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ORIGINAL PAPER

Solid phase extraction of chromium(VI) using Aliquat336 immobilized on a thin film of multiwall carbon nanotubes

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Abstract We report on a novel and selective method for the preconcentration and determination of Cr(VI) in aqueous samples. Cr(VI) is adsorbed - in a "batch mode" - on multi-walled carbon nanotubes covered with Aliquat 336 and then determined directly, i.e., on the solid, by X-ray fluorescence spectrometry. This reduces the number of reagents and minimizes sample handling. The method combines the advantages of solid-phase extraction with the benefits of the XRF method in that the large areas required by the carbon nanotubes make them a promising solid sorbent for preconcentration. The enrichment factor was calculated after considering that the thin film obtained from the 10 mL solution of 1 mgL^{-1} of Cr(VI) has a real thickness of 0.04 mm and a final diameter of 16.7 mm, so that the volume deposited on the pellet is 0.0088 cm^3 and the preconcentration factor is 1000.

Keywords Chromium · Preconcentration · Aliquat 336 · Nanotubes · Thin film · X-ray fluorescence

Introduction

Chromium occurs mainly in the oxidation states (III) and (VI) in the environment. As well known, Cr(III) is essential for plants and animals at trace concentrations, whereas Cr (VI) is considered to be a more toxic form because of its high oxidizing potential [1, 2]. For this reason, it is necessary to use a sensitive method for the determination of Cr(III) and Cr(VI) in drinking water samples. Also, the continuous monitoring of Cr(VI) in environmental and biological systems is of considerable relevance due to its elevated mobility in subsurface environments and bioaccumulative and toxic effects on living organisms [3, 4].

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

X-ray fluorescence (XRF) spectrometry has also been used for the analysis as well as speciation of Cr(III) and Cr (VI) [11, 13, 14]. The main advantage of XRF is its capability for direct analysis of solid and liquid samples, avoiding sample handling or at least reducing it to a minimum moreover it is a non-destructive technique [15].

The direct determination of metal ions in complex matrices is limited due to their usually low concentrations and matrix interferences [16]. In trace analysis, therefore, preconcentration and/or separation of analytes are necessary to improve sensitivity and selectivity of analysis. Solid-phase extraction (SPE) is the most common technique used for preconcentration of analytes in environmental waters and biological samples, due to its advantages as high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents, and the ability of combination with different detection techniques in the form of on-line or off-line mode [17].

The choice of appropriate adsorbent in a solid-phase extraction procedure is a critical factor to obtain full

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recovery and high enrichment factors. Many sorbents have been used for preconcentration of metal ions, such as polyurethane foam [18], modified silica gel [19], Amberlite XAD resins [20], microcrystalline naphthalene [21], nanometer titanium dioxide [22], cellulose [23], activated charcoal [14] and ion exchange resins [24].

In recent years, great attention has been paid to the application of nano-structure materials, especially carbon nanotubes (CNTs). In particular, there have been an increasing number of applications of CNTs in several fields of chemical analysis [25]. CNTs can be visualized as a sheet of graphite that has been rolled into a tube. These tubes are classified as multiwalled carbon nanotubes (MWCNTs) [26] and single-walled carbon nanotubes (SWCNTs) [27] according to the carbon atom layers in the wall of the nanotubes. Because of their special electronic, metallic, and structural characteristics as well as the unique tubular structures of nano diameter and large length/diameter ratio [28], CNTs have been exploited in analytical chemistry and other fields [29]. The highly developed hydrophobic surface of CNTs exhibits strong sorption properties toward various compounds and therefore CNTs have shown great potential in the adsorption, applications are screened in the care of the environment by removing toxic ions from wastewater and industrial processes have used as adsorbents to effect preconcentration step by solid-phase extraction [30, 31]. MWCNTs have also been used for the preconcentration of trace amounts of organic materials [32] and the extraction of some ions from environmental samples [16].

In our work, a novel method was developed for preconcentration and determination of Cr(VI) in aqueous solutions through their adsorption on a tertiary amine, ALIQUAT 336, a commercial anionic exchanger extractant widely used [10] for the 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.

Experimental

Reagents and apparatus

Commercial multiwall CNTs were obtained from Aldrich (Chemical Co., Milwauke, WI, USA, www.sigmaaldrich.com), diameter 110–170 nm, longitude 5–9 μm, 90 %. Membrane filter papers were Millipore of 0.45 mm pore size.

The extractant, Tricaprylmethylammonium chloride $CH_3N[(CH_2)_7CH_3]_3Cl$) (ALIQUAT 336) was purchased from Fluka (Switzerland www.sigmaaldrich.com). A 1000 mgL^{-1} Cr(VI) stock standard solution was prepared from 2.8290 g potassium dichromate ($K_2Cr_2O_7$), Merck (Darmstadt, Germany www.merck.de) dissolved in ultrapure water and diluted to a final volume of 1000 mL. Working standard solutions were prepared by stepwise dilution from this solution. Ultrapure water (18.1 MΩcm) was obtained from Barnstead EASY pure RF water system (Iowa, USA).

All the reagents used 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 the solutions was measured using an Orion 701-A pH meter with an Ag/AgCl electrode. A M-23 Digital Orbital shaker (Buenos Aires, Argentina www.vicking.com.ar), was used for sample agitation.

Activation of the MWCNTs

MWCNTs (25 mg) were added to 30 mL of 2.2 $molL^{-1}$ nitric acid solution, this mixture was sonicated at room temperature for 30 min in ultrasonic bath. After that, the MWCNTs were filtered, washed with distilled water. Then, to eliminate metal oxide catalysts, the MWCNT were dispersed in 60 mL of 6.0 $molL^{-1}$ HCl solution for 30 min under ultrasonic agitation, and then washed with distilled water until the pH was neutral and finally dried in an oven at 50 °C.

Preparation of the loaded MWCNTs

Under the optimized adsorption conditions previously published [14], the anion-exchanger extractant was loaded on the ground MWCNTs. A 50 mg MWCNTs mass was shaken overnight with 40 mL of 5 % Aliquat solution in methanol at room temperature. The MWCNTs were then filtered, washed with distilled water, and dried in an oven at 110 °C.

Batch adsorption experiment

A series of standards or sample solutions containing Cr(VI) were transferred into 25 mL beakers and the pH value was adjusted to the desired value with 0.1 $molL^{-1}$ HCl or 0.1 $molL^{-1}$ NaOH solutions. The volume was made up to 10 mL with ultrapure water and 5 mg of *ALIQUAT 336-MWCNTs* was added. This mixture was then placed in a shaker for 20 min to facilitate adsorption of the metal ions onto the sorbent.

Preparation of the thin film

Membrane filter papers were Millipore of 0.45 μm pore size. Different amounts (5, 10, 15, 20, 25 and 30 mg) of the loaded *ALIQUAT 336-MWCNTs* containing the preconcentrated Cr(VI) were used to prepare the films in order to

determine the critical thickness of the film. The filtrations were performed in a filtration apparatus equipped with a vacuum pump [33].

A series of aqueous properly diluted Cr solutions were preconcentrated. This was done on the *ALIQUAT 336-MWCNTs* by the method described above. The measuring X-ray parameters 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.

Result and discussion

Study of retention of chromium on activated and not activated MWNTs

To optimize the experimental parameters of the preconcentration system, the response of MWCNTs modified with Aliquat 336 with and without prior activation was evaluated. With this aim, a standard solution of Cr(VI) at increasing concentrations was preconcentrated and applied to the procedure described above. As shown in Fig. 1, a better response was obtained using MWCNTs with prior activation.

Effect of pH on the retention

In order to evaluate the effect of pH, 10 mL solutions containing 1 mgL^{-1} of Cr(VI) were adjusted to different pH values with sodium hydroxide or hydrochloric acid. They were mechanically shaken with 5 mg portions of ALIQUAT 336-MWCNTs for 20 min. Then, the ALIQUAT 336-MWCNTs was filtered, washed with distilled water, and later the Kα lines of the analyte were measured by the X-ray Fluorescence Spectrometer. As shown in Fig. 2, the XRF highest intensities of Cr Kα as function of pH were obtained between pH 5 and 9; therefore, pH 7.5 was selected for further experiments.

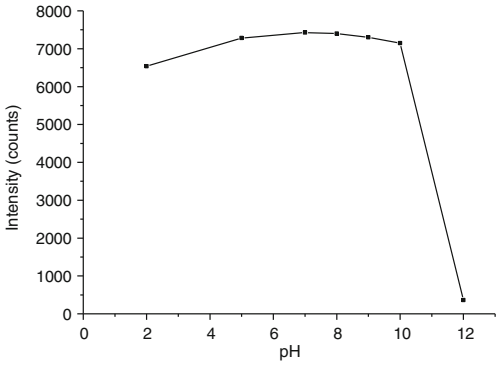

Fig. 2 Effect of pH on adsorption of 1.0 mgL^{-1} Cr(VI) on ALIQUAT 336-MWCNTs

Determination of the maximum capacity of retention of the ALIQUAT 336-MWCNTs

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-MWCNTs* material. In Fig. 3, the XRF intensity of Cr K_α as function of the Cr(VI) concentration is shown. For low Cr(VI) amounts, the concentration was proportional to the Cr K_α intensity. The curve was linear up to 0.5 mgL^{-1} of Cr(VI) and became constant at higher Cr concentrations. The total capacity retention was 100 mg of Cr(VI) per gram of sorbent material. The amount of Cr(VI) not retained by the ALIQUAT 336-MWCNTs was determined by inductively coupled plasma optical emission spectrometric analysis of the filtrate. The amount retained was always greater than 95 %.

Analytical performance

The enrichment factor is defined as EF = [QT/QM]/[QT_0/QM_0] [34], where: QT_0 and QT are the analyte quantities before and after the preconcentration, respectively; and

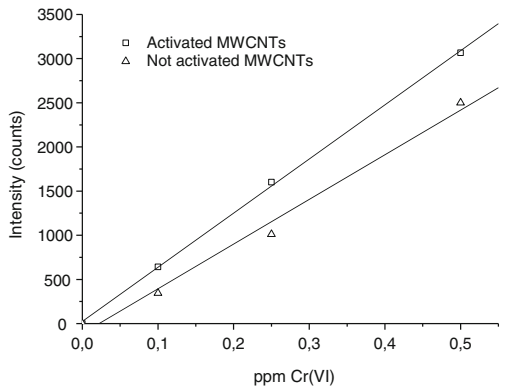

Fig. 1 Retention of Cr(VI) on MWCNTs modified with ALIQUAT 336 with and without prior activation

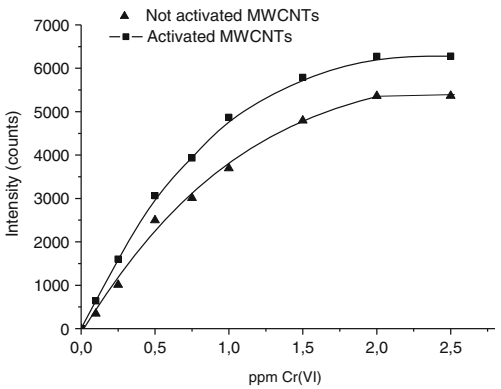

Fig. 3 Retention capacity of Cr(VI) on the ALIQUAT 336 on activated and not activated MWCNTs

Table 1 Procedures for preconcentration and determination of chromium

Detection limit (μg L^{-1})	Enrichment factor	Sample volume (mL)	Technique	References
0.5	10^3	10	XRF	This work
0.003	35	10	ETAAS	[5]
1.0	71	10	XRF	[14]
2.0–6.0	23–61	18	FAAS	[36]
0.002–0.005	100	100	ETAAS	[37]
0.056	25	25	ETAAS	[38]

QM_0, QM are the quantities of the matrix before and after the enrichment, respectively. The enrichment factor was calculated considering that the thin film obtained from the 10 mL solution of 1000 μgL^{-1} Cr(VI) had a final thickness of 0.04 mm and a final diameter of 16.7 mm, the volume deposited on the pellet was 0.0088 cm^3. The preconcentration factor obtained was 10^3 fold, which represented a highly satisfactory value for trace analysis by XRF.

One of the most important features of the use of a preconcentration method is the improvement of the detection limits. A detection limit of 0.5 μgL^{-1} was obtained for aqueous solutions, this was calculated as $(3/m)(I_b/t)^{1/2}$, where *m = slope of the calibration curve,* I_b = *background intensity (counts/*s^{-1}*) and t = counting time (s).*

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

Recovery study

Since a recovery study can be considered as a validation alternative [35], this procedure was applied to the developed methodology. Thus, we collected six samples with a volume of 100 mL of drinking water from different households in the city of San Luis and divided in ten aliquots of 10 mL each one. The methodology described above was applied to six portions for each sample and the average quantity of chromium obtained was taken as a base value. Then, increasing quantities of chromium were added to the other aliquots of sample, after that chromium was determined by the same method. The results are shown in Table 2. The other elements present in the sample do not showed spectral interferences in the determination. A full scan using the Cr Kα line was obtained and no spectral interferences were observed (Fig. 4).

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

Base (μg L^{-1})	Cr (VI) Added (μg L^{-1})	Cr (VI) Found (μg L^{-1})	Recovery (%)[a]
3.5	0.0	3.5±0.3	–
3.5	100.0	104±4.0	100.5
3.5	250.0	252±10.0	99.4
3.5	350.0	351±15.0	99.2
3.5	500.0	504±25.0	100.1

[a] [(Found−base)/added] × 100

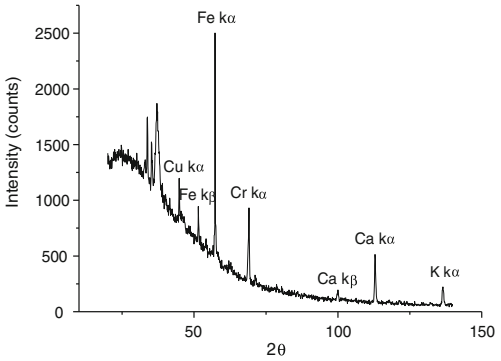

Fig. 4 Scanning XRF spectrum of a drinking water sample

Conclusions

Although the preconcentration procedure of this methodology was similar to the method developed in our research group where we employed activated carbon as adsorbent for solid-phase extraction coupled XRF [14]; furthermore, the method developed here is a promising method for Cr(VI) determination which joints the advantages of the minimal reagent employment, feasibility, low cost and sensibility.

The MWCNTs based procedure is superior to those reported chromium separation–preconcentration methods in term of selectivity, detection limit, pH range applicability, capacity, no need of consumption of organic solvents, and reproducibility and accuracy of the described method.

The high enrichment factors obtained encouraged us to propose this preconcentration methodology as a worthy tool for trace analysis by XRF analysis, which enables improvement of the detection limits and determination of trace elements with high precision.

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