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Cloud point microextraction involving graphene oxide for the speciation of very low amounts of chromium in waters

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ABSTRACT

A graphene oxide (GO) suspension was used to retain chromium (III) species in a neutral solution. The addition of Triton X-45 followed by heating resulted in a coacervate, to which the GO nanoparticles containing the analyte retained were transferred. Chromium was determined directly in the surfactant-rich phase by electrothermal atomic absorption spectrometry. The procedure was repeated using a second aliquot of sample to which sodium hydrogen sulphite was added to reduce chromium (VI) to chromium (III). By again obtaining the analytical signal of chromium in the condensed phase, the concentration of the hexavalent form was calculated by difference. Using 10 mL for the sample volume and 0.01% for the Triton X-45 concentration, the enrichment factor was 140, and the detection limit was 5 ng L^{-1}. The repeatability for five consecutive measurements at the 100 ng L^{-1} level was close to 5%. The reliability of the procedure was verified by analysing seven water samples with certified contents of total chromium. Speciation data are given for these standard materials and for seven potable waters and one seawater sample.

1. Introduction

Solid phase extraction is a widely used methodology considered appropriate for sample preparation and preconcentration purposes in the analytical laboratory. It is of even greater interest if the sorbent has a low particle size since the surface area available for the extraction stage considerably increases, and the process can be carried out with very small amounts of sorbent. Hence, among other advantages, the benefits inherent to microextraction approaches are fully exploited [1,2]. This is the case of graphene [3,4] and related materials. Graphene oxide (GO), which is obtained by chemical oxidation of graphite, has oxygen-containing functional groups (hydroxyl, epoxide and carboxylic acid) [5] which can retain polar chemical species [6–8] and facilitate dispersion to give stable aqueous colloids [9]. The first characteristic means that GO retains metallic species in solution as they are charged positively [1,3,10–16], but the second hinders application from an analytical point of view since separating the solid containing the retained analyte from the liquid is difficult, even after prolonged centrifugation. If the material is placed in small columns, high pressures will result from the low particle size [17]. Alternatives, such as aggregation of the GO dispersion by adding electrolytes [9,17–19], changing pH [18] or the incorporation of GO to a magnetic core [15,20–22] have been studied but the analytical potential these particles have has not been yet fully exploited.

Because of its hydrophilic and hydrophobic properties, GO could be incorporated in the coacervates obtained from solutions containing surfactants in a cloud point extraction (CPE) [23–25]. If this interaction occurs, the transfer to the coacervate of GO with the retained metallic species should result in a separation with a high enrichment factor due to the low volume of the condensed phase recovered in CPE. If, in addition, a sensitive analytical technique that operates with low-volume aliquots, such as electrothermal atomic absorption spectrometry (ETAAS), is used to measure the metallic ion, the resulting analytical procedure should have great sensitivity. To the best of our knowledge, this analytical possibility has not been exploited. This paper describes studies carried out to optimize a new procedure for the determination of very low concentrations of chromium in waters using GO, CPE and ETAAS. Although the literature reports analytical procedures for chromium involving GO, the nanoparticles are used from a different perspective [17,26–28], and no benefit is obtained from the simplicity that CPE offers in the analytical laboratory, as shown in recent studies [24,25].

2. Experimental

2.1. Instrumentation

A high-resolution continuum source (HR CS AAS) ContrAA 700

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spectrometer from Analytik Jena AG (Jena, Germany) was used for all the measurements. This instrument is equipped with a xenon short-arc lamp as the radiation source, a high-resolution double echelle monochromator, a linear charge-coupled device array for detection, a transversely heated graphite atomizer and an autosampler. Atomic absorption of chromium was measured at 357.87 nm. Data evaluation was carried out with the software ASPECT CS provided by Analytik Jena. For signal quantification, the integrated absorbance summed over three pixels was used. Argon with a purity of 99.999% (Messer, Spain) was used as purge and protective gas.

A 50 W ultrasound bath (ATU, Valencia, Spain) with temperature control, and a centrifuge (model Unicen 21, Madrid, Spain) equipped with a holder for conical tubes capable of working up to 4000 rpm (1540*g*) were also used. The particle size was studied with a Malvern Zetasizer Nano ZSP (Worcestershire, England) instrument. The homogenization of the coacervate after separation was carried out with a vortex accessory, model Reax from Heidolph (Germany).

2.2. Reagents and samples

All the solutions were prepared in pure water (18 MΩ cm resistivity) obtained with a Milli-Q system (Millipore, Bedford, MA, USA). The glassware and plastic ware (polypropylene) were washed with 1% (v/v) concentrated nitric acid solution and rinsed with water before use. The chromium (III) and (VI) stock standard solutions (1 g L^{-1} of the metal) were prepared from $Cr(NO_3)_3{\cdot}9H_2O$ and $K_2Cr_2O_7$ (Fluka, Buchs SG, Switzerland), respectively, and diluted daily to obtain appropriate working solutions. Concentrated nitric acid (65%), 2-amino-2-(hydroxymethyl)-1,3-propanediol hydrochloride (TRIS), palladium nitrate and Triton X-45 were obtained from Sigma-Aldrich (Steinheim, Germany). Other chemicals used were also obtained from Sigma-Aldrich or Merck (Darmstadt, Germany).

Graphene oxide was obtained from two manufacturers. A 2 mg mL^{-1} aqueous suspension was provided by Sigma-Aldrich, and Timesnano (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences) supplied the material as a solid from which suspensions were prepared with the aid of ultrasound in our laboratory. After preliminary studies, as indicated below, the home-prepared suspensions were discarded, and the product supplied by Sigma being used exclusively.

Five bottled water samples were purchased from a supermarket, and tap water was collected from the main supply of the University of Murcia. The seawater sample was obtained from near the shore, close to a harbour in south-eastern Spain. This sample was filtered and maintained in a plastic container at 4 °C until it was analysed (less than 48 h).

In addition, seven standard reference materials, namely NIST 1640a (trace elements in natural water), NASS-6 (seawater reference material for trace metals), SPS-SW2 Batch 125 (reference material for measurement of elements in surface waters), ERM-CA011b (hard drinking water), TMRAIN-04 (simulated rain sample), TM-23.4 (trace element fortified sample) and TM-25.4 (low level fortified sample) with a certified content of total chromium were obtained from the National Institute of Standards and Technology, National Research Council Canada, Spectrapure Standards, European Reference Materials and Environment Canada (TM materials).

2.3. Procedures

To a 10-mL aliquot of sample placed in a centrifuge tube, 400 µL of 0.1 M TRIS solution (pH 7) and 50 µL of 2 mg mL^{-1} GO suspension were added. The mixture was shaken for a few seconds and then left to stand for 10 min. Next, 100 µL of a 10% m/v Triton X-45 solution were incorporated, and the liquid was heated in a water bath at 60 °C for 10 min. The mixture was then centrifuged at 3000 rpm (1150*g*) for 10 min, the supernatant was discarded and the coacervate homogenized by vortexing for a few seconds. Aliquots (10 µL) were taken and introduced into the electrothermal atomizer followed by 10 µL of the chemical modifier solution (0.5 g L^{-1} Pd(II)). The heating program summarized in Table 1 was applied and the signal corresponding to chromium (III) was obtained. Unless otherwise stated, the measurements were made in duplicate.

For speciation purposes, 10 µL of a 1% v/v concentrated nitric acid solution were first added to a 10 mL sample aliquot (the pH should be close to 2.5) and 100 µL of a 1% sodium hydrogen sulphite solution were incorporated. After allowing to stand for 5 min, the TRIS solution was added to increase the pH, and the above described procedure was applied. The signal corresponding to the total chromium content allowed the Cr (VI) concentration to be calculated by difference. Calibration was carried out using Cr(III) and Cr(VI) standard solutions treated in the same way (Table 2).

3. Results and discussion

3.1. Optimization of CPE procedure

Preliminary experiments were carried out using GO obtained from two commercial sources. One of them provided the material as a 2 mg mL^{-1} aqueous suspension, while the other supplied the product as a solid, from which suspensions were prepared in our laboratory at the same concentration. In this latter case, the suspensions were sonicated for 30 min in a water bath. Both suspensions proved to be suitable sorbents for the effective collection of Cr(III) but they differed as regard their respective properties. Fig. S1, which is provided as Supplementary material, shows the results obtained when the particle size was measured. As can be seen in the graphs, the particles of the commercial suspension were very small, while the suspension prepared from the solid material contained much larger particles, probably as consequence of the inefficient action of the ultrasounds. Since, in addition, the commercial suspension led to very low blank values for chromium, this product was used for all the experiments.

The low particle size of GO meant a high surface area which, while appropriate for the retention of analytes, hindered the collection of the solid particles after the interaction. To overcome this difficulty, separation by cloud point extraction (CPE) was studied. To this effect, a large number of experiments were carried out using several common non-ionic surfactants, namely Triton X-114, Triton X-100 and Triton X-45, which contain different proportions of ethylene oxide in their

Table 1
Graphite furnace program for the determination of chromium in the coacervate.

Step	Temperature, °C	Heating rate, °C s^{-1}	Hold time, s
Drying 1	110	10	20
Drying 2	300	50	20
Pyrolisis	1300	300	10
Auto-zero[a]	1300	0	5
Atomization[a]	2400	3600	5
Cleaning	2450	500	4

[a] Inner gas (argon) stopped.

Table 2
Recovery values of Cr(III) and total Cr determined at different ratios.

Cr (III)/Cr (VI)	Cr (III), ng L^{-1}			Cr (total), ng L^{-1}	
	Added	Found[a]	Recovery, %	Found[b]	Recovery, %
0.1	40	38 ± 3	95 ± 7	445 ± 6	101 ± 2
1	100	102 ± 4	102 ± 4	198 ± 4	99 ± 2
5	200	199 ± 4	99 ± 5	247 ± 5	103 ± 2
10	250	253 ± 5	101 ± 2	270 ± 5	98 ± 2

[a] n=5.
[b] after reduction with sodium hydrogen sulphite at pH 2.5.