A simplified analysis of dimethylarsinic acid by wavelength dispersive X-ray fluorescence spectrometry combined with a strong cation exchange disk

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HIGHLIGHTS

- A simplified approach for the analysis of DMA^V has been developed.
- A strong cation exchange (SCX) disk was used to pre-concentrate DMA^V from water samples.
- The SCX disk adsorbing DMA^V was directly analyzed by WDXRF.
- A correction factor was derived to compensate for the Pb interference effect.
- The accuracy and precision of the SCX-WDXRF method were assessed by spike tests.

GRAPHICAL ABSTRACT
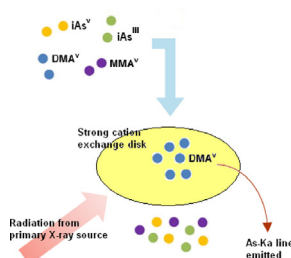
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ABSTRACT

Dimethylarsinic acid (DMA^V) was pre-concentrated from water samples using a strong cation exchange (SCX) disk functionalized with sulfonic groups, before being analyzed by wavelength dispersive X-ray fluorescence spectrometry (WDXRF). The adsorption of DMA^V occurred preferentially on the surface of the SCX disk, regardless of pH levels, probably due to interactions with the sulfonic functional groups. However, no other arsenic species, such as arsenate (iAs^V), arsenite (iAs^{III}), and monomethylarsonic acid (MMA^V), were retained. The SCX-WDXRF method produced a strongly linear calibration curve ($R^2 = 0.9996$) with its limit of detection at 0.218 µg L^{-1} when a one-liter water sample was used for pre-concentration. The As intensity of the system was sensitive to the Pb content retained on the SCX disk owing to the proximity of the As-Kα and Pb-Lα lines. To compensate for this interference, a correction factor was developed by considering the calibration slope ratio between the X-ray intensity measured at a *Bragg angle* of 48.781° and the Pb content of the SCX disks. The results of spike tests for iAs^V, iAs^{III}, MMA^V, and DMA^V with and without the addition of Pb in synthetic landfill leachate exhibited reasonable recoveries (i.e., 98–105%) after the spectral adjustment for the Pb interference.

1. Introduction

Arsenic (As), a highly toxic metalloid, is found throughout aquatic and terrestrial environments and originates from both anthropogenic and natural sources (e.g., arsenic bearing minerals like arsenopyrite (FeAsS)) [1–3]. It has been used in various industrial and agricultural applications such as pesticides [4] and wood preservatives (e.g., chromate copper arsenate) [5]. Evidence collected over the past decades suggests that dimethylarsinic acid (DMA^V) found in various environmental samples can be attributed to its extensive use as a component of herbicides [6]. In general, inorganic arsenic species (e.g., trivalent arsenite (iAs^{III}) and pentavalent arsenate (iAs^V)) are considered to be more toxic than

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organic forms such as monomethylarsonic acid (MMA^V), DMA^V, and arsenobetaine (AsB) [2,7]. However, DMA^V is now suspected to pose a potential health risk of its own (i.e., not only as a byproduct of the detoxification process of inorganic arsenic species) [6]. The presence of DMA^V can indirectly reflect the potential risk of inorganic arsenic transmission since it is a major metabolite in human and other animals via arsenic methylation process [2,6,8]. This, in turn, agrees with the general findings that DMA^V (60–80%) is dominant in terms of the As speciation in human excretion (with the remaining 10–30% as iAs^V and iAs^{III} and 10–20% as MMA^V) [9]. Furthermore, dimethylmonothioarsinic acid (DMMTA^V), which has drawn a great deal of attention due to its high toxicity toward human cells [10], has been observed in municipal landfill leachate [11]. Depending on the availability of sulfide in the surrounding environment, it can be formed from a reaction pathway of DMA^V. As such, the development of techniques to accurately measure arsenic species, not to mention DMA^V, is important to properly account for their potential health risks to humans and the environment.

A variety of methods have been reported for measuring arsenic speciation. The most promising approaches involve the use of hyphenated systems such as high performance liquid chromatography (HPLC) or ion chromatography linked to an inductively coupled plasma mass spectrometry (ICP-MS) that combine the separation and detection capabilities of the two methods [12,13]. A wide array of HPLC–ICP-MS applications has already been introduced for quantifying arsenic species in various environmental matrices such as landfill leachate [11], arsenic-rich spring water [14], and cell extracts [10,15]. However, such hyphenation methods have many drawbacks such as maintenance, expense, interface design, and lengthy separation procedures [16]. As a result, the operation of such a system has often been suspected to add biases to the pre-existing uncertainties. Furthermore, high concentrations of organic carbon in samples and organic solvents contained in the HPLC eluent may lead to carbon build-up in the plasma region (reduction of instrumental sensitivity), thus requiring costly maintenance [17]. In addition, $^{40}Ar^{35}Cl$ (i.e., the same mass to charge (m/z) ratio as arsenic) may be generated by argon from the plasma combining with chloride from the sample matrix. This seems to increase artifacts in the measurement of arsenic in samples with high chloride concentrations [13,17]. Although it can be overcome by using the ICP-MS equipped with the special apparatus such as dynamic and/or collision reaction cell and sector-field ICP-MS with a high resolution, they require the proficiency in multiple analytical skills. Clearly, these problems demonstrate the need to develop a simplified method for the separation and detection of arsenic species.

To attempt to resolve the difficulties associated with the analysis of arsenic species, we have, for the first time, investigated an experimental technique for the rapid and simple determination of trace levels of DMA^V in solution samples by using wavelength dispersive X-ray fluorescence spectrometry (WDXRF) with the aid of a solid phase extraction (SPE) disk. We have chosen a direct analysis technique such as WDXRF to avoid the multistage elution procedure and/or the additional use of solvents. In addition, a disk (i.e., thin layer) type SPE was reliable enough to provide an ideal support for the XRF analysis by eliminating additional experimental steps (e.g., preparation of the specimen) [18,19]. The feasibility of the SPE-WDXRF system for the analysis of DMA^V as an alternative tool to complex hyphenated systems has been investigated here. The correction for interference from lead (Pb) was evaluated because of the proximity of the As and Pb energy lines (i.e., 10.542 keV for As-Kα and 10.550 keV for Pb-Lα) when employing the WDXRF analysis. The limit of detection for this technique was also assessed and compared to those of conventional methods (i.e., HPLC–ICP-MS). In addition, its applicability to complex environmental media was tested with the

consideration of Pb interference. The new method introduced in this study has the advantages of eliminating time-consuming and complicated sample handling procedures, while allowing us to pursue more green analytical chemistry by minimizing the use of solvents [20].

2. Materials and methods

2.1. Instruments

The WDXRF (PW2404, Phillips, Netherlands) was used to determine As and Pb concentrations retained on the SPE disk. It is applicable to the qualitative measurement of most elements (i.e., beryllium (Be) to uranium (U)) at varying concentration levels by employing the appropriate wavelength-diffraction crystal. A rhodium (Rh) target X-ray (4 kW) tube equipped with a thin Be-window (i.e., thickness = 75 μm) was used. The X-ray pathway was positioned in a vacuum chamber (<3 Pa) to avoid adsorption by air. Diameters of X-ray collimator and aluminum (Al) sample holder used were both 27 mm.

The *Bragg angles* (i.e., 2θ degree) of As-Kα, Pb-Lα, and Pb-Lβ1 were 48.781, 48.742, and 40.382°, respectively, when using a LiF220 crystal. Details of the instrumental conditions used in this study are presented in Table 1(a).

The As and Pb concentrations in the solutions were determined using an Agilent 7700s ICP–MS spectrometer. Specific information concerning the instrumental setup is presented in Table 1(b). A tuning solution (1 ppb) of lithium (Li), cerium (Ce), yttrium (Y), and thallium (Tl) was used to optimize the ion intensity, resolution, and mass axis and to minimize the effect of oxide ions and doubly charged ions by monitoring the ^7Li, ^{89}Y, ^{205}Tl, $^{156}CeO^+/^{140}Ce^+$, and $^{70}Ce^{2+}/^{140}Ce^+$. The presence of As and Pb was monitored at an m/z ratio of 75 and 208 with the software Mass Hunter (Agilent Technologies, Yokogawa, Japan).

The analysis of arsenic species was made by HPLC linked to the ICP–MS. The separation of arsenic species was achieved by a Hamilton PRP X-100 anion exchange column (250 mm × 4.6 mm (id), 10 μm particle size, and 100 Å pore size). Mixture of 2 mM NaH$_2$PO$_4$ and 0.2 mM EDTA (pH 6.0 adjusted by 1 M NaOH) was used as a mobile phase (eluent) at a flow rate of 0.8 mL min^{-1}. Sample injection volume was 20 μL.

Table 1

Instrumental conditions of WDXRF and ICP-MS for the As and Pb analysis in this study.

Parameter	Setup conditions
(A) Wavelength dispersive X-ray fluorescence spectrometry (WDXRF)	
Crystal type	LiF220 (2d[a] = 0.2848 nm)
X-ray tube	Rhodium (Rh) target (60 kV, 50 mA)
Collimator	300 μm
Window	Be (d[a] = 75 μm)
Beam (tube) filter	Not used
Peak angle	48.781 ($^\circ 2\theta$) for As-Kα/40.382 ($^\circ 2\theta$) for Pb-Lβ1
Background offset[b]	0.6088 ($^\circ 2\theta$) for As-Kα/0.5816 ($^\circ 2\theta$) for Pb-Lβ1
Analyzing time	200 s (i.e., 100 s for As, 100 s for Pb)
(B) Inductively coupled plasma mass spectrometry (ICP-MS)	
RF power	1500 W
Carrier gas flow	Ar 0.70 L min^{-1}
Make-up gas flow	Ar 0.54 L min^{-1}
Extract 1 and 2 lens voltage	4.3 V for extract 1/−130 V for extract 2
Omega lens voltage	13.2 V
Torch	Standard quartz, 2.5 mm
Nebulizer	Quartz concentric
Sampling and skimmer cone	Nickel
Integration time/mass	0.33 s
Monitored mass	m/z 75 for As, m/z 208 for Pb

[a] Thickness.
[b] Angular difference between peak and background.