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Determination of vanadium (V) in drinking water by flow injection and pre-concentration in a knotted reactor by inductively coupled plasma optical emission spectrometry with ultrasonic nebulization

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Abstract

An on-line vanadium pre-concentration and determination system implemented with inductively coupled plasma optical emission spectrometry (ICP-OES) associated with a flow injection (FI) method with ultrasonic nebulization (USN) system was studied. The vanadium was retained as vanadium-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol V(V)-(5-Br-PADAP) complex, at pH 3.2. The vanadium complex was removed from the knotted reactor (KR) with 30% v/v nitric acid. A sensitivity enhancement factor of 180 was obtained with respect to ICP-OES using pneumatic nebulization (15 for USN and 12 for KR). The value of detection limit for the pre-concentration of 10 ml of aqueous solution was 19 ng l^{-1}. The precision for 10 replicate determinations at the 5 $\mu g\ l^{-1}$ V(V) level was 2.6% relative standard deviation (R.S.D.), calculated with the peak heights obtained. The calibration graph using the pre-concentration system for vanadium was linear with a correlation coefficient of 0.9995 at levels near the detection limits up to at least 100 $\mu g\ l^{-1}$. The method was successfully applied to the determination of vanadium in drinking water samples. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium determination; Drinking water; Inductively coupled plasma optical emission spectrometry; Ultrasonic nebulization; Knotted reactor; 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol reagent

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1. Introduction

Vanadium is widely distributed in the Earth's crust and has been recognized as a potentially dangerous pollutant [1]. Vanadium compounds can be highly toxic to man and animals [2] and their presence in the atmosphere is mainly due to the combustion of fossil fuels, which have important vanadium contents [3]. However, vanadium is an essential trace element possessing specific physiological functions [2] and its role in physiological systems includes normalization of sugar levels, participation in various enzyme systems as an inhibitor and a cofactor [4] and catalysis of the oxidation of various amines [5], therefore determination of vanadium is receiving increasing attention in pollution and nutritional studies.

Since one of the routes of incorporation of vanadium into the human body is drinking water [6–8], its determination in these type of samples becomes very important. Since the concentration of V in drinking water is very low [9–11], in the order of a few micrograms per liter, powerful techniques are required and only a few of them show sufficient sensitivity.

In the past years, several methods have been developed for the determination of V at low concentrations, among them, catalytic spectrophotometry [12,13], neutron activation analysis (NAA) [14], inductively coupled plasma mass spectrometry (ICP-MS) [8], inductively coupled plasma optical emission spectrometry (ICP-OES) [15] and electrothermal atomic absorption spectrometry (ETAAS) [16].

Although the detection levels reached by spectrophotometric catalytic methods are suitable, they are susceptible to multiple spectral interferences, a serious drawback for their application.

The NAA method is time-consuming, and routine analysis of numerous samples is laborious. This method also requires sophisticated instrumentation, which may not be available in most analytical laboratories. Within the last decade, ICP-MS has proved ideally suited as an alternative approach for the determination of vanadium in various matrices. ICP-MS is used for the determination of vanadium because of its high sensitivity, high selectivity, and high sample throughput. However, the cost of instrumentation may be prohibitive to many laboratories.

Although ICP-OES or ETAAS are the most used techniques in the determination of traces of vanadium, the low level of vanadium concentration in water is not compatible with the detection limit of these techniques. In order to achieve accurate, reliable and sensitive results, pre-concentrations and separations are needed when the concentrations of analyte elements in the sample are too low to be determined directly by ICP-OES.

Many pre-concentration techniques [6,17] for the determination of V have been proposed, including chelation and extraction, precipitation, coprecipitation, and ion-exchange resins. However, many of these methodologies are performed in batch, thus requiring great sample volumes in order to reach low detection limits. Besides, these systems present higher contamination risks.

When pre-concentration techniques are applied in a batch mode, the time of analysis increases and the operations are usually too tedious to be compatible with the ICP-OES measurements. Furthermore, these procedures are not practical for application in routine analysis. This situation has been significantly improved by utilizing flow injection (FI) associated with ICP-OES [18,19], such that the general drawbacks of batch pre-concentration procedures have been largely eliminated, and currently the pre-concentrations can be achieved almost as efficiently as with a simple ICP-OES determination. Reagent consumption is usually reduced to a small percentage of that in batch procedures. Sample contamination is also reduced, which becomes important when trace concentrations are determined. In fact, to date the most dramatic improvements achieved in FI-ICP-OES have been in the field of on-line pre-concentration. On the other hand, the use of an ultrasonic nebulizer can provide a 5–50 fold improvement in detection limits [20–22].

Flow injection on-line pre-concentration based on the sorption of metallic complexes on the inner walls of a PTFE knotted reactor (KR) has been successfully applied. So far, in most of the works using KRs, these have been coupled to FAAS [23,24] or to ETAAS [25–29]. On the other hand, unlike FAAS, the sensitivity of ETAAS is adequate for a variety of analytical situations, but not for coupling in a continuous system [30]. ICP-OES thus, appears to be an interesting alternative for coupling with KR in order to perform pre-concentrations and determinations of metal traces, since besides exhibiting a sensitivity similar to that of ETAAS, it has the advantage of coupling to systems working on-line. Additionally, KR has the advantage of a low hydrodynamic impedance, permitting high load sample rates and elevated throughput samples.

The most widely used reagents for metal pre-concentration in KR have, so far, been diethyldithiocarbamate (DDTC) [25,29] and ammonium pyrrolidine dithiocarbamate (APDC) [26,29]. Pyridylazo reagents form insoluble chelates with numerous metallic ions. However, we have not found any references in the literature to the use of these reagents in KR pre-concentration methodologies.

2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) has been used as a reagent in the spectrophotometric determination of numerous metallic ions [31–33], including vanadium [34], although precautions had to be taken in order to avoid the precipitation of the corresponding chelate, such as, the addition of surfactant agent. This fact suggested to us that, in the absence of a surfactant, 5-Br-PADAP could be a suitable reagent for the pre-concentration of vanadium on KR.

In the present work, a method for pre-concentration and determination of vanadium using a KR is proposed. Vanadium was retained under the form of V(V)-(5-Br-PADAP) complex. The determination was performed using ICP-OES associated with a FI methodology and ultrasonic nebulization system.

2. Experimental

2.1. Reagents

A solution of 5-Br-PADAP (Aldrich, Milwaukee, WI, USA) 10^{-2} mol l^{-1} was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution.

Vanadium (V) stock standard solution (1000 μg ml^{-1}) was prepared by dissolving 2.2966 g of ammonium metavanadate (99.99%, Merck) in 1000 ml of ultrapure water.

The acetic acid/acetate buffer solution was prepared from a 2 mol l^{-1} acetic acid solution adjusted to pH 3.2 by dissolution of sodium hydroxide.

Ultrapure water (18 MΩ cm^{-1}) was obtained from a EASYpure RF (Barnstedt, Iowa, USA).

All the reagents were of analytical-reagent grade and the presence of vanadium was not detected in the working range.

2.2. Apparatus

The measurements were performed with a sequential ICP spectrometer [Baird (Bedford, MA, USA) ICP 2070]. The 1-m Czerny-Turner monochromator had a holographic grating with 1800 grooves mm^{-1}. An ultrasonic nebulizer, U-5000 AT [CETAC Technologies (Omaha, NE, USA)], with desolvation system was used. The ICP and ultrasonic nebulizer operating conditions are listed in Table 1. The FI system used is shown in Fig. 1. A Minipuls 3 peristaltic pump [Gilson (Villiers-Le-Bell, France)] was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. For sorption of the complex, a KR was made from a 2-m length of PTFE tubing of 0.5 mm internal diameter by tying interlaced knots of approximately 5-mm diameter loops. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA)

Table 1
ICP and ultrasonic nebulizer instrumental parameters

ICP conditions	
RF generator power	0.8 kW
Frequency of RF generator	40.68 MHz
Plasma gas flow rate	8.5 l min^{-1}
Auxiliary gas flow rate	1 l min^{-1}
Observation height (above load coil)	15 mm
Analytical line: V	309.311 nm
Ultrasonic nebulizer conditions	
Heater temperature	140°C
Condenser temperature	4°C
Carrier gas flow rate	1 l min^{-1}

a high enhancement factor, a loading time of 120 s was used for pre-concentration.

3.1.2. KR length

An important parameter to be optimized was KR length. Fig. 3 shows that good results are obtained for a length of 200 cm, and further increases in length did not show any improvement in the enhancement factors.

3.1.3. Effect of solvent concentration

In order to avoid the precipitation of reagent complexing 5-Br-PADAP in aqueous medium the solution of the complexing reagent was prepared in the presence of ethanol. It was observed that with 10% v/v of ethanol, 5-Br-PADAP remained in solution up to concentrations in the order of 10^{-4} mol l^{-1}. Subsequently, the influence of ethanol concentration on the pre-concentration of complex V(V)-5-Br-PADAP was assessed. The pre-concentration decreases when ethanol concentrations above 20% v/v are used in the 5-Br-PADAP solution. This behavior was to be expected since increasing solvent concentrations leads to higher solubility of the V(V)-5-Br-PADAP complex, which hinders its precipitation and adsorption on the KR walls.

Ethanol concentration was set at 10% v/v, which enabled to achieve both stability of the complexation reagent solution and efficiency of the system for pre-concentration of the V(V)-5-Br-PADAP complex.

3.1.4. Concentration and flow rate of the 5-Br-PADAP solution

The concentration and loading flow rate of the 5-Br-PADAP solution were optimized. The minimum reagent-metal ratio necessary to achieve optimum pre-concentration was 5:1. However, the maximum possible concentration of 5-Br-PADAP was 10^{-4} mol l^{-1}, since at higher values the pre-concentration capacity of the system is decreased, which could be attributed to the fact that free complexing reagent and the V(V)-5-Br-

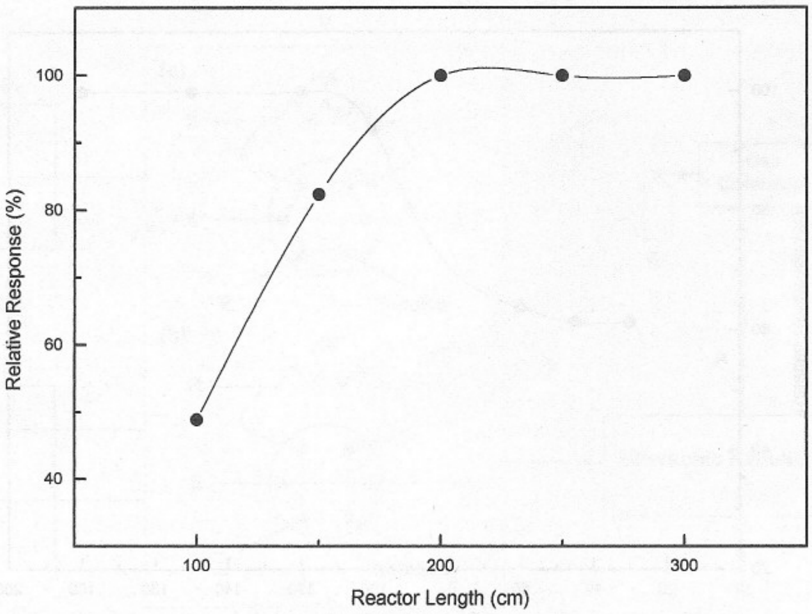

Fig. 3. Effect of the length of the KR on the recorder output signal. Sample loading period was 120 s; loaded flow rate was 5 ml min^{-1}; the elution flow rate was 1.75 ml min^{-1}; V(V) concentration was 50 μg l^{-1}; 5-Br-PADAP concentration was 5×10^{-5} mol l^{-1}.

PADAP complex compete for adsorption on the KR inert walls. The 5-Br-PADAP concentration selected was 5×10^{-5} mol l^{-1}.

The optimum load rate of the 5-Br-PADAP solution was 2.5 ml min^{-1}.

3.2. Optimization of the elution conditions

The selection of eluent for the complex was critical. Most of the reported literature uses ETAAS detection and, therefore, the use of an organic solvent does not cause any difficulties. This was not possible in this case since organic solvents generate instability in the ICP, which can eventually lead to its extinction. Nitric acid turned out to be a good eluent for the V(V)-5-Br-PADAP complex with 25% v/v as the minimum concentration necessary to obtain the best response. A concentration of 30% v/v nitric acid was adopted for the remainder of this work.

The effect of the flow rate of eluent was studied and the best ICP-OES signal was achieved at 1.75 ml min^{-1}.

3.3. Interferences

Experiments were performed to discover the degree to which the proposed method is susceptible to interference from Al (309.217 nm line) and Mg (309.299 nm line). The tailings of the aluminum and magnesium spectra served as important references when working with the most sensitive line of vanadium (309.311 nm line). The determination of vanadium was possible in the presence of a great excess of Al and Mg since these elements were not complexed with 5-Br-PADAP in the used operation conditions.

The effects of representative potential interferent species were tested. Thus, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{3+} could be tolerated up to at least 2500 μg l^{-1}. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not retained on the KR. The value of the reagent blank signal was not modified by the presence of the potentially interfering ions assayed.

3.4. Performance of the pre-concentration system with KR

The overall time required for pre-concentration of 10 ml of sample (2 min at a flow rate of 5 ml min^{-1}), elution (approx. 0.5 min at a flow rate of 1.75 ml min^{-1}) and washing (0.2 min at a flow rate of 1.75 ml min^{-1}) was approximately 2.7 min. Thus, sample throughput was approximately 22 samples h^{-1}.

A sensitivity enhancement factor of 180 was obtained with respect to ICP-OES using pneumatic nebulization (15 for USN and 12 for KR).

3.5. Method validation

In order to demonstrate the validity of this method, 1 l of drinking water was collected and divided into 10 portions of 100 ml each. The proposed method was applied to six portions and the average quantity of vanadium obtained was taken as a base value. Then, increasing quantities

Table 2
Method validation

Aliquots	Base value (μg l^{-1})	Quantity of V(V) added (μg l^{-1})	Quantity of V(V) found (μg l^{-1})	Recovery (%)[a]
1	–	0.00	5.52 ± 0.11	–
2	5.52	1.00	6.50	98.0
3	5.52	3.00	8.48	98.5
4	5.52	5.00	10.49	99.3
5	5.52	8.00	13.54	100.2

[a] 100 × [(found − base)/added].

of vanadium were added to the other aliquots of sample and vanadium was determined by the same method (Table 2).

Additionaly, the proposed method was applied to a standard reference material, NIST SRM 1640 Trace Elements in Natural Water, with a vanadium content of 12.99 ± 0.37 μg kg^{-1}, the density of SRM 1640 at 22°C is 1.0015 ± 0.0005 g ml^{-1}. Using the proposed method the content of vanadium determined in this SRM was 12.73 ± 0.07 μg kg^{-1}.

3.6. Determination of vanadium in drinking water samples

The relative standard deviation (R.S.D.) for 10 replicates containing 5 μg l^{-1} of V was 2.6%. The calibration graph was linear with a correlation coefficient of 0.9995 at levels near the detection limits up to at least 100 μg l^{-1}. The detection limit (DL), calculated as the amount of vanadium required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ) was 19 ng l^{-1}. Finally, the results of the method applied to vanadium determination in drinking water samples are shown in Table 3. The concentrations were in the range 5.52–8.11 μg l^{-1} of vanadium.

The results obtained are in good agreement with those of Sabbioni [8], Ahmed [10], and Bermejo-Barrera [11]. The mean values of vanadium concentration reported in drinking waters by these authors are 5.0 μg l^{-1}, 6.0 μg l^{-1}, and 6.63 μg l^{-1}, respectively.

Table 3
Concentrations of vanadium in drinking water samples[a]

Sample	V(V) concentration (μg l^{-1})
1	5.52 ± 0.11
2	7.40 ± 0.08
3	6.79 ± 0.08
4	5.82 ± 0.10
5	8.11 ± 0.06

[a] 95% confidence interval; $n = 6$.

4. Conclusions

The on-line coupling of a FI sorption pre-concentration system with a knotted reactor to FI-ICP-OES increases the speed of the pre-concentration and analysis process, besides reducing sample consumption and contamination risks.

The results in this work demonstrate the possibility of using 5-Br-PADAP for pre-concentration of vanadium, since the V(V)-5-Br-PADAP complex was effectively adsorbed on the inner surface of a KR made of PTFE. The manifold presented provided a sensitivity enhancement factor of 180 with respect to ICP-OES using pneumatic nebulization (15 for USN and 12 for KR).

The proposed system of pre-concentration associated with ultrasonic nebulization allows vanadium determinations in drinking water samples at levels of V as low as micrograms per liter with good accuracy and good reproducibility.

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