

粉煤灰的多环芳烃在海水中的溶出

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摘要 用荧光分光光度计测定浸泡粉煤灰海水中多环芳烃(PAHs)的含量, 用反相高效液体色谱紫外检测器/荧光检测器测定海水浸泡前后粉煤灰中多环芳烃。热电厂粉煤灰在海水中 2 种溶出结果表明, 其粉煤灰在海水中的静态溶出和吸附可逆, PAHs 的溶出极少。热电厂粉煤灰倾倒入海水中溶出的多环芳烃对海洋环境污染甚微。

关键词 粉煤灰, 多环芳烃, 溶出, 海水。

粉煤灰倾倒入海水其溶出的污染物对海洋环境的影响, 国内仅有溶出率的报道^[1]。有关粉煤灰多环芳烃在海水中的溶出, 尚未见报道。探讨热电厂粉煤灰中多环芳烃在海水中的溶出, 对于了解倾倒入粉煤灰时多环芳烃对海洋的污染十分重要。本试验用 2 种溶出方法, 对上海、天津、大连 3 个港口城市的热电厂粉煤灰中多环芳烃在海水中的溶出作初步研究。

1 实验部分

1.1 仪器和主要试剂

高效液相色谱计日立 656 型; 紫外检测器日立-638-0413; 荧光检测器日立-650-40 型; 荧光分光光度计日立-650-60 型; 层析柱 10×250 mm。

多环芳烃的标准物质: 蒽、菲分析纯。蒽、蒽、芘、蒽、苯并(e)芘, 菲、苯并(a)芘为色谱纯。

1.2 实验方法

取 10—15 g 细粉煤灰置于索氏提取器的滤纸套筒中, 用苯浸泡过夜, 往提取器的烧瓶中注入 200 ml, 苯和沸石, 控制 4—5 周期速率, 回流提取 8—10 h。将铜片脱硫的上述提取液置 K-D 浓缩器中, 在通入氮气下浓缩至约 0.5 ml, 后将挥发近干的浓缩液用 1 ml 石油醚溶解, 注入覆盖有 20 cm 氧化铝、15 cm 硅胶的层析柱上加以净化。分别用 30 ml 石油醚和 50 ml 苯冲

洗。取苯冲洗液于 K-D 浓缩器内, 在通入氮气下浓缩至 0.5 ml。将挥发近干的上述浓缩液用适量苯溶解洗涤, 定容摇匀测定。

1.3 粉煤灰的粒径分布

从现场取样的粉煤灰 A, 松散度为 0.99 g/cm³, 其粒径分布列于表 1。

表 1 粉煤灰 A 粒径分布

粒径[目]	比度(%)
$\Phi > 35$	1.21
$25 > \Phi > 35$	1.72
$35 > \Phi > 40$	4.24
$40 > \Phi > 60$	8.08
$60 > \Phi > 80$	33.03
$80 > \Phi > 100$	26.21
$\Phi < 100$	25.45

1.4 分析方法

(1) 试样 HPLC 分离测定 色谱条件: 色谱柱 Zorbax ODS, 4.6×150 mm; 柱温 40℃; 检测器 UVD, $\lambda=254$ nm; 流动相(等浓度法): CH₃OH:H₂O=90:10(V/V); 梯度洗脱法: 在 30 min 之内甲醇由 60% 增加到 100%, 水由 40% 降为 0%, 后用 100% 甲醇冲洗 20 min。

(2) 谱图的获取 待色谱条件稳定之后, 注入适量试样获取色谱图, 按照等浓度法的色谱条件获取 UVD-FLD 联用等浓度法色谱图; 按照梯度洗脱法色谱条件获取 UVD-FLD 联用

梯度洗脱法色谱图。

(3) 定性定量 PAHs 各组分对 UVD 和 FLD 的响应值各不相同, 使用 UVD 对 BeP 之前流出的各组分有较大的响应值, 而使用 FLD 时所得结果恰与 UVD 相反。当 UVD 与 FLD 串联使用时, 二者互为补充, PAHs 各组分均有较大的响应值。本实验, 由 UVD 测定 PA、AN、FA、PY 和 CH; 由 FLD 测定 BeP、PE 和 BaP。以标样的保留值法和标准物添加法加以定性, 以外标法定量。定量采用等浓度法。

(4) 分析方法的精密度 用上海粉煤灰作为样品, 以前处理至色谱测定做全过程分析法的重复性实验。结果表明, 本法的重复性变异系数随组分不同在 7%—27% 之间波动。

(5) HPLC 测定精密度 用上海粉煤灰配制成试样, 做色谱测定精密度, 在选定的色谱条件下色谱测定重复性变异系数均小于 6.1%。

(6) 分析方法的回收率及其最低检测限 按实验各步骤依次分析检测得多环芳烃各组分的回收率, 结果列于表 2。

表 2 PAHs 各组分回收率(%)

n	PA	AN	FA	PY	CH	BeP+PE	BaP
1	93.5	71.6	100.6	69.4	109.8	116.4	114.4
2	87.4	72.3	95.0	70.8	97.0	83.0	102.4
平均	90.4	72.0	97.8	70.1	103.4	99.7	108.4

按产生多环芳烃谱峰高于 2 倍噪音时所选择的色谱条件, 除 BeP 的最低检测限优于 0.01 ng 外, 其余各组分均优于 0.1 ng

1.5 海水溶出粉煤灰的方法

(1) 将未经任何前处理的干燥粉煤灰 148.4 g 置于 1000 ml 具塞三角瓶中, 注入 600 ml 海水, 振荡 30 min, 取出放置 30 min, 以 3000 r/min 离心分离 10 min。将溶液收集在 1000 ml 分液漏斗中, 分别用 15 nl 和 10 nl 环己烷萃取, 静止分层后, 把环己烷层移入 25 ml 具塞比色管中, 用环己烷稀释至刻度, 混匀待测。将试样移入 1 cm 石英吸收池中, 用 310 nm 波长激发, 在 360 nm 处测发射荧光强度, 用标准曲线法计算。

(2) 将干燥的粉煤灰 4 分法分样后, 经研磨使其全部通过 80 目筛网, 混匀后称取 16 g 加入 1000 nl 容量瓶中, 注入 800 ml 海水置于振荡器上振荡 10 h。弃去溶出液收集溶出后的粉煤灰, 置阴暗处自然风干。按未经海水浸泡前的粉煤灰的方式处理, 由 HPLC 分离测定试样中多环芳烃各组分的含量。

2 结果与讨论

2.1 粉煤灰中 PAHs 的含量

PAHs 各组分含量列于表 3。

表 3 表明, 粉煤灰中 PAHs 含量与海洋沉积物的 PAHs 含量^[2]比较不容忽视。远远高于我国浙江沿海沉积物的含量。

2.2 粉煤灰在海水中的溶出

空白海水采自北黄海, 海水经过 0.45 μm 滤膜过滤。用文献[3]分析方法测定, 其平均(n=7)浓度为 0.001 mg/L[CH/海水]。

以粉煤灰 A 作为试样, 按照溶出方法(1)分别考查溶出温度和时间对溶出液中多环芳烃总量的影响。

(1) 温度对 PHAs 溶出的影响 在不同温度下测溶出液中多环芳烃总量, 其结果如表 4。

由表 4 可见, 粉煤灰中 PAHs 不仅不被溶出, 反而使溶出液中 PAHs 含量降低。这可能是由于粒径分布很宽的粉煤灰对 PAHs 的吸附所致, 溶出和吸附是可逆的。温度在 10—25℃ 之间变化时对吸附无明显影响。

(2) 时间对 PAHs 溶出的影响 选择温度 10℃, 按溶出方法(1)各步骤分别溶出 10、30、60、120 min 之后测溶出液中 PAHs 的含量。结果见图 1, 表明溶出时间对 PAHs 的溶出量影响不明显。

2.3 溶出方法(2)的测定结果

表 3 粉煤灰与海洋沉积物中 PAHs 含量比较¹⁾($\mu\text{g}/\text{kg}$)

地区或国家	菲	蒽	荧蒽	芘	甾	苯并(a)芘	BeP+PE
大连粉煤灰 A	512.4	34.2	451.6	88.1	237.7	28.7	3139.0
天津粉煤灰 B	246.5	5.4	77.0		26.4	0.2	27.3
上海粉煤灰 C	219.8	7.8	135.2	47.4	68.6	7.2	608.3
象山港(浙江)				8	2	37	
台州湾(浙江)			49	9	15	0	
法 国						400	
意大利						3000	
日本(1 站)				630		320	
日本(2 站)				240		130	
美国(1 站)			101	100	40	75	
美国(2 站)			760	960	240	370	
澳大利亚							
汤斯维尔港			1400	4500	1500	2600	
格拉德斯通港			9	7	1	1	
约翰布鲁尔礁			<1	<1	<1	<1	

1) 粉煤灰 A、B、C 为本实验测得值。其余引用文献[4]

表 4 温度对 PAHs 溶出的影响

n	PAHs(mg/L)	CH/海水 ¹⁾
	1-±1℃	25±1.5℃
1	0.0005	0.0003
2	0.0010	0.0004
3	0.0006	0.0004
4	0.0006	0.0005
5	0.0010	0.0003
6	0.0005	0.0003
7	0.0003	0.0004
$\bar{x}$	0.0006	0.0004
S	0.00026	0.00008
CV%	43.3	19.6

1) 海水指溶出液，CH 指甾，表示荧光强度单位

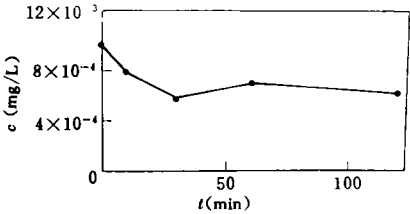


图 1 溶出时间对溶出液中 PAHs 总量的影响

以粉煤灰 C 作为试样，按溶出方法(2)及文献[4]测定经海水浸泡后粉煤灰中 PAHs 各组分的含量，对照溶出前的含量，结果见表 5。

表 5 海水浸泡前后粉煤灰中 PAHs 的含量

含量 ($\mu\text{g}/\text{kg}$ 干重)	PAHs				BeP+BKF+PE 以(BeP+PE)计	BaP
	AN	FA	PY	CH		
溶出前(n=6)	8.0	136.0	48.6	67.6	570.76	6.5
溶出后(n=2)	26.0	153.1	34.0	49.3	464.2	5.3
溶出情况	吸附	吸附	溶出	溶出	溶出	溶出

3 结论

从 2 种海水溶出方式处理粉煤灰后测定 PAHs 的含量结果可知，在温度 10—25℃，时间 10 min—120 min，其粉煤灰 PAHs 各组分总量

变化极不明显。

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to fluidize easily in the reactor. The treatment system can resist the loading fluctuation and possess high dehydrogenase activity.

Key words: fluidized, biofilm, treatment, phenolic wastewater, carrier.

Development of a New Type Dispelling Smoke Silencer of Diesel Engine. Zeng Defang (Turbine College, Wuhan University of Science and Technology of Traffic, Wuhan 430063); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 63—64

This paper introduces a kind of method of making a new type dispelling smoke silencer of diesel engine. The method includes adding a kind of solution which can clean the end gas of diesel engine to the bottom of the old silencer of diesel engine. The end gas of diesel engine can be both cleaned and silenced by passing through the dispelling smoke silencer. A comparison of new silencer with the old one under the same condition on the type 135 diesel engine has shown that the dispelling smoke silencer can reduce 80% of smoke and 14.1% of noise (from 99 dB to 85 dB).

Key words: diesel engine, dispelling smoke silencer, noise, end gas of diesel engine.

A Study on Treatment of Traditional Chinese Medicine Wastewater by SBR Process. Han Xiangkui et al. (Jilin Architectural and Civil Engineering Institute, Changchun 130021); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 65—67

Experimental results showed that at the concentration range of COD in influent from 1000 mg/L to 2500 mg/L, effluent COD can be reduced to less than 250 mg/L, BOD₅ and SS less than 100 mg/L. These levels conform to discharge permission standard of pharmaceutical wastewater. The variation behavior of dehydrogenase during the process of aeration is also discussed in this paper.

Key words: SBR process, wastewater treatment, traditional Chinese medicine wastewater.

Dioxins in Stack Ash from PCBs Incinerator. Ke Jiang et al. (Research Center for Eco-environmental Sciences, CAS, Beijing 100085); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 68—71

The PCDD/Fs in stack ash from a experimental incinerator for destruction of PCBs waste have been determined by ¹³C isotope HRGC/HRMS method. Seventeen 2, 3, 7, 8-substituted toxic dioxins congeners were quantitatively measured. The TEQ value of the stack ash is 47.2 ng/g.

Key words: stack ash, PCBs, dioxins.

Releasing of PAHs from Coal-ash in Seawater. Fu Yun-na and Liu Yiwen (Inst. of Mar. Environ. Prot., SOA, Dalian 116023); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 72—74

Releasing of PAHs from coal-ash in seawater was determined by fluorescence spectrophotometer. The amounts of PAHs from coal-ash soaked before and after in seawater were also analysed by reversed high performance liquid chromatography with UV or fluorescence detectors. The results show that the static state releasing and adsorption

of PAHs from coal-ash in seawater are reversible, releasing of PAHs is pool, and PAHs in the fine coal-ash dumped into sea from heat and power plant have little effect to the marine environment.

Key words: coal-ash, PAHs, releasing, seawater.

Spectrophotometric Determination of Anionic Surfactants in Water with Bromocresol Green and Cetylpyridinium Bromide. Wang Yongsheng et al. (Hengyang Medical College, Hengyang 421001); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 75—77

In this paper a spectrophotometric method has been developed for the determination of anionic surfactants in water with bromocresol green (BCG) and cetylpyridinium bromide (CPB). Sodium dodecylbenzenesulfonate (SDBS) and sodium dodecylsulfate (SDS) were determined at 614 nm and pH range of 5.5—9.0. In the concentration range of 0—80 µg/10 ml for SDBS and 0—75 µg/10 ml for SDS, both of them obey Beer's law in the presence of 86 µg CPB. The apparent molar absorptivities are $2.9 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for SDBS and $3.1 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for SDS. The proposed method has been applied to the determination of anionic surfactants in river water and wastewater. The average recovery of environmental water samples was 99.3% and the relative standard deviation was less than 3.0%.

Key words: anionic surfactants, bromocresol green, cetylpyridinium bromide, spectrophotometry.

Photometric Determinations of Nickel and Copper in Wastewater by Reversed Flow Injection Analysis. Wang Peng et al. (Department of Applied Chemistry, Harbin Institute of Technology, 150006); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 78—79

The new wastewater monitoring system by use of reversed flow injection spectrophotometry has been developed with injection of different reagents to produce similar color compounds by chemical reactions. The system has been used to simultaneous determination of nickel and copper in wastewater. The detection frequency of the method is 60 samples h⁻¹, the minimum detection limits are 0.03 µg Ni ml⁻¹ and 0.04 µg Cu ml⁻¹ respectively.

Key words: environmental monitoring, flow injection analysis, nickel, copper.

Acidification Models and Their Application to the Determination of Critical Load for Acid Deposition. Xie Shadong et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 80—84

This paper briefly discusses different models developed abroad in the study of precipitation effects to predict the long-term effects of acid deposition on soil, surface water, ground water and lakes in the past ten years. The basic methods to establish these models and the principles to apply them to the determination of critical load for acid deposition are presented based on through comparisons and analyses.

Key words: acidification model, critical load, acid deposition, acid rain.

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