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A flow-injection renewable surface sensor for the fluorimetric determination of vanadium(V) with Alizarin Red S

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Abstract

Vanadium(V) is determined by a simple bead injection spectroscopy–flow-injection analysis (BIS–FIA) system with spectrofluorimetric detection using a commercially available flow cell (Hellma 176-QS). The 500 μl of a homogeneous bead suspension of an anionic resin (Sephadex QAE A-25) previously loaded with the fluorogenic reagent 1,2-dihydroxyanthraquinone-3-sulfonic acid (Alizarin Red S) was injected to fill the flow cell. Next, V(V) is injected into the carrier and reacts with the immobilized reagent on the active solid support placed in the flow cell to form a fluorescent chelate in the absence of surfactant agents. The complex is so strongly retained on the beads that the regeneration of the solid support becomes extraordinarily difficult, so needing the renovation of the sensing surface which is achieved by means of bead injection. At the end of the analysis, beads are automatically discarded from the flow cell and transported out of the system by reversing the flow.

The measurement of fluorescence is continuously performed at an excitation wavelength of 521 nm and an emission wavelength of 617 nm. Using a low sample volume of 800 μl, the analytical signal showed a very good linearity in the range 2–60 ng ml^{-1}, with a detection limit of 0.45 ng ml^{-1} and a R.S.D. (%) of 4.22 for 50 ng ml^{-1} of V(V) concentration ($n = 10$). The sensor showed both a good selectivity, which could also be increased by the addition of EDTA and F^- as masking agents, and applicability to the determination of V(V) in waters, physiological samples (serum and urine) and mussel tissues.

Keywords: Bead injection spectroscopy; Flow-injection analysis; Vanadium

1. Introduction

It is known that vanadium is an essential trace element due to its significant role in environment [1], industry and physiological systems, involving participation in various enzyme systems as an inhibitor and cofactor [2], catalysis of the oxidation of various amines and normalisation of sugar levels (alternative or adjunct therapeutic agent in diabetes) [3]. Moreover, laboratory and epidemiological evidence suggests that vanadium may also play a beneficial role in the prevention of heart-disease [4], no forgetting that it is toxic at ml^{-1} levels [5]. Nevertheless, at high concentration levels, vanadium is a potentially dangerous chemical pollutant that can play havoc with the entire agricultural system. This toxicity is due to excessive industrial exposure and from emission into the environment from refineries, steel and chemical industries, as a result of the combustion of petroleum derivatives [6].

A few of methods for the determination of vanadium(V) have been described. UV–visible spectrophotometry [7–10] and atomic spectrometry (ICP-MS [11], AA [12], etc.) are two of the principal tools that have been extensively used for its determination. Molecular fluorescence spectrometry is also an important analytical technique for quantitative determination of trace and ultratrace of V. This is usually preceded by a reaction of the metal with different reagents [13,14] or oxidation reactions of organic compounds such as anthraquinone derivatives [15–17] where the metal acts as catalyst. In other fluorimetric methods, the fluorescence intensity has been greatly enhanced by addition of effective

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activators such as cationic surfactants [18]. As an alternative to conventional fluorimetry, a new spectrofluorimetric method is proposed.

Nowadays, there is a demanding need for the development of automatic analytical methods capable of detecting a large variety of metals in different media. Flow-injection analysis (FIA) methods have become an important means in these analyses. The large diffusion and utilisation of FIA is mainly due to their good properties: stability, robustness, reliability, no expensive, etc. Perhaps, two of the inconveniences of these methods, in some occasions, are the lack of sensibility and selectivity at low concentration levels. In order to overcome this problem, flow-injection (FI) can be used in combination with solid phase spectrometry (SPS) using different supports to obtain high sensitivity combined with a relatively simple procedure and good selectivity. These systems are called flow-through sensors [19], and beads of different material nature are acting as surface media for retaining reagents/catalysts/analytes/reacting products. Beads act as solid phase extractor, as the analyte is absorbed or exchanged on their surface and can be separated from the sample, and also as solid reagent, as the absorbed species reacts with the bead surface promoting a physical change in it which can be monitored by using an appropriate detector.

In this FI-SPS methodology it is possible that: (1) the species of interest is strongly retained, so the regeneration of the support becomes extraordinarily difficult, or (2) there is lost in the retention efficiency. In these cases a new methodology based on the concept of bead injection spectroscopy (BIS) [20] can be used, being beads surface renewed after each cycle. This methodology, flow-injection renewable surface (FI-RS) sensing methodology [21], can be seen as the third generation of FI microanalytical techniques. Although this concept was first introduced to use with sequential injection analysis (SIA), demonstrating that this new concept is feasible, it also can work with FIA (low-cost instrumentation) using a commercial flow cell (Hellma 176 QS) [22] as alternative to a jet ring cell [20,23].

The aim of this work is the development of a new flow method for the determination of V(V) in different media based in the continuous measurement of the fluorescence complex formed between V(V) and 1,2-dihydroxyanthraquinone-3-sulfonic acid, which is sorbed on anionic resin beads. The reagent, also called Alizarin Red S (ARS), is one of the most useful photometric reagents for the determination of metals because it forms chelates with a multitude of metal cations [24], but it has only been used for the fluorimetric determination of few elements (boron [25], molybdenum [26], etc.). In the proposed sensor, based on a system previously proposed by García Campaña et al. [18], the immobilization of the reagent in the solid support makes possible the production of a more rigid environment in which the fluorescence of the binary complex is enhanced and, in addition, very favourable selectivity conditions are introduced. The most important contributions of this new system are both (1) the renovation of the sensing surface for each individual sample analysis due to the difficulty of regenerating the sensing surface, and (2) the high sensitivity, avoiding the use of activators. The procedure is very simple, inexpensive and fast, and allows the selective determination at trace levels of V(V) in waters, physiological samples (serum and urine) and mussel tissues, without the use of extraction or pre-concentration off-line steps.

2. Experimental

2.1. Chemicals

All experiments were performed with reagents of analytical-reagent grade, pure solvents and deionized water (used for the dilution of samples and reagents).

Standard vanadium(V) solution (100 μg ml^{-1}) was prepared by dissolution of the appropriate amount of NH_4VO_3 (Panreac, Barcelona, Spain) in deionized water. Working solutions were daily prepared by appropriate dilution of this one with deionized water. Sodium 1,2-dihydroxyanthraquinone-3-sulfonate (Carlo Erba, Milano, Italy) solution (1×10^{-3} M), prepared weekly, was used as fluorescent reagent. Adequate fresh solution of reagent was prepared every day by appropriate dilution with deionized water. Rest of solutions were stable more than one month when they were protected from sunlight and kept at about 5 °C in a refrigerator.

A 0.15 M KCl solution (Panreac, Barcelona, Spain) at pH 7.5 was used in the FIA experiments as carrier solution.

Sephadex QAE A-25 anion exchanger gel (Aldrich, Madrid, Spain) was used in the chloride form as beads (40–120 μm, capacity: 3.1 meq/g). Another tested solid supports were Sephadex DEAE A-25, Sephadex SP C-25 and C_{18} bonded silica.

2.2. Apparatus

A chromatography column (i.d.: 16 mm, $l = 30$ cm) was used in order to obtain a homogeneous aqueous suspension of ARS-loaded beads (Sephadex QAE A-25) by purging air gently through it.

Fluorescence emission measurements were obtained with a Varian Cary-Eclipse Fluorescence Spectrofluorimeter (Varian Iberica, Madrid, Spain). The spectrofluorimeter was equipped with a xenon discharge lamp (75 kV), Czerny-Turner monochromators, two detectors (sample and internal reference), an R-928 photomultiplier tube which is red-sensitive (even 900 nm) with manual or automatic voltage controlled using the Cary-Eclipse software for Windows 95/98/NT system. Instrument excitation and emission slits were set at 10 and 20 nm, respectively, and the scan rate of the monochromators was 120 nm min^{-1}.

Two four-channel Gilson Miniplus-3 peristaltic pumps with rate selector were used to generate the flow stream and