

Original Paper

Application of full factorial design for the preconcentration of chromium by solid phase extraction with Amberlyst 36 resin

Erdal Kendüzler¹, Özcan Yalçınkaya², Sıtkı Baytak³, Ali Rehber Türker²

¹ Department of Primary Education, Faculty of Education, Ahi Evran University, Kırşehir, Turkey

² Department of Chemistry, Faculty of Science and Arts, Gazi University, Ankara, Turkey

³ Department of Chemistry, Faculty of Science and Arts, Harran University, Şanlıurfa, Turkey

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Abstract. The preconcentration of chromium(III) by solid phase extraction and its determination from aqueous solutions by flame atomic absorption spectrometry (FAAS) is investigated by applying an experimental design. The optimization of the preconcentration variables such as pH of the sample solution, flow rate of the sample solution and concentration of elution solution was carried out using 2^3 full factorial design. The most important parameter affecting the preconcentration of chromium is the concentration of eluent. In the established experimental conditions, chromium can be determined with a relative standard deviation of 2.0% ($N=7$) for a chromium concentration of $100\ \mu\text{g L}^{-1}$. The detection limit for chromium was $1\ \mu\text{g L}^{-1}$ ($N=20$). The adsorption capacity of Amberlyst 36 is found to be $90.9\ \text{mg g}^{-1}$ for chromium. Effect of other ions on the procedure was also evaluated. The method was validated by the analysis of certified reference materials (tea leaves GBW 07605 and fish tissue IAEA-407). The method was applied to the determination of chromium in waste water, dam water, carrot, parsley and lettuce.

Keywords: Chromium determination; factorial design; water and plant analysis; preconcentration; flame atomic absorption spectrometry

Procedures for the optimization of factors by multivariate techniques have been encouraged, as they are faster, more economical and effective. This optimization can be accomplished using experimental designs appropriate for determining first and second order models. The experimental designs not only determine the influence of the variables to be optimized for the response, but also enable the response function to be obtained and optimized [1]. The use of an experimental design combined with analysis of the variance is much more confident but, surprisingly, is still not extensively used in analytical applications. Multivariate methods involve simultaneous combinations of a number of parameters allowing evaluation of interdependence of variables, influence on response and optimization of these influential factors [2, 3].

In this study, factorial design was used for the optimization of the preconcentration conditions of chromium by solid phase extraction. The element chromium occurs in natural samples in two relatively stable valence states, i.e. in two different oxidation states, Cr(III) and Cr(VI) species, which exert quite different effects on biological systems. In fact, while Cr(III) is an essential component having an important role in the glucose, lipid and protein metabolism, Cr(VI) has a definitely adverse impact on living organism. Cr(VI) can easily penetrate the cell wall and exert its noxious influence in the cell

Correspondence: Ali Rehber Türker, Department of Chemistry, Faculty of Science and Arts, Gazi University, TR-06500 Ankara, Turkey, e-mail: aturker@gazi.edu.tr

itself, being also a source of various cancer diseases [4, 5].

The United State Environmental Protection Agency (USEPA), the European Communities Regulations [6] and World Health Organization (WHO) [7] have regulated the permissible limit of total chromium in drinking water as 100, 50 and $50 \mu\text{g L}^{-1}$, respectively. Therefore, it is very important to determine this element in drinking water and food.

The concentration of chromium in natural waters is very low [8]. In recent years, several methods have been developed for the determination of low concentrations of chromium [9–12]. Within the last decade, ICP-MS has proved ideally suited as an alternative approach for the determination of chromium from various media, however, the cost of instrumentation may be prohibitive to many laboratories. Although FAAS or ETAAS are the most commonly used techniques in the determination of chromium traces, the low level chromium concentration in ordinary aqueous environments is not compatible with the detection limit of FAAS. In order to achieve accurate, reliable and sensitive results, preconcentrations and separations are generally needed when the concentration of analyte elements in the sample are too low to determine directly by FAAS. On the other hand, FAAS is widely applied in routine laboratories due to its lower cost and greater simplicity as compared with ETAAS [13].

Various preconcentration techniques for the determination of chromium have been reported in the literature, including coprecipitation [14], solvent extraction [15], cloud point extraction [16] and solid phase extraction (SPE) [17, 18]. SPE offers a number of important benefits. It reduces solvent usage and exposure, disposal cost and extraction time for sample preparation. Different solid sorbents have been used for separation and preconcentration of chromium, such as Amberlite XAD-16 [19], modified silica [20], alumina [21] and biomass material [17, 22].

In many separation/preconcentration procedures [17–20, 22] either a known amount of chelating agent is added to solution to form the metal chelate or a chelating agent or microorganism is immobilized on a support material of column prior to enrichment procedure. However, in this work, any chelating agent was not used for increasing the enrichment factor and the recovery of analyte. Chromium(III) ions could retain sufficiently on Amberlyst 36 without using chelating agent or microorganism. This resin was firstly used in catalyst reactions of some organic components

[23]. Later, we have first reported the use of this resin as a solid phase extractor for the preconcentration of some metals in various media [24, 25].

In this work, factorial design was used for optimization of the experimental preconcentration variables of chromium. The experimental work was carried out using a 2^3 full factorial design in order to examine the effects of main parameters (pH of solution, flow rate of solution and concentration of elution solution) and their interactions. The proposed procedure was applied for the determination of chromium in dam water, waste water, carrot, parsley and lettuce samples using FAAS.

Experimental

Apparatus

A Philips PU 9285 model flame atomic absorption spectrometer, equipped with a chromium hollow-cathode lamp, a deuterium lamp for background corrector and air-acetylene flame as an atomizer, was used for the determination of chromium. The apparatus run under the conditions suggested by the manufacturer, i.e.: lamp current, 12.0 mA; wavelength, 357.9 nm; bandwidth of the slit, 0.5 nm; acetylene flow rate, 1.4 L min^{-1} [26]. A digital pH meter, Jenway 3010, was used for pH measurements. A Gallenkamp type thermostat shaker was used for adsorption capacity experiments.

Reagents and solutions

All chemicals used were of analytical reagent grade, unless stated otherwise. Aqueous reagents were prepared in triple distilled water. Laboratory glassware was kept overnight in 5% (v/v) nitric acid solution, rinsed with triple distilled water and dried before use. A stock aqueous solution of chromium(III) (1000 mg L^{-1}) was prepared by dissolving 0.7696 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) in 100 mL of water. A working aqueous solution of chromium(III) (10 mg L^{-1}) was also prepared by dilution from the stock solution of 1000 mg L^{-1} . Nitric acid (65%) and hydrochloric acid (37%) were from Merck. Amberlyst 36 (Aldrich) was used after washing with methanol, 1 mol L^{-1} HCl solution and water, respectively, and dried for 4 h at about 60°C .

Optimization strategy

The use of statistical design of experiments is advantageous as it allows one to obtain conditions through a relatively smaller number of systematic experiments. Details of how to achieve reduction of dimensionality in data sets are available in the chemometrical literature [27]. Using a proper design matrix one can obtain a regression equation, which highlights the effect of individual parameters and their relative importance in given operation/process. The interactional effects of two or more variables can also be known, which is not possible in a classical experiment [28].

The principal steps of statistically designed experiments are determination of response variables, factors and factor levels, choice of the experimental design and statistical analysis of the data. In recent years, the most widely used experimental design to estimate main effects, as well as interaction effects, is the 2^n factorial design, where

each variable is investigated at two levels. In this work, a 2^3 factorial design was selected. In this investigation for quantification of the effects of all the variables on the chromium sorption, a two level full factorial design of experiment was adopted. The variables studied are pH of sample solution, flow rate of sample solution and concentration of eluent solution. The number of experiments required for understanding the all effects is given by a^k , where a is the number of levels and k is the number of factors. The two levels assigned to each variable are the allowable limits i.e. the maximum and minimum values set on the basis of preliminary trials. These maximum and minimum levels are expressed in coded form as +1 and -1, respectively, to convert the absolute quantity into a dimensionless quantity convenience in handling the experimental data.

Column preparation

The glass column, having a stopcock and a tank of 250 mL, was 15 cm length and 0.8 cm internal diameter. A small amount of glass wool was placed at one end of the column in order to hold resin. 0.5 g dried resin was placed. Then, another small glass wool plug was inserted onto the tap of the resin. The bed height of the resin in the column was approximately 1.5 cm. It was washed successively with water, methanol and 1 mol L^{-1} hydrochloric acid, respectively. After each use, the resin in the column was washed with 2 mL of 6 mol L^{-1} HNO_3 and triply distilled water and stored in water for the next experiment.

Dissolution of CRMs

A portion (1.5 g) of standard reference tea leaves (GBW-07605, National Research Centre for Certified Reference Materials) and fish tissue (IAEA-407, International Atomic Energy Agency) was taken in a 250 mL PTFE beaker. For dissolution, a minimal volume of 5 mL of 1 mol L^{-1} nitric acid was added to moisten the sample thoroughly, followed by 10 mL of concentrated nitric acid. The beaker was heated on a hot plate at about $130 \pm 10^\circ\text{C}$ for 3 h. After cooling to room temperature, 10 mL perchloric acid was added drop wise. The beaker was heated to near dryness. This process was repeated twice. The resulting solution was transferred into 100 mL volumetric flask by washing the interior of beaker with small portions of 1 mol L^{-1} nitric acid, and diluted to the mark with triple distilled water.

Collection and preparation of samples

Carrot, parsley and lettuce samples were collected from a local market in the city of Şanlıurfa, Turkey. Firstly, the samples were cleaned with tap water and double distilled water, respectively. Then, the samples were dried at about 110°C for 24 h. Dried vegetable samples (0.5 g) were dissolved according to the procedure given above for tea leaves and fish tissue by using 5 mL of concentrated nitric acid and 5 mL of perchloric acid.

The surface dam water sample was collected from Atatürk Dam, Şanlıurfa, waste water sample was collected from Şanlıurfa, Turkey.

The water samples were filtered through a Millipore cellulose nitrate membrane of pore size $0.45 \mu\text{m}$ to remove the particulate matters. The water samples were acidified with 1.0 mL of concentrated hydrochloric acid per liter of sample.

In addition, ascorbic acid was added to real sample solutions to reduce the chromium ions in higher oxidation states to chromium(III). Finally, the general preconcentration procedure was applied.

Preconcentration and determination procedure

An aliquot of a solution (50 mL) containing $5 \mu\text{g}$ of the chromium(III) was placed in a beaker and adjusted to desired pH by using HCl and NH_3 solution. The column was preconditioned by passing the solution of working pH through the column and then, the solution was passed through the column. The adsorbed chromium(III) ion on the column was eluted into a 5 mL calibrated flask. The eluent was analyzed for the determination of chromium concentration by FAAS. Using the procedure described above, the recovery of the chromium was calculated from the ratio of the concentration found by FAAS and the concentration calculated theoretically.

Results and discussion

Statistical analysis

In order to examine the main factors and their interactions for the chromium preconcentration by adsorption, a factorial of the type 2^3 has been used. The experimental design involved 3 variables at 2 levels (i.e. low and high). In this case the total number of experiments becomes 8, but totally 16 experiments were performed, because each experiment was done two times. The variables and levels for the study are given in Table 1. The higher level variable was designated as +1, and the lower level as -1. These levels were chosen as input parameters to examine the analyte in subsequent experiment.

In Table 1, x_1 , x_2 and x_3 represent the level of pH of sample solution, flow rate of sample solution and the concentration of eluent solution, respectively, and X_1 , X_2 and X_3 are the corresponding values in coded forms.

The regression equation for the matrix is represented by the following expression [28].

$$R_i = b_0 + b_1X_{1i} + b_2X_{2i} + b_3X_{3i} + b_{12}X_{1i}X_{2i} + b_{13}X_{1i}X_{3i} + b_{23}X_{2i}X_{3i} + b_{123}X_{1i}X_{2i}X_{3i} \quad (1)$$

Table 1. Actual and corresponding coded values of parameters in 2^3 full factorial design for chromium preconcentration

Level of variables	pH of sample solution		Flow rate of sample solution (mL min^{-1})		Concentration of eluent solution (HNO_3 , mol L^{-1})	
	Actual (x_1)	Coded (X_1)	Actual (x_2)	Coded (X_2)	Actual (x_3)	Coded (X_3)
Low level	2	-	1	-	2	-
High level	4	+	5	+	4	+

Table 2. Design of trial runs (in coded form) for chromium preconcentration in two replicate experiments and calculated value of recovery of chromium

Trial No.	X_1	X_2	X_3	$X_1 X_2$	$X_1 X_3$	$X_2 X_3$	$X_1 X_2 X_3$	R (%)	R (%)	R_{average} (%)	$R_{\text{calculated}}$ (%)
1	-	-	-	+	+	+	-	48.5	44.0	46.3	46.2
2	+	-	-	-	-	+	+	45.5	42.3	43.9	43.9
3	-	+	-	-	+	-	+	49.3	50.9	50.1	50.1
4	+	+	-	+	-	-	-	53.5	58.7	56.1	56.1
5	-	-	+	+	-	-	+	90.9	88.5	89.7	89.7
6	+	-	+	-	+	-	-	85.0	87.1	86.1	86.0
7	-	+	+	-	-	+	-	90.8	92.9	91.9	91.8
8	+	+	+	+	+	+	+	91.1	91.8	91.5	91.4

The main and interaction coefficient have been calculated by the following equations.

$$b_0 = \sum \frac{R_i}{N} \quad (2)$$

$$b_j = \sum \frac{X_{ji} R_i}{N} \quad (3)$$

$$b_{nj} = \sum \frac{(X_{nj} X_{ji}) R_i}{N} \quad (4)$$

where R_i is the response (recovery of chromium); X_{ji} values ($j = 1, 2, 3; i = 1, 2, 3, \dots, 16$) represent the corresponding parameters in their coded forms; The design matrix and the results showing recovery of chromium are shown in Table 2. The values of the regression coefficients were determined.

The values of these coefficients were incorporated in Eq. (1), which takes the following form:

$$R = 69.4 - 0.05X_1 + 2.95X_2 + 20.34X_3 + 1.45X_1X_2 - 0.96X_1X_3 - 1.06X_2X_3 - 0.64X_1X_2X_3 \quad (5)$$

The effect of individual variables and inter-actional effects can be estimated from the above equation. In this equation, it can be seen that: (1) pH has a negative effect, while flow rate of the solution and concentration of the eluent solution have a positive effect; (2) concentration of eluent is the factor more significant for preconcentration procedure; (3) the chromium recovery slowly increases with the decreases of pH and increases flow rate.

The three studied variables have to be operated at lowest level of pH and highest level of flow rate of sample solution and concentration of eluent, (-, +, +). Thus, the two-level factorial design indicates that optimum values of pH of the sample solution, flow rate of the sample solution and eluent concentration to develop SPE procedure operation are 2.5 mL min^{-1} and $4 \text{ mol L}^{-1} \text{ HNO}_3$, respectively, for attain highest recoveries. But quantitative recoveries (>95%) were

not obtained under these conditions. Because the concentration of eluent is the factor more significant for preconcentration procedure, in order to choose a proper concentration of eluent for the elution of retained chromium, concentrations of 5 and $6 \text{ mol L}^{-1} \text{ HNO}_3$ were also examined. 5 mL of $6 \text{ mol L}^{-1} \text{ HNO}_3$ solution was found to be satisfactory (quantitative recovery >95%) for desorption. Therefore, the concentration of 6 mol L^{-1} of eluent was used for further studies.

Table 2 shows the experimental and calculated values of recovery of chromium. Since the differences between the experimental and calculated values of recovery of chromium are negligible, it can be said that the regression equation is adequate.

Variance of every factor and the sequence of importance of the factors were determined by the Fisher test (F -test) method [28]. Using F -test, not only effects and interactions without meaning can be eliminated, but the ones that have more influence on the recovery of chromium procedure can also be verified. Comparing the calculated F values with Fisher's F value [$F_{0.01}(1,8) = 11.26$] for probability levels of 1%, it can be verified that, the most important parameter affecting the preconcentration chromium is concentration of eluent, which is followed by flow rate of the sample solution (Table 3).

Table 3. F ratios and decisions according to analysis of variance

Source of variation	F ratio	Decision
X_1	0.009	not effective
X_2	30.13	effective
X_3	1408.05	effective
$X_1 X_2$	7.16	not effective
$X_1 X_3$	3.15	not effective
$X_2 X_3$	3.84	not effective
$X_1 X_2 X_3$	1.38	not effective

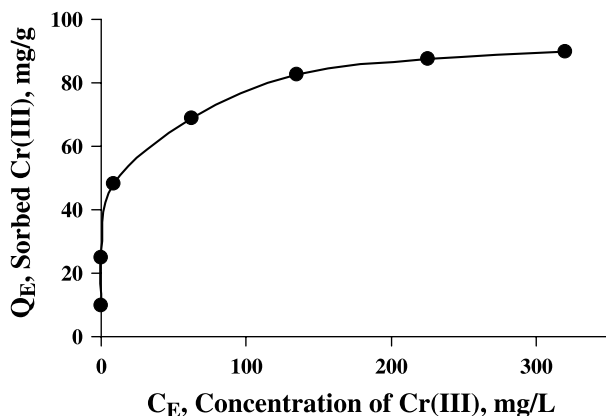


Fig. 1. Adsorption isotherm of Amberlyst 36 resin for chromium(III) at pH 2 in batch procedure

Adsorption isotherm and adsorption capacity

The adsorption isotherm of the chromium onto resin was also investigated by the batch technique described in Ref. [24] by employing the following experimental conditions: amount of resin, 100 mg; pH of the solution, 2; volume of sample solution, 50 mL; chromium concentration, 20–500 mg L⁻¹. The data obtained from the adsorption of chromium on the solution showed that a contact time of 60 min was sufficient to achieve equilibrium and the adsorption did not change with further increase in contact time. The adsorption behavior of Amberlyst 36 was determined by studying the amount of adsorbed chromium as a function of chromium concentration at pH 2. The profile of the adsorption isotherm of the resin for chromium is shown in Fig. 1, representing the amounts of adsorbed chromium versus the chromium concentration of the supernatant under equilibrium conditions. In Fig. 1, the graph shows an excellent fit to the data in the concentration interval studied in all cases for the Langmuir model.

The capacity value was calculated from the slope of the graph derived from the plot of the ratio of chromium concentration in solution (C_E , mg L⁻¹) to the amount of chromium in solid (Q_E , mg g⁻¹) at equilibrium vs. the concentration of chromium in solution. The obtained graph equation is $y = 0.0110x + 0.0832$ ($r^2 = 0.9969$), where, y is C_E/Q_E in g/L and x is C_E in mg/L. The value of adsorption capacity of Amberlyst 36 is found to be 90.9 mg g⁻¹ for chromium.

Influence of interfering species

The effects of potential interferences occurring in drinking water samples on the determination of chromium

Table 4. The effect of some ions on the recovery of chromium (pH, 2; eluent, 5 mL of 6 mol L⁻¹ HNO₃; flow rate of the sample solution, 5 mL min⁻¹; sample volume, 50 mL; amount of the chromium, 5 µg)

Interfering ions	Concentration (mg L ⁻¹)	R^a (%)	Interfering ions	Concentration (mg L ⁻¹)	R^a (%)
Na^+	1	102	K^+	1	98
	5	101		5	98
	25	98		25	96
	100	99		100	95
Mg^{2+}	1	96	Ca^{2+}	1	100
	5	100		5	103
	25	101		25	100
	100	97		100	98
Al^{3+}	1	99	Fe^{3+}	1	99
	5	102		5	95
	25	103		25	95
Zn^{2+}	1	101	Cd^{2+}	1	101
	5	97		5	101
	25	95		25	100
Cu^{2+}	1	98	Mn^{2+}	1	100
	5	98		5	95
	25	96		25	99

^a Mean of three replicates.

were investigated using the optimized preconcentration procedure. Metal ions were added individually to 50 mL of model solution containing 5 µg of chromium as their nitrate or chloride salts and the general preconcentration procedure was applied. The experimental results were given in Table 4. Results show that there is no interferences arise from tested cations. The procedure is suitable for the separation and preconcentration of chromium in the real samples examined in the present study, because the levels of alkaline, alkaline earth and transition metals in these samples are lower than their tested concentrations.

Analytical performance of the method

The precision of the column-SPE method evaluated as the standard deviation of recovery obtained from seven replicates under the optimum experimental conditions (amount of chromium, 5 µg; volume of solution, 50 mL; pH, 2; elution solution, 5 mL of 6 mol L⁻¹ HNO₃ solution; flow rate, 5 mL min⁻¹) was 2.0%. The mean recovery of seven replicates was 99 ± 2% at 95% confidence level.

By using direct aspiration without the preconcentration step in FAAS applying the preconcentration system the linear range for chromium determination was between 0.2 and 4.0 µg mL⁻¹. The calibration equa-

tion of chromium was $A = 0.0544 C + 0.0063$, where C is the chromium concentration in $\mu\text{g mL}^{-1}$, and A is the absorbance. Calibration equation calculations are based on the average of triplicate readings for each standard solution.

The limit of detection (LOD) of the proposed method for chromium has been studied under the optimized conditions. In order to determine the instrumental detection limit, 50 mL of blank solution was adjusted to pH 2 and then, this solution was passed through the column. Blank solution was prepared by adding a minimum amount of chromium to the dam water in order to obtain readable chromium signal. The column was washed by 50 mL of $6 \text{ mol L}^{-1} \text{ HNO}_3$ solution (there is no preconcentration). The instrumental detection limit based on mean of blank values plus three-times the standard deviation of the blank values was found to be $49 \mu\text{g L}^{-1}$ for chromium ($N=20$). The highest experimental preconcentration factor used for this method was 50, considering real water sample volumes of 250 mL and eluent volume of 5 mL. The analytical detection limit calculated by dividing the instrumental detection limit by the preconcentration factor (50) was $1 \mu\text{g L}^{-1}$ [24].

Validation of the method

The accuracy of the results was verified by analyzing the standard reference materials, tea leaves (GBW 07605) and fish tissue (IAEA-407). It was found that there is no significant difference between the results found by the proposed method ($0.73 \pm 0.06 \mu\text{g g}^{-1}$ for tea leaves, $0.69 \pm 0.05 \mu\text{g g}^{-1}$ for fish tissue) as the mean of five determinations at 95% confidence level and the certified values ($0.80 \mu\text{g g}^{-1}$ for tea leaves, $0.73 \mu\text{g g}^{-1}$ for fish tissue) according to the t -test. It can be concluded that there is no systematic error in the determination at 95% confidence level (the relative errors are below than 10%).

Application

The proposed preconcentration method was applied for the determination of chromium in dam water, waste water, carrot, parsley and lettuce samples under optimal experimental conditions. The accuracy of the method was also checked by measuring the recovery of spiked samples (Table 5). Relative errors, below 7%, demonstrate the applicability of the method and indicate that the proposed method is essentially free

Table 5. Determination of total chromium in water and food samples (volume of water samples: 250 mL)

Sample	Added	Found ^a $\bar{x} \pm \frac{fs}{\sqrt{N}}$	Relative error (%)
Dam water	–	$38.0 \pm 0.9 \mu\text{g L}^{-1}$	–
	$20.0 \mu\text{g L}^{-1}$	$54 \pm 2 \mu\text{g L}^{-1}$	–7
Waste water	–	$66 \pm 1 \mu\text{g L}^{-1}$	–
	$20.0 \mu\text{g L}^{-1}$	$82 \pm 2 \mu\text{g L}^{-1}$	–5
Carrot	–	$11 \pm 1 \mu\text{g g}^{-1}$	–
	$20 \mu\text{g g}^{-1}$	$30 \pm 2 \mu\text{g g}^{-1}$	–3
Parsley	–	$17 \pm 2 \mu\text{g g}^{-1}$	–
	$20 \mu\text{g g}^{-1}$	$35 \pm 2 \mu\text{g g}^{-1}$	–5
Lettuce	–	$12 \pm 1 \mu\text{g g}^{-1}$	–
	$20 \mu\text{g g}^{-1}$	$31 \pm 1 \mu\text{g g}^{-1}$	–3

^a Mean of five determinations at 95% confidence level.

from interferences when applied to the analysis of waters and vegetables.

Conclusion

Application of factorial design allowed the optimization of a procedure for the determination of chromium by FAAS, based on SPE, using a smaller number of experiments. When the factorial design is used, time savings are about 20% by considering total duration time of experiments and about 70% by considering the duration time of optimization steps by comparison with the classical optimization procedure without factorial design. The main advantages of the method over the many other solid-phase preconcentrated method are permitting to study in acidic medium and not requiring the chelating agent. Lower pH values are generally preferred for analysing real samples, because real samples (geological, biological, etc.) are dissolved generally with acids and there is no precipitation risk of sample components. The enrichment factor (50) and the adsorption capacity of this resin (90.9 mg g^{-1}) for chromium are satisfactory for analytical purposes.

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