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Non-chromatographic speciation of chromium at sub-ppb levels using cloud point extraction in the presence of unmodified silver nanoparticles



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ABSTRACT

The cloud point extraction (CPE) of silver nanoparticles (AgNPs) by Triton X-114 allows chromium (III) ions to be transferred to the surfactant-rich phase, where they can be measured by electrothermal atomic absorption spectrometry. Using 20 mL sample and 50 μL Triton X-114 (30% w/v), the enrichment factor was 1150, and calibration graphs were obtained in the 5–100 ng L^{-1} chromium range in the presence of 5 $\mu\text{g L}^{-1}$ AgNPs. Speciation of trivalent and hexavalent chromium was achieved by carrying out two CPE experiments, one of them in the presence of ethylenediaminetetraacetate. While in the first experiment, in absence of the complexing agent, the concentration of total chromium was obtained, the analytical signal measured in the presence of this chemical allowed the chromium (VI) concentration to be measured, being that of chromium (III) calculated by difference. The reliability of the procedure was verified by using three standard reference materials before applying to water, beer and wine samples.

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1. Introduction

In the environment chromium is present in two oxidation states, Cr(III) and Cr(VI), which have different physiological effects [1,2]. Due to the high toxicity of the hexavalent form, several countries have established severe restrictions concerning the presence of this metal in waters and, since both the authorized concentrations and those usually found in these samples are very low, at the $\mu\text{g L}^{-1}$ level [3,4], the need exists for sensitive, easy-to-carry out analytical procedures to facilitate routine control in the laboratory. The very low concentration involved means that inductively coupled plasma mass spectrometry (ICP-MS) should be a suitable analytical technique for the purpose. However, the difficulty of dealing with such low concentrations is increased by the need to speciate both forms of the metal due to the above mentioned toxicity, the result of which is that a liquid chromatographic (LC) step is often included in the analytical procedure [5]. The LC-ICP-MS combination allows the determination to be carried out but is not always easily available at the laboratory. Consequently, interest has increased in recent years to develop

other approaches involving instrumentation that is commonly present in the laboratory and which may be underused.

The analytical procedures for the speciation of chromium at low concentrations have been reviewed by several authors [4,6–9] and the recent literature shows an increasing use of miniaturized preconcentration techniques to achieve an improvement in sensitivity with minimal handling of the sample. As a result, a diversity of non-chromatographic alternative choices to LC-ICP-MS has been proposed. Leaving aside a number of liquid-liquid microextraction systems [10–16], sometimes involving ionic liquids or hollow fibers [17–19], followed by the use of an atomic or even molecular technique for the final measurement, cloud point extraction (CPE) would seem to be a promising method. CPE is based on the observation that solutions of non-ionic surfactants may form micelles and become turbid when heated above the cloud point temperature, giving rise to two fractions that can be separated by centrifugation. The surfactant-rich phase (coacervate) concentrates the analyte, as occurs with classical liquid-liquid extraction, but with no need for an organic solvent [20]. CPE followed by measurement of the chromium in the coacervate by means of an atomic technique has already been used for chromium determination and speciation [21–26]. A complexing agent is usually incorporated in the sample solution to facilitate the transfer of the metal to the surfactant-rich phase. Most authors

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have proposed electrothermal atomic absorption spectrometry (ETAAS) for the final measurement since, in addition to its high sensitivity, this analytical technique is selective and only requires a low volume of sample to be injected into the electrothermal atomizer.

During a study recently carried out in our laboratory on the CPE of silver nanoparticles (AgNPs) [27], it was observed that chromium species were also coextracted into the coacervate despite the absence of an auxiliary complexing agent. The AgNPs were used as obtained, with no modification by functionalization or physico-chemical treatment, so that they apparently acted directly as efficient carriers, transferring ultratraces of chromium to the coacervate. The direct interaction of chromium species with AgNPs has already been reported and represents the basis for sensitive molecular spectrophotometric and fluorimetric procedures [28–30] for determination in aqueous solutions but, to the best of our knowledge, there are no previous reports describing the analytical benefit that can be obtained by using the above mentioned co-extractant effect. Taking into account both the characteristics of CPE and ETAAS, a sensitive procedure for the speciation of extremely low chromium concentrations seemed feasible, and the results of the research into such a possibility are described in this manuscript.

2. Experimental

2.1. Instrumentation

All the measurements were carried out with a model 600 atomic absorption spectrometer (Perkin-Elmer, Shelton, USA) equipped with a transversely heated graphite atomizer and a Zeeman-effect background correction device. Pyrolytic graphite platforms inserted into pyrolytically coated tubes were obtained from the same manufacturer. Argon flowing at 250 mL min^{-1} was used as inert gas. Measurements were carried out using a chromium hollow cathode lamp (Perkin-Elmer) as the radiation source. Integrated absorbance was exclusively used as the analytical signal. The instrumental parameters are summarized in Table 1.

Once the procedure had been optimized, the autosampler provided with the instrument was not used. Instead, the aliquots were introduced

Table 1
Instrumental parameters for chromium determination.

Parameter			
Lamp current, mA	30 (HCL)		
Wavelength, nm	357.9		
Bandwidth, nm	0.7		
Atomizer type	Pyrolytic tube with L'Vov platform		
Injected volume, μL	10		
Chemical modifier	Pd(II) $2000 \mu\text{g mL}^{-1}$ (20 μL)		
Background correction	Zeeman		
Furnace heating program			
Step	Temperature, $^{\circ}\text{C}$	Ramp, s	Hold, s
1: Dry	110	10	30
2: Dry	300	5	30
2: Ash	900	10	20
3: Atomize ^{a,b}	2300	0	5
4: Clean	2450	1	5
Sequence			
Step A: Pipet the modifier and run step 1			
Step B: Pipet sample or standard and run the entire program			

^a Internal argon flow stopped;

^b Reading step.

into the atomizer by manual injection using a chromatographic-type syringe provided with a polytetrafluoroethylene tube in its tip to avoid physical contact between the plunger of the syringe and the solutions.

A 50 W ultrasound bath (ATU, Valencia, Spain) with temperature control was also used.

2.2. Reagents and samples

All the solutions were prepared with pure water ($18 \text{ M}\Omega \text{ cm}$ resistivity) obtained with a Milli-Q system (Millipore, Bedford, MA, USA). The glassware and plasticware (polypropylene) was washed with 1% (v/v) concentrated nitric acid solution, and then rinsed with water before use.

The chromium (III) and (VI) stock standard solutions ($1000 \mu\text{g mL}^{-1}$) were prepared from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$ (Fluka, Buchs SG, Switzerland), respectively, in water, and diluted daily to obtain appropriate working solutions. Triton X-114, sodium tetrahydroborate (NaBH_4) and silver nitrate (AgNO_3) were obtained from Fluka. Concentrated nitric acid (65%), disodium ethylenediaminetetraacetate (EDTA) and the rest of the chemicals used were obtained from Merck (Darmstadt, Germany).

Tap water was collected from the mains supply of the University of Murcia and analyzed both directly and after passing through a domestic water purifier system. Wine, beer and bottled water samples were purchased in a supermarket. The seawater samples were obtained from near the shore, close to a harbor in south-eastern Spain. These later samples were filtered and maintained in plastic containers at $4 \text{ }^{\circ}\text{C}$ until they were analyzed (less than 48 h) by the general procedure.

In addition, three standard reference materials, namely NIST 1640a (trace elements in natural water), NASS-6 (seawater reference material for trace metals) and SPS-SW2 Batch 125 (reference material for measurement of elements in surface waters) with a certified content of total chromium were obtained from the National Institute of Standards and Technology, National Research Council Canada and Spectrapure Standards, respectively.

2.3. Preparation of silver nanoparticles (AgNPs)

The silver nanoparticles (AgNPs) were prepared according to the scientific literature [28]. For this purpose, 100 mL of 0.1 mM silver nitrate solution were placed in a flat-bottomed flask and, while the solution was vigorously stirred, 0.012 g of solid NaBH_4 were incorporated, maintaining the stirring for 10 min. The mixture was aged overnight in the dark. The AgNPs suspension thus prepared was stable for several days at room temperature.

2.4. General procedure

The sample solution (20 mL) containing chromium in the $5\text{--}100 \text{ ng L}^{-1}$ range was placed in a centrifuge tube and 0.2 mL of a 1 mol L^{-1} nitric acid solution was incorporated to bring the pH close to 2, before heating to $60 \text{ }^{\circ}\text{C}$. Next, 10 μL of a 0.1 mM AgNPs suspension and 50 μL of a 30% w/v Triton X-114 solution were added. The tube was gently shaken for a few seconds and then maintained at $60 \text{ }^{\circ}\text{C}$ for 10 min. The turbid mixture obtained was centrifuged at 4000 rpm for 5 min and a 10 μL aliquot of the recovered surfactant-rich solution was injected into the electrothermal atomizer. The heating program given in Table 1 was run, and the analytical signal due to total chromium was obtained.

For speciation, the experiment was repeated but incorporating 0.4 mL of a 0.3 mol L^{-1} EDTA solution immediately before adding the AgNPs suspension, while the rest of the procedure was the same. The analytical signal obtained corresponded to Cr(VI) which permitted Cr(III) concentration to be calculated by difference.

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