

# 模式采样法采集尾气中 BaP 的研究

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**摘要** 用模式取样法采集汽车柴油发动机尾气中多环芳烃, 并重点对 BaP 采样方法进行研究。结果表明, 该法采样时间仅 1—2 s, 采样体积为 330 ml(s·次), 回收率 77.6%, 9 次重复的变异系数为 29.6%。测得 BaP 的数据与国际 ISO 规定的 CVS 定容取样法可比。

**关键词** 模式采样法, 多环芳烃(PAH), BaP, 柴油机尾气, 台架实验, 尾气采样。

碳氢化合物在缺氧和不完全燃烧的情况下形成大量多环芳烃化合物(PAHs), 其中包含苯并 a 芘(BaP)等多种致癌物。柴油、汽油等燃料在燃烧不完全时同样也有各种 PAHs 化合物从发动机尾气排出。在对发动机排气中的 PAHs 进行分析研究时, 关键问题之一是准确、可靠的采样技术。当前国际上通用的机动车辆排放废气中 PAHs 的采样法一般仍沿袭电脑控制的空气稀释法<sup>[1]</sup>, 设备和技术复杂, 价格昂贵, 国内迄今尚无标准方法。笔者在以往工作的基础上发展了一种新型采样技术, 命名为模式(Operomode)采样法, 经过初步应用, 得到了满意的结果<sup>[2]</sup>。

## 1 实验部分

### 1.1 设备和试剂

(1) 柴油发动机, 杭州发动机厂 6120 型柴油机; (2) 台架试验装置, 北京理工大学车辆工程学院提供; (3) 模式采样器, 浙江仪器仪表厂制作; (4) 高效液相色谱仪(HPLC), 岛津 LC-3A 型, 装备有 RF-510LC 和 UVD-2 检测器; (5) 荧光分光光度计, 岛津 RF-5000 型; (6) 滤膜, 上海红光造纸厂产品, 孔径 0.2  $\mu\text{m}$ ; (7) 聚氨基酯, 北京化工厂; (8) 乙酰化滤纸, 实验室制备; (9) 0# 柴油, 北京石油制品公司; (10) 索氏脂肪提取器, 60 ml; (11) KD 浓缩器(Kuderna-Danish 装置); (12) BaP 和其它 PAH 标准化合物, Alderich 公司产品; (13) 环己烷、苯、乙醚、甲醇、丙酮等溶剂均经  $E_{\lambda 367 \text{ nm}}$

$E_{\lambda 405 \text{ nm}}$  检查其荧光强度, 选用未检出者。

### 1.2 实验方法。

#### 1.2.1 尾气中 BaP 的采集

将玻璃纤维滤膜准确放置于模式取样器的滤器部位(图 1)。开动空气计量泵, 以 330 ml/s·次)的速度抽取发动机尾气, 使尾气中小于 10  $\mu\text{m}$  的颗粒包括蒸气相被滤料所吸附。

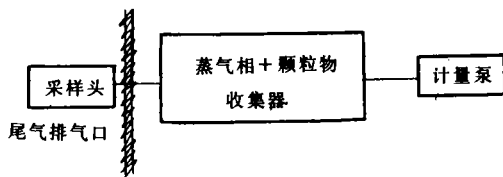


图 1 模式采样示意图

采样须注意下列事项: ① 采样器本身各结合点要结合紧密, 避免漏气现象; ② 采样探头在排气管的轴心线上是逆流安装; ③ 取样应在发动机运转稳定之后开始; ④ 取样用滤料应放在合理进气位置; ⑤ 空气泵力求平稳, 保证每次抽气时间和气量一致。

采足预定体积尾气之后, 取出滤料。根据滤料不同黑度取不同张数的滤膜, 用环己烷作溶剂进行索式提取, 提取液经浓缩操作后提供分析使用。

#### 1.2.2 BaP 的定量分析

按照国标 GB8971-88 规定的分析程序, 将前述浓缩液在乙酰化滤纸上层析分离后, 剪下

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收稿日期: 1995-02-14

BaP 斑点, 在 5 ml 离心管中用丙酮洗脱。荧光分光光度计测定条件,  $E_{\lambda}367\text{ nm}$  狭缝 5 nm,  $E_m406\text{ nm}$  狭缝 5 nm 进行测量, 标准曲线法定量。

1.2.3 PAH 的定量分析

前述样品浓缩液经纯化后用 HPLC-RF510LC 分析测定, 峰面积外标法定量。

2 结果和讨论

2.1 模式采样法的精密度

在柴油发动机自由加速工况下从尾气连续采样, 结果见表 1。

2.2 BaP 的回收量

向滤膜滴加 0.1 $\mu\text{g}$  标准 BaP 溶液, 其浸润直径不超过 5 mm, 将此滤膜置于模式采样器内适当位置上, 然后对自由加速工况下的柴油机尾气进行 BaP 采样。所采集加标样品的 5 次重复分析结果列于表 2。

上述数据统计处理时无任何舍弃, 平均回收率为 77.5%。与 $^{14}\text{C}$ 示踪法<sup>[1]</sup>测得尾气中 BaP

表 1 精密度实验结果( $\mu\text{g}/\text{m}^3$ )<sup>1)</sup>

统计编号	1	2	3	4	5	6	7	8	9
采样编号	13	11	15	10	14	16	9	12	8
BaP 实测值	0.046	0.048	0.057	0.059	0.072	0.073	0.077	0.100	0.105

1) 9 次重复 BaP 平均值为 0.0708, 为柴油机自由加速工况下尾气中 BaP 含量的本底值; 标准偏差 0.021; 变异系数为 29.7%

表 2 准确度实验结果( $\mu\text{g}/\text{m}^3$ )<sup>1)</sup>

统计编号	1	2	3	4	5	平均值	标准偏差	变异系数(%)
采样编号	20	22	19	17	18			
BaP 实测值	0.123	0.133	0.140	0.150	0.173	0.144	0.0191	13.2
BaP 回收量	0.0522	0.0622	0.0692	0.0792	0.102	0.073	0.019	26.0
回收率(%)	55.5	66.2	73.6	84.3	108	77.5	20.0	25.8

1) BaP 回收量为实测值减去本底值(0.0708), 回收率等于测得值比添加量

的回收率为 70%—75%相符。变异系数 26.0%与文献的 29.7%很接近, 均能表示采样方法的准确性。

2.3 滤料组合的分级采样效率

采样所用滤料组合共分 4 级, 第 1 级为滤膜、第 2—4 级均为聚氨基脂。采样后各级滤料分别进行索氏提取, 结果如表 3 所示。

由表 3 可见, 第 1 级滤料截留 BaP 达 99.1%, 第 2 级仅为 0.9%, 也即 BaP99%以上吸留在前级玻纤滤膜上。

表 3 滤料分级采集效率

层 次	材 料	BaP 吸留量( $\mu\text{g}$ )	采集效率(%)
1	玻纤滤膜	0.105	99.1
2	聚氨基脂	0.001	0.9
3	聚氨基脂	ND	—
4	聚氨基脂	ND	—

2.4 台架实验时尾气中 BaP 样品的采集分析

根据中国国家标准 GB6456-86 柴油机排放试验方法(简称 13 工况法)的规定程序, 用模式采样法对 6120 型柴油机尾气中的 BaP 进行了采样。各工况的 BaP 测定值如表 5 所示。表 5 中 BaP 的量以每 kg 耗油量产生的  $\mu\text{g}$  数表示。转速 1400 r/min 为中间转速, 2000 r/min 为额定转速。怠速为无负荷时空转, 相当于机车停驶时的发动机空转。

从表 4 可知: ① 在 13 种工况下, 除工况 7 (怠速、负荷为 0、油耗量为 0.28 kg/h)之外, 其余工况均检出了 BaP, 其含量分布范围为 0.262—0.578  $\mu\text{g}/\text{kg}$ ; ② 除怠速外, 各工况下 BaP 的检出量均随负荷量及油耗量的增加而增高, 反之则减低; ③ 额定转速的油耗量大于中等转速, 但前者尾气中的 BaP 排放量却小于后者。例如 2000 r/min、负荷 100%、油耗 7.77 kg/h 时 BaP 排量为 6.86  $\mu\text{g}/\text{kg}$ , 而 1400 r/min、负荷 100%、油耗 5.67 kg/h 时排 BaP

却为 19.4 $\mu\text{g/kg}$ 。这一现象对研究尾气排放污染物有重要意义。它说明发动机额定转速时处于最佳工作状态,油气比合理,燃烧完全,因此尾气中不完全燃烧产物排量最低。为此应考虑设计一种适合于公共交通使用的发动机,使之长期处于额定转速状态下运行,从而可以大大减少尾气中 PAHs 的排放量;④ 怠速状态下 BaP 排放量不稳定,表 4 中 3 种怠速工况测出 3 种不同浓度的 BaP。从而提示对车辆的怠速运行应予严格控制,以减少尾气中 PAHs 的排放。

表 4 柴油机台架实验时尾气中的 BaP 含量

工况 序号	转速 (r/min)	负荷 (%)	油耗量 (kg/h)	BaP ( $\mu\text{g/kg}$ )
1	怠速	0	0.37	0.578
2	1400	2	1.79	1.92
3	1400	25	2.46	4.39
4	1400	50	3.39	5.16
5	1400	75	4.42	13.7
6	1400	100	5.67	19.4
7	怠速	0	0.28	未检出
8	2000	100	7.77	6.86
9	2000	75	5.36	6.11
10	2000	50	4.41	3.31
11	2000	25	3.26	1.71
12	2000	2	2.46	0.262
13	怠速	0	0.34	4.42
平均				6.28

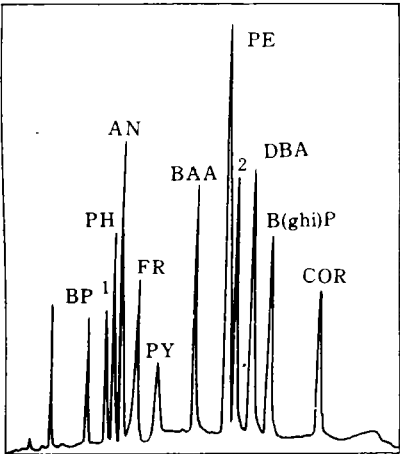


图 2 PAHs 标准 HPLC 谱图  
1. FL 2. BaP

2.5 模式采样法采集 PAHs 样的 HPLC 分析  
在 1400 r/min 工况下采集尾气中 PAHs, 采用 HPLC-荧光检测器进行色谱测定(图 2—3)。

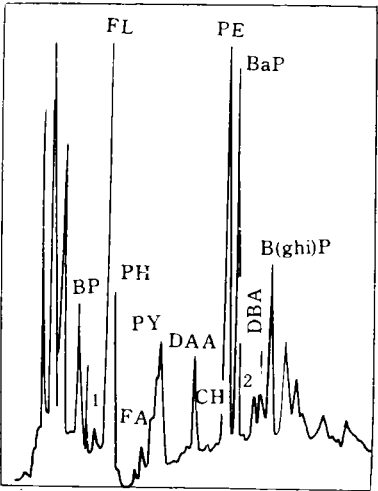


图 3 模式采样法采集 PAHs 样品 HPLC 分析谱图  
1. FL 2. DBA

3 小结

(1) 本文报道的模式采样技术成功地应用于柴油机尾气中 BaP 样品的采集,是迄今所见报道中采样时间最短(1—2s)、采样体积最小[330 ml/(s·次)]的气体采样法。

(2) 模式采样法具有回收率为 77.6%和高精密度,它表明采样技术和分析方法均高度可信。

(3) 根据国家标准 GB6456-86 柴油机排放试验法的规定,应用本方法采集到柴油机台架试验各种工况下尾气中的 BaP 含量平均值为 6.28  $\mu\text{g/kg}$ ,这与 CVS 法测得的 8.45  $\mu\text{g/kg}$  有可比性。

(4) 本采样法经历的采集时间极短,使采样过程中可能存在的氧化-还原或衍生化等反应可以被忽视,因而特别适于高温下 PAHs 的采样。本技术设备不复杂,也利于广泛推广。

参考文献

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spectrophotometry.

**Speciation of Arsenic in the Surface Microlayers of Natural Lakes.** Yu Jianshuan (Xiamen Environmental Monitoring Station, Xiamen 361004); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 61—63

Water samples were collected both from the surface microlayers of natural lakes by using a glass plate surface microlayer water sampler and from the surface layers in a depth of 0.5 m under water surface by using a conventional water sampler, and analyzed for arsenite, arsenate, monomethylarsonate (MMA) and dimethylarsinate (DMA) by using a high performance liquid chromatography/hydride generation/atomic absorption spectrometry technique. The concentrations of arsenic species in surface microlayer water were compared to those in surface layer water. The results show that the arsenic species in surface microlayer water had a significantly different distribution from these in surface layer water and had their concentrations usually higher than these in surface layer water, indicating that they were richer in surface microlayer water with an enrichment factor of 1.66, 1.35, 1.58 and 1.09 for As(III), As(V), MMA and DMA, respectively. As(V) is a dominant arsenic species present in both surface microlayer and surface layer of lake water, and DMA is a major organic arsenic species present in both layers. The distribution of arsenic species was dependent on sampling sites.

**Key words:** lake, surface microlayer water, surface layer water, arsenic species, speciation, sampler.

**Spectrophotometric Determination of Trace Chromium in Water Samples with Sym-Diphenylcarbazone.** Li Huizhi et al. (Dept. of Chemistry, Shandong Institute of Building Material, Jinan 250022); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 64—66

Chromium(VI) was reacted with sym-diphenylcarbazone to form a red complex in the presence of sodium dodecylbenzenesulfonate and 0.15 mol/L of  $H_2SO_4$ . The complex had a maximum absorbance at 560 nm with a molar absorptivity of  $9.74 \times 10^4$  L/(mol · cm). Beer's law was obeyed in the range of 0—10  $\mu$ g of Cr(VI) in 25 ml solution. The common metal ions were able to be separated and concentrated by amberlite 717, giving a better selectivity. The method has been applied to determining chromium in water samples with satisfactory results.

**Key words:** chromium, spectrophotometric, sym-diphenylcarbazone.

**Study on a General ICP-AES Method for Simultaneous Multielement Analysis of Water or Wastewater.** Sha Weinan et al. (Dept. of Chemistry, Nankai Univ., Tianjin 300070); *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 67—71

A general ICP-AES method for simultaneous multielement analysis of water or wastewater was studied and samples pretreatment process, experimental condition optimizing, interference judging, correction and the aspects needed for paying attention during the analysis were discussed. The results showed that analytical data were accurate, reliable, and coincident with the standard values of certified reference samples with a recovery of 90%—110%. The overall relative standard deviation is within 5%. The detection limits were 0.1—100  $\mu$ g/L. The calibration curve has a wide linearity range of 4—6 orders of magnitude.

**Key words:** water, wastewater, ICP-AES.

**Pretreatment for the Test of DEHP in Crops and Soil.** Pang Jinmei et al. (Soil and Fertilizer Institute, Shanxi Academy of Agri. Sci., Taiyuan 030031); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 72—74

This paper deals with the pretreatment method for testing DEHP from farm soil and crops with  $CHCl_3$  as a solvent and with the absorbent. Compared with those from Beijing, Denmark and United States of America, this method took a short extracting time of 0.5—0.7 h, 2—11 h shorter than others, and the solvent of 75—90 ml, 110—1200 ml less than others. This method is easy to use and has a high effective separation. There was a DEHP recovery rate of about 90%, except for cotton seeds. The coefficient of variability was less than  $\pm 3\%$ . It's very suitable to test phthalic acid esters.

**Key words:** DEHP, extraction,  $CHCl_3$ , absorbent.

**Methodological Study of the Operating-Mode Sampling Method Applied to Collecting PAH Compounds in Exhausts from Diesel Engines.** Sun Chen et al. (Beijing Municipal Environmental Monitoring Center, Beijing 100044); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 75—77

A new method, operomode sampling method was presented for the first time for collecting polycyclic aromatic hydrocarbons (PAHs) in the exhaust from diesel engines. With benzo-a-pyrene (BaP) as a main index, the efficiency, precision

and accuracy of the sampling technique were investigated. Results show that the operomode sampling method was a simple, rapid and reliable method. During the bench test of diesel engines it could be used to collect PAHs compounds quickly from exhausts of diesel engines under different operating modes such as idle motion, free acceleration etc. The BaP data measured were comparable with those from the constant volume sampling (CVS) method.

**Key words:** operomode sampling, polycyclic aromatic hydrocarbons, benzo-a-pyrene, exhausts of diesel engines, diesel engine test cycle, bench test.

**Hygienic Investigation of Different Rare Earth (RE) Mining Areas in China: RE Levels of Farmer's Natural Living Environment and Head Hair.** Lu Guocheng et al. (Dept. of Environ. Health, Beijing Medical University, Beijing 100083); *Chin. J. Environ. Sci.*, 16(4), 1995, pp. 78—82

In order to get a preliminary estimation of RE exposure and absorption (or accumulation) levels of inhabitants living in RE mining areas, RE contents of natural environment (including soil of cultivated land, well water, natural plants, vegetables and cereals) and head hair of farmer's living in three representative RE mining areas in China were examined. All samples were analyzed for RE content by spectrophotometric method. Results show that RE levels of soil samples from RE mining areas (680—1200 mg/kg) were obviously higher than those from control areas. some natural plants are capable of accumulating RE (16.8—57.2  $\mu\text{g/g}$ ). However, RE levels of shallow well water (2.6—21.0  $\mu\text{g/g}$ ), cereals (0.05—3.15  $\mu\text{g/g}$ ) and fresh vegetables (0.06—1.82 g/g) from RE mining areas had only a trend of slight increase. The estimated amount of average daily RE intake person (RE EADI) (554.1—1708.1  $\mu\text{g/d} \cdot \text{person}$ ) of farmer's in RE mining areas were almost the same as those of farmer's in control areas, but RE EADI of farmer's of the two RE mining areas of southern China (554.4—659.4  $\mu\text{g/d} \cdot \text{person}$ ) were lower than that of the RE mining area of northern China (1708.1  $\mu\text{g/d} \cdot \text{person}$ ). On the

contrast, RE levels of head hair samples from RE mining areas of southern China (0.53—15.02  $\mu\text{g/g}$ ) were significantly higher than those of samples from control areas, and also markedly higher than those (0.20—1.12  $\mu\text{g/g}$ ) from RE mining area of northern China. Reasons leading to the differences in head hair RE contents among these mining areas were discussed. Hypothesis and suggestions were made. It was concluded that RE exposure and / or absorption levels of farmer's living in the two RE mining areas of southern China were markedly increased. They should be regarded as RE highly exposed groups.

**Key words:** rare earth elements, soil, well water, natural plant, human head hair, estimated exposure dose, highly exposed group.

**Construction of the Aquatic Environment Management Information system in Dachang District, Nanjing City, China.** Wang Xuejun et al. (Dept. of Urban and Environ. Sci., Peking University, Beijing 100871); *Chin. J. Environ. Sci.*, 16(4), 1995, pp. 83—85

The aquatic environment management information system, a MIS/GIS software package for environmental management, in Nanjing city was constructed. Unlike conventional MIS, a lot of GIS modules were offered in this system to extend its perspective usage in future environmental management, planning and decision-making.

**Key words:** Nanjing, aquatic environment management information system, GIS.

**A Review on Ten Problems of the Global Environmental.** Cao Lei (Gansu Provincial Bureau of Environment Protection, Lanzhou, 730030); *Chin. J. Environ. Sci.*, 16(3), 1995, pp. 86—88

A brief review was made on ten problems of the global environmental, including the depletion of ozone layer, greenhouse effect and global warming, acid deposition, simplification of ecosystem, soil degeneration, deforestation, crisis in water resources, marine pollution, solid waste pollution and toxic chemicals pollution.

**Key words:** global environment, environmental problem, review.