

Solidified floating organic drop micro-extraction (SFODME) for simultaneous separation/pre-concentration and determination of cadmium by atomic absorption spectroscopy

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In the present study, a method using solidified floating organic drop micro-extraction (SFODME) using atomic absorption spectroscopy was developed for determination of trace amounts of cadmium in various environmental water matrices including well water, qanat influent and effluent. Ammonium pyrrolidine-N-dithiocarbamate (APDC) acted as chelating agent. The main parameters affecting the performance of SFODME, such as pH, concentration of APDC, stirring rate, extraction time, extraction temperature, volume of the solvent (1-Dodecanol), dilution solvent (ethanol), and concentration of salt were optimized. Under the optimum experimental conditions, enhancement factors of 63 and 300 were obtained for 5 and 25 ml of sample solution, respectively. The calibration graph was found to be linear in a range of 2.0 – 400 μgL^{-1} . The limit of detection (3S) and the limit of quantification (10S) were 0.57 and 1.91 μgL^{-1} , respectively. The relative standard deviation (RSD) for 8 replicate measurements were found to be 3.04 %, 1.8%, 2.33% for 10 μgL^{-1} , 20 μgL^{-1} , and 300 μgL^{-1} of cadmium, respectively. The developed procedure was successfully applied to standard and several water samples (well, qanat and waste water) to determine trace amounts of cadmium. The method accuracy was assessed either by determination of cadmium in a certified reference material of water or by addition-recovery experiments, in which satisfactory results were obtained.

Keywords: solidified floating organic drop micro extraction; pre-concentration; cadmium ion determination; pyrrolidine-N-dithiocarbamate

INTRODUCTION

Cadmium is one of the most hazardous pollutants found in the environment. Due to its increased utilization in industries, cadmium concentration has increased which is of great concern to human health. This heavy metal is easily absorbed; it remains in tissues for a relatively long time and thus, poses serious health risks to both humans and animals. The adverse physiological effects due to high cadmium exposure commonly include depressed growth rate, anemia hypertension, damage to renal tubules and poor mineralization of bones [1]. Therefore, development of sensitive and selective methods for cadmium speciation is of great importance, and some solid-phase separation/pre-concentration systems coupled with spectro-analytical techniques (FAAS, EAAS, and ICP-MS) have been employed to eliminate matrix interferences and enhance detectability. The FAAS is one of the most commonly applied techniques for determination of trace amount of heavy metals. This method is a relatively inexpensive one, which provides adequate sensitivity and simple sample preparation as well.

Determination and analysis of untreated samples falls into two main categories, direct and indirect methods. Indirect methods employ a preliminary separation or concentration of the analyte. Typically, field samples contain high concentrations of matrix ions, which produce a high background level. An alternative method applied to improve the efficiency of these kinds of techniques is the use of a suitable ligand, which can be added to the aquatic sample to complex metal ions before their accumulation on a hydrophobic adsorbent [2]. To solve this problem ammonium pyrrolidine dithiocarbamate (APDC) is widely used to determine the metal ions, such as Cd^{+2} , Pb^{+2} , Ni^{+2} , Co^{+2} , etc, that could form slightly soluble complexes in an aqueous solution [3]. Usually, metal APDC complexes are measured by flame atomic absorption spectrometry [4], after extraction with nonpolar organic solvent [5]. Thus, development of pre-concentration methods using APDC can be very desirable for the chemical speciation using minimal sample treatment.

In other studies, pre-concentration techniques such as liquid-liquid extraction (LLE), solid-phase extraction (SPE) and cloud point extraction (CPE) have been developed and applied [6-8].

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However, there are a few drawbacks that should be considered for these methods. They are time-consuming and require large volumes of organic solvents which are not only toxic to human health and the environment, but also are expensive. Solvent – free sample preparation methods or those employing less organic solvent are becoming increasingly important and have induced a major advance in analytical methodology. Therefore, liquid phase micro-extraction (LPME) has emerged as a new alternative for sample preparation [9]. This method has been developed in different modes, including single drop micro extraction (SDME) [9,10], direct single drop micro extraction (Direct-SDME) [11], head space single drop micro-extraction (HS-SDME) [12], liquid-liquid-liquid micro-extraction (LLL-ME) [13], continuous-flow micro-extraction (CFME) [15], hollow fiber liquid phase micro-extraction (HF-LPME) [16], dispersive liquid/liquid micro-extraction (DLLME) [15], and solidified floating organic drop (SFODME) [17-19]. The present research focuses on the SFODME. In this technique, a micro drop of the organic solvent with a density lower than water and a melting point close to room temperature (10-30°C) is floated on the surface of an aqueous sample while being agitated by a stirring bar in the bulk of the solution. After completion of the extraction, the sample is transferred into an ice bath, to freeze the organic phase. The solidified micro drop is transferred into a new conical vial, where it melts immediately. Finally, it dilutes by sufficient ethanol and injects to FAAS to determine the species in the extract. In this method, no specific holders are required for supporting the micro drop. Moreover, operation simplicity, low cost, fast operation, high enrichment factor, and low consumption of the extraction solvent are the advantages of the proposed method.

The aim of this study is to investigate the feasibility of the novel LPME technique based on solid organic drop combined with FAAS, in order to determine trace amounts of cadmium in environmental samples. The accuracy of the proposed method was assessed either by determination of cadmium in a certified reference material of water or by addition-recovery experiments.

EXPERIMENTAL

Instruments

A Varian AA-240 Flame atomic absorption spectrometer (Varian Australia Pty Ltd) coupled with an acetylene-air burner and a hollow cathode

lamp (current 4mA, 228.8nm wave length, and slit width 0.5 nm) was applied in the study.

All pH measurements were carried out using a digital pH meter equipped with a combined glass-calomel electrode (WTW-GmbH). The solution was stirred with a magnetic heater-stirrer (IKAMAG – RET, Germany). A simple water bath placed on the heater-stirrer was used for controlling the temperature of the sample solution.

Reagents and chemical

The stock cadmium standard solution, $\beta_{(Cd)} = 1000 \text{mgL}^{-1} (\text{CdCl}_2 \text{ in } \text{H}_2\text{O})$ was prepared by dissolving standard titrisol (Merck, KGaA, Darmstadt, Germany) with distilled water. The working standard solutions were prepared daily by serial dilutions of the stock solution with distilled water. The chelating agent 0.02gL^{-1} APDC solution was prepared daily by dissolving the appropriate amount of APDC (Merck Company, KGaA Darmstadt-Germany for syntheses) in distilled water. The extraction solvent, 1-Dodecanol and dilution solvent, ethanol were purchased from (Merck Company, KGaA Darmstadt-Germany for syntheses) Nitric acid (0.1molL^{-1}) and sodium hydroxide (0.1molL^{-1}) were used to adjust the pH levels 1-11.

Di - ammonium hydrogen citrate buffers (113gL^{-1}) was prepared by adding an appropriate amount of di-ammonium hydrogen citrate to ammoniac (25% w/v) to produce a pH range of 9 to 10. Coexisting ions (1000mgL^{-1}) were prepared by serial dilution of a Titrisol-Merk solution.

RESULT AND DISCUSSION

The suggested method is based on equilibrium between the analyte concentration in the sample and that in the extracting solvent. The thermodynamics and kinetic equations of LLE are demonstrated in previous studies [20]. In this method APDC forms a stable amphoteric chelate with cadmium if the pH is adjusted. It was observed that cadmium from the aqueous phase could be extracted into a small volume of 1-dodecanol. Furthermore, its stability, low vapor pressure and low water solubility at extraction conditions made 1-dodecanol the best extraction solvent to be used in the present experiment.

To obtain a suitable enrichment factor, the influence of different parameters that affect the chelate formation and the extraction conditions such as amount of APDC, sample stirring rate, extraction time, extraction temperature, volume of solvent, were optimized.

Effect of pH

The separation and pre-concentration of metal ions by SFODME involve prior formation of a complex with sufficient amount of hydrophobicity that allows it to be extracted into small volumes of organic solvent. The pH plays a unique role in the process of formation and extraction of chalets. The pH of solution (5 ml of solution involves 200ng ml^{-1} of cadmium) was adjusted between 1.0 – 11.0, using nitric acid and sodium hydroxide. The stirred solution was kept at 30°C for 20 min (300rpm) using $140\mu\text{L}$ of the organic solvent.

The results depicted in fig.1 shows the influence of pH on the analytical signal (absorbance). According to the figure, at the pH values lower than 10, as the pH increased absorbance rose from 1.0 to 9.0. At pH levels higher than 10, the absorbance showed a declining trend. The decrease in extraction efficiency at lower or higher pH levels depends on distribution of APDC between water and organic solvent at the specific pH. The highest extraction efficiency of cadmium using 1-dodecanol was obtained at $\text{pH}=9.0$. Thus $\text{pH}=9$ was selected for subsequent work and the real sample analysis.

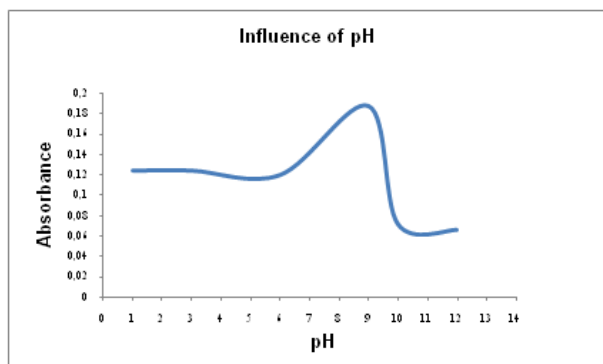


Fig 1. The influence of pH on the extraction efficiency

Effect of amount of APDC

The formation of hydrophobic ions complex strongly depends on concentration and amount of added chelate which also has influence on extraction efficiency. It is known that Cd^{+2} ions are stoichiometrically combined with ammonium pyrrolidine dithiocarbamate (APDC) to form 1:2 complexes ($\text{Cd}(\text{PDC})_2$). At constant pH levels in an aqueous phase, up to the solubility limit of the chelate in the organic phase, the value of the distribution ratio and consequently the extraction efficiency will increase as the concentration of the chelate increases [21]. Therefore the influence of concentration of APDC was studied by varying the amount of APDC 0.02 gL^{-1} between 0.2 to 1 ml. As

shown fig.2, the absorbance signal was increased by addition of 0.6ml of APDC and maximum absorbance was adjusted by addition of 0.8 ml of APDC 0.02gL^{-1} . 0.8ml was selected as the optimum amount for further studies.

Stirring rate

The stirring rate is an important parameter that enhances the kinetics of chelate formation and its extraction. According to the film theory of convective-diffusive mass transfer in the LPME system, faster sample agitation causes lower thickness of diffusion film in the aqueous phase. The optimum stirring rate was evaluated at different stirring rates, between 100 and 400rpm at a constant extraction time of 20 min. As shown in fig.3 up to 400 rpm, the absorbance signal rose as the stirring rate was increased. Afterwards, it remained constant. Higher stirring rate were not used, because at such rates, the spattering damaged the micro drops. Hence a stirring rate of 200rpm was adopted for further study.

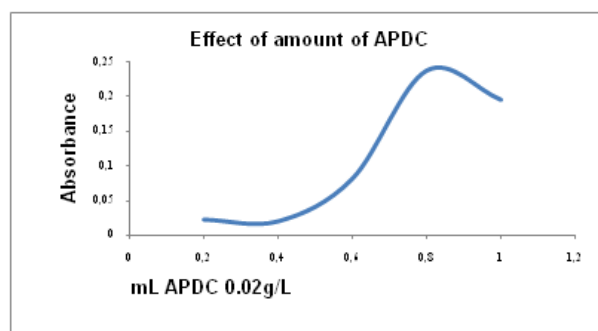


Fig 2. The effect of amount of APDC on the extraction efficiency.

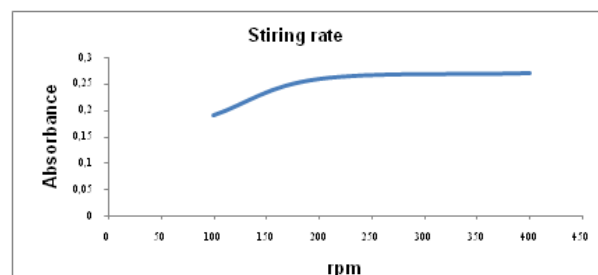


Fig 3. The effect of stirring rate on the extraction efficiency.

Effect of extraction time

The optimal extraction efficiency is obtained when equilibrium is established. The extraction time performs a very essential role in the whole process of equilibrium extraction. The effect of extraction time on the extraction efficiency was examined by varying the extraction time from 15 to 60 min at constant experimental conditions. Fig.4 shows a corresponding rise in absorbance within

time of extraction ranges between 10 and 30 minute. Micro drop was damaged on the higher extraction time. Finally, an extraction time of 30 min was selected as a reasonable compromise between enrichment factor and analysis time.

Extraction temperature

It was expected that an increase in temperature would lead to an enhancement of the mass transfer coefficients of the goal compounds from the aqueous sample into the micro drop and consequently, to higher extraction efficiencies. On the other hand, the sample temperature has significant effect on , not only the kinetics and thermodynamics of the analyte extraction, but also on those of the water molecules in the sample[22, 23].The effect of sample temperature on extraction efficiency was studied at different temperatures raging between 30 to 60 °C(30, 40, 50, 60)°C.The lower extraction efficiencies obtained at 40°Candbelow could be due to an increase in viscosity of 1-dodecanol , resulting in a decrease of the mass transfer between aqueous solvent an organic solvent.

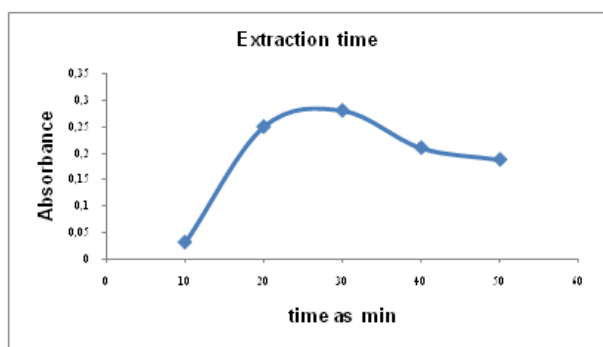


Fig 4. The effect of extraction time on the extraction efficiency.

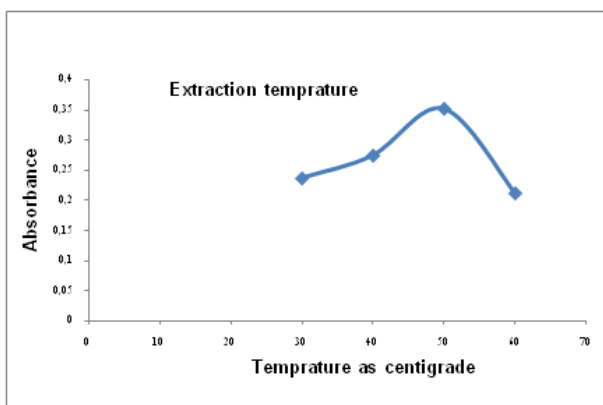


Fig 5. The effect of extraction temperature on the extraction efficiency.

In fact, a significant reduction in sensitivity was observed at higher temperature values (>50°C). This declining trend is shown in fig.5 which is

likely to be explained by considering the effects of high temperature; on the one side, it has been reported that high temperature can decrease the portion coefficients of analytes in the micro drop, resulting in a decrease of the rate of analyte adsorption on the outer surface of the micro drop. On the other side, solubility of 1-dodecanol in water decreases at temperature values higher than 50°C. So, the optimum extraction temperature was set at 50°C.

Volume of extraction solvent

Selection of an appropriate solvent is considered a crucial parameter in LPME methods. The range of proper solvents to be used in the previously mentioned method is limited as the solvent must have qualities such as, low volatility and low solubility in water, in order to be immiscible with water and as the analytes must be soluble in it. The solvent melting point should be close to the room temperature [24]. Because of low melting point, low vapor pressure, and low water solubility, 1-dodecanol seemed to be suitable for this investigation.

The influence of micro drop volume on the analytical signal was studied in the range of 50.0 to 300µL. Volume of extraction solvent was evaluated for the extraction of 5.0mL of sample containing 200.0µL⁻¹of cadmium. The stirred solution (200rpm) was kept at 50°C for 30 minute until the extraction was completed. Then, the extract was diluted using 500µLof ethanol, and its absorption was measured.

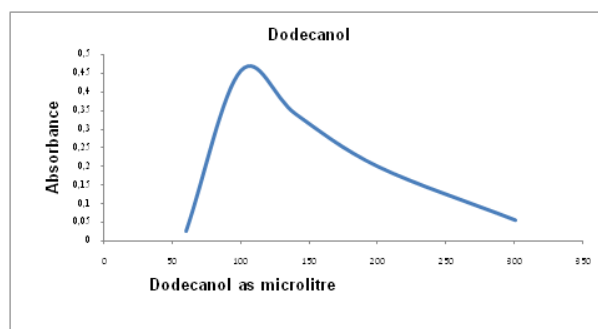


Fig 6. The effect of volume of extraction solvent on the extraction efficiency.

The result (Fig.6) shows that the rewas a corresponding growth in the absorbance of target compounds for solvent volumes ranging from 50.0 to 100.0µL. Based on LLE equations, rate of the analyte migration into the micro drop is directly related to the surface area between the two liquid phases and is inversely related to the organic phase volume [25].Thus, an increase in the drop volume raises the interfacial area following the analytical

signals. However, any further increase in the micro drop volume results in a decrease in the absorbance [26]. Hence, an organic volume of $100\mu\text{L}$ was selected as optimum.

Volume of ethanol as dilution solvent

Aqueous samples can be generally introduced for analysis directly without any prior treatment. But that is remarkably dependent on the viscosity of the solution; In flame atomic absorption spectroscopy (FAAS) analysis, the viscosity should be similar to that of water for which most nebulizers are designed.

Only some organic liquids such as ethanol or methyl isobutyl-keton fulfill this condition, and as a result, these solvents are often used to dilute the organic liquids; during the analysis, volatile solvents (such as methanol, acetone, diethyl ether, etc.), evaporate before reaching the flame. The burning rate is increased by expanded steam, and then increasing the gases flow into the spray chamber, leading to erratic results. Due to the high viscosity of dodecanol, the atomic absorption direct injection is not possible.

In this work, extraction solvent was diluted with ethanol prior to injection. Therefore, the influence of dilution solvent was also investigated by varying the volume of ethanol between 0.1 to 0.4 ml. As shown in fig.7, the absorbance signal was increased by additional amount of ethanol to a certain point. Further increase in the dilution solvent volume resulted in a decline in the absorbance and enrichment factor. Hence, a dilution solvent volume of 0.4mL ($400\mu\text{L}$) was selected as a reasonable compromise between enrichment factor and dilution solvent volume.

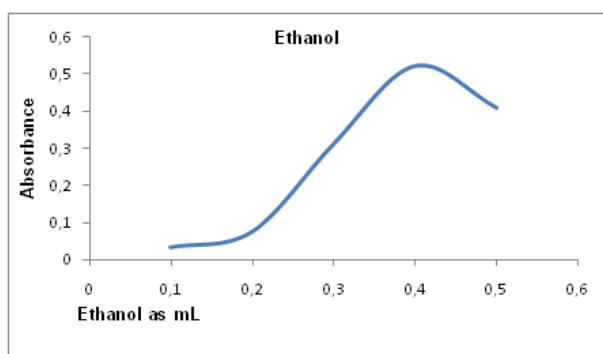


Fig 7. The effect of dilution solvent volume on the extraction efficiency

Ionic strength

The Ionic strength is one of the key parameters that must be taken into account in the extraction process. Depending on the target compounds, the presence of salt in aqueous sample can potentially

result in contrary effects: it may improve [27], not influence [28], or diminish the extraction process [29,30]. Apart from the salting-out effect improving extraction efficiency, it also leads to altered physical properties of the Nernst diffusion film in the interface of aqueous and organic phases; consequently, the diffusion rate of analytes into the solvent reduces [31,32]. To investigate this effect on the proposed LPME, the extraction was performed with a 5.0mL water sample containing various concentration of NaCl (0% to 30%, w/v). The result confirmed (figure 8) that adding salt to increase the concentration from 5% (w/v) to 10% (w/v) caused a growth in absorbance which then remained constant at concentrations up to 25% (w/v). The absorbance then showed a declining trend at higher concentrations of salt. This observation suggests the possibility of using this method for the separation and determination of cadmium from saline solutions.

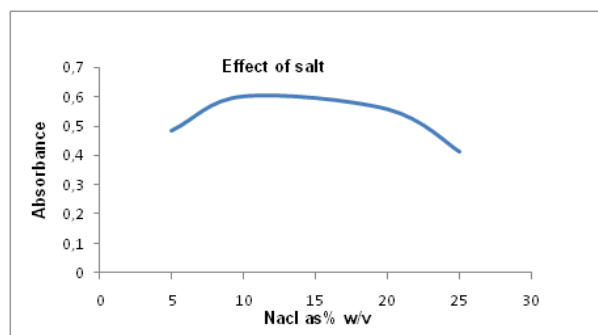


Fig 8. The effect of salt on the extraction efficiency.

Interference study

The sensitivity and utility of the SFODME in the pre-concentration of cadmium in the presence of potential interfering ions at an initial mole ratio of 5000 (ion/cadmium) was examined. In these experiments, 5.0 ml of solutions containing $200\mu\text{g/L}$ cadmium and various amounts of interfering ions were treated according to the recommended procedure. When interference was observed, the concentration of the interfering ion was lowered. The results of this investigation are given in Table 1. A relative error of less than 5% was considered to be within the range of experimental error. As is shown, the presence of high concentrations of alkali, alkali earth cat ions, did not cause any interference, but the presence of some metals that formed ionic complex, did interfere in the determination of cadmium.

Figures of merit

Under the optimum experimental condition described above, method validation was carried out, in terms of linearity, precision, limit of detection

(LOD) and quantifications (LOQ) for each analyte. The analytical characteristics of the proposed method are presented in Table 2. The calibration curve was found to be linear in the range of 2.00 to 400 μgL^{-1} and the resulting equation was $A=0.002C+0.122$, where A is the absorbance of the extract and C is the concentration of cadmium (μgL^{-1}) in the initial solution. Precision was assessed by determination of repeatability, which could express the precision of the method under the same operating conditions

Table 1. The effect of diverse ions on the recovery of Cadmium.

Ion	Molar ratio (ion/Cd)	Recovery (%)
Pb	5000	98.87
K	5000	99.87
Mg ²⁺	5000	99.62
Ca ²⁺	5000	99
Cu ²⁺	5000	88.75
Li	5000	101.25
Na	5000	100
As	5000	91
Hg	5000	87

Concentrated volume, 5mL; cadmium concentration 200 μgL^{-1} .

Table 2. Figure of merit of the proposed method for pretreatment and determination of cadmium

Analytical parameter	Results
LR (μgL^{-1})	2-400
Slope	2.7×10^{-3}
Correlation coefficient	0.9995
LOD (μgL^{-1})	0.57
LOQ (μgL^{-1}) (LOQ)	1.91
RSD (%) (n=8, 10 μgL^{-1})	3.04
RSD (%) (n=10, 20 μgL^{-1})	1.85
RSD (%) (n=8, 300 μgL^{-1})	2.3
PF (25mL)	300
PF (5mL)	63

LR, Linearity range; (LOD) Detection limit (μgL^{-1}); (LOQ), Quantification Limit; RSD, Relative standard deviation; PF, Pre-concentration factor.

It also identified intraday precision which is explained as relative standard deviation (RSD%).

The results of 10 standard replicate measurements of 20 μgL^{-1} of cadmium is given in Table 2. The relative standard deviation was then evaluated to be 1.85% which shows acceptable error and reliability of the experiments. The limit of detection, defined as ($\text{LOD}=3S_B/m$) and quantification of limit defined as ($\text{LOQ}=10S_B/m$) where (S_B and m are the standard deviation of the blank, and the slope of the calibration curve), were 0.57 and 1.91 μgL^{-1} respectively. Furthermore, the pre-concentration factor was calculated as the ratio of the cadmium concentration in the solidified floating organic drop to that initially in the bulk phase which was 63 [33,34].

Application to real sample

Finally, the reliability of the recommended procedure, the method was evaluated by the analysis of the real samples including well, qanat and waste water. For this purpose a volume of 5 mL of each sample was pre-concentrated according to the proposed method, the result indicated that no traces of cadmium were detected in qanat and well water samples but cadmium was detected in the waste water. The accuracy of the method was verified by the analysis of the sample spiked with (50 and 200 μgL^{-1}) levels of cadmium to assess the matrix effect. The relative recovery defined as the concentration of cadmium ion ratio of a natural water sample and ultrapure water sample spiked with analytes at the same level, was applied. The relative recoveries of the analytes are given in Table 3, which varies from 98% to 101%; it shows that the influence of the matrix is not significant on the extraction.

Table 3. The results obtained from analysis of real water sample

Sample	Added Cadmium (μgL^{-1})	Found cadmium (μgL^{-1})	Recovery (%)
Well water	-	ND	-
Well water	200	201.4±0.02	101
Qanat water	-	ND	-
Qanat water	200	196.4±0.02	98.2
Waste Water	-	31±0.02	-
Waste Water	50	80.55±0.02	98.8

ND, not detected; Results are mean and standard deviation of three independent measurements (n=3).

Table 4. Comparison of the proposed method with other methods for pretreatment and determination of cadmium

Methods	LOD (μgL^{-1})	LR (μgL^{-1})	r^2	RSD (%)	Recovery (%)	PF	References
CPE-FAAS	0.3	3-250	0.999	4.0(at100 μgL^{-1})(n=7)	95.6-102.8	70	35
DLL-ME	1.2	5-150	0.9997	2.1(at100 μgL^{-1})(n=8)	69-99	34.5	36
USAE-SFODM	0.66	10-450	0.9985	3.34(at20 μgL^{-1})(n=10)	95.2-100.6	81	37
Proposed method	0.57	2-400	0.9995	1.85(at20 μgL^{-1})(n=10)	98.2-101	63	*

CPE, Cloud point extraction; DLL-ME, Dispersive liquid-liquid micro extraction; USA-SFODM, Ultrasound – assisted emulsification solidified floating organic drop micro extraction.

A comparison between the proposed FAAS-SFODM method and some of the other published methods used for extraction and determination of cadmium are summarized in table 4. The results of the investigation indicate that solidified floating organic drop micro extraction (SFODME) combined with flame atomic absorption spectrometry can be used as a simple and powerful technique for pre-concentration and determination of metal ions in aqueous samples.

CONCLUSION

In the present work, the application of the solidified floating organic drop micro-extraction (SFODME) method in determination of cadmium in aqueous samples was investigated. This technique made the separation and quantification of cadmium in the aqueous samples possible. The proposed SFODME method permits an effective separation and pre-concentration of cadmium and also its final determination using spectrometry in several categories of natural waters. The sample preparation time as well as the consumption of organic solvent was minimized and the figures of merit of the developed method were comparable to other reported methods for the determination of cadmium [35-37]. In conclusion the SFODME method is a simple, fast operation, economic, rejection of matrix constituent, high enrichment factor and environmentally friendly technique that can be applied to extraction process and can be used for determination of the cadmium ions in environmental samples in order to obtain satisfactory results. In this study, this method significantly improved the performance of the FAAS detection for cadmium. These features appears promising for the future studies on extraction of metals other than cadmium, aiming at the development of novel speciation methods that would deliver better analytical performance.

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