Talanta 116 (2013) 205–209

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Graphite furnace atomic absorption spectrometric detection of vanadium in water and food samples after solid phase extraction on multiwalled carbon nanotubes

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ARTICLE INFO

Article history:
Received 9 April 2013
Received in revised form
4 May 2013
Accepted 10 May 2013
Available online 16 May 2013

Keywords:
Solid phase extraction
Vanadium
8-hydroxyquinoline
Multiwalled carbon nanotubes
Atomic absorption spectrometry

ABSTRACT

Vanadium(V) ions as 8-hydroxyquinoline chelates were loaded on multiwalled carbon nanotubes (MWNTs) in a mini chromatographic column. Vanadium was determined by graphite furnace atomic absorption spectrometry (GFAAS). Various analytical parameters including pH of the working solutions, amounts of 8-hydroxyquinoline, eluent type, sample volume, and flow rates were investigated. The effects of matrix ions and some transition metals were also studied. The column can be reused 250 times without any loss in its sorption properties. The preconcentration factor was found as 100. Detection limit (3 s) and limit of quantification (10 s) for the vanadium in the optimal conditions were observed to be 0.012 μg L^{-1} and 0.040 μg L^{-1}, respectively. The capacity of adsorption was 9.6 mg g^{-1}. Relative standard deviation (RSD) was found to be 5%. The validation of the method was confirmed by using NIST SRM 1515 Apple leaves, NIST SRM 1570a Spinach leaves and GBW 07605 Tea certified reference materials. The procedure was applied to the determination of vanadium in tap water and bottled drinking water samples. The procedure was also successfully applied to microwave digested food samples including black tea, coffee, tomato, cabbage, zucchini, apple and chicken samples.

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1. Introduction

Vanadium(V) is an essential element for living organisms [1]. The estimated daily intake of vanadium ranges from 6 to 18 μg [2]. It can exist in many oxidation states from −1 to +5, but it is most commonly found in the +4 and +5 states. The coexistence of these species depends on pH, redox potential and ionic strength of the aqueous media [3–6]. The toxicity of vanadium(V) is higher than vanadium(IV) [7]. Vanadium mainly enters the environment from natural sources and combustion of fossil fuels, fuel oils and coal. The burning of petroleum fuels and coal releases vanadium into the air, soil and water [8]. V is toxic to living organisms at mg L^{-1} level [1].

Several analytical techniques such as inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectrometry, and graphite furnace atomic absorption spectrometry have been used for the determination of vanadium concentrations in water, food and environmental samples [9–11]. The determination of trace quantities of vanadium requires the use of sensitive and selective techniques such as graphite furnace atomic absorption spectrometry is an important instrument. The level of vanadium in natural water samples is very low such as μg L^{-1} [12]. In order to achieve accurate, reliable and sensitive results, separation–enrichment steps are often necessary prior to the analysis of vanadium.

Various separation and preconcentration techniques including coprecipitation, cloud point extraction, flotation, solvent extraction, solid phase extraction have been used prior to the determination of vanadium [13–16]. Solid phase extraction of vanadium for preconcentration is preferred to other techniques due to simple application, easy methodology, high preconcentration factor, sensitivity and low organic solvent consumption.

Carbon nanotubes have become attractive materials for the adsorption of metal ions at trace level because of their structure characteristics with high surface area. The large surface areas make them a promising solid sorbent for preconcentration procedures [17–19]. Surface area and density of multiwalled carbon nanotubes used in this work are 600 m^2 g^{-1} and 2.1 g mL^{-1}, respectively [17]. Multiwalled carbon nanotubes (MWNTs) and 8-hydroxyquinoline combination was not used for solid phase extraction of vanadium according to our literature survey.

In this study, a simple solid phase extraction method was used for the separation and enrichment of vanadium. Various analytical parameters were optimized prior to graphite furnace atomic absorption

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0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.05.020

spectrometric detection of vanadium in water, food samples and certified materials.

2. Experimental

2.1. Apparatus

Vanadium was determined by a PerkinElmer AAnalyst 700 model (Norwalk, CT, USA) atomic absorption spectrometry equipped with HGA graphite furnace and with deuterium background corrector. The operating parameters for vanadium are given in Table 1. Pyrolytic-coated graphite tubes with a platform were used. 20 μL of sample plus 5 μL of 1000 μg mL^{-1} $Mg(NO_3)_2$ as matrix modifier during the study were injected into the furnace using a PerkinElmer AS-800 autosampler. pH values were measured with a Sartorius pp-15 model pH meter using a glass-electrode (Göttingen, Germany). A Milestone Ethos D (Sorisole-Bg Italy) closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used for solving solid samples. Digestion conditions of microwave system for the samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min [17,20].

2.2. Reagents and solutions

Analytical reagent grade chemicals were used in this work. Deionised water (Milli-Q Millipore (Bedford, MA, USA) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1+9) and were rinsed with distilled water prior to use. The stock solution of 1000 μg mL^{-1} vanadium(V) was prepared by dissolving appropriate amount of NH_4VO_3 (Merck, Darmstadt, Germany). Multiwalled carbon nanotube (Aldrich no: 636630) was purchased from Aldrich, Milwaukee, WI, USA. 1 mol L^{-1} HCl and 1 mol L^{-1} NaOH were used for adjustment of pH value of the solutions.

2.3. Preparation of the MWNTs column

Two hundred milligrams of MWNTs was loaded into a 10 mm × 100 mm glass column equipped with porous disc. The thickness of resin bed was approximately 1.0 cm. Then, the column was conditioned to the desired pH values. After each elution, the MWNTs column was washed with 10 mL of water.

2.4. Test procedure

The preconcentration method was tested with 50 mL of model solutions containing 1.0 μg of vanadium(V). pH values of this solution were adjusted to desired pH and 1 mL of 8-hydroxyquinoline solution was added to this solution for complexation. Vanadium(V)-8-hydroxyquinoline solution was passed through the MWNTs column at a flow rate of 8 mL min^{-1}. The sample solution was permitted to flow through the SPE column under gravity. The flow rates of the solutions were controlled by using stopcock of the column. The adsorbed chelate on MWNTs column was eluted with 5 mL of 1 mol L^{-1} HCl. The eluent was analyzed for the determination of vanadium by graphite furnace atomic absorption spectrometry.

Table 1
Instrument settings for GFAAS determination of vanadium.

Wavelength (nm)	318.4
Slit width (nm)	0.7
Lamp current (mA)	40
Argon flow (mL min^{-1})	250
Reading time	5 s
Heating program temperature	
	°C (ramp time (s), hold time (s))
Drying 1	100 (5, 20)
Drying 2	140 (15, 15)
Ashing	1100 (10, 20)
Atomization	2600 (0, 5)
Cleaning	2650 (1, 3)

2.5. Applications

NIST SRM 1515 Apple leaves, NIST SRM 1570a Spinach leaves and GBW 07605 Tea standard reference materials (250 mg), black tea, coffee, tomato, cabbage, zucchini, apple and chicken (1.0 g) were digested with 6 mL of HNO_3 (65%) and 2 mL of H_2O_2 (30%) in a closed microwave digestion system. It was filtered through a blue band filter paper and diluted to 50 mL with deionized water. A blank digest was also carried out. Then the procedure given in Section 2.4 was applied.

Tap water and bottled drinking water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 5.0 with 1 mol L^{-1} HCl and 1 mol L^{-1} NaOH. Then the procedure given in Section 2.4 was applied. Vanadium concentration was determined by GFAAS.

3. Results and discussion

3.1. Influences of pH

pH is a critical factor on the adsorption studies for quantitative recoveries of analytes [21–26]. The influences of pH on the recovery values of vanadium(IV) and vanadium(V) as 8-hydroxyquinoline chelates on MWNTs were investigated in the pH range of 2–8. Quantitatively recoveries were found in the pH range of 5–7 for vanadium(V). The recoveries of vanadium(IV) were found below 60% in all pH values. So, we studied only vanadium(V) in all next studies. The results are given in Fig. 1 for vanadium(V). The recovery values were decreased after pH 7 due to the onset of precipitation of V(V) ions as hydroxide. All subsequent studies were carried out at pH 5.0. pH values were adjusted by using 1 mol L^{-1} HCl and 1 mol L^{-1} NaOH.

3.2. Effects of amounts of 8-hydroxyquinoline

The influences of amounts of 8-hydroxyquinoline on the recoveries of vanadium(V) on MWNTs column were also examined. The results are shown in Fig. 2. Vanadium(V) recoveries were found to be 75% without ligand. The recoveries of vanadium (V) were enhanced to quantitative values (95%) by using 1–3 mg

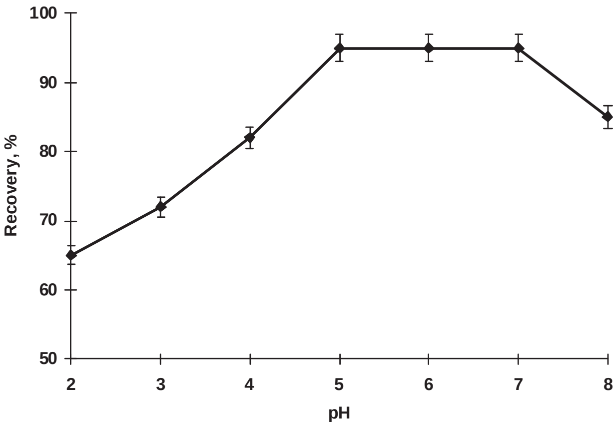

Fig. 1. Effect of pH on recoveries of vanadium ($N=3$).

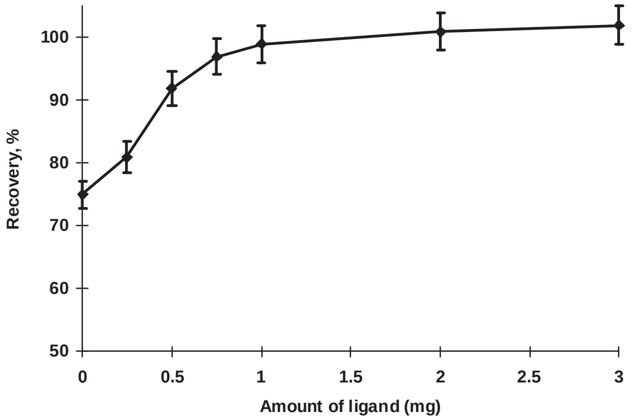

Fig. 2. Effect of amount of 8-hydroxyquinoline on the recoveries of vanadium (*N*=3).

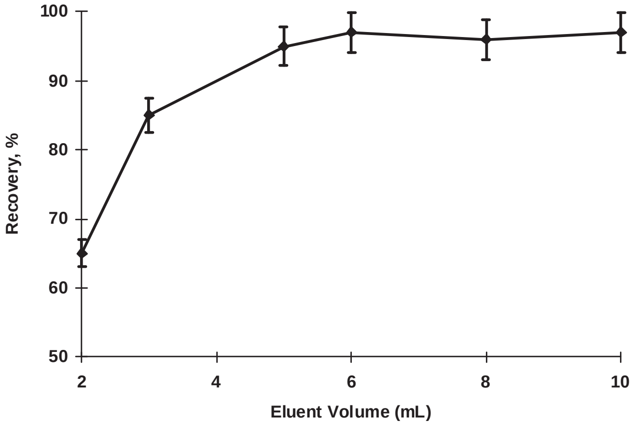

Fig. 3. Effect of eluent volume on recoveries of vanadium (*N*=3).

of 8-hydroxyquinoline. All subsequent studies were carried out at pH 5 by using 1 mg of 8-hydroxyquinoline.

3.3. *Eluent*

Various concentrations of HCl and HNO_3 were used as eluent for the desorption of vanadium(V) ions from the MWNTs column. The recoveries were quantitative (> 95%) by using 1–3 mol L^{-1} HCl for vanadium(V). So, 1 mol L^{-1} HCl was selected as eluent.

Because eluent volume plays a key role in solid phase extraction studies to achieve a high preconcentration factor, the influence of eluent volume was investigated. The results are shown in Fig. 3. Quantitative recoveries were found by using 5–10 mL of 1 mol L^{-1} HCl. Therefore, 5 mL of 1 mol L^{-1} HCl was used as eluent in the next studies.

3.4. *Flow rates*

Effect of flow rates of sample and eluent solutions is also very important in solid phase extraction studies because of retention of analyte ions on column system. Low flow rates can be time consuming. The flow rates were investigated in the range of 1–10 mL min^{-1}. The recoveries of vanadium(V) were found to be quantitative in the sample and eluent flow rate in the range of 1–8 mL min^{-1}. Therefore, 8 mL min^{-1} was selected as sample and eluent flow rate in next studies. The flow rates of the solutions were controlled by using stopcock of the column.

3.5. *Effect of sample volume*

To obtain high enrichment factors, sample volume is an important factor in solid phase extraction studies [27–31]. The effects of sample volume on the recovery values of vanadium on a MWNTs column were studied over the range of 10–1000 mL. The recoveries of vanadium were found quantitative up to 500 mL of sample solution. The results are shown in Fig. 4. The preconcentration factor (PF) is calculated by the ratio of the highest sample volume (500 mL) and the lowest eluent volume (5 mL). The preconcentration factor was calculated as 100.

3.6. *Effects of concomitants*

The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and determination of vanadium. The influences of matrix ions on the recoveries of vanadium ions were investigated at pH 5. Maximum amounts of matrix ions including alkaline, alkaline earth and some metal were separately added to solution containing 1.0 μg of vanadium(V). The results are given in Table 2. Vanadium was quantitatively recovered. The recovery values were also found quantitative for vanadium ions in the presence of all foreign ions together.

3.7. *Analytical performance*

The capacity of MWNTs was investigated by using the batch method [17]. The capacity of MWNTs for vanadium(V) was found to be 9.6 mg g^{-1}. The relative standard deviation (RSD) was found to be 5% in the model solutions. Multiwalled carbon nanotubes (MWNTs) could be reused 250 times without any loss in its sorption behavior.

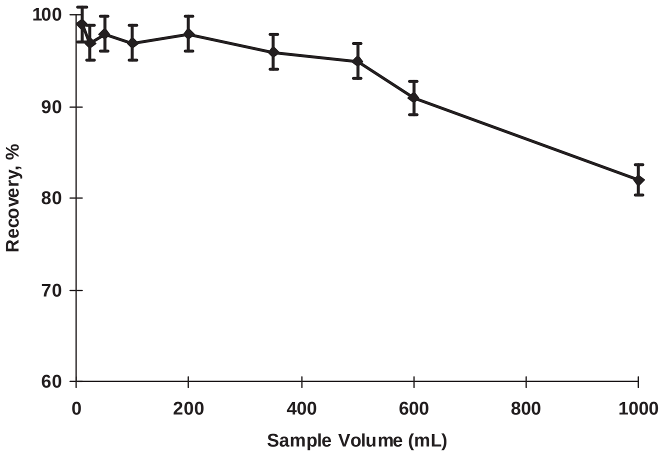

Fig. 4. Effect of sample volume on recoveries of vanadium (*N*=3).

Table 2
Influences of some foreign ions on the recoveries of vanadium (*N*=3).

Ion	Added salt	Concentration (mg L^{-1})	Recovery (%)
Ca^{2+}	$CaCl_2$	3500	95 ± 2
Zn^{2+}	$ZnSO_4$	100	95 ± 1
Fe^{3+}	$FeCl_3$	100	96 ± 2
Fe^{2+}	$FeCl_2$	100	95 ± 2
NH_4^+	CH_3COONH_4	5000	95 ± 2
SO_4^{2-}	Na_2SO_4	4000	101 ± 4
PO_4^{3-}	Na_3PO_4	1000	97 ± 3
CO_3^{2-}	Na_2CO_3	4000	95 ± 2
CH_3COO^-	CH_3COONH_4	10,000	95 ± 2

Table 3
The results for tests of addition/recovery for vanadium determination in some water samples (sample volume: 500 mL, final volume: 5 mL (N=4).

Added (μg L^{-1})	Tap water		Bottled drinking water	
	Found (μg L^{-1})	Recovery (%)	Found (μg L^{-1})	Recovery (%)
–	0.23 ± 0.01*	–	BDL	–
1.0	1.20 ± 0.04	98	0.99 ± 0.03	99
2.0	2.21 ± 0.07	99	1.95 ± 0.01	98
3.0	3.19 ± 0.09	99	2.90 ± 0.02	97

* Standard deviation, BDL: below the detection limit.

Table 4
The results for reference standard materials for vanadium (N=5).

Certified reference material	Concentration (μg g^{-1})		
	Certified value	Experimental value	Recovery (%)
NIST SRM 1515 Apple leaves	0.26	0.27 ± 0.02*	104
NIST SRM 1570a Spinach leaves	0.57	0.54 ± 0.04	95
GBW 07605 Tea	0.86	0.82 ± 0.06	95

* Standard deviation

Table 5
Concentration of vanadium in food samples after application of presented procedure (N=4).

Food samples	Concentration (μg g^{-1})
Black tea	1.58 ± 0.10*
Coffee	0.40 ± 0.01
Tomato	0.17 ± 0.01
Cabbage	BDL
Zucchini	0.10 ± 0.01
Apple	0.25 ± 0.02
Chicken	0.13 ± 0.01

* Standard deviation, BDL: below the detection limit.

The limit of detection (LOD) and limit of quantification (LOQ) of the presented study were calculated after application of the present procedure to blank solutions. Detection limit (3 s) and limit of quantification (10 s) for the vanadium in the optimal conditions were found to be 0.012 μg L^{-1} and 0.040 μg L^{-1}, respectively. The regression equation of calibration curve was linear in the range of 0.05–3.0 μg L^{-1}, A=0.0043C–0.01422 (A: absorbance, C: concentration), r^2=0.9993. Peak height was used as the analytical signal.

3.8. Applications to real samples

The solid phase extraction procedure was also applied to the determination of vanadium in tap water and bottled drinking water samples. Various amounts of vanadium were also spiked to these water samples. The results are given in Table 3. A good agreement was obtained between the added and measured vanadium amounts. These results confirm the validity of the proposed preconcentration method.

The presented solid phase extraction method was checked to certified reference materials (NIST SRM 1515 Apple leaves, NIST SRM 1570a Spinach leaves and GBW 07605 Tea). The results are given in Table 4. The results are in good agreement with the certified values. The procedure was also successfully applied to microwave digested food samples including black tea, coffee, tomato, cabbage, zucchini, apple and chicken samples. The results are given in Table 5.

4. Conclusion

A simple, sensitive, selective and reliable separation and preconcentration method for the determination of vanadium in water and food samples has been successfully validated. The accuracy, precision, linearity, LOD and LOQ values are satisfactory for this method. Trace amounts of vanadium at ng L^{-1} levels can be determined accurately. The results of the present method are comparable with literature values (Table 6) [32–38]. The limit of detection, PF and RSD values of vanadium are superior to those of other methods for vanadium [39–44].

Table 6
Comparative data from some recent studies on preconcentration of vanadium.

System	Ligand	Technique	pH	PF	LOD	RSD (%)	References
H-point standard addition method and partial least squares	Gallic acid	UV–vis	5	–	0.03 μg mL^{-1}	2.2	[32]
Silicagel modified with 3-aminopropyltriethoxysilane	–	GFAAS	8	40	0.1 μg mL^{-1}	2.2	[11]
Diphenylamine and hydrogen peroxide	Diphenylamine	UV–vis		–	0.40 μg mL^{-1}	0.5	[33]
Chelex-100	dithizone, luminol, or 8-hydroxyquinoline	ICP-AES	5	50	4.09 μg mL^{-1}		[9]
Chelex 100 chelating resin	–	ICP-AES	3–5	100	40 μg kg^{-1}	3.9	[34]
Ultrasonic slurry sampling	–	GFAAS			0.6 μg L^{-1}		[35]
Solidified floating organic drop microextraction	8-Hydroxyquinoline	UV–vis	5	38	0.97 μg L^{-1}	3.9	[13]
Ionic liquid-based microextraction	5-Br-PADAP, CDTA	GFAAS	4.75	40	4.9 ng L^{-1}	4.3	[6]
Amberlite XAD-7 resin	5-Br-PADAP, CDTA	ICP-OES	3.7	225	19 ng L^{-1}	2.3	[36]
On-line temperature-assisted ionic liquid dispersive microextraction system	5-Br-PADAP	GFAAS	4	25	4.8 ng L^{-1}	4.1	[14]
Dispersive liquid–liquid microextraction based on solidification of floating organic drop (DLLME-SFO)	N-benzoyl-N-phenylhydroxylamine (BPHA)	GFAAS	3	184	7 ng L^{-1}	4.6	[37]
Flow injection (FI) using a micro-column packed with quinine modified resin	–	FETV-ICP-OES	3.8	62.5	0.072 ng mL^{-1}	4.9	[38]
Ion-exchange (Dowex 1 × 8–100)	–	GFAAS	7.2	60	0.02 μg L^{-1}	3.2	[39]
L-methionine immobilized on controlled pore glass (CPG)	L-methionine	ICP-OES	9	90	0.008 ng mL^{-1}	2	[40]
Cetyltrimethylammonium bromide (CTAB)-modified alkyl silica microcolumn	–	ICP-OES	5–7	28	0.03 μg L^{-1}	4	[41]
Histidine functionalized multiwalled carbon nanotubes as sorbent (MWCNTs-His)	–	GFAAS	5.5	35	9 ng L^{-1}	1.5	[42]
Multiwalled carbon nanotubes	8-Hydroxyquinoline	GFAAS	5	100	0.012 μg L^{-1}	5	Present work

LOD: limit of detection, PF: preconcentration factor.

Acknowledgment

The authors are thankful for the financial support from the Unit of the Scientific Research Projects of Gaziosmanpasa University. Dr. Mustafa Tuzen thanks the Turkish Academy of Sciences for financial support. Sham Kumar Wadhwa thanks TUBITAK BIDEB 2216 for scholarship support.

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