

Cloud point extraction–flame atomic absorption spectrometry method for preconcentration and determination of trace cadmium in water samples

Jinyan Ning, Yang Jiao, Jiao Zhao, Lifan Meng and Yaling Yang

ABSTRACT

A method based on cloud point extraction (CPE) separation/preconcentration of trace cadmium (Cd) as a prior step to its determination by flame atomic absorption spectrometry has been developed. Cadmium reacted with 8-hydroxyquinoline to form hydrophobic chelates, which were extracted into the micelles of nonionic surfactant oligoethylene glycol monoalkyl ether (Genapol X-080) in an alkaline medium. Octanol was used to depress the cloud point of Genapol X-080 in the extraction process. The chemical variables that affect the CPE, such as pH of complexation reaction, amount of chelating agent, Genapol X-080 and octanol were evaluated and optimized. Under optimized conditions, linearity was obeyed in the range of 10–500 µg/L, with the correlation coefficient of 0.9993. For 5 mL of sample solution, the enhancement factor was about 20. The limit of detection and limit of quantification of the method were 0.21 and 0.63 µg/L, respectively. The relative standard deviations ($n = 6$) was 3.2% for a solution containing 100 µg/L of Cd. The accuracy of the preconcentration system was evaluated by recovery measurements on spiked water samples. Recoveries of spiked samples varied in the range of 94.1–103.8%.

Key words | 8-hydroxyquinoline, cadmium, cloud point extraction, flame atomic absorption spectrometry, Genapol X-080, octanol

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INTRODUCTION

Heavy metals in the environment and their effects on human health have been studied (Sarkar 2002; Järup 2003; Reilly 2008). Cadmium (Cd) is one of the most toxic elements (Järup *et al.* 1998; Nordberg 2009; Mudgal *et al.* 2010). Widespread use of the compounds of Cd, burning of oil and coal and incineration of waste has led to extensive contamination of environmental sources such as waters (Moore 1991). Cd is hazardous both by inhalation and ingestion. Food and water are the most important sources of Cd exposure (Khan *et al.* 2010; Wen *et al.* 2011). Once absorbed, Cd accumulates in the human body and it is highly toxic even at very low concentrations. Excessive Cd exposure may give rise to renal (Huang *et al.* 2009), pulmonary (Corradi & Mutti 2011), hepatic (Kyriakou *et al.* 2011) and skeletal problems (Trzcinka-Ochocka *et al.* 2004) and cancer (Joseph 2009).

Flame atomic absorption spectrometry (FAAS) is widely used to determine cadmium ions in various samples because of low costs, operational ease and high sample throughput (Ferreira *et al.* 2007). However, the method lacks sufficient

sensitivity and selectivity and usually requires preconcentration procedures before the determination of trace elements. Sample pretreatment can separate and enrich the analyte and solve the problem of matrix effects and low concentrations. Cloud point extraction (CPE) is an alternative preconcentration method because of its efficiency, low cost of commercially available surfactants, rapidity and safety. The aqueous solutions of nonionic surfactant materials become cloudy when their temperature reaches the cloud point temperature. And additives, such as salts, alcohols, carboxylic acids and ionic surfactant, have been added to change the cloud point of aqueous solution of nonionic surfactant (Sadaghiania & Khan 1991; Sharma *et al.* 2003; Zhang & Yin 2005). CPE has been used for the extraction and preconcentration of Cd after chelation with diethyldithiocarbamate (DDTC) (Escaleira *et al.* 2009), 1-(2-thiazolylazo)-2-naphthol (TAN) (Silva & Roldan 2009), 1-(2-pyridylazo)-2-naphthol (PAN) (Zhu *et al.* 2006), 8-hydroxyquinoline (8-HQ) (Shemirani *et al.* 2005), O,O-diethyldithiophosphate

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(DDTP) (Maranhão *et al.* 2005), and dithizone (Manzoori & Karim-Nezhad 2004).

In this paper, nonionic surfactant Genapol X-080 was used for the extraction and preconcentration of trace Cd chelating with 8-HQ (Figure 1) from water. The cloud point of Genapol X-080 was about 70 °C and octanol was used to drop the cloud point of Genapol X-080 to room temperature. Low cloud point in extraction has many advantages such as the extraction of thermally unstable substances, and being safe and simple. Compared with classical CPE, this method can obtain lower cloud point temperature and comparative extraction efficiency.

EXPERIMENTS

Reagents and solutions

Stock standard solution (1000 µg/mL) of Cd was purchased from China National Institute of Standards (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution. A solution of 100 µg/mL of 8-HQ (E. Merck, Darmstadt, Germany) was prepared by dissolving appropriate amounts of this reagent in ethylalcohol. The nonionic surfactants Genapol X-080, Triton X-114, Triton X-100 and TMN-6 were obtained from Sigma (St Louis, MO, USA). Octanol was purchased from Aladdin (Shanghai, China). All reagents were of analytical reagent grade.

Instrumentation

A 6300 C atomic absorption spectrometer (AAS) (Shimadzu, Japan) with ethyne flame and Cd hollow-cathode lamp as radiation source was used throughout the measurements. The operating conditions were those recommended by the manufacturer, unless specified otherwise. A pH meter, Elico Li-129 model glass-calomel combined electrode (Shanghai,

China) was used to measure pH values. A vortex-mixing apparatus (Shanghai, China) was prepared for assisting the mixture emulsification. A thermostated bath (Shanghai, China) was used to control the temperature of the extraction process. A centrifuge with calibrated centrifugal tubes (Shanghai, China) was used for the phase separation and the volume of the calibrated centrifugal tubes was 10 mL.

Sample pretreatment

The investigated area is located in Green Lake in Kunming, Yunnan Province (China). Four kinds of water samples from areas suffering different levels of industrial pollution were collected. Each sample was acidified to about pH 1.5 with concentrated HNO₃. The samples of water were digested with 2 mL HCl (1.179 g/mL) and 2 mL HNO₃ (1.405 g/mL) in an electric hot plate digestion system and diluted to 10 mL with deionized water.

CPE procedure

One hundred microlitres of 8-HQ (100 µg/mL) was added to 5 mL of the sample or standard solution containing the analyte which was adjusted to pH 9 with either 1 mol/L HCl or NaOH for 10 min. One hundred microlitres of Genapol X-080 and 100 µL of octanol were added to the sample. Then the mixture was vortex-mixed for 60 s and kept for 20 min in a thermostated bath at 30 °C. Separation of the two phases was accomplished by centrifugation for 5 min at 3500 rpm. The mixture was separated into two phases. The aqueous phase was carefully removed by using a syringe with a long needle and the enrichment phase was diluted to 500 µL with methanol and determined by FAAS. Figure 2 is the schema of the CPE process. Surfactant micelles consist of a hydrophilic surface and a hydrophobic core. The hydrophobic core can entrap and thus isolate hydrophobic substances (Paleologos *et al.* 2005). A phase separation occurs after increasing the temperature up to the cloud point. After centrifugation, the mixture was

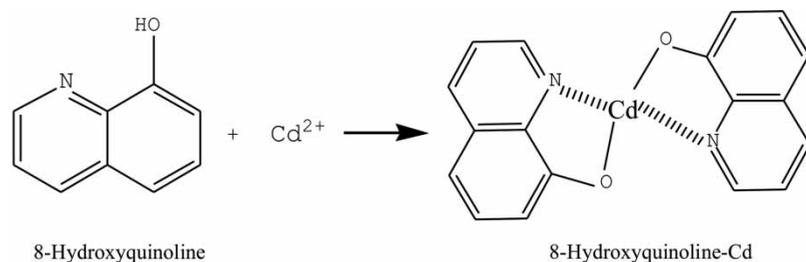


Figure 1 | The reaction equation Cd and 8-hydroxyquinoline.

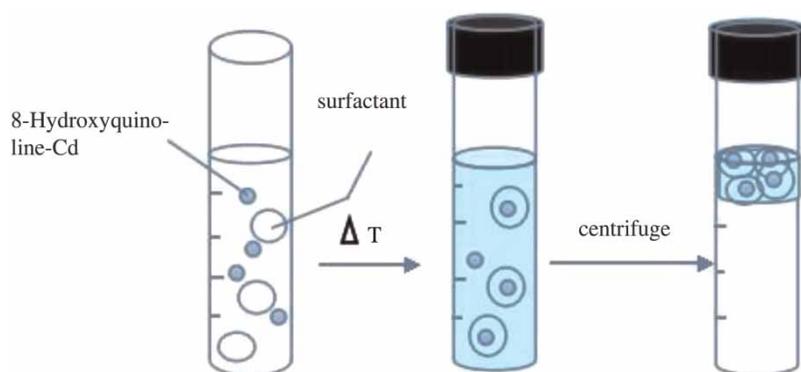


Figure 2 | Schema of the CPE process.

separated into two phases and the surfactant-rich phase containing the complexed ions was removed and analysed by FAAS.

RESULTS AND DISCUSSION

The enrichment factor (EF) was calculated from the following equation:

$$EF = C_S / C_0$$

where C_S and C_0 are the metal concentrations in the surfactant-rich phase and the initial concentration in the aqueous phase, respectively.

The extraction efficiency of the CPE method, defined as the percentage of total analyte amount extracted into the surfactant-rich phase, can be expressed as the following equation:

$$E(\%) = C_S V_S / C_0 V_0 \times 100$$

where $E(\%)$, C_S , C_0 , V_S , V_0 are the extraction efficiency, the metal concentrations in the surfactant-rich phase, the initial concentration in the aqueous phase, the volume of the surfactant-rich phase and the volume of the aqueous phase, respectively.

Effect of pH

pH plays a unique role in metal chelate formation and subsequent extraction. 8-HQ is amphiprotic in aqueous solution, and can ionize in alkaline conditions and can bind hydrogen ions in an acidic environment. Complexation reaction is easier in alkaline conditions, and hydrophobic

metal chelate was extracted in a small amount of the surfactant-rich phase. Figure 3 shows the effect of pH on CPE of Cd, and pH 9 was chosen in this test.

Effect of concentration of 8-HQ

The effect of the chelating agent on the analytical response was examined. Major improvement on the responses was obtained as the chelating concentrations increased up to certain values, which are sufficient for total complexation, and levelled off thereafter. The concentration of 8-HQ ranged between 0.2 and 3 $\mu\text{g}/\text{mL}$ in this part of the study (Figure 4) and 2 $\mu\text{g}/\text{mL}$ was chosen for further experiments.

Effect of concentration of Genapol X-080

The concentration of surfactant that is used in CPE is a critical factor. To obtain the optimal concentration of Genapol X-080, the effect of surfactant concentration on the

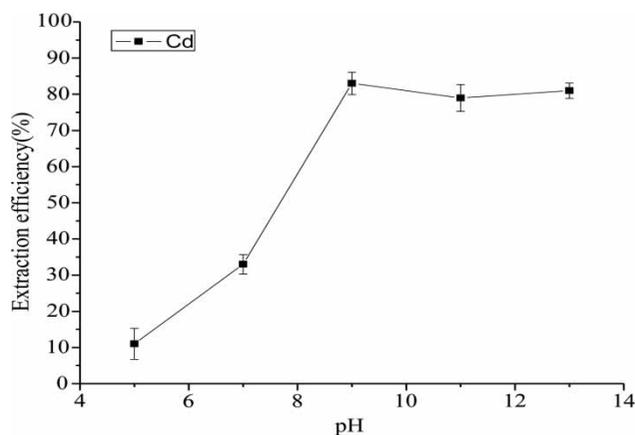


Figure 3 | Effect of pH. Fixed parameters: 100 $\mu\text{g}/\text{L}$ Cd, 2 $\mu\text{g}/\text{mL}$ 8-HQ, 2% Genapol X-080, 2% octanol.

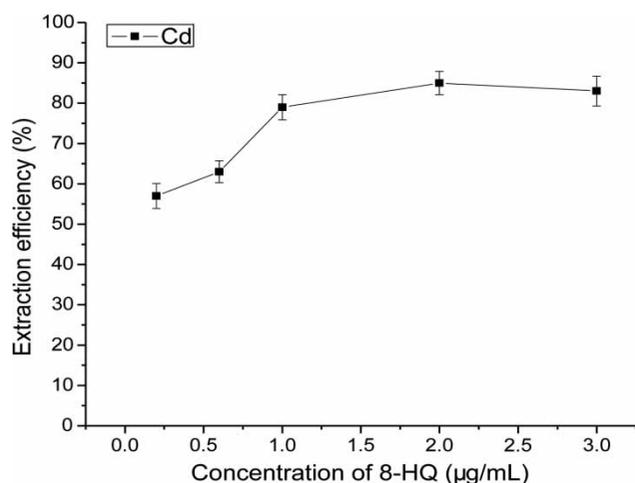


Figure 4 | Effect of concentration of 8-HQ. Fixed parameters: 100 µg/L Cd, 2% Genapol X-080, 2% octanol, pH 9.

preconcentration of cadmium was investigated in the range 0.2–4% (v/v). When the concentration of Genapol X-080 was 0.2–2% (v/v), the extraction efficiency of the complexes increased (Figure 5). When the concentration of Genapol X-080 was above 2%, the viscosity of the system increased and interfered with the separation of the two phases, which is unfavorable for the complex extracted into the surfactant-rich phase, and the extraction efficiency of complexes decreased. Hence, 2% Genapol X-080 was chosen as optimum surfactant amount for CPE.

Effect of concentration of octanol

Effects of alcohol on the cloud point of nonionic surfactant have been reported. When the number of carbon atoms of

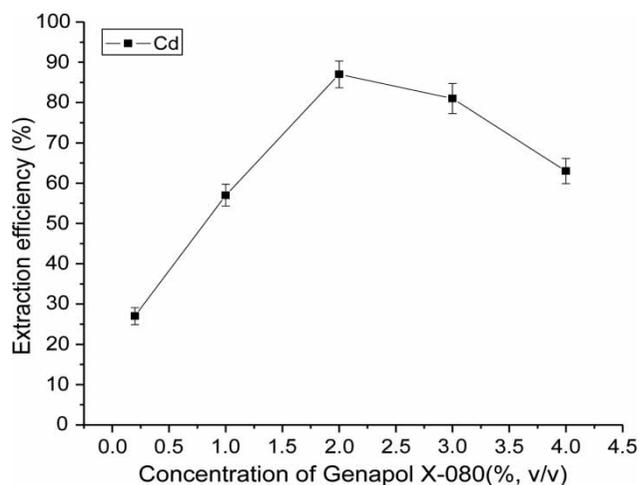


Figure 5 | Effect of concentration of Genapol X-080. Fixed parameters: 100 µg/L Cd, 2 µg/mL 8-HQ, 2% octanol, pH 9.

straight-chain alcohol is greater than four, it can depress the cloud point of nonionic surfactant (Guo & Zhu 1995). When the polar organic liquid was partially soluble in water, the molecules of additive may be solubilized in the micelles and adsorbed at the interface micelle water, which could justify a micellar growth and a depression in cloud point (Zhang & Yin 2005). In this paper, octanol was used to depress the cloud point of Genapol X-080. Figure 6 shows the effect of the concentration of octanol on CPE, and 2% (v/v) octanol was chosen for following experiment.

Effects of equilibration temperature and time

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature. It was found that 30 °C was adequate, as a compromise between completion of extraction and efficient separation of phases. The dependence of extraction efficiency on equilibration time was studied for a time span of 10–60 min. An equilibration time of 20 min was chosen as the optimal to achieve quantitative extraction.

Effect of foreign ions

Several metal ions that might react with 8-HQ were examined for their effect on the recoveries of cadmium. An ion was considered as interferent, when it caused a variation in the absorbance of the sample greater than ±5%. Five millilitres of sample solution containing Cd (10 µg/L) and other ions was prepared and treated with the proposed procedure. The results are shown in Table 1. It was found that the tolerable concentration ratio of foreign ions to Cd was

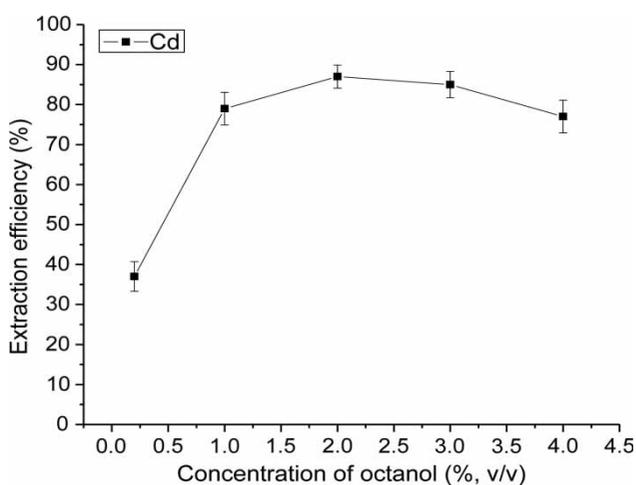


Figure 6 | Effect of the concentration of octanol. Fixed parameters: 100 µg/L Cd, 2 µg/mL 8-HQ, 2% Genapol X-080, pH 9.

Table 1 | Effect of foreign ions on Cd preconcentration and determination

Foreign ions	Foreign ions/Cd ²⁺ (w/w)	Recovery (%)
Mg ²⁺	100	93.2
Cu ²⁺	100	92.8
Fe ³⁺	500	97.2
Hg ²⁺	500	103.9
Pb ²⁺	100	93.6
Zn ²⁺	500	100.1
Mn ²⁺	500	97.3
Ni ²⁺	500	101.3
Cr ⁶⁺	100	96.4

100 for Mg²⁺, Cu²⁺, Pb²⁺, and Fe³⁺; and 500 for Hg²⁺, Zn²⁺, Mn²⁺ and Ni²⁺. The recovery was quantitative and satisfactory in the presence of the major cations in the water samples, which had no obvious influence on CPE of Cd under the selected conditions.

Effect of additives in CPE

Salts are classical additives added to change the cloud point of aqueous solution of nonionic surfactant. A comparison of the proposed method (surfactant + octanol) with other classical preconcentration procedures (surfactant + salt) is given in Table 2. The proposed method can obtain lower cloud point and higher extraction efficiency. The extraction procedure of compared methods was as follows: 100 µL surfactant and 0.3 g NaCl were added into 5 mL of standard solutions and vortex-mixed for 60 s and kept for 20 min in a thermostated bath. Centrifugation was run for 5 min at 3500 rpm.

Analytical features

Calibration curves were obtained by preconcentrating 5 ml of standard solutions with CPE. Table 3 shows the analytical

Table 2 | Effect of additives in CPE

Surfactant	Additive	Cloud point (°C)	Extraction efficiency (%)
Triton X-114	NaCl	40	71
Triton X-100	NaCl	55	67
TMN-6	NaCl	65	19
Genapol X-080	NaCl	35	56
Genapol X-080	octanol	30	87

Table 3 | Analytical characteristics of the method

Parameters	Cd
Concentration range	10–500 µg/L
Correlation coefficient (<i>r</i>)	0.9993
Relative standard deviation (<i>n</i> = 6)	3.2%
Limit of detection	0.21 µg/L
Limit of quantification	0.63 µg/L
Enhancement factor	20

characteristics of the proposed method. Under the optimal conditions, the calibration curves were linear in the range of 10–500 µg/L (*r* = 0.9993). The enhancement factor was about 20. The limit of detection (LOD) of the method, calculated as three times the standard deviation of the blank signals, was 0.21 µg/L for the preconcentration of 5 mL of sample solution. The limit of quantification (LOQ) usually equals about three times the LOD value. Therefore, the LOQ value was 0.63 µg/L. The precision of the method was determined by analyzing standard solution at 100 µg/L of Cd for six times in continuous and the relative standard deviation (RSD) was 3.2%.

Recovery of Cd in water samples

Samples were analysed to assess their content of Cd. For this purpose, the samples were digested and filtered. Then 5 ml of each of the samples was preconcentrated using CPE procedure. In addition, recovery experiments for different amounts of Cd were carried out. The recovery for the addition of different concentrations of Cd to water samples, was in the range of 94.1–103.8% (Table 4). The results show that the proposed method is suitable for determination of Cd in such water samples.

Comparison of the results obtained by the proposed method and standard methods

To evaluate the accuracy of the proposed method, a comparison between results obtained by the suggested method and other standard methods was performed. In the paper by Ma et al. (2009), ultrasound-assisted emulsification micro-extraction with FAAS (USAEME-FAAS) was applied for the extraction and preconcentration of Cd from water samples in which NaDDTC·3H₂O was used as a chelating agent and carbon tetrachloride as extraction solvent. Afkhami et al. (2006) developed a method which was based on the CPE of cadmium in iodide media with Triton X-114. Cd

Table 4 | Recovery of Cd in water samples

Sample	Cd concentration ($\mu\text{g/L}$)		Recovery (%)	RSD (%; $n = 3$)
	Added	Found		
Industrial wastewater	0	8.2		5.1
	10	17.9	97	3.4
	50	60.1	103.8	4.7
	100	105.3	94.1	5.3
Wastewater	0	not detected		
	10	10.3	103	3.9
	50	49.1	98.2	3.1
	100	101.5	101.5	4.3
River water	0	not detected		
	10	9.7	97	2.6
	50	51.1	102.2	1.8
	100	103.7	103.7	3.4
Tap water	0	not detected		
	10	10.1	101	3.1
	50	48.3	96.6	2.8
	100	99.7	99.7	2.8

Table 5 | The results obtained by this method and other methods

sample	Cd concentration ($\mu\text{g/L}$) obtained		
	This method	USAEME-FAAS (Ma et al. 2009)	CPE-FAAS (Afkhami et al. 2006)
Industrial wastewater	8.3	7.9	8.1

content in industrial wastewater samples were tested by the proposed method as well as standard methods by J. J. Ma et al. (2009) and A. Afkhami et al. (2006). The obtained results are shown in Table 5. In samples, the concentrations obtained by both methods were in agreement.

CONCLUSION

This paper proposed a method for the determination of Cd in water samples by CPE combined with FAAS using 8-HQ as chelating reagent. In CPE, octanol was firstly used to depress the cloud point of Genapol X-080 (70 °C) to room temperature (30 °C). Phase separation can be achieved at relatively low temperature which is a safe and simple operation and this procedure might well be extended to detect thermally unstable substances. Using octanol instead of inorganic salts lowers the cloud point and can avoid desalination and reduce salt damage to the

instrument. In short, compared with classical CPE, this method can obtain comparative extraction efficiency and recovery. It extends the application of CPE.

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REFERENCES

- Afkhami, A., Madrakian, T. & Siampour, H. 2006 Flame atomic absorption spectrometric determination of trace quantities of cadmium in water samples after cloud point extraction in Triton X-114 without added chelating agents. *Journal of Hazardous Materials* **138** (2), 269–272.
- Corradi, M. & Mutti, A. 2011 Metal ions affecting the pulmonary and cardiovascular systems. *Metal Ions in Life Sciences* **8**, 81–105.
- Escaleira, L. A., Santelli, R. E. & Oliveira, E. P. 2009 Preconcentration procedure for determining trace amounts of Ni, Cd, Pb and Cu in high-salinity waters after cloud-point extraction. *International Journal of Environmental and Analytical Chemistry* **89** (7), 515–527.
- Ferreira, S. L. C., de Andrade, J. B., Korn, M. G. A., Pereira, M. G., Lemosc, V. A., dos Santos, W. N. L., Rodrigues, F. M., Souza, A. S., Ferreira, H. S. & da Silva, E. G. P. 2007 Review of procedures involving separation and preconcentration for the determination of cadmium using spectrometric techniques. *Journal of Hazardous Materials* **145** (3), 358–367.
- Guo, R. & Zhu, W. Q. 1995 Effect of alcohol on cloud point of nonionic surfactant. *Chemical Journal of Chinese Universities* **16**, 1104–1108.
- Huang, M., Choi, S. J. & Kim, D. W. 2009 Risk assessment of low-level cadmium and arsenic on the kidney. *Journal of Toxicology and Environmental Health, Part A* **72** (21–22), 1493–1498.
- Järup, L. 2003 Hazards of heavy metal contamination. *British Medical Bulletin* **68** (1), 167–182.
- Järup, L., Berglund, M. & Elinder, C. G. 1998 Health effects of cadmium exposure – a review of the literature and a risk estimate. *Scandinavian Journal of Work, Environment & Health* **24**, 1–51.
- Joseph, P. 2009 Mechanisms of cadmium carcinogenesis. *Toxicology and Applied Pharmacology* **238** (3), 272–279.
- Khan, S. I., Ahmed, A. K. M. & Yunus, M. 2010 Arsenic and cadmium in food-chain in Bangladesh – an exploratory study. *Journal of Health, Population, and Nutrition* **28** (6), 578–584.

- Kyriakou, L. G., Tzirogiannis, K. N. & Demonakou, M. D. 2011 Gadolinium chloride pretreatment ameliorates acute cadmium-induced hepatotoxicity. *Toxicology and Industrial Health* **29** (7), 624–632.
- Ma, J. J., Du, X., Zhang, J. W., Li, J. C. & Wang, L. Z. 2009 Ultrasound-assisted emulsification–microextraction combined with flame atomic absorption spectrometry for determination of trace cadmium in water samples[J]. *Talanta* **80** (2), 980–984.
- Manzoori, J. L. & Karim-Nezhad, G. 2004 Development of a cloud point extraction and preconcentration method for Cd and Ni prior to flame atomic absorption spectrometric determination. *Analytica Chimica Acta* **521** (2), 173–177.
- Maranhão, T. A., Borges, D. L. G. & da Veiga, M. A. M. S. 2005 Cloud point extraction for the determination of cadmium and lead in biological samples by graphite furnace atomic absorption spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy* **60** (5), 667–672.
- Moore, J. W. 1991 *Inorganic Contaminants of Surface Water: Research and Monitoring Priorities*. Springer-Verlag, New York.
- Mudgal, V., Madaan, N. & Mudgal, A. 2010 Effect of toxic metals on human health. *The Open Nutraceuticals Journal* **3**, 94–99.
- Nordberg, G. F. 2009 Historical perspectives on cadmium toxicology. *Toxicology and Applied Pharmacology* **238** (3), 192–200.
- Paleologos, E. K., Giokas, D. L. & Karayannis, M. I. 2005 Micelle-mediated separation and cloud-point extraction. *TrAC Trends in Analytical Chemistry* **24** (5), 426–436.
- Reilly, C. 2008 *Metal Contamination of Food: its Significance for Food Quality and Human Health*. Wiley, Oxford, UK.
- Sadaghiana, A. S. & Khan, A. 1991 Clouding of a nonionic surfactant: the effect of added surfactants on the cloud point. *Journal of Colloid and Interface Science* **144** (1), 191–200.
- Sarkar, B. 2002 *Heavy Metals in the Environment*. CRC Press.
- Sharma, K. S., Patil, S. R. & Rakshit, A. K. 2003 Study of the cloud point of nonionic surfactants: effect of additives. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **219** (1), 67–74.
- Shemirani, F., Abkenar, S. D. & Mohammad, R. J. 2005 Determination of cadmium (II), copper (II) and zinc (II) in water samples by flame atomic absorption spectrometry after cloud point extraction. *Indian Journal of Chemistry. Sect. A: Inorganic, Physical, Theoretical & Analytical* **44** (6), 1211–1214.
- Silva, E. L. & Roldan, P. S. 2009 Simultaneous flow injection preconcentration of lead and cadmium using cloud point extraction and determination by atomic absorption spectrometry. *Journal of Hazardous Materials* **161** (1), 142–147.
- Trzcinka-Ochocka, M., Jakubowski, M. & Razniewska, G. 2004 The effects of environmental cadmium exposure on kidney function: the possible influence of age. *Environmental Research* **95** (2), 143–150.
- Wen, X., Yang, Q. & Yan, Z. 2011 Determination of cadmium and copper in water and food samples by dispersive liquid–liquid microextraction combined with UV–vis spectrophotometry. *Microchemical Journal* **97** (2), 249–254.
- Zhang, Z. G. & Yin, H. 2005 Effect of additives on the cloud point of nonionic surfactant AEO-9 in aqueous solution. *Acta Petrolei Sinica (Petroleum Processing Section)* **21** (5), 70–75.
- Zhu, X., Zhu, X. & Wang, B. 2006 Determination of trace cadmium in water samples by graphite furnace atomic absorption spectrometry after cloud point extraction. *Microchimica Acta* **154** (1–2), 95–100.

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