



ELSEVIER

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Tungsten coil atomic emission spectrometry combined with dispersive liquid–liquid microextraction: A synergistic association for chromium determination in water samples



Lorena Vidal^{a,*}, Sidnei G. Silva^b, Antonio Canals^a, Joaquim A. Nóbrega^b

^a Departamento de Química Analítica, Nutrición y Bromatología e Instituto Universitario de Materiales, Universidad de Alicante, P.O. Box 99, E-03080 Alicante, Spain

^b Group of Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, P.O. Box 676, São Carlos, SP 13560-970, Brazil

ARTICLE INFO

Article history:

Received 14 November 2014

Received in revised form

3 April 2015

Accepted 7 April 2015

Available online 16 April 2015

Keywords:

Atomic emission

Chromium

Dispersive liquid–liquid microextraction

Ionic liquids

Speciation

Tungsten coil atomizer

Water samples

ABSTRACT

A novel and environment friendly analytical method is reported for total chromium determination and chromium speciation in water samples, whereby tungsten coil atomic emission spectrometry (WCAES) is combined with *in situ* ionic liquid formation dispersive liquid–liquid microextraction (*in situ* IL–DLLME). A two stage multivariate optimization approach has been developed employing a Plackett–Burman design for screening and selection of the significant factor involved in the *in situ* IL–DLLME procedure, which was later optimized by means of a circumscribed central composite design. The optimum conditions were complexant concentration: 0.5% (or 0.1%); complexant type: DDTC; IL anion: PF₆⁻; [Hmim][Cl] IL amount: 60 mg; ionic strength: 0% NaCl; pH: 5 (or 2); centrifugation time: 10 min; and centrifugation speed: 1000 rpm. Under the optimized experimental conditions the method was evaluated and proper linearity was obtained with a correlation coefficient of 0.991 (5 calibration standards). Limits of detection and quantification for both chromium species were 3 and 10 µg L⁻¹, respectively. This is a 233-fold improvement when compared with chromium determination by WCAES without using pre-concentration. The repeatability of the proposed method was evaluated at two different spiking levels (10 and 50 µg L⁻¹) obtaining coefficients of variation of 11.4% and 3.6% (*n*=3), respectively. A certified reference material (SRM-1643e NIST) was analyzed in order to determine the accuracy of the method for total chromium determination and 112.3% and 2.5 µg L⁻¹ were the recovery (trueness) and standard deviation values, respectively. Tap, bottled mineral and natural mineral water samples were analyzed at 60 µg L⁻¹ spiking level of total Cr content at two Cr(VI)/Cr(III) ratios, and relative recovery values ranged between 88% and 112% showing that the matrix has a negligible effect. To our knowledge, this is the first time that combines *in situ* IL–DLLME and WCAES.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Miniaturization of analytical methods has become very popular in recent years, and many efforts have focused on carrying out chemical analysis at a reduced scale. Miniaturization of sample preparation has significantly increased with the development of a great number of solid-phase and liquid-phase microextraction techniques [1,2]. Liquid-phase microextraction (LPME) offers simplicity, ease of handling, minimal sample and solvent consumptions, and an important reduction in residues generated, in contrast with traditional liquid–liquid extraction techniques. Since its appearance in the nineties, several LPME techniques have been

developed and the most commonly used are single drop microextraction, hollow-fiber liquid-phase microextraction and dispersive liquid–liquid microextraction (DLLME) [3]. Although classical organic solvents have traditionally been used as extractants in LPME techniques, the use of ionic liquids (ILs) has recently attracted interest as a promising alternative [4]. ILs are melted salts at room temperature that possess unique properties among which we can highlight their high thermal and chemical stability with negligible vapor pressure, tuneable viscosity, electrolytic conductivity, wide electrochemical window and good extractability of organic compounds and metal ions [5]. The utilization of ILs has helped to overcome problems associated with LPME techniques using classical organic solvents [4], and enabled the development of new methods such as temperature-controlled IL dispersive liquid–liquid microextraction [6] and *in situ* IL formation dispersive liquid–liquid microextraction (*in situ* IL–DLLME)

* Corresponding author. Tel.: +34 5903400x2232; fax: +34 965903697.

E-mail address: lorena.vidal@ua.es (L. Vidal).

[7,8]. During *in situ* IL-DLLME the extractant phase is formed into sample solution *via* a metathesis reaction between a water-miscible IL and an ion exchange reagent to form a water-immiscible IL. Homogeneously dispersed fine drops of the extractant phase are generated and high enrichment factors are obtained with low extraction times due to the high contact surface between phases. Dispersion of the IL takes place *via* metathesis reaction, and a disperser agent is not needed, thus avoiding competition with the IL and decreasing extraction efficiency. Moreover, additional devices are avoided such as vortex or ultrasound bath, which have also been used to assist IL-DLLME [9,10].

In most cases, LPME procedures are followed by chromatographic separations, in either liquid or gas modalities, coupled with different detection systems (UV-vis, atomic absorption/emission spectrometry (AAS/AES), inductively coupled plasma optical emission spectrometry or mass spectrometry, among others). Most of these detection systems are slow, expensive and bulky, so analytical instrumentation employed for detection has not achieved the same degree of miniaturization as miniaturized sample preparation methods, which are more widely used. Accordingly, devices based on tungsten coil as atomizer, such as atomic emission spectrometry (WCAES) are presented as an attractive option for use in detection of metals. Tungsten coil AES was proposed in 2005 by Rust et al. [11] and several applications were developed [12–15]. However, the low temperature of the gas phase when using the tungsten coil atomizer [16] limits its application to elements with low excitation energies. New strategies are being investigated for improving the sensitivity such as recently demonstrated using Co as a chemical modifier to change the excitation mechanism of Cr [17]. Despite being effective, this strategy will not be applied when simultaneous analysis also requires the determination of Co. Consequently, the coupling with a microextraction procedure will improve the sensitivity for Cr and also will avoid interference processes that are critical in WCAES.

Recently, tungsten coil atomic absorption spectrometry (WCAAS) has been combined to LPME employing ILs as extracting phases for the extraction of Pb and Cu [18], and Cd [19] in water samples. The combination of LPME techniques with tungsten coil-based devices has been mostly restricted to WCAAS measurements, but this synergistic association remains unexplored for WCAES. In comparison to WCAAS, some favorable characteristics are associated with WCAES, especially the multi-element capacity and portability [20].

To our knowledge, this is the first report of an analytical method in which WCAES is used as detection system for LPME. Considering the low volume of the IL formed during *in situ* IL-DLLME (10–25 μL), WCAES seems to be a perfect working partner for analyzing IL drop after microextraction, offering simplicity, a rapid response, low-cost instrumentation with portable options, as well as analytical requirements of sensitivity and reproducibility.

Chromium speciation has been the target to develop this method due to its environmental concern and that Cr species are usually determined by bulky and expensive instrumentation, such as graphite furnace atomic absorption spectrometer and inductively coupled plasma-mass spectrometer. In addition, Cr(III) is an essential nutrient for human health, and some studies have demonstrated that its deficiency is associated with maturity-onset diabetes and/or cardiovascular diseases [21]. In the environment (*e.g.*, water samples) Cr(III) and Cr(VI) are the two common oxidation states. Although Cr(III) is considered to be a trace element essential for living organisms as stated above, Cr(VI) compounds are related as toxic element and exhibiting carcinogenic effects on humans [22].

The research presented here combines the advantages of LPME techniques with the benefits that WCAES offers as detection system. The resulting novel method includes size-reduced systems in both sample preparation and in detection step. The proposed

method has been developed using a multivariate optimization strategy and has been evaluated in order to demonstrate its applicability to determine Cr species in real-world water samples.

2. Experimental section

2.1. Reagents and real-world water samples

Cr(VI) stock solution of 1000 mg L^{-1} was prepared in distilled-deionized water (18.2 $\text{M}\Omega\text{ cm}$, Milli-Q[®], Millipore, Bedford, MA, USA) from K_2CrO_4 (99.5% purity, Ecibra, São Paulo, SP, Brazil) and stored in the dark at 4 °C. Cr(VI) and Cr(III) working solutions were prepared in ultrapure water from the previous stock solution and from single element standard 1000 mg L^{-1} (Qhemis, High Purity, Hexis, Jundiaí, SP, Brazil), respectively.

1-Hexyl-3-methylimidazolium chloride ([Hmim][Cl]) IL (98%) was purchased from Iolitec (Heilbronn, Germany). The lithium bis[(trifluoromethyl)sulfonyl]imide (LiNTf_2) and the potassium hexafluorophosphate (KPF_6) salts, ammonium pyrrolidinedithiocarbamate (APDC, $\approx 99\%$) and sodium diethyldithiocarbamate trihydrate (DDTC, ACS reagent) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium chloride and acetonitrile HPLC-grade ($\geq 99.93\%$) were from Synth (Diadema, SP, Brazil) and Merck (Darmstadt, Germany), respectively. Acetic acid, sodium acetate and sodium hydroxide were from Sigma-Aldrich, and sodium dihydrogen phosphate and disodium hydrogen phosphate from Synth were used to prepare buffer solutions at different pH values.

The certified reference material “trace elements in water” SRM-1643e from National Institute of Standards and Technology (Gaithersburg, MD, USA) with a total Cr content of 20.40 ± 0.24 ($U, k=2$) $\mu\text{g L}^{-1}$ was used to assess the accuracy of the developed method. Tap water (collected from the laboratory, São Carlos, SP, Brazil), bottled mineral water (purchased in local market) and natural mineral water (Mogi das Cruzes, SP, Brazil) were utilized as real-world water samples. Samples were collected in amber glass containers and stored in the dark at 4 °C and were used without any further treatment. The real-world water samples were previously analyzed and the target analytes were not detected.

2.2. *In situ* IL-DLLME procedure

Under optimum conditions for total Cr determination at pH 5, 0.2 mL [Hmim][Cl] IL solution, corresponding to 60 mg, was placed in a conical-bottom glass tube and dissolved in 10 mL of aqueous standards or sample solutions. Then, 0.5 mL DDTC complexant solution (10%, w/v) and 0.5 mL buffer solution (pH 5, 2 mol/L) were added. Next, an equimolar quantity of KPF_6 (55 mg) relative to [Hmim][Cl] was added and a cloudy solution was immediately formed. The mixture was manually shaken for 0.5 min. In order to accelerate the phases separation, the tube was then introduced in an ice bath for 5 min. Next, the phases were separated by centrifugation for 10 min at 1000 rpm. The aqueous phase was removed with a glass pipette, and 15 μL of the formed IL (*i.e.*, [Hmim][PF₆]) was withdrawn with a syringe, and deposited in a vial for dilution with 15 μL of acetonitrile. Finally, 10 μL of the mixture was deposited on a tungsten coil surface for analysis. A schematic diagram of the analytical method is depicted in Fig. 1.

For Cr(VI) determination, the only difference was that the volume of DDTC solution was reduced to 0.1 mL and the pH of the sample was fixed at 2 with buffer solution.

2.3. Tungsten coil atomic emission spectrometer

Instrumental arrangement is identical to that recently described by Silva et al. [17]. The main features of the labmade tungsten

Download English Version:

<https://daneshyari.com/en/article/1243825>

Download Persian Version:

<https://daneshyari.com/article/1243825>

[Daneshyari.com](https://daneshyari.com)