Solid-Phase Microextraction Coupled with Capillary Electrophoresis for Doping Analysis of Propranolol Enantiomers in Urine Using a Sol-Gel Derived Calix[4]arene Fiber

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Abstract A new type fiber coated with diglycidyloxy calix[4]arene/hydroxy-terminated silicone oil diglycidyloxy-calix[4]arene/OH-TSO made by sol-gel method was prepared for capillary electrophoresis CE sample pretreatment. By using headspace solid-phase microextraction HS-SPME combined with a novel back-extraction facility coupled off-line to capillary zone electrophoresis CZE the determination of propranolol enantiomers in urine was achieved with combination of ultrasonic back-extraction and field amplified sample injection FASI technologies. Extraction and back-extraction parameters were optimized. The clean-up effect and preconcentration effect were realized without derivatization during the SPME process in terms of this strongly polar and thermally stable compound. Preconcentration of the sample by calix[4]arene fiber increased the sensitivity yielding a limit of detection LOD of 0.01 mg/L by CZE-diode array detection DAD. Method repeatability relative standard deviations RSD < 6.5% and fiber reusability > 150 extraction procedures were observed over a wide linear range of propranolol 0.05 – 10 mg/L in urine samples. Compared with commercial SPME stationary phases the new coating showed higher extraction efficiency and this SPME-CZE-DAD procedures could meet the demand of minimum required performance limits MRPL set by the World Anti-Doping Agency WADA for the detection of propranolol in urine samples.

Key words calix[4]arene solid-phase microextraction capillary electrophoresis doping analysis propranolol enantiomers
1

1.1

P/ACE MDQ  

1.2

SPME

1.3

1 mol/L NaOH

1.4

10 min

1.5

NaOH

2

2.1
For the extraction efficiency of propanolol.

2.2 Extraction conditions

- Extraction temperature: 90 °C
- Extraction time: 30 min
- Desorption time: 3 min
- Salting-out: 300 g/L NaCl
- Propanolol: 2.5 mg/L
- FID detector

Fig. 1 Influence of NaOH concentration on the extraction efficiency of propanolol

HS-SPME conditions: extraction temperature: 90 °C, extraction time: 30 min, desorption time: 3 min, NaCl: 300 g/L, propanolol: 2.5 mg/L, FID detector.

2.3 Comparison of extraction abilities of different fibers

HS-SPME conditions: 90 °C for 30 min with 4 mol/L NaOH and 300 g/L NaCl in aqueous solution spiked with 5 mg/L propanolol hydrochloride with magnetic stirring.

Back extraction conditions: water without ultrasonic back extraction at 40 °C for 15 min, DAD detector. Identification of the peaks of S-propanolol and R-propanolol in the electropherograms was referred to reference 8.

Fig. 3 Comparison of extraction abilities of different fibers

Fiber type

- C[4]
- PDMS
- PDMS-DVB
- PA
Table 1 Influence of back-extraction combined with field amplified sample injection on preconcentration effect

<table>
<thead>
<tr>
<th>Compound</th>
<th>FASI area</th>
<th>ESI area</th>
</tr>
</thead>
<tbody>
<tr>
<td>-[J]-Propanol</td>
<td>2.52 x 10^3</td>
<td>3.72 x 10^3</td>
</tr>
<tr>
<td>+[J]-Propanol</td>
<td>2.45 x 10^3</td>
<td>3.64 x 10^3</td>
</tr>
</tbody>
</table>

1 Back-extraction solution composition: water-acetonitrile 40:10 v/v sample water spiked with 0.5 mg/L propanolol hydrochloride; electokinetic sample injection: 10 kV x 12 s; 2 ESI electokinetic sample injection: without sample stacking; 30 kV x 12 s; 4 back-extraction solution composition: 50 µL phosphate buffer solution; pH 2.5; sample water spiked with 10 mg/L propanolol hydrochloride.

3.4

2.4

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Fig. 4 Comparison of electropherograms obtained by different modes for the determination of propanolol enantiomers in human urine

- direct CE-DAD analysis
- sample spiked with 10 mg/L propanolol hydrochloride
- b. calii 4 arene-coated SPME-CZE-DAD analysis with sample stacking
c. calii 4 arene-coated SPME-CZE-DAD analysis without sample stacking.

SPME conditions: extraction medium 5 mL urine sample spiked with 0.5 mg/L propanolol hydrochloride containing 1.5 g NaCl 4 mol/L NaOH with stirring speed 1 000 r/min, temperature 90 °C, time; 30 min headspace SPME mode.

Back-extraction conditions: water-acetonitrile 40:10 v/v with ultrasonic back-extraction at 40 °C for 15 min.