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Ligandless-solidified floating organic drop microextraction method for the preconcentration of trace amount of cadmium in water samples

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A B S T R A C T

In this article, a new ligandless solidified floating organic drop microextraction (LL-SFODME) method has been developed for preconcentration of trace amount of cadmium as a prior step to its determination by flow injection-flame atomic absorption spectrometry (FI-FAAS). The methodology is based on the SFODME of cadmium with 1-dodecanol in the absence of chelating agent. Several factors affecting the microextraction efficiency, such as, pH, sodium dodecylbenzenesulfonate (SDBS) concentration, extraction time, stirring rate and temperature were investigated and optimized. Under optimized experimental conditions an enhancement factor of 205 was obtained for 100 mL of sample solution. The calibration graph was linear in the range of 1.0–25.0 ng mL^{-1}, the limit of detection (3*s*) was 0.21 ng mL^{-1} and the limit of quantification (10*s*) was 0.62 ng mL^{-1}. The relative standard deviation (RSD) for 10 replicate measurements of 10 ng mL^{-1} cadmium was 4.7%. The developed method was successfully applied to the extraction and determination of cadmium in standard and several water samples and satisfactory results were obtained.

1. Introduction

Heavy metals occur naturally in the environment and are found in varying levels in all ground and surface waters [1]. Heavy metal pollution is one of the five major types of toxic pollutants commonly present in surface waters [2,3]. However, some heavy metals are essential elements for the normal metabolism of organisms, while others are nonessential and play no significant biological roles [4]. Cadmium is a nonessential heavy metal, it has a cumulative polluting effect and could cause toxicity to aquatic organisms even in minute concentrations [5]. Cd is widely used in metallurgical alloying, the manufacture of batteries and paints, ceramics, metal plating, photograph development, pigment works, textile printing industries, [6–9] and is commonly found in fertilizers. Cadmium is not biodegradable [10,11] and is likely to cause a number of acute and chronic disorders. Long-term effects from cadmium poisoning includes kidney damage and changes to the constitution of the bone, liver, and blood. Short-term effects include nausea, vomiting, diarrhea, and cramps. So minimizing production of hazardous waste and heavy metals became one of the most important environmental challenges that the world faces today [12]. So, maximum tolerable level for Cd(II) in drinking water has been strictly regulated. Recommended cadmium concentration in drinking water by The World Health Organization (WHO) is smaller than 0.005 mg L^{-1}.

Therefore, it is necessary from an analytical point of view to develop sensitive and economical methods for the determination of trace amount of cadmium. Because of its experimental rapidity, simplicity, and wide application, flame atomic absorption spectrometry is the one of the most widely applied methods. But the direct determination of metal ions at trace levels with FAAS is limited not only due to insufficient sensitivity, but also by matrix interference. Despite the selectivity and sensitivity of analytical techniques, there is a pivotal need for the preconcentration and/or separation of trace elements before their analysis. Recently, a powerful microextraction technique, SFODME, has been used to effectively enhance the sensitivity and selectivity of atomic absorption spectrometry [13–15]. In this technique, a free microdrop of the organic solvent which has a melting point near room temperature in the range of 10–30 °C is transferred to the surface of an aqueous sample, while being agitated by a stirring bar in the bulk of the solution. Under the proper stirring conditions, the suspended microdrop can remain in the top-center position of the aqueous sample. After the completion of the extraction, the sample vial is cooled and the solidified microdrop is transferred into a conical vial, where it melts immediately. Finally, the analytes can be determined in the extractant. There are several reports about the application of SFODME for the analysis of heavy metal ions [14–24].

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However, until to present, all of these SFODME applications to preconcentrate the metals are based on the formation of hydrophobic chelates or ion pairs in the extracting solvent choosing a specific chelating agent. It may be useful to emphasize that using less number of reagent increases the ease of the procedure. Starting from this idea, a new LL-SFODME method has been proposed. In this method, quantitative extraction of Cd in the absence of a chelating agent is demonstrated. In the literature, there are a few studies on ligandless liquid–liquid microextraction for the preconcentration and determination of metal ions [25–29].

2. Experimental

2.1. Instrumentation

A PerkinElmer Model AAnalyst 800 Atomic Absorption Spectrophotometer equipped with deuterium background correction and air–acetylene burner was used for Cd(II) measurements in standard and sample solutions. Cadmium hollow cathode lamp was used as the radiation source. The most sensitive wavelength was 228.8 nm and lamp current was 4 mA and slit width was 0.7 nm for the determination of the analyte. All of the absorbance measurements were carried out in air and acetylene flame at flow rates of 17 and 2.0 L min^{-1}, respectively. The nebulizer flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal by aspirating a solution containing the analyte in methanol. A Fisher Scientific Accumet Model 15 pH meter was used to measure pH values. A Variomag magnetic stirrer from Thermo Fisher Scientific Inc. (Waltham, MA, USA) and an 8 mm × 1.5 mm PTFE coated stirring bar were used to stir the solutions. A PerkinElmer model flow injection system, FIAS 400, was used for sample loading and carrying. FIAS 400 system comprises two peristaltic pumps, a two-positional and five-port valve and a 200 μL sample loop.

2.2. Reagents and solutions

All chemicals used were of analytical reagent grade. All solutions were prepared with deionized water (18.1 MΩ cm) obtained from a Barnstead, Nanopure Diamond purification system. Stock solution for cadmium ions was prepared from appropriate amounts of the $Cd(NO_3)_2·4H_2O$ (Merck, Darmstadt, Germany) as 1000 mg L^{-1} in deionized water, and diluted daily for obtaining working solutions prior to use. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with deionized water. Extraction solvent, 1-dodecanol, was purchased from Merck and sodium dodecylbenzenesulfonate (SDBS) was supplied by Sigma–Aldrich. A solution of 5 mmol L^{-1} SDBS was prepared by dissolving proper amount of SDBS in 1-dodecanol. A buffer solution of pH 4.5 was prepared by using sodium acetate (Merck) and acetic acid (Merck) at appropriate concentrations. Methanol (Merck) was used for dilution and elution. Laboratory glassware were kept overnight in 10% nitric acid solution. Before use, the glassware were rinsed with deionized water and dried in dust free environment. The following certified reference materials were used for method validation: surface water (SPS-SW2) and fortified water (TMDA-51.3) samples purchased from LGC (Teddington, UK) and National Water Research Institute (Ontario, Canada), respectively.

2.3. Procedure

For LL-SFODME, aliquots of 100 mL containing sample or standard solution of cadmium was prepared and placed in 100 mL beaker containing a stirrer bar. After pH adjustment with 2 mL of pH: 4.5 acetate buffer, 100 μL of 5 mmol L^{-1} SDBS in 1-dodecanol were added. Then, magnetic stirrer was turned on and the solution was stirred for 10 min at 300 rpm. Under the proper stirring conditions, the organic solvent droplet floating on the surface of the aqueous solution due to its lower density than water was obtained. During the stirring step Cd(II) ions were extracted into 1-dodecanol. After extraction time was over, the beaker was placed in the refrigerator (4 °C) in order to solidify the organic solvent. Because melting point of 1-dodecanol is close to room temperature (24 °C) the solidified drop was obtained in 10 min. Then the solidified drop was immediately transferred to a conical vial by a mini spatula and was diluted to 300 μL with methanol. After this step, 200 μL sample loop of FI 400 system was filled with the diluted organic phase in fill position of valve. Then the valve was switched to the inject position and the solution was directly introduced into the FAAS nebulizer in the presence of methanol as carrier solution.

3. Results and discussion

In this study, combination of LL-SFODME with FI-FAAS was developed for the determination of trace amounts of cadmium. 1-Dodecanol was selected as extraction solvent, because of its low volatility, low water solubility, melting point close to room temperature and low cost. One of the greatest limitations of SFODME is the lower extraction efficiencies of hydrophilic inorganic species. To overcome this limitation, at pH around 4.5, an anionic surfactant, SDBS, has been added to the extraction solvent. The surfactant molecules aggregate and form the spherical micelles when the surfactant concentration is higher than its critical micellar concentration (cmc). Micelles with negative charges cause the cations to bind to or adsorb onto the micelle interface. Because of the strong tendency of the metal ions to be attracted by the micelle surface, a large fraction of the metal ions can be extracted by micelles [30,31]. The anionic micelles, which are negatively charged, can bind to cadmium ions, which are positively charged. So, Cd(II) ions gained hydrophobic character by using SDBS and can be extracted into 1-dodecanol phase. Thereby, a high extraction efficiency factor was reached. In order to obtain maximum extraction efficiency for cadmium ions, some analytical parameters such as pH, extraction solvent and anionic surfactant concentrations, stirring rate and time, temperature and interfering ions were examined.

3.1. Effect of pH

As preconcentration effectiveness of an analyte with a given SFODME method may vary depending on the pH of the analyte solution, finding the proper pH is one of the most crucial issues in the optimization of working conditions. For this reason, a set of Cd(II) solutions (10 μg L^{-1}) were prepared within the pH range of 3–9 and subjected to the LL-SFODME procedure. pH values of the solutions were adjusted by using 2 mL of appropriate buffer solutions. The influence of the solution pH on analytical signal was presented in Fig. 1. This figure indicates that the quantitative extraction of Cd(II) ions were observed within a broad pH range of 3.5–6.0, therefore for further studies all samples were buffered to a pH value 4.5.

3.2. Effect of SDBS concentration

In LL-SFODME of Cd(II) ions, the anionic surfactants have been shown to be very effective since their opposite charge with metal ions. However, the concentrations of surfactant greater than their cmc must be used for effective extraction. Cmc for SDBS is 2.9 mmol L^{-1} [32]. The effect of SDBS concentration on analytical signals were evaluated in the range of 0–20 mmol L^{-1}. The results were given in Fig. 1 and showed that the absorbance values increased with the increase in SDBS concentration up to 3 mmol L^{-1}

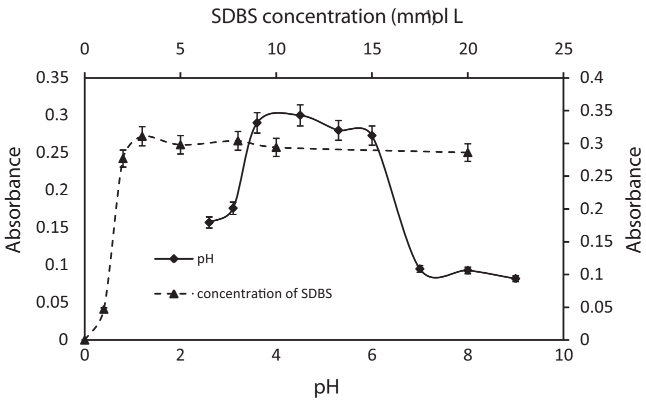

Fig. 1. Effect of pH and SDBS concentration on the extraction efficiency. Conditions: pH, 4.5; (for SDBS concentration optimization); SDBS concentration, 5 mmol L^{-1} (for pH optimization); organic solvent volume, 100 μL; sample volume, 100 mL containing 10 ng mL^{-1} of cadmium; extraction time, 10 min; stirring rate, 300 rpm; temperature, room temperature.

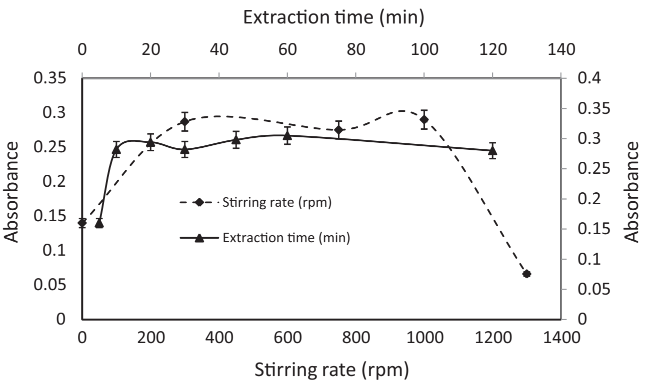

Fig. 2. Effect of extraction time and stirring rate on the extraction efficiency. Conditions: pH, 4.5; SDBS concentration, 5 mmol L^{-1}; organic solvent volume, 100 μL; sample volume, 100 mL containing 10 ng mL^{-1} of cadmium; temperature, room temperature.

and then remained constant up to 20 mmol L^{-1}. So, a 5 mmol L^{-1} SDBS concentration was chosen for subsequent experiments.

3.3. *Effect of extraction solvent volume*

In all extraction techniques extracting solvent volume is one of the essential factors which influence the extraction efficiency. The rate of the analyte transport into the solvent microdrop is directly related to the interfacial area between the aqueous phase and extracting phase and inversely related to the extracting phase volume [33,34]. So, by increasing the drop volume, interfacial area and also extraction efficiency is enhanced. By further increase in the drop volume, the effect of the solvent volume is predominated and extraction efficiency is decreased. To examine the effect of extraction solvent volume, different volumes of 1-dodecanol in the range of 10–200 μL were used in the extraction procedure. The results showed that absorbance of the analyte increased with the increase of 1-dodecanol volume in the range of 10–75 μL, and then remained constant in the range of 75–150 μL and for 1-dodecanol volume greater than 150 μL, the extraction efficiency slightly decreased because of insufficient dilution of solid drop by ethanol to final volume. So, a volume of 100 μL 1-dodecanol was selected as optimum for further experiment.

3.4. *Effect of extraction time*

The extraction of analytes at a given time is dependent on the mass transfer of analyte from aqueous samples to the organic solvent drop. So, extraction time is an important parameter that may have significant effects on extraction efficiency. The effect of extraction time on extraction efficiency was studied within a range of 5–120 min under the constant experimental conditions. The results given in Fig. 2 showed that absorbance values increased by the increase in time up to 10 min and then remained constant. Thus the extraction time of 10 min was selected for further experiments.

3.5. *Effect of stirring rate*

For all liquid phase microextraction techniques, stirring of sample is an important parameter that enhances the mass transfer between the aqueous solution and the extraction solvent. Stirring of the sample reduces the time required to reach the equilibrium condition between the sample solution and the droplet by enhancing the diffusion of the analytes towards the organic phase. Furthermore, convection is induced in the organic drop by the stirring of the aqueous phase. On the other hand very high stirring rate can cause a decrease in extraction efficiency because of spattering and damaging of the droplet. For this purpose, experiments were carried out at stirring rate between 0 and 1300 rpm. From the results given in Fig. 2 it can be seen that, the analytical signal increased with increasing stirring rate from 0 to 300 rpm, and then remained constant with further increase in stirring rate up to 1000 rpm. Higher stirring rates (>1000 rpm) caused a decrease in absorbance. Thus, 300 rpm was selected as the optimum stirring rate.

3.6. *Effect of temperature*

Temperature can also affect process by influencing the extraction efficiency. The effect of extraction temperature was studied over the temperatures ranging from 20 °C to 60 °C. In the whole temperature range from 20 °C to 40 °C, the extraction efficiency was found as constant. But further increase in temperature caused a decrease in analytical signal, which might be due to increase in solubility of organic phase at higher temperatures. Therefore, the extractions were carried out at room temperature (25 ± 2 °C) for the convenience.

3.7. *Effect of salt*

For investigation of the influence of ionic strength on performance of SFODME, various experiments were performed by adding varying NaCl amounts from 0% to 5% (w/v) while other experimental conditions were kept constant. According to the obtained experimental results, salt addition has no significant effect on extraction recovery. Therefore, all the extraction experiments were carried out without adding a salt.

3.8. *Effect of other ions*

In order to evaluate the possibility of selective recovery of analyte ions in the presence of foreign ions, the procedure has been performed with 100 mL of 10 ng mL^{-1} of cadmium solution containing concomitant ions at different concentrations. The tolerance limit was defined as the concentration of added ion that caused less than ±5% relative error in the determination of Cd(II). The maximum tolerance limits of the investigated cations and anions are given in Table 1. As it is seen from the table, large numbers of ions used have no considerable effect on the determination of ultra-trace cadmium in water samples.

Table 1
Tolerance limits of interfering ions in the determination of 10 ng mL^{-1} cadmium.

Ion	Added as	[Cadmium]/[interferent]	Ion	Added as	[Cadmium]/[interferent]
K^+	KCl	>1/5000	Al^{3+}	$Al(NO_3)_3$	1/500
Na^+	NaCl	>1/5000	Fe^{3+}	$Fe(NO_3)_3$	1/500
Zn^{2+}	$Zn(NO_3)_2$	1/2000	Cr^{3+}	$Cr(NO_3)_3$	1/1000
Ca^{2+}	$CaCO_3$	>1/5000	Sr^{2+}	$Sr(NO_3)_2$	1/1500
Cu^{2+}	$Cu(NO_3)_2$	1/1000	As^{3+}	As_2O_3	1/1500
Pb^{2+}	$Pb(NO_3)_2$	1/1000	SCN^-	NH_4SCN	1/1000
Mn^{2+}	$Mn(NO_3)_2$	1/2000	NO_3^-	KNO_3	1/5000
Ni^{2+}	$Ni(NO_3)_2$	1/2000	Cl^-	NaCl	>1/5000
Mg^{2+}	$MgSO_4$	1/2000	CH_3COO^-	NH_4CH_3COO	1/2000
Hg^{2+}	$HgCl_2$	1/2000	SO_4^{2-}	$MgSO_4$	1/2000
Co^{2+}	$Co(NO_3)_2$	1/2000	PO_4^{3-}	$(NH_4)_3PO_4$	1/2000

Table 2
Optimum conditions for LL-SFODME of cadmium ions.

Optimum conditions for LL-SFODME of Cd	Value
Extraction solvent	1-Dodecanol
Diluent/carrier	Ethanol
pH	4.5
Complexing agent	None
SDBS concentration (mmol L^{-1})	5
Extraction time (min)	10
Stirring rate (rpm)	300
Sample volume (mL)	100
Extracted phase volume (mL)	0.300
Extraction temperature (°C)	Room temperature

Table 3
Analytical characteristics of the method.

Parameter	Analytical feature
Enhancement factor	205
Linear range, ng mL^{-1}	1.0–25.0
Limit of detection, ng mL^{-1} (3*s*)	0.21
Limit of quantification, ng mL^{-1} (10*s*)	0.62
Precision (10 ng mL^{-1}, $n = 10$) RSD (%)	4.7

A summary of optimum condition values obtained for SFODME for preconcentration and determination of cadmium is presented in Table 2.

3.9. *Analytical performance of the method*

Calibration graphs obtained by using the optimized conditions for the SFODME procedure were linear in the range of 1.0–25.0 ng mL^{-1} cadmium. The regression equation for cadmium determination was $A = 2.07 \times 10^{-2}C + 3.50 \times 10^{-2}$, where A is the absorbance and C is the metal ion concentration in solution (ng mL^{-1}). The correlation coefficient of the calibration curve equation was higher than 0.99. The equation obtained by direct aspiration in FAAS without the preconcentration procedure was $A = 1.01 \times 10^{-4}C + 1.63 \times 10^{-2}$ ($R^2 = 0.99$); linear range between 250–4000 ng mL^{-1}. The enhancement factor calculated as the ratio of the slope of calibration curve of the analytes after preconcentration to that of prior preconcentration was found as 205.

The limit of detection (LOD), defined as the concentration equivalent to three times the standard deviation (3 s) of 10 measurements of the blank was found as 0.21 ng mL^{-1}. The limit of quantification (LOQ) is the lowest level of analyte that can be accurately and precisely measured. LOQ, defined as ten times the standard deviation (10 s) of 10 measurements was found as 0.62 ng mL^{-1}. The relative standard deviation (RSD) was found as ±4.7% ($n = 10$) for 10 ng mL^{-1} cadmium. Table 3 gives the summary of analytical features of the method.

Table 4
Determination of cadmium in certified reference materials ($n = 3$).

Sample	Certified (μg L^{-1})	Found (μg L^{-1})	Recovery %
TMDA-51.3	25.8	25.1 ± 0.3	97.3
SPS-SW2	2.50 ± 0.02	2.46 ± 0.4	98.4

Table 5
Determination of cadmium in several water samples ($n = 3$).

Sample	Added (μg L^{-1})	Found (μg L^{-1})	Recovery %
Tap water	0	N.D.[a]	–
	5.0	4.72 ± 0.43	94.4
	10.0	9.57 ± 0.81	95.7
Spring water	0	N.D.	–
	5.0	4.85 ± 0.72	97.0
	10.0	9.75 ± 1.15	97.5
Mineral water	0	N.D.	–
	5.0	4.90 ± 0.67	98.0
	10.0	9.60 ± 1.09	96.0
Izmit Bay	0	2.21 ± 0.56	–
	5.0	7.08 ± 0.77	98.2
	10.0	11.78 ± 0.89	96.5

[a] N.D.: Not detected

3.10. *Accuracy of the method*

To demonstrate the performance of the proposed method, recovery experiments were carried out by certified reference materials. TMDA-51.3 (fortified water) and SPS-SW2 (surface water) were used for method validation. Results are the average of three replicates. As Table 4 indicates there is a good agreement between the obtained results and the known values. The recoveries indicate that the proposed system was successful for the determination of cadmium.

3.11. *Analysis of real samples*

The recovery experiments were carried out by spiking different water samples in order to validate the method. For this purpose, different amounts of cadmium were added to 100 mL of tap (Ankara, Turkey), spring, mineral and Izmit Bay water samples. The results are shown in Table 5. The recovery values calculated for the added amounts were always higher than 96%, and these results confirm the validity of the method.

4. Conclusion

This paper proposes a novel method for the preconcentration and determination of trace amounts of cadmium by LL-SFODME combined with FI-FAAS. Suggested procedure does not need any chelating agent. A comparison of the represented method with the other liquid–liquid microextraction methods with dif-

Table 6
Comparison of characteristic performance data obtained by using LL-SFODME and other liquid–liquid microextraction techniques for determination of cadmium.

Analytical technique	Detection technique	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	RSD (%)	Enrichment factor	Sample volume (mL)	Final volume (μL)	Time (min)	Ref.
USAE-SFODME[a]	FAAS	0.66	10–450	2.42	81.0	6.0	500	10	[35]
ISFME[b]	FAAS	0.07	0.2–40.0	2.42	78	5	50	5	[36]
IL-based DLLME[c]	FAAS	0.03	0.1–15	2.3	311	10	100	5	[37]
SI-DLLME[d]	ETAAS[f]	0.002	0.006–0.150	4.1	34	8.1	30	1.5	[38]
SFODME	FAAS	0.0079	0.08–30	5.4	640	160	250	15	[14]
IL-based USA-DLLME[e]	ETAAS	0.0074	0.02–0.15	3.3	63	10.0	73	2	[39]
LPME[g]	GFAAS	0.0035	0.008–1	4.5	450	2	4	10	[40]
SI-SDME[h]	ETAAS	0.01	0.03–0.6	3.9	10	15	60	10	[41]
CFME[i]	ETV-ICP-MS	4.6	0.01–50	16	140	1.5	4	15	[42]
HF-LPME[j]	ETV-ICP-MS	0.0045	0.02–30	9.4	29	2.5	4	15	[43]
LL-SFODME	FAAS	0.21	1.0–25.0	4.7	205	100	300	10	This work

[a] USAE-SFODME: Ultrasound-assisted emulsification-solidified floating organic drop microextraction
[b] ISFME: In situ solvent formation microextraction.
[c] IL-based DLLME: Ionic liquid-based dispersive liquid–liquid microextraction.
[d] SI-DLLME: Sequential injection dispersive liquid–liquid microextraction.
[e] IL-based USA-DLLME: Ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction.
[f] ETAAS: Electrothermal atomic absorption spectrometry.
[g] LPME: Liquid phase microextraction.
[h] SI-SDME: Sequential injection single-drop micro-extraction.
[i] CFME: Continuous flow microextraction.
[j] HF-LPME: Hollow-fiber liquid-phase microextraction.

ferent detection techniques for the cadmium extraction and determination is given in Table 6. Some of the methods in this table are ultrasound-assisted emulsification-solidified floating organic drop microextraction [35], In situ solvent formation microextraction [36], ionic liquid-based dispersive liquid–liquid microextraction [37], sequential injection dispersive liquid–liquid microextraction [38], ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction [39], sequential injection single-drop micro-extraction [41], continuous flow microextraction [42] and hollow-fiber liquid-phase microextraction [43]. The main advantages of the LL-SFODME methodology are simplicity, rapidity, reliability, safety and low cost and these advantages of the method make it very convenient for the determination of trace amount of cadmium in natural water samples.

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