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Pre-concentration and separation of vanadium on Amberlite IRA-904 resin functionalized with porphyrin ligands

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Abstract

Among several methods, enrichment techniques based on sorption onto chelating resins seem convenient, rapid and capable to achieve a high concentration factor. Amberlite IRA-904 resin modified with tetrakis (*p*-carboxyphenyl) porphyrin (TCPP) was used to pre-concentrate vanadium species. Several parameters, such as sorption capacity of the chelating resin, pH for retention of V(IV) and V(V), volume of sample and eluent, were evaluated. Both vanadium species sorbed on TCPP-modified resin were eluted by use of 2 M nitric acid and determined by atomic absorption spectrometry. The recovery values were >94% and pre-concentration factor of 110 was obtained. For speciation studies, CDTA was added to the sample for complexing vanadium(IV), which was not retained on the microcolumn. The proposed method was examined for reference standard material (TM-25.2) and river water sample.

Keywords: Vanadium; Pre-concentration; Speciation; Water analysis

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1. Introduction

Determination of vanadium at trace levels is important for an understanding of its geochemical and biological effects as well as for a monitoring of environmental pollution. Major sources for the emission of vanadium in the environment include combustion of fuel oils, dyeing, ceramics, ink, catalyst and steel manufacturing. Vanadium at trace amounts represents an essential element for normal cell growth, but can be toxic when present at higher concentration. Commonly ETAAS [1,2] or ICP-MS [3,4] have been applied for vanadium analysis. However, in many cases, when the level of vanadium in natural samples is very low, an enrichment step is necessary to improve the precision and accuracy.

Pre-concentration/separation procedures based on sorption are considered to be superior to the liquid–liquid extraction due to their simplicity and ability to obtain high enrichment factors. Application of sorbents obtained by immobilization of chelating agents on solid supports has the advantage of controlling the capacity and selectivity of metal sorption by the appropriate choice of loading organic agents, thus controlling the efficiency of the process. Chelating resins [5–7], activated carbon [8] and various modified polymers [9–11] have been applied for the pretreatment of vanadium. Hirayama et al. [11] applied a two-column system containing chelating functionalised immobilised silica gel for vanadium pre-concentration and speciation analysis. Under suitable conditions, each species was adsorbed onto a differently prepared (ethylenediamine-bonded and ethylenediaminetriacetate-bonded) silica gel columns, from which they were separately eluted and detected by ICP-AES. This procedure, however, requires a considerable time for each analysis.

The aim of the presented work is to check the possibility of tetrakis (*p*-carboxyphenyl) porphyrin (TCPP) as a complexing agent for pre-concentration of vanadium. The strong affinity of metal ions towards porphyrin ligands leads to ideas of their application in solid phase extraction technique [12]. As a support for TCPP the macroporous anion-exchange resin

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Amberlite IRA-904 was examined. The suitability of TCPP for vanadium enrichment was also evaluated using the formation of complexes in a solution followed by their retention on non-modified anionic resin.

2. Experimental

2.1. Instrument and reagents

A Perkin-Elmer model AAnalyst 300 atomic absorption spectrometer equipped with a deuterium background correction system utilised vanadium 318.5 nm line. HGA-800 furnace and pyrolitically coated graphite tubes were employed. The instrumental settings of the manufacturers were followed.

The chemicals used were of analytical grade, and all solutions were prepared with deionised water obtained from a Milli-Q system (Millipore).

A commercial atomic absorption standard solution (Merck) containing 1000 mg/l of V(IV) ($VOSO_4$ in 0.5 mol/l H_2SO_4) was used. Vanadium(V) solutions were prepared by dissolving V_2O_5 in 1% (v/v) HNO_3.

5,10,15,20-tetrakis (4-carboxyphenyl) porphyrin (TCPP) from Fluka was used without further purification.

The macroporous anion-exchange resin Amberlite IRA-904 (50–100 mesh) from Bio Rad Laboratories was applied. It was preliminary washed with 6 M HCl, water, then with 2 M NaOH and water again. For modification sorbent was shaken with 0.1 M TCPP solution at pH 9 for 2 h until the supernatant solution became colourless. It was then filtered out, washed with water and ethanol.

2.2. Retention of vanadium as a function of pH

Retention of vanadium ions was determined using batch technique separately for V(IV) and V(V) in the pH range of 3–11. About 100 mg of dry sorbent (modified or non-modified) was gently shaken for 60 min with 10 ml of 1 µg/ml vanadium solution or with vanadium in the presence of 0.04 mM TCPP solution at selected pH value. The pH was changed by addition of acetate, phosphate and borate buffers, respectively. The metal concentrations were then determined in the filtrate by AAS method. Retention of vanadium ions was expressed in terms of percent of sorption calculated in comparison to the initial metal concentration. The results are based on at least three replicates.

2.3. Pre-concentration and speciation procedure

The proposed method was tested with model solution before its application to the natural waters. For pre-concentration of total vanadium species appropriate volume of aliquots was adjusted (if necessary) to pH 6.5 with phosphate buffer and passed through the microcolumn containing 0.1 g of Amberlite IRA-904 resin loaded with TCPP (0.22 mmol/g) at a flow rate of 1.5 ml/min. Metal chelates were then eluted by using 1 ml of 2 M nitric acid and analysed by atomic absorption spectrometry.

In speciation studies before enrichment step, CDTA solution was added to the sample to reach its final concentration of 0.27 M. The solution was then passed through the microcolumn with TCPP-loaded resin. Vanadium(V) content was determined after elution with 1 ml of 2 M HNO_3.

3. Results and discussion

3.1. Sorption of vanadium ions

The complexation of vanadium and also its retention depends on the protonation of chelating agent. The sorption of both vanadium species on Amberlite IRA-904 modified with TCPP was examined in pH range of 3–11 (Fig. 1A). The used sorbent contained 0.022 mmol of TCPP per gram. Vanadium complexation with porphyrin could be also realised in a solution when ligand is added to the sample and the resulting complexes are then retained on an anion-exchange resin due to π–π interaction between aromatic structure of resin polymeric matrix and chelating agent. Thus, this procedure was evaluated for sorption of vanadium(V) and vanadium(IV) complexes with TCPP in solution (0.04 mM) on

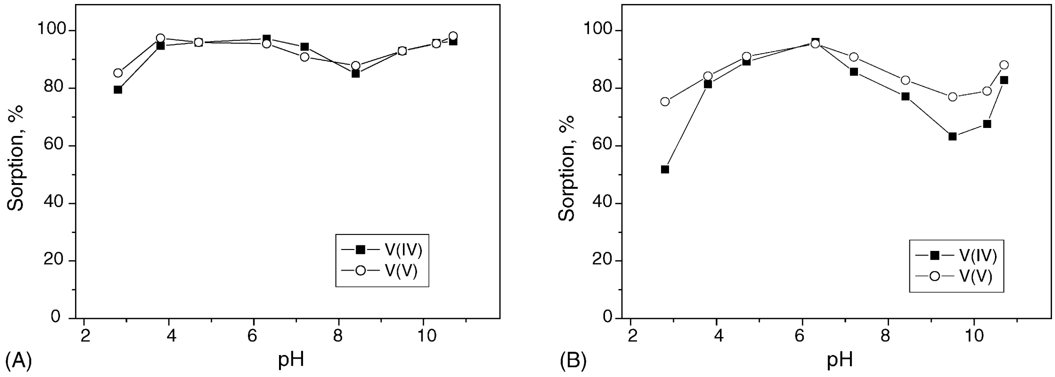

Fig. 1. Effect of retention of vanadium ions on: (A) TCPP-modified sorbent; (B) non-modified sorbent in the presence of TCPP in a solution.