Analytical and Bioanalytical Chemistry

Electronic Supplementary Material

Boronate affinity solid-phase extraction of cis-diol compounds by a one-step electrochemically synthesized selective polymer sorbent

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The Supplementary data provides additional relevant details of this work, including:

- Optimization of the polymerization conditions
- Optimization of parameters for online solid-phase microextraction
- Figure S1. Chemical structure of adrenaline, noradrenaline and dopamine
- Figure S2. Polymerization mechanism of poly (thiophene-3-boronic acid)
- Figure S3. Extraction selectivity of the method for phenols
- Figure S4. Optimization for polymerization conditions
- Figure S5. Cyclic voltammogram comparison of carbon fiber in 1 mM potassium ferricyanide solution
- Figure S6. Amplified image of poly (thiophene-3-boronic acid)
- Figure S7. FT-IR spectra of bare carbon fiber and poly (thiophene-3-boronic acid)
- Figure S8. Energy Dispersive Spectrometry characterization of poly (thiophene-3-boronic acid)
- Figure S9. Optimization for extraction conditions
- Table S1. Optimization for extraction conditions
- Table S2. Recoveries of 3 catecholamines in spiked plasma samples
Optimization of polymerization conditions

The polymerization process of thiophene-3-boronic acid on carbon fiber can be strongly influenced by many factors, such as monomer and supporting analyte concentration, scan rates. To obtain higher extraction efficiency, several main affecting factors were investigated as discussed as follows.

**Effect of thiophene-3-boronic acid concentration.** Sufficient thiophene-3-boronic acid in the supporting electrolyte solution is vital for the synthesis of the polymer and thus affecting the extraction efficiency. Therefore, it is necessary to investigate the effect of thiophene-3-boronic acid concentration on extraction efficiency. In our experiment we investigated five different concentrations gradient and triple respectively for each concentration. From the result shown in Fig. S4A, we can see that when the concentration is blew 0.075 mol·L\(^{-1}\), the extraction efficiency kept increasing gradually. However, when the concentration was higher than 0.075 mol·L\(^{-1}\), the thiophene-3-boronic acid cannot totally dissolve and uniformly distribute in the solution, which may cause waste of thiophene-3-boronic acid. As a result, we chose 0.075 mol·L\(^{-1}\) of thiophene-3-boronic acid for our experiment.

**Effect of scan rates.** Scanning rates is a core kinetic parameter, which helps to increase the homogeneity of the coating obviously, thus improving extraction efficiency and reducing extraction time. The effect of the scanning rate (0.025, 0.05, 0.075, 0.1, 0.125 V·s\(^{-1}\)) on the extraction efficiency was investigated. Results in Fig. S4B shows that the peak areas reached maximum amounts at a scan rate of 0.025 V·s\(^{-1}\). The results revealed that slow scan rate leads to better the extraction efficiency.
However, slow scan rate would take longer time to modify the fiber bundle. Therefore, slower scan rates less than 0.025 V·s\(^{-1}\) were not tested and it was chosen as an optimal option.

*Effect of scan segments.* The thickness of the electro-polymerized sorbent is influenced by scan segments in cyclic voltammetry. When it was varied between 120 and 160, the extraction efficiency increased sharply simultaneously as Fig. S4C showed. When scan segments increased from 160 to 180, the extraction efficiency varied slice. We deduce that an increase of cyclic voltammetry segments up to 160 gave rise to a smoother surface of the modified fiber bundle, as more poly (thiophene-3-boronic acid) immobilized during polymerization. Concerning about the time for modification, we choose 160 scan segments for next step extraction.

**Optimization of parameters for online solid-phase microextraction**

The sorption of catecholamines onto the surface of modified fibers was mainly attributed to the interaction of cis-diol compounds and boronic acid group of poly (thiophene-3-boronic acid) in alkaline condition, hydrogen bonds and \(\pi - \pi\) electrostatic force. The sample solution was pushed through the packed PEEK tube loop, thus the sample flow rate had potential effect on the contact between catecholamines and the adsorbent. In our experiment, the effect of sample flow rate was studied; the values were ranged from 0.6 to 1.0 mL-min\(^{-1}\) controlled by a syringe pump. As shown in Fig. S7A, peak areas fell off gradually in the examined sample flow rate, indicating that sample flow rate has big influence on extraction efficiency.
Considering analysis time and pressure, which might increase along with the flow rate, 0.6 mL·min⁻¹ of flow rate was applied for further studies.

In alkaline condition, the cis-diol catecholamines reacted with boronic acid group of poly (thiophene-3-boronic acid) and were adsorbed onto the surface of modified fibers. The sample pH value would affect extent of the reaction and the hydrogen bonds between catecholamines and the polymer. The effect of sample pH value was studied; the values were ranged from 7.0 to 11.0 and were adjusted with HCl and ammonia. As shown in Fig. S7B, the peak areas increase rapidly along with increase of the sample pH value from 7.0 to 11.0, exception that of adrenaline when pH value increased from 10.0 to 11.0. The reason was that adrenaline was easier to be oxidized than noradrenaline and dopamine. Thus sample pH value of 11.0 was selected for further studies and higher pH value was not tested.

In-tube SPME based on packed sorbents is a nonequilibrium absorption process and the extraction efficiency is closely related to sample volume. Volumes of pre-extraction solution in the range of 2.5–20 mL were loaded onto the PEEK tube separately, and the extraction efficiencies were investigated. As shown in Fig. S7C, the peak areas increase rapidly along with increase of the sample volume from 2 to 15 mL and increased slowly from 15 to 20 mL. Sample volume of 20 mL was selected for ultimate extraction.
**Fig. S1** Chemical structure of adrenaline, noradrenaline and dopamine

**Fig. S2** Polymerization mechanism of poly (thiophene-3-boronic acid)

**Fig. S3** Extraction selectivity of the method for phenols. 20 ml sample solution (200 ng·mL⁻¹, pH 8.5) was loaded at 0.6 mL·min⁻¹
Fig. S4 Optimization for polymerization conditions: (A) thiophene-3-boronic acid concentration, (B) scan rates, (C) scan segments. 20 ml sample solution (200 ng·mL⁻¹, pH 7) was loaded at 1 mL·min⁻¹ by syringe pump.

Fig. S5 Cyclic voltammogram comparison of carbon fiber in 1 mM potassium ferricyanide solution (monomer concentration: 7.5 mmol·L⁻¹, scan rate: 0.025 V·s⁻¹, 160 scan segments)
**Fig. S6** Amplified image of poly (thiophene-3-boronic acid): lateral image (A) and cross section image (B)

**Fig. S7** FT-IR spectra of bare carbon fiber (A) and poly (thiophene-3-boronic acid) (B)

**Fig. S8** Energy Dispersive Spectrometry characterization of poly (thiophene-3-boronic acid)
Fig. S9 Optimization for extraction: (A) Sample flow rates, (B) Sample pH value, (C) Sample volume
**Table S1** Analytical performance of the online SPME-HPLC methods for analysis of 3 catecholamines in spiked plasma samples (n=3)

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Linear equation</th>
<th>Range (ng·mL⁻¹)</th>
<th>LOD (ng·mL⁻¹)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adrenaline</td>
<td>Y=6.77X+3239.1</td>
<td>1-8000</td>
<td>0.5</td>
<td>0.9923</td>
</tr>
<tr>
<td>Noradrenaline</td>
<td>Y=6.82X+6814.3</td>
<td>1-8000</td>
<td>0.5</td>
<td>0.9696</td>
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<tr>
<td>Dopamine</td>
<td>Y=21.84X+5437.4</td>
<td>1-8000</td>
<td>0.5</td>
<td>0.9954</td>
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</tbody>
</table>

*S/N=3

**Table S2** Recoveries of 3 catecholamines in spiked plasma samples

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Concentration</th>
<th>Added</th>
<th>Found</th>
<th>Recovery %</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ng·mL⁻¹)</td>
<td>(ng·mL⁻¹)</td>
<td>(ng·mL⁻¹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adrenaline</td>
<td>100</td>
<td>100</td>
<td>194.02</td>
<td>94.02</td>
<td>3.08</td>
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<tr>
<td>Noradrenaline</td>
<td>100</td>
<td>100</td>
<td>195.72</td>
<td>95.72</td>
<td>4.65</td>
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<tr>
<td>Dopamine</td>
<td>100</td>
<td>100</td>
<td>192.55</td>
<td>92.55</td>
<td>2.18</td>
</tr>
</tbody>
</table>

*Mean value. N=3