Preconcentration and Trace Determination of Cadmium in Spinach and Various Water Samples by Temperature-controlled Ionic Liquid Dispersive Liquid Phase Microextraction

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Abstract

A sensitive and selective method for the preconcentration and separation of sub μg L^{-1} levels of cadmium ions in aqueous solutions with high salt contents is described. The developed method is based on temperature-controlled ionic liquid dispersive liquid phase microextraction of cadmium using the 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (ionic liquid (IL)) as an extractant followed by flame atomic absorption spectrometry determination. The extraction of cadmium ions from the aqueous solution into the fine droplets of IL was performed with dithizone as the chelating agent. Some predominant factors affecting the preconcentration of cadmium ions were evaluated and optimized. Under the optimum conditions, the calibration graph was linear over the concentration range from 0.6–20.0 μg L^{-1} of cadmium and the limit of detection (LOD) was 0.2 μg L^{-1}. The enrichment factor was found to be 25. The developed method was successfully applied to the determination of cadmium in spinach and water samples.

Keywords: Temperature-controlled ionic liquid dispersive liquid phase microextraction, Flame atomic absorption spectrometry, Dithizone, Cadmium, Spinach, Water samples

1. Introduction

The pollution of natural waters by heavy metals is a great concern nowadays due to their potentially toxic effects on living organisms. Urbanization, industrial development, and heavy traffic lead to contamination of waters by heavy metals.[1–3]

Cadmium is a very toxic metal which naturally exists as a contaminant of zinc, copper and lead ores as well as phosphate rock. Cadmium is also a component of alloys, protective metal plating, dental materials, pigments, and nickel–cadmium batteries. Various industrial applications of cadmium have recently been developed and the direct production of this metal has increased. Cadmium is not regarded as essential to human life and is known to damage organs including the kidneys, liver and lungs.[4,5] According to World Health Organization (WHO) the upper permissible level of cadmium in drinking water is 3.0 μg L^{-1}.[6] Consequently, the determination of this element, at trace level, in food and water samples is of great interest from the public health and environmental point of view.[7]

In spite of great improvements in the sensitivity and selectivity of modern instrumental analysis such as ICP-MS, ICP-OES and ET-AAS, direct determination of very low concentrations of target elements by the majority of atomic spectrometric techniques is generally troublesome as a consequence of insufficient sensitivity and matrix interfering effects.[8] Thus, a chemical separation and preconcentration step is often required prior to analysis.

The most common preconcentration and separation techniques for Cd determination at trace levels are liquid–liquid extraction,[9] solid phase extraction,[10] coprecipitation,[11] and ion-exchange.[12] Liquid–liquid extraction is a very effective analytical technique for removing metallic and organometallic species as well as organic com-

pounds from liquid samples. However, this technique requires large amounts of organic solvents, some of which are harmful and contaminate the environment due to their high vapor pressure. Considering this aspect, for reducing the amounts of organic solvents, various microextraction techniques such as cloud point extraction (CPE),[13] homogeneous liquid–liquid extraction (HLLE),[14] liquid-phase microextraction (LPME)[15] and solid-phase microextraction (SPME)[16] can be used for the preconcentration of pollutants. These techniques are less time-consuming, more effective, simple, and fast and require smaller amounts of organic solvents.[17,18] Also, recently, considerable interest has been raised by using room temperature ionic liquids (ILs) as replacement solvents in the sample preparation, due to their unique chemical and physical properties such as negligible vapor pressure, non-flammability, good extractability for various organic compounds and metal ions as neutral or charged complexes, as well as tunable viscosity and miscibility with water and organic solvents.[19]

More recently, temperature-controlled ionic liquid dispersive liquid phase microextraction (TC-IL-DLPME) was developed by Zhou et al.,[20] which was initially applied for the enrichment and determination of pyrethroid pesticides. The mechanism is similar to that of DLLME, but the dispersion of extraction solvent into the water sample is realized by high temperature rather than the use of expensive and toxic organic disperser solvent which decreases the extraction efficiency to some extent. It is based on the temperature change that permit ILs to completely disperse in the aqueous phase and increase the mass transfer of the target analytes into the IL phase. Due to the environment friendly behavior and good extraction capability of ILs, and the avoidance of disperser solvent, TC-IL-LPME has many benefits such as simplicity, environmental friendliness and high extraction efficiency. This technique has been applied to the determination of trace organic pollutants and metal ions in environmental samples.[21,22]

In this paper, a new, sensitive and highly selective preconcentration method (TC-IL-DLPME) is reported for the determination of cadmium by using dithizone (DTZ) as chelating agent. Cadmium determination by flame atomic absorption spectrometry (FAAS) can be performed with appreciable sensitivity and accuracy using an air–acetylene flame. Due to its reliability and freedom from interferences it is still the recommended approach in some official analytical methods.[23] The proposed method overcame the demerits of the use of relatively large amounts of toxic solvents in DLLME. Various factors affecting extraction efficiency (such as pH, volume of IL, temperature, salt addition, extraction time and DTZ concentration) were evaluated and optimized. Under the optimum conditions, this method was used for cadmium determination in spinach and various water samples with satisfactory results.

2. Experimental

2. 1. Instrumentation

A SensAA (GBC, Australia) atomic absorption spectrometer equipped with deuterium background correction and cadmium hollow cathode lamp was used for the determination of cadmium at a wavelength of 228.8 nm. A centrifuge model Hettich, EBA 20 was used. The pH-meter model 827 from Metrohm (Herisau, Switzerland) with combined glass electrode was used for the pH measurements.

2. 2. Reagents and Solutions

All chemicals were of analytical reagent grade. Dithizone (DTZ), Cd $(NO_3)_2 \cdot 4H_2O$, hydrochloric acid, nitric acid, sodium hydroxide, ethanol, methanol, acetone, acetonitrile, and sodium nitrate were obtained from Merck (Darmstadt, Germany). 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (99%) was provided by Io-li-tec (Germany). Stock standard solution (1 g L^{-1}) of cadmium was prepared using Cd $(NO_3)_2 \cdot 4H_2O$ in 0.5 mol L^{-1} HNO_3. The working standard solutions (100 and 10 μg L^{-1}) were prepared by appropriate stepwise dilution of the stock standard solution with bidistilled water (BDW). A solution of 10^{-3} mol L^{-1} DTZ was prepared by dissolving an appropriate amount of DTZ in methanol. All glassware was rinsed with BDW, decontaminated for at least 24 h in 10 % (v/v) nitric acid solution and rinsed again five times with BDW.

2. 3. Extraction Procedure

25 mL of 10 μg L^{-1} standard solution containing cadmium, 0.6 mol L^{-1} ammonia buffer (pH = 9) and 6 × 10^{-4} mol L^{-1} DTZ solution was placed in a screw cap glass conical tube and 50 μL IL was added. Then, the conical tube was heated in a water bath at 60 °C for 5 min. The IL completely dissolved in the solution under these conditions. The tube was thereafter cooled on an ice bath for 5 min. Then, the solution was centrifuged for 5 min at 5000 rpm. The sedimented IL was made up to 1 mL by adding a mixture of 0.1 mol L^{-1} HNO_3 in methanol. The final solution was injected manually into FAAS. Triplicate extractions were performed for all experiments, and the average of these results was reported in figures or tables and optimal conditions were applied to extract and detect cadmium in spinach and various water samples.

2. 4. The Preparation of Real Samples

Spinach sample was purchased from local supermarket at Sari in Iran. First, spinach sample was cleaned with tap water and DDW. Then, this sample was dried at 110 °C and was ground to reduce particle size and then thoroughly mixed to homogenize. Mass of 500 mg of spi-

nach was transferred into 250 mL beaker and 5 mL of 0.5 mol L^{-1} nitric acid was added to moisten the sample thoroughly. This was followed by adding 10 mL of concentrated nitric acid and heating on a hot plate (130 °C) for 3 h. After cooling to room temperature, 5 mL of concentrated perchloric acid was added drop wise. The beaker was heated gently until completion of sample decomposition. This was left to cool down and then was transferred into a 100 mL volumetric flask and the solution was filled to the mark with 0.1 mol L^{-1} nitric acid.[24]

All of the collected water samples (tap, mineral, river and sea water) were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm and after acidification to 1% with concentrated nitric acid, were stored in polyethylene bottles.

3. Results and Discussion

3. 1. The Effect of pH

Separation of metal ions by temperature-controlled ionic liquid dispersive liquid phase microextraction involves a complex formation with sufficient hydrophobicity to be extracted into the small volume of the IL-phase. pH plays a unique role on the metal-chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of cadmium from water samples was studied in the range of 1–11 by using HNO$_3$ and NaOH. Since the recovery is nearly constant in the pH range of 8–10 (Figure 1). Therefore, pH 9 was chosen for the subsequent experiments, the ammonia buffer was used for pH adjustment.
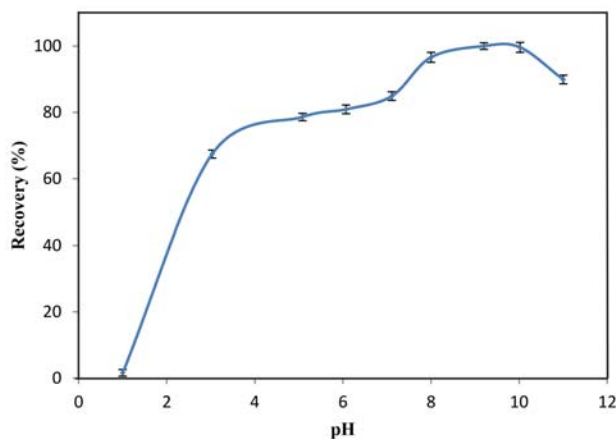
Figure 1. Effect of pH on the recovery of cadmium. Extraction conditions: 6×10^{-4} mol L^{-1} DTZ; 50 μL IL; temperature = 60 °C

3. 2. The Effect of DTZ Concentration

The influence of DTZ concentration was also evaluated in the range from $2.0 \times 10^{-5} - 1.2 \times 10^{-3}$ mol L^{-1} (Figure 2). It was observed that increasing of DTZ con-
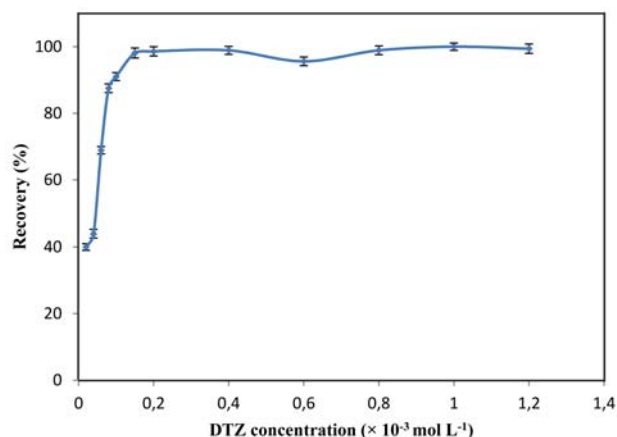

Figure 2. Effect of DTZ concentration on the recovery of cadmium. Extraction conditions: pH 9; 50 μL IL; temperature = 60 °C

centration, up to 1.5×10^{-4} mol L^{-1} results in higher recovery (cadmium extraction), which is not further improved by increasing of DTZ concentration. Lower extraction recovery at a concentration below 1.5×10^{-4} mol L^{-1} is due to incomplete formation of the complex. Thus, 6.0×10^{-4} mol L^{-1} DTZ was chosen as the optimum to account for other extractable species.

3. 3. The Effect of the Volume of IL

The volume of the extraction solvent was a crucial parameter that seriously influenced the extraction performance in liquid phase microextraction. Theoretically, larger volumes of exaction solvent resulted in higher extraction efficiency. Developing new technologies for improving the extraction performance has been an essential research field in recent years. In the present study, the volume of extraction solvent may be enlarged according to the needed enrichment. In the light of these points, the extraction efficiency of different volumes (20 to 150 μL) of ionic liquid was investigated, with a spiked concentration of 10 μg L^{-1} (Figure 3). It is clear that at volumes of IL
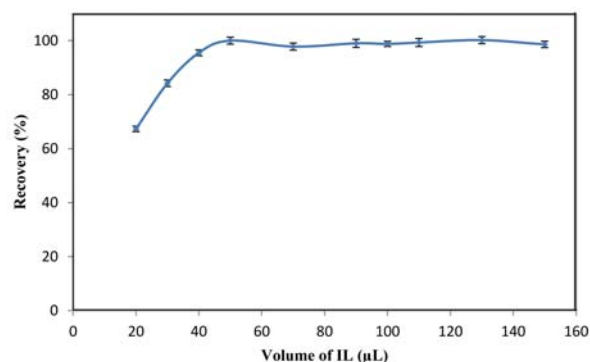
Figure 3. Effect of the volume of IL on the recovery of cadmium. Extraction conditions: pH 9; 6×10^{-4} mol L^{-1} DTZ; temperature = 60 °C
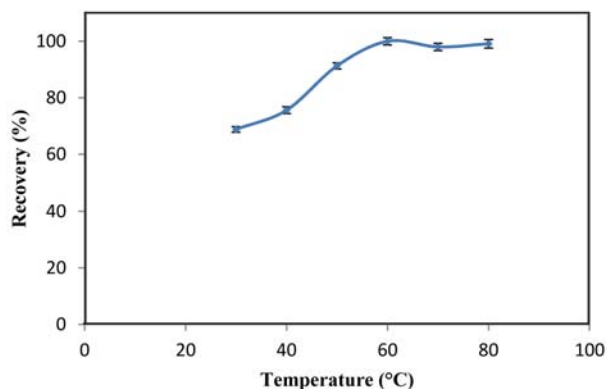
Figure 4. Effect of temperature on the recovery of cadmium. Extraction conditions: pH 9; 6×10^{-4} mol L^{-1} DTZ; 50 μL IL

lower than 50 μL the recovery is low. Hence 50 μL was selected for use in the subsequent experiments.

3. 4. The Effect of Temperature

Temperature is the driving force for the complete dispersion of IL into the aqueous solution and plays an important role, whether the achieved sensitivity of the developed method is satisfactory or not (Figure 4). In our case, the highest extraction efficiency was achieved at 60 °C and was not affected by further temperature increase. Consequently, 60 °C was chosen as the optimal temperature for extraction.

3. 5. The Effect of Extraction Time

In this experiment, extraction time was defined as the time interval between the placement of the solution containing the completely dissolved IL into ice water bath and centrifugation. The effect of the extraction time was examined in the range of 2–15 min. Experiments demonstrated that when 50 μL IL was used for extracting cadmium in 25 mL aqueous sample solution, the recovery after 4 min was quantitative. Therefore, 5 min was applied to all experiments as the optimum extraction time.

3. 6. The Effects of Centrifuge Conditions

Centrifugation is applied for separating IL from the aqueous solution in the proposed method. In order to attain the best phase separation, the centrifugation rate and time was optimized. The results showed that for the optimum conditions, 5000 rpm and 5 min were the optimum points.

3. 7. The Effect of Salt Addition

$NaNO_3$ was chosen to study the salt effect. It was observed that phase separation occurred successfully up to 20 % $NaNO_3$ (Figure 5). Consequently, it was noticed that temperature-controlled ionic liquid dispersive liquid phase microextraction is a powerful sample preparation technique for salinity solutions.
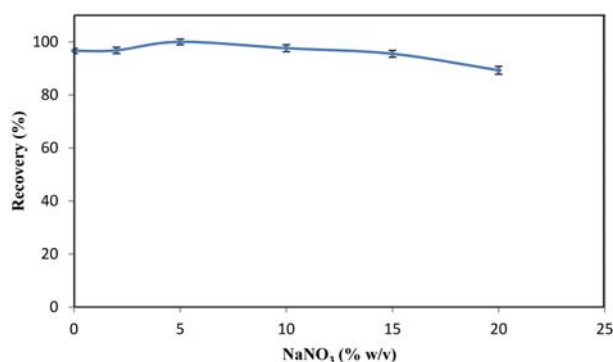
Figure 5. Effect of salt addition on the recovery of cadmium. Extraction conditions: pH 9; 6×10^{-4} mol L^{-1} DTZ; 50 μL IL; temperature = 60 °C

3. 8. Selectivity of the Method

In order to investigate the selectivity of the developed microextraction method for the determination of cadmium, the effect of coexisting ions on the recovery of cadmium complex was evaluated. For this purpose, 25 mL of sample solutions containing 10 μg L^{-1} of cadmium and different quantities of coexisting ions were treated in accordance with the recommended procedure. An ion was considered to be interfering when it caused a variation greater than ± 5% in the absorption of the sample. The results (Table 1) indicate that cadmium recoveries are almost quantitative in the presence of interfering ions.

Table 1: Effect of interfering ions on the extraction of cadmium.

Interfering ions	Ion/Cd (II) ratio (w/w)	Recovery (%)
K^+, Na^+, Li^+ , Ca^{2+}, Mg^{2+}, Br^-,F^-, I^-, NO_3^- PO_4^{3-}, Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Ba^{2+}	1000	100
Pb^{2+}, Zn^{2+}, Cr^{3+}, Cr (VI), CO_3^{2-}, HCO_3^-	125	99
Cu^{2+}	50	100
Ag^+	30	98

3. 9. Figures of Merit

The analytical performance of temperature-controlled ionic liquid dispersive liquid phase microextraction coupled with FAAS for the preconcentration and determination of cadmium was systematically investigated under optimized experimental conditions. The results exhibited that there was an excellent linear correlation between the absorbance and the concentration of cadmium from 0.6 to 20 μg L^{-1} and a good correlation coefficient of 0.9983. The precision of this method was 1.5% (RSD, n = 10) at the spiked concentration of 10 μgL^{-1} and the extraction recovery of cadmium 99 % was obtained. The LOD calculated as the concentration corresponding to three times the standard deviation of 10 runs of the blank samples of the proposed method was 0.2 μg L^{-1} of cadmium. The preconcentration factor was 25 for 25 mL sample solution.

3. 10. Analysis of Real Samples

During the present investigation, matrix effects on the extraction were also evaluated by investigating the applicability of the proposed method in determining cadmium concentration in spinach as well as river, tap, mineral and seawater samples. The water samples were extracted using the proposed method and analyzed by FAAS. These results (Table 2) show that water samples were free of cadmium contamination. These samples were spiked with cadmium at different concentration levels to assess matrix effects. As can be seen from Table 2, the spiked recoveries were very good in the range of 96.0–102.0%. The results of the determination of cadmium in spinach sample (Table 3) indicate that cadmium concentration was 1.60 μg g^{-1}. Relative recoveries of cadmium from spinach sample at spiking levels of 1.00 and 2.00 μg g^{-1} were 102.0 and 101.5% respectively. These results demonstrate that these water and spinach matrices, in our present context, had little effect on the proposed method.

4. Conclusions

The main difficulty in the determination of cadmium in real samples is its low concentration level. This study demonstrates the successful application of the temperature-controlled ionic liquid dispersive liquid phase microextraction method whereby separation and preconcentration of ng mL^{-1} levels of cadmium in spinach and several water samples can be achieved. Environmental friendliness, simplicity of operation, sensitivity, rapidity, minimum use of toxic organic solvent and selectivity are the advantages of the present method. The results of the analysis of real samples indicate that the proposed method is excellent and would be very competitive in routine analysis of cadmium.

5. Acknowledgment

Table 2: Determination of cadmium in water samples.

| Sample | cadmium (μg L^{-1}) | | | Recovery (%) |
	Added	Found	RSD (%) (n = 3)	
Tap water	0.0	n.d.[a]	–	–
(Drinking water system of Sari, Iran)	5.0	4.9	1.3	98.0
	15.0	14.9	1.5	99.3
Mineral water	0.0	n.d.	–	–
(Surprise mineral water, Iran)	5.0	4.9	1.4	98.0
	15.0	14.7	1.3	98.0
River water	0.0	n.d.	–	–
(Chalous river, Chalous, Iran)	5.0	4.8	1.5	96.0
	15.0	15.1	1.5	100.7
Sea water	0.0	n.d.	–	–
(Caspian sea water, Chalous, Iran)	5.0	5.1	1.7	102.0
	15.0	15.2	1.6	101.3

[a] Not detected

Table 3: Determination of cadmium in spinach sample.

| Sample | cadmium (μg L^{-1}) | | | Recovery (%) |
	Added	Found	RSD (%) (n = 3)	
Spinach sample	0.00	1.60	–	–
	1.00	2.62 (1.7)[a]	1.7	102.0
	2.00	3.63 (1.6)	1.6	101.5

6. References

1. E. Luiz Silva, P. Santos Roldan, M. Fernanda Gine, *J. Hazard. Mater.*, **2009**, *171*, 1133–1138.
2. R. Lertlapwasin, N. Bhawawet, A. Imyim, S. Fuangswasdi, *Sep. Purif. Technol.*, **2010**, *72*, 70–76.
3. M. Ghaedi, K. Niknam, K. Taheri, H. Hossainian, M. Soylak, *Food Chem. Toxicol.*, **2010**, *48*, 891–897.
4. H. C. Rezende, C. C. Nascentes, N. M. M. Coelho, *Microchem. J.*, **2011**, *97*, 118–121.
5. N. Pourreza, K. Ghanemi, *J. Hazard. Mater.*, **2010**, *178*, 566–571.
6. Guidelines for Drinking-water Quality, Volume 1, Recommendations, 3nd edition Geneva, *World Health Organization*, **2008**.
7. M. Shirani Bidabadi, S. Dadfarnia, A. M. Haji Shabani, *J. Hazard. Mater.*, **2009**, *166*, 291–296.
8. N. H. Bings, A. Bogaerts, J. A. C. Broekaert, *Anal. Chem.*, **2010**, *82*, 4653–4681.
9. E. Zeini Jahromi, A. Bidari, Y. Assadi, M. R. Milani Hosseini, M. R. Jamali, *Anal. Chim. Acta*, **2007**, *585*, 305–311.
10. M. Soylak, I. Narin, *Chem. Anal.*, **2005**, *50*, 705–715.
11. S. Tokalioglu, T. Oymak, S. Kartal, *Microchim. Acta*, **2007**, *159*, 133–139.
12. E. Pehlivan, T. Altun, *J. Hazard. Mater.,* **2007**, *140,* 299–307.
13. J. L. Manzoori, Gh. Karim-Nezhad, *Anal. Chim. Acta*, **2004**, *521*, 173–177.
14. A. N. Anthemidis, K. I. G. Ioannou, *Talanta,* **2009,** *80*, 413–421.
15. T. S. Ho, J. L. E. Reubsaet, H. S. Anthonsen, S. Pedersen-Bjergaard, K. E. Rasmussen, *J. Chromatogr. A,* **2005**, *1072*, 29–36.
16. C. L. Arthur, J. Pawliszyn, *Anal. Chem.,* **1990**, *62*, 2145–2148.
17. D. E. Raynie, *Anal. Chem.*, **2004**, *76,* 4659–4664.
18. C. Wang, C. R. Li, X. H. Zang., D. D. Han, Z. M. Liu, Z. Wang, *J. Chromatogr. A*, **2007**, *1143*, 270–275.
19. X. Han, D. W. Armstrong, *Acc. Chem. Res.,* **2007**, *40*, 1079–1086.
20. Q. X. Zhou, H. H. Bai, G. H. Xie, J. P. Xiao, *J. Chromatogr. A,* **2008**, *1177*, 43–49.
21. Q. Zhou, H. Bai, G. Xie, J. Xiao, *J. Chromatogr. A*, **2008**, *1188*, 148–153.
22. F. Shah, T. G. Kazi, Naeemullah, H. I. Afridi, M. Soylak, *Microchemical J.*, **2012**, *101*, 5–10.
23. Official Methods of Analysis (AOAC), 17th ed., Sec. 999.17, Arlington, VA, **2002**.
24. S. Baytak, *Acta. Chim. Slov.*, **2007**, *54*, 385–391.

Povzetek

Za določanje sledov kadmija v vodnih raztopinah z visoko vsebnostjo soli smo razvili občutljivo in selektivno metodo predkoncentracije in ločevanja. Metoda temelji na temperaturno kontrolirani disperzivni mikroekstrakciji s tekočo fazo (TC-IL-DLPME) v kombinaciji s plamensko atomsko absorpcijsko spektrometrijo. Za ekstrakcijo smo uporabili ionsko tekočino (IL) 1-heksil-3-metilimidazol bis (trifluorometilsulfonil) imid in ditizon kot kelator. Proučevali smo vpliv parametrov, ki vplivajo na predkoncentracijo kadmija in jih optimizirali. Pri optimalnih pogojih je bila umeritvena krivulja linearna v območju 0,6–20,0 µg L^{-1} kadmija, meja zaznave pa 0,2 µg L^{-1}, faktor obogatitve pa 25. Razvito metodo smo uspešno uporabili za določanje kadmija v špinači in v vodnih vzorcih.