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Quantification of volatile-alkylated selenium and sulfur in complex aqueous media using solid-phase microextraction

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ABSTRACT

Biologically produced volatile-alkylated Se and S compounds play an important role in the global biogeochemical Se and S cycles, are important constituents of odorous industrial emissions, and contribute to (off-)flavors in food and beverages. This study presents a fully automated direct-immersion solid-phase microextraction (DI-SPME) method coupled with capillary gas chromatography–mass spectrometry (GC/MS) for the simultaneous quantification of 10 volatile-alkylated Se and S compounds in complex aqueous media. Instrumental parameters of the SPME procedure were optimized to yield extraction efficiencies of up to 96% from complex aqueous matrices. The effects of sample matrix composition and analyte transformation during sample storage were critically assessed. With the use of internal standards and procedural calibrations, the DI-SPME–GC/MS method allows for trace-level quantification of volatile Se and S compounds in the ng/L range (e.g. down to 30 ng/L dimethyl sulfide and 75 ng/L dimethyl selenide). The applicability and robustness of the presented method demonstrate that the method may be used to quantify volatile Se and S compounds in complex aqueous samples, such as industrial effluents or food and beverage samples.

1. Introduction

The chemical elements selenium (Se) and sulfur (S) have similar chemical properties and are essential to many organisms [1,2]. In the natural environment, the distribution and bioavailability of these elements is significantly affected by a process called biomethylation: the biological production of volatile-alkylated Se and S compounds that may be emitted to the atmosphere [3,4]. The alkylation of Se and S is performed by a wide range of organisms (bacteria, fungi, algae, plants, animals, and even humans [5]) and leads to the formation of biogenic volatiles (e.g. dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and Se analogs dimethyl selenide (DMSe), and dimethyl diselenide (DMDSe) [3,4,6]) that have been identified in soils, fresh waters, oceans, and air [4,7]. However, quantitative field measurements of volatile-alkylated Se and S species are relatively scarce, which causes large uncertainties in global atmospheric budget estimates [8–10]. Volatile S species (and possibly Se species as well) can contribute to malodor of industrial emissions (e.g. at wastewater treatment facilities [11,12]) and to (off-)flavors of food (e.g. fruit [13] and cheese [14,15]) and beverages (e.g. wine [16–18] and milk [19]). It is thus important that volatile-alkylated Se and S species can be accurately quantified in a wide variety of sample matrices.

Because volatile-alkylated S and (particularly) Se species are typically present in low concentrations in the aqueous phase in the natural environment (ng/L range), their speciation analysis is usually preceded by a pre-concentration procedure. Although several methods for the preconcentration and speciation analysis of volatile S compounds are available [20,21], preconcentration and speciation methods for Se have focused on the major aqueous Se species, i.e. selenate and selenite [22,23]. Dissolved volatile-alkylated Se species have received less attention than anionic Se compounds, even though their presence in aqueous samples may compromise Se quantification by ICP/MS [24]. Hyphenated analytical procedures such as purge-and-trap combined with cryotrapping [25], solid-phase extraction with preconcentration columns and cartridges [23], liquid-phase (micro) extraction [26,27], and solid-phase (micro) extraction [20,23] have been deployed to preconcentrate volatile Se and S species from aqueous samples. Compared with other preconcentration procedures, solid-phase microextraction (SPME) may be preferred because it is relatively fast, solvent-free and requires only small sample volumes [28].

Solid-phase microextraction has previously been used for the analysis of alkylated S species [29–33], volatile Se species [34–42], or both S and Se species [43,44]. In addition, SPME has been

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employed in combination with derivation techniques for aqueous inorganic Se speciation analysis [45–49]. The majority of SPME methods for volatile Se and S species have been conducted in headspace extraction mode (e.g. for the analysis of volatile compounds in beverages [43] and human specimens [34,47], or in controlled laboratory incubation experiments [44]), where the SPME fiber is exposed to (relatively) clean gaseous sample headspace. Solid-phase microextraction of volatile-alkylated Se and S compounds is rarely performed directly in the aqueous phase, especially in complex and/or turbid samples. However, many volatile alkylated Se and S species are highly soluble in water and are therefore preferably extracted from the aqueous phase: the Henry constants of volatile Se and S species (defined as the ratio of aqueous-phase concentrations over gas-phase concentrations at equilibrium, see Table S1) illustrate that, at equilibrium, their concentrations in the aqueous phase greatly exceed those in the gas phase.

Here, we present a direct-immersion SPME (DI-SPME) procedure for the direct in situ extraction of 10 (semi)-volatile-alkylated Se and S compounds from complex aqueous samples. For analyte separation and quantification, the SPME procedure is coupled with GC/MS. We systematically evaluated and optimized the instrumental- and sample parameters of the SPME procedure (e.g. fiber coating type, extraction parameters, as well as sample salinity, pH, and organic matter content) and assessed potential analyte transformations during prolonged sample storage. We applied the method for the quantification of volatile-alkylated Se and S analytes in aqueous samples from a peat bog and in raw wastewater. The high degree of repeatability of quantification, as well as the low method detection limits, demonstrates that the method may be applied to a variety of complex and even turbid aqueous samples.

2. Material and methods

2.1. Chemicals and reagents

The following analytes were purchased from Sigma Aldrich (Buchs, Switzerland) and used without further purification: dimethyl sulfide (DMS, ≥99%), dimethyl disulfide (DMDS, ≥99%), diethyl sulfide (DES, 98%), diethyl disulfide (DEDS, ≥99%), ethylmethyl sulfide (EMS, 96%), dipropyl sulfide (DPS, 97%), methyl phenyl sulfide (MPS, ≥99%), and ethane thiol (ESH, 97%). Dimethyl selenide (DMSe, 99%) and dimethyl diselenide (DMDSe, 96%) were purchased from Alfa Aesar, Zurich, Switzerland. Dipropyl ether (DPE, ≥ 99%), deuterated dimethyl sulfide (DMS-d_6, 99 atom-% D), deuterated *p*-xylene (XYL-d_{10}, 99 atom-% D), deuterated toluene (TOL-d_8, 99.96 atom-% D) (all Sigma Aldrich, Buchs, Switzerland) and ^{13}C-labeled methyl-tert-butyl ether (MTBE, ≥99 atom-% ^{13}C) (CDN isotopes Canada) were used as internal standards. Selected chemical properties of the analytes and internal standards are listed in the Table S1. The following chemicals were used for optimization of the SPME procedure: sodium chloride (NaCl, ≥ 99.0%), sodium hydroxide (NaOH, ≥99.0%), a humic acid (CAS 1415-93-6), monosodium phosphate and disodium phosphate (≥98%) (all obtained from Sigma Aldrich, Buchs, Switzerland), and HPLC-grade methanol (Alfa Aesar, Zürich, Switzerland). Sodium selenite (> 98.0%) was obtained from Sigma-Aldrich, Switzerland. The sample pH was adjusted with NaOH or ultrapure nitric acid (HNO_3, Carl Roth GmbH, Karlsruhe, Germany). All chemicals were of analytical grade or higher.

2.2. Preparation of standards and samples

All glassware, vials, and syringes were cleaned and rinsed with diluted HNO_3, ultrapure water, and methanol before use. Headspace-free stock solutions of individual analyte standards were prepared using 10 and 100 μL gas-tight micro-syringes (Hamilton, Bonaduz, Switzerland) in ultrapure HPLC-grade methanol, hexadecane, or undecane (≥99%, Sigma-Aldrich, Buchs, Switzerland) in amber glass crimp vials (2 or 10 mL, BGB Analytics, Boeckten, Switzerland) with silicone-PTFE septa (BGB Analytics, Boeckten, Switzerland). From these stock solutions, headspace-free working solutions of individual or combined analytes were freshly prepared in methanol, undecane, hexadecane (for calibration of on-column injections), or ultrapure water (for calibration of SPME analyses, 18 MΩ, Thermo Fisher, NANOpure, Reinach, Switzerland). In order to account for variability in GC/MS sensitivity and SPME−fiber wearing, a mixture of internal standards (~1 μg/L DPE, MTBE, DMS-d_6, TOL-d_8, and *p*-XYL-d_{10}) in methanol was added to all standards and samples measured with the combined DI-SPME−GC/MS method. The internal standards were injected into the crimped vials directly before (< 1 min) the start of extraction. All solutions were stored at 4 °C in the dark until use.

2.3. GC/MS analysis

Separation and quantification of analytes was performed using a GC/MS system (Thermo Scientific DSQ II with Trace GC Ultra Gas Chromatograph, Thermo Fisher, Switzerland), equipped with a Stabilwax polyethylene glycol column (60 m, 0.32 mm ID, 1 μm coating) (BGB Analytics, Boeckten, Switzerland). For optimization of the GC/MS procedure, standards were injected directly into the GC/MS via a cold splitless on-column injector port with He as the carrier gas at a constant injector head pressure of 100 kPa. The optimized temperature program of the GC consisted of a 4 min hold time at 40 °C, heating with 7 °C/min−140 °C, heating at 25 °C/min−200 °C, followed by a 20 min hold time at 200 °C. With this program, the separation of 30 investigated compounds was achieved within 40 min (Fig. 1). The retention of the investigated compounds was inversely correlated with the analytes' volatility (Fig. S1).

The GC was connected to the MS through a heated transfer line (deactivated TSP-FS tubing, 530 μm ID, 660 μm OD, BGB Analytics, Boeckten, Switzerland) at 220 °C. The MS was operated in the positive ion electron impact mode with a source temperature of 250 °C. The MS was tuned on a daily basis. Obtained chromatograms were processed and integrated using the Xcalibur software (Thermo Scientific, Switzerland). Eluted analytes were identified by their specific masses (using species-specific target ions and qualifier ions, see Table S2), either in a selective ion mode (SIM) or in a scanning mode (SCAN). The SCAN mass range was set to 50–250 amu in order to capture the mass fragments of interest for the identification of the target analytes and to guarantee sufficient sensitivity by omitting redundant masses (particularly masses below 50 amu suffer from minor interferences caused by bleeding of alkyl-groups from the glycol- and siloxane phases of the GC column and SPME−fiber, respectively). Calibrations of on-column injections of standards were based on a three point plus blank linear fit over at least two orders of magnitude in the ng/L concentration range. An overview of the investigated target analytes, their retention factors, the linear calibration ranges, and the calibration regressions of the on-column injections are given in Table S2.

2.4. DI-SPME Extraction

Analyte preconcentration with DI-SPME was conducted using a CombiPal autosampler system (CTC, Zwingen, Switzerland). For DI-SPME, the GC/MS system was equipped with a splitless injector that contained a Merlin Microseal septum (Merlin Instruments), a SPME liner of 0.75 mm ID (Supelco, Bellefonte, PA, USA), and a