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Indirect spectrophotometric determination of ultra trace amounts of selenium based on dispersive liquid–liquid microextraction–solidified floating organic drop

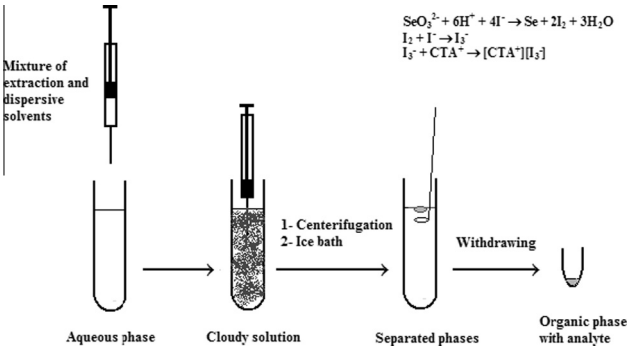
Ali Mohammad Haji Shabani, Shayessteh Dadfarnia *, Mahnaz Nozohor

Department of Chemistry, Faculty of Science, Yazd University, 89195-741 Yazd, Iran

HIGHLIGHTS

- Development of an indirect spectrophotometric method for the determination of Se.
- The first application of DLLME–SFOD for indirect spectrophotometric determination of Se.
- Combination of DLLME–SFOD with fiber optic-linear array spectrophotometry.
- Develop. of a rapid, simple and sensitive method for deter. of Se in water and Se plus tablet.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel dispersive liquid–liquid microextraction–solidified floating organic drop (DLLME–SFOD) method combined with fiber optic-linear array detection spectrophotometry has been developed for the indirect determination of selenium. The method is based on the oxidation of the I^- to iodine by inorganic Se(IV). The produced I_2 reacts with the excess of I^- ions in acidic media to give triiodide ions. The I_3^- is then extracted into 1-undecanol by DLLME–SFOD upon the formation of an ion pair with cetyltrimethylammonium cation. The extracted ion pair is determined by measuring its absorption at 360 nm. The absorbance signal is proportional to the selenium concentration in the aqueous phase. Under optimum conditions, the method provided an enrichment factor of 250 with a detection limit of 16.0 μg L^{-1} and a linear dynamic range of 40.0–1000.0 μg L^{-1}. The relative standard deviation was found to be 2.1% ($n = 7$) at 100.0 μg L^{-1} concentration level. The method was successfully applied to the determination of selenium in water samples and selenium plus tablet.

Introduction

Selenium at trace levels is an essential element for plants, animals and humans, while at high concentrations it can produce chronic toxicity symptoms such as liver carcinoma, cirrhosis, paralysis, loss of teeth, hair, nails and irritation of the eyes [1,2]. Selenium enters the environment from natural process, human activities or the combustion of fuel oils, and can enter the human body from food, from contact with soil, or from the air containing large quantities of selenium. A safe and adequate range of selenium intake of 50–200 μg per person per day has been recommended for adults [3]. In the majority of environmental matrices including natural water, selenium is present as Se(IV) (selenite) and Se(VI) (selenate). Biogeochemical behavior, bioavailability and toxicity of selenium depend on its chemical forms and oxidation states. Inorganic Se(IV) has been found to be about 500 times more toxic than common organic forms of selenium and is considered to be more dangerous to aquatic organisms than the Se(VI). Thus, development of an accurate and sensitive method for the determination

* Corresponding author. Tel.: +98 351 8122667; fax: +98 351 8210644.
E-mail address: sdadfarnia@yazd.ac.ir (S. Dadfarnia).

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of inorganic selenium in environmental water samples is a challenging subject. However, in spite of the development of modern analytical instruments, an extraction and preconcentration step for the determination of low concentration of selenium is still required. Different methods such as solid phase extraction (SPE) [4,5], cloud point extraction (CPE) [6–8], solid phase microextraction (SPME) [9–11] and liquid phase microextraction (LPME) [12–16] have been applied for the separation, preconcentration and speciation of selenium. Among these methods, the liquid phase microextraction has the advantages of the use of low volumes of the organic phase, low cost, ease of operation and the possibility of obtaining a high preconcentration factor.

In 2008, Leong and Huang introduced a new microextraction technique named dispersive liquid–liquid microextraction–solidified floating organic drop (DLLME–SFOD). As the title implies, the method is a combination of dispersive liquid–liquid microextraction (DLLME) and solidified floating organic drop microextraction (SFODME). In this method, the extraction solvent is an immiscible solvent with a melting point near room temperature (10–30 °C) which is mixed with the disperser solvent and is rapidly injected into the aqueous sample by a syringe. Thus, a cloudy solution with a vast contact area between the extraction solvent and the sample is formed resulting in fast mass transfer and short extraction time. The mixture is centrifuged and the organic drop floats on the top of the solution. The extraction vial is then placed in an ice bath until the organic drop is solidified. The solidified organic drop is then removed and the amount of the analyte in the melted drop is determined via a suitable technique. This method has been used for the determination of various analytes [17–24].

Several reagents including 3,3′-diaminobenzidine, o-phenylenediamine, dithizone, diethyldithiocarbamate and dithiolate have been used for the separation and spectrophotometric determination of selenium. However, the reaction between selenium and most of these reagents is slow so that the completion of the reaction usually lasts about 30 min [25].

In this paper, an indirect spectrophotometric method for the determination of selenium in water samples and selenium plus tablet is described. The procedure is based on the oxidation of the iodide ions by selenium (IV). The produced triiodide anion then forms ion pair with cetyltrimethylammonium cation (I_3^-—CTA^+), is extracted by DLLME–SFOD method and is determined by fiber optic-linear array detection spectrophotometry. The amount of selenium is proportional to the amount of the produced triiodide ions. To the best of our knowledge, this is the first study on the application of DLLME–SFOD for indirect spectrophotometric determination of ultra trace amounts of selenium.

Experimental

Apparatus

An Avantes photodiode array spectrophotometer model Ava-Spec-2048 equipped with a source model of Ava Light-DH-S-BAL and a 10-mm micro flow cell, an Ismatic peristaltic pump model MS-REGLO/8-100 (Switzerland), and a rotary injection valve (Rheodyne, CA, USA) with a 60 μL loop were used. All measurements were made against a reagent blank solution. The pH measurements were carried out by means of a Metrohm pH meter (model 827) using a combined glass calomel electrode. The centrifuge (Hitachi, Universal 320, Tuttlingen, Germany) was used for the phase separation.

Reagents

All the reagents used were of analytical reagent grade and were obtained from Merck Company (Darmstadt, Germany). Distilled deionized water was used for all the sample preparations. The stock standard solution (1000 mg L^{-1}) of sodium selenite was prepared by dissolving an appropriate amount of Na_2SeO_3 in distilled water. The surfactant solution, cetyltrimethylammonium bromide (CTAB) (2.6×10^{-5} mol L^{-1}), was prepared by dissolving an appropriate amount of the reagent in 100 mL of ethanol. 1-Undecanol was used as the extracting solvent.

Sample preparation

Water samples were filtered through a 0.45 μm Millipore filter and were treated according to the given procedure.

Five selenium plus tablets were grinned and homogenized. To 0.04 g of it, 2 mL of hydrochloric acid solution (4 mol L^{-1}) was added and the mixture was heated for a few minutes. Then, the solution was passed through a 0.45 μm Millipore filter and was diluted with distilled water to 50.0 mL in a volumetric flask. Finally, 20 mL of it was treated according to the given procedure.

Procedure

An aliquot of the sample or standard solution containing 1–20 μg of selenium was transferred into a ~25 mL sample vial and the Se(VI) was effectively reduced to Se(IV) upon the addition of 0.5 mL of hydrochloric acid (4.0 mol L^{-1}) [16] and heating the solution in a boiling water bath for 30 min. Then, 2 mL sodium iodide (4.0×10^{-2} mol L^{-1}) was added and the solution was mixed until a yellow color was appeared. At this stage, the selenium (IV) oxidizes I^- into I_2 species which react with the I^- and produce triiodide anion (I_3^-). The pH of the solution was adjusted to ~3 using either diluted ammonia or hydrochloric acid solutions. Then, a mixture of 1.0 mL ethanol containing CTAB (2.6×10^{-5} mol L^{-1}) as the dispersive solvent and 40 μL 1-undecanol as the extraction solvent was rapidly injected into the aqueous sample. The solution became cloudy and the triiodide ion (I_3^-) reacted with the CTAB and extracted into the fine droplet of 1-undecanol in a few seconds. Then, the mixture was centrifuged and the organic solvent drop containing CTA^+—I_3^- ion pair floated on the surface of the aqueous solution. The vial was transferred into an ice bath for 5 min and the organic solvent was solidified. The solidified solvent was easily transferred into a conical vial where it melted immediately at room temperature and its viscosity was decreased through dilution with 40 μL of ethanol. Finally, the extract was transferred into the quartz micro flow-cell of a photodiode array spectrophotometer via the sample loop of the injection valve; the pump was stopped for 2 s and the absorption was measured at 360 nm.

Results and discussion

The primary study indicated that in acidic media Se(IV) may quantitatively oxidize the iodide ions into I_2 species which react with the excess I^- and produce triiodide ion I_3^-. The I_3^- then reacted with cetyltrimethylammonium cation (CTA^+) forming a hydrophobic ion association species which was extractable into 1-undecanol. The reactions were as follows:

$$SeO_3^{2-} + 6H^+ + 4I^- \rightarrow Se + 2I_2 + 3H_2O$$

$$I_2 + I^- \rightarrow I_3^-$$

$$I_3^- + CTA^+ \rightarrow [CTA^+][I_3^-]$$

The color of the extracted ion pair in the 1-undecanol was yellow with a relatively sharp absorption maximum around 360 nm (Fig. 1a) which was proportional to the Se(IV) concentration in the aqueous phase. The reagent blank spectrum (Fig. 1b) also showed some absorbance at this wavelength due to the oxidation