

Analytical Methods

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4 1 **Ultrasound-assisted cloud point extraction coupled with flame**
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6 2 **atomic absorption spectrometry for the determination of lead and**
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9 3 **cadmium in water samples**
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4 28 **Abstract:** A new method based on ultrasound-assisted cloud point extraction (UA-CPE)
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6 29 using the mixture of non-ionic surfactant alkylphenol ethoxylate NP-7 and alkylphenol
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8 30 ethoxylate NP-9 for the preconcentration of trace amount of lead (Pb) and cadmium (Cd) in
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10 31 water samples prior to determination by FAAS had been developed. In this method, Pb and
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12 32 Cd reacts with ammonium pyrrolidinedithiocarbamate (APDC) yielding hydrophobic
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14 33 complexes, which then are extracted into the surfactant-rich phase. Comparing with the
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16 34 traditional CPE, a faster phase separation speed and higher recovery were obtained by using
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18 35 ultrasound-assisted process and non-ionic surfactant NP series in the present UA-CPE.
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20 36 Variable parameters affecting the CPE procedure were evaluated and optimized. Under the
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22 37 optimized condition, the calibration graph was linear in the range of 10-500 $\mu\text{g L}^{-1}$ for Pb and
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24 38 Cd. The detection limits were 0.5 $\mu\text{g L}^{-1}$ and 0.28 $\mu\text{g L}^{-1}$ with the relative standard deviations
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26 39 of 2.6% and 3.4% for Pb and Cd, respectively. The enrichment factors are 57 and 63 for Pb
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28 40 and Cd, respectively, for 10 mL of preconcentrated solution. The method was successfully
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30 41 applied to the determination of Pb and Cd in water samples.

31 **Keywords:** Ultrasound-assisted cloud point extraction, Flame atomic absorption
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33 spectrometry, APDC, NP-7 and NP-9, Pb and Cd
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38 45 1. Introduction

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40 46 In recent years, the pollution of environment by heavy metals, such as Pb, Cd, Cr, and Hg,
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42 47 has received considerable attention. Heavy metals are very toxic because, as ions or in
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44 48 compound forms, they are soluble in water and may be readily absorbed into living
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46 49 organisms.¹

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48 50 Pb and Cd are among the most toxic elements used industrially, which exist in different
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50 51 chemical and physical forms in the environment. Pb has no known biological function, and
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52 52 high levels of exposure have serious detrimental effects on human health. In addition to acute
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54 53 toxicity, Pb has an extremely long half-life in bone.² It is known to associate with osteoporosis.
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55 54 Cd is highly toxic even at very low concentrations, causing damage to organs such as the
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57 55 kidneys, the liver and the lungs.³ Due to these reasons, determination of Pb and Cd at trace

level in environmental and in biological samples have become of increasing interest.

At present, several analytical techniques such as spectrophotometry, inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) have been widely used for the detection of metal ions in samples.⁴⁻⁸ However, the direct determination of noxious trace Pb and Cd in real samples may not be possible because of low concentrations and matrix interferences, so some separation and preconcentration techniques were necessary.⁹ Many separation and preconcentration techniques such as solid-phase extraction (SPE), single drop microextraction (SDME) and dispersive liquid-liquid microextraction (DLLME) have been widely used for the determination of trace heavy metals in samples.¹⁰⁻¹⁵

Nowadays, cloud point extraction (CPE) using non-ionic surfactant has attracted considerable attention as an alternative to the conventional extraction techniques for separation and preconcentration.¹⁶ It is based on the non-ionic surfactant properties in aqueous a sample to form micelles which becomes turbid by heating up to cloud point temperature. By exposing to a temperature higher than cloud point temperature, the micellar solution separates into two phases: a surfactant rich phase in a small volume and an aqueous phase.¹⁷ CPE based on surfactant-mediated phase separation has been recognized as an alternative to the conventional extraction because of its high-efficiency, low cost and low toxicity. It has been successfully used for the preconcentration of trace heavy metals prior to FAAS.

In this study, APDC was used as the chelating agent, and its structure was shown in Fig. 1. In virtue of its ligand possesses nitrogen and sulfur donor atoms and a conjugated π system, APDC could form stable complexes with Pb and Cd. The complex reaction was shown in Fig. 2. NP-7 and NP-9 were selected as the extractant in the preconcentration and treatment of Pb and Cd in water samples. NP-7 and NP-9 are both nonyl phenol ethoxylate, their cloud point are about 20°C and 54°C, respectively. To our knowledge, NP-7 and NP-9 have never been applied in CPE for the determination of Pb and Cd. APDC is a commonly used chelating agent, which has been reported to use along with Triton X-114 in classical CPE.¹⁸⁻²⁰ Compared with Triton X-114, a better recovery and higher enrichment factor were obtained

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3 86 by the CPE system with NP-7 and NP-9 under the same experimental conditions. Other
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5 87 experimental conditions were also investigated to obtain the optimal condition for the
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7 88 determination of Pb and Cd.
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10 11 90 **2. Experimental**

12 13 91 **2.1 Chemicals**

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16 92 Stock standard solution ($1000 \mu\text{g mL}^{-1}$) of Pb and Cd were obtained from the National
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18 93 Institute of Standards (Beijing, China). APDC was of analytical grade and obtained from
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20 94 Shanghai Chemistry Reagent Company (Shanghai, China). Britton-Robinson buffer solution
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22 95 was composed of phosphoric acid, boric acid and acetic acid (all analytical grade). Triton
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24 96 X-114, NP-7 and NP-9 (10%, v/v) (Aladdin, China) were used for CPE. All the other reagents
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26 97 used were of analytical grade.

27 28 98 **2.2 Apparatus**

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30 99 Flame atomic absorption spectrometer (Z-2000, Hitachi, Japan) was used for the
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32 100 determination of metal ions. An ultrasonic cleaner with temperature control (Shanghai, China)
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34 101 was used to assist the CPE procedure. A centrifuge with calibrated centrifugal tubes (Shanghai,
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36 102 China) was used for the phase separation process.

37 38 103 **2.3 Cloud point extraction procedure**

39
40 104 An aliquot of 10 mL of a solution containing Pb and Cd ($100 \mu\text{g L}^{-1}$) were placed into a
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42 105 calibrated centrifuge tube containing $10 \mu\text{g mL}^{-1}$ APDC. And 1 mL of buffer solution (pH 5.0)
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44 106 and 0.5 mL mixed surfactant (60% NP-7) (10%, v/v) solutions were added. The solutions
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46 107 were mixed and left in an ultrasonic cleaner ultrasound-assisted 10 min, then kept in a
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48 108 thermostatic water bath for 25 min at 55°C . And centrifugation for 5 min at 3000 rpm was
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50 109 adopted for complete separation of the surfactant-rich phase. The surfactant -rich phase was
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52 110 cooled down in an ice bath in order to increase the viscosity of the phase. The aqueous phase
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54 111 was then carefully removed by using a syringe with a long needle. And the surfactant-rich
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56 112 phase was diluted with methanol solution containing 1.0 mol L^{-1} HNO_3 to 0.5 mL. The
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58 113 obtained solution was then directly determined by FAAS.
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115 **3. Results and Discussion**

116 **3.1 Effect of pH**

117 The pH of the sample solution plays a unique role on the metal complex formation and
118 subsequent extraction.²¹ The metal ions could react with complex agent sufficiently in a
119 specific pH conditions. In this study, the effect of pH on the extraction efficiency of Pb and
120 Cd was investigated in the range of 1.0-9.0. As can be seen in Fig. 3, with the increase in the
121 pH range, the extraction efficiency of Pb and Cd complex rise gradually, and the maximum
122 extraction efficiency was obtained at the pH 5.0. Thus, pH 5.0 was used as the optimum pH
123 for extraction of Pb and Cd in the following work.

124 **3.2 Effect of APDC concentration**

125 The effect of the APDC concentration on the CPE of Pb and Cd was evaluated in the
126 concentration range of 1-50 $\mu\text{g mL}^{-1}$. The results are shown in Fig. 4. The obtained results
127 showed that the extraction efficiency of the solutions increased by increasing the APDC
128 concentration up to 10 $\mu\text{g mL}^{-1}$ and remained nearly constant at higher concentrations. So, a
129 10 $\mu\text{g mL}^{-1}$ APDC was chosen for the subsequent experiment.

130 **3.3 The distribution ratios of metal complexes in different CPE systems**

131 The distribution ratio (D), calculated from the experimental data, are defined by the
132 following expression:

$$133 \quad D = C_{\text{ep}}/C_{\text{ap}} \quad (1)$$

134 where C_{ep} and C_{ap} are the analyte concentration in extraction phase and aqueous phase,
135 respectively. In this study, the distribution ratios of metal complexes in four CPE systems
136 were investigated under the same experimental conditions. The results are shown in Table 1.
137 As can be seen from Table 1, the value of D in NP-7+NP-9 CPE system was the biggest,
138 which might indicate that the metal complexes could transfer from the aqueous phase to
139 NP-7+NP-9 easier than three other CPE systems.

140 **3.4 Comparison of between NP series CPE and Triton X-114 CPE**

141 Different surfactants may demonstrate different efficiencies of extraction for certain targets

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3 142 based on various factors. Therefore, Triton X-114, the most commonly used surfactant in CPE,
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5 143 was selected to compare with NP-7 and NP-9 CPE method in this study. As shown in Fig. 5,
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7 144 NP-7+NP-9 CPE and NP-7 CPE had a significantly advantage over Triton X-114 CPE in
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9 145 terms of extraction efficiency. By contrast, NP-7+NP-9 had the best extraction efficiency. This
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11 146 may be explained for the synergistic effect between NP-7 and NP-9. That is, the obtained
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13 147 surfactant has more excellent performance such as the lower critical micelle concentration
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15 148 (CMC) and surface tension than the single surfactant. Thus, the mixed surfactant, NP-7+NP-9
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17 149 was chosen as the optimal extraction agent for its highest extraction efficiency.

18 19 150 **3.5 Effect of mixed surfactant ratio and concentration**

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21 151 In order to find the best ratio and concentration of the mixed surfactant (NP-7+NP-9), a
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23 152 variation of extraction efficiency upon the mixed surfactant ratio and concentration were
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25 153 investigated in the range of 10%-90% (proportion of NP-7 in mixed surfactant) and 0.1%-2%,
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27 154 respectively. The results are shown in Figs. 6 and 7. The extraction efficiency increased by
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29 155 increasing the proportion of NP-7 in mixed surfactant up to 60% and then gradually decreases.
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31 156 While the extraction efficiency increased by increasing the concentration of the mixed
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33 157 surfactant up to 0.5% and remained nearly constant between 0.5% and 2%. Therefore, a
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35 158 mixed surfactant ratio of 60% NP-7 and 0.5% concentration of mixed surfactant were chosen
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37 159 as the optimal experimental conditions in all further studies.

38 39 160 **3.6 Effects of the equilibrium temperature and time**

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41 161 Equilibrium temperature and time are two important parameters in CPE. And it was
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43 162 desirable to employ the shortest equilibration time and the lowest possible equilibration
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45 163 temperature as a compromise between completion of extraction and efficient separation of
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47 164 phases. In this study, the dependence of extraction efficiency upon equilibrium temperature
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49 165 and time was studied over the ranges of 40-75 °C and 10-50 min, respectively. As can be seen
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51 166 from Figs. 8 and 9, an equilibration temperature of 55 °C and an equilibration time of 25 min
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53 167 were adequate to achieve satisfying extraction efficiency.

54 55 168 **3.7 Effects of Ultrasound-assisted CPE**

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57 169 Ultrasonic process plays an important role in ultrasound-assisted CPE.²²⁻²⁴ An ultrasonic
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59 170 process was applied to accelerate the formation of a fine cloudy solution and obtain faster

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3 171 phase separation speed and higher recovery. As shown in Fig.10, a higher recovery of Pb and
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5 172 Cd was obtained by using ultrasound-assisted CPE than direct CPE. This may be because
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7 173 ultrasound can accelerate the interactive rate between the non-ionic surfactant and aqueous
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9 174 phase so that the hydrophobic complexes could be well extracted into the surfactant-rich
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11 175 phase. The effect of ultrasound time, which was defined as the time before heating, was varied
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13 176 within the range of 0-40 min. The extraction efficiency increased with the increase of the
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15 177 ultrasound time in the range of 0-10 min, and then remained almost constant after 10 min. So,
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17 178 10 min ultrasound time was chosen as the most appropriate ultrasound time. Fig. 11 describes
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19 179 the phase separation condition of ultrasound-assisted CPE and direct CPE at 20 min
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21 180 equilibrium time. As shown in Fig. 11, the phase separation time was reduced when using the
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23 181 ultrasound-assisted CPE. Therefore, ultrasound process was used for the further experiments.

182 **3.8 Interferences**

183 The effect of potential interference of some metal ions on the preconcentration and
184 determination of Pb and Cd was investigated. In these experiments, solutions of $100 \mu\text{g L}^{-1}$ Pb
185 and Cd and the added interfering ions were treated according to the recommended procedure
186 under optimum conditions. The tolerance limits were determined for a maximum error of
187 $\pm 5\%$ and the results are given in Table 2. The results demonstrate that the common coexisting
188 ions did not have significant effect on the determination of the analyte ions under the selected
189 conditions.

190 **3.9 Analytical features**

191 Under the optimized conditions, the analytical performance of the proposed method was
192 evaluated. A calibration curve was constructed by preconcentrating of 10 mL of sample
193 solutions with NP-7 and NP-9. The calibration graph was linear in the range of $10\text{-}500 \mu\text{g L}^{-1}$
194 for Pb and Cd. The calibration equation is $A=0.037C+0.005$ and $A=0.387C+0.03$ (where A is
195 the absorbance and C is the concentration of metal ions) with a correlation coefficient of
196 0.999 and 0.996 for Pb and Cd, respectively. The limit of detection (LOD), defined as
197 $C_L=3S_B/m$ (where C_L , S_B , and m are the limit of detection, standard deviation of the blank,
198 and slope of the calibration graph, respectively), are $0.5 \mu\text{g L}^{-1}$ and $0.28 \mu\text{g L}^{-1}$ for Pb and Cd,
199 with the relative standard deviation (RSD) were 2.6% and 3.4%, respectively. The enrichment

200 factor (EF), calculated as the ratio of slope of calibration curves of preconcentrated sample to
201 that obtained without preconcentration, were 57 and 63 for Pb and Cd, respectively.

202 **3.10 Comparison with other methods**

203 A comparison of the proposed method with other reported methods for Pb and Cd
204 determination after CPE is shown in Table 3. Some characteristics such as complexing agent,
205 extracting agent, LOD, RSD and EF for the extraction and determination of Pb and Cd are
206 summarized for comparison. As shown in Table 3, the proposed method has higher
207 enrichment factor and consequently lower detection limit when compared with other methods.
208 The high sensitivity and low detection limit suggests that the present method is efficient and
209 sensitive for determination of very low concentrations of the Pb and Cd in various water
210 samples.

211 **3.11 Determination of Pb and Cd in water samples**

212 The proposed method was applied for the determination of Pb and Cd in different water
213 samples. Under the recommended experimental conditions, the developed method is
214 employed to determine Pb and Cd in tap water, river water, and industrial waste water
215 samples. All the water samples are spiked with Pb and Cd standard solutions at different
216 concentration levels to assess the matrix effects, and non-spiked samples are also analyzed.
217 The results are shown in Table 4. As can be seen from Table 4, the recovery for the added
218 metal ions is in the range of 96.9%-100.4%, demonstrating that the proposed method can be
219 reliably used for determination of Pb and Cd in real water samples.

221 **4. Conclusions**

222 In this study, a new simple, efficient and reliable ultrasound-assisted cloud point extraction
223 method coupled with FAAS was successfully applied for the determination of Pb and Cd in
224 water samples with low detection limit, accuracy and high enrichment factor. NP-7 and NP-9
225 as non-ionic surfactant were selected in cloud point extraction procedure with good recovery
226 and higher enrichment factor than traditional non-ionic surfactant such as Triton X-114. An
227 ultrasound-assisted process was employed to accelerate the formation of a fine cloudy
228 solution and obtain faster phase separation speed and higher recovery. The mixture of

229 non-ionic surfactant NP-7 and NP-9 was successfully used in the present UA-CPE, which has
230 certain significance for the development of CPE technology.

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288 **Table 1** The distribution ratios of metal complexes in different CPE systems

CPE system	Distribution ratio (D) \pm S.D ^a	
	Pb	Cd
NP-7 CPE system	3.42 \pm 2	4.08 \pm 3
NP-9 CPE system	2.61 \pm 3	3.52 \pm 2
NP-7+NP-9 CPE system	3.81 \pm 3	4.19 \pm 3
Triton X-114 CPE system	3.13 \pm 4	3.88 \pm 1

289 ^aStandard deviation (n=6)

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Ions	Interfering ion to analyte ratio
K^+ , Na^+ , Ca^{2+} , Mg^{2+}	2000
Al^{3+} , Fe^{3+} , Mn^{2+}	1000
Cu^{2+} , Ni^{2+} , Zn^{2+}	100
Cl^- , HCO_3^- , SO_4^{2-} , PO_4^{3-} ,	1500
NO_3^- , CH_3COO^-	1000
Hg^{2+} , Cr^{3+}	500

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335 **Table 3** Comparison of the present cloud point extraction method with other previously
 336 reported methods using FAAS for Pb and Cd detection

Complexing agent	Surfactant	Element	LOD ($\mu\text{g L}^{-1}$)	Linear range ($\mu\text{g L}^{-1}$)	EF	RSD (%)	Technique	Reference
KI and methyl green (MG)	Triton X-114	Cd	0.9	2-200	13.5	4.2	FAAS	16
1-PTSC	Triton X-114	Pb	3.42	500-10000	25	4.8	FAAS	25
Methyltrioctylammonium chloride	Triton X-114	Cd	0.3	3-250	63	4.0	FI-FAAS	26
APDC and DDTC	Triton X-114	Pb	1.14	5-20	56	6.88	FAAS	27
Dimethylglyoxime (DMG)	Triton X-114	Pb	1.4	4.5-250	44	1.0	FI-FAAS	28
TAN	Triton X-114	Pb	4.5	25-2000	15.1-20.3	1.6-3.2	FAAS	29
		Cd	0.75	2.5-500				
APDC	NP-7 and NP-9	Pb	0.5	10-500	57	2.6	FAAS	This work
		Cd	0.28		63	3.4		

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349 **Table 4** Determination of Pb and Cd in water samples

Samples	Added ($\mu\text{g L}^{-1}$)		Found ($\mu\text{g L}^{-1}$)		Recovery (%)	
	Pb	Cd	Pb	Cd	Pb	Cd
Tap Water	-	-	not detected	not detected	-	-
	50	50	48.5	49.3	97	98.6
	100	100	99.4	98.8	99.4	98.8
River	-	-	8.6	9.2	-	-
Water	50	50	56.8	57.9	96.9	97.8
	100	100	106.3	107.9	97.9	98.8
Industrial	-	-	23.5	16.8	-	-
Waste	50	50	71.5	67.1	97.3	100.4
Water	100	100	122.8	114.7	99.4	98.2

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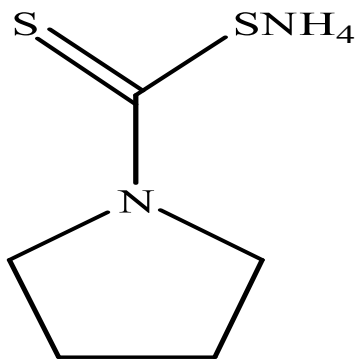


Fig. 1 The structure of APDC.

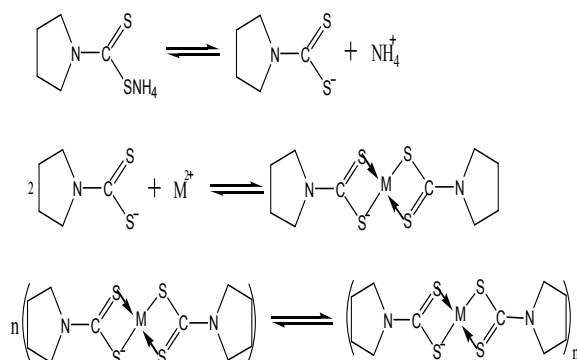


Fig. 2 The complex reaction of APDC with M (M stand for the Pb and Cd).

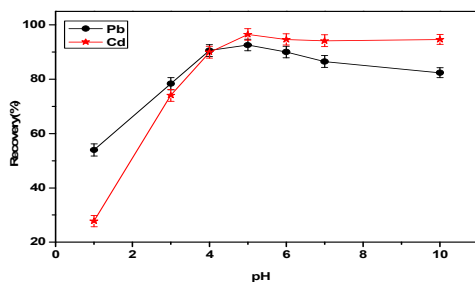


Fig. 3 Effect of pH; Experimental conditions: $100 \mu\text{g L}^{-1}$ Pb and Cd, $10 \mu\text{g mL}^{-1}$ APDC and 0.5 mL mixed surfactant (NP-7+NP-9) (10%, v/v) solutions. Other experimental conditions are described under procedures.

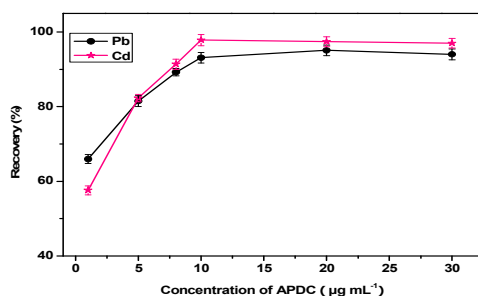


Fig. 4 Effect of the concentration of APDC; Experimental conditions: 100 µg L⁻¹ Pb and Cd, 0.5 mL mixed surfactant (NP-7+NP-9) (10%, v/v) solutions and pH 5.0. Other experimental conditions are described under procedures.

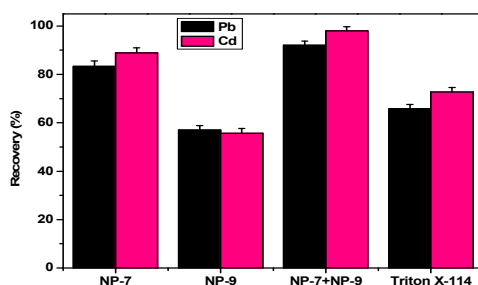


Fig. 5 Effect of different surfactants; Experimental conditions: 100 µg L⁻¹ Pb and Cd, 10 µg mL⁻¹ APDC and pH 5.0. Other experimental conditions are described under procedures.

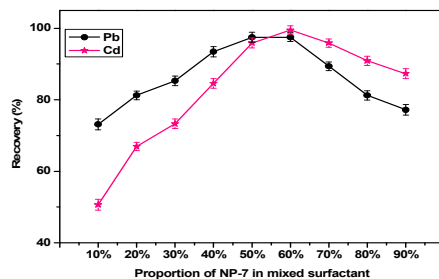


Fig. 6 Effect of the proportion of NP-7 in mixed surfactant; Experimental conditions: 100 µg L⁻¹ Pb and Cd, 10 µg mL⁻¹ APDC and pH 5.0. Other experimental conditions are described under procedures.

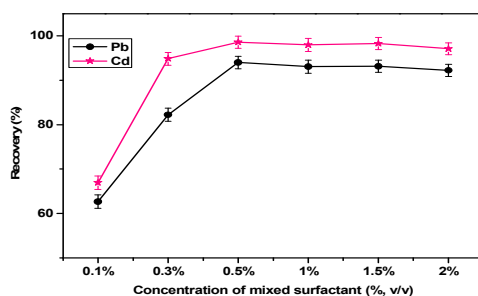


Fig. 7 Effect of the concentration of mixed surfactant; Experimental conditions: $100 \mu\text{g L}^{-1}$ Pb and Cd, $10 \mu\text{g mL}^{-1}$ APDC and pH 5.0. Other experimental conditions are described under procedures.

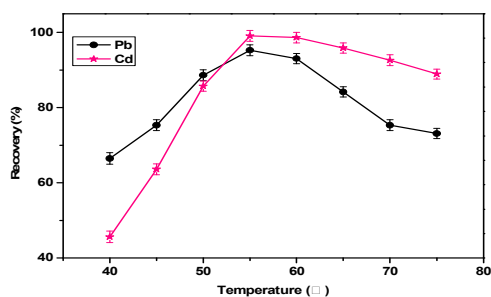


Fig. 8 Effect of the equilibrium temperature; Experimental conditions: $100 \mu\text{g L}^{-1}$ Pb and Cd, $10 \mu\text{g mL}^{-1}$ APDC, 0.5 mL mixed surfactant (NP-7+NP-9) (10%, v/v) solutions and pH 5.0. Other experimental conditions are described under procedures.

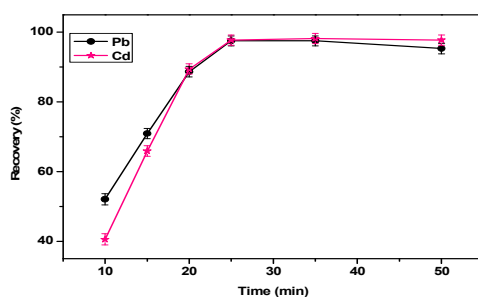


Fig. 9 Effect of the equilibrium time; Experimental conditions: $100 \mu\text{g L}^{-1}$ Pb and Cd, $10 \mu\text{g mL}^{-1}$ APDC, 0.5 mL mixed surfactant (NP-7+NP-9) (10%, v/v) solutions and pH 5.0. Other experimental conditions are described under procedures.

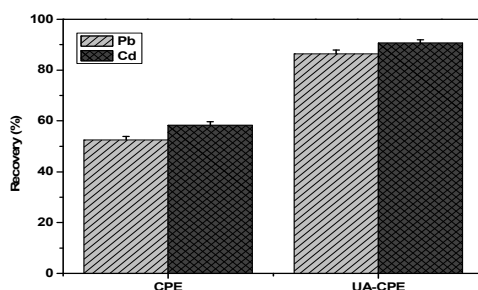


Fig. 10 Comparison of UA-CPE with direct CPE on the recovery of Pb and Cd; Experimental conditions: $100 \mu\text{g L}^{-1}$ Pb and Cd, $10 \mu\text{g mL}^{-1}$ APDC, 0.5 mL mixed surfactant (NP-7+NP-9) (10%, v/v) solutions and pH 5.0. Other experimental conditions are described under procedures.

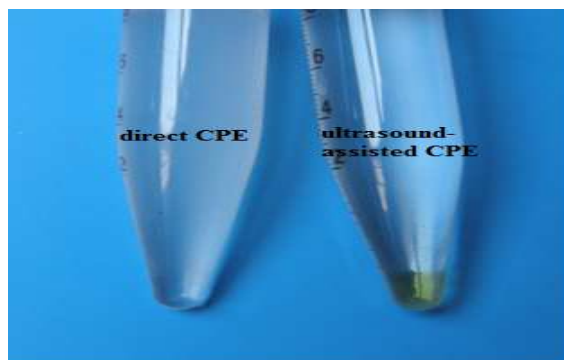


Fig. 11 Comparison of ultrasound-assisted CPE with direct CPE in terms of phase separation condition; Experimental conditions: $100 \mu\text{g L}^{-1}$ Pb and Cd, $10 \mu\text{g mL}^{-1}$ APDC, 0.5 mL mixed surfactant (NP-7+NP-9) (10%, v/v) solutions and pH 5.0. Other experimental conditions are described under procedures.