*Article*

# Speciation and Preconcentration of Chromium from Water and Food Samples by Synthesized Chelating Resin

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A resina poli(ácido *N*,*N*'-dipropionitrila metacrilamida-*co*-divinilbenzeno-*co*-2-acrilamida-2-metil-1-propanosulfonico) foi sintetizada com um novo adsorvente quelante para especiação de cromo em amostras de água e alimento por espectrometria de absorção atômica com chama (FAAS). A resina foi caracterizada por espectroscopia no infravermelho por transformada de Fourier (FTIR), análise elementar, microscopia eletrônica de varredura (SEM) e análise termogravimétrica (TGA). Os efeitos do pH, concentração da solução eluente, vazão e volume de amostra e íons interferentes na recuperação de Cr(III) foram investigados. A capacidade de sorção da resina foi 12,1 mg g$^{-1}$ para Cr(III). Elevado fator de pre-concentração (150) e baixo desvio padrão relativo (2,0%, n = 10) foram obtidos. O limite de detecção do método foi 1,11 µg L$^{-1}$. A validação do método foi realizada pelas análises de materiais de referencia de padrão certificado (TMDA-70 água de lago adulterada e SRM 1568a farinha de arroz) e de amostras adulteradas de água e alimento. O método desenvolvido foi aplicado na determinação de cromo em várias amostras de água e alimentos.

The poly(*N*,*N*'-dipropionitrile methacrylamide-*co*-divinylbenzene-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid) resin was synthesized as a new chelating adsorbent for speciation of chromium in water and food samples by flame atomic absorption spectrometry (FAAS). The resin was characterized using Fourier transform infrared spectroscopy (FTIR), elemental analysis, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Effects of pH, concentration of elution solution, sample flow rate, sample volume and interfering ions on the recovery of Cr(III) were investigated. The sorption capacity of the resin was found to be 12.1 mg g$^{-1}$ for Cr(III). A high preconcentration factor (150) and low relative standard deviation (2.0%, n = 10) were obtained. The limit of detection of the method was 1.11 µg L$^{-1}$. The method validation was performed by analyzing certified standard reference materials (TMDA-70 lake water and SRM 1568a rice flour) and spiked water and food samples. The developed method was applied to the determination of the chromium in various water and food samples.

**Keywords:** speciation, chelating resin, chromium, water, food, flame atomic absorption spectrometry

## Introduction

Speciation analysis of an element yields information on the individual concentrations of the various chemical forms of that element in environmental samples. The importance of chromium speciation is related with the toxicity and reactivity of their chemical form or oxidation state.[1,2] Two stable chromium species are known in the environment: Cr(III) and Cr(VI). Cr(III) appears to be essential for the mammals, and together with insulin, they are responsible for removing the glucose from the bloodstream. On contrary, the hexavalent chromium has toxic and carcinogenic effects. The toxic nature of the Cr(VI) ions is attributed to their high oxidation potential and their relatively small size, which enables them to penetrate through biological cell membranes.[3-5] Chromium is widely used in various industries, such as plating, tanning, paint and pigment production and metallurgy, which possibly contaminate the environment. Speciation analysis of trace amounts of Cr(III) and Cr(VI) ions has become an important topic in environmental and biological sciences.[6] Therefore, the knowledge on the speciation of chromium is of particular necessity.

The speciation analysis of chromium is carried out by separation and determination of the different chromium

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species and then by the determination of total chromium. Coprecipitation,[7,8] solvent extraction,[3] ion exchange,[9-11] cloud point extraction[12-14] and solid phase extraction[15-17] have been developed in order to determine the different chromium species by using various techniques such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

Solid phase extraction (SPE) is one of the widely utilized techniques for the separation and preconcentration of metal ions due to its simplicity, selectivity, flexibility, low cost, safety, ease of automation and high preconcentration factor. The adsorption materials play an important role in SPE process. Hence, the preparation of new materials for selective solid phase extraction of analytes is an important trend of solid phase extraction.[18-20] Chelating resins are superior in selectivity to solvent extraction and ion exchange due to their triple function of ion exchange, chelate formation and physical adsorption. Many researches are concentrated on metal ion recovery using chelating polymers because they are reusable and have higher adsorption capacities as well as high selectivity to some metal ions.[21-23]

In the present study, poly[*N,N'*-dipropionitrile methacrylamide (DPMAAm)-*co*-divinylbenzene (DVB)-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS)] resin (poly(DPMAAm-*co*-DVB-co-AMPS) resin) was synthesized and used for the speciation of chromium in various samples. Cr(III) was separated from Cr(VI) and preconcentrated by using a column containing chelating resin. Total chromium was determined after reducing Cr(VI) to Cr(III). The concentration of Cr(VI) was found by subtracting the Cr(III) concentration from the total Cr concentration. Factors affecting the separation and preconcentration of Cr such as pH of the sample, concentration of eluting reagent, flow rate, sample volume, adsorption capacity and matrix components were investigated.

## Experimental

### Instrument

Spectrometric measurements were carried out with a PerkinElmer AAnalyst 800 model flame atomic absorption spectrometry (Waltham, MA, USA) equipped with hollow cathode lamp operated at 25 mA. The wavelength and spectral band pass were set at 357.9 and 0.7 nm, respectively. A 10 cm long slot burner head and an air-acetylene flame were used. Acetylene/air flow rate

was $2.0/17$ L min$^{-1}$. The pH measurements were carried by using a WTW pH315i apparatus equipped with combined pH electrode. The Fourier transform infrared spectra (FTIR) of the resin were recorded on a PerkinElmer Spectrum 400 FTIR spectrometer (Waltham, MA, USA). Elemental analyses were carried out by a Leco CHNSO-932 auto microanalyzer (St. Joseph, MI, USA). The microstructure of the polymer was examined by a Leo 440 model scanning electron microscopy (SEM). Thermal data were obtained by using a Perkin Elmer Diamond TGA-DTA thermobalance in $N_2$ atmosphere.

### Reagents and solutions

All chemicals were of analytical reagent grade. Stock solutions (1000 mg L$^{-1}$) of Cr(III) and Cr(VI) were prepared by dissolving appropriate amounts of Cr(NO$_3$)$_3$.9H$_2$O (Merck, Darmstadt, Germany) and K$_2$CrO$_4$ (Merck) in 1 mol L$^{-1}$ HNO$_3$, respectively. The working solutions were prepared by dilution of the stock solutions immediately prior to their use. For the preparation of pH 1 and pH 2 solutions, diluted HCl and diluted NaOH solutions were used. The other pH adjustments were made by the use of buffer solutions. Buffer solutions were prepared by using 1 mol L$^{-1}$ acetic acid-sodium hydroxide (pH 3-6) and 1 mol L$^{-1}$ ammonia-hydrochloric acid (pH 8). 3,3'-Iminodipropionitrile (Aldrich) and methacryloyl chloride (Alfa Easer, MA, USA) were used as received. *N,N'*-Dipropionitrile methacrylamide was synthesized according to the literature.[24] 2,2'-Azobisisobutyronitrile (AIBN) (Merck) was purified by successive crystallizations from chloroform-methanol mixture. The crosslinker divinylbenzene (Merck) was used as received. 2-Acrylamido-2-methyl-1-propanesulfonic acid (Merck, 99%) was used without further purification. A glass column (100 mm length and 10 mm i.d.) with a glass wool over its stopcock was used throughout all the study. A total of 900 mg of chelating resin was placed into the column and washed thoroughly with distilled-deionized water. The column was preconditioned by the buffer solution having the same pH with the sample solution prior to use.

### Synthesis of *N,N'*-dipropionitrile methacrylamide (DPMAAm) monomer

Triethylamine (180 mmol), 3,3'-iminodipropionitrile (60 mmol) and acetone (200 mmol) were placed in a three-necked flask equipped with magnetic stirrer, reflux condenser and dropping funnel and the contents were cooled to approximately 0 °C. Methacryloyl chloride (60 mmol) was added dropwise from dropping funnel with
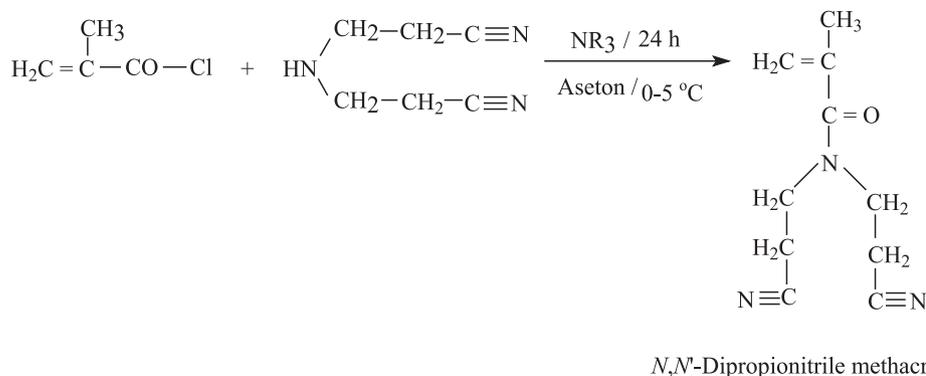
*N,N'*-Dipropionitrile methacrylamide

**Figure 1.** Synthesis of *N,N'*-dipropionitrile methacrylamide monomer.

constant stirring, purged with nitrogen gas for 30 min and the system was closed. This mixture was stirred for 3 h at approximately 0 °C in an ice bath. The product, quaternary ammonium salt, was washed with distilled water, extracted with chloroform, dried over anhydrous sodium sulfate and the solvent was evaporated in vacuum. The resultant monomer was obtained and recrystallized from ethanol as a yellow powder (yield: 75%). The reaction scheme of the monomer is shown in Figure 1.

### Synthesis of chelating resin

The preparation of poly(DPMAAm-*co*-DVB-*co*-AMPS) resin was carried out with a radical initiator in dimethylformamide solution. To a polymerization flask, the two appropriate monomers, DPMAAm (1.09 g, 6.0 mmol) and AMPS (0.41 g, 2.0 mmol), the crosslinking

reagent, DVB (0.26 g, 2.0 mmol), and the initiator, AIBN (0.018 g, 0.1 mmol), were added. The system was kept under $N_2$ for 3 h at 70 ± 1 °C. Subsequently, the resin was filtered, washed with abundant diethylether and dried under vacuum at 50 °C until a constant weight was obtained. The conversion of monomer to polymer resin was gravimetrically determined (yield: 80%). The structure of the chelating resin is shown in Figure 2.

### Characterization of chelating resin

Characterization of poly(DPMAAm-*co*-DVB-*co*-AMPS) resin was carried out as described below.

### Elemental analysis

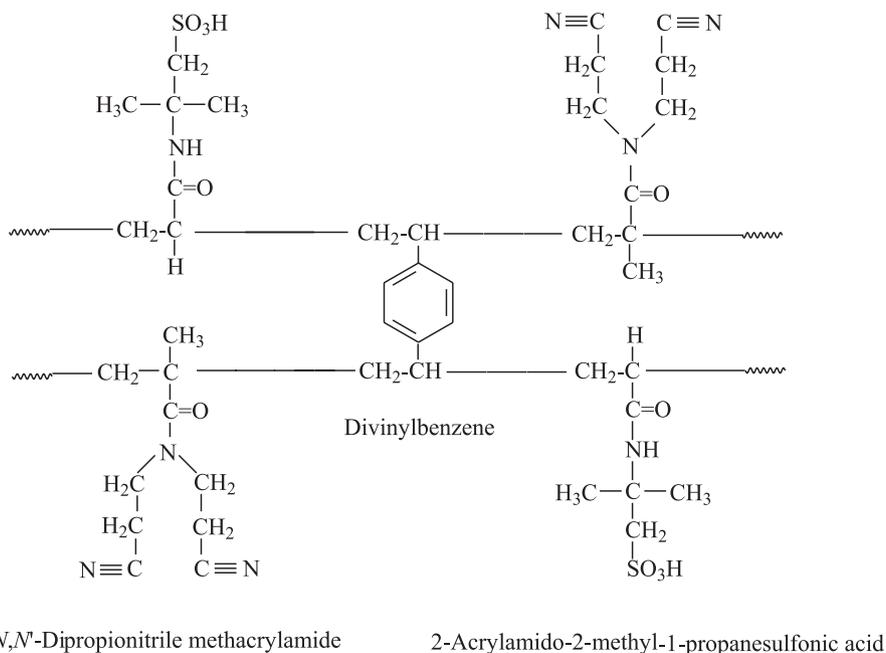The elemental analysis results of the poly(DPMAAm-*co*-DVB-*co*-AMPS) resin are as follows: found (%): C,



*N,N'*-Dipropionitrile methacrylamide          2-Acrylamido-2-methyl-1-propanesulfonic acid

**Figure 2.** The structure of the poly(DPMAAm-*co*-DVB-*co*-AMPS) resin.

61.36; H, 6.98; O, 14.52; N, 10.76; S, 6.38; calculated (%): C, 61.55; H, 6.95; O, 14.44; N, 10.81; S, 6.25. The results showed that there is a good agreement between experimental and theoretical values.

### FTIR spectra

The FTIR spectrum of chelating resin shows a small band at 3320 cm$^{-1}$ which is attributed to $\nu_{NH}$. The peak at 3050 cm$^{-1}$ corresponds to the C−H stretching of the aromatic ring. The asymmetrical and symmetrical C-H stretching due to the methylene and methyl groups are observed at 2980 and 2860 cm$^{-1}$, respectively. In the FTIR spectrum of resin, a small band at 2245 cm$^{-1}$ for the C≡N group is clearly seen. The absorption at 1651 cm$^{-1}$ can be assigned for a complex stretching vibrations of N−C=O. The ring breathing vibrations of the aromatic nuclei are observed at 1600, 1538 and 1480 cm$^{-1}$. The broad band at 1446 cm$^{-1}$ is due to the C−N scissoring vibration of the –N−C=O group. The asymmetrical and symmetrical bending vibrations of methyl groups are seen at 1380 and 1365 cm$^{-1}$, respectively. A strong band at 1034 cm$^{-1}$ is attributed to $\nu_{SO}$. The C−H and C=C out of plane bending vibrations of the aromatic ring nuclei of DVB are observed at 799 and 623 cm$^{-1}$, respectively.

### Morphology of polymer

Scanning electron microscopy (SEM) image of poly(DPMAAm-*co*-DVB-*co*-AMPS) resin is given in Figure 3. The resin has the morphology with standard cauliflower structure. SEM micrograph of resin reveals big droplets whereas it is cauliflower-like structure in pristine polymers. Microscopic observation suggests that the resin was immersed in a partially haematic exudate. SEM revealed an existence of organized fibrin clot, matrix which is usually evident AMPS and DPMAAm unit after implant. Platelet adhesion and aggregation involved the whole gel surface.
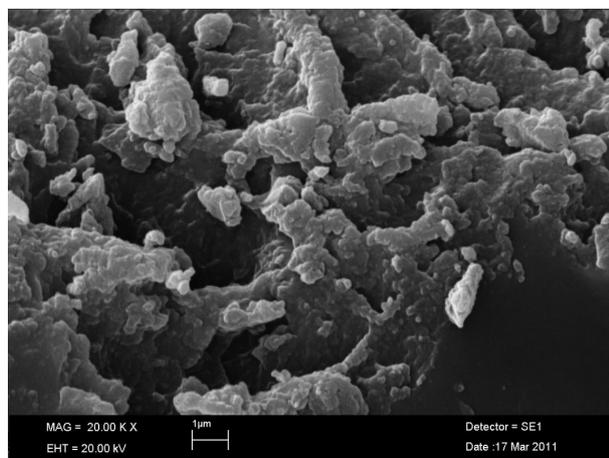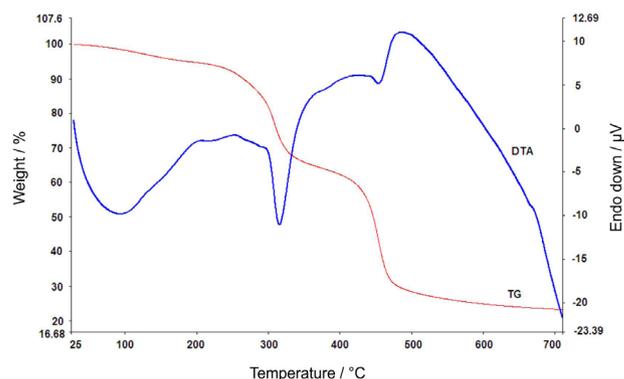


**Figure 3.** SEM image of poly(DPMAAm-*co*-DVB-*co*-AMPS) resin.

A few eritrocytes and leukocytes were detected in limited areas of the samples. Monocytes, macrophages, and/or fibroblasts from fibrotic tissue of the surrounding cage were absent. Interestingly, the presence of neoangiogenesis was evident only in the capsule surrounding the Hyal cage.

### Thermogravimetric analysis

The TGA-DTA curves of poly(DPMAAm-*co*-DVB-*co*-AMPS) resin are given in Figure 4. The first weight loss region appears around 100-200 °C associated with dehydration of partially degradated of amide groups. The initial degradation temperature and 73% weight loss of resin were found to be 215 and 700 °C, respectively. Thermal degradation of resin was formed by three steps. The weight loss of the first step was found to be 30% between 215-350 °C. The weight loss of the second step was found to be 34% between 350-480 °C. The weight loss of the third step was found to be 9% between 480-700 °C.



**Figure 4.** TGA-DTA curves of poly(DPMAAm-*co*-DVB-*co*-AMPS) resin.

### Recommended procedure

An aliquot of 25 mL of solution containing 40 µg Cr(III) was used for the optimization of column separation and preconcentration. The pH of the solution was adjusted to the desired value (pH 2). The column was preconditioned by passing pH 2 solution and the resulting solution was passed through the column at a flow rate of 6 mL min$^{-1}$. The retained Cr(III) was eluted with 10 mL of 1.5 mol L$^{-1}$ HCl. The chromium in the eluate was determined by FAAS.

### Determination of total chromium

Total chromium was determined as Cr(III) by the method described above after reducing Cr(VI) to Cr(III). The reduction of Cr(VI) to Cr(III) was performed by the procedure in the literature.[4,25] 2 mL of 2 mol L$^{-1}$ HCl and then 1 mL of 5% (m/v) hydroxylamine hydrochloride were added to 80 mL of sample solution containing 40 µg Cr(III) and 40 µg Cr(VI), respectively. The solution was left at room temperature for 45 min. After the reduction of

Cr(VI) to Cr(III), the pH was adjusted to 2 and the volume of the solution made up to 100 mL with distilled-deionized water. The preconcentration procedure was applied and total chromium was determined by FAAS. The concentration of Cr(VI) was calculated by subtracting the concentration of Cr(III) from total chromium concentration.

## Sample preparation

The tap water from our research laboratory, river water from Yeşilırmak River (Amasya, Turkey), well water from Kayseri city (Turkey) and two waste water samples from plating plants in Kayseri Organized Industrial Region (Turkey) were collected in pre-washed polyethylene bottles. The samples (except for tap water) were filtered through a Millipore cellulose membrane filter with 0.45 μm of pore size. The pH of the water samples was adjusted to pH 2 by using diluted HCl and diluted NaOH solutions and the developed method was applied.

The food samples (apple, parsley, wheat, marrow and quince) were purchased from a local market in Kayseri city, washed thoroughly with tap water followed by distilled water and dried at 100 ℃. 0.20 g of the rice flour (SRM 1568a) and 0.50 g of the food samples were placed in a 100 mL beaker, and 10 mL of concentrated $HNO_3$ was added to the beaker. The mixture was evaporated near to dryness on a hot plate at about 130 ℃. After cooling to room temperature, 3 mL of concentrated hydrogen peroxide were added. The mixture was again evaporated to dryness. The resulting solution was diluted to 25 mL with distilled-deionized water and the described method was applied.

## Results and Discussion

### Effect of pH

The pH plays an important role on the metal complex formation and subsequent extraction. The effect of pH on the solid phase extraction efficiency of Cr(III) and Cr(VI) was investigated separately. The pH of model solutions containing one of the chromium species (40 μg Cr(III) or 40 μg Cr(VI)) was adjusted in the range of 1-8 and passed through the column. The retained ions were eluted by 10 mL of 2 mol $L^{-1}$ $HNO_3$ and determined by FAAS. The results are shown in Figure 5. It can be seen that the extraction was quantitative (recovery $\geq 95\%$) for Cr(III) in the pH range of 1.0-3.0 and the recovery of Cr(VI) was negligible in this pH range. In this case, it is possible to separate Cr(III) from Cr(VI) by checking the pH of the solution. pH 2 was selected for subsequent works. The recovery for Cr(VI) at this pH was 8%. The adsorption efficiency for Cr(III) at the

higher pH values was gradually decreased due to increase in the precipitation of Cr(III) ions in the form of hydroxyl complexes. Similar curve for Cr(III) and Cr(VI) was also found in our previous work.[4]
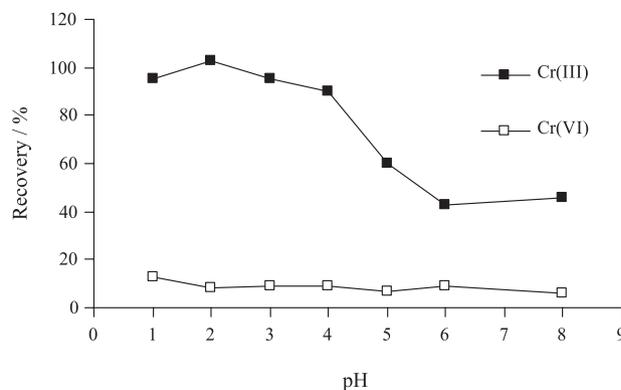


**Figure 5.** Recoveries of Cr(III) and Cr(VI) on chelating resin as a function of pH (40 μg Cr(III) and 40 μg Cr(VI), eluent: 10 mL of 2 mol $L^{-1}$ $HNO_3$, resin amount: 0.90 g, n = 3).

### Effect of concentrations of eluting reagents

The elution of Cr(III) from chelating resin by $HNO_3$ and HCl at different concentrations (0.5-2 mol $L^{-1}$) was investigated. The recovery values for Cr(III) were found to be quantitative for 10 mL of 1.5 mol $L^{-1}$ HCl, 10 mL of 2.0 mol $L^{-1}$ HCl and 10 mL of 2.0 mol $L^{-1}$ $HNO_3$ eluents. 10 mL of 1.5 mol $L^{-1}$ HCl were chosen as eluent in subsequent studies due to the low acid concentration. In addition, the elution of Cr(III) ions with HCl is an advantage that, chloride ion is an acceptable matrix for the AAS techniques.[17]

### Effect of sample flow rate

The sample flow rate should be optimized to ensure quantitative retention along with minimization of the time required for sample processing.[26] For this purpose, the adsorption of Cr(III) ions was investigated at different flow rates (4-14 mL $min^{-1}$) under the optimum conditions. It was found that the retention of Cr(III) was quantitative up to 8 mL $min^{-1}$ flow rate. Above this value, it decreased gradually due to the insufficient contact time of the sample solution with the resin. For this reason, 6 mL $min^{-1}$ was chosen as the optimum flow rate.

### Effect of sample volume

In order to explore the possibility of enriching low concentrations of analytes from large volume of solution, the effect of sample volume on the retention of metal ions

was also investigated. For this purpose, 50, 100, 200, 250, 500, 750, 1000 and 1500 mL of model solutions containing 40 μg of Cr(III) were passed through the column at the optimum flow rate. Quantitative recovery of Cr(III) was obtained for all the studied volumes. The adsorbed metal ions could be eluted with 10 mL of 1.5 mol L$^{-1}$ HCl. So, the preconcentration factor achieved by this method was 150 when used 1500 mL of sample volume and 10 mL of eluent volume.

### Effect of coexisting ions

The effect of various metal ions found in water and solid samples on the determination of Cr(III) was studied. For this purpose, interferent ions Na(I), K(I), Ca(II), Mg(II), Fe(III), Pb(II), Al(III), Cu(II), Ni(II), Mn(II), Co(II), Zn(II), Cd(II), Cl$^-$, PO$_4^{3-}$, SO$_4^{2-}$ and NO$_3^-$ having different concentrations were added individually to the model solutions containing 40 μg of Cr(III) and the general procedure was applied. It can be seen that the presence of major cations and anions, 1500 mg L$^{-1}$ Na(I) and K(I), 100 mg L$^{-1}$ Ca(II) and Mg(II), 1000 mg L$^{-1}$ Cl$^-$, 250 mg L$^{-1}$ SO$_4^{2-}$, NO$_3^-$ and PO$_4^{3-}$, 10 mg L$^{-1}$ Al(III), Fe(III), Pb(II), Cu(II), Zn(II), Ni(II), and Cd(II) did not show a significant influence on the determination of Cr(III), except for 10 mg L$^{-1}$ Mn(II). The results show that the chelating resin has a good selectivity for Cr(III) and is suitable for the analysis of various samples.

### Sorption capacity of the resin

The adsorption isotherm of the resin for Cr(III) was studied by the column method. The adsorption at the solid-liquid interface is commonly described by Langmuir isotherm which is based on the equation given below:

$$\frac{C}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m}\right) \times C \qquad (1)$$

where C (mg L$^{-1}$) is the concentration of Cr(III) in solution at equilibrium and *n* (mg g$^{-1}$) is the amount of adsorbed Cr(III) *per* g of resin at equilibrium (mg g$^{-1}$). $n_m$ is the maximum adsorption in monolayered adsorption systems (mg g$^{-1}$) and *K* is the adsorption equilibrium constant related to adsorption energy (L mg$^{-1}$). A plot of C/n *vs.* C shows a linear relationship, and Langmuir constants $n_m$ and *K* can be calculated from the slope and intercept of the plot, respectively.[20] Aliquots of 25 mL of the model solutions containing 10-950 mg L$^{-1}$ Cr(III) were passed through the column containing 0.90 g of chelating resin. Adsorption capacity of resin for Cr(III) and adsorption equilibrium

constant were found to be 12.1 mg g$^{-1}$ and 0.218 L mg$^{-1}$, respectively.

### Analytical performance

The precision of the method for Cr(III) was investigated under optimum experimental conditions. For this, ten successive retentions and elution cycles were performed. The recovery for Cr(III) was found to be 98 ± 2%. The limit of detection (LOD, n = 10) evaluated as three times the standard deviation of the blank solutions divided by the slope of the calibration curve was found to be 1.11 μg L$^{-1}$. In the calculation of LOD, a 150 fold preconcentration factor was taken into consideration.[27]

### Accuracy and applications of the method

The accuracy of the method was verified by the recovery studies in water and food samples and by analyzing certified reference materials (TMDA-70 and SRM 1568a). Different concentrations of Cr(III) and Cr(VI) were spiked to aliquots of 100 mL of distilled water and tap water, of 250 mL of river water and well water and of 25 mL of waste water samples. The results are given in Table 1. A good agreement was achieved between the added and found concentrations of chromium species. The recovery values for both chromium species changed from 90 to 104%. The concentration of Cr(III) in river water sample was found to be 22.9 ± 2.0 μg L$^{-1}$. Cr(III), Cr(VI) and total chromium concentrations in waste water were found to be 3.97 ± 0.21, 9.43 ± 0.37 and 13.4 ± 0.3 mg L$^{-1}$, respectively. The analysis results for chromium in various food samples are shown in Table 2. The recovery values found for total chromium were satisfactorily (91-101%). In order to estimate the accuracy of the method, the total chromium in certified reference materials (TMDA-70 and SRM 1568a) was also determined. The found results are in a good agreement with the certified and/or spiked total chromium values (Table 3).

### Comparison of the method with the other solid phase extraction methods

A comparison with some of the previous works is given in Table 4. The proposed method for chromium speciation has much higher preconcentration factor and lower relative standard deviation (RSD, %) than the other chelating matrices. The adsorption capacity of the chelating resin is higher and/or comparable to those of the other solid phase extraction methods. The LOD value of the method is comparable to the LOD values of the other methods which use FAAS as detection technique. When compared

**Table 1.** Speciation of chromium in various water samples (sample volume: 100 and 250 mL, final solution: 10 mL)

| Sample | Added for final solution / (mg L$^{-1}$) | | Found[a] / (mg L$^{-1}$) | | Total[a] / (mg L$^{-1}$) | Recovery / % | | |
|---|---|---|---|---|---|---|---|---|
| | Cr(III) | Cr(VI) | Cr(III) | Cr(VI)[b] | | Cr(III) | Cr(VI) | Total |
| Distilled water | 4.0 | – | 3.99 ± 0.07 | – | – | 100 | | |
| | 3.0 | 1.0 | 2.98 ± 0.01 | 1.03 ± 0.01 | 4.01 ± 0.01 | 99 | 103 | 100 |
| | 1.0 | 3.0 | 1.07 ± 0.08 | 2.91 ± 0.08 | 3.98 ± 0.03 | 107 | 97 | 100 |
| | 2.0 | 2.0 | 2.04 ± 0.17 | 1.92 ± 0.18 | 3.96 ± 0.06 | 102 | 96 | 99 |
| | – | 4.0 | – | 3.92 ± 0.18 | – | | 98 | |
| Tap water | – | – | < LOD | < LOD | < LOD | | | |
| | 1.0 | 2.0 | 0.99 ± 0.10 | 2.07 ± 0.15 | 3.07 ± 0.11 | 99 | 104 | 102 |
| | 2.0 | 1.0 | 2.04 ± 0.15 | 0.98 ± 0.17 | 3.02 ± 0.09 | 102 | 98 | 101 |
| River water | – | – | 0.57 ± 0.05 | < LOD | 0.57 ± 0.05 | | | |
| | 2.0 | 2.0 | 2.50 ± 0.12 | 2.07 ± 0.24 | 4.57 ± 0.21 | 97 | 104 | 100 |
| Well water | – | – | < LOD | < LOD | < LOD | | | |
| | 2.0 | 2.0 | 2.02 ± 0.17 | 1.81 ± 0.34 | 3.83 ± 0.30 | 101 | 90 | 96 |
| Wastewater[c] | – | – | < LOD | < LOD | < LOD | | | |
| | 2.0 | 2.0 | 1.95 ± 0.08 | 2.09 ± 0.12 | 4.04 ± 0.09 | 98 | 105 | 101 |
| | 2.0 | 4.0 | 2.01 ± 0.06 | 4.00 ± 0.06 | 6.01 ± 0.02 | 100 | 100 | 100 |
| Wastewater[d] | – | – | 0.79 ± 0.04 | 1.89 ± 0.07 | 2.68 ± 0.06 | | | |
| | 2.0 | – | 2.76 ± 0.03 | – | – | 99 | | |
| | – | 2.0 | – | – | 4.72 ± 0.02 | | | 102 |
| | 4.0 | – | 4.74 ± 0.05 | – | – | 99 | | |
| | – | 4.0 | – | – | 6.65 ± 0.06 | | | 100 |
| | 2.0 | 4.0 | 2.76 ± 0.03 | 6.07 ± 0.04 | 8.83 ± 0.02 | 99 | 105 | 103 |

[a]Mean value ± standard deviation, n = 3. [b]Calculated value. [c]From the copper plating plant, contains 2500 mg L$^{-1}$ Cu. [d]From the chromium plating plant. It was 25 fold diluted.

**Table 2.** Determination of chromium in various food samples (sample amount: 0.5 g)

| Sample | Added / (µg g$^{-1}$) | | Found[a] / (µg g$^{-1}$) | Recovery / % |
|---|---|---|---|---|
| | Cr(III) | Cr(VI) | Total Cr | |
| Apple | – | – | < LOD | – |
| | 40 | 40 | 80.5 ± 0.6 | 101 |
| Parsley | – | – | < LOD | – |
| | 40 | 40 | 80.3 ± 0.6 | 100 |
| Wheat | – | – | < LOD | – |
| | 40 | 40 | 78.6 ± 1.4 | 98 |
| Marrow | – | – | < LOD | – |
| | 40 | 40 | 80.2 ± 1.7 | 100 |
| Quince | – | – | < LOD | – |
| | 40 | 40 | 72.5 ± 1.1 | 91 |

[a]Mean value ± standard deviation, n = 3.

**Table 3.** Determination of total chromium in certified reference materials by described method (sample volume: 50 mL)

| | TMDA-70 fortified lake water | | Recovery / % | SRM 1568a rice flour | | Recovery / % |
|---|---|---|---|---|---|---|
| | Certified[a] / (µg L$^{-1}$) | Found[b] / (µg L$^{-1}$) | | Added[c] / (mg L$^{-1}$) | Found[b] / (mg L$^{-1}$) | |
| Total Cr | 389 ± 2.3 | 386 ± 7 | 99 | 4.0 | 3.9 ± 0.1 | 98 |

[a]At 95% confidence level. [b]Mean value ± standard deviation, n = 3. [c]Not certified; 2.0 mg L$^{-1}$ Cr(III) and 2.0 mg L$^{-1}$ Cr(VI) were added to the SRM solution.

**Table 4.** Comparison of some solid phase extraction methods for chromium speciation

| Reagent/adsorbent/technique | PF | AC / (mg g$^{-1}$) | LOD / (µg L$^{-1}$) | RSD / % | Reusability | Sample | Reference |
|---|---|---|---|---|---|---|---|
| Activated carbon produced from tea-industry wastes / FAAS | 50 | 61 | 0.27 | 3.9 | 6 | stream, tap and sea water, tobacco and dried eggplant | 18 |
| Cr(III)-imprinted silica gel / ICP-MS | 40 | 30.5 | 0.004 | 4.44 | 100 | lake, tap and well water | 26 |
| Immobilized moss on a polysilicate matrix / ICP-MS and FAAS | 20 | 11.5 | 0.15,145 | 1.0 | | bottled, lake, ground and waste water | 28 |
| A fiber / FI-FAAS | 32 | 25.2 | 0.3 | 4.3 | | drinking water | 29 |
| *Saccharomyces cerevisiae* immobilized on sepiolite / FAAS | 75 | 11.9 | 94 | | 20 | river water | 30 |
| Diphenylcarbazide / Amberlite XAD-4 resin / Spectrophotometry | 27 | 0.85 | 6 | 3.8 | 7 | tap, well and waste water | 31 |
| Nanometer TiO$_2$ / ICP-AES | 50 | 7.6 | 0.32 | 2.4 | | tap and lake water | 32 |
| Melamine based polymeric sequestering succinic acid resin / FAAS | 4 | 3.8 | 4.2 | 2-3 | 20 | waste water | 33 |
| Acetylacetone modified Amberlite XAD-16 / FAAS | 100 | 15 | 0.02 | 2 | 8 | industrial waste water samples | 34 |
| Poly(DPMAAm-*co*-DVB-*co*-AMPS) / FAAS | 150 | 12.1 | 1.11 | 2 | 200 | tap, river, well, waste water and various food samples | this work |

PF: preconcentration factor; AC: adsorption capacity; LOD: limit of detection.

to the other adsorbent, the reusability of the chelating resin is perfect.

## Conclusions

In this work, a new chelating resin was synthesized and characterized. A new solid phase extraction method for the determination of Cr(III) by chelating resin was developed. The method was successfully applied to the separation, preconcentration and speciation of chromium in various water and food samples. Cr(III) is quantitatively recovered in the acidic pH range (pH 1-3). The method has high flow rate (6 mL min$^{-1}$), low eluting acid concentration (1.5 mol L$^{-1}$ HCl) and low limit of detection (1.11 µg L$^{-1}$). The precision, accuracy and selectivity of the method are satisfactory. The recovery values for chromium species and total chromium changed in the range of 90-107%. The synthesized resin is highly stable and the recovery value of the Cr(III) after 200 cycles of adsorption and desorption was still quantitative.

## Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

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