Determination of Trace Polycyclic Aromatic Hydrocarbons in Surface Sediments of Huangpu River by High-Performance Liquid Chromatography

LIU Ying¹, CHEN Ling¹, TANG Yinjian¹, HUANG Qinghui², ZHAO Jianfu¹
¹. State Key Laboratory of Pollution Control and Resources Reuse, School of Environmental Science and Engineering, Tongji University, Shanghai 200092, China ². Key Laboratory of Yangtze Aquatic Environment, Ministry of Education, School of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

Abstract The 16 polycyclic aromatic hydrocarbons included in US EPA Priority Pollutant List in surface sediments from Huangpu River were qualified and quantified using high-performance liquid chromatography (HPLC) coupled with photodiode array detector (PDA). On the basis of qualification by retention times, the ultraviolet spectra of 16 PAHs obtained from PDA were used to improve the qualification. Furthermore, benz[a]anthracene, fluoranthene, benz[k]fluoranthene, benz[a]pyrene and benz[e]pyrene in sediment samples were identified with the differences of ultraviolet spectra of isomers. The quantitative method for 16 trace PAHs in the sediments was developed. In order to intensify ultraviolet response of target components and reduce those of the interferents, detection wavelengths of 16 PAHs were optimized. The limits of detection were improved further and were from 1.1 to 18.3 ng/g on dry basis and spiked recoveries from environmental samples were 87% – 113%. Therefore, the quantitative method in this study was sensitive and accurate and was satisfied for the determination of trace PAHs in environmental samples. Finally, the quantitative method was successfully used for the analysis of the surface sediments of Huangpu River. All the PAHs except acenaphthylene were detected. The concentrations of the PAHs were 10.1 – 253.0 ng/g and their relative standard deviations RSD were less than 10%.

Key words high performance liquid chromatography, HPLC, polycyclic aromatic hydrocarbons, PAHs, surface sediment, Huangpu River
测定沉积物中的高效液相色谱（HPLC）方法以富集目标组分和测定两个基本过程。由于环境样品的基质复杂且含有大量干扰物，样品的富集必将增加基质的干扰，加大测定难度。现有文献报道了环境样品（如大颗粒物）中多环芳烃（PAHs）、苯并α芘（BAP）、苯并[a]芘（BaP）、二苯并[a,h]蒽（BghiP）的大量存在也将导致定量误差大。气相色谱（GC）和质谱（MS）联合检测是多环芳烃测定的常用方法，但该方法定性准确，但是质谱无法区分同分异构体，仅能用于准确定性定量分析。环境样品中异构体化合物的准确测定尤为重要。气相色谱（GC）-质谱（MS）联合检测是近年来常用于多环芳烃测定的方法，具有灵敏度高、选择性好的优点。但是GC-MS方法检测波长固定，不能提供目标组分的详细信息。气相色谱-质谱-质量检测器（GC-MS-MS）联合检测提供更丰富的信息，可用于多环芳烃的准确检测。对不同环境样品（如沉积物、土壤和水）中多环芳烃的测定，GC-MS-MS联合检测方法简便实用，灵敏度和专一性高。表1列出了美国环保局（EPA）优先控制污染物（PAHs）中各组分的定性。为了更好地探讨不同环境样品中多环芳烃的含量，取上海市黄浦江上游（淀峰）、中游（青浦）、下游（吴淞口码头）表层沉积物，置于美国公司购得的组分有萘（Nap）、苊（AcN）、菲（Fl）、苯并[a]蒽（B[a]A）、苯并[a]芘（B[a]P）、苯并[k]荧光（BghiP）、苯并[k]芘（BghiP）等7种组分已被美国环保局（EPA）列入优先控制污染物（PAHs）中。

### 表1 检测波长、方法检出限、加标回收率及黄浦江表层沉积物样品中的多环芳烃含量

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Detection wavelength/ nm</th>
<th>LOD/ ng/g</th>
<th>Recovery mean ± SD/ %</th>
<th>Sediment from upstream</th>
<th>Sediment from midstream</th>
<th>Sediment from downstream</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>mean ± SD/ ng/g</td>
<td>RSD/ %</td>
<td>mean ± SD/ ng/g</td>
</tr>
<tr>
<td>1</td>
<td>Nap</td>
<td>218</td>
<td>3.6</td>
<td>90 ± 4</td>
<td>68.9 ± 1.7</td>
<td>2</td>
<td>111.5 ± 3, 1</td>
</tr>
<tr>
<td>2</td>
<td>AcN</td>
<td>226</td>
<td>4.8</td>
<td>103 ± 5</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>Fl</td>
<td>254</td>
<td>18.3</td>
<td>98 ± 5</td>
<td>18.8 ± 5.1</td>
<td>27</td>
<td>51 ± 1.4</td>
</tr>
<tr>
<td>4</td>
<td>AcN</td>
<td>226</td>
<td>1.9</td>
<td>93 ± 8</td>
<td>10.1 ± 1.1</td>
<td>11</td>
<td>32 ± 1.9</td>
</tr>
<tr>
<td>5</td>
<td>PhA</td>
<td>254</td>
<td>1.1</td>
<td>98 ± 8</td>
<td>86.4 ± 1.5</td>
<td>2</td>
<td>168.4 ± 6.8</td>
</tr>
<tr>
<td>6</td>
<td>An</td>
<td>254</td>
<td>1.8</td>
<td>113 ± 6</td>
<td>13.5 ± 1.1</td>
<td>8</td>
<td>44.7 ± 2.4</td>
</tr>
<tr>
<td>7</td>
<td>FIA</td>
<td>286</td>
<td>5.1</td>
<td>111 ± 5</td>
<td>123.3 ± 1.1</td>
<td>1</td>
<td>224.2 ± 3.3</td>
</tr>
<tr>
<td>8</td>
<td>Py</td>
<td>334</td>
<td>7.1</td>
<td>106 ± 7</td>
<td>165 ± 1.3</td>
<td>1</td>
<td>237.7 ± 1.4</td>
</tr>
<tr>
<td>9</td>
<td>Chy</td>
<td>266</td>
<td>2.2</td>
<td>104 ± 8</td>
<td>97.8 ± 1.5</td>
<td>2</td>
<td>25.7 ± 4.7</td>
</tr>
</tbody>
</table>
图具有显著特征且受干扰物影响不明显，在保留时间定性的基础上，通过紫外光谱图对比可方便地识别目标组分。在保留时间的基础上，利用质谱检测器对分析物进行定性分析，再通过选择组分在离子色谱进行定量分析。该方法选择性好、灵敏度高，但是对同分异构体的鉴别能力较弱，而多环芳烃类物质中，多种组分属于同分异构体，例如苯并[...]

### 2.1 PAHs
GC-MS/LC-MS/LC-PDA

PDA

BeP

BeP

BbF

BbF

BkF

BkF

BaP

BaP

DBahA

IP

IP

BghiP

BghiP

Table 1 Continued

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Detection wavelength/ nm</th>
<th>LOD/ ng/g</th>
<th>Recovery</th>
<th>Sediment from upstream</th>
<th>Sediment from midstream</th>
<th>Sediment from downstream</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>mean ± SD/ %</td>
<td>mean ± SD/ %</td>
<td>mean ± SD/ %</td>
</tr>
<tr>
<td>10</td>
<td>BaA</td>
<td>285</td>
<td>4.9</td>
<td>95 ± 7</td>
<td>112.1 ± 8.6</td>
<td>8.9 ± 2.3</td>
<td>99.5 ± 4.9</td>
</tr>
<tr>
<td>11</td>
<td>BbF</td>
<td>300</td>
<td>6.9</td>
<td>97 ± 8</td>
<td>60.9 ± 1.7</td>
<td>3 ± 1.8</td>
<td>100.7 ± 1.8</td>
</tr>
<tr>
<td>12</td>
<td>BkF</td>
<td>300</td>
<td>3.1</td>
<td>101 ± 6</td>
<td>70.2 ± 5.5</td>
<td>8 ± 1.7</td>
<td>42.2 ± 1.8</td>
</tr>
<tr>
<td>13</td>
<td>BaP</td>
<td>300</td>
<td>6.5</td>
<td>102 ± 8</td>
<td>76.3 ± 4.7</td>
<td>2 ± 1.8</td>
<td>152.0 ± 6.3</td>
</tr>
<tr>
<td>14</td>
<td>DBahA</td>
<td>300</td>
<td>6.4</td>
<td>97 ± 2</td>
<td>22.2 ± 1.0</td>
<td>5 ± 1.1</td>
<td>38.2 ± 2.1</td>
</tr>
<tr>
<td>15</td>
<td>IP</td>
<td>249</td>
<td>6.4</td>
<td>102 ± 5</td>
<td>70.8 ± 6.3</td>
<td>9 ± 1.9</td>
<td>94.7 ± 7.8</td>
</tr>
<tr>
<td>16</td>
<td>BghiP</td>
<td>300</td>
<td>6.1</td>
<td>87 ± 7</td>
<td>19.5 ± 2.0</td>
<td>10.9 ± 3.0</td>
<td>110.9 ± 2.4</td>
</tr>
</tbody>
</table>

1. Nap[...]naphthalene[...], AcNyl[...]acenaphthylene[...], FL[...]fluorene[...], AcNe[...]acenaphthene[...], PhA[...]phenanthrene[...], An[...]anthracene[...], FLA[...]fluoranthenes[...], Py[...]pyrene[...], Chy[...]chrysene[...], BaA[...]benz[a]anthracene[...], BbF[...]benz[b]fluoranthene[...], BkF[...]benz[k]fluoranthene[...], BaP[...]benz[a]pyrene[...], DBahA[...]dibenzo[a,h]anthracene[...], IP[...]indeno[1,2,3-c,d]pyrene[...], BghiP[...]benz[g,h,i]perylene.

Fig. 1 Ultraviolet spectra of a) benz[a]fluoranthene, b) benz[b]fluoranthene, c) benz[a]pyrene and d) benz[g,h,i]perylene.
2.2 PAHs

The chromatograms of the mixed standards of 16 PAHs and a sediment sample at 254 nm are shown in Figure 4. The chromatograms were obtained using a high-performance liquid chromatography (HPLC) system equipped with a UV detector. The retention times of the PAHs were used for qualitative analysis, and the UV spectra were used for quantitative analysis.

The retention times of the PAHs in the mixed standards and the sediment sample are shown in Table 1. The results show that the PAHs were eluted in the following order: BbF, BkF, AcN, 1-b, 1, 3, BeP, BbF, 256 nm, BkF, AcN, 1-b, 1, 3, BeP, BbF, 256 nm, BkF, AcN, 1-b, 1, 3, BeP, BbF, 256 nm, BkF, AcN, 1-b, 1, 3, BeP, BbF, 256 nm, BkF, AcN, 1-b, 1, 3, BeP, BbF, 256 nm, BkF, AcN, 1-b, 1, 3, BeP, BbF, 256 nm, BkF, AcN, 1-b, 1, 3, BeP, BbF, 256 nm, BkF, AcN, 1-b, 1, 3, BeP, BbF, 256 nm.

The UV spectra of the PAHs in the mixed standards and the sediment sample are shown in Figure 5. The spectra were obtained using a UV-visible spectrophotometer. The UV absorption maxima of the PAHs were used for quantitative analysis.

The UV absorption maxima of the PAHs in the mixed standards and the sediment sample are shown in Table 2. The results show that the UV absorption maxima of the PAHs were in the range of 200-300 nm. The absorbance at these wavelengths was used for quantitative analysis.

The quantitative analysis of the PAHs in the sediment sample was performed using the external standard method. The standard solutions of the PAHs were prepared at concentrations of 50-500 μg/L. The absorbance of the standard solutions was measured at 254 nm, and the absorbance of the sediment sample was measured at 254 nm. The concentration of the PAHs in the sediment sample was calculated using the following equation:

\[ C = \frac{A_{\text{sample}}}{A_{\text{standard}}} \cdot C_{\text{standard}} \]

where \( C \) is the concentration of the PAHs in the sediment sample (μg/g), \( A_{\text{sample}} \) is the absorbance of the sediment sample at 254 nm, \( A_{\text{standard}} \) is the absorbance of the standard solution at 254 nm, and \( C_{\text{standard}} \) is the concentration of the standard solution (μg/L).

The results of the quantitative analysis are shown in Table 3. The results show that the concentrations of the PAHs in the sediment sample were in the range of 0.1-10 μg/g. The analysis indicates that the PAHs were present in the sediment sample at low concentrations.
常常导致定量测定不准确或无法定量。针对前一类情况，可选择在响应值较大的波长（如306 nm）下进行定量；而后一类情况，可以选择干扰物无吸收或弱吸收的波长进行定量。总之，强化目标响应，弱化干扰响应。

将图（图）中# fragment放大（见图#），未观察到#峰，而#峰拖尾。未观察到#峰的原因有两个。第一，#在样品中的含量较低；第二，通过前面的定性分析可知，该处至少有#个组分共洗脱，依次为#、#、#、#和#。前三者在#下都有较强的吸光度，而#相对较弱，所以#峰被前面的组分峰掩盖。当选择在#响应值较大而其他三者响应值略弱的*+*下进行观察（见图#），#峰便显现出来，可以精确地定量。在图#中的#附近基线噪声较大，影响其定量的准确性和最低检出限，但在其最大吸收波长#处定量（见图#），信号被强化且基线噪声大大减小，基线从约*，**降到约*，**。

在图#中，在#出峰位置附近，有一明显的峰，如仅从保留时间来分析，很容易被误认为是#。通过分析附近的光谱图，会发现#其实被该峰附近的噪声所掩盖。在#下检测（图#），干扰峰变弱，噪声降低，#的峰显现出来。前面提到在本实验中#与#有共洗脱现象，所以对#定量应避免样品中#的干扰。

图#和图#表明，#在#之间的吸光度相对较低，而#在#处有次强吸收峰，所以在#处定量可以大大减少#对#的干扰。同时，在#处，#也有较强的吸收，#和#在该处吸收相对较弱，但受干扰较小，因此，本文在#处对#、#、#和#进行定量。本研究中其他目标组分的检测波长详见表#，共计#个波长。

采用该方法分析黄浦江表层沉积物的结果表明，#种多环芳烃中除二氢苊外，#种#都被检出，各组分的含量介于#之间。（详见表#）。

次平行样品测定结果表明，本方法测定#种#具有较好的重现性，相对标准偏差小于#。上游沉积物样品中的#值较大与其含量接近检出限有关。通过空白样品加标，按#倍信噪比计的检出限列于表#。除#外，其他组分检出限（以干基计）均低于#，满足沉积物样品中痕量多环芳烃的分析要求。将#种#混合标准品加到环境样品中，加标量为#，实际样品中各组分的加标回收率为#。
15 期 刘颖, 等: 高效液相色谱法测定黄浦江表层沉积物中的痕量多环芳烃

检出限均低于 0.01%, 实际样品中各组分的加标回收率为 90%。该方法具有较好的灵敏度和准确性。

参考文献:


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