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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 ± 6) mg kg^{-1} ($k = 2$), that is, As concentration was (433.8 ± 2.5) 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 ± 0.47) mg kg^{-1} ($k = 2$), at the same time, As concentration was (8.43 ± 0.20) 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 ($[As] = (9.933 \pm 0.055)$ 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; $99.9926 \pm 0.0030\%$) 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 μg 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 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 mg kg^{-1}, those in the As(V)-1 1.99 and 1.61 mg kg^{-1}, those in the As(V)-2 4.92 and 2.65 mg kg^{-1}, those in the As(V)-3 7.95 and 1.88 mg kg^{-1}, those in the As(V)-4 11.6 and 2.50 mg kg^{-1}, and those in the As(V)-5 21.5 and 1.87 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 ± 0.10 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 mg kg^{-1}, those in the As(III)-1 2.02 and 1.81 mg kg^{-1}, those in the As(III)-2 4.59 and 2.00 mg kg^{-1}, those in the As(III)-3 9.09 and 1.99 mg kg^{-1}, those in the As(III)-4 13.7 and 2.39 mg kg^{-1}, and those in the As(III)-5 24.1 and 2.48 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