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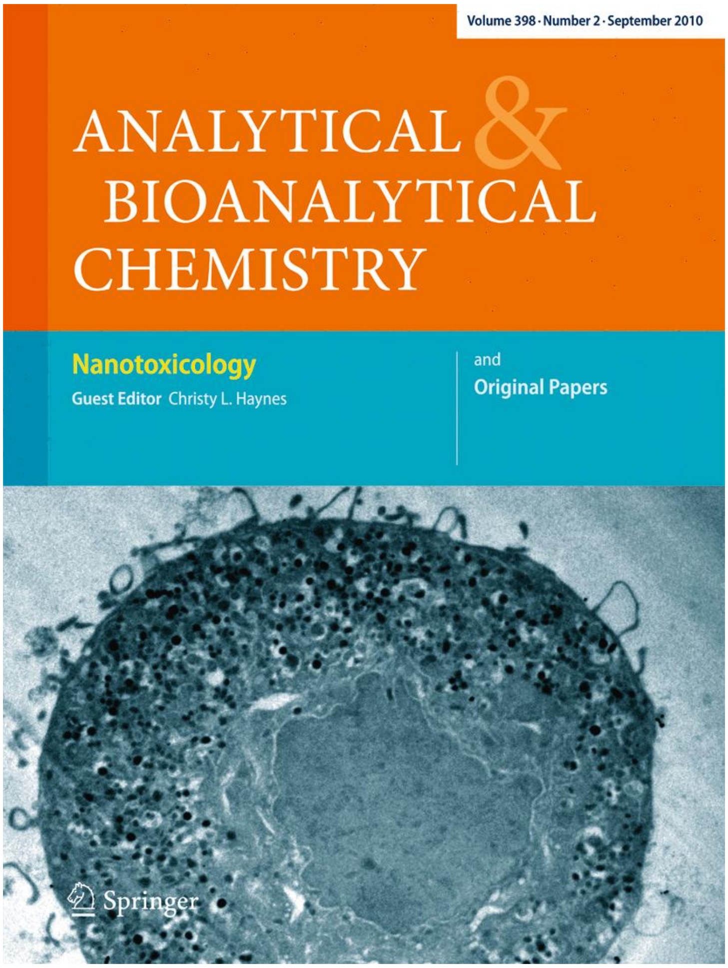

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ORIGINAL PAPER

Determination of trace chromium(VI) in drinking water using X-ray fluorescence spectrometry after solid-phase extraction

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Abstract A new, simple, and selective method for preconcentration and determination of Cr(VI) in aqueous samples. After adsorption in "batch mode" on Aliquat 336-AC, determinations were made directly on the solid by X-ray fluorescence spectrometry, which had the advantage of not requiring the step of elution of the chromium retained. The enrichment factor was calculated considering that the tablets obtained from 10 mL solution of Cr(VI) (1000 μgL^{-1}) had a final thickness of 0.64 mm and a diameter of 16.7 mm; the volume deposited on the pellet was 0.14 cm^3. The preconcentration factor obtained was 71-fold, which was highly satisfactory for chromium trace analysis by XRF. Finally, the method was successfully applied to the determination of Cr(VI) in drinking water samples.

Keywords Chromium · Preconcentration · Aliquat 336 · Activated carbon (AC) · X-ray fluorescence

Introduction

Chromium species exist in the environment mainly in two oxidation states, Cr(III) and Cr(VI), which have contrasting physiological effects [1]. Trivalent chromium is essential to normal carbohydrate, lipid, and protein metabolism. In contrast, chromium(VI) can induce carcinogenesis because of its ability to cross biological membranes easily and react with protein components and nucleic acids inside the cell [2]. The US Environmental Protection Agency (EPA) recommends that the concentration of Cr(VI) in drinking water should be less than 0.05 μgmL^{-1}. Consequently, the determination of Cr(VI) species in environmental samples has great importance. Continuous monitoring of Cr(VI) in environmental and biological systems is also of considerable relevance because it is highly mobile in the subsurface environment, is bioaccumulative, and toxic to living organisms [3].

A wide range of analytical techniques are available for the determination of Cr: atomic absorption spectrometry [4, 5], flow-injection analysis (FIA) combined with inductively coupled plasma-mass spectrometry (ICP-MS) [6, 7], liquid chromatography [8, 9], and spectrophotometric approaches based on the reaction of Cr(VI) with 1,5-diphenylcarbazide [10, 11], among others. Most of these methods need a previous preconcentration step to enrich the analyte or to eliminate matrix effects [7, 8, 12].

X-ray fluorescence (XRF) spectrometry has also been used for analysis and speciation of Cr(III) and Cr(VI) [12–14]. The main advantage of this technique is its capability of direct analysis of solid and liquid samples, avoiding sample handling or at least reducing it to a minimum. However, XRF has a number of limitations when dealing with aqueous samples, such as short linear range, the requirement of closely matching standards to overcome matrix effects, and poor sensitivity. The use of preconcentration materials as retention media for the analytes of interest offers the possibility of overcoming these problems, ensuring lower limits of detection, extending the linear range, and unifying matrix effects by fixing the same conditions for both standards and samples. Moreover, it has to be taken into consideration that unlike other methods, in which an elution step is required to recover the metal from the solid sorbent used to preconcentrate, X-ray spectrometry offers the possibility of direct quantification of metal

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species held in the solid sorbents, reducing the number of chemicals required and minimizing sample handling. Different sorbents such as ion-exchange materials [13] or activated charcoal [14] have been used to concentrate Cr before analysis by XRF.

For monitoring of environmental pollutants at ultra-trace levels an effective sample preconcentration step is necessary. Solid-phase extraction (SPE) is the most common technique used for preconcentration of analytes in environmental waters, because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents, and the possibility of combination with different detection techniques in on-line or off-line mode [15].

In an SPE procedure, the choice of appropriate adsorbent is a critical factor to obtain full recovery and high enrichment factor. Many sorbents have been used for preconcentration of metal ions, for example C_{18} [16], XAD resins [17], polyurethane foam [18], microcrystalline naphthalene [19], modified silica gel [20], cellulose [21], nanometer titanium dioxide [22], and ion-exchange resins [23]. Activated carbon (AC) is still by far the most important adsorbent in current use in environmental pollution control because of its large surface area, high adsorption capacity, porous structure, selective adsorption, and high purity [24]. However, without any surface treatment, activated carbon has adsorption capacity for metal ions from fair to as low as none, because metal ions often exist in solution either as ions or as hydrous ionic complexes [25]. For this reason, modification and impregnation techniques have been used to increase the surface adsorption and the removal capacity in order to add selectivity to activated carbon.

Because the sorption capacity of modified activated carbon is higher than that of untreated activated carbon, there are several recent reports on the use of modified activated carbon for metal enrichment. Activated carbon functionalized with pyrocatechol violet [26], 1,2-cyclohexanediondioxime [27], tetrabutylammonium iodide (TBAI) and sodium diethyl dithiocarbamate (SDDC) [28], tartrazine [29], ammonium pyrrolidine dithiocarbamate [30], and *N*,*N*-ethylenebis-(ethane sulfonamide) [31] have been reported as chelating collectors for metal ions, i.e. Fe(III), Cu(II), Cr(III), Zn(II), Cd(II), Co(II), Ni(II), Pb(II), Mn(II), and U(VI).

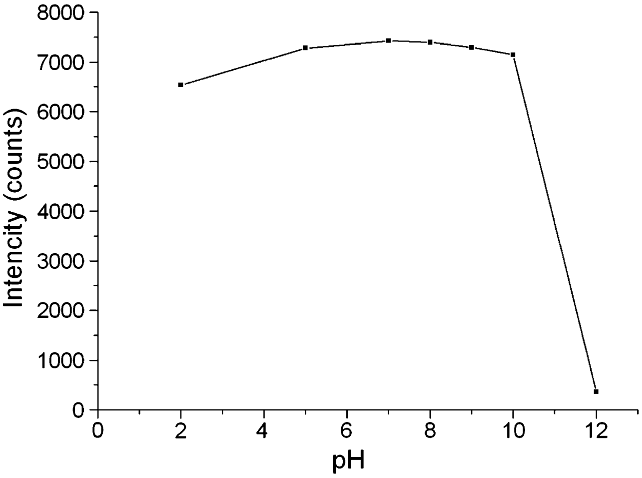

Fig. 1 Effect of pH on adsorption of 1.0 gmL^{-1}Cr(VI) on to Aliquat 336-AC

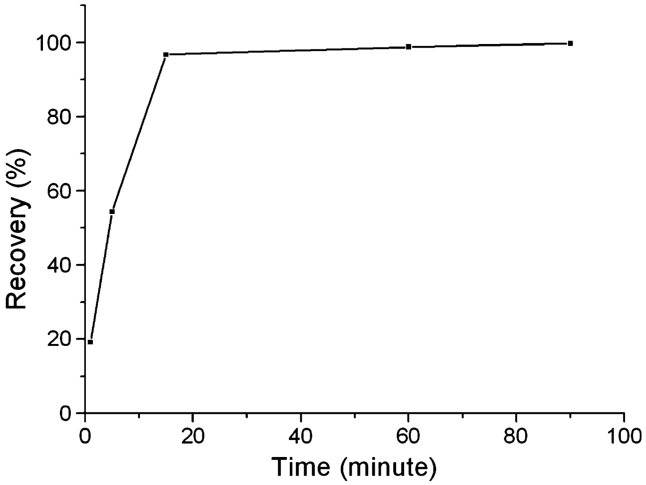

Fig. 2 Effect of shaking time on the adsorption of 1.0 gmL^{-1}Cr(VI) on to Aliquat 336-AC

Solvent extraction is a convenient technique for the removal of chromate from aqueous solutions. It has been reported that the tertiary amine extractants Alamine 336 and Aliquat 336 are effective reagents for the removal of Cr(VI) [11, 32].

In our work, a novel method was developed for preconcentration and determination of Cr(VI) in aqueous solutions. Cr(VI) was adsorbed on Aliquat 336-AC, a commercial anion-exchange extractant widely used [11, 12] for selective extraction of Cr(VI) over Cr(III). The determinations were made directly on the solid by XRF spectrometry, which had the advantage of eliminating the step of elution of the chromium retained. A high preconcentration factor was achieved for a very low volume of sample.

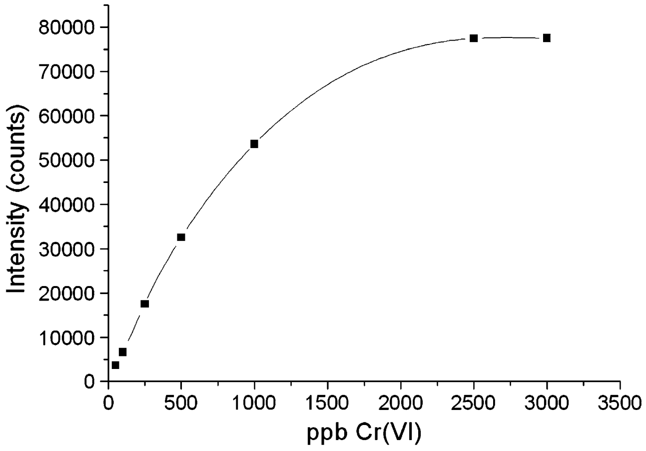

Fig. 3 Retention capacity of Aliquat 336-AC for Cr(VI)

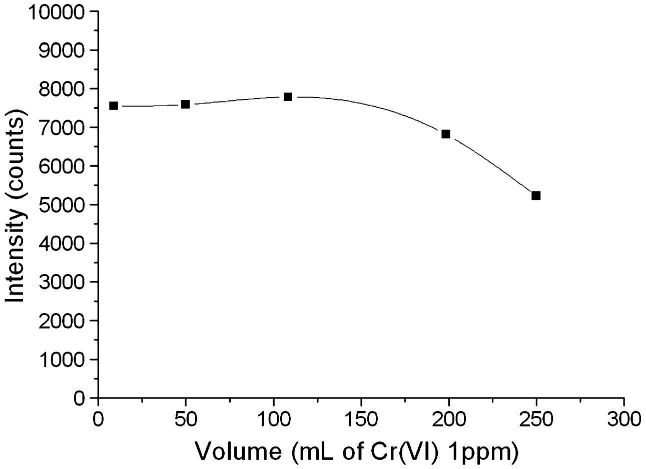

Fig. 4 Effect the sample volume on SPE recovery of Cr(VI)

Experimental

Reagents and apparatus

The extractant tricaprylmethylammonium chloride ($CH_3N[(CH_2)_7CH_3]_3Cl$; Aliquat 336) was purchased from Fluka, Switzerland. A 1000 mgL^{-1} Cr(VI) stock standard solution of was prepared by dissolving 2.8290 g potassium dichromate ($K_2Cr_2O_7$; Merck, Darmstadt, Germany) in ultrapure water and diluting to a final volume of 1000 mL. Working standard solutions were prepared from this solution by stepwise dilution. Ultrapure water (18.1 M Ω cm) was obtained from a Barnstead (Iowa, USA) Easy Pure RF water system.

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

Measurements were performed with a Philips PW1400 X-ray fluorescence spectrometer. The Cr K_α line was used for measurements. The conditions were selected appropriately. The pH of solutions was measured using an Orion 701-A pH meter with an Ag/AgCl electrode. An M-23 Digital Orbital shaker (Buenos Aires, Argentina) was used for sample agitation.

Preparation of the activated carbon

The activated carbon (AC; Merck; 200 mesh) was used after pretreatment with acid. (Activated carbon was heated 60ºC with 10% (*v*/*v*) hydrochloric acid (Merck) for 30 min, then with 10% (*v*/*v*) nitric acid (Merck) for 20 min, and finally washed with deionized water until neutral pH [33].)

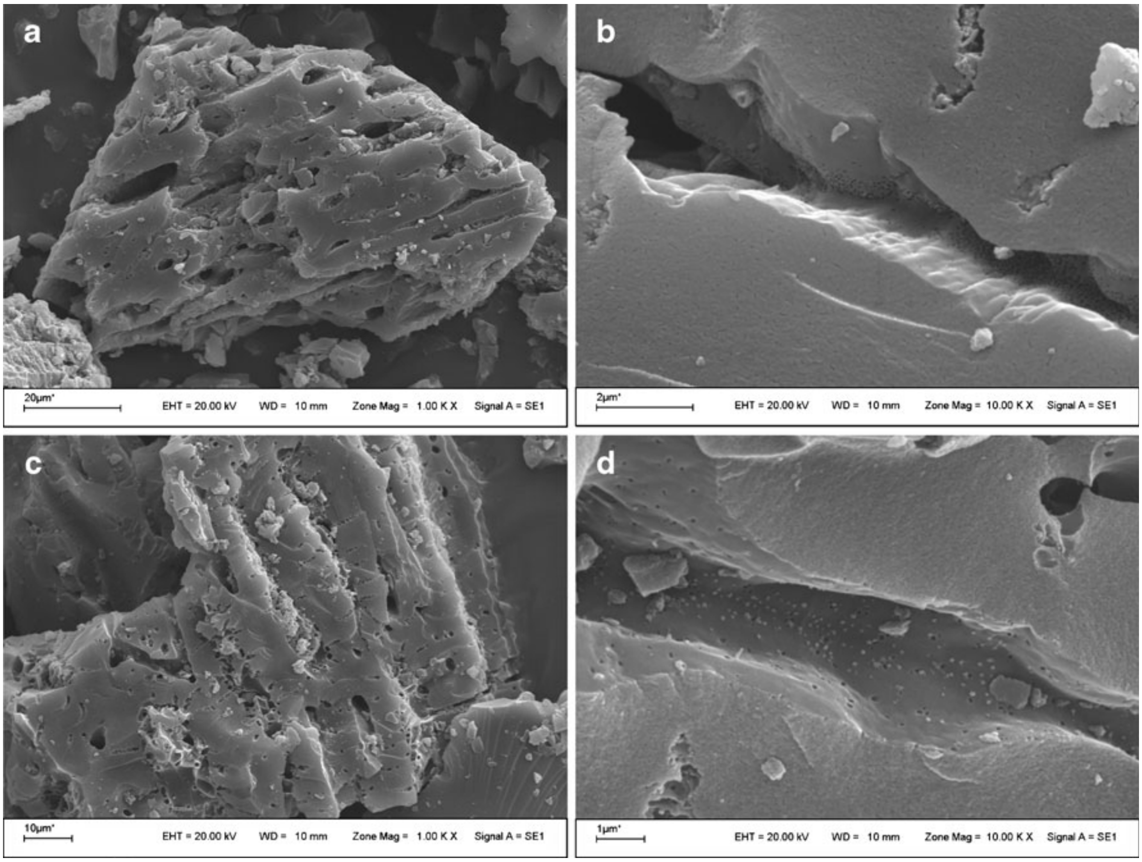

Fig. 5 Scanning electron micrographs (SEM) of (**a**, **b**) AC and (**c**, **d**) AC after Aliquat 336 adsorption

Table 1 Preconcentration procedures developed for analysis of chromium

Type of sample	Detection limit (μgL^{-1})	Enrichment factor	Sample volume (mL)	Technique	Ref.
Drinking water	1	71	10	XRF	This work
Drinking water	0.003	35	10	ETAAS	5
Aqueous solution	13.6	–	25	Spectrophotometry	10
Aqueous solution	2.0-6.0	23-61	18	FAAS	36

Preparation of the loaded activated carbon

Under the optimized adsorption conditions, the anion-exchanger extractant was loaded on the ground activated carbon. The AC (1 g) was shaken overnight with 40 mL 5% Aliquat solution in methanol at room temperature. The AC was then filtered, washed with distilled water, and dried in an oven at 110ºC.

Batch adsorption experiment

A series of standards or sample solutions containing Cr(VI) were transferred into 25-mL beakers and the pH was adjusted to the desired value with 0.1 $molL^{-1}$HCl or 0.1 $molL^{-1}$NaOH. The volume was then adjusted to 10 mL with ultrapure water and 100 mg Aliquat 336-AC was added. This mixture was then placed in a shaker for 20 min to facilitate adsorption of the metal ions on to the sorbent.

Preparation of the pellet

Tablets were made from boric acid, which was deposited on 100 mg Aliquat 336-AC–Cr (IV), as a powder, and then compacted, always working within infinite thickness [34]. The powdered and pelletizing forms of the solid material were used in this work. Thus, speed was achieved by avoiding the traditional step of elution of the retained chromium.

A series of solutions and appropriately diluted standards of Cr in water and synthetic water samples for human consumption were preconcentrated on the Aliquat 336-AC by the method described above. The settings used for X-ray measurement were: 66.23 2θ for Cr; Rh tube, 50 kV 50 mA, LiF (200) crystal; 75-25 window width, counting time for peak and background 100 s; gas proportional scintillation counter in tandem.

Results and discussion

Effect of pH on retention

In order to evaluate the effect of pH, 10-mL solutions containing 1 mgL^{-1}Cr(VI) were adjusted to different pH with sodium hydroxide or hydrochloric acid. They were mechanically shaken with 100 mg portions of Aliquat 336-AC for 20 min. The Aliquat 336-AC was then isolated by filtration, washed with distilled water, and later the K_α lines of the analyte were measured by X-ray fluorescence spectrometry. As shown in Fig. 1, the highest Cr(VI) recovery values were obtained between pH 5 and 9; therefore, pH 7.5 was selected for further experiments.

Effect of shaking time on sorption

The shaking time is an important factor in determining the possibility of application of Aliquat 336-AC to extraction of metal ions. In this work, considering the percentage extraction of Cr(VI) on Aliquat 336-AC, different shaking times (ranging from 1 to 90 min) were studied. The results (Fig. 2) indicated that more than 95% Cr(VI) was extracted within 20 min.

Determination of the maximum retention capacity of the Aliquat 336-AC

Solutions containing different concentrations of Cr(VI) were adjusted to pH 7.5, shaken, and filtered to determine the quantity of analyte that saturated the Aliquat 336-AC.

Table 2 Concentrations of Cr (VI) in water for human consumption (95% confidence level; $n=6$)

Base (μgL^{-1})	Cr(VI) added (μgL^{-1})	Cr(VI) found (μgL^{-1})	Recovery (%)[a]
4.0	0.0	4.0±0.3	–
4.0	100.0	104±5.0	100
4.0	250.0	251±10	98.8
4.0	500.0	503±26.0	99.8
4.0	1000.0	1006±16.0	100.2

[a] [(Found−base)/added] ×100

The metal K_α line was measured by XRF. The XRF intensity of Cr K_α as function of the Cr(VI) concentration is shown in Fig. 3. For very low amounts of Cr(VI) the concentration is proportional to Cr K_α intensity. The curve was linear up to 1.0 $\mathrm{mg L^{-1}}$ Cr(VI) and became constant at higher Cr concentrations. The total retention capacity was 10 mg Cr(VI) per gram of sorbent material. The amount of Cr(VI) not retained by the Aliquat 336-AC was determined by inductively coupled plasma optical emission spectrometric analysis of the filtrate. The amount retained was always greater than 95%.

Sample volume and preconcentration factor

Because of the importance of obtaining high preconcentration factors, the effect of sample volume on recovery of Cr on the solid phase was also examined. The results are given in Fig. 4. Cr(VI) ions were quantitatively (>95%) recovered within the volume range 10–100 mL. Therefore, 10–100 mL sample solution was adopted as volume range for separation and preconcentration of Cr.

Scanning electron microscopy (SEM)

SEM micrographs were obtained before and after adsorption of Aliquat 336 on to AC. The SEM images of AC showed the porosity and surface structure. After adsorption of the anionic exchanger, a significant change in the structure of the adsorbent was observed (Fig. 5a, b, c and d). The adsorbent seemed to have a rough surface and pores containing shiny and bulky particles.

Analytical performance

The enrichment factor is defined as $EF = [QT/QM]/[QT_0/QM_0]$ [35], where QT_0 and QT are the quantities of analyte before and after preconcentration, respectively, and QM_0 and QM are the quantities of the matrix before and after enrichment, respectively. The enrichment factor was calculated considering that the tablets obtained from 10 mL of a solution of 1000 $\mu\mathrm{g L^{-1}}$ Cr(VI) had a final thickness of 0.64 mm and a final diameter of 16.7 mm, and the volume deposited on the pellet was 0.14 $\mathrm{cm^3}$. The preconcentration factor obtained was 71-fold, which was a highly satisfactory value for trace analysis by XRF.

One of the most important features of use of a preconcentration method is improvement of detection limits. A detection limit of 1.00 $\mu\mathrm{g L^{-1}}$ was obtained for aqueous solutions, this was calculated as $(3/m)(I_b/t)^{1/2}$, where m is the slope of the calibration plot, I_b is the background intensity (counts s^{-1}), and t is the counting time (s). Preconcentration procedures developed for determination of chromium are compared in Table 1.

Recovery and validation studies

In order to evaluate and demonstrate the validity of this method, 100 mL drinking water sample was collected in our laboratory and divided into ten aliquots of 10 mL each. The proposed method was applied to six portions and the average quantity of chromium obtained was taken as the base value. Increasing quantities of chromium were then added to the other aliquots then chromium was determined by the same method. The results are shown in Table 2. The other elements present in the sample did not cause spectral interferences with the determination.

Conclusions

Adsorption on Aliquat 336-AC enabled efficient separation and preconcentration of Cr(VI) from drinking water. This system of preconcentration enabled determination of Cr(VI) in drinking water samples at $\mu\mathrm{g L^{-1}}$ levels. A 71-fold *EF* was obtained. The reproducibility and accuracy of the described method were excellent. The high enrichment factors obtained encouraged us to propose this preconcentration method as a worthy tool for trace analysis by XRF analysis, which enables improvement of detection limits and determination of trace elements with high precision.

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