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Review

A critical review of selenium analysis in natural water samples

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ABSTRACT

This paper critically reviews the current understanding of the analysis of selenium in the natural environment. Several inorganic species of Se (−2, 0, +4, and +6) and organic species (monomethylated and dimethylated) have been reported in aquatic systems. Inorganic speciation of Se varies with pH and E_h. Many different analytical methods including UV–visible spectrophotometry, spectrofluorimetry, atomic fluorescence spectroscopy (AFS), chromatography, flameless atomic absorption spectroscopy (FAAS), electrochemistry, and inductively coupled plasma with atomic emission (ICP-AES) or mass spectrometry (ICP-MS) are available for quantification of selenium levels in different matrices. In recent years, analytical speciation techniques made a great leap in separating and detecting low levels of Se, but analyzing reduced species such as Se(0), polyselenides, and sulfur–selenium mixed species in the environment need further development. A number of selenium compounds has been identified in biota, but positive identification of such compounds in environmental samples is needed to understand the speciation of selenium in natural waters, sediments, and soils.

Contents

1. Introduction

The narrow concentration range between essentiality and toxicity for Se and adverse effects for fish and wildlife populations experienced in many world regions require a thorough understanding of processes responsible for Se mobilization. The complex

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speciation of Se, which is governed by biological processes occurring at the sediment and in the water column as well as by physicochemical factors including redox conditions, pH and availability of sorbing surfaces [1,2], makes the analysis of selenium species more important than total selenium itself. The most relevant species include Se(VI), Se(IV), Se(0), Se(-II) and a number of Se-containing organic compounds [1]. Selenium is reduced to hydrogen selenide, H_2Se, or other selenides at relatively low redox potentials. Hydrogen selenide by itself is not expected to exist in the aquatic environment since the Se(0)/H_2Se couple falls even below the H^+/H_2 couple. Aqueous solutions of H_2Se are actually unstable in air due to its decomposition into elemental selenium and water. Under moderately reducing conditions, heavy metals are precipitated as the selenides, which have extremely low solubilities. The following are log *K*s values of some heavy metal selenides of environmental interest: −11.5 (Mn^{2+}), −26.0 (Fe^{2+}), −60.8 (Cu^{+}), −48.1 (Cu^{2+}), −29.4 (Zn^{2+}), −35.2 (Cd^{2+}), and −64.5 (Hg^{2+}). The precipitation of selenium as heavy metal selenides can be an important factor affecting the cycling of the element in soils and natural waters.

2. Analysis

A strong interest in the dual role of Se as an essential element and a toxic one led to the development of various analytical techniques for the determination of selenium species in environmental matrices [3–10]. The evaluation of the role of elemental selenium in the speciation of this element is a critical point, due to the difficulty in the detection of Se(0) at environmental concentrations. Se(0) is commonly considered an unavailable form of Se because of its insolubility and its presence as a colloidal species, which represents a criticity in the separation of selenium species. More recently, Se(0) was determined in sediments by using X-ray based techniques, including X-ray absorption and X-ray fluorescence spectroscopy [11–13]. Although in recent years the performances of analytical speciation techniques have been greatly improved providing both good separation and powerful detection levels, quantitative evaluation of the speciation of Se in the environment still presents many challenges, particularly in reducing environments [10,12,14]. Recent studies seem to suggest that Se(0) is one of the largest pools of Se in aquatic systems since it may account for about 30–60% of total Se in sediments [9,15].

2.1. Atomic absorption and atomic fluorescence spectroscopy

Flameless atomic absorption spectroscopy (FAAS) has been employed with three main configurations [4]: electrothermal atomization with direct sample injection in a graphite furnace (ETAAS) [16], hydride generation with quartz tube atomization (HG-AAS) and hydride generation with in situ trapping in a graphite furnace (HG-ETAAS). HG-AAS and HG-ETAAS offer reduced chemical interferences but require larger sample volumes than does ETAAS. HG-ETAAS including pretreatment with an iridium coating, represents an elegant and reliable technique for the determination of Se and other elements such as Te, and As, allowing preconcentration and better control of interferences both in the liquid phase and in the atomization step [4]. When coupled with a flow injection technique, the detection limit is at the ng L^{-1} level (Fig. 1).

Sodium borohydride ($NaBH_4$) is the most common reducing agent used to obtain Se hydride species. Se(IV) is the only species able to produce hydrides, thus the sample analyzed without any pretreatment provides the Se(IV) concentration. Total inorganic selenium in the sample may be obtained after a preliminary reduction of Se(VI) to Se(IV) by reaction with $NaBH_4$, HBr, HBr/$KBrO_3$, HCl or HCl/KBr at high temperature [17]. UV photolysis in alkaline or acid solution is also used for the reduction of Se(VI) to Se(IV) [18]. The more traditional approach consists of heating the sample with 2–6 M HCl in a microwave oven at 90–100 °C for 20–45 min. In the case of samples containing Se(-II), oxidation to Se(IV) with 0.04 M potassium peroxodisulfate solution in HCl solution is possible. Hydride generation atomic absorption spectroscopy (HGAAS) using quartz tube atomization was recently applied to determine the concentration of Se(IV) in several Se(IV)-reductant systems [19–21]. Measurements were preceded by tests proving that Se(0) was kinetically unable to develop hydrogen selenide by reaction with sodium borohydride [20]. To prove the inability of red Se(0) to react with sodium borohydride forming hydrogen selenide, we monitored the HGAAS response during the reaction of Se(IV) with ascorbic acid at pH 2. The decrease of the analytical response during the reaction was a clear indication that Se(0) produced by the reduction with ascorbic acid did not respond to the HGAAS analysis and, upon completion of the reaction, no analytical response was obtained. These results proved that Se(0) was not determined by HGAAS under our experimental conditions, in agreement with similar evidences [22]. Therefore, the selenide developed in the HGAAS system reflects the concentration of residual selenite present in the sample.

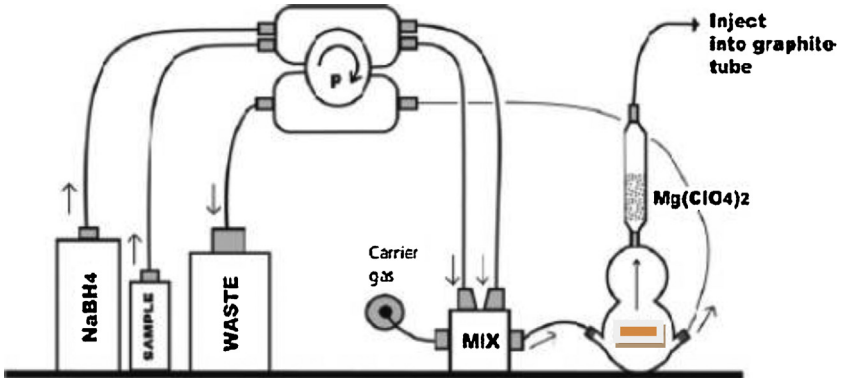

Fig. 1. Schematic representation of the flow injection system and the hydride generation chamber (adapted from Pettine et al. [28] with the permission of Elsevier Inc.).