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Development of a new on-line system for the sequential speciation and determination of chromium species in various samples using a combination of chelating and ion exchange resins

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ABSTRACT

A new on-line flow injection (FI) procedure for the sequential separation, preconcentration and speciation of Cr(III)/Cr(VI) species in different matrices is described based on the combining of solid phase extraction and flame atomic absorption spectrometry (FAAS). Poly 2-(5-methylisoxazol)methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinyl-benzene and Dowex 21K resins were used as chelating and ion-exchange materials for the separation/preconcentration of Cr(III) and Cr(VI) ions, respectively. Trace amounts of chromium retained on the resins were eluted sequentially with HNO_3 and then introduced directly to the nebulizer-burner system of FAAS. The optimum conditions such as pH of the sample solution, amount of the resin, volume of the sample and interfering ions, which are effective on the quantitative recovery of the analytes, were investigated for sequential determination of Cr(III) and Cr(VI) ions. The preconcentration factors were found to be 48 and 30 for Cr(III) and Cr(VI), and the detection limits corresponding to three times the standard deviation of the blank (3s/b) were 0.05 and 0.3 $\mu g\ L^{-1}$, respectively. The method was verified by analyzing a certified reference material. The proposed method was applied to the determination based on the speciation of chromium in various real samples with satisfactory results.

1. Introduction

Toxic metal ions are major sources of pollution in environmental and water resources. Chromium is ubiquitous in nature, occurring in various chemically, physically and morphologically different forms. The metal ions may also enter tap water supply systems from the corrosion inhibitors used in water pipes and containers [1]. Chromium is one of the most abundant elements with the potential to contaminate groundwater, and so can be a major source of drinking water contamination [2,3]. Chromium is considered to be necessary for the production of electroplating and metal finishing processes, tanning of leather, and for the pigment and chemical industries [4]. Research purposes, industrial applications and ecotoxicological concerns are some of the fields in which the determination of chromium at trace levels has attracted considerable interest [1].

Toxicological studies have indicated that the degree of toxicity of metal ions depends on its chemical form. Chromium is mainly found in solution form in two oxidation states, III and VI, both showing well differentiated chemical properties and environmental consequences [5,6]. Such difference in toxicity is one of the main reasons for the recent enormous development of analytical methods for differentiating the various forms of Cr existing in the medium of interest [7]. Chromium species can enter into the environment from their discharge [8]. Cr(III) is relatively non-toxic and an essential nutrient for humans; and trace amounts of Cr(III) are considered as essential to mammals for their maintenance of normal glucose tolerance factor, lipid and protein metabolism, and are therefore essential for human health [9]. Chromium deficiency is associated with cardiovascular diseases and diabetes, while excessive amounts of this element, particularly in the more toxic Cr(VI) valence state, are detrimental to health as it may be involved in the pathogenesis of some diseases such as lung and gastrointestinal cancer [10]. The toxic nature of Cr(VI) is attributed to its higher oxidation potential and relatively smaller size, which enables it to penetrate through biological cell membranes. Moreover, in air, chromium particulates play an important role in the oxidation of sulfur dioxide, leading to the formation of acidic aerosols responsible for global acid rain [7]. Cr(VI) has an adverse impact on the liver, lunsland, kidneys [2] and causes cancer by oxidizing biological species such as DNA and some proteins [3].

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Owing to these two contrasting effects, the precise and accurate determination of Cr(VI); especially at ultratrace levels; in environmental samples is urgently required for environmental protection, food and agricultural chemistry. However, the direct determination of Cr(III) and Cr(VI) at ultratrace levels is limited due to their low concentrations. Therefore, in ultratrace analysis, a preconcentration/separation is necessary to improve sensitivity and selectivity of determination [11]. Various preconcentration techniques such as solvent extraction [9,10], ion-exchange [12], cloud point extraction [13], hollow fiber microextraction [14], and solid phase extraction [5,15] have been applied for the extraction of trace levels of chromium ions from environmental samples. Flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma–mass spectrometry (ICP–MS) can only yield the total amount of chromium. As a result, preliminary species separation and preconcentration are required before the determination of analytes by any of the techniques mentioned above [6].

Flow injection analysis (FIA) has appeared as a powerful tool for on-line operations such as separation/preconcentration [16,17]. On-line solid phase extraction (SPE) may be used in order to improve the sensitivity and selectivity of FAAS. In addition it has some extra advantages: large availability, easy recovery of the solid phase, attainability of large preconcentration factors and facility for separation using various flow injection systems [18–21].

Chelating sorbents can provide a better separation of interferent ions, high efficiency and higher rate of process, and the possibility of combining with on-line SPE–FAAS [22]. Chelating resins are typically characterized by functional groups containing O, N, S and P donor atoms which coordinate to different metal ions [23,24]. Ion exchange resins are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers) [25]. Metal separation in aqueous solutions by using adsorbents is also very important.

In this study, the synthesized chelating resin, poly 2-(5-methylisoxazol) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene [MIAAm/AMPS/DVB] [5] and Dowex 21K as ion-exchange resin were used for the separation, preconcentration and speciation of Cr(III) and Cr(VI), respectively. Using the new flow injection (FI) system which combined a solid phase extraction procedure and FAAS technique, the analyte ions in aqueous solutions were sequentially determined. The accuracy of the method was verified by analysis of a certified reference material (CWW-TMD wastewater) and recovery measurements made with spiked natural water samples. The results showed good agreement with the certified value and the recoveries were sufficiently high.

2. Experimental

2.1. Instrument

A Perkin-Elmer (Norwalk, CT, USA) model AAnalyst 800 flame atomic absorption spectrometer equipped with a deuterium background correction system and an air-acetylene burner was used for the determination of chromium. The wavelength used for chromium was 357.9 nm. A spectral bandwidth of 0.7 nm, acetylene flow rate of 1.4 L min^{-1}, and nebulizer flow rate of 10.0 mL min^{-1} were the conventional working parameters. For measuring pH values in the aqueous phase, a Consort model C533 pH meter combined with a glass-electrode and a magnetic stirrer (Chiltern) were used.

The flow injection system comprises a peristaltic pump with variable speed (Watson-Marlow Inc., Wilmington, MA, USA), a multichannel peristaltic pump (Ismatec SA, Glattbrugg, Switzerland) furnished with silicone tubes to deliver all solutions, and two three-way valves (Cole-Parmer Inc. Co., IL, USA) to select solution ways. The peristaltic pumps (PP) and valves (V) are controlled by a five channel timer and each channel has 36 different timing periods adjustable with thumble switches. This unit was of home-made construction. The flow injection system was constructed using fittings, unions and tees made of plastic and high density polyethylene (HDPE) materials. The chelating resin and anion exchange resin (Dowex 21K) packed into the minicolumns (glass, 2.0 cm length and 0.2 cm i.d.) were used for the on-line separation/preconcentration and sequential speciation of the chromium ions.

2.2. Reagents and standard solutions

All reagents used were of the highest available purity and of at least analytical reagent grade (Merck, Darmstadt, Germany). Deionized pure water was used for the preparation of the stock solutions. Cr(III) and Cr(VI) stock solutions (1000 mg L^{-1}) were prepared from $Cr(NO_3)_3 \cdot 9H_2O$ and K_2CrO_4, respectively [5]. Test solutions were prepared from these stock solutions on a daily basis at pH 3.0 by adjusting with respect to the buffer solution. The following buffer solutions were used for the presented separation/preconcentration procedure: HCl/KCl buffer for pH 1.0–2.0; CH_3COONa/CH_3COOH buffer for pH 3.0–5.0; CH_3COONH_4/CH_3COOH buffer for pH 6.0–7.0. A 3.0 mol L^{-1} HNO_3 was used as eluent throughout the experiments.

Poly-2-(5-methylisoxazole) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene, the chelating resin was synthesized according to the literature [5]. The adsorption capacity of the chelating resin for Cr(III) was 34.3 mg g^{-1} and the binding equilibrium constant was 1.5 L mg^{-1} [5]. Dowex 21K was purchased from Sigma-Aldrich. It is a strong base anion exchange resin (in Cl^- form) and has quaternary amine functional groups. Its total exchange capacity is 1.2 eq L^{-1} min^{-1} and has excellent kinetics, excellent regeneration efficiency and outstanding physical stability [26].

The reusability of the resins (life-time) was also investigated using proposed minicolumn procedures. It was found that the life-time is quantitative without any loss in the recovery throughout the study. The both of the resins can be used for quantitative recovery of chromium ions even after 550 cycles. Therefore, the resins show better reusability and stability towards chromium ions.

2.3. Column preparation

The chelating and anion exchange resins were washed successively with 1 mol L^{-1} HNO_3, 1 mol L^{-1} NaOH, acetone, ethyl alcohol and deionized water and were then dried in an oven at about 60 °C. The minicolumns made of glass were 2 cm in length and 0.2 cm in diameter contained 0.1 g of each resin in water suspension. The resin bed heights in the column were approximately 0.3 cm. The minicolumns were washed thoroughly with deionized water and then conditioned at the working pH 3.0 using the buffer solution.

2.4. Procedure for Cr(III)and Cr(VI)

First, the proposed method was tested by using model solutions before the application of the speciation procedure for Cr(III) and Cr(VI) ions to real samples. For that purpose, the pH of the test solutions including 0.1 mg L^{-1} of Cr(III) and 0.6 mg L^{-1} of Cr(VI) was adjusted to pH 3.0 using acetic acid/sodium acetate buffer. The minicolumn was conditioned by passing the buffer solution with pH 3.0 through it and then the test solutions were passed through the column at a flow rate of 1.7 mL min^{-1}. The chromium ions retained on the resins were eluted with HNO$_3$ solution. The concentration of the analytes in the eluate was determined by FAAS.

The schematic diagram of the on-line system is illustrated in Fig. 1. In the preconcentration step, P1 is running while P2 and V are not running, and the sample solutions with pH 3.0 are continuously passed through the minicolumns (MC) for 3.4 min at a flow rate of 1.7 mL min^{-1}. The optimum sample volume was 5.78 mL. The Cr(III) and Cr(VI) ions are retained simultaneously on the minicolumns, MC1 and MC2, respectively, while the effluent is sent to the burner system of FAAS. Afterwards, the minicolumns are washed with water in order to remove the matrix ions from the resins. In this period, P1 is running while P2 and V are not running. Finally, in the elution step; the eluent (E), HNO$_3$, is aspirated by the pump P2 for 3.6 s at a flow rate of 4.4 mL min^{-1} to the minicolumn MC1 to elute Cr(III) ions. The optimum eluent volume was 0.264 mL. Then, the elution stream is directed to the second minicolumn MC2 to elute Cr(VI) ions. During the elution period, P1 does not operate while pump P2 and valve V are running. The released chromium ions are directly introduced to the FAAS. First, Cr (III) ions arrive at FAAS and then Cr(VI) ions, and they are determined by FAAS each in turn, as can be seen in Fig. 2.

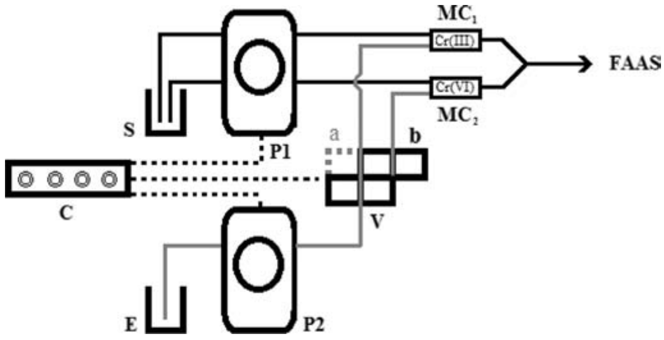


Fig. 1. Schematic diagram of on-line preconcentration system (V: valve, P1: peristaltic pump 1, P2: peristaltic pump 2, E: eluent, MC1: minicolumn 1 (MIAAm/AMPS/DVB chelating resin), MC2: minicolumn 2 (Dowex 21K anion exchange resin), T: timer, and a–b: solution ways; S: sample).

2.5. Determination of total chromium

In order to determine the total chromium, model solutions that contain different amounts of both Cr(III) and Cr(VI) ions were prepared. Then, the described on-line separation/preconcentration procedure was applied to these solutions and the determination of the chromium species was carried out by FAAS. The total chromium concentration was found via the summation of Cr(III) and Cr(VI) levels.

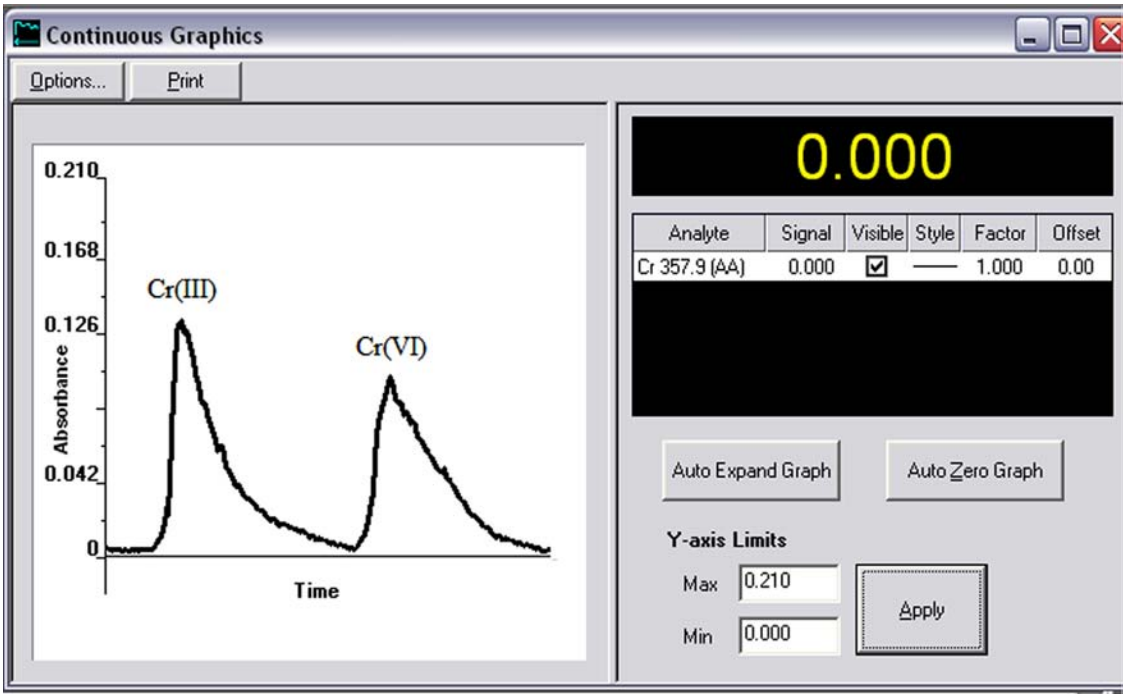
The method was also applied to the certified reference material, CWW-TMD waste water. Ten milliliters of CWW-TMD waste water were used to determine the levels of Cr(III) and Cr(VI) ions.

In order to determine the total chromium, 10 mL portions of CWW-TMD waste water containing both Cr(III) and Cr(VI) were taken. In order to oxidize Cr(III) ions to Cr(VI) ions, 4 mL of 3% (w/v) H$_2$O$_2$ at pH 12 was added to the sample and then heated on a hot plate adjusted to 80 °C for 40 min [27]. Then the sample was boiled for 10 min in order to remove excess H$_2$O$_2$. This sample was allowed to cool at room temperature for 30 min. After, pH of the sample was adjusted to 3 and completed to 10 mL with deionized water. The on-line preconcentration procedure was applied and total chromium was determined.

In another application, various amounts of these chromium species were also spiked to real aqueous samples, i.e., various waste water and tap water samples. Blanks were prepared in the same way as the sample solutions, but by omitting the addition of the analytes.

2.6. Application

The presented speciation procedure for Cr(III) and Cr(VI) based on the solid phase extraction method was applied to various water and certified reference material (CRM) samples. The tap water samples were taken from our laboratory and analyzed without



0.000

Analyte	Signal	Visible	Style	Factor	Offset
Cr 357.9 (AA)	0.000	☑	——	1.000	0.00

Y-axis Limits
Max 0.210
Min 0.000

Fig. 2. Signals of Cr(III) and Cr(VI) ions arrive at FAAS.

pretreatment. The total chromium concentration in the water samples was found by analyzing sequentially the Cr(III) and Cr(VI) levels by the proposed on-line procedure.

3. Results and discussion

The optimized chemical and hydrodynamic conditions in the flow system were determined by using the solutions each including 0.1 mg L^{-1} of Cr(III) and 0.6 mg L^{-1} of Cr(VI) ions. After the optimization process, the separation/preconcentration/speciation procedure was applied to the real samples.

3.1. Effect of pH on signals of Cr(III) and Cr(VI)

In order to determine the retention characteristics of Cr(III) and Cr(VI) ions on the columns, the effect of pH was studied. Various buffer solutions involving the pH range between 1 and 10 were used to obtain the model solutions with different pHs. The retained chromium ions on the minicolumns were eluted with HNO_3. Cr(III) and Cr(VI) ions present in the eluate solution were determined sequentially by FAAS. The effect of pH on the signals of Cr(III) and Cr(VI) ions are illustrated in Fig. 3. The signals of Cr(III) were maximum at around pH 3, while Cr(VI) was not observed at any pH for the chelating resin. The absorbances (signal) of Cr(VI) were maximum at pH 3 for the ion-exchange resin, while Cr(III) did not give any signal. These results show that both the chromium species could be determined quantitatively at pH 3. In all subsequent studies for the separation/preconcentration of Cr(III)/Cr(VI) ions, pH 3 was used as optimum. The findings related to the optimal pH value for this study agree with those which are given in the literature [5].

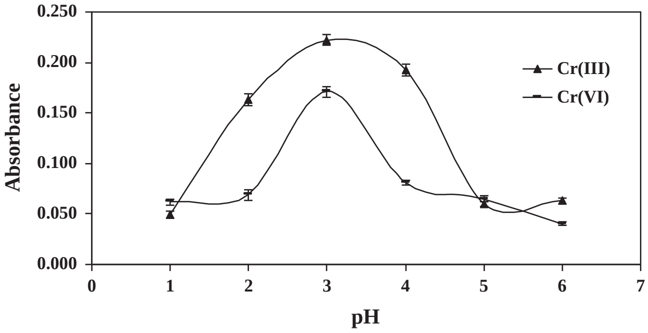


Fig. 3. Effect of pH of the sample solution on the Cr(III) and Cr(VI) signals.

3.2. Effect of type, concentration and volume of elution solutions

In order to get the best eluent conditions, various dilute strong acid and salt solutions with different volumes and concentrations were investigated for the elution of the retained Cr(III) and Cr(VI) ions on the chelating and ion-exchange resins, respectively, by using model solutions adjusted to pH 3.0 and containing 0.1 mg L^{-1} of Cr(III) and 0.6 mg L^{-1} of Cr(VI) ions. The main purpose of this study was to find a common eluent for the two chromium species. For the elution of the retained chromium ions from each minicolumn dilute HCl, HNO_3, H_2SO_4, NH_4NO_3, NH_4NO_3 in HNO_3, NH_4NO_3 in NH_3, and NaCl solutions were tested. The results are shown in Fig. 4, from which it is clear that the HNO_3 solution is the best eluent for the species. Then, different HNO_3 concentrations from 1 to 7 mol L^{-1} were tested and, except for 2–3 mol L^{-1} HNO_3, the other HNO_3 solutions did not give any improvement on the chromium signals. Therefore, 3 mol L^{-1} HNO_3 was chosen for stripping off Cr(III) and Cr(VI) ions from the columns in subsequent experiments (see Fig. 5). In all further studies, 3 mol L^{-1} HNO_3 was preferred as eluent due to its giving maximum absorbances and good repeatability.

3.3. Effect of flow rate of sample and eluent

The sample flow rate is an important parameter in on-line systems because it affects the retention of the ion on the minicolumn. At high sample flow rates, metal ions probably could not equilibrate properly with the resin due to the increase in the velocity of the ions, which reduces the contact time between the mobile and stationary phases. In contrast, low flow rates decrease the sample throughput, resulting in long analysis times. For this reason, the effect of sample flow rate on the sorption of the

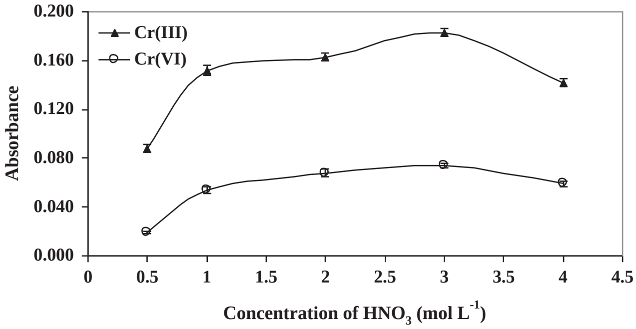


Fig. 5. Effect of the concentration of nitric acid as eluent on the Cr(III) and Cr(VI) signals (n=3).

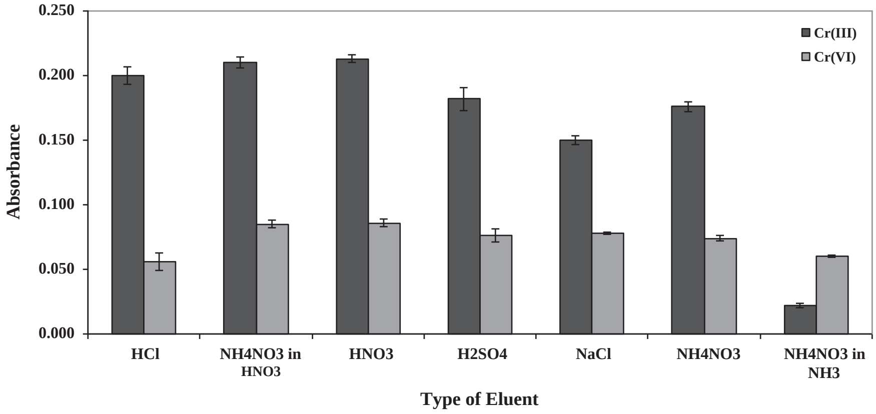


Fig. 4. Effect of type of the elution solutions on the signals of Cr(III)/Cr(VI) ions (n=3).

chromium species was investigated. The results are illustrated in Fig. 6. The sample flow rate was nearly constant from 0.5 to 1.7 mL min^{-1} for Cr(III) ions while it slowly increased in the range up to 1.7 mL min^{-1} for Cr(VI) ions. Beyond the sample flow rates of 1.7 mL min^{-1} the analytical signals decreased at similar speed for the two chromium species. Consequently, the optimum flow rate of the sample was chosen to be 1.7 mL min^{-1} in subsequent experiments as a compromise between efficiency and stability.

The eluent flow rate is another important parameter for stripping the analytes off the columns. In order to get an as high as possible analytical signal, the eluent flow rates were scanned from 2.5 to 5 mL min^{-1}. The optimum flow rate was selected to be 4.4 mL min^{-1} for subsequent studies in order to match the elution and the nebulization flow rates. As can be seen from Fig. 7, this flow rate was optimum for both the chromium species.

3.4. Effect of the amounts of the resins

The effect of the amount of chelating resin on adsorption of the metals was investigated at the flow rate of 1.7 mL min^{-1} for the sample and at a flow rate of 4.4 mL min^{-1} for the elution solutions. The analytical signal values increased with increasing the amounts of resins and reached maximum values at 15 mg. The analytical signals of the chromium ions decreased with increasing the amounts of resins beyond 15 mg due to insufficient eluent volume. In all the subsequent studies, the glass columns were filled with 15 mg of the both resins.

3.5. Effect of matrix ions on analytical signal

The effect of interferences on the determination of the two chromium species was investigated using the optimized on-line separation/preconcentration procedure. The possible interfering metal ions were added individually to the model solutions containing 0.5 mg L^{-1} from both Cr(III) and Cr(VI) ions and then the proposed procedure was applied. The effect of each interfering species was considered as interference when the analytical signal in the presence of the species resulted in an absorbance deviation of more than ±5%. The results are shown in Table 1. The results indicate that various substances commonly present in water and/or wastewater samples do not interfere in the analysis of these two chromium species under the experimental conditions.

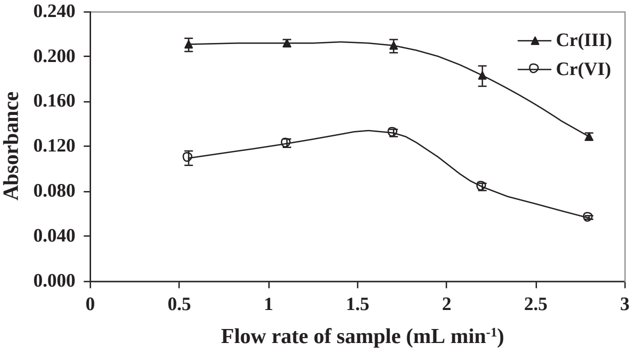


Fig. 6. Effect of the flow rate of sample solution on the Cr(III) and Cr(VI) signals (n=3)

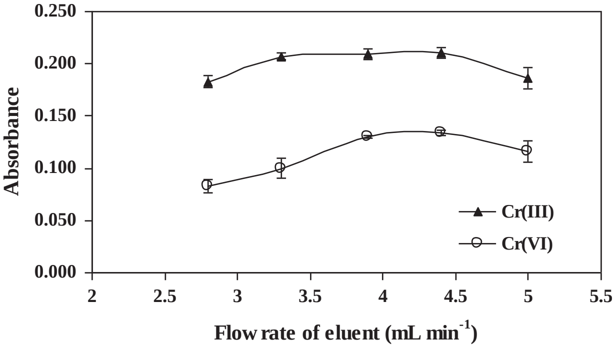


Fig. 7. Effect of the flow rate of eluent on the Cr(III) and Cr(VI) signals (n=3).

3.6. Analytical performance of the method

The characteristic data for the performance of the on-line separation/preconcentration system under the optimum conditions were studied. Linear regression equations were obtained for the on-line calibration curve, i.e., A=0.0015+0.8037$C_{\mathrm{Cr(III)}}$ (R^2=0.9997) and A=0.0001+0.4980$C_{\mathrm{Cr(VI)}}$ (R^2=0.9997), and for the off-line calibration curve, i.e., A=0.0039+0.0167C_{Cr} (R^2=0.9984); where A is the absorbance and C is the Cr(III) and/or Cr(VI) concentration in the standard solution. The enrichment factor (EF) was carried out by slope ratio of on-line calibration curve to off-line calibration curve. The enrichment factor was found to be 48 and 30 for Cr(III) and Cr(VI) ions, respectively. The detection limit as the concentration that gives a response equivalent to three times the standard deviation for the blank solutions (n=21) was 0.05 μg L^{-1} for Cr(III) and 0.3 μg L^{-1} for Cr(VI), respectively. The precision (as relative standard deviation, R.S.D.) was 2.3 and 4%, for the concentration of 0.4 μg L^{-1} Cr(III) and 0.4 μg L^{-1} Cr(VI) ions. Also the precisions (as intra and inter days) were 2.33% and 1.13% respectively. The accuracy of the developed method was tested by measuring the Cr(III) and Cr(VI) contents in the certified reference materials (CWW-TMD waste water). The samples were digested using the procedure described in Section 2.5. The chromium contents established with the present procedure agreed very well with the certified values (see Table 2).

The results indicate that the developed procedure can be applied for the determination of inorganic chromium species in the reference water sample being free from interferences.

3.7. Application to real samples

The method was extended for the on-line determination of the chromium(III)/(VI) species in various real samples. Preparation of the real samples for analysis was performed as described above in Section 2.5. The results are shown in Table 3. The proposed method was applied to the analysis of various water samples and satisfactory results were obtained for the two chromium species.

The recoveries for the additions of 0.05 mg L^{-1} of each chromium species varied from 96% to 102% (see Table 3). These results prove the accuracy of the proposed method. There was good agreement between the added and the found amounts of the analytes.

The proposed separation/preconcentration method was also successfully applied for the determination of total chromium in environmental water samples.

4. Conclusion

The data from the presented method have been compared with those of reported methods on speciation of chromium (Table 4). Some parameters obtained are comparable to those presented by the other methods. The system proposed in this paper allows the separate determination of both species of chromium. It is rapid, easy to use, automatic, selective and has a good sensitivity for the determination of Cr(III) and Cr(VI) ions in water samples. The minicolumns life is very long, and the only preparation process required for the columns prior to their use is a washing step with diluted nitric acid. This system also has the advantage being able to be fully automated without complicated hardware or software;

Table 1
Effect of foreign ions in the determination of 0.5 mg L^{-1} Cr(III) and 0.5 mg L^{-1} Cr(VI) ions.

Ions	**Added**	**Cr(III)**		**Cr(VI)**	
		Concentration (mg L^{-1})	**Recovery** (%)	**Concentration** (mg L^{-1})	**Recovery** (%)
Na^+	$NaNO_3$	2500	98 ± 1[a]	10000	100 ± 2
K^+	KNO_3	3500	99 ± 1	8000	98 ± 3
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	750	99 ± 2	5000	99 ± 2
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	500	96 ± 1	2000	100 ± 2
Fe^{3+}	$Fe(NO_3)_3 \cdot 6H_2O$	100	98 ± 2	100	98 ± 3
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	–	–	250	104 ± 2
Zn^{2+}	$Zn(NO_3)_2$	250	95 ± 1	200	99 ± 2
Cu^{2+}	$Cu(NO_3)_2 \cdot 4H_2O$	25	95 ± 1	500	97 ± 3
Cl^-	KCl	2250	100 ± 1	5000	98 ± 2
$SO_4{}^{2-}$	K_2SO_4	5250	98 ± 1	400	96 ± 2
$H_2PO_4{}^-$	KH_2PO_4	4000	100 ± 1	300	96 ± 2
$Cr_2O_7{}^-$	$K_2Cr_2O_7$	150	103 ± 1	–	–

[a] Average of three measurements ± standard deviation.

Table 2
The determination of the chromium species in the certified reference materials ($n=3$).

Sample	CWW-TMD waste water (mg L^{-1})				
	Found			Certified value	
	Cr(III)	Cr(VI)	Total Cr	Total Cr	Recovery (%)
CRM	0.805 ± 0.016[a]	0.188 ± 0.004	0.99 ± 0.02	1.00 ± 0.05	99 ± 2
Oxidation of Cr(III) (CRM)	–	1.020 ± 0.003	1.020 ± 0.003	1.00 ± 0.05	102 ± 3

[a] Average of three measurements ± standard deviation.

Table 3
Recoveries of the chromium species from water samples ($n=3$, mg L^{-1}).

Sample	Added		Found		Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tap water	–[a]	–	–	–	–	–
	0.05	0.05	0.049 ± 0.002[b]	0.05 ± 0.003	98 ± 3	100 ± 5
Synthetic sample	0.02	–	0.020 ± 0.001	–	100 ± 4	–
	0.02	0.04	0.020 ± 0.001	0.041 ± 0.002	99 ± 4	103 ± 3
Water of Kızılırmak	–	–	0.010 ± 0.001	–	–	–
	0.02	0.04	0.030 ± 0.001	0.039 ± 0.002	100 ± 3	98 ± 4
Nevşehir thermal spring water	–	–	–	–	–	–
	0.02	0.04	0.021 ± 0.001	0.049 ± 0.002	105 ± 4	98 ± 4
Antalya sea water	–	–	–	–	–	–
	0.02	0.04	0.011 ± 0.001	–	55 ± 8	0 ± 0
Gebze industry water	–	–	0.0050 ± 0.0002	–	–	–
	0.02	0.04	0.024 ± 0.001	0.041 ± 0.003	96 ± 4	103 ± 5
Water of battery factory	–	–	0.011 ± 0.001	0.032 ± 0.001	–	–
	0.02	0.04	0.031 ± 0.001	0.070 ± 0.001	100 ± 3	99 ± 2

[a] Below detection limit.
[b] Average of three measurements ± standard deviation.

Table 4
A comparative study for on-line speciation and determination of chromium species.

Method/system/technique	Detection limit for Cr(III)/Cr(VI) (µg L^{-1})	Quantification limit (µg L^{-1})	Enrichment factor	Sample throughput (h^{-1})	Sampling volume (mL)	References
On-line HPLC–ICP–AES/MS	4.6/3.7	15.2/12.2	–	–	2	[28]
On-line FAAS	0.8 only Cr(VI)	2.6	80	18	37.8	[29]
On-line FAAS	0.02/0.02	0.2/0.2	90/100	10	30	[30]
On-line FAAS	0.2 for Cr(III)/total Cr	–	36	30	2.2	[31]
On-line FAAS	1.9/2.3	–	20.8/24.9	12	15	[32]
On-line ICP–MS	0.02	0.1	11.5	12	7	[33]
On-line FAAS	0.05/0.3	0.2/1.0	48/30	17	5.8	This work

in fact, modification of the software of the spectrometer and the use of additional computers were not necessary. It is an accurate and economic method. This method also uses less chemicals than those of similar works given in the literature. The proposed method was successfully applied for the determination of chromium (III) and (VI) species in various aqueous samples with a low detection limit, high preconcentration factor, accuracy and precision. By using this proposed on-line separation/preconcentration system, the following advantages are attained: (a) elimination of the matrix effect, (b) increase of sensitivity by the preconcentration, (c) automatization of different steps of the analysis, and (d) separation/preconcentration and sequentially speciation of the Cr(III) and Cr(VI) ions in aqueous samples.

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