

Application of factorial designs and Doehlert matrix in optimization of experimental variables associated with the preconcentration and determination of vanadium and copper in seawater by inductively coupled plasma optical emission spectrometry[☆]

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Abstract

In the present paper a procedure for preconcentration and determination of vanadium and copper in seawater using inductively coupled plasma optical emission spectrometry (ICP OES) is proposed, which is based on solid-phase extraction of vanadium (IV), vanadium (V) and copper (II) ions as 1-(2-pyridylazo)-2-naphthol (PAN) complexes by active carbon. The optimization process was carried out using two-level full factorials and Doehlert matrix designs. Four variables (PAN mass, pH, active carbon mass and shaking time) were regarded as factors in the optimization. Results of the two-level full factorial design 2^4 with 16 runs for vanadium extraction, based on the variance analysis (ANOVA), demonstrated that the factors pH and active carbon mass, besides the interaction (pH \times active carbon mass), are statistically significant. For copper, the ANOVA revealed that the factors PAN mass, pH and active carbon mass and the interactions (PAN mass \times pH) and (pH \times active carbon mass) are statistically significant. Doehlert designs were applied in order to determine the optimum conditions for extraction. The procedure proposed allowed the determination of vanadium and copper with detection limits ($3\sigma/S$) of 73 and 94 ng l⁻¹, respectively. The precision, calculated as relative standard deviation (R.S.D.), was 1.22 and 1.37% for 12.50 μ g l⁻¹ of vanadium and copper, respectively. The preconcentration factor was 80. The recovery achieved for determination of vanadium and copper in the presence of several cations demonstrated that this procedure improved the selectivity required for seawater analysis. The procedure was applied to the determination of vanadium and copper in seawater samples collected in Salvador City, Brazil. Results showed good agreement with other data reported in the literature.

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1. Introduction

Procedures for optimization of factors by multivariate techniques [1,2] have been encouraged, 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 [3], which can be of first or second order. The second-order designs have advantages, because they not only determine the influence of the variables to be optimized on the response, but also enable the response function to be obtained and optimized.

The Doehlert matrix [4] is an optimization system, defined as a second-order design. For a process involving two variables (A and B) and an experimental response (Y), the model is described as:

$$Y = a + bA + cB + dA^2 + eB^2 + fAB \quad (1)$$

where Y is the experimental response, A and B represent the variables to be optimized, a is an independent term, b and c are coefficients of the linear terms, d and e are coefficients of the quadratic terms and f is the coefficient of the interaction term. The identification of the critical points (maximum, minimum or saddle point) is carried out with application of the Lagrange criterion in the equation obtained during the optimization process using experimental data. In analytical chemistry, the Doehlert matrix [5–16] has been widely used in several situations, such as: development of an on-line procedure for preconcentration and determination of zinc by inductively coupled plasma optical emission spectrometry (ICP OES) [5]; optimization of experimental variables in solid-phase spectrophotometry [6,7]; optimization process for simultaneous solvent extraction of several metals [8,9]; methodology for spectrophotometric determination [10]; optimization for spectrofluorimetric determination [11]; methodology for separation process using micellar electrokinetic capillary chromatography [12]; extraction process using microwaves [13]; optimization for voltammetry determination [14]; and investigation of matrix effects in ICP OES [15]. In our laboratory, Doehlert designs were used for the optimization of variables for the

preconcentration and determination of molybdenum in seawater by ICP OES [16].

Vanadium is an essential trace element for plants and animals, which stimulates the synthesis of chlorophyll and promotes the growth of young animals. Copper is also an essential trace element for humans, higher mammals and numerous plants. The blood of marine mollusks and crabs contains the Cu complex hemocyanin rather than the Fe complex hemoglobin, which is taken up from the seawater and acts as a respiratory catalyst [17]. Thus, these metals are frequently determined in seawater. However, their determination by ICP OES [18] is difficult because of its relatively low sensitivity and the high saline concentration of seawater. The concentration ranges for vanadium and copper in seawater are 2.0–3.0 and 0.2–4.0 $\mu\text{g l}^{-1}$, respectively [19].

The reagent 1-(2-pyridylazo)-2-naphthol (PAN) forms complexes with several metal ions, including vanadium (IV), vanadium (V) and copper (II). In preconcentration procedures, PAN was repeatedly used for different analytical separation strategies, such as: solid phase extraction using an active carbon column [20]; silica gel [21,22]; naphthalene [23]; Amberlite XAD-2000 [24]; alumina [25]; Amberlite XAD-2 [26,27]; Amberlite XAD-4 [28]; and chloromethylated polystyrene [29], as well as by cloud-point extraction [30,31].

In this work, a procedure for the preconcentration and determination of vanadium and copper in seawater using ICP OES is proposed. Factorial designs and a Doehlert matrix were used for optimization of the experimental variables. It is based on the solid-phase extraction of vanadium and copper ions as PAN complexes on active carbon.

2. Experimental

2.1. Instrumentation

A Research Laboratories model 3410 minitorch sequential inductively coupled plasma optical emission spectrometer (Dearborn, MI, USA) coupled to an IBM PC-AT computer was used. Emission intensities were measured under the conditions shown in Table 1. The calibration curves (0–2.0

Table 1
Operating parameters for the inductively coupled plasma optical emission spectrometer

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
Emission line (nm)	
V(II)	309.311
Cu(II)	324.754

μg ml⁻¹) for vanadium and copper were plotted with solutions prepared from a 100.0 μg ml⁻¹ stock solution. A Digimed pH meter (Santo Amaro, Brazil) was used to measure pH values. An Etica mechanical shaker (São Paulo, Brazil) at 100 counts min⁻¹ was also used.

2.2. Reagents

All reagents were of analytical grade unless otherwise stated. Ultrapure water was obtained from an EASYpure RF set-up (Barnstedt, Dubuque, IA, USA). Nitric and hydrochloric acid were of Suprapur quality (Merck). Laboratory glassware was kept overnight in 10% nitric acid solution, rinsed with deionized water before use, and dried in a dust-free environment.

Vanadium solution (10.0 μg ml⁻¹) was prepared by diluting a 1000 μg ml⁻¹ vanadium solution (Merck) with 1% (v/v) hydrochloric acid.

Copper solution (10.0 μg ml⁻¹) was prepared by diluting a 1000 μg ml⁻¹ copper solution (Merck) with 1% (v/v) hydrochloric acid.

PAN solution 0.25% (w/v) was prepared by dissolving 1.25 g of 1-(2-pyridylazo)-2-naphthol (Aldrich) in 500 ml of ethanol (Merck).

Acetate buffer (pH 3.75) was prepared by mixing 14.76 g of sodium acetate with 104.1 ml of concentrated acetic acid and diluting it to 1 l with ultrapure water.

Acetate buffer (pH 5.75) was prepared by mixing 149.24 g of sodium acetate with 10.3 ml of

concentrated acetic acid and diluting it to 1 l with ultrapure water.

Synthetic seawater was prepared with a composition [5] of: 27.9 μg ml⁻¹ NaCl; 1.4 g l⁻¹ KCl; 2.8 g l⁻¹ MgCl₂; 0.5 g l⁻¹ NaBr; and 2.0 g l⁻¹ MgSO₄.

2.3. Surface seawater samples

Seawater samples were collected in polypropylene bottles, previously cleaned by soaking in 2 mol l⁻¹ 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 they were analyzed. Sampling stations were beaches on the Atlantic Ocean in Salvador City, Brazil.

2.4. General procedure

A sample volume of 800 ml, containing vanadium and copper ions, was transferred into a stoppered flask; 10 ml of acetate buffer solution and a volume of PAN solution (0.25%) were added. After fast shaking, a mass of active carbon was added and the mixture was shaken again for a certain time. The system was then filtered under vacuum through a 2.5-cm-diameter cellulose membrane. The residue of active carbon was transferred to an Erlenmeyer flask and digested at 120 °C with 4.00 ml of concentrated nitric acid solution until dryness. The residue was treated with 10.0 ml of 3 mol l⁻¹ nitric acid, and filtered through a paper filter (Whatman no 40). The filtrate was collected and used for determination of vanadium and copper by ICP OES using the emission lines V(II) 309.311 and Cu(II) 324.754 nm.

2.5. Procedure used in the factorial design

The general procedure was applied using the variable experimental conditions for PAN mass, pH, active carbon mass and shaking time shown in Table 2. Maximum and minimum levels of each factor were chosen according to data from previous experiments.

Table 2

Factors and levels used in the factorial design for extraction of vanadium and copper

Variable	Low (-)	High (+)
PAN mass (A) (μg)	1250	12500
pH (B)	3.75	5.75
Active carbon mass (C) (mg)	50	200
Shaking time (D) (min)	10	50

2.6. Procedures used in the Doehlert matrix

The general procedure was applied and the experimental conditions for pH, PAN mass, active carbon mass and shaking time were established in agreement with requirement by the optimization process.

2.7. Optimization strategy

The optimization process was carried out using two-level full factorial and Doehlert matrix designs. All experiments were carried out in duplicate, using 800 ml of synthetic seawater containing 10.0 μg of vanadium and copper. Four variables (PAN mass, pH, active carbon mass and shaking time) were regarded as factors, and the experimental data were processed using the STATISTICAL program.

2.8. Lagrange criterion

The Lagrange criterion [5,16] was used for determination of the critical point of the second-order equation and is based on the calculation of the Hessian determination of Y :

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

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 $\delta^2 Y / \delta B^2 = 0$.

3. Results and discussion

3.1. Factorial design

The procedure proposed is based on the solid phase extraction of vanadium (IV), vanadium (V) and copper (II) ions as PAN complexes using active carbon. The following factors were evaluated: PAN mass, pH, active carbon mass and shaking time. A two-level full factorial of 2^4 with 16 runs was carried out in order to determine the main factors of the extraction process. Table 2 list the maximum and minimum values given to each factor and Tables 3 and 4 show the experimental design matrix and the results derived from each run in duplicate for vanadium and copper, respectively. The significance of the effects was checked by analysis of the variance (ANOVA) and using P -value significance levels.

The ANOVA results for vanadium produced the Pareto chart [32,33] of main effects shown in Fig. 1. Bar lengths are proportional to the absolute value of the estimated effects, which helps in comparing the relative importance of effects. The interpretation of this chart demonstrates that the factors pH and active carbon mass are highly significant. An increase in pH and in active carbon

Table 3
Design matrix and the results of vanadium extraction

No	PAN mass	pH	Active carbon mass	Shaking time	Vanadium extraction (%)
1	+	+	+	+	100/110
2	+	+	+	-	98/102
3	+	+	-	+	90/98
4	+	+	-	-	94/88.4
5	+	-	+	+	98/95
6	+	-	+	-	97/94.4
7	+	-	-	+	62/70.8
8	+	-	-	-	53/55.6
9	-	+	+	+	104/104
10	-	+	+	-	100/108
11	-	+	-	+	90/97.8
12	-	+	-	-	91/95
13	-	-	+	+	90/92
14	-	-	+	-	88/94
15	-	-	-	+	72/76.6
16	-	-	-	-	55/65

Table 4
Design matrix and the results of copper extraction

No	PAN mass	pH	Active carbon mass	Shaking time	Copper extraction (%)
1	+	+	+	+	96.7/102
2	+	+	+	–	107/107
3	+	+	–	+	97.7/101
4	+	+	–	–	92/94
5	+	–	+	+	97.8/102
6	+	–	+	–	99.2/104
7	+	–	–	+	96.3/99
8	+	–	–	–	97/101
9	–	+	+	+	97/95.4
10	–	+	+	–	92.1/90.2
11	–	+	–	+	80/83
12	–	+	–	–	80/79
13	–	–	+	+	75.6/73
14	–	–	+	–	70/69.7
15	–	–	–	+	71/72.5
16	–	–	–	–	71.5/68.9

mass increases the extraction efficiency. The shaking time is a less significant factor. The interaction (pH \times active carbon mass) is also statistically significant. The factor PAN mass has an insignificant effect.

The Pareto chart in Fig. 2 demonstrates that PAN mass provides a more significant effect for copper extraction. An increase in this complexing agent leads to higher extraction efficiency. The factors pH and active carbon mass also produce significant effects. The interactions (PAN mass \times pH) and (pH \times active carbon mass) are also statistically significant. The shaking time in the range 10–50 min has no significant effect on the extraction.

3.2. Final optimization by Doehlert design

The factorial design demonstrated that the variables at the levels studied need final optimization, for which the Doehlert designs were used. Firstly, designs were developed for the optimization of pH

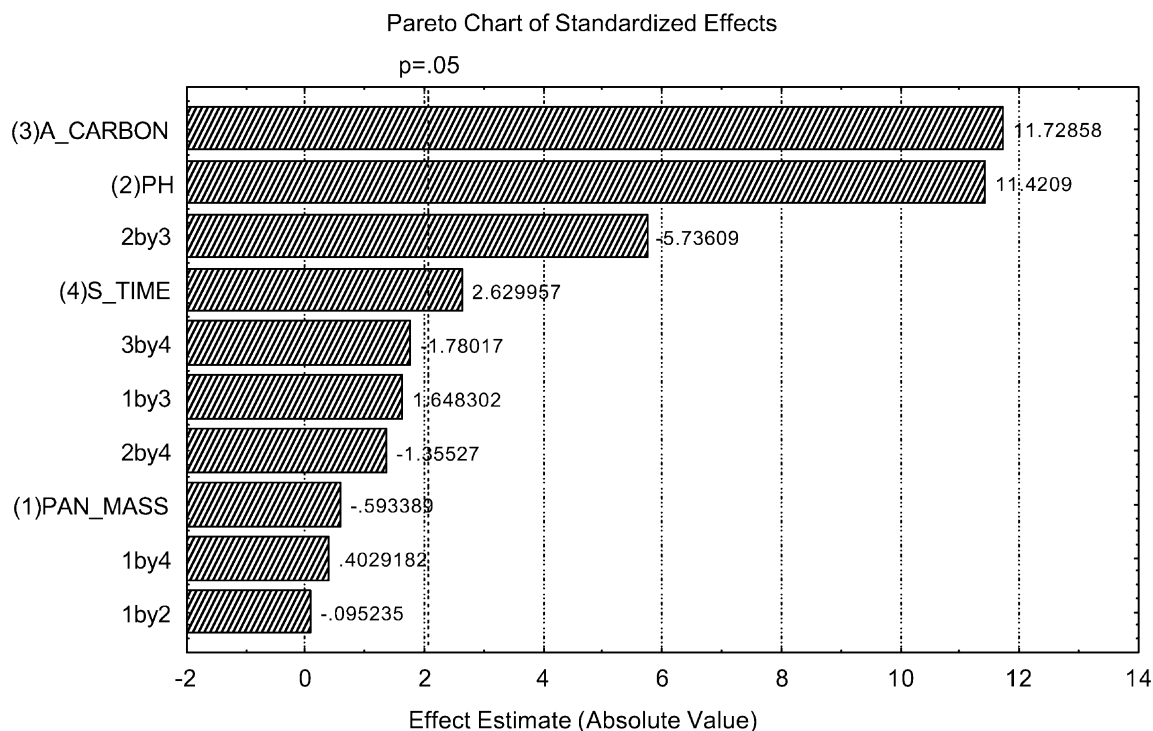


Fig. 1. Pareto chart of standardized effects for variables in the vanadium extraction.

and PAN mass and then designs for the optimization of active carbon mass and shaking time.

3.2.1. Design 1—conditions of pH and PAN mass for vanadium extraction

In this design the optimized variables were pH and PAN mass, setting the active carbon mass and shaking time at 200 mg and 50 min, respectively. The seven experiments required by the Doehlert design are described in Table 5. The pH and PAN mass varied from 2.5 to 8.0 and from 1250 to 12 500 μg, respectively.

The data obtained were used in the Doehlert matrix and Eq. (3) illustrates the relationship between pH, PAN mass and vanadium extraction (%):

$$\begin{aligned} \% \text{ V extraction} = & -36.202 + 48.202 \text{ pH} \\ & + 0.003m_{\text{PAN}} - 3.998 \text{ pH}^2 \\ & - 4.52 \times 10^{-4}m_{\text{PAN}} \text{ pH} \\ & - 1.277 \times 10^{-7}m_{\text{PAN}}^2 \end{aligned} \quad (3)$$

The corresponding surface response is shown in Fig. 3.

Application of the Lagrange criterion in this equation demonstrates that:

Table 5
Doehlert matrix for design 1

Experiment	pH	PAN mass (μg)	Vanadium recovery (%)	
			Experimental	Expected
1	3.75	1250	90	90
2	3.75	12500	90	85
3	4.75	7500	105	102
4	8.00	7500	85	82
5	2.50	7500	70	66
6	5.75	12500	100	94
7	5.75	1250	110	109

$R^2 = 0.9781$.

$$H(a_o, b_o) = 1.838 \times 10^{-6}$$

$$\delta^2 Y / \delta pH^2 = -7.996$$

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

$$\begin{aligned} \delta V \text{ extraction} / \delta pH = 0 \\ = 48.202 - 7.996 \text{ pH} \\ - 4.52 \times 10^{-4}m_{\text{PAN}} \end{aligned} \quad (3a)$$

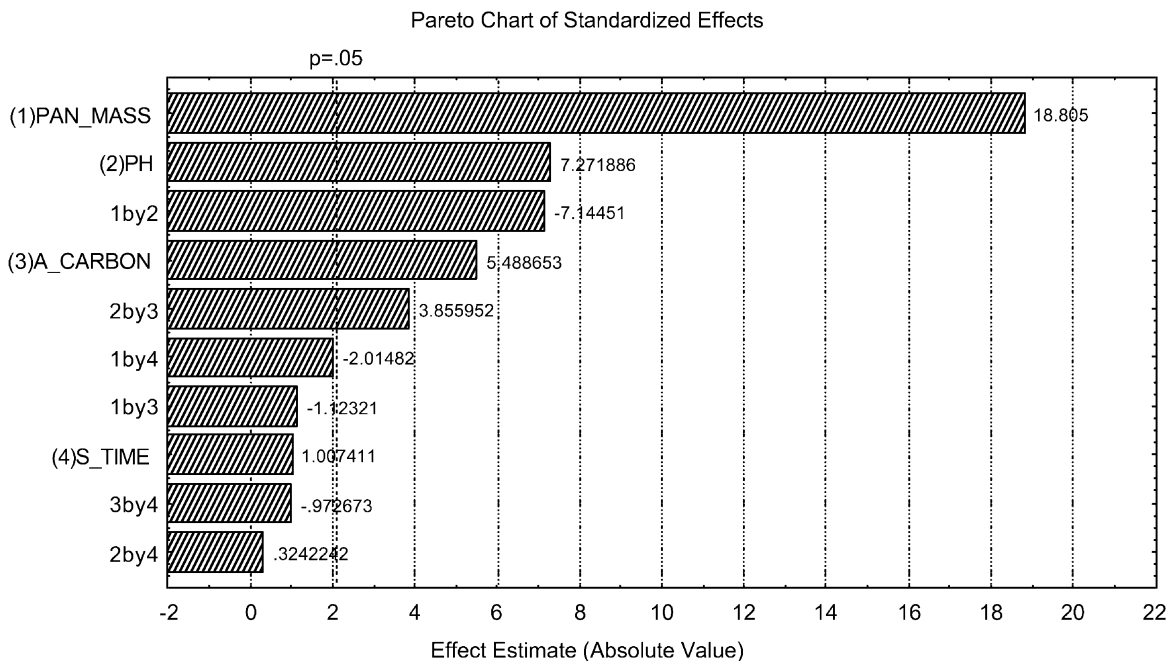


Fig. 2. Pareto chart of standardized effects for variables in the copper extraction.

$$z = -36,202 + 48,202 * x + 0,003 * y - 3,998 * x * x - 4,52e-4 * x * y - 1,277e-7 * y * y$$

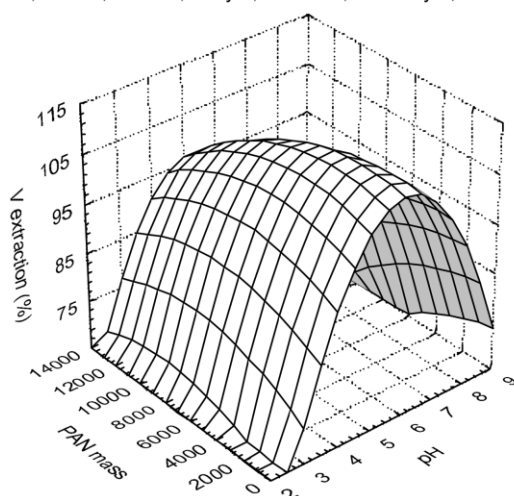


Fig. 3. Surface response for vanadium extraction (%). Vanadium concentration, $12.50 \mu\text{g l}^{-1}$; synthetic seawater volume, 800 ml; active carbon mass, 200 mg; shaking time, 50 min; pH 2.5–8.0; PAN mass, 1250–12 500 μg .

$$\begin{aligned} \delta V \text{ extraction} / \delta m_{\text{PAN}} &= 0 \\ &= 0.003 - 4.52 \times 10^{-4} \text{ pH} - 2.554 \\ &\quad \times 10^{-7} m_{\text{PAN}} \end{aligned} \quad (3b)$$

The maximum values are pH 5.96 and $m_{\text{PAN}} = 1197 \mu\text{g}$.

3.2.2. Design 2—conditions of pH and PAN mass for copper extraction

In this design, the experimental conditions (pH, PAN mass, active carbon mass and shaking time) are in agreement with design 1. The seven experiments required by the Doehlert design are described in Table 6.

The data obtained were used in the Doehlert matrix and Eq. (4) illustrates the relationship between pH, PAN mass and copper extraction (%):

$$\begin{aligned} \% \text{ Cu extraction} &= -63.968 + 35.595 \text{ pH} \\ &\quad + 0.017 m_{\text{PAN}} - 2.276 \text{ pH}^2 \\ &\quad - 9.605 \\ &\quad \times 10^{-4} m_{\text{PAN}} \text{ pH} - 6.264 \\ &\quad \times 10^{-7} m_{\text{PAN}}^2 \end{aligned} \quad (4)$$

The corresponding surface response is shown in Fig. 4.

Table 6
Doehlert matrix for design 2

Experiment	pH	PAN mass (μg)	Copper recovery (%)	
			Experimental	Expected
1	3.75	1250	52.6	53.3
2	3.75	12500	104	107.1
3	4.75	7500	110	111.8
4	8.00	7500	108	109.8
5	2.50	7500	84	85.1
6	5.75	12500	109	111.1
7	5.75	1250	79	78.6

$$R^2 = 0.9986.$$

Application of the Lagrange criterion in this equation demonstrates that:

$$H(a_0, b_0) = 4.781 \times 10^{-6}$$

$$\delta^2 Y / \delta \text{pH}^2 = -4.552$$

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

$$\begin{aligned} \delta \text{Cu extraction} / \delta \text{pH} &= 0 \\ &= 35.595 - 4.552 \text{ pH} \\ &\quad - 9.605 \\ &\quad \times 10^{-4} m_{\text{PAN}} \end{aligned} \quad (4a)$$

$$z = -63,968 + 35,595 * x + 0,017 * y - 2,276 * x * x - 9,605e-4 * x * y - 6,264e-7 * y * y$$

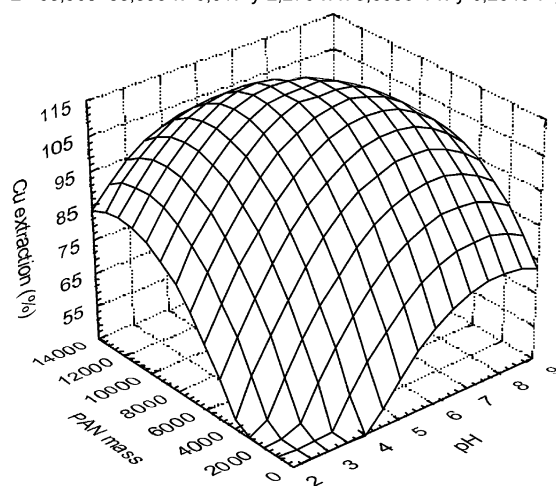


Fig. 4. Surface response for copper extraction (%). Copper concentration, $12.50 \mu\text{g l}^{-1}$; synthetic seawater volume, 800 ml; active carbon mass, 200 mg; shaking time, 50 min; pH 2.5–8.0; PAN mass, 1250–12 500 μg .

Table 7
Doehlert matrix for design 3

Experiment	Active carbon mass (mg)	Time (min)	Vanadium recovery (%)	
			Experimental	Expected
1	50	10	91	92
2	200	10	99.5	100
3	125	30	101	101
4	125	60	99	100
5	125	5	99.5	98.5
6	200	50	100	100
7	50	50	96	96
CP	157	33	–	102.17
RC	150	30	–	102.10

CP, critical point; RC, recommended conditions for this procedure. $R^2=0.9624$.

$$\begin{aligned} \delta \text{Cu extraction} / \delta m_{\text{PAN}} &= 0 \\ &= 0.017 - 9.605 \times 10^{-4} \text{pH} - 1.253 \\ &\quad \times 10^{-6} m_{\text{PAN}} \end{aligned} \quad (4b)$$

The maximum values are pH 5.91 and $m_{\text{PAN}} = 9035 \mu\text{g}$.

3.2.3. Design 3—conditions of active carbon mass and shaking time for vanadium extraction

In this design, pH and PAN mass were fixed, and active carbon mass and shaking time were varied. Considering the results obtained in designs 1 and 2, pH was fixed at 5.75 (maximum pH allowed for the acetate buffer) and PAN mass at $12\,500 \mu\text{g}$. The seven experiments required for the new Doehlert design are described in Table 7. Time and active carbon mass varied from 5 to 60 min and from 50 to 200 mg, respectively.

The data obtained were used in the Doehlert matrix and Eq. (5) illustrates the relationship between active carbon mass, shaking time and vanadium extraction (%):

$$\begin{aligned} \% \text{ V extraction} &= 79.741 + 0.219 m_{\text{AC}} \\ &\quad + 0.316 t - 6.178 \\ &\quad \times 10^{-4} (m_{\text{AC}})^2 - 7.5 \\ &\quad \times 10^{-4} m_{\text{AC}} t - 0.003 t^2 \end{aligned} \quad (5)$$

The corresponding surface response is shown in Fig. 5.

Application of the Lagrange criterion in this equation demonstrates that:

$$H(a_o, b_o) = 6.851 \times 10^{-6}$$

$$\delta^2 Y / \delta m_{\text{AC}}^2 = -1.236 \times 10^{-3}$$

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

$$\begin{aligned} \delta V \text{ extraction} / \delta m_{\text{AC}} &= 0 \\ &= 0.219 - 1.236 \\ &\quad \times 10^{-3} m_{\text{AC}} - 7.5 \\ &\quad \times 10^{-4} t \end{aligned} \quad (5a)$$

$$\begin{aligned} \delta V \text{ extraction} / \delta t &= 0 = 0.316 - 7.5 \\ &\quad \times 10^{-4} m_{\text{AC}} \\ &\quad - 0.006 t \end{aligned} \quad (5b)$$

The maximum values are $m_{\text{AC}} = 157 \text{ mg}$ and $t = 33 \text{ min}$.

3.2.4. Design 4—conditions of active carbon mass and shaking time for copper extraction

In this design, the experimental conditions (pH, PAN mass, active carbon mass and shaking time) are in agreement with design 3. The seven exper-

$$z = 79.741 + 0.219x + 0.316y - 6.178e-4x^2 - 7.5e-4x^2y - 0.003y^2$$

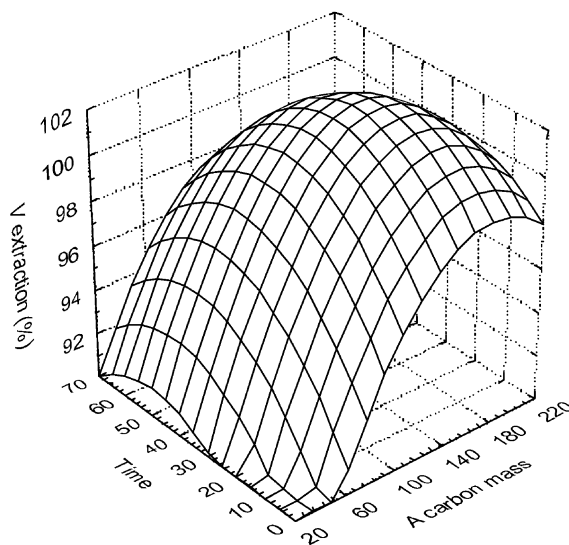


Fig. 5. Surface response for vanadium extraction (%). Vanadium concentration, $12.50 \mu\text{g l}^{-1}$; synthetic seawater volume, 800 ml; pH 5.75; PAN mass, $12\,500 \mu\text{g}$; active carbon mass, 50–200 mg; shaking time, 5–60 min.

Table 8
Doehlert matrix for design 4

Experiment	Active carbon mass (mg)	Time (min)	Copper recovery (%)	
			Experimental	Expected
1	50	10	94	94
2	200	10	99	99
3	125	30	102	102
4	125	60	100	99
5	125	5	99	99
6	200	50	99	98
7	50	50	98	97
CP	143	31	–	101.84
RC	150	30	–	101.81

CP, critical point; RC, recommended conditions for this procedure. $R^2=0.9522$.

iments required by the Doehlert design are described in Table 8.

The data obtained were used in the Doehlert matrix and Eq. (6) illustrates the relationship between active carbon mass, shaking time and copper extraction (%):

$$\begin{aligned} \% \text{ Cu extraction} = & 83.826 + 0.18m_{AC} + 0.34t \\ & - 5.595 \times 10^{-4}(m_{AC})^2 \\ & - 6.667 \times 10^{-4}m_{AC}t - 4 \\ & \times 10^{-3}t^2 \end{aligned} \quad (6)$$

The corresponding surface response is shown in Fig. 6.

Application of the Lagrange criterion in this equation demonstrates that:

$$H(a_o, b_o) = 8.508 \times 10^{-6}$$

$$\delta^2 Y / \delta m_{AC}^2 = -1.119 \times 10^{-3}$$

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

$$\begin{aligned} \delta \text{Cu extraction} / \delta m_{AC} &= 0 \\ &= 0.18 - 1.119 \times 10^{-3}m_{AC} - 6.667 \\ &\quad \times 10^{-4}t \end{aligned} \quad (6a)$$

$$\begin{aligned} \delta \text{Cu extraction} / \delta t &= 0 \\ &= 0.34 - 6.667 \\ &\quad \times 10^{-4}m_{AC} - 8 \\ &\quad \times 10^{-3}t \end{aligned} \quad (6b)$$

The maximum values are $m_{AC}=143$ mg and $t=31$ min.

3.3. Procedure for determination of vanadium and copper in seawater

Considering the results obtained in the designs, the procedure for the determination of vanadium and copper in seawater recommends the use of the general procedure, described in the experimental part, using a PAN mass of 12 500 μg , pH 5.75, active carbon mass of 150 mg and shaking time of 30 min.

3.4. Analytical features

The precision calculated as the relative standard deviation (RSD) for a series of 11 replicates was 1.22 and 1.37% for 12.50 $\mu\text{g l}^{-1}$ of vanadium and copper, respectively, in synthetic seawater solution.

The preconcentration factor was 80, considering the sample volume of seawater (800 ml) and a solution volume for analysis of 10.0 ml.

The sensitivity [34] was studied by means of the limits of detection (LOD) and quantification (LOQ), defined as $\text{LOD}=(3\sigma)/S$ and $\text{LOQ}=\text{LOD}/0.1$.

$$z=83,826+0,18*x+0,34*y-5,595e-4*x*x-6,667e-4*x*y-0,004*y*y$$

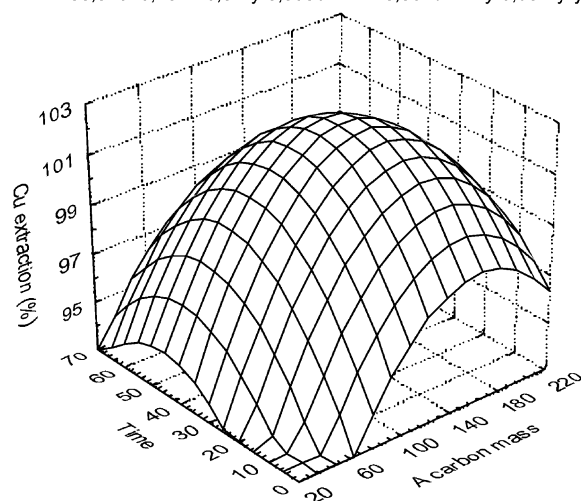


Fig. 6. Surface response for copper extraction (%). Copper concentration, 12.50 $\mu\text{g l}^{-1}$; synthetic seawater volume, 800 ml; pH 5.75; PAN mass, 12 500 μg ; active carbon mass, 50–200 mg; shaking time, 5–60 min.

Table 9

Determination of vanadium in unspiked and spiked seawater samples ($n=3$)

Seawater sample	Vanadium ($\mu\text{g l}^{-1}$)		Recovery (%)
	Added	Found ^a	
Synthetic	0	<LOD	–
	12.50	12.26 ± 0.10	98.1
	12.50 ^b	11.55 ± 0.19	92.4
Jardim Alah	0	1.73 ± 0.06	–
	12.50	14.16 ± 0.17	99.4
Stella Mares	0	3.45 ± 0.08	–
	12.50	15.38 ± 0.14	95.4
Porto da Barra	0	3.13 ± 0.09	–
	12.50	14.68 ± 0.17	92
Corsário	0	3.05 ± 0.08	–
	12.50	15.33 ± 0.16	98.2
Ondina	0	1.77 ± 0.04	–
	12.50	14.90 ± 0.16	105

Sample volume, 800 ml.

^a At 95% confidence level.^b Vanadium in the presence of several metal ions.

$(10\sigma)/S$, where S is the slope of the analytical curve and σ is the standard deviation of 10 consecutive measurements of the blank. For vanadium, LOD and LOQ were 73 and 243 ng l^{-1} , and for copper, 94 and 313 ng l^{-1} , respectively.

3.5. Effect of other metal ions on the procedure proposed

In order to check the effect of other metal ions on the method proposed, vanadium and copper ($10.00 \mu\text{g}$) and other metal ions (all $10.00 \mu\text{g}$) were added to 800 ml of synthetic seawater and the procedure was applied. The values measured were $9.24 \pm 0.16 \mu\text{g}$ ($n=3$) for vanadium and $9.45 \pm 0.15 \mu\text{g}$ ($n=3$) for copper, with recovery of 92.4 and 94.5%, respectively. This experiment was carried out using a multi-elemental ICP OES solution Quality Control Standards (QCS-19), which had arsenic, antimony, beryllium, cadmium, calcium, chromium, cobalt, iron, molybdenum, nickel, thallium, titanium, zinc, lead, magnesium, manganese and selenium at a concentration of $100 \mu\text{g l}^{-1}$ each.

3.6. Accuracy

In order to evaluate the accuracy of the procedure developed, vanadium and copper were deter-

Table 10

Determination of copper in unspiked and spiked seawater samples ($n=3$)

Seawater sample	Copper ($\mu\text{g l}^{-1}$)		Recovery (%)
	Added	Found ^a	
Synthetic	0	<LOD	–
	12.50	12.38 ± 0.11	99.0
	12.50 ^b	11.78 ± 0.18	94.2
Jardim Alah	0	<LOD	–
	12.50	12.65 ± 0.18	101.2
Stella Mares	0	0.94 ± 0.02	–
	12.50	13.21 ± 0.14	98
Porto da Barra	0	0.38 ± 0.11	–
	12.50	13.51 ± 0.17	105
Corsário	0	0.38 ± 0.04	–
	12.50	12.56 ± 0.06	97.4
Ondina	0	0.48 ± 0.10	–
	12.50	12.25 ± 0.16	94

Sample volume, 800 ml.

^a At 95% confidence level.^b Copper in the presence of several metal ions.

mined in the CASS-4 Nearshore Seawater Reference Material for Trace Metals (National Research Council Canada). For vanadium, the result achieved was $1.16 \pm 0.18 \mu\text{g l}^{-1}$ compared to the certified value of $1.18 \pm 0.16 \mu\text{g l}^{-1}$. For copper, the result achieved was $0.602 \pm 0.064 \mu\text{g l}^{-1}$ compared to the certified value of $0.592 \pm 0.055 \mu\text{g l}^{-1}$. This test was carried out using 150 ml of solution.

3.7. Analytical application

The optimized methodology was applied to the analysis of seawater samples collected during the winter of 2001 from several beaches in Salvador City, Brazil. The results are shown in Tables 9 and 10, together with recovery data for added vanadium and copper. The data found in this study were consistent with those reported in literature [19], including former data for the same city using a different procedure for copper determination [35]. The recovery of vanadium and copper added to the samples before application of the method proposed demonstrates its efficiency.

4. Conclusions

Application of factorial designs and a Doehlert matrix allowed the optimization of a procedure for

the determination of vanadium and copper by ICP OES, based on solid phase extraction, to be more efficient using a smaller number of experiments. The data obtained for vanadium and copper from seawater samples collected in beaches in Salvador City, Brazil were consistent with those reported in the literature.

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