

固体废弃物浸出液中酞酸酯的测定*

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摘要 报道高效液相色谱测定固体废弃物浸出液中酞酸酯的方法。实验建立了 Zorbax-CN 柱和含 0.1% 异丙醇的正己烷为洗脱液, 在 224nm 处紫外检测的液相色谱系统, 并应用该系统测定了北京市城市垃圾浸出液中的酞酸酯。该系统可有效地分离浸出液中非极性有机物和酞酸酯组分, 并有效地避开了一部分与酞酸酯极性相近的有机物的干扰。浸出液经正己烷萃取、浓缩后, 不需净化(如柱层析)即可直接进入液相色谱系统进行分析。5 种酞酸酯的检出限为 0.2—1.0ng, 浸出液定量分析线性范围为 0.1^{-9} — 450×10^{-9} , 回收率为 70%—110%, 垃圾浸出液 7 次平行测试的变异系数在 10% 以内。

关键词 酞酸酯, 固体废弃物, 浸出液, 高效液相色谱。

酞酸酯(PAE)又称邻苯二甲酸酯, 在工业上主要用作增塑剂。由于塑料在工业、农业和日常生活中应用广泛, 酞酸酯不断进入环境, 近些年来塑料垃圾大量增加, 也增加了酞酸酯进入环境的机会, 因而酞酸酯已成为全球性的最为普遍的一类污染物^[1]。酞酸酯的污染已经受到世界各国的普遍重视。美国、日本以及欧洲许多国家都将酞酸酯列入优先污染物名单中^[2], 我国水中优先控制污染物黑名单中也包括酞酸二甲酯、酞酸二丁酯和酞酸二辛酯。

酞酸酯的分析国际上一般采用 GC 或 GC/MS 法^[3]。我国关于环境样品中酞酸酯的分析都是应用 GC 或 GC/MS 法, 目前已经在一些水体、土壤和大气颗粒物样品中不同程度地检出了酞酸酯^[4—6], 但固体废弃物中酞酸酯的测试还未见报道。

本文报告了以高效液相色谱法测定固体废弃物浸出液中酞酸酯的方法。实验建立了 Zorbax-CN 柱和含 0.1% 异丙醇的正己烷为洗脱液, 于 224nm 处紫外检测的液相色谱系统。该系统可有效地分离浸出液的正己烷萃取物中的非极性有机物和酞酸酯组分, 并避开了一部分与酞酸酯极性相近的化合物的干扰。固体废弃物浸出液经正己烷萃取、浓缩后, 不需净化(如柱层析), 即可直接进入液相色谱系统进行分析。

1 实验部分

1.1 仪器和试剂

玻璃仪器、器皿在使用前在 400℃ 下烘 30min, 或用二次蒸馏水、丙酮和正己烷依次冲

洗。所用试剂主要有: 正己烷(宜兴市试剂二厂), AR, 现用现蒸; 无水硫酸钠(天津塘沽南中化工厂), AR, 用前在 400℃ 下烘 16h; 二次蒸馏水, 现用现蒸。酞酸酯标样有: 酞酸二甲酯(DMP), AR; 酞酸二乙酯(DEP), AR; 酞酸二正丁酯(DBP), AR; 酞酸二正辛酯(DOP), AR; 酞酸-双-(2-乙基己基)酯(DEHP), AR。以上均为北京化工厂产品。

1.2 固体废弃物样品的采集

固体废弃物采自北京市区及郊区垃圾场。样品采集后, 室温下自然风干、破碎, 20 目筛分后, 装入棕色玻璃瓶内待用。样品在红外干燥箱内 60—70℃ 下烘 24h 后测其水分含量。

1.3 浸出液制备

取上述处理好的城市垃圾样品约 50g 与 500ml 二次蒸馏水相混合(固液比约为 1:10), 复式水平振荡 24h, 振荡频率为 200 次/min, 振幅为 100mm, 静置 48h, 混合物以中速滤纸过滤后, 再以 0.45μm 滤膜过滤, 滤液置于 0—4℃ 冰箱内保存浸出液需在 7d 之内进行萃取, 30d 之内完成全分析^[5]。

1.4 浸出液预处理

取上述浸出液 500ml, 以 3×70ml 正己烷萃取, 萃取时手动剧烈振摇 15min, 静置 10min。有机层转移到 500ml 三角瓶中, 以无水硫酸钠干燥。萃取液 250mlK-D 浓缩器在 80℃ 水浴下浓缩

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到约 1ml, 然后转移到 5ml 棕色容量瓶中, 并以少许正己烷洗净浓缩瓶, 洗液并入容量瓶中, 再以正己烷定容到 5ml。用高效液相色谱系统按下述条件进行分析。

空白组(取二次蒸馏水 500ml)和标准物水溶液也按上述步骤进行处理。

1.5 高效液相色谱分析

1.5.1 色谱条件

仪器: 日本岛津 LC-4A 型高效液相色谱仪; 色谱柱: Zorbax-CN 柱 (250mm × 4.6mmID); 检测器: 岛津 SPD-2A 型紫外检测器, 测试波长为 224nm; 洗脱液: 正己烷/异丙醇 (100 : 0.1), 流速 1.5ml/min; 柱温: 室温 (20—25℃); 进样量 10μl。

1.5.2 定性及定量分析

定性分析: 用酞酸酯单标和混合标准溶液测定各种酞酸酯的保留时间, 样品的定性分析采用与标样的保留时间相对照的方法进行。

定量分析: 用酞酸酯各种标准溶液与二次蒸馏水配制成 500ml 酞酸酯混合物标准溶液, 经过与实际浸出液相同的处理后, 进入色谱系统进行分析。用峰高对溶液中各种酞酸酯的浓度作图, 根据峰高与浓度比值为一常数 ($RSD < 10\%$) 来确定方法的线性工作范围, 并绘制工作曲线。对测浸出液和空白样同时进行分析。每个样品连续进样 3 次。用绝对校准曲线法求出待测浸出液中酞酸酯的含量。

2 结果与讨论

2.1 液相色谱条件的选择

本实验在 Zorbax-CN 柱上, 以含 0.1% 异丙醇的正己烷为洗脱液, 对 5 种酞酸酯进行了分离, 取得了良好的分离效果 (见图 1)。利用这种色谱系统成功地分离了城市垃圾浸出液的正己烷萃取物 (见图 2)。CN 柱的特点是按照化合物的极性进行分离^[7], 在实际样品分析时, 浸出液的正己烷萃取物中非极性有机物与酞酸酯组分得到了良好的分离。

实验将紫外检测器工作波长选为 224nm, 提高了检测器对酞酸酯组分的选择性和分析灵敏度。在 224nm 处, 紫外检测器可有选择地检测酞

酸酯, 5 种酞酸酯在 224nm 处均有最大吸收峰,

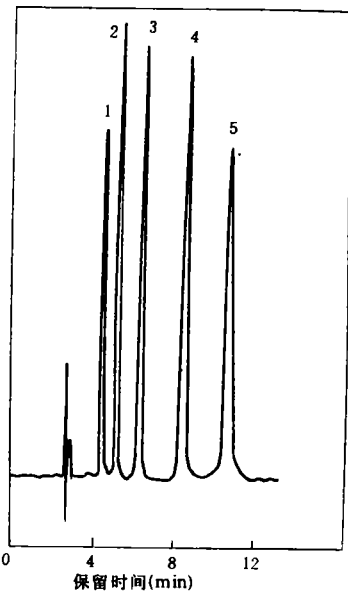


图 1 5 种酞酸酯在 Zorbax-CN 柱上的液相色谱分离图

1. DEHP 2. DOP 3. DBP 4. DEP 5. DMP

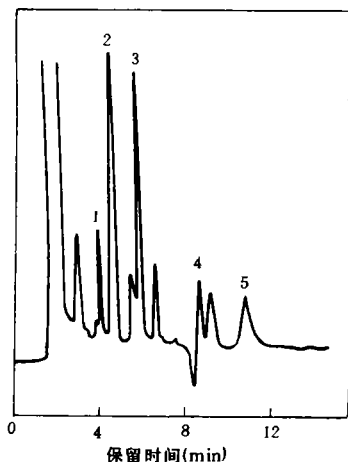


图 2 立水桥垃圾浸出液的正己烷萃取物液相色谱分离图

1. DEHP 2. DOP 3. DBP 4. DEP 5. DMP

其克分子吸光系数是 254nm 处的 10 倍^[8]。因此, 在 224nm 处吸收很小或没有吸收的化合物在紫外检测器上几乎没有响应。这样有效地避开了一部分极性与酞酸酯相近的化合物的干扰。实测时没有发现明显的干扰峰。酞酸酯的检出限在该系统中为: 酞酸二甲酯 1.0ng; 酞酸二乙酯 0.4ng; 酞酸二正丁酯 0.2ng; 酞酸二正辛酯 0.2ng; 酞酸-双-(2-乙基己基)酯 0.2ng。紫外检测器线性检测范围为 0.1—500ng。

2.2 萃取条件选择

用 400×10^{-9} 、 100×10^{-9} 、 40×10^{-9} 的酞酸酯二次蒸馏水溶液,测试了在不同萃取条件下的回收率,结果表明,在实验萃取条件(见“实验部分”)下,5 种酞酸酯在 3 种浓度下均获得了稳定的回收率,在 77% 以上和 110% 以下,5 次平行测试的变异系数均在 10% 以内。

2.3 工作曲线及准确度和精密度

表 1 立水桥垃圾浸出液(500ml)酞酸酯含量分析结果

样品 序号	DEHP		DOP		DBP		DEP		DMP	
	c	W	c	W	c	W	c	W	c	W
1	38.4	317.7	52.8	436.8	38.2	316.0	6.6	54.6	7.1	58.7
2	39.7	328.8	52.2	431.8	37.3	308.6	6.9	57.1	7.5	62.0
3	37.8	312.7	51.6	426.9	37.0	306.1	6.3	52.1	7.8	64.5
4	39.0	322.6	52.5	434.3	36.3	300.3	6.6	54.6	6.7	55.4
5	41.0	339.2	54.0	446.7	37.7	311.9	6.3	52.1	6.4	52.9
6	37.1	306.9	53.1	439.3	38.7	320.2	7.2	59.6	6.7	55.4
7	40.3	333.4	54.6	451.7	39.1	323.5	6.1	50.5	7.5	62.0
平均	39.04	322.9	52.9	438.2	37.7	312.4	6.6	54.4	7.1	58.7
CV(%)	3.6		2.0		2.6		5.8		7.3	

c 为浸出液中酞酸酯的浓度($\times 10^{-9}$),W 为垃圾样品干基(约 50g)中酞酸酯的含量($\mu\text{g}/\text{kg}$)

表 2 浸出液(500ml)酞酸酯加标回收率

含量($\times 10^{-9}$)	39.1(DEHP)	52.9(DOP)	37.7(DBP)
加标量(μg)	50	50	50
回收率(%)	85.4	95.6	105.5
	89.0	99.4	100.8
	90.5	93.2	95.6
平均	88.3	96.1	100.6
CV(%)	3.0	3.2	4.9

2.4 实验室内酞酸酯的干扰

由于酞酸酯在环境中普遍存在,实验室所用蒸馏水、仪器以及样品处理用具等,都有可能引起空白酞酸酯增高^[9]。本文在实验过程中杜绝使用塑料容器、器皿;所用玻璃仪器、器皿以及试剂等都作了相应处理(见“实验部分”)。经过处理后测试的空白水样中酞酸酯的含量显著降低,分别为酞酸二正丁酯 0.06×10^{-9} ;酞酸-双-(2-乙基己基)酯 0.05×10^{-9} 。

2.5 实际浸出液的分析

将浸出液经过正己烷萃取、浓缩后,直接进入液相色谱系统进行分析。垃圾样品中酞酸酯主要是酞酸二正丁酯和酞酸二辛酯(DOP 和 DEHP),其含量在 $300 \mu\text{g}/\text{kg}$ 干基左右,而酞酸二

用不同浓度的酞酸酯二次蒸馏水的混合标准溶液绘制出工作曲线,方法的线性工作范围为 0.2×10^{-9} — 450×10^{-9} 。加标回收率实验表明,3 种酞酸酯的加标回收率很稳定,在 85%—100% 之间,3 次平行测试的变异系数在 10% 以内(见表 2)。实际浸出液 7 次平行测试的变异系数在 10% 以内(见表 1)。

甲酯和酞酸二乙酯含量较低,在 $50 \mu\text{g}/\text{kg}$ 干基左右。实验对垃圾浸出液具有较好的定量重复性,朝阳区立水桥样品 7 次平行测试的变异系数在 10% 以内(见表 1)。

本文首次用高效液相色谱法测定了固体废弃物浸出液中酞酸酯。实验表明,本法可适用于固体废弃物浸出液中酞酸酯的分析。

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Since the main industrial sources of mercury discharged into the Songhua Jiang River were eliminated eight years ago, the total mercury and methylmercury contaminations in fish from the reaches of the river from Jilin City to Sanchahekou and from Sanchahekou to Tongjiang have been reduced to a light level of contamination and a medium level of contamination, respectively. The average levels of total mercury and methylmercury contaminations in fish from both reaches of the river exhibited; the highest in carnivorous fish, lower in omnivorous fish, and the lowest in herbivorous fish; higher in the underlayer fish than in the medium and upper layer fish; and higher in the scaleless fish than in the scaled fish. In the muscle of each species of fish from both reaches of the river, the level of methylmercury was in a significantly positive correlation with the level of total mercury while being in a significantly negative correlation with the activities of urease and lactate dehydrogenase (LDH). The level of total mercury in the muscle of fish was in a significantly multiple linear, multiple logarithmic or multiple exponential correlation with the level of total mercury in river water. The level of methylmercury in the muscle of fish was in a significantly multiple logarithmic correlation with the level of methylmercury in river water.

Key words: the Songhua Jiang River, total mercury, methylmercury, contamination, fish.

Study on the Level of Mercury in Fishmen's Hair Since the Elimination of Major Sources of Mercury Pollution in the Songhua Jiang River. Wu Shi'an et al. (Jilin Provincial Station of Sanitation and Antiepidemics, Changchun 130021); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 39—40

Since the major sources of mercury pollution in the Songhua Jiang River were eliminated 8 years ago, the level of mercury in the hairs of fishmen living along the river has reduced by 78.30%—82.5% as compared with that in the 1970s, and by 71.48% as compared with that in the early 1980s, showing that obvious health benefit and environmental benefit have been obtained. However, it was found that so far the fishmen living along the river still have a significantly higher level of hair mercury than those living in a non-mercury polluted area, and 1.92% of them have a level of hair mercury exceeding the national diagnostic standards. They were found to be mainly distributed along the first Songhua Jiang reaches of the river downstream Sanchahekou. Extremely less number of cases for the fishmen living along the second Songhua Jiang reaches of the river were found to have a level of hair mercury exceeding the national diagnostic standards, and the causes for this were discussed also.

Key words: mercury poisoning, water pollution,

biological monitoring, Songhua Jiang River.

Determination of Phthalic Esters in Aqueous Extracts from Solid Wastes. Dai Tianyou, Wang Shufang (China National Environmental Monitoring Center, Beijing 100012); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 41—43

The HPLC determination of phthalic esters in aqueous extracts from solid wastes were reported. In this study, a HPLC system equipped with a Zorbax-CN column and a 224 nm UV detector and using a n-hexane mixed with 0.1% isopropanol as eluting agent was established and used to determine the phthalic esters in aqueous extracts from municipal refuses in Beijing. The system was effective to separate phthalic esters from non-polar organics in the extracts and to eliminate the interference likely resulted from some organic compounds which had a polarity similar to phthalic esters. Having been extracted with n-hexane and then concentrated, the extracts in organic phase could be directly analysed with the HPLC system without a further purification (e.g., column chromatography). Water samples fortified with phthalic esters at a level in the range of 1—500 ppb were analysed, with a linear response in the range of 0.1—450 ppb, a recovery for phthalic esters of 70%—110%, and the detectable limits of 1.0 ng for dimethyl phthalate (DMP), 0.4 ng for diethyl phthalate (DEP), and 0.2 ng for each of di-n-butyl phthalate (DBP), di-n-octyl phthalate (DOP) and di(2-ethylhexyl) phthalate (DEHP), at 224 nm. The phthalic esters in aqueous extracts from several solid waste samples were found by using this system to be at a level of 5 ppb. The variation coefficient for 7 parallel tests on the extracts from solid wastes was within 10%.

Key words: phthalic esters, extracts, HPLC.

Study on the removal of Arsenic in Different States of Valence from Acidic Wastewater. He Shaoxian et al. (Dept. of Environmental Engineering and Chemical Engineering, Kunming Institute of Technology, Kunming 650093); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 44—46

Based on the process of iron salts neutralization to remove arsenic from wastewater, theoretical analysis and experiments indicated that, at a ratio of $Fe/As = 0.5—0.6$, $As(III)$ was removed at a rate of about 60% lower than that of $As(V)$, demonstrating that $As(III)$ was more difficult to be removed from wastewater than $As(V)$. In a further study, it was found that it was most suitable to oxidize $As(III)$ in acidic wastewater containing a high level of arsenic by using a bleaching powder, $Ca(ClO)_2$. For an acidic wastewater containing 782.5 mg/L of As at pH = 1, the oxidation/iron salts neutralization process used in a primary treatment produced an effluent containing less than 8 mg/L of As, with an arsenic removal of more than 99%. If followed by a further secondary treatment, the level of arsenic in the effluent produced would be lower