Chromate surface-imprinted silica gel sorbent for speciation of Cr in surface waters

Mariya MITREVA, Ivanka DAKOVA, Tanya YORDANOVA, Irina KARADJOVA*

Department of Analytical Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia “St. Kliment Ohridski”, Sofia, Bulgaria

*Correspondence: kardjoya@chem.uni-sofia.bg

Abstract: This study is focused on the synthesis of chromate anion imprinted sorbent supported on silica gel for non-chromatographic Cr speciation in surface waters. The preparation procedure is based on grafting of 3-methyl-1-trimethoxysilylpropylimidazolium, preliminarily coordinated to \( \text{CrO}_4^{2-} \) as a template ion, onto the surface of silica gel. Sorption and desorption characteristics of surface imprinted sorbent toward Cr(III) and Cr(VI) were examined by batch solid phase extraction. An excellent separation of Cr(VI), selectively retained on the sorbent, from Cr(III) remained in the solution was achieved at pH 2-3 for 20 minutes. A freshly prepared mixture of ascorbic acid and nitric acid was selected as the most efficient eluent for quantitative desorption of the retained Cr(VI). An analytical procedure for Cr speciation in surface waters was developed and validated through analysis of certified reference materials. Detection limits achieved and relative standard deviations for typical concentration levels of Cr(VI) in surface waters matched the requirements of analytical procedures used in monitoring programs.

Key words: Chromate anion surface imprinted sorbent, chromium speciation, solid phase extraction, surface waters
1. Introduction

Nowadays, it is commonly accepted that a lot of elements can naturally exist in the environment under various chemical forms with considerably different properties and behaviour in the environment, which resulted insubstantial distinctions in their toxicity, mobility and bioavailability. Undoubtedly this means that, determination of total element concentrations is generally not sufficient for comprehensive clinical and environmental considerations. Therefore, speciation analysis has reasonably become an important topic of the present-day analytical research.

During the recent years, one of the most investigated problems is the speciation analysis of chromium, mainly because of totally contrasting physiological effects of its predominantly existing chemical forms, i.e. Cr(III) and Cr(VI). The former is identified as an essential nutrient for humans, required for glucose and fats metabolism \(^1\), while the latter and its compounds are definitely recognized as carcinogenic and mutagenic substances. \(^2\)

From practical point of view, application of expensive and complicated hyphenated methods such as chromatographic separation followed by ICP-MS measurement might be replaced by simple off line quantitative separation of Cr species followed again by instrumental measurement. Solid phase extraction (SPE) is a widely used separation technique that offers several significant benefits such as low solvent consumption, high enrichment factors, fastness, simple operation in batch and column mode, good reproducibility as well as relatively low cost compared to other methods.\(^3\) Furthermore, the correct selection of suitable sorbent is very important because the reliable species separation is a crucial stage of each successful SPE procedure. A large variety of materials were proposed as effective sorbents in non-chromatographic speciation analysis of chromium, e.g. nanosized TiO\(_2\) \(^4\)–\(^6\), silver nanoparticles \(^7\), graphene oxide \(^8\), single walled \(^9\) and multiwalled carbon nanotubes \(^10\)–\(^12\), ion-imprinted polymers \(^13\)–\(^17\), functionalized polymeric sorbents \(^18\)–\(^25\), Fe\(_3\)O\(_4\) coated with ZrO\(_2\) \(^26\), Al\(_2\)O\(_3\) \(^27\)–\(^28\), chitosan \(^29\), etc. It might be accepted, that from analytical point of view,
sorption and enrichment of more toxic Cr(VI) is a preferable step of SPE procedure for Cr speciation especially in surface waters.

In the present study, we report on the synthesis of chromate surface-imprinted silica gel sorbent prepared by grafting of 3-methyl-1-trimethoxysilylpropylimidazolium chloride onto the surface of silica gel particles and its further application for chromium speciation analysis. The imprinting process was carried out in the presence of chromate anion as a template, which further ensures high selectivity toward Cr(VI). The optimal chemical conditions for separation and enrichment of Cr(VI) were defined. The analytical procedure for Cr(VI) determination in surface waters was developed and validated through analysis of certified reference materials.

2. Results and discussion

2.1. Synthesis and characterization of chromate surface-imprinted silica gel sorbent (Cr(VI)-SIS)

The synthesis of chromate anion surface-imprinted silica gel sorbent (Cr(VI)-SIS) via a multistep procedure is described in Section 3.3. and shown in Figure 1. After successful leaching of Cr(VI) from the surface of the synthesized sorbent, some specific binding sites with functional groups in a predetermined orientation and cavities with special size of CrO$_2^-$ were formed. Non-imprinted sorbent (NIS) is synthesized in the same way as described above, in the absence of template. To evaluate the degree of 1-methylimidazole incorporation, the elemental analysis of the synthesized Cr(VI)-SIS was performed. The obtained results, 8.32 wt.% C and 2.44 wt.% N (for Cr(VI)-SIS) and 7.27 wt.% C and 1.84 wt.% N (for NIS), suggested that 1-methylimidazole was successfully introduced onto the silica gel surface. The content of 1-methylimidazole units/groups in Cr(VI)-SIS was calculated as 0.87 mmol per gram of the dry sorbent.
2.2. Optimization of Cr(VI) separation procedure

2.2.1. Effect of pH on sorption efficiency of Cr(VI)-SIS

Sorption affinity of Cr(VI)-SIS particles toward Cr(III) and Cr(VI) strongly depends on pH of the aqueous media first because of its surface properties and second because of the different Cr species distribution under acidic and basic conditions. The optimal pH value for quantitative separation of Cr species was defined by batch experiments carried out in pH range between 1 and 8. The results obtained, presented in Figure 2 showed quantitative retention of Cr(VI) on Cr(VI)-SIS particles in nearly the whole investigated pH range (2–6) because both anionic HCrO$_4$– and CrO$_4^{2–}$ are electrostatically attracted by the positively charged methylimidazolium groups. The degree of sorption of Cr(III) is below 5% at lower pH values and tend to increase after pH 4. This behaviour of Cr(III) might be explained with the presence of free silanol groups on the surface of silica gel, which are deprotonated at pH higher than 5 and could retain the positively charge Cr(III) ions, i.e. Cr$^{3+}$, Cr(OH)$_2^{+}$ and Cr(OH)$^{2+}$. Accordingly, the range of pH 2–3 was selected as an optimal for quantitative separation of Cr(VI) from Cr(III).

Kinetic of sorption was investigated under optimal conditions (pH 2–3), the sorbent 50 mg Cr(VI)-SIS particles was mixed with 10 mL aqueous solution, containing 2 µg Cr(VI) and then vigorously shaken for 40 minutes. Aliquots (0.2 mL) of the supernatant solution were recurrently removed and Cr was measured by ETAAS. Results obtained showed that retention of Cr(VI) is a relatively fast process and 20 minutes are completely enough to achieve quantitative sorption.

2.2.2. Capacity and adsorption isotherms

The experimental adsorption capacity (Q) of the Cr(VI)-SIS was determined after saturation of the sorbents with chromate anions under optimum conditions at room temperature (Figure 3). For this
purpose, increasing amounts (2 µg – 30 µg) of Cr(VI) anions were added to 50 mg sorbent and the equilibrium chromium concentration after adsorption was measured by FAAS. The sorption capacity $Q$ was calculated using the following equation:

$$Q = \frac{(C_0 - C_e) \times V}{m}$$  \hspace{1cm} (1)

where $Q$ is the mass of chromate anions adsorbed per unit mass of the sorbent, µmol g$^{-1}$; $V$ is volume of the solution, L; $m$ is the mass of the sorbent, g; $C_0$ and $C_e$ are the initial and equilibrium concentrations after adsorption of the chromium anions in aqueous solution, respectively, µmol L$^{-1}$. The results presented in Figure 3(A) showed that the amount of chromate anions adsorbed per unit mass of Cr(VI)-SIS increased with the initial concentration of Cr(VI) and reached plateau values, determining the adsorption capacity values. The experimentally determined $Q$ was 6.42 µmol Cr(VI) per gram of Cr(VI)-SIS.

Langmuir isotherm model was used for curve fitting to derived adsorption data. According to the Langmuir isotherm theory the sorption process occurs in a surface monolayer of homogenous sites which number is fixed.$^{31}$ The expression of the linearized Langmuir isotherm (Eq. (2)) is:

$$\frac{C_e}{Q_e} = \frac{C_0}{Q_{max}} + \frac{1}{(b \times Q_{max})}$$  \hspace{1cm} (2)

Where $C_e$ is the equilibrium concentration of chromate anions in the solution, µmol L$^{-1}$; $Q_e$ is the adsorption capacity of the adsorbed chromium ions onto the sorbents at equilibrium, µmol g$^{-1}$; $Q_{max}$ is the maximum adsorption capacity, µmol g$^{-1}$; $b$ is the Langmuir constant that relates to the affinity of binding sites, L µmol$^{-1}$. Calculated coefficients of the Langmuir model for the isotherms presented in Figure 3(B) were $Q_{max} = 6.54$ µmol g$^{-1}$ and $b$ =1.18 L µmol$^{-1}$ and the obtained regression coefficient was $R^2 = 0.992$. The high $R^2$ value achieved for the adsorption of chromium anions onto Cr(VI)-SIS show that the Langmuir equation gives a good mathematical fit to the adsorption isotherm. The experimental value of sorption capacity, determined according to the procedure described in paragraph 3.5 was 6.42 µmol g$^{-1}$ sorbent, very close to the calculated value by Langmuir model (Eq.
The sorption capacity of NIS sorbent was found to be 4.75 µmol g⁻¹ sorbent, around 25% lower than this obtained for imprinted particles.

2.2.3. Elution study

Taking into account that the separation of Cr species is based on electrostatic interactions, various solutions were tested as an appropriate eluents for quantitative desorption of Cr(VI). The initial idea was that elution of Cr(VI) could be realized by ion exchange, but the results obtained were unsatisfactory (Figure 4). The highest degree of elution achieved by using (NH₄)₂CO₃ as ion-exchanger was a little bit above 80%. A possible explanation for the superiority of (NH₄)₂CO₃ over the other ion exchangers used could be the stronger competitive action of the doubly charged carbonate anions at pH 9-10, but even though, quantitative elution was not acquired.

A suitable alternative to overcome this obstacle was elution based on reduction of Cr(VI) to Cr(III). For this purpose ascorbic acid was used as a mild and environmentally friendly reducing agent. It was experimentally verified that Cr(VI) was entirely eluted (Dₑ > 98%) with freshly prepared solution of ascorbic acid (3 mmol L⁻¹) in 2 mol L⁻¹ HNO₃.

Kinetics of elution process was studied after the loading of the sorbent with 10 µg Cr(VI) and subsequent elution with 10 mL 3 mmol L⁻¹ ascorbic acid in 2 mol L⁻¹ HNO₃ for 10-40 min. Aliquot samples (0.2 mL) were taken and measured by ETAAS. The results showed that 20 min elution time ensures quantitative elution of retained Cr(VI).

2.3. Effects of competitive ions

The separation of Cr species is a result of electrostatic attraction between Cr(VI), i.e. HCrO₄⁻, and the positively charged methylimidazolium groups. In this regard, the extend of possible interferences of another anions, e.g. SO₄²⁻, HCO₃⁻, Cl⁻, PO₄³⁻, HPO₄²⁻, etc., on the extraction efficiency of Cr(VI)-SIS particles toward Cr(VI) have to be evaluated. As far as these anions exists at various concentration levels in surface waters, known amounts of Cr(VI) were directly spiked in several spring, river and
mineral water samples (previously acidified to pH 2–3 by adding of HNO₃) and SPE procedure was carried out under the optimized chemical conditions. Recoveries obtained for Cr(VI) for all studied samples were in the range 97 – 99 %, with relative standard deviations (RSD) less than 7%, which can be accepted as an evidence for the absence of matrix interferences on the extraction efficiency of Cr(VI)-SIS sorbent toward Cr(VI) in real samples. However, the degree of sorption of Cr(VI) in the presence of Black sea water varied between 55% and 60%, which means that highly mineralized samples should be preliminary diluted in order to remove matrix interferences from high concentration of SO₄²⁻ and Cl⁻ in sea water.

The batch-to-batch reproducibility of the synthesis of Cr(VI)-SIS was tested by using sorbents prepared independently from different batches. The relative standard deviation of the degree of sorption of 0.2 µg mL⁻¹ Cr(VI) with different sorbents was 4% which confirms very good reproducibility of the applied synthesis procedure. Experiments performed showed that Cr(VI)-SIS particles can be used for at least 50 sorption/desorption cycles of without significant loss of extraction efficiency.

2.4. Analytical figures of merit and applications to real samples

The accuracy and precision of the developed SPE procedure has been evaluated by the analysis of parallel samples of procedural blank (5 parallel blanks, containing 10 mL Milli-Q water and 50 mg Cr(VI)-SIS particles) and certified reference material Chromium VI-WS (Fluka) (5 parallel solutions of 10 mL CRM and 50 mg Cr(VI)-SIS particles). Results obtained (Table 1) were used for the calculation of limit of detection (LOD, 3σ criteria), quantification limits (LOQ, 10σ criteria) and relative standard deviations (RSD%) for studied concentration level. For the validation of the developed procedure, a CRM, Chromium VI in Sea water after 100 times dilution was additionally analyzed. The results obtained (Table 1) were in reasonable agreement with the certified values (Student t-test, 95% confidence limit) which indicates the absence of systematic errors and confirms
the validity of proposed analytical method for selective determination of Cr(VI) in various types of surface waters.

2.5. Conclusions

Sorbent based on surface Cr(VI) imprinted silica gel has been characterized for selective and efficient solid phase extraction of Cr(VI) and incorporated in analytical procedure developed for Cr speciation in surface waters. The synthesis procedure for sorbent preparation and enrichment procedure for Cr(VI) selective determination are simple and easy to perform. The analytical characteristics (LOD, LOQ, RSD) meet the requirements of European Directive 2009/90/EC, which renders analytical procedures applicable to River Basin monitoring programs.

Comparison of the proposed method with some other methods and strategies for Cr speciation (employing also nanomaterials as sorbents) is presented in Table 2. It is worth mention that the detection limits achieved depend on the instrumental method used and direct comparison of different procedures with different measurements methods is often misleading. The value of enrichment factor, typically, is in relation with measurement method and sorbent properties, however sample throughput has been also taken into account. It can be seen from Table 2, that the proposed analytical method for selective determination of Cr(VI) ensures detection limits, which are close to those of methods employing ETAAS as measurement method and fit well with environmentally relevant concentrations of Cr in surface waters even at background level in unpolluted sites.

3. Experimental

3.1. Reagents

The stock standard solutions for Cr(VI) and Cr(III) (1000 µg mL\(^{-1}\)) were Titrisol, Merck (Darmstadt, Germany, www.merck.de) in 2% HNO\(_3\). Silica gel 60 (Merck, Darmstadt, Germany), 1-methylimidazole (MIA), (3-chloropropyl)trimethoxysilane (CPTMS) (Sigma – Aldrich, Germany),
methanol (Labscan, Dublin, Ireland), were used to prepare the Cr(VI)-SIS. Certified reference materials used for method validation: Chromium VI-WS, Fluka, LOT:01453; Cromium VI in Sea water, Fluca, Lot: LRAA8706. All reagents were of analytical-reagent grade and all aqueous solutions were prepared in high-purity water (Milli-Q; Millipore Corp., Milford, MA, USA).

3.2. Apparatus

The Flame AAS/Electrothermal AAS measurements were carried out with a Perkin-Elmer Model Analyst 400 atomic absorption spectrometer equipped with HGA 900. Instrumental parameters for flame AAS measurements, in air/acetylene flame, were optimized according to the Instrument Manual. For ETAAS measurements pyrolytically coated graphite tubes were used as atomizers, sample solutions (10–20 µL) were introduced into the graphite furnaces using Perkin-Elmer autosampler AS 800. All measurements were carried out with at least three replicates and based on integrated absorbance. Optimal instrumental parameters for ETAAS measurements were defined according to the manufacturer’s recommendations for Cr e.g. pretreatment temperature 1100 °C and atomization temperature 2500 °C.

Elemental analysis was performed using Euro EA CHNS-O elemental analyzer (EuroVector, Italy). The centrifuge EBA 20 (DJB Labcare Ltd, Buckinghamshire, England) was used to separate modified silica and extracted metal solution in batch experiments.

A microprocessor pH-meter (Hanna Instruments, Portugal, www.hannacom.pt) was used for pH measurements.

3.3. Synthesis of the chromate anion surface imprinted sorbent

The synthesis scheme of chromate anion surface imprinted sorbent involves several steps (Figure 1).

(i) Silica gel (SiG) surfaces were first activated by refluxing 10 g silica gel with 80 mL 6 mol L⁻¹
hydrochloric acid under stirring for 8 h. Activated silica gel (aSiG) was filtered and washed with deionized water to neutral reaction and then dried under vacuum at 60 °C for 8 h. (ii) The synthesis of 1-(trimethoxysilylpropyl)-3-methylimidazolium chloride ([TMSP-MIA]Cl) was adapted from the procedure reported by Valkenberg et al. 32 A mixture of 1-methylimidazole (2.84 g, 34.5 mmol) and 3-(chloropropyl)trimethoxysilane (6.86 g, 34.5 mmol) were stirred and refluxed under nitrogen flow at 70 °C for 48 h. The resulting liquid product was extracted twice with ether and then dried under vacuum at room temperature. The final compound [TMSP-MIA]Cl was obtained as a yellow viscous liquid. (iii) To prepare chromate anion complex with [TMSP-MIA]Cl, 0.456 g ammonium chromate were dissolved in 30 mL of methanol containing 0.150 mg NaOH (used to prevent the reduction of Cr(VI) in methanol) and 1.689 g [TMSP-MIA]Cl were added to this solution. The complex formation was carried out for 1 h at room temperature with continuous stirring. (iv) Afterward, to prepare the chromate anion surface imprinted sorbent, this solution was gradually added to activated silica gel (1.0 g) dispersed into methanol (10 mL) in a flask of total volume of 100 mL. The suspension was refluxed with stirring for 24 h. The obtained product was recovered by filtration, washed with methanol to remove the residual [TMSP-MIA]Cl. Chromium anions were removed from the sorbents by several, sequential elution steps using 4 mol L⁻¹ nitric acid and 3 mmol L⁻¹ ascorbic acid as eluent. This procedure was repeated until the Cr concentration (template ions) in the washing solution is below the LOD as measured by ETAAS. Finally, the prepared material was dried under vacuum at 60 °C for 8 h.

3.4. Sorption/elution studies

A model experiments were carried out using 10.00 mL of aqueous standard solution, containing 2 µg (A_initial) of Cr(VI) or Cr(III) and 50 mg of Cr(VI)-SIS in polypropylene centrifuge tubes. The pH of these solutions was varied in the range 1–8, using HNO₃ or NH₄OH. The mixture was shaken on an
electric shaker for 20 minutes and then centrifuged at 5000 rpm for 20 minutes. The supernatant, as an effluante, was removed and Cr content \( (A_{\text{end}}, \mu g) \) determined by FAAS. The degree of sorption \( (D_s) \) was defined as \( D_s, \% = \left( \frac{A_{\text{end}}}{A_{\text{initial}}} \right) \times 100 \).

The Cr(VI)-SIS after sorption was washed with deionized water and retained Cr was eluted from the sorbent particles for 20 minutes with 3 mL of various elution solutions. After centrifugation Cr content in the eluate solution \( (A_{\text{el}}, \mu g) \) was measured by FAAS. The degree of elution \( (D_e) \) was defined as \( D_e, \% = \left( \frac{A_s}{A_{\text{el}}} \right) \times 100 \), where \( A_s \) is Cr content retained on the sorbent.

### 3.5. Sorbent capacity

The total sorption capacity (mg Cr(VI) g\(^{-1}\) sorbent) of the synthesized Cr(VI)-SIS was determined by shaking model solutions of Cr(VI) with increasing concentration with 50 mg sorbent for 20 min at optimal sorption pH=3. The amount of Cr in the effluante is determined by ETAAS.

### 3.6. Analytical procedure for Cr(VI) and Cr(III) determination in surface waters.

The water samples were filtered through 0.45 µm membrane filters, on site, during sampling and acidified with 1 mL 1 mol L\(^{-1}\) HNO\(_3\) per 100 mL sample, before transportation to the laboratory.

**Determination of total Cr**: Total Cr content in water sample is determined by ETAAS under optimized instrumental parameters.

**Determination of Cr(VI)**: The water sample of 20 mL was directly (if acidified during sampling or acidified before analysis to pH 2-3) mixed with 50 mg sorbent Cr(VI)-SIS and the suspension was shaken for 20 minutes. After centrifugation for 10 minutes, the supernatant was discarded, the sorbent was washed with deionized water and then 1 mL of the eluate solution (3 mmol L\(^{-1}\) ascorbic acid in 2 mol L\(^{-1}\) HNO\(_3\)) was added. The suspension was shaken for 20 minutes and after centrifugation Cr(VI) was determined in the eluate solution by ETAAS under optimized instrumental parameters.
**Determination of Cr(III):** If necessary, Cr(III) content could be simply calculated as a difference between both measurements for total Cr and Cr(VI).

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Figure 1. Schematic illustration of preparation process of Cr(VI)-SIS.

Figure 2. pH-dependence of the degree of sorption (\(D_s\)%) of Cr(VI) anions on Cr(VI)-SIS.
Figure 3. Experimental adsorption capacity of Cr(VI) onto Cr(VI)-SIS (A) and the fitting curve of Langmuir adsorption isotherm (B). Experimental conditions: pH 3, sorption time 20 min, temperature 25 °C.
Figure 4. Effect of various eluents on the degree of desorption $D_e\%$ of Cr(VI)

Table 1. Analysis results, mean±SD, µg L$^{-1}$.

| Sample                     | Certified value, µg L$^{-1}$ | Found, µg L$^{-1}$ | RSD, % | Recovery, % |
|----------------------------|------------------------------|-------------------|-------|-------------|
| CRM Chromium VI-WS         | 19.5 ± 0.221                 | 19.32 ± 0.57      | 3     | 98 ± 2      |
| CRM Chromium VI in sea water | 450 ± 13.9                   | 438 ± 0.13        | 2     | 97 ± 3      |

LOD - 0.02 µg L$^{-1}$; LOQ-0.06 µg L$^{-1}$
**Table 2** Comparison of analytical procedures for Cr(III)/Cr(VI) speciation.

| Specie(s)     | Sorbent                                      | Instrumental method | Sample                  | LOD, µg L⁻¹/Enrichment factor | Ref. |
|---------------|----------------------------------------------|---------------------|-------------------------|-------------------------------|------|
| Cr(III)       | Nanometer-sized TiO₂ microcolumn             | ICP-OES             | Water                   | 0.32/50                       | 4    |
| Cr(VI)        |                                              |                      |                         |                               |      |
| Cr(III)       | Nanometer-sized TiO₂ immobilized on silica gel| ICP-OES             | Water                   | 0.22 Cr(III)/50               | 5    |
| Cr(VI)        |                                              |                      |                         |                               |      |
| Cr(III)       | Nanometer-sized TiO₂ FI ETAAS                | Drinking water      |                         | 0.01 Cr(VI) 0.006 Cr(III)     | 6    |
| Cr(VI)        |                                              |                      |                         |                               |      |
| Cr(III)       | Ag-NPs                                       | ETAAS               | Water; Beer; Wine       | 0.002 Cr(III)                 | 7    |
| Total Cr      | CPE by Triton X-114                          |                     |                         |                               |      |
| Cr(VI)        | Graphene oxide, decorated with magnetite modified with triethylenetetramine | FAAS               | Tannery waste water; River water; Industry water | 1.4 Cr(VI) 1.6 Cr(III)         | 8    |
| Cr(III)       | SWCNTs, oxidized                             | ICP-MS              | Natural water; Waste waters | 0.01 Cr(III) 0.024 Cr(VI)   | 9    |
| Cr(VI)        |                                              |                      |                         |                               |      |
| Cr(III)       | MWCNTs, oxidized with conc HNO₃              | FAAS                | Natural water           | 1.15 Cr(III)/22               | 10   |
| Cr(III)       | MWCNTs, impregnated with D2EHPA              | ICP AES             | Tap and well water      | 0.05 Cr(III)/60               | 11   |
| Cr(VI) | MWCNTs, APDC | FAAS | Industrial waste water | 0.9 Cr(VI) | 12 |
| Cr(III) | Cr(III)–Cr(VI) pyrroldinedithiocarbamate complex/acrylamide/ethylene glycol dimethacrylate | ETAAS | Tap and river water | 0.018 Cr(III) | 13 |
| Cr(III) | Cr(III)–Cr(VI) pyrroldinedithiocarbamate complex/acrylamide/ethylene glycol dimethacrylate | ETAAS | CRM of waste water | 7.0 Cr(III) | 14 |
| Cr(III) | Cr(III)/3-(2-aminoethylamino)propyltrimethoxysilane (on silica gel) | ICP-MS | ICP-MS | 4.43 ng L⁻¹ Cr(III) | 15 |
| Cr(III), Cr(VI) | Cr(III)/3-aminopropyltriethoxysilane/tetraethylorthosilicate on silica gel | ICP-AES | Lake water | 0.11 Cr(III) | 16 |
| Cr(III) | Cr(VI) | Adsorbent | Detection Method | Application | Concentration | Ref. |
|---------|--------|-----------|-----------------|-------------|--------------|------|
| Cr(III) | Cr(VI) | Cr(III)/3-aminopropyltriethoxysilane on SBA-15 | ICP-AES and UV-vis | Plating and leather wastewater | 0.53 Cr(III) | 17 |
| Cr(III) | Cr(VI) | poly N-(4-bromophenyl)-2-methacryl-mide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzeneP-3 resin | FAAS | Tap water, Lake water, Spring water, Wastewater | 1.58 Cr(III)/100 | 18 |
| Cr(III) | Cr(VI) | poly(N,N’-dipropionitrile methacrylamide-co-divinylbenzene-co-2-acrylamido-2-methyl-1-propanesulfonic acid) resin | FAAS | Water, food samples | 1.1 Cr(III) | 19 |
| Cr(III) | Cr(VI) | β-Cyclodextrin cross-linked polymer | ETAAS | Environmental waters | 0.056 Cr(III)/25 | 20 |
| Cr(III) | Cr(VI) | Poly(1,3-thiazol-2-yl methacrylamide-co-4-vinyl pyridine-co-divinylbenzene) | FAAS | Stream water, Wastewater | 2.4 Cr(VI)/30 | 21 |
| Cr(III) | Cr(VI) | Adsorbent/Functionality | Analysis Method | Sample Type     | Concentration (Cr(VI)/Cr(III)) |
|-------|-------|-------------------------|----------------|-----------------|------------------------------|
| Poly(methacrylic acid) and poly(vinylimidazole) cross-linked with ethylene glycol dimethacrylate | | FAAS | Tap water, Mineral water, Lake water | 0.84 Cr(III)/47.3 Cr(VI)/8.6 |
| N,N-bis(2-aminoethyl)ethane-1,2-diamine functionalized poly(chloromethyl styrene-co-styrene) adsorbent | | HPLC/ICP-MS | Waste water | 0.0068 Cr(VI)/105 0.0041 Cr(III)/128 |
| Fe₃O₄@ZrO₂ | | FAAS | Environmental samples, Biological samples | 0.69 Cr(III)/25 |
| Fe₃O₄@Al₂O₃ modified by surfactant Triton X-114 | | FAAS | Water, Soil | 1.4 - 3.6 Cr(III) for waters 5.6 for soil |
| Fe₃O₄@Al₂O₃ | | FAAS | Water, Waste water | 0.083 Cr(III)/140 |
| Cr(III)  | Chitosan-modified Fe$_3$O$_4$ nanoparticles | ICP-OES  | Waters                      | 0.02 Cr(III)/100          | 0.03 total Cr |
|----------|--------------------------------------------|----------|-----------------------------|---------------------------|---------------|
| Cr(VI)   | Chromate surface imprinted silica gel sorbent | ETAAS   | Surface waters              | 0.02 Cr(VI)               | This work     |