Preparation and application of perfluorodecyl modified silica monolithic capillary column in extraction and enrichment of perfluoroocane sulfonates

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Abstract A perfluorodecyl modified silica monolithic capillary column has been prepared by using sol-gel method. The preparation steps included hydrolysis of alkoxy silane, fasculation of silanol gelation, aging, meso-pore preparation, drying and surface modification. It could be used as a solid phase extraction (SPE) microcolumn for extraction and enrichment of perfluoroocane sulfonate (PFOS). The enrichment characteristics and efficiency of the perfluorodecyl modified monolithic silica capillary column has been investigated and compared with C18 silica monolithic capillary column. The results indicated that the perfluorodecyl modified silica monolithic capillary column 15 cm × 75 μm had a higher adsorption capacity and a better enrichment selectivity for PFOS. The average adsorption capacity of the perfluorodecyl modified silica monolithic capillary column was 75 ng. And when the PFOS mass concentration in sample was 0.25 mg/L, the enrichment factor was 29-fold in average. Owing to the good performance of the perfluorodecyl modified silica monolithic capillary column, it can be used for the extraction and enrichment of trace PFOS in water to meet the requirements of water quality monitoring and analysis.

Key words perfluorodecyl modified silica monolithic capillary column, solid phase extraction, SPE, enrichment, perfluoroocane sulfonate, PFOS


通过溶胶-凝胶法制备全氟辛烷磺酸(PFOS)溶液，其中氟代物常用来制造皮革、纺织品、家具、地毯、农药等产品。

1. 实验材料与试剂

1.1 材料

JEOL JSM-6490LV 电子扫描电子显微镜
KQ3200E 实验超声波清洗仪
DF-101S 电热恒温水浴锅
DZKW 电热恒温干燥箱
HP-5890 气相色谱仪
Palo Alto CA USA LSP02-1B 气相色谱柱
API 4000 液相色谱质谱联用仪
LC-20A 液相色谱仪
Finnigen 串联质谱仪

1.2 API 4000 液相色谱质谱条件

毛细管整体柱的发展，使得待萃取样品的用法(1%-2%)大大降低，而且还可以减少萃取溶剂的消耗，提高萃取效率的富集倍数。可以预见，毛细管萃取整体柱在样品前处理领域将具有良好的发展前景。

1.3 LCQ ADVANTAGE MAX 液相色谱质谱条件

通过毛细管整体柱进行富集，考察了所制备的整体柱的萃取富集特性和富集效率，并与传统填充型萃取柱，整体柱制备简单，可以避免填充柱繁琐的装填过程，固定相内部是由微米级的通部接触，实现了较快的对流传质，多反应监测(2. 1% 2% 3% 5% 8% 10% 15% 20%)扫描，多反应监测。通过溶胶-凝胶法制备全氟辛烷磺酸(PFOS)，相比较为常见的全氟化合物(PFOS)具有稳定性很高，在自然环境下很难发生分解，一般在多种环境样品中检测到了 PFOS，是危害性有机污染物。以永光明医疗仪器厂(2. 1% 2% 3% 5% 8% 10% 15% 20%)和分离实验进行富集，得到的样品中 PFOS 含量为 100 mg/L，1 mL 毛细管整体柱的萃取富集特性，与传统填充型萃取柱，其传质阻力大，萃取效率较低，需要较大浓度的样品和萃取溶剂，且杂质干扰难以去除。近来，整体柱技术的迅速发展使得其在固相萃取领域得到了越来越广泛的应用。毛细管整体柱在样品前处理领域将具有良好的发展前景。
2.1 20 h 330 °C 100 μL 900 μL 3 h 110 °C 3 h 110 °C 900 μL 900 μL

PFOS 7.25 mg/L
PFOS 96.6% C18 29 1.05 mg/L
PFOS 20% 1b

2.2

PFOS 10 μL/min 2.5 mg/L
PFOS 10 μL 110 μL 10 μL 40 μL
PFOS 2 1 2 1 2
PFOS 75 ng C18
PFOS 10 μL

Fig. 2 Breakthrough curves of PFOS on a C18 and b perfluorodecyl modified silica monolithic columns

2. Scanning electron micrographs SEM of a C18 and b perfluorodecyl modified silica monolithic capillary columns

Fig. 1
2.3 C18 PFOS

Table 1 Elution of PFOS adsorbed on perfluorodecyl modified and C18 silica monolithic capillary columns

<table>
<thead>
<tr>
<th>Elution volume/μL</th>
<th>PFOS concentration μg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7520.0</td>
</tr>
<tr>
<td>20</td>
<td>204</td>
</tr>
<tr>
<td>30</td>
<td>11.8</td>
</tr>
<tr>
<td>40</td>
<td>3.7</td>
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</tbody>
</table>

2.5 MS total ion current chromatogram of sodium heptane-1-sulphonate in pre-column liquid and post-column liquid of perfluorodecyl modified silica monolithic capillary column and post-column liquid of C18 silica monolithic capillary column

Fig. 3 HPLC-MS/MS chromatograms of a) PFOS standard and b) Xiangjiang River water
Table 2  Spiked recoveries of PFOS in 3 real samples\( n = 3 \) 

<table>
<thead>
<tr>
<th>Sample</th>
<th>Background/ Added/</th>
<th>Found/ Recovery/</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ng/L</td>
<td>ng/L</td>
</tr>
<tr>
<td>Xiangjiang River</td>
<td>6.2</td>
<td>8.0</td>
</tr>
<tr>
<td>Running water</td>
<td>ND</td>
<td>8.0</td>
</tr>
<tr>
<td>bottled drinking water</td>
<td>ND</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>ND</td>
<td>12.0</td>
</tr>
</tbody>
</table>

* ND not detected.