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Ultrasound-assisted cloud point extraction coupled with flame atomic absorption spectrometry for the determination of lead and cadmium in water samples

Zonghao Li\textsuperscript{a,b}, Jiaxi Chen\textsuperscript{c}, Mousheng Liu\textsuperscript{a}, Yaling Yang\textsuperscript{a*}

\textsuperscript{a}Faculty of Life Science and Technology, Kunming University of Science and Technology, Kunming 650500, R.P. China

\textsuperscript{b}Kunming Guiyan Pharmaceutical Co., Ltd., Kunming, 650106, China;

\textsuperscript{c}Yunnan Metallurgy Group Co., Ltd., Kunming, Yunnan 650031, China;

*Corresponding author: Tel.: +86-13888316388

E-mail address: yilyil8@163.com (Y.L. Yang)
Abstract: A new method based on ultrasound-assisted cloud point extraction (UA-CPE) using the mixture of non-ionic surfactant alkylphenol ethoxylate NP-7 and alkylphenol ethoxylate NP-9 for the preconcentration of trace amount of lead (Pb) and cadmium (Cd) in water samples prior to determination by FAAS had been developed. In this method, Pb and Cd reacts with ammonium pyrrolidinedithiocarbamate (APDC) yielding hydrophobic complexes, which then are extracted into the surfactant-rich phase. Comparing with the traditional CPE, a faster phase separation speed and higher recovery were obtained by using ultrasound-assisted process and non-ionic surfactant NP series in the present UA-CPE. Variable parameters affecting the CPE procedure were evaluated and optimized. Under the optimized condition, the calibration graph was linear in the range of 10-500 µg L\(^{-1}\) for Pb and Cd. The detection limits were 0.5 µg L\(^{-1}\) and 0.28 µg L\(^{-1}\) with the relative standard deviations of 2.6% and 3.4% for Pb and Cd, respectively. The enrichment factors are 57 and 63 for Pb and Cd, respectively, for 10 mL of preconcentrated solution. The method was successfully applied to the determination of Pb and Cd in water samples.

Keywords: Ultrasound-assisted cloud point extraction, Flame atomic absorption spectrometry, APDC, NP-7 and NP-9, Pb and Cd

1. Introduction

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

Pb and Cd are among the most toxic elements used industrially, which exist in different chemical and physical forms in the environment. Pb has no known biological function, and high levels of exposure have serious detrimental effects on human health. In addition to acute toxicity, Pb has an extremely long half-life in bone.\(^2\) It is known to associate with osteoporosis. Cd is highly toxic even at very low concentrations, causing damage to organs such as the 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. 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. 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.

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. 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. 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 $\pi$ 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° and 54°, 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. Compared with Triton X-114, a better recovery and higher enrichment factor were obtained.
by the CPE system with NP-7 and NP-9 under the same experimental conditions. Other experimental conditions were also investigated to obtain the optimal condition for the determination of Pb and Cd.

2. Experimental

2.1 Chemicals

Stock standard solution (1000 µg mL$^{-1}$) of Pb and Cd were obtained from the National Institute of Standards (Beijing, China). APDC was of analytical grade and obtained from Shanghai Chemistry Reagent Company (Shanghai, China). Britton-Robinson buffer solution was composed of phosphoric acid, boric acid and acetic acid (all analytical grade). Triton X-114, NP-7 and NP-9 (10%, v/v) (Aladdin, China) were used for CPE. All the other reagents used were of analytical grade.

2.2 Apparatus

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

2.3 Cloud point extraction procedure

An aliquot of 10 mL of a solution containing Pb and Cd (100 µg L$^{-1}$) were placed into a calibrated centrifuge tube containing 10 µg mL$^{-1}$ APDC. And 1 mL of buffer solution (pH 5.0) and 0.5 mL mixed surfactant (60% NP-7) (10%, v/v) solutions were added. The solutions were mixed and left in an ultrasonic cleaner ultrasound-assisted 10 min, then kept in a thermostatic water bath for 25 min at 55℃. And centrifugation for 5 min at 3000 rpm was adopted for complete separation of the surfactant-rich phase. The surfactant-rich phase was cooled down in an ice bath in order to increase the viscosity of the phase. The aqueous phase was then carefully removed by using a syringe with a long needle. And the surfactant-rich phase was diluted with methanol solution containing 1.0 mol L$^{-1}$ HNO$_3$ to 0.5 mL. The obtained solution was then directly determined by FAAS.
3. Results and Discussion

3.1 Effect of pH

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

3.2 Effect of APDC concentration

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

3.3 The distribution ratios of metal complexes in different CPE systems

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

\[ D = \frac{C_{ep}}{C_{ap}} \]  

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

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

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

3.5 Effect of mixed surfactant ratio and concentration

In order to find the best ratio and concentration of the mixed surfactant (NP-7+NP-9), a variation of extraction efficiency upon the mixed surfactant ratio and concentration were investigated in the range of 10%-90% (proportion of NP-7 in mixed surfactant) and 0.1%-2%, respectively. The results are shown in Figs. 6 and 7. The extraction efficiency increased by increasing the proportion of NP-7 in mixed surfactant up to 60% and then gradually decreases. While the extraction efficiency increased by increasing the concentration of the mixed surfactant up to 0.5% and remained nearly constant between 0.5% and 2%. Therefore, a mixed surfactant ratio of 60% NP-7 and 0.5% concentration of mixed surfactant were chosen as the optimal experimental conditions in all further studies.

3.6 Effects of the equilibrium temperature and time

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

3.7 Effects of Ultrasound-assisted CPE

Ultrasonic process plays an important role in ultrasound-assisted CPE. An ultrasonic process was applied to accelerate the formation of a fine cloudy solution and obtain faster
phase separation speed and higher recovery. As shown in Fig.10, a higher recovery of Pb and Cd was obtained by using ultrasound-assisted CPE than direct CPE. This may be because ultrasound can accelerate the interactive rate between the non-ionic surfactant and aqueous phase so that the hydrophobic complexes could be well extracted into the surfactant-rich phase. The effect of ultrasound time, which was defined as the time before heating, was varied within the range of 0-40 min. The extraction efficiency increased with the increase of the ultrasound time in the range of 0-10 min, and then remained almost constant after 10 min. So, 10 min ultrasound time was chosen as the most appropriate ultrasound time. Fig. 11 describes the phase separation condition of ultrasound-assisted CPE and direct CPE at 20 min equilibrium time. As shown in Fig. 11, the phase separation time was reduced when using the ultrasound-assisted CPE. Therefore, ultrasound process was used for the further experiments.

3.8 Interferences

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

3.9 Analytical features

Under the optimized conditions, the analytical performance of the proposed method was evaluated. A calibration curve was constructed by preconcentrating of 10 mL of sample solutions with NP-7 and NP-9. The calibration graph was linear in the range of 10-500 µg L$^{-1}$ for Pb and Cd. The calibration equation is $A=0.037C+0.005$ and $A=0.387C+0.03$ (where $A$ is the absorbance and $C$ is the concentration of metal ions) with a correlation coefficient of 0.999 and 0.996 for Pb and Cd, respectively. The limit of detection (LOD), defined as $C_L=3S_B/m$ (where $C_L$, $S_B$, and $m$ are the limit of detection, standard deviation of the blank, and slope of the calibration graph, respectively), are 0.5 µg L$^{-1}$ and 0.28 µg L$^{-1}$ for Pb and Cd, with the relative standard deviation (RSD) were 2.6% and 3.4%, respectively. The enrichment
factor (EF), calculated as the ratio of slope of calibration curves of preconcentrated sample to that obtained without preconcentration, were 57 and 63 for Pb and Cd, respectively.

### 3.10 Comparison with other methods

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

### 3.11 Determination of Pb and Cd in water samples

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

### 4. Conclusions

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

Acknowledgements

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

<table>
<thead>
<tr>
<th>CPE system</th>
<th>Distribution ratio (D)±S.D&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
</tr>
<tr>
<td>NP-7 CPE system</td>
<td>3.42±2</td>
</tr>
<tr>
<td>NP-9 CPE system</td>
<td>2.61±3</td>
</tr>
<tr>
<td>NP-7+NP-9 CPE system</td>
<td>3.81±3</td>
</tr>
<tr>
<td>Triton X-114 CPE system</td>
<td>3.13±4</td>
</tr>
</tbody>
</table>

<sup>a</sup> Standard deviation (n=6)
Table 2 Tolerance limits for ions interfering with the determination of 100 µg L\(^{-1}\) Pb and Cd (n=6)

<table>
<thead>
<tr>
<th>Ions</th>
<th>Interfering ion to analyte ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(^+), Na(^+), Ca(^{2+}), Mg(^{2+})</td>
<td>2000</td>
</tr>
<tr>
<td>Al(^{3+}), Fe(^{3+}), Mn(^{2+})</td>
<td>1000</td>
</tr>
<tr>
<td>Cu(^{2+}), Ni(^{2+}), Zn(^{2+})</td>
<td>100</td>
</tr>
<tr>
<td>Cl(^-), HCO(_3^-), SO(_4^{2-}), PO(_4^{3-})</td>
<td>1500</td>
</tr>
<tr>
<td>NO(_3^-), CH(_3)COO(^-)</td>
<td>1000</td>
</tr>
<tr>
<td>Hg(^{2+}), Cr(^{3+})</td>
<td>500</td>
</tr>
</tbody>
</table>
Table 3 Comparison of the present cloud point extraction method with other previously reported methods using FAAS for Pb and Cd detection

<table>
<thead>
<tr>
<th>Complexing agent</th>
<th>Surfactant</th>
<th>Element</th>
<th>LOD (µg L⁻¹)</th>
<th>Linear range (µg L⁻¹)</th>
<th>EF</th>
<th>RSD (%)</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI and methyl green (MG)</td>
<td>Triton X-114</td>
<td>Cd</td>
<td>0.9</td>
<td>2-200</td>
<td>13.5</td>
<td>4.2</td>
<td>FAAS</td>
<td>16</td>
</tr>
<tr>
<td>1-PTSC</td>
<td>Triton X-114</td>
<td>Pb</td>
<td>3.42</td>
<td>500-10000</td>
<td>25</td>
<td>4.8</td>
<td>FAAS</td>
<td>25</td>
</tr>
<tr>
<td>Methyltriocetyl ammonium chloride</td>
<td>Triton X-114</td>
<td>Cd</td>
<td>0.3</td>
<td>3-250</td>
<td>63</td>
<td>4.0</td>
<td>FI-FAAS</td>
<td>26</td>
</tr>
<tr>
<td>APDC and DDTC</td>
<td>Triton X-114</td>
<td>Pb</td>
<td>1.14</td>
<td>5-20</td>
<td>56</td>
<td>6.88</td>
<td>FAAS</td>
<td>27</td>
</tr>
<tr>
<td>Dimethylglyoxine (DMG)</td>
<td>Triton X-114</td>
<td>Pb</td>
<td>1.4</td>
<td>4.5-250</td>
<td>44</td>
<td>1.0</td>
<td>FI-FAAS</td>
<td>28</td>
</tr>
<tr>
<td>TAN</td>
<td>Triton X-114</td>
<td>Pb</td>
<td>4.5</td>
<td>25-2000</td>
<td>15.1-20.3</td>
<td>1.6-3.2</td>
<td>FAAS</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>0.75</td>
<td>2.5-500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APDC</td>
<td>NP-7 and NP-9</td>
<td>Pb</td>
<td>0.5</td>
<td>10-500</td>
<td>57</td>
<td>2.6</td>
<td>FAAS</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>0.28</td>
<td></td>
<td>63</td>
<td>3.4</td>
<td></td>
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</table>
Table 4 Determination of Pb and Cd in water samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Added (µg L$^{-1}$)</th>
<th>Found (µg L$^{-1}$)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
<td>Cd</td>
<td>Pb</td>
</tr>
<tr>
<td>Tap Water</td>
<td>-</td>
<td>-</td>
<td>not detected</td>
</tr>
<tr>
<td></td>
<td>50 50</td>
<td>48.5 49.3</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>100 100</td>
<td>99.4 98.8</td>
<td>99.4</td>
</tr>
<tr>
<td>River Water</td>
<td>-</td>
<td>-</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>50 50</td>
<td>56.8 57.9</td>
<td>96.9</td>
</tr>
<tr>
<td></td>
<td>100 100</td>
<td>106.3 107.9</td>
<td>97.9</td>
</tr>
<tr>
<td>Industrial Waste</td>
<td>-</td>
<td>-</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td>50 50</td>
<td>71.5 67.1</td>
<td>97.3</td>
</tr>
<tr>
<td>Water</td>
<td>100 100</td>
<td>122.8 114.7</td>
<td>99.4</td>
</tr>
</tbody>
</table>
Fig. 1 The structure of APDC.

\[
\text{SNH}_4^+ \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{N} \quad \text{C} \\
\text{S} \quad \text{S} \quad \text{M} \quad \text{N} \quad \text{C} \\
\text{S} \quad \text{S} \quad \text{N} \quad \text{C} \quad \text{S} \\
\text{S} \quad \text{S} \quad \text{N} \quad \text{C} \quad \text{S} \\
\text{S} \quad \text{S} \quad \text{M} \quad \text{N} \quad \text{C} \\
\text{S} \quad \text{S} \quad \text{N} \quad \text{C} \quad \text{S} \\
\text{S} \quad \text{S} \quad \text{M} \quad \text{N} \quad \text{C} \\
\text{S} \quad \text{S} \quad \text{N} \quad \text{C} \quad \text{S} \\
\text{S} \quad \text{S} \quad \text{M} \quad \text{N} \quad \text{C} \\
\text{S} \quad \text{S} \quad \text{N} \quad \text{C} \quad \text{S} 
\]

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

Fig. 3 Effect of pH; Experimental conditions: 100 µg L\(^{-1}\) Pb and Cd, 10 µg 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 µg L\(^{-1}\) Pb and Cd, 10 µg mL\(^{-1}\) APDC and pH 5.0. Other experimental conditions are described under procedures.

Fig. 8 Effect of the equilibrium temperature; Experimental conditions: 100 µg L\(^{-1}\) Pb and Cd, 10 µg 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 µg L\(^{-1}\) Pb and Cd, 10 µg 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 µg L\(^{-1}\) Pb and Cd, 10 µg 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 µg L\(^{-1}\) Pb and Cd, 10 µg 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.