



Speciation of Cr(III) and Cr(VI) in environmental samples determined by selective separation and preconcentration on silica gel chemically modified with niobium(V) oxide

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ABSTRACT

In this study a new method for chromium speciation in water using solid phase extraction coupled to a flow injection system and flame atomic absorption spectrometry was developed. The adsorption behavior of Cr(III) and Cr(VI) on Nb₂O₅-SiO₂ allowed the selective separation of Cr(III) from Cr(VI) in the pH range of 6–9. Thus, a method for Cr(III) preconcentration and extraction using Nb₂O₅-SiO₂ was developed. Total chromium was determined after the reduction of Cr(VI) to Cr(III) using sodium sulfite in acidic medium. The operational variables of the preconcentration and reduction procedures were optimized through full factorial and Doehlert designs. The limit of detection for Cr(III) was 0.34 μg L⁻¹ and the precision was below 4.6%. Results for recovery tests using different environmental samples were between 90 and 105%. Certified reference materials (NIST 1640 and NIST 1643e) were analyzed in order to check the accuracy of the proposed method, and the results were in agreement with the certified values.

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1. Introduction

Chromium has been increasingly introduced into the environment as a result of the growth in industrial activities which use chromium, such as, tanning factories, steelworks, industrial electroplating and wood preservation. The wastes generated as a consequence of such activities are the main contamination sources of chromium in water bodies.

Chromium is not an essential element for plants, but it is for animals at trace levels, being involved in carbohydrate and lipid metabolism and its function is related to the mechanism of insulin action [1]. However, Cr(VI) has exhibited carcinogenic properties [2]. Due to the differences between the oxidation states of the chromium species, there has been increasing interest in monitoring the concentration of the chromium species individually, as well as the total chromium concentration.

The determination of chromium species can be carried out using flame or graphite AAS, ICP-OES and ICP-MS, but accuracy and sensitivity are often difficult to achieve with direct measurements. The use of prior separation/preconcentration of the samples can aid in improving the determination of Cr(III) and Cr(VI) by the above methods [3].

Of the sample preparation techniques, solid phase extraction (SPE) based on the selective or simultaneous retention of Cr(III) and Cr(VI) on sorbents is the most widely employed procedure for the study of chromium speciation in water samples. Currently, one of the most important focuses in relation to studies on SPE for chromium speciation determination is the use of new solid sorbents. Methods based on the quantitative sorption of Cr(III) on *Bacillus sphaericus*-loaded Diaion SP-850 at pH 5 [4], crosslinked chitosan-bound FeC nanoparticles at pH 6–10 [5], nanometer titanium dioxide at pH 7–9 [6], and nanometer-sized zirconium oxide immobilized on silica gel [7] have been proposed. In all of these cases, total chromium was determined after reduction of Cr(VI) to Cr(III). The Cr(VI) in the original mixture can be calculated as the difference. On the other hand, XAD-2010 [3], a poly(styrene-divinylbenzene) copolymer with high adsorption capacity, and multiwalled carbon nanotubes [8], have been used to concentrate Cr(VI). After oxidation of Cr(III) to Cr(VI) the proposed methods were applied to the determination of total chromium. The level of Cr(III) is calculated as the difference between the total chromium and Cr(VI) levels. Another strategy [9] used for chromium speciation is to adsorb Cr(III) and Cr(VI) sequentially onto silica gel modified with zirconium phosphate and silica gel modified with zirconium oxide.

Recently, our research group proposed new sorbent materials for SPE to determine heavy metals in aqueous samples. These included silica gel chemically modified with niobium(V) oxide,

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which demonstrated a great potential for metal determination [10–12]. As a continuation of these studies, the possibility of developing a sensitive and selective on-line FI-FAAS procedure for the speciation of Cr(III) and Cr(VI) was investigated. The procedure is based on the selective retention of Cr(III) on silica gel chemically modified with niobium(V) oxide at pH 6–9. Cr(VI) was calculated as the difference between the total chromium concentration obtained after the reduction procedure and the Cr(III) concentration. Also, in this study a two-level full factorial experimental design and Doehlert matrix were the multivariate tools used not only for optimization of the factors affecting the preconcentration system but also to optimize the reduction process.

2. Experimental

2.1. Instrumentation

A Varian SpectrAA 50 (Victoria, Australia) flame atomic absorption spectrometer, equipped with deuterium lamp background correction and a Hitachi chromium hollow cathode lamp (Ibaraki, Japan) was used. The hollow cathode lamp was operated at 5 mA and the selected wavelength was 357.9 nm. All measurements were carried out in an air/acetylene flame. Atomic absorption grade acetylene purchased from White Martins (São Paulo, Brazil) was used. The absorbance reading mode was peak height. A 320 Mettler Toledo pH meter was used to adjust the pH of the solutions.

2.2. Reagents and solutions

All chemicals were of analytical grade and were used without prior purification. Nitric and hydrochloric acids obtained from Merck (Darmstadt, Germany) were double distilled below their boiling points in a quartz distillation apparatus (Kürner Analysentechnik, Rosenheim, Germany). Deionized water from a Milli-Q Millipore® 18.2 M Ω cm⁻¹ conductivity purification system (Bedford, MA, USA) was used to prepare all solutions. Prior to use, the laboratory glassware was kept for 24 h in 2% (v/v) Extran® solution (Merck) and then rinsed with distilled water. It was then transferred to a 20% (v/v) nitric acid solution (Vetec, Rio de Janeiro, Brazil) where it remained for another 48 h followed by 1 h in an ultrasonic bath. Finally, the glassware was washed with deionized water and dried in a dust-free environment.

The following buffer solutions were used to adjust the solution pH when necessary: (i) potassium acid phthalate–hydrochloric acid (or sodium hydroxide) buffer solution was prepared by mixing 0.1 mol L⁻¹ potassium acid phthalate obtained from Carlo Erba (Milan, Italy) and 0.1 mol L⁻¹ hydrochloric acid (Merck) to obtain pH 2. In order to obtain pH 4.0, 5.0 and 6.0, adequate volumes of 0.1 mol L⁻¹ sodium hydroxide (Vetec) were mixed with 0.1 mol L⁻¹ potassium acid phthalate solution and (ii) Tris(hydroxymethyl)aminomethane buffer solution obtained from Aldrich (Mallinckrodt, Paris, France) was prepared by dissolving 1.2 g of the chemical in water and adjusting the pH to 8 and 9 using a 0.1 mol L⁻¹ nitric acid solution to give a final volume of 100 mL.

Chromium(VI) and chromium(III) working standard solutions were all prepared by appropriate dilution of, respectively, 1000 mg L⁻¹ K₂Cr₂O₇ (Merck) and 1000 mg L⁻¹ CrCl₃·6H₂O (Vetec) stock solutions.

Reduction of Cr(VI) to Cr(III) was carried out using sodium sulfite as the reducing reagent (Vetec). The stock solution of 50 mmol L⁻¹ sodium sulfite was prepared by dissolving 630.2 mg of the chemical in water to give a final volume of 100 mL.

Silica gel chemically modified with niobium(V) oxide (Nb₂O₅–SiO₂) was used to preconcentrate chromium(III) and total

chromium. The synthesis and characterization of the adsorbent material are described in the literature [13].

2.3. On-line preconcentration system

The on-line flow system used for the development of the proposed method is illustrated in Fig. 1. The flow system consists of two peristaltic pumps equipped with Tygon tubes, four three-way solenoid valves and a minicolumn (43 mm × 3 mm) filled with 100 mg of the sorbent Nb₂O₅–SiO₂. The flow system was coupled to the FAAS. During the preconcentration step (A), valve V1 is open and the other valves remain closed; the sample or working solutions are pumped through the minicolumn and the effluent is discarded. After this first step, water is pumped for 5 s in the same way as in the preconcentration procedure to eliminate any sample matrix that might be present in the dead volume of the minicolumn.

In the elution step (B), V1 is closed and valves V2, V3 and V4 are open. Thus, the eluent percolates through the minicolumn in the opposite direction to that of the preconcentration step. The eluate is carried directly to the nebulization system of the FAAS.

2.4. Optimization strategy for the chromium speciation

In the first step, the best working conditions for Cr(III) sorption onto the sorbent Nb₂O₅–SiO₂ were determined using an experimental design. The chemical and flow rate variables were optimized through a two-level full factorial design and Doehlert matrix. All experiments were carried out in duplicate, using 15.0 mL of a 100.0 μ g L⁻¹ Cr(III) solution. The experimental data were processed using the Statistica 6.0 computer program. In the second step the best conditions to reduce Cr(VI) were determined using a Doehlert design. The two variables considered in this second step were: sodium sulfide (reducing reagent) concentration and reaction time. The reduction was carried out at pH 1, the medium being acidified with hydrochloric acid.

2.5. Calibration, validation and application of the proposed method

The procedure for quantification of Cr(III) and Cr(VI) was carried out using an external calibration procedure. The analytical curve was obtained in the range of 5.0–120.0 μ g L⁻¹ of Cr(III) and submitting each solution to the previously optimized preconcentration system.

A calibration curve with concentrations between 1.0 and 3.0 mg L⁻¹ was constructed without preconcentration for estimation of the enrichment and recovery factors.

Water samples of a river located close to a tanning factory, as well as of the public domestic water system and well water, were collected in Florianópolis (Santa Catarina, Brazil). All water samples were filtered through 0.45 μ m cellulose membranes (Millipore), acidified with HNO₃ and stored in PTFE flasks under refrigeration at 4 °C until the analysis. The Cr(VI) concentration was estimated indirectly by subtracting the Cr(III) concentration before reduction from the total chromium concentration.

The accuracy of the method was demonstrated through recovery tests and determining the concentration of the analytes in the following certified reference materials: NIST 1643e and NIST 1640 (trace elements in freshwater) from the National Institute of Standards & Technology (Gaithersburg, USA).

3. Results and discussion

Initially the proposed preconcentration system was optimized to reach the best sorption of Cr(III) on the sorbent Nb₂O₅–SiO₂.

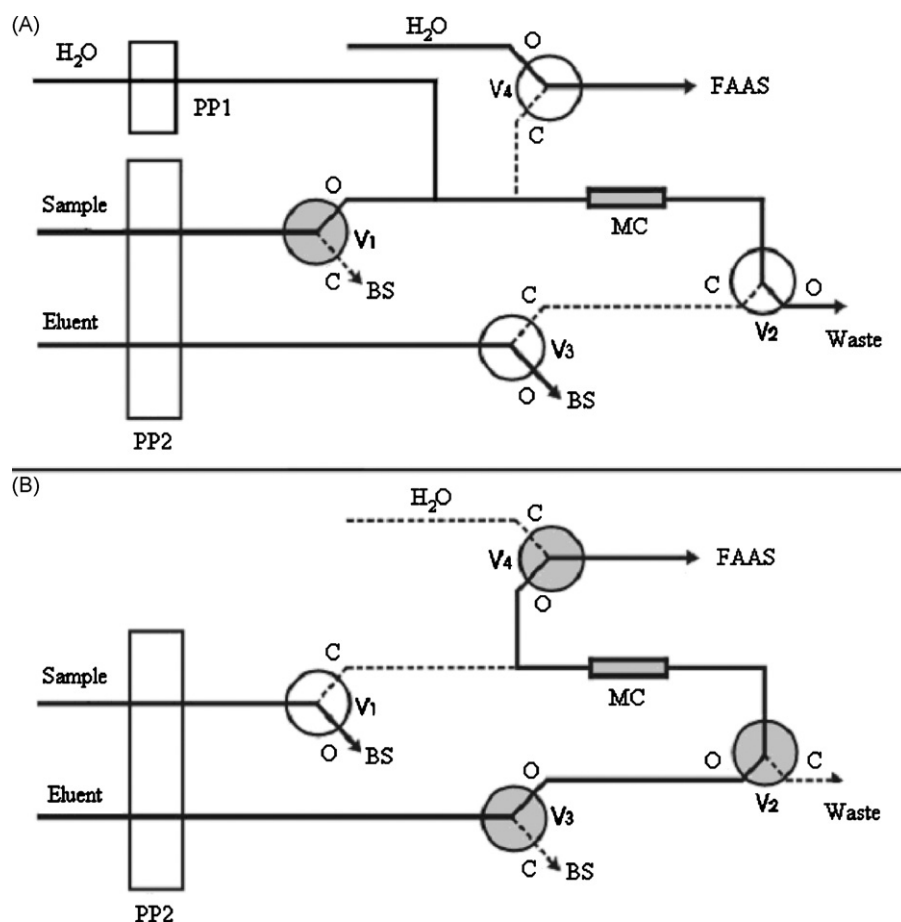


Fig. 1. Diagram of the on-line pre-concentration system. (A) Adsorption step and (B) desorption step. V, valve; L, open; D, closed; MC, minicolumn containing adsorbent; R, sample or eluent back stream; hatched circle, valve on and white circle, valve off.

In this step some parameters were fixed: the sample volume used for the optimization was 15 mL with a $100 \mu\text{g L}^{-1}$ Cr(III) solution, nitric acid was selected as the eluent, and the quantity of sorbent was 100 mg.

3.1. Factorial design

The significance of each operational parameter selected in this study (sample and eluent flow rates, eluent concentration and sample pH) and their interactions in the pre-concentration system were determined using a 2^4 full factorial design with a central point. Table 1 shows the minimum and maximum levels selected for each variable. The 17 combinations used for this design and their respective analytical responses, obtained in duplicate, are summarized in Table 2. The analytical response used for this study was the sensitivity efficiency (SE), which is defined as the analytical signal of an on-line enrichment system for a pre-concentration time of 1 min [14]. The SE was used because it includes the sampling time as an implicit factor in the analytical response, and consequently it

takes the best sensitivity with the highest sampling frequency into consideration.

An analysis of variance (ANOVA) was performed to determine whether the experimental factors studied were significant (at a *p*-value of 0.05) in the performance of the pre-concentration system. The main effects and their interactions are presented in the Pareto chart shown in Fig. 2. According to this chart, sample flow rate (51.59), sample pH (21.26) and eluent flow rate (-2.19) are statistically significant at the 95% confidence level. Furthermore, interaction between sample flow rate and sample pH (13.18) as well as between eluent concentration and sample pH (3.12) are also significant. The results indicate that these variables have a synergistic effect on the analytical response, that is, the use of sample flow rate and sample pH (1/4) both at the high level studied, and eluent concentration in combination with sample pH (3/4) also at the high level evaluated, leads to a better analytical response. This information on the interactions between factors would be neglected if a univariate approach had been employed, possibly leading to a false optimum. The positive values indicate that increasing these factors will result in an increase in the analytical signal. On the other hand, the negative values for eluent flow rate indicate an improvement in the analytical response when the level changes from maximum to minimum. However, in an on-line procedure the use of low eluent flow rate can be incompatible with the aspiration rate of the nebulizer-burner system of the FAAS. Thus, an eluent flow rate of 4.5 mL min^{-1} was selected to continue the study. The factorial study also demonstrated that the eluent concentration was not significant (at the 0.05 level). However, an effect of the interaction between

Table 1
Levels and factors used in the factorial design

Factors	Minimum (-)	Central point (0)	Maximum (+)
Sample pH	3.0	6.0	9.0
Sample flow rate (mL min^{-1})	3.3	5.6	7.8
Eluent concentration (mol L^{-1})	1.0	2.0	3.0
Eluent flow rate (mL min^{-1})	3.3	4.5	5.6

Table 2

Matrix of full factorial design and the analytical response (SE) for each experiment for pre-concentration of Cr(III)

Experiments	Sample flow rate (mL min ⁻¹)	Eluent flow rate (mL min ⁻¹)	Eluent concentration (mol L ⁻¹)	Sample pH	SE replicates	
					1	2
1	-1	-1	-1	-1	0.0143	0.0147
2	1	-1	-1	-1	0.0314	0.0291
3	-1	1	-1	-1	0.0117	0.0120
4	1	1	-1	-1	0.0302	0.0302
5	-1	-1	1	-1	0.0133	0.0127
6	1	-1	1	-1	0.0280	0.0281
7	-1	1	1	-1	0.0112	0.0112
8	1	1	1	-1	0.0291	0.0280
9	-1	-1	-1	1	0.0272	0.0256
10	1	-1	-1	1	0.0521	0.0505
11	-1	1	-1	1	0.0230	0.0220
12	1	1	-1	1	0.0460	0.0436
13	-1	-1	1	1	0.0261	0.0263
14	1	-1	1	1	0.0559	0.0508
15	-1	1	1	1	0.0228	0.0232
16	1	1	1	1	0.0513	0.0555
17	0	0	0	0	0.0345	0.0334

eluent concentration and sample pH was observed. Considering the algebraic sign of the main effect of these variables, one can conclude that the sample pH leads to a more pronounced enhancement of the analytical response. Thus, the eluent concentration was fixed at 2.0 mol L⁻¹. The results obtained for the full factorial study indicated that the variables sample flow rate and sample pH required a final optimization. Therefore, the aforementioned variables were optimized using a Doehlert design.

3.2. Doehlert design

Table 3 summarizes the seven experiments carried out to construct the Doehlert matrix, as well as their respective analytical responses (SE). The response surface obtained through application of the Doehlert matrix is shown in Fig. 3 and it is described by a quadratic equation (Eq. (1)).

The Lagrange criterion was applied to confirm whether the critical point of the response surface corresponded to a maximum, minimum or saddle point. Eqs. (2)–(4) were generated by application of the Lagrange criterion.

$$SE = -0.239 + 0.03 \times \text{pH} + 0.054 \times \text{Flow} - 0.003 \times \text{pH}^2 + 0.003 \times \text{pH} \times \text{Flow} - 0.006 \times \text{Flow}^2 \quad (1)$$

$$H(\text{pH}_0, \text{Flow}_0) = (-0.006)(-0.012) - (0.003)^2 = 6.3 \times 10^{-5} \quad (2)$$

$$\frac{\partial^2 SE}{\partial \text{pH}_{\text{sample}}^2} = -0.006 \quad (3)$$

Table 3Response surface for optimization of sample pH and sample flow rate (sample volume 15.0 mL, sample concentration 100.0 µg L⁻¹, sorbent mass 100.0 mg and eluent concentration 2.0 mol L⁻¹ HNO₃)

Experiment	Sample pH	Sample flow rate (mL min ⁻¹)	SE ^a
1	7.5	5.3	0.0420
2	6	5.8	0.0458
3	9	5.8	0.0432
4	7.5	6.3	0.0532
5	6	6.8	0.0405
6	9	6.8	0.0468
7	7.5	7.3	0.0518

^a Average.

$$\frac{\partial^2 SE}{\partial \text{Flow}_{\text{sample}}} = -0.012 \quad (4)$$

The critical point is a maximum if $H(x_0, y_0) > 0$ and $\partial^2 R / \partial x^2(x_0, y_0) < 0$, minimum if $H(x_0, y_0) > 0$ and $\partial^2 R / \partial x^2(x_0, y_0) > 0$ and saddle if $H(x_0, y_0) < 0$. Therefore, the critical point obtained in this study corresponds to a maximum point. The maximum point of the response surface was obtained by making the partial derivative of Eq. (1) equal to zero, generating Eqs. (5) and (6). The critical points obtained were 8.3 and 6.6 for sample pH and sample flow rates (mL min⁻¹), respectively.

$$\frac{\partial SE}{\partial \text{pH}} = +0.03 - 0.006 \times \text{pH} + 0.003 \times \text{Flow} = 0 \quad (5)$$

$$\frac{\partial SE}{\partial \text{Flow}} = +0.054 + 0.003 \times \text{pH} - 0.012 \times \text{Flow} = 0 \quad (6)$$

In short, the optimized conditions to adsorb Cr(III) onto Nb₂O₅-SiO₂ in the proposed on-line system obtained using full factorial and Doehlert designs are: eluent concentration of 2.0 mol L⁻¹, eluent flow rate of 4.5 mL min⁻¹, sample flow rate of 6.6 mL min⁻¹ and sample pH of 8.0.

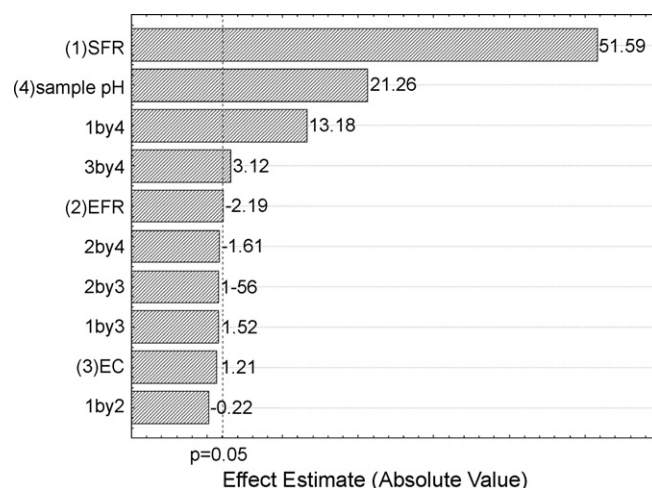


Fig. 2. Pareto chart of standardized effects for the variables of the pre-concentration system using SE as analytical response. SFR = sample flow rate, EFR = eluent flow rate and EC = eluent concentration.

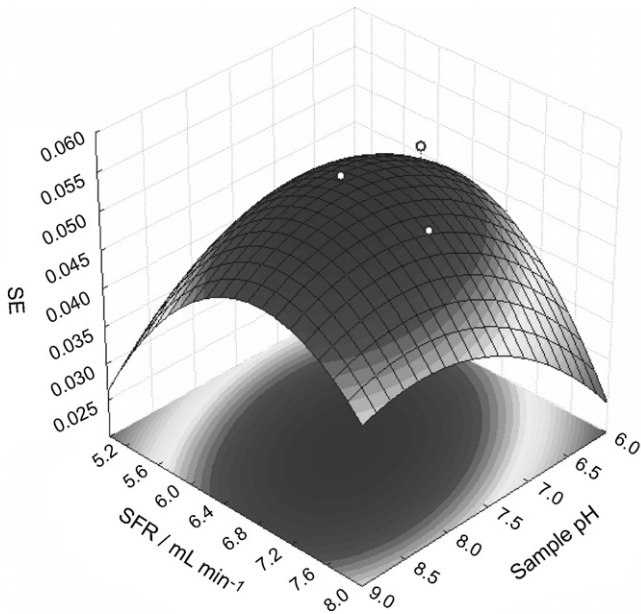


Fig. 3. Response surface for optimization of sample pH and sample flow rate (sample volume 15.0 mL, sample concentration 100.0 $\mu\text{g L}^{-1}$, sorbent mass 100.0 mg, eluent concentration 2.0 mol L^{-1} HNO_3 and eluent flow rate 4.5 mL min^{-1}).

3.3. Optimization of Cr(VI) reducing conditions

A possible retention of Cr(VI) onto $\text{Nb}_2\text{O}_5\text{-SiO}_2$ within the pH range of 6–9 was investigated. As expected, Cr(VI) was not adsorbed. This is because $\text{Nb}_2\text{O}_5\text{-SiO}_2$ has cationic exchange capacity and the Cr(VI) can be present as different anionic species, such as CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- .

The reducing conditions for Cr(VI) were optimized through a response surface methodology using a Doehlert matrix. Reducing agent concentration (sodium sulfite) and reaction time were considered to be the most important factors. Table 4 summarizes the seven experiments required for the Doehlert matrix and their respective analytical responses (peak height). Each solution obtained in the reduction experiments was submitted to the previously optimized Cr(III) preconcentration. The response surface obtained is shown in Fig. 4.

The quadratic equation that describes the response surface (Eq. (7)) and its partial derivative equations (Eqs. (8) and (9)) are described below.

$$\text{Abs} = -0.011 + 0.003 \times \text{RT} + 0.001 \times \text{AC} - 7.6 \times 10^{-5} \times \text{RT}^2 + 9.05 \times 10^{-6} \times \text{RT} \times \text{AC} - 6.204 \times 10^{-6} \times \text{AC}^2 \quad (7)$$

$$\frac{\partial \text{Abs}}{\partial \text{RT}} = 0.003 - 15.27 \times 10^{-5} \times \text{RT} + 9.05 \times 10^{-6} \times \text{RT} = 0 \quad (8)$$

Table 4

Response surface for optimization of reducing agent concentration and reaction time to reduce Cr(VI)

Experiments	Reaction Time (min)	Na_2SO_3 concentration ($\mu\text{mol L}^{-1}$)	Absorbance ^a
1	10	30	0.0459
2	5	60	0.0529
3	10	90	0.0783
4	20	90	0.0909
5	25	60	0.0809
6	20	30	0.0555
7	15	60	0.0744

^a Average.

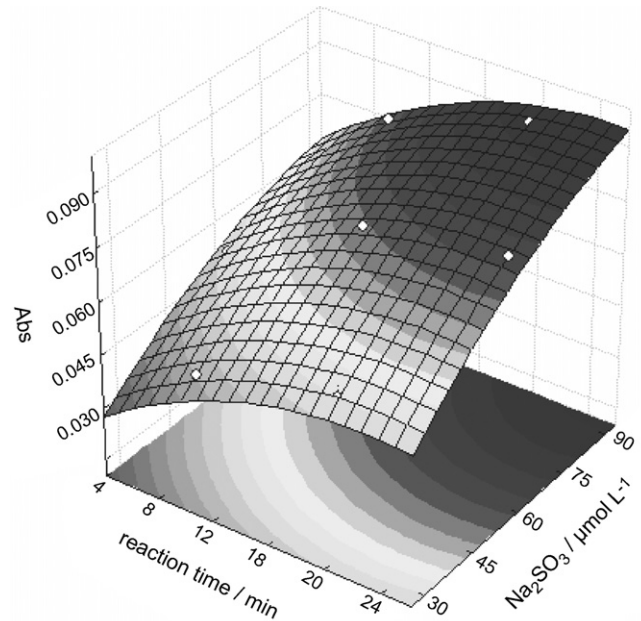


Fig. 4. Response surface for optimization of reducing conditions for Cr(VI) (sample volume 15.0 mL, Cr(VI) concentration 100.0 $\mu\text{g L}^{-1}$, sorbent mass 100.0 mg, eluent concentration 2.0 mol L^{-1} HNO_3 , eluent flow rate 4.5 mL min^{-1} and sample flow rate 6.6 mL min^{-1}).

$$\frac{\partial \text{Abs}}{\partial \text{RT}} = 0.001 + 15.27 \times 10^{-5} \times \text{RT} + 9.05 \times 10^{-6} \times \text{AC} = 0 \quad (9)$$

According to these equations, the maximum analytical signal is reached when a reaction time of 26.5 min and reducing agent concentration of 99.4 $\mu\text{mol L}^{-1}$ are used. For practical reasons, the reaction time and reducing agent concentration used to continue this study were, respectively, 26 min and 100 $\mu\text{mol L}^{-1}$.

3.4. Sample load time

The effect of time on the Cr(III) adsorption rate was investigated in the range of 60–300 s using a sample flow rate of 6.6 mL min^{-1} . As can be seen in Fig. 5, the analytical signal increased linearly with time at a constant sample flow rate. However, an increase in load

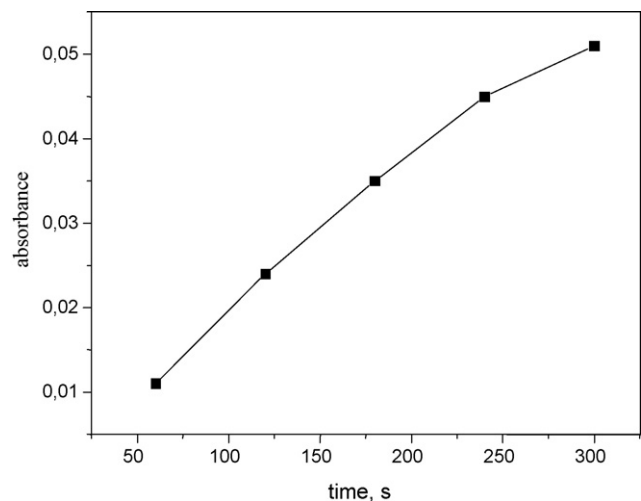


Fig. 5. Effect of the sample load time on the retention of Cr(III) at 30 $\mu\text{g L}^{-1}$. Mini-column contained 100 mg of $\text{Nb}_2\text{O}_5\text{-SiO}_2$, sample flow rate 6.6 mL min^{-1} ; sample pH 8.0 and eluent concentration 2.0 mol L^{-1} .

Table 5
Analytical parameters of merit for the proposed method

Working linear range	1.2–120 $\mu\text{g L}^{-1}$
Correlation coefficient (<i>R</i>)	0.997
Relative standard deviation (RSD) (30 $\mu\text{g L}^{-1}$, <i>n</i> = 7)	4.6% for Cr(III) 5.5% for Cr(VI)
Slope	0.0015 L μg^{-1}
Limit of detection ^b (LOD)	0.34 $\mu\text{g L}^{-1}$
Limit of quantification (LOQ)	1.2 $\mu\text{g L}^{-1}$
Enrichment factor (EF)	23 times
Analytical frequency ^a	15 samples h ⁻¹

^a Taking into consideration only the preconcentration step.

^b Based on a signal to noise ratio of 3 and sample volume of 15 mL.

time reduces the analytical frequency and uses larger volumes of sample. In addition, it is less cost-effective since it requires the use of larger quantities of chemicals. Taking this into consideration, a preconcentration time of 120 s was used in this study.

3.5. Analytical features

The analytical data of interest for the optimized proposed method are summarized in Table 5. The limit of detection (LOD) was calculated as three times the standard deviation of a blank solution (*n* = 10) divided by the slope of the analytical curve obtained with the preconcentration procedure. An enrichment factor of 23 was obtained through the ratio between the slopes of the analytical curves with and without preconcentration. The method precision was determined by submitting 15 mL of sample solution containing 30 $\mu\text{g L}^{-1}$ of Cr(III) and 30 $\mu\text{g L}^{-1}$ of Cr(VI) to the optimized procedure. The analytical curve was also used to assess the sensitivity and linear range of the method. The detection limits obtained in this study are comparable to those found in the literature. Ghaedi et al. obtained detection limits of 0.28 $\mu\text{g L}^{-1}$ [15] and 0.8 $\mu\text{g L}^{-1}$ [16], while Maltez and Carasek [9], Wu et al. [5], Tuzen et al. [4] and Bulut et al. [3] obtained detection limits of 2 $\mu\text{g L}^{-1}$, 0.05 $\mu\text{g L}^{-1}$ (for 100 mL sample), 0.5 $\mu\text{g L}^{-1}$ and 1.28 $\mu\text{g L}^{-1}$, respectively.

3.6. Application of the proposed method to the chromium speciation

The optimized reduction procedure and on-line preconcentration system were used to determine the chromium speciation in water samples collected from a river close to a tanning factory,

Table 6
Cr concentration obtained by the preconcentration of 15 mL water samples through the proposed method

Samples		Spiked ((g L^{-1}))	Found ((g L^{-1}))	Recovery (%)
River water	Cr(III)	0	9.8 ± 1.0	–
		30	39.3 ± 1.3	98
	Cr(VI)	0	1.5 ± 0.1	–
		30	28.1 ± 2.0	94
	Total Cr	0	11.3 ± 0.2	–
	60	67.4 ± 1.5	95	
Tap Water	Cr(III)	0	<LOQ	–
		20	21.0 ± 1.1	105
	Cr(VI)	0	<LOQ	–
		20	18.2 ± 1.8	91
	Total Cr	0	<LOQ	–
	40	39.2 ± 1.4	98	
Well water	Cr(III)	0	<LOQ	–
		30	31.1 ± 0.7	104
	Cr(VI)	0	<LOQ	–
		30	26.9 ± 1.9	90
	Total Cr	0	<LOQ	–
	60	58.0 ± 1.8	97	

Table 7

Concentrations obtained for Cr in certified reference materials analyzed using the preconcentration procedure here developed (*n* = 5)

Samples	Certified ((g L^{-1}))	Found ((g L^{-1}))
NIST 1643e	20.40 ± 0.24	20.10 ± 0.40
NIST 1640	38.6 ± 1.6	37.9 ± 2.0

domestic tap water and well water, all in Florianópolis, Brazil. Recovery tests were performed and two certified reference materials were analyzed in order to check the accuracy of the method. The results are given in Tables 6 and 7, respectively. Good recoveries of between 90 and 105% were obtained for the environmental samples, demonstrating that the method can be successfully applied to these samples. For the certified reference materials, there was good agreement between found and certified values.

4. Conclusions

In this study a new application of silica gel chemically modified with niobium(V) oxide as the sorbent was described for the determination of chromium speciation. The use of a multivariate procedure for optimization of the parameters affecting the preconcentration system, as well as the procedure to reduce Cr(VI), was found to be very efficient, requiring a reduced number of experiments. The procedure to reduce Cr(VI) was relatively simple and fast since only sodium sulfite in acid medium and a reaction time of less than 30 min are required. The instrumentation and method described provided a fast and convenient way to determine chromium speciation in aqueous samples in a simple analytical cycle.

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