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Development of on-line single-drop micro-extraction sequential injection system for electrothermal atomic absorption spectrometric determination of trace metals

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ABSTRACT

A novel automatic sequential injection (SI) single-drop micro-extraction (SDME) system is proposed as versatile approach for on-line metal preconcentration and/or separation. Coupled to electrothermal atomic absorption spectrometry (ETAAS) the potentials of this SI scheme are demonstrated for trace cadmium determination in water samples. A non-charged complex of cadmium with ammonium diethyldithiophosphate (DDPA) was produced and extracted on-line into a 60 μL micro-drop of di-isobutyl ketone (DIBK). The extraction procedure was performed into a newly designed flow-through extraction cell coupled on a sequential injection manifold. As the complex Cd(II)-DDPA flowed continuously around the micro-droplet, the analyte was extracting into the solvent micro-drop. All the critical parameters were optimized and offered good performance characteristics and high preconcentration ratios. For 600 s micro-extraction time, the enhancement factor was 10 and the sampling frequency was 6 h^{-1}. The detection limit was 0.01 μg L^{-1} and the precision (RSD at 0.1 μg L^{-1} of cadmium) was 3.9%. The proposed method was evaluated by analyzing certified reference material.

1. Introduction

Despite the valuable advances in separation and quantification the conventional liquid–liquid extraction (LLE) is still the most widely used sample pretreatment technique in routine analyses for improvement of sensitivity and/or selectivity of analytical methods. The implementation of LLE in flow manifolds simulating the same sequences performed in batch procedures contributes advantages inherent in automatic methods. Recently, efforts have been focused on the miniaturizing of the LLE procedure by reducing the organic solvent, leading to the development of micro-extraction methodologies [1,2].

The first attempt to miniaturize LLE in a flowing stream assembly was carried out by Liu and Dasgupta [3] reporting a flow-through drop-in-drop micro extraction system where a 1.3 μL drop of an organic solvent was immersed into a larger flowing aqueous drop to accomplish the extraction of ion-paired species. Further research led to the development of the so-called single-drop microextraction (SDME) where a droplet of organic solvent was suspended at the tip of a microsyringe needle and immersed into the aqueous sample [4]. Psillakis and Kalogerakis [5] and recently Xu et al. [6] overviewed the principles of SDME as well as its latest developments and applications. The implementation of SDME in a continuous flow micro-extraction mode (CF-SDME) was firstly described by Liu and Lee for trace nitroaromatic compounds and chlorobenzens in environmental samples [7]. The proposed procedure differs from other SDME approaches in the fact that the solvent is continuously surrounded by fresh aqueous solution, thus leading to improved extraction efficiencies.

Hitherto, the majority of the reported SDME papers have been focused on preconcentration of organic pollutants, and only few efforts have been devoted to metal extraction using SDME coupled to electrothermal vaporization (ETV)-ICP-MS [8–10] and electrothermal atomic absorption spectrometry (ETAAS) [11–13]. Pena et al. [14] proposed the combination of sequential injection analysis (SIA) with electrothermal atomic absorption spectrometry (ETAAS) for determination of Cr(VI) in waters using a home-made micro-extraction vial but for limited sample volume and extended cycling times, when high preconcentration factors are demanded.

Recently, Kokosa developed an automatically performing liquid phase micro-extraction method on liquid samples in discrete vials for GC, HPLC and GC/MS [15]. Thus, still there is need for automation of on-line continuous flow micro-extraction procedure coupled with atomic spectrometric techniques.

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On the other hand, the significant advantages of sequential injection (SI) systems are the ability for even small volumes (down to a few tenths of micro-liters) handling of solutions with great success, thanks to the use of syringe pump and advanced software [1,16,17]. Moreover, they are much economical regarding to the sample, reagents and hence the waste production.

The aim of present work is to develop a new completed automatic sequential injection single-drop micro-extraction (SI-SDME) system for metal determination in water samples using ETAAS, based on the on-line complex formation of metals with chelating agents. For this purpose a newly designed flow-through micro-extraction cell was manufactured, while the effectiveness and efficiency of the proposed SI-SDME system has been demonstrated for cadmium determination, due to its high toxicity and the very low concentration levels in the environmental water samples. Ammonium diethyldithiophosphate (DDPA) was also selected as chelating agent due to its good selectivity for cadmium in strong acidic medium [18].

2. Experimental

2.1. Apparatus

The SI manifold and its operation for on-line SDME and cadmium determination by ETAAS is depicted schematically in Fig. 1.

A FIAlab®-3000 sequential injection system (Alitea FIAlab, USA) equipped with an internally incorporated six-port multiposition valve (MV) and a syringe pump (SP, Cavro, Sunnyvale, CA) with a capacity of 1000 μL was used. The FIAlab®-3000 system was controlled by a personal computer and the FIAlab for windows v. 5.9.245 application program, written by FIAlab instruments (http://www.flowinjection.com).

A PerkinElmer, Norwalk, Connecticut, USA (http://las.perkinelmer.com) model 5100 PC atomic absorption spectrometer with Zeemann effect background correction and a transversely heated graphite tube atomizer (THGA), equipped with AS-71 furnace auto-sampler and a circulating cooling unit, was employed throughout measurements. Pyrolytically coated THGA graphite tubes (PerkinElmer) with integrated L'vov platform were used. A cadmium electrodeless discharge lamp (EDL) was used as radiation source operated at 5 W. The wavelength was set at 228.8 nm resonance line and the monochromator spectral bandpass at

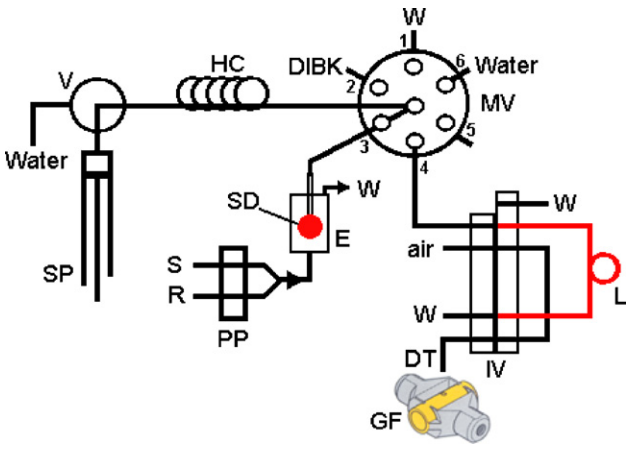

Fig. 1. SI-SDME manifold of the on-line solvent micro-extraction system coupled to ETAAS for cadmium determination. For details see text and Table 1. S, sample; R, DDPA solution; W, waste; PP, peristaltic pump; SP, syringe pump; MV, multi-position valve; IV, injection valve in "Load" position; V, valve in "OUT" position; HC, holding coil; L, loop; E, micro-extraction cell; SD, solvent droplet; DT, delivery tube; GF, graphite furnace ETAAS.

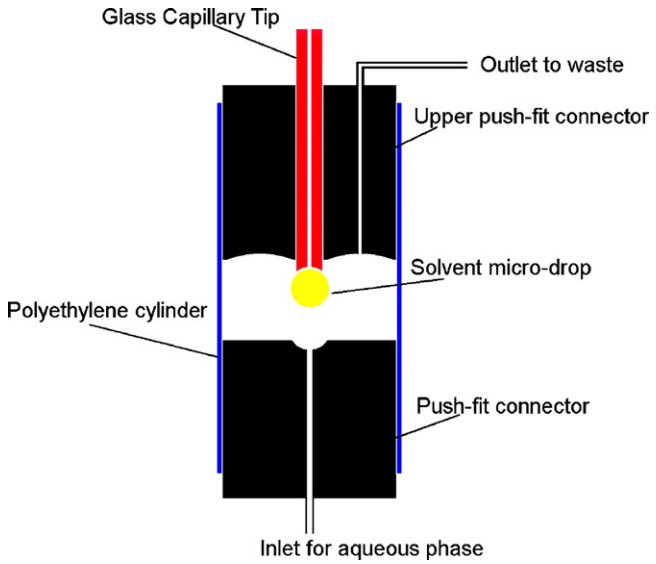

Fig. 2. Schematic diagram of the micro-extraction flow-through cell and the capillary tip.

0.7 nm. The graphite furnace (GF) temperature program for the Cd determination in DIBK includes preheating/drying steps at 90/110 °C for gradual drying of the organic solvent and a pyrolysis step at 400 °C. Argon 99.996% was used as purge and protective gas. Integrated absorbance (peak area) was used exclusively for signal evaluation.

A PerkinElmer Norwalk, Connecticut, USA model FIAS-400 flow injection analysis system was coupled to the SI system and to the ETAAS for automatic processing of the whole procedure. The FIAS-400 system was controlled by a personal computer and the AA Lab. Benchtop version 7.2 software program. The FIAS-400 system consisted of two peristaltic pumps (only one is used for the proposed manifold) and a 5-port 2-position injection valve.

A 35 μL extract loop (L) of PTFE tubing was employed with the injection valve IV in order to grab and transfer an accurate portion of the DIBK micro-drop into the graphite tube for atomization. A 30 cm length/0.3 mm i.d. delivery tube (DT) was used to connect the FI manifold with the atomizer. An air compressor (air flow rate: 0.1 mL min^{-1}) was used in association with the injection valve, IV for loop evacuation into the graphite tube.

2.2. The micro-extraction flow-through cell and the capillary tip

The micro-extraction flow-through cell (E) and the capillary tip were constructed in the laboratory and are presented schematically in Fig. 2. The flow-through cell was made of a polyethylene cylinder 3.0 cm length/9.0 mm internal diameter/11.0 mm external diameter. At the two ends of the cylinder there are push-fit connectors. The capillary tube, for organic micro-drop suspension, passes through the upper push-fit connector and was made of a glass tube with 0.15 mm i.d./4.5 mm o.d. The glass material (hydrophilic) is necessary for suspension of the organic solvent drop into the flowing aqueous solution. As it is proved from preliminary experiments a hydrophobic material like PTFE cannot be used as capillary tube because the organic solvent (hydrophobic material), wets the end of the capillary tube and glides towards the exit of the cell. Thus, in this case it is impossible to be generated a suspended micro-drop. The above configuration of the flow-through cell together with the capillary tube facilitates the generation and suspension of a stable DIBK micro-drop. With this extraction cell

the volume of stable drops that can be produced are ranged up to 80 μL into an aqueous flowing stream with flow rate ranged up to 4.0 mL min^{-1}.

2.3. Reagents

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany, http://www.merck.de). Ultra-pure quality water was used throughout which was produced by a Milli-Q system (Millipore, Bedford, USA, http://www.millipore.com). All standard solutions were prepared immediately before use, by stepwise dilution of a 1000 mg L^{-1} Cd(II) stock standard solution (Merck Titrisol) to the required sub μg L^{-1} levels. The chelating reagent, 1.2% (m/v) ammonium diethyldithiophosphate (DDPA) solution were prepared daily by dissolving appropriate amount of DDPA (Aldrich) in ultra-pure water without any further purification. Di-isobutyl ketone (DIBK) was previously saturated with ultra-pure water.

2.4. Procedure

The operation steps of the proposed SI-SDME method for cadmium determination are summarized in Table 1.

In step 1–4 segments of water, DIBK, water DIBK at volumes of 300, 100, 100, and 60 μL, respectively, are aspirated into the holding coil (HC). In step 5, the micro-drop of DIBK is generated and suspended at the glass capillary tip into the flow-through micro extraction cell (E). In step 6, the peristaltic pump (PP) is activated and the on-line formed complex Cd(II)-DDPA is flowing continuously around the DIBK drop for a micro-extraction time (preconcentration time) as it is shown in Fig. 1. As the fresh complex Cd(II)-DDPA flowed around micro-droplet continuously, the analyte was kept extracting into the solvent. After that the drop is retracted back into the holding coil. In the next step the drop is delivered into the loop (35 μL) of the injection valve (IV) and the delivery tube (DT) mounted at the auto-sampler of the furnace is moved into the dosing hole of the graphite tube. In step 9, the injection valve IV is switched to the "inject" position, so that 35 μL of the drop is propelled by an air stream (Air) and introduced into the graphite tube. Thereinafter, the auto-sampler arm is moved back to the "wash" position and the atomization program starts. During the ETAAS atomization program the washing of the loop is performed (step 11), while a new sample solution is pumped through the micro-extraction cell. Three replicate measurements were made in all instances.

3. Results and discussion

3.1. Organic solvent

The selection of an appropriate organic solvent for SDME is an important task. It should be highly immiscible with water, with high extraction efficiency and selectivity. In addition, drop stability during micro-extraction is a necessary requirement for SDME applications.

On the other hand, the use of volatile organic solvents and halogen-containing organic solvents should be avoided for injection into the graphite furnace of ETAAS because they result to lower precision and many interferences in metal determinations [14]. Usually the recommended organic solvent for conventional liquid–liquid extraction of metal-chelate complexes and determination by atomic spectrometry is isobutyl-methyl-ketone (IBMK). However, IBMK cannot be used in SDME systems due to its high solubility in water (2%, v/v at 20 °C). Alternative, DIBK is an excellent organic solvent with analogous extraction properties, high boiling point and very low miscibility with water (0.05%, v/v at 20 °C) [19]. Practically, no decrease in drop volume during extraction was observed with DIBK even for long extraction times (>20 min), while the drop was stable for drop-volume up to 80 μL. Finally, DIBK was used throughout, which in turn, facilitates the use of long preconcentration time.

3.2. Optimization of SDME parameters

3.2.1. Sample acidity and DDPA concentration

The pH value of the sample plays a significant role in the overall performance of the on-line solvent extraction affecting the complex formation and the extraction efficiency.

Ammonium diethyldithiophosphate (DDPA) has been used successfully in on-line liquid–liquid extraction and solid phase extraction methodologies, and compared with other dithiocarbamate reagents proved to be more selective and stable for cadmium, copper and lead in very low pH values [20]. The main advantage of the DDPA is that forms stable complexes with several metals even in strong acidic medium due to its resistance against hydrolysis, avoiding thus the addition of buffer solutions which are a significant source of contamination [21]. Another significant advantage of DDPA is that it does not react with alkali, alkaline earth metals and others such as Mn, V, Ti, Co, Cr, Zn allowing the separation of major components of the matrix.

Therefore, the influence of sample pH on the absorbance was studied in the range 0.5 ± 0.2 to 7.0 ± 0.1 by adjusting it with dilute

Table 1
Operational sequence of the SI-SDME on-line preconcentration system for ETAAS cadmium determination (for manifold details see Fig. 1).

Step	V position	MV position	SP flow-rate (μL s−1)	SP operation	IV position	PP	Commentary
1	IN	2	30	Aspirate 300 μL	Load	OFF	Water into HC
2	OUT	2	30	Aspirate 100 μL	Load	OFF	DIBK into HC
3	OUT	6	30	Aspirate 100 μL	Load	OFF	Water into HC
4	OUT	2	5.0	Aspirate 60 μL	Load	OFF	DIBK into HC
5	OUT	3	3.0	Dispense 100 μL	Load	OFF	Micro-drop generation
6	–	–	–	–	–	ON[a]	Preconcentration (600 s)
7	OUT	3	5.0	Aspirate 110 μL	Load	OFF	Drop into HC
8	OUT	4	20	Dispense 150 μL	Load	OFF	Drop into the loop (L) of the IV
–	–	–	–	–	–	–	Capillary movement into GF of ETAAS
9	–	–	–	–	Inject	OFF	Delivery 35 μL of the drop into GF
–	–	–	–	–	–	–	Capillary movement to waste
10	–	–	–	–	–	–	Starting of the atomization program/measurement of absorption
11	OUT	4	30	Empty	Inject	OFF	Washing of the loop (L)

[a] Sample flow rate, 1.5 mL min^{-1}; DDPA flow rate, 0.3 mL min^{-1}. V, valve; MV, multi-position valve; SP, syringe pump; IV, injection valve; PP, peristaltic pump.

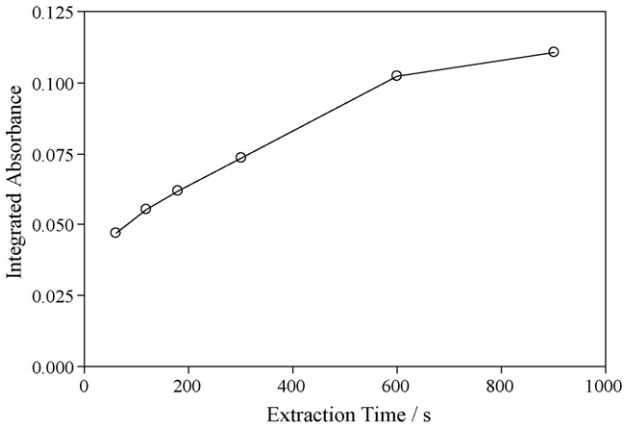

Fig. 3. Effect of extraction time on integrated absorbance of 0.2 μg L^{-1} Cd(II). 1.2% (m/v) DDPA; 1.5 mL min^{-1} sample flow rate; 60 μL micro-drop volume.

nitric acid or ammonia solution. The maximum absorbance was recorded within a pH range from 0.5 to 3.0. Thus, the samples and standards solutions were fixed to pH 2.0 ± 0.2. This optimum pH value enables the use of the method directly in many aqueous samples after common acid preservation.

The effect of DDPA concentration was studied in the range of 0.05–1.5% (m/v). The maximum absorbance was observed over the concentration range 0.8–1.5% (m/v). Given its competitive complexation with other coexisting ions in the real samples a DDPA concentration of 1.2% (m/v) was adopted for all further experiments.

3.2.2. Extraction time

The process of mass transfer is time-dependent and the extraction rate is reduced, as well as the maximum integrated absorbance is attained, when the system approaches equilibrium. However, in automatic systems reaching equilibrium is not necessary, as long as the extraction conditions are reproducible. On the other hand, continuous flow micro-extraction systems keep the mass transfer rate almost constant because fresh analyte solution flows into the extraction cell around the micro-droplet. The influence of extraction time was investigated in the range 60–900 s. The results are shown in Fig. 3. The integrated absorbance increases significantly with the increase of extraction time up to 600 s and after that, the increase is slower. As a compromise between sensitivity and sampling frequency, an extraction time of 600 s was adopted throughout the experiments.

3.2.3. Micro-drop volume

Generally, the volume of micro-drop determines the extraction efficiency, because it affects the surface area of the drop and the interfacial layer of both aqueous and organic phases. As the surface area increases with an increase in drop volume, it is expected more efficient mass transfer from aqueous solution to the organic drop. With the proposed manifold, stable DIBK drop with volume up to 80 μL into a flowing stream (<4.0 mL min^{-1}) of aqueous phase can be preserved. The micro-extraction was performed for 10 min at 1.5 mL min^{-1} sample flow rate. It has been shown that a slight increase on integrated absorbance was observed by increasing the drop volume from 30 μL to 60 μL. For volumes over 60 μL no notable effect observed. Thus, a droplet of 60 μL was selected in this study.

3.2.4. Aqueous phase flow rate

In continuous flow SDME, aqueous phase flow rate affects remarkably the extraction dynamics. An increase of flow rate results in decreasing the thickness of the interfacial layer surrounding the solvent droplet, increasing mass transfer of analytes, and speeding up extraction process. However, at very high flow rates the much higher linear velocity of the analyte solution does not to allow establishment of extraction equilibrium in the interfacial layer of both phases involved in extraction [8].

The effect of aqueous phase (sample + DDPA) flow rate was evaluated in the range of 0.5–3.9 mL min^{-1}. The ratio of sample flow rate to DDPA flow rate was fixed at ∼5 throughout the study. With a constant sampling period (extraction time) increasing the aqueous phase flow rate up to 1.8 mL min^{-1} an increased integrated absorbance was observed. For flow rate above 1.8 mL min^{-1} the signal was levelled off. The possible reason for this is the fact that at higher flow rates the linear velocity of the sample solution was being too high to allow efficient extraction in the interfacial layer of both phases during extraction process [8]. An aqueous phase flow rate 1.8 mL min^{-1} (1.5 mL min^{-1} sample flow rate and 0.3 mL min^{-1} DDPA flow rate) was adopted for the proposed method.

3.3. Interference studies

The effect of potential interferents encountered in natural waters on the absorbance of cadmium was examined using the SI-SDME manifold shown in Fig. 1, under the optimum conditions described above for 0.1 μg L^{-1} Cd(II) standard solution with individual potential interferents added. Interference was defined to be significant if a variation more than ±10% in the absorbance was recorded. The results showed that, Al(III), Co(II), Cr(III), Cr(IV), Fe(III), Mn(II), and Zn(II) are tolerated up to 5 mg L^{-1} while Cu(II), Pb(II) and Hg(II) are tolerated up to 2 mg L^{-1}. Moreover, the potential interferences from some common matrix cations such as Ca(II), Mg(II), Ba(II), Na(I) and K(I) were also investigated. No significant variation in the absorbance was observed at concentrations up to1000 mg L^{-1} and NaCl up to 30 g L^{-1}.

3.4. Analytical performance and analysis of natural waters

The performance data of the SI-SDME on-line preconcentration method for ETAAS cadmium determination are presented in Table 2.

For sample consumption 15.0 mL, the detection limit was 0.01 μg L^{-1} and the enhancement factor was 10. The performance characteristics of the proposed method are comparable to some recently published works reporting also on automation interface of SIA with ETAAS [1,16].

The accuracy of the proposed method was evaluated, by the analysis of the certified reference materials: NIST CRM 1643e (National Institute of Standard and Technology, Trace elements in

Table 2
Analytical performance of the SI-SDME method for cadmium determination.

Enrichment factor[a]	10
Preconcentration Time (s)	600
Sample consumption (mL)	15.0
Sampling frequency (h^{-1})	6
Linear range (μg L^{-1})	0.03–0.6
Regression equation ([Cd] in μg L^{-1})	$A = 0.5015\ [Cd] + 0.0016$
Correlation coefficient	$r = 0.9988$
Detection limit (3s) (μg L^{-1})	$c_L = 0.01$
Precision (RSD, $n = 9$; 0.1 μg L^{-1}) (%)	$s_r = 3.9$

[a] Compared with the direct injection of 35 μL aqueous standard solution.

Table 3
Analytical results of the cadmium determination in certified reference material and spiked natural water samples.

Sample	Certified value ($\mu g L^{-1}$)	Added ($\mu g L^{-1}$)	Found[a] ($\mu g L^{-1}$)	Recovery (%)
CRM 1643e	6.568 ± 0.073		6.371 ± 0.355	97
Tap water		0	0.050 ± 0.004	
		0.200	0.242 ± 0.011	96
River water		0	0.180 ± 0.012	
		0.200	0.376 ± 0.020	98
Seawater		0	0.125 ± 0.008	
		0.200	0.313 ± 0.025	94

[a] Mean value ± standard deviation based on three replicate measurements.

water). The proposed method was applied to the analysis of tap water, river water and coastal seawater samples collected from river and gulf of Northern Greece. Natural water samples were filtered through 0.45 μm membrane filters and acidified to 0.01 mol L^{-1} HNO_3 (pH ≈ 2). The results are presented in Table 3. The determined concentration of cadmium were in good agreement with the certified values and the recovery ranged between 94–97% showing the good performance of the method in all type of natural water samples.

4. Conclusions

A new completed automatic SDME method for metal determination in water samples using sequential injection analysis coupled with ETAAS has been developed. The most important features of the system are: (i) facility of automated operation in micro-scale analysis, (ii) the successfully interfacing of the continuous operating process of liquid–liquid extraction with the extremely sensitive but of discrete nature ETAAS technique and (iii) extremely low consumption of organic solvent thanks to the use of a syringe pump and a SIA manifold. The effectiveness and efficiency of the proposed SI-SDME system was successfully demonstrated for cadmium determination and applied in water samples.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.aca.2008.10.078.

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