



Flow based determination of Cr(VI) by adsorptive cathodic stripping voltammetry on an immobilized magnetic poly(ionic liquid) modified electrode



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ABSTRACT

In this work an electrochemical procedure for Cr(VI) flow based determination in tap water is presented. An AdCSV method was developed using a screen printed electrode modified with magnetic poly(1-allyl-3-methylimidazolium) chloride and the procedure does not require the addition of complexing agents in the solution unlike the methodologies reported so far for Cr(VI) determination. The flow based system is described and the control variables were studied in detail and optimized using a Taguchi parameters design. Under optimal conditions, the electrochemical sensor offered an excellent response to Cr(VI) and the limit of detection estimated from 3σ was $0.5 \mu\text{g L}^{-1}$ ($n = 3$) allowing the analysis of tap water samples. The effect of interfering ions was also investigated below the maximum permissible limits for tap water according to Mexican standards. The presence of the magnetic particles on the sorbent allowed its easy modification on the electrode surface between each determination when removing the magnetic field placed in the wall-jet cell. Finally, the precision of the method was tested with tap water samples using standard addition method for Cr(VI) quantification and the accuracy was evaluated comparing the results with the diphenylcarbazide method and by analyzing a certified water sample. The method shows good repeatability and reproducibility (%RSD less than 5%) making it feasible for Cr(VI) flow based determination and no significant difference is observed in the results obtained by both methods.

1. Introduction

Chromium is found in two oxidation states in water, as Cr(III) and Cr(VI). The former is considered an essential trace element related to lipid metabolism whereas Cr(VI) is a highly toxic specie considered carcinogenic and mutagenic from group A, according to the international agency for research on cancer [1]. The main source of Cr(VI) is associated with anthropogenic activities such as electroplating, textile industries, and pigments. Depending on the conditions of the media, such as pH and concentration this element can be found as CrO_4^{2-} , HCrO_4^- , or $\text{Cr}_2\text{O}_7^{2-}$; these species are oxidizing agents and highly soluble in water [1,2]. The Environmental Protection Agency of the United States and the World Health Organization have established a concentration of $50 \mu\text{g L}^{-1}$ as the maximum permitted level for Cr(VI) [3]; therefore, methods for quantification of Cr(VI) are of great importance.

The conventional techniques for determination of chromium(VI)

such as atomic absorption spectroscopy [4,5] and ICP-MS [6] require separation of the species prior to analysis. These methods do not satisfy the requirements for routine analysis due to instrumentation cost, time consumption and complexity of the methods. Electroanalytical techniques have been widely reported for Cr(VI) determination, in particular adsorptive stripping voltammetry (AdSV) because of their advantages such as low limits of detection, high sensitivity and the possibility of coupling to batch injection [7–11], flow injection [12] and on-line determination methods [13–15] facilitating routine testing.

Adsorptive cathodic stripping voltammetric methods (AdCSV) allow the determination of Cr(VI) in trace levels; in these procedures the determination is based on the adsorptive accumulation of a Cr electroactive complex on the electrode surface followed by voltammetric measurements [7,13–19]. The application of AdCSV techniques for the determination of Cr(VI) commonly involves the use of discontinuous systems and although the adsorption phenomena are favored by forced convection (agitation or flow), the contact time is an important factor

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for the process efficiency. Flow based stripping techniques have a greater flexibility in terms of sample volume used during analyte accumulation related to analytical sensitivity, and also pre-concentration efficiency, precision and accuracy are higher than batch methodologies [12,20].

Mercury based electrodes [13,14,21,22] were commonly used for the AdCSV determination of Cr(VI) but due to mercury toxicity different electrode materials like bismuth [16,19] or carbon [8,10] were proposed for Cr(VI) determination.

Imidazolium based ionic liquids (ILs) have been used as binders for the preparation of carbon paste electrodes. A lower background, larger potential window, lower resistance, higher ionic conductivity and controllable ion-pairing properties were observed during the determination of dopamine, catechol, ascorbic acid, NADH and Hg(II) [23,24]. Alternatively, ILs can be immobilized using them as monomers during the synthesis of poly(ionic liquids) (PILs) based sorbents [25,26]. It has been proved that the use of PILs improves the adsorption capacity and selectivity during Cr(VI) retention due to anionic exchange interactions [27]. On the other hand, the use of magnetic nanoparticles is of great interest because the solid can be easily isolated by an external magnetic field facilitating its application to routine analysis.

The present work describes the synthesis and application of a magnetic poly(1-allyl-3-methylimidazolium) chloride modified electrode for flow based determination of Cr(VI) in tap water samples by adsorptive cathodic stripping voltammetry. The control variables: sample volume, flow rate, sorbent amount and pH were investigated. The analytical parameters were obtained under optimal conditions and the method was applied to the analysis of tap water samples.

2. Material and methods

2.1. Reagents and solutions

All solutions were prepared with deionized water (Millipore Milli-Q system) with a resistance of 18.2 MΩ cm or greater. All the chemicals used were analytical grade and used without further purification. Potassium dichromate was purchased from Sigma Aldrich (St. Louis, MO, USA). A stock solution of 500 mg L⁻¹ of Cr(VI) was prepared and Cr(VI) working standards were prepared daily by dilution. The supporting electrolyte consists on a Britton-Robinson buffer solution (0.01 M H₃PO₄, 0.01 M CH₃COOH, 0.01 M H₃BO₃ and 0.1 M NaCl). A 0.02 M of 1,5-Diphenylcarbazide solution was prepared by dissolving 0.050 g in 10 mL of acetone. Sodium persulfate, ethylene glycol dimethacrylate (EGDMA), 1-allyl-3-methylimidazolium chloride (IL), iron (II) sulfate heptahydrate (FeSO₄·7H₂O), sodium hydroxide, sulfuric acid, methanol, hydrochloric acid, sodium chloride, boric acid, acetic acid, and phosphoric acid were also purchased from Sigma Aldrich.

2.2. Apparatus

Micrographs for sorbent characterization were taken using scanning electron microscopy (FEI Model Quanta 200 F, Amsterdam, Netherlands). The analysis of the samples was also carried out using the UV-Vis technique in a HACH spectrophotometer (DR-2700, Dusseldorf, Germany) [28].

Voltammetric measurements were carried out in a Bipotentiostat μStat 200 by Dropsens (Asturias, Spain) controlled with a DropView software for Windows. The detector consists on a wall jet cell (Dropsens, model DRP-FLWCL) with a carbon screen printed electrode (Dropsens, model DRP-110). The sample and the supporting electrolyte were introduced into the cell using a peristaltic pump (Gilson minipuls 3, France) and an injection valve (Gilson, France). The distance between the injection valve and the electrochemical cell is 25 cm. The different components of the flow system were connected using Omnifit Teflon tubing (0.8 mm internal diameter).

2.3. Synthesis of magnetic poly(1-allyl-3-methylimidazolium) chloride

Magnetic poly(1-allyl-3-methylimidazolium)chloride was prepared according to the following methodology. Briefly 12.96 mmol (3.6 g) of FeSO₄·7H₂O were dissolved in 100 mL of deionized water, and NaOH (6 M) was added until pH 10.0 ± 0.2 and dark green color were obtained. The suspension was stirred at 300 rpm, aerated, and heated at 100 °C during 45 min, keeping pH value at 10.0 ± 0.2. Magnetite was washed with deionized water (3 × 10 mL) followed by cold ethanol (2 × 10 mL). Magnetite was dispersed in methanol (15 mL), and it was then transferred into a ball flask containing IL monomer (2.0 mmol), and EGDMA (4.0 mmol). The mixture was stirred for 15 min. Then, 0.5 mmol of sodium persulfate (0.12 g) were added as radical initiator, and a reflux system was mounted. The temperature was set from room temperature to 60 °C during the first 2 h, and maintained for 2 h. The solid obtained was washed with deionized water, and left in the oven at 60 °C for 8 h to dry.

2.4. Flow based procedure

Initially, the screen printed electrode was placed in the electrochemical detector (D) and 10 μL of an aqueous dispersion of the magnetic sorbent (1.0 mg mL⁻¹) were placed on the working electrode surface in the presence of an external magnetic field. The configuration of the flow based system (Fig. 1) consists of a peristaltic pump (PP) used to propel the water samples (S) and supporting electrolyte solution (SE). The determination procedure consists in two steps, once the electrode was prepared, the injection valve (V) was placed in adsorption position, S and SE were mixed and propelled through the electrochemical cell during 10 min, during this time no potential was applied. Under this condition, Cr(VI) specie in the sample HCrO₄⁻ was exchanged for the Cl⁻ contained on the PIL phase of the magnetic sorbent. When the adsorption period was completed, V was switched to stripping position introducing a clean solution of SE to the electrochemical cell during 30 s, this step minimizes interferences and promotes Cr(VI) desorption of the PIL phase in order to facilitate the mass transport of the specie to the electrode surface. Subsequently, a cathodic scan is applied from 0.6 to -0.6 V (vs. Ag electrode) in stopped-flow condition. Differential pulse voltammograms were recorded using an amplitude of 50 mV, step potential of 6 mV, modulation time of 4 ms and scan rate of 50 mV s⁻¹. The flow rate of each individual channel was 0.5 mL min⁻¹.

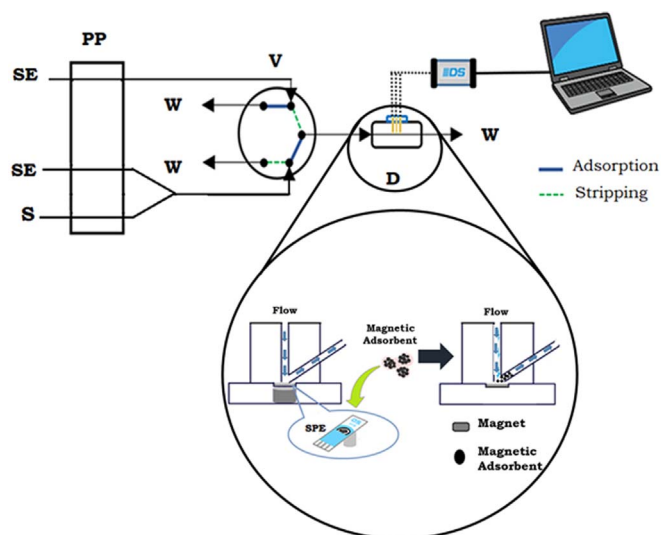


Fig. 1. Flow system for Cr(VI) on-line determination. SE: supporting electrolyte Britton-Robinson, S: sample, Cl⁻ chloride solution, PP: peristaltic pump, V: 4-way valve, W: waste, D: detector, SPE: screen-printed electrode.

Once the determination is concluded, the sorbent was renewed by removing the magnetic external field. Using this methodology, flow condition improves the analyte convection to the sorbent surface enhancing the interaction Cr(VI)-sorbent and also the retention. Experimental parameters such as sample volume, flow rate, pH of the solution and the sorbent weight were evaluated and optimized using a Taguchi experimental design.

2.5. Sample preparation

Ten samples of drinking water from different regions of Pachuca, Hidalgo were analyzed using the standard addition method. The sample and two additions were prepared and analyzed independently, 5.0 mL of the sample (with Cr(VI) additions of 0.0, 1.0 and 2.0 $\mu\text{g L}^{-1}$), 2.5 mL of the Britton-Robinson buffer solution H_3BO_3 , H_3PO_4 and CH_3COOH (pH = 2.5, all components 0.1 M) and 2.5 mL of a 1.0 M NaCl solution were placed in a 25 mL volumetric flask. The volume was completed with deionized water.

In order to evaluate the accuracy of the method, the results obtained with the electrochemical technique were compared with those obtained by the diphenylcarbazide official methodology using UV-Vis determination [28]. Ten tap water samples were collected from different zones in Pachuca Hidalgo, Mexico and were analyzed employing both methodologies. A certified water sample was also evaluated using the proposed method. The certified sample (DMR-3ag) was purchased from the National metrology center (CENAM, Mexico).

3. Results and discussion

3.1. Sorbent characterization

The morphology of the particles was studied by scanning electron microscopy. The micrograph of bare magnetite particles (Fig. 2a) shows the formation of spherical particles with diameter around 50 nm. In the case of coated magnetite particles (Fig. 2b), it is possible to observe the formation of aggregates. Magnetite surface was covered with PIL promoting the particle stability in solution and avoiding air oxidation [29,30].

3.2. Optimization of Cr(VI) determination

Several factors affecting the flow based procedure such as flow rate (FR, mL min^{-1}), sample volume (SV, mL), sorbent amount (SA, μg) and pH value were optimized, using a Taguchi parameters design which use orthogonal arrays in which the factors (columns) and trials (rows) are arranged in a conveniently fixed manner. The analytical response evaluated was the peak current (μA) of the reduction wave of Cr(VI).

The selected orthogonal array used was an $L_9(3^4)$, the control factors and their corresponding settings were chosen according to preliminary experiments.

The control factor settings used in the optimization experiments and the analytical responses obtained are shown in the factorial design matrix presented in Table 1. All experiments were performed in triplicate in order to calculate the residual error and the measurements were carried out using a solution containing a Cr(VI) concentration of 10.0 $\mu\text{g L}^{-1}$. The effects of the control factors on the mean signal are shown in Fig. 3.

The analytical response was evaluated using different amounts of sorbent on the electrode surface varying between 1.0 and 3.0 mg mL^{-1} . It was found that the peak current decreases with the sorbent amount. The analyte diffusion is better when lower amount of the magnetic sorbent is employed. An increment on the amount of sorbent, difficult the mass transport of the analyte to the electrode surface [31]. A sorbent amount of 10 μg was selected then as the optimum to modify the electrode surface.

The effect of the adsorption time on the response was evaluated in function of the flow rate and sample volume. As a result, if the flow rate is very high and the sample volume is small, the contact time is not enough and therefore the analytical signal of Cr(VI) is lower. A flow rate of 0.5 mL min^{-1} and a sample volume of 5.0 mL were chosen.

The pH value of the buffer solution is a very important parameter for the adsorption and thus for the electrochemical detection of Cr(VI). The pH was evaluated in the range of 2.0–3.0, because of the adsorption process is preferential in acidic media. It was found that the optimum pH value was 2.5, at this pH value electrostatic interaction between sorbent surface and HCrO_4^- is adequate [32]. It has been reported that PILs are chemically tolerant to different chemical conditions, however re-arrangement reactions in the structure or degradation of the polymer can occur in acidic conditions, decreasing their adsorption capacity [33]. The combination of settings allowing the highest peak current was: FR of 0.5 mL min^{-1} , SV of 5.0 mL, SA of 10 μg and a pH value of 2.5.

3.3. Analytical parameters of the methodology

Once the experimental conditions for the determination were optimized, a calibration line for Cr(VI) was constructed using standard solutions in a concentration interval of 1.5–7.1 $\mu\text{g L}^{-1}$. The peak height of the analytical response was measured in triplicate. Table 2 shows the regression parameters taken from the calibration line, limit of detection and limit of quantification were calculated according to IUPAC criteria for voltammetric determinations [34].

The methodology presents an adequate LOD (0.5 $\mu\text{g L}^{-1}$) which allows the effective detection of Cr(VI) according with the range of Cr

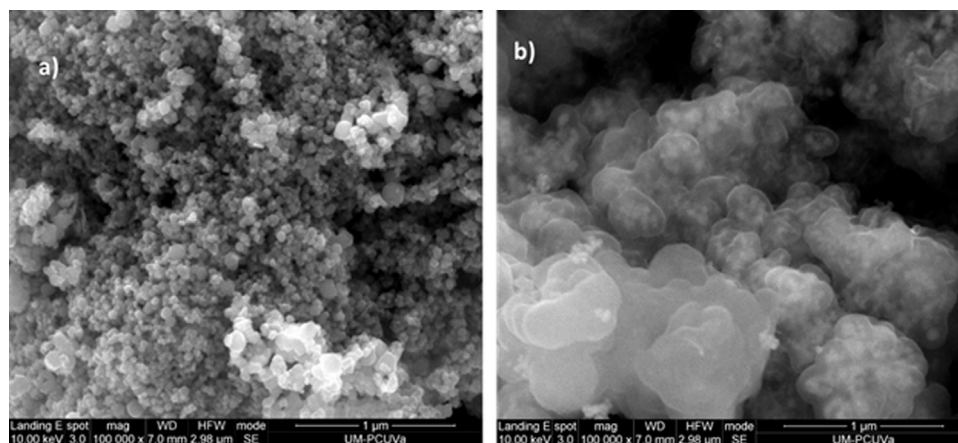


Fig. 2. SEM images obtained of the synthesized adsorbents a) Fe_3O_4 , b) coated Fe_3O_4 .

Table 1
L₉(3⁴) orthogonal array and the mean of the peak current obtained.

Experiment	Factors and Levels				Peak current (μA)
	FR (mL.min ⁻¹)	SV (mL)	SA (μg)	pH value (pH)	
1	0.3	3.0	10	2.0	3.97
2	0.3	5.0	20	2.5	6.08
3	0.3	7.0	30	3.0	3.88
4	0.5	3.0	20	3.0	4.04
5	0.5	5.0	30	2.0	5.87
6	0.5	7.0	10	2.5	7.97
7	0.7	3.0	30	2.5	4.25
8	0.7	5.0	10	3.0	4.21
9	0.7	7.0	20	2.0	4.17

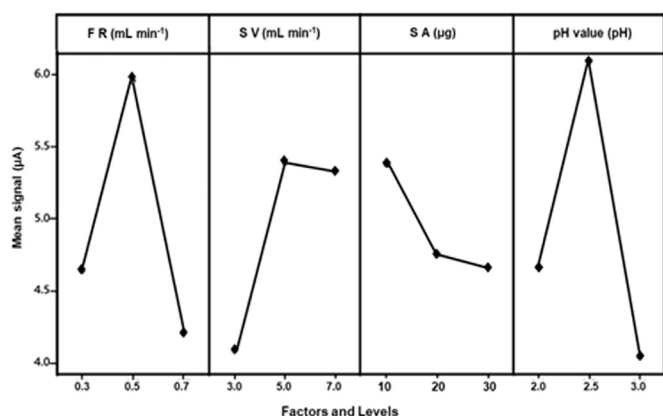


Fig. 3. Effect of the control factors on the mean peak current obtained. F R: Flow rate, S V: sample volume, S A: sorbent amount.

Table 2
Analytical parameters of the calibration line.

Parameter	Value
Square root of residual variance (<i>Sy</i>)	0.023
Limit of detection (μg L ⁻¹)	0.5
Limit of quantification (μg L ⁻¹)	1.5
Linear range (μg L ⁻¹)	1.5–7.1
Number of standards (N)	7
Slope and confidence interval (μA μg ⁻¹)	0.145 ± 0.005
Intercept and confidence interval (μA) <i>b</i> ₀ ± <i>t</i> (<i>Sb</i> ₀)	-0.018 ± 0.023
Repeatability (%RSD, [Cr(VI)] = 2.5 μg L ⁻¹ , n = 3)	0.6
(%RSD, [Cr(VI)] = 3.8 μg L ⁻¹ , n = 3)	0.3
(%RSD, [Cr(VI)] = 5.0 μg L ⁻¹ , n = 3)	0.5
Reproducibility (%RSD, [Cr(VI)] = 2.5 μg L ⁻¹ , n = 9)	4.2
(%RSD, [Cr(VI)] = 3.8 μg L ⁻¹ , n = 9)	2.2
(%RSD, [Cr(VI)] = 5.0 μg L ⁻¹ , n = 9)	2.8

Table 3
Cr(VI) concentrations determined in water samples by the proposed flow based AdCSV method and the UV-Vis method.

Muestra	Flow based AdCSV (μg L ⁻¹)	UV-Vis (μg L ⁻¹)	<i>t</i> calculated value
1	13.7 ± 1.3	14.3 ± 1.4	0.5
2	14.5 ± 1.2	17.6 ± 1.6	1.4
3	16.1 ± 1.5	15.4 ± 1.4	0.6
4	18.7 ± 1.3	17.3 ± 1.6	1.2
5	24.0 ± 1.6	24.5 ± 1.9	0.4
6	16.7 ± 1.5	14.3 ± 1.4	2.0
7	14.4 ± 1.0	13.9 ± 1.4	0.5
8	6.8 ± 0.4	6.9 ± 0.8	0.2
9	12.7 ± 1.3	12.3 ± 1.1	0.4
10	6.2 ± 0.8	6.9 ± 0.9	1.0
Certified sample (DMR – 3ag, 2.747 ± 0.055 mg L ⁻¹)	2.5 ± 0.1 mg L ⁻¹	-	3.0

(VI) concentrations required to be measured for most of contaminated consumption waters according to EPA, WHO and Mexican standards for Cr(VI) content [3,28].

The intermediate precision of the procedure was evaluated in terms of repeatability and reproducibility and expressed in terms of relative standard deviation (%RSD). The %RSD for nine determinations (made in three different days) using the concentrations mentioned above were less than 5.0% in all cases indicating that the method shows a good repeatability and reproducibility.

In order to study the selectivity of the method, the influence of interfering ions usually found in tap water was evaluated considering at the maximum permissible limits established by a Mexican standard [35]. A Cr(VI) solution of 5.0 μg L⁻¹ containing the interfering ion was analyzed, the anions produced a slight decrease of the analytical signal at the following concentrations: CO₃²⁻ (97.6%, 50.0 μg L⁻¹), SO₄²⁻ (90.9%, 500.0 μg L⁻¹), Hg(II) (94.8%, 1.0 μg L⁻¹) and NO₃⁻ (93.1%, 10.0 mg L⁻¹) but the diminishing on the analytical signal is lower than 10.0%. PO₄³⁻, Fe(III), Zn(II), Cu(II), Cd(II), Pb(II), Cr(III) affected the signal < 5.0% at the concentrations reported as maximum permissible limits. Therefore the proposed stripping method is adequate to analyze tap water using standard addition method.

3.4. Cr(VI) determination in water samples

The proposed method was applied to the determination of Cr(VI) in ten tap water samples from different zones of Pachuca, Hidalgo and a certified water sample. The standard addition method was followed for the Cr(VI) determination and the results obtained are shown in Table 3. Measurements of the resulting current for each determination were made in triplicate, plotting the averages of the determinations. Overall all the samples presented positive results under the maximum permissible limits for Cr(VI) in tap water samples.

The accuracy of the method was evaluated comparing the results obtained for the tap water samples with those obtained using the UV-Vis method [28]. For each sample, the results obtained with both methods were compared using a Student *t*-test (n = 3), assuming comparable variances. The values of *t* calculated does not exceed *t* critical value (2.8, α = 0.05, d.f. = 4 for the tap water samples and 4.3, α = 0.05, d.f. = 2 for the certified sample), thus there are no significant differences between the results obtained by both methods.

Table 4 shows other methods for Cr(VI) voltammetric determination in water samples. It can be seen that the lowest LOD were achieved using mercury based electrodes, however toxicity of mercury limits the application of these electrodes. In this sense, the proposed method is an adequate alternative to control Cr(VI) concentration in tap water samples. Additionally, this is the first report of Cr(VI) flow based determination using a magnetic poly(ionic liquid) modified electrode.

Table 4
Limits of detection of described voltammetric methods for Cr(VI) determination.

Electrode	Analysis mode	LOD (nM)	Flow rate (mL min ⁻¹)	Reference
Au carbon composite	Batch	80	–	[8]
AuNPs-GCE	Batch	50	–	[10]
Ag-SPCE	Batch	850	–	[11]
Au-SPCE	Batch	400	–	[11]
Ag amalgam microwire	Batch	0.20	–	[22]
HMDE	Flow based	0.003	18.0	[13]
HMDE	Flow based	0.20	8.0	[36]
PANI/GQDs- SPCE	Flow based	1860	0.1	[37]
Magnetic poly(1-allyl-3-methylimidazolium)-SPE	Flow based	9.6	0.5	This work

4. Conclusions

In this work a feasible on-line system was developed for the AdCSV determination of Cr(VI) in tap water samples. The modification of the working electrode with magnetic poly(1-allyl-3-methylimidazolium) chloride allowed the combination of the advantages of PILs, magnetic materials and flow based voltammetric methods. The proposed method is an alternative for Cr(VI) determination in tap water samples.

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