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Tungsten Coil Atomic Emission Spectrometry Combined with Dispersive Liquid-Liquid Microextraction: a Synergistic Association for Chromium Determination in Water Samples

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## ABSTRACT

A novel and environmentally 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: PF<sub>6</sub><sup>-</sup>; [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<sup>-1</sup>, respectively. This is a 233-fold improvement when

compared with chromium determination by WCAES without using preconcentration. The repeatability of the proposed method was evaluated at two different spiking levels (10 and 50  $\mu\text{g L}^{-1}$ ) obtaining coefficients of variation of 11.4 and 3.6% (n=3), respectively. A certified reference material (SRM-1643e NIST) was analysed in order to determine the accuracy of the method for total chromium determination and 112.3% and 2.5  $\mu\text{g L}^{-1}$  were the recovery (trueness) and standard deviation values, respectively. Tap, bottled mineral and natural mineral waters were analysed at 60  $\mu\text{g L}^{-1}$  spiking level of total Cr content at two Cr(VI)/Cr(III) ratios, and relative recovery values were 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.

Keywords: Atomic emission; Chromium; Dispersive liquid-liquid microextraction; Ionic liquids; Speciation; Tungsten coil atomizer; Water samples.

## 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 vapour 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) [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) is 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 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 favourable 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  $\mu\text{L}$ ), WCAES seems to be a perfect working partner for analysing 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<sup>-1</sup> was prepared in distilled-deionized water (18.2 MΩ cm, Milli-Q<sup>®</sup>, Millipore, Bedford, MA, USA) from K<sub>2</sub>CrO<sub>4</sub> (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<sup>-1</sup> (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<sub>2</sub>) and the potassium hexafluorophosphate (KPF<sub>6</sub>) salts, ammonium pyrrolidinedithiocarbamate (APDC, ≈99%) and sodium diethyldithiocarbamate trihydrate (DDTC, ACS reagent) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium chloride and acetonitrile HPLC-grade (≥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) µg L<sup>-1</sup> 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 analysed 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, were 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  $\text{KPF}_6$  (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  $\mu\text{L}$  of the formed IL (i.e., [Hmim][PF<sub>6</sub>]) was withdrawn with a syringe, and deposited in a vial for dilution with 15  $\mu\text{L}$  of acetonitrile. Finally, 10  $\mu\text{L}$  of the mixture was deposited on tungsten coil surface for analysis. A schematic diagram of the analytical method is depicted in Figure 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 coil atomic emission



spectrometer are: (1) use of a ten-turn tungsten coil atomizer (Osram, Pullach, Germany) easily heated using a solid state power supply (0-14 V, Anacom Científica, Sao Bernardo do Campo, SP, Brazil); (2) acquisition of emission signals using a handheld spectrometer (Ocean Optics, HR 4000, Dunedin, FL, USA). The CCD detector system consists of a two-dimensional array of 3648 pixels. A fixed 50  $\mu\text{m}$  entrance slit was used in all measurements and all data were acquired in peak area. This system is easily miniaturized and there is no need of using an additional refrigeration system for cooling down the atomizer between successive heating cycles due to the low mass and low specific heat of the tungsten coil.

A volume of 10  $\mu\text{L}$  of IL/acetonitrile mixture containing the analyte was directly deposited on the tungsten coil surface, with the aid of mechanical micropipette (Eppendorf 10-100  $\mu\text{L}$ , Brinkman, Westbury, NY, USA). A heating program (Table 1) was optimized in order to avoid sample losses due to overheating the coil during the drying steps. All measurements were carried out in triplicate and emission signals were obtained from peak area for chromium at 425.1 nm.

#### 2.4. Data processing

A multivariate optimization strategy was carried out to determine the optimum conditions of the microextraction method. Statgraphics Statistical Computer Package "Statgraphics Plus 5.1." (Warrenton, VA, USA) was used to build the experimental design matrices and evaluate the results. Cr(VI) was selected for the sample preparation optimization study because complexes formation with this specie is kinetically faster than Cr(III) complexes. The peak

area was used as response function to identify and quantify the analyte in order to assess the developed method.

### 3. RESULTS AND DISCUSSION

#### 3.1. Heating program of WCAES

In a recent work, some changes in the heating program for biodiesel decomposition to prevent sample losses by sample splashing during the heating was proposed for Na, K, Cr and V determination [23]. Additionally, longer steps, lower applied voltages and stop of the flow rate of the purge gas during the drying steps were also implemented for reaching better performance. Sample losses occurred by two different ways: (i) first phenomenon was related to capillarity, when the biodiesel sample drains back to the copper electrodes connected to the tungsten coil and; (ii) the sample splashes. The former behaviour can be explained by the decrease of the surface tension with the increase of the temperature [24], inducing the sample outflow. The same effect was not observed in aqueous solution due to the difference of the surface tension of water and biodiesel, in the order of 70 and 30 mN/m (40 °C), respectively [24,25]. On the other hand, sample splashing may be related to temperature differences between the internal and external parts of the sample drop, such as observed when a drop of water are sprinkled onto a hot pan. Whereupon a liquid contacts with a surface significantly hotter than the liquid boiling point, gases formed between the liquid and the hotter surface produce an insulating layer which keeps that liquid from boiling rapidly; this phenomenon is known as Leidenfrost effect [26]. Due to the fact that the tungsten coil atomizer is an open system with a constant gas flow rate, a pronounced gas

phase temperature gradient was observed, decreasing ca. 250 °C for every millimeter away from the coil [16].

Associating these phenomena with the experimental observation in the present work, we may speculate that when an electric current is applied through the tungsten coil the heat is transferred to IL drop by conduction, the bottom part of the IL drop vaporizes in contact with the heated coil, and the resulting gas suspends the rest of the drop causing the splashing. Taking into account the hypotheses related to the experimental observations, the heating program for IL containing the analyte was optimized to promote the matrix decomposition and prevent outflow and splashing (Table 1).

The optimization was carried out employing 10  $\mu\text{L}$  of IL. The first four heating steps (0.48, 0.50, 0.70 and 0.90 V for 50, 50, 50 and 10 s, respectively) were implemented to dry the IL drop and decompose the organic matrix. The gradual and small increase of the output voltage prevents outflow IL drop due to overheating of the coil. To minimize temperature gradients among parts of the IL drop in contact with the hot metallic surface and with the gas flow at room temperature, the purge gas flow rate was stopped during these matrix decomposition/drying steps. This prevented IL drop splashing and contributed to improving repeatability. In the next steps, the purge gas flow rate was re-established to remove the smoke generated and 1.0, 3.0 and 4.0 V for 20, 10 and 10 s, respectively, was applied to promote the pyrolysis of the IL drop. Next, a cooling step of 5 s with gas flowing was applied, and, finally, a 14.0 V, 5 s step was applied for atomizing and exciting chromium and generating emission signals (gas on).

Since the viscosity of the IL presented a difficulty to ensure the complete dryness/pyrolysis, the effect of a dilution of the IL extract after the in situ IL-DLLME was studied. Extractions of Cr(VI) with the two ion exchange reagents (i.e.,  $\text{KPF}_6$  and  $\text{LiNTf}_2$ ) at  $50 \mu\text{g L}^{-1}$  concentration level were carried out. After the in situ IL-DLLME the  $15 \mu\text{L}$  extracts were diluted with acetonitrile testing three different ratios, 20/80, 50/50 and 80/20 (IL/acetonitrile, v/v). Results are presented in Figure 2.

As can be seen, the result obtained at 20/80 ratio (i.e., the highest dilution) provided a signal slightly lower than the others dilution ratios. However, there is no significant difference between responses obtained at 50/50 and 80/20 ratios, therefore, 50/50 was selected due to its lower viscosity and better behaviour in the WCAES. On the other hand, Figure 2 also shows the difference in the response obtained for the two ion exchange reagents tested. As can be seen,  $[\text{Hmim}][\text{PF}_6]$  IL provides better extraction of chromium complexes than  $[\text{Hmim}][\text{NTf}_2]$ .

### 3.2. Multivariate optimization

#### 3.2.1. Screening step

Plackett-Burman design is a two-level fractional factorial design for studying  $k = N - 1$  variables in  $N$  runs, where  $N$  is a multiple of 4 [27]. Fractional factorial designs are useful in the first steps of a project when many variables are initially considered but only a few show important effects. The Plackett-Burman design ignores interaction between variables so the main effects can be calculated with a reduced number of experiments, thereby leading to more economical experimentation. A saturated Plackett-Burman design was used to construct the

matrix of experiments, including 11 variables: eight real variables and three dummy variables. The effects of dummy variables were used to evaluate the experimental error [28,29].

Based on the literature and previous experience of the research group [30,31], the eight real experimental variables selected at two levels were: complexant type and concentration, IL anion, amount of [Hmim][Cl], ionic strength, pH, and centrifugation time and speed. Table 2 shows the experimental variables and levels considered in the Plackett-Burman design. A total of twelve experiments were carried out using aqueous standards of Cr(VI) at  $50 \mu\text{g L}^{-1}$  concentration level.

Data obtained were evaluated using an ANOVA test and results were visualized with the Pareto chart shown in Figure 3. The length of each bar is proportional to the influence of the corresponding factor and the effects that exceed the reference vertical line can be considered significant with a 95% probability.

According to Figure 3, IL anion was the most significant factor, with 95% probability, causing a positive effect (in agreement with the previous one-at-a-time study, Figure 2). The following significant factors were centrifugation speed and IL amount with negative effect. The latter is in agreement with the fact that if a lower amount of [Hmim][Cl] is used, a smaller volume of IL is formed in the microextraction procedure, thus a higher concentration of the analyte is obtained in the extraction phase. The next important factor was the pH being non-significant with a negative effect. However, it is important to point out that pH is a key factor for speciation of Cr(III) and Cr(VI), and therefore, it was considered as a mandatory factor to study in the following optimization step.

The other factor included in the next optimization step was the IL amount, however, IL anion and centrifugation speed were excluded due to levels limitation and were fixed at PF<sub>6</sub><sup>-</sup> and 1000 rpm values, respectively.

The other four factors, complexant concentration and type and centrifugation time with non-significant positive effect, and ionic strength with non-significant negative effect were fixed at their corresponding values (complexant concentration: 0.5%; complexant type: DDTC; centrifugation time: 10 min; and ionic strength: 0% NaCl).

### 3.2.2. Optimization of significant variables

Circumscribed central composite design (CCCD) was employed in this optimization step. This design combines a two-level full factorial design ( $2^k$ ) with  $2k$  star points, where  $k$  is the number of variables being optimized, and one point at the center of the experimental region, that can be run  $n$  times. In order to ensure the rotatability of the model, star points were set at  $\alpha = \sqrt{k} = 1.41$  whereas the central point was repeated five times to provide an orthogonal design [27]. CCCD was used to evaluate and optimize main effects, interaction effects and quadratic effects of the two considered variables. Table 3 shows the low and high levels, the central and star points of the considered variables in the CCCD. Thirteen experiments were carried out using aqueous standards of Cr(VI) at  $50 \mu\text{g L}^{-1}$  concentration level.

Data obtained were also evaluated using an ANOVA test and results were visualized with a Pareto chart (results not shown). The amount of [Hmim][Cl] was a significant variable, with a 95% probability, confirming the predicted importance of the extractant phase volume effect. One of the quadratic effects

was also significant, assuming the curvature of the system and fitting the second-grade polynomial model proposed. The response surface obtained using the CCCD is shown in Figure 4. The surface graph shows a pronounced increase in the analytical signal as the amount of [Hmim][Cl] and pH value decrease. This is in agreement with the previous results obtained by Plackett-Burman design, where decreasing the amount of IL leads to an increase of the concentration of Cr(VI) in the extract, and the Cr(VI) complex formation is higher at lower pH.

In summary, results obtained from the overall optimization process lead to the following experimental conditions: complexant concentration: 0.5% (or 0.1%, see next Section); complexant type: DDTC; IL anion:  $\text{PF}_6^-$ ; [Hmim][Cl] IL amount: 60 mg; ionic strength: 0% NaCl; pH: 2 (or 5, see next Section); centrifugation time: 10 min; and centrifugation speed: 1000 rpm.

### 3.3. Speciation study

Speciation study was focused on pH effect because the influence of this parameter was previously shown using IL-DLLME [32]. The pH range studied was from 1 to 6, since at pH higher than 6 there was a pronounced decrease on Cr(III) complexes extraction. As can be seen from Figure 5, a significant effect on Cr(VI) complexes extraction was not observed in the whole pH range studied. On the other hand, the extraction of Cr(III) complexes was negligible at all pH values except at pH 5. Therefore, it can be concluded that by varying the pH it was possible to determine Cr(VI) at pH 2, optimum pH value obtained from the previous experimental design analysis, and total chromium at pH 5.

Consequently, a speciation study was carried out at pH 2 and 5. A water

sample was spiked at the same concentration level of Cr(VI) and Cr(III),  $25 \mu\text{g L}^{-1}$ , and two successive extractions following the procedure described in Section 2.2. were carried out. Results obtained are shown in Table 4. As can be seen, measurements at pH 2 provided a 103% recovery of Cr(VI), and at pH 5 led to a 106% recovery of total chromium. Cr(III) was obtained subtracting Cr(VI) to the total chromium amount and the recovery was 108%. Therefore, the microextractions at different pH values confirmed the feasibility to determine the two species of Cr just by variation of pH. It is important to highlight that the concentration of DDTC in the water sample was reduced to 0.1%, instead of 0.5%, when only Cr(VI) was determined at pH 2, because there was an increasing of 65% in the signal due to partial Cr(III) extraction if 0.5% of DDTC was employed.

#### 3.4. Analytical figures of merit of the proposed method

Quality parameters of the proposed method were evaluated for Cr(VI) extraction. A concentration range from 10 to  $100 \mu\text{g L}^{-1}$  was studied at pH 2 and 5 and the linear range was finally established from 10 to  $60 \mu\text{g L}^{-1}$ . The resulting analytical calibration curves gave a high level of linearity with a correlation coefficient ( $r$ ) of 0.991 (5 calibration standards). The repeatability of the proposed method, expressed as coefficient of variation (CV), was evaluated at two different spiking levels ( $10$  and  $50 \mu\text{g L}^{-1}$ ) by extracting six consecutive aqueous standards, and CV values were found to be 11.4% and 3.6%, respectively.

The limit of detection (LOD) and the limit of quantification (LOQ) were estimated using the mean signal of the blank ( $n = 3$ ) plus three or ten times its



standard deviation. The LOD was  $3 \mu\text{g L}^{-1}$  whereas the LOQ was  $10 \mu\text{g L}^{-1}$ . These limits were obtained for Cr(VI) and Cr(III). It should be pointed out that the LOD of the developed method fulfils the European Legislation Council Directive 98/83/EC (total Cr  $50 \mu\text{g L}^{-1}$ ) and the United States Environmental Protection Agency regulation (total Cr  $100 \mu\text{g L}^{-1}$ ) employing low-cost instrumentation compared to other previous works [32,33]. In addition, this is a 233-fold improvement when compared with Cr determinations by WCAES without using preconcentration [17]. Therefore the developed method presents unique benefits.

The SRM-1643e certified reference material "trace elements in water" was analysed in order to determine the accuracy of the method. The analysis was done at pH 5 because Cr content of the sample was specified as total Cr. The recovery (i.e., trueness) of the method was 112.3%, and the precision expressed as standard deviation was  $2.5 \mu\text{g L}^{-1}$ . These results confirm the capability of the method to determine Cr at trace levels. It is important to highlight that this was the first time that Cr was determined in water certified material by WCAES.

### 3.5. Real-world water samples analysis

The applicability of the proposed method to determine Cr in real-world water samples was evaluated. Three replicate analyses of tap, bottled mineral and natural mineral water samples were carried at  $60 \mu\text{g L}^{-1}$  spiking level of total Cr content. Analyses were done at pH 5 to determine the total Cr content, and two Cr(VI) and Cr(III) ratios were studied, being Cr(VI)/Cr(III) equal to 3 or equal to 0.33. It should be noted that in previous analyses none of the selected water

samples had initial detectable Cr concentrations. In order to assess matrix effects, relative recoveries were calculated as the ratio of the signals found in real and ultrapure water samples spiked at the same concentration level. Relative recoveries for tap, bottled mineral and natural mineral water samples were found to be 108%, 93% and 88% with CV values of 10%, 21% and 17% ( $n = 3$ ), respectively, when Cr(VI)/Cr(III) ratio was 3 (Table 5). On the other hand, the relative recoveries obtained, when the Cr(VI)/Cr(III) ratio was 0.33, were 95%, 93% and 112% with CV values of 21%, 16% and 13% ( $n = 3$ ) for tap, bottled mineral and natural mineral water samples, respectively (Table 5).

According to these results, it can be concluded that the matrix effects were not significant in total Cr determination in the three water samples. In addition, the different contents of Cr(VI) and Cr(III) in the samples did not affect the total Cr determination. Therefore, the developed method can be successfully applied to water sample matrices.

## CONCLUSIONS

Tungsten coil atomic emission spectrometry has been successfully combined with LPME for the first time. The suggested analytical method employs size-reduced systems both in sample preparation and in detection step to allow on site determination of total chromium and chromium species in water samples. The presented method is fast, sensitive, low-cost and environmentally friendly, and presents a new step forward on the miniaturization of analytical methodologies.

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## REFERENCES

- [1] S. Risticovic, V.H. Niri, D. Vuckovic, J. Pawliszyn, Recent developments in solid-phase microextraction, *Anal. Bioanal. Chem.* 393 (2009) 781–795.
- [2] F. Pena-Pereira, I. Lavilla, C. Bendicho, Liquid-phase microextraction techniques within the framework of green chemistry, *TrAC Trends Anal. Chem.* 29 (2010) 617–628.
- [3] M. Rezaee, Y. Assadi, M.-R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, Determination of organic compounds in water using dispersive liquid-liquid microextraction, *J. Chromatogr. A* 1116 (2006) 1–9.
- [4] E. Aguilera-Herrador, R. Lucena, S. Cárdenas, M. Valcárcel, The roles of ionic liquids in sorptive microextraction techniques, *TrAC Trends Anal. Chem.* 29 (2010) 602–616.
- [5] P. Sun, D.W. Armstrong, Ionic liquids in analytical chemistry, *Anal. Chim. Acta* 661 (2010) 1–16.
- [6] Q. Zhou, H. Bai, G. Xie, J. Xiao, Temperature-controlled ionic liquid dispersive liquid phase micro-extraction, *J. Chromatogr. A* 1177 (2008) 43–49.
- [7] M. Baghdadi, F. Shemirani, In situ solvent formation microextraction based on ionic liquids: a novel sample preparation technique for determination of inorganic species in saline solutions, *Anal. Chim. Acta* 634 (2009) 186–191.
- [8] C. Yao, J.L. Anderson, Dispersive liquid-liquid microextraction using an in situ metathesis reaction to form an ionic liquid extraction phase for the preconcentration of aromatic compounds from water, *Anal. Bioanal. Chem.* 395 (2009) 1491–1502.
- [9] X.-M. Sun, Y. Sun, L.-W. Wu, C.-Z. Jiang, X. Yu, Y. Gao, L.-Y. Wang, D.-Q. Song, Development of a vortex-assisted ionic liquid microextraction method for the determination of aromatic amines in environmental water samples, *Anal. Methods* 4 (2012) 2074–2080.
- [10] Y. Zhang, H.K. Lee, Ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction followed high-performance liquid chromatography for the determination of ultraviolet filters in environmental water samples, *Anal. Chim. Acta* 750 (2012) 120–126.
- [11] J.A. Rust, J.A. Nobrega, C.P. Calloway, B.T. Jones, Advances with tungsten coil atomizers: Continuum source atomic absorption and emission spectrometry, *Spectrochim. Acta Part B* 60 (2005) 589–598.

- [12] J.A. Rust, J.A. Nobrega, C.P. Calloway, B.T. Jones, Tungsten coil atomic emission spectrometry, *Spectrochim. Acta Part B* 61 (2006) 225–229.
- [13] G.L. Donati, J. Gu, J.A. Nobrega, C.P. Calloway, B.T. Jones, Simultaneous determination of the lanthanides by tungsten coil atomic emission spectrometry, *J. Anal. At. Spectrom.* 23 (2008) 361–366.
- [14] G.L. Donati, R.B. Wildman, B.T. Jones, A new atomization cell for trace metal determinations by tungsten coil atomic spectrometry, *Anal. Chim. Acta* 688 (2011) 36–42.
- [15] J. Gu, S.R. Oliveira, G.L. Donati, G. Neto, B.T. Jones, Rugged, portable tungsten coil atomic emission spectrometer, *Anal. Chem.* 83 (2011) 2526–2531.
- [16] Z.F. Queiroz, F.J. Krug, P. V. Oliveira, M. Silva, J.A. Nobrega, Electrothermal behavior of sodium, potassium, calcium and magnesium in a tungsten coil atomizer and review of interfering effects, *Spectrochim. Acta Part B* 57 (2002) 49–61.
- [17] S.G. Silva, G.L. Donati, L.N. Santos, B.T. Jones, J.A. Nobrega, Cobalt as chemical modifier to improve chromium sensitivity and minimize matrix effects in tungsten coil atomic emission spectrometry, *Anal. Chim. Acta* 780 (2013) 7–12.
- [18] X. Wen, Q. Deng, J. Wang, X. Zhao, Application of portable spectrometer for ultra trace metal analysis after ionic liquid based microextraction, *Anal. Methods* 5 (2013) 2978–2983.
- [19] X. Wen, Q. Deng, J. Wang, S. Yang, X. Zhao, A new coupling of ionic liquid based-single drop microextraction with tungsten coil electrothermal atomic absorption spectrometry, *Spectrochim. Acta Part A* 105 (2013) 320–325.
- [20] J.A. Rust, G.L. Donati, M.T. Afonso, J.A. Nobrega, B.T. Jones, An overview of electrothermal excitation sources for atomic emission spectrometry, *Spectrochim. Acta Part B* 64 (2009) 191–198.
- [21] R.A. Anderson, Essentiality of chromium in humans, *Sci. Total Environ.* 86 (1989) 75–81.
- [22] M. Ding, X. Shi, Molecular mechanisms of Cr(VI)-induced carcinogenesis, *Mol. Cell. Biochem* 234 (2002) 293–300.
- [23] S.E. Dancsak, S.G. Silva, J.A. Nobrega, B.T. Jones, G.L. Donati, Direct determination of sodium, potassium, chromium and vanadium in biodiesel fuel by tungsten coil atomic emission spectrometry, *Anal. Chim. Acta* 806 (2014) 85–90.

- [24] G.J. Gittens, Variation of surface tension of water with temperature, *J. Colloid Interface Sci.* 30 (1969) 406–412.
- [25] C.A.W. Allen, K.C. Watts, R.G. Ackman, Predicting the surface tension of biodiesel fuels from their fatty acid composition, *J. Am. Oil Chem. Soc.* 76 (1999) 317–323.
- [26] J.C. Burton, A.L. Sharpe, R.C.A. van der Veen, A. Franco, S.R. Nagel, Geometry of the vapor layer under a Leidenfrost drop, *Phys. Rev. Lett.* 109 (2012) 074301(1)–074301(4).
- [27] D.C. Montgomery, *Design and Analysis of Experiments*, seventh ed, Wiley, New Jersey, 2009.
- [28] Y.V. Heyden, C. Hartmann, D.L. Massart, L. Michel, P. Kiechle, F. Erni, Ruggedness tests for a high-performance liquid Chromatographic assay: Comparison of an evaluation at two and three levels by using two-level Plackett-Burman designs, *Anal. Chim. Acta* 316 (1995) 15–26.
- [29] H. Fabre, N. Mesplet, Robustness testing for a capillary electrophoresis method using the “short-end injection” technique, *J. Chromatogr. A* 897 (2000) 329–338.
- [30] E. Fernández, L. Vidal, J. Iniesta, J.P. Metters, C.E. Banks, A. Canals, Screen-printed electrode-based electrochemical detector coupled with in-situ ionic-liquid-assisted dispersive liquid-liquid microextraction for determination of 2,4,6-trinitrotoluene, *Anal. Bioanal. Chem.* 406 (2014) 2197–2204.
- [31] C. Cortada, L. Vidal, A. Canals, Determination of geosmin and 2-methylisoborneol in water and wine samples by ultrasound-assisted dispersive liquid-liquid microextraction coupled to gas chromatography-mass spectrometry, *J. Chromatogr. A* 1218 (2011) 17–22.
- [32] S. Wen, J. Wu, X. Zhu, Room temperature ionic liquid-based dispersive liquid-liquid microextraction combined with flame atomic absorption spectrometry for the speciation of chromium(III) and chromium(VI), *J. Mol. Liq.* 180 (2013) 59–64.
- [33] I. López-García, Y. Vicente-Martínez, M. Hernández-Córdoba, Determination of very low amounts of chromium(III) and (VI) using dispersive liquid-liquid microextraction by in situ formation of an ionic liquid followed by electrothermal atomic absorption spectrometry, *J. Anal. At. Spectrom.* 27 (2012) 874–880.

## Figure Captions

Figure 1. In situ IL-DLLME coupled with WCAES.

Figure 2. Effect of the extract dilution on Cr emission signals by WCAES.

Figure 3. Pareto chart of the main effects of Plackett-Burman design for Cr(VI) extraction.

Figure 4. Response surface of circumscribed central composite design for Cr(VI) extraction.

Figure 5. pH study for chromium species extraction.

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Fig. 1

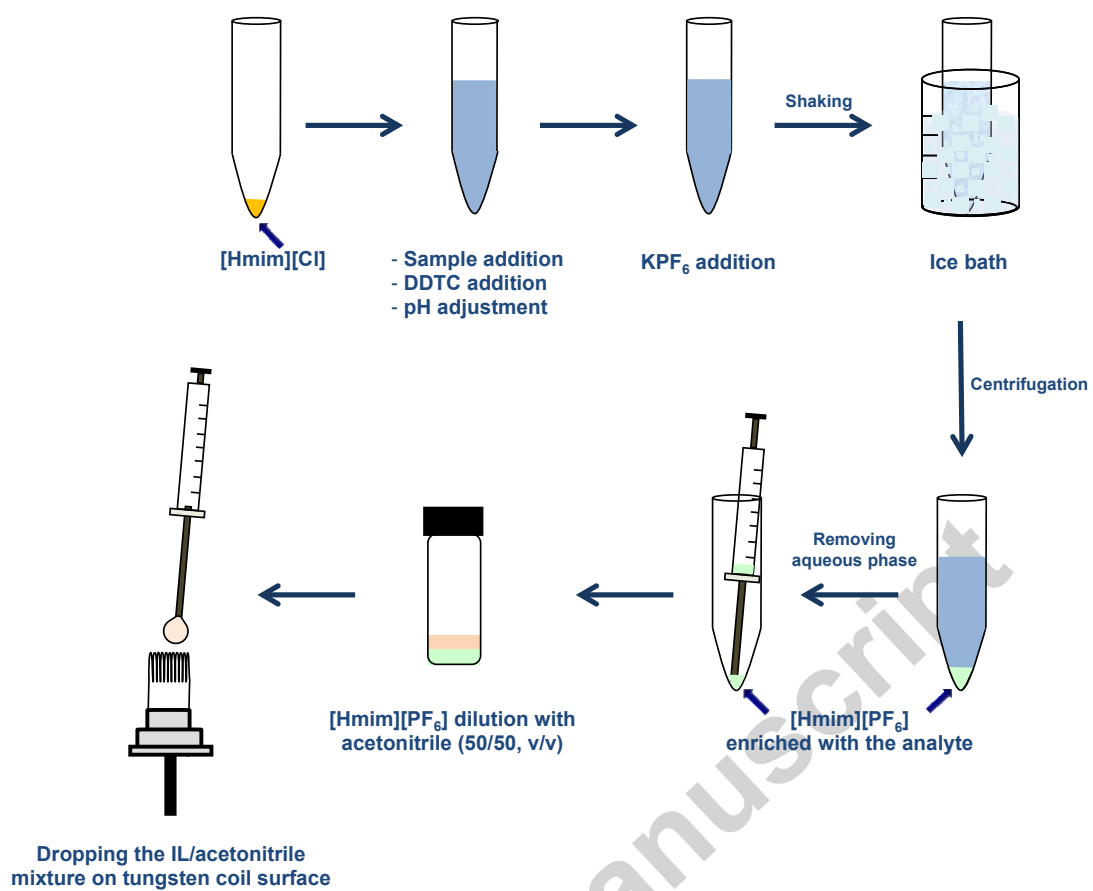
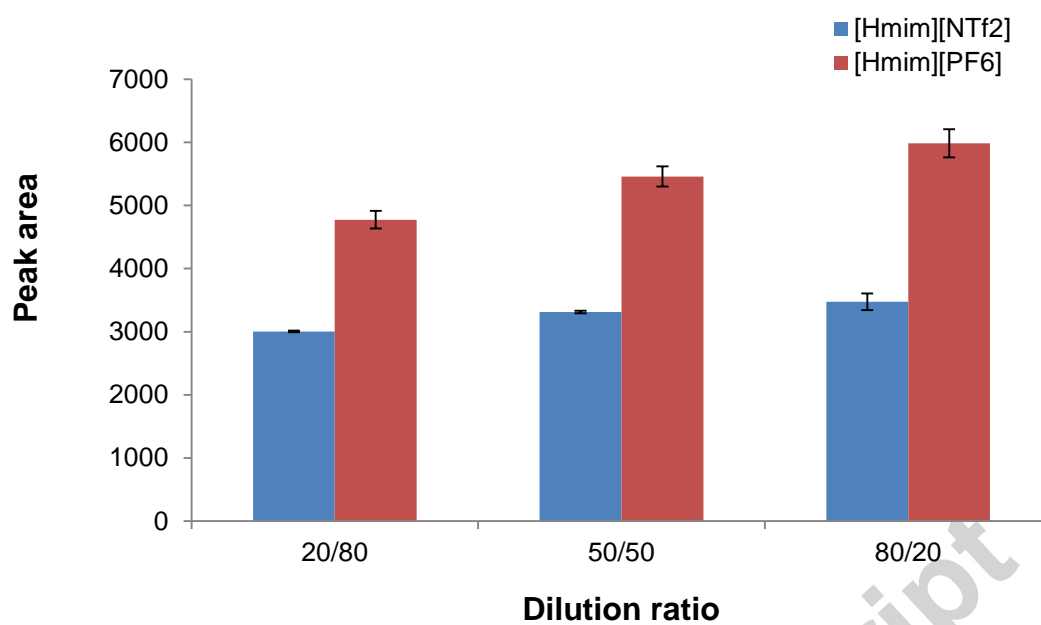




Fig. 2



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Fig. 3

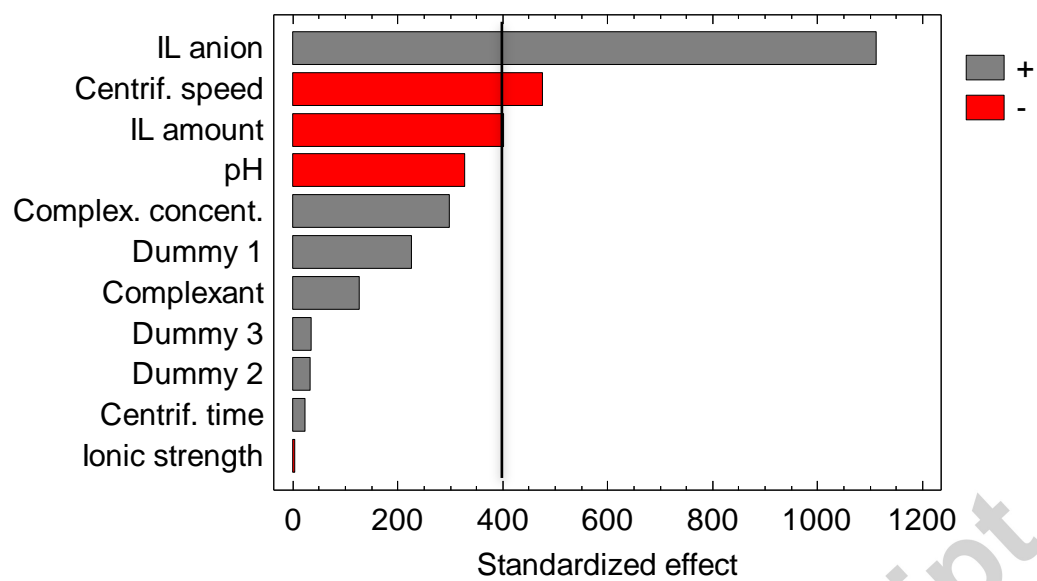


Fig. 4

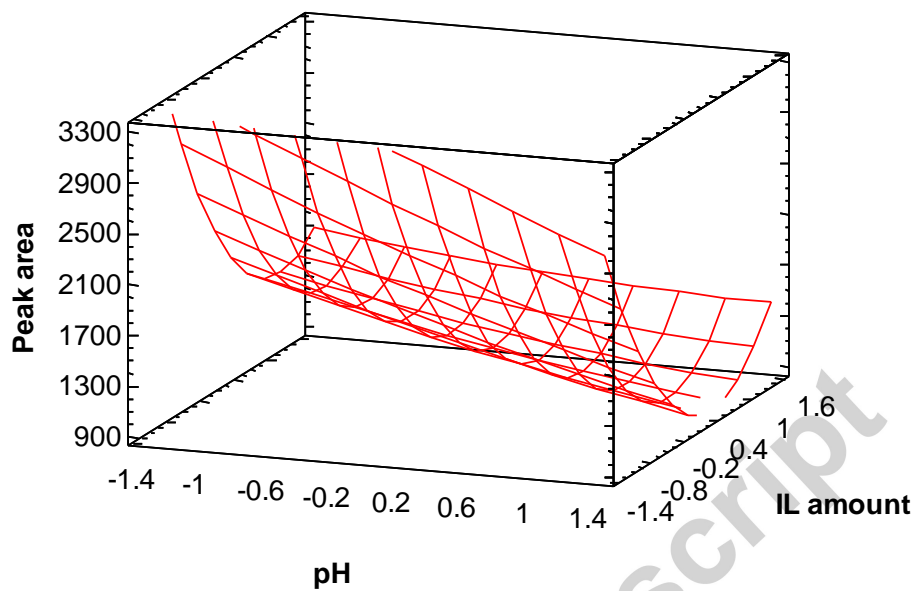


Fig. 5

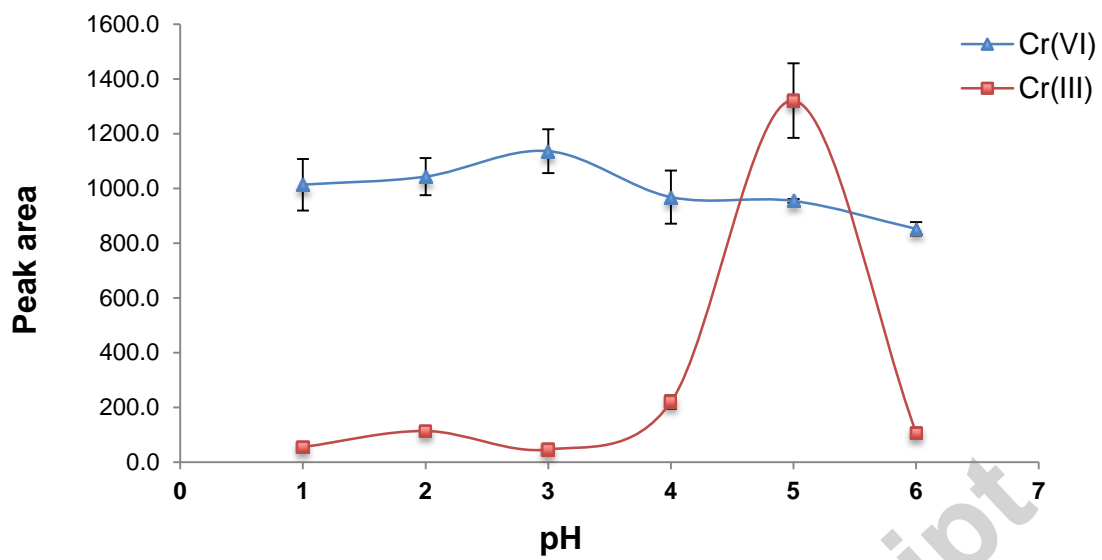


Table 1. Heating program for chromium atomization-excitation by WCAES.

Step	Voltage (V)	Time (s)	Process
1	0.48	50	Drying and decomposition of organic matrix (purge gas off)
2	0.50	50	
3	0.70	50	
4	0.90	10	
5	1.0	20	Pyrolysis (purge gas on)
6	3.0	10	
7	4.0	10	
8	0	5	Cooling (purge gas on)
9	14.0	5	Atomisation/excitation/emission/measurement (purge gas on)

Table 2. Factors and levels of Plackett-Burman design.

Factor	Level	
	Low (-1)	High (+)
Complexant type	APDC	DDTC
Complexant concentration (% w/v)	0.1	0.5
Ionic liquid anion	NTf <sub>2</sub> <sup>-</sup>	PF <sub>6</sub> <sup>-</sup>
[Hmim][Cl] amount (mg)	60	120
Ionic strength, NaCl (% w/v)	0	5
pH	5	7
Centrifugation time (min)	5	10
Centrifugation speed (rpm)	1000	2000

Table 3. Factors, levels and star points of the circumscribed central composite design.

Factor	Level			Star points ( $\alpha=1.41$ )	
	Low (-1)	Central (0)	High (+1)	$-\alpha$	$+\alpha$
[Hmim][Cl] amount (mg)	70	100	130	60	142
pH	3	5	7	2	8

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Table 4. Water sample analysis spiked at  $25 \mu\text{g L}^{-1}$  Cr(VI) and  $25 \mu\text{g L}^{-1}$  Cr(III) concentration levels.

Chromium specie	Recoveries (%) and CV in parenthesis
Total Cr <sup>a</sup>	106 (12)
Cr(VI) <sup>b</sup>	103 (19)
Cr(III) <sup>c</sup>	108 (19)

<sup>a</sup> Extraction carried out at pH 5; Mean of three replicated analysis

<sup>b</sup> Extraction carried out at pH 2; Mean of three replicated analysis

<sup>c</sup> Calculated by subtracting Cr(VI) to the total Cr



Table 5. Relative recoveries and coefficient of variation in total chromium determination at different ratios of Cr(VI) and Cr(III) in real-world water samples.

Water sample	Relative recoveries (%) and CV in parenthesis <sup>a</sup>
Tap water	108 (10) <sup>b</sup>
	95 (21) <sup>c</sup>
Bottled mineral water	93 (21) <sup>b</sup>
	93 (16) <sup>c</sup>
Natural mineral water	88 (17) <sup>b</sup>
	112 (13) <sup>c</sup>

<sup>a</sup> Spiking level: 60  $\mu\text{g L}^{-1}$ ; mean of three replicated analysis

<sup>b</sup> Cr(VI)/Cr(III): 3

<sup>c</sup> Cr(VI)/Cr(III): 0.33

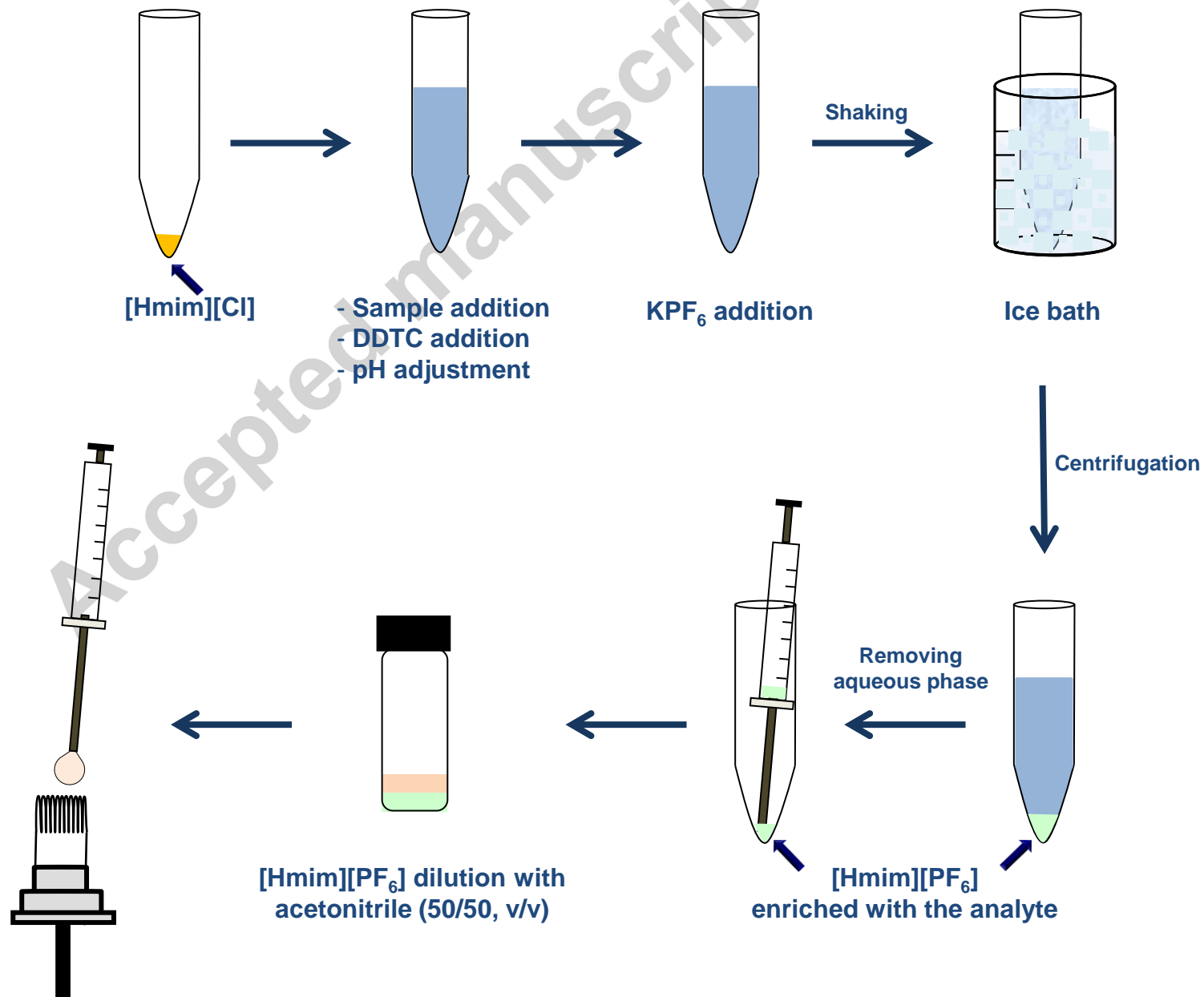
#### Highlights

Total chromium determination and chromium speciation in drinking waters

In situ IL-DLLME for extraction of chromium complexes

WCAES is successfully combined with LPME for the first time

Limits of detection lower than European and North American Legislation



Dropping the IL/acetonitrile mixture on tungsten coil surface