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Determination of Trace Cadmium in Food Samples by Electrothermal Atomic Absorption Spectrometry After Cloud Point Extraction

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A new method for the determination of trace cadmium in food samples by cloud point extraction combined with electrothermal atomic absorption spectrometry is presented and evaluated. The method based on the fact that formation of a hydrophobic complex of cadmium(II) with ammonium pyrrolidine dithiocarbamate at pH 4.0 and subsequently enter surfactant-rich phase. Cadmium(II) in surfactant-rich phase was determined by electrothermal atomic absorption spectrometry after dilution by 0.2 mL nitric acid in methanol (0.1 mol L^{-1}). The main factors affecting the cloud point extraction, such as pH, concentration of ammonium pyrrolidine dithiocarbamate and Triton X-114, equilibrium temperature and incubation time, sample volume were investigated in detail. Under the optimum conditions, the limit of detection of this method was 0.004 ng mL^{-1} for cadmium and the relative standard deviation was 4.3 % (c = 0.5 ng mL^{-1}, n = 7). The analytical results for the certified reference rice sample (GBW08510) were in a good agreement with the certified value. The proposed method was successfully applied to determination of trace cadmium in the liquor, rice and drinking water with satisfactory results.

Key Words: Cloud point extraction, Cadmium, Food samples, Electrothermal atomic absorption spectrometry.

INTRODUCTION

It is now widely accepted that cadmium is among the most dangerous of all metal contaminants in environmental systems. Cadmium can accumulate in living organisms and its toxic potential is very high. Long-term consumption of drinking water containing cadmium at levels higher than 0.005 mg L^{-1} can cause nausea, salivation, diarrhea, muscular cramps, renal degradation, lung insufficiency, bone lesions, cancer and hypertension in humans[1]. Cadmium ions are easily uptaken by vegetables and in animal foods, are principally deposited in the liver and kidneys. The highest cadmium concentrations are found in rice, wheat, oyster, mussels and the kidney cortex of animals[2]. Excessive accumulation of dietary heavy metals in the human body may cause serious health problems and there is growing concern about the effects of dairy food contaminants on human health[3,4]. Therefore, there is an increasing need to monitor cadmium levels in food samples at ever decreasing concentrations. For this purpose, very sensitive, simple, rapid and inexpensive methods are necessary.

Several atomic spectrometric techniques such as flame and electrothermal atomic absorption spectrometry (FAAS and ETAAS)[5-8], atomic fluorescence spectrometry (AFS)[9,10], inductively coupled plasma atomic emission spectrometry (ICP-AES)[11], inductively coupled plasma mass spectrometry (ICP-MS)[12] have been proposed for the determination of trace cadmium in different food samples. Since the concentrations of cadmium in food samples is very typically well below 1 mg kg^{-1} and the sample matrixs are very complicated, various separation and preconcentration procedures have been used in combination with the above mentioned techniques for accurate, reliable and sensitive results. These procedures include coprecipitation[13], solid phase extraction[14], solvent microextraction[15] and cloud point extraction[16,17].

Nowadays, cloud point extraction (CPE) using non-ionic surfactants has attracted considerable attention as an alternative to the conventional extraction techniques for separation and preconcentration[18-20]. Briefly, above the cloud point temperature, the surfactant solution easily separates into two distinct phases: a surfactant-rich phase of a small volume and a diluted aqueous phase, in which the surfactant concentration is close to the critical micelle concentration. When metal ion form hydrophobic complex with an appropriate chelating reagent under the adequate conditions, the hydrophobic complex can be trapped in the hydrophobic micelle core and then extracted into the surfactant-rich phase. As a new separation technique, CPE offers many advantages over traditional liquid-liquid extraction, such as simple, cheap, rapid, no use of organic

solvents, high capacity to concentrate a wide variety of analytes with high recoveries and high concentration factors[21].

When CPE technique was used for the extraction of metal chelates, FAAS was often used as detector for its advantages, such as simple, rapid and low cost. However, considered the poor sensitivity of FAAS, ETAAS is an efficient alternative. Besides of the excellent detection limits, the need of a very small sample injection volume is another advantage of ETAAS. Furthermore, the surfactant matrix in the injection solution can be eliminated at least in part during the appropriate ashing temperature and time. In this sense, ETAAS is suitable for determination of small volume of the surfactant-rich phase obtained in CPE schemes.

The aim of this present paper is to evaluate the feasibility of combining CPE preconcentration with ETAAS for determination of trace cadmium in food samples. In this procedure, ammonium pyrrolidine dithiocarbamate was used as chelating reagent and Triton X-114 as the extracting one. The main factors affecting CPE were investigated in detail. The developed method was applied to determine trace cadmium in different food samples with satisfactory results.

EXPERIMENTAL

A TAS-986 atomic absorption spectrometer (Beijing purkinje general Instrument Limited Company, Beijing, China) equipped with a GFA-4A transverse heated graphite furnace atomizer was used for the determination of cadmium in the surfactant-rich phase. Deuterium lamp background correction was employed to correct the non-specific absorbance. A cadmium hollow cathode lamp (Beijing Shuguangming Electronic Lighting Source Instrument Limited Company, Beijing, China) was used as the radiation source. The operation conditions of cadmium hollow cathode lamp were those recommended by the manufacture. Pyrolytic graphite-coated and transverse heated platform graphite tubes were used throughout. Argon 99.999 % (Beijing Praxair Inc., Beijing, China) with 450 mL min^{-1} was used as a protective and purge gas. Measurements were performed in the peak area mode. The detailed instrumental parameters and graphite furnace temperature program used for the determination of cadmium were shown in Table-1. A thermostatic bath(Jintan Instrument Limited Company, Jiangsu, China) was used for cloud point preconcentration experiments and phase separation was assisted by a centrifuge (80-1 model, Jintan Instrument Limited Company, Jiangsu, China) in 15 mL calibrated centrifuge tubes. All pH measurements were carried out using a PHS-25B digital pH meter equipped with a combined glass-calomel electrode (Shanghai Dapu Instrument Limited Company, Shanghai, China).

A stock standard cadmium(II) solution(1000 μg mL^{-1}) was prepared by dissolving 0.2032 g cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) (Tianjin Reagent Company, Tianjin, China) with 100 mL double distilled water. All stock standard solutions were stored in polyethylene bottles in a refrigerator at 6 ºC. Working standard solutions were obtained by appropriate dilution of the stock standard solution just before use. Solution (1.0 %, v/v) of Triton X-114 (Sigma, USA) was prepared in double distilled water and was used without further purification.

TABLE-1
INSTRUMENTAL PARAMETERS AND TEMPERATURE PROGRAM FOR CADMIUM DETERMINATION

Spectrometer				
Wavelength/nm	228.8			
Current(mA)	2			
Bandwidth/nm	0.4			
Background correction	Deuterium			
Sample volume/μL	10			
Graphite furnace				
Step	Temp. (ºC)	Ramp time (s)	Step time (s)	Flow rate of argon (mL min^{-1})
Drying	100	5	10	450
Ashing	400	10	30	450
Atomization	1900	0	4	0
Cleaning	2000	0	1	450

An ammonium pyrrolidine dithiocarbamate solution (2.0 %, w/v) (Shanghai Reagent Company, Shanghai, China) was prepared daily by dissolving 0.5000 g ammonium pyrrolidine dithiocarbamate in 25 mL double distilled water. The buffer solution was prepared by dissolving 20.0 g sodium acetate and 134 mL 6 mol L^{-1} acetic acid into 500 mL double distilled water. All chemicals and reagents used in this study were of analytical-reagent grade or higher purity. Double distilled water was used thoughout.

Procedure for CPE: For the cloud point extraction, aliquots of 8.00 mL sample or standard solution, 1.0 mL 2.0 % (w/v) ammonium pyrrolidine dithiocarbamate solution and 1.00 mL 1.0 % (v/v) Triton X-114 solution was added into a 15 mL centrifuge tube and the mixture were buffered to pH 4.0 with acetic-acetate and then diluted to 15 mL with double distilled water. The solution was kept in a thermostatic water bath at 50 ºC for 15 min, separation of the aqueous and surfactant-rich phase was accomplished by centrifugation for 5 min at 3500 rpm. After cooling in an ice bath, the surfactant-rich phase became viscous and the supernatant aqueous phase was then separated completely by a syringe centered in the tube. To decrease the viscosity of the surfactant-rich phase, 0.2 mL nitric acid in methanol (0.1 mol L^{-1}) was added and then 10 μL the resultant solution was directly introduced into graphite tube for determination of cadmium.

Sample preparation

Liquor: A volume of 50 mL of liquor(purchased in the supermarket, produced by old village chief liquor limited company, Shuangcheng City, Heilongjiang province, China) was introduced into a 100 mL flask and 5.0 mL of concentrated nitric acid and 5.0 mL of 30 % (w/v) hydrogen peroxide were added. The samples were heated and evaporated to dryness on a hot plate. The residue was dissolved in 5 % (v/v) nitric acid and was transferred to a 50 mL volumetric flask and diluted to volume with deionized water.

Rice: The rice sample was digested by pressure assisted closed digestion. 0.5000 g of rice (purchased in the supermarket) was weighed into a 60 mL closed digestion vessels and 1.0 mL concentrated nitric acid and 3.0 mL H_2O_2 (30 %, w/v) were added. The vessels were put into stainless steel containers and the container were closed and heated in a drying oven at temperature of 100 ºC for 1 h, then at temperature of 140 ºC for 3 h. After that, the vessels were cooled to natural

temperature. The samples were heated and evaporated to dryness on a hot plate; the residue was dissolved in 5 % (v/v) nitric acid and was transferred to a 25 mL volumetric flask and diluted to volume with deionized water.

Purified water: The purified water was purchased in the supermarket and no special sample pretreatment was required for this clean water samples.

Certified reference rice sample (GBW08510): The sample was treated as the rice sample above.

RESULTS AND DISCUSSION

Optimization of the electrothermal atomic absorption spectrometry conditions: The selection of an appropriate pyrolysis temperature is very important for removing the matrix as much as possible and preventing pyrolysis loss of the analytes prior to atomization. This decreases the possibility of chemical interference and reduces the magnitude of the background signal. The influence of pyrolysis temperature (200-600 ºC) on the absorbance of the cadmium in surfactant-rich phase was investigated. The results showed that maximum absorbance obtained when the pyrolysis temperature was near 400 ºC. However, when pyrolysis temperature was higher than 450 ºC, the absorbance of cadmium was decreased rapidly with the increasing pyrolysis temperature. Therefore, 400 ºC was selected as the optimized pyrolysis temperature for the determination of cadmium. The effect of pyrolysis time on the absorbance of cadmium was also investigated at the selected pyrolysis temperature of 400 ºC. The results showed that the signal of the background decreased when the pyrolysis time(hold time) changed from 5 to 30 s and no appreciable improvements were observed for longer time. As a result, a pyrolysis time of 30 s was chosen.

With the selected pyrolysis temperature of 400 ºC and pyrolysis time 30 s, the effect of the atomization temperature on signal of cadmium was studied in the temperature range of 1500 to 2200 ºC and the results showed that the maximum analytical signal of cadmium was obtained when the atomization temperature was between 1800 and 2000 ºC. The experimental results showed that atomization time has little effect on the analytical signal of cadmium. Therefore, an atomization temperature of 1900 ºC and an atomization time of 4 s were selected for atomization of cadmium.

Effect of pH: The pH plays an important role on metal-chelate formation and subsequent extraction. In this part of study, the effect of pH on the signal intensity of cadmium in the surfactant-rich phase was evaluated at pH values varying from 1.0 to 7.0. As illustrated in Fig. 1, the maximum extraction of cadmium began at pH 3.0, being constant until pH 5.0. At lower or higher pH values, the hydrophobic complex of Cd(II)-ammonium pyrrolidine dithiocarbamate does not form completely, so the extraction efficiency of cadmium is low. Hence, pH 4.0 was selected as the working value.

Effect of ammonium pyrrolidine dithiocarbamate concentration: The CPE efficiency depends on the hydrophobicity of the ligand and the complex formation, the apparent equilibrium constants in the micelle medium, the kinetics of the complex formation and the transference between the phases. Ammonium pyrrolidine dithiocarbamate is one of the

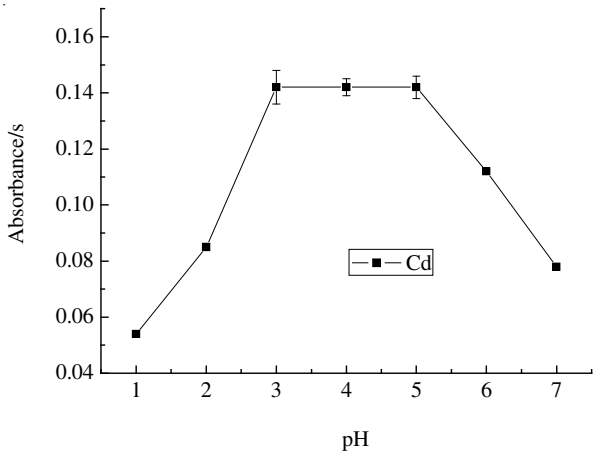

Fig. 1. Effect of pH on the signal intensity of cadmium in surfactant-rich phase. Condition: Cadmium(II) standard solutions (0.5 ng mL^{-1}, 6.00 mL), 1.0 mL 2.0 % (w/v) ammonium pyrrolidine dithiocarbamate, 1.0 mL 1.0 % (v/v) Triton X-114, pH 1.0-7.0, equilibrium temperature 50 ºC and incubation time 15 min

widely used chelating agents for the preconcentration of trace metals from solution[22]. The variation of the analytical signal as a function of the concentration of ammonium pyrrolidine dithiocarbamate in the range of 0.2-2.5 % (w/v) was studied and the experimental result was demonstrated in Fig. 2. It could be seen that the analytical signal of cadmium increased rapidly as the concentration of ammonium pyrrolidine dithiocarbamate increased from 0.2 to 1.5 % (w/v) and kept constant with concentration of ammonium pyrrolidine dithiocarbamate up to 2.5 % (w/v). For further studies, an ammonium pyrrolidine dithiocarbamate concentration of 2.0 % (w/v) was selected.

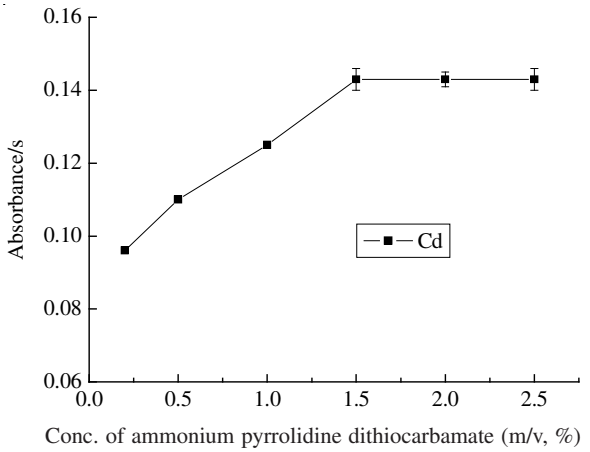

Fig. 2. Effect of ammonium pyrrolidine dithiocarbamate concentration on the analytical signal intensity of cadmium. Condition: Cadmium(II) standard solutions (0.5 ng mL^{-1}, 6.00 mL), 1.0 mL 0.2-2.5 % (m/v) ammonium pyrrolidine dithiocarbamate, 1.0 mL 1.0 % (v/v) Triton X-114, pH 4.0, equilibrium temperature 50 ºC and incubation time 15 min

Effect of Triton X-114 concentration: Compared with Triton X-100, Triton X-114 has lower cloud point temperature (18 ºC) and higher density of the surfactant-rich phase. It is more convenient for inducing the phase separation and collecting the surfactant-rich phase by centrifugation. The effect of Triton X-114 concentration upon sensitivity and extraction was studied within the concentration of surfactant varied from

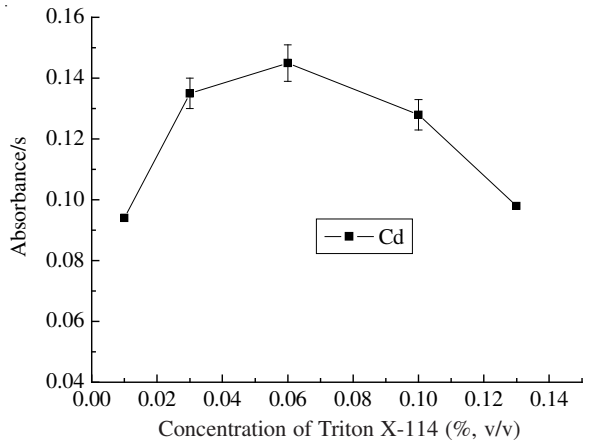

Fig. 3. Effect of Triton X-114 concentration on the analytical signal intensity of cadmium. Condition: Cadmium(II) standard solutions (0.5 ng mL^{-1}, 6.00 mL), 1.0 mL 2.0 % (w/v) ammonium pyrrolidine dithiocarbamate, Triton X-114 concentration 0.01-0.13 % (v/v), pH 4.0, equilibrium temperature 50 ºC and incubation time 15 min

0.01-0.13 % (v/v). Fig. 3 showed the effect of Triton X-114 concentration on signal intensity of cadmium in surfactant-rich phase. It is obvious that a maximum extraction was observed with the Triton X-114 concentration in the range of 0.03-0.06 % (v/v). Therefore, 0.06 % (v/v) of Triton X-114 concentration was employed for further studies.

Effects of equilibrium temperature and incubation time: The effect of equilibrium temperature was investigated from room temperature to 70 ºC. It was found that the solutions became turbid as soon as the solutions were put into the water bath with temperature higher than 40 ºC and the temperature had no considerable effect upon the extraction efficiency and the analytical signal kept constant at temperature range of 40-70 ºC. Thus, 50 ºC was chosen as the equilibrium temperature. Keeping the equilibrium temperature of 50 ºC, the influence of incubation time on CPE was studied within range of 5-30 min. It was observed that, 15 min was sufficient to achieve a quantitative extraction of analyte. Then, 15 min incubation time was employed for CPE procedure.

Effect of sample volume: In order to obtain a higher enrichment factor, a large volume of sample solution is required. For this purpose, 5.00, 6.00, 7.00, 8.00, 9.00, 10.00 mL of standard solutions containing 3.0 ng of cadmium were extracted according to the procedure of CPE. It was shown that quantitative extraction of the analyte was obtained with the sample volumes no more than 8.00 mL. For further studies, 8.00 mL of sample volume was selected.

Interferences of coexisting ions: The effect of potential interference of some metal ions on the preconcentration and determination of cadmium was examined. In these experiments, solutions containing cadmium (0.5 ng mL^{-1}) and the added interfering ions were treated according to the recommended procedure under the optimum conditions and the results were given in Table-2.

Analytical performance: Under the optimum conditions described above, the limit of detection (LOD, calculated as 3s/a, where s is the standard deviation of ten measurements of a reagent blank and a is the slope of the calibration graph with preconcentration) of this method for cadmium was 0.004 ng mL^{-1} and the relative standard deviation (RSD) was 4.3 % (c = 0.5 ng mL^{-1}, n = 7). The linear calibration range was from 0.05 to 2.5 ng mL^{-1}. The enrichment factor (EF, calculated as the ratio of the slopes of the calibration graphs with preconcentration and direct injection, respectively) was 14. The consumptive index (CI) was 0.57 mL. This factor (calculated based on the ratio of the sample volume in milliliters and the enrichment factor) reflects the volume of the sample consumed to achieve the enrichment factor value[23].

TABLE-2
INTERFERENCES OF COEXISTING IONS ON EXTRACTION AND DETERMINATION OF CADMIUM(II)

Coexisting ions	Mass ratio*	Recovery (%)	Coexisting ions	Mass ratio*	Recovery (%)
K^+	1000	99.6	Co^{2+}	20	104.0
Na^+	1000	101.0	Ni^{2+}	20	101.0
Mg^{2+}	1000	102.0	Mn^{2+}	15	106.0
Ca^{2+}	1000	104.0	Zn^{2+}	15	92.2
Al^{3+}	50	102.0	Pb^{2+}	15	94.1
Cu^{2+}	20	94.8	Fe^{3+}	15	96.1

*Coexisting ion/cadmium(II) (The concentration of cadmium(II) was 0.5 ng mL^{-1}).

Analysis of real samples: For real sample analysis, the standard calibration curve was employed. In order to establish the validity of the proposed procedure, the method has been applied to the determination of trace cadmium in the certified reference materials (GBW08510 rice sample). The analytical results showed a good agreement between determined values (2.53 ± 0.18 μg g^{-1}) and the certified values (2.60 ± 0.14 μg g^{-1}).

The method was also applied to the determination of trace cadmium in liquor, rice and drinking water samples. The analytical results and the recoveries for the spiked samples were given in Table-3. It can be seen that the recovery for the spiked samples is between 96 and 110 %.

TABLE-3
ANALYTICAL RESULTS FOR CADMIUM IN FOOD SAMPLES (n = 3)

Samples	Added	Found	Recovery (%)
Liquor (ng mL^{-1})	0.0	0.600 ± 0.030	–
	0.5	1.150 ± 0.050	110.0
	1.0	1.640 ± 0.100	104.0
Rice (μg g^{-1})	0.0	0.041 ± 0.003	–
	0.1	0.140 ± 0.050	99.0
	0.2	0.240 ± 0.010	99.5
Drinking water (ng mL^{-1})	0.0	Not detected	–
	0.5	0.530 ± 0.030	106.0
	1.0	0.960 ± 0.050	96.0

Conclusion

A new method for the determination of trace cadmium by CPE combined with ETAAS was proposed in this paper. The advantages of the proposed method are summarized as follows:

(1) Simplicity, selectivity, safety and low cost.

(2) By combination cloud point extraction with ETAAS, lower detection limit could be achieved. The proposed method was successfully applied to determination of trace cadmium in the liquor, rice and drinking water with satisfactory results. Compared with other similar methods for cadmium determi-

nation by CPE, the proposed procedure is very fast and simple, the whole CPE could be completed within 0.5 h, which is much quicker than other similar procedures[24,25]. And the comparable analytical performance was obtained with a smaller sample volume and without a matrix modifier[26,27].

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