



Young Scientist Feature

## Development of an apple juice certified reference material for cadmium, lead, total arsenic and arsenic species



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### ABSTRACT

In the development of the apple juice certified reference material, isotope dilution mass spectrometry method was used for the assignment of certified values and long-term stability study for cadmium and lead. For total arsenic, inorganic arsenic, as well as dimethylarsenic acid, standard addition method was used. The analytes were found to be homogenous and stable over a period of at least 4.5 months at storage temperature of  $-20^{\circ}\text{C}$  (long-term stability). The certified mass fraction values were  $(0.220 \pm 0.011)$  mg/kg for cadmium,  $(0.245 \pm 0.014)$  mg/kg for lead,  $(0.185 \pm 0.015)$  mg/kg for total arsenic,  $(0.124 \pm 0.012)$  mg/kg for inorganic arsenic [As(III)+As(V)] and  $(0.0601 \pm 0.0052)$  mg/kg for DMAA. The recovery of the arsenic species was over 99%. This apple juice certified reference material can be used for method validation or as a quality control material by routine testing laboratories.

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### 1. Introduction

For drinking water, the maximum contaminant level for cadmium has been set at  $3\ \mu\text{g/L}$  according to the World Health Organization (WHO) and  $5\ \mu\text{g/L}$  according to the US Food and Drug Administration (FDA) and the Environmental Protection Agency (EPA) [1–3]. FDA has also established a guidance level of 50 ppb of lead in ready-to-drink fruit juices, in line with the Codex Alimentarius Commission standard [4,5]. In addition, FDA has proposed an “action level” for inorganic arsenic in apple juice to be  $10\ \mu\text{g/L}$  [6]. It is the same level as for arsenic in drinking water set by the EPA [3]. Meanwhile, the Agri-Food and Veterinary Authority of Singapore (AVA) has regulated the maximum amount of lead and arsenic in fruit juices to be 300 and 200 ppb, respectively [7]. There is no limit specified for cadmium in fruit juices. However, the Sale of Food Act mentions that natural mineral water and any article of food shall not contain more than 10 ppb and 200 ppb of cadmium, respectively [7].

Cadmium is considered a cumulative nephrotoxicant, whose level in human organs increases with age due to the lack of an active biochemical process for its elimination coupled with renal

reabsorption. There has been accumulating evidence for the carcinogenic risk of chronic cadmium exposure [8]. Lead, on the other hand, has the ability to affect almost every system in the human body, including the reproductive, neurological, hematopoietic, hepatic and renal systems [9]. Long term low level exposure in children is harmful for the brain and nervous system [10]. As in cadmium and lead, acute and chronic exposures to arsenic can also cause adverse health effects to human including dermal changes, damage to internal organs and carcinogenic effects [11,12].

Arsenic found in fruits and vegetables is primarily organic arsenic and only less than 10% of the arsenic is present in the inorganic form [11]. Inorganic arsenic in apple juice may come from processing aids, prior and/or current use of pesticides containing arsenic on apple orchards, natural arsenic in soil or water and atmospheric deposition from industrial activities [13]. In human, organoarsenic compounds including monomethylarsinic acid (MMAA) and dimethylarsinic acid (DMAA) are not readily taken up by the cell, subjected to limited metabolism and excreted close to their original form in the urine [11]. In contrast, the soluble inorganic arsenic can be absorbed and accumulated in tissues and body fluids. Hence, inorganic arsenic species are more toxic than the organic ones and As(III) is more toxic than As(V) [11,12]. Arsenic speciation gives valuable information that helps in judging the actual level of toxicity.

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This paper describes the development of an apple juice certified reference material (CRM) containing cadmium, lead, inorganic [As(III) and As(V)] as well as organoarsenic (DMAA) species. The development of the CRM, including procedures for sample preparation, homogeneity study, stability study, assignment of reference values and uncertainty evaluation, was carried out in accordance with the requirements of ISO Guides 34 and 35 [14,15].

Prior to establishing the certified mass fraction values for the analytes in the material, a method development was conducted using CRMs from the National Metrology Institute of Japan (NMIJ) (Tsukuba, Japan). The results obtained were in good agreement with certified concentration levels. To the best of our knowledge, there are currently no available CRMs for arsenic speciation in fruit juice matrix. Hence, rice flour CRMs were used in the method development.

## 2. Material and methods

### 2.1. Reagents, standard solutions and CRMs

All experimental work was carried out in class 100 low laminar flow fumehoods or a class 10,000 clean room. Standard and sample solutions were prepared gravimetrically on a microanalytical balance (Mettler Toledo XP205 or XP26, Greifensee, Switzerland).

The certified reference standards for cadmium, lead and total arsenic were obtained from the National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA). Isotopically enriched isotopes were purchased from Oak Ridge National Laboratory (Oak Ridge, TN, USA). For determination of cadmium, lead and total arsenic, all working solutions were diluted with 5% HNO<sub>3</sub> (aq). Nitric acid (67–70% HNO<sub>3</sub>, Ultrapur-100, Kanto Kagaku Singapore Pte Ltd) used was distilled twice using DST-1000 sub-boiling distillation system (Savillex Corporation, MN, USA). The As(III), As(V) and DMAA standards were obtained from the National Metrology Institute of Japan (NMIJ) (Tsukuba, Japan). Stock solution for As(III) was prepared by dissolving As(III) trioxide powder in 1% NaOH (aq), while stock solution for As(V) and DMAA were prepared by diluting with Milli-Q element water (18.2 MΩ cm, Millipore Corporation, MA, USA). The certified reference standards and isotopically enriched isotopes used are listed in Table 1.

The brown rice (CRM 7532-a) and white rice (CRM 7503-a) CRMs used for method development were obtained from NMIJ.

The high-performance liquid chromatography (HPLC) buffer solution used for arsenic speciation was prepared by adding 0.7 g tetramethylammonium hydroxide pentahydrate (99%, Aik Moh Paints and Chemicals, Singapore), 1.6 g sodium 1-butanefulfonate ( $\geq 99.0\%$ , Sigma Aldrich, MO, USA), 0.7 g malonic acid (Reagentplus 99%, Sigma Aldrich, MO, USA) and 0.5 mL methanol (HPLC grade, J.T. Baker, PA, USA) into 1 L of Milli-Q water. The pH of the buffer solution was approximately 3.0.

### 2.2. Instrumentations

An Agilent Technologies 7700x ICP-MS system (ICP-MS) (Agilent Technologies International Japan, Ltd., Tokyo, Japan) equipped with an octopole collision cell was used for measurements of cadmium and lead. Measurements of total arsenic were carried out using a Finnigan Element 2 (Finnigan MAT GmbH, Bremen, Germany) sector-field ICP-MS (SF-ICP-MS) using a self-aspirating PFA MicroFlow nebulizer. For arsenic speciation, an Agilent Technologies 1200 HPLC was coupled with the ICP-MS system to separate and measure the different arsenic species [As(III), As(V) and DMAA]. The HPLC was equipped with an automatic sample injector for direct sample introduction into the ICP-MS. The instruments were conditioned and optimized daily to achieve optimum

sensitivity and stability. The typical operating conditions and data acquisition parameters are summarized in Table 2.

### 2.3. Preparation of candidate CRM sample

The apple juice material, obtained from a local supermarket, was screened and found to contain negligible amount of cadmium, lead and arsenic. The material was filtered using Nalgene Rapid-Flow™ Filter Units (90 mm nylon membrane, 0.2 μm pore, VWR, PA, USA), preserved with sodium benzoate (1.2 g/L, >98.0%, HPLC grade, Tokyo Chemical Industry, Tokyo, Japan) and spiked with cadmium nitrate tetrahydrate, lead (II) nitrate from Sigma Aldrich (MO, USA) as well as As(III) trioxide, As(V) and DMAA from NMIJ. The mixture was then homogenized by mixing on a shaker for 1 h and bottled into 125-mL high-density polyethylene (HDPE) bottles. Each bottle containing 100 mL of apple juice was flushed with nitrogen gas for 15 s before sealing and labelled according to its dispensing sequence number. A total of fifty four bottles were prepared. The targeted ranges of concentration for cadmium, lead, inorganic arsenic and DMAA in the apple juice were 0.2–0.4 mg/kg, 0.2–0.4 mg/kg, 0.02–0.2 mg/kg and 0.01–0.1 mg/kg, respectively. The apple juice was not acidified so that it would closely match in terms of matrix, measurands and concentrations to the type of materials encountered in routine testing or calibration. For long term storage, the material was stored in frozen state at –20 °C to reduce the risk of deterioration.

### 2.4. Homogeneity study, stability study and assignment of reference values

The homogeneity of the material was established by selecting six bottles using a stratified random sampling scheme. The samples were analyzed by ICP-MS using isotope dilution mass spectrometry (IDMS) for cadmium and lead, by SF-ICP-MS using standard addition method for total arsenic and by HPLC-ICP-MS using external calibration method for arsenic species. The homogeneity of each analytes was tested using the one-way analysis of variance (ANOVA) on duplicate results from these six bottles. The result from the homogeneity study of total arsenic was also used for assignment of reference value.

For the assignment of reference values three bottles were randomly selected and two subsamples were taken from each bottle. The measurements were carried out using IDMS (cadmium and lead) and standard addition (arsenic species) methods. The results were taken as the first point ( $t=0$  month) in the long-term stability study. Two more stability points were determined at time interval of 3 and 4.5 months, using the classical design [16].

### 2.5. Sample preparation for analysis

For determination of cadmium, lead and total arsenic content, a multiple spiking approach was used for the sample preparation. Calculated amounts of enriched isotope spike solutions (<sup>111</sup>Cd and <sup>206</sup>Pb) were added gravimetrically into approximately 1 g of apple juice. The mixture was digested with 2.5 mL of concentrated HNO<sub>3</sub> at room temperature overnight. Afterwards, a calculated amount of gallium (Ga) standard solution (SRM 3119a, NIST, Gaithersburg, MD, USA) was added into the digest and the mixture was diluted to 50 g using Type I Milli-Q water. The final weight of the diluted digest was recorded. The digest was then used to prepare sample blends (cadmium and lead) as well as unspiked and spiked solutions (total arsenic). This protocol was employed for the homogeneity testing, assignment of reference values as well as long-term stability studies.

For arsenic speciation, approximately 0.5 g (for external calibration) or 1 g (for standard addition) of apple juice was diluted with

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