au metal was less than $30\,\mu\mathrm{g\,kg^{-1}}$, which was determined by ICP-SFMS after dissolution.

2.3. Instruments

A Mettler Toledo XP205 semi-microbalance was used for weighing. The gamma ray measurement system consisted of ORTEC GMX-30190 Ge semiconductor gamma ray detector and SEIKO EG&G MCA7700. The energy resolution of the detector was 1.9 keV at 1332 keV gamma ray peak of ^{60}Co. The system was emulated by SEIKO EG&G spectrum navigator (DS-P100/W32). The shield system was made of iron brick (50 mm thick) of the battleship Mutsu.

2.4. Internal standard solution and As comparator standards

The Au standard solution was prepared as follows: an aliquot amount of the Au metal (1.03515 g) was dissolved in aqua-regia and the solution was diluted to make up 0.1 kg with 7% HCl in a polypropylene (PP) bottle. The Au standard solution was further diluted by 50 times with the acid mixture of 10% HCl and 1% HNO_3 to prepare the Au working solution. The concentration of Au in the working solution was $220\,\mathrm{mg\,kg^{-1}}$.

Six concentration levels of the As(V) working solutions [As(V)-0 to As(V)-5] were prepared as follows: proper amounts of NIST SRM 3103a and the Au working solution were gravimetrically poured into PP bottles with a PP syringe, and then the acid mixture of 10% HCl and 1% HNO_3 was added into them. The concentrations of As and Au in the As(V)-0 working solution were 0 and $2.44\,\mathrm{mg\,kg^{-1}}$, those in the As(V)-1 1.99 and $1.61\,\mathrm{mg\,kg^{-1}}$, those in the As(V)-2 4.92 and $2.65\,\mathrm{mg\,kg^{-1}}$, those in the As(V)-3 7.95 and $1.88\,\mathrm{mg\,kg^{-1}}$, those in the As(V)-4 11.6 and $2.50\,\mathrm{mg\,kg^{-1}}$, and those in the As(V)-5 21.5 and $1.87\,\mathrm{mg\,kg^{-1}}$, respectively.

The As(III) standard solution was prepared from NIST SRM 83d As_2O_3. An aliquot amount (1.22402 g) of NIST SRM 83d was precisely weighed and dissolved in diluted NH_4OH solution to avoid the oxidation. The pH of the As(III) solution was adjusted to pH 4 by adding 6% H_2SO_4 and then diluted to make up 0.928261 kg with H_2O. The concentration of As(III) was $998.704 \pm 0.10\,\mathrm{mg\,kg^{-1}}$ (expanded uncertainty, $k = 2$), which was confirmed by coulometric titration [16].

Six concentration levels of the As(III) working solutions were prepared with the same manner as the As(V) ones. The concentrations of As and Au in the As(III)-0 working solution were 0 and $1.94\,\mathrm{mg\,kg^{-1}}$, those in the As(III)-1 2.02 and $1.81\,\mathrm{mg\,kg^{-1}}$, those in the As(III)-2 4.59 and $2.00\,\mathrm{mg\,kg^{-1}}$, those in the As(III)-3 9.09 and $1.99\,\mathrm{mg\,kg^{-1}}$, those in the As(III)-4 13.7 and $2.39\,\mathrm{mg\,kg^{-1}}$, and those in the As(III)-5 24.1 and $2.48\,\mathrm{mg\,kg^{-1}}$, respectively.

2.5. Preparation of irradiation sample

Five bottles of BCR-626 and 5 bottles of NMIJ CRM 7901-a were used in the experiment. BCR-626 were diluted by 50 times with H_2O in order to conform their concentration levels to that of NMIJ CRM 7901-a. An aliquot amounts of samples were taken from 5

Table 1
Nuclear properties of As and Au [14,18,19].

Isotopes	Natural isotopic abundances, %	Induced radioactive nuclides	σ_0[a]	Q_0[b]	Half lives
^{75}As	100	^{76}As	3.86	13.6	1.09379 d
^{197}Au	100	^{198}Au	98.7	15.7	2.6951 d

[a] The thermal neutron cross-section, b.

[b] The ratio of epithermal neutron cross-section to thermal neutrons cross-section.

bottles of diluted BCR-626 and 5 bottles of NMIJ CRM 7901-a into PP bottles and then the proper amount of the Au working solution were added to them.

The irradiation samples were prepared as follows: Polyethylene (PE) film bags were made from PE film (0.005 mm thick, free from Al catalyst process, Hitachi Cable, Ltd., Tokyo, Japan) in our laboratory. The PE film bags and ADVANTEC No.5C paper filters were soaked in 2% HNO_3 to eliminate metallic impurities before use. After drying, a paper filter was put into a PE film bag. The sub-samples from each 5 samples of BCR-626 and NMIJ CRM 7901-a were gravimetrically poured on a paper filter in a bag by a PP syringe, while the weight of sample poured was weighed by a semi-microbalance. Then the PE film bags were doubly heat-sealed to make a sample package of 25 mm × 25 mm.

Two comparator standard series of As(III) and As(V) were prepared by the same manner as the AB irradiation samples. The amounts of As(III) and Au in the As (III) comparator standards were (0 μg As, 0.149 μg Au), (0.12 μg As, 0.107 μg Au), (0.119 μg As, 0.0950 μg Au), (0.340 μg As, 0.0744 μg Au), (0.660 μg As, 0.115 μg Au) and (1.15 μg As, 0.119 μg Au). The amounts of As(V) and Au in the As (V) ones were (0 μg As, 0.0990 μg Au), (0.0920 μg As, 0.0746 μg Au), (0.189 μg As, 0.102 μg Au), (0.268 μg As, 0.0632 μg Au), (0.636 μg As, 0.137 μg Au) and (1.13 μg As, 0.0986 μg Au). Two blank test samples were prepared, one of which was the paper filter in the PE film bag and the other was just the PE film bag. The AB samples and the comparator standards were placed in an irradiation capsule (33 mm diameter × 95 mm length).

All the AB samples and comparator standards were in the same shape and had the same matrix, so that the gamma ray attenuation was almost the same in the samples and the comparator standards.

2.6. Neutron irradiation and gamma ray measurements

The samples and comparator standards in the capsule were irradiated in the pneumatic irradiation system (PN-1, thermal neutron flux: $5.2 \times 10^{17}\ \mathrm{m^{-2}\ s^{-1}}$, irradiation time: 20 min, Cd ratio: 23) of Japan Research Reactor No. 3 (JRR-3) in Japan Atomic Energy Agency.

After cooling for 1 day, the gamma rays of ^{76}As (559.1 keV, $T_{1/2}$ = 1.09379 d) and ^{198}Au (411.8 keV, $T_{1/2}$ = 2.69517 d) were measured with the Ge semiconductor gamma ray detector. The AB samples and the comparator standards were placed 0.3 cm away from the detector on an acrylic resin plate. The emitted gamma ray was measured for 1000–3600 s, since the net gamma ray intensities of the peaks were required more than 6×10^4 counts in order to reduce counting statistics errors. The measured gamma ray spectrum was analyzed by SEIKO EG&G spectrum navigator (DS-P100/W32) and Hypermet-PC program [17].

3. Results and discussions

3.1. Selection of an internal standard radionuclide

An isotope suitable for an internal standard should have the sufficient sensitivity, the Q_0 value similar to a target isotope, the half-life longer than a target radionuclide, and no interfering emission. The nuclear properties of ^{75}As and ^{197}Au are shown in Table 1 [14,18,19]. The Q_0 value is the ratio of an epithermal neutron cross-section of nucleus to a thermal one and expresses the difference of reactivity of a nucleus irradiated by epithermal and thermal neutrons. The isotopes with the similar Q_0 value are affected equally by the difference of neutron flux and the sample matrix. The Q_0 value and the half-life of induced radionuclide of ^{197}Au are very similar to those of ^{75}As. Furthermore, ^{198}Au has simple gamma ray spectrum and does not interfere with ^{76}As measurement. Therefore, Au is a suitable element as an internal standard for As measurement. In addition, Au was not found in the BCR-626, NMIJ CRM 7901-a, As(III) and As(V) standard solutions, PE, and the paper filter, so it was quite preferable to be used as an internal standard in this experiment.

The background radiation of natural radionuclides was low enough not to affect the measurement of ^{76}As and ^{198}Au. There was no significant peak to interfere with gamma-ray peaks of ^{76}As 559.1 keV and ^{198}Au 411.8 keV under these experimental conditions.

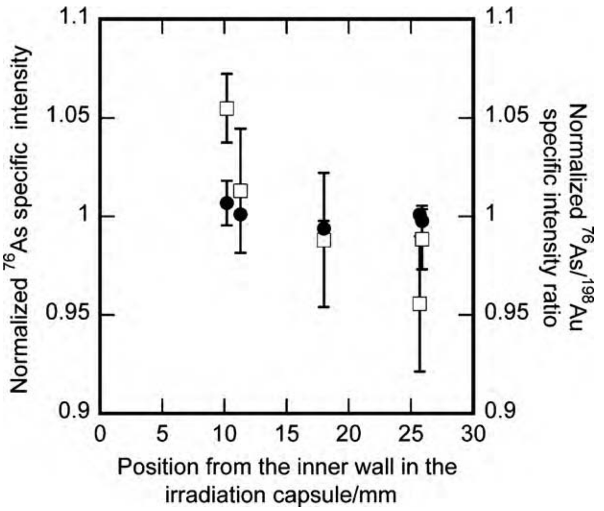

Fig. 1. Variation of the ^{76}As specific intensity (cps μg^{-1}) of As(III) comparator standards at 559.1 keV gamma ray peak in the irradiation capsule. (●) ^{76}As/^{198}Au specific intensity ratio normalized to the mean value; (□) ^{76}As specific intensity (cps μg^{-1}) normalized to the mean value. Half of each bar indicates the standard deviation of the measurement repetition (n = 2) on each comparator standard.

3.2. Homogeneity of reactor neutron flux

It is well known that the neutron flux significantly differs from position to position in an irradiation capsule, even when a steady state nuclear reactor is used. The variation of the specific intensity (cps μg^{-1}) of ^{76}As and ^{198}Au was investigated.

The specific intensities of ^{76}As and their ratios to ^{198}Au of As(III) comparator standards at different irradiation positions in the irradiation capsule are shown in Fig. 1, where they were normalized by their mean values, respectively. The deviation of ^{76}As/^{198}Au specific intensity ratios with position was 0.6%, although that of ^{76}As specific intensities was 4.0%. The uncertainty related to the neutron flux difference improved by 6 times when the ^{198}Au was used as an internal standard, as mentioned in the previous papers [10,11].

Table 2
Analytical results of BCR-626 and NMIJ CRM 7901-a by NAA.

Method	Bottle no.	BCR-626 As (mg kg^{-1}) Mean ± SD[a] (RSD)[b]	Bottle no.	NMIJ CRM 7901-a As (mg kg^{-1}) Mean ± SD (RSD)	Number of replicates
Proposed method	813	473 ± 1.9 (0.41%)	30	10.25 ± 0.11 (1.1%)	4
	903	477 ± 6.4 (1.4%)	116	10.15 ± 0.010 (0.10%)	4
	1138	489 ± 3.3 (0.68%)	268	10.10 ± 0.044 (0.43%)	4
	1285	518 ± 2.9 (0.56%)	365	10.09 ± 0.019 (0.19%)	4
	1599	538 ± 5.6 (1.1%)	401	10.19 ± 0.18 (1.8%)	4
	Mean	499 ± 28 (5.6%)	Mean	10.16 ± 0.066 (0.65%)	
k_0-NAA	258	504 ± 14 (2.8%)		10.2 ± 0.26 (2.6%)	5
Certified value		433.8[c] ± 2.5[d] (0.58%)		8.43 ± 0.20[d] (2.4%)	

[a] Standard deviation.
[b] Relative standard deviation.
[c] The certified value of BCR-626 was converted from the arsenobetaine concentration (As/$C_5H_{11}AsO_2$: 0.42077).
[d] Expanded uncertainty (k = 2).

Moreover, the specific intensity ratios of ^{76}As to ^{198}Au showed an excellent reproducibility of 0.13% (n = 2), when the different comparator standards were irradiated and measured in the different days. It shows the NAA potentially has high robustness in measurement when the proper internal standard is used.

3.3. Comparison of analytical sensitivity between As(III) and As(V) in NAA measurement

The measurement sensitivities of As(III) and As(V) are generally different when they were measured by ICP-OES and ICP-MS [15,20].

As(III) and As(V) were measured independently by NAA to compare their measurement sensitivities, although neutron capture and decay of a product nuclide are not influenced by the oxidation state and chemical form. Fig. 2 shows the two calibration curves prepared by As(III) and As(V) working solutions when Au was used as an internal standard. It is anticipated that both the calibration curves completely overlapped with each other and showed sufficient linearity up to 1 μg of As. Their correlation coefficients were larger than 0.999. The relative standard uncertainty related to the linearity of calibration curve was 0.20%. These results indicate that the sensitivity of NAA is not affected by the valence states of As and that NAA is a reliable method to measure total As concentration.

A minimum detectable value (MDV) is known to be a good indication to evaluate the performance of an analytical method. According to Currie and Svehla [21], MDV is calculated from the following equation

$$\mathrm{MDV} = \frac{3.29 \times \sqrt{(S_a{}^2 + S_y{}^2)}}{b}$$

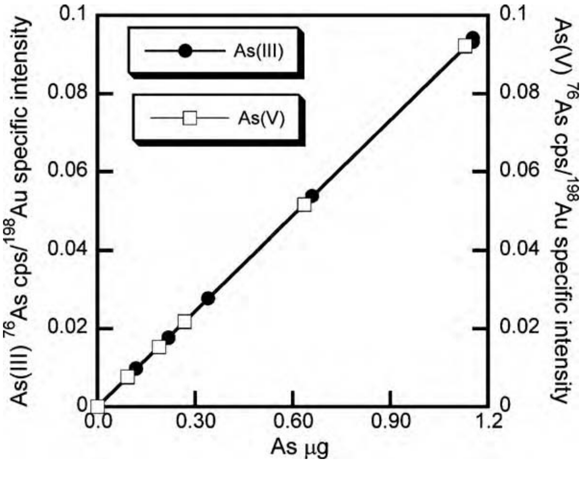

Fig. 2. The calibration curves of As(III) and As(V). (●) As(III); (□) As(V).

where S_a is the standard deviation of the calibration curve at the y-intercept, S_y the residual standard deviation of the calibration curve and b the slope of the calibration curve. In this experiment, S_a, S_y, and b were obtained as 3.98×10^{-5}, 8.13×10^{-5}, and 8.14×10^{-2} from Fig. 2, respectively. The MDV of As was calculated 4 ng. It was sufficiently lower than As amounts in the present samples, since the As amounts had been expected about 400 ng.

3.4. Determination of As in AB standard solutions

Total As concentrations of the AB standard solutions of BCR-626 and NMIJ CRM 7901-a were determined and the analytical results are shown in Table 2. Table 2 also shows the analytical results obtained by k_0-NAA, in which Al–0.1% Au alloy of IRMM-530 was used as a single comparator [14,22]. The analytical result of As in BCR-626 was (499 ± 28) mg kg^{-1} (RSD: 5.6%) when 4 sub-samples from each 5 bottles were measured, although the that by k_0-NAA method was (504 ± 14) mg kg^{-1} (RSD: 2.8%) when 5 sub-samples from 1 bottle were measured. The analytical result of As in NMIJ CRM 7901-a was (10.16 ± 0.066) mg kg^{-1} (RSD: 0.65%) when 4 sub-samples from each 5 bottles were measured, although that by k_0-NAA was (10.2 ± 0.26) mg kg^{-1} (RSD: 2.5%) when 5 sub-samples from 1 bottle were measured. The analytical results obtained by both methods were in good agreement with each other for both CRMs. These agreements denote the reliability of the proposed method.

As can be seen in Table 2, the RSDs of measurements were in the range from 0.1% to 1.8%, when 5 measurements of each bottle of BCR-626 and NMIJ CRM 7901-a were carried out. Those results suggest that the sample-to-sample repeatability of the proposed method is about 1% even when it is applied to actual samples. This value is almost the same as the variation of the intensity ratio (As/Au) mentioned in the previous section. On the other hand, RSDs of the mean values of BCR-626 and NMIJ CRM 7901-a were 5.6% and 0.65%, respectively. For BCR-626, it was 6 times higher than the sample-to-sample repeatability, although it was almost the same as its sample-to-sample repeatability for NMIJ CRM 7901-a. These results suggest that there may be large bottle-to-bottle inhomogeneity for BCR-626. As for k_0-NAA, the sample-to-sample repeatability was 2.8% for BCR-626 and 2.5% for NMIJ CRM 7901-a. It means that the sample-to-sample repeatability of k_0-NAA is about 3%.

3.5. Evaluation of the uncertainty

Each uncertainty component of the proposed method was evaluated to calculate the expanded uncertainty. The uncertainty budget of As measurement is shown in Table 3.

The uncertainty related to the difference of neutron exposure was not taken into consideration for the budget calculation,

Table 3
Uncertainty budget for analytical results of BCR-626 and NMIJ CRM 7901-a.

Component	BCR-626 Relative standard uncertainty, %	NMIJ CRM 7901-a Relative standard uncertainty, %
Preparation of sample		
Weighing	0.015	0.016
Internal standard addition	0.020	0.019
Preparation of standard solution		
Uncertainty of As(III) standard solution	0.010	0.010
Weighing	0.015	0.016
Internal standard addition	0.020	0.019
Peak integration	0.086	0.086
Calibration	0.24	0.20
Measurement variability (ANOVA)	0.48	0.71
Between-bottle homogeneity (s_{bb})	5.5	0.055
Neutron flux homogeneity[a]	–	–
Pulse pile-up	0.089	0.089
Gamma ray attenuation[b]	–	–
Decay correction	0.049	0.049
Arsenobetaine molecular weight	0.048	0.048
Combined standard uncertainty	**5.5%**	**0.76%**
Coverage factor	2	2
Expanded uncertainty ($k = 2$)	**11%**	**1.5%**

[a] Neutron flux homogeneity is corrected by internal standard method.
[b] All samples and comparator standards were same shape and had the same matrix, so gamma ray attenuation effects were equal.

because it was eliminated by the internal standard method. In addition, the AB samples and comparator standards were in the same shape and had the same matrix, so that gamma-ray attenuation was almost the same among all the irradiated samples. Therefore, the uncertainty related to the gamma ray attenuation was not taken into account for the calculation, neither.

The measurement variability of BCR-626 and NMIJ CRM 7901-a were calculated from analysis of variance (ANOVA). They were 0.48% for BCR-626 and 0.71% for NMIJ CRM 7901-a. The measurement variability of NAA with the proposed method was excellent. The uncertainty related to calibration was about 0.2%. As mentioned above, BCR-626 was expected to observe large variability among bottles, so that the between-bottle homogeneity of both CRMs was calculated based on the measurement data in Table 2 according to ISO Guide 35 [23,24]. The between-bottle homogeneity (s_{bb}) was calculated by following equation:

$$s_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}}$$

where MS_{among} is the mean squares among bottles, MS_{within} the mean squares within bottles, and n the number of observations for calculation of s_{bb}. The s_{bb} value of BCR-626 was calculated 5.51%, although that of NMIJ CRM 7901-a was 0.055%. The s_{bb} value of BCR-626 was much larger than the expanded uncertainty of the certified value. It suggests that there is a great possibility for BCR-626 to involve higher inhomogeneity among bottles than expected and that the between-bottle variation of NMIJ CRM 7901-a is sufficiently low in comparison to the measurement variability. The other uncertainty components were too small to affect the combined standard uncertainty.

As the results, the combined standard uncertainty of BCR-626 was 5.54% and that of NMIJ CRM 7901-a was 0.71%. The difference between them was due to the uncertainty of between-bottle homogeneity (s_{bb}). The combined standard uncertainty of NMIJ CRM 7901-a indicates that NAA coupled with the internal standard method possesses an excellent capability of precise analysis.

3.6. Comparison of analytical results and the certified values

As can be seen in Table 2, the analytical results of BCR-626 and NMIJ CRM 7901-a were 499 mg kg^{-1} and 10.16 mg kg^{-1}, although their certified values were 433.8 mg kg^{-1} and 8.43 mg kg^{-1}. The analytical results were 15–20% higher than the certified values. The relative expanded uncertainties of measurement result were 11% ($k = 2$) for BCR-626 and 1.5% ($k = 2$) for NMIJ CRM 7901-a, although those of the certified values were 0.58% and 2.4%, respectively. The expanded uncertainties could not give an appropriate explanation to the discrepancies between the certified values and analytical results. Furthermore, the production reports describe that BCR-626 and NMIJ CRM 7901-a were prepared from synthetic AB and that both CRMs do not contain significant amounts of other As species such as As(III), As(V), and organoarsenic compounds [1,2]. The As impurities could not be attributed to the discrepancies, neither. In addition, the between-bottle variation of BCR-626 was much larger than the expanded uncertainty, although that of NMIJ CRM 7901-a was almost negligible and although the uncertainty of the measurement of NAA was less than 1%. These experimental results suggest that the valid values of As of BCR-626 and NMIJ CRM 7901-a are higher than their certified values.

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