



# Multivariate optimization of a solid phase extraction system employing *L*-tyrosine immobilized on carbon nanotubes applied to molybdenum analysis by inductively coupled plasma optical emission spectrometry with ultrasound nebulization



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## ABSTRACT

A method for Mo solid phase extraction on *L*-tyrosine immobilized on carbon nanotubes (*L*-tyr-CNTs) is presented. *L*-tyr-CNTs were used to fill a minicolumn and introduced into a FI system employing inductively coupled plasma optical emission spectrometry with ultrasound nebulization (USN-ICP OES). Five FI parameters such as buffer flow rate (BFR) and concentration (BC); sample flow rate (SFR); eluent flow rate (EFR) and concentration (EC); and pH were chosen for optimization employing a half fraction composite design (HFFD). Multivariate optimization through central composite design (CCD) allowed establishing the statistical ideal parameter values to reach maximum Mo signal. From HFFD and CCD it was established that SFR was not affecting the system significantly and that the optimal experimental conditions were: pH, 4.0; BC, 5 mM ammonium acetate; EC, 15% ( $v v^{-1}$ ) and EFR, 2 mL  $min^{-1}$ . Under these conditions an enhancement factor of 750-fold (25 for preconcentration system and 30 for USN) was obtained reaching a detection limit of 40 ng  $L^{-1}$  with a precision of 1.32%. The system was successfully applied to a certified reference material NIST CRM 1643e (trace elements in water) and river, thermal, mine and tap water samples.

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## 1. Introduction

The transition element molybdenum is an essential micronutrient for microorganisms, plants, and animals and is one of the ten biologically active elements [1]. Molybdenum (Mo) is the only second-row transition metal with biological activity. Among the existing compounds of Mo in nature, oxyanion molybdate ( $MoO_4^{2-}$ ) is the predominant form in solution at pH higher than 4.2, and therefore cells take up Mo from the external medium in the form of molybdate [2].

Mo is present in low and diverse amounts in continental (5 nmol  $L^{-1}$ ) and marine (100 nmol  $L^{-1}$ ) waters, and in soils (1.1 mg  $kg^{-1}$ ) [3–5]. In biological tissues, Mo is one of the scarcest elements. In human serum, molybdenum concentration lower than 1  $\mu g L^{-1}$  was reported [6], while mean concentration in urine was 42.5  $\mu g L^{-1}$  [7]. In contrast, many elements that are present in considerably larger amounts have no apparent biological function (e.g., Al, Ti, or Zr) [8]. These low Mo concentrations in environmental and biological samples, along with the high concentration of interfering matrix components, require sensitive instrumentation to reach its determination.

In this sense ICP OES has been applied to molybdenum determination [9]. Despite the fact that it has been used by a good number of researchers, it does not possess the necessary sensitivity for trace and ultra-trace analysis, and the use of a separation–preconcentration procedure is inevitable [10]. Spectral interferences in Mo determination by ICP-OES have been reported. Baucells et al. [11] reported the spectral interference of aluminium and magnesium and Dos Santos et al. [12] noted the spectral interference of aluminium, magnesium, and iron in Mo determination. For all the aforementioned considerations, determination of trace amounts of Mo using ICP-OES is almost always preceded by a previous pre-concentration step, using separation techniques [13].

Among the methods reported for preconcentration and matrix separation of molybdenum, sorbent extraction has proved to be especially effective [14]. Nowadays, carbon nanotubes (CNTs) have been proposed as a novel solid phase extractant for metal ions [15]. The hexagonal arrays of carbon atoms in graphite sheets of CNTs' surface are ideal for strong interactions with other molecules. The large surface areas of CNTs make them a promising solid sorbent for preconcentration procedures. In addition a proper surface treatment of CNTs can improve metal sorption and selectivity in SPE [16]. In this context different amino acids have been immobilized on CNTs for metal retention like *L*-tyrosine [17, 18].

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The introduction of on-line systems to solid phase extraction (SPE) systems provides the possibility of automation which increases precision and accuracy [19]. However an on-line system requires optimization of several variables leading to a tedious and time consuming work. As an alternative, multivariate techniques have been introduced for analytical method optimization [20]. These techniques allow several variables to be optimized simultaneously representing several advantages, such as speed of analysis, practicality, economy, and reduction in the number of experiments that need to be carried out [21]. In addition, these methods are able to generate mathematical models that estimate the relevance as well as statistical significance of the factors' effects on the processes and also evaluate the interactions' effects among the factors. Factorial design is one of the mathematical models for multivariate optimization and is widely applied in chemistry. In order to determine the real functionality established among the analytical response and the significant factors, second order designs eventually are also necessary.

The present research introduces *L*-tyr immobilized on carbon nanotubes (*L*-tyr-CNTs) as an alternative for Mo retention and preconcentration. To this end *L*-tyr-CNTs were packed in a minicolumn and introduced into an FI system employing USN-ICP OES as detection system. A two-level fractional factorial design was used to evaluate the experimental variables including buffer flow rate and concentration; sample flow rate; acid flow rate and concentration; and pH. The experiments for the final system optimization were performed according to the central composite response surface experimental design. The system was successfully applied to Mo determination in QC-LL2 standard reference material (metals in natural water) and different water samples.

## 2. Experimental

### 2.1. Instrumentation

Measurements were performed with a sequential ICP spectrometer Baird ICP 2070 (Bedford, MA, USA). The 1 m Czerny–Turner monochromator had a holographic grating with 1800 grooves  $\text{mm}^{-1}$ . The FI system used is shown in Fig. 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. A Minipulse 3 peristaltic pump Gilson (Villiers-Le-Bell, France) was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way and of 6 ports, 2 positions, rotary valves. The conical minicolumn was prepared by placing 25 mg of *L*-tyr-CNTs into an empty conical tip using the dry packing method. To avoid loss of filling when the sample solution passed through the conical

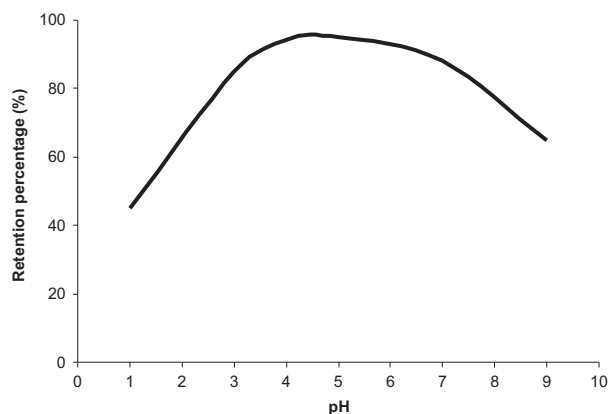


Fig. 1. Dependence of Mo retention on pH of loading solutions. Volume of sample: 10 mL; Mo (VI) concentration: 1  $\text{mg L}^{-1}$ ; eluent concentration: 10.0% (v/v).

Table 1  
ICP and ultrasonic nebulizer instrumental parameters.

<i>ICP conditions</i>	
RF generator power plasma	0.8 kW
Frequency of RF generator	40.68 MHz
Gas flow rate	8.5 $\text{L min}^{-1}$
Auxiliary gas flow rate	1 $\text{L min}^{-1}$
Observation height-above load coil.	15 mm
Analytical line	Mo 202.030 nm
<i>Ultrasonic nebulizer conditions</i>	
Heater temperature	140 °C
Condenser temperature	4.0 °C
Carrier gas flow rate	1 $\text{L min}^{-1}$

minicolumn, a small amount of quartz wool was placed at both ends of conical minicolumn. The column was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system. Tygon type pump tubing (Ismatec, Cole Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagents and eluent. The Mo 202.030 nm spectral line was used.

### 2.2. Reagents

Unless otherwise stated, the chemicals used were of analytical grade, and therefore no further purification was required. A molybdenum stock solution ( $1000 \text{ mg L}^{-1}$ ) was prepared by dissolving 920.3 mg  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in water and the volume was filled up to 500 mL with water and a few drops of concentrated nitric acid (Fluka). Commercial multiwall CNTs were obtained from Sunnano (Jiangxi, China). *L*-Tyrosine was obtained from MP Biomedicals Inc. (Chicago, IL, USA).

### 2.3. Sample collection

Mine water samples were obtained from La Carolina (San Luis, Argentina) abandoned mine. River water samples were obtained from Conlara River (San Luis, Argentina) and Quinto River (San Luis–Córdoba, Argentina). Thermal water samples were obtained from San Gerónimo (San Luis, Argentina) pools. Tap water samples were obtained directly from San Luis City (Argentina) water system. Immediately after collection, samples were filtered through 0.45  $\mu\text{m}$  pore size membrane filters, acidified with nitric acid, and stored at 4 °C in Nalgene bottles.

The method accuracy was checked by applying it to Mo determination in the standard reference material NIST CRM 1643e (Trace Elements in Water).

### 2.4. Immobilization procedure

About 50 mg of commercial multiwall CNTs were treated with concentrated  $\text{HNO}_3$  to clean them and eliminate possible Mo residues present in CNTs since metallic impurities are inherently present in CNT samples because CNTs are typically synthesized by using metallic (typically Fe, Ni, Co, Mo) catalyst nanoparticles [22]. This procedure also allowed the generation of –COOH and –OH groups on CNTs' surface, improving their solubility [23]. After this, CNTs were centrifuged, filtrated and dried.

The resultant powder was suspended in phosphate buffer pH 7.0 and an aliquot of 50 mg of the amino acid (*L*-tyr) was added to the buffer solution. After this, the solution was heated for 48 h at 45 °C. Finally, it was filtered, and CNTs were dried at room temperature.

### 2.5. Procedure

The flow injection system used for preconcentration, separation and subsequent determination of Mo has been reported before [24,25]. Before loading, the column was conditioned for preconcentration at the

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