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A new portable micropipette tip-syringe based solid phase microextraction for the determination of vanadium species in water and food samples

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ABSTRACT

Simple, rapid and miniaturized portable micropipette tip-syringe solid phase microextraction method was developed for speciation of vanadium in water and food samples. Tetra ethylene pentamine functionalized multiwalled carbon nanotubes were synthesized and packed in micropipette tip-syringe system. The surface morphology of adsorbent was characterized, and the effective factors that influence the efficiency of developed method such as pH, amount of adsorbent, concentration of acid solution for desorption cycles were studied. The V(V) could be adsorbed on the modified adsorbent surface with tetra ethylene pentamine, while V(IV) could not be retained. The assay of V(IV) was based on subtracting values of V(V), from total vanadium. The extracted total vanadium and V(V) were injected directly into the electrothermal atomic absorption spectrometry for analysis. Enhancement factor and detection limit were found 50 and 0.008 $\mu g\,L^{-1}$, respectively. Accuracy of the method was checked by analysis of certified reference materials. The developed method was applied to water and food samples.

1 Introduction

Vanadium is considered to be one of the most important and strategic metals having widespread application in many fields [1]. Generally, vanadium exists in two oxidation states. tetravalent (IV) and pentavalent (V) in aquatic environment. It was reported that V (V) is highly toxic species as compared to V(IV), and have a strong inhibiting activity of the essential metal with enzymes [2,3]. Therefore, a great effort has needed to quantify the low concentration of vanadium in different environmental and biological samples. The different species of vanadium determination have hold a great deal of space in modern literature due to their different chemical, toxic behavior and effects on the environment, animal and human health [3–5].

Q3 Vanadium exists in different charge species such as V(V), which exists as VO_2^+ and VO_4^{3-} at different pH values. The V(IV), mainly exists as VO^{2+}, in the reducing environmental solution and stable in acidic conditions, whereas at higher pH oxidized to V(V) [4–8]. Several instrumental analytical techniques have been launched to quantify and determined vanadium species at trace levels in different environmental samples [7,9–12]. Electrothermal atomic absorption spectrometry (ETAAS) is one of the most applicable technique for the elemental determination in trace levels with low detection limit, reduced the usage and exposure of toxic chemicals to the environment [12–17]. Vanadium is found to be in trace levels in real water samples [18,19]. Separation and preconcentration process is one of the most growing trend to obtain reliable, precise and accurate trace metals results, thus separation-enrichment steps is an important step prior to the quantification of traces of analytes [20,21]. There are number of separation approaches, which have been used for preconcentration and determination of the trace levels of vanadium in different environmental and biological samples [22,23].

Solid phase microextraction (SPME) is one of the most applicable sample preparation trend due to their unique properties and environmental perspectives [24]. The SPME method is preferred approaches due to their simple operation, reduced consumption of the toxic organic chemicals, high extraction capability, excellent sensitivity and high preconcentration factor [25]. Carbon nanotubes have grabbed a great space in the materials and separation science, due to excellent adsorption of metal ions at trace levels, because of their structural characteristics with high

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surface area. Their high surface area and excellent extraction capability of carbon nanotubes, make it a popular solids event for the extraction approaches [26,27]. Multiwalled carbon nanotubes (MWNTs) is one of the most popular and applicable attractive materials due to unique physical and chemical structure [28]. According to our literature survey, miniaturized portable micropipette tip-syringe solid phase microextraction (MTS-SPME) method has not been used for the speciation of inorganic vanadium in real samples.

In the current study a novel approach of modified/functionalized MWCNTs with tetra ethylene pentamine (TEPA), retained by a micropipette tip couple with syringe system was designed for the determination of total and species of vanadium in real water and food samples. The factors that influence the enrichment capability of the portable TEPA-MWCNTs retained micropipette tip-syringe system was studied and optimized. The optimized (MTS-SPME) procedure was applied to determine the trace levels of vanadium species in the real samples.

2 Experimental

2.1 Chemical, reagents and glassware

The stock standard solution of 1000 mg L^{-1} V(V) and V(IV) were prepared by dissolving appropriate amount of NH_4VO_3 and $VOSO_4 \cdot 5H_2O$, respectively (Merck, Darmstadt, Germany). Tetra ethylene pentaamine was obtained from Merck. Phosphate, acetate, borate and ammonia buffer solutions (0.1 mol L^{-1}) were used throughout the experiment to obtained the desired pH of the solutions. The pipette tip and syringe were obtained from Huaxin chemical reagent (Baoding, China) was used. Multi-walled carbon nanotubes (Aldrich Milwaukee, WI, USA) were used according to the information reported by the manufacturer [28].

2.2 Instrumentation

A Perkin Elmer Analyst model 700 and atomizer HGA-800 (Norwalk, CT, USA) atomic absorption spectrometer was used for the vanadium determination, using V hollow cathode lamp at 318.5 nm with a slit width of 0.7 nm. The previously operating instrumental conditions were used for the vanadium determination [29]. A Perkin Elmer AS-800 autosampler was used to automatically injected 20 μL sample containing 5 μL of a matrix modifier $Mg(NO_3)_2$ and $Pd(NO_3)_2$ into the graphite furnace tube.

2.3 Preparation and characterization of TEPA-MWCNTs

The TEPA immobilized MWCNTs were prepared in a beaker with magnet stirring. The detail of preparation and characterization was presented in our previous work [28].

2.4 Procedure of MTS-SPME method

The desired portable MTS-SPME operating in-syringe system is quite easy, the micropipette tip was preconditioned with acidic ethanol to the make surface free of matrix which might affect on the extraction efficiency and results. Then 1–10 mg of MWCNTs-TEPA was introduced into the micropipette tips and coupled with the syringe. Replicate 5 mL of each standard (0.5–10.0 μg L^{-1}) of V (V) and real sample were taken in beakers separately and the pH of solutions were maintained in the range of 2–8 using related buffer solutions. Then the solution was sucked up into the syringe system and push back into the beaker. These two steps are known as one MTS-SPME operating in-syringe system cycle. In the proposed method, 2–12 cycles were applied for optimum adsorption, during two min. Finally, analyte retained on MWCNTs-TEPA were eluted with 50–200 μL of 2.0 mol L^{-1} of HNO_3 from the syringe system into a small vial (2 mL in capacity) using 2–10 desorption cycles. A 20 μL aliquot of the eluate sucked up into the syringe and injected manually into the graphite furnace for vanadium determination in the standards/real samples. Total inorganic vanadium was determined after the oxidation of V(IV) to V(V) with 8 μmol L^{-1} of $KMnO_4$. The amount of V(IV) was calculated by subtracting V(V) from the total vanadium.

3 Result and discussion

3.1 Optimization of ETAAS parameters

The optimization of the pyrolysis and atomization temperatures has a key role on the signal intensity and efficiency of vanadium determination by desired method. The effect of different pyrolysis and atomization temperature under optimized conditions were investigated. The efficient and reliable analytical response were obtained by using pyrolysis and atomization temperature at 1400 and 2000 °C, respectively, as shown in Fig. 1.

3.2 Optimization of MTS-SPME procedures

Several factors have a key role on the extraction capability and performance of the proposed methods were studied and optimized.

3.2.1 Effect of pH

Functionalized surface of the MWCNTs has an important task on the extraction efficiency and vanadium speciation of the proposed method. Vanadium has a variety of oxidation state in the sample solution, but mostly V(IV) and V(V) are exist in environmental samples. Vanadium (V) exists in both cationic VO_2^+ and anionic forms VO_4^{3-}, respectively. Vanadium(IV) is found in cationic form VO_2^+. It can be seen in Fig. 2 that V(V) could be quantitatively adsorbed on the surface of MWCNT at pH >3, while on other side V (IV) could not retained at that pH. In the proposed method, pH 4 was chosen for the selective separation of V(V) from V(IV), as shown in Fig. 2. The different adsorption behaviors of V(V) and V (IV) on the surface of modified MWCNTs could be elaborated on the basis of functional group and chemical behavior of the two-oxidation state of vanadium. In the slightly acidic condition the amine functional group has a positive charge and function as a weak-base anion-exchange resin, while V(V) present in the anionic form such as ($H_2VO_4^-$), therefore V(V) quantitatively retained on the surface of the MWCNTs by electrostatic interaction. Whereas V

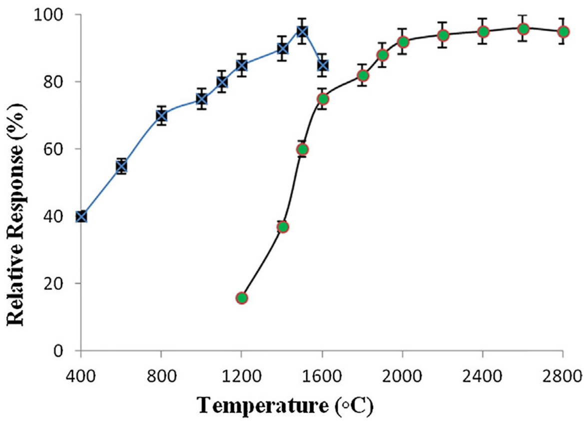

Fig. 1. Pyrolysis (■) and atomization (●) temperature curves for 2.0 μg L^{-1} V(V) in the presence of 4.5 mg of TEPA-MWCNTs, pH 3, 3 mL sample volume, 8 adsorption cycles of extraction (2.0 min), 5 desorption cycles with 100 μL of 2 mol L^{-1} HNO_3.

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