Modification of mid-point restrictor of heart cut multidimensional gas chromatography-mass spectrometry system and its application in analysis of benz[a]pyrene in cigarette smoke

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Abstract The mid-point restrictor known as the key spare part of multidimensional gas chromatography MDGC was modified and applied in the determination of benz[a]pyrene in cigarette smoke. The graphite restrictor was replaced by a 0.25 mm i.d. fused silica open tubular and the two-hole graphite ferrule was replaced by a press-fit glass Y-splitter to improve the stability of retention time on the 1st dimensional column and eliminate the carry-over effects of graphite. The cigarette samples were prepared as follows The mainstream cigarette smoke collected on Cambridge pad was extracted with cyclohexane then the extractant was analyzed by heart cut MDGC-mass spectrometry MS directly with benz[a]pyrene-d12 as internal standard. The method was proved to be simple, sensitive, fast and reliable with good linearity linear range of 1.47 – 29.4 μg/L \( r^2 \) of 0.9999 reproducibility, relative standard deviation RSD of 1.94%, recovery 90.74% – 101.86% and low quantitative and qualitative detection limits. Moreover, the amount of benz[a]pyrene in the 2R4F Kentucky reference cigarette smoke obtained by this method was close to that reported in literature.

Key words mid-point restrictor multidimensional capillary gas chromatography MDGC mass spectrometry MS benz[a]pyrene cigarette smoke

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并市售卷烟样品
连接器取代两孔石墨垫,确保了一维保留时间的长
芘,卷烟样品不需要经过净化,利用大孔径毛细管柱
谱联用(\(\text{MS}^{+}\))来检测卷烟烟气中的苯并\(\text{a}\)芘质量浓度为

点关注的烟气有害物之一。由于卷烟烟气的组成十
复杂的分离和富集过程,都需要经过不同方式的净
化。本课题组也曾利用具备在线富集功能的大孔径
毛细管柱取代石墨限流管,用一段
形玻璃压合连接器代替两孔石墨垫,消除了吸附和记忆效应。长期的分析过程中容易产生一维色谱保留时间漂移,
影响中心切割范围的准确性,不利于常规批量检测。

样品
<br/>

仪器与材料
<br/>

已报道的卷烟烟气中苯并\(\text{a}\)芘含量一般仅为几至几十纳克
原液,制成一级储备液,苯并\(\text{a}\)芘标准品(纯度
<br/>

\(\text{MS}^{+}\))进行改进,用一段
小孔径毛细管柱多维气相色谱系统和质

本工作对
<br/>

装置(\(\text{MS}^{+}\)来检测卷烟烟气中的苯并\(\text{a}\)芘质量浓度为
<br/>

对烟气进行初步分离
<br/>

的吸烟条件
<br/>

的中点限流器(见图
<br/>

系统应用于卷烟烟气中苯
<br/>

中点限流器的改进
<br/>
史佳沁,等:中心切割式多维气相色谱质谱系统中中点限流器的改进及其在卷烟烟气中苯并[a]芘检测中的应用

图3 改进后的中点限流装置

图4 使用改进的中点限流器分析多环芳烃混合标准溶液进样1, 2, 3, 4次、5, 6次和7, 8次的一维色谱图

图5 使用原中点限流器进行样品分析后第1次和第2次空白溶剂进样所得到的二维色谱图

第1.2.2

SIM的2a

MDS6890的3a

Fig. 3 Diagram of improved mid-point restrictor
1. 2nd column 2. mid-point pressure 3. quartz capillary column 4. pre-column 5. fused silica restrictor 6. glass Y-splitter.

Fig. 4 Chromatograms of first dimensional GC of a mixed standard solution of polycyclic aromatic hydrocarbons for the 1st and 10th and 20th injection used improved mid-point restrictor
1. benz@ a-pyrene IS internal standard.
2.2 GC-MS

2.2.1 0.147 ~ 29.4 μg/L. y = 0.0404x + 0.0092

2.2.2 1.47 ~ 29.4 ng/L.

1.03 ng/L 1 0SD

Table 1 Benzene a-pyrene delivery levels of 12 cigarette products

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<thead>
<tr>
<th>Sample</th>
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2.2.3

2.2.4

2.2.5

2.3 2R4F

2.4

Fig. 6 2D GC-SIM-MS chromatogram of pure solvent for the first time with improved mid-point restrictor after the injection of samples.

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结论

对多维气相色谱的核心部件中点限流器进行了改进,用一段毛细管柱取代石墨限流管,\textit{V} 形玻璃压合连接器取代两孔石墨垫,显著提高了一维色谱保留时间的稳定性,保证了中心切割范围的准确性,且消除了石墨对苯并芘的吸附残留。将本系统应用于卷烟烟气中苯并芘的检测,不需要任何净化程序。方法的重复性、回收率、灵敏度和线性范围均令人满意。对不同配方、滤嘴类型和焦油含量的卷烟样品的测定结果表明,苯并芘含量随着\textit{V}的增加而上升,两者具有较好相关性。按单位\textit{V}计算,烟气苯并芘与配方类型、滤材类型都有一定关系。

参考文献: