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A novel on-line preconcentration method for trace molybdenum determination by USN–ICP OES with biosorption on immobilized yeasts

Raúl A. Gil [a,b], Sergio Pasini-Cabello [a], Andrés Takara [a], Patricia Smichowski [b,c], Roberto A. Olsina [a,b], Luis D. Martínez [a,b,*]

[a] *Área de Química Analítica, Departamento de Química, Facultad de Química Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco y Pedernera, San Luis, 5700, Argentina*
[b] *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina*
[c] *Comisión Nacional de Energía Atómica, Unidad de Actividad Química, Av. General Paz 1499, San Martín-Buenos Aires, B1650KNA, Argentina*

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Abstract

A new system for on-line preconcentration of molybdenum by sorption on a minicolumn associated to inductively coupled plasma — optical emission spectrometry with ultrasonic nebulization was studied. It is based on the sorption of molybdenum on a column packed with immobilized baker's yeasts on controlled pore glass without further complexing reagent. The molybdenum preconcentrated by biosorption was subsequently eluted with hydrochloric acid. Considering a sample flow rate of 5.0 mL min^{-1}, 10 mL of sample was preconcentrated in 2 min achieving a sensitive total enhancement factor of 480-fold, and the detection limit (3 s) obtained was 21 ng L^{-1}. Additionally, the calculated precisions expressed as percent relative standard deviation (RSD%) was 1.9%.

Satisfactory results were obtained for the determination of molybdenum in standard reference material NIST 1643e Trace Elements in Water and real water samples.

Keywords: On-line preconcentration; Immobilized baker's yeasts on CPG; FI–USN–ICP OES; Molybdenum; Water samples

1. Introduction

As early as 1953 [1] molybdenum was recognized to be an essential trace element for many species including man. It is a component of many enzymes responsible for the initial stages of nitrogen, carbon and sulphur metabolism of plants, animals and man [2,3]. There is an absolute dependence by plants on Mo as it plays a vital role in the earth nitrogen cycle where it is involved both in nitrate reduction and nitrogen fixation. Although molybdenum is essential for animals it shows evidence of toxicity at high levels [4,5]. Molybdenum intoxication depends on its speciation and is also influenced by the uptake of other elements such as S, W, Cu, Pb and Zn. It must be emphasized that studies of Mo roles in man or environment have often be hampered by the lack of sufficiently sensitive analytical methods for determining trace Mo levels. For this reason in many cases it is difficult to determine whether the symptoms attributed to Mo deficiency or excess are due to biological variations or simply to experimental error [6]. A better understanding of the role of Mo in human, plants or animal nutrition as well as in the environment depends on improving the sensitivity and accuracy of the analytical methods involved [7].

One of the major routes of incorporation of Mo is water. In this context, inductively coupled plasma mass spectrometry (ICP-MS) [8] has the analytical capability for the determination of Mo at trace and ultra-trace levels because of its high sensitivity, selectivity and sample throughput. However, the cost of the instrumentation is not affordable to many laboratories. Trace

* Corresponding author. Área de Química Analítica, Departamento de Química, Facultad de Química Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco y Pedernera, San Luis, 5700, Argentina. Fax: +54 2652 430224.
E-mail address: ldm@unsl.edu.ar (L.D. Martínez).

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Table 1
ICP and ultrasonic nebulizer instrumental parameters

ICP conditions	
RF generator power plasma	0.8 kW
Frequency of RF generator	40.68 MHz
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: Mo	202.030 nm
Ultrasonic nebulizer conditions	
Heater temperature	140 °C
Condenser temperature	4.0 °C
Carrier gas flow rate	1 L min^{-1}

molybdenum determination in water samples has been carried out by atomic absorption with electrothermal atomization (ETAAS) [9], atomic emission spectrometry with inductively coupled plasma (ICP OES) [10]. The concentration of molybdenum is too low to be directly determined with these technique in well water, tap water [11], seawater samples [12], etc. Preconcentration is an effective means for extending the detection limits of ICP OES technique. However, when practised manually in the batch mode, the operations are usually too tedious to be compatible with the ICP OES measurements.

Therefore, many preconcentration procedures for determination of molybdenum have been developed involving different analytical techniques. Preconcentration and determination of trace molybdenum had been developed by using different complexing agents in liquid–liquid extraction and several adsorbent materials for its on-line solid phase extraction (SPE) assisted by complexing reagents [10–16].

Metal preconcentration using living organisms, such as algae, fungi, bacteria, red cells, and yeasts [17–20], has been used as an attractive alternative to other adsorbent material for SPE because of its low cost, high accumulation capacity and the large variety of microorganisms available. One of the reasons why the adsorption ability of living organisms is higher than that of chemical adsorbents is due to the many functional groups available (amine, hydroxyl, carboxyl groups, phosphate, and sulfhydryl groups) to bind the metal without complexing reagents and the high apparent diffusion coefficients [21]. Yeast cells have been widely used because of its easy growth, non-hazardous nature, considerable tolerance towards metals and high cell-binding capacity. *Saccharomyces cerevisiae* is the specie of yeast most commonly used for metal accumulation [22–27].

In the present work, a method for on-line preconcentration and determination of inorganic Mo is proposed. Molybdenum has various oxidation states and ionic forms in aqueous solution. However, it exists in one oxidation state, Mo(VI), in well aerated water samples.

The coupling of flow injection (FI)-SPE and ICP OES with ultrasonic nebulization (USN) was used for Mo determination at trace levels. Molybdenum was retained by sorption on a conical minicolumn packed with immobilized yeast cells in the absence of complexing reagent. The pH adjustment of the solution suffices to retain Mo.

2. Experimental

2.1. Instrumentation

All measurements were performed with a sequential ICP spectrometer [Baird (Bedford, MA, USA) ICP2070]. The 1 m Czerny–Turner monochromator had a holographic grating with 1800 grooves mm^{-1}. A U-5000 AT ultrasonic nebulizer (CETAC Technologies, Omaha, NE, USA), involving a desolvation system, was used.

The ICP OES and NUS conditions are listed in Table 1. Minipuls 3 peristaltic pumps [Gilson (Villiers-Le-Bel, France)] were used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA), Model 50, four-way rotary valve. A conical minicolumn (40 mm length, 4.5 mm internal upper diameter and 1.5 mm internal lower diameter) was used as the *S. cerevisiae* holder. Pump tubes, Tygon type (Ismatec, Cole-Parmer Instrument Company, Niles. IL, USA), were employed to propel the sample, reagent and eluent. The FI system used is shown in Fig. 1. The 202.030 nm spectral line was used and FI

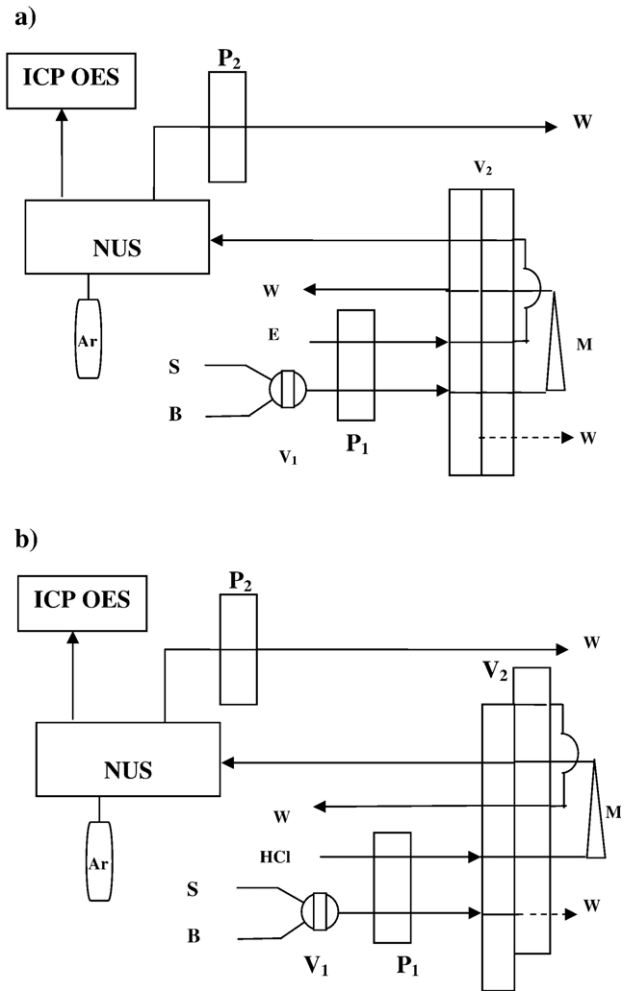

Fig. 1. Schematic diagram of the instrumental setup. B, conditioning line; S, sampling line; W, waste; V_1, two way rotary valve, V_2, load injection valve (a, load position; b, injection position); M, conical minicolumn; NUS, ultrasonic nebulizer, Ar, argon gas suplyeither for plasma and for NUS.