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Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination

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Abstract

An on-line flow injection (FI) preconcentration-electrothermal atomic absorption spectrometry (ETAAS) method is developed for trace determination of chromium in drinking water samples by sorption on a conical minicolumn packed with activated carbon (AC) at pH 5.0. The chromium was removed from the minicolumn with 1.0% (v/v) nitric acid. An enrichment factor (EF) of 35-fold for a sample volume of 10 ml was obtained. The detection limit (DL) value for the preconcentration method proposed was 3.0 ng l^{-1}. The precision for 10 replicate determinations at the 0.5 μg l^{-1} Cr level was 4.0% relative standard deviation (R.S.D.), calculate with the peak heights obtained. The calibration graph using the preconcentration system for chromium was linear with a correlation coefficient of 0.9992 at levels near the detection limits up to at least 50 μg l^{-1}. The method was successfully applied to the determination of Cr(III) and Cr(VI) in drinking water samples.

Keywords: Chromium speciation; On-line preconcentration; Activated Carbon; ETAAS; Drinking water

1. Introduction

The element chromium occurs in natural samples in two relatively stable valence states, i.e. in the form of Cr(III) and Cr(VI) species, which exert quit different effects on biological systems. In fact, while Cr(III) is an essential component having an important role in the glucose, lipid and protein metabolism, Cr(VI) has a definitely adverse impact on living organisms. Cr(VI) can easily penetrate the cell wall and exert its noxious influence in the cell itself, being also a source of various cancer diseases [1,2].

Since once of the routes of Cr incorporation into the human body is by ingestion [3,4], several analytical methods have been developed in order to separate and determine Cr(III) and Cr(VI) species in water samples [5,6]. The concentration of Cr in natural waters is very low [4–6], in order of a few μg l^{-1}. Therefore, powerful techniques are required, but of those currently available only a few show sufficient detection power.

Flow injection analysis (FIA) combined with inductively coupled plasma-mass spectrometry (ICP-MS) [7,8]; flame atomic absorption spectrometry (FAAS) [9,10] and electrothermal atomic absorption spectrometry (ETAAS) [11,12] are the most used techniques in the determination of low chromium amounts.

However, the low level of chromium in drinking waters is not compatible with the detection limit of ETAAS. Thus, preconcentration and separation steps are frequently required in order to improve the detection capability of this technique.

Various preconcentration procedures for the determination of chromium have been reported [13–17], including, among others, chelation, extraction, precipitation, co-precipitation, and ion-exchange. Table 1 shows a

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Table 1
Procedures for preconcentration and determination of chromium

Sampling frequency (h^{-1})	Detection limit ($\mu g\,l^{-1}$)	Relative standard deviation (%)	Enrichment factor	Sample volume (ml)	Technique	References
33	0.003	4.0	35	10	ETAAS	This work
17	2.0	2.8	25	–	Spectrophotometry	[5]
–	0.5	–	–	–	HPLC-ICP-MS	[7]
10	0.02	3.8	50	50	FAAS	[9]
18	0.8	3.2	80[a]	–	FAAS	[10]
–	0.14	–	7.4	–	ETAAS	[11]
–	0.002–0.005	1.8–2.3	100	100	ETAAS	[12]
–	0.4–1.1	9.0	–	–	FAAS	[14]
–	2.0–6.0	–	23–61	18	FAAS	[15]
10	0.02	2.9	50	50	FAAS	[17]

[a] Enhancement factor.

comparison among preconcentration procedures developed for chromium determination. However, many of these methodologies are performed in a batch mode. When preconcentration techniques are applied in batch, the time of analysis is increased, thus turning these procedures unpractical for application in routine analysis. This situation has been significantly improved utilizing flow injection associated with ETAAS [11,18,19].

In this sense, procedures for the preconcentration of chromium have been proposed. These methodologies usually make use of a packed column filled with C_{18} bonded silica [20] or activated alumina [21] and most recently with small Teflon beads [22] where the hydrophobicity of the beads is exploited for the appropriate preconcentration of metallic ion species. Based on the hydrophobicity, have also been developed other procedures where the generated complex is sorbed on the inner walls of a knotted reactor [23].

Activated carbon has been widely used for many purposes both in laboratory and industrial settings, due to its ability to adsorb organic compounds and inorganic metal complexes. Since its introduction in analytical chemistry, enrichment of trace metals using AC has been favorably performed with very high concentration factors in different matrices [24–27].

The mechanism of sorption on AC is still under investigation and the adsorption of metals on activated carbon could be explained using Langmuir and Freundlich equations. The adsorption equilibrium studies have revealed that pH is the dominant parameter controlling the adsorption [28].

In this study, a simple preconcentration system, achieved by replacing the sample tip of the autosampler arm by a minicolumn packed with activated carbon, is developed for the speciation and determination of chromium. Chromium was retained on the AC in absence of complexing reagent; the adjustment of pH value of the solution suffices to retain chromium (III) ion. A step of reduction was necessary in order to determinate the total chromium content. The Cr(VI) content was then calculated by the difference by total chromium concentration and that for Cr(III). The determination was then carried out by ETAAS associated with a FI methodology.

2. Experimental

2.1. Reagents

The activated carbon (Merck, Darmstadt, Germany, 50–70 mesh) was used after pretreatment with acid [activated carbon was heated with 10% (v/v) hydrochloric acid for 30 min and then with 10% (v/v) nitric acid for 20 min and finally washed with deionized water at neutral pH was reached].

A stock standard solution of 1000 mg l^{-1} Cr(III) was prepared from 7.6960 g chromium nitrate ($Cr(NO_3)_3$. 9 H_2O, Merck, Darmstadt, Germany) dissolved in ultrapure water and diluted to a final volume of 1000 ml. A stock standard solution of 1000 mg l^{-1} Cr(VI) was prepared from 2.8290 g potassium dichromate ($K_2Cr_2O_7$, Merck, Darmstadt, Germany) dissolved in ultrapure water and diluted to a final volume of 1000 ml.

A buffer solution was prepared by diluting a 2.0 mol l^{-1} acetic acid solution adjusted to pH 5.0 with sodium hydroxide.

Ultrapure water (18 MΩ cm) was obtained from EASY pure RF (Barnsted, Iowa, USA).

All the reagents were of analytical-reagent grade and the presence of chromium was not detected within the working range.

2.2. Apparatus

The measurement were performed with a Shimadzu Model AA-6800 Atomic Absorption Spectrometer (Tokyo, Japan), equipped with a deuterium background corrector, a 6500-electrothermal atomizer and an ASC-6100 autosampler. Pyrolytic graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. Chromium hollow-cathode lamp (Hamamatsu, Photonics K.K., Japan) was employed as radiation source. The ETAAS instrumental and operating conditions are listed in Table 2. A Minipulse peristaltic pump [Gilson (Villiers, Le-Bell, France)] was used. Sample injection was achieved using a Rheodine Model 50 4-way (Cotati, CA, USA). A conical minicolumn (40 mm length, 4.5 mm internal upper-diameter and 1.5 mm internal lower-

Table 2
Main instrument parameters and furnace temperature program for Cr determination

Parameters				
Wavelength (nm)				357.9
Slit width (nm)				0.5
Lamp current (mA)				10
Background correction				Deuterium
Stage	Temperature (°C)	Time (s)		Argon gas flow (l min^{-1})
		Ramp	Hold	
Furnace program				
Drying	150	20	–	0.1
	250	10	–	0.1
Pyrolisis	800	10	–	1.0
	800	–	10	1.0
	800	–	3	0.0
Atomization	2300	–	2	0.0 (read)
Cleaning	2500	–	2	1.0

diameter) was used as the AC holder. Pump tubes-Tygon type (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA) were employed to propel the sample and eluent. The 357.9 chromium wavelength was used in the subsequent determinations.

2.3. Column and sample preparation

The conical minicolumn was prepared by replacing 30 mg of AC into an empty conical tip using the dry packing method. To avoid loss of AC when the sample solution passed through the conical minicolumn, a small amount of quartz wool was placed a both sides of conical minicolumn. The column was then mounted at the furnace autosampler to form the preconcentration system.

The water samples were filtered through 0.45 μm pore size membrane filters immediately after sampling, and were adjusted to pH 5.0 with buffer solution immediately before use.

2.4. Reduction of Cr(VI) to Cr(III) prior to total chromium determination

In order to determine the total chromium content, it is necessary to reduce Cr(VI) to Cr(III) prior to sorption on AC. This was made by heating solutions in 0.1 mol l^{-1} hydrochloric acid at 50 °C using 0.2 ml of 99.8% (v/v) ethanol as reductant reagent. Then, the solution was diluted up to 10 ml. After that, Cr(VI) is completely reduced in an hour.

2.5. Preconcentration procedure and determination

Before loading, the conical minicolumn was conditioned for preconcentration at the correct pH value (5.0) with diluted buffer solution, valve $\mathbf{V_1}$ in position **B** (Fig. 1); the chromium solution was then loaded on the activated carbon at flow rate of 15 ml min^{-1} with valve $\mathbf{V_1}$ in position **S** and valve $\mathbf{V_2}$ in load position **(a)**.

After the loading time, the conical minicolumn mounted at the furnace autosampler was automatically moved into the dosing hole of the graphite tube. Finally, peristaltic pump P was stopped and the injection valve $\mathbf{V_2}$ was switched on the injection position **(b)** and the retained metal was eluted with 50 μl volume of 1.0% (v/v) nitric acid at a flow rate of 0.2 ml min^{-1} directly into the graphite furnace. After that, the autosampler arm was moved back to the wash position and

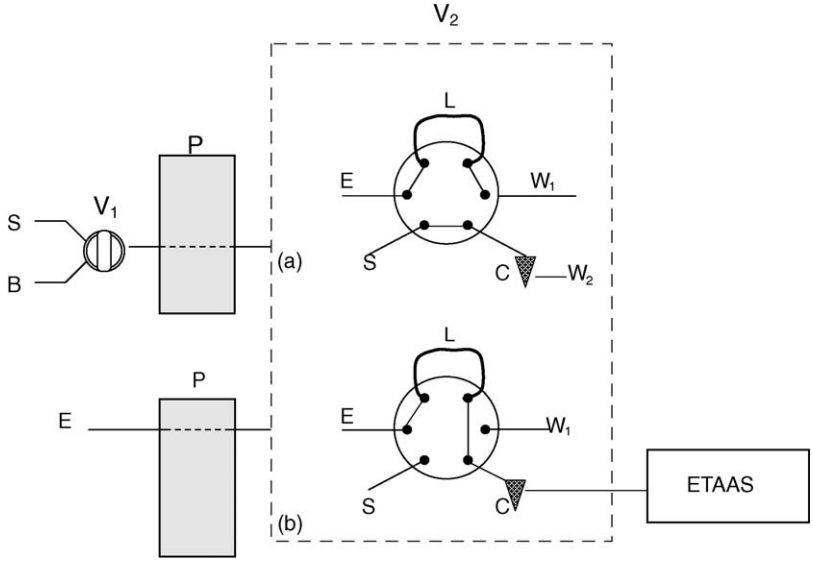

Fig. 1. Schematic diagram of the instrumental set-up. **S**, sample (flow rate: 15.0 ml min^{-1}); **B**, buffer; **E**, eluent (flow rate: 0.2 ml min$-^{1}$); **L**: loop 50 μl volume; $\mathbf{W_1}$,$\mathbf{W_2}$, wastes; **P**, peristaltic pump; **C**, minicolumn packed with activated carbon; $\mathbf{V_1}$ and $\mathbf{V_2}$, injection valves. Valve positions: **(a)** sample loading; **(b)** injection.

the temperature program was started. The absorbance measurements were proportional to the chromium concentration in the sample and were used for all meaurements. The operating conditions were established and the determination was carried out.

3. Results and discussion

3.1. Coupling of the packed minicolumn with ETAAS

Owing to the discrete non-flow-through nature of the ETAAS, the limited capacity of the graphite tube and, the necessity for quantitative elution of the retained analyte, there are some difficulties when coupling the ETAAS directly with FI on-line sorption systems. In order to adapt the minicolumn packed with activated carbon, which is used in our previous work for Cd and Ni determination with inductively coupled plasma optical emission spectrometry [25,26], to the requirements of ETAAS, the mass of the sorbent material was reduced to 30 mg. The volume of activated carbon busy in the new minicolumn was 35 μl, while it was proved that 50 μl of 1.0% (v/v) nitric acid was enough for quantitative elution.

3.2. Effect of pH

In order to optimize the sorption conditions for the retention of the chromium on AC, the chromium signal was monitored by measuring it with ETAAS while changing the pH of the solution that passes through the conical minicolumn packed with AC. Fig. 2 shows that the optimal pH values were in the range of 4.5–5.5. Considering these results, the selected pH was 5.0.

3.3. Effect of sample flow rate

The sample flow rate through the column packed with AC is a very important parameter, since this is one of steps that controls the time of analysis. We could verify that with flow rates up to 15 ml min^{-1} there is no effect on the analyte recovery. Fig. 3 shows that at higher flow rates the response decreases.

3.4. Effect of eluent concentration

A satisfactory eluent should effectively elute the sorbed metal which a discrete volume due to the limited graphite tube capacity. In order to elute the chromium adsorbed on the AC, 50 μl volume of 1.0% (v/v) nitric acid at 0.2 ml min^{-1} flow rate was chosen as optimal.

3.5. Interferences

The effects of representative potential interference species (at the concentration levels at which they may occur in the sample under study) were tested. Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+},

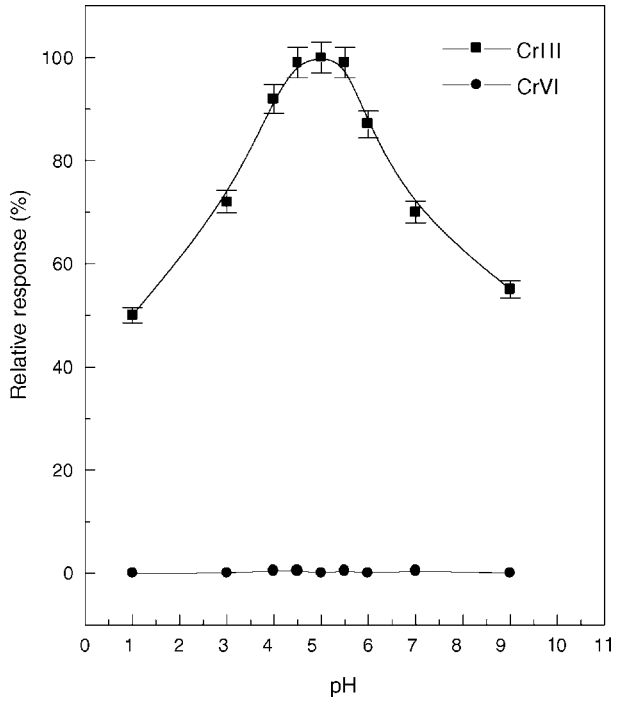

Fig. 2. Dependence of Cr(III) and Cr(VI) retention on pH of loading solutions. Preconcentration of 10 ml of Cr(III) and Cr(VI) solutions; chromium concentration was 0.5 μg l^{-1}; nitric acid concentration was 1.0% (v/v).

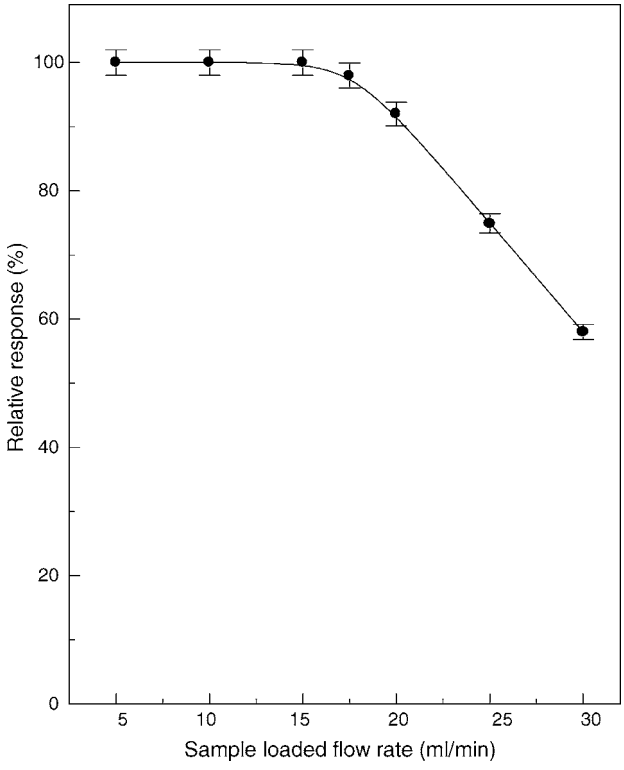

Fig. 3. Dependence of recovery of metal on sample flow rate. Preconcentration of 10 ml of Cr(III) and Cr(VI) at pH 5.0; chromium concentration was 0.5 μg l^{-1}; nitric acid concentration was 1.0% (v/v).

Table 3
Recovery study (95% confidence interval; $n = 6$)

Aliquots	Base value ($\mu g\,l^{-1}$)	Quantity of Cr added ($\mu g\,l^{-1}$)	Quantity of Cr found ($\mu g\,l^{-1}$)	Recovery (%)[a]
1–6[b]	–	0.00	0.71 ± 0.03	–
7[b]	0.71	0.20	0.92	101.4
8[b]	0.71	0.40	1.09	97.1
9[b]	0.71	0.60	1.30	98.5
10[b]	0.71	0.80	1.50	98.5
11–16[c]	–	0.00	0.59 ± 0.02	–
17[c]	0.59	0.20	0.79	100.0
18[c]	0.59	0.40	1.00	101.6
19[c]	0.59	0.60	1.18	98.3
20[c]	0.59	0.80	1.40	101.6

[a] $100 \times$ [(found-base)/added].
[b] Recuperation study for Cr (III).
[c] Recuperation study for Cr (VI).

Ni^{2+}, Co^{2+}, Mn^{2+}, and Fe^{3+} could be tolerated up to at least $500\ \mu g\,l^{-1}$. Commonly encountered matrix components such alkali and alkaline elements are not retained on the activated carbon under the working conditions. On the other hand, anions such as CO_3^{2-}, F^-, SO_4^{2-}, Cl^-, PO_4^{3-}, malonate and ascorbate could be tolerated up to at least $1000\ \mu g\,l^{-1}$.

3.6. Validation study

In order to demonstrate the validity of this method, 200 ml of drinking water was collected and divided into twenty portions of 10 ml each. The proposed method was applied to 12 portions and the average quantities of Cr(III) and Cr(VI) obtained were taken as a base values. Then increasing quantities of Cr(III) and Cr(VI) were added to the other aliquots of sample and the analyte was determined by the same method. As it is shown in Table 3, the recovery values are between 97.1 and 101.4% for Cr(III) and 98.3 and 101.6% for Cr(VI). The results were compared with the *t*-test and no significant differences were observed at 95% confidence level [29,30].

3.7. Analytical performance

Under the optimum conditions described above, the performance data of the on-line minicolumn preconcentration-ETAAS system for chromium determination are summarized in Table 4.

The overall time required for preconcentration of 10 ml of sample (0.66 min, at flow rate of $15\ ml\,min^{-1}$), elution (0.25 min, at flow rate of $0.2\ ml\,min^{-1}$), and washing and conditioning (1 min) was about 1.91 min; hence, throughput was approximately 31 samples h^{-1}. An enrichment factor of 35-fold was obtained with respect to the chromium determination in drinking water by ETAAS without preconcentration.

Table 4
Performance of the FI-on-line activated carbon sorption preconcentration-ETAAS system determination of chromium under the optimized conditions

Correlation coefficient	0.9992
Sampling frequency (f) (h^{-1})	31
Precision ($500\ ng\,l^{-1}$) (%R.S.D., $n = 10$)	4.0
Detection limit (3σ) ($ng\,l^{-1}$)	3.0
Enrichment factor (EF)	35.0
Concentration efficience (CE = EF $\times$ (f/60))	19.2

Table 5
Concentration of chromium in drinking water samples (95% confidence interval; $n = 6$)

Sample	Cr(III) concentration ($\mu g\,l^{-1}$)	Cr(VI) concentration ($\mu g\,l^{-1}$)
A (1st week)	0.68 ± 0.03	0.58 ± 0.02
B (2nd week)	0.70 ± 0.02	0.61 ± 0.02
C (3rd week)	0.71 ± 0.02	0.59 ± 0.02
D (4rd week)	0.70 ± 0.03	0.57 ± 0.03

The drinking water samples were collected at different times in our laboratory.

The reproducibility of the preconcentration method was evaluated by passing 10 ml of standard solution of chromium ($0.5\ \mu g\,l^{-1}$) through the minicolumn and repeating this procedure 10 times. The relative standard deviation (R.S.D.) was 4.0%, calculated from the peaks heights obtained. The calibration graph using the preconcentration system for chromium was linear with a correlation coefficient of 0.9992 at levels close to the detection limit up to at least $50\ \mu g\,l^{-1}$. The detection limit (DL) was calculated as the amount of chromium required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ). The value of DL obtained for the preconcentration of 10 ml of aqueous solutions of Cr was $3.0\ ng\,l^{-1}$. Finally, the results of the method applied to the chromium determination in drinking water samples are shown in Table 5. The concentrations of total chromium were in the range 1.26–1.33 $\mu g\,l^{-1}$ of chromium. The results obtained are in good agreement with those reported by Siles Cordero et al. [11].

4. Conclusions

The FI on-line separation and preconcentration system using activated carbon as a sorbent material for ETAAS has been evaluated and demonstrated to be a promising for routine speciation and determination of chromium at low levels

in drinking water samples. A 35-fold EF was obtained. The methodology proposed has shown adequate accuracy and selectivity, besides being simple and economical, as only AC is used for preconcentration of chromium without to use a complexing reagent.

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