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Speciation of inorganic selenium in environmental samples after suspended dispersive solid phase microextraction combined with inductively coupled plasma spectrometric determination



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ABSTRACT

A rapid and effective suspended dispersive solid phase microextraction (SDSPME) was developed for the speciation of inorganic selenium using alumina nanoparticles functionalized with Aliquat-336. The target analytes were preconcentrated and determined by inductively coupled plasma optical emission spectrometry. Alumina nanoparticles were characterized using XRD, BET, SEM and EDX while the functionalized nano- Al_2O_3 was characterized by FTIR. The effect of pH of the solution on speciation Se in water samples was optimized separately. It was observed that when the pH values of sample solution ranged from 2.0 to 7.0, successful separation of inorganic Se species was achieved. The percentage recoveries for Se (IV) and Se (VI) were > 90% and 5%, respectively. The two-level fractional factorial design was used to optimize experimental parameters affecting the preconcentration system. Under optimal conditions, the enrichment factor (EF), limit of detection (LOD) and limit of quantification for Se (IV) were found to be 850, 1.4 ng L^{-1} and 4.6 ng L^{-1} , respectively. Furthermore, intra-day and inter-day precisions expressed in terms of relative standard deviation (RSD) were found to be 1.9% and 3.3%, respectively. The effect of coexisting ions on the recovery of Se (IV) was investigated. The accuracy of the developed method was checked by analysis of standard reference material (NIST SRM 1643e). The optimized method was applied for the determination of targets in surface water samples.

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1. Introduction

In the past decades, metal ion speciation has become one of the most important subjects in environmental and toxicological studies [1]. This is because the toxicity, biological availability and transport mechanisms of an element highly depend on the chemical form in which it exists [1]. This is definitely the case for selenium. The latter is an essential nutrient for plant, animal and human body. However at high concentration Se can become toxic whereas at very low concentrations can result in chronic and sometimes fatal deficiency [2,3]. For this reason, there is a thin line in terms of concentration range from sufficiency to deficiency and toxicity [2,4]. Selenium is toxic at concentrations 3–5 times higher than the acceptable concentration [5]. In general, inorganic species of Se are more toxic than the organic forms, with Se (IV) being more toxic than Se (VI) [6].

Conventionally, the determination of the total concentration of

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elements was considered to be satisfactory for precarious and environmental considerations [1]. Even though the total metal concentration is still worthwhile to know and essential from many analytical aspects, the determination of the species is an important analytical and environmental task [1,7,8]. Therefore, the information about the Se species concentrations in water can assist to make more accurate assessments of the environmental impact and health risks [1,8].

Recently, non-chromatographic based methods have been developed for speciation of trace elements in environmental samples. Fu et al. [9] reported a method for speciation of selenium in water samples using hydride generation atomic fluorescence spectrometry (HG-AFS). The Se species were separated using nano-sized TiO_2 colloid as an adsorbent. The speciation of Se was aided by pH of the solution. For instance, when the pH of the solution is between 6.0 and 7.0, Se (IV) was successful adsorbed onto nano-sized adsorbent while Se (VI) was hardly adsorbed. Ghasemi et al. [10], on the other hand, reported the application hollow fiber liquid phase microextraction for speciation of trace Te and Se in environmental samples prior to electrothermal atomic absorption spectrometric determination. Ammonium

pyrrolidinedicarbodithioate (APDC) was used as a selective chelating agent for extraction of Te (IV) and Se (IV) species and toluene was used as acceptor phase. Other sample preparation methods used for speciation of trace elements are reported by Sun et al. [4], Xu et al. [11], Duan et al. [12], Najafi et al. [13], Peng et al. [14], and Zou et al. [15], among others.

Notwithstanding various analytical methodologies reported for a selenium speciation in the last decade, there is still a need for reliable, rapid and sensitive techniques, which allow selective determination of the species in environmental samples. In addition, our research team has been working on the separation and preconcentration of trace metals using modified nanometer-sized metal oxides as adsorbent combined with atomic spectrometric techniques [16,17]. According to a recent review by Hu et al. [18], the use of nanometer-sized materials as adsorbent has increased significantly. This is because these adsorbents display unique size and physical properties that result to high surface area and more activated sites for metal adsorption [18].

Therefore, the objective of this work is to develop a suspended dispersive solid phase microextraction (SDSPME) procedure coupled to ICP-OES for the determination of the inorganic selenium species in environmental samples. Nano-alumina modified with Aliquat 336 was used as an adsorbent for speciation of Se. Nano-alumina was chosen because of its preferential adsorption towards Se (IV) in water samples and its amphoteric nature [19]. Aliquat 336 was chosen because it acts as anion exchanger at wide pH ranges. In addition, Aliquat 336 was used in order to enhance the selectivity of the nanoadsorbent. The method was validated by analyzing the certified reference material (NIST SRM 1643e) and applied for the analysis of real river water samples. The possible factors affecting the speciation of inorganic Se were studied using fractional factorial design. These factors include eluent concentration (EC), the amount of sorbent (AS) and extraction time (EXT), among others.

2. Experimental

2.1. Reagents and material

All chemicals were of analytical reagent grade unless stated otherwise and double distilled water (Millipore-Q-plus purification system, Bedford, USA) was used throughout the experiments. Anhydrous aluminium chloride (99.999% trace metal basis), Aliquat 336, absolute ethanol (99.9%), ammonium hydroxide solution (28%) and ultrapure nitric acid (69%) were purchased from Sigma-Aldrich (St. Louis MO, USA). Spectrascan single element standard (1000 mg L⁻¹) of Se (IV) and Se (VI) species (Teknolab, Norway) were used to prepare working solutions for SDSPME at concentration of 50 µg L⁻¹. A Spectrascan multi-elemental standard solution at a concentration of 100 mg L⁻¹ (Teknolab, Norway) was used to prepare working standard solutions for quantification of analyte concentrations in the model and sample solutions.

2.2. Instrumentation

The quantification of the analyte (Se (IV) and Se (VI)) was performed using an ICP-OES spectrometer (iCAP 6500 Duo, Thermo Scientific, UK) equipped with a charge injection device (CID) detector. The samples were introduced with a concentric nebulizer and a cyclonic spray chamber. The operating parameters of the instrument are presented in Table 1.

Branson 5800 Ultrasonic Cleaner – 2 1/2 gallon and Eppendorf 5702 Series Centrifuge, Rotor Cell Culture Packages. The morphology Al₂O₃ nanomaterials was observed using scanning electron microscope (SEM) (JSM-6360LVSEM, JEOL Co., Japan) after

Table 1
Operating parameter of an ICP-OES.

ICP-OES parameters	
RF generator power/W	1150
Frequency of RF generator/MHz	40
Coolant gas flow rate/L min ⁻¹	12
Carrier gas flow rate/L min ⁻¹	0.7
Auxiliary gas/L min ⁻¹	1.0
Max integration times/s	15
Pump rate/rpm	50
Viewing configuration/Touch mode	Axial
Replicate	3
Flush time/s	30

gold coating and the diameter of the mixed metal oxide was measured by image processing software. The specific surface area value was determined from adsorption isotherms by the Brunauer, Emmett and Teller (BET) multipoint method using Surface Area and Porosity Analyzer (ASAP2020 V3. 00H, Micromeritics Instrument Corporation, Norcross, USA). All the gases used for analysis were of instrument grade. X-ray powder diffraction (XRD) measurements were carried out with a Philips X-ray generator model PW 3710/31 a diffractometer with automatic sample changer model PW 1775 (scintillation counter, Cu-target tube and Ni-filter at 40 kV and 40 mA). The infrared spectrum was recorded using Spectrum 100 FT-IR (PerkinElmer, USA) spectrometer equipped with Universal Attenuated Total Reflectance (ATR).

2.3. Sample collection and preparation

Surface water was collected from Soweto area, (Johannesburg Gauteng, South Africa). Three sampling sites (S1, S2, and S3) were chosen. After sampling, the samples were filtered through 0.45 µm filter membrane and subjected to the sample preparation procedure.

2.4. Preparation, functionalization and characterization of Al₂O₃ composite nanoparticles

The preparation of nano-alumina was carried out according to the procedures reported previously [16,20]. The procedure for the functionalization of nano-alumina was adopted from the literature with some modification [16]. Briefly, the nano-Al₂O₃ was first activated by mixing Al₂O₃ with 5 mol L⁻¹ HNO₃ and then refluxed for 6 h at 60 °C with continuous stirring by a magnetic stirrer. The activated Al₂O₃ was filtered, washed several times with ultrapure water and ethanol then dried under vacuum. An appropriate amount of activated Al₂O₃ (5 g) was mixed with 20 mL of 5% Aliquat-336 in ethanol. The resulting slurry was gently stirred for 2 h and the ethanol was evaporated at room temperature. The nanoadsorbent was then dried in the oven at 70 °C. The nano-Al₂O₃ was characterized by SEM, BET, and XRD. The SEM images (Fig. S1) illustrate that the alumina nanoparticles were well dispersed and according to DLS measurement the particle size of the nano-Al₂O₃ ranged between 2 nm and 50 nm.

The XRD patterns (Fig. S2) revealed that the synthesized nano-alumina had crystalline peaks, which are attributed to two crystallization phases of alumina, that is, α-Al₂O₃ and γ-Al₂O₃ [16]. The nitrogen adsorption/desorption isotherms showed that the nanoadsorbent had a surface area of about 321 m² g⁻¹. These results were similar to our previous findings [16].

The functionalized nano-Al₂O₃ was characterization with ATR-FTIR spectroscopy. The infrared spectrum of nano-Al₂O₃/Aliquat 336 (results not included) showed characteristic bands at 2971 and 2848 cm⁻¹ which were attributed to stretching vibrations of

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