Application of Doehlert matrix and factorial designs in optimization of experimental variables associated with preconcentration and determination of molybdenum in sea-water by inductively coupled plasma optical emission spectrometry

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A simple and efficient procedure for the preconcentration and determination of molybdenum in sea-water was developed using solid-phase extraction (SPE) of molybdenum(v) ion as the thiocyanate complex by polyurethane foam and inductively coupled plasma optical emission spectrometry (ICP-OES). The optimization process was carried out using two-level full factorial and Doehlert matrix designs. Four variables (solution volume, shaking time, thiocyanate concentration and hydrochloric acid concentration) were regarded as factors in the optimization. Results of the two-level full factorial design, 2^4 with 16 runs based on the variance analysis (ANOVA), demonstrated that all four factors, as well as the interactions between thiocyanate concentration and time and hydrochloric acid concentration and time, are statistically significant. Doehlert designs were applied in order to determine the optimum conditions for molybdenum preconcentration. The proposed procedure allowed molybdenum determination with a detection limit of 1.5 μg L^{-1} and a precision, calculated as relative standard deviation (RSD), of 1.8% for a set of 10 measurements for a molybdenum concentration of 10.0 μg L^{-1} in synthetic sea-water solution. The recovery of molybdenum in the presence of several cations achieved demonstrated that this procedure improved the required selectivity for sea-water analysis. The studied procedure was applied to molybdenum determination in surface sea-water samples collected in Salvador City, Brazil. Results showed good agreement with other reported data from the literature, including data obtained for samples from this same city by another procedure.

Introduction

Most procedures proposed by analytical chemists are optimized by development of univariate methodology (one variable at each time). This simple optimization methodology is supposed to have an easier interpretation. However, this process requires a large number of experiments, expends a great amount of reagent and time and is only valid if the variables to be optimized do not interact. Procedures involving optimization by multivariate techniques[1–3] have been increasingly used as they are faster, more economical and effective, and allow more than one variable to be optimized simultaneously. This optimization can be accomplished using experimental designs of two types.[4,5]

1. Primary order designs, for which the equation is:

$$Y = a_1 + b_1 A + c_1 B + d_1 AB \qquad (1)$$

where Y is the experimental response, A and B represent the variables to be optimized, a_1 is an independent term, b_1 and c_1 coefficients of the linear terms and d_1 is the coefficient of the interaction term.

2. Second order designs, which are described by the equation:

$$Y = a_2 + b_2 A + c_2 B + d_2 A^2 + e_2 B^2 + f_2 AB \qquad (2)$$

where Y is the experimental response, A and B represent the variables to be optimized, a_2 is an independent term, b_2 and c_2 are coefficients of the linear terms, d_2 and e_2 coefficients of the quadratic terms and f_2 is the coefficient of the interaction

term. The choice of design type is made with regard to the experimental conditions and purpose.

The second order designs have advantages because they not only determine the influence of the variables to be optimised on the response, but also enable the response function to be obtained and optimized.

The Doehlert matrix[3–21] is a second order design, which has been widely used in several situations. It allows identification of critical points (maximum, minimum and saddle points) at each step of the optimization process. This consists of an experimental design in which a set of points is uniformly distributed in a rhombic lattice (a hexagon in the case of two variables). The whole experimental domain is assayed with a minimum number of experiments following a sequential approach. For a number of factors k, $(k^2 + k + 1)$ experiments are required and a minimum of three levels is assigned to each factor. Thus, for a two-factor design, the Doehlert matrix dimension is {5,3}. This property allows the free choice of factors to be assigned either to a large or to a small number of levels.

The Doehlert design has been used for: optimization of experimental variables in solid-phase spectrophotometry;[4,8–10] methodology for separation processes by using micellar electrokinetic capillary chromatography;[11] extraction processes by using microwaves;[12] simultaneous solvent extraction of several metals;[13,14] development of an on-line procedure for preconcentration and determination of zinc by ICP-OES; methodology for spectrophotometric determination;[15] investigation of matrix effects in ICP-OES;[16] voltammetric determination;[17] and other applications.[18–21]

Table 1 Results for molybdenum determination in several sea-water samples

Sampling place/year	Achieved results/μg l^{-1}	Analytical technique	Preconcentration process	Ref.
Philippine Sea, 1995	10.15	Voltammetry	—	23
Kanagawa, Japan, 1996	9.0	ETAAS	Adsorption onto active carbon	27
Salvador, Brazil, 1999	7.9–8.5	ICP-OES	Adsorption onto active carbon	28
Pacific Ocean, 1990	7.0–10.0	ICP-OES	Cellulose phosphate column	31
Fukaura, Japan, 1994	10.7	Solid phase spectrometry	—	37
Taiwan, R. of China, 1996	10.03	ETAAS	Chelating resin column	38
South Pacific, 1998	9.3	Voltammetry	—	39

The evaluation of molybdenum in sea-water is very important, since this metal is part of biochemical phenomena in most marine flora and fauna organisms. Under normal conditions the molybdenum concentration[22,23] in the sea-water samples is around of 10 μg L^{-1}. However, analysis of these samples by ICP-OES[24] is difficult because this technique has a low sensitivity for molybdenum and problems occur with samples of high saline concentration. Thus, many preconcentration procedures have been proposed for molybdenum determination in sea-water samples using several separation techniques, such as liquid–liquid extraction,[25,26] adsorption processes with activated carbon,[27,28] coprecipitation[29,30] and others.[31] Table 1 shows molybdenum concentrations determined in sea-water samples collected from around the world.

In this paper, a procedure for the preconcentration and determination of molybdenum in sea-water, based on the solid-phase extraction of molybdenum(v) as the thiocyanate complex using polyurethane foam as sorbent, is proposed.

The sorption mechanism of the molybdenum(v) thiocyanate complex in aqueous media by unloaded polyurethane foam was studied by Farag et al.[32] In a previous paper,[33] we proposed a procedure for molybdenum determination in iron matrices by ICP-OES, after iron separation and adsorption of molybdenum(v) thiocyanate complex onto polyurethane foam. The analytical conditions were set by univariate optimization. Molybdenum(vi) ions also form thiocyanate complexes and are extracted by polyurethane foam, but the extraction kinetic is much slower than for the molybdenum(v) thiocyanate complex.

Experimental

Instrumentation

A Research Laboratories Model 3410 minitorch sequential inductively coupled plasma spectrometer linked to an IBM PC-AT computer was used. Emission intensity was measured under conditions shown in Table 2. The calibration curve (0–4.0 μg mL^{-1}) for molybdenum was plotted with solutions prepared from a 1 mg mL^{-1} stock solution.

A 300 Analyser pH meter was used to measure pH values. A VKS-100 mechanical shaker at 100 counts min^{-1} was also used.

Reagents

All reagents were of analytical grade unless otherwise stated. Doubly distilled water was used to prepare all solutions.

Table 2 Operating parameters for ICP-OES

Incident output power	650 W
Reflected power	<5 W
Nebulizer	Glass, Meinhard
Plasma gas flow rate	7.5 L min^{-1}
Auxiliary gas flow rate	0.81 L min^{-1}
Aerosol carrier gas flow	0.81 mL min^{-1}
Solution uptake rate	2.5 L min^{-1}
Signal integration time	5 s
Integration for determination	3

Nitric and hydrochloric acid were of Suprapur quality (Merck). Laboratory glassware was kept overnight in 10% nitric acid solution. Before use the glassware was rinsed with deionized water and dried in a dust free environment.

A 5.00 μg mL^{-1} molybdenum solution was prepared by diluting a 1000 μg mL^{-1} molybdenum solution (Merck) with a 1% hydrochloric acid solution.

A 4.0 M potassium thiocyanate solution was prepared by dissolving the reagent in water.

To prepare polyurethane foam (PUF), a commercial, open cell polyether-type PUF (Trorion TR-110, 43% resilience and 10–12 cells per linear cm) was ground in a householder blender with water. The foam was used as described by Carvalho et al.[34]

Synthetic sea-water was prepared with the composition[5] (in g L^{-1}): 27.9 of NaCl, 1.4 of KCl, 2.8 of MgCl$_2$, 0.5 of NaBr and 2.0 of MgSO$_4$.

Sea-water samples

Surface sea-water samples were collected in polypropylene bottles previously cleaned by soaking in 2 M nitric acid. Samples were filtered through a membrane of 0.45 μm pore size, acidified to 1% (v/v) with concentrated nitric acid and stored frozen until analysis. Sampling stations were beaches of the Atlantic Ocean in Salvador City, Brazil. Salvador is in the eastern region of the Brazilian coast.

Procedures used in the factorial design

10.0 μg of molybdenum(vi) were added to synthetic sea-water in all experiments. Molybdenum was reduced by addition of 1 mL of ascorbic acid solution (1%). Firstly, molybdenum(v) was preconcentrated in polyurethane foam (PUF) within the range of experimental conditions of volume of synthetic sea-water, shaking time, thiocyanate concentration and hydrochloric acid concentration, which are shown in Table 3. After extraction, the PUF was separated by filtration and molybdenum was desorbed by addition of 2 mL of concentrated nitric acid and 8.0 mL of demineralized water. The foam was filtered and molybdenum was determined in the filtrate by ICP-OES. Maximum and minimum levels of each factor were chosen according to data presented in a previous paper.[33]

Procedures used in the Doehlert matrix

500 mL of synthetic sea-water containing 10.0 μg of molybdenum(vi) salt and 1 mL of ascorbic acid solution (1%) was preconcentrated in PUF under the conditions of shaking time, thiocyanate concentration and hydrochloric acid

Table 3 Factors and levels used in factorial design

Variable	Low (−)	High (+)
Solution volume/mL	50	500
Shaking time/min	2	20
Thiocyanate concentration/M	0.02	0.2
Hydrochloric acid concentration/M	0.05	1.0

Table 4 Design matrix and the results of molybdenum extraction (%)

No.	[SCN⁻]	[HCl]	t^a	$V_s{}^b$	Recovery (%)	
1	+	+	+	+	90	92
2	+	+	+	−	99	101
3	+	+	−	+	15.2	16.5
4	+	+	−	−	52.6	49
5	+	−	+	+	25.6	24.2
6	+	−	+	−	76.6	70.5
7	+	−	−	+	10	9.5
8	+	−	−	−	25.1	28.5
9	−	+	+	+	21.3	23.1
10	−	+	+	−	62.4	66
11	−	+	−	+	8.4	5
12	−	+	−	−	25.4	22
13	−	−	+	+	0	0
14	−	−	+	−	0	0
15	−	−	−	+	0	0
16	−	−	−	−	0	0

$^a t$—time in minutes. $^b V_s$—volume in mL.

concentration shown in Tables 6 and 7. After extraction, PUF was separated by filtration and the molybdenum was desorbed by addition of 2 mL of concentrated nitric acid and 8.0 mL of demineralized water. The foam was then filtered and molybdenum was determined in the filtrate by ICP-OES.

Proposed procedure for molybdenum determination in sea-water

1 mL of ascorbic acid solution (1%), 86 ± 1 mL of 6.0 M hydrochloric acid solution and 24 ± 1 mL of 4.0 M thiocyanate solution were added to 500 mL of sea-water sample in a plastic lidded vessel. Next, 100 ± 5 mg of ground PUF were added and the vessel was mechanically shaken for at least 16 min. The PUF was separated by vacuum filtration and washed with 0.2 mol L^{-1} thiocyanate solution. The solid phase was transferred to a dry beaker, and 2 mL of concentrated nitric acid and 8.0 mL of demineralized water were added. The foam was then filtered and molybdenum was determined in the filtrate by ICP-OES, using the Mo II 281.615 nm line.

Optimization strategy

The optimization process was carried out using two-level full factorial and Doehlert matrix designs. All the experiments were done in duplicate. Four variables (solution volume, shaking time, thiocyanate concentration and hydrochloric acid concentration) were regarded as factors and the experimental data were processed by using the STATISTICAL program.

Lagrange's criterium

Lagrange's criterium[5,13] was used for the determination of the critical point of the 2nd order equation and is based on the calculation of the Hessian determination of Y.

$$H(A,B) = (\delta^2 Y/\delta A^2)(\delta^2 Y/\delta B^2) - (\delta^2 Y/\delta A\delta B)^2 \quad (3)$$

The critical point (a_o, b_o) is maximum if $H(a_o, b_o) > 0$ and $\delta^2 Y/\delta A^2 (a_o, b_o) < 0$ and it is minimum if $H(a_o, b_o) > 0$ and $\delta^2 Y/\delta A^2 (a_o, b_o) > 0$. A saddle point exists if $H(a_o, b_o) < 0$. If the response surface has a maximum, this point is calculated by solving the equation systems, $\delta^2 Y/\delta A^2 = 0$ and $\delta^2 Y/\delta B^2 = 0$.

Results and discussion

Factorial design

The proposed preconcentration procedure has several variables. However, the factors that may potentially affect the extraction process are solution volume, shaking time, thiocyanate concentration and hydrochloric acid concentration. A two

Table 5 Analysis of data given in Table 4

Factor	SS^a	DF^b	MS^c	F-ratio	P level^d
[SCN⁻]	9511.65	1	9511.653	104.699	0.000000
[HCl]	7167.04	1	7167.038	78.8908	0.000000
t	7335.63	1	7335.633	80.7466	0.000000
V_s	3555.35	1	3555.353	39.1354	0.000003
[SCN⁻]−[HCl]	4.28	1	4.278	0.0471	0.830305
[SCN⁻]−t	2120.63	1	2120.633	23.3428	0.000089
[SCN⁻]−V_s	320.68	1	320.678	3.5298	0.074226
[HCl]−t	1753.80	1	1753.800	19.3049	0.000253
[HCl]−V_s	173.45	1	173.445	1.9092	0.181577
t−V_s	117.43	1	117.428	1.2926	0.268380
Error	1907.80	21	90.848		
Total	33967.74	31			

^{a}SS = sum of squares. ^{b}DF = degrees of freedom. ^{c}MS = mean squares. ^{d}P level = probability level.

level full factorial, 2^4 with 16 runs, was carried out in order to determine the main factors of the extraction process. Table 3 lists the maximum and minimum values of each factor and Table 4 shows the experimental design matrix and the results derived from each run in duplicate. Significance of the effects was checked by analysis of the variance (ANOVA) and using P-value significance levels. This value expresses how much the probability of a factor is due to random errors. A factor is considered significant if P is less than 5%. Results (Table 5) demonstrated that all the four factors (solution volume, shaking time, thiocyanate concentration and hydrochloric acid concentration) and the interactions (thiocyanate concentration–time and hydrochloric acid concentration–time) were statically significant.

Doehlert design

The factorial design demonstrated that the solution volume was a significant factor in the process of molybdenum extraction. However, taking into account that the main purpose of this procedure is molybdenum preconcentration for sea-water analysis by ICP-OES, the hydrochloric acid concentration, thiocyanate concentration and shaking time were optimized for a sample volume of 500 mL by using Doehlert designs. In the optimization process two designs of two factors were performed and two response surfaces were derived for each pair of studied factors.

Design 1. In design 1 the optimized variables were thiocyanate concentration and hydrochloric acid concentration, and the sample volume and shaking time were fixed at 500 mL and 20 min, respectively. The seven experiments required by the Doehlert design are described in Table 6. Concentration of hydrochloric acid and thiocyanate varied from 0.05 to 1.0 M and from 0.02 to 0.20 M, respectively.

The data obtained were used in the Doehlert matrix and the equation below illustrates the relationship of the thiocyanate concentration, hydrochloric acid concentration and molybdenum extraction (%).

Table 6 Doehlert matrix for design 1; $R = 0.991$

Experiment	HCl concentration/ mol L^{-1}	SCN concentration/ mol L^{-1}	Mo recovery (%)	
			Experimental	Expected
1	0.05	0.06	7	1.92
2	1	0.06	79.5	74.4
3	0.525	0.11	92.5	92.5
4	0.525	0.2	86.6	83
5	0.525	0.02	14	19.6
6	1	0.16	101.5	106.6
7	0.05	0.16	35	40

Table 7 Doehlert matrix for design 2; $R = 0.996$

Experiment	Time/ min	SCN concentration/ mol L^{-1}	Mo recovery (%)	
			Experimental	Expected
1	2	0.06	0	3.80
2	20	0.06	8.5	12.50
3	11	0.11	87.5	87.50
4	11	0.2	83	87.3
5	11	0.02	7	2.8
6	20	0.16	98.5	94.4
7	2	0.16	19.5	15.7
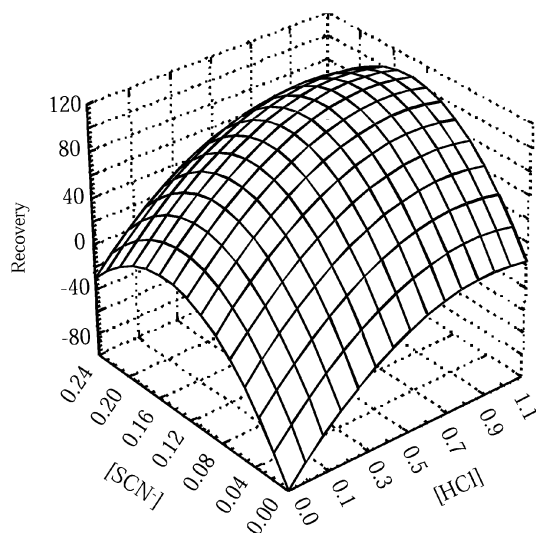
Fig. 1 Surface response for molybdenum extraction by polyurethane foam: sample volume = 500 mL; shaking time = 20 min; hydrochloric acid concentration = 0.05–1.0 M; and thiocyanate concentration = 0.02–0.20 M.

$$\% \text{ Mo extraction} = -79.15 + 191.95[\text{HCl}] + 1503.85[\text{SCN}]$$
$$- 106.52[\text{HCl}]^2 - 63.16[\text{HCl}][\text{KSCN}] - 5086.42[\text{KSCN}]^2 \quad (4)$$

The corresponding surface response is shown in Fig. 1.

The application of Lagrange's criterium in this equation demonstrates that:

$$H(a_o,b_o) = (-213.04)(-10172.84) - (63.16)^2 = 216323.65$$

$$\delta^2 \text{ Mo Ext}/\delta[\text{HCl}]^2 = (-213.04)$$

These results indicated that there was a maximum on the surface response, and it was calculated by the following equations:

$$\delta^2\text{Mo Ext}/\delta[\text{HCl}]^2 = 0 =$$
$$191.95 - 213.04[\text{HCl}] - 63.16[\text{SCN}] \quad (4a)$$

$$\delta^2\text{Mo Ext}/\delta[\text{SCN}]^2 = 0 =$$
$$1503.85 - 63.16[\text{HCl}] - 10172.84[\text{SCN}] \quad (4b)$$

The maximum values are $[\text{HCl}] = 0.86$ M and $[\text{SCN}] = 0.14$ M.

Design 2. Taking into account that thiocyanate is the complexing agent in the extraction process and has a strong interaction with the time variable, as demonstrated by results of the full factorial design, the concentration of this ligand was again optimized using a Doehlert design with these two variables. The sample volume was 500 mL and the hydrochloric acid concentration was 0.86 M: values set by Doehlert

design 1. The seven experiments required for the new Doehlert design are shown in Table 7. Time and thiocyanate concentration varied from 2 to 20 min and from 0.02 to 0.2 M, respectively.

The obtained data were applied in the Doehlert matrix and the equation below shows the relationship of the thiocyanate concentration (M), shaking time (min) and molybdenum extraction (%).

$$\% \text{ Mo extraction} = -71.17 + 9.79t + 1195.63 [\text{SCN}]$$
$$- 0.53t^2 + 38.89t [\text{KSCN}] - 5246.91 [\text{KSCN}]^2 \quad (5)$$

The corresponding surface response is shown in Fig. 2.

The application of Lagrange's criterium in this equation demonstrates that:

$$H(a_o,b_o) = (1.06)(10493.83) - (38.89)^2 = 9611.02$$

$$\delta^2 \text{ Mo Ext}/\delta t^2 = (-1.06)$$

These results indicated that there was a maximum on the surface response, and it was calculated by the following equations:

$$\delta^2 \text{ Mo Ext}/\delta t^2 = 0 = 9.79 - 1.06t + 38.89 [\text{SCN}] \quad (5a)$$

$$\delta^2 \text{ Mo Ext}/\delta [\text{SCN}]^2 = 0 = 1195.63 + 38.89t$$
$$- 10493.83 [\text{SCN}] \quad (5b)$$

The maximum values are $t = 15.6$ min and $[\text{SCN}] = 0.16$ M.

Thus, the general proposed procedure suggests a hydrochloric acid concentration of 0.86 M, thiocyanate concentration of 0.16 M and a shaking time of 15.6 min for maximum molybdenum extraction.

Analytical features of procedure

The detection limit was calculated as ($3s/S$), where S is the slope of the analytical curve and s is the standard deviation of ten consecutive measurements of the blank, and found to be 1.5 µg L^{-1}.

The precision of the procedure evaluated as relative standard deviation (RSD) obtained after analysing a series of 10 replicates was 1.8% for a molybdenum concentration of 10.0 µg L^{-1} in synthetic sea-water solution.

The factor preconcentration was 50, assuming a sample
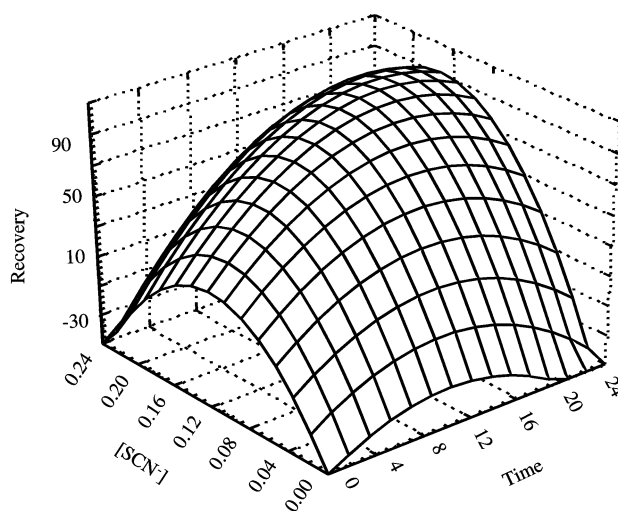
Fig. 2 Surface response for molybdenum extraction using polyurethane foam: sample volume = 500 mL; hydrochloric acid concentration = 0.86 M; thiocyanate concentration = 0.02–0.20 M; and shaking time = 2–20 min.

Table 8 Determination and recovery of molybdenum in sea-waters ($n = 3$); sample volume = 500 mL

Sample	Added molybdenum/ μg L^{-1}	Achieved molybdenum[a]/ μg L^{-1}	Recovery (%)
Synthetic sea-water	0	<LOD	—
	12.5	12.2 ± 0.1	97.6
	18.75	18.78 ± 0.2	101
	25.00	24.01 ± 0.2	96
	10.00[b]	9.64 ± 0.3	96
Sea-water: Pedra da Sereia	0	9.1 ± 0.5	—
	10.0	18.5 ± 0.6	94
Sea-water: Porto da Barra	0	6.4 ± 0.3	—
	10.0	15.5 ± 0.7	99
Sea-water: Ondina	0	7.9 ± 0.2	—
	10.0	17.8 ± 0.9	99
Sea-water: Pituba	0	10.1 ± 0.4	—
	10.0	19.7 ± 0.4	96

[a]At 95% confidence level. [b]Molybdenum in presence of several metallic ions.

volume of sea-water of 500 mL and a solution volume for analysis of 10.0 mL.

Effect of other metallic ions on the proposed procedure

Metal ions such as zinc(II), copper(II), copper(I), iron(III) and cobalt(II), which form complexes with thiocyanate, are easily extracted by polyurethane foam.[35,36] However, they did not affect the applicability of this procedure for molybdenum determination in sea-water because the molybdenum concentration in these samples was significantly higher than for these ions. Addition of ascorbic acid also prevents the iron interference, since ascorbic acid reduces iron(III) to iron(II), which does not form complexes with thiocyanate.

In order to check the accuracy of the studied methodology and the effect of other metallic ions, molybdenum (10.00 μg) and other metallic ions (10.00 μg of each) were added to 500 mL of synthetic sea-water and the proposed procedure was applied. The achieved result was 9.64 ± 0.30 μg, $n = 3$, for a recovery of 96.4%. This experiment was carried out using a multielemental ICP-OES solution quality control standard (QCS-19), which had antimony, arsenic, beryllium, cadmium, calcium, chromium, cobalt, nickel, copper, iron, lead, magnesium, manganese, selenium, titanium, thallium, vanadium and zinc at a concentration of 100 μg L^{-1} each.

Analytical application

The optimized methodology was applied to the analysis of surface sea-water samples collected during the winter of 2001 from several beaches of Salvador City, Brazil. Data found were consistent with those reported in the literature, as can be seen in Table 1, including former data for the same city by other procedures for molybdenum determination.[28] Results are shown in Table 8. Results of the recovery of added molybdenum in the samples before application of the proposed methodology demonstrated its efficiency.

Conclusions

Application of the factorial designs and Doehlert matrix allowed the optimization of a procedure based on solid-phase extraction, which was found to be more efficient and have a fewer number of experiments.

The developed methodology in this paper is feasible and allows molybdenum preconcentration with a preconcentration

factor of 50, making it suitable for sea-water analysis by ICP-OES.

Achieved data for molybdenum concentration in sea-water samples collected from beaches in Salvador City, Brazil, were consistent with those reported in the literature (Table 1).

Acknowledgement

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