Preconcentration and Speciation of Cr(III) and Cr(VI) in Water Samples Using Amberlite XAD-16 Resin and Determination by Flow Injection-Flame AAS

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INTRODUCTION

Chromium exists in two oxidation states (III and VI) with different thermodynamic, kinetic, biochemical, and toxicological behaviors in environmental and biological systems (1-4). In fact, while Cr(III) is an essential component having an important role in 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 (3). Therefore, the separation of Cr(III) and Cr(VI) and the determination of their species is receiving considerable attention in pollution and nutritional studies.

Since one of the routes of Cr incorporation into the human body is water (1,5,6), determination in these types of samples becomes very important. The concentration of Cr in natural water is very low (6-8), in the order of a few µg/L. Therefore, powerful techniques are required, but of those currently available only few show sufficient sensitivity. The neutron activation analysis (NAA) (9) method has been applied to the determination of Cr; however, it is time-consuming, and routine analysis of numerous samples is laborious. This method also requires sophisticated instrumentation which may not be available in most analytical laboratories. Inductively coupled plasma mass spectrometry (ICP-MS) (10,11) is used for the determination of Cr because of its high sensitivity, selectivity, and sample throughput. However, in the case

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ABSTRACT

A method for the preconcentration and speciation of chromium was developed. On-line preconcentration and determination were obtained using flame atomic absorption spectrometry (FAAS) coupled with flow injection (FI). To determine the total chromium present in water samples, the chromium species were retained on an Amberlite XAD-16 resin as chromium-4-(2-Thiazolylazo)-resorcinol (Cr-TAR) complex, at pH 5.0. On the other hand, Cr(VI) was determined by selective formation of Cr-TAR complexes with the use of 1,2 cyclohexane-diaminetetracetic acid (CDTA) as masking agent of Cr(III). The Cr-TAR complexes were formed by heating the reagents at 90°C for 50 minutes and then retained on the resin. The Cr-TAR complexes were removed from the micro-column with ethanol. The Cr(III) concentration was determined by the difference between the total chromium concentration and that of Cr(VI). A sensitivity enhancement factor of 250 was obtained with respect to the chromium determination in aqueous medium by FAAS (50 for preconcentration and 5 due to the use of ethanol as solvent). The detection limit for the preconcentration of 50 mL of aqueous solution was 20 ng/L. The precision for 10 replicate determinations at the 2.0-µg/L Cr level was 3.8% relative standard deviation (RSD), calculated from the peak heights obtained. The calibration graph using the separation and preconcentration method for chromium species was linear with a correlation coefficient of 0.9994 at levels near the detection limits up to at least 100 µg/L. The method was successfully applied to the speciation of chromium in water samples.

of chromium determination, it suffers from matrix effects by molecular ion peaks (6,12). Additionally, the cost of ICP-MS instrumentation may be prohibitive for many laboratories.

Flame atomic absorption spectrometry (FAAS) or electrothermal atomic absorption spectrometry (ETAAS) are the most used techniques in the trace determination of Cr. However, the low-level concentration of Cr in water is not compatible with the detection limit of FAAS. In order to achieve accurate, reliable and sensitive results, preconcentrations and separations are needed when the concentrations of the analyte elements in the sample are too low to be determined directly by FAAS, or when the determination of species is required. On the other hand, unlike FAAS, the sensitivity of ETAAS is adequate for a variety of analytical situations, but not for coupling in a continuous detection system (13). Although the sensitivity of ETAAS is sufficient for the determination of Cr in water samples, a previous separation stage becomes necessary in order to determine the different Cr species.

Over the past years, several methods for speciation of chromium using atomic spectroscopy have been investigated. These methods include previous preparation of the sample by liquid-liquid extraction (14,15), solid-liquid extraction (16,17), or the direct coupling of liquid chromatography with FAAS (18,19). However, many of these methodologies are performed in batch, thus requiring great sample volumes in order to reach low detection limits. Besides, these sys-

tems present higher contamination risks and are not practical for application in routine analysis. This situation has been significantly improved by utilizing flow injection (FI) associated with FAAS. In fact, to date the most dramatic improvements achieved in FI-FAAS have been in the field of on-line preconcentration (20,21).

In order to be used as packing in preconcentration columns for FI (22), the materials have to meet several requirements. XAD resins meet many of these requirements and since they have good physical properties such as porosity, uniform pore size distribution, high surface area as chemical homogeneous non-ionic structures, and good adsorbent properties for great amounts of uncharged compounds (23), they have been used as supports for immobilization of chelating agents and metal complexes (24-30).

4-(2-Thiazolylazo)-resorcinol (TAR) forms stable complexes with numerous metal ions (31,32), and it is therefore a suitable reagent for Cr preconcentration on XAD resin (33).

On the other hand, the selectivity in metal complexing with organic reagents can be enhanced by the use of masking agents. Chromium can react selectively with the 1,2-cyclohexanediaminetetracetic acid (CDTA) (34,35) reagent and this behavior could be used to obtain the specific complexing of Cr with other reagents.

In the present work, an on-line method is proposed for the preconcentration of Cr(III) and Cr(VI) using XAD-16 resin. Chromium was retained on the resin under the form of Cr-TAR complex. Determination selectivity was obtained by using CDTA as the masking agent for Cr(III). The determination was performed by FAAS associated with a FI methodology.

EXPERIMENTAL

Instrumentation

The measurements were performed with a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan), equipped with a chromium hollow cathode lamp. The FAAS instrumental and operating conditions that provided the best sensitivity and no differences between the Cr(III) and Cr(VI) signal are listed in Table I. The flow injection system used is shown in Figure 1. A Minipuls™ 3 peristaltic pump (Gilson, Villiers Le-Bell, France) was used. The sample injection was achieved using a Rheodyne® (Cotati, CA, USA) Model 50, four-way rotary valve. A micro-

bore glass column (50-mm length; 3-mm internal diameter) fitted with porous 25-µm glass frits was used as the resin holder. Tygon™ type pump tubes (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA) were employed to propel the sample, reagent and eluent.

Reagents and Chemicals

Amberlite XAD-16 resin (Rohm & Haas, Philadelphia, PA, USA) was used. The particle size was between 20 - 50 mesh with a surface area of 825 m²/g. Before use, the surface of the resin was activated by immersion in a solution of methanol-4 mol/L HCl (1+1). Subsequently, metal impurities were removed by further washing with 2 mol/L HCl

TABLE I
FAAS Instrumental Parameters Employed to Cr Determination

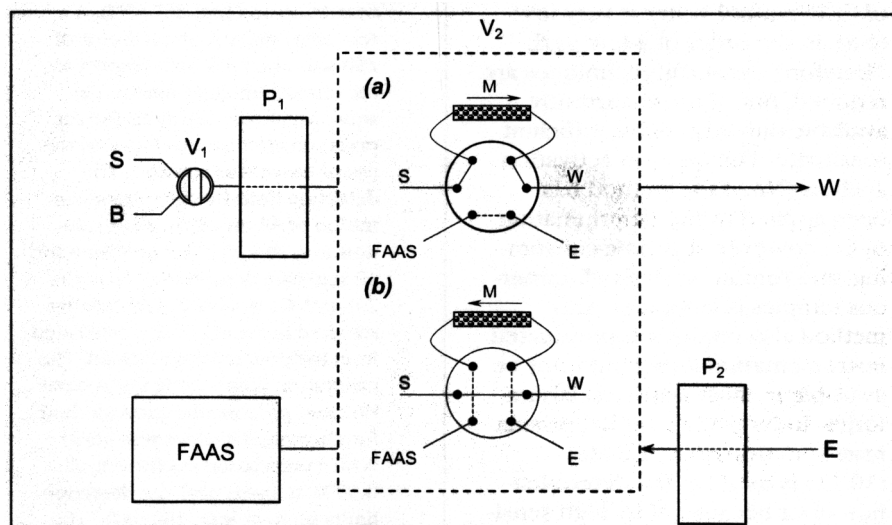| Flame type	Air-C_2H_2
Burner height	13 mm
Wavelength	357.9 nm
Slit width	0.5 nm
Lamp current	10 mA
Measurement mode	Height
Air flow rate	8.0 L/min
Acetylene flow rate	2.8 L/min
Sample introduction flow rate	3.0 mL/min

Fig. 1. Schematic diagram of the instrumental setup.
S: sample; B: buffer diluted; E: eluent ; W: waste; P_1 and P_2: peristaltic pumps; M: micro-column; V_1: two-way valve; V_2: load-injection valve [(a) Load position; (b) Injection position].

solution and finally with deionized water.

A solution of 4-(2-Thiazolylazo)-resorcinol (Merck, Darmstadt, Germany) 10^{-2} mol/L was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution with ethanol.

A 10^{-2} mol/L solution of CDTA (Aldrich, Milwaukee, WI, USA) was prepared by dissolution in 0.1 mol/L sodium hydroxide (Merck, Darmstadt, Germany) solution.

A stock standard solution of 1000 mg/L Cr(III) was prepared from 7.6930 g chromium nitrate (99.99%) $(Cr(NO_3)_3 \cdot 9H_2O)$ (Merck, Darmstadt, Germany) dissolved in ultrapure water and diluted to 1000 mL with a final HNO_3 concentration of 0.05 mol/L. Working solutions were prepared by dilution of the stock solution.

A stock standard solution of 1000 mg/L Cr(VI) was prepared from 2.8287 g sodium dichromate (99.99%) $(K_2Cr_2O_7)$ (Merck, Darmstadt, Germany) dissolved and diluted to 1000 mL with ultrapure water. Working standard solutions were prepared daily by appropriate dilution with ultrapure water.

A buffer solution was prepared by diluting a 2.0 mol/L acetic acid solution adjusted to pH 5.0 with sodium hydroxide.

Ultrapure water (18 MΩ cm^{-1}) was obtained from an EASYpure RF (Barnstedt, Iowa, USA).

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

Sample Collection and Preparation

The water samples were filtered through 0.45-μm pore size membrane filters (Millipore Corporation, Bedford, MA, USA) immediately after sampling and were stored in bottles at 4°C (Nalgene; Nalge, Rochester, NY, USA).

In order to avoid the reduction of Cr(VI) with the organic matter present in natural water, the samples were not acidified. The analysis was performed immediately after sampling in order to minimize the adsorption of chromium in solution on the walls of the container. All instruments used were previously washed with a 10% (v/v) HNO_3 water solution and then with ultrapure water.

Formation of Cr(III) and Cr(VI) Complexes with TAR Reagent

Prior to the preconcentration and determination of total chromium, a procedure was developed in order to reach the formation of the Cr-TAR complex. 1.0 mL of 10^{-2} mol/L TAR solution and 2.0 mL of acetic/acetate buffer solution (pH=5.0) were added to a precipitation vessel containing 50 mL of sample solution. The mixture was placed in a water bath at a temperature of 90°C for 50 min. Finally, it was allowed to cool to room temperature (25°C).

Selective Complexing of Cr(III) with CDTA

A volume of 50 mL of sample solution was placed in a precipitation vessel, 5 mL of 10^{-2} mol/L CDTA solution was added, and the solution subsequently heated at 80°C in a water bath for 5 minutes. A similar procedure to that described for total chromium was followed for the formation of the Cr(VI)-TAR complex.

Study of the Retention of the Cr-TAR Complex on the Resin

In order to optimize the retention of the Cr(III) and Cr(VI) complexes on the column, the following variables were assessed: pH, TAR concentration, and loading flow rate.

Solutions were prepared with a known amount of chromium and 100-fold excess in moles of TAR to form the metal complex, and the

pH was varied by adding diluted HCl or NaOH solutions, so that 50 mL of each solution was obtained at the corresponding pH, containing 50 μg/L of chromium. Each of the solutions was loaded on the XAD-16 resin and the retained metal complex was eluted with 10 mL of ethanol in a 10-mL volumetric flask.

The optimum TAR concentration was determined by the same procedure, working at pH 5.0.

Assessment of the retention with respect to the loading flow rate of the solutions was performed at flow rates between 2 - 15 mL/min.

The concentration of chromium was determined by FAAS. Recovery was calculated against the theoretical concentration.

Separation and Preconcentration Procedure

Before loading, the column was conditioned for preconcentration at the correct pH with the diluted (1:10) buffer solution, valve V_1 in position B (Figure1). The complex was then loaded on the XAD-16 resin at a flow rate of 10 mL/min, with valve V_1 in position S and valve V_2 in load position (a). After the loading time, the sample still present in the lines and on the column was removed with further washing with the diluted buffer solution, with valve V_1 again in position B. Finally, valve V_2 was switched to the injection position (b) and the retained metal complex was eluted in countercurrent (i.e., reversal of the flow direction through the column during elution with respect to sample loading), with ethanol at a flow rate of 3.0 mL/min, directly into the nebulizer and subsequently the flame. Since the Cr-TAR metal complex is not totally retained on the resin (approximately 80%), the standard solution must also be passed through the micro-column. The operating conditions were established and the determination was

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carried out. For the Cr(VI) precon-centration and determination, the above described procedure was followed but using CDTA as the masking reagent of Cr(III). Therefore, the concentration of Cr(III) was calculated as the difference between the total concentration of Cr and that of Cr(VI).

RESULTS AND DISCUSSION

Optimization of the Loading Variables

The retention conditions of the metal complexes were optimized and the Cr signal was monitored by measuring it with FAAS while changing the pH of the solution that passes through the sorption micro-column. The optimal pH values were in the 4.5-5.6 range. This phenomenon is understandable, since better complexing occurs within this range. Considering these results, the pH selected was 5.0. Working at this pH value had the advantage of selectively complexing and preconcentrating Cr, since most metal ions which can form complexes with TAR do so at higher pH values (31,32).

In the present work, a bead size of resin (20-50 mesh) was considered adequate for the preconcentration procedure in the micro-column. Smaller resin particles could have improved retention capacity, but would have increased back-pressure of the micro-column, and the flow rate ought to have been reduced, with the subsequent increase in preconcentration time. Choice of the Amberlite XAD-16 resin was motivated by the fact that it is highly stable in both acidic and basic solution and exhibits a large surface area. This allows the use of the micro-column for an indefinite number of samples without degradation of performance. Besides, many researchers have studied the behavior of Amberlite XAD resins as adsorbents of organic substances and as supports for chelating agent-

impregnated resins (23,36,37). The dimensions of the micro-column used here have been optimized and previously reported (27).

It is well known that complex retention on XAD resins is modified by the concentration of organic solvents (36). Furthermore, the formation of metal complexes with TAR is also affected by the solvent. Higher retention was observed for lower ethanol percentages. The value selected was 2.0% (v/v), since it was the lowest value compatible with the complex stability.

Chromium did not react with the complexing reagent at room temperature; however, the complex was formed on heating the reactants to 85-95°C. The effect of the temperature on the progress of the complexing reaction is shown in Figure 2(a). Another important parameter in the complexing reaction was the heating time. As can be seen in Figure 2(b), the minimum heating time needed to obtain the best results was 50 minutes.

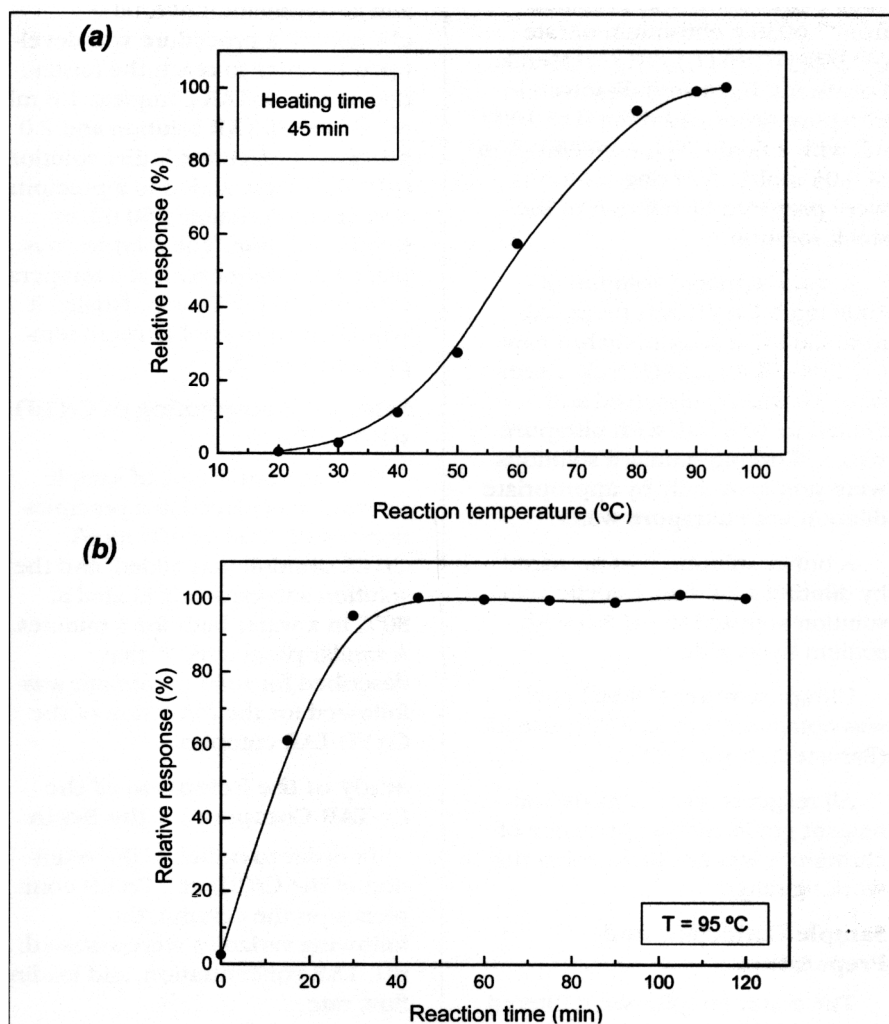As regards the variation of pre-concentration with the TAR con-

Fig. 2. Effect of reaction temperature (a) and heating time (b) on the formation of Cr-TAR complex. Preconcentration of 50 mL of Cr-TAR complex. Cr(III) concentration was 50 µg/L; ethanol concentration 2% (v/v); TAR concentration was 2.0 x 10⁻⁴ mol/L.

centration, the signal remained constant between 10^{-4} mol/L and at least 5×10^{-3} mol/L.

The sample flow rate through the micro-column is a very important parameter, since this is one of the steps that controls the time of analysis. It was verified that with flow rates up to 10 mL/min there is no effect on analyte recovery, which in optimum conditions is approximately 80%. As can be seen in Figure 3, at higher flow rates the retention of the Cr-TAR complex decreases.

Optimization of the Elution Variables

In order to elute the Cr-TAR complex adsorbed on the resin, ethanol in countercurrent (i.e., reversal of sample loading flow direction) was used as the eluent. Countercurrent elution substantially improves the elution profiles as compared to unidirectional flow. Chromium was completely eluted from the resin with 1.0 mL of ethanol. The use of ethanol as eluent and carrier solution had the advantage of increasing the sensitivity value for chromium determination by five times with respect to aqueous medium. The effect of the eluent flow rate was studied, achieving the best response at 3.0 mL/min. A typical elution profile for Cr obtained with the preconcentration system is shown in Figure 4.

Masking Effect of CDTA and Selectivity

It must be noted that no differences were found between the behavior of Cr(III) and Cr(VI) in any of the steps included in the proposed methodology (complexing, micro-column retention, elution, and determination). Under these conditions, the present methodology appears suitable for the determination of total chromium. The proposed method was separately applied to the deter-
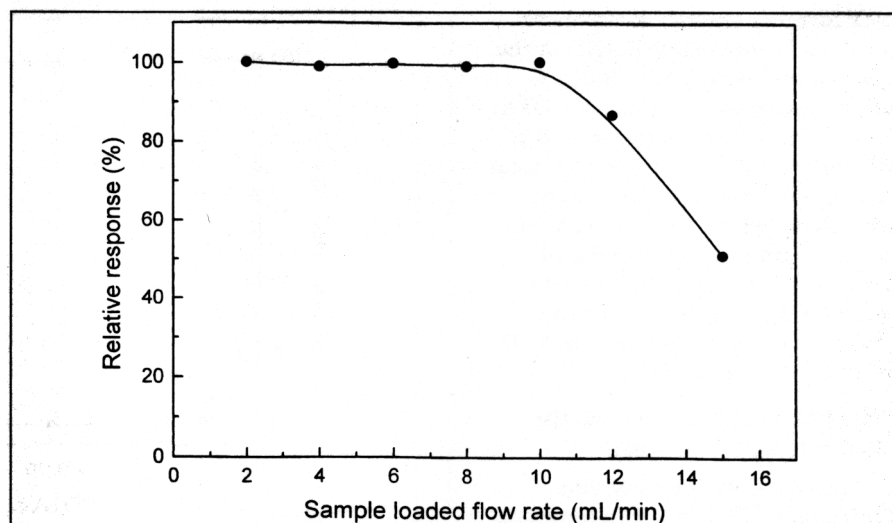

Fig. 3. Dependence of recovery of metal complex on sample flow rate. Preconcentration of 50 mL of Cr-TAR complex at pH 5.0. Cr concentration was 50 µg/L; TAR concentration was 2.0×10^{-4} mol/L.
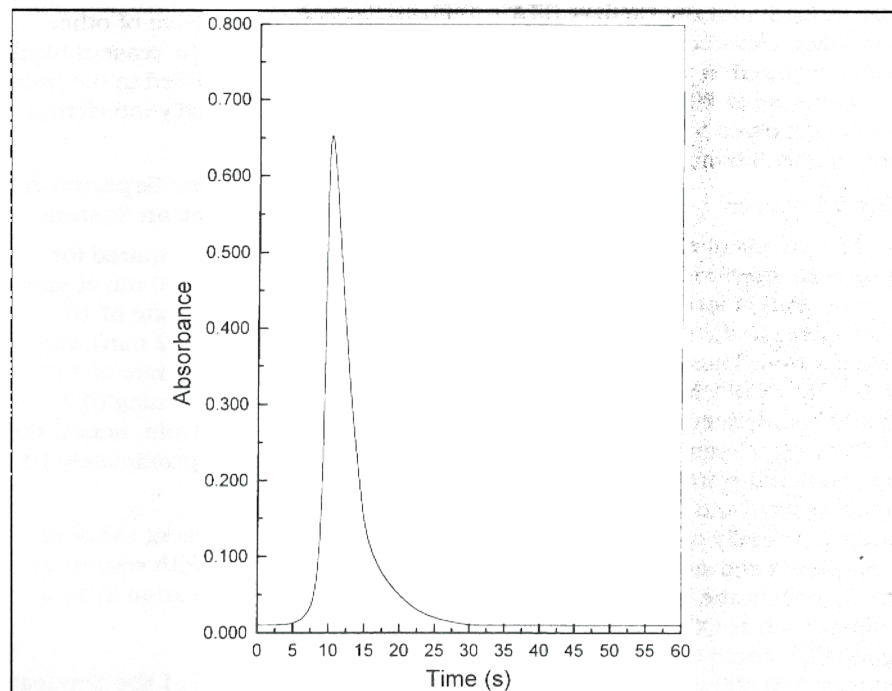

Fig. 4. Peak profile obtained by preconcentration of 50 mL of Cr-TAR complex using the system depicted in Fig. 1. Loaded flow rate was 10 mL/min; the elution flow rate was 3.0 mL/min. Cr concentration was 50 µg/L ; TAR concentration was 2.0×10^{-4} mol/L.

mination of Cr(III) and Cr(VI) in deionized water at levels of 50 µg/L, obtaining 80% recovery for both oxidation states.

With the purpose of obtaining total separation of Cr(III) and Cr(VI), we studied the use of a masking agent. CDTA, which has been widely used as the masking agent in the determination of several metal ions that involve com-

plex-forming reactions, was here proposed for masking Cr(III) in the complexing with TAR. Figure 5 shows the masking effect of CDTA on Cr(III), with a concentration of 10^{-3} mol/L CDTA, allowing for total masking of Cr(III). It can also be seen from Figure 5 that CDTA had no effect on the complexing of Cr(VI) with reagent TAR. On the other hand, no retention of the Cr(III)-CDTA complex on the XAD-16 resin was observed.

Effect of Temperature on the Masking Reaction Time

The reaction rate between Cr(III) and CDTA at room temperature is too slow to complete total complexing within an acceptable time (34,35). In order to accelerate the formation of the Cr(III)-CDTA complex, elevated temperatures were required. It was verified that a temperature of 80°C was adequate since it allowed for complete masking in only 5 minutes.

Interferences

The effects of representative potential interfering species (at the concentration levels at which they may occur in the sample studied) were tested. Thus, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Fe^{3+} could be tolerated up to at least 2,500 µg/L. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not retained on the resin. On the other hand, anions such as CO_3^{2-}, F^-, SO_4^{2-}, Cl^-, and PO_4^{3-} could be tolerated up to at least 500,000 µg/L.

The recoveries were not influenced by these ions because they are not complexed with the TAR reagent at the working pH value of 5.0. Thus, they are not retained on the resin prior to the elution of the retained Cr and can be easily washed out through the Amberlite XAD-16 resin, resulting in a highly selective determination of Cr
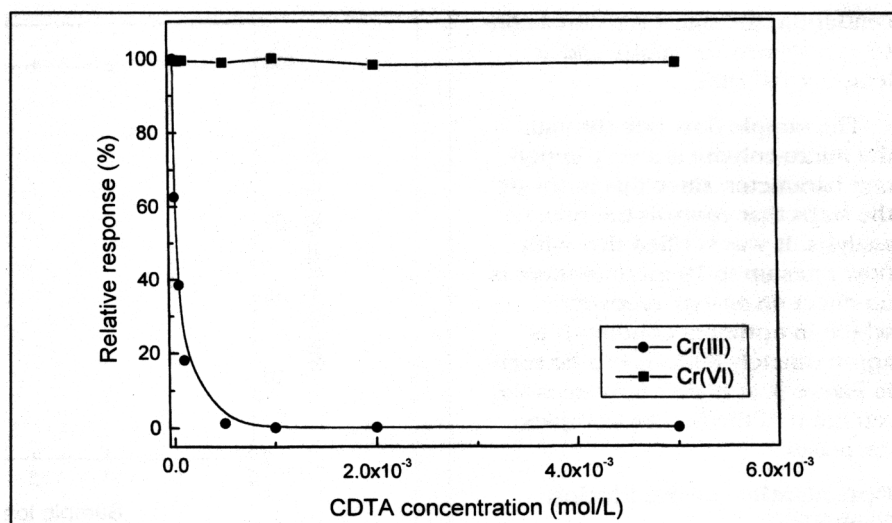

Fig. 5. Effect of the CDTA concentration on the separation of Cr(III) and Cr(VI). Loaded flow rate was 10 mL/min; Cr concentration was 50 µg/L; TAR concentration was 2.0 x 10⁻⁴ mol/L.

species in the presence of other ions. The value of the reagent blank signal was not modified in the presence of the potentially interfering ions assayed.

Performance of the Separation and Preconcentration System

The overall time required for preconcentration of 50 mL of sample (5.0 min, at flow rate of 10 mL/min), washing (0.2 min), elution (0.4 min, at flow rate of 3.0 mL/min) and conditioning (0.2 min) was about 5.8 min; hence, the throughput was approximately 10 samples per hour.

A total enhancement factor of 250 was obtained with respect to chromium determination in aque-

ous medium by FAAS (50 for the preconcentration system and 5 due to the use of ethanol as the solvent).

Separation of Cr(III) and Cr(VI)

In order to assess the selectivity of the proposed method on Cr(III) and Cr(VI), it was applied to various synthetic samples using different concentration relations between the two oxidation states. Table II shows that using the proposed method, the two Cr species are completely separated and also recovered quantitatively. The method was thus shown to have an acceptable accuracy under different conditions.

TABLE II
Evaluation of the Separation of Cr(VI) and Cr(III) Species

Cr(VI)/Cr(III) ratio	Chromium(VI)			Chromium(III)		
	Added (µg/L)	Found (µg/L)	Recovery (%)	Added (µg/L)	Found (µg/L)	Recovery (%)
20	80	79.2	99.0	4	3.9	97.5
3.3	40	39.4	98.5	12	12.1	100.8
1	24	23.4	97.5	24	23.8	99.2
0.3	12	11.8	98.3	40	41.0	102.5
0.05	4	3.8	95.4	80	79.8	99.8

Determination of Cr(III) and Cr(VI) in Water Samples

The relative standard deviation (RSD) for ten replicates containing 2.0 µg/L of Cr was 3.8%. The calibration graph was linear with a correlation coefficient of 0.9994 at levels near the detection limits up to at least 100 µg/L. The detection limit, calculated as the amount of Cr required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ), was 20 ng/L. Finally, the results of the method applied to Cr(III) and Cr(VI) determination in water samples are shown in Table III. The concentrations were in the 2.16–9.12 µg/L range for Cr(III) and <0.02–1.94 µg/L for Cr(VI). The results obtained are in good agreement with those of Matsuoka et al. (6) and Luo et al. (7). These authors found similar Cr(III) and Cr(VI) concentrations in water samples.

CONCLUSION

The use of CDTA as the masking agent of Cr(III) in the formation of the Cr-TAR complex and the retention on the XAD-16 resin allowed the separation and determination of Cr(III) and Cr(VI). The complexing of Cr with the TAR reagent resulted in highly selective conditions in the presence of other elements, which is due to the low pH value required for the formation of Cr-TAR complexes. The on-line coupling of a FI sorption preconcentration system with FI-FAAS increases the speed of the preconcentration and analysis processes, in addition to reducing sample consumption and contamination risks. The proposed system of preconcentration associated with FAAS allows the separation and determination of Cr(III) and Cr(VI) species in natural water samples at levels as low as µg/L with good accuracy and good reproducibility.

TABLE III
Analysis of Cr(VI) and Cr(III) in Natural Water Samples
(95% confidence interval; n = 6)

Sample	Chromium(VI)			Chromium(III)		
	Added (µg/L)	Found (µg/L)	Recovery (%)[a]	Added (µg/L)	Found (µg/L)	Recovery (%)[a]
Tap water	0	1.94 ± 0.09	—	0	2.16 ± 0.09	—
	5	6.98 ± 0.10	100.9	5	7.15 ± 0.10	99.8
Lake water	0	<0.02	—	0	2.80 ± 0.10	
	5	4.85 ± 0.09	97.0	5	7.81 ± 0.15	100.2
River water	0	<0.02	—	0	3.98 ± 0.10	—
	5	4.94 ± 0.10	98.7	5	9.02 ± 0.15	100.8

[a]100 x [(Found-base)/added].

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