Comparison of two derivatizing agents for the simultaneous determination of selenite and organoselenium species by gas chromatography and atomic emission detection after preconcentration using solid-phase microextraction

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Abstract

Two methods for the simultaneous determination of selenite and two organoselenium compounds, dimethylselenide (DMSe) and dimethyldiselenide (DMDSe), are proposed. Both methods involve sample preconcentration by solid-phase microextraction (SPME) and capillary gas chromatography coupled to atomic emission detection (GC–AED). The main difference between the methods is the derivatizing agent used to complex the inorganic species: sodium tetraethylborate and 4,5-dichloro-1,2-phenylenediamine. The parameters affecting the derivatization and preconcentration steps, chromatographic separation as well as detection of the compounds were optimized. Direct immersion (DI) mode and a relatively long extraction time were selected for the method involving the formation of the piazselenol complex, better sensitivity being achieved for the three analytes under study. In this case, detection limits ranged between 3 and 25 ng L$^{-1}$, depending on the compound. Headspace mode (HS) and extraction times of 20 min were selected for the method involving tetraalkylborate, and detection limits of between 7.3 and 55 ng L$^{-1}$ were obtained. DMSe and Se(IV) were found in several of the water samples analyzed at concentrations of 0.07–1.0 ng mL$^{-1}$.

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1. Introduction

Trace levels of selenium occur naturally in waters and is also released into the environment from anthropogenic sources, because this element is used in the microelectronic, semiconductor and optoelectronic industries [1]. Selenium concentration levels ranging between 0.03 and 6000 ng mL$^{-1}$ have been found in waters, depending on the origin of the sample [2,3]. Selenium is an essential trace element with only a small difference between essential and toxic levels, depending on the chemical form in which it is present [1]. The concentration permitted in drinking water is federally regulated in the USA and must not exceed 10 μg L$^{-1}$ [4].

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The biomethylation process of inorganic selenium by micro-organisms in environmental matrices produces mainly dimethylselenide (DMSe) and dimethyldiselenide (DMDSe), and is well documented in the literature [5], methylation being an effective detoxification mechanism. Volatile methylated species are considered to be 500 times less toxic than selenite [1].

The importance of selenium speciation is evident as regards the great number of reviews related with this point [6–10]. The volatility of DMSe and DMDSe means that gas chromatography is frequently used for their determination, while application of this technique to determine selenite involves its volatilisation by suitable derivatization agents. Sodium tetraethylborate [11–13], sodium tetrapropylborate [11], 4,5-dichloro-1,2-phenylenediamine [14,15], and 4-chloro-o-phenylenediamine [2,16] have been used to transform selenite into less polar compounds which are amenable for gas chromatography to be carried out.