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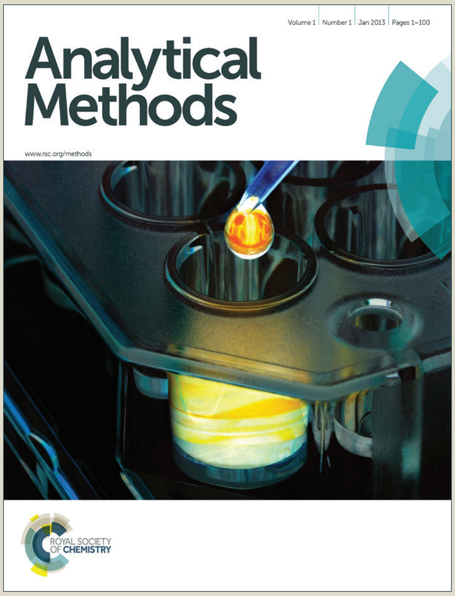

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Determination of heavy metals in water samples[1] using Dual-cloud point extraction coupled with inductively coupled plasma mass spectrometry

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Abstract

A dual-cloud point extraction (d-CPE) 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 OA_{25} (5^6) 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,

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60□; 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 μgL^{-1} with correlation coefficients of 0.9974-0.9999, the limits of detection(LODs) were between 0.012 and 0.36μg L^{-1}. Relative standard deviations (RSDs, C=10 μg L^{-1}, n=6) were 1.29%–5.56%. Finally, the developed method was successfully applied to extraction and determination of the mentioned metal ions real water samples and satisfactory results were obtained.

Key words: dual-cloud point extraction; inductively coupled plasma mass spectrometry; orthogonal array design; metal ions

1. Introduction

As the rapid development of industry, more and more waste water containing hazardous heavy metals was discharged into river, which is harmful to living beings and the environment around[1]. Trace heavy metals are one of the most common pollutants that have severely deteriorated the aquatic ecosystems, their release in aquatic ecosystem is triggered by both natural and anthropogenicprocesses[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 level directly in the environmental samples because of interfering species in the surrounding matrix, or the

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concentration of the analyte being 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], 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 also has 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 CPE method is viscous and must be diluted with organic solvent such as methanol and further, 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 torch tube and influencing the stability of ICP [26].

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A novel dual-cloud point extraction (d-CPE) 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. d-CPE technique includes two cloud point extraction processes. The first part of d-CPE procedure is done just as traditional CPE. But, instead of the direct analysis, another round of CPE procedure, in which, surfactant-rich phase is treated with another aqueous solution is done. After heating at control temperature in thermostatic bath and centrifugation, finally the analyte is back-extracted into aqueous phase at the second cloud point step. The obtained aqueous extract is introduced into ICP-MS as sample for analysis. The potential interfering species were also eliminated to some extent[28]. The removal of interfering species through the d-CPE procedure improves the analysis method selectivity 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 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 effect of different variables, concentration of complexing reagent, back extraction agent, Triton X-114, pH, salt addition, equilibrium time and temperature was investigated and

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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).

(Table 1 here)

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 (1000mgL^{-1}) were purchased from Merck (Darmstadt, Germany).. The

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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 chelating agent, prepared by dissolving 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. A 0.7 mol L^{-1} HNO_3 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 (Beijing, China). Real water samples were collected from Changjiang river (Chongqin), and filtered through filter paper and stored in the refrigerator.

2.3. Procedure of d-CPE

The procedure of d-CPE was based on conventional cloud point extraction process. A 50.0mL of solutions was placed in a 55.0mL screw cap glass tube and spiked with the metal ions (Cr, Ga, Ag, Cd, Mn, Fe, In, Cu, Ni,Co, Pb and Zn)at 10 μgL^{-1} level. 0.2-1.5 mL of Triton X-114 (5%, m/v) and appropriate amounts of 8-HQ solutions were added, buffered at pH 6.5. The tube was kept in a thermostatic bath at 60 □ 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

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for 30 min to increase the viscosity of the surfactant-rich phase. Then, the bulk aqueous phase was easily decanted. Instead of addition of diluents or analysis, the surfactant-rich phase containing the complexes was treated with 2 mL 0.7 mol L^{-1} HNO_3, and then the second round of cloud point extraction was applied to the solution with thermostatic bath at 60 □ for 30 min and centrifugation for 10 min at 3500 rpm. After d-CPE, 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 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 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

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respected 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 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 (r1, r2, r3, r4 and r5) 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 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 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 complexing reagent(8-HQ), 0.25 mmol L^{-1} ; pH, 6.5; equilibrium temperature(T), 60□; surfactant Triton X-114(TX), 0.1%; equilibrium time(Time), 30 min and without salt addition.

(Figure 1, here)

(Table 2 here)

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3.1. Effect of pH on the 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. A, 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.

3.2. Effect of Triton X-114 concentration on the d-CPE

The non-ionic surfactant Triton X-114 was chosen because of its low toxicological properties and cost. its high density that facilitates phases 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 reach 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.

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3.3. Effect of 8-HQ concentration on the d-CPE

For d-CPE, 8-HQ was used as chelating agent, due to 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 reach maximum when the concentration of 8-HQ was 0.2 5mmol L^{-1}. When the concentration continues to increase, it seems that slight reduction of extraction in high concentration 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.

3.4. Effect of equilibration temperature and time on the d-CPE

The greatest pre-concentration efficiency would achieve 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 present study the

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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. the second CPE procedure, water bath temperature and time was also 60 °C and 30 min, respectively.

3.5. 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.

3.6. Effect of concentrations of back extraction agent

The influences of back-extraction solution concentrations on the preconcentration in the second step were investigated. For this purpose HCl and HNO_3 of 0.5 to 1.0 mol L^{-1} were employed to extract the ions from their hydrophobic complexes trapped in miceller media form back into aqueous phase. It is found that HNO_3 shows an excellent efficiency of back extraction by d-CPE for all the metal ions. However, when HCl

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was used, the back extraction efficiencies of all metal ions were lower than those using HNO_3, 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 HNO_3 is 0.7 mol L^{-1}. Therefore, in second phase of d-CPE, HNO_3 at 0.7 mol $L^{-1}$was selected for back extraction of elemental ions into aqueous phase.

(Figure 2, here)

3.7. 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 μgL^{-1} of the analytes containing the interfering ions were treated according to the optimized procedures. The amount of interfering ions were determined according to the metal-to-interferent ratios. Table 3 shows 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 have no significant effect on the recovery of the analytes.

(Table 3here)

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3.8. Analytical properties of merit

The figures of merit of the developed d-CPE procedure were 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 measurement and m is the slope of the calibration graph. LODs were in the range of 0.012-0.36μg L^{-1} . The limit of quantifications (LOQs)were calculated based on the standard deviation of the blank to the slope of the calibration graph(Sd/m). It was equal to10. The relatives tandard deviations (RSDs, n=6, C= 10 μgL^{-1}) were1.29%–5.56%.

Comparison of the efficiency by the new developed d-CPE method and the other CPE methods to extract and determine the similar metal ions is given in Table 5. We see that our method has lower detection limit 0.012-0.36 μgL^{-1}, higher enhancement factor 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 surfactant Triton X-114 on ICP can be significantly eliminated.

(Table 4 here)

(Table 5 here)

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3.9. Analysis of real samples

The proposed method was applied to determine of 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 6 here)

4.0. Conclusions

A novel dual-cloud point extraction technique which can eliminate the effects of surfactant on the performance of ICP-MS has been investigated. Comparing with the traditional CPE, the proposed method has extensive application in sample pretreatment for separation and analysis of trace heavy metal ions in water samples. In d-CPE procedure, metal ions could be back extracted into aqueous phases as target samples in the followed analysis and the surfactant is left at the bottom of centrifuge tube. The results indicated that while it eliminates the influence of surfactant in the surfactant-rich phase on ICP, the interferences from the sample matrix can also be decreased to some extent. Furthermore, the method is characterized by simplicity, ease of

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operation, cheap and environmental-friendly.

Acknowledgement

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Figure captions

Fig.1. The effects of each factor on d-CPE-ICP-MS using OAD. (A) Effect of the PH, (B) Effect of the Triton X-114(TX), (C)Effect of the concentration of 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 μgL^{-1}.

Fig.2. Effects of HNO_3 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, 0.1% (m/v) Triton X-114.

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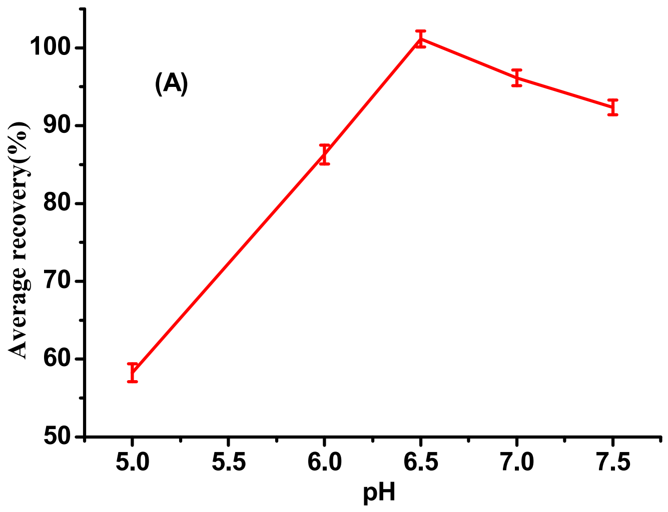

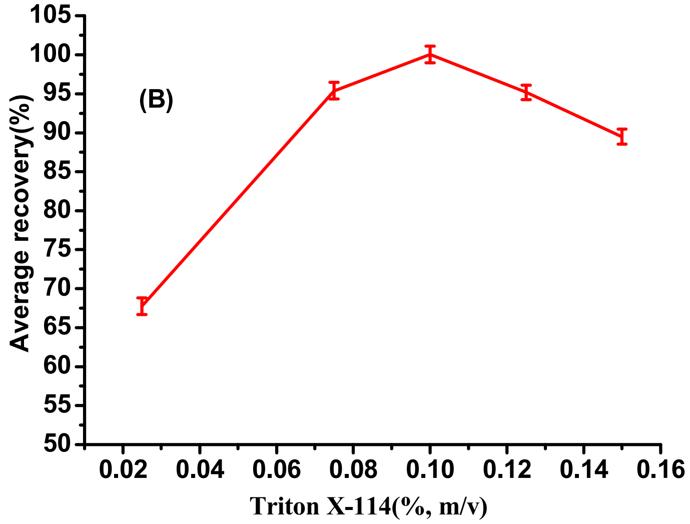

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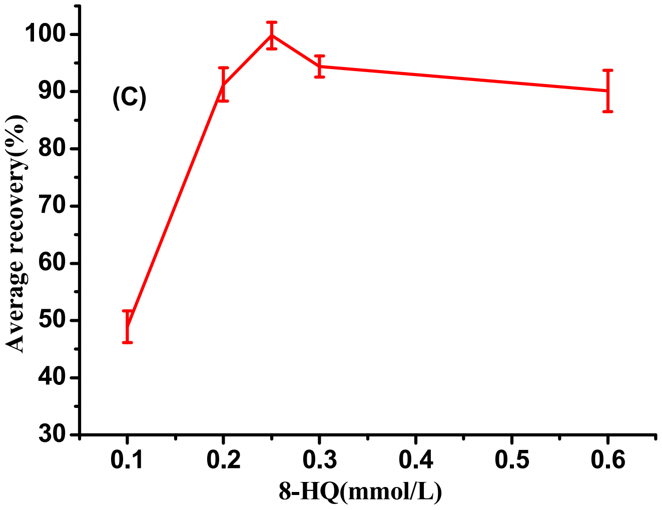

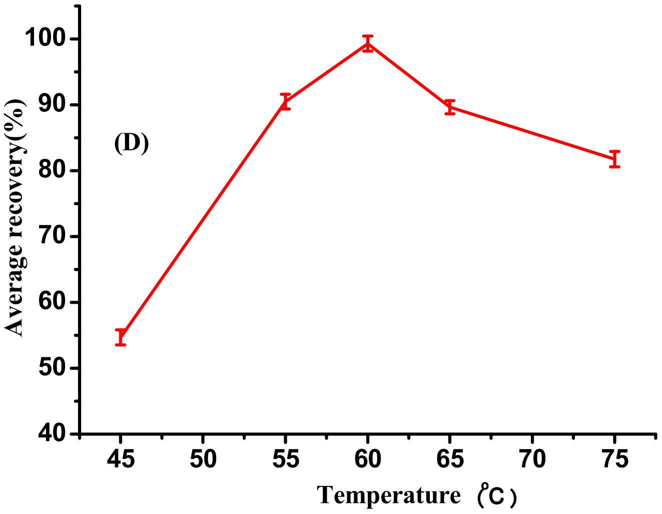

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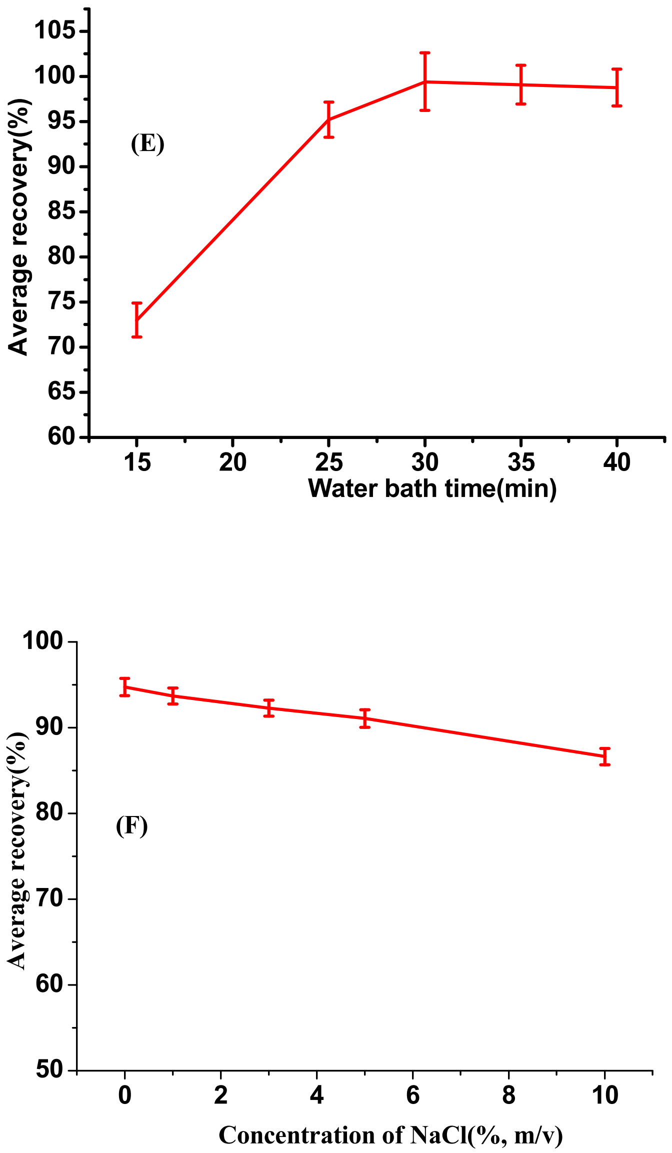

F.g.1.

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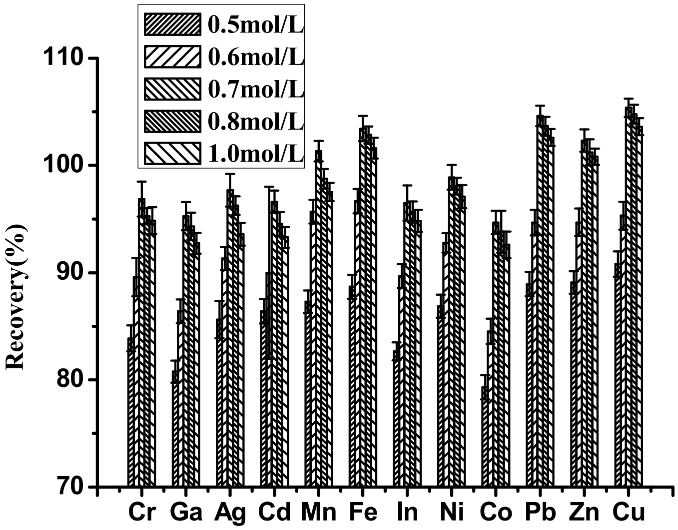

Fig. 2.

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, ^{66}Zn

Table 2

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OA$_{25}$ (5^6)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 3

Effect of interfering ions on the recovery of heavy metal in water sample.

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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
Mg2+	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

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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

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Concentration of each analyte is 20 μgL^{-1}

Table 4

Analytical figures of merit of the proposed method

Metal	LDR[a]	Slope	EF[b]	LOD[d]	LOQ[e]	RSD[f]
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 dynamicrange(μg L^{-1}).

[b] Enrichment factor.

[d] Limit of detection(μg L^{-1}).

[e] Limit ofquantification(μg L^{-1}).

[f] Relative standard deviation(C=10 μgL^{-1}, n=6).

Table 5

Comparison of the proposed method with other CPE methods for extraction and determination of the metal ions.

Element	Method	EF	LDR (μgL^{-1})	LOD(μgL^{-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

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Table 6

Recoveries and determination results in water samples (n = 3).

Metal	Measured(μgL^{-1})	Added(μgL^{-1})	Found(μgL^{-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

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