

Determination of Cadmium at the Nanogram per Liter Level in Seawater by Graphite Furnace AAS Using Cloud Point Extraction

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INTRODUCTION

It is well known that cadmium can accumulate in human organs and cause serious diseases such as cancer, hypercalciuria, and the very painful illness called itai-itai ('ouch-ouch') disease (1). Genotoxic studies show that cadmium acts as an inhibitor of DNA mismatch repair in yeast (2). In a recent rat study, it was reported that cadmium can also act as an estrogen mimic and exert adverse effects on the estrogen-responsive tissues of the uterus and the mammary glands (3). These study results have drawn renewed attention to the pollution and toxic effects of cadmium, and will contribute in revising the regulatory standards for cadmium exposure. Because of the generally low concentration levels of cadmium in nature, noticeable adverse effects to the environment and human beings are very low. It is therefore very important to develop effective analytical methods for the trace level determination of cadmium in samples with complex matrices. To investigate cadmium concentrations at the ppb or ppt levels, graphite furnace atomic absorption spectrometry (GFAAS) is one of the most favored choices. Unfortunately, the determination of cadmium in seawater is difficult even with GFAAS, equipped with Zeeman-effect background correction, not only due to the low Cd levels in the samples but also due to the severe interferences caused by high-salinity matri-

ABSTRACT

A method based on cloud point extraction was developed to determine cadmium at the nanogram per liter level in seawater by graphite furnace atomic absorption spectrometry. Diethyldithiocarbamate (DDTC) was used as the chelating reagent to form Cd-DDTC complex; Triton X-114 was added as the surfactant. The parameters affecting sensitivity and extraction efficiency (i.e., pH of the solution, concentration of DDTC and Triton X-114, equilibration temperature, and centrifugation time) were evaluated and optimized. Under the optimum conditions, a preconcentration factor of 51.6 was obtained for a 20-mL water sample. The detection limit was as low as 2.0 ng L⁻¹ and the analytical curve was linear in the 10.0–200.0 ng L⁻¹ range with satisfactory precision (RSD <4.7%). The proposed method was successfully applied to the trace determination of cadmium in seawater.

ces. To decrease matrix interferences during GFAAS analysis, different kinds of atomizers (4–8) have been developed. Although these types of atomizers are effective to some extent, they are not available in many laboratories for routine analysis. The use of chemical matrix modifiers is another way to decrease the interferences from the matrix (9,10), but it is not usually adequate for seawater sample analysis. In this case, some sample pretreatment (preconcentration and separation from matrices) including electrolysis (11), coprecipitation (12), liq-

uid-liquid extraction (LLE) (13–16), and solid-phase extraction (SPE) (17–21) is necessary before routine determination of cadmium at the nanogram per liter level in seawater with ordinary graphite tubes. Unfortunately, all of these methods require a large sample volume and they are time-consuming. In particular, the traditional liquid-liquid extraction method is not only time-consuming and labor-intensive but is also dangerous to analysts because of the large volume of volatile organic solvent required.

As a green liquid-liquid extraction method, cloud point extraction (CPE) has been employed in analytical chemistry to separate and preconcentrate organic compounds (22–24) and metal ions (25–29). Compared with the traditional organic liquid-liquid extraction, cloud point extraction requires a very small amount of relatively nonflammable and nonvolatile surfactants that are benign to the environment. Aqueous solutions of non-ionic surfactants may separate in two phases in a narrow temperature range, called the cloud point. Using appropriate conditions such as temperature, pressure, and pH value, the solution containing the surfactant becomes turbid and separates into a surfactant-rich phase (in very small volume) and the remaining larger volume (bulk amount) into the diluted aqueous solution with the surfactant concentration, which is approximately equal to its critical micelle concentration (CMC). The hydrophobic analytes of the solution are extracted into the surfactant-rich phase. Since the surfactant-rich phase volume is very small in com-

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parison to the initial solution volume, a high enrichment factor can be obtained.

Pinto et al. (25) reported using 1-(2-pyridylazo)-2-naphthol (PAN) and Chen et al. (27) used 1-(2-thiazolylazo)-2-naphthol (TAN) as the chelating reagent with Triton® X-114 as the surfactant to extract ultratrace cadmium in seawater after cloud point extraction. The determination was performed using flame atomic absorption spectrometry. Although higher enrichment factors were achieved, the concentration of cadmium in seawater was too low to be compatible for the detection limit capability of a FAAS system. Cadmium determination at the nanogram per liter levels in seawater samples has only been successfully performed by complexing O,O-diethyl-dithiophosphate (DDTP) with cadmium, followed by cloud point extraction and ultrasonic nebulization inductively coupled plasma mass spectrometry (ICP-MS) (30).

In the present study, a method was developed for the trace level determination of cadmium (ng L⁻¹ level) in seawater employing cloud point extraction coupled with GFAAS using diethyldithiocarbamate (DDTC) as the chelating reagent and Triton X-114 as the surfactant. The results obtained after extraction show that cadmium was determined successfully, with satisfactory recoveries and precision.

EXPERIMENTAL

Instrumentation

A Hitachi Z-5700 atomic absorption spectrometer (Hitachi High-Technologies Corporation, Japan), equipped with Zeeman background correction and a cadmium hollow-cathode lamp as the radiation source, was used. The working conditions (listed in Table I) were adjusted in accordance with the

manufacturer's recommendations. The absorbance signals were measured as peak height with manual injection. A thermostated bath (TB-85 Therma Bath, Shimadzu, Japan), maintained at the desired temperature, was used to obtain cloud point preconcentration. A centrifuge and calibrated centrifuge tubes (Beijing Medicinal Instrument Company, P.R. China) were used to accelerate the phase separation process. The Easypure System (Model D7382-33, Barnstead Thermolyne Corporation, Dubuque, IA, USA) produced the deionized water (18 MΩ) used for this study.

Reagents and Standard Solutions

All reagents used were of analytical grade. Working standard solutions were obtained by appropriate dilution of the stock standard solution (1000 µg mL⁻¹) with distilled water. The non-ionic surfactant Triton X-114 (Acros Organics, New Jersey, USA) was used without further purification. The DDTC aqueous solution was prepared by dissolving appropriate amounts of sodium diethyldithiocarbamate (NaDDTC) (Beijing Chemical Factory, P.R. China) immediately before each experiment.

The materials and vessels used for trace analysis were kept in 10% (v/v) nitric acid for at least 48 h and

were subsequently washed four times with deionized water (obtained from the Easypure System) before use.

Cloud Point Extraction Procedure

For the preconcentration of Cd, aliquots of 20.0 mL of the cold sample solution containing the analyte, 1.5 g L⁻¹ Triton X-114 and 0.01 g L⁻¹ DDTC, buffered at a suitable pH, were mixed and kept for 20 min in the thermostatic bath at 40°C. Then the phase separation was accelerated by centrifugation for 6 min at 3000 rpm. After cooling in an ice-bath for 5 min, the surfactant-rich phase was separated with a syringe. After removing the bulk aqueous phase, the remaining micellar phase (about 100 µL) was treated with 100 µL of the methanol solution of 1% (v/v) nitric acid to reduce its viscosity. Then, 20 µL of the sample was introduced into the GFAAS by manual injection. During the experiment, 10 µL of 200 mg L⁻¹ Pd(NO₃)₂ of the chemical modifier was applied.

The conventional liquid-liquid extraction of Cd in Cd-DDTC complex form in the samples using CCl₄ was carried out to compare these results with the cloud point extraction method results.

TABLE I
Instrumental Operating Conditions

Lamp Current	9 mA	Cuvette	A-type
Wavelength	228.8 nm	Gas Flow	30 mL min ⁻¹
Slit	1.3 nm	Sample Volume	20 µL
<u>Temperature Program</u>			
Stage	Temperature (°C)	Ramp Time	Hold Time
	Start	End	
Drying	80	140	40 s
Ashing	300	300	20 s
Atomizing	1600	1600	5 s
Cleaning	2000	2000	4 s

Extraction of Cd in Real Samples

The seawater samples were filtered through a 0.45- μm pore size membrane filter to remove the suspended particulate matter and then stored at 4°C in the dark. A 20-mL sample, adjusted at pH 9 with ammonia and nitric acid, was submitted to the cloud point extraction procedure for preconcentration using 1.5 g L⁻¹ Triton X-114 and 0.01 g L⁻¹ DDTC. After phase separation, a 100- μL methanol solution containing 1% (v/v) nitric acid was added to the surfactant-rich phase. The treated samples were introduced into the GFAAS by manual injection.

RESULTS AND DISCUSSION

Effect of pH

The extraction efficiency, depending on the pH values at which the cloud point extraction of Cd was performed, was optimized. As an important parameter, the effect of pH on the extraction of Cd was investigated in the 1–13 pH range and the results are illustrated in Figure 1. It was found that the atomic absorbance reached maximum at

pH 9, at which point maximum extraction efficiency was obtained. For this study, pH 9 was selected as the working pH.

Effect of DDTC Concentration

In general, the concentration of a chelating reagent has a remarkable influence on the extraction efficiency. In order to select the optimum concentration of DDTC (while keeping other experimental parameters constant), the effect of the concentration of the chelating reagent on the extraction efficiency was examined and the results are presented in Figure 2. It can be seen that maximum signals were obtained at 0.01 g L⁻¹ DDTC ($-\log C_{\text{DDTC}} = 2$); therefore, 0.01 g L⁻¹ DDTC was chosen as the chelating reagent for this study.

Effect of Concentration of Triton X-114

For a successful cloud point extraction procedure, Triton X-114 was chosen for the formation of the surfactant-rich phase due to its low cloud point temperature (23–25°C) and high density of the surfactant-rich phase (31). The properties of Triton X-114 facilitate the extrac-

tion procedure and phase separation by centrifugation. In this experiment, the variation of extraction efficiency upon the surfactant concentration in the 0.1–4.0 g L⁻¹ range was investigated and the results are shown in Figure 3. It can be seen that the absorbance signal increased with an increase in concentration of Triton X-114 up to 1.0 g L⁻¹. When the concentration of Triton X-114 was varied between 1.0 and 2.5 g L⁻¹, the signal kept a plateau, which shows that a quantitative extraction by cloud point extraction was obtained. With an increase in Triton X-114 concentration over 2.5 g L⁻¹, the signal decreased because of an increase in the volume and viscosity of the surfactant phase. Based on these experimental results, 1.5 g L⁻¹ Triton X-114 was adopted as the optimum amount to achieve best analytical signals and highest extraction efficiency.

Effect of Equilibration Temperature

The best analyte preconcentration factor was achieved when the cloud point extraction procedure was processed at equilibration tem-

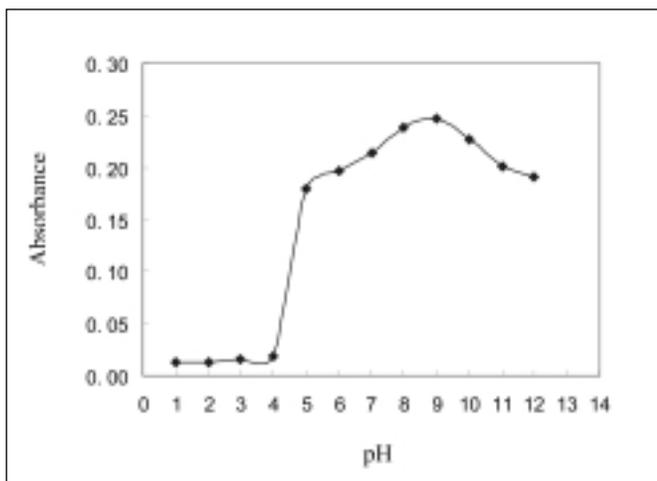


Fig. 1. Effect of pH on preconcentration of Cd. Conditions: 0.20 ng mL⁻¹ Cd 20 mL, 0.01 g L⁻¹ DDTC, 1.5 g L⁻¹ Triton X-114 at 40°C. Other experimental conditions are described in Cloud point extraction procedure section.

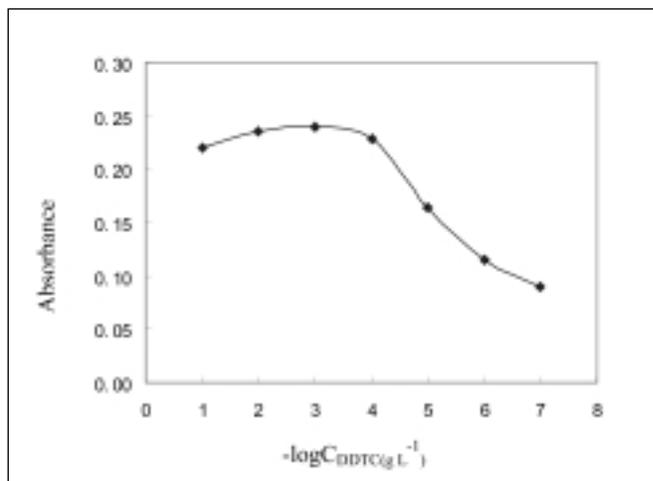


Fig. 2. Influence of DDTC concentration on the absorbance signal of Cd. Conditions: 0.20 ng mL⁻¹ Cd 20 mL, pH 9.0, 1.5 g L⁻¹ Triton X-114 at 40°C. Other experimental conditions are described in Cloud point extraction procedure section.

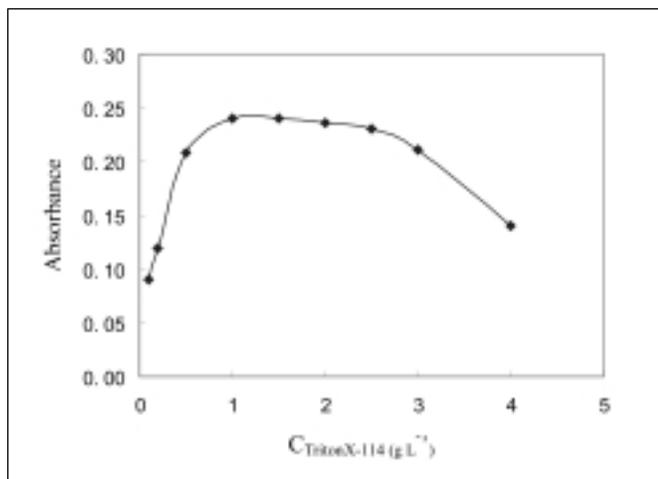


Fig. 3. Variation of the analytical signal of the Cd with Triton X-114 concentrations. Conditions: 0.20 ng mL^{-1} Cd 20 mL , pH 9.0, 0.01 g L^{-1} DDTC at 40°C . Other experimental conditions are described in Cloud point extraction procedure section.

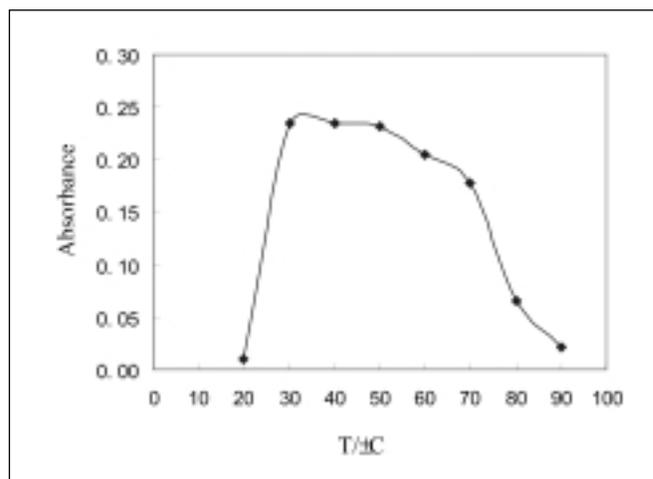


Fig. 4. Effect of equilibration temperature on the analytical signal. Conditions: 0.20 ng mL^{-1} Cd 20 mL , pH 9.0, 0.01 g L^{-1} DDTC, 1.5 g L^{-1} Triton X-114 at 40°C . Other experimental conditions are described in Cloud point extraction procedure section.

peratures that were well above the cloud point temperature of the surfactant (32). The enrichment factor was also affected by time (33). Thus, it was necessary to examine the effect of temperature on cloud point extraction. In order to employ the shortest incubation time and the lowest possible equilibration temperature, and to ensure the completion of the reaction and the efficient separation of phases, the effects of equilibration temperature and time were examined. Figure 4 shows the effects of equilibration temperature on the absorbance signal. Maximum signals were obtained at temperatures between $30\text{--}50^\circ\text{C}$. At 20°C , which was below the cloud point temperature of Triton X-114, two phases cannot be formed and the metal complex cannot be extracted. When the temperature was above 60°C , the signal decreased due to the decomposition of the Cd-DDTC complex. Therefore, 40°C was selected as the working equilibration temperature.

The equilibration time was also selected based on the best signal and efficient extraction obtained in the time span between 5–60 min. It

was found that an incubation time of 20 min was sufficient for quantitative extraction, and 20 min was subsequently chosen as the equilibration time for our experiments.

Effect of Centrifugation Time

The effect of centrifugation time on extraction efficiency was studied in the time range of 1–30 min at $3000 \text{ rev. min}^{-1}$. The results showed that there were no appreciable improvements time periods longer than 5 min at which complete separation occurred. A centrifugation time of 6 min was therefore selected as optimum.

Figures of Merit

Calibration curves were constructed by preconcentrating 20 mL of standard solutions with 1.5 g L^{-1} Triton X-114. The surfactant-rich phase was diluted with $100 \mu\text{L}$ of a solution of methanol containing 1% (v/v) nitric acid to reduce its viscosity. Then, $20 \mu\text{L}$ of diluted solution was introduced into the GFAAS by manual injection. Under the optimum experimental conditions, the calibration curve for Cd was linear from 0.01 to 0.20 ng mL^{-1} with

good relative standard deviation ($\text{RSD} < 4.7\%$) and a detection limit (3δ) (reagent blank, $n=6$) as low as 0.002 ng mL^{-1} was obtained. Figures of cloud point extraction and conventional liquid-liquid extraction by CCl_4 are compared in Table II. An enrichment factor of 51.6-fold was obtained by preconcentrating a 20-mL solution. Further improvement can be obtained by employing larger amounts of the sample solution or by diluting the surfactant-rich phase to a smaller volume with the methanol solution.

Interferences

Cations that may react with DDTC and anions that may form complexes with cadmium were the two main interferences affecting the preconcentration process. The effects of representative potential interfering species were tested and the results are listed in Table III. The results show that cadmium recoveries were almost quantitative in the presence of most foreign cations, except for Hg^{2+} , Sn^{4+} , Pb^{2+} which led to negative interferences with recoveries of 62.9%, 71.3%, 79.8%, respectively. The absorbance profiles are shown in

TABLE II
Analytical Characteristics of the Different Preconcentration Methods for Cd

Method	Solvent	Enrichment Factor	D.L. (ng mL ⁻¹) ^c	R.S.D. (%)	Regression Equation	R ²
Without Preconcentration	--	1	0.101	2.7	A=0.026C+0.0056	0.9992
Liquid-liquid Extraction ^a	CCl ₄	16.2	0.007	3.9	A=0.4216C+0.0092	0.9945
Cloud-point Extraction ^b	Triton X-114	51.6	0.002	4.7	A=1.3402C+0.0087	0.9961

^a Sample volume was 100 mL, CCl₄ volume was 5 mL.

^b Sample volume was 20 mL, Triton X-114 rich phase volume was 0.10 mL.

^c D.L. means detection limit (3δ) (reagent blank).

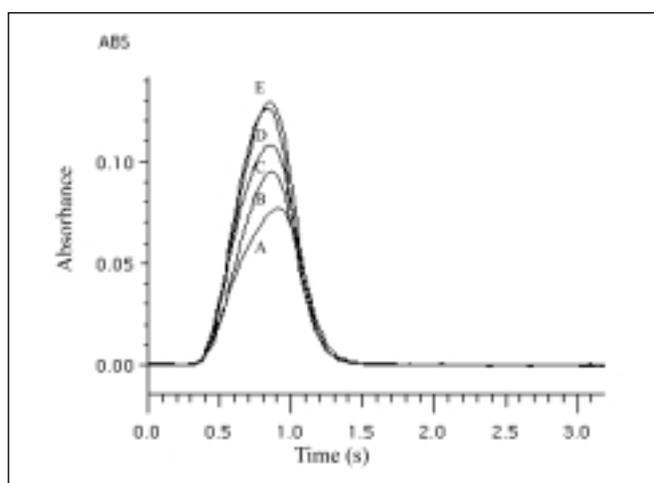


Fig. 5. Absorbance profiles of Cd obtained with and without interferences.

*A: 0.10 ng mL⁻¹ Cd²⁺ with 1.0 ng mL⁻¹ Hg²⁺, 0.01 g L⁻¹ DDTC;
B: 0.10 ng mL⁻¹ Cd²⁺ with 5.0 ng mL⁻¹ Sn⁴⁺, 0.01 g L⁻¹ DDTC;
C: 0.10 ng mL⁻¹ Cd²⁺ with 5.0 ng mL⁻¹ Pb²⁺, 0.01 g L⁻¹ DDTC;
D: 0.10 ng mL⁻¹ Cd²⁺ with 1.0 ng mL⁻¹ Hg²⁺, 5.0 ng mL⁻¹ Sn⁴⁺ and 5.0 ng mL⁻¹ Pb²⁺, 0.10 g L⁻¹ DDTC;
E: Standard solution of 0.10 ng mL⁻¹ Cd²⁺ without any interference, 0.01 g L⁻¹ DDTC, other conditions in this test are the optimal as described in the text.*

Figure 5. The peak shapes were not changed for co-extraction of Hg²⁺, Sn⁴⁺, Pb²⁺ and these interferences can be avoided by employing a higher concentration of DDTC reagent (0.10 g L⁻¹). The results indicated that the interferences by Hg²⁺, Sn⁴⁺, Pb²⁺ resulted mainly from the metal complex formation with DDTC. Under the experiment conditions employed, interferences were not detected in the real samples, resulting in satisfactory recoveries of 84.8–108.9%.

Real Sample Analysis

The method proposed was applied to the determination of Cd in seawater samples to test its reliability and practicality. Six seawater samples from the East China Sea (collected in November 2002) were preconcentrated

TABLE III
Influence of Foreign Ions on the Preconcentration and Determination of Cd*

Foreign Ion	Foreign Ion to Analyte Ratio	Recovery (%) ^a
Cl ⁻	2.5×10 ⁸	98.1±2.1
SO ₄ ²⁻	8×10 ⁷	96.7±1.7
HCO ₃ ⁻	1×10 ⁴	103.2±3.1
CO ₃ ²⁻	1×10 ⁴	94.6±1.2
NO ₃ ⁻	1×10 ⁴	99.0±3.4
F ⁻	1×10 ⁴	97.7±2.7
Fe ³⁺	2000	98.7±1.9
Fe ²⁺	2000	95.4±4.2
Zn ²⁺	2000	105.2±3.5
As ³⁺	1000	94.2±1.8
As ⁵⁺	1000	103.2±2.4
Cr ⁶⁺	500	102.4±2.9
Cr ³⁺	500	98.5±1.1
Mo ⁶⁺	500	89.1±2.9
Bi ³⁺	500	97.9±3.4
Cu ²⁺	200	101.8±2.6
Mn ²⁺	100	94.2±3.1
Co ²⁺	50	91.3±0.9
Ni ²⁺	50	99.1±4.1
Pb ²⁺	50	79.8±3.8
Sn ⁴⁺	50	71.3±2.9
Hg ²⁺	10	62.9±3.7

^a Mean±standard deviation (95% confidence interval, n=6).

*Preconcentration step: 0.10 ng mL⁻¹ Cd²⁺, pH 9.0, 0.01 g L⁻¹ DDTC, 1.5 g L⁻¹ Triton X-114 at 40°C.

by cloud point extraction and analyzed by GFAAS. For this purpose, 20 mL of each water sample was preconcentrated with 1.5 g L⁻¹ Triton X-114 and 0.01 g L⁻¹ DDTC. The results of the real sample analysis are listed in Table IV. The concentrations of Cd in these samples were in the range of 0.051–0.156 ng mL⁻¹. Recovery tests were carried out with standard cadmium-spiked real seawater samples at three different concentrations. The obtained recoveries (84.8–108.9%) were satisfactory and indicated that the method can be successfully applied to real samples.

CONCLUSION

Compared with conventional liquid–liquid extraction, cloud point extraction (CPE) is a much more environmentally friendly method and is safer for the analysts because of the small volume of innocuous surfactants used in place of toxic organic solvents. The surfactant can be easily introduced into the GFAAS by manual injection after dilution with a methanol solution containing nitric acid. Interferences from anions such as chlorine and humic acid can be avoided since the metal complexes are separated. Under optimum conditions, a preconcentration factor of 51.6 was

obtained for a 20-mL water sample. The detection limit was as low as 2.0 ng L⁻¹ and the analytical curve was linear in the 10.0–200.0 ng L⁻¹ range with satisfactory precision (RSD <4.7%). The proposed method was successfully applied to the trace determination of cadmium in seawater with satisfactory recoveries (84.8–108.9%). The experiment proved that cloud point extraction is a convenient, safe, simple, rapid, and inexpensive preconcentration method for cadmium determination at the nanogram per liter levels in seawater samples, resulting in a high enrichment factor.

TABLE IV
Determination of Cd in Real and Spiked Samples

Sample No.	Location	Measured (ng mL ⁻¹) *	Spiked (ng mL ⁻¹)	Found (ng mL ⁻¹) *	Recovery ^a (%)
			0.050	0.110±0.003	118.0
W1	31°59.893' N; 123°30.195' E	0.051±0.002	0.085	0.142±0.005	107.1
			0.120	0.163±0.006	93.3
			0.050	0.117±0.004	96.0
W2	31°30.092' N; 123°00.272' E	0.069±0.004	0.085	0.149±0.005	94.1
			0.120	0.193±0.003	103.3
			0.050	0.161±0.005	104.0
W3	31°00.460' N; 122°29.870' E	0.109±0.005	0.085	0.179±0.007	82.4
			0.120	0.213±0.006	86.7
			0.100	0.241±0.009	85.0
W4	30°41.866' N; 122°43.798' E	0.156±0.003	0.150	0.283±0.010	84.7
			0.200	0.312±0.008	78.0
			0.050	0.135±0.004	98.0
W5	30°30.603' N; 123°29.623' E	0.086±0.004	0.085	0.176±0.006	105.9
			0.120	0.199±0.009	94.2
			0.100	0.219±0.008	98.0
W6	30°00.220' N; 123°00.507' E	0.121±0.003	0.150	0.248±0.011	84.7
			0.200	0.286±0.007	82.5

* Mean ± standard deviation (95% confidence interval, n=6).

^a 100 × [(Found-base)/spiked].

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