



# Development of a new aerosol phase extraction method for metal determination through inductively coupled plasma atomic emission spectrometry

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## ABSTRACT

In this work, a new extraction method termed aerosol phase extraction has been developed for the first time. The new method was based on the nebulisation of the sample onto the extracting solution to maximize the contact surface. The influential parameters are: agitation time, chelating agent concentration and inorganic acid concentration. The method has been applied to the extraction of molybdenum with organophosphorus chelating agents such as tributyl phosphate (TBP) and bis(2-Ethylhexyl) phosphoric acid (D2EHPA) dissolved in *n*-hexane from aqueous hydrochloric and phosphoric acid solutions. In order to test the efficiency of the method, the aqueous phase has been analyzed by means of Inductively Coupled Plasma Atomic Emission Spectrometry. The extraction of molybdenum under aerosol phase was found to be faster than the conventional extraction method. Equilibrium time was shortened under aerosol phase extraction and molybdenum extraction yields were comparable, or better as compared to the conventional method.

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## 1. Introduction

The solvent extraction is one of the most versatile and widely used procedures for the removal, separation and concentration of various metals [1,2]. In classical liquid–liquid extraction, small droplets are generated by agitation, which increases the contact surface area and improves the extraction efficiency. However, the classical procedure has not proved to be effective enough in some cases and presents some disadvantages (e.g. laborious manipulation, large volumes of solvents, high operation costs, possible formation of emulsions, large equipments and long analysis time, it is often time-consuming and equilibrium cannot be attained after shaking for a long time).

In the last few years, research activities are oriented towards the development of more efficient, economical, and miniaturized sample preparation methods in order to increase the extraction yields obtained under conventional solvent extraction. The advantages of miniaturization are the reduction of the sample size. In addition, transport phenomena are faster in microsystems than in ordinary systems, and therefore, one may expect that liquid extraction takes less time to be achieved in miniaturized

devices. This feature was demonstrated recently with many configurations [2,3].

One of the means for increasing the extraction efficiency is to disperse the extracting solvent into the liquid sample. For example, Rezaee et al. [4] developed a dispersive liquid–liquid microextraction (DLLME) method which is a miniaturized green sample preparation method. In their method a dispersing agent (acetone) was added to the extracting one (carbon tetrachloride) to extract organic compounds in water. A cloudy solution was then formed. Then this solution was centrifuged and the two phases were separated.

Molybdenum acidified aqueous solutions were chosen as the model metallic cation and organophosphorous extractants, such as tributyl phosphate (TBP) and bis(2-Ethylhexyl) phosphoric acid (D2EHPA) were employed to extract this element. This choice was based on the fact that molybdenum is considered as a bio-essential trace nutrition element for both plants and animals, including humans where it plays an important role [5–7]. Very low concentrations of molybdenum can be found in plants, natural water and seawater, and other aqueous matrices. For example, the assay of molybdenum in seawater is very important, since this metal is part of biochemical phenomena in most marine flora and fauna. Under normal conditions the reported concentrations are included within the 6–20  $\mu\text{g L}^{-1}$  range [2,3]. The complexity of the sample matrix makes advisable the development of

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methodologies capable to separate the Mo from possible matrix interferences prior to the analysis by Inductively Coupled Plasma (ICP) techniques, which are the most commonly used for trace elemental determinations (minimization of matrix effects by dilution is not recommended because it would compromise the detection capability). On the other hand, this metal is commercially important and widely used in a variety of industrial processes, e.g. alloying agent in steels and cast iron; high-temperature alloys; tool steels; pigments for printing inks, paints, and ceramics; catalyst; solid lubricants; missile and aircraft parts; reactor vessels; cermet; die-casting copper base alloys and special batteries [8–11]. Therefore, the extraction and purification processes of molybdenum are important.

The goal of the present paper was thus to evaluate the suitability of a new method for liquid–liquid extraction based on the trapping of an aerosol, previously generated from the extracting solution, into the aqueous sample. The aerosol was generated by means of a pneumatic nebulizer in which the droplets were produced through the interaction between the solvent and a high velocity gas stream. The nebulizer was placed close to the sample surface. Therefore, the resulting emulsion agitation was assisted by the nebulizer gas stream, hence favoring the metal extraction. To the best of our knowledge none of the liquid–liquid extraction methods existing so far are based on the collection of an aerosol on the sample solution.

## 2. Experimental

### 2.1. Reagents and solutions

Two organophosphorus extractants were employed: tributyl phosphate (TBP) and bis(2-ethylhexyl) phosphoric acid (D2EHPA). TBP 97% (w/w) had a 193 °C boiling point whereas for D2EHPA 97% (w/w) this physical property was 130 °C and were from Aldrich (Barcelona, Spain). Additional reagents were ammonium molybdate 4-hydrate ( $\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6 \cdot 4\text{H}_2\text{O}$ ), 37% (w/w) hydrochloric acid (HCl), 85% (w/w) phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and *n*-hexane ( $\text{C}_6\text{H}_{14}$ ). Reagent grade were purchased from Panreac (Barcelona, Spain).

Molybdenum (VI) stock solution (1000 mg/L) was prepared by dissolving 0.1856 g of ammonium molybdate 4-hydrate (purity 99%) in deionized water. Working solutions were prepared daily by suitable dilution of the master standard stock solution with deionized water and the addition of a given volume of either 37% (w/w) HCl or 85% (w/w)  $\text{H}_3\text{PO}_4$ . The initial concentration of molybdenum in the aqueous solutions was 100 mg/L (nearly  $10^{-3}$  mol/L) for all the experiments. The organic solutions were prepared by dissolving and diluting either TBP or D2EHPA at a definite concentration in *n*-hexane.

### 2.2. Analytical technique

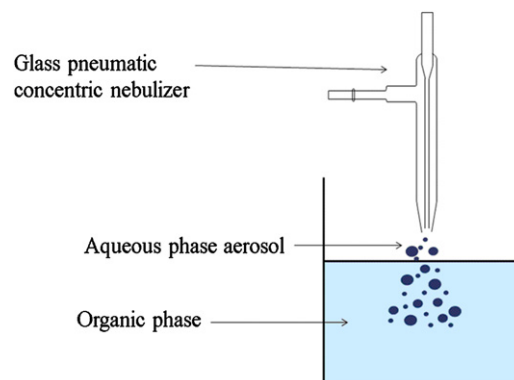
Molybdenum concentrations in the aqueous phase solutions were analyzed by a model Optima 4300 DV Perkin Elmer inductive coupled plasma atomic spectrometry (ICP-AES) (Uberlingen, Germany) at a wavelength of 202.031 nm. The experimental conditions of the ICP-AES system are summarized in Table 1.

### 2.3. Conventional extraction procedure

Conventional liquid–liquid extraction was performed by shaking thoroughly a mixture consisting of equal volumes (i.e., 10 mL) of aqueous and organic phase solutions ( $V_{aq}/V_{org}=1$ ) in 125-mL separating funnels for a specified time defined as agitation time of

**Table 1**  
ICP-AES operating conditions.

RF power/kW	1.45
Integration time/ms	100
Liquid flow rate (mL/min)	0.05
Outer gas flow rate (L/min)	15
Intermediate gas flow rate (L/min)	0.5
Central gas flow rate (L/min)	0.7
Viewing height above load coil/mm	5
Injector tube inner diameter/mm	2



**Fig. 1.** Scheme of the experimental setup employed in the present work.

the two phases during (30–1800 s) for experiments conducted with D2EHPA and during (20–900 s) for those conducted with TBP at a constant temperature. During a specified agitation time portions of molybdenum were extracted from aqueous to organic phase. The two phases were stirred with a mechanical shaker (Promax 1020, Heidolph Instruments, Schwabach, Germany) at 8.5–9 rpm stirring speed. This speed ensured a perfect agitation of the mixture. Then the separating funnels were allowed to stay for 10 min and the aqueous and organic phases were separated. Aqueous phases were stocked for their further analysis.

### 2.4. Aerosol phase extraction

A new extraction procedure termed “aerosol phase extraction” was developed. The experimental set-up is shown in Fig. 1. In this method the required volume of both aqueous and organic phase was lower than that commonly needed in classical methods. First, 0.5 mL of the organic solution were poured into the extraction vessel (Fig. 1). Then the aqueous solution containing molybdenum was delivered at a 1 mL/min liquid flow rate to a glass pneumatic concentric nebulizer (Meinhard Glass Products, Santa Ana, CA) through a peristaltic pump (Perimax, Spetec, Erding, Germany). As Fig. 1 reveals, the nebulizer tip was located about 5 mm above the organic solution surface. An aerosol was therefore generated at the nebulizer tip as a result of the interaction of the liquid stream with the gas one. The gas backpressure was set at 0.5 bar, what corresponded to a 0.3 L/min flow rate. The generated droplets were thus directed towards the organic phase. In this way the metal extraction occurred at the interface of each generated droplet, thus giving rise to a larger contact surface.

Once the solutions were separated, the molybdenum concentration in the aqueous phase was determined through ICP-AES. These concentrations values were used to compute the extraction percentage values,  $E(\%)$ , according to the following mathematical relationship:

$$E(\%) = \left( \frac{[\text{Mo(VI)}]_{\text{initial}} - [\text{Mo(VI)}]_{\text{final}}}{[\text{Mo(VI)}]_{\text{initial}}} \right) \times 100 \quad (1)$$

where the subscript “initial” denotes the initial molybdenum concentration in aqueous phase. The subscript “final” denotes the molybdenum concentration in aqueous phase at equilibrium.

All the experiments and measurements were carried out at room temperature (*i.e.*, 26–28 °C). Three extraction ( $n=3$ ) and five measurements replicates were performed for all the evaluated conditions. In all the cases good precisions were achieved, the RSD being lower than 3%.

Volume drop size distribution was measured for the aerosols generated by the nebulizers (*i.e.*, primary aerosols). This was done by means of a laser Fraunhofer diffraction system (model 2600c, Malvern Instruments, Malvern Worcestershire, UK). The sizer was equipped with a 63 mm lens focal length which enabled the system to measure droplets with diameters included within the 1.2 to 118  $\mu\text{m}$  range. The nebulizer tip was placed at 30 mm from the lens and at 2 mm from the laser beam center.

### 3. Results and discussion

#### 3.1. Kinetics of molybdenum extraction

The primary studies on kinetics involved some batch preliminary experiments which were carried out in order to study the role of agitation time on the extraction of molybdenum with TBP from a 5 M HCl aqueous solution and with D2EHPA from a 0.30 M  $\text{H}_3\text{PO}_4$  solution.

##### 3.1.1. Extraction of molybdenum with TBP

Fig. 2 shows the variation of the extraction efficiency ( $E$ , %) with agitation time for the two studied methods. For the classical method, it was found that as the agitation time increased from 20 to 180 s, the efficiency went up from about 57 to 100%. Beyond 180 s, there was no significant increase in molybdenum extraction. Therefore, it was assumed that 180 s agitation time was sufficient to reach a practical equilibrium state. This time was suitable for the quantitative extraction of molybdenum.

For a given agitation time, the extraction percentages of molybdenum were substantially enhanced under aerosol phase extraction (Fig. 2). As the agitation time increased from 5 to 30 s, the extraction percentage went from 92 to 100%. The extraction was very fast and the equilibrium was reached only within the

first 30 s. Comparatively speaking, the equilibrium time was about 6 times shorter when the aerosol based method was employed as compared to the conventional one. The comparison of extraction percentages (Fig. 2) with the two methods showed, that for a 30 s agitation time (the equilibrium time under aerosol phase extraction) the percentage of molybdenum mass extracted was about 40% higher for the aerosol than the conventional methodology.

##### 3.1.2. Extraction of molybdenum with D2EHPA

The effect of agitation time on the extraction of molybdenum from 0.30 M  $\text{H}_3\text{PO}_4$  solution with 0.10 M D2EHPA in *n*-hexane was also investigated. Fig. 3 shows that for the conventional method, the longer the agitation time, the higher the mass of molybdenum extracted. This trend was found up to 900 s (equilibration time corresponding to an extraction of 88%). A further increase in agitation time had no significant change on the extraction of molybdenum.

When the aerosol based method was employed (Fig. 3) the extraction process was accelerated. In this case the equilibrium (87% of molybdenum extracted) was afforded after agitating for 180 s (5 times shorter time than for the conventional method). Extraction percentages were substantially higher under aerosol phase extraction over the whole range of agitation time investigated (5–900 s). For example at 180 s agitation time, the recovery was three times higher for the former methodology than that for the latter one.

The improvement of the molybdenum extraction efficiency for a given agitation time incorporated by the aerosol based method with respect to the conventional one could be attributed to the different aqueous–organic interfacial area. Since aerosol phase extraction is based on the extraction from the aqueous sample after its breakage in small droplets the mass transfer coefficient increases as a result of the high specific interfacial area. Thus, for example, for the aqueous solution, the aerosol generated by the nebulizer had a measured liquid surface of 2.4  $\text{m}^2/\text{cm}^3$ . This was possible, because droplets with diameters below 15  $\mu\text{m}$  were produced. Meanwhile, in conventional extraction the interfacial area is much lower hence making the extraction to be less efficient.

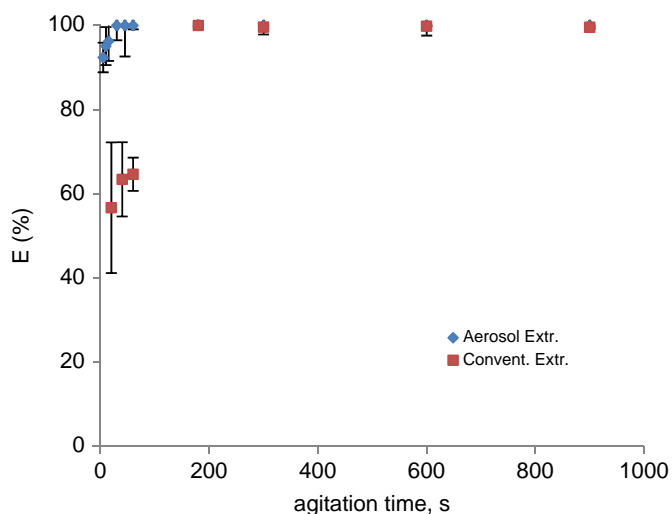


Fig. 2. Effect of agitation time on molybdenum extraction under aerosol phase extraction and conventional extraction.  $C_{\text{Mo(initial)}}=100$  mg/L,  $[\text{HCl}]=5$  M,  $\phi=40\%$  v/v TBP,  $V_{\text{aq}}/V_{\text{org}}=1$ .

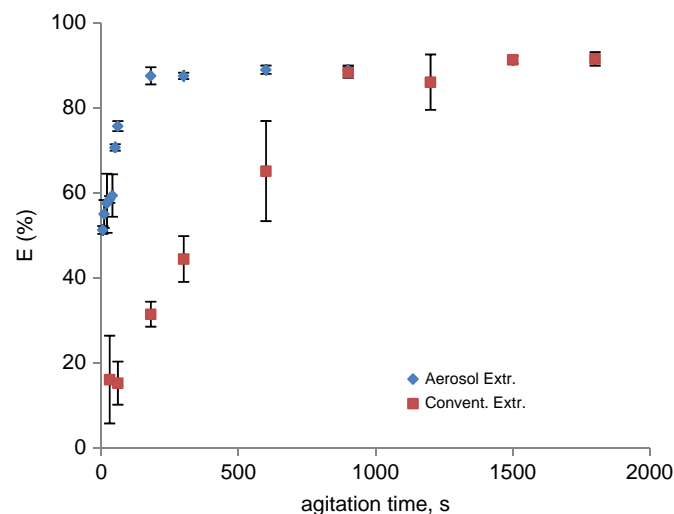


Fig. 3. Effect of agitation time on molybdenum extraction under aerosol phase extraction and conventional extraction.  $C_{\text{Mo(initial)}}=100$  mg/L,  $[\text{H}_3\text{PO}_4]=0.30$  M,  $[\text{D2EHPA}]=0.10$  M,  $V_{\text{aq}}/V_{\text{org}}=1$ .

### 3.2. Effects of D2EHPA and TBP concentrations

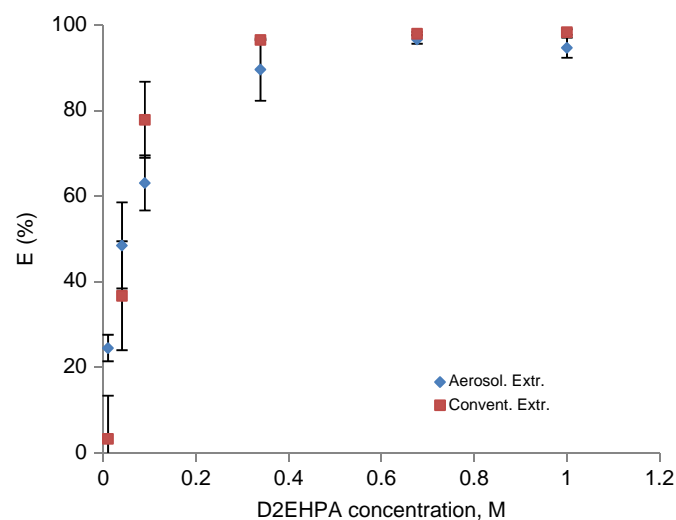
The influence of TBP and D2EHPA concentrations on the extraction efficiency of molybdenum present in aqueous acidic solutions was investigated under conventional extraction and aerosol phase extraction. Agitation times of the aqueous and organic phases were 10 and 15 min for experiments conducted with TBP and D2EHPA as extracting agents, respectively. The ratio of aqueous to organic phase volume was kept at 1.

The percentage extraction of molybdenum when using D2EHPA solutions in *n*-hexane containing varying molar concentrations (0.01–1 M) is shown in Fig. 4 for the two methods investigated. For the conventional method, molybdenum extraction percentage increased strongly from 3 to 97% when the concentration of D2EHPA increased from 0.01 to 0.34 mol/L. A further increase in the D2EHPA concentration to 1 M did not have a significant effect. The extraction percentage attained a mean stable value of 98% for concentrations of D2EHPA between 0.34 and 1.00 M. Therefore the optimum concentration of D2EHPA chosen was 0.34 M.

It was observed, that under aerosol phase extraction, the extraction percentage of molybdenum increased considerably from 24 to 97% with increase in D2EHPA concentration from 0.01 to 0.68 M. A mean extraction percentage value of 96% was obtained for the D2EHPA concentrations in the range 0.68–1 M.

The aerosol phase extraction was especially interesting at low extracting agent concentrations. Extraction percentages were found to be higher in the 0.01–0.04 M D2EHPA concentration range. Under these circumstances, the extraction yield was up to 7 times higher for the aerosol method than for the conventional one. Nonetheless, this parameter was lower for the former method in the 0.08–0.34 M D2EHPA concentration range.

Molybdenum was also extracted from 5 M HCl solution with different TBP concentration varying in the range 10–40% (v/v) in *n*-hexane. The results indicated that TBP concentration did not significantly affect molybdenum extraction percentages compared with other experimental parameters. In the examined conditions the extraction percentages kept in a very high constant extraction percentage nearly 99% under both conventional and aerosol phase extraction.

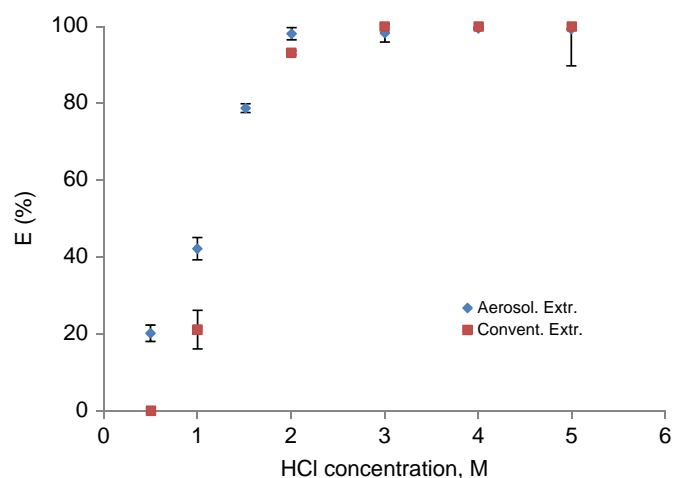


**Fig. 4.** Effect of D2EHPA concentration on molybdenum extraction under aerosol phase extraction and conventional extraction.  $C_{Mo(initial)} = 100$  mg/L,  $[H_3PO_4] = 0.30$  M,  $V_{aq}/V_{org} = 1$ , agitation time = 15 min.

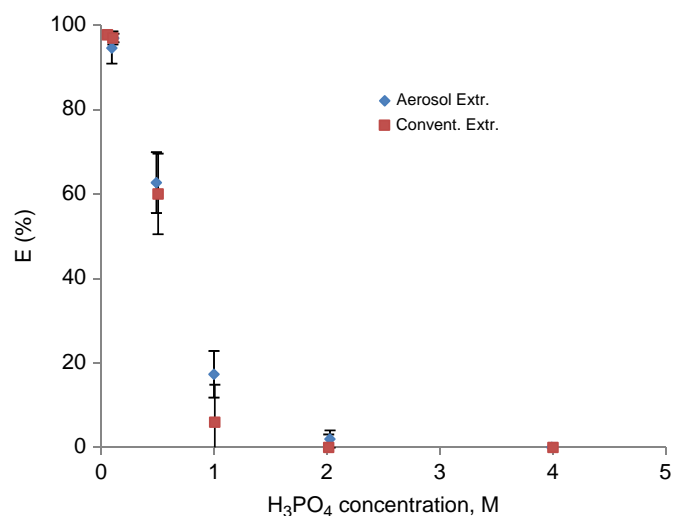
### 3.3. Effect of acid concentration

The extraction profiles for molybdenum from HCl solutions with TBP or from  $H_3PO_4$  solutions with D2EHPA are shown in Figs. 5 and 6, respectively. These data indicated that both reagents had a substantial effect on molybdenum extraction. The effect of HCl concentration on the extraction of molybdenum with 40% (v/v) TBP was studied in the range 0.5–5 M. It was observed that percentage extraction increased rapidly with increase of acid concentration in aqueous phase up to 3 M. After that, a plateau was reached. Under these conditions, the extraction of molybdenum was complete (i.e.,  $E \cong 100\%$ ). Higher extraction percentages were found under aerosol extraction than under conventional extraction particularly in the range 0–1 M HCl concentration.

As regards phosphoric acid, quantitative extraction (98%) was observed at 0.055 M acid concentration and with increase in acidity the extraction rapidly dropped down to 6% (for conventional method) and 17% (for aerosol based method) at 1 M acid concentration (Fig. 6). With further increase in  $H_3PO_4$  concentration the percentage of molybdenum extraction decreased slowly and was 0% beyond 2 M.



**Fig. 5.** Effect of HCl concentration on molybdenum extraction under aerosol phase extraction and conventional extraction.  $C_{Mo(initial)} = 100$  mg/L,  $\phi = 40\%$  v/v TBP,  $V_{aq}/V_{org} = 1$ , agitation time = 10 min.



**Fig. 6.** Effect of  $H_3PO_4$  concentration on molybdenum extraction under aerosol phase extraction and conventional extraction.  $C_{Mo(initial)} = 100$  mg/L,  $[D2EHPA] = 0.10$  M,  $V_{aq}/V_{org} = 1$ , agitation time = 15 min.

### 3.4. Analytical figures of merit

A given volume of extracting solution (*i.e.*, 1 mL) was taken and 10 mL of an aqueous standard was nebulized over this solution. The obtained sensitivity was 12 times higher than that observed for the aqueous standard. The obtained sensitivity was higher than the preconcentration factor (*i.e.*, 10) because of the effect of the organic solvent over the sensitivity. It has been widely indicated that the presence of an organic solvent leads to the generation of finer aerosols than those found for water. Furthermore, the extracting solution volatility is higher than that for water. Both facts lead to high ICP-AES sensitivities. However, in order to prevent plasma degradations problems caused by an excessively high solvent plasma load, a rather high RF power value must be employed (see Table 1). With the same aim, the nebulizer liquid flow rate was decreased down to 0.05 mL/min. Under these circumstances, the obtained limit of detection calculated according to the  $3s_b$  criterion, where  $s_b$  was the standard deviation of twenty consecutive blank measurements, was 2 µg/L. This value allowed to carry out molybdenum determination in a wide range of samples. Note that this LOD compared favorably against the value obtained in plain water solutions (15 µg/L).

Precision was determined by performing five consecutive extractions for various molybdenum concentrations. The obtained signal RSD was 3%.

### 3.5. Sea water analysis

The aerosol extraction methodology was applied to the analysis of two different spiked sea water samples. The advantages of the used methodology were: the analyte (Mo) and the complicated salty matrix were quantitatively separated thus avoiding matrix effects; and Mo was preconcentrated. The two samples were spiked with a 10 µg/L Mo concentration. Then 10 mL of sample were nebulized over 1 mL of extracting solution. The results indicated that the recovery was 98% with a 3% RSD (five replicates).

## 4. Conclusion

The solvent extraction study of molybdenum has been carried out from hydrochloric acidic (HCl) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>)

solutions using TBP and D2EHPA as extractants and *n*-hexane as diluting agent. The experimental results show that extraction time, hydrochloric and phosphoric acid concentrations have significant effect on the molybdenum extraction yields. The results reported in this paper show that the molybdenum-TBP extraction system reaches equilibrium faster than the system molybdenum-D2EHPA and that the extraction efficiency of molybdenum is dependent upon the acid concentration of the aqueous phase and upon the D2EHPA concentration. However, when varying TBP concentration the extraction percentages were nearly 99% under both conventional and aerosol phase extraction. Under optimal conditions, the extraction percentage of molybdenum in the organic phase was found to be more than 99%. The use of the new extraction technique termed aerosol phase extraction reduced significantly the time required for the quantitative extraction of molybdenum and increased the molybdenum extraction yields at short times and low concentrations of reagents.

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