Research Article

Use of Dispersive Liquid-Liquid Microextraction and UV-Vis Spectrophotometry for the Determination of Cadmium in Water Samples

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A simple and inexpensive method for cadmium determination in water using dispersive liquid-liquid microextraction and ultraviolet-visible spectrophotometry was developed. In order to obtain the best experimental conditions, experimental design was applied. Calibration was made in the range of 10–100 $\mu\text{g/L}$, obtaining good linearity ($R^2 = 0.9947$). The obtained limit of detection based on calibration curve was 8.5 $\mu\text{g/L}$. Intra- and interday repeatability were checked at two levels, obtaining relative standard deviation values from 9.0 to 13.3%. The enrichment factor had a value of 73. Metal interferences were also checked and tolerable limits were evaluated. Finally, the method was applied to cadmium determination in real spiked water samples. Therefore, the method showed potential applicability for cadmium determination in highly contaminated liquid samples.

1. Introduction

Cadmium is one of the most toxic heavy metals [1, 2]. Due to its low damaging concentration levels and to the complexity of the matrix of samples, a prior preconcentration and separation step is frequently necessary in its determination. Liquid-liquid microextraction (LLME) emerged from the classic liquid-liquid extraction (LLE) overcoming one of its major drawbacks by reducing the amount of organic solvents. From the LLME introduction, different approaches have been developed [3]; among them is dispersive liquid-liquid microextraction (DLLME) presented by Rezaee et al. in 2006 [4]. In this method, a cloudy solution is formed after the fast injection of a suitable mixture of extraction and disperser solvents into the aqueous phase. Thus, due to the large superficial area in contact between the phases, analytes in the aqueous sample are rapidly extracted into the fine droplets of extraction solvent. After extraction, phase separation is achieved by centrifugation. This technique offers several advantages such as high recoveries, high enhancement factors, and rapidity. Moreover, it may be considered

environmentally friendly, due to the use of reduced amount of organic solvents. In addition, it is simple and inexpensive, since neither very specific reagents nor costly laboratory equipment is required [5, 6].

For cadmium determination DLLME has been coupled to different spectrometry detection techniques, such as atomic absorption (AAS), atomic fluorescence, inductively coupled plasma with optical emission (ICP-OES), and total reflection X-ray [7–11]. Due to the difficulty in adapting the micro-volume of extraction solvent to the necessary volume in conventional UV-Vis spectrophotometers, the coupling to UV-Vis spectrophotometry has only been recently achieved. This problem has been sometimes solved by evaporation and/or dilution of the organic phase or by using special instrumentation [12, 13].

The goal of this work was to develop a simple and inexpensive method for determination of cadmium in aqueous samples by coupling DLLME and UV-Vis spectrophotometry with a microcapacity cuvette. In this way, loss of sensitivity linked to the dilution of the organic phase and increase of the price due to the special instrumentation may be avoided. In

order to select the best experimental conditions, a planned experimental design was run. The chosen procedure was validated and applied to the determination of cadmium in different water samples.

2. Materials and Methods

2.1. Reagents and Apparatus. All analytical grade reagents and solvents used were purchased from Panreac Química S.A. (Barcelona, Spain), except for carbon tetrachloride that was obtained from VWR International Eurolab S.L. (Barcelona, Spain). Working solutions of cadmium and dithizone were daily prepared. The pH of the extraction was adjusted just before the use with a weekly prepared NaOH/KCl solution. All solutions were preserved in the fridge while not being used. Doubly distilled water was used throughout the whole work.

A Spectrophotometer 8453 UV-Vis Diode Array System (Agilent Technologies, Spain) with the software "UV-Visible Chemstation Rev. A. 10.01" and an 80 μL cuvette (Hellma GmbH & Co. KG, Germany) were used.

The extractions were made in a vessel with a thermostatic jacket joined to a Lauda Ecoline Re 104 E100 thermobath (Lauda, Germany). Values of cadmium concentration for the enrichment factor evaluation were obtained by measurements in the 7700X ICP-MS (Agilent Technologies, Spain). Experimental design was performed and the results were evaluated using Statistica Software (StatSoft, Tulsa, USA).

2.2. Procedure. Microextraction was accomplished in a tube containing 7.5 mL of sample at pH 12.8 ± 0.2 and 1.5 mL of disperser solvent (methanol). The mixture sample/dispersant was brought to 40°C. Then, 150 μL of a 34 mg/L solution of dithizone (chelating agent) in chloroform (extraction solvent) was added. The mixture was stirred at 1000 rpm for 3 min to form a cloudy solution, in which chloroform was dispersed as fine droplets to extract the complex cadmium dithizone. This solution was centrifuged at 3500 rpm for 1 min, and the dispersed droplets were deposited at the bottom of the tube. 60 μL of the sedimented phase was transferred to the microcuvette for determination in the spectrophotometer. The extraction procedure is schematically shown in Figure 1.

2.3. Water Samples. Two commercial drinking mineral water samples (DW1, DW2), tap water (TW), snow water (SW), river water (RW1), and irrigation channel water (RW2) were analyzed. All samples were filtered through a 0.45 μm micropore filter, and different volumes (from 0.5 to 2.5 mL) were diluted up to 10 mL with the NaOH/KCl solution.

3. Results and Discussion

3.1. Study on the Absorption Spectra. Due to its high efficiency, dithizone was selected as chelating agent for extraction and determination of cadmium by UV-Vis spectrophotometry [14]. Absorbance of the complex $(\text{Cd}(\text{HDz})_2)$ was measured in the wavelength of the maximum absorption

(516 nm for chloroform, 517 nm for carbon tetrachloride), which corresponded to the wavelength of the minimum absorption for dithizone.

3.2. Selection of Working Conditions. There are several parameters affecting the extraction process. Some of the experimental conditions were fixed according to working characteristics.

In stirring step, agitation speed and time were high enough to form the cloudy solution (1000 rpm, 3 min). In the sedimentation step, centrifugation rate and time were the minimum that allowed collecting the cloudy solution into a sedimented drop (3500 rpm, 1 min).

Other variables were univariately studied. pH was studied in the range of 4.0–13.0, obtaining better results at high levels of pH, where extraction efficiency is higher and the dithizone does not interfere in the analysis [15]. Effect of salt addition was investigated at two levels, without salt and at 10% (W/V) addition. The best results were obtained without salt addition.

The remaining considered experimental variables were studied using experimental design. Taking into account their high density, extraction capacity, and low solubility in water, chloroform and carbon tetrachloride were selected as extraction solvents [6]. Due to their different characteristics (boiling points, water solubility, and interactions with the different dispersants) efficiency of both solvents could not be compared in the same conditions. Hence, two different designs for finding the better experimental conditions for each solvent were done. Regarding the volume of extraction solvent, the minimum volume which gave manageable sedimented phase (100 μL for carbon tetrachloride and 150 μL for chloroform) was chosen.

A 2^4 full factorial design with temperature, volume and type of dispersant, and dithizone concentration was made for each extraction solvent [16]. Levels of the factors were chosen based on previous experiments. Concentration of dithizone was selected in the way that in both cases the net amount of chelating agent was the same. A summary of experimental design and its results are included in Table 1.

The levels of the nonsignificant variables were fixed at the values which gave better responses, 0.5 mL of dispersant and ethanol for carbon tetrachloride and 34 mg/L concentration of dithizone and methanol for chloroform. Temperature was fixed at the high level in both cases because a further increase of the temperature led to problems in the collection of the sedimented phase. For the same reason, when chloroform was used, the disperser solvent volume was fixed at high level. When carbon tetrachloride was used the concentration of dithizone was fixed at 154 mg/L.

Absorbance in the best conditions of both extraction solvents was compared. Carbon tetrachloride gave a slightly higher value of absorbance but not enough to compensate its higher toxicity and cost compared with those ones of chloroform. Hence, chloroform was selected for further experiments.

Taking into account the experimental design, 1.5 mL of methanol, 150 μL of a 34 mg/L solution of dithizone in chloroform, and 40°C of temperature were the chosen experimental

FIGURE 1: Extraction procedure scheme for determination of cadmium.

TABLE 1: Resume of the experimental designs' conditions and results for determination of cadmium with two extraction solvents using DLLME and UV-Vis spectrophotometry.

Factor	Low level	High level	Factor significance	Sign of effect
Carbon tetrachloride				
Temperature ($^{\circ}\text{C}$)	25	50	Significant	Positive
Volume of dispersant (mL)	0.5	1.5	Nonsignificant	Negative
Dithizone concentration (mg/L)	52	154	Significant	Positive
Type of dispersant	Ethanol	Methanol	Nonsignificant	Negative
Chloroform				
Temperature ($^{\circ}\text{C}$)	25	40	Significant	Positive
Volume of dispersant (mL)	0.5	1.5	Significant	Positive
Dithizone concentration (mg/L)	34	102	Nonsignificant	Negative
Type of dispersant	Ethanol	Methanol	Nonsignificant	Positive

Screening designs.

 2^4 full factorial designs.

Total number of runs: 32 (with duplicates, in four blocks).

conditions. Those levels, 7.5 mL of aqueous phase, pH 12.8 ± 0.2 , no salt addition, 3 min of extraction at 1000 rpm, and 1 min of centrifugation at 3500 rpm were the final working conditions.

3.3. Analytical Characteristics. The correlation coefficient ($R^2 = 0.9947$) showed a good linearity in the studied range (10–100 $\mu\text{g/L}$). Limit of detection (LOD) was calculated based on the residual standard deviation of the calibration curve [17]. The obtained value (8.5 $\mu\text{g/L}$) was little higher than some of those obtained when more sensitive techniques such as FAAS and ICP-OES are coupled to DLLME [8, 10]. Precision of the method was evaluated at two concentration levels (20 and 80 $\mu\text{g/L}$). For intraday repeatability ten measurements were carried out in the same day. For interday repeatability twelve experiments were performed in three days during two weeks. The relative standard deviation percentages (RSD) ranged from 9.0 to 13.0% for intraday repeatability and from 9.0 to 10.9% for interday repeatability. For these analyte concentrations, RSDs between 15 and 21% are acceptable [18]. Hence, the obtained results showed satisfactory precision.

Enrichment factor (EF) was calculated as the relation between the concentration of cadmium in the sedimented

phase obtained after the extraction and the initial concentration in the sample. Both concentrations were evaluated by inductively coupled plasma-mass spectroscopy (ICP-MS). EF had a value of 73, which is among the EFs obtained in the previous mentioned works [7, 8, 10].

3.4. Interferences. Due to the fact that dithizone can form complexes with other metals, interferences from other present cations in samples may occur frequently. The effect of potentially interfering ions in the developed method was studied in an 80 $\mu\text{g/L}$ cadmium solution. Tolerable limit was taken when the interfering ion/cadmium molar ratio did not cause a relative error in the signal higher than 10%. Molar ratio tolerable limits were the following: 250 for Al^{3+} , 100 for Ca^{2+} , 10 for Pb^{2+} , 1 for Mg^{2+} , Mn^{2+} , Co^{2+} , and Zn^{2+} , and 0.1 for Fe^{3+} , Ni^{2+} , and Cu^{2+} .

3.5. Application to Real Samples. No cadmium was found in the collected water samples. All of them were spiked at 40 $\mu\text{g/L}$, except for DW1 that was spiked at 20 and 80 $\mu\text{g/L}$. Each determination was made in triplicate and the results were evaluated on the basis of recovery (R, %) and repeatability (RSD, %). The results showed recoveries

ranging from 90 to 109% and RSDs between 3 and 9%. Thus, the proposed method can be successfully applied to the determination of cadmium in real water samples giving accurate and reproducible results.

4. Conclusions

A simple and inexpensive method for determination of cadmium has been developed by coupling DLLME and UV-Vis. DLLME confers some advantages since it is rapid, simple, and environmentally friendly. On its behalf, UV-Vis spectrophotometry, in spite of its lower sensitiveness compared with other techniques for determination of cadmium, grants the mentioned benefits. Coupling of these two techniques has been successfully achieved by the use of a microliter-capacity cuvette. This form of connection allows avoiding the inconveniences of previous DLLME-UV-Vis coupling ways.

The proposed method showed good precision, repeatability, and reproducibility, and it was successfully applied to real spiked samples. This method is especially suitable when the analytical laboratories have no funds for acquisition of high cost equipment. In conclusion, the proposed method could be applied to the determination of cadmium in highly contaminated water samples.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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