Analytical Methods

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Cite this: *Anal. Methods*, 2013, **5**, 2971

# Supramolecular dispersive liquid–liquid microextraction based solidification of floating organic drops for speciation and spectrophotometric determination of chromium in real samples

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A novel, sensitive and inexpensive supramolecular dispersive liquid–liquid microextraction method based on the solidification of floating organic drops (SM-DLLME-SFO) has been proposed for the speciation and preconcentration of trace quantities of chromium as a precursor to its determination by UV-Vis spectrophotometery for the first time. The chromium ions are micro-extracted with coacervates composed of reverse micelles formed using decanoic acid and dispersed in tetrahydrofuran–water mixtures. THF plays a double role, as a dispersing solvent and also in the self-assembly of decanoic acid. The method involves the partitioning of the metal chelates, produced from the reaction of Cr(VI) with diphenylcarbazide and sodium dodecyl sulfate in an acidic medium and a combination of SM-DLLME with the solidification of floating organic drops. It combines the advantages of dispersive liquid–liquid microextraction with those based on coacervation and reverse micelles and solidification. All the critical parameters affecting the analytical performance were studied. Under the optimum conditions, the enhancement factor was 50. The detection limit and precision (RSD) were 0.23 μg $L^{-1}$ and 3.8% ($n = 6$), respectively. The accuracy of the developed method was evaluated by analyzing a certified reference material and applied successfully to the analysis of several water samples.

Received 6th January 2013
Accepted 1st April 2013

DOI: 10.1039/c3ay00036b

www.rsc.org/methods



## Introduction

Speciation analysis of toxic heavy metals is of great importance due to its impact on environmental chemistry, food, medicine and clinical toxicology.[1] Cr(VI) is highly toxic and shows carcinogenic effects as a result of its reaction with protein components and nucleic acids inside the cell.[2] Cr(III) is normally an essential element for biological mechanisms, controlling glucose, lipid, and protein metabolism. Due to the difference in toxicities of Cr(III) and Cr(VI), the use of an accurate and reliable method for the speciation of chromium is highly required.[3] Water and soil are the main sources of chromium pollution, therefore a fast, simple, environmentally friendly and sensitive preconcentration technique for Cr determination is in demand. One of the traditional extraction methods is the liquid–liquid extraction (LLE) technique.[4–6] Despite the wide use, LLE is tedious and suffers from large consumption of toxic organic solvents. To overcome these drawbacks, different types of liquid phase microextraction (LPME) such as single drop microextraction (SDME),[7,8] hollow fiber-protected microextraction (HF-LPME)[9,10] and dispersive liquid–liquid microextraction (DLLME)[11,12] have been developed. However, there are some shortcomings in these techniques *e.g.* long extraction times and high stirring rates causing the suspended organic drop to become unstable in SDME; the long pretreatment time and creation of air bubbles on the surface of the HF decreases the transport rate and also manual cutting of the membrane results in poor reproducibility in HF-LPME; hazardous organic solvents with densities greater than water are also employed in the DLLME method. The use of toxic, flammable and environmentally damaging solvents is one of the major drawbacks of recent analytical techniques and much attention has been paid towards the use of green solvents such as ionic liquids.[13] However, they are very expensive and their handling poses some difficulties because of their high viscosities. In this respect the use of other organic solvents friendly to environment, easy to handle and inexpensive are of great importance. Recently, Ruiz and coworkers,[14] and others have developed a novel strategy based on the coacervation of decanoic acid reverse micelles for the extraction of organic compounds with wide polarity ranges.[15–17] Coacervates are water immiscible liquids that are separated out from the bulk of colloidal solutions with the aid of dehydrating agents. Based on studies of the coacervation

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process on various dissolved alkanoic acids in miscible binary mixtures of water and a variety of solvents, decanoic acid in tetrahydrofuran (THF) has been chosen as the most suitable system for analytical applications.[14] However, this technique is tedious, labor-intensive and a time-consuming procedure. The SM-DLLME method is a combination of DLLME with a coacervation-based microextraction technique which has been introduced by our group for the first time. This technique provides enhanced sensitivity and a high preconcentration factor for the extraction of inorganic metals and dyes.[18–20] The method, beside the advantages of DLLME (simplicity of operation, high recovery, very short extraction time due to the very large surface area between the organic and aqueous phases), benefits from other useful factors such as employing nontoxic, inflammable and less expensive decanoic acid as an extraction solvent whereby it is handled when dissolved and does not have the limitations associated with applying solvents with densities higher than water. The removal of the extracted phase on the top of the solution can be also performed without taking out the aqueous phase which is time consuming. Considering the characteristics of decanoic acid such as lower density than water and a melting point near room temperature, a novel combination of SM-DLLME with the solidification of a floating organic drop microextraction technique as a sensitive and powerful preconcentration technique, termed supramolecular dispersive liquid–liquid microextraction based on the solidification of floating organic drops (SM-DLLME-SFO), has been introduced for the first time. The main advantage of this method compared to SM-DLLME is the elimination of the handmade narrow neck centrifuge tube for removing the extracting phase due to the solidification of this extracting phase. In the present study, the applicability of SM-DLLME-SFO was examined for the speciation and preconcentration of trace amounts of chromium in real samples and was determined by UV-Vis spectrophotometry for the first time. Cr(VI) reacts with 1,5-diphenylcarbazide (DPC) in an acidic medium to form a cationic complex which is extracted into the coacervative phase as an ion pair using sodium dodecyl sulfate (SDS).

## Experimental

### Instrumentation

A UV-Vis spectrophotometer (Agilent 8453) with a 250 μL quartz microcell was used for measuring the absorbance of the complex at 540 nm. A Metrohm pH meter model 632 (Herisau, Switzerland) with a combined glass electrode was used for pH measurements. A centrifuge (Hettich, Germany) was used to accelerate the phase separation process.

### Reagents and solutions

All solutions were prepared with analytical grade chemicals and deionized water. DPC, SDS, THF, decanoic acid, $H_2SO_4$ and metal salts were obtained from Merck (U. S. A.). A $4 \times 10^{-3}$ mol $L^{-1}$ DPC solution was prepared daily by dissolving appropriate amounts of DPC in a mixture of ethanol and deionized water (1 : 4, v/v). The SDS and $H_2SO_4$ solutions were prepared in deionized water without further purification. Stock solutions of Cr(VI) and Cr(III) (1000 mg $L^{-1}$) were prepared by dissolving appropriate amounts of $K_2Cr_2O_7$ and $Cr(NO_3)_3$ in 100 mL deionized water and working standard solutions were prepared by appropriate dilutions of the stock standard solutions daily. Decanoic acid working solutions were prepared by dissolving 90 mg of this reagent in 0.6 mL of tetrahydrofuran for each extraction step.

### Recommended SM-DLLME-SFO procedure

For SM-DLLME-SFO, 10 mL of a standard solution containing Cr(VI) at concentrations in the linear range of the calibration curve, 0.05 mL of a $4 \times 10^{-3}$ mol $L^{-1}$ DPC solution, 0.2 mL of a 0.5% (w/v) SDS solution and 0.5 mL of 1 mol $L^{-1}$ $H_2SO_4$ was delivered into a centrifuge tube. A solution of 90 mg decanoic acid (microextraction solvent) in 0.6 mL THF (self-assembly agent and disperser solvent) was then rapidly injected by a long needle syringe causing a cloudy state to appear in the whole solution resulting in increased sensitivity and reproducibility of the method. As a result, the water immiscible decanoic acid rich coacervate was immediately produced in the solution. The Cr–DPC–SDS complex was extracted into fine coacervative and the mixture was centrifuged at 4000 rpm for 5 min to accelerate the separation of the coacervate from the bulk of the solution. After centrifugation, the fine droplets of the extraction phase containing dispersed fine droplets of the coacervate phase were floating at the top of the test tube. The test tube was then transferred into a beaker containing crushed ice for cooling. After 1.5 min, the extraction phase solidified and was then transferred into a conical vial, where it melted immediately at room temperature. It was then diluted with pure acetonitrile up to 150 μL, and transferred to a microcell by the aid of a micro syringe. Absorbance of the complex was measured at 540 nm. A diagrammatic sketch of SM-DLLME-SFO is shown in Fig. 1.

### Determination of total chromium content

The total chromium content was determined as Cr(VI) by the method described above after oxidizing Cr(III) to Cr(VI) by the addition of $KMnO_4$ in an acidic medium. For this purpose, 3 or 4 drops of 0.02 mol $L^{-1}$ $KMnO_4$ solution and 0.5 mL of concentrated $H_2SO_4$ were added into a 25 mL beaker containing the spiked solution of Cr(VI) and Cr(III). The beaker was covered with a watch glass and heated gently (50 °C) for about 15 min to complete the oxidation. The solution was cooled and it was followed by the dropwise addition of sodium azide solution [2.5% (w/v)] to remove the excess $KMnO_4$ by decolorizing the pink solution.[21]

### Sample preparation

In order to establish the accuracy of the recommended SM-DLLME-SFO procedure, a standard rock reference material, JSD3 was analyzed. The rock sample (0.5 g) was transferred into a Teflon beaker and then a mixture of concentrated HF (7 mL), $HNO_3$ (0.5 mL) and $H_2SO_4$ (2.5 mL) was added. The solution was heated until 2 mL of the solution remained. It was followed by adding 6 mL of concentrated nitric acid and, after heating,

 

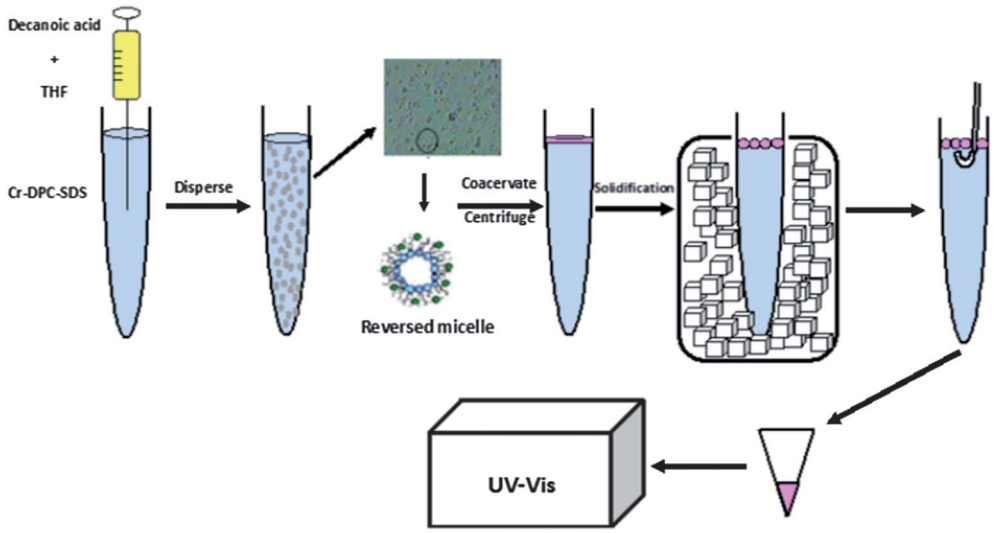


**Fig. 1** Schematic diagram of the proposed SM-DLLME-SFO procedure.

treatment with water to give a clear solution and was finally made to 100 mL by the further addition of deionized water.

The method was also employed for determination of chromium species in several water samples including tap water (Ferdowsi University of Mashhad, Iran), spring water (Dehsorkh, Neyshaboor, Iran) and two different well waters (Ghasemabad and Now chah, Mashhah, Iran). All aqueous samples were filtered using a 0.45 μm pore size membrane filter to remove suspended particulate matter and were collected in cleaned polyethylene bottles.

## Results and discussion

For the formation of a hydrophobic complex, Cr(VI) reacts with DPC($H_4L$) in an acidic medium as a cationic complex which is made as an ion pair using SDS as follows:[22]

$$2CrO_4^{2-} + 3H_4L + 8H^+ \rightarrow Cr(III)(HL)_2^+ + Cr^{3+} + H_2L + 8H_2SO_4$$

$$Cr(III)(HL)_2^+ + SDS \rightarrow [Cr(III)\,(HL)_2^+][SDS]$$

In order to evaluate the optimized experimental conditions for achieving a high enrichment factor and quantitative extraction for the determination of the chromium species, the effects of different parameters on the performance of the method were investigated.

### Volume of sulfuric acid

The complex formation between Cr(VI) and DPC occurs in an acidic medium. On the other hand, the coacervation phenomenon should be performed with protonated decanoic acid ($pK_a = 4.8 \pm 0.2$), which is already provided at a pH below 4.[14] Therefore, the volume of 1 mol $L^{-1}$ sulfuric acid as a unique parameter was studied. A series of experiments were performed using 0–1.5 mL of 1 mol $L^{-1}$ sulfuric acid. The results show that the absorbance increased up to 0.5 mL and then decreased, and hence 0.5 mL of 1 mol $L^{-1}$ sulfuric acid was chosen as the optimum value.

### DPC and SDS concentrations

In this work, DPC was selected as a complexing agent for the extraction of Cr(VI) in an acidic medium. In order to study the influence of DPC concentration on the analytical response for Cr(VI), different concentrations of DPC in the range $4 \times 10^{-6}$ to $3.6 \times 10^{-5}$ mol $L^{-1}$ were prepared and followed the present procedure. As the results show (Fig. 2), the absorbance increased rapidly as the concentration of DPC increased from $4 \times 10^{-6}$ to $1.4 \times 10^{-5}$ mol $L^{-1}$, and then nearly leveled off at higher concentrations. Therefore, a DPC concentration of $2 \times 10^{-5}$ mol $L^{-1}$ was chosen for subsequent experiments.

The effect of SDS concentration on the recovery of the method was studied in the range 0 to 0.025% (w/v). Absorbance was increased up to 0.005% (w/v) and was gradually decreased

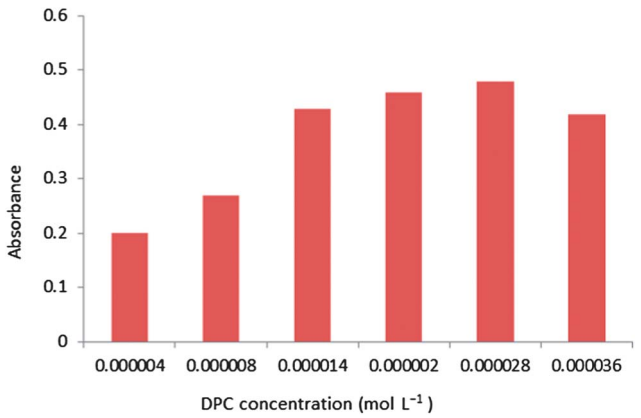


**Fig. 2** Effect of DPC concentration on the absorbance of Cr(VI). Extraction conditions: sample volume, 10 mL; amount of decanoic acid, 50 mg; volume of THF, 0.8 mL; volume of 1 M $H_2SO_4$, 0.5 mL; SDS concentration 0.005% (w/v); concentration Cr(VI), 25 μg $L^{-1}$.

afterwards and hence 0.01% (w/v) was chosen as the optimum value.

### Types of extraction and disperser solvents

The choice of extraction and disperser solvents is very important in SM-DLLME-SFO. The extraction solvent must have several characteristics such as low volatility, low toxicity, low melting point near room temperature, good solubility in disperser solvent and a density less than water. In the previous study[14] decanoic acid in THF was chosen as the most suitable system for analytical applications in reversed micelles. Decanoic acid is an extraction solvent having all the above-mentioned requirements. THF plays a double role, it not only acts as a disperser solvent but also causes self-assembly of decanoic acid. As a result, decanoic acid and THF were selected as extraction and disperser solvents, respectively.

### Amount of extraction solvent

In order to examine the effect of the extraction solvent amount, solutions containing different amounts of decanoic acid were examined with the recommended SM-DLLME-SFO procedure. The results show that the absorbance increases with the increase of decanoic acid up to 90 mg and then started to diminish (Fig. 3). This is due to the enhancement of the extracted phase volume, and as a result the extraction efficiency was decreased. To obtain reasonable precision and higher enrichment factor, 90 mg of decanoic acid was chosen as the optimal amount for further experiments.

### Volume of disperser solvent

The volume of the disperser solvent is one of the important factors to be evaluated. Thus, under the same experimental conditions, a series of sample solutions were prepared using different volumes of THF containing 90 mg of decanoic acid and the experimental procedure was followed. The results indicate (Fig. 4) that the maximal absorbance signal was obtained for 0.6 mL of THF. At lower volumes, the coacervation process was not complete due to the deficiency of the disperser solvent. It is probable that at higher volumes of THF, the solubility of the coacervate phase in water–THF would increase causing the decrease of absorbance.[23]

### Type of diluent solvent

To select the best diluting solvent, pure ethanol, methanol, acetone and acetonitrile were studied individually. The results showed that when ethanol and acetonitrile were used as a diluent, the analytical signals were at their maximum. However, the turbid solution in the case of ethanol hinders its use. Thereby, acetonitrile was selected to dilute the extraction phase up to 150 μL.

### Ionic strength

To investigate the influence of ionic strength on the micro-extraction efficiency, various experiments were performed by adding different amounts of $NaNO_3$ (0–10% w/v) to the standard solution (25 μg $L^{-1}$ of Cr(VI)), while other experimental conditions were kept constant. The results show (Fig. 5) that the absorbance decreased by increasing the $NaNO_3$ concentration in the studied range followed by a decrease in extraction efficiency. This suppression may be due to the disruption of original charge distribution with the addition of an electrolyte which hinders the coacervation formation at high ionic strengths. Hence, all the extraction experiments were performed without salt addition.[24]

### Extraction time

The extraction time is defined as the interval time between the injection of disperser and extraction solvent mixtures, and

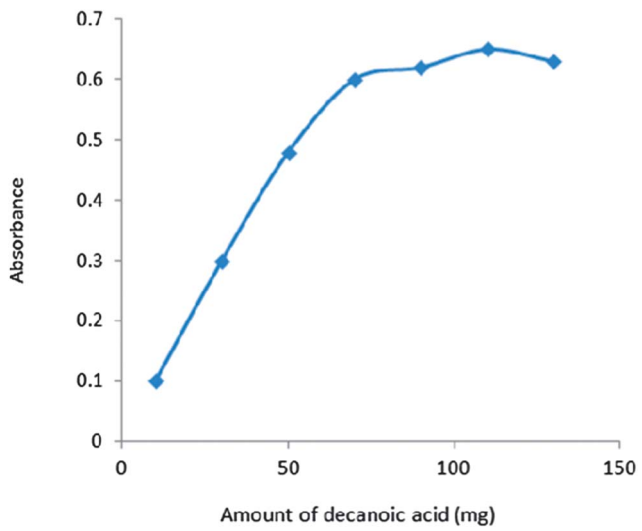


**Fig. 3** Effect of the amount of extraction solvent (decanoic acid) on the absorbance of Cr(VI). Extraction conditions: sample volume, 10 mL; volume of THF, 0.8 mL; volume of 1 M $H_2SO_4$, 0.5 mL; DPC concentration, $2 \times 10^{-5}$ mol $L^{-1}$; SDS concentration, 0.01% (w/v), concentration Cr(VI), 25 μg $L^{-1}$.

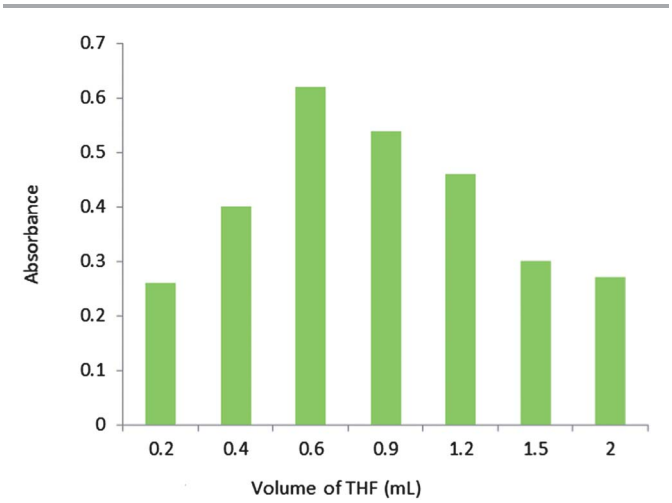


**Fig. 4** Effect of the volume of disperser solvent (THF) on the absorbance of Cr(VI). Extraction conditions: sample volume, 10 mL; amount of decanoic acid, 90 mg; volume of 1 M $H_2SO_4$, 0.5 mL; DPC concentration, $2 \times 10^{-5}$ mol $L^{-1}$; SDS concentration 0.01% (w/v), concentration Cr(VI), 25 μg $L^{-1}$.

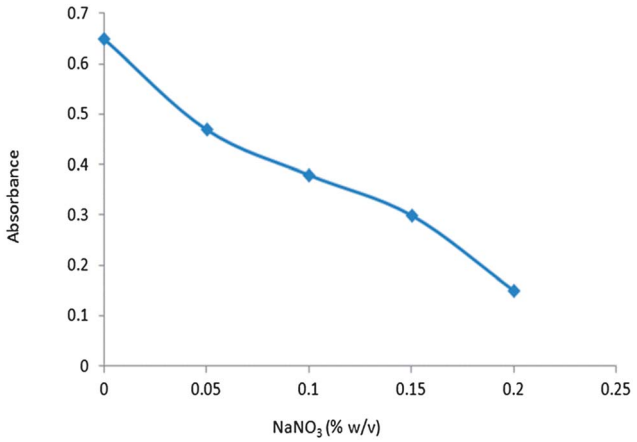


**Fig. 5** Effect of ionic strength on the absorbance of Cr(VI). Extraction conditions: sample volume, 10 mL; amount of decanoic acid, 90 mg; volume of THF, 0.6 mL; volume of 1 M $H_2SO_4$, 0.5 mL; DPC concentration, $2 \times 10^{-5}$ mol $L^{-1}$; SDS concentration 0.01% (w/v), concentration Cr(VI), 25 μg $L^{-1}$.

before the start of centrifuge. The effect of this parameter was investigated on the extraction efficiency of chromium from aqueous phase to coacervate phase. As the data show, extraction time has no effect on the extraction efficiency, because attaining the equilibrium in SM-DLLME-SFO is very fast.

### Centrifuge time

The effect of centrifuge time upon the analytical signal was also studied in the range of 2–10 min. A centrifugation time of 5 min at 4000 rpm was selected for the entire procedure, since complete separation occurred at this time and no appreciable improvements were observed at longer times.

### Interference studies

The effect of diver ions on determination of Cr(VI) was investigated under the optimized conditions. This study was performed by analyzing 10 mL of 20 μg $L^{-1}$ Cr(VI) solution containing concomitant ions at different concentrations. The tolerance limit is defined as the concentration of added ion that causes less than ±5% relative error in the determination of Cr(VI). The results are summarized in Table 1. The data show that chromium(VI) recoveries would be almost quantitative in the presence of all interfering cations and anions studied. The interferences of $Fe^{3+}$ and $Hg^{2+}$ could be completely removed by using EDTA and KCl respectively.

### Figures of merit

Under the optimum conditions, the calibration graph was linear in the range of 1–40 μg $L^{-1}$ of Cr(VI). The detection limit, based on 3Sb was 0.23 μg $L^{-1}$. The relative standard deviation (RSD) for six replicate analyses of 20 μg $L^{-1}$ Cr(VI) was 3.8%. The enrichment factor, calculated as the ratio of the slopes of the calibration graphs after and before the preconcentration step was 50.

**Table 1** Effect of interference on determination of 20 μg $L^{-1}$ Cr(VI) in optimum conditions

| Coexisting ions | Interference/Cu(II) ratio | Recovery (%) |
|---|---|---|
| $K^+$ | 1000 | 105 |
| $Ca^{2+}$ | 1000 | 105 |
| $Na^+$ | 500 | 96 |
| $Mg^{2+}$ | 500 | 97 |
| $SO_4^{2-}$ | 500 | 95 |
| $Br^-$ | 250 | 97 |
| $NO_3^-$ | 250 | 97 |
| $Cu^{2+}$ | 250 | 96 |
| $Cd^{2+}$ | 100 | 97.4 |
| $Ni^{2+}$ | 100 | 103 |
| $Co^{2+}$ | 100 | 103 |
| $Mn^{2+}$ | 100 | 95 |
| $Zn^{2+}$ | 100 | 96 |
| $Cl^-$ | 100 | 95 |
| $CO_3^{2-}$ | 50 | 98 |
| $Fe^{3+}$ | 10 | 96 |
| $Hg^{2+}$ | 10 | 98 |

### Analysis of standard reference material and water samples

The accuracy of the proposed method was evaluated by the spike method using a certified reference material JSD3. The chromium content was determined to be 32.4 ± 4.3 μg $g^{-1}$ which is in good agreement with its certified value (35.3 μg $g^{-1}$) with a recovery of 92%. In addition, this procedure was used for determination of chromium species in different water samples. The results are given in Table 2.

### Comparison to other methods

A comparison of the proposed method with other reported preconcentration methods for determination of chromium is presented in Table 3. In the recommended method, better LOD

**Table 2** Analysis of species chromium in water samples using proposed methods

| | Spiked (μg $L^{-1}$) | | Found[a] (μg $L^{-1}$) | | Recovery (%) | |
|---|---|---|---|---|---|---|
| Samples | Cr(III) | Cr(VI) | Cr(III) | Cr(VI) | Cr(III) | Cr(VI) |
| Tap water[b] | 0.0 | 0.0 | 5.5 ± 0.3 | 1.7 ± 0.3 | — | — |
| | 5.0 | 5.0 | 10.3 ± 0.4 | 6.5 ± 0.4 | 98.0 | 97.0 |
| | 10.0 | 10.0 | 15.0 ± 0.6 | 11.4 ± 0.4 | 97.0 | 97.0 |
| Well water[c] | 0.0 | 0.0 | 4.2 ± 0.3 | 1.5 ± 0.2 | — | — |
| | 3.0 | 3.0 | 7.3 ± 0.4 | 4.4 ± 0.3 | 101.10 | 97.0 |
| | 6.0 | 6.0 | 10.5 ± 0.5 | 6.2 ± 0.4 | 102.0 | 104.0 |
| Well water[d] | 0.0 | 0.0 | 3.0 ± 0.2 | 0.23 ± 0.02 | — | — |
| | 3.0 | 3.0 | 6.1 ± 0.3 | 3.2 ± 0.2 | 102.0 | 98.0 |
| | 6.0 | 6.0 | 8.8 ± 0.4 | 6.1 ± 0.3 | 97.0 | 97.50 |
| Spring water[e] | 0.0 | 0.0 | 4.5 ± 0.3 | 0.7 ± 0.02 | — | — |
| | 3.0 | 3.0 | 7.5 ± 0.4 | 3.7 ± 0.3 | 101.0 | 98.0 |
| | 6.0 | 6.0 | 10.6 ± 0.5 | 6.5 ± 0.3 | 101.0 | 96.0 |

[a] Mean ± standard deviation ($n = 3$). [b] Ferdowsi University of Mashhad, Iran. [c] Ghasemabad, Mashhad, Iran. [d] Nowshad, Mashhad, Iran. [e] Dehsorkh, Neyshaboor, Iran.

**Table 3** Comparison of the proposed method with other reported procedures

| System | Analysis method | Extraction solvent | Extraction time (min) | Enrichment factor | Linear range ($\mu g\ L^{-1}$) | LOD ($\mu g\ L^{-1}$) | Ref. |
|---|---|---|---|---|---|---|---|
| LLE[a] | UV-Vis | *n*-Pentanol | 10 | 5 | 7.5–350 | 7.5 | 25 |
| UACPE[b] | UV-Vis | $I_3^-$ + CTAB | 30 | 20 | 20–400 | 20 | 26 |
| DLLME | FAAS[e] | $CCL_4$ | 2 | 275 | 0.3–20 | 0.07 | 11 |
| DLLME | ICP-OES[f] | $CCL_4$ | 2 | 8 | 1–1000 | 0.27 | 12 |
| LLE | HPLC | [C4MIM][PF6] | 4 | — | 25–200 | 1 | 27 |
| SPE[c] | FAAS | — | 70 | 25 | — | 45 | 28 |
| CPE[d] | FAAS | Triton X-114 | 17 | 75 | Up to 85 | 0.65 | 29 |
| CPE | FAAS | Triton X-114 | 11 | 48 | 2.5–80 | 0.7 | 30 |
| CPE | HPLC | Triton X-114 | 11 | 19 | 50–2000 | 5.2 | 31 |
| SPE[g] | FAAS | — | 20 | 24.9 | 25–250 | 2.3 | 32 |
| SPE | FAAS | — | 35 | 100 | 10–100 | 0.47 | 1 |
| SM-DLLME-SFO | UV-Vis | Decanoic acid | <2 | 50 | 1–40 | 0.23 | This work |

[a] Liquid–liquid extraction. [b] Ultrasonic-assisted cloud point extraction. [c] Solid phase extraction. [d] Cloud point extraction. [e] Flame atomic absorption spectrometry. [f] Inductively coupled plasma optical emission spectrometry. [g] Solid phase extraction.



were obtained for Cr(VI) ions in comparison with other methods. Also, the enrichment factor and linear range are comparable to those reported techniques. Although the extraction equilibrium is achieved very quickly the same as DLLME but apart from using friendly extraction solvent, the present SM-DLLME-SFO is inexpensive and requires basic equipment which is available in almost every analytical laboratory. In comparison with CPE this method requires no heating step, and the extraction time would be greatly decreased. As compared to SPE procedures eliminates the use of any column and, also the sorbent preparation step is omitted. Moreover, this procedure uses an extracting solvent which is nontoxic and the whole extraction procedure is performed at a shorter period.

## Conclusions

The combination of SM-DLLME with a solidification of floating organic drop microextraction technique and UV-Vis spectrophotometry was used for the determination of trace amounts of chromium species in real samples with a low detection limit, high accuracy and good reproducibility for the first time. The DLLME method cannot be usually used in a complex sample, however, as the DPC reagent is highly selective for Cr(VI), this technique could be successfully employed for matrix samples such as soil. Reverse micelle coacervates are produced *in situ* through self-assembly processes in which reversed micelles of decanoic acid are dispersed in tetrahydrofuran–water. This technique involves all the advantages of conventional DLLME such as the simplicity of operation, high recovery and speed. Moreover, it uses decanoic acid as an extraction solvent which is not expensive and no report has been yet published with respect to its toxicity. Also, the limitation of using solvents of higher densities than water has been avoided.

## Acknowledgements

The authors wish to thank the Ferdowsi University of Mashhad for the financial support of this work (code: 15604/3 dated: February 2011).

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