Canadian Chemical Transactions

ISSN 2291-6458 (Print), ISSN 2291-6466 (Online)
Year 2014 | Volume 2 | Issue 1| Page 12-23

Research Article

DOI:10.13179/canchemtrans.2014.02.01.0049

Separation/Preconcentration and Determination of Trace Levels of Cadmium in Saffron Samples by Dispersive Liquid–Liquid Based on Solidification of Floating Organic Drop Microextraction Coupled to UV-Vis Spectrophotometry

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Received: *October18, 2013* ***Revised:*** *November 25, 2013* ***Accepted:*** *November 30, 2013* ***Published:*** *November 30, 2013*

Abstract: This study, dispersive liquid–liquid microextraction based on solidification of floating organic drop, was developed as a simple and rapid technique for separation and determination of cadmium ions in saffron samples. The extracted cadmium was separated, identified, and quantified by UV-Vis spectrophotometry. In this technique, a mixture of 200 µL 1-undecanol containing dithizone as complexing agent (1 mg/L) (extraction solvent) and 500 µL ethanol (dispersive solvent) was rapidly injected into the 10 mL analyte sample in a test tube. The test tubes were sonicated, centrifuged and then some effective parameters on extraction and complex formation, such as type and volume of extraction and disperser solvent, salt effect, pH, the amount of chelating agent and extraction time were optimized. The effect of the interfering ions on the analytes recovery was also investigated. The calibration graph was linear in the range of 0.001–0.5 µg/mL with detection limit of 0.0005 µg/mL. The proposed method was applied to the determination of cadmium in saffron samples with satisfactory analytical results.

Keywords: Dispersive Liquid–Liquid Microextraction; Solidification of Floating Organic Drop; Cadmium, Saffron, UV-Vis Spectrophotometry

1. INTRODUCTION

Heavy metal contamination presents a significant threat to the ecosystem due to severe toxicological effects on living organisms. Cadmium is one of the most hazardous elements to human health, because it results in adverse effects on metabolic processes. Cadmium has been pointed as the sixth most poisonous substance jeopardizing human health with biological half- life in the range of 10- 30 years [1]. Food can be contaminated by environmental Cd that is present in air (by deposition), soil (by transfer) or water (by deposition and transfer), or during processing and cooking. Saffron is the dried stigmas of Crocus sativus L and the most expensive spice used in industry, with different uses as drug, textile dye and culinary adjunct. It is mainly valued as a food additive for tasting, flavoring and coloring

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Table 1. Selection of the type of disperser solvents

	ethanol	acetone	acetonitrile
1- undecanol	0.36±0.05	0.25±0.06	0.21±0.05

Table 2. Effect of diverse ions on recovery of cadmium

M^n	Interference/cadmium ratio	Recovery/%
K^+	100	100.3±2.1
Ca^{2+}	100	109.1±3.4
Mg^{2+}	100	95.0±3.2
Cu^{2+}	100	102.2±4.1
Fe^{2+}	100	103.3±3.1
Zn^{2+}	100	101.8±4.5
Co^{2+}	100	101.6±3.6
Pb^{2+}	100	109.0±5.1
Sn^{2+}	100	105.6±3.3

Table 3. Determination of cadmium in saffron samples

Saffron samples	Spiked/(μg/mL)	Found/(μg/mL)	RSD/%	Recovery/%
saffron of torbate heydariyeh	1×10^{-1}	$1.02\times10^{-1}\pm0.04$	2	103
saffron of ghaen	1×10^{-1}	$1.03\times10^{-1}\pm0.05$	3	102
saffron of bakharz	1×10^{-1}	$1.05\times10^{-1}\pm0.07$	5	105

[2, 3]. But recently some saffron samples have been introduced in the market with a higher presence of

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contaminants and pollutants [4]. Several studies have been carried out in different countries on spices and medical plants, but only a few studies were found on the analysis of contaminants residues in saffron samples [5, 6]. In recent years, the development of fast, precise, accurate and sensitive methodologies has become an important issue. However, despite the advances in the development of highly efficient analytical instrumentation for the endpoint determination of analytes, sample pre-treatment is usually necessary in order to extract, isolate and concentrate the analytes of interest from complex matrices [7].

Liquid–liquid extraction (LLE) is one of the most widely used preconcentration and matrix isolation techniques for determination of metal ions. Although it offers high reproducibility and high sample capacity, it is considered to be a time and labor consuming procedure. It also has the tendency for emulsion formation, and uses large amount of hazardous and costly organic solvents. To overcome these problems, microextraction methods such as drop- in- drop system [8], single-drop microextraction (SDME) [9,10], homogenous liquid–liquid microextraction (HLLME) [11,12], solid phase microextraction (SPME) [13,14], and dispersive liquid–liquid microextraction (DLLME) [15–17] have been developed. The advantages of these techniques are; the negligible volume of solvents and their ability to detect analytes at very low concentration. Recently, a liquid–liquid microextraction method based on solidification of floating organic drop (DLLME-SFO) was successfully used for determination of polycyclic aromatic hydrocarbons [18]. The DLLME-SFO is a modified solvent extraction method, and has the advantages of simplicity, short extraction time, minimum organic solvent consumption, and achievement of high enrichment factor [19].

In many applications, other techniques could be employed but none rival UV–Vis spectrophotometry for its availability, simplicity, versatility, speed, accuracy, precision, and cost-effectiveness. This technique is routinely used in analytical chemistry for quantitative determination of different analytes such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Ultraviolet and visible spectrophotometer has become a popular analytical instrument in the modern day laboratories. However, the low concentrations of many analytes in samples make it difficult to directly measure them by UV–Vis spectrophotometry. The low concentrations of many analytes in the complex real samples make it difficult to directly measure by spectrophotometry, even by these new instruments. Moreover, the wide bandwidth in the UV–Vis spectrum of the species makes the technique unselective. Therefore, a sample preparation step is necessary before spectroscopic measurements to improve the selectivity and sensitivity [20].

The objective of this study is to consider the possibility of implementation of DLLME-SFO in combination with UV–Vis spectrophotometry in trace cadmium analysis. The applicability of the approach was demonstrated for the determination of cadmium in saffron samples. Factors affecting the extraction efficiency, such as solution pH, type and volume of extraction solvent, the amount of chelating agent and extraction time were optimized.

2. MATERIALS AND METHODS

2.1. Apparatus

Absorbance measurements were carried out on a UV–Vis spectrophotometer model JENWAY 6300 using quartz microcell. A digital pH meter Metrohm, Model NANO Technic was used for all pH measurements. A Denley bench centrifuge model BS400 (Denley Instruments Ltd., Billingshurst, UK) was used to accelerate the phase separation. A Hamilton syringe was used for rapid injection.

2.2. Reagents

Saffron samples were obtained from different area of Khorasan state of Iran contain 3 regions

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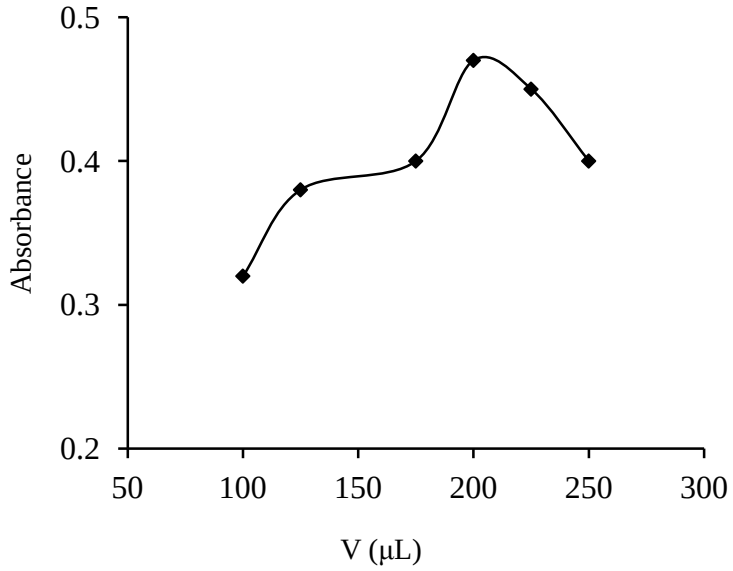

Fig. 1. Effect of volume of the extraction solvent (1-undecanol) on the absorbance of cadmium by DLLME-SFO. Extraction conditions: concentration of cadmium, 0.5 µg⁄mL; aqueous volume, 10 mL; dispersive solvent 500 µL ethanol, dithizone as complexing agent, 500 µg/L; pH, 5; λ_{max}, 420 nm; dilution solvent, acetone.

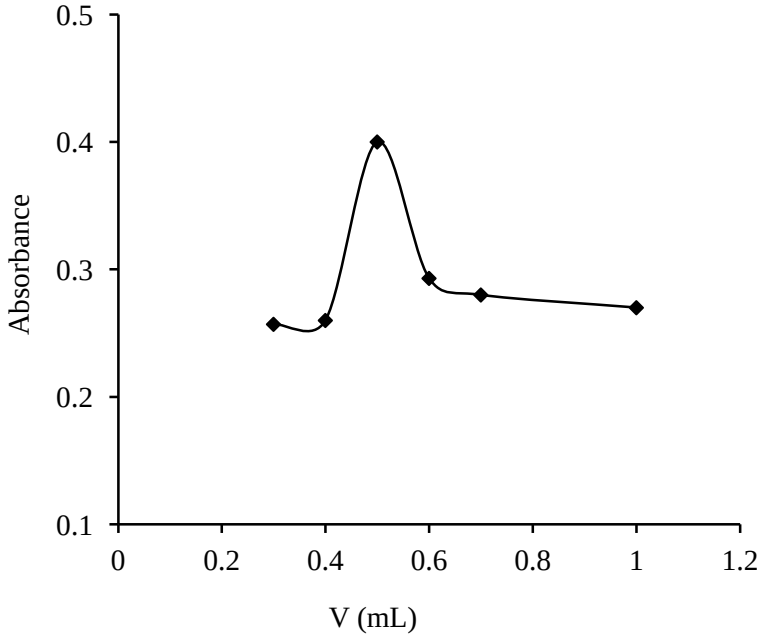

Fig. 2. Effect of disperser solvent volume (ethanol) on the absorbance of cadmium by DLLME-SFO. Extraction conditions: concentration of cadmium, 0.5 µg/mL; aqueous volume, 10 mL; extraction solvent 200 µL 1-undecanol containing 500 µg/L dithizone as complexing agent; pH, 5; λ_{max}, 420 nm; dilution solvent, acetone.

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(Ttorbatheydariyeh-Ghaen–Bakharz) in the year 2013. All of the chemicals used were of analytical reagent grade. All solution was diluted with de-ionized water. A stock solution of cadmium at a concentration of 1000.0 μg/mL was prepared by dissolving 1.000 g of cadmium in 1.0 L de-ionized water. The working reference solutions were obtained daily by stepwise dilution from stock solution with de-ionized water. The solutions of alkali metal salts and various metal salts were used to study the interference of anions and cations, respectively. The chelating agent, dithizone (Merck) and the rest of the used chemicals were 1-undecanol (Merck) as the extraction solvent. Acetonitrile, acetone and ethanol as dispersive solvents were purchased from Merck. Sodium chloride (Merck) was of the highest purity available.

2.3. Sample preparation

Saffron samples were obtained from different area of Khorasan state of Iran contain 3 regions (Ttorbatheydariyeh-Ghaen–Bakharz) in the year 2013. Saffron samples were milled to make a fine powder before spectrophotometry. 125 mg of saffron was dissolve in 200 mL water slowly using magnetic shaker for 1 hour and the final volume made to 250 mL. Sample was ten times diluted prior to analysis.

2.4. DLLME-SFO procedure

10 mL of cadmium solution, the pH was adjusted to 9, was placed into 10 mL test tube, and a mixture of 200 μL 1-undecanol containing dithizone as complexing agent (1 mg/L) (extraction solvent) and 500 μL ethanol (dispersive solvent) was rapidly injected into the sample solution. In this stage, a cloudy solution containing many dispersed fine droplets of dithizone in 1-undecanol was formed, the cadmium ions reacted with dithizone and were extracted into 1-undecanol in a few seconds. Then, the mixture was centrifuged 6 min at 4000 rpm, the organic solvent droplet was floated on the surface of the aqueous solution due to its low density. The vial was then transferred into an ice bath and the organic solvent was solidified after 10 min and the solidified solvent was transferred into a conical vial where it melted immediately. After this process, the extract was collected and was dilute in 250.0 μL by acetone and was transported to a UV–Vis spectrophotometer to measure its absorbance at λ_{max} (420 nm) for the determination of cadmium. In the experiment, some conventional solvents including methanol, ethanol and acetone were investigated for the determination of the best dilution solvent. The results indicated the acetone was the best dilution solvent for the determination of Cd. During the determination, it was found that acetone has an obvious sensitization to the spectrophotometric determination of Cd, which could contribute to the high sensitivity for the determination of Cd.

3. RESULTS AND DISCUSSION

In this study, a DLLME-SFO technique combined with UV–Vis spectrophotometry was developed for the determination of cadmium in saffron samples. In order to obtain a high recovery, the effect of different parameters such as kind of extraction, dispersive solvents, volumes of solvent, extraction time, and salt addition were examined and the optimum conditions were selected.

3.1. Study on the absorption spectra of complex

In order to carry out the quantification analysis, the maximum wavelength of absorption should be found out. For the determination of cadmium, absorbance of the complex of Cd- dithizone was determined in the range from 350 nm to 700 nm. The results showed the maximum absorption wavelength was 420 nm for Cd- dithizone complex. During the determination, the blank absorbance of

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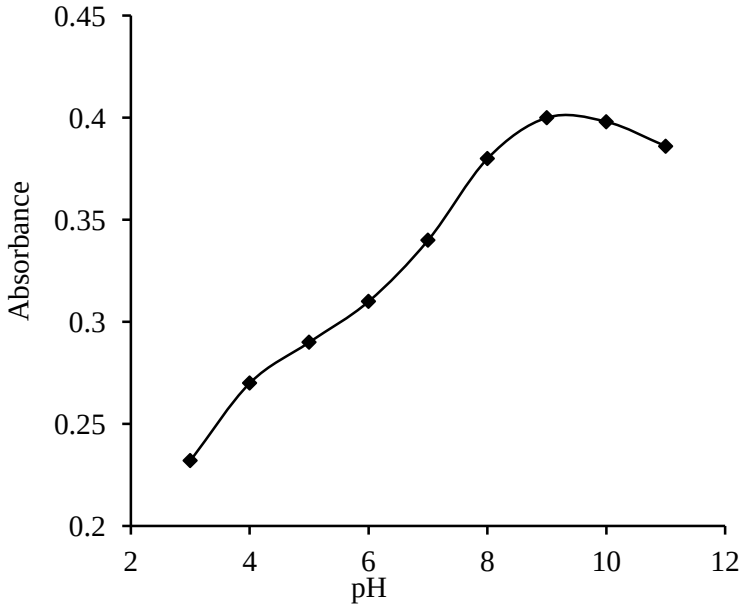

Fig. 3. Effect of sample pH on the absorbance of Cd by DLLME-SFO. Extraction conditions: concentration of cadmium, 0.5 µg/mL; aqueous volume, 10 mL; extraction solvent, 200 µL of 1-undecanol containing 500 µg/L dithizone as complexing agent; dispersive solvent 500 µL ethanol; λ_{max}, 420 nm; dilution solvent, acetone.

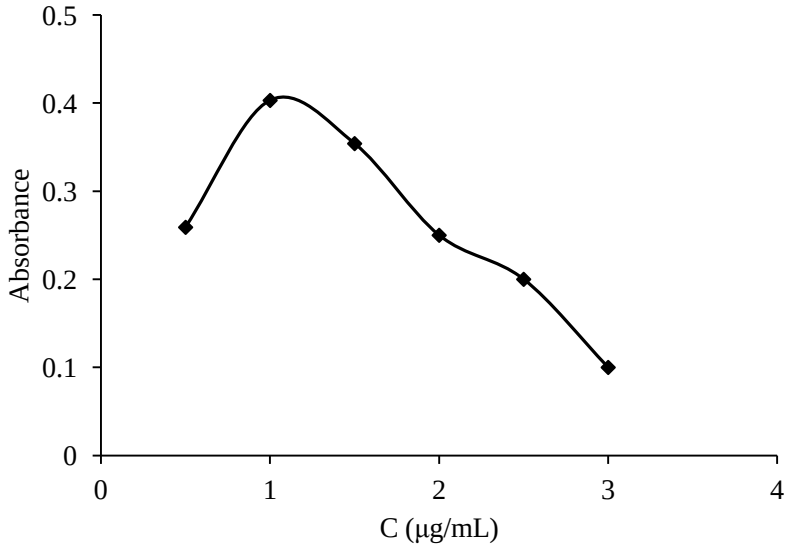

Fig. 4. Effect of dithizone concentration on the absorbance of Cd by DLLME-SFO. Extraction conditions: concentration of cadmium, 0.5 µg/mL; aqueous volume, 10 mL; extraction solvent, 200 µL of 1-undecanol containing dithizone as complexing agent; dispersive solvent 500 µL ethanol; pH, 9; λ_{max}, 420 nm; dilution solvent, acetone.

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reagents was corrected. For the extraction of Cd, the pH value was in the range of neutral or weak basicity, which was different from some conventional works in alkaline solution.

3.2. Effect of DLLME-SFO parameters

3.2.1. Selection of extraction solvent and disperser solvent

In order to obtain high recovery, the selection of extraction solvent has an important role in the DLLME-SFO system. Extraction solvent should have special characteristics; it should have lower density rather than water, high efficiency in the extraction of the interested compounds and low solubility in water and it should have a melting point near room temperature (in the range of 10–30 ◦C) was floated on the surface of aqueous solution. [21]. According to these considerations, 1-undecanol was chosen as the extracting solvent.

Miscibility of a disperser with organic phase (extraction solvent) and aqueous phase (sample solution) is the most important point for the selection of a disperser. Therefore, acetone, acetonitrle and ethanol, which have this ability, are selected for this purpose. For obtaining maximum extraction recovery, all combinations using 1-undecanol as extractant with acetone, acetonitrile, ethanol as dispersive solvent, were examined. According to the results shown in Table 1, ethanol as the disperser solvent provided maximum absorbance. Therefore, we selected ethanol /1-undecanol as a suitable set for subsequent experiments.

3.2.2. Effect of volume of extractant

To examine the effect of the extraction solvent volume, solutions containing different volumes of 1-undecanol were subjected to the same DLLME-SFO procedures. The experimental conditions were fixed and included the use of 500 μL ethanol and 1 mg L^{-1} of dithizone and different volume of 1-undecanol (100.0, 125.0, 150.0, 175.0, 200.0, 225.0 and 250.0 μL). According to the Fig.1, by increasing volume of 1-undecanol, the absorbance increased till 200 μL. With the increase of extractant volume, the concentration of cadmium in the sediment phase was decreased due to the dilution effect. Therefore, 200 μL was the reasonable volume for the experiment. After extraction procedure, the enriched samples were diluted to 250 μL by acetone for the subsequent determination.

3.2.3. Effect of disperser solvent volume

To study the effect of disperser volume on the absorbance of cadmium, all experimental conditions were fixed except volume of ethanol (0.3 to 1 mL). The results are shown in Fig. 2. According to the obtained results, the extraction efficiencies increased till 0.5 mL and then decreased by increasing the volume of ethanol for cadmium. The cloudy state is not formed well, thereby the extraction is disturbed. On the other hand, in the high volumes of ethanol, solubility of the cadmium in water increases, therefore, the extraction efficiencies decrease because of distribution coefficients decreasing. A 0.5 mL volume was chosen as an optimum volume for disperser.

3.2.4. Effect of sample pH

Sample pH has a significant effect on the formation of Cd- dithizone complex and its subsequent extraction into organic phase. So the effect of sample pH on the extraction of cadmium (Cd) was studied by varying the pH within the range of 3–11. Fig. 3 shows the influence of the sample pH on the analytical signal intensity. As it is demonstrated, the highest signal intensity of cadmium obtained at pH 9.

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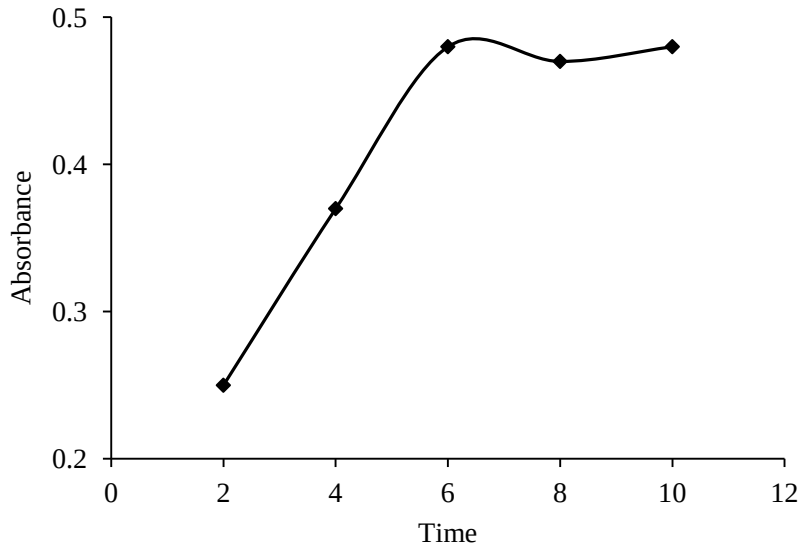

Fig. 5. Effect of the extraction time on the absorbance of Cd by DLLME-SFO. Extraction conditions: concentration of cadmium, 0.5 µg/mL; aqueous volume, 10 mL; extraction solvent, 200 µL of 1-undecanol containing 1000 µg/L dithizone as complexing agent; dispersive solvent 500 µL ethanol; pH, 9; λ_{max}, 420 nm; dilution solvent, acetone.

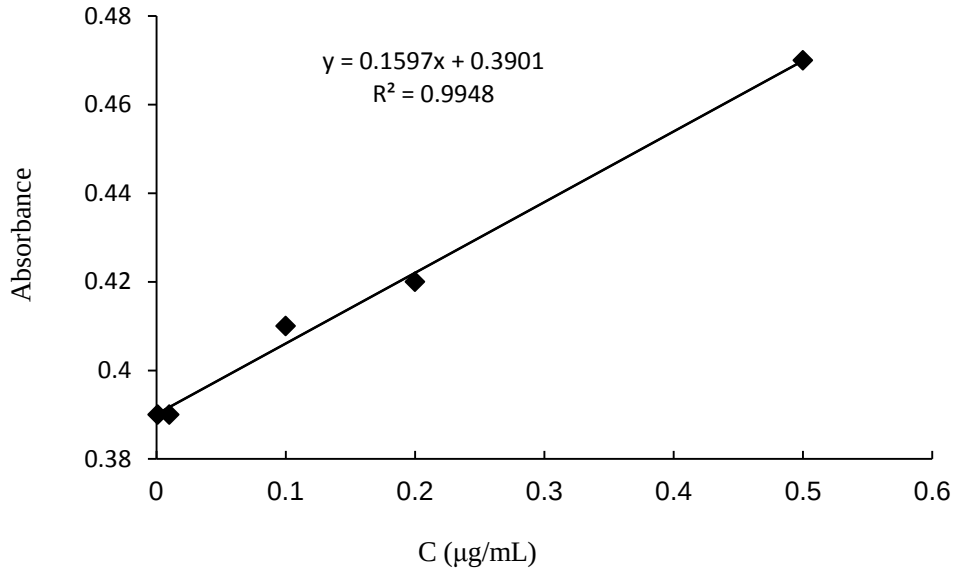

Fig. 6. Calibration curve of Cd by DLLME-SFO. Extraction conditions: concentration of cadmium, 0.5 µg/mL; aqueous volume, 10 mL; extraction solvent, 200 µL of 1-undecanol containing 1000 µg/L dithizone as complexing agent; dispersive solvent 500 µL ethanol; pH, 9; λ_{max}, 420 nm; dilution solvent, acetone.

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Therefore, pH 9 was selected for further studies. Moreover, to adjust pH 9, sodium hydroxide was used. At the higher and lower pH values cadmium absorbance decreases.

3.2.5. Effect of dithizone concentration

The efficiency of cadmium extraction was dependent on dithizone concentration as shown in Fig. 4. The recovery was increased by increasing the dithizone concentration up to 1 μg/mL, quantitative extraction results within the dithizone concentration in the range of 0.5 to 3 μg/mL. A further excess of dithizone would cause decrease in extraction probably due to saturation of extracting solvent, which results in its extraction into aqueous phase [21]. Therefore, a dithizone concentration of 1 μg/mL was chosen for further study.

3.2.6. Salt addition

Addition of salt often improves extraction of analytes in liquid- liquid extraction due to the salting- out effect. To study the effect of salt addition on the analytical signal of the cadmium, the concentration of NaCl was changed in the range of 0–10% (w/v). The results showed that extraction efficiency of the analyte was independent of NaCl concentration. Thus, the strategy of no salt addition was performed.

3.2.7. Study of the extraction time

In DLLME-SFO, extraction time is defined as the interval time between the injection of the solution of disperser and extraction solvents before starting to centrifuge. According to previous studies [22–27], time has no influence on extraction efficiency in DLLME and the result is similar for DLLME-SFO. After the formation of a cloudy solution, the surface area between the extraction solvent and the aqueous phase is very large. Thereby, transition of the complex from the aqueous phase to the extraction solvent is fast. Subsequently, equilibrium state is achieved quickly after injection of the extraction solvent into the sample solution. Thus, the most important advantage of DLLME-SFO is time independence of the method. In this method, time-consuming steps are centrifuging of the sample solution in the extraction procedure. The effect of extraction time was examined in the range of 2–10 min while the other experimental conditions remained constant. The obtained results are shown in Fig 5. As a result, 6 min was selected for further studies.

3.3. Interference studies

Because dithizone is versatile chelating agent, interferences may occur due to the competition of other metal ions for dithizone and their subsequent co- extraction with Cd. To evaluate the selectivity of the proposed method, the effect of typical potential interfering ions was investigated. The effects of some alkali and alkaline earth metals and some transition metals were studied under the optimized conditions. In this experiment, solutions containing 0.5 μg/mL of cadmium and 50 μg/mL interfering ions were treated according to the recommended procedure. The results of this investigation are summarized in Table 2, indicating that the cadmium recoveries were almost quantitative in the presence of the excessive amount of the possible interfering cations. This shows that the proposed method is suitable for the determination of cadmium in real samples such as saffron.

3.4. Quantitative aspects

A calibration curve was constructed by preconcentrating 10 mL of the sample standard solution

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(0.001 –0.5 µg/mL) (Fig. 6). Under the optimum experimental conditions, the equation of calibration graph was A = 0.1597C + 0.3901 (where A is the absorbance and C is the concentration of cadmium (µg/mL) in the aqueous phase) with the correlation coefficient of 0.9948. The limit of detection (LOD) calculated based on 3 Sb/m (where, Sb and m are the standard deviation of the blank and slop ratio of the calibration graph respectively) was 0.0005 µg/mL.

3.5. Real sample analysis

The procedure was applied to the determination of cadmium in Saffron samples that obtained from different area of Khorasan state of Iran contain 3 regions (Ttorbatheydariyeh-Ghaen-Bakharz) in the year 2013. All the samples were spiked with cadmium standard at 0.1 µg/mL, and were extracted subsequently by using the DLLME-SFO technique and finally the extracts were analyzed by UV–Vis method. Three replicate experiments were carried out for each concentration level. The results are shown in Table.3. These results demonstrate that the saffron matrices have a little effect on the DLLME-SFO procedure. As shown in Table 3, the relative recoveries obtained clearly demonstrated that the accuracy of the developed method for the analysis of cadmium in real saffron samples was quite satisfactory. The precision for the determination of the saffron samples is also satisfactory, with the RSD value below 6%.

4. CONCLUSION

It has been demonstrated that DLLME-SFO combined with UV-Vis Spectrophotometry can be used as a powerful tool for the preconcentration and determination of metal ions from aqueous samples. It has also been shown that the cadmium-dithizone can be extracted into 1-undecanol. Furthermore, the proposed DLLME-SFO method, permits effective separation and preconcentration of cadmium and final determination by UV-Vis Spectrophotometry in several saffron samples. The main benefits of the DLLME-SFO method were the minimum use of toxic organic solvent consumption, rejection of matrix constituent, low cost and enhancement of sensitivity. The spectrophotometric instrumentations own merits of simplicity, cheapness, portability and so on. Through this hyphenation investigated in this work, the conventional spectrophotometer can accomplish trace metal detection thus to expand its applications. The LOD of Cd was better than those obtained by FAAS (0.3 µg/L) [28] or (1.4 ng/ml) [29].

REFERENCES AND NOTES

[1] Feriberg, L.; Nordbery, G. F.; Wouk, VB. Hand book on toxicology of metal. *Amsterdam: Elsevier* **1986**, 2, 130- 184, 158- 210, 298- 354.
[2] Madan, C. L.; Kapur, B. M.; Gupta, U.S. Saffron. *Econ Bot* **1996**, *20*, 377–385.
[3] Sampathu, S. R.; Shivashankar, S.; Lewis Y. S. Saffron (Crocus Sativus Linn.) Cultivation, processing, chemistry and standardization. *CRC Crit Rev Food Sci Nutr* **1984**, *20*, 123–157.
[4] *USEPA Method 8310 polynuclear aromatic hydrocarbons*. In USEPA (Ed.), EPA test methods SW-846 on-line, **1986.**
[5] Maggi, L.; Carmona, M.; Prisciladel Campo, C.; Zalacain, A.; Hurtado de Mendoza, J.; Mochol, F.A.; Alonso, G.L. Multi-residue contaminants and pollutants analysis in saffron spice by stir bar sorptive extraction and gas chromatography–ion trap tandem mass spectrometry. *J. Chromatogr A.* **2008**, *120*9, 55–60.
[6] Abou-Arab, A. A. K.; Abou-Donia, M. A.; Pesticide residues in some Egyptian spices and medicinal plants as affected by processing, *Food Chem.* **2001**, *72*, 439–445.
[7] Sarafraz-Yazdi, A.; Amiri, A. Liquid-phase microextraction. *Trends Anal Chem* **2010**, *29*, 1–14.

ISSN 2291-6458 (Print), ISSN 2291-6466 (Online)
Year 2014 | Volume 2 | Issue 1| Page 12-23

[8] Liu, H. G.; Dasgupta, P. K. Analytical chemistry in a droop solvent extraction in a microdrop, *Anal. Chem.* **1996,** *68*, 1817-1821.

[9] Jeannot, M. A.; Cantwell, F. F. Solvent Microextraction into a Single Drop, *Anal. Chem.* **1996**, *68*, 2236–2240.

[10] Xia, L.; Hu, B.; Jiang, Z.; Wu, Y.; Liang, Y. Single-drop microextraction combined with low-temperature electrothermal vaporization ICPMS for the determination of trace Be, Co, Pd, and Cd in biological samples, *Anal. Chem.* **2004**, *76*, 2910–2915.

[11] Ghiasvand, A. R.; Shadabi, S.; Mohagheghzadeh, E.; Hashemi, P. Homogeneous liquid–liquid extraction method for the selective separation and preconcentration of ultra trace molybdenum, *Talanta* **2005**, *66*, 912–916.

[12] Igarashi, S.; Ide, N.; Takagai, Y. High-performance liquid chromatographic- spectrophotometric determination of copper(II) and palladium(II) with 5,10,15,20-tetrakis (4N-pyridyl) porphine following homogeneous liquid-liquid extraction in the water-acetic acid-chloroform ternary solvent system. *Anal. Chim. Acta* **2000**, *424*, 263–269.

[13] Arthur, C. L.; Pawliszyn, J. Solid Phase Microextraction with Thermal Desorption Using Fused Silica Optical Fibers, Anal. Chem. **1990**, *62*, 2145–2148.

[14] Kumazawa, T.; Lee, X. P.; Sato, K.; Suzuki, O. Solid-phase microextraction and liquid chromatography/mass spectrometry in drug analysis, *Anal. Chim. Acta*. **2003**, *492*, 49–67.

[15] Rezaee, M.; Assadi, Y.; Milani-Hosseini, M. R.; Aghaee, E.; Ahmadi, F.; Berijani, S. Determination of organic compounds in water using dispersive liquid-liquid microextraction, *J. Chromatogr. A.* **2005**, *1116*, 1–9.

[16] Berijani, S.; Assadi, Y.; Anbia, M.; Milani-Hosseini, M. R.; Aghaee, E. Dispersive liquid-liquid microextraction combined with gas chromatography-flame photometric detection. Very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water, *J. Chromatogr. A.* **2006**, *1123*, 1–9.

[17] Zeini-Jahromi, E.; Bidari, A.; Assadi, Y.; Milani Hosseini, M. R.; Jamali, M. R. Dispersive liquid-liquid microextraction combined with graphite furnace atomic absorption spectrometry. Ultra trace determination of cadmium in water samples, *Anal. Chim. Acta.* **2007**, *585*, 305–311.

[18] Khalili-Zanjani, M. R.; Yamini, Y.; Shariati, S.; Jonsson, J. A. A new liquid-phase microextraction method based on solidification of floating organic drop, *Anal. Chim. Acta* **2007**, *585*, 286–293.

[19] Lopez-Garcia, I.; Rivas, R. E.; Hernadez-cordoba, M. Liquid-phase microextraction with solidification of the organic floating drop for the preconcentration and determination of mercury traces by electrothermal atomic absorption spectrometry, *Anal. Bioanal. Chem.* **2010**, *396*, 3097–3102.

[20] Shokoufi, N.; Shemirani, F.; Memarzadeh, F. Fiber optic-linear array detection spectrophotometry in combination with cloud point extraction for simultaneous preconcentration and determination of cobalt and nickel, Anal. Chim. Acta **2007**, *601*, 204-211.

[21] Dadfarnia, S.; Salmanzadeh, A. M.; Haji Shabani, A. M, A novel separation/preconcentration system based on solidification of floating organic drop microextraction for determination of lead by graphite furnace atomic absorption spectrometry, *Anal. Chim. Acta* **2008**, *623*, 163–167.

[22] Rezaee, M.; Assadi, Y.; Milani Hosseini, M. R.; Aghaee, E.; Ahmadi, F.; Berijani, S. Determination of organic compounds in water using dispersive liquid–liquid microextraction, *J. Chromatogr. A.* **2006**, *1116*, 1–9.

[23] Naseri, M. T.; Hemmatkhah, P.; Milani Hosseini, M. R.; Assadi, Y, Combination of dispersive liquid–liquid microextraction with flame atomic absorption spectrometry using microsample introduction for determination of lead in water samples, *Anal. Chim. Acta* **2008**, *610*, 135–141.

[24] Shamsipur, M.; Ramezani, M. Selective determination of ultra trace amounts of gold by graphite furnace atomic absorption spectrometry after dispersive liquid–liquid microextraction, *Talanta* **2008**, *75*, 294–300.

ISSN 2291-6458 (Print), ISSN 2291-6466 (Online)
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[25] Garcia-Lopez, M.; Rodriguez, I.; Cela, R. Development of a dispersive liquid–liquid microextraction method for organophosphorus flame retardants and plasticizers determination in water samples, *J. Chromatogr. A.* **2007**, *116*6, 9–15.

[26] Farina, L.; Boido, E.; Carrau, F.; Dellacassa, E. Determination of volatile phenols in red wines by dispersive liquid–liquid microextraction and gas chromatography–mass spectrometry detection, *J. Chromatogr. A.* **2007**, *1157*, 46–50.

[27] Rezaee, M.; Yamini, Y.; Shariati, S.; Esrafili, A.; Shamsipur, M. Dispersive liquid–liquid microextraction combined with high-performance liquid chromatography-UV detection as a very simple, rapid and sensitive method for the determination of bisphenol A in water samples, *J. Chromatogr. A* **2009**, *121*6, 1511–1514.

[28] Fang. Z.; Guo, T.; Welz. B. Determination of cadmium, lead and copper in water samples by flame atomic-absorption spectrometry with preconcentration by flow-injection on-line sorbent extraction, *Talanta*, **1991**, *38*, 613–619.

[29] Ghaedi. M.; Shokrollahi. A.; Niknam. K.; Niknam. E.; Najibi. A.; Soylak M. Cloud point extraction and flame atomic absorption spectrometric determination of cadmium(II), lead(II), palladium(II) and silver(I) in environmental samples, *J. Hazardous Materials*, **2009**, *168*, 1022–1027.

The authors declare no conflict of interest

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