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Automated in-chip kinetic-catalytic method for molybdenum determination

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ABSTRACT

In this work, the automation of a catalytic spectrophotometric method for the determination of molybdenum is presented. For this purpose, a multisyringe flow injection system was coupled to an integrated microconduit that we have called "chip". Reagents and sample were simultaneously dispensed to the chip where complete mixing, heating, and measurement were carried out. The spectrophotometric method is based on the oxidation of 4-amino-3-hydroxy-naphthalenesulphonic acid (AHNA) by hydrogen peroxide catalyzed by Mo (VI). Absorbance of the reaction product was measured at 465 nm. Two optical fibers were used to conduct the light, one from the source to the chip, and the other from the output of the cell to the spectrophotometer. The detection cell was incorporated in the thermostated zone of the chip. The initial rate method, at controlled temperature, was employed to determine the Mo (VI) concentration. The estimated precision was 3.7%, with the working range of 4.0–40 μg L^{-1} of Mo (VI), and the limit of detection of 1.2 μg L^{-1} of Mo (VI). The system was successfully applied to water samples and pharmaceutical products with a sampling throughput of 20 injections h^{-1}.

1. Introduction

Molybdenum (VI) is an essential trace element for plants and animals, including humans. In plants, this element is necessary to fix atmospheric nitrogen by bacteria to begin the protein synthesis. In animals, it is a component of xanthine oxidase and other redox enzymes. Molybdenum is also widely used in a variety of industrial processes such as metal alloys, pigments, lubricants and catalysts [1–3]. However, at high concentration molybdenum can be toxic to humans, plants and animals [2,4]. Most natural waters contain low levels of molybdenum in the range of <2–3 μg L^{-1}, unless local anthropogenic sources have contaminated the waters [5]. The concentration of molybdenum in seawater is reported in the range of 6–20 μg L^{-1} [3,6–8], and in mineral waters in the range of 0.25–1.0 μg L^{-1} [9]. The U.S. EPA drinking water health advisories recommended long term limits of 10 μg L^{-1} for children and 50 μg L^{-1} for adults in daily drinking water, and the United Nations Food and Agriculture Organization recommends a maximum level for irrigation water of 10 μg L^{-1} [10,11]. Therefore, the development of a rapid, selective and sensitive method for determination of molybdenum is required.

There are a number of sensitive techniques for molybdenum determination in the μg L^{-1} range, such as spectrofluorimetry [12], voltammetry [13], inductively coupled plasma–mass spectrometry (ICP–MS) [5,14], inductively coupled plasma–atomic emission spectrometry (ICP–AES) [15,16], cloud point extraction and quantification by isotope dilution inductively coupled plasma mass spectrometry (CP/ICP-MS) [17] and electrothermal atomic absorption spectrometry (ETAAS) [9,18]. However, the need for pre-concentration and/or separation and the relatively high instrumental costs are disadvantages. Catalytic spectrophotometric methods offer low cost, simple and sensitive alternatives for the determination of trace levels of Mo (VI) [1,2,19–21].

There are some works using the initial rate method for catalytic determinations. Advantages of these methods are its wide working range, i.e. two or three orders of magnitude, and also its high sampling throughput [22,23]. However this method requires a strict control of the experimental conditions such as the mixture temperature in the detection cell and the measurement time. For that reason it is convenient to use automatic methods such as flow techniques to guaranty the reproducibility of the determination.

Flow techniques have some unique advantages, such as they do not require reaction to reach the equilibrium, and the use of very

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small sample and reagent volumes (μL). They also provide sample throughput, low carry over, high degree of flexibility, and ease of automation. We have selected Multisyringe Flow Injection Analysis (MSFIA) as the flow-based technique since it includes the advantages of Flow Injection Analysis (FIA), in terms of mixing of flowing solutions, and of Sequential Injection Analysis (SIA) in relation to its robustness and versatility [24]. MSFIA is a low cost technique, which employs up to four syringes working in parallel as the liquid pumps. In this way, MSFIA overcomes some drawbacks of the peristaltic pumps, eliminates the presence of pulses, the needs of often recalibrations, and the corrosion effect of aggressive reagents and solvents. Moreover, MSFIA is computer controlled, and is therefore very well adapted for the stopped-flow technique. This technique also offers a reliable flow rate, unaffected by neither the flow resistance, nor sample viscosity. Therefore, MSFIA is a very appropriate technique for the kinetics method with homogeneous and highly reproducible mixing of the solutions, a critical requirement for this kind of determinations [25].

This work presents a multisyringe flow injection system coupled to a monolithic flow conduit, called Chip, for the automation of a catalytic spectrophotometric method. This chip was made of poly(methylmethacrylate) (PMMA). It integrated different steps of the analytical procedure such as: the confluent point, the mixing coil, the detection cell, all these on the thermostated chamber to control the temperature during the measurement step. This new device allowed the application of initial rate determination method at controlled temperature for the determination of molybdenum in waters and pharmaceutical samples.

2. Experimental

2.1. Reagents and standards

All chemicals were of analytical reagent grade. MilliQ water (Milli-Q plus, 18.2 MΩ cm^{-1}) was employed for standard and reagent preparations. 1000 mg L^{-1} Mo (VI) stock standard solution was prepared by dissolving 1841 mg of ammonium heptamolybdate tetrahydrate ($Mo_7O_{24}(NH_4)_6 \cdot 4H_2O$) (Scharlau, Spain) [26]. Working molybdenum standard solutions were prepared daily from their respective stocks. A 0.0168 mol L^{-1} 4-amino-3-hydroxy-naphthalenesulfonic acid (AHNA) (Sigma-Aldrich, USA) was prepared, by dissolving 804 mg AHNA, 804 mg of Na_2SO_3 (Fluka, Switzerland) and 102 mg of diethylenetriaminepentaacetic acid (DTPA) (Sigma-Aldrich, USA) in ca. 100 mL of water. The solution was then made up to 200 mL in a volumetric flask, and kept at room temperature [2,20]. The shelf life of the solution was 2 days. A 0.42 mol L^{-1} hydrogen peroxide (H_2O_2) solution was prepared daily from a concentrated (9.79 mol L^{-1}) (Scharlau, Spain) solution. A 0.48 mol L^{-1} acetate buffer was prepared using 6.82 mL of 17.60 mol L^{-1} of acetic acid (Sigma-Aldrich, USA), adjusting pH to 5.00 with NaOH (suprapure Sigma-Aldrich, USA), and making up to volume in a 250 mL volumetric flask.

2.2. Reagents for the interference study

A stock solution of 1000 mg L^{-1} Fe (II) was prepared by dissolving 1404 mg of ammonium iron (II) sulfate 6-hydrate (Panreac, Spain) in water and made up to 20.0 mL. A stock 1000 mg L^{-1} I^- was prepared by dissolving 262 mg of potassium iodide (KI) (Scharlau, Spain) in water and made up to 20.0 mL. A stock 1000 mg L^{-1} S^{2-} was prepared by dissolving 1498 mg of sodium sulfide ($Na_2S \cdot 9H_2O$) (ACROS Organics) in water and made up to 20.0 mL. Appropriate dilutions of these solutions were employed for the interference study. Appropriate dilution of Fe (III), Cr (VI), Mn (VII), and V (V) solutions were prepared from AAS grade of stock 1000 mg L^{-1} Fe (III), Cr (VI), Mn (VII), and V (V), respectively (Scharlau, Spain).

2.3. Sample collection and preparation

One tablet of Hydropolivit is equivalent to 100 μg of molybdenum (Hydropolivit 1.91 ± 0.02 g/tablet), whereas Multicentrum has 50 μg of molybdenum per tablet (Multicentrum 1.39 ± 0.01 g/tablet).

For each product, 10 tablets were powdered in a mortar. Then 285 mg of the Hydropolivit and 417 mg of Multicentrum powder were accurately weighed, and transferred into 100 mL Teflon digestion vessels. 10 mL of ultrapure concentrated HNO_3 (65%) (Scharlau, Spain) were added and the closed vessels, placed in a microwave oven (Milestone, START D) to digest the samples. The oven is equipped with a 2450 MHz microwave power supply of 0–1200 W output, a 6-position turntable and 100-mL Teflon liners with 355° rotatable pressure release valves, resistant up to 350 psi and 210 °C (microwave program included in supporting information Table A-1). The digested solutions were cooled to room temperature and then evaporated to reduce their volume to a small drop. Finally, the volume was adjusted to 100 mL with MilliQ water to obtain a 150 μg L^{-1} molybdenum solution. The pharmaceutical samples were filtered with 0.45 μm cellulose acetate membrane (Sartorious Stedium Biotech, Germany) before analysis. A demolition leachate wastewater and several seawater samples were collected from different area of Mallorca (Balearic Islands, Spain). The water samples were filtered through a 0.45 μm cellulose acetate membrane (Sartorious Stedium Biotech, Germany).

The ICP–AES technique was used as a reference method for the quantification of Mo (VI) in waters and pharmaceutical samples previously acidified with concentrated HNO_3 (65%) (Scharlau, Spain) to 2 %v/v. An ICP–AES (Optima 5300 DV, Perkin Elmer® Inc.) equipped with a Gem Tip Cross-flow pneumatic nebulizer (Waltham, MA, USA) was used under the following instrumental operating conditions: RF generator power 1300 W, frequency of RF generator 40 MHz, plasma argon flow 15 L min^{-1}, nebulizer argon flow 0.8 L min^{-1}, auxiliary argon flow 0.5 L min^{-1}, integration time 5 s and aspiration rate 1.5 mL min^{-1}. Wavelength for intensity measurements was 202.031 nm. All measurements were in triplicate.

2.4. Flow analyzer

The flow system is shown in Fig. 1. A multisyringe piston pump module (model Bu 4S) was purchased from Crison Instruments S.A. (Allela, Barcelona, Spain). The module was equipped with two 1 mL glass syringes (S3, and S4) and two 5 mL glass syringes of (S1, and S2). Solenoid valves (V1, V2, V3, and V4) allowed the connection of each syringe with either the chip (position ON, activated) or with the respective solution reservoir (position OFF, deactivated) for refilling. Solutions in the syringes were AHNA reagent in S1, Milli-Q water in S2, H_2O_2 reagent in S3, and acetate buffer in S4. Furthermore, two external three-way solenoid valves (V5, V6) from Takasago (STV-3 1/4UKG, Nagoya, Japan) were powered and controlled using an auxiliary supply port of the multisyringe module. V5 was used for sample introduction (position ON). In position OFF V5 was connected to V6, and its common position was connected to a holding coil of 255 cm length and 1.00 mm i.d. which was connected to S2. V6 was used for introduction of air (position ON) which allowed the removal of small bubbles remaining inside the chip. All tubes of the flow system were of PTFE of 0.8 mm i.d.

The chip was constructed from three PMMA pieces, 85 × 44 × 10 mm^3, similar to that previously reported by Abouhiat et.al. [25]. Threads of ¼ in. 28 fittings were drilled in the upper part to connect the supply tubings for reagents and sample/carrier as well for the output of the integrated detection flow cell. On its