

学校编码: 10384

分类号 _____ 密级 _____

学号: 200434066

UDC _____

厦 门 大 学

硕 士 学 位 论 文

新型嵌入式被动采样膜的制备
及其富集水体中溶解态 PAHs 的效能研究

Preparation of Cyclodextrin-Triolein Embedded Cellulose
Acetate Membrane and Its Uptake Efficiency of Dissolved
PAHs in Aqueous Solution

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论文提交日期: 2007 年 10 月

论文答辩时间: 2007 年 11 月

学位授予日期: 2007 年 月

答辩委员会主席: _____

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2007 年 11 月

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廈門大學博碩士論文摘要庫

中文摘要

本论文共分为以下四个部分：

第一部分是绪论部分。首先介绍了多环芳烃(Polycyclic aromatic hydrocarbons, PAHs)的性质、来源、迁移以及对人类健康和生态环境的危害；详细综述了水体中 PAHs 生物有效性部分的研究进展，介绍了目前几种评价 PAHs 生物有效性的方法，其中着重论述了半透膜被动采样装置(Semi-permeable membrane device, SPMD)研究进展；介绍了 PAHs 几种常见的分析方法；随后介绍了环糊精(Cyclodextrins, CDs)的结构、性质及其在环境领域的应用；最后在上述讨论的基础上提出了本文的设想及研究内容。

第二部分是新型嵌入式被动采样膜的制备及表征。在嵌入式被动采样膜(Triolein embedded cellulose acetate membrane, TECAM)的基础上，采用具有疏水性空腔结构的 β -CD 作为致孔剂，制备了一种新型嵌入式被动采样膜(Cyclodextrin-Triolein embedded cellulose acetate membrane, C-TECAM)。采用沉浸凝胶相转化技术，以醋酸纤维素为膜材料，丙酮和二甲亚砜为混合溶剂，在制膜过程中将 β -CD 和三油酸甘油酯(Triolein)同时嵌入到高分子材料中。表征实验结果表明，C-TECAM 外观上是乳白色半透明的均匀膜，具备一定的厚度(115-122 μ m)；亲水性能良好，含水率介于 64.83%-65.77%之间，孔隙率介于 33.80%-35.65%之间； β -CD 和 Triolein 的加入能显著地提高膜的机械强度，拉伸强度平均较纯醋酸纤维素膜提高了 38.22%。C-TECAM 在典型的现实环境酸碱条件(pH=4.49-9.18)下基本性能保持稳定；在正己烷和环己烷中未发生溶胀、溶解或其他化学反应，但在二氯甲烷中则有部分溶解。纯净水可作为 C-TECAM 的保存液，己烷类溶剂可作为后续处理的透析溶剂。

第三部分是水溶液和环己烷溶液中萘(Naphthalene, Na)、蒽(Anthracene, An)和苯并(a)芘(Benzo(a)pyrene, BaP)三组分 PAHs 同步荧光同时测定方法的建立。水溶液中，Na、An 和 BaP 线性范围分别为 0.5-20.0 μ g/L、0.5-20.0 μ g/L 和 0.5-5.0 μ g/L，Na 和 An 线性范围均在溶解度以内，而 BaP 在助溶剂无水乙醇的存在下则可扩展至溶解度以外；检测限分别为 0.37、0.021 和 0.048 μ g/L；三者相对标准偏差最高不超过 10%(n=5)；合成样品回收率介于 84.4%-123.9%之间。与标

准方法相比，本方法具有灵敏度高，无需复杂前处理的优点，能够为考察 C-TECAM 富集水体中 PAHs 的效能提供一种简便、灵敏、快速的研究手段，也为今后的在线研究奠定良好的方法基础。另一方面，为进一步从膜富集的角度研究 C-TECAM 富集水溶液中 PAHs 的效能，本文同时建立了环己烷溶液中 Na、An 和 BaP 三组分 PAHs 同步荧光同时测定方法。鉴于 PAHs 在环己烷中有较高的荧光量子产率，为使环己烷溶液中三种 PAHs 的分析灵敏度和水溶液中的灵敏度保持在一个相应的范围内，实验时对仪器参数作适当的调整。结果表明，分别在 5.0-80.0 $\mu\text{g/L}$ 、2.0-80.0 $\mu\text{g/L}$ 和 2.0-80.0 $\mu\text{g/L}$ 范围内，环己烷溶液中 Na、An 和 BaP 的同步荧光光谱强度与其浓度有良好的线性关系；检测限分别为 0.62、0.056 和 0.082 $\mu\text{g/L}$ ；三者相对标准偏差不超过 5%(n=5)；合成样品回收率则介于 90.8%-103.8%之间。

第四部分是新型嵌入式被动采样膜的实验室模拟暴露实验研究。采用静水暴露实验系统，利用第三部分所建方法，初步考察了 C-TECAM 富集水体中 Na、An 和 BaP 的效能。在实验条件下，三种 PAHs 均可被 C-TECAM 快速富集，平衡富集量以及达到富集平衡所需的时间与 PAHs 的 K_{ow} 值呈正相关。Na($\log K_{ow}=3.45$) 在 2h 左右就能基本达到平衡，但平衡富集量最小，An($\log K_{ow}=4.54$) 达到富集平衡的时间约在 6h，而 BaP($\log K_{ow}=6.35$) 至少需要暴露 12 h 以上才能接近富集平衡状态，但其平衡富集量在三种 PAHs 中最大。与“夹心式”SPMD 相比，C-TECAM 能够缩短富集达到平衡所需的时间。同时，与 TECAM 相比， β -CD 的加入能够提高 C-TECAM 对 Na、An 和 BaP 的平衡富集量，但对 Na 和 An 的富集速率有所降低，而 BaP 在 β -CD 添加量为 0.5% 时富集速率有一定的提高。此外，三种 PAHs 在 C-TECAM 中的膜-水分配系数 $\log K_m$ 与其辛醇-水系数 $\log K_{ow}$ 以及生物富集系数 $\log K_{BCF}$ 之间都有良好的线性关系，可作为研究 PAHs 生物有效性的评价手段。最后本文考察了 C-TECAM 的再生性能，达到富集平衡的膜经净化后可进行二次重复富集，是一种更为经济的富集技术。因此，C-TECAM 有望提供一种更为高效、经济替代手段，用于 PAHs 的模拟生物富集研究，评估污染物的生物有效性。

关键词：环糊精；三油酸甘油酯；新型嵌入式被动采样膜；多环芳烃

Abstract

This dissertation is composed of four chapters.

Chapter one is the preface. First, the properties, sources, fate of polycyclic aromatic hydrocarbons (PAHs) and its effects on human and environment were present. The progress on bioavailability of PAHs and its estimated methods, especially the semi-permeable membrane device (SPMD) method, were introduced. The determination methods of PAHs were then discussed. Besides, the structure, properties of cyclodextrins (CDs) and their applications to environmental science were also introduced. Finally, the proposal of dissertation was illuminated.

Chapter two is the preparation and characterization of a novel passive sampling membrane, cyclodextrin-triolein embedded cellulose acetate membrane (C-TECAM). On the basis of the triolein embedded cellulose acetate membrane (TECAM), β -CD was introduced to C-TECAM as a novel pore-forming material. C-TECAM was prepared by wet phase inversion technique in which triolein and β -CD were embedded. C-TECAM was ivory-white apparently and 115-122 μ m in thickness. C-TECAM was hydrophilic with water content between 64.83%-65.77% and porosity between 33.80%-35.65%. The mechanical strength of C-TECAM was improved 38.22% averagely compared to cellulose acetate membrane. C-TECAM was stable in typical acidic and basic conditions (pH=4.49-9.18) and in organic solvents such as hexane and cyclohexane, except dichloromethane.

Chapter three is the establishment of simultaneous determination of Naphthalene (Na), Anthracene (An) and Benzo(a)pyrene (BaP) by synchronous fluorimetry. With the new method, Na, An and BaP can be simultaneously determined in a mixture aqueous solution and in a mixture cyclohexane solution respectively. The linear ranges for the determination of Na, An and BaP in aqueous solution were 0.5-20.0 μ g/L, 0.5-20.0 μ g/L and 0.5-5.0 μ g/L with the limits of detection 0.37、0.021 and 0.048 μ g/L, respectively and the relative standard deviations were less than 10% (n=5). Satisfactory recovery experimental results were between 84.4%-123.9% in

spiked water samples. The advantage of the established method was sensitive and did not necessitate a complex pretreatment. It could be a simple, sensitive and rapid method to investigate the accumulation efficiency of C-TECAM to PAHs in aquatic environment and be a useful method for further on-line study. On the other hand, simultaneous determination of Na, An and BaP by synchronous fluorimetry in cyclohexane solution was also established to study the accumulation efficiency of C-TECAM from the membrane phase. As the fluorescence quantum yield of PAHs was higher in cyclohexane solution, apparatus parameters were changed to get a corresponding sensitivity in cyclohexane solution as well as that in aqueous solution. The linear ranges for the determination of Na, An and BaP in cyclohexane were 5.0-80.0 $\mu\text{g/L}$ 、 2.0-80.0 $\mu\text{g/L}$ and 2.0-80.0 $\mu\text{g/L}$ with the limits of detection 0.62、 0.056 and 0.082 $\mu\text{g/L}$, respectively and the relative standard deviations were less than 5% (n=5). Satisfactory recovery experimental results were between 90.8%-103.8% in spiked cyclohexane samples.

Chapter four is the laboratory simulated exposure experiment of C-TECAM to Na, An and BaP. The exposure of C-TECAM to three PAHs in aquatic environment was studied in static exposure system by synchronous fluorimetry. Na, An and BaP could be accumulated rapidly by C-TECAM, concentrations of three PAHs increased in C-TECAM while those decreased in aqueous solution till uptake equilibrium. Equilibrium time was directly proportional to octane-water partition coefficient ($\log K_{ow}$). Na, with $\log K_{ow}$ 3.45, could reach equilibrium in about 2 hours, while An and BaP, with $\log K_{ow}$ 4.54 and 6.35, needed 6 and 12 hours to equilibrium, respectively. C-TECAM was proved to be a more rapid accumulation method which could shorten equilibrium time compared to “sandwich” SPMD. The equilibrium concentrations of Na, An and BaP were increased with the introduction of β -CD to C-TECAM. Meanwhile, the uptake rates of Na and An were decreased and the uptake rate of BaP were improved with the addition of 0.5% β -CD. The membrane-water partition coefficient ($\log K_m$) of three PAHs in C-TECAM was linear correlated to their $\log K_{ow}$ as well as bioconcentration factors ($\log K_{BCF}$). Besides, C-TECAM could be regeneration for another accumulation of three PAHs. The results indicated that

C-TECAM could be a more efficient and economic method for the estimation of the bioavailable concentrations of PAHs.

Key words: β -cyclodextrin, Triolein, Cyclodextrin-triolein embedded cellulose acetate membrane, Polycyclic aromatic hydrocarbons

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