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Determination of heavy metals in water samples using dual-cloud point extraction coupled with inductively coupled plasma mass spectrometry

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A dual-cloud point extraction (d-CPE) technique combined with inductively coupled plasma mass spectrometry (ICP-MS) was used for preconcentration and determination of Cr, Ga, Ag, Cd, Mn, Fe, In, Cu, Ni, Co, Pb and Zn in real water samples. An orthogonal array design (OAD) with the OA₂₅ (5⁶) matrix was employed to study the effects of different parameters on the extraction efficiency. Under the best experimental conditions (concentration of complexing reagent 8-hydroxyquinoline, 0.25 mmol L⁻¹, pH, 6.5; equilibrium temperature, 60 °C; surfactant Triton X-114, 0.1%; equilibrium time, 30 min and without salt addition), the enhancement factor ranged from 9.85 to 35.98. The linear dynamic range (LDR) was 1–800 µg L⁻¹ with correlation coefficients of 0.9974–0.9999 and the limits of detection (LODs) were between 0.012 and 0.36 µg L⁻¹. Relative standard deviations (RSDs, *C* = 10 µg L⁻¹ and *n* = 6) were 1.29%–5.56%. Finally, the developed method was successfully applied to extraction and determination of the mentioned metal ions in real water samples and satisfactory results were obtained.

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1. Introduction

With the rapid development of industries, more and more waste water containing hazardous heavy metals is being discharged into rivers, which are harmful to living beings and the environment around us.¹ Trace heavy metals are one of the most common pollutants that have severely deteriorated aquatic ecosystems, their release into aquatic ecosystems is triggered by both natural and anthropogenic processes.^{2,3} Therefore, determination of trace levels of heavy metals is very critical in the context of environmental protection.⁴ However, it is generally impossible to determine metal ions at trace levels directly in environmental samples because of interfering species in the surrounding matrix, or the concentration of analytes below the detection limit of the instrument.⁵ So preconcentration and separation techniques are still necessary.

Various sample preparation methods including solid-phase extraction (SPE),^{6–8} solid phase microextraction (SPME),^{9–11} dispersive liquid–liquid microextraction (DLLME),^{12–15} and the dispersive liquid–liquid microextraction method based on solidification of floating organic drop (DLLME-SFO)^{16–18} have been developed for the preconcentration and separation of

heavy metals. Recently, cloud point extraction (CPE)^{19–24} as an important and powerful method has also been widely applied to extract and preconcentrate various metal ions. This method has some advantages such as low cost, rapidity, simplicity of operation, high preconcentration factors and extraction efficiency. However, traditional CPE is primarily based on the hydrophobic interaction between the solutes and surfactant, other hydrophobic species can be extracted into the surfactant-rich phase and may interfere with the analysis of interested analytes.²⁵ The as-obtained surfactant phase by the CPE method is viscous and must be diluted with organic solvents such as methanol and furthermore, they are not often compatible with inductively coupled plasma mass spectrometry (ICP-MS). Additionally, it is easy to form carbon particles, depositing at the mouth of the torch tube and influencing the stability of ICP.²⁶

A novel dual-cloud point extraction (d-CPE) technique was successfully developed for electrophoretic speciation of mercury by Yin,²⁷ which can eliminate the adsorbed surfactant on the capillary wall, since the adsorbed surfactant might affect the sample injection and separation in traditional CPE. The d-CPE technique includes two cloud point extraction processes. The first part of the d-CPE procedure is done just as traditional CPE. But, instead of direct analysis, another round of CPE procedure, in which the surfactant-rich phase is treated with another aqueous solution, is done. After heating at controlled temperature in a thermostatic bath and centrifugation, finally the analyte is back extracted into the aqueous phase at the second cloud point step. The obtained aqueous extract is introduced into ICP-MS as the sample for analysis. The potential interfering

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species were also eliminated to some extent.²⁸ The removal of interfering species through the d-CPE procedure improves the selectivity of the analysis method extensively, and besides, the aqueous sample solution is naturally compatible with the conditions of ICP-MS.

In this study, d-CPE was used to eliminate the surfactant. Nitric acid was chosen as the back extraction agent to extract metal ions Cr, Ga, Ag, Cd, Mn, Fe, In, Cu, Ni, Co, Pb and Zn. 8-Hydroxyquinoline (8-HQ) was employed as a chelating agent in d-CPE. The effects of different variables, the concentrations of the complexing reagent, back extraction agent, and Triton X-114, pH, salt addition, equilibrium time and temperature, were investigated and discussed in detail. The method was validated by the simultaneous determination of the target metals in river water samples. To the best of our knowledge, no report has been published on d-CPE in combination with ICP-MS for the determination of heavy metals in water samples.

2. Experiment

2.1. Instrumentation

The detection system used for the determination of heavy metal ions was NexION 300X ICP-MS (Perkin-Elmer, USA). The instrumental operating conditions for the determination of the elements are summarized in Table 1. The pH values were measured using a Model PHB-5 pH-meter (Switzerland), equipped with a E201-combination electrode. A Hettich Rotanta 460 centrifuge (Germany) was used to accelerate the phase separation. Double deionized water was prepared from a SZ-2 system (Shanghai Lu West Analytical Instruments, Shanghai, China).

2.2. Chemicals and samples

All chemicals used were of analytical reagent grade. Stock standard solutions of Cr, Ga, Ag, Cd, Mn, Fe, In, Cu, Ni, Co, Pb and Zn (1000 mg L⁻¹) were purchased from Merck (Darmstadt, Germany). The standard solutions were diluted with double deionized water to prepare the mixed standard solutions. Reagent grade 8-HQ (Sigma, St. Louis, MO, USA) was used as the chelating agent, prepared by dissolving an appropriate amount

of this chelating agent in ethanol. A 5% (m/v) Triton X-114 solution (Sigma, St. Louis, MO, USA) was used. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution. 0.7 mol L⁻¹ HNO₃ was prepared with double deionized water for back extraction. The solutions of other metals as well as those used for the interference study were obtained from the respective inorganic salts (Tianjin Reagent Factory, Tianjin, China). Real water samples were collected from the Changjiang River (Chongqing), and filtered through a filter paper and stored in the refrigerator.

2.3. Procedure of d-CPE

The procedure of d-CPE was based on the conventional cloud point extraction process. A 50.0 mL of solution was placed in a 55.0 mL screw cap glass tube and spiked with the metal ions (Cr, Ga, Ag, Cd, Mn, Fe, In, Cu, Ni, Co, Pb and Zn) at the 10 µg L⁻¹ level. 0.2–1.5 mL of Triton X-114 (5%, m/v) and appropriate amounts of 8-HQ solutions were added and buffered at pH 6.5. The tube was kept in a thermostatic bath at 60 °C for 30 min. The separation of the two phases was accelerated by centrifugation of the solution for 10 min at 3500 rpm. The tube was then placed in an ice bath for 30 min to increase the viscosity of the surfactant-rich phase. Then, the bulk aqueous phase was easily

Table 2 OA₂₅ (5⁶) experimental design for the extraction of metal ions

No.	A (PH)	B (TX)	C (8-HQ)	D (T)	E (time)	F (NaCl)	Recovery (%)
1	5	0.025	0.1	45	15	0	66.22
2	5	0.075	0.2	55	25	1	87.38
3	5	0.1	0.25	60	30	3	91.51
4	5	0.125	0.3	65	35	5	87.93
5	5	0.15	0.6	75	40	10	84.17
6	6	0.025	0.2	60	35	10	85.73
7	6	0.075	0.25	65	40	0	94.10
8	6	0.1	0.3	75	15	1	88.19
9	6	0.125	0.6	45	25	3	85.63
10	6	0.15	0.1	55	30	5	84.28
11	6.5	0.025	0.25	75	25	5	89.45
12	6.5	0.075	0.3	45	30	10	88.60
13	6.5	0.1	0.6	55	35	0	95.94
14	6.5	0.125	0.1	60	40	1	89.50
15	6.5	0.15	0.2	65	15	3	89.47
16	7	0.025	0.3	55	40	3	89.97
17	7	0.075	0.6	60	15	5	90.83
18	7	0.1	0.1	65	25	10	86.10
19	7	0.125	0.2	75	30	0	93.08
20	7	0.15	0.25	45	35	3	88.59
21	7.5	0.025	0.6	65	30	1	88.83
22	7.5	0.075	0.1	75	35	3	84.96
23	7.5	0.1	0.2	45	40	5	88.02
24	7.5	0.125	0.25	55	15	10	89.57
25	7.5	0.15	0.3	60	25	0	94.24
r1	83.44	84.04	82.21	83.41	84.86	88.71	
r2	87.59	89.17	88.74	89.43	88.56	88.47	
r3	90.60	89.95	90.64	90.36	89.26	88.36	
r4	89.71	89.14	89.79	89.29	88.63	88.10	
r5	89.12	88.15	89.08	87.97	89.15	86.83	
R	7.15	5.91	8.43	6.95	4.40	1.88	

Table 1 Operating conditions for ICP-MS

Nebulizer	Meinhard
Spray chamber	Cyclonic
RF power (kW)	1.20
Auxiliary gas flow rate (L min ⁻¹)	1.20
Plasma gas flow rate (L min ⁻¹)	18.00
Sample uptake rate (mL min ⁻¹)	1.50
Detection mode	Auto
No. of replicates per sample	3
Dwell time (ms)	100
Sweeps/reading	5
Analytical masses	⁵² Cr, ⁶⁹ Ga, ¹⁰⁷ Ag, ¹¹¹ Cd, ⁵⁵ Mn, ⁵⁷ Fe, ¹¹⁵ In, ²⁰⁸ Pb, ⁵⁹ Co, ⁶³ Cu, ⁶⁰ Ni, and ⁶⁶ Zn

decanted. Instead of addition of diluents or analysis, the surfactant-rich phase containing the complexes was treated with 2 mL of 0.7 mol L⁻¹ HNO₃, and then the second round of cloud point extraction was applied to the solution with a thermostatic bath at 60 °C for 30 min and centrifugation for 10 min at 3500 rpm. After d-CPE, a supernatant was introduced into ICP-MS for analysis. Blanks and real samples were also prepared in the similar way.

3. Results and discussion

3.1. Experimental design and data analysis

Orthogonal array design (OAD), also known as a type of fractional factorial design, in which an orthogonal array is used to

arrange different factors for effective optimization of experimental conditions, is believed to incorporate the advantages of a simplex method and factorial design.^{29,30} The use of OAD can simplify the experiment procedure without affecting the quality of results. A six-factor, five-level factorial design was used to evaluate the effects of the concentration of the complexing reagent (8-HQ) and surfactant Triton X-114 (TX), equilibrium time (time) and temperature (*T*), pH and concentration of NaCl (NaCl) on the extraction efficiency of the metal ions. 25 experiments were performed. Each experiment was repeated twice and the factors and their respective levels are reported in Table 2. The effects of different parameters on the d-CPE method combined with ICP-MS experiments based on the average

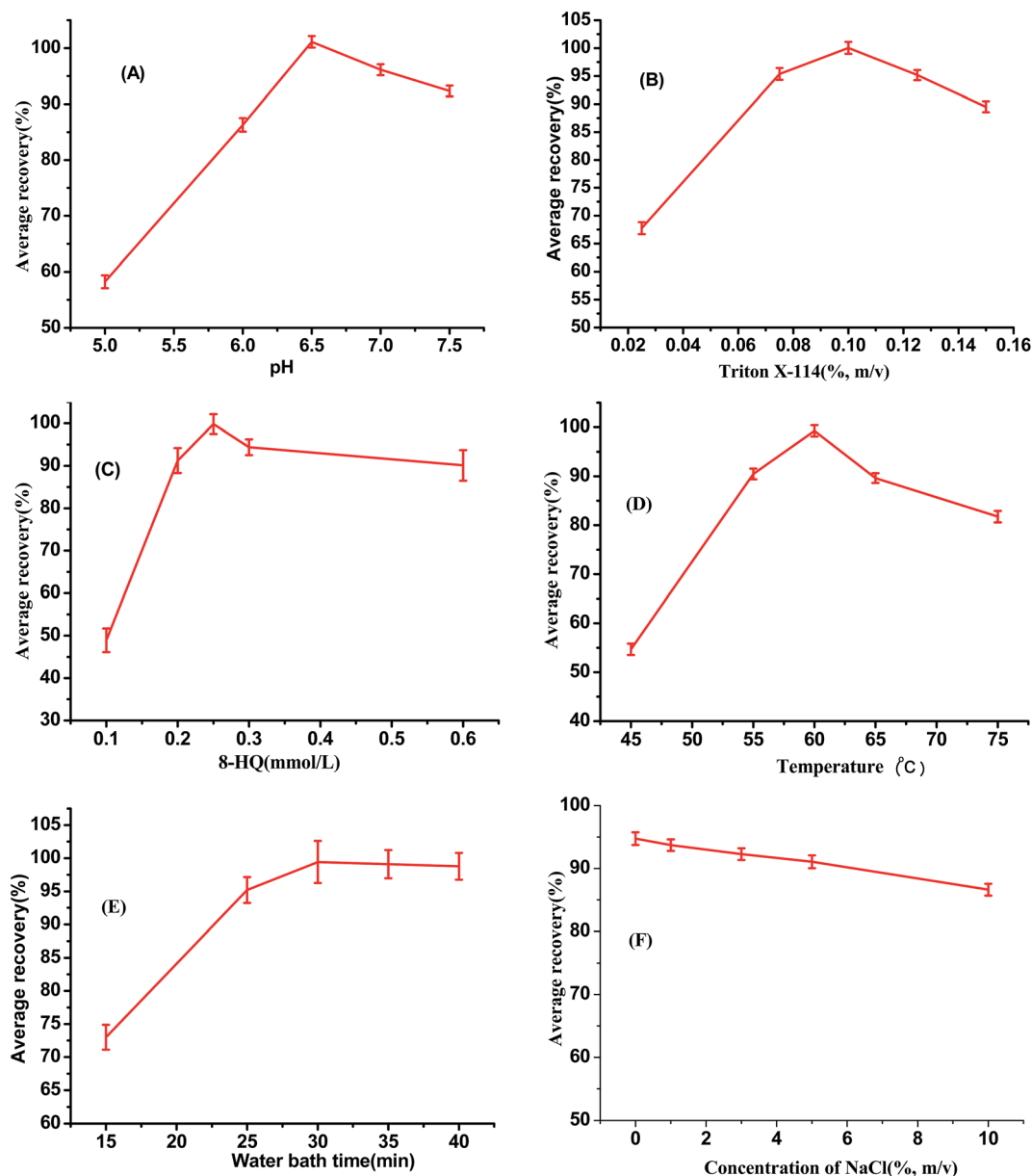


Fig. 1 The effects of each factor on d-CPE-ICP-MS using OAD. (A) Effect of pH, (B) effect of Triton X-114 (TX), (C) effect of the concentration of the complexing reagent (8-HQ), (D) effect of the temperature, (E) effect of the equilibrium time, and (F) effect of the concentration of NaCl. Concentration of metal ions, 20 $\mu\text{g L}^{-1}$.

extraction recovery of the metal ions are given in Fig. 1. The results of the OAD experiment can be statistically treated by two ways: analysis of variance (ANOVA) and direct observation analysis. From ANOVA and direct observation analysis of experimental results, factors that significantly affect the output responses can be found and optimal parameters for an analytical procedure can be obtained.³¹ The mean values (r_1 , r_2 , r_3 , r_4 and r_5) of different factors at different levels revealed the change of extraction efficiency. The extreme difference (r) was applied to analyze the data and the results indicated that the influence (R) of extraction factors on the extraction recovery is $R(C) > R(A) > R(D) > R(B) > R(E) > R(F)$. Namely, concentration of the complexing reagent $>$ pH $>$ equilibrium temperature $>$ surfactant Triton X-114 $>$ equilibrium time $>$ concentration of NaCl. Therefore, the best values of the selected factors for the extraction of the ions were obtained as: concentration of the complexing reagent (8-HQ), 0.25 mmol L⁻¹; pH, 6.5; equilibrium temperature (T), 60 °C; surfactant Triton X-114 (TX), 0.1%; equilibrium time (time), 30 min and without salt addition.

3.2. Effect of pH on d-CPE

The pH plays a unique role on metal chelate formation and subsequent extraction, and is proved to be a main parameter for d-CPE. Extraction yield depends on the pH at which complex formation is carried out. In this work, the effect of pH upon the extraction of Cr, Ga, Ag, Cd, Mn, Fe, In, Cu, Ni, Co, Pb and Zn ions was studied by using five replicate mixed standard solutions of each analyte in the pH range of 5–7.5. As shown in Fig. 1A, the effect of pH on the average recovery of the metal ions was significant and at the pH of 6.5, the maximum extraction of metal ions was obtained. Hence, the pH of 6.5 was chosen for the subsequent extractions and real sample analysis.

3.3. Effect of Triton X-114 concentration on d-CPE

The non-ionic surfactant Triton X-114 was chosen because of its low toxicological properties and cost. Its high density facilitates phase separation. Also, the high density of the surfactant rich phase facilitates phase separation by centrifugation.³² The effect of Triton X-114 concentrations on the extraction efficiencies was evaluated in the range of 0.025–0.15% (m/v) in this study. As shown in Fig. 1B, the recovery of metal ions reaches the highest at the concentration of 0.10% for all ions. Therefore, a concentration of 0.10% (m/v) of Triton X-114 was selected in the following experiments.

3.4. Effect of 8-HQ concentration on d-CPE

For d-CPE, 8-HQ was used as the chelating agent, as it can react with metal ions to form hydrophobic chelates, which can be extracted into Triton X-114. The optimization of 8-HQ concentration was an important parameter for extraction efficiency. The extraction efficiency of Cr, Ga, Ag, Cd, Mn, Fe, In, Cu, Ni, Co, Pb and Zn as a function of 8-HQ concentrations ranged from 0.10 to 0.60 mmol L⁻¹ as shown in Fig. 1C. The recovery of analytes reached the maximum when the concentration of 8-HQ was 0.25 mmol L⁻¹. When the concentration continues to increase, it seems that there is a slight reduction of extraction in

high concentrations of 8-HQ, this is because the excess of non-ionic 8-HQ molecules are presumably trapped in the micelles. Hence, 0.25 mmol L⁻¹ of the 8-HQ was selected for further studies.

3.5. Effect of equilibration temperature and time on d-CPE

The greatest pre-concentration efficiency would be achieved when the CPE process is carried out at the equilibration temperature above the cloud point temperature of the surfactant (Triton X-114). Sufficient incubation time is required for completing the formation of extractable ion associated and chelating and their effective interaction and quantitative transfer into the solubilizing sites.³³ In the present study the equilibration temperature of the thermostatic bath was investigated at the range of 45–75 °C (Fig. 1D). It was found that the temperature of 60 °C was adequate for all the studied elements. The dependence of extraction efficiency upon equilibration time was studied for a time span of 15–40 min (Fig. 1E). It was observed that 30 min was sufficient to achieve a quantitative extraction of analytes. Therefore, an equilibration time of 30 min was employed for the separation process. In the second CPE procedure also, the water bath temperature and time were 60 °C and 30 min, respectively.

3.6. Salt effect

The influence of ionic strength on d-CPE performance was evaluated by adding various amounts of NaCl in the range 0–10.0% (m/v) (Fig. 1F). The obtained results showed that by increasing the NaCl%, the extraction recovery decreases, therefore, further experiments were performed without salt addition.

3.7. Effect of concentrations of back extraction agent

The influence of back-extraction solution concentrations on the preconcentration in the second step was investigated. For this purpose HCl and HNO₃ of 0.5 to 1.0 mol L⁻¹ were employed to extract the ions from their hydrophobic complexes trapped in

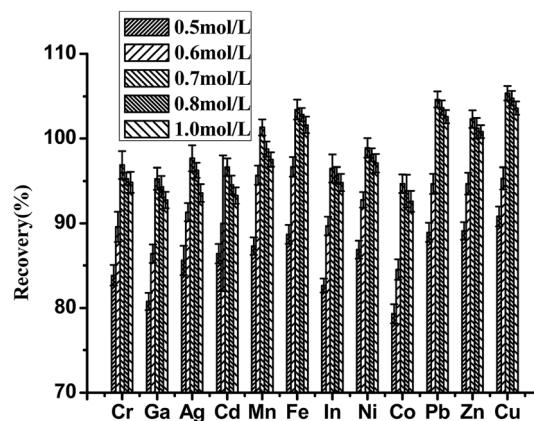


Fig. 2 Effects of HNO₃ concentrations on d-CPE efficiency. Conditions: 50 mL solution, pH 6.5, 10 μg L⁻¹ metal ions, 0.25 mmol L⁻¹ 8-HQ, and 0.1% (m/v) Triton X-114.

micellar media form back into the aqueous phase. It is found that HNO₃ shows an excellent efficiency of back extraction by d-CPE for all the metal ions. However, when HCl was used, the back extraction efficiencies of all metal ions were lower than those using HNO₃, so HCl is not a good back extraction agent for this study. As shown in Fig. 2, the back extraction efficiency is the highest when the concentration of HNO₃ is 0.7 mol L⁻¹. Therefore, in the second phase of d-CPE, HNO₃ at 0.7 mol L⁻¹ was selected for back extraction of elemental ions into the aqueous phase.

3.8. Effects of interfering ions

The effects of the common coexisting ions were investigated for efficient extraction of elements by d-CPE. In these experiments, solutions of 20 µg L⁻¹ of the analytes containing the interfering ions were treated according to the optimized procedures. The amounts of interfering ions were determined according to the metal-to-interferent ratios. Table 3 shows the tolerance limits of every interfering ion. Recoveries of 95.39–107.37% for all heavy metal ions were obtained. Therefore, the presence of the common cations and anions in real water samples has no significant effect on the recovery of the analytes.

3.9. Analytical properties of merit

The figures of merit of the developed d-CPE procedure are summarized in Table 4. Enrichment factors, defined as the ratios of the slopes of the analytical curves before and after the d-CPE, were in the range of 9.85–35.98. The detection limits (LODs) were calculated based on the expression $LOD = 3S_b/m$, where, S_b is the standard deviation of ten replicate blank measurements and m is the slope of the calibration graph. LODs were in the range of 0.012–0.36 µg L⁻¹. The limits of quantification (LOQs) were calculated based on the standard deviation of the blank to the slope of the calibration graph (S_d/m). It was equal to 10. The relative standard deviations (RSDs, $n = 6$ and $C = 10$ µg L⁻¹) were 1.29%–5.56%.

Table 4 Analytical figures of merit of the proposed method

Metal	LDR ^a	Slope	EF ^b	LOD ^c	LOQ ^d	RSD ^e
Cr	1–800	0.184	14.23	0.32	1.07	1.82
Ga	1–800	0.0413	20.39	0.36	1.20	2.35
Ag	1–800	0.154	10.59	0.014	0.047	3.12
Cd	1–800	0.00438	11.74	0.016	0.053	1.56
Mn	1–800	0.0546	13.28	0.26	0.087	2.42
Fe	1–800	0.000981	29.15	0.055	1.83	2.68
In	1–800	0.0702	12.08	0.059	0.20	3.37
Ni	1–800	0.0411	13.16	0.086	0.29	5.18
Co	1–800	0.205	11.28	0.064	0.21	5.56
Pb	1–800	10.0321	9.85	0.17	0.57	2.09
Zn	1–800	0.184	16.04	0.077	0.26	1.62
Cu	1–800	0.0413	35.98	0.012	0.04	1.29

^a Linear dynamic range (µg L⁻¹). ^b Enrichment factor. ^c Limit of detection (µg L⁻¹). ^d Limit of quantification (µg L⁻¹). ^e Relative standard deviation ($C = 10$ µg L⁻¹ and $n = 6$).

A comparison of the efficiency by the newly developed d-CPE method and the other CPE methods to extract and determine similar metal ions is given in Table 5. We see that our method has a lower detection limit of 0.012–0.36 µg L⁻¹ and a higher enhancement factor of 9.85–35.98. The advantage of d-CPE embodies in the very little amount of surfactant in the aqueous phase for analysis by ICP-MS, indicating that the influence of the surfactant Triton X-114 on ICP can be significantly eliminated.

3.10. Analysis of real samples

The proposed method was applied to determine the heavy metal ions in real river water samples. In addition, reliability was checked by analysis of spiking experiments. The obtained results are given in Table 6. As can be seen, the recoveries in the range of 92.34–109.13% are reasonably well for ultra trace analysis.

Table 3 Effects of interfering ions on the recovery of heavy metals in water samples^a

Interference	Interference to analyte ratio (w/w)	Recovery (%)											
		Cr	Ga	Ag	Cd	Mn	Fe	In	Ni	Co	Pb	Zn	Cu
K ⁺	3000	103.36	98.21	96.43	101.72	104.62	106.63	97.82	98.83	102.33	105.25	104.41	107.37
Ca ²⁺	3000	101.37	97.39	104.32	98.37	99.33	98.79	102.31	97.38	99.67	98.83	101.77	103.76
Na ⁺	4000	99.38	99.58	98.22	101.32	97.81	95.48	103.43	101.11	100.88	97.12	99.67	103.68
Mg ²⁺	2000	100.28	103.21	101.18	95.87	96.73	97.85	97.12	99.51	96.68	95.91	102.83	99.57
Al ³⁺	2000	98.84	97.82	106.69	98.83	97.79	95.39	96.56	103.35	98.89	98.37	100.18	98.48
Ba ²⁺	3000	97.31	104.53	99.53	102.22	101.63	96.83	100.32	98.67	100.18	96.62	98.89	105.52
SO ₄ ²⁻	1000	98.79	100.21	101.00	96.68	98.28	99.39	98.57	101.29	98.36	99.09	101.2	102.28
CO ₃ ²⁻	1000	101.51	97.39	97.50	98.39	95.68	97.08	95.82	96.68	95.67	96.08	97.71	98.31
NO ₃ ⁻	3000	102.22	100.61	101.67	99.38	98.86	99.39	96.76	100.08	97.37	102.21	98.68	104.16
Cl ⁻	4000	101.51	100.43	98.83	98.83	100.68	98.59	98.39	97.39	101.31	98.69	102.28	103.72
Hg ²⁺	1500	95.53	98.65	97.17	96.57	97.21	95.49	98.87	96.08	95.79	97.61	101.77	102.58
Li ⁺	4000	100.88	99.83	98.03	98.38	102.37	98.07	96.39	103.42	98.51	99.64	100.27	103.36

^a Concentration of each analyte is 20 µg L⁻¹.

Table 5 comparison of the proposed method with other CPE methods for extraction and determination of the metal ions

Element	Method	EF	LDR ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	R	RSD/%	Ref.
Cu, Cd, Ni, Zn	CPE-ICP-OES	9.4–10.1	10–2500	1.0–6.3	0.9926–0.9982	1.3–2.6	1
Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	CPE-ICP-OES	13	2–5000	0.3–40	0.9911–0.999	1.5–11	34
Cd, Cu, Pb, Zn	CPE-FAAS	55.6–64.3	0.095–100	0.095–1.1	0.9982–0.9995	1.5–3.5	35
Cu	CPE-ST	125	4–115	1.2	0.9996	0.8–1.5	36
Cr	CPE-GFAAS	83.5	—	0.02	0.9998	2.6	37
Cr, Ga, Ag, Mn, Fe, In, Cu, Ni, Co, Pb, Zn	d-CPE-ICP-MS	9.85–35.98	1–800	0.012–0.36	0.9971–0.9999	1.29–5.56	This work

Table 6 Recoveries and determination results in water samples ($n = 3$)

Metal	Measured ($\mu\text{g L}^{-1}$)	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Cr	1.85	1.50	3.21	92.43
		2.00	3.93	104.32
		3.00	4.78	96.22
Ga	1.69	1.50	3.21	101.18
		2.00	3.82	107.69
		3.00	4.53	90.53
Ag	0	0.20	0.21	105.00
		0.40	0.39	97.50
		0.60	0.61	101.67
Cd	0.24	0.20	0.43	95.83
		0.40	0.65	104.17
		0.60	0.83	95.83
Mn	1.51	1.00	2.46	96.69
		1.50	2.92	94.04
		3.00	4.41	93.38
Fe	125.52	100.00	226.32	100.64
		120.00	246.72	100.96
		150.00	276.89	101.09
In	0.32	0.20	0.53	103.13
		0.40	0.71	96.88
		0.60	0.89	90.63
Ni	2.41	2.00	4.38	98.76
		2.50	5.13	109.13
		3.00	5.55	105.81
Co	0.14	0.10	0.24	100.00
		0.20	0.33	92.86
		0.30	0.45	107.14
Pb	0.26	0.20	0.45	96.15
		0.30	0.57	103.85
		0.40	0.68	107.69
Zn	4.12	3.0	6.97	96.36
		4.00	8.01	97.33
		6.00	9.87	93.93
Cu	0.41	0.20	0.62	102.44
		0.40	0.80	97.56
		0.60	1.03	104.88

4. Conclusions

A novel dual-cloud point extraction technique that can eliminate the effects of the surfactant on the performance of ICP-MS has been investigated. Comparing with the traditional CPE, the proposed method has extensive applications in sample pretreatment for separation and analysis of trace heavy metal ions in water samples. In the d-CPE procedure, metal ions could be back extracted into aqueous phases as target samples in the

analysis that followed and the surfactant is left at the bottom of the centrifuge tube. The results indicated that while it eliminates the influence of the surfactant in the surfactant-rich phase on ICP, the interference from the sample matrix can also be decreased to some extent. Furthermore, the method is characterized by its simplicity, ease of operation, cheapness and environmental friendliness.

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