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Evaluation of liquid chromatography inductively coupled plasma mass spectrometry for arsenic speciation in water from industrial treatment of shale ☆

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Abstract

This work describes an arsenic speciation analysis in aqueous effluent from a shale industrial plant using liquid chromatography coupled to inductively coupled plasma mass spectrometry (LC–ICP–MS). Arsenic species have been separated through an anion-exchange column and several parameters investigated, such as retention time, pH, flow rate and concentration of the mobile phase (ammonium carbonate), chloride interference and column conditioning time. The best conditions have been found by fixing the pH of the mobile phase at 8.7. Keeping the mobile phase flow rate at 1.5 ml min^{-1}, arsenic species were separated by varying the concentration of the mobile phase and the time of elution, as follow: 1.5 mmol l^{-1} for 10 min, 12 mmol l^{-1} for 10 min and 20 mmol l^{-1} for 10 min, respectively. Up to 13 As species present in the samples were separated under these conditions and the following species could be identified and quantified: arsenite [As(III)], dimethylarsinic acid (DMA), monomethylarsonic acid (MMA) and arsenate [As(V)]. The limits of detection of the LC–ICP–MS method were 0.02, 0.06, 0.04 and 0.10 μg l^{-1} of As(III), DMA, MMA, and As(V), respectively. The concentration of these species in the samples were from 3.7 to 6.4 μg l^{-1}, 6.9 to 13.2 μg l^{-1}, 100 to 142 μg l^{-1} and 808 to 1363 μg l^{-1} for As(III), DMA, MMA and As(V), respectively. The accuracy, evaluated by recovery tests, varied from 94 to 105% and the precision, evaluated by the relative standard deviation was typically lower than 10%.

Keywords: Arsenic speciation analysis; Liquid chromatography inductively coupled plasma mass spectrometry; Industrial effluent

1. Introduction

Arsenic is widely distributed in soils, sediments, water, air and living organisms. For example, arsenic concentration in igneous and sedimentary rocks is about 2 mg kg^{-1} [1]. Other sources of natural occurrence of arsenic are fossil fuels, such as petroleum, coal and shale. Shale, or bituminous shale, is a sedimentary rock with high levels of argillaceous constituents and about 8% of carbonaceous material (kerogen). Shale has been used for oil production based on a pyrolysis process in a retort, where the shale is heated at 500 °C in inert atmosphere while the kerogen is converted to oil and separated. In this process, which is called retorting, other by-products are generated, such as naphtha, combustible gas, liquefied gas, sulfur, retorted residues, ashes and considerable amounts of waste water. This water originates from mineral dehydration, combustion, groundwater seepage and steam and moisture in the input gas. The presence of impurities in the shale can affect oil production and previous purification is currently necessary. Purifying is usually made by water washing of the raw shale, partially retorted shale and oil shale. The water that comes from the retort shale contains a high amount of organic substances (mainly phenols and sulfur-containing compounds), as well as a great number of trace metals and metalloids that are potentially toxic for aquatic biota and humans [2]. Among the trace elements, arsenic can be found at relatively high concentration and in quite different forms [3]. However, not a single publication could be found dealing with the quantification of these arsenic

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species in shale retort water, most likely due to difficulties of speciation analysis.

Nowadays, the knowledge about the different species of elements present in environmental and biological materials is important, since the effects and/or toxicity of an element, besides its concentration depends to a great extent on its chemical form [4]. Extensive studies concerning As toxicity have already shown that different arsenic species exhibit different toxicities; inorganic As compounds are more toxic than organic compounds and the acute toxicity generally decreases with increasing degree of methylation [5]. Depending on the source, a metal or metalloid can enter the environment, where it might be converted into another compound [6]. Therefore, in order to get information on the activity and toxicity of a specific element it is necessary to know its specific chemical and physical forms [4].

A wide variety of techniques has been used for arsenic species separation and detection [7–13]. However, in most cases it was necessary to decompose the sample, which might transform arsenic species and impede speciation analysis [14]. Electrospray–mass spectrometry (ES–MS) and high-performance liquid chromatography ES–MS (HPLC–ES–MS) [15] are frequently used for speciation analysis. With the use of ES–MS it is possible to identify unknown species, even without the use of standards. However, it has some limitations, such as difficult ionization of some arsenic species as dimethylarsenic acid (DMA) [10]. In addition, signal suppression up to 50% has been reported in HPLC–ES–MS [16]. As a consequence, these techniques are more feasible for screening purposes.

Currently, inductively coupled plasma mass spectrometry (ICP-MS) is the most widely used detector for elemental speciation analysis because it provides high sensitivity, wide linear dynamic range and it can be easily combined with many separation techniques [12,16,17]. Thus, liquid chromatography inductively coupled plasma mass spectrometry (LC–ICP–MS) [18,19] has become an established technique for arsenic speciation analysis [17]. One of the most important advantages of LC is the extended range of separation mechanisms available using different mobile and stationary phases, which provide nearly all conditions necessary for the separation of element species [20].

Although inorganic and organic arsenic compounds have already been determined in a variety of materials, little information is available in the literature with respect to arsenic speciation in oil shale [2,21,22] and related wastes [2]. The aim of this work was to develop a method for arsenic speciation analysis in aqueous effluent from shale processing using LC–ICP–MS. Parameters related to sample preparation, As species separation and quantification by LC were evaluated (pH of sample and mobile phase, mobile phase flow rate, mobile phase concentration and column conditioning). The isobaric chloride interference (as $^{40}Ar^{35}Cl^{+}$) on $^{75}As^{+}$ determination in shale retort water was also evaluated.

2. Experimental

2.1. Reagents

Distilled, deionized water was purified using a Milli-Q system (Millipore Corp., Bedford, USA). Calibration solutions for total As determinations were prepared from a 10 mg l^{-1} As stock solution (Spex CertiPrep, Metuchen, USA). Stock solutions of 1000 mg l^{-1} arsenic were prepared in water from dimethylarsinic acid ($C_2H_6AsO_2Na$, Sigma, St. Louis, USA), arsenite (As(III) — $NaAsO_2$, Merck, Darmstadt, Germany), arsenate (As(V) — Na_2HAsO_4 7 H_2O, Riedel-de Haën, Seelze, Germany) and monomethylarsonic acid (MMA — CH_5AsO_3, donated by Dr. J. Feldmann, University of Aberdeen, Aberdeen, UK). Stock solutions of 1000 mg l^{-1} arsenic were prepared in ammonium hydroxide (Merck) from *p*-arsanilic acid (*p*-ASA — $C_6H_8AsNO_3$, Sigma) and arsenobetaine (AsB — $C_3H_6AsCH_2COOH$, donated by Dr. W. Goessler, Karl-Franzens-University, Graz, Austria). Reference solutions of these arsenicals were calibrated against an arsenic standard solution (Spex CertiPrep) using ICP-MS. Individual stock solutions of 10 mg l^{-1} As for As(III), As(V), DMA, MMA, *p*-ASA and AsB were prepared in Milli-Q water, and stored at 4 °C in the dark [23].

The mobile phase used was ammonium carbonate (Merck) and it was prepared in Milli-Q water and filtered through a membrane filter (0.45 μm). The pH of this eluent was adjusted by using ammonium hydroxide (Merck) or nitric acid (Merck), when necessary.

High-purity concentrated nitric acid, obtained by sub-boiling distillation of reagents grade (Merck) and H_2O_2 30% (v/v) (Synth, Diadema, Brazil) were used for acid digestion of the samples. All other reagents used were of analytical grade. Working solutions were prepared daily.

2.2. Instrumentation

An inductively coupled plasma mass spectrometer (PerkinElmer SCIEX, Model ELAN DRC II, Thornhill, Canada), equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a cyclonic spray chamber (Glass Expansion, Inc., West Merbourne, Australia) and a quartz torch with a quartz injector tube (2 mm i.d.), was used throughout. Instrumental performance optimization, including nebulizer gas flow rate, ion lens voltage and torch alignment, was carried out following the instructions of the manufacturer, using conventional nebulization. The operational conditions are shown in Table 1. Single ion monitoring at *m/z* 75 was used to colleted the data, which were obtained by integrating peak area, using the Chromera software (PerkinElmer, version 1.2, 2006).

The LC system consisted of a quaternary pump (Model Series 200, PerkinElmer) equipped with a Rheodyne six-port injector valve, a 200 μl sample loop and a separation column (Dionex,

Table 1
Operational parameters for ICP-MS

RF power	1400 W
Plasma gas flow	15 l min^{-1}
Auxiliary gas flow	1.2 l min^{-1}
Nebulizer gas flow	1.15 l min^{-1}
Sampler and skimmer cones	Pt
Ion lens	7.2 V
Data collection mode	Single monitoring ^{75}As
Dwell time	250 ms