



Application of multivariate designs in the development of a method for vanadium determination in natural waters by HR-CS GF AAS after cloud-point extraction



Valdinei S. Souza^{a,c}, Leonardo S.G. Teixeira^a, Marcos A. Bezerra^{b,*}

^a Universidade Federal da Bahia, Instituto de Química, Departamento de Química Analítica, Campus Universitário de Ondina, 40170-115 Salvador, Bahia, Brazil

^b Universidade Estadual do Sudoeste da Bahia, Laboratório de Química Analítica, 45206-190 Jequié, Bahia, Brazil

^c Instituto Federal de Educação, Ciência e Tecnologia Baiano, Campus de Santa Inês, 45320-000 Santa Inês, Bahia, Brazil

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ABSTRACT

A method for trace vanadium determination in natural waters was developed using multivariate approaches (two-level fractional factorial, Doehlert and constrained mixture designs). The preconcentration method was based on the cloud point extraction of vanadium after its complexation with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP), separation of a micellar phase on the cloud point of the non-ionic surfactant polyethylene glycol tert-octylphenyl ether (Triton X-114) and subsequent determination using high resolution continuous source graphite furnace atomic absorption spectrometry (HR-CS GF AAS). The developed method presented limits of detection and quantification of 0.13 and 0.42 $\mu\text{g L}^{-1}$ respectively, an enrichment factor of 13.3-fold and precision expressed as a repeatability (% RSD, $n = 10$, $2 \mu\text{g L}^{-1}$) of 2.5%. Analysis of a certified reference material (Trace elements water, NIST 1643e) and spike tests with recoveries between 84% and 123% showed that the proposed method presents adequate accuracy. The proposed method was applied in the analysis of natural waters collected in an area with naturally occurring vanadium (Maracás, Bahia, Brazil) and groundwater collected from artesian wells located at gas stations.

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1. Introduction

Vanadium is a metal widely distributed in the earth's crust and is the twentieth most abundant element [1]. It can be found in trace amounts in foods, soils, sediments, natural waters, air, plants, animals, fossil fuels, etc. [2–4]. It is also a micronutrient necessary for the adequate functioning of metabolism, as it is a cofactor for enzymes such as haloperoxidase and nitrogenase. Some vanadium compounds stimulate glucose uptake and inhibit lipid breakdown [5]. Vanadium has toxic effects on health when its concentration in the environment is above safe levels. Moreover, this metal can undergo bioaccumulation and biomagnification processes, thus damaging the biota and, consequently, humans [6,7]. Vanadium compounds also contribute to environmental pollution and the control of its emission, mainly from burning fossil fuels, has been a concern due to its mutagenic and carcinogenic effects [8,9]. In the petroleum and derivatives processing industry, control of this metal is required due to its ability to poison catalysts [10].

Due to its toxic nature in biological systems, there is increasing interest in the determination of vanadium in environmental samples. To

meet this demand, a large variety of analytical techniques have been reported on the determination of vanadium. Adsorptive anodic stripping voltammetry [11], spectrophotometry [12], spectrofluorimetry [14], neutron-activation analysis (NAA) [15], graphite furnace atomic absorption spectrometry (GF AAS) [13,16], inductively coupled plasma optical emission spectrometry (ICP OES) [17] and inductively coupled plasma mass spectrometry (ICP MS) [18] have been used extensively for this task. The need for the determination of vanadium and other metals in trace concentrations has motivated the development of strategies to improve the characteristics of the commonly used analytical techniques and allow for the detection of low concentrations of this metal. Methods of pre-concentration and separation can contribute not only to achieving lower limits of quantification, but can also eliminate matrix effects and possible interference in this determination [19]. Although GF AAS presents high sensitivity for several elements of environmental concern, this technique still presents a limit of quantification insufficient for determining some refractory metals, such as vanadium, in very small amounts such those found in natural waters [20].

Cloud point extraction (CPE) is a separation and pre-concentration technique based on the use of a surfactant to induce the formation of a micellar environment and phase separation that a surfactant (anionic, amphoteric or non-ionic) presents when it reaches the cloud point temperature. At this temperature, the surfactant-rich phase separates from

* Corresponding author.

E-mail address: mbezerra@uesb.edu.br (M.A. Bezerra).

the bulk phase, dragging into a small volume hydrophobic substances such as some metal complexes [21].

Cloud point extraction has the advantages of low cost, operational safety due to the poor flammability of the surfactant, speed, operational simplicity and high pre-concentration factors. Furthermore, CPE is considered to be an environmentally friendly technique as it replaces the toxic solvents typically used in liquid-liquid extraction with surfactants that are used in small amounts and have low toxicity [22,23]. CPE has been used in analytical chemistry to determine levels of synthetic dyes in food samples by molecular spectrophotometry [24], traces of inorganic arsenic in water samples by hydride generation atomic fluorescence spectrometry [25], inorganic antimony species in beverages and biological samples using flame atomic absorption spectrometry [26], flavonoids in vegetal samples using high performance liquid chromatography [27], trace levels of copper in the serum of patients with viral hepatitis using flame atomic absorption spectrometry [28], silver nanoparticles and Ag(I) species determination by electrothermal atomic absorption spectrometry [29], and cadmium, copper and nickel in sediment samples by inductively coupled plasma emission spectrometry [30], among others applications.

In this work, three multivariate methods (two-level fractional factorial, Doehlert and constrained mixture designs) were used to develop a method for the pre-concentration of vanadium by CPE and determination by high resolution continuous source graphite furnace atomic absorption spectrometry (HR-CS GF AAS). This method was applied for the determination of vanadium in natural water samples (well water and river water) collected in a region rich in vanadium minerals and groundwater samples from wells located close to gas stations.

2. Experimental

2.1. Instrumentation

All spectrometric measures were obtained using a high resolution continuous source graphite furnace atomic absorption spectrometry (HS-CS GF AAS) model ContrAA 700 (Analytik Jena AG, Jena, Germany) equipped with transversely heated pyrolytically coated graphite tubes with an integrated platform, a AS-GF autosampler (Analytik Jena AG, Jena, Germany), a 300 W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany) operating in hot-spot mode as the source of continuous radiation, a coupled charge detector (CCD) and a compact double Echelle monochromator. High purity argon (99.99%) was always used as the purge and tube protective gas. The graphite furnace program for the determination of vanadium in this study is given in Table 1. Acquisition, treatment and storage of analytical signals (absorbance peak integrated area) were carried out by the software Aspect CS 2.1.2.0. Data were obtained by selecting three pixels (central pixel ± 1). All measurements were carried out at the wavelength 318.3982 nm.

A centrifuge model Q022T294 (Quimis, São Paulo, SP, Brazil) was used to accelerate the separation of the surfactant rich-phase from the aqueous phase. An ultrasonic cleaner (Maxclean model 1450, Unique, Indaiatuba, SP, Brazil) was used for the solubilization of the surfactant in water during its preparation.

Table 1

Temperature program used for the determination of vanadium by HS-CS GF AAS after cloud point extraction procedure.

Steps	Temperature, °C	Ramp, °C/s	Hold, s	Ar flow rate, mL min ⁻¹
Drying 1	120	3	20	250
Drying 2	150	5	20	250
Drying 3	200	10	10	250
Pyrolysis 1	350	30	10	250
Pyrolysis 2	1600	100	15	250
Gas adaptation	1600	0	5	0
Atomization	2700	FP	8	0
Clean	2710	500	4	250

2.2. Reagents and solutions

All reagents used in the analysis were of analytical grade purity. Ultrapure water was obtained using an Elga system (Purelab Classic model, High Wycombe, UK). All glassware was decontaminated with 10% (v/v) HNO₃ solution for at least 12 h. After this period, they were rinsed with deionized water and dried in a dust-free environment.

Vanadium solutions were prepared by diluting a standard solution (Merck, Kenilworth, NJ, USA) with a concentration of 1000 µg mL⁻¹ in a 1% HCl solution. A solutions of 100 mg L⁻¹ (m/v) 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP) was prepared by dissolving 0.0200 g in a volume of 200 mL in ethyl alcohol (PA). A 10% (v/v) Triton X-114 surfactant solution was prepared from the dilution of 10 mL of the concentrated surfactant (Vetec, Rio de Janeiro, RJ, Brazil) to a final aqueous volume of 100 mL followed by solubilization using ultrasound energy. A solution of 1% (v/v) HNO₃ in ethanol (Synth) was used to decrease the viscosity of the surfactant-rich phase obtained after extraction. Acetate buffer solutions (pH 3.7 to 5.7), Tris (pH 7.0 to 8.0) and borate (pH 9.0) were used for pH adjustment of the solutions.

2.3. Sample collection

Samples of natural waters were collected from rivers and wells in the city of Maracás, Bahia, Brazil (a region with natural deposits of vanadium ores) and samples of groundwater collected from artesian wells located close to gas stations in the cities of Salvador, Jaguaquara and Itaquara (Bahia, Brazil). The samples were filtered, preserved by the addition of 100 µL of HNO₃ for each liter and stored in polyethylene flasks previously decontaminated overnight with 10% (v v⁻¹) nitric acid solution.

2.4. Pyrolysis and atomization curves

The electrothermal behavior of vanadium was investigated by obtaining its respective pyrolysis and atomization curves without the presence of any modifier. To obtain the pyrolysis curve, the atomization temperature was fixed to 1600 °C and the pyrolysis temperature was varied in the range from 700 to 2000 °C. After selecting the optimum pyrolysis temperature, it was fixed and the atomization temperature was varied in the range from 2400 to 2700 °C. All measurements were based on the integrated absorbance for the measurement of a vanadium standard solution with a concentration of 20 µg L⁻¹.

2.5. Multivariate optimization

For the optimization of the CPE procedure, three types of multivariate experimental designs were applied: (i) a fractional two-level factorial design, i.e. 2⁶⁻¹, (ii) a Doehlert design, and (iii) a constrained mixture design [31,32]. All experiments were carried out in random order in the application of these designs and a 40.0 mL of a 10.0 µg L⁻¹ vanadium standard solution was used in all optimization steps. Two-level factorial design was used to screen the variables and discover which of them presented a significant effect. Low and high levels were established according to the values presented in Table 2a.

The Doehlert design was used to find the optimal values of method variables and the mixture design allowed for optimizing the proportions of the solutions of extraction-promoting agents. The Doehlert matrix (Table 3) allowed for studying the variables pH at five levels (3.7 to 7.7), complexing at three levels (2.86 × 10⁻³ to 14.32 × 10⁻³ mmol L⁻¹) and the surfactant concentration at three levels (0.1 to 0.3% v/v). In relation to the mixture design, some constraints (upper and lower limits) for the levels of the variables were established (Table 4a). These constraints were necessary to avoid the absence of some extraction promoting agent in certain experiments set by the experimental matrix. The experiments were

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