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Comparison of ultrasound-assisted emulsification and dispersive liquid–liquid microextraction methods for the speciation of inorganic selenium in environmental water samples using low density extraction solvents

Nahid Mashkouri Najafi[a,*], Hamed Tavakoli[a], Yaser Abdollahzadeh[b], Reza Alizadeh[a]

[a] *Department of Chemistry, Faculty of Science, Shahid Beheshti University, P.O. Box 19397-4716, Evin, Tehran, Iran*
[b] *Department of Chemistry, Faculty of Science, K.N. Toosi University of Technology, Tehran, Iran*

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ABSTRACT

Herein, ultrasound-assisted emulsification microextraction (USAEME) and dispersive liquid–liquid microextraction (DLLME) methods based on applying low-density organic solvents have been critically compared for the speciation of inorganic selenium, Se(IV) (selenite) and Se(VI) (selenate) in environmental water samples by gas chromatography-flame ionization detection (GC-FID). At pH 2 and $T = 75\,^{\circ}C$ for 7 min, only Se(IV) was able to form the piazselenol complex with 4-nitro-*o*-phenylenediamine. Piazselenol was extracted using an extraction solvent and was injected into a GC-FID instrument for the determination of Se(IV). Conveniently, Se(VI) remained in the aqueous phase. Total inorganic selenium was determined after the reduction of Se(VI) to Se(IV) and prior to the above procedures. The Se(VI) concentration was calculated as the difference between the measured total inorganic selenium and Se(IV) content. The effect of various experimental parameters on the efficiencies of the two methods and their optimum values were studied with the aid of response surface methodology and experimental design. Under the optimal conditions, the limit of detections (LODs) for Se(IV) obtained by USAEME-GC-FID and DLLME-GC-FID were 0.05 and 0.11 ng mL^{-1}, respectively. The relative standard deviations (RSDs, $n = 6$) for the measurement 10 ng mL^{-1} of Se(IV) were 5.32% and 4.57% with the enrichment factors of 2491 and 1129 for USAEME-GC-FID and DLLME-GC-FID, respectively. Both methods were successfully applied to the analysis of inorganic selenium in different environmental water samples and certified reference material (NIST SRM 1643e).

1. Introduction

Selenium is an essential element for plants, animals and the humans, but at high concentrations it can produce chronic toxicity symptoms, such as liver carcinoma, cirrhosis, the loss of teeth, hair and nails, irritation of the eyes and paralysis [1–4]. Selenium's toxicity, bioavailability and chemoprotective activities depend strongly on its chemical form and oxidation state. Inorganic Se(IV) has been found to be 500 times more toxic than common organic forms of selenium [5] and is considered more dangerous to aquatic organisms compared to Se(VI) due to its higher solubility and bioavailability [6]. Thus, the development of accurate and sensitive methods for the determination and speciation of inorganic selenium in environmental water samples is necessary.

Several instrumental techniques have been applied for the determination of selenium; these include UV–vis spectrophotometry [7], voltammetry [8], X-ray absorption spectroscopy [9], high performance liquid chromatography (HPLC) [10], gas chromatography (GC) [11], atomic absorption spectrometry [12], etc. Low concentration and matrix interference are two problems in the detection of selenium compounds. Thus, in spite of developments in modern analytical instruments, extraction and preconcentration processes are needed for the determination and speciation of selenium. In literatures, several sample preparation methods such as liquid–liquid extraction (LLE) [13], solid phase extraction (SPE) [14], phase microextraction (SPME) [15], liquid phase microextraction (LPME) [16,17], cloud point extraction (CPE) [18] and homogeneous liquid–liquid microextraction (HLLME) [19] have been developed to solve these problems. Each of them has its advantages and disadvantages and should be chosen according to the analytical problem.

The dispersive liquid–liquid microextraction (DLLME) technique is one of the LPME techniques that was suggested by Assadi and co-workers [20]. It is based on ternary component solvent systems, such as HLLME and CPE. The advantages of DLLME are

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[*] Corresponding author at: Department of Chemistry, Faculty of Science, Shahid Beheshti University, 1983963113 Evin, Tehran, Iran. Tel.: +98 2129903233; fax: +98 2122209442.
E-mail address: n-najafi@sbu.ac.ir (N.M. Najafi).

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simplicity of operation, rapidity, low cost, and high recovery and enrichment factor. This method has been successfully applied to the extraction and preconcentration of selenium [21] and other organic [22] and inorganic species [23]. The variety of the solvents that could be used as extraction solvents in DLLME was limited to organic solvents that are denser than water. By designing a new extraction vessel, Farajzadeh et al. succeeded in performing a DLLME using safe and nontoxic solvents, such as hydrocarbons that are lighter than water [24].

Another drawback of the DLLME method is the necessity of using a third component (dispersion solvent), which usually decreases the partition coefficients of analytes into the extraction solvent and increases the cost and environmental pollution. Regueiro et al. reported the application of ultra sonic radiation as a substitution for the dispersion solvent and named the procedure ultrasound-assisted emulsification microextraction (USAEME) [25]. In USAEMEs, similar to DLLMEs, the selected extracting solvent must have been denser than the aqueous samples due to the difficulty of collecting micro volumes of the organic solvents. Saleh et al. have recently reported a solution to this technical hurdle [26]. They used a home-designed glass centrifuge vial, which had a conical head and a glass tube fixed on the side of the vial to explore the possibility of applying low-density organic solvents to ultrasound-assisted emulsification microextractions.

The aim of this study was to compare the efficiencies of USAEMEs and DLLMEs using low-density organic solvents as the extraction solvents for speciation of inorganic selenium in different environmental water samples by a GC-FID. GC methods for the analysis of inorganic selenium require the conversion of these compounds to volatile and thermal-stable species. Herein, 4-nitro-*o*-phenylenediamine was used as the derivatizing reagent to form 5-nitropiazselenol. The advantages and disadvantages of both methods for the GC-FID analysis of inorganic selenium species have been discussed.

2. Experimental

2.1. Reagents and solutions

All the reagents and standards were of analytical grade unless otherwise stated, and all dilutions were made using high-purity, de-ionized water (18 MΩ cm resistivity) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Stock solution standards (1000 mg L^{-1}) of Se(IV) and Se(VI) were obtained by respectively dissolving appropriate amounts of Na_2SeO_3 (Merck, Darmstadt, Germany) and Na_2SeO_4 (Aldrich, Milwaukee, WI, USA) in 0.1 mol L^{-1} HCl and storing the solutions in a refrigerator at 4 °C. The chelating agent solution, 4-nitro-*o*-phenylenediamine (2 g L^{-1}), was prepared daily by dissolving the appropriate amount of 4-nitro-*o*-phenylenediamine (97% Merck, Darmstadt, Germany) in water. All other chemicals, such as toluene, n-hexane, 1-dodecane, undecan-1-ol, and octan-1-ol were used as extraction solvents; ethanol, acetone, and acetonitrile were used as disperser solvents, HCl (37%), and NaOH (99% purity) were purchased from Merck (Darmstadt, Germany). The water standard reference material, SRM 1643e, from the National Institute of Standards and Technology (NIST) was employed for validating the proposed method.

River water samples (Haraz and Tajan, Iran), Caspian sea water, tap water, drinking water and waste water were collected in pre-washed (soaked in dilute HNO_3 and rinsed with de-ionized distilled water) polytetrafluoroethylene (PTFE) bottles; after adjusting the pH to 3 by adding an appropriate amount of HCl, the samples were stored at 4 °C and analyzed during 48 h from the sample collection without any previous treatment or filtration.

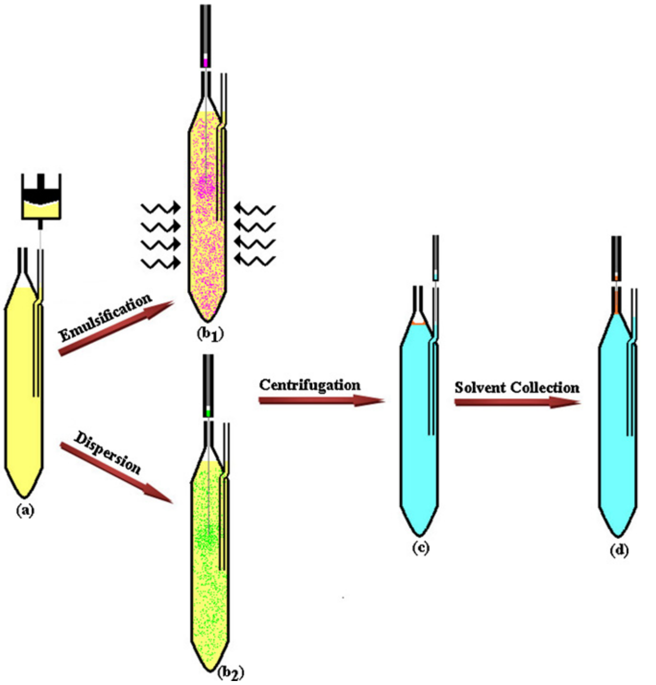

Fig. 1. Schematic diagram of the USAEME and DLLME procedures applying low-density organic solvent [11]. (a) Water sample solution in the home-designed glass vial, (b_1) simultaneous injection and emulsification of extraction solvent (toluene) into water sample, (b_2) injection of a mixture of disperser solvent (acetonitrile) and extraction solvent (toluene) into a water sample, (c) addition of a few microliters of distilled water into vial and (d) collection of toluene transferred into the capillary tube at the top of the vial.

2.2. Instrumental

A Shimadzu 14B gas chromatograph with a 30 m BP-5 (SGE, Australia) fused-silica capillary column (0.32 mm i.d. and 0.5 μm film thickness) equipped with a split–splitless injector and a flame ionization detector (FID) was used for the analysis of the samples. Helium (purity 99.999%) was used as the carrier gas at a constant flow rate of 4 mL min^{-1}. The temperatures of the injector and detector were set at 260 and 280 °C, respectively. The injection port was operated at the splitless mode. The oven temperature program was set as follows: 100 °C for 3 min, increase to 175 °C at 8 °C min^{-1}, hold for 5 min, increase to 260 °C at 15 °C min^{-1} and then hold at 260 °C for 2 min. A research pH-meter (model 3520, Jenway, UK) with a precision of 0.001 units, a centrifuge (model Z200A, HERMLE, Germany) and a 40 kHz and 0.138 kW ultrasonic water bath (Tecno-Gaz SpA, Italy) were employed for pH adjusting, centrifuging and emulsifying the organic solvent, respectively. Home-designed centrifuge glass vials were used for the extraction and collection procedures (Fig. 1).

2.3. Procedures

2.3.1. Derivatization of Se(IV)

The derivatization of Se(IV) was carried out according to previous reports [27,11].12 mL of ultra-pure water, containing 0.12 mL of HCl (1 mol L^{-1}) and 0.0006 g of 4-nitro-*o*-phenylenediamine were placed in a home-designed centrifuge glass vial (Fig. 1a), and the solution was spiked at the level of 10 ng mL^{-1} of selenite. The resulting solution was heated at 75 °C for 7 min in a water bath. Once the derivatization was completed and the solution was cooled to room temperature, the selenium derivative (5-nitropiazselenol) was extracted using the USAEME and DLLME techniques using low-density extraction solvents.