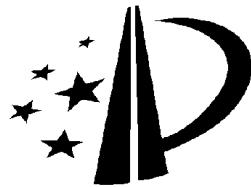


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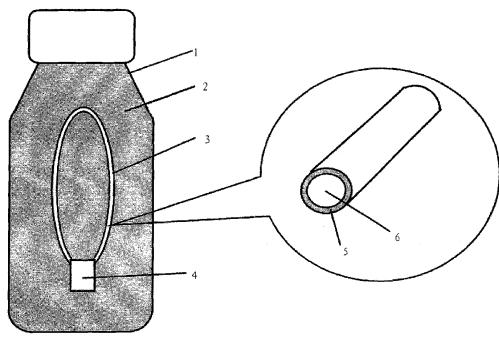
权利要求书 1 页 说明书 6 页 附图 1 页

[54] 发明名称

一种具有中空纤维膜的被动采样装置

[57] 摘要

本发明提供一种具有中空纤维膜的被动采样装置，所述的被动采样装置包括被动采样器和采样瓶，被动采样器置于采样瓶内，其中所述的被动采样器是首尾密闭连接的中空纤维膜，中空纤维膜的膜壁的微孔中充满液膜溶剂，中空纤维膜的内腔中充满接受相。被动采样装置用于采集样品和完成被采集样品中的待测物在分析之前的预处理。本发明的被动采样装置在采集和富集样品中的待测物的操作简单、省时，并且该被动采样装置在采样完毕后，不需要从被动采样器中解析出待测物，就可以测定样品中的待测物含量，同时发明所用的中空纤维膜、液膜溶剂和接受相溶液均为价格便宜的商品化材料、制作成本低，可以一次性使用。



1. 一种具有中空纤维膜的被动采样装置，所述的被动采样装置包括被动采样器和采样瓶，被动采样器置于采样瓶内，其特征在于所述的被动采样器是首尾密闭连接的中空纤维膜，中空纤维膜的膜壁的微孔中充满液膜溶剂，中空纤维膜的内腔中充满接受相。
2. 根据权利要求 1 所述的被动采样装置，其特征在于还在所述的被动采样器的底部安装一部件，该部件用于当采样瓶内充满被采集的样品时，将被动采样器没入被采集的样品中，并且该部件为不与被采集的样品反应的部件，优选为玻璃管。
3. 根据权利要求 1 或 2 所述的被动采样装置，其特征在于所述的中空纤维膜的壁厚为 30—200  $\mu\text{m}$ ，优选为 30—50  $\mu\text{m}$ 。
4. 根据权利要求 1-3 中任一项所述的被动采样装置，其特征在于所述的中空纤维膜由疏水性材料制成，所述的疏水性材料优选为聚丙烯、聚偏氟乙烯或聚四氟乙烯中的一种。
5. 根据权利要求 1-4 中任一项所述的被动采样装置，其特征在于所述的液膜溶剂为脂肪烷烃、脂肪醇或脂肪醚中的一种，优选地，还在所述的溶剂中添加特异性液膜载体，所述的特异性液膜载体优选为三正辛基氧化膦或者双硫腙。
6. 根据权利要求 1-4 中任一项所述的被动采样装置，其特征在于所述的接受相为酸、碱、脂肪烷烃、脂肪醇或脂肪醚中的一种，所述的酸优选为盐酸或硝酸，所述的碱优选为氢氧化钠或碳酸氢钠。
7. 根据权利要求 5 或 6 所述的被动采样装置，所述的脂肪烷烃为正十一烷。
8. 根据权利要求 5 或 6 所述的被动采样装置，其特征在于所述的脂肪醇为正辛醇。
9. 根据权利要求 5 或 6 所述的被动采样装置，其特征在于所述的脂肪醚为正己基醚。
10. 权利要求 1-9 中任一项所述的被动采样装置用于采集样品和完成被采集样品中的待测物在分析之前的预处理，所述的样品优选为水样并且所述的待测物优选为极性有机物、非极性有机物或金属离子中的一种。

## 一种具有中空纤维膜的被动采样装置

### 技术领域

本发明涉及一种具有中空纤维膜的被动采样装置，特别是，基于中空纤维膜液相微萃取的被动采样装置。

### 背景技术

样品的采集和前处理是环境分析化学中最为关键的操作步骤。传统的方法是将采样和前处理分别进行，其步骤包括：大量样品采集——样品运输——样品保存——样品预处理，即：样品富集净化——分析测定，该方法操作繁琐、耗时、耗人力和财力，且容易损失样品。为了克服这些缺点，被动采样装置由于集样品的采集和样品的富集于一体，从而得到了环境工作者的亲睐。被动采样装置操作步骤包括：现场被动采样——采样装置运输保存——样品解析——分析测定。该方法操作简单，已经有一些成功地应用典范。如：J. N. Huckins 发明的半透膜采样装置（以下简称 SPMD），基于装在低密度聚乙烯膜袋中的脂质对疏水性有机污染物进行采样；J. Pawliszyn 发明的固相微萃取（以下简称 SPME）技术，基于涂有聚合物涂层的熔融石英纤维对疏水性有机污染物进行采集；W. Davison 发明的扩散梯度薄膜（以下简称 DGT）技术，基于双层聚丙烯酰胺凝胶对金属离子和某些无机阴离子进行采集。尽管这些被动采样装置得到了很广泛的应用，但是也存在一些缺陷。具体表现在：在采样过程中，耗时很长，一般 1 天到 6 个月；在样品解析过程中，SPMD 需要使用大量的有机溶剂进行繁琐的透析处理，SPME 也需要少量有机溶剂进行至少 1 天的解吸，而 DGT 需要使用数毫升强酸浸泡洗脱 1 天；这些被动采样多数没有达到萃取平衡，样品浓度校正复杂。另外，这些被动采样装置针对的污染物范围比较窄，如 SPMD 和 SPME 只适用于疏水性有机污染物，而 DGT 仅适用于金属离子和某些无机阴离子。

《中国环境科学》在 2000 年（2）发表了题为“利用两种采样技术监测淮河水中的有毒有机污染物”的文章，该文章中采用三油酸酯——半渗

透膜采样装置采集并测定水样中的有毒有机污染物浓度。其中的采样装置是按如下方法制作得到的：将聚乙烯薄膜切割成双层长带，夹层内均匀涂布中性三油酸酯，立即密封冷冻保存（-20℃），采样器外部是洁净的PVC板支撑结构。

在《湖泊科学》2002年3月发表的“用生物模拟采样技术模拟研究不同取代氯酚在金鱼体内的富集和降解”一文中，文中三油酸酯/半渗透膜采样装置是如下制作的：将鱼体内的一种典型中性脂封装在一个半渗透膜内，允许水相污染物跨膜在内侧脂相富集，这种三油酸酯/半渗透膜采样装置将被采集样品中的待测物富集之后，还需要将其进行解析、浓缩、提纯后，才可以将待测物向分析色谱上样，从而进行待测物的分析检测。

## 发明内容

因此，本发明的任务是提供一种具有中空纤维膜的被动采样装置，特别是，基于中空纤维膜液相微萃取的被动采样装置。所述的被动采样装置集采样、运输、富集和样品的前处理于一体，并且适合样品中的多种待测物的采集。

本发明提供了一种具有中空纤维膜的被动采样装置，所述的被动采样装置包括被动采样器和采样瓶，被动采样器置于采样瓶内，其中所述的被动采样器是首尾密闭连接的中空纤维膜，中空纤维膜的膜壁的微孔中充满液膜溶剂，中空纤维膜的内腔中充满接受相。采样器的选择性由液膜溶剂和接受相共同决定。当样品被采集进入采样瓶内，液膜溶剂与样品中的待测物的极性相近，因此样品中的待测物首先结合于中空纤维膜的微孔中，接着中空纤维膜内腔中的接受相与待测物相络合或者相反应，络合或者反应后的产物溶解于接受相，这样就达到了富集和提纯样品中的待测物的目的。例如：如果检测水中的碱性有机极性污染物，就需要在中空纤维膜的膜壁中充满有机液膜溶剂，它可以和极性污染物相结合，在膜腔中的接受相为无机的酸：如盐酸或者硝酸，无机酸可以和碱性极性污染物反应，反应后的产物溶解于接受相中。

优选地，中空纤维膜的首尾密闭连接是将中空纤维膜的两端相结合，形成环状，然后用铝箔封口完成的。

优选地，采样瓶是密封的玻璃瓶。

优选地，还在所述的被动采样器的底部安装一部件，该部件用于当

采样瓶内充满被采集的样品时，将被动采样器没入被采集的样品中，并且该部件为不与被采集的样品反应的部件，更优选为玻璃管。如果被采集的样品为液体时，被动采样器由于它的重量轻，容易浮在样品上，这就容易造成样品的不完全富集，因此需要物体将被动采样器没入被采集样品中。

优选地，所述的中空纤维膜的壁厚为30—200 $\mu\text{m}$ ，更优选为30—50 $\mu\text{m}$ 。

优选地，所述的中空纤维膜由疏水性材料制成，所述的疏水性材料优选为聚丙烯、聚偏氟乙烯或聚四氟乙烯中的一种。

优选地，所述的液膜溶剂为脂肪烷烃、脂肪醇或脂肪醚中的一种，更优选地，还在所述的溶剂中添加特异性液膜载体，所述的特异性液膜载体为三正辛基氧化膦或双硫腙。

优选地，所述的接受相为酸、碱、脂肪烷烃、脂肪醇或脂肪醚中的一种。

优选地，所述的酸为盐酸或硝酸，所述的碱为氢氧化钠或碳酸氢钠。

优选地，所述的脂肪烷烃为正十一烷。

优选地，所述的脂肪醇为正辛醇。

优选地，所述的脂肪醚为正己基醚。

优选地，所述的被动采样装置用于采集样品和完成被采集样品中的待测物在分析之前的预处理。

更优选地，所述的样品为水样，并且所述的待测物为极性有机物、非极性有机物或金属离子中的一种。

本发明的有益效果是：由于采样器的液膜溶剂和接受相溶液分别具有萃取和结合样品中的待测物的作用，所以在采集和富集样品中的待测物的操作简单、省时。由于本发明中的被动采样装置具有的特殊结构，所以除了采集样品和富集样品中的待测物的作用，它还可以将被采集的样品向实验室运输，并且由于本发明中的被动采样装置不需要特殊的保存，在样品的运输过程中，被动采样装置中的被动采样器也在完成样品中的待测物的富集作用。

由于本发明中的采样瓶的中空纤维膜内腔中充满接受相，中空纤维膜的膜壁的微孔中充满液膜溶剂，待测物扩散快，所以本发明的被动采样装置的萃取效率高，易于达到萃取平衡。

与现有的半渗透膜（SPMD）采样装置相比。本发明的被动采样装置

在采样完毕后，不需要从被动采样器中解析出待测物，也不需要对解析出的待测物进行提纯，只需将中空纤维膜的两端剪开，取出膜腔中的富集了待测物的接受相，直接取接受相进行分析就可以测定样品中的待测物含量。所以相对于现有的采样装置，本发明的被动采样装置不但可以采集样品，富集样品中的待测物，同时还可以对样品中的待测物进行前处理，因此本发明的被动采样装置更为高效、省时。

针对样品中的待测物的性质，可以选择液膜溶剂和膜腔中的接受相溶液，所以通过选择液膜溶剂和膜腔中的接受相溶液，就可以采样和前处理不同类型的样品中的不同类型的待测物。所以与现有技术中的仅能够采集和富集样品中的疏水性有机待测物相比，本发明的被动采样装置针对的待测物范围广范，包括极性有机待测物、疏水性有机待测物和金属离子待测物。

本发明中采用的中空纤维膜、液膜溶剂和接受相溶液均为价格便宜的商品化材料、制作成本低，可以一次性使用。

#### 附图说明

图 1 表示根据本发明的具有中空纤维膜的被动采样装置的一个实施方式的示意图，其中，采样瓶 1、样品 2、被动采样器 3、玻璃管 4、膜壁 5、内腔 6。

#### 具体实施方式

以下，结合附图来详细说明本发明的实施例，本发明的实施例用于解释本发明而非限制本发明。

#### 实施例 1

采集环境水样中的卤代苯氧酸型除草剂，该除草剂中含有2, 4-二氯苯氧乙酸、2-甲基-4-氯苯氧乙酸、2-(2,4-二氯苯氧)-丙酸和2-甲基-4-氯苯氧丙酸。本实施例中采用如图1所示的被动采样装置，该装置具有如下结构，包括：采样瓶 1 和被动采样器 3，采样瓶是 4ml 的具塞玻璃瓶，被动采样器是首尾连接的中空纤维膜 3，玻璃管 4，中空纤维膜的膜壁 5 的微孔中充满液膜溶剂，中空纤维膜的内腔 6 中充满接受相。本实施例中空纤维膜为聚丙烯材料，中空纤维膜的内腔 6 的接受相是 0.2M 的氢氧化钠溶液，

中空纤维膜的膜壁的微孔中充满液膜溶剂是溶解于正己基醚的质量浓度为 2.0% 的三正辛基氧化膦。本实施例中的被动采样装置是通过以下方法制备而成的：

- (1) 将经裁剪的 30 cm 长的聚丙烯中空纤维膜（内径 240 微米，膜壁厚 30 微米）的内腔中用注射器充满 0.2M 的氢氧化钠溶液，即：接受相；
- (2) 将中空纤维膜浸泡在含有 2.0% 质量浓度的三正辛基氧化膦的正己基醚溶液中：即液膜溶剂中 60 秒，使中空纤维膜的膜壁上的微孔中充满液膜溶剂；
- (3) 将中空纤维膜从三正辛基氧化膦的正己基醚溶液中取出，使其两端合在一起，形成环，两端折叠 2 次，用铝箔封口，并将铝箔插入一小截玻璃管中，形成被动采样器；
- (4) 将被动采样器的表面用样品液冲洗五次，去除过剩的正己基醚和三正辛基氧化膦；
- (5) 用镊子将被动采样器放置于 4mL 的具塞玻璃样品瓶中密封，形成被动采样装置。

为了防止被动采样器的液膜溶剂挥发，本发明的被动采样装置制成功后应立即使用，本实施例中的被动采样装置是通过以下方式进行工作的：

- (1) 在采样现场将 4ml 样品装入 4ml 的被动采样装置内，并加适量盐酸调节样品的 pH 值为 1.5；
- (2) 将盛有样品的被动采样装置运往实验室；
- (3) 在实验室中，将被动采样装置中的中空纤维膜被动采样器取出，采样器的表面用滤纸吸干；
- (4) 将中空纤维膜的两端剪开，用注射器将膜腔中的 10 微升氢氧化钠接受相（已富集了样品中的待测物）完全吹到一个 50 微升的玻璃样品瓶中，再取样品瓶中的样品向分析色谱进样。

本实施例中，中空纤维膜壁 5 中，含有质量浓度为 2.0% 的三正辛基氧化膦的正己基醚，中空纤维膜腔 6 中，含有 10 微升 0.2 M 的氢氧化钠接受相。本实施例方法的萃取效率高，8 个小时所有的目标物的萃取效率都达到了 90% 以上，1 天即可达到完全萃取；在 1-7 天内萃取效率稳定在 95%—110%。对本实施例的方法进行了反复测试，在 1-7 天内具有很好的

稳定性，在 7 天重复测定中其相对标准偏差为 4 ~ 15%。

### 实施例 2

本实施例中，所述样品为环境水样，中空纤维膜的内径 240 微米，膜壁厚 50 微米并且中空纤维膜是聚四氟乙烯材料，待测物是水样中的氯酚类，所述液膜溶剂为正十一烷，接受相为 0.2M 的氢氧化钠，其它与实施例 1 相同。

### 实施例 3

本实施例中，所述样品为环境水样，待测物是其中的苯胺和氯代苯胺，所述样品的 pH 值调为 5，所述疏水性中空纤维膜为 5cm 长的聚偏氟乙烯中空纤维膜（内径 450 微米，膜壁厚 125 微米），所述接受相为 4M 的盐酸，所述液膜溶剂为正辛醇，其它与实施例 1 相同。

### 实施例 4

本实施例中，待测物是含有金属离子镉的水样，所述样品的 pH 值调为 5，所述疏水性中空纤维膜为 5cm 长聚丙烯中空纤维膜，内径 600 微米，膜壁厚 200 微米，所述接受相为 0.05M 的硝酸，所述液膜溶剂为含有 0.002% 质量浓度的双硫腙的正十一烷溶液，其他与实施例 1 相同。

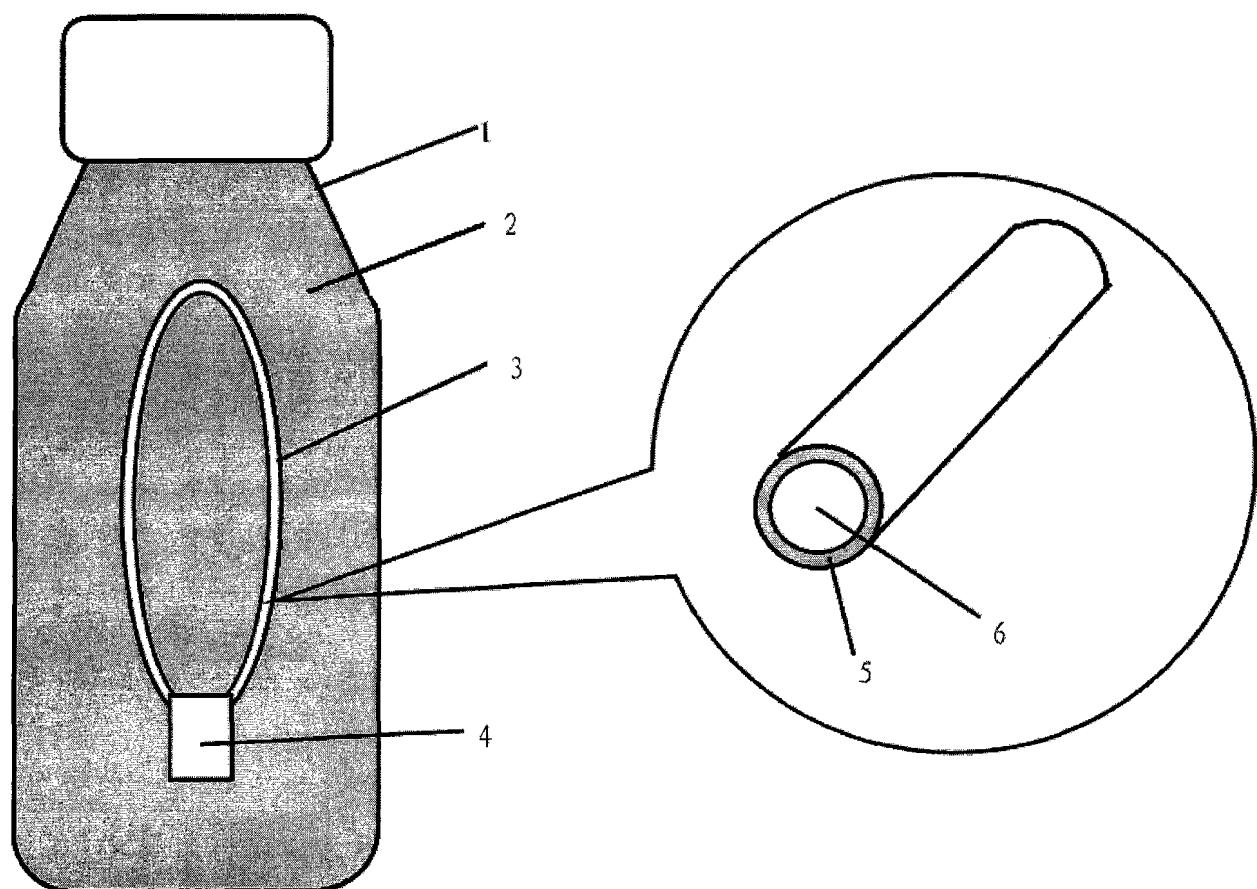


图 1

## Notice

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## DESCRIPTION CN101532921A

*10* A passive sampling device with a hollow fiber membrane

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*12* 一种具有中空纤维膜的被动采样装置

[0001]

*18* technical field

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*20* 技术领域

[0002]

*26* The invention relates to a passive sampling device with a hollow fiber membrane, in particular, a passive sampling device based on liquid-phase microextraction of the hollow fiber membrane.

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*29* 本发明涉及一种具有中空纤维膜的被动采样装置，特别是，基于中空纤维膜液相微萃取的被动采样装置。

[0003]

*36* Background technique

---

[0004]

44 Sample collection and pretreatment are the most critical steps in environmental analytical chemistry.

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46 样品的采集和前处理是环境分析化学中最为关键的操作步骤。

49 The traditional method is to carry out sampling and pretreatment separately, and the steps include: a large number of sample collection - sample transportation - sample storage - sample pretreatment, that is: sample enrichment and purification - analysis and determination, this method is cumbersome to operate and consumes Time-consuming, manpower-consuming and financial resources, and easy to lose samples. In order to overcome these shortcomings, passive sampling devices are favored by environmental workers because they integrate sample collection and sample enrichment. The operation steps of the passive sampling device include: on-site passive sampling—transportation and storage of the sampling device—sample analysis—analysis and determination. The method is simple to operate, and there are already some successful application examples. Such as: the semi-permeable membrane sampling device (hereinafter referred to as SPMD) invented by J.N.Huckins, based on the lipid contained in the low-density polyethylene film bag, the hydrophobic organic pollutants are sampled; the solid-phase microextraction (hereinafter referred to as SPME) technology, based on polymer-coated fused silica fibers to collect hydrophobic organic pollutants; W.Davison invented diffusion gradient thin film (hereinafter referred to as DGT) technology, based on double-layer polyacrylamide gel Ions and some inorganic anions are collected. Although these passive sampling devices have been widely used, they also have some drawbacks. The specific manifestations are: in the sampling process, it takes a long time, generally 1 day to 6 months; in the sample analysis process, SPMD needs to use a large amount of organic solvent for tedious dialysis treatment, and SPME also needs a small amount of organic solvent for at least 1 Days of desorption, while DGT requires a few milliliters of strong acid soaking and elution for 1 day; most of these passive samples have not reached the extraction equilibrium, and the correction of sample concentration is complicated. In addition, the range of pollutants targeted by these passive sampling devices is relatively narrow, such as SPMD and SPME are only suitable for hydrophobic organic pollutants, while DGT is only suitable for metal ions and certain inorganic anions.

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73 传统的方法是将采样和前处理分别进行，其步骤包括：大量样品采集——样品运输——样品保存——样品预处理，即：样品富集净化——分析测定，该方法操作繁琐、耗时、耗人力和财力，且容易损失样品。为了克服这些缺点，被动采样装置由于集样品的采集和样品的富集于一体，从而得到了环境工作者的亲睐。被动采样装置操作步骤包括：现场被动采样——采样装置运输保存——样品解析——分析测定。该方法操作简单，已经有一些成功的应用典范。如：J.N.Huckins发明的半透膜采样装置(以下简称SPMD)，基于装在低密度聚乙烯膜袋中的脂质对疏水性有机污染物进行采样；J.Pawliszyn发明的固相微萃取(以下简称SPME)技术，基于涂有聚合物涂层的熔融石英纤

维对疏水性有机污染物进行采集；W.Davison发明的扩散梯度薄膜(以下简称DGT)技术，基于双层聚丙烯酰胺凝胶对金属离子和某些无机阴离子进行采集。尽管这些被动采样装置得到了很广泛的应用，但是也存在一些缺陷。具体表现在：在采样过程中，耗时很长，一般1天到6个月；在样品解析过程中，SPMD需要使用大量的有机溶剂进行繁琐的透析处理，SPME也需要少量有机溶剂进行至少1天的解吸，而DGT需要使用数毫升强酸浸泡洗脱1天；这些被动采样多数没有达到萃取平衡，样品浓度校正复杂。另外，这些被动采样装置针对的污染物范围比较窄，如SPMD和SPME只适用于疏水性有机污染物，而DGT仅适用于金属离子和某些无机阴离子。

## [0005]

<sup>92</sup> "China Environmental Science" published an article entitled "Using Two Sampling Techniques to Monitor Toxic Organic Pollutants in Huaihe River Water" in 2000 (2). Determination of the concentration of toxic organic pollutants in water samples.

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<sup>96</sup> 《中国环境科学》在2000年(2)发表了题为“利用两种采样技术监测淮河水中的有毒有机污染物”的文章，该文章中采用三油酸酯——半渗透膜采样装置采集并测定水样中的有毒有机污染物浓度。

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<sup>101</sup> The sampling device is produced as follows: cut polyethylene film into double-layer long strips, evenly coat neutral trioleate in the interlayer, immediately seal and freeze (-20 ° C), and the outside of the sampler is clean. PVC board support structure.

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<sup>105</sup> 其中的采样装置是按如下方法制作得到的：将聚乙烯薄膜切割成双层长带，夹层内均匀涂布中性三油酸酯，立即密封冷冻保存(-20 °C)，采样器外部是洁净的PVC板支撑结构。

## [0006]

<sup>112</sup> In the article "Simulating the Accumulation and Degradation of Different Substituted Chlorophenols in Goldfish Using Biomimetic Sampling Technology" published in "Lake Science" in March 2002, the trioleate/semi-permeable membrane sampling device was made as follows : A typical neutral lipid in the fish body is encapsulated in a semi-permeable membrane, allowing water-phase pollutants to accumulate in the inner lipid phase across the membrane. This trioleate/semi-permeable membrane sampling device will be collected in the sample After the analyte is enriched, it needs to be analyzed, concentrated, and purified before the analyte can be loaded on the analytical chromatogram, so as to analyze and detect the analyte.

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<sup>120</sup> 在《湖泊科学》2002年3月发表的“用生物模拟采样技术模拟研究不同取代氯酚在金鱼体内的富集和降解”一文中，文中三油酸酯/半渗透膜采样装置是如下制作的：将鱼体内的一种典型中性脂

封装在一个半渗透膜内，允许水相污染物跨膜在内侧脂相富集，这种三油酸酯/半渗透膜采样装置将被采集样品中的待测物富集之后，还需要将其进行解析、浓缩、提纯后，才可以将待测物向分析色谱上样，从而进行待测物的分析检测。

## [0007]

130 Contents of the invention

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132 发明内容

## [0008]

138 Therefore, the task of the present invention is to provide a passive sampling device with hollow fiber membranes, in particular, a passive sampling device based on liquid phase microextraction with hollow fiber membranes.

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142 因此，本发明的任务是提供一种具有中空纤维膜的被动采样装置，特别是，基于中空纤维膜液相微萃取的被动采样装置。

146 The passive sampling device integrates sampling, transportation, enrichment and sample pretreatment, and is suitable for collecting various analytes in the sample.

---

149 所述的被动采样装置集采样、运输、富集和样品的前处理于一体，并且适合样品中的多种待测物的采集。

## [0009]

156 The invention provides a passive sampling device with a hollow fiber membrane, the passive sampling device includes a passive sampler and a sampling bottle, the passive sampler is placed in the sampling bottle, wherein the passive sampler is hermetically connected head to tail In the hollow fiber membrane, the micropores of the membrane wall of the hollow fiber membrane are filled with a liquid membrane solvent, and the inner cavity of the hollow fiber membrane is filled with an accepting phase.

---

162 本发明提供了一种具有中空纤维膜的被动采样装置，所述的被动采样装置包括被动采样器和采样瓶，被动采样器置于采样瓶内，其中所述的被动采样器是首尾密闭连接的中空纤维膜，中空纤维

膜的膜壁的微孔中充满液膜溶剂，中空纤维膜的内腔中充满接受相。

---

<sup>167</sup> The selectivity of the sampler is jointly determined by the liquid film solvent and the receiving phase.

<sup>169</sup> 采样器的选择性由液膜溶剂和接受相共同决定。

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<sup>172</sup> When the sample is collected into the sampling bottle, the polarity of the liquid membrane solvent and the analyte in the sample are similar, so the analyte in the sample is first combined in the micropores of the hollow fiber membrane, and then the analyte in the cavity of the hollow fiber membrane. The accepting phase is complexed or reacted with the analyte, and the complexed or reacted product is dissolved in the accepting phase, thus achieving the purpose of enriching and purifying the analyte in the sample.

---

<sup>178</sup> 当样品被采集进入采样瓶内，液膜溶剂与样品中的待测物的极性相近，因此样品中的待测物首先结合于中空纤维膜的微孔中，接着中空纤维膜内腔中的接受相与待测物相络合或者相反应，络合或者反应后的产物溶解于接受相，这样就达到了富集和提纯样品中的待测物的目的。

---

<sup>183</sup> For example: if detecting alkaline organic polar pollutants in water, it is necessary to fill the membrane wall of the hollow fiber membrane with an organic liquid membrane solvent, which can combine with polar pollutants, and the accepting phase in the membrane cavity is inorganic Acids: such as hydrochloric acid or nitric acid, inorganic acids can react with basic polar pollutants, and the reacted products dissolve in the receiving phase.

---

<sup>189</sup> 例如：如果检测水中的碱性有机极性污染物，就需要在中空纤维膜的膜壁中充满有机液膜溶剂，它可以和极性污染物相结合，在膜腔中的接受相为无机的酸：如盐酸或者硝酸，无机酸可以和碱性极性污染物反应，反应后的产物溶解于接受相中。

[0010]

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<sup>197</sup> Preferably, the end-to-end airtight connection of the hollow fiber membrane is completed by combining the two ends of the hollow fiber membrane to form a ring, and then sealing it with aluminum foil.

---

<sup>200</sup> 优选地，中空纤维膜的首尾密闭连接是将中空纤维膜的两端相结合，形成环状，然后用铝箔封口完成的。

## [0011]

<sup>207</sup> Preferably, the sampling bottle is a sealed glass bottle.

---

<sup>209</sup> 优选地，采样瓶是密封的玻璃瓶。

## [0012]

<sup>215</sup> Preferably, a part is also installed at the bottom of the passive sampler, which is used to submerge the passive sampler into the collected sample when the sampling bottle is full of collected sample, and this part is not compatible with the collected sample. The component for collecting the sample reaction is more preferably a glass tube.

---

<sup>220</sup> 优选地，还在所述的被动采样器的底部安装一部件，该部件用于当采样瓶内充满被采集的样品时，将被动采样器没入被采集的样品中，并且该部件为不与被采集的样品反应的部件，更优选为玻璃管。

<sup>225</sup> If the collected sample is liquid, the passive sampler is easy to float on the sample due to its light weight, which is easy to cause incomplete enrichment of the sample, so an object is required to submerge the passive sampler into the collected sample.

---

<sup>229</sup> 如果被采集的样品为液体时，被动采样器由于它的重量轻，容易浮在样品上，这就容易造成样品的不完全富集，因此需要物体将被动采样器没入被采集样品中。

## [0013]

<sup>236</sup> Preferably, the hollow fiber membrane has a wall thickness of 30-200  $\mu\text{m}$ , more preferably 30-50  $\mu\text{m}$ .

---

<sup>238</sup> 优选地，所述的中空纤维膜的壁厚为30—200  $\mu\text{m}$ ，更优选为30—50  $\mu\text{m}$ 。

## [0014]

<sup>244</sup> Preferably, the hollow fiber membrane is made of hydrophobic material, and the hydrophobic material is preferably one of polypropylene, polyvinylidene fluoride or polytetrafluoroethylene.

---

<sup>247</sup> 优选地，所述的中空纤维膜由疏水性材料制成，所述的疏水性材料优选为聚丙烯、聚偏氟乙烯或

聚四氟乙烯中的一种。

[0015]

<sup>254</sup> Preferably, the liquid film solvent is one of aliphatic alkanes, fatty alcohols or fatty ethers, more preferably, a specific liquid film carrier is added to the solvent, and the specific liquid film carrier is Tri-n-octylphosphine oxide or dithizone.

---

<sup>258</sup> 优选地，所述的液膜溶剂为脂肪烷烃、脂肪醇或脂肪醚中的一种，更优选地，还在所述的溶剂中添加特异性液膜载体，所述的特异性液膜载体为三正辛基氧化膦或双硫腙。

[0016]

<sup>265</sup> Preferably, the receiving phase is one of acid, alkali, fatty alkane, fatty alcohol or fatty ether.

---

<sup>267</sup> 优选地，所述的接受相为酸、碱、脂肪烷烃、脂肪醇或脂肪醚中的一种。

[0017]

<sup>273</sup> Preferably, the acid is hydrochloric acid or nitric acid, and the base is sodium hydroxide or sodium bicarbonate.

---

<sup>276</sup> 优选地，所述的酸为盐酸或硝酸，所述的碱为氢氧化钠或碳酸氢钠。

[0018]

<sup>282</sup> Preferably, the aliphatic alkane is n-undecane.

---

<sup>284</sup> 优选地，所述的脂肪烷烃为正十一烷。

[0019]

<sup>290</sup> Preferably, the fatty alcohol is n-octanol.

---

<sup>292</sup> 优选地，所述的脂肪醇为正辛醇。

#### [0020]

<sup>298</sup> Preferably, the fatty ether is n-hexyl ether.

---

<sup>300</sup> 优选地，所述的脂肪醚为正己基醚。

#### [0021]

<sup>306</sup> Preferably, the passive sampling device is used for collecting samples and completing the pretreatment of the analytes in the collected samples before analysis.

---

<sup>309</sup> 优选地，所述的被动采样装置用于采集样品和完成被采集样品中的待测物在分析之前的预处理。

#### [0022]

<sup>315</sup> More preferably, the sample is a water sample, and the analyte is one of polar organic matter, non-polar organic matter or metal ions.

---

<sup>318</sup> 更优选地，所述的样品为水样，并且所述的待测物为极性有机物、非极性有机物或金属离子中的一种。

#### [0023]

<sup>325</sup> The beneficial effects of the present invention are: since the liquid film solvent and the receiving phase solution of the sampler have the functions of extracting and binding the analyte in the sample respectively, the operation of collecting and enriching the analyte in the sample is simple and time-saving .

---

<sup>329</sup> 本发明的有益效果是：由于采样器的液膜溶剂和接受相溶液分别具有萃取和结合样品中的待测物的作用，所以在采集和富集样品中的待测物的操作简单、省时。

333 Due to the special structure of the passive sampling device in the present invention, in addition to collecting samples and enriching the analyte in the sample, it can also transport the collected samples to the laboratory, and due to the passive sampling in the present invention The device does not require special storage, and the passive sampler in the passive sampling device is also completing the enrichment of the analyte in the sample during the transportation of the sample.

---

339 由于本发明中的被动采样装置具有的特殊结构，所以除了采集样品和富集样品中的待测物的作用，它还可以将被采集的样品向实验室运输，并且由于本发明中的被动采样装置不需要特殊的保存，在样品的运输过程中，被动采样装置中的被动采样器也在完成样品中的待测物的富集作用。

#### [0024]

347 Because the cavity of the hollow fiber membrane of the sampling bottle in the present invention is full of accepting phase, the micropores of the membrane wall of the hollow fiber membrane are full of liquid film solvent, and the analyte diffuses quickly, so the extraction efficiency of the passive sampling device of the present invention is high , easy to achieve extraction balance.

---

352 由于本发明中的采样瓶的中空纤维膜内腔中充满接受相，中空纤维膜的膜壁的微孔中充满液膜溶剂，待测物扩散快，所以本发明的被动采样装置的萃取效率高，易于达到萃取平衡。

#### [0025]

359 Compared with existing semi-permeable membrane (SPMD) sampling devices.

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361 与现有的半渗透膜(SPMD)采样装置相比。

364 After the passive sampling device of the present invention has finished sampling, it does not need to analyze the analyte from the passive sampler, nor does it need to purify the analyzed analyte. It only needs to cut the two ends of the hollow fiber membrane, take out The receiving phase in the membrane cavity is enriched with the analyte, and the content of the analyte in the sample can be determined by directly taking the receiving phase for analysis.

---

370 本发明的被动采样装置在采样完毕后，不需要从被动采样器中解析出待测物，也不需要对解析出的待测物进行提纯，只需将中空纤维膜的两端剪开，取出膜腔中的富集了待测物的接受相，直接取接受相进行分析就可以测定样品中的待测物含量。

<sup>375</sup> Therefore, compared with the existing sampling device, the passive sampling device of the present invention can not only collect samples, enrich the analyte in the sample, but also perform pretreatment on the analyte in the sample, so the passive sampling device of the present invention More efficient and time-saving.

---

<sup>379</sup> 所以相对于现有的采样装置，本发明的被动采样装置不但可以采集样品，富集样品中的待测物，同时还可以对样品中的待测物进行前处理，因此本发明的被动采样装置更为高效、省时。

## [0026]

<sup>386</sup> According to the properties of the analyte in the sample, the liquid film solvent and the accepting phase solution in the membrane cavity can be selected, so by selecting the liquid film solvent and the accepting phase solution in the membrane cavity, it is possible to sample and pre-treat different types of samples different types of analytes.

---

<sup>391</sup> 针对样品中的待测物的性质，可以选择液膜溶剂和膜腔中的接受相溶液，所以通过选择液膜溶剂和膜腔中的接受相溶液，就可以采样和前处理不同类型的样品中的不同类型的待测物。

<sup>395</sup> Therefore, compared with the prior art that can only collect and enrich hydrophobic organic analytes in samples, the passive sampling device of the present invention is aimed at a wide range of analytes, including polar organic analytes, hydrophobic Organic analytes and metal ion analytes.

---

<sup>399</sup> 所以与现有技术中的仅能够采集和富集样品中的疏水性有机待测物相比，本发明的被动采样装置针对的待测物范围广范，包括极性有机待测物、疏水性有机待测物和金属离子待测物。

## [0027]

<sup>406</sup> The hollow fiber membrane, the liquid membrane solvent and the accepting phase solution used in the present invention are all cheap commercial materials with low manufacturing cost and can be used once.

---

<sup>409</sup> 本发明中采用的中空纤维膜、液膜溶剂和接受相溶液均为价格便宜的商品化材料、制作成本低，可以一次性使用。

## [0028]

418 附图说明

[0029]

424 1 shows a schematic diagram of an embodiment of a passive sampling device with a hollow fiber membrane according to the present invention, wherein a sampling bottle 1 , a sample 2 , a passive sampler 3 , a glass tube 4 , a membrane wall 5 , and an inner chamber 6 .

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428 图1表示根据本发明的具有中空纤维膜的被动采样装置的一个实施方式的示意图，其中，采样瓶1、样品2、被动采样器3、玻璃管4、膜壁5、内腔6。

[0030]

435 Detailed ways

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437 具体实施方式

[0031]

443 Hereinafter, embodiments of the present invention will be described in detail in conjunction with the accompanying drawings, and the embodiments of the present invention are used to explain the present invention rather than limit the present invention.

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447 以下，结合附图来详细说明本发明的实施例，本发明的实施例用于解释本发明而非限制本发明。

[0032]

453 Example 1

---

455 实施例1

### [0033]

461 Collect the halogenated phenoxy acid herbicides in the environmental water samples, which contain 2,4-dichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid, 2-(2,4-dichlorophenoxyacetic acid, Chlorophenoxy)-propionic acid and 2-methyl-4-chlorophenoxypropionic acid.

---

465 采集环境水样中的卤代苯氧酸型除草剂，该除草剂中含有2,4-二氯苯氧乙酸、2-甲基-4-氯苯氧乙酸、2-(2,4-二氯苯氧)-丙酸和2-甲基-4-氯苯氧丙酸。

469 Adopt the passive sampling device as shown in Figure 1 in the present embodiment, this device has following structure, comprises: sampling bottle 1 and passive sampler 3, and sampling bottle is the tool stopper glass bottle of 4ml, and passive sampler is the hollow that connects end to end. The fiber membrane 3, the glass tube 4, and the micropores of the membrane wall 5 of the hollow fiber membrane are filled with a liquid membrane solvent, and the inner chamber 6 of the hollow fiber membrane is filled with a receiving phase.

---

475 本实施例中采用如图1所示的被动采样装置，该装置具有如下结构，包括：采样瓶1和被动采样器3，采样瓶是4ml的具塞玻璃瓶，被动采样器是首尾连接的中空纤维膜3，玻璃管4，中空纤维膜的膜壁5的微孔中充满液膜溶剂，中空纤维膜的内腔6中充满接受相。

480 In this embodiment, the hollow fiber membrane is made of polypropylene, and the receiving phase of the cavity 6 of the hollow fiber membrane is 0.2M sodium hydroxide solution. The mass concentration is 2.0% tri-n-octylphosphine oxide.

---

484 本实施例中空纤维膜为聚丙烯材料，中空纤维膜的内腔6的接受相是0.2M的氢氧化钠溶液，中空纤维膜的膜壁的微孔中充满液膜溶剂是溶解于正己基醚的质量浓度为2.0%的三正辛基氧化膦。

488 The passive sampling device in this embodiment is prepared by the following method:

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490 本实施例中的被动采样装置是通过以下方法制备而成的：

### [0034]

496 (1) Fill the inner cavity of the cut 30cm long polypropylene hollow fiber membrane (inner diameter 240 microns, membrane wall thickness 30 microns) with 0.2M sodium hydroxide solution with a syringe, that is: receiving phase;

---

500 (1) 将经裁剪的30cm长的聚丙烯中空纤维膜(内径240微米，膜壁厚30微米)的内腔中用注射器充满0.2M的氢氧化钠溶液，即：接受相；

#### [0035]

507 (2) soak the hollow fiber membrane in the n-hexyl ether solution containing 2.0% mass concentration of tri-n-octylphosphine oxide: that is, in the liquid membrane solvent for 60 seconds, the micropores on the membrane wall of the hollow fiber membrane are filled with liquid membrane solvent;

---

511 (2) 将中空纤维膜浸泡在含有2.0%质量浓度的三正辛基氧化膦的正己基醚溶液中：即液膜溶剂中60秒，使中空纤维膜的膜壁上的微孔中充满液膜溶剂；

#### [0036]

518 (3) Take the hollow fiber membrane out of the n-hexyl ether solution of tri-n-octylphosphine oxide, bring the two ends together to form a ring, fold the two ends twice, seal with aluminum foil, and insert the aluminum foil into a small section In a glass tube, a passive sampler is formed;

---

522 (3) 将中空纤维膜从三正辛基氧化膦的正己基醚溶液中取出，使其两端合在一起，形成环，两端折叠2次，用铝箔封口，并将铝箔插入一小截玻璃管中，形成被动采样器；

#### [0037]

529 (4) The surface of the passive sampler is washed five times with the sample solution to remove excess n-hexyl ether and tri-n-octylphosphine oxide;

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532 (4) 将被动采样器的表面用样品液冲洗五次，去除过剩的正己基醚和三正辛基氧化膦；

#### [0038]

538 (5) Use tweezers to place the passive sampler in a 4mL stoppered glass sample bottle and seal it to form a passive sampling device.

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541 (5) 用镊子将被动采样器放置于4mL的具塞玻璃样品瓶中密封，形成被动采样装置。

[0039]

547 In order to prevent the liquid film solvent of the passive sampler from volatilizing, the passive sampling device of the present invention should be used immediately after it is made. The passive sampling device in the present embodiment works in the following manner:

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551 为了防止被动采样器的液膜溶剂挥发，本发明的被动采样装置制后应立即使用，本实施例中的被动采样装置是通过以下方式进行工作的：

[0040]

558 (1) 4ml samples are packed into a 4ml passive sampling device at the sampling site, and an appropriate amount of hydrochloric acid is added to adjust the pH value of the samples to 1.5;

---

561 (1) 在采样现场将4ml样品装入4ml的被动采样装置内，并加适量盐酸调节样品的pH值为1.5；

[0041]

567 (2) Transport the passive sampling device containing the sample to the laboratory;

---

569 (2) 将盛有样品的被动采样装置运往实验室；

[0042]

575 (3) In the laboratory, the hollow fiber membrane passive sampler in the passive sampling device is taken out, and the surface of the sampler is blotted dry with filter paper;

---

578 (3) 在实验室中，将被动采样装置中的中空纤维膜被动采样器取出，采样器的表面用滤纸吸干；

[0043]

<sup>584</sup> (4) Cut the two ends of the hollow fiber membrane, and use a syringe to completely blow 10 microliters of sodium hydroxide receiving phase in the membrane cavity (which has been enriched with the analyte in the sample) to a 50 microliter glass sample. Then take the sample in the sample bottle and inject it into the analytical chromatogram.

---

<sup>589</sup> (4) 将中空纤维膜的两端剪开，用注射器将膜腔中的10微升氢氧化钠接受相(已富集了样品中的待测物)完全吹到一个50微升的玻璃样品瓶中，再取样品瓶中的样品向分析色谱进样。

#### [0044]

<sup>590</sup> In this embodiment, the hollow fiber membrane wall 5 contains n-hexyl ether of tri-n-octylphosphine oxide with a mass concentration of 2.0%, and the hollow fiber membrane chamber 6 contains 10 microliters of 0.2M sodium hydroxide receiving phase. The extraction efficiency of the method in this embodiment is high, and the extraction efficiency of all target substances has reached more than 90% in 8 hours, and complete extraction can be achieved in 1 day; the extraction efficiency is stable at 95%-110% in 1-7 days. The method of this embodiment has been repeatedly tested, and it has good stability within 1-7 days, and its relative standard deviation is 4-15% in the 7-day repeated measurement.

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<sup>604</sup> 本实施例中，中空纤维膜壁5中，含有质量浓度为2.0%的三正辛基氧化膦的正己基醚，中空纤维膜腔6中，含有10微升0.2M的氢氧化钠接受相。本实施例方法的萃取效率高，8个小时所有的目标物的萃取效率都达到了90%以上，1天即可达到完全萃取；在1-7天内萃取效率稳定在95%—110%。对本实施例的方法进行了反复测试，在1-7天内具有很好的稳定性，在7天重复测定中其相对标准偏差为4~15%。

#### [0045]

<sup>614</sup> Example 2

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#### 616 实施例2

#### [0046]

<sup>622</sup> In this embodiment, the sample is an environmental water sample, the inner diameter of the hollow fiber membrane is 240 microns, the wall thickness of the membrane is 50 microns and the hollow fiber membrane is made of polytetrafluoroethylene material, and the analyte is chlorophenols in the water sample, so The liquid film solvent is n-undecane, the receiving phase is 0.2M sodium hydroxide, and the others are the same

as in Example 1.

---

628 本实施例中，所述样品为环境水样，中空纤维膜的内径240微米，膜壁厚50微米并且中空纤维膜是聚四氟乙烯材料，待测物是水样中的氯酚类，所述液膜溶剂为正十一烷，接受相为0.2M的氢氧化钠，其它与实施例1相同。

[0047]

636 Example 3

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638 实施例3

[0048]

644 In this embodiment, the sample is an environmental water sample, and the analyte is aniline and chloroaniline in it, the pH value of the sample is adjusted to 5, and the hydrophobic hollow fiber membrane is a polyvinylidene fluoride with a length of 5 cm. Hollow fiber membrane (inside diameter 450 microns, membrane wall thickness 125 microns), described accepting phase is the hydrochloric acid of 4M, and described liquid film solvent is n-octanol, other is identical with embodiment 1.

---

650 本实施例中，所述样品为环境水样，待测物是其中的苯胺和氯代苯胺，所述样品的pH值调为5，所述疏水性中空纤维膜为5cm长的聚偏氟乙烯中空纤维膜(内径450微米，膜壁厚125微米)，所述接受相为4M的盐酸，所述液膜溶剂为正辛醇，其它与实施例1相同。

[0049]

658 Example 4

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660 实施例4

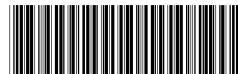
[0050]

666 In this embodiment, the test object is a water sample containing metal ion cadmium, the pH value of the sample is adjusted to 5, and the hydrophobic hollow fiber membrane is a 5 cm long polypropylene hollow

fiber membrane with an inner diameter of 600 microns and a membrane wall thickness of 5 cm. 200 microns, the accepting phase is 0.05M nitric acid, the liquid film solvent is n-undecane solution containing dithizone at a mass concentration of 0.002%, and the others are the same as in Example 1.

---

672 本实施例中，待测物是含有金属离子镉的水样，所述样品的pH值调为5，所述疏水性中空纤维膜为5cm长聚丙烯中空纤维膜，内径600微米，膜壁厚200微米，所述接受相为0.05M的硝酸，所述液膜溶剂为含有0.002%质量浓度的双硫腙的正十一烷溶液，其他与实施例1相同。



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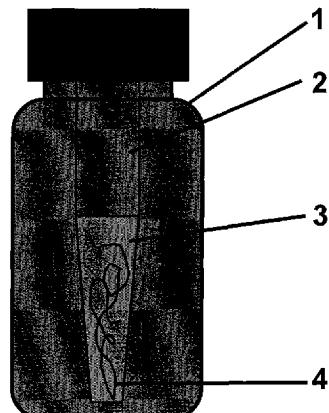
权利要求书 1 页 说明书 3 页 附图 1 页

(54) 发明名称

一种用于解吸和保存微型被动采样装置所采集的目标物的微量解吸瓶

(57) 摘要

本发明属于环境分析化学领域，涉及到一种用于解吸和保存微型被动采样器所采集的分析物的微量解吸瓶。该微量解吸瓶由 0.05-0.3mL 的玻璃内插衬管、带含聚四氟乙烯密封垫的瓶盖的 2mL 棕色玻璃瓶等组成。使用操作如下：在采样现场待采样完成后，将微型被动采样装置完全浸没在盛于内插衬管中的有机溶剂中；将内插衬管置于样品瓶中，盖紧带聚四氟乙烯密封垫的样品瓶盖，即可室温解吸和保存目标物。将微量解吸瓶室温运输回实验室后，直接取衬管中的解吸溶液进行样品分析即可。本发明所用组件为价格便宜的商品化材料，可供一次性使用；密封性好，可用于挥发和半挥发性有机化合物目标污染物的解吸与保存；装置微型化且可室温使用，方便保存和运输。



1. 一种用于解吸和保存微型被动采样器所采集的分析物的微量解吸瓶，其由内插衬管、带含聚四氟乙烯密封垫的瓶盖的玻璃瓶组成。
2. 权利要求 1 的微量解吸瓶，其中在内插衬管中可放置有机溶剂。
3. 权利要求 1 或 2 的微量解吸瓶，其中在内插衬管中放置微型被动采样器。
4. 前述权利 1-3 任一项的微量解吸瓶，其中所述内插衬管为 0.05-0.3mL 的玻璃内插管。
5. 权利要求 2 的微量解吸瓶，其中所述有机溶剂为烷烃、醇类、卤代烃类。
6. 权利要求 5 的微量解吸瓶，其中所述有机溶剂为甲醇。
7. 权利要求 1-6 中任一项的微量解吸瓶，所述样品瓶为 2mL 的带含聚四氟乙烯密封垫的瓶盖的玻璃瓶。
8. 权利要求 1-6 中任一项的微量解吸瓶，所述样品瓶为棕色的玻璃瓶。
9. 权利要求 1 的微量解吸瓶，其中所述分析物为挥发和半挥发性有机化合物。
10. 权利要求 1 的微量解吸瓶，其中所述分析物为 2-甲基异莰醇、土腥素、氯酚类、苯胺或氯代苯胺。
11. 一种使用权利要求 1-10 中任一项的微量解吸瓶的方法，所述方法包括下列步骤：
  - (1) 将内插衬管置于样品瓶中，再将一定体积的有机溶剂盛入内插衬管，盖紧带聚四氟乙烯密封垫的样品瓶盖，即组装成微型解吸瓶。
  - (2) 在采样现场待采样完成后，将微型被动采样装置完全浸没在盛于内插衬管中的有机溶剂中，盖紧带聚四氟乙烯密封垫的样品瓶盖；
  - (3) 将微量解吸瓶室温储存、运输回实验室。
12. 按权利要求 11 所述的方法，其特征在于，所述样品瓶为 2mL 的带含聚四氟乙烯密封垫的瓶盖的玻璃瓶。
13. 按权利要求 11 所述的方法，其特征在于，所述微量解吸瓶为棕色的样品瓶。
14. 按权利要求 11 所述的方法，其特征在于，所述有机溶剂为烷烃、醇类、卤代烃类。
15. 按权利要求 11 所述的方法，其特征在于，所述内插衬管为容量为 0.05-0.3mL 的玻璃管。

# 一种用于解吸和保存微型被动采样装置所采集的目标物的 微量解吸瓶

## 技术领域

[0001] 本发明属于环境分析化学领域,涉及到一种用于解吸和保存微型被动采样器所采集的分析物的微量解吸瓶。

## 背景技术

[0002] 本发明技术领域的背景和发展现状大致如下:样品采集和前处理是环境水样中污染物的分析测定中非常关键的步骤。传统的方法是到现场采集大体积的水样(数百毫升至数升)运输回实验室,进行分离富集和测定等操作。对于一些特殊的目标物如2-甲基异莰醇和土腥素等异味物质,运送过程中需要4℃低温储藏,以防止水中微生物代谢生成或降解,确保样品能够代表采样点的真实污染状况。基于被动采样装置的被动采样技术可以避免这种繁琐和高能耗的样品运输过程。该技术可在现场将环境水体中的目标化合物直接富集于被动采样装置中,再将富集了目标物的被动采样装置带回实验室,进行目标物的解吸和分析测定。但是对于一些挥发性强和易的分析物,这些富集了目标分析物的被动采样装置在运输和储存过程中仍然需要进行低温和避光保存等繁琐的操作。尽管近年发展起来的基于固相微萃取的微型被动采样装置,可以显著减少采样器采样后所需的低温保存容器(如液氮罐等)的空间,但液氮罐等低温容器的运输仍然十分麻烦。

## 发明内容

[0003] 本发明的微量解吸瓶可在室温下解吸和保存微型采样装置所采集的目标物,便于运输,很好地克服了以上缺点。

[0004] 本发明的微量解吸瓶由内插衬管、带含聚四氟乙烯密封垫瓶盖的样品瓶、有机溶剂等组成。具体使用操作如下:

[0005] (1) 将内插衬管置于样品瓶中,再将一定体积的有机溶剂盛入内插衬管,盖紧带聚四氟乙烯密封垫的样品瓶盖,即组装成微型解吸瓶。

[0006] (2) 在采样现场待采样完成后,将微型被动采样装置完全浸没在盛于内插衬管中的有机溶剂中,盖紧带聚四氟乙烯密封垫的样品瓶盖;

[0007] (3) 将微量解吸瓶室温储存、运输回实验室。

[0008] 所述样品瓶为2mL的带含聚四氟乙烯密封垫的瓶盖的玻璃瓶。

[0009] 所述样品瓶为棕色的玻璃瓶。

[0010] 所述有机溶剂为烷烃、醇类、卤代烃类。

[0011] 所述内插衬管为0.05-0.3mL的玻璃内插管。

[0012] 具体地,本发明提供下列内容:

[0013] 1. 一种用于解吸和保存微型被动采样器所采集的分析物的微量解吸瓶,其由内插衬管、带含聚四氟乙烯密封垫的瓶盖的玻璃瓶组成。

[0014] 2. 1的微量解吸瓶,其中在内插衬管中可放置有机溶剂。

- [0015] 3.1 或 2 的微量解吸瓶,其中在内插衬管中放置微型被动采样器。
- [0016] 4.1-3 中任一项的微量解吸瓶,其中所述内插衬管为 0.05-0.3mL 的玻璃内插管。
- [0017] 5.2 的微量解吸瓶,其中所述有机溶剂为烷烃、醇类、卤代烃类。
- [0018] 6.5 的微量解吸瓶,其中所述有机溶剂为甲醇。
- [0019] 7.1-6 中任一项的微量解吸瓶,所述样品瓶为 2mL 的带含聚四氟乙烯密封垫的瓶盖的玻璃瓶。
- [0020] 8.1-6 中任一项的微量解吸瓶,所述样品瓶为棕色的玻璃瓶。
- [0021] 9.1 的微量解吸瓶,其中所述分析物为挥发和半挥发性有机化合物。
- [0022] 10.1 的微量解吸瓶,其中所述分析物为 2-甲基异莰醇、土腥素、氯酚类、苯胺或氯代苯胺。
- [0023] 11. 一种使用 1-10 中任一项的微量解吸瓶的方法,所述方法包括下列步骤:
- [0024] (1) 将内插衬管置于样品瓶中,再将一定体积的有机溶剂盛入内插衬管,盖紧带聚四氟乙烯密封垫的样品瓶盖,即组装成微型解吸瓶。
- [0025] (2) 在采样现场待采样完成后,将微型被动采样装置完全浸没在盛于内插衬管中的有机溶剂中,盖紧带聚四氟乙烯密封垫的样品瓶盖;
- [0026] (3) 将微量解吸瓶室温储存、运输回实验室。
- [0027] 12.11 所述的方法,其特征在于,所述样品瓶为 2mL 的带含聚四氟乙烯密封垫的瓶盖的玻璃瓶。
- [0028] 13.11 所述的方法,其特征在于,所述微量解吸瓶为棕色的样品瓶。
- [0029] 14.11 所述的方法,其特征在于,所述有机溶剂为烷烃、醇类、卤代烃类。
- [0030] 15.11 所述的方法,其特征在于,所述内插衬管为容量为 0.05-0.3mL 的玻璃管。
- [0031] 本发明主要有以下优点:
- [0032] 1. 集解吸和保存于一体,室温保存,微型化,方便运输,操作简单;
- [0033] 2. 在微型采样装置储存和运输的过程中完成目标物的解吸过程,节省时间;
- [0034] 3. 密封性好,样品损失少、回收率高;
- [0035] 4. 适应范围广,可应用的目标污染物包括各类挥发和半挥发性有机化合物;
- [0036] 5. 成本低,本发明中采用的微量样品瓶、内插衬管和有机溶剂均为价格便宜的商品化材料,制作成本低,可供一次性使用。

## 附图说明

- [0037] 图 1 是微量解吸瓶示意图。
- [0038] 其中,1 为微量样品瓶,2 为内插衬管,3 为有机溶剂,4 为微型被动采样装置。

## 具体实施方式

[0039] 下面结合实施例,对本发明的微量解吸瓶做进一步的详细描述,但本发明不限于这些实施例:

[0040] 实施例 1

[0041] 如图 1 所示,采用本发明的微量解吸瓶解吸和保存富集于中空纤维微型被动采样装置中的 2-甲基异莰醇和土腥素等异味物质,具体步骤如下:

[0042] 中空纤维微型被动采样装置的制备：

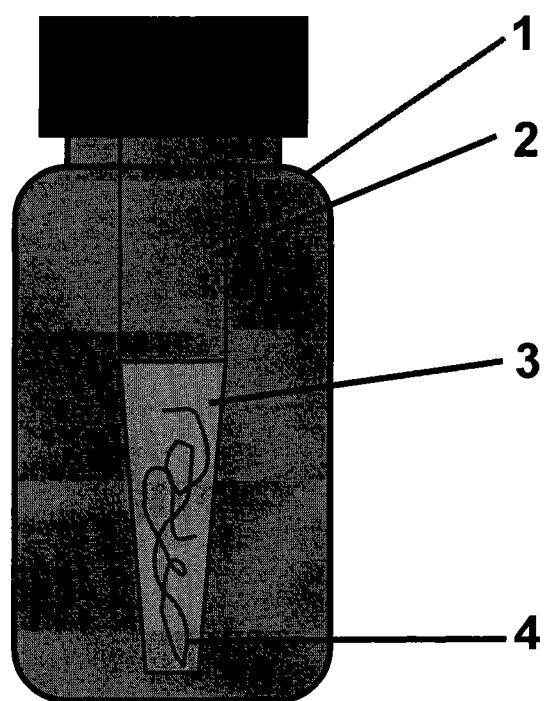
[0043] 将平均分子量为 4000 的聚丙二醇 (PPG 4000) 和甲醇以体积比 2 : 1 混合制得 PPG/ 甲醇涂层液备用。首先通过微量注射器将水注入一段长 52cm 的聚丙烯中空纤维 (PP50/280, 内径 280 μm, 壁厚 50 μm, 孔径 0.1 μm) 的腔内, 然后用加热过的不锈钢镊子将纤维的两端热封 ;其次, 将封好的纤维置于 PPG/ 甲醇涂层液中浸渍 30min, 在纤维膜壁的微孔中形成液体液膜 ;然后, 将中空纤维取出后, 剪开封口, 用水冲洗其内、外表面, 以洗去残留在表面的涂层液体。通过这种制作方法制得的液体薄膜中空纤维萃取器, 有效长度 50cm, 液膜涂层厚度约 38 μm。

[0044] 1. 在采样现场 (江苏太湖) 将中空纤维微型被动采样装置完全浸没于太湖湖水中, 1-2 小时后采样完成, 将中空纤维微型被动采样装置置于盛有 100 μL 甲醇的玻璃内插衬管中, 使采样装置完全浸没在甲醇中。

[0045] 2. 将内插衬管置于 2mL 样品瓶中, 盖紧带聚四氟乙烯密封垫的样品瓶盖 ;

[0046] 3. 将微量解吸瓶运输回实验室。

[0047] 本实施例中, 微量解吸瓶运输回实验室后, 将解吸瓶中的甲醇解吸液全部转移到装有 10mL 水的萃取瓶 (25mL) 中, 将商品 PDMS 固相微萃取纤维 (美国 Supelco 公司) 置于所述萃取瓶内, 在室温下搅拌进行顶空固相微萃取 40min, 再将固相微萃取纤维取出并直接插入进入 GC/MS 进样口进样分析测定 2- 甲基异莰醇和土腥素含量, 对 2- 甲基异莰醇和土腥素的检测限分别为 9ng/L 和 5ng/L, 满足实际分析测定的需求。GC/MS 的工作条件如下 : 载气 : 高纯 He (99. 999%), 流速 1mL/min ; 恒压 120kPa ; 进样口温度 : 225°C ; 进样方式 : 无分流进样 ; 溶剂延迟 : 4min ; 程序升温 : 100°C (1min) - 10°C /min 280°C - 280°C (2min) ; 传输线温度 280°C ; 离子源温度 230°C ; 电子能量 70eV。鉴定水样中的未知化合物采用质谱全扫描方式, 质量范围为 40 ~ 350amu。定量测定水样中异化合物时, 采用质谱选择离子方式, 特征离子 m/z 95、112 分别作为 MBI, GSM 的定量离子, 同时检测特征离子 m/z 135、125 分别作为两种异味化合物的监控离子。



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## DESCRIPTION CN101936834A

*10* A micro-desorption bottle used for desorbing and preserving target objects collected by a miniature passive sampling device

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*13* 一种用于解吸和保存微型被动采样装置所采集的目标物的微量解吸瓶

[0001]

*19* technical field

---

*21* 技术领域

[0002]

*27* The invention belongs to the field of environmental analysis chemistry and relates to a micro desorption bottle used for desorbing and storing analytes collected by a micro passive sampler.

---

*30* 本发明属于环境分析化学领域，涉及到一种用于解吸和保存微型被动采样器所采集的分析物的微量解吸瓶。

[0003]

*37* Background technique

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39 背景技术

[0004]

45 The background and development status of the technical field of the present invention are generally as follows: sample collection and pretreatment are very critical steps in the analysis and determination of pollutants in environmental water samples.

---

49 本发明技术领域的背景和发展现状大致如下：样品采集和前处理是环境水样中污染物的分析测定中非常关键的步骤。

53 The traditional method is to collect large-volume water samples (hundreds of milliliters to several liters) on site and transport them back to the laboratory for separation, enrichment and determination. For some special target substances such as 2-methylisobutyritol and geosin, low-temperature storage at 4 ° C is required during transportation to prevent the metabolic generation or degradation of microorganisms in water and ensure that the samples can represent the real pollution status of the sampling point. Passive sampling technology based on passive sampling devices can avoid this tedious and energy-intensive sample transportation process. This technology can directly enrich the target compound in the environmental water body in the passive sampling device on site, and then bring the passive sampling device enriched with the target compound back to the laboratory for desorption and analysis of the target compound. However, for some highly volatile and easy analytes, these passive sampling devices enriched with target analytes still need cumbersome operations such as low temperature and light-proof storage during transportation and storage. Although the miniature passive sampling device based on solid-phase microextraction developed in recent years can significantly reduce the space of cryopreservation containers (such as liquid nitrogen tanks, etc.) required by the sampler after sampling, the transportation of cryogenic containers such as liquid nitrogen tanks is still very difficult trouble.

---

68 传统的方法是到现场采集大体积的水样(数百毫升至数升)运输回实验室，进行分离富集和测定等操作。对于一些特殊的目标物如2-甲基异茨醇和土腥素等异味物质，运送过程中需要4 低温储藏，以防止水中微生物代谢生成或降解，确保样品能够代表采样点的真实污染状况。基于被动采样装置的被动采样技术可以避免这种繁琐和高能耗的样品运输过程。该技术可在现场将环境水体中的目标化合物直接富集于被动采样装置中，再将富集了目标物的被动采样装置带回实验室，进行目标物的解吸和分析测定。但是对于一些挥发性强和易的分析物，这些富集了目标分析物的被动采样装置在运输和储存过程中仍然需要进行低温和避光保存等繁琐的操作。尽管近年发展起来的基于固相微萃取的微型被动采样装置，可以显著减少采样器采样后所需的低温保存容器(如液氮罐等)的空间，但液氮罐等低温容器的运输仍然十分麻烦。

[0005]

82 Contents of the invention

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84 发明内容

[0006]

90 The micro-volume desorption bottle of the present invention can desorb and store the target objects collected by the micro-sampling device at room temperature, is convenient for transportation, and well overcomes the above disadvantages.

---

94 本发明的微量解吸瓶可在室温下解吸和保存微型采样装置所采集的目标物，便于运输，很好地克服了以上缺点。

[0007]

101 The micro desorption bottle of the present invention is composed of an inserting liner, a sample bottle with a bottle cap containing a polytetrafluoroethylene sealing gasket, an organic solvent and the like.

---

104 本发明的微量解吸瓶由内插衬管、带含聚四氟乙烯密封垫瓶盖的样品瓶、有机溶剂等组成。

107 The specific operation is as follows:

---

109 具体使用操作如下：

[0008]

115 (1) Place the insert liner in the sample bottle, then fill a certain volume of organic solvent into the insert liner tube, and close the sample bottle cap with a Teflon gasket to assemble a miniature desorption bottle.

---

118 (1) 将内插衬管置于样品瓶中，再将一定体积的有机溶剂盛入内插衬管，盖紧带聚四氟乙烯密封垫的样品瓶盖，即组装成微型解吸瓶。

[0009]

<sup>125</sup> (2) After the sampling is completed at the sampling site, completely immerse the miniature passive sampling device in the organic solvent contained in the insert liner, and tightly cover the sample bottle cap with the Teflon gasket;

---

<sup>129</sup> (2)在采样现场待采样完成后，将微型被动采样装置完全浸没在盛于内插衬管中的有机溶剂中，盖紧带聚四氟乙烯密封垫的样品瓶盖；

[0010]

<sup>136</sup> (3) Store the micro desorption bottle at room temperature and transport it back to the laboratory.

---

<sup>138</sup> (3)将微量解吸瓶室温储存、运输回实验室。

[0011]

<sup>144</sup> The sample bottle is a 2 mL glass bottle with a cap containing a polytetrafluoroethylene seal.

---

<sup>146</sup> 所述样品瓶为2mL的带含聚四氟乙烯密封垫的瓶盖的玻璃瓶。

[0012]

<sup>152</sup> The sample bottle is a brown glass bottle.

---

<sup>154</sup> 所述样品瓶为棕色的玻璃瓶。

[0013]

<sup>160</sup> The organic solvents are alkanes, alcohols, halogenated hydrocarbons.

---

<sup>162</sup> 所述有机溶剂为烷烃、醇类、卤代烃类。

[0014]

<sup>168</sup> The inserting liner is a 0.05-0.3mL glass inserting tube.

---

<sup>170</sup> 所述内插衬管为0.05-0.3mL的玻璃内插管。

[0015]

<sup>176</sup> Specifically, the present invention provides the following:

---

<sup>178</sup> 具体地，本发明提供下列内容：

[0016]

<sup>184</sup> 1.

---

<sup>186</sup> 1.

<sup>189</sup> A micro-desorption bottle used for desorbing and storing analytes collected by a micro-passive sampler is composed of an inner liner and a glass bottle with a bottle cap containing a polytetrafluoroethylene sealing gasket.

---

<sup>193</sup> 一种用于解吸和保存微型被动采样器所采集的分析物的微量解吸瓶，其由内插衬管、带含聚四氟乙烯密封垫的瓶盖的玻璃瓶组成。

[0017]

<sup>200</sup> 2.1 The micro desorption bottle, in which the organic solvent can be placed in the insert liner.

---

<sup>202</sup> 2.1的微量解吸瓶，其中在内插衬管中可放置有机溶剂。

[0018]

<sup>208</sup> 3. The micro desorption bottle of 1 or 2, wherein a micro passive sampler is placed in the insert liner.

---

<sup>210</sup> 3.1或2的微量解吸瓶，其中在内插衬管中放置微型被动采样器。

[0019]

<sup>216</sup> 4. The micro desorption bottle according to any one of 1-3, wherein the insert liner is a 0.05-0.3mL glass insert tube.

---

<sup>219</sup> 4.1-3中任一项的微量解吸瓶，其中所述内插衬管为0.05-0.3mL的玻璃内插管。

[0020]

<sup>225</sup> The micro desorption bottle of 5.2, wherein said organic solvent is alkanes, alcohols, halogenated hydrocarbons.

---

<sup>228</sup> 5.2的微量解吸瓶，其中所述有机溶剂为烷烃、醇类、卤代烃类。

[0021]

<sup>234</sup> The micro desorption bottle of 6.5, wherein said organic solvent is methanol.

---

<sup>236</sup> 6.5的微量解吸瓶，其中所述有机溶剂为甲醇。

[0022]

<sup>242</sup> 7. The micro desorption bottle according to any one of 1-6, the sample bottle is a 2mL glass bottle with a cap containing a polytetrafluoroethylene sealing gasket.

---

<sup>245</sup> 7.1-6中任一项的微量解吸瓶，所述样品瓶为2mL的带含聚四氟乙烯密封垫的瓶盖的玻璃瓶。

[0023]

<sup>251</sup> 8. The microdesorption bottle of any one of 1-6, the sample bottle is a brown glass bottle.

---

<sup>253</sup> 8.1-6中任一项的微量解吸瓶，所述样品瓶为棕色的玻璃瓶。

[0024]

<sup>259</sup> 9. The microdesorption vial of 1, wherein the analytes are volatile and semi-volatile organic compounds.

---

<sup>261</sup> 9.1的微量解吸瓶，其中所述分析物为挥发和半挥发性有机化合物。

[0025]

<sup>267</sup> 10.1 The microdesorption vial, wherein the analyte is 2-methylisobutyric alcohol, geoxanthin, chlorophenols, aniline or chloroaniline.

---

<sup>270</sup> 10.1的微量解吸瓶，其中所述分析物为2-甲基异茨醇、土腥素、氯酚类、苯胺或氯代苯胺。

[0026]

<sup>276</sup> 11.

---

<sup>278</sup> 11.

<sup>281</sup> A method of using any one of 1-10 micro desorption bottles, said method comprising the steps of:

---

<sup>283</sup> 一种使用1-10中任一项的微量解吸瓶的方法，所述方法包括下列步骤：

[0027]

<sup>289</sup> (1) Place the insert liner in the sample bottle, then fill a certain volume of organic solvent into the insert liner

tube, and close the sample bottle cap with a Teflon gasket to assemble a miniature desorption bottle.

---

292 (1) 将内插衬管置于样品瓶中，再将一定体积的有机溶剂盛入内插衬管，盖紧带聚四氟乙烯密封垫的样品瓶盖，即组装成微型解吸瓶。

[0028]

299 (2) After the sampling is completed at the sampling site, completely immerse the miniature passive sampling device in the organic solvent contained in the insert liner, and tightly cover the sample bottle cap with the Teflon gasket;

---

303 (2) 在采样现场待采样完成后，将微型被动采样装置完全浸没在盛于内插衬管中的有机溶剂中，盖紧带聚四氟乙烯密封垫的样品瓶盖；

[0029]

310 (3) Store the micro desorption bottle at room temperature and transport it back to the laboratory.

---

312 (3) 将微量解吸瓶室温储存、运输回实验室。

[0030]

318 The method described in 12.11 is characterized in that the sample bottle is a 2mL glass bottle with a cap containing a polytetrafluoroethylene sealing gasket.

---

321 12.11所述的方法，其特征在于，所述样品瓶为2mL的带含聚四氟乙烯密封垫的瓶盖的玻璃瓶。

[0031]

327 The method described in 13.11 is characterized in that, the micro desorption bottle is a brown sample bottle.

---

329 13.11所述的方法，其特征在于，所述微量解吸瓶为棕色的样品瓶。

[0032]

<sup>335</sup> 14. The method described in 11, wherein the organic solvent is alkanes, alcohols, halogenated hydrocarbons.

---

<sup>337</sup> 14.11所述的方法，其特征在于，所述有机溶剂为烷烃、醇类、卤代烃类。

[0033]

<sup>343</sup> 15. The method described in 11, wherein the inserting liner is a glass tube with a capacity of 0.05-0.3mL.

---

<sup>345</sup> 15.11所述的方法，其特征在于，所述内插衬管为容量为0.05-0.3mL的玻璃管。

[0034]

<sup>351</sup> The present invention mainly has the following advantages:

---

<sup>353</sup> 本发明主要有以下优点：

[0035]

<sup>359</sup> 1.

---

<sup>361</sup> 1.

<sup>364</sup> Integrating desorption and storage, storage at room temperature, miniaturization, convenient transportation, and simple operation;

---

<sup>367</sup> 集解吸和保存于一体，室温保存，微型化，方便运输，操作简单；

[0036]

<sup>373</sup> 2.

---

375 2.

---

378 The desorption process of the target is completed during the storage and transportation of the micro-sampling device, saving time;

---

381 在微型采样装置储存和运输的过程中完成目标物的解吸过程，节省时间；

[0037]

387 3.

---

389 3.

392 Good sealing, less sample loss and high recovery rate;

---

394 密封性好，样品损失少、回收率高；

[0038]

400 4.

---

402 4.

405 Wide range of applications, applicable target pollutants include various volatile and semi-volatile organic compounds;

---

408 适应范围广，可应用的目标污染物包括各类挥发和半挥发性有机化合物；

[0039]

414 5.

---

416 5.

419 The cost is low, the micro sample bottle, the insert liner and the organic solvent used in the present invention are all cheap commercial materials, the production cost is low, and they can be used for one-time use.

---

422 成本低，本发明中采用的微量样品瓶、内插衬管和有机溶剂均为价格便宜的商品化材料，制作成本低，可供一次性使用。

[0040]

429 Description of drawings

---

431 附图说明

[0041]

437 Figure 1 is a schematic diagram of a micro desorption bottle.

---

439 图1是微量解吸瓶示意图。

[0042]

445 Among them, 1 is a micro sample bottle, 2 is an insert liner, 3 is an organic solvent, and 4 is a miniature passive sampling device.

---

448 其中，1为微量样品瓶，2为内插衬管，3为有机溶剂，4为微型被动采样装置。

[0043]

454 Detailed ways

---

456 具体实施方式

#### [0044]

<sup>462</sup> Below in conjunction with embodiment, micro desorption bottle of the present invention is described in further detail, but the present invention is not limited to these embodiments:

---

<sup>465</sup> 下面结合实施例，对本发明的微量解吸瓶做进一步的详细描述，但本发明不限于这些实施例：

#### [0045]

<sup>471</sup> Example 1

---

<sup>473</sup> 实施例1

#### [0046]

<sup>479</sup> As shown in Fig. 1, adopt micro desorption bottle of the present invention to desorb and preserve the peculiar smell substances such as 2-methylisobutyrylaldehyde and geosin that are enriched in the hollow fiber miniature passive sampling device, concrete steps are as follows:

---

<sup>483</sup> 如图1所示，采用本发明的微量解吸瓶解吸和保存富集于中空纤维微型被动采样装置中的2-甲基异茨醇和土腥素等异味物质，具体步骤如下：

#### [0047]

<sup>490</sup> Preparation of the hollow fiber miniature passive sampling device:

---

<sup>492</sup> 中空纤维微型被动采样装置的制备：

#### [0048]

<sup>498</sup> Polypropylene glycol (PPG 4000) with an average molecular weight of 4000 and methanol were mixed at a volume ratio of 2:1 to prepare a PPG/methanol coating solution for use.

---

501 将平均分子量为4000的聚丙二醇(PPG 4000)和甲醇以体积比2 1混合制得PPG/甲醇涂层液备用。

---

504 First, inject water into the cavity of a 52cm-long polypropylene hollow fiber (PP50/280, inner diameter 280  $\mu$  m, wall thickness 50  $\mu$  m, pore diameter 0.1  $\mu$  m) through a micro-syringe, and then use heated stainless steel tweezers to heat seal the two ends of the fiber; Next, immerse the sealed fiber in the PPG/methanol coating solution for 30 minutes to form a liquid liquid film in the micropores of the fiber membrane wall; then, after taking out the hollow fiber, cut off the seal, and rinse the inside and outside with water. surface to wash away the remaining coating liquid on the surface.

---

511 首先通过微量注射器将水注入一段长52cm的聚丙烯中空纤维(PP50/280，内径280  $\mu$  m，壁厚50  $\mu$  m，孔径0.1  $\mu$  m)的腔内，然后用加热过的不锈钢镊子将纤维的两端热封；其次，将封好的纤维置于PPG/甲醇涂层液中浸渍30min，在纤维膜壁的微孔中形成液体液膜；然后，将中空纤维取出后，剪开封口，用水冲洗其内、外表面，以洗去残留在表面的涂层液体。

---

517 The liquid film hollow fiber extractor prepared by this manufacturing method has an effective length of 50 cm and a liquid film coating thickness of about 38  $\mu$  m.

---

520 通过这种制作方法制得的液体薄膜中空纤维萃取器，有效长度50cm，液膜涂层厚度约38  $\mu$  m。

[0049]

526 1.

---

528 1.

---

531 At the sampling site (Taihu Lake, Jiangsu Province), the hollow fiber micro-passive sampling device was completely immersed in the water of Taihu Lake. After 1-2 hours, the sampling was completed, and the hollow fiber micro-passive sampling device was placed in a glass insert liner filled with 100  $\mu$  L of methanol. Completely submerge the sampling device in methanol.

---

536 在采样现场(江苏太湖)将中空纤维微型被动采样装置完全浸没于太湖湖水中，1-2小时后采样完成，将中空纤维微型被动采样装置置于盛有100  $\mu$  L甲醇的玻璃内插衬管中，使采样装置完全浸没在甲醇中。

[0050]

544 2.

---

546 2.

549 Place the insert liner in a 2mL sample bottle, and tightly cap the sample bottle with a PTFE seal;

---

551 将内插衬管置于2mL样品瓶中，盖紧带聚四氟乙烯密封垫的样品瓶盖；

[0051]

557 3.

---

559 3.

562 Transport the microdesorption bottle back to the laboratory.

---

564 将微量解吸瓶运输回实验室。

[0052]

570 In this example, after the trace desorption bottle was transported back to the laboratory, all the methanol desorption solution in the desorption bottle was transferred to an extraction bottle (25 mL) containing 10 mL of water, and the commercial PDMS solid-phase microextraction fiber (Supelco, USA) Place in the extraction bottle, stir at room temperature to carry out headspace solid-phase microextraction for 40min, then take out the solid-phase microextraction fiber and directly insert it into the GC/MS inlet for sample analysis and determination of 2-methylisobutyrylaldehyde and Geostin content, the detection limits of 2-methylisobutyrylaldehyde and geostin are 9ng/L and 5ng/L respectively), which meets the needs of actual analysis and determination.

---

579 本实施例中，微量解吸瓶运输回实验室后，将解吸瓶中的甲醇解吸液全部转移到装有10mL水的萃取瓶(25mL)中，将商品PDMS固相微萃取纤维(美国Supelco公司)置于所述萃取瓶内，在室温下搅拌进行顶空固相微萃取40min，再将固相微萃取纤维取出并直接插入进入GC/MS进样口进样分析测定2-甲基异茨醇和土腥素含量，对2-甲基异茨醇和土腥素的检测限分别为9ng/L和5ng/L)，满足实际分析测定的需求。

586 The working conditions of GC/MS are as follows: carrier gas: high-purity He (99.999%), flow rate 1mL/min; constant pressure 120kPa; inlet temperature: 225 ° C; sampling method: splitless injection; solvent delay: 4min; Temperature program: 100 ° C (1min)-10 ° C/min 280 ° C-280 ° C (2min); transfer line temperature 280 ° C; ion source temperature 230 ° C; electron energy 70eV.

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591 GC/MS的工作条件如下：载气：高纯He(99.999%)，流速1mL/min；恒压120kPa；进样口温度：225；进样方式：无分流进样；溶剂延迟：4min；程序升温：100 (1min)-10 /min 280 - 280 (2min)；传输线温度280 ；离子源温度230 ；电子能量70eV。

596 The identification of unknown compounds in water samples adopts mass spectrometry full-scan mode, and the mass range is 40-350 amu.

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599 鉴定水样中的未知化合物采用质谱全扫描方式，质量范围为40 ~ 350amu。

602 When quantitatively determining foreign compounds in water samples, mass spectrometry is used to select ion methods. The characteristic ions m/z 95 and 112 are used as the quantitative ions of MBI and GSM respectively, and the characteristic ions m/z 135 and 125 are respectively used as the monitoring of two odor compounds. ion.

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607 定量测定水样中异化合物时，采用质谱选择离子方式，特征离子m/z 95、112分别作为 MBI，GSM的定量离子，同时检测特征离子m/z 135、125分别作为两种异味化合物的监控离子。

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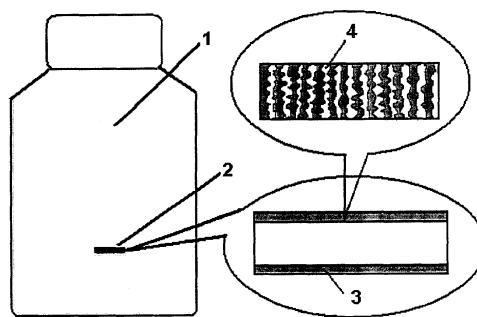
权利要求书 1 页 说明书 5 页 附图 1 页

### [54] 发明名称

一种被动采样方法

### [57] 摘要

本发明涉及一种中空纤维液膜被动采样方法，其步骤包括：将内腔充满水的疏水性中空纤维膜段浸泡在脂质或非水溶性有机溶剂中，使中空纤维膜壁上的微孔中充满脂质或非水溶性有机溶剂，得到中空纤维支载液膜被动采样器；再将该采样器经清洗后，浸没在待取样的样品液中进行采样；之后，将进行了采样的采样器浸没在盛有可将目标物质从采样器中溶解出来的溶剂的密闭容器中，使采集于中空纤维支载液膜被动采样器中的目标物质定量解析到所述溶剂中，完成采样。本采样方法具有微型化、灵活性高、低成本和采样速率高等优点，而且还可方便地与液相色谱等检测仪器联用，其稳定性和重复性好。



1、一种中空纤维液膜被动采样方法，包括以下步骤：

- (1) 将经裁剪的疏水性中空纤维膜段的内腔中充满水；
- (2) 将内腔中充满水的疏水性中空纤维膜段浸泡在脂质或非水溶性有机溶剂中，使疏水性中空纤维膜段的膜壁上的微孔中充满脂质或非水溶性有机溶剂，形成中空纤维支载液膜被动采样器；
- (3) 将中空纤维支载液膜被动采样器由所述脂质或非水溶性有机溶剂取出，并置于水中清洗，去除其表面吸附的过剩脂质或非水溶性有机溶剂；
- (4) 将经清洗后的中空纤维支载液膜被动采样器浸没在待取样的样品液中 20 分钟～5 天；
- (5) 将中空纤维支载液膜被动采样器取出，并清除其外表面的颗粒物；
- (6) 再将中空纤维支载液膜被动采样器浸没在盛有可将目标物质从采样器中溶解出来的溶剂的密闭容器中，并使采集于中空纤维支载液膜被动采样器中的目标物质定量解析到所述溶剂中，完成采样。

2. 按权利要求 1 所述的方法，其特征在于，所述疏水性中空纤维膜为聚丙烯膜、聚偏氟乙烯膜或聚四氟乙烯膜。

3. 按权利要求 1 所述的方法，其特征在于，所述非水溶性有机溶剂为高级烷烃、高级醇类或高级醚类。

4. 按权利要求 3 所述的方法，其特征在于，所述高级烷烃为正十一烷；所述高级醇类包括正辛醇；所述高级醚类包括正己基醚。

5. 按权利要求 1 所述的方法，其特征在于，所述可将目标物质从采样器中溶解出来的溶剂为甲醇、甲苯或正己烷。

6. 按权利要求 1 所述的方法，其特征在于，所述脂质为动物油或植物油。

7. 按权利要求 6 所述的方法，其特征在于，所述动物油为鱼油，所述植物油为菜籽油。

## 一种被动采样方法

### 技术领域

本发明涉及一种被动采样方法，特别是涉及一种中空纤维支载液膜被动采样方法。

### 背景技术

本技术领域的背景和发展现状大致如下：J. N. Huckins 等首次将脂质装在低密度聚乙烯膜袋中作为被动采样器，用于监测疏水性有机污染物，他们将该技术命名为半透膜采样装置（以下简称 SPMD）。Davison 等发明了扩散梯度薄膜（以下简称 DGT）技术，用于采集具有生物有效性的金属离子和某些无机阴离子。这两种被动采样器尺寸较大，采样相体积和富集倍数较大，需要较大的样品体积和很长的时间才能够达到平衡，一般用于远未达到平衡的动态采样。

为了克服 SPMD 和 DGT 的缺点，人们又将固相微萃取（以下简称 SPME）应用于采集疏水性有机污染物，如 Hermens 等人在文献：*Trends Anal. Chem.* 2003, 22, 575-587 中所述，将环境介质中的目标污染物富集于有聚合物涂层的石英纤维上，再直接插入气相色谱进样口进行热解析、分离和测定。SPME 已成功地用于测定土壤和沉积物的孔隙水（pore water）中的多氯联苯、多环芳烃和氯代苯等污染物，其富集倍数高达  $2.5 \times 10^6$ 。由于 SPME 的涂层很薄且体积极小（亚微升级），采样所需要的平衡时间较短且样品体积小，故该技术既可以用于远未达到平衡的动态采样，又可以用于平衡采样，具有很好的应用前景。遗憾的是，作为采样相的 SPME 的涂层一般为固态或者高粘度的液态高聚物，目标分子在其中的扩散速度较慢，故其采样富集速度依然相对较慢；另外，SPME 与高效液相色谱（以下简称 HPLC）的联用技术还不够成熟，二者匹配使用还有一些技术

问题待解决。

## 发明内容

本发明的目的是为了克服上述现有的被动采样方法的缺陷，从而提供一种有很高采样速率且能够方便与 HPLC 联用、稳定性和重复性好的被动采样方法。

本发明的技术方案如下：

本发明提供的中空纤维液膜被动采样方法，包括以下步骤：

1、将经裁剪的疏水性中空纤维膜段的内腔中充满水；  
2、将内腔中充满水的疏水性中空纤维膜段浸泡在脂质或非水溶性有机溶剂中，使疏水性中空纤维膜段的膜壁上的微孔中充满脂质或非水溶性有机溶剂，形成中空纤维支载液膜被动采样器；

3、将中空纤维支载液膜被动采样器由所述脂质或非水溶性有机溶剂取出，并置于水中清洗，去除其表面吸附的过剩脂质或非水溶性有机溶剂；

4、将经清洗后的中空纤维支载液膜被动采样器浸没在待取样的样品液中 20 分钟～5 天；

5、将中空纤维支载液膜被动采样器取出，并清除其外表面的颗粒物；

6、再将中空纤维支载液膜被动采样器浸没在盛有可将目标物质从采样器中溶解出来的溶剂的密闭容器中，并使采集于中空纤维支载液膜被动采样器中的目标物质定量解析到所述溶剂中，完成采样。

所述疏水性中空纤维膜为聚丙烯膜、聚偏氟乙烯膜或聚四氟乙烯膜。

所述非水溶性有机溶剂为高级烷烃、高级醇类或高级醚类。

所述高级烷烃为正十一烷；所述高级醇类包括正辛醇；所述高级醚类包括正己基醚。

所述可将目标物质从采样器中溶解出来的溶剂为甲醇、甲苯或正己烷。

所述脂质为动物油或植物油。所述动物油为鱼油，所述植物油为菜籽油。

本发明可以用于富集环境样品（如水和沉积物）和生物样品（如血清）的目标物质，与现有的被动采样方法相比，本发明主要有以下优点：

1. 高效率，由于采用了中空纤维支载液膜，当使用壁厚较小（如 30 微米）

的中空纤维膜作为支载体时即可得到很薄（如30微米）的采样相液膜，获得很高的萃取富集速率，大大缩短达到平衡所需要的时间；

2. 微型化，采用本发明的方法，制备得到的中空纤维膜壁中的脂质或非水溶性有机溶剂体积仅数十纳升，从而大大减少了进行非耗尽性（non-depletion）采样所需的样品体积；
3. 灵活性，可以根据研究目的和目标物的性质选择非水溶性有机溶剂、动物脂肪或植物油；
4. 低成本，本发明的方法中采用的中空纤维膜（如聚丙烯中空纤维膜）和脂质或非水溶性有机溶剂（如正辛醇）均为价格便宜的商品化材料，制作成本低，可供一次性使用。

#### 附图说明

图1为使用本发明的方法进行被动采样的示意图。

其中，1为样品液，2为中空纤维支载液膜被动采样器，3为中空纤维膜壁，4为填充于膜壁微孔中的脂质或非水溶性有机溶剂所形成的薄液膜。

#### 具体实施方式

下面结合实施例，对本发明的采样方法做进一步的详细描述，但本发明不限于这些实施例：

#### 实施例 1

如图1所示，采用本发明提供的方法采集环境水样1中的双酚A，具体步骤如下：

- (1) 将经裁剪的5mm长度聚丙烯中空纤维膜段的内腔中充满水；
- (2) 在正辛醇中将内腔中充满水的聚丙烯中空纤维膜段浸泡5秒，使聚丙烯中空纤维膜段的膜壁上的微孔中充满正辛醇，形成中空纤维支载液膜被动采样器2；
- (3) 将中空纤维支载液膜被动采样器2由正辛醇中取出，并置于水中清洗，去除其表面吸附的过剩的正辛醇；

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- (4) 在待取样的样品液 1 中将经清洗后的中空纤维支载液膜被动采样器 2 浸没 20 分钟，完成采样；
  - (5) 将所述中空纤维支载液膜被动采样器 2 取出，并清除其外表面的颗粒物；
  - (6) 然后将中空纤维支载液膜被动采样器浸没在盛有 30 微升甲醇的小瓶中并密闭，使采集于中空纤维支载液膜被动采样器 2 中的双酚 A 定量解析到甲醇中。

本实施例中，中空纤维膜壁 3 中，正辛醇液膜 4 薄 30 微米，其体积仅 60 纳升，对本实施例的方法进行了反复测试，具有很好的稳定性，其相对标准偏差为 4~10%（三次重复测定），本实施例中制备的聚丙烯中空纤维支载液膜被动采样器对于双酚 A 的采样平衡时间为 16 min，而 SPME 的采样平衡时间一般为 260 min，故本实施例的采样器萃取采样效率比 SPME 被动采样器高 16 倍。

#### 实施例 2

本实施例中，所述疏水性中空纤维膜选用 5mm 聚偏氟乙烯中空纤维膜段，所述非水溶性有机溶剂选用正十一烷，内腔中充满水的聚偏氟乙烯中空纤维膜段在正十一烷中浸泡 60 秒，所述目标物质为环境水样中的壬基酚，中空纤维支载液膜被动采样器在环境水样中浸没 1 天，所述能够将目标物质从采样器中溶解出来的溶剂选用正己烷，其他与实施例 1 相同。

#### 实施例 3

本实施例中，所述疏水性中空纤维膜选用 5mm 聚四氟乙烯中空纤维膜段，所述非水溶性有机溶剂选用正己基醚，内腔中充满水的聚四氟乙烯中空纤维膜段在正己基醚中浸泡 30 秒，所述目标物质为环境水样中的壬基酚，中空纤维支载液膜被动采样器在环境水样中浸没 2 天，其他与实施例 1 相同。

#### 实施例 4

采用本发明提供的方法采集环境水样中的多环芳烃，具体步骤如下：

- (1) 将经裁剪的 5mm 长度聚四氟乙烯中空纤维膜段的内腔中充满水；

- (2) 在鱼油中将内腔中充满水的聚四氟乙烯中空纤维膜段浸泡 15 秒，使聚四氟乙烯中空纤维膜段的膜壁上的微孔中充满鱼油，形成中空纤维支载液膜被动采样器；
- (3) 将中空纤维支载液膜被动采样器由鱼油中取出，并置于水中清洗，去除其表面吸附的过剩的鱼油；
- (4) 在待取样的样品液中将经清洗后的中空纤维支载液膜被动采样器浸没 5 天，完成采样；
- (5) 将所述中空纤维支载液膜被动采样器取出，并清除其外表面的颗粒物；
- (6) 然后将中空纤维支载液膜被动采样器浸没在盛有 50 微升甲苯的小瓶中并密闭，使采集于中空纤维支载液膜被动采样器中的壬基酚定量解析到甲苯中。

#### 实施例 5

本实施例中，所述疏水性中空纤维膜选用 5mm 聚四氟乙烯中空纤维膜段，所述脂质选用菜籽油，内腔中充满水的聚四氟乙烯中空纤维膜段在菜籽油中浸泡 45 秒，所述目标物质为环境水样中的多环芳烃，中空纤维支载液膜被动采样器在环境水样中浸没 5 天，其他与实施例 4 相同。

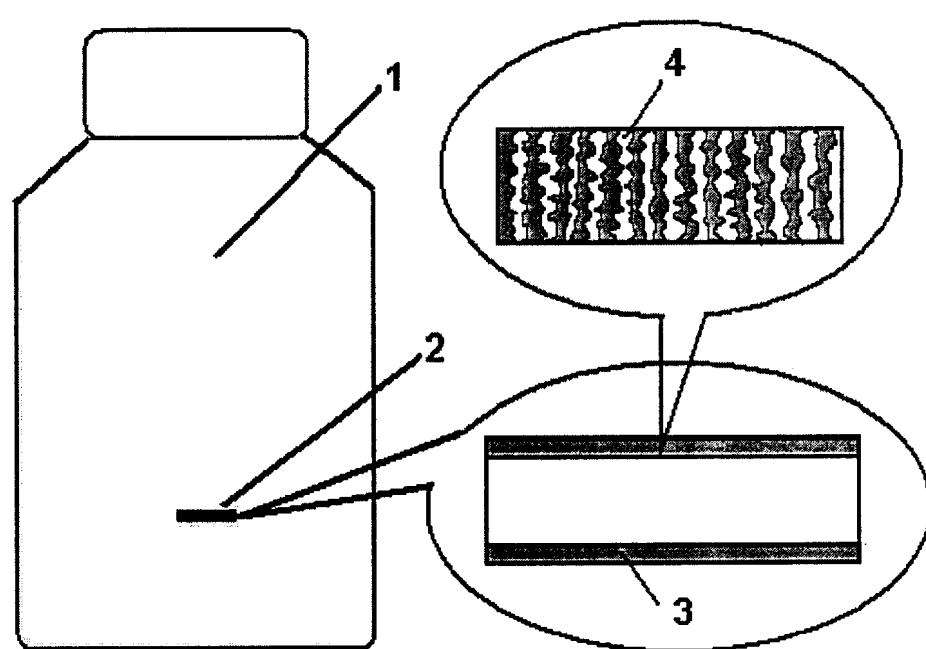


图 1

## Notice

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## DESCRIPTION CN101097214A

*10* A Passive Sampling Method

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*12* 一种被动采样方法

[0001]

*18* technical field

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*20* 技术领域

[0002]

*26* The invention relates to a passive sampling method, in particular to a passive sampling method for a liquid membrane supported by a hollow fiber.

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*29* 本发明涉及一种被动采样方法，特别是涉及一种中空纤维支载液膜被动采样方法。

[0003]

*35* Background technique

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*37* 背景技术

## [0004]

<sup>43</sup> The background and development status of this technical field are roughly as follows: J.N.Huckins and others first packed lipids in low-density polyethylene film bags as passive samplers for monitoring hydrophobic organic pollutants, and they named the technology semi-permeable membranes Sampling device (hereinafter referred to as SPMD).

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<sup>48</sup> 本技术领域的背景和发展现状大致如下：J.N.Huckins等首次将脂质装在低密度聚乙烯膜袋中作为被动采样器，用于监测疏水性有机污染物，他们将该技术命名为半透膜采样装置(以下简称SPMD)。

<sup>53</sup> Davison et al. invented the diffusion gradient film (hereinafter referred to as DGT) technology, which is used to collect biologically effective metal ions and certain inorganic anions. These two passive samplers are larger in size, larger in sampling phase volume and enrichment multiple, and require a larger sample volume and a long time to reach equilibrium, and are generally used for dynamic sampling that is far from equilibrium.

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<sup>58</sup> Davison等发明了扩散梯度薄膜(以下简称DGT)技术，用于采集具有生物有效性的金属离子和某些无机阴离子。这两种被动采样器尺寸较大，采样相体积和富集倍数较大，需要较大的样品体积和很长的时间才能够达到平衡，一般用于远未达到平衡的动态采样。

## [0005]

<sup>66</sup> In order to overcome the shortcomings of SPMD and DGT, people apply solid-phase microextraction (hereinafter referred to as SPME) to collect hydrophobic organic pollutants again, as Hermens et al. in the literature: Trends Anal.

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<sup>70</sup> 为了克服SPMD和DGT的缺点，人们又将固相微萃取(以下简称SPME)应用于采集疏水性有机污染物，如Hermens等人在文献：Trends Anal.

<sup>74</sup> As described in Chem.2003, 22, 575-587, the target pollutants in the environmental medium are enriched on the polymer-coated quartz fiber, and then directly inserted into the gas chromatography inlet for thermal analysis, separation and determination. SPME has been successfully used to determine pollutants such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and chlorinated benzenes in soil and sediment pore water (pore water), and its enrichment factor is as high as  $2.5 \times 10^6$ . Since the coating of SPME is very thin and the volume is extremely small (submicron upgrade), the equilibration time required for sampling is

short and the sample volume is small, so this technology can be used for dynamic sampling far from equilibrium, and for equilibrium Sampling has a good application prospect. Unfortunately, the SPME coating used as the sampling phase is generally a solid or high-viscosity liquid polymer, and the diffusion rate of target molecules in it is relatively slow, so its sampling enrichment rate is still relatively slow; in addition, SPME and high-efficiency The combined technology of liquid chromatography (hereinafter referred to as HPLC) is not yet mature enough, and there are still some technical problems to be solved for the matching of the two.

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<sup>87</sup> Chem.2003 , 22 , 575-587中所述，将环境介质中的目标污染物富集于有聚合物涂层的石英纤维上，再直接插入气相色谱进样口进行热解析、分离和测定。SPME已成功地用于测定土壤和沉积物的孔隙水(pore water)中的多氯联苯、多环芳烃和氯代苯等污染物，其富集倍数高达 $2.5 \times 10^6$ 。由于SPME的涂层很薄且体积极小(亚微升级)，采样所需要的平衡时间较短且样品体积小，故该技术既可以用于远未达到平衡的动态采样，又可以用于平衡采样，具有很好的应用前景。遗憾的是，作为采样相的SPME的涂层一般为固态或者高粘度的液态高聚物，目标分子在其中的扩散速度较慢，故其采样富集速度依然相对较慢；另外，SPME与高效液相色谱(以下简称HPLC)的联用技术还不够成熟，二者匹配使用还有一些技术问题待解决。

## [0006]

<sup>100</sup> Contents of the invention

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<sup>102</sup> 发明内容

## [0007]

<sup>108</sup> The purpose of the present invention is in order to overcome the above-mentioned defective of existing passive sampling method, thereby provide a kind of passive sampling method that has very high sampling rate and can be used conveniently with HPLC, good stability and repeatability.

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<sup>112</sup> 本发明的目的是为了克服上述现有的被动采样方法的缺陷，从而提供一种有很高采样速率且能够方便与HPLC联用、稳定性和重复性好的被动采样方法。

## [0008]

<sup>119</sup> Technical scheme of the present invention is as follows:

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<sup>121</sup> 本发明的技术方案如下：

[0009]

<sup>127</sup> The hollow fiber liquid membrane passive sampling method provided by the invention comprises the following steps:

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<sup>130</sup> 本发明提供的中空纤维液膜被动采样方法，包括以下步骤：

[0010]

<sup>131</sup> 1. Fill the cavity of the cut hydrophobic hollow fiber membrane segment with water;

---

<sup>138</sup> 1、将经裁剪的疏水性中空纤维膜段的内腔中充满水；

[0011]

<sup>144</sup> 2. Soak the hydrophobic hollow fiber membrane section filled with water in the inner cavity in lipid or water-insoluble organic solvent, so that the micropores on the membrane wall of the hydrophobic hollow fiber membrane section are filled with lipid or water-insoluble organic solvent. Solvent, forming a hollow fiber supported liquid membrane passive sampler;

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<sup>149</sup> 2、将内腔中充满水的疏水性中空纤维膜段浸泡在脂质或非水溶性有机溶剂中，使疏水性中空纤维膜段的膜壁上的微孔中充满脂质或非水溶性有机溶剂，形成中空纤维支载液膜被动采样器；

[0012]

<sup>156</sup> 3. Take the hollow fiber-supported liquid membrane passive sampler out of the lipid or water-insoluble organic solvent, and wash it in water to remove excess lipid or water-insoluble organic solvent adsorbed on its surface;

---

<sup>160</sup> 3、将中空纤维支载液膜被动采样器由所述脂质或非水溶性有机溶剂取出，并置于水中清洗，去除其表面吸附的过剩脂质或非水溶性有机溶剂；

[0013]

<sup>167</sup> 4. Immerse the cleaned hollow fiber supported liquid membrane passive sampler in the sample solution to be sampled for 20 minutes to 5 days;

---

<sup>170</sup> 4、将经清洗后的中空纤维支载液膜被动采样器浸没在待取样的样品液中20分钟~5天；

[0014]

<sup>176</sup> 5. Take out the hollow fiber-supported liquid membrane passive sampler and remove the particles on its outer surface;

---

<sup>179</sup> 5、将中空纤维支载液膜被动采样器取出，并清除其外表面的颗粒物；

[0015]

<sup>185</sup> 6. Submerge the hollow fiber-supported liquid membrane passive sampler in a closed container containing a solvent that can dissolve the target substance from the sampler, and make the target collected in the hollow fiber-supported liquid membrane passive sampler The substance is quantitatively resolved into the solvent and the sampling is completed.

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<sup>190</sup> 6、再将中空纤维支载液膜被动采样器浸没在盛有可将目标物质从采样器中溶解出来的溶剂的密闭容器中，并使采集于中空纤维支载液膜被动采样器中的目标物质定量解析到所述溶剂中，完成采样。

[0016]

<sup>198</sup> The hydrophobic hollow fiber membrane is polypropylene membrane, polyvinylidene fluoride membrane or polytetrafluoroethylene membrane.

---

<sup>201</sup> 所述疏水性中空纤维膜为聚丙烯膜、聚偏氟乙烯膜或聚四氟乙烯膜。

[0017]

<sup>207</sup> The non-water-miscible organic solvent is higher alkanes, higher alcohols or higher ethers.

---

<sup>209</sup> 所述非水溶性有机溶剂为高级烷烃、高级醇类或高级醚类。

[0018]

<sup>215</sup> The higher alkanes are n-undecane; the higher alcohols include n-octanol; and the higher ethers include n-hexyl ether.

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<sup>218</sup> 所述高级烷烃为正十一烷；所述高级醇类包括正辛醇；所述高级醚类包括正己基醚。

[0019]

<sup>224</sup> The solvent capable of dissolving the target substance from the sampler is methanol, toluene or n-hexane.

---

<sup>226</sup> 所述可将目标物质从采样器中溶解出来的溶剂为甲醇、甲苯或正己烷。

[0020]

<sup>232</sup> The lipid is animal oil or vegetable oil.

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<sup>234</sup> 所述脂质为动物油或植物油。

<sup>237</sup> The animal oil is fish oil, and the vegetable oil is rapeseed oil.

---

<sup>239</sup> 所述动物油为鱼油，所述植物油为菜籽油。

[0021]

<sup>245</sup> The present invention can be used for enriching the target substance of environmental sample (as water and sediment) and biological sample (as serum), compared with existing passive sampling method, the present invention mainly has the following advantages:

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<sup>249</sup>本发明可以用于富集环境样品(如水和沉积物)和生物样品(如血清)的目标物质，与现有的被动采样方法相比，本发明主要有以下优点：

[0022]

<sup>256</sup>1.

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<sup>258</sup>1.

<sup>261</sup>High efficiency, due to the use of the hollow fiber supporting liquid membrane, when using the hollow fiber membrane with a small wall thickness (such as 30 microns) as the supporting carrier, a very thin (such as 30 microns) sampling phase liquid film can be obtained, and a very High extraction and enrichment rate greatly shortens the time required to reach equilibrium;

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<sup>266</sup>高效率，由于采用了中空纤维支载液膜，当使用壁厚较小(如30微米)的中空纤维膜作为支载体时即可得到很薄(如30微米)的采样相液膜，获得很高的萃取富集速率，大大缩短达到平衡所需要的时间；

[0023]

<sup>274</sup>2.

---

<sup>276</sup>2.

<sup>279</sup>Miniaturization, adopting the method of the present invention, the volume of the lipid or water-insoluble organic solvent in the prepared hollow fiber membrane wall is only tens of nanoliters, thereby greatly reducing the need for non-depletion (non-depletion) sampling. the sample volume;

---

<sup>283</sup>微型化，采用本发明的方法，制备得到的中空纤维膜壁中的脂质或非水溶性有机溶剂体积仅数十纳升，从而大大减少了进行非耗尽性(non-depletion)采样所需的样品体积；

[0024]

290 3.

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292 3.

295 Flexibility, you can choose non-water-soluble organic solvents, animal fats or vegetable oils according to the research purpose and the nature of the target;

---

298 灵活性，可以根据研究目的和目标物的性质选择非水溶性有机溶剂、动物脂肪或植物油；

[0025]

304 4.

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306 4.

309 Low cost, the hollow fiber membranes (such as polypropylene hollow fiber membranes) and lipids or water-insoluble organic solvents (such as n-octanol) adopted in the method of the present invention are all cheap commercial materials, the production cost is low, and can be used for one-time use.

---

313 低成本，本发明的方法中采用的中空纤维膜(如聚丙烯中空纤维膜)和脂质或非水溶性有机溶剂(如正辛醇)均为价格便宜的商品化材料，制作成本低，可供一次性使用。

[0026]

320 Description of drawings

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322 附图说明

[0027]

328 Fig. 1 is a schematic diagram of passive sampling using the method of the present invention.

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330 图1为使用本发明的方法进行被动采样的示意图。

[0028]

<sup>336</sup> Among them, 1 is the sample liquid, 2 is the hollow fiber supported liquid membrane passive sampler, 3 is the hollow fiber membrane wall, and 4 is the thin liquid film formed by the lipid or non-water-soluble organic solvent filled in the micropores of the membrane wall .

---

<sup>340</sup> 其中，1为样品液，2为中空纤维支载液膜被动采样器，3为中空纤维膜壁，4为填充于膜壁微孔中的脂质或非水溶性有机溶剂所形成的薄液膜。

[0029]

<sup>347</sup> Detailed ways

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<sup>349</sup> 具体实施方式

[0030]

<sup>355</sup> Below in conjunction with embodiment, sampling method of the present invention is described in further detail, but the present invention is not limited to these embodiments:

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<sup>358</sup> 下面结合实施例，对本发明的采样方法做进一步的详细描述，但本发明不限于这些实施例：

[0031]

<sup>364</sup> Example 1

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<sup>366</sup> 实施例1

[0032]

<sup>372</sup> As shown in Figure 1, the bisphenol A in the environmental water sample 1 is collected by the method provided by the invention, and the specific steps are as follows:

---

375 如图1所示，采用本发明提供的方法采集环境水样1中的双酚A，具体步骤如下：

[0033]

381 (1) Fill the inner cavity of the cut 5mm length polypropylene hollow fiber membrane section with water;

---

383 (1) 将经裁剪的5mm长度聚丙烯中空纤维膜段的内腔中充满水；

[0034]

389 (2) Soak the polypropylene hollow fiber membrane section filled with water in the inner cavity for 5 seconds in n-octanol, so that the micropores on the membrane wall of the polypropylene hollow fiber membrane section are filled with n-octanol to form a hollow fiber support Liquid film passive sampler 2;

---

393 (2) 在正辛醇中将内腔中充满水的聚丙烯中空纤维膜段浸泡5秒，使聚丙烯中空纤维膜段的膜壁上的微孔中充满正辛醇，形成中空纤维支载液膜被动采样器2；

[0035]

400 (3) The hollow fiber-supported liquid membrane passive sampler 2 is taken out from n-octanol, and placed in water for cleaning to remove excess n-octanol adsorbed on its surface;

---

403 (3) 将中空纤维支载液膜被动采样器2由正辛醇中取出，并置于水中清洗，去除其表面吸附的过剩的正辛醇；

[0036]

410 (4) Submerge the cleaned hollow fiber supported liquid membrane passive sampler 2 in the sample solution 1 to be sampled for 20 minutes to complete the sampling;

---

413 (4) 在待取样的样品液1中将经清洗后的中空纤维支载液膜被动采样器2浸没20分钟，完成采样；

[0037]

419 (5) Take out the passive sampler 2 supported by the hollow fiber supported liquid membrane, and remove the particles on its outer surface;

---

422 (5) 将所述中空纤维支载液膜被动采样器2取出，并清除其外表面的颗粒物；

[0038]

428 (6) The hollow fiber supported liquid membrane passive sampler is then submerged in a vial filled with 30 microliters of methanol and airtight, so that the bisphenol A collected in the hollow fiber supported liquid membrane passive sampler 2 is quantitatively resolved to methanol middle.

---

432 (6) 然后将中空纤维支载液膜被动采样器浸没在盛有30微升甲醇的小瓶中并密闭，使采集于中空纤维支载液膜被动采样器2中的双酚A定量解析到甲醇中。

[0039]

439 In the present embodiment, in the hollow fiber membrane wall 3, the n-octanol liquid membrane 4 is 30 microns thinner, and its volume is only 60 nanoliters. The method of the present embodiment has been repeatedly tested and has good stability, and its relative standard deviation It is 4 ~ 10% (repeated determination three times), the polypropylene hollow fiber supported liquid membrane passive sampler prepared in the present embodiment is 16min for the sampling equilibrium time of bisphenol A, and the sampling equilibrium time of SPME is generally 260min, so The extraction and sampling efficiency of the sampler of this embodiment is 16 times higher than that of the SPME passive sampler.

---

447 本实施例中，中空纤维膜壁3中，正辛醇液膜4薄30微米，其体积仅60纳升，对本实施例的方法进行了反复测试，具有很好的稳定性，其相对标准偏差为4~10%（三次重复测定），本实施例中制备的聚丙烯中空纤维支载液膜被动采样器对于双酚A的采样平衡时间为16min，而SPME的采样平衡时间一般为260min，故本实施例的采样器萃取采样效率比SPME被动采样器高16倍。

[0040]

456 Example 2

---

[0041]

464 In this embodiment, the hydrophobic hollow fiber membrane is selected from a 5 mm polyvinylidene fluoride hollow fiber membrane section, the water-insoluble organic solvent is selected from n-undecane, and the polyvinylidene fluoride hollow fiber membrane section filled with water in the inner cavity Soak in n-undecane for 60 seconds, the target substance is nonylphenol in the environmental water sample, the hollow fiber supported liquid membrane passive sampler is immersed in the environmental water sample for 1 day, and the target substance can be sampled from The solvent that dissolves out in the device selects normal hexane, and others are identical with embodiment 1.

---

472 本实施例中，所述疏水性中空纤维膜选用5mm聚偏氟乙烯中空纤维膜段，所述非水溶性有机溶剂选用正十一烷，内腔中充满水的聚偏氟乙烯中空纤维膜段在正十一烷中浸泡60秒，所述目标物质为环境水样中的壬基酚，中空纤维支载液膜被动采样器在环境水样中浸没1天，所述能够将目标物质从采样器中溶解出来的溶剂选用正己烷，其他与实施例1相同。

[0042]

481 Example 3

---

483 实施例3

[0043]

489 In this embodiment, the hydrophobic hollow fiber membrane is selected from a 5mm polytetrafluoroethylene hollow fiber membrane section, the water-insoluble organic solvent is selected from n-hexyl ether, and the polytetrafluoroethylene hollow fiber membrane section filled with water in the inner cavity is Soak in n-hexyl ether for 30 seconds, the target substance is nonylphenol in the environmental water sample, the hollow fiber supported liquid membrane passive sampler is immersed in the environmental water sample for 2 days, the other is the same as in Example 1.

---

496 本实施例中，所述疏水性中空纤维膜选用5mm聚四氟乙烯中空纤维膜段，所述非水溶性有机溶剂选用正己基醚，内腔中充满水的聚四氟乙烯中空纤维膜段在正己基醚中浸泡30秒，所述目标物质为环境水样中的壬基酚，中空纤维支载液膜被动采样器在环境水样中浸没2天，其他与实施例1相同。

[0044]

505 Example 4

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507 实施例4

[0045]

513 Using the method provided by the invention to collect polycyclic aromatic hydrocarbons in environmental water samples, the specific steps are as follows:

---

516 采用本发明提供的方法采集环境水样中的多环芳烃，具体步骤如下：

[0046]

522 (1) Fill the inner cavity of the cut 5mm length polytetrafluoroethylene hollow fiber membrane section with water;

---

525 (1) 将经裁剪的5mm长度聚四氟乙烯中空纤维膜段的内腔中充满水；

[0047]

531 (2) Soak the polytetrafluoroethylene hollow fiber membrane section filled with water in the inner cavity for 15 seconds in fish oil, so that the micropores on the membrane wall of the polytetrafluoroethylene hollow fiber membrane section are filled with fish oil to form a hollow fiber support Liquid film passive sampler;

---

535 (2) 在鱼油中将内腔中充满水的聚四氟乙烯中空纤维膜段浸泡15秒，使聚四氟乙烯中空纤维膜段的膜壁上的微孔中充满鱼油，形成中空纤维支载液膜被动采样器；

[0048]

542 (3) The hollow fiber supported liquid membrane passive sampler is taken out from the fish oil, and placed in water for cleaning to remove excess fish oil adsorbed on its surface;

---

545 (3) 将中空纤维支载液膜被动采样器由鱼油中取出，并置于水中清洗，去除其表面吸附的过剩的鱼油；

[0049]

552 (4) immerse the cleaned hollow fiber supported liquid membrane passive sampler in the sample liquid to be sampled for 5 days to complete the sampling;

---

555 (4) 在待取样的样品液中将经清洗后的中空纤维支载液膜被动采样器浸没5天，完成采样；

[0050]

561 (5) Take out the passive sampler of the hollow fiber supported liquid membrane, and remove the particles on its outer surface;

---

564 (5) 将所述中空纤维支载液膜被动采样器取出，并清除其外表面的颗粒物；

[0051]

570 (6) The hollow fiber supported liquid membrane passive sampler is then submerged in a vial filled with 50 microliters of toluene and sealed, so that the nonylphenol collected in the hollow fiber supported liquid membrane passive sampler is quantitatively resolved into toluene .

---

574 (6) 然后将中空纤维支载液膜被动采样器浸没在盛有50微升甲苯的小瓶中并密闭，使采集于中空纤维支载液膜被动采样器中的壬基酚定量解析到甲苯中。

[0052]

581 Example 5

---

583 实施例5

[0053]

<sup>589</sup> In this embodiment, the hydrophobic hollow fiber membrane is selected from a 5 mm polytetrafluoroethylene hollow fiber membrane section, the lipid is selected from rapeseed oil, and the polytetrafluoroethylene hollow fiber membrane section filled with water in the inner cavity is prepared from rapeseed oil. Soak in the water for 45 seconds, the target substance is polycyclic aromatic hydrocarbons in the environmental water sample, the hollow fiber supported liquid membrane passive sampler is immersed in the environmental water sample for 5 days, and the others are the same as in Example 4.

---

<sup>590</sup> 本实施例中，所述疏水性中空纤维膜选用5mm聚四氟乙烯中空纤维膜段，所述脂质选用菜籽油，内腔中充满水的聚四氟乙烯中空纤维膜段在菜籽油中浸泡45秒，所述目标物质为环境水样中的多环芳烃，中空纤维支载液膜被动采样器在环境水样中浸没5天，其他与实施例4相同。



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# United States Patent [19]

## Vroblesky et al.

[11] Patent Number: 5,804,743  
[45] Date of Patent: Sep. 8, 1998

[54] **DOWNHOLE PASSIVE WATER SAMPLER AND METHOD OF SAMPLING**

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[21] Appl. No.: **700,047**

[22] Filed: **Aug. 20, 1996**

[51] Int. Cl.<sup>6</sup> ..... **E21B 49/08**

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[58] Field of Search ..... **73/863.23, 864.51, 73/64.56, 19.12; 166/264**

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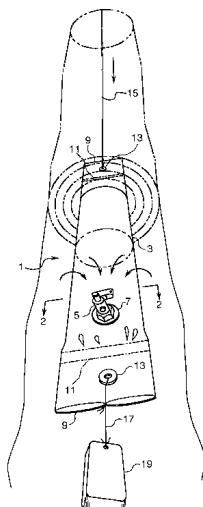
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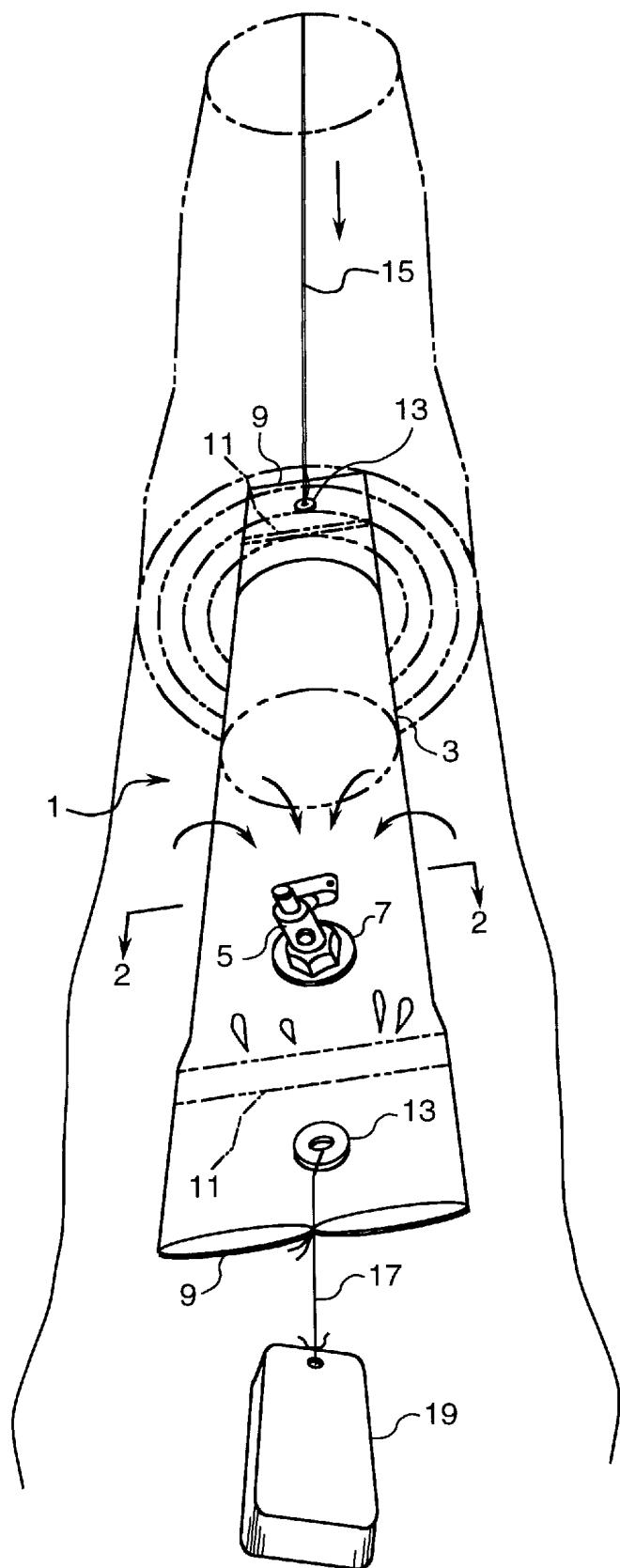
Primary Examiner—Thomas P. Noland  
Attorney, Agent, or Firm—James Magee, Jr.; Douglas E. Stoner

[57] **ABSTRACT**

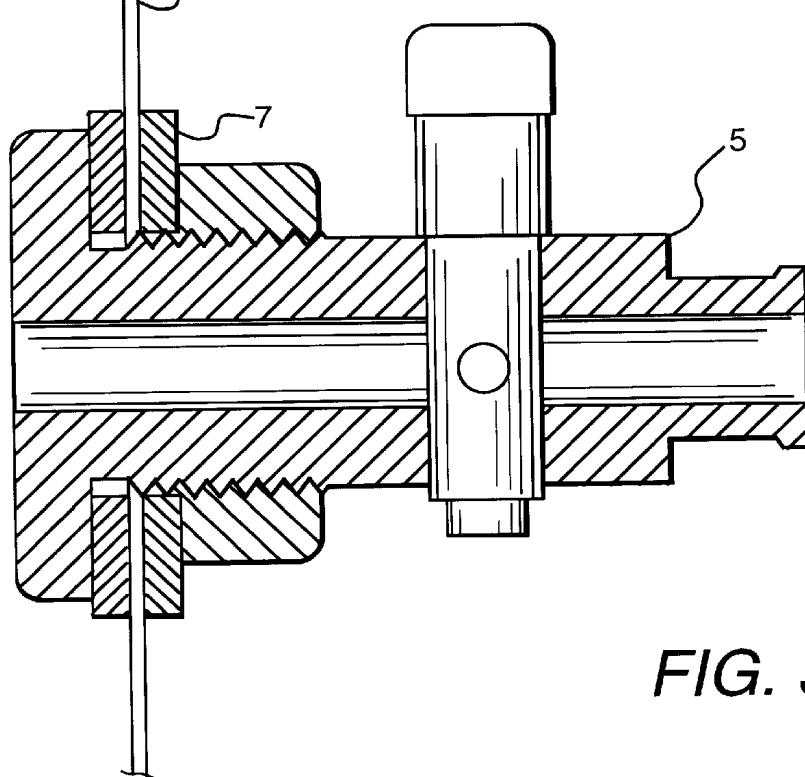
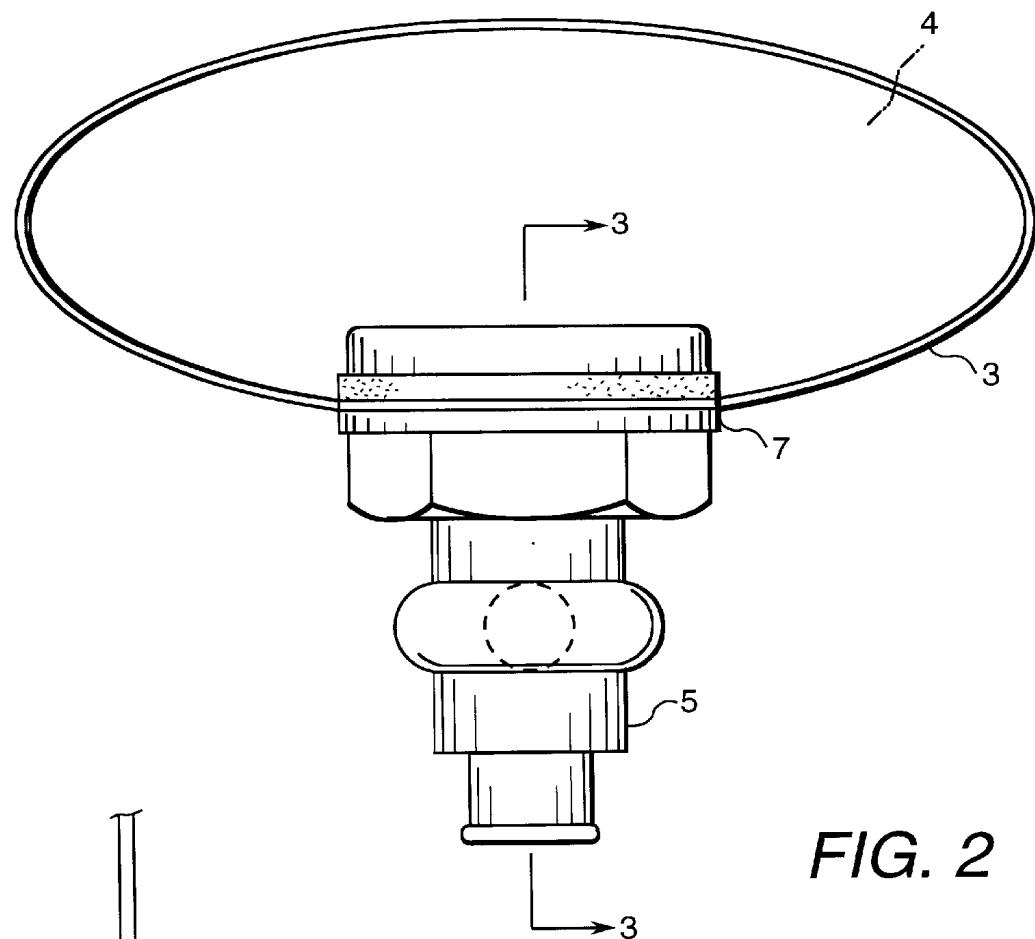
An improved method and apparatus for monitoring the concentration of contaminants, including volatile organic compounds, in groundwater is provided comprising a semipermeable membrane defining an inner chamber therein. The membrane is permeable to contaminants but impermeable to a reference fluid, which is preferably distilled water. The method of sampling comprises placing the semipermeable membrane, which contains the reference fluid, in contact with contaminated groundwater, thereby allowing contaminants to diffuse through the semipermeable membrane and into the inner chamber. Sufficient time is allowed for the contaminant concentrations in the groundwater and in the reference fluid to reach equilibrium. The semipermeable membrane is then removed from contact with the groundwater, and a sample withdrawn from the inner chamber for analysis, preferably through a port communicating with the inner chamber.

**20 Claims, 3 Drawing Sheets**





*FIG. 1*



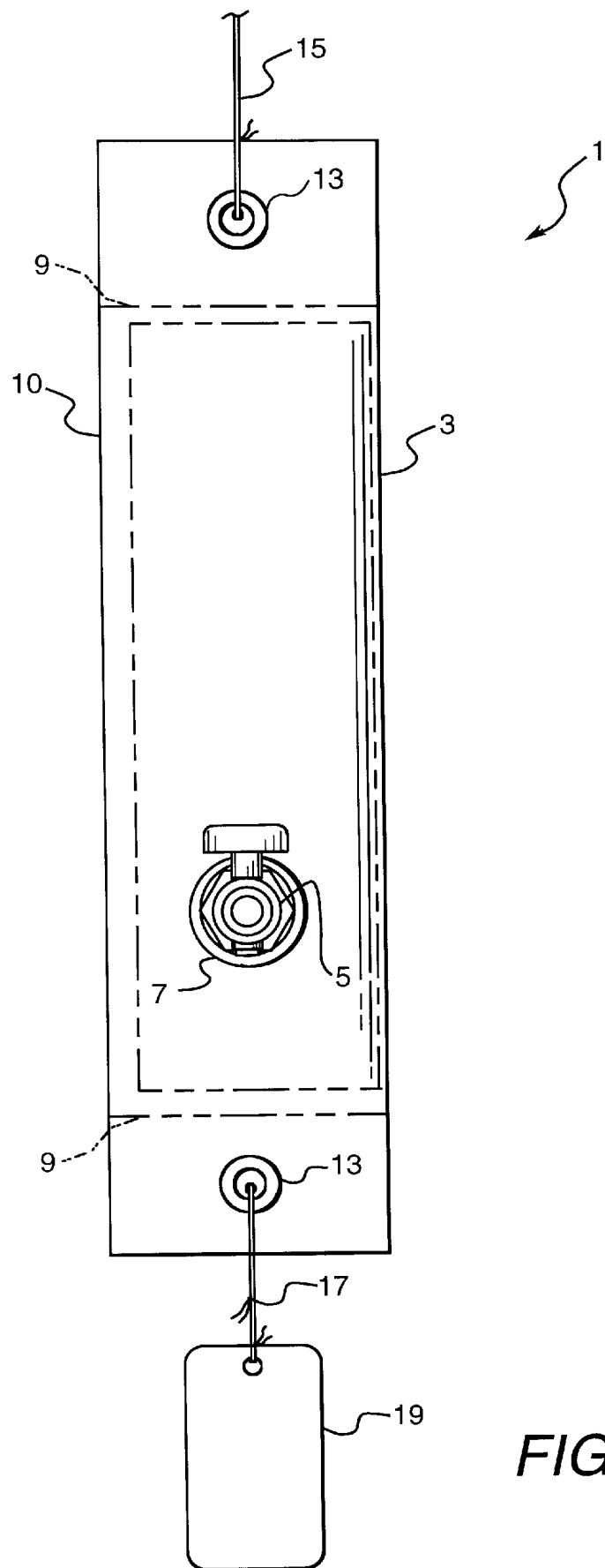


FIG. 4

**1****DOWNHOLE PASSIVE WATER SAMPLER  
AND METHOD OF SAMPLING****BACKGROUND OF THE INVENTION**

This invention relates generally to a liquid sampling device, and more particularly to an improved method and apparatus for monitoring the concentration of contaminants, including volatile organic compounds, in groundwater.

Various devices exist for sampling a liquid. DMLS™ is a passive, multi-layer sampling device which is used to extract groundwater samples. DMLS™ is comprised of a rod (or connector rods) with apertures at specific intervals to accommodate dialysis cells. Contaminants enter the dialysis cells by diffusion.

U.S. Pat. No. 5,454,275 to Kabis discloses a groundwater sampler which makes use of pressure differentials that result during sampling. U.S. Pat. No. 5,147,561 to Burge et al. teaches a sampling device containing a stripping chamber for stripping a groundwater sample of its volatile components at or near the point of collection. U.S. Pat. No. 4,078,433 to McCabe, Jr. et al. discloses a liquid sampling device comprising a length of pipe having a cap screwed onto each end thereof. The upper cap has an aperture for admitting the liquid to be sampled into the pipe.

Despite the prior art devices, there is much room for improvement in the art of groundwater sampling.

**SUMMARY OF THE INVENTION**

It is therefore an object of this invention to provide an improved method and apparatus for sampling groundwater.

It is another object of this invention to provide an improved method and apparatus for sampling groundwater that does not require the purging of a well.

It is another object of this invention to provide an improved method and apparatus for sampling groundwater that can be used subaqueously.

It is yet another object of this invention to provide an improved method and apparatus for sampling groundwater that precludes the need for an organic-carbon sorbent.

It is yet another object of this invention to provide an improved method and apparatus for sampling groundwater that precludes the need for dialysis cells.

It is still another object of this invention to provide an improved method and apparatus for sampling groundwater that utilizes water as a carrier for volatile organic compounds and other contaminants.

It is still another object of this invention to provide an improved method and apparatus for sampling groundwater that is both economical and environmentally friendly.

It is still a further object of this invention to provide an improved method and apparatus for sampling groundwater that is easy to construct and use.

These and other objects of the invention are achieved by a passive water sampler comprising: a semipermeable membrane, the semipermeable membrane being permeable to contaminants and impermeable to a reference fluid; the semipermeable membrane defining an inner chamber herein; and the inner chamber being at least partially filled with the reference fluid, the partially filled semipermeable membrane being placed in contact with the groundwater thereby allowing the contaminants to diffuse through the semipermeable membrane and into the inner chamber, the concentrations of the contaminants in the groundwater and in the reference fluid coming into equilibrium.

**2****BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a front elevational view of a preferred embodiment of the present invention.

5 FIG. 2 is a cross-sectional plan view of a preferred embodiment of the present invention taken along line 2—2 of FIG. 1.

FIG. 3 is a side view of a port suitable for use in a preferred embodiment of the present invention.

10 FIG. 4 is a front elevational view of an alternative embodiment of the present invention.

**DETAILED DESCRIPTION**

The method and apparatus according to this invention can be used to monitor the concentrations of volatile organic compounds (VOCs) and other contaminants in groundwater without the need to purge a well. Purging a well is presently a regulatory requirement if samples are to be withdrawn from the well, and is a large part of the expense associated with routine monitoring of groundwater contamination. Regulatory agencies typically require removal of at least three casing volumes of water prior to sampling. The large number of observation wells typically sampled at groundwater contamination sites results in a large volume of contaminated purge water that must be disposed of. Thus, sampling costs are incurred that include not only personnel time, but also the proper transport and disposal of the contaminated purge water. These costs can be substantial when multiplied over the lifetime of the contamination. Moreover, the costs associated with remediation and monitoring of existing groundwater contamination must be factored in as a loss when the market value of particular businesses are calculated. The method and apparatus of sampling according to the present invention eliminates the need to purge wells, thus resulting in a substantial cost savings as well as an increased corporate value. Also, the absence of purging makes the present invention environmentally friendly.

40 Furthermore, the method and apparatus according to the present invention precludes the need for using either dialysis cells or an organic-carbon sorbent. Both of these can be very costly in terms of sampler preparation and analysis. Also, when using a carbon sorbent, the results obtained yield only relative concentrations because the sorbent continues to collect contaminants, including VOCs, as long as the sampler is in the sampling area. Thus, using the sorbent system, the measured contaminant concentration is a function of the time the sampler was in place. On the other hand, the present invention allows the contaminant concentration in the sampler to change in response to fluctuations in contaminant concentrations outside of the sampler, thereby maintaining equilibrium and providing an accurate contaminant concentration in the sampler at any time after equilibrium is reached. Consequently, great flexibility is allowed in the length of time that the present invention can be left in the sampling area.

60 Additionally, the present invention is used subaqueously, thus accomplishing its objectives without requiring the pumping or bailing of water samples from within a well. It has been found that water immediately adjacent to a well screen can be representative of an aquifer without having to purge, and may even be more favorable than samples achieved after purging due to the sampling bias that can result from the purging itself.

Therefore, according to this invention, it has been found that an improved method and apparatus for water sampling

**3**

can be utilized. This and other features of the invention will become apparent from the description that follows with particular reference to the figures of drawing.

Referring to the drawings, FIG. 1 shows a front elevational view of the preferred embodiment of the downhole passive water sampler 1 according to the present invention. Downhole passive water sampler 1 comprises at least semipermeable membrane 3. Semipermeable membrane 3 is constructed to be permeable to contaminants, including VOCs, but impermeable to a reference fluid. The reference fluid employed is preferably distilled water, but may be undistilled water or any other suitable fluid. The use of water simplifies the analytical aspects of the system. Semipermeable membrane 3 can be made from a variety of materials which fit the above-stated criteria, but is preferably made from polyethylene. It is envisioned that other polymers, such as polypropylene, may also be employed. Semipermeable membrane 3 may be manufactured in a wide variety of shapes and sizes depending on the application. Water sampler 1 is relatively small, making it easily transportable.

Semipermeable membrane 3 defines inner chamber 4 therein (FIG. 2). Preferably, semipermeable membrane 3 is provided in the shape of a tube having open ends. In this case, inner chamber 4 is formed by sealing the open ends of the tubes, thus providing a leakage-free inner chamber 4. This sealing may be achieved by: heat sealing, sonic welding, or any other suitable bonding method. FIG. 1 shows the resulting top and bottom seals 11.

Alternatively, semipermeable membrane 3 may be provided as a flat piece. In this case, inner chamber 4 is formed by folding semipermeable membrane 3 over and onto itself, thereby forming one folded edge and three overlapping edges. Next, the three overlapping edges are respectively sealed together, forming top and bottom seals 9 and a side seal 10 (as shown in FIG. 4).

Prior to placing water sampler 1 in contact with contaminated groundwater, inner chamber 4 is at least partially filled with the reference fluid. Preferably, the reference fluid is added to inner chamber 4 through port 5 which communicates with both inner chamber 4 and an area outside of semipermeable membrane 3 (FIG. 3) through hole 6. Other appropriate means for adding or withdrawing fluid that communicates with both inner chamber 4 and an area outside of semipermeable membrane 3 may also be employed. Port 5 is preferably made from TEFLON™, but the material of construction may vary depending on the application. Port 5 can also employ a locking nut. Port 5 is preferably connected to semipermeable membrane 3 by washer 7 in a manner that prevents leakage of the reference fluid from inner chamber 4. Washer 7 is preferably a Viton Washer, but the material of construction may vary depending on the application. Hole 6 can be opened or closed by the turning of handle 8.

Upon placing partially filled semipermeable membrane 3 in contact with contaminated groundwater, the contaminants in the groundwater come into contact with semipermeable membrane 3. The contaminants begin to diffuse through semipermeable membrane 3 and into inner chamber 4. As discussed above, semipermeable membrane 3 is impermeable to the reference fluid contained therein, and thus the reference fluid does not diffuse into the groundwater. Likewise, semipermeable membrane 3 is impermeable to the groundwater itself, and thus only contaminants in the groundwater diffuse into inner chamber 4. Contaminants continue to diffuse into inner chamber 4 until the concentration of contaminants in the reference fluid and the con-

**4**

centration of contaminants in the groundwater reach equilibrium. As discussed above, water sampler 1 may be submerged in a well for great lengths of time without jeopardizing analysis results. This is because, once equilibrium has been reached, any changes in contaminant concentration outside of water sampler 1 are compensated for diffusion of contaminants into or out of inner chamber 4. Thus, equilibrium is consistently maintained. For example, if the concentration of contaminants in the groundwater falls, contaminants will diffuse out of inner chamber 4 and into the groundwater until the contaminant concentrations in the reference fluid and in the groundwater are the same again. Conversely, if the contaminant concentration in the groundwater rises, contaminants will diffuse from the groundwater into inner chamber 4 until the concentrations are the same again.

When water sampler 1 is to be used in a well, as is preferred, it is preferred to attach plastic members 9 to opposite sides of semipermeable membrane 3. Plastic members 9 have grommets 13 therein, grommets 13 being made of plastic, metal, or other suitable material depending on the application. Attached to one of grommets 13 is support line 15. Support line 15 is of suitable length and construction for supporting water sampler 1 while inside a well. Support line 15 may be tied to an above ground portion of the well during sampling. Support line 15 is used to raise water sampler 1 up and out of the well after sampling.

Weight 19 can be hung from the other of grommets 13 either directly or by support line 17 (as shown in FIG. 1). Weight 19 is used to assist in submerging water sampler 1 once it is inside of a well. Weight 19 may be made of a variety of materials and sizes depending on the application. Support lines 15 and 17 may be made from a variety of materials including galvanized steel cable, stainless steel cable, or monofilament line.

Alternatively, a weighted support line can be attached to at least one of grommets 13 for raising and lowering water sampler 1 and to assist in the submerging of water sampler 1.

The method of sampling according to the present invention involves using water sampler 1 in any of its many variations as described above. In the preferred embodiment, inner chamber 4 is first at least partially filled with a reference fluid, preferably distilled water. The reference fluid is preferably added to inner chamber 4 through port 5 communicating therewith. Next, semipermeable membrane 3 is lowered into a well using support line 15. As discussed above, means for submerging water sampler 1 within the groundwater in a well can also be provided.

When the contaminants in the groundwater begin to contact semipermeable membrane 3, they diffuse through semipermeable membrane 3 and into inner chamber 4. After sufficient time, the concentrations of contaminants in the reference fluid and in the groundwater reach equilibrium, as described above.

Once sampling is complete (i.e., once equilibrium has been reached), water sampler 1 is raised up and out of a well using support line 15. A portion of the equilibrium mixture of reference fluid and contaminants within inner chamber 4 can be withdrawn, preferably through port 5, for analysis. Analysis of the sample is carried out by conventional means, for example, through the use of a gas chromatograph. Because the water adjacent to a well screen in an unpurged well is potentially representative of the water in the adjacent aquifer, the concentration of contaminants in the water sampler can be related to the concentration of contaminants in the aquifer at the screened interval.

At each well to be sampled, an initial comparison should be done between the method of sampling according to the present invention and conventional sampling methods. The purpose of this comparison would be to account for potential borehole-specific interferences and to verify that data obtained using the present invention adequately represents data obtained using the standard sampling methodology.

It is thus seen that an improved method and apparatus for sampling groundwater can be utilized. It is also seen that the method and apparatus for water sampling according to this invention does not require purging of a well. It is also seen that the method and apparatus for water sampling according to this invention can be used subaqueously. It is also seen that the method and apparatus according to this invention precludes the need for using costly sorbents or dialysis cells. It is also seen that the method and apparatus according to this invention can utilize water as a carrier for volatile organic compounds and other contaminants. Furthermore, it is seen that the method and apparatus according to the present invention is economical, environmentally friendly, and easy to construct and use.

It is understood that many variations will become apparent to one of ordinary skill in the art upon reading the specification. Such variations are within the spirit and scope of the invention as defined by the following appended claims.

That which is claimed:

**1. A passive water sampler for monitoring the concentration of contaminants in groundwater comprising:**

a semipermeable membrane, said semipermeable membrane being permeable to said contaminants and impermeable to water;

said semipermeable membrane defining an inner chamber therein; and

said inner chamber being at least partially filled with water, said partially filled semipermeable membrane being placed in contact with said groundwater thereby allowing said contaminants to diffuse through said semipermeable membrane and into said inner chamber, the concentrations of said contaminants in said groundwater and in said water coming into equilibrium.

**2. The water sampler according to claim 1 wherein said water is distilled water.**

**3. The water sampler according to claim 1 further comprising a port communicating with said inner chamber, said port for adding or withdrawing water from said inner chamber.**

**4. The water sampler according to claim 3 wherein said port is connected to said semipermeable membrane by a washer.**

**5. The water sampler according to claim 3 wherein said port further comprises a locking nut.**

**6. The water sampler according to claim 3 wherein said port is made of polytetra fluoroethylene.**

**7. The water sampler according to claim 1 wherein said semipermeable membrane is made from polyethylene.**

**8. The water sampler according to claim 1 wherein said semipermeable membrane is provided in generally the shape of a tube having open ends, said open ends being sealed to form said inner chamber.**

**9. The water sampler according to claim 1 wherein said semipermeable membrane is provided as generally a flat piece, said flat semipermeable membrane being folded over and onto itself thereby creating a folded edge and three overlapping edges, said three overlapping edges being respectively sealed together to form said inner chamber.**

**10. The water sampler according to claim 1 further comprising two members attached to opposite sides of said semipermeable membrane, each said member having a grommet therein.**

**11. The water sampler according to claim 10 further comprising a weight hanging from one said grommet and a support line connected to the other said grommet, said weight to assist in submerging said water sampler in a well, said line for supporting said water sampler in said well and for raising said water sampler up and out of said well.**

**12. The water sampler according to claim 10 further comprising a weighted support line attached to at least one of said grommets, said weighted support line to assist in submerging said water sampler in a well, for supporting said water sampler in said well, and for raising and lowering said semipermeable membrane into and out of said well.**

**13. A method for determining the concentration of contaminants in groundwater comprising the steps of:**

providing a semipermeable membrane, said semipermeable membrane being permeable to said contaminants and impermeable to water,

manipulating said semipermeable membrane to define an inner chamber therein;

at least partially filling said inner chamber with said water;

placing said partially filled semipermeable membrane in contact with said groundwater,

allowing said contaminants to diffuse through said semipermeable membrane and into said inner chamber;

allowing sufficient time for the concentrations of said contaminants in said groundwater and in said water to come into equilibrium;

withdrawal at least a portion of said water containing said contaminants from said inner chamber for analysis.

**14. The method according to claim 13 further comprising the step of providing a port communicating with said inner chamber, and wherein said step of at least partially filling said inner chamber with water further comprises passing said water through said port and into said inner chamber, and wherein said step of withdrawing at least a portion of said water containing said contaminants from said inner chamber further comprises passing said contaminants out of said inner chamber through said port.**

**15. The method according to claim 13 wherein said step of at least partially filling said inner chamber with said water further comprises at least partially filling said inner chamber with distilled water.**

**16. The method according to claim 13 wherein said step of providing a semipermeable membrane further comprises providing a semipermeable membrane in the shape of a tube having open ends, and wherein said step of manipulating said semipermeable membrane to define an inner chamber therein further comprises sealing said open ends.**

**17. The method according to claim 13 wherein said step of providing a semipermeable membrane further comprises providing a semipermeable membrane as generally a flat piece, and wherein said step of manipulating said semipermeable membrane to define an inner chamber therein further comprises folding said flat semipermeable membrane over and onto itself, thereby forming a folded edge and three overlapping edges, said three overlapping edges being respectively sealed together.**

**18. The method according to claim 13 wherein said step of placing said partially filled semipermeable membrane in contact with said groundwater further comprises lowering**

said semipermeable membrane into a well, and wherein said step of removing said semipermeable membrane from contact with said groundwater further comprises raising said semipermeable membrane up and out of said well.

19. The method according to claim 18 further comprising the step of hanging a weight from said semipermeable membrane, said weight to assist in submerging said semipermeable membrane in said groundwater within said well.

20. The method according to claim 18 further comprising the step of attaching a weighted support line to said semipermeable membrane, said weighted support line to assist in submerging said semipermeable membrane in said groundwater within said well and for raising and lowering said semipermeable membrane into and out of said well.

\* \* \* \* \*



(12) 实用新型专利

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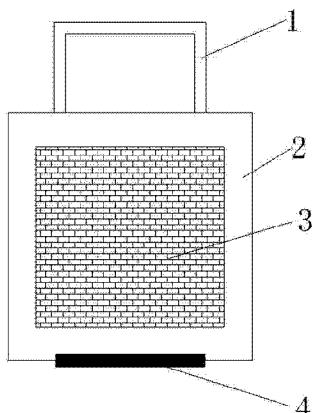
权利要求书1页 说明书2页 附图1页

(54) 实用新型名称

一种持久性有机污染物的被动采样装置

(57) 摘要

本实用新型公开了一种持久性有机污染物的被动采样装置，是由把手、采样材料放置支架和采样材料组成，把手设置在采样材料放置支架上端，采样材料放置支架包括前放置层和后放置层，前放置层与后放置层底端用合页铰接在一起，采样材料放置于采样材料放置支架的前放置层和后放置层之间。采样材料固定于采样材料放置支架内。将整个采样装置插入待分析的水体、沉积物中，静置一定时间后分析采样材料上的持久性有机污染物的含量，便可得到水体、沉积物中有机污染物的含量。能够准确反映出 POPs 在自然环境中的分布情况。



1. 一种持久性有机污染物的被动采样装置,其特征在于:是由把手(1)、采样材料放置支架(2)和采样材料(3)组成,把手(1)设置在采样材料放置支架(2)上端,采样材料放置支架(2)包括前放置层和后放置层,前放置层与后放置层底端用合页(4)铰接在一起,采样材料(3)放置于采样材料放置支架(2)的前放置层和后放置层之间。

2. 根据权利要求1所述的一种持久性有机污染物的被动采样装置,其特征在于:所述的把手(1)为304不锈钢材质。

3. 根据权利要求1所述的一种持久性有机污染物的被动采样装置,其特征在于:所述的采样材料为经过化学药剂处理的半渗透膜。

## 一种持久性有机污染物的被动采样装置

### 技术领域

[0001] 本实用新型涉及环境保护技术领域,特别涉及一种持久性有机污染物的被动采样装置。

### 背景技术

[0002] 持久性有机污染物 POPs 具有长期残留性、生物富集性、半挥发性和高毒性,是当前国际上备受关注的全球环境问题。关于持久性有机污染物在自然水体、沉积物中的迁移转化规律一直是环境科学领域的研究热点。持久性有机污染物在水体、沉积物中浓度不高,对其检测分析的传统方法是采集大量水样、沉积物样品,在实验室内对样品进行液液萃取、固相萃取以及超声萃取等手段,最后测得持久性有机污染物的含量。这种方法虽然应用比较广泛,但是需要采集大量样品,处理样品步骤相对复杂,而且不能很好地反映出持久性有机污染物在水体、沉积物中的空间分布规律。因此人们迫切需要一种针对水体、沉积物中持久性有机污染物的采样装置,可以减轻人们的工作量,同时能够准确的反映出持久性有机污染物在自然水体、沉积物中的空间分布情况,为人们研究各种有机污染物在自然环境中的迁移转化规律提供数据支持。

### 发明内容

[0003] 本实用新型是针对目前持久性有机污染物采样方式工作量大、不能准确反映出持久性有机污染物在水体、沉积物中的空间分布规律等问题,提出一种操作简单、设计合理、能够准确反映出 POPs 在自然环境中的分布情况的被动采样装置。

[0004] 本实用新型是由把手、采样材料放置支架和采样材料组成,把手设置在采样材料放置支架上端,采样材料放置支架包括前放置层和后放置层,前放置层与后放置层底端用合页铰接在一起,采样材料放置于采样材料放置支架的前放置层和后放置层之间。

[0005] 所述的把手为 304 不锈钢材质,

[0006] 本实用新型的使用过程 :

[0007] 将经过化学药剂处理的采样材料放置于前放置层和后放置层之间,合起采样材料放置支架,使采样材料固定于采样材料放置支架内。将整个采样装置插入待分析的水体、沉积物中,静置一定时间后分析采样材料上的持久性有机污染物的含量,便可得到水体、沉积物中有机污染物的含量。

[0008] 所述的采样材料为经过化学药剂处理的半渗透膜。

[0009] 本实用新型的有益效果 :

[0010] 本实用新型是针对目前持久性有机污染物采样方式工作量大、不能准确反映出持久性有机污染物在水体、沉积物中的空间分布规律等问题,提出一种操作简单、设计合理、能够准确反映出 POPs 在自然环境中的分布情况的被动采样装置,具有广阔的应用前景。

### 附图说明

[0011] 图 1 为本实用新型的结构示意图。

### 具体实施方式

[0012] 请参阅图 1 所示,本实施例是由把手 1、采样材料放置支架 2 和采样材料 3 组成,把手 1 设置在采样材料放置支架 2 上端,采样材料放置支架 2 包括前放置层和后放置层,前放置层与后放置层底端用合页 4 铰接在一起,采样材料 3 放置于采样材料放置支架 2 的前放置层和后放置层之间。

[0013] 所述的把手 1 为 304 不锈钢材质,

[0014] 所述的采样材料 3 为经过化学药剂处理的半渗透膜。

[0015] 本实施例的使用过程:

[0016] 将经过化学药剂处理的采样材料 3 放置于前放置层和后放置层之间,合起采样材料放置支架 2,使采样材料 3 固定于采样材料放置支架 2 内。将整个采样装置插入待分析的水体、沉积物中,静置一定时间后分析采样材料 3 上的持久性有机污染物的含量,便可得到水体、沉积物中有机污染物的含量。

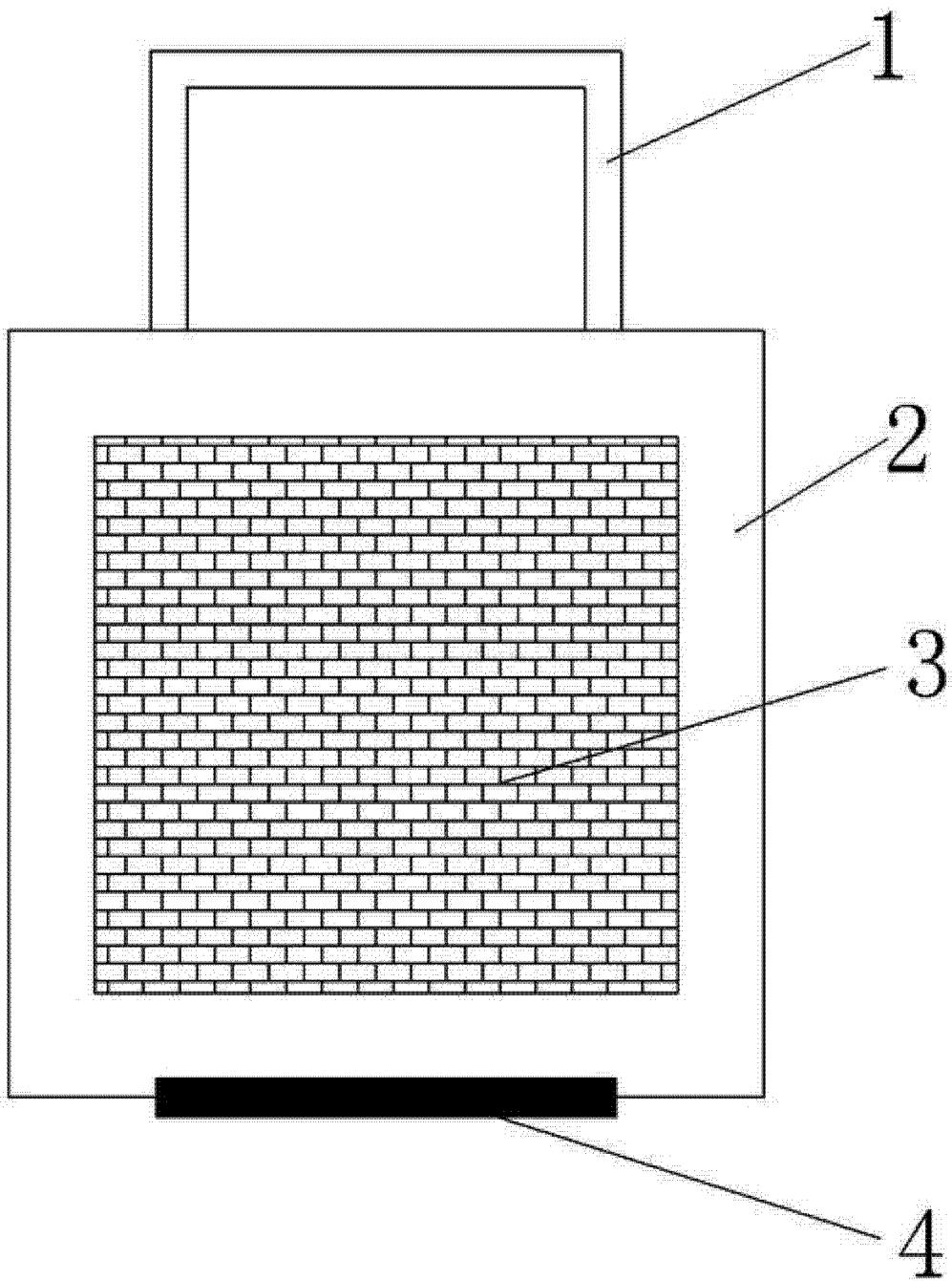


图 1

## Notice

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## DESCRIPTION CN204439408U

*10* A passive sampling device for persistent organic pollutants

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*12* 一种持久性有机污染物的被动采样装置

[0001]

*18* technical field

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*20* 技术领域

[0002]

*26* The utility model relates to the technical field of environmental protection, in particular to a passive sampling device for persistent organic pollutants.

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*29* 本实用新型涉及环境保护技术领域，特别涉及一种持久性有机污染物的 被动采样装置。

[0003]

*35* Background technique

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*37* 背景技术

[0004]

43 Persistent organic pollutants (POPs) have long-term persistence, bioaccumulation, semi-volatility and high toxicity, and are currently a global environmental issue that has attracted much attention internationally.

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46 持久性有机污染物POPs具有长期残留性、生物富集性、半挥发性和高毒性，是当前国际上备受关注的全球环境问题。

50 The migration and transformation of persistent organic pollutants in natural water bodies and sediments has always been a research hotspot in the field of environmental science.

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53 关于持久性有机污染物在自然水体、沉积物中的迁移转化规律一直是环境科学领域的研究热点。

56 The concentration of persistent organic pollutants in water bodies and sediments is not high. The traditional method for its detection and analysis is to collect a large number of water samples and sediment samples, and perform liquid-liquid extraction, solid-phase extraction, and ultrasonic extraction on the samples in the laboratory. means, and finally measure the content of persistent organic pollutants.

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61 持久性有机污染物在水体、沉积物中浓度不高，对其检测分析的传统方法是采集大量水样、沉积物样品，在实验室内对样品进行液液萃取、固相萃取以及超声萃取等手段，最后测得持久性有机污染物的含量。

66 Although this method is widely used, it needs to collect a large number of samples, the sample processing steps are relatively complicated, and it cannot well reflect the spatial distribution of persistent organic pollutants in water bodies and sediments. Therefore, people urgently need a sampling device for persistent organic pollutants in water bodies and sediments, which can reduce people's workload and accurately reflect the spatial distribution of persistent organic pollutants in natural water bodies and sediments., to provide data support for people to study the migration and transformation laws of various organic pollutants in the natural environment.

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74 这种方法虽然应用比较广泛，但是需要采集大量样品，处理样品步骤相对复杂，而且不能很好地反映出持久性有机污染物在水体、沉积物中的空间分布规律。因此人们迫切需要一种针对水体、沉积物中持久性有机污染物的采样装置，可以减轻人们的工作量，同时能够准确的反映出持久性有机污染物在自然水体、沉积物中的空间分布情况，为人们研究各种有机污染物在自然环境中的迁移转化规律提供数据支持。

## [0005]

*84* Contents of the invention

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*86* 发明内容

## [0006]

*92* The utility model aims at the problems that the current persistent organic pollutant sampling method has a large workload and cannot accurately reflect the spatial distribution of persistent organic pollutants in water bodies and sediments, and proposes a simple operation, reasonable design, and accurate A passive sampling device that reflects the distribution of POPs in the natural environment.

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*97* 本实用新型是针对目前持久性有机污染物采样方式工作量大、不能准确反映出持久性有机污染物在水体、沉积物中的空间分布规律等问题，提出一种操作简单、设计合理、能够准确反映出 POPs 在自然环境中的分布情况的被动采样装置。

## [0007]

*105* The utility model is composed of a handle, a sampling material placement bracket and sampling materials. The handle is arranged on the upper end of the sampling material placement bracket. Hinged together, the sampling material is placed between the front placement layer and the rear placement layer of the sampling material placement bracket.

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*110* 本实用新型是由把手、采样材料放置支架和采样材料组成，把手设置在采样材料放置支架上端，采样材料放置支架包括前放置层和后放置层，前放置层与后放置层底端用合页铰接在一起，采样材料放置于采样材料放置支架的前放置层和后放置层之间。

## [0008]

*118* The handle is made of 304 stainless steel,

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*120* 所述的把手为304不锈钢材质，

## [0009]

<sup>126</sup> The use process of the utility model:

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<sup>128</sup> 本实用新型的使用过程：

## [0010]

<sup>134</sup> Place the sampling material treated with chemicals between the front placement layer and the rear placement layer, close the sampling material placement bracket, and fix the sampling material in the sampling material placement bracket.

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<sup>138</sup> 将经过化学药剂处理的采样材料放置于前放置层和后放置层之间，合起采样材料放置支架，使采样材料固定于采样材料放置支架内。

<sup>142</sup> Insert the entire sampling device into the water body and sediment to be analyzed, and after standing for a certain period of time, analyze the content of persistent organic pollutants on the sampling material to obtain the content of organic pollutants in the water body and sediment.

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<sup>146</sup> 将整个采样装置插入待分析的水体、沉积物中，静置一定时间后分析采样材料上的持久性有机污染物的含量，便可得到水体、沉积物中有机污染物的含量。

## [0011]

<sup>153</sup> The sampling material is a semi-permeable membrane treated with chemicals.

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<sup>155</sup> 所述的采样材料为经过化学药剂处理的半渗透膜。

## [0012]

<sup>161</sup> The beneficial effects of the utility model:

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<sup>163</sup> 本实用新型的有益效果：

## [0013]

<sup>169</sup> The utility model aims at the problems that the current persistent organic pollutant sampling method has a large workload and cannot accurately reflect the spatial distribution of persistent organic pollutants in water bodies and sediments, and proposes a simple operation, reasonable design, and accurate Passive sampling devices that reflect the distribution of POPs in the natural environment have broad application prospects.

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<sup>174</sup> 本实用新型是针对目前持久性有机污染物采样方式工作量大、不能准确反映出持久性有机污染物在水体、沉积物中的空间分布规律等问题，提出一种操作简单、设计合理、能够准确反映出 POPs 在自然环境中的分布情况的被动采样装置，具有广阔的应用前景。

## [0014]

<sup>182</sup> Description of drawings

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<sup>184</sup> 附图说明

## [0015]

<sup>190</sup> Fig. 1 is the structural representation of the utility model.

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<sup>192</sup> 图1为本实用新型的结构示意图。

## [0016]

<sup>198</sup> Detailed ways

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<sup>200</sup> 具体实施方式

## [0017]

<sup>206</sup> Please refer to Fig. 1, the present embodiment is composed of a handle 1, a sampling material placement bracket 2 and a sampling material 3, the handle 1 is arranged on the upper end of the sampling material placement bracket 2, and the sampling material placement bracket 2 includes a front placement layer and a rear placement layer , the bottom ends of the front placement layer and the rear placement layer are hinged together with a hinge 4, and the sampling material 3 is placed between the front placement layer and the rear placement layer of the sampling material placement bracket 2.

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<sup>213</sup> 请参阅图1所示，本实施例是由把手1、采样材料放置支架2和采样材料3组成，把手1设置在采样材料放置支架2上端，采样材料放置支架2包括前放置层和后放置层，前放置层与后放置层底端用合页4铰接在一起，采样材料3放置于采样材料放置支架2的前放置层和后放置层之间。

#### [0018]

<sup>221</sup> The handle 1 is made of 304 stainless steel,

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<sup>223</sup> 所述的把手1为304不锈钢材质，

#### [0019]

<sup>229</sup> The sampling material 3 is a semi-permeable membrane treated with chemicals.

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<sup>231</sup> 所述的采样材料3为经过化学药剂处理的半渗透膜。

#### [0020]

<sup>237</sup> The use process of this embodiment:

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<sup>239</sup> 本实施例的使用过程：

#### [0021]

<sup>245</sup> The sampling material 3 processed by the chemical agent is placed between the front placement layer and the back placement layer, and the sampling material placement bracket 2 is closed so that the sampling material 3 is fixed in the sampling material placement bracket 2.

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<sup>249</sup> 将经过化学药剂处理的采样材料3放置于前放置层和后放置层之间，合起采样材料放置支架2，使采样材料3固定于采样材料放置支架2内。

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<sup>253</sup> The entire sampling device is inserted into the water body and sediment to be analyzed, and after standing for a certain period of time, the content of persistent organic pollutants on the sampling material 3 can be analyzed to obtain the content of organic pollutants in the water body and sediment.

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<sup>257</sup> 将整个采样装置插入待分析的水体、沉积物中，静置一定时间后分析采样材料3上的持久性有机污染物的含量，便可得到水体、沉积物中有机污染物的含量。

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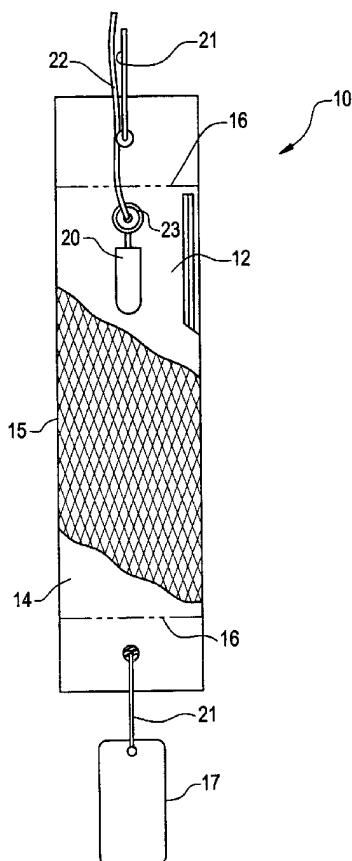
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[Continued on next page]

(54) Title: MONITORING OF VOLATILE ORGANIC COMPOUNDS IN GROUNDWATER WITH AN IN-SITU SAMPLING DEVICE



(57) Abstract: A sampling device (10) can monitor contaminants in groundwater. The sampling device comprises a semi-permeable membrane (14) for contact with groundwater, in which the semi-permeable membrane is permeable to contaminants and impermeable to groundwater; an inner chamber (12) formed by the semi-permeable membrane for containing the contaminants from the groundwater that diffuse through the semi-permeable membrane; and a sensor device (20) communicating with the inner chamber. The sensor device is in contact with the contaminants contained within the inner chamber for monitoring the contaminants.

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MONITORING OF VOLATILE ORGANIC  
COMPOUNDS IN GROUNDWATER WITH AN IN-  
SITU SAMPLING DEVICE

**BACKGROUND OF THE INVENTION**

The invention relates to an in-situ sampling device for monitoring compounds. In particular, the invention relates to a method and device for monitoring of volatile organic compounds in groundwater wells.

Presently, large amounts of time, energy, and money are spent monitoring groundwater, for example monitoring groundwater at remediation sites. In recent years, attempts have been made to develop in-situ samplers that can passively sample volatile organic compounds (VOCs) in groundwater wells. Diffusive vapor samplers with sorbent tube and water samplers, as disclosed in U.S. Patent Nos. 5,481,927 and 5,804,743, provide passive in-situ methods for monitoring VOCs in groundwater and unsaturated soils (vadose) zones.

The diffusive vapor sampler of U.S. Patent No. 5,804,743, assigned to the assignee of this invention, comprises a diffusion membrane that has a high permeability rate for organic vapors and impermeable to water. Upon retrieval from the well, the samples are sent to a laboratory for analysis or analyzed by gas chromatography on site.

Diffusive vapor samplers provide advantages over traditional groundwater sampling methods because these samplers do not need purging of groundwater wells in order to collect representative water samples. Purging can increase project costs because removal of water from each well results in large amounts of contaminated purge water that must be disposed. Moreover, purging potentially confounds analytical results by creating sediments, particulates, and erroneous concentration readings. Although in-situ diffusive vapor samplers promote minimization of wastes, they may not provide yield real-time monitoring of groundwater wells.

Therefore, a need exists for methods to monitor groundwater and remediation processes. Further, a need exists for an in-situ device that can be used to monitor volatile organic compounds (VOCs) continuously in groundwater.

## SUMMARY OF THE INVENTION

An aspect of the invention provides a sampling device that can monitor 5 contaminants in groundwater. The sampling device comprises a semi-permeable membrane for contact with groundwater, in which the semi-permeable membrane is permeable to contaminants and impermeable to groundwater; an inner chamber formed by the semi-permeable membrane for containing the contaminants from the groundwater that diffuse through the semi-permeable membrane; and a sensor device 10 communicating with the inner chamber. The sensor device is in contact with the contaminants contained within the inner chamber for monitoring the contaminants.

Further, the invention provides a method for the monitoring of 15 contaminants in ground water. The method comprises steps of: providing a semi-permeable membrane, the membrane being permeable only to the contaminants in groundwater; forming an inner chamber with the semi-permeable membrane for containing the contaminants that diffuse into the chamber; disposing the semi-permeable membrane within the groundwater; and detecting the contaminants with a sensor device. The sensor device is in communication with the inner chamber of the semi-permeable membrane for the monitoring of contaminants in groundwater.

20 Yet another aspect of the invention sets forth a sampling system for the monitoring of contaminants in groundwater and transmission of information from the monitoring. The sampling system comprises a sampling device and a data receiving and transmission system. The sampling device comprises a semi-permeable membrane for contact with groundwater, the semi-permeable membrane being permeable to contaminants and impermeable to groundwater; an inner chamber 25 formed by the semi-permeable membrane for containing the contaminants from the groundwater that diffuse through the semi-permeable membrane; and a sensor device communicating with the inner chamber, the sensor device being in contact with the

-contaminants contained within the inner chamber. The data receiving and transmission system communicates monitored information from the sampling system.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Other features and advantages of the present invention will become apparent from the following description of embodiments of the invention, which refers to the accompanying drawings, wherein:

Figure 1 is a cross-sectional view of an embodiment of a sampling device, as embodied by the invention;

Figure 2 is a cross-sectional view of another embodiment of a sampling device, as embodied by the invention; and

Figure 3 is a perspective view of a sampling system, as embodied by the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

An in-situ sampling device, as embodied by the invention, can provide monitoring of contaminants, such as, but not limited to, solvents in groundwater, in which the monitoring can be at least one of continuous and non-continuous monitoring. The in-situ sampling device includes a sampling chamber that encloses a sensor device, for example at least one of a gas sensor and a gas chromatograph (gc). Alternatively, the in-situ sampling device comprises a chamber that is connected to a sensor device, such as, but not limited to, at least one of a gas sensor and gas chromatograph (gc) through tubing. The sensor device will be discussed hereinafter as one or both of gas chromatograph and a gas sensor, however, this description is merely exemplary, and is not intended to limit the invention in any manner.

As illustrated in Fig. 1, the in-situ sampling device 10 comprises a gas sensor 20 disposed within the sampling chamber 12 of a semi-permeable membrane 14. The sensor 20 detects contaminants in the groundwater, such as, but not limited to, chlorinated solvents, hydrocarbons, VOCs, light non-aqueous phase liquid

(LNAPL), and dense non-aqueous phase liquid (DNAPL). The contaminant is referred to hereinafter as a VOC, however, this description is merely exemplary, and is not intended to limit the invention in any manner. Further, although only one sensor is illustrated, the scope of the invention comprises an in-situ sampling device comprising a plurality of sensors.

The in-situ sampling device 10 comprises a semi-permeable, hydrophobic membrane 14 (hereinafter "semi-permeable membrane"), which can comprise low-density polyethylene. Alternatively, the semi-permeable membrane 14 can comprise any appropriate material, such as, but not limited to, silicone, polyethylene, and Mylar<sup>®</sup>. The semi-permeable membrane material is selected so VOCs can diffuse therethrough, with the semi-permeable membrane material being generally impermeable to water. This semi-permeable membrane feature makes the membrane effective in protecting an in-situ sampling device if exposed to at least one of groundwater and heavy particulate. The impermeable feature also expands utility of the in-situ sampling device into areas and applications where environmental considerations previously limited use.

The gas sensor 20 can comprise a metal oxide semiconductor (MOS) hydrocarbon sensor. The gas sensor 20 can be located within the sampling chamber 12 that is formed by membrane 14. The gas sensor 20 can be located in a approximate middle portion of the sampling chamber 12 formed by the semi-permeable membrane 14. As illustrated in Fig. 1, the membrane 14 can be covered with a mesh protective sleeve or cover 15 (hereinafter "mesh cover"). The mesh cover 15 can prevent abrasion or puncturing of the semi-permeable membrane 14 and the chamber formed thereby. Although not illustrated, the in-situ sampling chamber 12 can enclose a gas that is disposed over an open end of the gas sensor 20.

To use the in-situ sampling device 10 in a well, a support line 21 is attached to the in-situ sampling device 10. The support line 21 comprises a suitable length of line 21 to support the in-situ sampling device 10. The support line 21 can be formed of any appropriate material, for example, but not limited to, nylon and other inert materials. The support line 21 can support the mesh cover 15, for example by an

appropriate fastening structure. The support line 21 can be used to raise the in-situ sampling device 10 out of a well after a sampling operation. Further, a weight 17 can be hung from a lower portion of the mesh cover 15 and in-situ sampling device 10 to assist in submerging the in-situ sampling device 10 in the well.

5                 The chamber of semi-permeable membrane 14 is filled, for example partially or completely, prior to placement of the in-situ sampling device 10 within a well. The chamber 12 can be filled with a reference fluid, for example, but not limited to, air. The semi-permeable membrane 14 can be permeable to the reference fluid, and can be impermeable to groundwater. Thus, only contaminants can flow  
10 therethrough.

Once the in-situ sampling device 10 is in contact with contaminated groundwater, contaminants can begin to diffuse through the semi-permeable membrane 14 into chamber 12. Air that is displaced from the in-situ sampling device 10 diffuses into the groundwater, as contaminants from the groundwater diffuse into the chamber 12 of the in-situ sampling device 10. The contaminants continue to diffuse into the chamber 12 until a concentration of contaminants in the chamber 12 and concentration of contaminants in the groundwater reach a state of equilibrium at  
15 which time the diffusion halts.

20                 The semi-permeable membrane 14 comprises a seal 16 disposed on both ends. The seal 16 may be formed by any appropriate sealing function, such as but not limited to, by an impulse heat sealer to form the chamber 12. An adhesive seal 16 (not illustrated) can also seal the semi-permeable membrane 14.

25                 Figure 2 illustrates a further in-situ sampling device 10, as embodied by the invention. Like elements will be provided with like reference characters. In Fig. 2, the sampling device 10 is placed into a well 18 and connected to a gas sensor or gas chromatograph for monitoring groundwater contamination. The in-situ sampling device 10 of Fig. 2 comprises a length of tubing 22 that is connected to sampling chamber 12. The length of tubing 22 is connected to the sampling chamber 12 through a compressor fitting 23. The in-situ sampler 10 can then be connected to a

gas chromatograph through the length of tubing 22. A sensing device, including at least one of a gas chromatograph, a micro-gas chromatograph, and a gas sensor, can take a sample via an automated pump (not illustrated) that can be installed therewith. The above description of the gas chromatograph is merely illustrative, and is not intended to limit the invention. The scope of the invention comprises any kind of sensing device that can detect hydrocarbon, as embodied by the invention.

Figure 3 illustrates a transceiver 24, which sends data signal(s) from the gas sensor 20 to a data collection station 26, for use with the in-situ sampling device 10, as embodied by the invention. The transceiver 24 can send these signals by any appropriate communications link 31. The communications link 31, and other communications links described herein, comprise, but are not limited to, at least one of a phone modem, wired networks, modem, radio, network connection, communication, radio communication and other wireless communication systems, cellular communication, satellite communication, web access communication, and Internet access communication, and combinations thereof.

The gas sensor 20 can be connected to an explosion-proof transmitter via sensor wires on a well head. The sensor transmitters can be mounted at any suitable distance from the collection system. The sensor transmitters provide linear output signals over a range of gas concentrations, regardless of a sensor type. The sensor transmitters can be connected to a data logger, such as, but not limited to, a database, Web page, or other storage device, for recording of the information. Further, any party so authorized by the in-situ sampling device 10 owner or operator can access the data logger to review the information. For example, regulatory agencies can access the data logger.

A data receiving and transmission system can comprise a data transmission system 28 and a data processing and reporting system 30 that are also provided in the in-situ sampling device 10 for communicate of data and information. Any suitable data transmission system 28 and a data processing and reporting system 30 for data transmission and retrieval can be used with the in-situ sampling device 10. For example, a data transmission system 28 and a data processing and reporting

system 30 as set forth in U.S. Serial No. 09/201,385, entitled "Monitoring, Diagnostic, and Reporting System and Process" and U.S. Patent No. 5,999,643, entitled Passive Water Sampler and method of Sampling (both of which are assigned to the assignee of the present invention) can be used with the in-situ sampling device 10, as embodied by the invention. The teachings of both U.S. Serial No. 09/201,385 and U.S. Patent No. 5,999,643 are fully incorporated by reference herein.

The method of sampling groundwater contaminants, as embodied by the invention, comprises positioning an in-situ sampling device 10 in a well 18. The in-situ sampling device 10 is positioned in the well 18 so the semi-permeable membrane 14 contacts contaminated groundwater. The semi-permeable membrane 14 has been configured to form an inner chamber 12 prior to insertion of the in-situ sampling device 10 in the groundwater. The inner chamber 12 contains the contaminants that diffuse through semi-permeable membrane 14 during use of the in-situ sampling device 10. The in-situ sampling device 10 remains in the well for a time that is sufficient to allow contaminants in the groundwater to diffuse through the semi-permeable membrane 14 and reach an equilibrium state.

The gas sensor 20, which can be disposed within chamber 12 and alternatively disposed outside of the well 18. The gas sensor 20 can provide total hydrocarbons in the groundwater. Alternatively, the gas sensor 20 can quantitatively identify individual contaminant species in the groundwater in a relatively continuous manner. The in-situ sampling device 10 provides information about contaminants in the groundwater in a relatively fast manner, such as but not limited to real-time and near real-time. The term "real-time" means that any delays from the time the information is attained, and then made available is minimal, for example on the order of minutes, and possibly a few seconds, or even longer, if the need for the information is defined as such and the data may still be relevant and of value to the interested party, if any delay is present. Also, the term real time can mean a time required by a user to obtain data.

The in-situ sampling device 10, as embodied by the invention, has been described with respect to monitoring groundwater wells. The scope of the

invention comprises use of the in-situ sampling device 10 in other such applications. For example, and in no way limiting of the invention, the in-situ sampling device 10 can be used chemical process applications to determine contaminants.

5 While various embodiments are described herein, it will be appreciated from the specification that various combinations of elements, variations or improvements therein may be made by those skilled in the art, and are within the scope of the invention.

**WHAT IS CLAIMED IS:**

1. A sampling device (10) for the monitoring of contaminants in groundwater, the sampling device comprising:

a semi-permeable membrane (14) for contact with groundwater, the semi-permeable membrane being permeable to contaminants and impermeable to groundwater;

an inner chamber (12) formed by the semi-permeable membrane for containing the contaminants from the groundwater that diffuse through the semi-permeable membrane; and

a sensor device (20) communicating with the inner chamber, the sensor device being in contact with the contaminants contained within the inner chamber for monitoring the contaminants.

2. The sampling device according to claim 1, wherein the semi-permeable membrane comprises polyethylene.

3. The sampling device according to claim 1, wherein the sensor device is disposed in the inner chamber.

4. The sampling device according to claim 1, the sampling device further comprising tubing, wherein the sensor device is connected to the inner chamber via the tubing.

5. The sampling device according to claim 1, wherein the sensor device comprises a metal oxide semiconductor sensor.

6. The sampling device according to claim 1, the sampling device further comprising a protective covering disposed on the semi-permeable membrane.

7. The sampling device according to claim 1, wherein the sampling device continuously monitors the groundwater.

8. A method for the monitoring of contaminants in ground water, the method comprising the steps of:

providing a semi-permeable membrane (14), the membrane being permeable only to the contaminants in groundwater;

5 forming an inner chamber (12) with the semi-permeable membrane for containing the contaminants that diffuse into the chamber;

disposing the semi-permeable membrane within the groundwater; and

detecting the contaminants with a sensor device, the sensor device being in communication with the inner chamber of the semi-permeable membrane for 10 the monitoring of contaminants in groundwater.

9. The method according to claim 8, wherein the step of detecting the contaminants comprises positioning the sensor device within the inner chamber in contact with the contaminants.

10. The method according to claim 8, wherein the step of detecting the contaminants comprises connecting the sensor device with the inner chamber of the membrane.

11. The method according to claim 8, further comprising a step of receiving data from the sensor device and transmitting the data to a remote location.

12. The method according to claim 8, wherein the step of detecting the contaminants comprises determining a total amount of hydrocarbons present within 20 the groundwater.

13. The method according to claim 8, wherein the step of detecting the contaminants comprises identifying individual species quantitatively in the groundwater in a manner.

14. The method according to claim 8, wherein the monitoring comprises continuous monitoring.

15. A sampling system for the monitoring of contaminants in groundwater and transmission of information from the monitoring, the sampling system comprising:

5 a sampling device comprising:

10 semi-permeable membrane (14) for contact with groundwater, the semi-permeable membrane being permeable to contaminants and impermeable to groundwater;

15 an inner chamber (12) formed by the semi-permeable membrane for containing the contaminants from the groundwater that diffuse through the semi-permeable membrane; and

15 a sensor device communicating with the inner chamber, the sensor device being in contact with the contaminants contained within the inner chamber; and

20 a data receiving and transmission system (24, 26, 28, 30) that communicates monitored data from the sampling device.

25 16. A sampling system according to claim 15, wherein the data receiving and transmission system provides the data via communications link (31) in at least one of near real-time and real time.

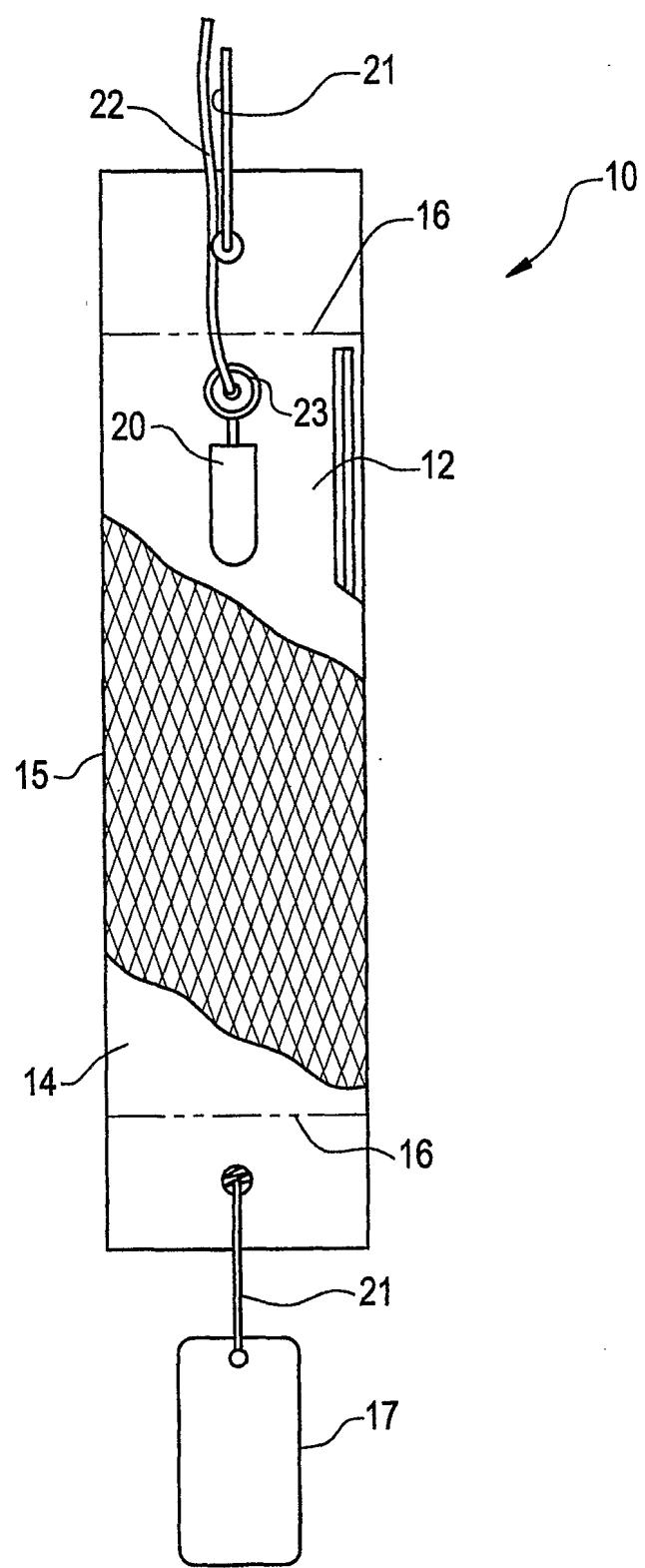
25 17. A sampling system according to claim 15, wherein the communications link comprises at least one of phone modem, wired networks, modem, radio, network connection, communication, radio communication and other wireless communication systems, cellular communication, satellite communication,

web access communication, and Internet access communication, and combinations thereof.

18. A sampling system according to claim 15, wherein the data receiving and transmission system can transmit the data to a remote location from the  
5 sensor device.

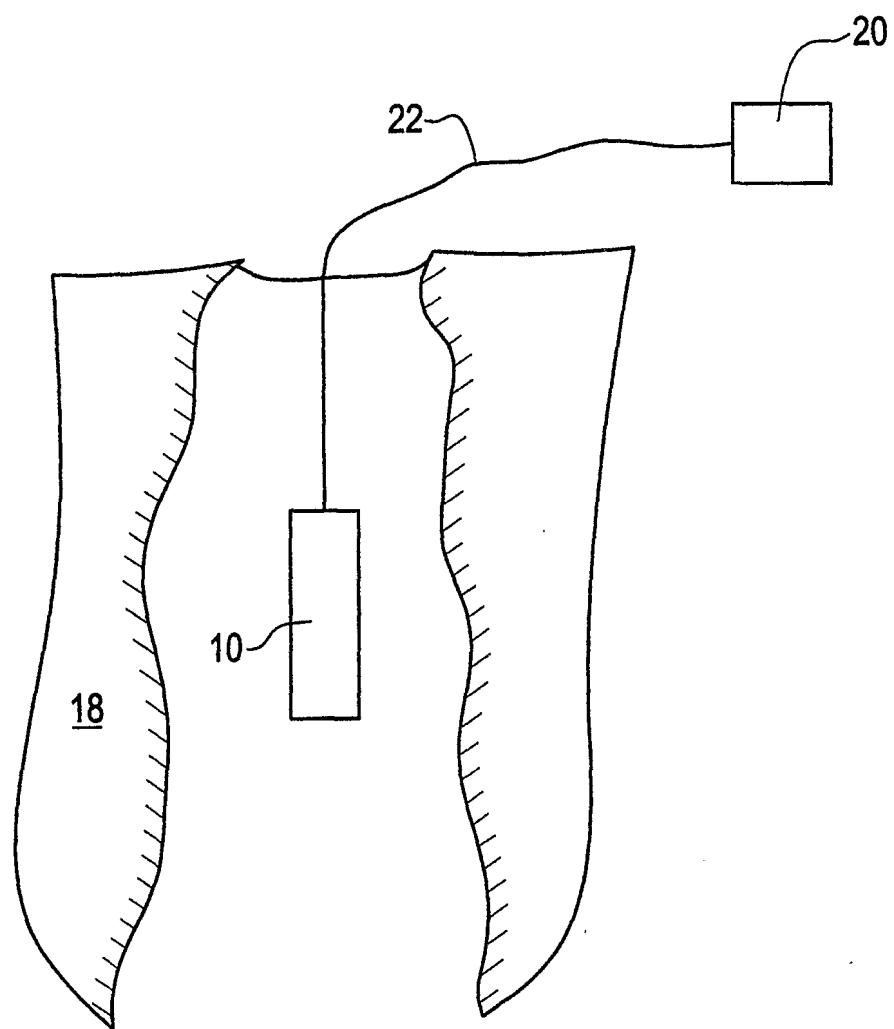
1/3

**FIG. 1**



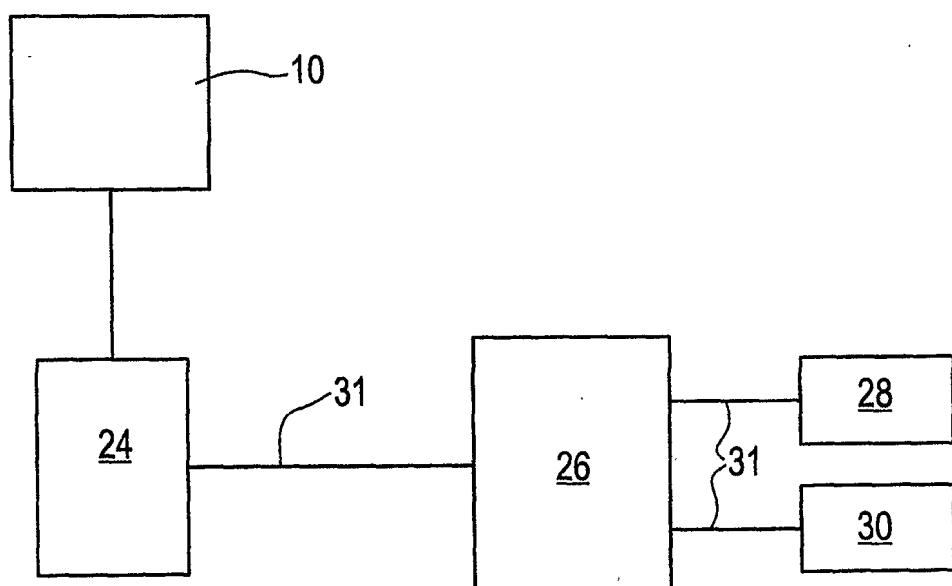
2/3

FIG. 2



3/3

FIG. 3



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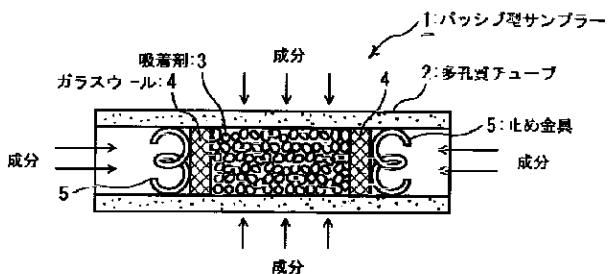
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(54)【発明の名称】 パッシブ型サンプラー及び分析方法

(57)【要約】

【課題】 検定精度が良好で分析操作がきわめて容易であるとともに、多数回繰り返しサンプリングに使用できるパッシブ型サンプラー及びこのパッシブ型サンプラーを用いた雰囲気中の成分の分析方法を提供する。

【解決手段】 パッシブ型サンプラー1は、両端が開口した円筒形の多孔質チューブ2と、この多孔質チューブ2内部に収容された吸着剤3とを有している。この吸着剤3は、多孔質チューブ2の両端以外の部分に配置されている。多孔質チューブ2の両端側からガラスウール4、4を充填し、さらにその外端に止め金具5、5を設置することによって移動可能に保持されている。このパッシブ型サンプラー1を測定環境に配置し、サンプリングを行う。サンプリング終了後、パッシブ型サンプラー1を測定管10内部に挿入し、止め金具11で保持する。この測定管10を加熱して成分を脱着させ、機器分析する。



## 【特許請求の範囲】

【請求項1】 多孔質チューブと、該多孔質チューブ内に充填された吸着剤とを有するパッシブ型サンプラー。

【請求項2】 請求項1において、前記吸着剤は前記多孔質チューブ内で移動不能に保持されていることを特徴とするパッシブ型サンプラー。

【請求項3】 請求項1又は2において、前記多孔質チューブの軸心部分に多孔質の細管が配置されており、前記吸着剤は該細管と前記多孔質チューブとの間に充填されていることを特徴とするパッシブ型サンプラー。

【請求項4】 請求項1ないし3に記載のパッシブ型サンプラーを用いて大気等の雰囲気中の成分の分析を行う方法であって、

該パッシブ型サンプラーを雰囲気と接触させて該パッシブ型サンプラーの吸着剤に成分を吸着させた後、該パッシブ型サンプラーを非通気性の測定管に入れ、該測定管内に通気しながら吸着剤を加熱して成分を脱着させて分析することを特徴とする雰囲気中の成分の分析方法。

【請求項5】 請求項3に記載のパッシブ型サンプラーを用いて大気等の雰囲気中の成分の分析を行う方法であって、

該パッシブ型サンプラーを雰囲気と接触させて該パッシブ型サンプラーの吸着剤に成分を吸着させた後、該パッシブ型サンプラーを非通気性の測定管に入れ、前記細管内に脱着用のキャリアガスを供給すると共に、吸着剤を加熱して成分を脱着させて分析することを特徴とする雰囲気中の成分の分析方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、屋外、屋内の大気等の雰囲気中に含まれる成分特に微量成分を吸着剤に吸着させて捕集するパッシブ型サンプラーと、このパッシブ型サンプラーを用いた成分の分析方法とに関する。

## 【0002】

【従来の技術】各種産業分野や居住環境で生じるガス状物質の環境監視モニターや環境測定等においては、大気中の特定のガス状物質やエアロゾルなどを採取、捕集し、捕集した大気物質を分析装置で分析を行っている。

【0003】大気中のガス状物質やエアロゾルを採取する方法としては、従来より真空瓶法、吸引瓶法、捕集バック法等の方法が知られている。これらの捕集方法は、吸引ポンプで減圧した各種容器内に試料を気体状態で採取するものや、ポンプを通して試料袋に直接試料を採取するものであるため、減圧装置や吸引ポンプ等の装置を必要とする。そのため、これらの装置のための設置スペースを必要とし、また装置の設備費、捕集、採取のための人的経費が増加する等の問題がある。また、ポンプによる騒音が居住者に不快感を与えていた。

【0004】これに対して、小型でポンプ等の装置を必要としないパッシブ型サンプラーが提案されている。パ

ッシブ型サンプラーは、サンプラーを測定環境中に配置するだけでサンプリングを行うものであり、ポンプ等の装置を持たず、測定環境内の気体の流れのみによって吸着物質と吸着剤とを接触させて、吸着剤に被吸着物質を吸着させるものである。

【0005】従来のパッシブ型サンプラーとしては、特開平10-300647号に記載されているものがある。このパッシブ型サンプラーは、容器と、吸着部とかなる。容器は、一端が栓によって閉止された円筒形をしており、内部に吸着剤が充填されている。吸着部は、一端が栓によって閉止された略円筒形をしており、吸着部の開口端が前記容器の開口端に着脱可能に外嵌されている。この吸着部は被吸着物質の通過が可能な分子拡散フィルタによって構成されている。

【0006】このように構成されたサンプラーは、サンプリング時には、吸着部が下側、容器が上側となるようにして測定環境中に配置される。このとき、吸着剤は下側の吸着部に移動しているため、吸着部を通過してきた被吸着物質を吸着する。

【0007】サンプリング終了後は、サンプラーを反転し、吸着剤を吸着部側から容器側に移動させる。

【0008】サンプリング終了後に分析を行う場合は、容器から吸着部及び栓を取り外し、容器を分析装置に取り付けて分析を行う。このとき、容器は分析装置内で測定管として使用される。

## 【0009】

【発明が解決しようとする課題】上記特開平10-300647号のパッシブ型サンプラーにあっては、サンプリング後に吸着剤を吸着部から容器に移動させる場合、吸着部に吸着剤が残存し、被吸着物質の分析値に誤差を生じさせる。また、吸着剤が容器及び吸着部間を移動する間に、吸着剤同士がぶつかって磨耗するため、パッシブ型サンプラーを多数回繰り返し使用することはできない。なお、吸着剤が磨耗すると、吸着特性が変化するため、成分の分析精度が変化するようになる。

【0010】本発明は、前記した従来のパッシブ型サンプラーの問題点を解決し、測定精度が良好なパッシブ型サンプラーと、このパッシブ型サンプラーを用いた大気等の雰囲気の成分を分析する方法を提供することを目的とする。

【0011】また、本発明は、多数回繰り返しサンプリングに使用することができるパッシブ型サンプラーと、このパッシブ型サンプラーを用いた雰囲気中の成分の分析方法を提供することを目的とする。

## 【0012】

【課題を解決するための手段】本発明（請求項1）のパッシブ型サンプラーは、多孔質チューブと、該多孔質チューブ内に充填された吸着剤とを有するものである。

【0013】かかるパッシブ型サンプラーによれば、吸着剤を収納している多孔質チューブ自体がガス透過性を

有するため、サンプリング時に吸着剤を多孔質チューブから他の容器等に移動させることなく、吸着剤を多孔質チューブ内にそのまま位置させたまま目的成分を該吸着剤に吸着させてサンプリングすることができる。従って、移動によって吸着剤同士がぶつかって磨耗し、劣化するということではなく、吸着剤を多数回繰り返しサンプリングに使用することができる。

【0014】本発明のパッシブ型サンプラーは、前記吸着剤が前記多孔質チューブ内で移動不能に保持されていることが好ましい(請求項2)。この場合、該吸着剤は磨耗による劣化が全くないため、きわめて多数回繰り返し使用することができる。

【0015】本発明のパッシブ型サンプラーは、前記多孔質チューブの軸心部分に多孔質の細管が配置されており、前記吸着剤は該細管と前記多孔質チューブとの間に充填されているものであってもよい(請求項3)。この場合も、吸着剤を多孔質チューブ内に収容したままサンプリングすることができるため、移動によって吸着剤同士がぶつかって磨耗し、劣化するということなく、吸着剤を多数回繰り返しサンプリングに使用することができる。

【0016】本発明(請求項4)の分析方法は、前記パッシブ型サンプラーを用いて大気等の雰囲気中の成分の分析を行う方法であって、該パッシブ型サンプラーを雰囲気と接触させて該パッシブ型サンプラーの吸着剤に成分を吸着させた後、該パッシブ型サンプラーを非通気性の測定管に入れ、該測定管内に通気しながら吸着剤を加熱して成分を脱着させて分析するものである。

【0017】かかる分析方法によれば、サンプリングした後、吸着剤をパッシブ型サンプラーから取り出さずに分析することができる。従って、分析操作がきわめて容易であると共に、吸着剤を取り出すときに吸着剤の一部がパッシブ型サンプラー内に残存して分析値に誤差が生じるということなく、測定精度が良好なものとなる。また、吸着剤を取り出さないため、吸着剤が磨耗することができなく、吸着剤を多数回繰り返し使用することができる。

【0018】本発明(請求項5)の分析方法は、請求項3に記載のパッシブ型サンプラーを用いて大気等の雰囲気中の成分の分析を行う方法であって、該パッシブ型サンプラーを雰囲気と接触させて該パッシブ型サンプラーの吸着剤に成分を吸着させた後、該パッシブ型サンプラーを非通気性の測定管に入れ、前記細管内に脱着用のキャリアガスを供給すると共に、吸着剤を加熱して成分を脱着させて分析することを特徴とするものである。

【0019】かかる分析方法によれば、前記細管内に供給されたキャリアガスは、多孔質チューブの軸心部分に導入され、該軸心部分から吸着剤及び多孔質チューブの周壁を透過して多孔質チューブの外側に流出する。この分析方法においても、加熱により吸着剤から脱着した成

分は、このキャリアガスに搬送されて効率的に多孔質チューブの外側に流出するため、脱着した成分が多孔質チューブ内に滞留して分析値に誤差が生じるということなく、測定精度が良好なものとなる。また、サンプリングした後、吸着剤をパッシブ型サンプラーから取り出すことなく分析することができるため、分析操作がきわめて容易であると共に、吸着剤を取り出すときに吸着剤の一部がパッシブ型サンプラー内に残存して分析値に誤差が生じるということなく、測定精度が良好なものとなる。さらに、吸着剤を取り出さないため、吸着剤が磨耗することができなく、吸着剤を多数回繰り返し使用することができる。

【0020】なお、本発明のパッシブ型サンプラーでは、成分は多孔質チューブを拡散して吸着剤に吸着されるため、多孔質チューブ内に充填された吸着剤のうち多孔質チューブの内周壁に近いものほど多くの成分を吸着する。従って、請求項5の分析方法のように、キャリアガスを軸心部分の多孔質細管を通して吸着剤に供給すると、キャリアガスは細管から放射方向に流れて吸着剤層を通り抜けるため、多孔質チューブの内周壁近傍の吸着剤から脱着された成分は、脱着後直ちに多孔質チューブを通過し、取り出される。従って、この請求項5の方法によると、成分の脱着を迅速に行うことができる。

#### 【0021】

【発明の実施の形態】以下、本発明の実施の形態を図を参照にして詳細に説明する。図1は本発明の実施の形態に係るパッシブ型サンプラーの断面図、図2(a), (b)は図1のパッシブ型サンプラーの多孔質チューブの斜視図である。

【0022】パッシブ型サンプラー1は、両端が開口した円筒形の多孔質チューブ2と、この多孔質チューブ2の内部に収容された吸着剤3とを有する。この吸着剤3は、多孔質チューブ2の両端以外の部分に配置されている。吸着剤3は、多孔質チューブ2の両端側からガラスウール4, 4を充填し、さらにその外端に止め金具5, 5を設置することによって移動不能に保持されている。この止め金具5としては、耐食性の金属線をU字形状、α字形状やW字形状等に湾曲させたものが好適であるが、これ以外のものを用いてもよい。

【0023】多孔質チューブ2としては、雰囲気及び該雰囲気中の分析目的成分を透過可能なものが使用される。多孔質チューブ2の材質は、サンプリング後に加熱脱着法による成分分析を行う際の加熱温度に耐え得るものであることが好ましい。具体的には、多孔質セラミックス、多孔質金属、多孔質耐熱性合成樹脂などが使用される。多孔質チューブ2は硬質のものであってもよく、柔軟性を有したものであってもよい。

【0024】多孔質チューブ2としては、図2(a)に示す如く、その全体が多孔質材料とされた多孔質チューブ2Aであっても良く、また、図2(b)に示す如く、

多孔質材料よりなるチューブの両端の、内側に吸着剤が存在せず、実質的にガス成分の拡散が生じない部分2a, 2aを、ガスが透過しないように多孔質の孔をふさいだ処理を施した多孔質チューブ2Bであっても良い。この両端部分2a, 2aの封孔処理の目的は、主に多孔質チューブの強度を高めることにあり、その具体的な方法としては、多孔質チューブの表面に焼成によりガラス質となるような成分をスプレー、もしくはディッピングによりコーティングし、乾燥後、焼成する方法が挙げられる。

【0025】この場合、焼成によりガラス質となる成分の具体例としては、ガラス質フリット95～97%、粘土3～5%の組成物を水に分散させたものが挙げられる。このガラス質成分は、吸着成分の分析の際に加熱するときの加熱温度に耐え得るものであれば良く、特に限定されるものではない。

【0026】吸着剤3は、目的成分の吸着量が多く、また脱着が容易なものが好適である。具体的には、吸着剤としては活性炭、シリカゲル、モレキュラーシーブ、ポーラスopolマー（Tenax樹脂等）等が好適であり、特に活性炭が好ましい。この吸着剤3は微細な顆粒状のものが好ましい。顆粒状の吸着剤は、多孔質チューブ2への充填が容易であると共に、吸着剤3の粒子同士の間にガスが通気するので、多孔質チューブ2の芯部分付近に充填された吸着剤にも目的成分が十分に吸着されるようになる。

【0027】このように構成されたパッシブ型サンプラー1を測定環境下に設置することによりサンプリングを行う。このとき、多孔質チューブ2の側周面を透過してきた雰囲気中の成分及び多孔質チューブ2の開口端から侵入してきた雰囲気中の成分が、吸着剤3によって吸着される。所定時間経過後、測定環境からパッシブ型サンプラー1を取り出し、サンプリングを終了する。

【0028】このパッシブ型サンプラー1にあっては、多孔質チューブ2の開口端から侵入してきた成分が吸着剤3に吸着されるのに加え、多孔質チューブ2の側周面から透過してきた成分も吸着剤3に吸着されるため、吸着効率が高く、比較的短時間でサンプリングを行うことができる。ただし、多孔質チューブ2の一端又は両端に着脱可能なキャップを装着し、サンプリング時には多孔質チューブ2を透過した雰囲気中の成分のみが吸着剤3に吸着されるようにしてよい。このようにすれば、塵や異物、生物などが該多孔質チューブ2内に入り込むことを防止できる。このキャップは脱着時に外せばよい。

【0029】このパッシブ型サンプラー1にあっては、吸着剤3がガラスウール4及び止め金具5によって移動不能に保持されているため、吸着剤3同士がぶつかって磨耗、劣化することなく、多数回繰り返し使用することができる。

【0030】また、図2(b)に示す如く、両端のガス

成分が拡散しない部分2a, 2aを封孔処理して補強した多孔質チューブ2Bであれば、多孔質チューブの強度が高く、より一層多数回の繰り返し使用に耐え得るパッシブ型サンプラーとすることができる。また、この多孔質チューブ2Bであれば、ガス成分が透過する多孔質部分2bと透過しない封孔処理部分2a, 2aとが外見上区別され、サンプラーの取扱いの際に、ガス成分が透過する部分2bを素手で触ることを防ぎ、この部分2bが油成分などのガス成分の透過を妨げる不純物で汚染されることを防止する効果も期待される。

【0031】図3は、図1のパッシブ型サンプラー1によってサンプリングされた成分を分析する方法を説明する断面図である。

【0032】サンプリング終了後のパッシブ型サンプラー1は、両端が開口した円筒形の測定管10の内部に挿入され、止め金具11等によって移動不能に保持される。この測定管10の内径は多孔質チューブ2の外径よりも大きいため、測定管10の内周面と多孔質チューブ2の外周面との間には隙間が存在する。

【0033】パッシブ型サンプラー1を収容した測定管10は、公知の加熱脱着法による装置内部に設置される。この装置内において、測定管10の内部にキャリアガスが流されると共に、測定管10が加熱され、吸着剤3も加熱される。この加熱によって、吸着剤3に吸着していた成分が吸着剤3から脱着し、脱着した成分は多孔質チューブ2の開口端から、あるいは多孔質チューブ2の周面を透過して流出する。そして、キャリアガスに搬送され、測定管10の下流に設置されたガスクロマトグラフィー等の分析機器（図示略）に導入され、分析される。

【0034】なお、測定管10の測定条件は、例えば温度：50～500°C、時間：1分～60分、キャリアガス：ヘリウム、チゾ、圧力：50～300 kPaとする。

【0035】この成分の分析方法にあっては、パッシブ型サンプラー1をそのまま測定管10内に挿入して分析するため、操作が簡単である。また、吸着剤3を多孔質チューブ2から他の容器等に移動する必要がないため、移動時に吸着剤3の一部が残留し、成分の分析値に誤差を生じさせるということはない。さらに、移動時に吸着剤3同士がぶつかって磨耗し、劣化するということもない。

【0036】このパッシブ型サンプラー1にあっては、測定環境中の分析目的成分の多くは、多孔質チューブ2の側周面を通過して吸着剤3に吸着される。従って、多孔質チューブ2の長手方向と垂直方向の断面においては、多孔質チューブ2の芯部分ほど吸着剤3の成分吸着量が少なく、多孔質チューブ2の内周面に近づくほど吸着量が多くなることが通常である。従って、このパッシブ型サンプラー1を脱着処理する場合、脱着する成分の

かなりの部分が多孔質チューブ2を内周側から外周側に透過するようになる。図3の脱着装置では多孔質チューブ2の外周と測定管10の内周との間の隙間にキャリアガスが流通されるため、吸着剤3から脱着して多孔質チューブ2を透過した成分が、この測定管10と多孔質チューブ2との間のキャリアガスに搬送されて効率的に測定管10から流出させることができる。

【0037】図4(a)は本発明の別の実施の形態に係るパッシブ型サンプラーの斜視図、図4(b)は図4(a)のパッシブ型サンプラーの細管の斜視図、図4(c)は図4(a)のパッシブ型サンプラーの多孔質チューブの斜視図である。図5は図4(a)のパッシブ型サンプラーによってサンプリングされた成分を分析する方法を説明する断面図、図6は図5のVI-VI線に沿う断面図、図7は図5のVII-VII線に沿う断面図である。

【0038】このパッシブ型サンプラー21は、円筒形状をした多孔質チューブ22と、この多孔質チューブ22の軸心部分に配置された多孔質の細管25と、この多孔質チューブ22と細管25との間に充填された吸着剤3とを有する。この多孔質チューブ22の一端は、平たい円盤状の封止板23によって封止されており、他端は金属、ガラス、セラミックスあるいは耐熱性のゴム又は合成樹脂製(この実施の形態では耐熱性のゴム製)の封止蓋24によって封止されている。封止板23は、例えば耐熱性の接着剤などにより多孔質チューブ22の端面に接着される。

【0039】封止蓋24は略円盤形であり、その外周縁からは多孔質チューブ22の外周面に被さる短い筒状の周壁部24aが突設されている。この周壁部24aの内径は多孔質チューブ22の外径よりも若干小さく設定されており、該周壁部24aが前記多孔質チューブ22の外周面の縁部に外嵌されている。

【0040】この封止蓋24の中心部分には貫通孔24bが設けられ、この貫通孔24b内に細管25が挿通されている。この細管25の先端は前記封止板23にまで達し、該細管25の先端面は該封止板23に当接している。なお、該封止板23の板央部に凹みを設け、該細管25の先端を該凹みに嵌入させてもよい。この細管25の外周面と前記多孔質チューブ22の内周面との間隙には、吸着剤3が充填されている。

【0041】多孔質チューブ22としては、先の実施の形態に係る多孔質チューブ2と同等の材質のものが使用される。

【0042】封止板23は好ましくは非通気性のものが用いられるが、通気性のものであってもよい。この封止板23は、サンプリング後に加熱脱着法による成分分析を行う際の加熱温度に耐え得るもののが用いられ、具体的には耐熱性のゴム又は合成樹脂、金属、ガラス、セラミックスなどが使用される。この封止板23は、耐熱性の接着剤のほか、超音波振動法等により直接、多孔質チュ

ーブ22に接合されてもよい。この封止板23は、封止蓋24と同様に多孔質チューブ22の外周端部に被さる形状のものであってもよく、ゴム栓の如く多孔質チューブ22に内嵌される栓状体であってもよい。

【0043】細管25としては、サンプリング時や分析時の雰囲気ガス、分析目的成分、キャリアガス等を透過可能なものが使用される。細管25の材質は、サンプリング後に加熱脱着法による成分分析を行う際の加熱温度に耐え得るものであることが好ましく、例えば、焼結ガラスや多孔質セラミックス等が好適であるが、ガラス管や金属管の側面に小口径の孔を多数あけたものであってもよい。

【0044】このように構成されたパッシブ型サンプラー21は、前記パッシブ型サンプラー1と同様に、測定環境下に設置することによりサンプリングを行う。このとき、多孔質チューブ22の周面を透過してきた雰囲気中の成分が、吸着剤3によって吸着される。所定時間経過後、測定環境からパッシブ型サンプラー22を取り出し、サンプリングを終了する。

【0045】サンプリング終了後のパッシブ型サンプラー21は、測定管10の内部に挿入される。このとき、封止蓋24の外径が該測定管10の内径と同一もしくは若干小さい寸法となっており、パッシブ型サンプラー21はこの封止蓋24によって測定管10内部に略同軸状に保持される。なお、封止板23の外周面から突起を突設し、この突起を測定管10の内周面に当接させることにより多孔質チューブ22を測定管10内部に同軸状に保持させるようにしてもよい。

【0046】このパッシブ型サンプラー21を収容した測定管10は、公知の加熱脱着法による装置内部に設置され、加熱されると共に測定管10内部にキャリアガスが流される。このとき、測定管10内には封止蓋24が配置されているため、殆ど全てのキャリアガスは細管25を通じて多孔質チューブ22内部に導入される。細管25内に導入されたキャリアガスは、多孔質チューブ22内において細管25の周面を透過して流出し、吸着剤3及び多孔質チューブ22の側周面を透過して多孔質チューブ22の外側に流出する。

【0047】なお、多孔質チューブ22の一端は非通気性の封止板23によって封止されているため、全てのガスは多孔質チューブ22の側周面から流出する。この加熱によって吸着剤3から脱着した分析目的成分がキャリアガスによって多孔質チューブ22の外側に搬出される。このキャリアガスと分析目的成分は、測定管10の下流に設置されたガスクロマトグラフィー等の分析装置(図示略)に導入され、分析される。

【0048】このパッシブ型サンプラー21にあっては、多孔質チューブ22の側周面から透過してきた成分が吸着剤3に吸着されるため、吸着効率が高く、比較的短時間でサンプリングを行うことができる。多孔質チュ

ープ22の両端は封止板23及び封止蓋24によって封止されているため、該チューブ22内に塵や異物、生物などが入り込むことが防止できる。また、多孔質チューブ22の内部に充填された吸着剤3が封止板23及び封止蓋24によって移動不能に保持されているため、吸着剤3同士がぶつかって磨耗し、劣化する事なく、多数回繰り返し使用することができる。

【0049】この成分の分析方法にあっては、パッシブ型サンプラー21をそのまま測定管10内に挿入して分析するため、操作が簡単である。また、吸着剤3を多孔質チューブ22から他の容器等に移動する必要がないため、移動時に吸着剤3の一部が残留し、成分の分析値に誤差を生じさせるということはない。さらに、移動時に吸着剤3同士がぶつかって磨耗し、劣化するということもない。

【0050】また、この成分の分析方法にあっては、加熱により脱着した成分が、キャリアガスによって効率的に多孔質チューブ22の外側に搬送される。このため、脱着した成分が多孔質チューブ22内に滞留して分析値に誤差が生じるということなく、測定精度が良好なものとなる。

【0051】なお、この実施の形態に係るパッシブ型サンプラーでは、雰囲気中の成分は多孔質チューブ22を拡散して吸着剤3に吸着されるため、多孔質チューブ22内に充填された吸着剤3のうち多孔質チューブ22の内周壁に近いものほど多くの成分を吸着する。従って、図5の分析方法のように、キャリアガスを軸心部分の多孔質細管25を通して吸着剤に供給すると、キャリアガスは細管25から放射方向に流れて吸着剤3の層を通り抜けるため、多孔質チューブ22の内周壁近傍の吸着剤3から脱着された成分は、脱着後直ちに多孔質チューブ22を通過し、取り出される。従って、この図5の分析方法によると、成分の脱着を迅速に行うことができる。

【0052】上記実施の形態は本発明の一例であって、本発明は上記実施の形態に限定されるものではない。例えば、上記実施の形態では多孔質チューブ2, 22は直管状であるが、湾曲ないし屈曲した管であってもよく、コイル状とされたものであってもよい。また、多孔質チューブ2, 22は円形断面形状のものに限定されるものではなく、角筒状や偏平状のものであってもよい。さらに、多孔質チューブ2, 22の両端にキャップを留める

ための凹凸やねじを設けてもよい。この多孔質チューブ2, 22には、室内に吊り下げるための紐等を係止するための係止部を設けてもよい。

#### 【0053】

【発明の効果】以上の通り、本発明のパッシブ型サンプラー及びその分析方法によれば、分析操作がきわめて容易であるとともに、多数回繰り返し使用することができ、且つ測定精度の良好なパッシブ型サンプラー及びその分析方法を提供することができる。

#### 【図面の簡単な説明】

【図1】実施の形態に係るパッシブ型サンプラーを示す断面図である。

【図2】図1のパッシブ型サンプラーの多孔質チューブの斜視図である。

【図3】図1のパッシブ型サンプラーによってサンプリングされた雰囲気中の成分を分析する方法を説明する断面図である。

【図4】(a)は本発明の別の実施の形態に係るパッシブ型サンプラーの斜視図、(b)は(a)のパッシブ型サンプラーの細管の斜視図、(c)は(a)のパッシブ型サンプラーの多孔質チューブの斜視図である。

【図5】図4のパッシブ型サンプラーによってサンプリングされた成分を分析する方法を説明する断面図である。

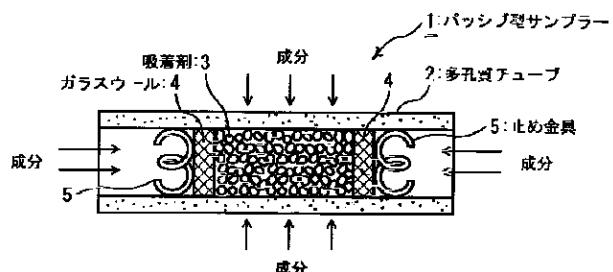
【図6】図5のVI-VI線に沿う断面図である。

【図7】図5のVII-VII線に沿う断面図である。

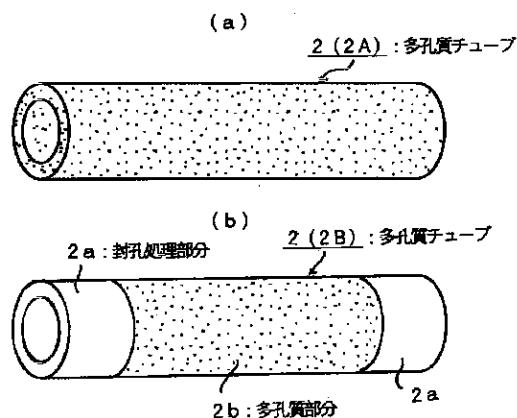
#### 【符号の説明】

- 1 パッシブ型サンプラー
- 2, 2A, 2B 多孔質チューブ
- 3 吸着剤
- 4 ガラスウール
- 5 止め金具
- 10 測定管
- 11 止め金具
- 21 パッシブ型サンプラー
- 22 多孔質チューブ
- 23 封止板
- 24 封止蓋
- 24a 周壁部
- 25 細管

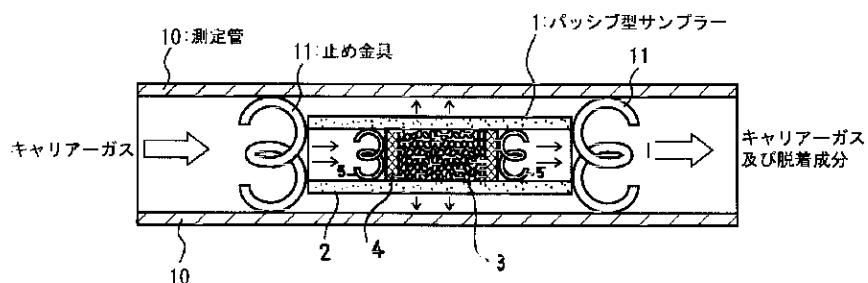
【図1】



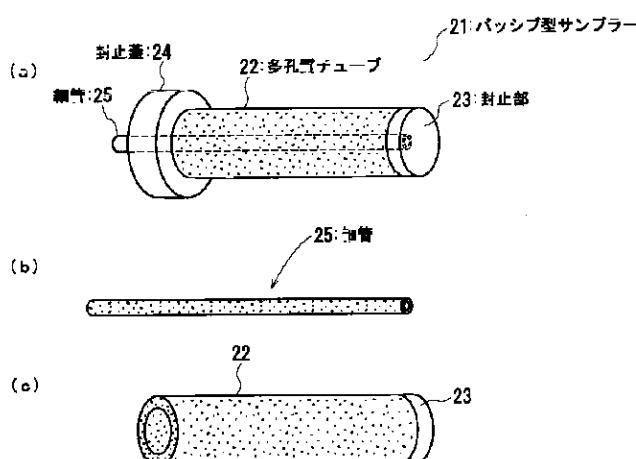
【図2】



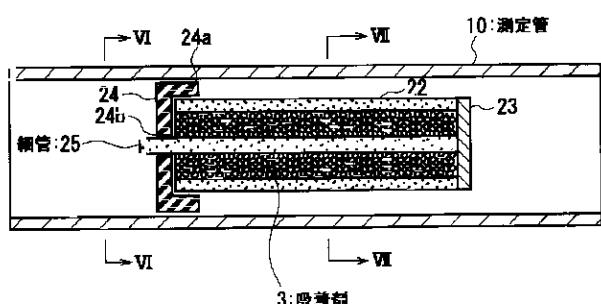
【図3】



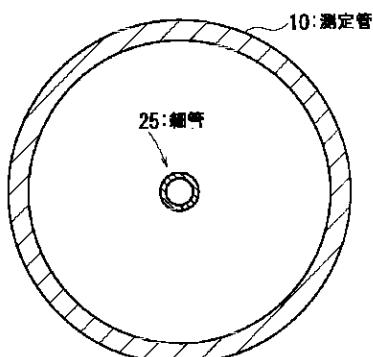
【図4】



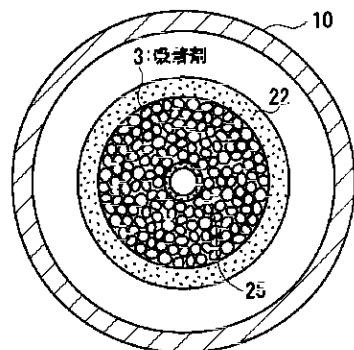
【図5】



【図6】



【図7】



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フロントページの続き

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ED09 GA27 JA09

## Notice

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## DESCRIPTION JP2002310863A

### [0001]

13 BACKGROUND OF THE INVENTION 1. Field of the Invention The present invention relates to a passive sampler for collecting components, particularly trace components, contained in atmospheres such as outdoor and indoor air by adsorbing them to adsorbents, and components using this passive sampler. and related to the analysis method of

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18 【発明の属する技術分野】本発明は、屋外、屋内の大气等の雰囲気中に含まれる成分特に微量成分を吸着剤に吸着させて捕集するパッシブ型サンプラーと、このパッシブ型サンプラーを用いた成分の分析方法とに関する。

### [0002]

26 2. Description of the Related Art In environmental monitoring and environmental measurement of gaseous substances generated in various industrial fields and living environments, specific gaseous substances and aerosols in the atmosphere are sampled, collected, and collected atmospheric substances. is analyzed with an analyzer.

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31 【従来の技術】各種産業分野や居住環境で生じるガス状物質の環境監視モニターや環境測定等においては、大気中の特定のガス状物質やエアロゾルなどを採取、捕集し、捕集した大気物質を分析装置で分析を行っている。

## [0003]

39 As methods for collecting gaseous substances and aerosols in the atmosphere, methods such as the vacuum bottle method, the suction bottle method, and the collection bag method have been conventionally known.

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43 大気中のガス状物質やエアロゾルを採取する方法としては、従来より真空瓶法、吸引瓶法、捕集バック法等の方法が知られている。

47 In these collection methods, the sample is collected in a gaseous state in various containers evacuated by a suction pump, or the sample is collected directly into a sample bag through a pump. I need.

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51 これらの捕集方法は、吸引ポンプで減圧した各種容器内に試料を気体状態で採取するものや、ポンプを通して試料袋に直接試料を採取するものであるため、減圧装置や吸引ポンプ等の装置を必要とする。

56 Therefore, installation space for these devices is required, and there are problems such as an increase in equipment costs for the devices and personnel expenses for collection and extraction. In addition, the noise from the pump was giving discomfort to the residents.

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60 そのため、これらの装置のための設置スペースを必要とし、また装置の設備費、捕集、採取のための人的経費が増加する等の問題がある。また、ポンプによる騒音が居住者に不快感を与えていた。

## [0004]

68 On the other hand, a passive sampler that is small and does not require a device such as a pump has been proposed.

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71 これに対して、小型でポンプ等の装置を必要としないパッシブ型サンプラーが提案されている。

75 A passive sampler performs sampling simply by placing the sampler in the measurement environment, and does not have a device such as a pump. The adsorbent is made to adsorb a substance to be adsorbed.

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79 パッシブ型サンプラーは、サンプラーを測定環境中に配置するだけでサンプリングを行うもの

であり、ポンプ等の装置を持たず、測定環境内の気体の流れのみによって吸着物質と吸着剤とを接触させて、吸着剤に被吸着物質を吸着させるものである。

## [0005]

<sup>87</sup> A conventional passive sampler is disclosed in JP-A-10-300647.

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<sup>89</sup> 従来のパッシブ型サンプラーとしては、特開平10-300647号に記載されているものがある。

<sup>93</sup> This passive sampler consists of a container and an adsorption section. The container has a cylindrical shape, one end of which is closed with a stopper, and the inside is filled with an adsorbent. The adsorption part has a substantially cylindrical shape with one end closed by a plug, and the open end of the adsorption part is detachably fitted to the open end of the container. This adsorption part is composed of a molecular diffusion filter through which the substance to be adsorbed can pass.

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<sup>100</sup> このパッシブ型サンプラーは、容器と、吸着部とからなる。容器は、一端が栓によって閉止された円筒形をしており、内部に吸着剤が充填されている。吸着部は、一端が栓によって閉止された略円筒形をしており、吸着部の開口端が前記容器の開口端に着脱可能に外嵌されている。この吸着部は被吸着物質の通過が可能な分子拡散フィルタによって構成されている。

## [0006]

<sup>109</sup> The sampler configured in this manner is placed in the measurement environment so that the adsorption portion faces downward and the container faces upward during sampling.

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<sup>112</sup> このように構成されたサンプラーは、サンプリング時には、吸着部が下側、容器が上側となるようにして測定環境中に配置される。

<sup>116</sup> At this time, since the adsorbent has moved to the lower adsorbing portion, it adsorbs the substance to be adsorbed that has passed through the adsorbing portion.

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<sup>119</sup> このとき、吸着剤は下側の吸着部に移動しているため、吸着部を通過してきた被吸着物質を吸着する。

## [0007]

126 After completion of sampling, the sampler is turned over to move the adsorbent from the adsorption part side to the container side.

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129 サンプリング終了後は、サンプラーを反転し、吸着剤を吸着部側から容器側に移動させる。

## [0008]

135 When analysis is performed after sampling is completed, the adsorption part and stopper are removed from the container, and the container is attached to the analyzer for analysis.

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138 サンプリング終了後に分析を行う場合は、容器から吸着部及び栓を取り外し、容器を分析装置に取り付けて分析を行う。

142 The container is then used as a measuring tube in the analyzer.

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144 このとき、容器は分析装置内で測定管として使用される。

## [0009]

150 In the passive sampler disclosed in Japanese Patent Application Laid-Open No. 10-300647, when the adsorbent is transferred from the adsorption section to the container after sampling, the adsorbent remains in the adsorption section and is adsorbed. It causes an error in the analytical value of the substance.

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155 【発明が解決しようとする課題】上記特開平10-300647号のパッシブ型サンプラーにあっては、サンプリング後に吸着剤を吸着部から容器に移動させる場合、吸着部に吸着剤が残存し、被吸着物質の分析値に誤差を生じさせる。

160 In addition, the passive sampler cannot be used repeatedly many times because the adsorbent collides with each other and wears out while the adsorbent moves between the container and the adsorption part.

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<sup>164</sup> また、吸着剤が容器及び吸着部間を移動する間に、吸着剤同士がぶつかって磨耗するため、パッシブ型サンプラーを多数回繰り返し使用することはできない。

<sup>168</sup> It should be noted that when the adsorbent is worn out, the adsorption characteristics change, so the component analysis accuracy changes.

<sup>171</sup> なお、吸着剤が磨耗すると、吸着特性が変化するため、成分の分析精度が変化するようになる。

。

## [0010]

<sup>178</sup> The present invention solves the problems of the conventional passive samplers described above, and aims to provide a passive sampler with good measurement accuracy and a method of analyzing atmospheric components such as the atmosphere using this passive sampler. aim.

<sup>183</sup> 本発明は、前記した従来のパッシブ型サンプラーの問題点を解決し、測定精度が良好なパッシブ型サンプラーと、このパッシブ型サンプラーを用いた大気等の雰囲気の成分を分析する方法を提供することを目的とする。

## [0011]

<sup>191</sup> Another object of the present invention is to provide a passive sampler that can be used for repeated sampling many times, and a method for analyzing components in an atmosphere using this passive sampler.

<sup>195</sup> また、本発明は、多数回繰り返しサンプリングに使用することができるパッシブ型サンプラーと、このパッシブ型サンプラーを用いた雰囲気中の成分の分析方法を提供することを目的とする。

## [0012]

<sup>203</sup> SUMMARY OF THE INVENTION A passive sampler of the present invention (claim 1) has a porous tube and an adsorbent filled in the porous tube.

206 【課題を解決するための手段】本発明（請求項1）のパッシブ型サンプラーは、多孔質チューブと、該多孔質チューブ内に充填された吸着剤とを有するものである。

### [0013]

213 According to such a passive sampler, since the porous tube itself containing the adsorbent has gas permeability, the adsorbent is allowed to pass through the porous tube without moving the adsorbent from the porous tube to another container or the like during sampling. The target component can be adsorbed to the adsorbent and sampled while being placed in the sample tube.

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219 かかるパッシブ型サンプラーによれば、吸着剤を収納している多孔質チューブ自体がガス透過性を有するため、サンプリング時に吸着剤を多孔質チューブから他の容器等に移動させることなく、吸着剤を多孔質チューブ内にそのまま位置させたまま目的成分を該吸着剤に吸着させてサンプリングすることができる。

225 Therefore, the adsorbents can be repeatedly used for sampling many times without the adsorbents colliding with each other due to movement and being worn and deteriorated.

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228 従って、移動によって吸着剤同士がぶつかって磨耗し、劣化するということがなく、吸着剤を多数回繰り返しサンプリングに使用することができる。

### [0014]

235 In the passive sampler of the present invention, it is preferable that the adsorbent is immovably held within the porous tube (claim 2).

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238 本発明のパッシブ型サンプラーは、前記吸着剤が前記多孔質チューブ内で移動不能に保持されていることが好ましい（請求項2）。

242 In this case, the adsorbent does not deteriorate due to wear, and can be used repeatedly a very large number of times.

---

245 この場合、該吸着剤は磨耗による劣化が全くないため、きわめて多数回繰り返し使用することができる。

## [0015]

252 In the passive sampler of the present invention, a porous thin tube is arranged in the axial center portion of the porous tube, and the adsorbent is filled between the thin tube and the porous tube. (Claim 3).

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256 本発明のパッシブ型サンプラーは、前記多孔質チューブの軸心部分に多孔質の細管が配置されており、前記吸着剤は該細管と前記多孔質チューブとの間に充填されているものであってもよい（請求項3）。

261 Also in this case, since the adsorbent can be sampled while it is housed in the porous tube, the adsorbents do not collide with each other due to movement and wear and deteriorate, and the adsorbent can be repeatedly used for sampling many times. be able to.

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265 この場合も、吸着剤を多孔質チューブ内に収容したままサンプリングすることができるため、移動によって吸着剤同士がぶつかって磨耗し、劣化するということがなく、吸着剤を多数回繰り返しサンプリングに使用することができる。

## [0016]

273 The analysis method of the present invention (claim 4) is a method of analyzing components in an atmosphere such as air using the passive sampler, wherein the passive sampler is brought into contact with the atmosphere to After the component is adsorbed by the adsorbent, the passive sampler is placed in a non-air-permeable measuring tube, and the adsorbent is heated while air is being passed through the measuring tube to desorb the component for analysis.

---

280 本発明（請求項4）の分析方法は、前記パッシブ型サンプラーを用いて大気等の雰囲気中の成分の分析を行う方法であって、該パッシブ型サンプラーを雰囲気と接触させて該パッシブ型サンプラーの吸着剤に成分を吸着させた後、該パッシブ型サンプラーを非通気性の測定管に入れ、該測定管内に通気しながら吸着剤を加熱して成分を脱着させて分析するものである。

## [0017]

289 According to this analysis method, after sampling, analysis can be performed without

removing the adsorbent from the passive sampler.

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292 かかる分析方法によれば、サンプリングした後、吸着剤をパッシブ型サンプラーから取り出すことなく分析することができる。

296 Therefore, the analytical operation is extremely easy, and when the adsorbent is taken out, a part of the adsorbent remains in the passive sampler, which causes an error in the analytical value, resulting in good measurement accuracy. .

---

300 従って、分析操作がきわめて容易であると共に、吸着剤を取り出すときに吸着剤の一部がパッシブ型サンプラー内に残存じて分析値に誤差が生じるということがなく、測定精度が良好なものとなる。

305 Moreover, since the adsorbent is not taken out, the adsorbent is not worn out and can be used repeatedly many times.

---

308 また、吸着剤を取り出すことがないため、吸着剤が磨耗することがなく、吸着剤を多数回繰り返し使用することができる。

## [0018]

315 The analysis method of the present invention (Claim 5) is a method of analyzing components in an atmosphere such as air using the passive sampler of Claim 3, wherein the passive sampler is brought into contact with the atmosphere. After the component is adsorbed by the adsorbent of the passive sampler, the passive sampler is placed in a non-air-permeable measurement tube, a carrier gas for desorption is supplied into the narrow tube, and the adsorbent is heated to obtain the component. is characterized by desorption and analysis.

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322 本発明（請求項 5）の分析方法は、請求項 3 に記載のパッシブ型サンプラーを用いて大気等の雰囲気中の成分の分析を行う方法であって、該パッシブ型サンプラーを雰囲気と接触させて該パッシブ型サンプラーの吸着剤に成分を吸着させた後、該パッシブ型サンプラーを非通気性の測定管に入れ、前記細管内に脱着用のキャリアガスを供給すると共に、吸着剤を加熱して成分を脱着させて分析することを特徴とするものである。

## [0019]

332 According to this analysis method, the carrier gas supplied into the narrow tube is introduced into the axial center portion of the porous tube, permeates through the adsorbent and the peripheral wall of the porous tube from the axial center portion, and enters the porous tube. flow outside.

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337 かかる分析方法によれば、前記細管内に供給されたキャリアガスは、多孔質チューブの軸心部分に導入され、該軸心部分から吸着剤及び多孔質チューブの周壁を透過して多孔質チューブの外側に流出する。

342 In this analysis method as well, the components desorbed from the adsorbent due to heating are transported by this carrier gas and efficiently flow out of the porous tube. measurement accuracy is improved.

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346 この分析方法においても、加熱により吸着剤から脱着した成分は、このキャリアガスに搬送されて効率的に多孔質チューブの外側に流出するため、脱着した成分が多孔質チューブ内に滞留して分析値に誤差が生じるということがなく、測定精度が良好なものとなる。

351 In addition, since the adsorbent can be analyzed without removing it from the passive sampler after sampling, the analysis operation is extremely easy, and some of the adsorbent remains in the passive sampler when the adsorbent is removed. As a result, there is no error in the analytical value, and the measurement accuracy is good.

---

356 また、サンプリングした後、吸着剤をパッシブ型サンプラーから取り出すことなく分析することができるため、分析操作がきわめて容易であると共に、吸着剤を取り出すときに吸着剤の一部がパッシブ型サンプラー内に残存して分析値に誤差が生じるということがなく、測定精度が良好なものとなる。

362 Furthermore, since the adsorbent is not taken out, the adsorbent is not worn out and can be used repeatedly many times.

---

365 さらに、吸着剤を取り出すことがないため、吸着剤が磨耗することなく、吸着剤を多数回繰り返し使用することができる。

## [0020]

372 In the passive sampler of the present invention, the component diffuses through the porous tube and is adsorbed by the adsorbent. adsorbs the components of

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375 なお、本発明のパッシブ型サンプラーでは、成分は多孔質チューブを拡散して吸着剤に吸着されるため、多孔質チューブ内に充填された吸着剤のうち多孔質チューブの内周壁に近いものほど多くの成分を吸着する。

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380 Therefore, when the carrier gas is supplied to the adsorbent through the porous thin tube at the axial center portion as in the analysis method of claim 5, the carrier gas flows radially from the thin tube and passes through the adsorbent layer. Components desorbed from the adsorbent near the inner peripheral wall pass through the porous tube immediately after desorption and are taken out.

---

386 従って、請求項 5 の分析方法のように、キャリアガスを軸心部分の多孔質細管を通して吸着剤に供給すると、キャリアガスは細管から放射方向に流れて吸着剤層を通り抜けるため、多孔質チューブの内周壁近傍の吸着剤から脱着された成分は、脱着後直ちに多孔質チューブを通過し、取り出される。

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392 Therefore, according to the method of claim 5, the components can be desorbed rapidly.

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394 従って、この請求項 5 の方法によると、成分の脱着を迅速に行うことができる。

## [0021]

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400 DETAILED DESCRIPTION OF THE INVENTION Embodiments of the present invention will now be described in detail with reference to the drawings.

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403 【発明の実施の形態】以下、本発明の実施の形態を図を参照にして詳細に説明する。

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406 FIG. 1 is a sectional view of a passive sampler according to an embodiment of the present invention, and FIGS. 2(a) and 2(b) are perspective views of porous tubes of the passive sampler of FIG.

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410 図 1 は本発明の実施の形態に係るパッシブ型サンプラーの断面図、図 2 ( a ) , ( b ) は図 1 のパッシブ型サンプラーの多孔質チューブの斜視図である。

## [0022]

417 A passive sampler 1 has a cylindrical porous tube 2 with both ends open and an adsorbent 3 housed inside the porous tube 2 .

---

420 パッシブ型サンプラー 1 は、両端が開口した円筒形の多孔質チューブ 2 と、この多孔質チューブ 2 の内部に収容された吸着剤 3 を有する。

424 This adsorbent 3 is arranged in portions other than both ends of the porous tube 2 .

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426 この吸着剤 3 は、多孔質チューブ 2 の両端以外の部分に配置されている。

429 The adsorbent 3 is held immovably by filling glass wool 4, 4 from both ends of the porous tube 2, and installing fasteners 5, 5 on the outer ends thereof. As the fastener 5, a corrosion-resistant metal wire bent in a U-shape, an L-shape, a W-shape, or the like is suitable, but other than this may be used.

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434 吸着剤 3 は、多孔質チューブ 2 の両端側からガラスウール 4, 4 を充填し、さらにその外端に止め金具 5, 5 を設置することによって移動不能に保持されている。この止め金具 5 としては、耐食性の金属線を U 字形状、L 字形状やW字形状等に湾曲させたものが好適であるが、これ以外のものを用いてもよい。

## [0023]

443 As the porous tube 2, one that is permeable to the atmosphere and the components for analysis in the atmosphere is used.

---

446 多孔質チューブ 2 としては、雰囲気及び該雰囲気中の分析目的成分を透過可能なものが使用される。

450 It is preferable that the material of the porous tube 2 can withstand the heating temperature when performing the component analysis by the thermal desorption method after sampling. Specifically, porous ceramics, porous metals, porous heat-resistant synthetic resins, and the like are used. The porous tube 2 may be rigid or flexible.

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455 多孔質チューブ 2 の材質は、サンプリング後に加熱脱着法による成分分析を行う際の加熱温度に耐え得るものであることが好ましい。具体的には、多孔質セラミックス、多孔質金属、多孔質耐熱性合成樹脂などが使用される。多孔質チューブ 2 は硬質のものであってもよく、柔

軟性を有したものであってもよい。

## [0024]

464 As the porous tube 2, as shown in FIG. 2(a), a porous tube 2A made entirely of a porous material may be used, or as shown in FIG. Portions 2a, 2a at both ends of the tube where there is no adsorbent inside and diffusion of the gas component does not substantially occur, and the porous pores are blocked so that the gas does not permeate. It may be the tube 2B.

---

469 多孔質チューブ 2 としては、図 2 ( a ) に示す如く、その全体が多孔質材料とされた多孔質チューブ 2 A であっても良く、また、図 2 ( b ) に示す如く、多孔質材料よりなるチューブの両端の、内側に吸着剤が存在せず、実質的にガス成分の拡散が生じない部分 2 a , 2 a を、ガスが透過しないように多孔質の孔をふさいだ処理を施した多孔質チューブ 2 B であっても良い。

476 The purpose of the sealing treatment of the end portions 2a, 2a is mainly to increase the strength of the porous tube. is coated by spraying or dipping, dried and then baked.

---

479 この両端部分 2 a , 2 a の封孔処理の目的は、主に多孔質チューブの強度を高めることにあり、その具体的な方法としては、多孔質チューブの表面に焼成によりガラス質となるような成分をスプレー、もしくはディッピングによりコーティングし、乾燥後、焼成する方法が挙げられる。

## [0025]

488 In this case, as a specific example of the component that becomes vitrified by firing, a composition of 95 to 97% vitreous frit and 3 to 5% clay is dispersed in water.

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491 この場合、焼成によりガラス質となる成分の具体例としては、ガラス質フリット 9 5 ~ 9 7 %、粘土 3 ~ 5 %の組成物を水に分散させたものが挙げられる。

495 This vitreous component is not particularly limited as long as it can withstand the heating temperature during the analysis of the adsorbed component.

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498 このガラス質成分は、吸着成分の分析の際に加熱するときの加熱温度に耐え得るものであれば良く、特に限定されるものではない。

## [0026]

505 It is preferable that the adsorbent 3 has a large adsorption amount of the target component and is easily desorbed.

---

508 吸着剤3は、目的成分の吸着量が多く、また脱着が容易なものが好適である。

511 Specifically, as the adsorbent, activated carbon, silica gel, molecular sieves, porous polymers (Tenax resin, etc.) and the like are suitable, and activated carbon is particularly preferable. This adsorbent 3 is preferably in the form of fine granules. The granular adsorbent is easy to fill into the porous tube 2, and gas passes between the particles of the adsorbent 3. Therefore, the adsorbent filled near the core portion of the porous tube 2 Also, the target component is sufficiently adsorbed.

---

518 具体的には、吸着剤としては活性炭、シリカゲル、モレキュラーシーブ、ポーラスopolマー（Tenax樹脂等）等が好適であり、特に活性炭が好ましい。この吸着剤3は微細な顆粒状のものが好ましい。顆粒状の吸着剤は、多孔質チューブ2への充填が容易であると共に、吸着剤3の粒子同士の間にガスが通気するので、多孔質チューブ2の芯部分付近に充填された吸着剤にも目的成分が十分に吸着されるようになる。

## [0027]

528 Sampling is performed by installing the passive sampler 1 configured as described above in a measurement environment.

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531 このように構成されたパッシブ型サンプラー1を測定環境下に設置することによりサンプリングを行う。

535 At this time, the components in the atmosphere that have permeated the side peripheral surface of the porous tube 2 and the components in the atmosphere that have entered from the open end of the porous tube 2 are adsorbed by the adsorbent 3 . After a predetermined time has elapsed, the passive sampler 1 is taken out from the measurement environment, and sampling ends.

---

541 このとき、多孔質チューブ2の側周面を透過してきた雰囲気中の成分及び多孔質チューブ2の

開口端から侵入してきた霧囲気中の成分が、吸着剤 3 によって吸着される。所定時間経過後、測定環境からパッシブ型サンプラー 1 を取り出し、サンプリングを終了する。

## [0028]

549 In this passive-type sampler 1, in addition to the components entering through the open end of the porous tube 2 being adsorbed by the adsorbent 3, the components permeating through the side peripheral surface of the porous tube 2 are also adsorbed by the adsorbent. 3, the adsorption efficiency is high, and sampling can be performed in a relatively short time.

---

554 このパッシブ型サンプラー 1 にあっては、多孔質チューブ 2 の開口端から侵入してきた成分が吸着剤 3 に吸着されるのに加え、多孔質チューブ 2 の側周面から透過してきた成分も吸着剤 3 に吸着されるため、吸着効率が高く、比較的短時間でサンプリングを行うことができる。

559 However, a detachable cap may be attached to one end or both ends of the porous tube 2 so that only the components in the atmosphere that have passed through the porous tube 2 are adsorbed by the adsorbent 3 during sampling. By doing so, it is possible to prevent dust, foreign matter, living things, etc. from entering the porous tube 2 . This cap should be removed when removing.

---

565 ただし、多孔質チューブ 2 の一端又は両端に着脱可能なキャップを装着し、サンプリング時には多孔質チューブ 2 を透過した霧囲気中の成分のみが吸着剤 3 に吸着されるようにしてよい。このようにすれば、塵や異物、生物などが該多孔質チューブ 2 内に入り込むことを防止できる。このキャップは脱着時に外せばよい。

## [0029]

574 In this passive-type sampler 1, since the adsorbent 3 is immovably held by the glass wool 4 and the fastener 5, the adsorbent 3 does not collide with each other to be worn or deteriorated, and can be used repeatedly many times. can do.

---

578 このパッシブ型サンプラー 1 にあっては、吸着剤 3 がガラスウール 4 及び止め金具 5 によって移動不能に保持されているため、吸着剤 3 同士がぶつかって磨耗、劣化することがなく、多数回繰り返し使用することができる。

## [0030]

586 Further, as shown in FIG. 2(b), if the porous tube 2B is reinforced by sealing the portions 2a, 2a at both ends where the gas component does not diffuse, the strength of the porous tube is high, and the porous tube can be repeated more times. can be a passive sampler that can withstand repeated use.

---

591 また、図 2 ( b ) に示す如く、両端のガス成分が拡散しない部分 2 a , 2 a を封孔処理して補強した多孔質チューブ 2 B であれば、多孔質チューブの強度が高く、より一層多数回の繰り返し使用に耐え得るパッシブ型サンプラーとすることができる。

596 In addition, with this porous tube 2B, the porous portion 2b through which the gas component permeates and the sealing treated portions 2a, 2a through which the gas component does not permeate are visually distinguished, and when the sampler is handled, the portion through which the gas component permeates. It is also expected to prevent the portion 2b from being touched with bare hands and to prevent the portion 2b from being contaminated with impurities that hinder permeation of gas components such as oil components.

---

604 また、この多孔質チューブ 2 B であれば、ガス成分が透過する多孔質部分 2 b と透過しない封孔処理部分 2 a , 2 a とが外見上区別され、サンプラーの取扱いの際に、ガス成分が透過する部分 2 b を素手で触ることを防ぎ、この部分 2 b が油成分などのガス成分の透過を妨げる不純物で汚染されることを防止する効果も期待される。

## [0031]

613 FIG. 3 is a cross-sectional view explaining a method of analyzing components sampled by the passive sampler 1 of FIG.

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616 図 3 は、図 1 のパッシブ型サンプラー 1 によってサンプリングされた成分を分析する方法を説明する断面図である。

## [0032]

623 After completing sampling, the passive sampler 1 is inserted into a cylindrical measuring tube 10 with both ends opened, and held immovably by fasteners 11 and the like.

---

626 サンプリング終了後のパッシブ型サンプラー 1 は、両端が開口した円筒形の測定管 10 の内部に挿入され、止め金具 11 等によって移動不能に保持される。

630 Since the inner diameter of the measuring tube 10 is larger than the outer diameter of the porous tube 2 , there is a gap between the inner peripheral surface of the measuring tube 10 and the outer peripheral surface of the porous tube 2 .

---

634 この測定管 10 の内径は多孔質チューブ 2 の外径よりも大きいため、測定管 10 の内周面と多孔質チューブ 2 の外周面との間には隙間が存在する。

### [0033]

641 A measuring tube 10 containing a passive sampler 1 is installed inside an apparatus using a known thermal desorption method.

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644 パッシブ型サンプラー 1 を収容した測定管 10 は、公知の加熱脱着法による装置内部に設置される。

648 In this device, the carrier gas is flowed inside the measuring tube 10 and the measuring tube 10 is heated, so that the adsorbent 3 is also heated.

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651 この装置内において、測定管 10 の内部にキャリアガスが流されると共に、測定管 10 が加熱され、吸着剤 3 も加熱される。

655 Due to this heating, the components adsorbed on the adsorbent 3 are desorbed from the adsorbent 3, and the desorbed components flow out from the open end of the porous tube 2 or through the peripheral surface of the porous tube 2.

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659 この加熱によって、吸着剤 3 に吸着していた成分が吸着剤 3 から脱着し、脱着した成分は多孔質チューブ 2 の開口端から、あるいは多孔質チューブ 2 の周面を透過して流出する。

663 Then, it is transported to a carrier gas, introduced into an analytical instrument (not shown) such as a gas chromatograph installed downstream of the measuring tube 10, and analyzed.

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666 そして、キャリアガスに搬送され、測定管 10 の下流に設置されたガスクロマトグラフィー等の分析機器（図示略）に導入され、分析される。

## [0034]

673 The measurement conditions of the measuring tube 10 are, for example, temperature: 50-500 ° C., time: 1-60 minutes, carrier gas: helium, nitrogen, pressure: 50-300 kPa.

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676 なお、測定管 10 の測定条件は、例えば温度：50～500 、時間：1分～60分、キャリアガス：ヘリウム、チッソ、圧力：50～300 kPa とする。

## [0035]

683 In this component analysis method, since the passive sampler 1 is directly inserted into the measurement tube 10 for analysis, the operation is simple.

---

686 この成分の分析方法にあっては、パッシブ型サンプラー 1 をそのまま測定管 10 内に挿入して分析するため、操作が簡単である。

690 Moreover, since there is no need to move the adsorbent 3 from the porous tube 2 to another container or the like, there is no possibility that part of the adsorbent 3 remains during the transfer and causes an error in the analytical values of the components.

---

694 また、吸着剤 3 を多孔質チューブ 2 から他の容器等に移動する必要がないため、移動時に吸着剤 3 の一部が残留し、成分の分析値に誤差を生じさせるということがない。

698 Furthermore, the adsorbents 3 do not collide with each other during movement and are worn and deteriorated.

---

701 さらに、移動時に吸着剤 3 同士がぶつかって磨耗し、劣化するということもない。

## [0036]

707 In this passive sampler 1 , most of the components for analysis in the measurement environment pass through the side peripheral surface of the porous tube 2 and are adsorbed by the adsorbent 3 .

---

711 このパッシブ型サンプラー 1 にあっては、測定環境中の分析目的成分の多くは、多孔質チューブ 2 の側周面を通過して吸着剤 3 に吸着される。

715 Therefore, in the cross section in the longitudinal direction and the vertical direction of the porous tube 2, the amount of adsorption of the component of the adsorbent 3 decreases toward the core portion of the porous tube 2, and increases toward the inner peripheral surface of the porous tube 2. It is normal to become Therefore, when the passive sampler 1 is desorbed, a considerable portion of the components to be desorbed permeate the porous tube 2 from the inner peripheral side to the outer peripheral side. In the desorption device of FIG. 3, the carrier gas is circulated in the gap between the outer circumference of the porous tube 2 and the inner circumference of the measurement tube 10. Therefore, the components that are desorbed from the adsorbent 3 and permeate the porous tube 2 are It can be transported by the carrier gas between the measuring tube 10 and the porous tube 2 to efficiently flow out from the measuring tube 10 .

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727 従って、多孔質チューブ 2 の長手方向と垂直方向の断面においては、多孔質チューブ 2 の芯部分ほど吸着剤 3 の成分吸着量が少なく、多孔質チューブ 2 の内周面に近づくほど吸着量が多くなることが通常である。従って、このパッシブ型サンプラー 1 を脱着処理する場合、脱着する成分のかなりの部分が多孔質チューブ 2 を内周側から外周側に透過するようになる。図 3 の脱着装置では多孔質チューブ 2 の外周と測定管 10 の内周との間の隙間にキャリアガスが流通されるため、吸着剤 3 から脱着して多孔質チューブ 2 を透過した成分が、この測定管 10 と多孔質チューブ 2 との間のキャリアガスに搬送されて効率的に測定管 10 から流出させることができる。

## [0037]

740 FIG. 4(a) is a perspective view of a passive sampler according to another embodiment of the present invention, FIG. 4(b) is a perspective view of a narrow tube of the passive sampler of FIG. 4(a), and FIG. 4(c) is a perspective view of the porous tube of the passive sampler of Figure 4(a);

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745 図 4 ( a ) は本発明の別の実施の形態に係るパッシブ型サンプラーの斜視図、図 4 ( b ) は図 4 ( a ) のパッシブ型サンプラーの細管の斜視図、図 4 ( c ) は図 4 ( a ) のパッシブ型サンプラーの多孔質チューブの斜視図である。

750 FIG. 5 is a cross-sectional view explaining a method of analyzing the components sampled by the passive sampler of FIG. 4(a), FIG. 6 is a cross-sectional view along line VI-VI of FIG. It is a

cross-sectional view along line VII.

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754 図5は図4(a)のパッシブ型サンプラーによってサンプリングされた成分を分析する方法を説明する断面図、図6は図5のVI-VI線に沿う断面図、図7は図5のVII-VII線に沿う断面図である。

## [0038]

762 This passive sampler 21 includes a cylindrical porous tube 22, a porous thin tube 25 arranged at the axial center of the porous tube 22, and a space between the porous tube 22 and the thin tube 25, and an adsorbent 3.

---

766 このパッシブ型サンプラー21は、円筒形状をした多孔質チューブ22と、この多孔質チューブ22の軸心部分に配置された多孔質の細管25と、この多孔質チューブ22と細管25との間に充填された吸着剤3とを有する。

771 One end of this porous tube 22 is sealed by a flat disk-shaped sealing plate 23, and the other end is made of metal, glass, ceramics, or heat-resistant rubber or synthetic resin (heat-resistant in this embodiment). It is sealed by a sealing lid 24 made of rubber. The sealing plate 23 is adhered to the end surface of the porous tube 22 with, for example, a heat-resistant adhesive.

---

777 この多孔質チューブ22の一端は、平たい円盤状の封止板23によって封止されており、他端は金属、ガラス、セラミックスあるいは耐熱性のゴム又は合成樹脂製（この実施の形態では耐熱性のゴム製）の封止蓋24によって封止されている。封止板23は、例えば耐熱性の接着剤などにより多孔質チューブ22の端面に接着される。

## [0039]

786 The sealing lid 24 has a substantially disk shape, and a short cylindrical peripheral wall portion 24a that covers the outer peripheral surface of the porous tube 22 protrudes from the outer peripheral edge thereof.

---

790 封止蓋24は略円盤形であり、その外周縁からは多孔質チューブ22の外周面に被さる短い筒状の周壁部24aが突設されている。

794 The inner diameter of the peripheral wall portion 24 a is set slightly smaller than the outer diameter of the porous tube 22 , and the peripheral wall portion 24 a is fitted around the edge of the outer peripheral surface of the porous tube 22 .

---

798 この周壁部 2 4 a の内径は多孔質チューブ 2 2 の外径よりも若干小さく設定されており、該周壁部 2 4 a が前記多孔質チューブ 2 2 の外周面の縁部に外嵌されている。

#### [0040]

805 A through hole 24b is provided in the central portion of the sealing lid 24, and a thin tube 25 is inserted through the through hole 24b.

---

808 この封止蓋 2 4 の中心部分には貫通孔 2 4 b が設けられ、この貫通孔 2 4 b 内に細管 2 5 が挿通されている。

812 The tip of the thin tube 25 reaches the sealing plate 23 , and the tip surface of the thin tube 25 is in contact with the sealing plate 23 . A recess may be provided in the central portion of the sealing plate 23, and the tip of the thin tube 25 may be fitted into the recess. The gap between the outer peripheral surface of the thin tube 25 and the inner peripheral surface of the porous tube 22 is filled with the adsorbent 3 .

---

818 この細管 2 5 の先端は前記封止板 2 3 にまで達し、該細管 2 5 の先端面は該封止板 2 3 に当接している。なお、該封止板 2 3 の板央部に凹みを設け、該細管 2 5 の先端を該凹みに嵌入させてもよい。この細管 2 5 の外周面と前記多孔質チューブ 2 2 の内周面との間隙には、吸着剤 3 が充填されている。

#### [0041]

827 As the porous tube 22, a material equivalent to that of the porous tube 2 according to the previous embodiment is used.

---

830 多孔質チューブ 2 2 としては、先の実施の形態に係る多孔質チューブ 2 と同等の材質のものが使用される。

## [0042]

837 The sealing plate 23 is preferably non-breathable, but may be breathable.

---

839 封止板 23 は好ましくは非通気性のものが用いられるが、通気性のものであってもよい。

842 The sealing plate 23 is made of a material that can withstand the heating temperature during the component analysis by the thermal desorption method after sampling. be.

---

845 この封止板 23 は、サンプリング後に加熱脱着法による成分分析を行う際の加熱温度に耐え得るものが用いられ、具体的には耐熱性のゴム又は合成樹脂、金属、ガラス、セラミックスなどが使用される。

850 The sealing plate 23 may be directly joined to the porous tube 22 by an ultrasonic vibration method or the like, instead of using a heat-resistant adhesive. The sealing plate 23 may be shaped to cover the outer peripheral edge of the porous tube 22 like the sealing lid 24, and may be a plug-like body fitted inside the porous tube 22 like a rubber plug. There may be.

---

855 この封止板 23 は、耐熱性の接着剤のほか、超音波振動法等により直接、多孔質チューブ 22 に接合されてもよい。この封止板 23 は、封止蓋 24 と同様に多孔質チューブ 22 の外周端部に被さる形状のものであってもよく、ゴム栓の如く多孔質チューブ 22 に内嵌される栓状体であってもよい。

## [0043]

864 As the narrow tube 25, one that is permeable to atmospheric gases during sampling and analysis, components to be analyzed, carrier gases, and the like is used.

---

867 細管 25 としては、サンプリング時や分析時の雰囲気ガス、分析目的成分、キャリアガス等を透過可能なものが使用される。

871 The material of the capillary tube 25 is preferably capable of withstanding the heating temperature at which the component analysis is performed by the thermal desorption method after sampling. A tube having a large number of small-diameter holes in its side surface may also be used.

---

876 細管 25 の材質は、サンプリング後に加熱脱着法による成分分析を行う際の加熱温度に耐え得るものであることが好ましく、例えば、焼結ガラスや多孔質セラミックス等が好適であるが

、ガラス管や金属管の側面に小口径の孔を多数あけたものであってもよい。

## [0044]

884 Like the passive sampler 1, the passive sampler 21 configured in this manner performs sampling by being placed under the measurement environment.

---

887 このように構成されたパッシブ型サンプラー 21 は、前記パッシブ型サンプラー 1 と同様に、測定環境下に設置することによりサンプリングを行う。

891 At this time, the components in the atmosphere that have permeated the peripheral surface of the porous tube 22 are adsorbed by the adsorbent 3 . After a predetermined time has elapsed, the passive sampler 22 is taken out from the measurement environment, and sampling ends.

---

896 このとき、多孔質チューブ 22 の周面を透過してきた雰囲気中の成分が、吸着剤 3 によって吸着される。所定時間経過後、測定環境からパッシブ型サンプラー 22 を取り出し、サンプリングを終了する。

## [0045]

904 After sampling, the passive sampler 21 is inserted into the measurement tube 10 .

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906 サンプリング終了後のパッシブ型サンプラー 21 は、測定管 10 の内部に挿入される。

909 At this time, the outer diameter of the sealing lid 24 is the same as or slightly smaller than the inner diameter of the measuring tube 10, and the passive sampler 21 is held substantially coaxially inside the measuring tube 10 by the sealing lid 24. A projection is provided from the outer peripheral surface of the sealing plate 23 and brought into contact with the inner peripheral surface of the measuring tube 10 so that the porous tube 22 is coaxially held inside the measuring tube 10. good too.

---

916 このとき、封止蓋 24 の外径が該測定管 10 の内径と同一もしくは若干小さい寸法となっており、パッシブ型サンプラー 21 はこの封止蓋 24 によって測定管 10 内部に略同軸状に保持される。なお、封止板 23 の外周面から突起を突設し、この突起を測定管 10 の内周面に当接させることにより多孔質チューブ 22 を測定管 10 内部に同軸状に保持させるようにして

もよい。

## [0046]

926 The measurement tube 10 containing the passive sampler 21 is installed inside an apparatus using a known thermal desorption method, and is heated and a carrier gas is caused to flow inside the measurement tube 10 .

---

930 このパッシブ型サンプラー 21 を収容した測定管 10 は、公知の加熱脱着法による装置内部に設置され、加熱されると共に測定管 10 内部にキャリアガスが流される。

934 At this time, since the sealing lid 24 is arranged inside the measuring tube 10 , almost all the carrier gas is introduced into the inside of the porous tube 22 through the fine tube 25 . The carrier gas introduced into the thin tube 25 passes through the peripheral surface of the thin tube 25 in the porous tube 22 and flows out, permeates the adsorbent 3 and the side peripheral surface of the porous tube 22, and passes through the porous tube 22. flow outside.

---

941 このとき、測定管 10 内には封止蓋 24 が配置されているため、殆ど全てのキャリアガスは細管 25 を通って多孔質チューブ 22 内部に導入される。細管 25 内に導入されたキャリアガスは、多孔質チューブ 22 内において細管 25 の周面を透過して流出し、吸着剤 3 及び多孔質チューブ 22 の側周面を透過して多孔質チューブ 22 の外側に流出する。

## [0047]

950 In addition, since one end of the porous tube 22 is sealed by the air-impermeable sealing plate 23 , all the gas flows out from the side peripheral surface of the porous tube 22 .

---

953 なお、多孔質チューブ 22 の一端は非通気性の封止板 23 によって封止されているため、全てのガスは多孔質チューブ 22 の側周面から流出する。

957 The component for analysis desorbed from the adsorbent 3 by this heating is carried out to the outside of the porous tube 22 by the carrier gas. The carrier gas and the component to be analyzed are introduced into an analyzer (not shown) such as a gas chromatograph installed downstream of the measuring tube 10 and analyzed.

---

962 この加熱によって吸着剤 3 から脱着した分析目的成分がキャリアガスによって多孔質チューブ 22 の外側に搬出される。このキャリアガスと分析目的成分は、測定管 10 の下流に設置されたガスクロマトグラフィー等の分析装置（図示略）に導入され、分析される。

## [0048]

970 In this passive sampler 21, since the component transmitted through the side peripheral surface of the porous tube 22 is adsorbed by the adsorbent 3, the adsorption efficiency is high and sampling can be performed in a relatively short time.

---

974 このパッシブ型サンプラー 21 にあっては、多孔質チューブ 22 の側周面から透過してきた成分が吸着剤 3 に吸着されるため、吸着効率が高く、比較的短時間でサンプリングを行うことができる。

979 Since both ends of the porous tube 22 are sealed by the sealing plate 23 and the sealing lid 24 , it is possible to prevent dust, foreign substances, organisms, etc. from entering the tube 22 . In addition, since the adsorbent 3 filled inside the porous tube 22 is immovably held by the sealing plate 23 and the sealing lid 24, the adsorbent 3 does not collide with each other, wears out, and deteriorates. , can be used repeatedly.

---

985 多孔質チューブ 22 の両端は封止板 23 及び封止蓋 24 によって封止されているため、該チューブ 22 内に塵や異物、生物などが入り込むことが防止できる。また、多孔質チューブ 22 の内部に充填された吸着剤 3 が封止板 23 及び封止蓋 24 によって移動不能に保持されているため、吸着剤 3 同士がぶつかって磨耗し、劣化することがなく、多数回繰り返し使用することができる。

## [0049]

995 In this component analysis method, since the passive sampler 21 is directly inserted into the measurement tube 10 for analysis, the operation is simple.

---

998 この成分の分析方法にあっては、パッシブ型サンプラー 21 をそのまま測定管 10 内に挿入して分析するため、操作が簡単である。

1002 Moreover, since there is no need to move the adsorbent 3 from the porous tube 22 to another container or the like, there is no possibility that part of the adsorbent 3 remains

during the transfer and causes an error in the analytical values of the components. Furthermore, the adsorbents 3 do not collide with each other during movement and are worn and deteriorated.

---

1008 また、吸着剤 3 を多孔質チューブ 2 2 から他の容器等に移動する必要がないため、移動時に吸着剤 3 の一部が残留し、成分の分析値に誤差を生じさせるということはない。さらに、移動時に吸着剤 3 同士がぶつかって磨耗し、劣化するということもない。

## [0050]

1016 Further, in this component analysis method, the components desorbed by heating are efficiently transported to the outside of the porous tube 22 by the carrier gas.

---

1019 また、この成分の分析方法にあっては、加熱により脱着した成分が、キャリアガスによって効率的に多孔質チューブ 2 2 の外側に搬送される。

1023 Therefore, the desorbed component does not stay in the porous tube 22 and cause an error in the analysis value, and the measurement accuracy is improved.

---

1026 このため、脱着した成分が多孔質チューブ 2 2 内に滞留して分析値に誤差が生じるということなく、測定精度が良好なものとなる。

## [0051]

1033 In the passive sampler according to this embodiment, the components in the atmosphere diffuse through the porous tube 22 and are adsorbed by the adsorbent 3 . The closer to the inner peripheral wall of the quality tube 22, the more components are adsorbed.

---

1037 なお、この実施の形態に係るパッシブ型サンプラーでは、雰囲気中の成分は多孔質チューブ 2 2 を拡散して吸着剤 3 に吸着されるため、多孔質チューブ 2 2 内に充填された吸着剤 3 のうち多孔質チューブ 2 2 の内周壁に近いものほど多くの成分を吸着する。

1042 Therefore, when the carrier gas is supplied to the adsorbent through the porous thin tube 25 at the axial center portion as in the analysis method of FIG. Components desorbed from the adsorbent 3 near the inner peripheral wall of the porous tube 22 pass through the porous tube 22 immediately after desorption and are taken out. Therefore, according to the

analysis method of FIG. 5, desorption of the components can be rapidly performed.

---

1048 従って、図5の分析方法のように、キャリアガスを軸心部分の多孔質細管25を通して吸着剤に供給すると、キャリアガスは細管25から放射方向に流れて吸着剤3の層を通り抜けるため、多孔質チューブ22の内周壁近傍の吸着剤3から脱着された成分は、脱着後直ちに多孔質チューブ22を通過し、取り出される。従って、この図5の分析方法によると、成分の脱着を迅速に行うことができる。

## [0052]

1058 The above embodiment is an example of the present invention, and the present invention is not limited to the above embodiment.

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1061 上記実施の形態は本発明の一例であって、本発明は上記実施の形態に限定されるものではない。

1065 For example, although the porous tubes 2 and 22 are straight tubes in the above embodiments, they may be curved or bent tubes, or may be coiled. Moreover, the porous tubes 2 and 22 are not limited to those having a circular cross-sectional shape, and may have a rectangular tubular shape or a flat shape. Furthermore, unevenness or screws for fastening caps may be provided at both ends of the porous tubes 2 and 22. The porous tubes 2 and 22 may be provided with locking portions for locking a string or the like for hanging in the room.

---

1073 例えば、上記実施の形態では多孔質チューブ2, 22は直管状であるが、湾曲ないし屈曲した管であってもよく、コイル状とされたものであってもよい。また、多孔質チューブ2, 22は円形断面形状のものに限定されるものではなく、角筒状や偏平状のものであってもよい。さらに、多孔質チューブ2, 22の両端にキャップを留めるための凹凸やねじを設けてもよい。この多孔質チューブ2, 22には、室内に吊り下げるための紐等を係止するための係止部を設けてもよい。

## [0053]

1084 INDUSTRIAL APPLICABILITY As described above, according to the passive sampler and the analysis method thereof of the present invention, the analysis operation is extremely easy, the passive sampler can be repeatedly used many times, and the measurement accuracy is good. and its analysis method can be provided.

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1089 【発明の効果】以上の通り、本発明のパッシブ型サンプラー及びその分析方法によれば、分析操作がきわめて容易であるとともに、多数回繰り返し使用することができ、且つ測定精度の良好なパッシブ型サンプラー及びその分析方法を提供することができる。



US005996423A

# United States Patent [19]

Baghel et al.

[11] Patent Number: 5,996,423

[45] Date of Patent: \*Dec. 7, 1999

[54] **PASSIVE WATER SAMPLER AND METHOD OF SAMPLING**[75] Inventors: **Sunita Singh Baghel**, Rensselaer; **Angelo Anthony Bracco**, Albany; **Patricia Denise Mackenzie**, Clifton Park, all of N.Y.[73] Assignee: **General Electric Company**, Schenectady, N.Y.

[\*] Notice: This patent is subject to a terminal disclaimer.

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[22] Filed: Oct. 6, 1998

[51] Int. Cl.<sup>6</sup> G01N 1/22

[52] U.S. Cl. 73/863.23

[58] Field of Search 73/863.21, 863.23, 73/864.51

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Primary Examiner—Robert Raevis

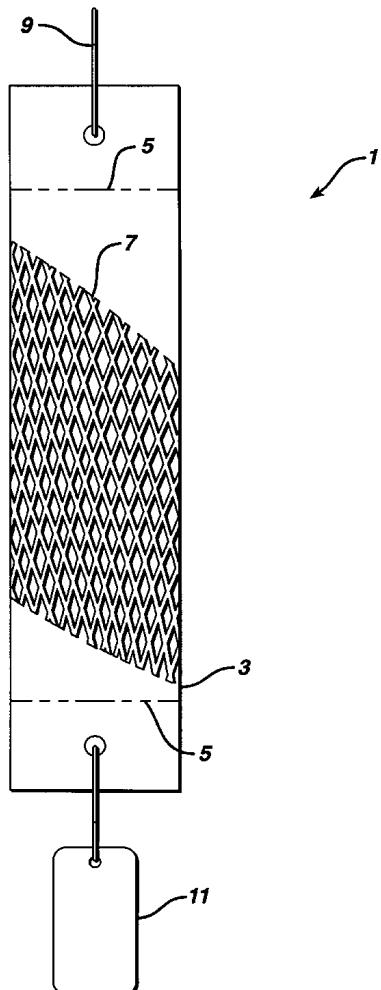
Attorney, Agent, or Firm—Ernest G. Cusick; Noreen C. Johnson

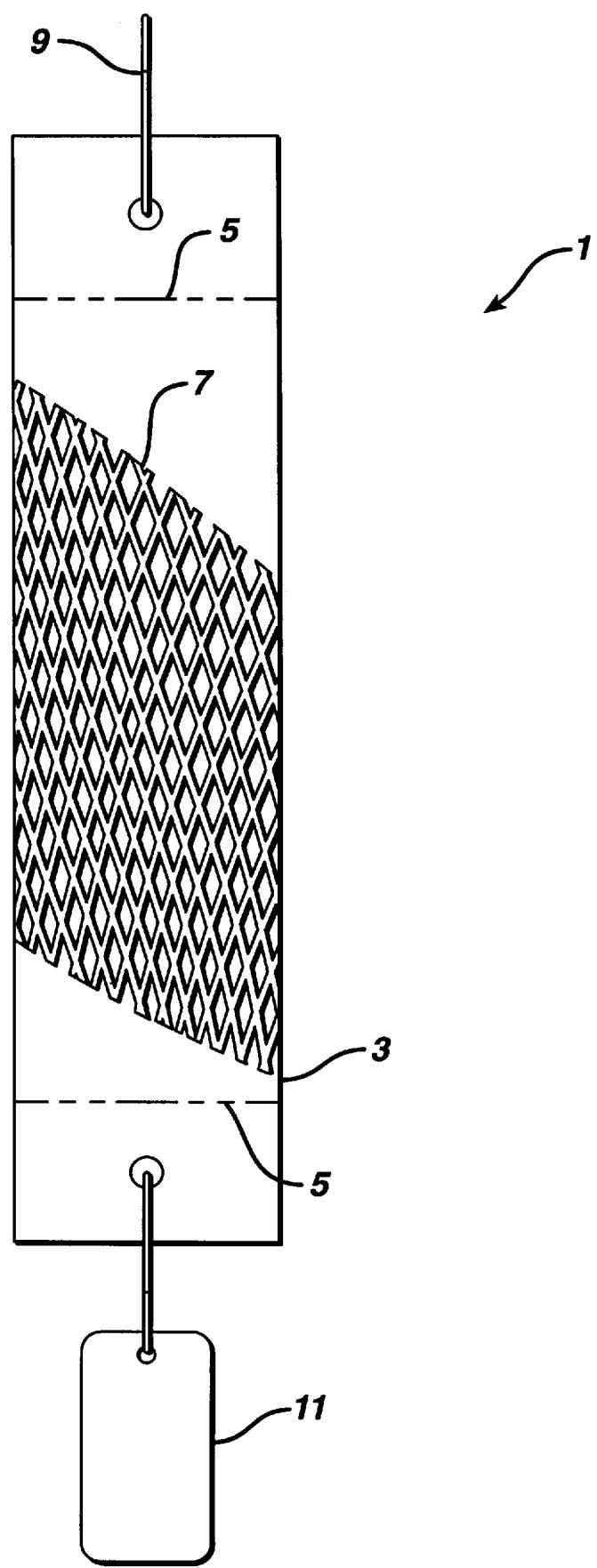
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## ABSTRACT

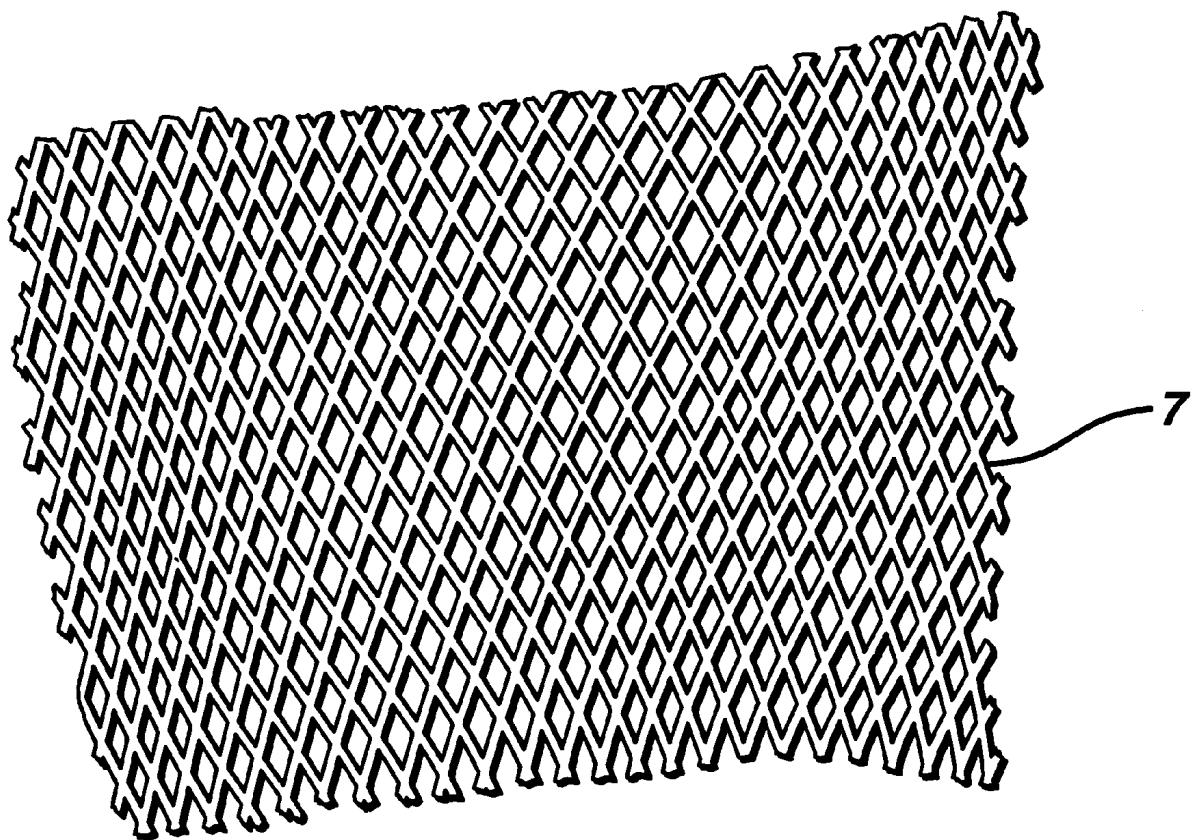
An improved method and apparatus for monitoring the concentration of contaminants, including volatile organic compounds, in groundwater is provided comprising a semipermeable membrane defining an inner chamber. The chamber is carried within a mesh protective sleeve of cover to prevent abrasion or puncture of the chamber. The membrane is permeable to contaminants but impermeable to a reference fluid, which is distilled water. The method of sampling comprises placing the semipermeable membrane chamber, which contains the reference fluid, in contact with contaminated groundwater, thereby allowing contaminants to diffuse through the semipermeable membrane.

10 Claims, 2 Drawing Sheets



**FIG. 1**

***FIG. 2***



**PASSIVE WATER SAMPLER AND METHOD  
OF SAMPLING**

**BACKGROUND OF THE INVENTION**

This invention relates generally to a liquid sampling device, and more particularly to an improved method and apparatus for monitoring the concentration of contaminants, including volatile organic compounds, in groundwater. Various devices exist for sampling a liquid. A known type of passive, multi-layer sampling device which is used to extract groundwater samples is comprised of a rod (or connector rods) with apertures at specific intervals to accommodate dialysis cells.

U.S. Pat. No. 5,454,275 to Kabis discloses a groundwater sampler which makes use of pressure differentials that result during sampling. U.S. Pat. No. 5,147,561 to Burge et al. teaches a sampling device containing a stripping chamber for stripping a groundwater sample of its volatile components at or near the point of collection. U.S. Pat. No. 4,078,433 to McCabe, Jr. et al. discloses a liquid sampling device comprising a length of pipe having a cap screwed onto each end thereof. The upper cap has an aperture for admitting the liquid to be sampled into the pipe. Despite the prior art devices, there is a need for improvement in the art of groundwater sampling. The use of thin semipermeable membrane materials in water sampling devices presents certain problems due to the very sensitive nature of the membrane. Such membrane are easily damaged in the course of use during placement in a well and removal.

**SUMMARY OF THE INVENTION**

The water sampling apparatus of this invention comprises a reference liquid chamber constructed of a semipermeable material, a protective mesh cover which conforms to the shape and outer surface of the chamber, and associated attaching means for carrying a weight and lowering line for positioning the device in the body of water to be sampled such as a monitoring well. The term "mesh" as used herein means a material of open texture with evenly spaced holes or openings between the threads, lines, or cords like the fabric of a net. The openings are of sufficient size to permit effective contact between the groundwater and the semipermeable material of which the chamber is formed. "Effective contact" means sufficient water to membrane contact to permit equilibration of contaminants between the groundwater and the reference fluid within a reasonable period of time.

Practice of the invention provides a number of advantages including an improved method and apparatus for sampling groundwater; a method and apparatus for sampling groundwater in a test well that does not require purging or bailing of the well; method and apparatus for sampling groundwater that does not require dialysis cells; a method and apparatus for sampling groundwater that utilizes water as a reference liquid or carrier for volatile organic compounds and other contaminants. Use of the protective mesh cover prevents loss of samples resulting from puncture or tearing of the semipermeable membrane chamber or bag caused by contact with sharp or rough parts of the well screen or casing.

The passive water sampler comprises a sample chamber or container constructed of a semipermeable membrane material, the semipermeable membrane being permeable to contaminants and impermeable to a reference fluid; the semipermeable membrane defining an inner chamber therein; and the inner chamber being at least partially filled with the reference fluid such as distilled water, the partially

filled chamber semipermeable membrane being placed in contact with the groundwater thereby allowing the contaminants to diffuse through the semipermeable membrane and into the inner chamber, the concentrations of the contaminants in the groundwater and in the reference fluid coming into equilibrium. In an embodiment the fluid chamber is substantially completely filled with reference fluid. The sample chamber is carried within a protective covering constructed of a mesh material such that the semipermeable membrane is exposed to contact by the well water and is shielded from contact with the inner walls of the bore of the well or any screen lining the bore of the well. The mesh acts to prevent abrasion or puncture of the membrane chamber by any roughness or protrusions inside the well. The mesh cover is constructed of a stretchable plastic which can be expanded to receive the fluid filled bag and then return to its original dimensions and conform to the shape of the bag or chamber. In embodiments the chamber is of tubular shape heat sealed at both ends after at least partially filling with water and the cover is in the form of a sleeve of mesh material into which the tubular chamber can be inserted. It is generally that the fluid chamber be substantially filled with reference fluid.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a front elevational view of the present invention.  
FIG. 2 is plan view of a mesh material suitable for use as the protective cover.

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**DETAILED DESCRIPTION**

The method and apparatus according to this invention can be used to monitor the concentrations of volatile organic compounds (VOCs) and other contaminants in groundwater in a test or monitoring well without the need to purge or bail the well. Purging a well is presently a regulatory requirement if samples are to be withdrawn from the well, and is a large part of the expense associated with routine monitoring of groundwater contamination. Regulatory agencies typically require removal of at least three casing volumes of water prior to sampling. The large number of observation wells typically sampled at groundwater contamination sites results in a large volume of contaminated purge water that must be disposed of. Thus, sampling costs are incurred which include not only personnel time, but also the proper transport and disposal of the contaminated purge water. These costs can be substantial when multiplied over the lifetime of the contamination. Moreover, the costs associated with remediation and monitoring of existing groundwater contamination must be factored in as a loss when the market value of particular businesses are calculated. The method and apparatus of sampling according to the present invention eliminates the need to purge wells, thus resulting in a substantial cost savings as well as an increased corporate value. Also, the absence of purging makes the present invention environmentally friendly. Use of the protective mesh cover makes the device less subject to accidental damage during use.

Furthermore, the method and apparatus according to the present invention precludes the need for using either dialysis cells or a carbon sorbent. Both of these can be very costly in terms of sampler preparation and analysis. Also, when using a carbon sorbent, the results obtained yield only relative concentrations because the sorbent continues to collect contaminants, including as long as the sampler is in the sampling area. Thus, using the sorbent system, the measured contaminant concentration is a function of the

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time the sampler was in place. On the other hand, the present invention allows the contaminant concentration in the sampler to change in response to fluctuations in contaminant concentrations outside of the sampler, thereby maintaining equilibrium and providing an accurate contaminant concentration in the sampler at any time after equilibrium is reached. Consequently, great flexibility is allowed in the length of time that the present invention can be left in the sampling area.

Additionally, the present sampling device is used subaqueously, without requiring the pumping or bailing of water samples from within a well. It has been found that water immediately adjacent to a well screen can be representative of an aquifer without having to purge, and may even be more representative than samples obtained after purging due to the sampling bias that can result from the purging itself. The mesh cover prevents damage resulting from contact with the screen or casing of the well.

Referring to the drawings, FIG. 1 shows a front elevational view of a mesh material covered passive water sampler 1 according to the present invention. The water sampler 1 comprises a semipermeable membrane material in the form of a tube 3 with heat seal at the ends 5. Protective mesh 7, shown in partial view, encloses the fluid filled tube. Semipermeable membrane 3 is permeable to contaminants but impermeable to the reference fluid, e.g., contaminant-free water. The reference fluid employed is distilled water, but may be undistilled water or any other suitable fluid in which the contaminants are soluble or miscible. Use of distilled water as the reference fluid simplifies the analysis of the sample. Semipermeable membrane 3 can be made from a variety of materials which fit the above-stated criteria but can be made from polyethylene. Polypropylene, may also be employed. Semipermeable membrane 3 may be manufactured in a wide variety of shapes and sizes depending on the application. Water sampler 1 is relatively small, making it easily transportable. Semipermeable membrane 3 defines an internal fluid chamber which can be any size or shape required for use. For example, semipermeable membrane 3 is provided in the shape of a tube having open ends which can be sealed. The inner chamber is formed by sealing the open ends of the tube, thus providing a leakage-free inner chamber. This sealing may be achieved by: heat sealing, sonic welding, or any other suitable bonding method.

Alternatively, the semipermeable membrane may be provided as a flat piece. The chamber is formed by folding the semipermeable material over and onto itself, thereby forming one folded edge and three overlapping edges. The three overlapping edges are respectively sealed.

Prior to placing the water sampler in contact with contaminated groundwater, inner chamber is at least partially filled with the reference fluid in which the contaminants are soluble or miscible and sealed. Other appropriate means for adding or withdrawing fluid may also be employed.

Upon placing a partially filled sampling device 1 in contact with contaminated groundwater, the contaminants begin to diffuse through the semipermeable membrane and into the chamber. The reference fluid does not diffuse into the groundwater. Only contaminants in the groundwater diffuse into the chamber of the device. Contaminants continue to diffuse into the chamber until the concentration of contaminants in the reference fluid and the concentration of contaminants in the groundwater reach equilibrium. As discussed above, water sampler 1 may be submerged in a well for great lengths of time without jeopardizing analysis

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results. This is because, once equilibrium has been reached, any changes in contaminant concentration outside of water sampler 1 are compensated for by diffusion of contaminants into or out of the chamber. Thus, equilibrium is consistently maintained. For example, if the concentration of contaminants in the groundwater falls, contaminants, will diffuse out of inner chamber 4 and into the groundwater until the contaminant concentrations in the reference fluid and in the groundwater are the same again. Conversely, if the contaminant concentration in the groundwater rises, contaminants, will diffuse from the groundwater into the chamber until the concentrations are the same again.

When water sampler 1 is to be used in a well, support line 9 of suitable length and construction for supporting water sampler 1 while inside a well is attached to the mesh cover 15 by any suitable hook or fastening means. The support line is used to raise water sampler up and out of the well after sampling. The mesh cover serves to prevent abrasion or puncture of the fluid filled device during placement in and removal from the well.

Weight 11 can be hung from the lower portion of the mesh either directly or by a length of support line to assist in submerging water sampler 1 once it is inside of a well. Weights and support lines may be made of a variety of materials and sizes depending on the application.

The method of sampling according to the present invention involves using water sampler 1 in any of its many variations as described above.

The vertical profile of the extent of contamination at different levels in an aquifer can be monitored by setting a series of mesh covered sampling devices at various levels in a monitoring well. Each device will come to equilibrium with the contaminant at the corresponding level in the well.

Sampling is complete when equilibrium has been reached. The sampling device 1 is raised up and out of a well. A portion of the equilibrium mixture of reference fluid and contaminants within the chamber is withdrawn for analysis by cutting the bag or chamber open or by opening any sealed port.

Analysis of the sample is carried out by conventional means, for example, through the use of a gas chromatograph. Because the water adjacent to a well screen in an unpurged well is potentially representative of the water in the adjacent aquifer, the concentration of contaminants in the water sampler can be related to the concentration of contaminants in the aquifer at the screened interval.

At each well to be sampled, an initial comparison should be done between the method of sampling according to the present invention and conventional sampling methods. The purpose of this comparison would be to account for potential borehole-specific interferences and to verify that data obtained using the present invention adequately represents data obtained using the standard sampling methodology.

It is thus seen that an improved method and apparatus for sampling groundwater can be utilized. It is also seen that the method and apparatus for water sampling according to this invention does not require purging of a well. It is also seen that the method and apparatus for water sampling according to this invention can be used subaqueously. It is also seen that the method and apparatus according to this invention precludes the need for using costly sorbents or dialysis cells. It is also seen that the method and apparatus according to this invention can utilize water as a carrier for volatile organic compounds and other contaminants. Furthermore, it is seen that the method and apparatus according to the present invention is economical, environmentally friendly, and easy to construct and use.

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Use of a protective mesh cover is a useful and expedient way to reduce loss of water samples resulting from damage to the fluid filled chamber during handling and transportation to and from the well site.

Thin membranes are particularly vulnerable to damage when being placed in a well and when being removed from a well. The mesh cover makes the use of thindifusion films a practical method for monitoring the concentration of contaminants in groundwater.

It is understood that many variations will become apparent to one of ordinary skill in the art upon reading the specification. Such variations are within the spirit and scope of the invention as defined by the following appended claims.

**What is claimed:**

**1. A passive water sampler for monitoring the concentration of contaminants in groundwater comprising:**

a semipermeable membrane, said semipermeable membrane being permeable to said contaminants and impermeable to a reference fluid;

said semipermeable membrane defining an inner chamber therein;

said inner chamber being at least partially filled with reference fluid, said partially filled semipermeable membrane placed in contact with said groundwater thereby allowing said contaminants to diffuse through said semipermeable membrane and into said inner chamber, the concentrations of said contaminants in said groundwater and in said reference fluid coming into equilibrium; and an elastic stretchable mesh protective cover surrounding the chamber.

**2. The water sampler according to claim 1 wherein said reference fluid is water.**

**3. The water sampler according to claim 2 wherein said water is distilled water.**

**4. The water sampler according to claim 1 wherein said semipermeable membrane is made from polyethylene.**

**5. The water sampler according to claim 1 wherein said semipermeable membrane is provided in generally the shape of a tube having open ends, said open ends being sealed to form said inner chamber.**

**6. The water sampler according to claim 1 wherein said semipermeable membrane is provided as generally a flat piece, said flat semipermeable membrane being folded over**

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and onto itself thereby creating a folded edge and three overlapping edges, said three overlapping edges being respectively sealed together to form said inner chamber.

**7. The water sampler according to claim 1 further comprising a weight and a support line said weight to assist in said water sampler in a well, said line for supporting said water sampler in said well and for raising said water sampler up and out of said well.**

**8. A method for determining the concentration of contaminants in groundwater comprising the steps of:**

providing a semipermeable membrane, said semipermeable membrane being permeable to said contaminants and impermeable to a reference fluid, manipulating said semipermeable membrane to define an inner chamber therein;

at least partially filling said inner chamber with said reference fluid; placing the chamber in an elastic stretchable protective sheath;

placing said partially filled chamber in contact with said groundwater,

allowing said contaminants to diffuse through said semipermeable membrane and into said inner chamber;

allowing sufficient time for the concentrations of said contaminants in said groundwater and in said reference fluid to come into equilibrium;

removing said semipermeable membrane from contact with said groundwater;

withdrawing at least a portion of said reference fluid containing said contaminants from said inner chamber for analysis.

**9. The method according to claim 8 wherein said step of at least partially filling said inner chamber with said reference fluid further comprises substantially completely filling said inner chamber with distilled water.**

**10. The method according to claim 8 wherein said step of providing a semipermeable membrane further comprises providing a semipermeable membrane in the shape of a tube having open ends, and wherein said step of manipulating said semipermeable membrane to define an inner chamber therein further comprises sealing said open ends and providing said mesh in the form of a sleeve.**

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## Research Article

# A Simple and Quick Method for the Determination of Pesticides in Environmental Water by HF-LPME-GC/MS

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This paper describes a simple and quick method for sampling and also for carrying out the preconcentration of pesticides in environmental water matrices using two-phased hollow fiber liquid phase microextraction (HF-LPME). Factors such as extraction mode, time, solvents, agitation, and salt addition were investigated in order to validate the LPME method. The following conditions were selected: 6 cm of polypropylene hollow fiber, ethyl octanoate as an acceptor phase, and extraction during 30 min under stirring at 200 rpm. The optimized method showed good linearity in the range of 0.14 to 200.00  $\mu\text{g L}^{-1}$ ; the determination coefficient ( $R^2$ ) was in the range of 0.9807–0.9990. The LOD ranged from 0.04  $\mu\text{g L}^{-1}$  to 0.44  $\mu\text{g L}^{-1}$ , and LOQ ranged from 0.14  $\mu\text{g L}^{-1}$  to 1.69  $\mu\text{g L}^{-1}$ . The recovery ranged from 85.17% to 114.73%. The method was applied to the analyses of pesticides in three environmental water samples (a spring and few streams) collected in a rural area from the state of Minas Gerais, Brazil.

## 1. Introduction

The extensive use of pesticides harms the soil [1–4], air [5, 6], food [7–10] surface and ground waters [11–14], and quality causing serious impacts on the environment and on human health. In natural waters pesticide residues are present at very low levels and can be degraded when submitted to lower pH levels or exposed to solar radiation [15]. Furthermore the complexity of environmental matrices and large variations in physical and chemical properties of the target compounds requires the use of sensitive and selective techniques. Several analytical techniques, such as high-performance liquid chromatography (HPLC) [16, 17], gas chromatography (GC) [18, 19], micellar electrokinetic chromatography (MEKC) [20, 21], enzyme-linked immunosorbent assays (ELISA) [22–24], and gas and liquid chromatography coupled to mass spectrometry (GC/MS, LC-MS) [25, 26], have been used for analyses of pesticides in different matrices. The chromatographic techniques combine separation capabilities with sensitivity from the mass systems such as ion trap (IT),

triple quadrupole (QqQ), and time of flight (TOF). However, these techniques still remain as challenges related to low detection limits, the variety of pesticides classes, and sample preparation. The analytes extraction in chromatographic analysis is critical to the method's performance since it enables the elimination of possible array interferences and the preconcentration of analytes. Traditional extraction methods such as solid phase extraction (SPE) [27, 28] and liquid-liquid extraction (LLE) are multistage consuming toxic solvents and require a long time to execute. Solid phase microextraction (SPME) [29–31] is a technique that is based on the partition between the analyte present in the matrix and the fiber coating over a small fused silica rod. This technique is solvent-free and gathers in a single step extraction and preconcentration. However problems such as low resistance, short lifetime, and high cost remain. Recently, several materials have been proposed to increase the strength and durability of SPME coatings such as carbon materials [32]. Hollow fiber liquid phase microextraction (HF-LPME) [33–37] and dispersive liquid-liquid microextraction

(DLLME) [38, 39] have been used for the concentration and clean-up step of pesticides analyses in waters. HF-LPME was developed by Pedersen-Bjergaard and Rasmussen [40] and has been used by many researchers in recent years due to its low cost, which enables the rejection of the material after use, eliminating problems of cross-contamination or low reproducibility as well as its decreased consumption of organic solvents. Moreover, the process is simple and a clean-up step is not necessary and can be applied to a variety of arrays reaching high enrichment factors [41]. The technique consists of a capillary porous hydrophilic fiber, impregnated with organic solvent and its interior filled with an acceptor phase, so that it does not come into direct contact with the matrices allowing for the application of agitation during extraction [42]. HF-LPME can be used in two or three phases. With two phases the analyte is extracted from the donor through an organic solvent immiscible in water that fills the membrane pores passing to the acceptor stage, which corresponds to the same solvent [43]. With three phases the analyte is extracted from a donor phase through an organic solvent immiscible in water for an aqueous solution (acceptor phase) inside the fiber. The organic phase acts as a barrier preventing contact between the phases. Despite the extensive use of HF-LPME for extraction of pesticides in water [33, 44, 45], the reported studies using GC/MS are generally for just one pesticide class. Therefore, this study presents the development of a simple and low-cost two-phase HF-LPME methodology for multiresidue microextraction of organophosphorus, phthalimides, organochlorines, and triazoles pesticides from environmental water using GC/MS. The pesticides selected were parathion-methyl (*O,O*-dimethyl-*O-p*-nitrophenyl phosphorothioate), chlorpyrifos (*O,O*-diethyl *O-3,5,6-trichloro-2-pyridyl* phosphorothioate), captan (*N-(trichloromethylthio)cyclohex-4-ene-1,2-dicarboximide*), procymidone (*N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide*),  $\alpha$ -endosulfan (1,4,5,6,7,7-hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylene sulfite), prothiofos ((*RS*)-(O-2,4-dichlorophenyl *O*-ethyl S-propyl phosphorodithioate)), cyproconazole ((2*RS,3RS; 2RS,3SR*)-2-(4-chlorophenyl)-3-cyclopropyl-1-(1*H*-1,2,4-triazol-1-yl)butan-2-ol), ethion (*O,O,O',O'*-tetraethyl S,S'-methylene bis(phosphorodithioate)), triazophos (*O,O*-diethyl *O-1-phenyl-1H-1,2,4-triazol-3-yl* phosphorothioate), and phosmet (*O,O*-dimethyl S-phthalimidomethyl phosphorodithioate). The main parameters affecting the extraction efficiency were optimized using GC/MS determination. The procedure presented good accuracy and precision and low limits of quantification and detection, besides good recovery.

## 2. Materials and Methods

**2.1. Chemical and Materials.** Parathion-methyl, chlorpyrifos, captan, procymidone,  $\alpha$ -endosulfan, prothiofos, cyproconazole, ethion, triazophos, and phosmet of 98% w/w purity grade were purchased from Sigma-Aldrich (St. Louis, MO, USA). The choice of pesticides was based on their use on the region of samples collection. A work solution of 20.00 mg L<sup>-1</sup> was prepared by the appropriate dilution in HPLC-grade methanol, Sigma-Aldrich (St. Louis, Missouri,

United States). This work solution was used for the matrix spike in different concentration levels (5.00 to 160.00  $\mu\text{g L}^{-1}$ ) to optimize the extraction conditions during the validation study. Calibration standards were prepared at 5.00, 10.00, 20.00, 40.00, 80.00, and 160.00  $\mu\text{g L}^{-1}$  concentrations using ultrapure water produced in a Purelab UVMK2 purifier from Elga (Marlow, Buckinghamshire, England). 1-Octanol HPLC grade was purchased from Sigma-Aldrich (St. Louis, Missouri, United States), ethyl decanoate, acetonitrile, and ethyl octanoate were purchased from J. T. Baker (Xalostoc, Edo MEX, Mexico). Hollow fiber was purchased from Underlying Performance Co. (Wuppertal, Germany).

**2.2. Instrumentation for GC/MS.** The analysis was carried out with a Shimadzu (Kyoto, Japan) GC/MS system model GC-2010/QP-2010 high-performance quadrupole. The mass spectrometer operated within the electron impact mode (EI) at 70 eV. A capillary column (30 m × 0.25 mm × 0.25  $\mu\text{m}$ ) containing 5% diphenyl and 95% dimethylpolysiloxane HP-5MS from Agilent Technology, Inc. (Santa Clara, California, United States), was used. The oven temperature program began at 80°C and raised to 200°C at a rate of 8 °C min<sup>-1</sup> up to 300°C at 30 °C min<sup>-1</sup> and held there for 3 min. Helium (99.999%) was the carrier gas at a flow rate of 1.0 mL min<sup>-1</sup>. The injector was operated at 280°C in splitless mode for 3 min, followed by a 1: 20 split ratio (RD). The ion source temperature was 200°C, and the GC/MS interface temperature was 300°C. The analysis was carried out in the selected ion monitoring (SIM) mode. The quantification was achieved using the ion fragments shown in Table 2. The collection of raw data was carried out using a LabSolution software, Shimadzu (Kyoto, Japan).

**2.3. HF-LPME Extraction Procedure.** Aqueous standards of pesticides were prepared by spiking an appropriate amount of the working standard. The extraction and desorption conditions were based on Psillakis and Kalogerakiss's study [49]. LPME sampling was tested in two and three phases, study of salt addition, stirring speed, and extraction time. The extractions were carried out with propylene hollow fiber of 6.0 cm length, 600  $\mu\text{m}$  of internal diameter, and wall thickness of 200  $\mu\text{m}$ . Before the extraction, the hollow fiber was filled with 30.0  $\mu\text{L}$  of solvent using a microsyringe. Then, the U-shaped solvent-filled fiber was connected to two syringe needles and immersed into the vial containing 15.00 mL of aqueous donor solutions spiked with 100.0  $\mu\text{g L}^{-1}$  of standard pesticides solutions for the extraction under magnetic stirring. After the extraction, the acceptor phase was removed with a microsyringe and transferred to a 2.0 mL vial to the injection of 1.0  $\mu\text{L}$  in GC/MS. All experiments were performed in replicates (*n* = 3).

**2.4. Samples Collection.** Real samples of surface water were collected in a rural area of the state of Minas Gerais, Brazil. In this region the main crops are coffee, eucalyptus, and tomatoes. Samples of surface water were sampled 2 km downstream of these crops. The collected samples showed clear appearance and no suspended particles. The amber-glass

collection bottles were previously washed with a solution of 5.0% v/v alkaline detergent under ultrasound bath for 15 minutes and rinsed with ultrapure water. Water samples collected with these bottles were carefully filled to the brim to avoid trapping air. After filling the bottles they were sealed with Teflon lined screw caps, kept in ice, and transported to the laboratory before 24 h where they were stored at 4°C until the extraction and analysis.

**2.5. Quality Control and Quality Assurance.** The quality control and the quality assurance method were carried out according to EURACHEM guidelines [50]. The limits of detection (LOD) and limits of quantification (LOQ) were calculated from mean and standard deviation of 10 blank measurements with 95% confidence. Linearity was established for all the analytes (from 0.04 to 150.0  $\mu\text{g L}^{-1}$ ). Six concentration levels were analyzed with three measurements at each concentration level. The Hartley test using Origin 8.0 from OriginLab Co. software (Northampton, MA, United States) was used to verify the instrumental response homogeneity of variances. The result of this test indicated heteroscedasticity of variances, so the linear models for the calibration curves were constructed by the least squares method weighted by the experimental variance. Intraday repeatability was calculated with four replicates. Recovery was evaluated using blank sample water spiked with 10.0  $\mu\text{g L}^{-1}$ .

### 3. Results and Discussion

**3.1. Optimization of HF-LPME Method.** The most important factors related to the HF-LPME extraction method such as the extraction mode, solvents, agitation, salt addition, and extraction time were optimized before the validation tests. The pesticides studied were chosen based on the information of their broad use (higher quantity retailed) in the cultures of the region where the samples were collected. Table 1 shows few relevant physicochemical properties of the selected pesticides [51].

**3.1.1. Extraction Mode and Solvents.** The extraction mode with three phases was evaluated using acetonitrile as the acceptor phase; 1-octanol, ethyl decanoate, and ethyl octanoate were tested as the organic phase. Aqueous solutions spiked with standard pesticides were used as donor solutions.

A significant loss of the organic phase during the three-phased extraction process significantly affected the recovery of the acceptor phase for further analysis. Subsequently, the two-phase mode was tested using 1-octanol or ethyl decanoate and ethyl octanoate as the acceptor phase and the aqueous solutions spiked with standard pesticides as donor solutions. The two-phase extraction method provided significant improvement in the recovery due to good immobilization of the acceptor phase in the fiber. Ethyl octanoate was selected as the acceptor phase due to its superior response to most pesticides as shown in Figure 1.

The results obtained with 1-octanol were relatively lower compared to the other acceptor phases studied. This can be explained by the difference in polarity between them since

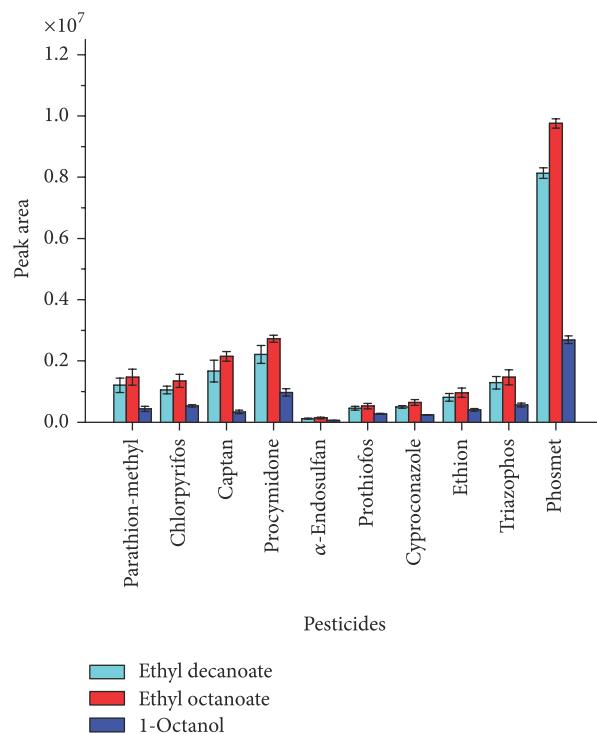


FIGURE 1: Effect of organic solvent on pesticide's extraction efficiency. Conditions of the donor phase: 15 mL of water spiked at 100  $\mu\text{g L}^{-1}$  of each pesticide; extraction time of 60 min; and stirring speed of 100 rpm. Error bars represented the standard deviation of the mean peak area for  $n = 3$  replicates.

ethyl decanoate and ethyl octanoate are less polar than 1-octanol. Therefore, the studied analytes are best extracted in more hydrophobic solvents because all  $K_{ow}$  values are greater than 1. This indicates that there is greater solubility in nonpolar solvent increasing the distribution ratio between the organic acceptor solution and the donor solution [52]. The different areas observed for organochlorine pesticides in relation to organophosphorus areas are mainly due to the fact that the electron impact mode used in MS detector show extensive fragmentation. Electron impact produces relatively low signal intensity with poor sensitivity for organochlorines compounds [53].

**3.1.2. Agitation.** Agitation provides continuous exposure of the extraction surface for the aqueous sample. The fiber is depleted of the analytes due to their partitioning in the donor phase; hence, the agitation diminishes this depletion area by bringing fresh undepleted sample close to the fiber. Agitation also reduces the time required to reach thermodynamic equilibrium and induces convection in the membrane phase. To optimize sample agitation, ethyl octanoate was used as the acceptor phase, and aqueous pesticide was used as the donor phase. The stirring rates studied were 0; 200; 400; 800; and 1600 rpm using metallic stir bars of 0.5 cm. The extraction time was 60 min. The results presented in Figure 2 show that the largest areas were obtained using 200 rpm of agitation speed. It was also observed that the agitation speed higher

TABLE 1: Physicochemical properties of the selected pesticides.

Pesticide	CAS number	Chemical class	Molecular formula	Structural formula	$\log K_{ow}$	Water solubility ( $\text{mg L}^{-1}$ )
Triazophos	24017-47-8	Organophosphorus	$\text{C}_{12}\text{H}_{16}\text{N}_3\text{O}_3\text{PS}$		3.34	35.00
Prothiofos	34643-46-4	Organophosphorus	$\text{C}_{11}\text{H}_{15}\text{Cl}_2\text{O}_2\text{PS}_2$		5.67	0.07
Chlorpyrifos	2921-88-2	Organophosphorus	$\text{C}_9\text{H}_{11}\text{Cl}_3\text{NO}_3\text{PS}$		4.70	1.05
Parathion-methyl	298-00-0	Organophosphorus	$\text{C}_8\text{H}_{10}\text{NO}_5\text{PS}$		2.86	37.7
Captan	133-06-2	Dicarboximide	$\text{C}_9\text{H}_8\text{Cl}_3\text{NO}_2\text{S}$		5.20	2.50
Cyproconazole	94361-06-5	Triazole	$\text{C}_{15}\text{H}_{18}\text{ClN}_3\text{O}$		3.09	93.00

TABLE 1: Continued.

Pesticide	CAS number	Chemical class	Molecular formula	Structural formula	$\log K_{ow}$	Water solubility ( $\text{mg L}^{-1}$ )
Ethion	563-12-2	Organophosphorus	$\text{C}_9\text{H}_{22}\text{O}_4\text{P}_2\text{S}_4$		5.07	2.00
Procymidone	32809-16-8	Dicarboximide	$\text{C}_{13}\text{H}_{11}\text{Cl}_2\text{NO}_2$		3.30	2.46
$\alpha$ -Endosulfan	115-29-7	Organochloride	$\text{C}_9\text{H}_6\text{Cl}_6\text{O}_3\text{S}$		4.75	0.32
Phosmet	732-11-6	Organophosphorus	$\text{C}_{11}\text{H}_{12}\text{NO}_4\text{PS}_2$		2.96	15.20

TABLE 2: Analytical performance of GC/MS method using HF-LPME for the extraction of pesticides in environmental water.

<sup>a</sup> Pesticide	Quantification ion ( $m z^{-1}$ )	Linearity ( $R^2$ )	<sup>b</sup> Precision RSD (%)	<sup>c</sup> Recovery (%)	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )
Parathion-methyl	263	0.9932	2.80	110.05	0.04	0.14
Chlorpyrifos	97	0.9950	3.98	114.73	0.44	1.46
Captan	79	0.9955	14.98	100.65	0.20	0.67
Procymidone	67	0.9996	4.77	113.68	0.17	0.57
$\alpha$ -Endosulfan	195	0.9903	6.50	110.75	0.12	1.69
Prothiofos	113	0.9990	0.90	112.17	0.35	1.16
Cyproconazole	125	0.9943	9.31	85.17	0.14	0.48
Ethion	125	0.9807	2.36	113.36	0.13	0.42
Triazophos	161	0.9906	13.56	91.08	0.09	0.31
Phosmet	160	0.9874	15.16	111.10	0.23	0.76

<sup>a</sup>Compounds are listed in sequence of elution. <sup>b,c</sup>Concentration  $10 \mu\text{g L}^{-1}$ ;  $n = 3$ .

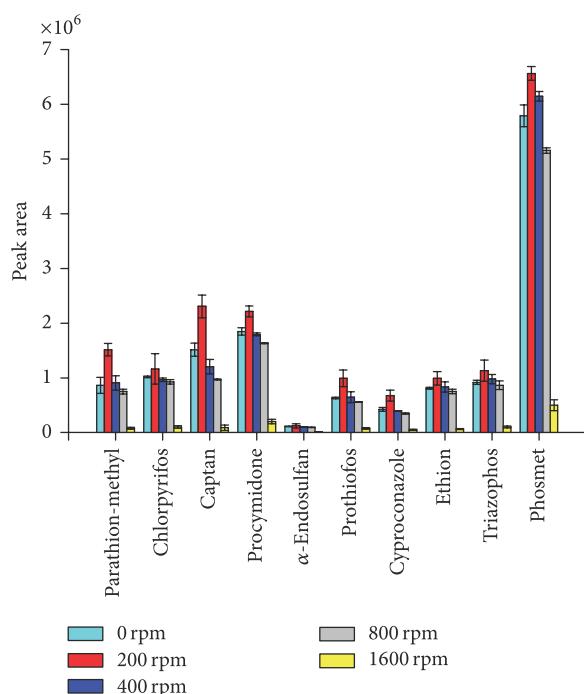


FIGURE 2: Effect of the stirring speeds on pesticide extraction efficiency. Extraction conditions of the donor phase:  $15.0 \text{ mL}$  of water spiked at  $100.0 \mu\text{g L}^{-1}$  of each pesticide; extraction time of  $60 \text{ min}$ ; and ethyl octanoate in the acceptor phase. Error bars represented the standard deviation of the mean peak area for  $n = 3$  replicates.

than  $200 \text{ rpm}$  decreases extraction efficiency despite the fact that stirring promotes mass transfer between the donor and acceptor phases. The relative decreased extraction yield was due to the fact that vigorous agitation promotes the formation of air bubbles which adhere to the fiber surface [54]. The efficiency of the extraction at  $0 \text{ rpm}$  and  $400 \text{ rpm}$  are similar because in the static stage the diffusion layer close to the fiber is not renewed; this effect decreases the mass transfer to the donor layer. However, the formation of bubbles on the outer surface of the fiber starts from  $400 \text{ rpm}$ , which contribute to reducing the mass transfer of the acceptor phase.

**3.1.3. The Salting-Out Effect.** The effect of salt addition to the LPME extraction of the pesticides was examined in the presence of different concentrations of NaCl:  $0.0$ ;  $5.0$ ;  $10.0$ ; and  $15.0\% \text{ w/v}$ . The extraction time was  $60 \text{ min}$ . The acceptor phase was ethyl octanoate with agitation at  $200 \text{ rpm}$ . The addition of salt in the aqueous samples generally improves the extraction of analytes in the organic phase. The salt increases the ionic strength decreasing the solubility of hydrophobic analytes in the donor phase; therefore, it enhances their partitioning into the acceptor phase. However, in this study the addition of salt did not present a positive influence on the extraction process of most analytes (Figure 3). Phosmet presented a large improvement in the extraction efficiency of  $5.0\%$  NaCl concentration, although at higher concentrations the peak area decreased drastically. The presence of higher concentrations of salt can change the physical properties of the extraction film reducing the diffusion rates of the analytes into the organic phase [55]. Therefore, the increase in ionic strength resulting from the addition of salt increased the salting-in effect. This effect has been observed in other studies regarding environmental water samples [35, 56].

**3.1.4. Extraction Time.** LPME sampling is an equilibrium process, in which analytes are partitioned between the donor phase and acceptor phase. The equilibrium time refers to the time after which the amount of extracted analyte remains constant. Extraction times of  $10.0$ ;  $20.0$ ;  $30.0$ ;  $40.0$ ; and  $60.0 \text{ minutes}$  were tested for the extraction using the best conditions of the variables previously assessed. As seen in Figure 4, the extraction efficiency reached its maximum value after  $30 \text{ min}$  for most of the pesticides evaluated. Therefore this was the extraction time selected. Periods above  $30 \text{ min}$  reduced extraction efficiency in some analytes, such as parathion-methyl, captan, phosmet, and triazophos. This reduction occurs due to the prolonging of the stirring time, which originates the formation of bubbles in the outer fiber, contributing to increased losses of the donor phase.

**3.2. Chromatographic Evaluation.** After evaluating the different parameters that could affect the extraction the following optimized conditions were selected for all experiments:  $6 \text{ cm}$  polypropylene hollow fiber impregnated and filled with  $30 \mu\text{L}$

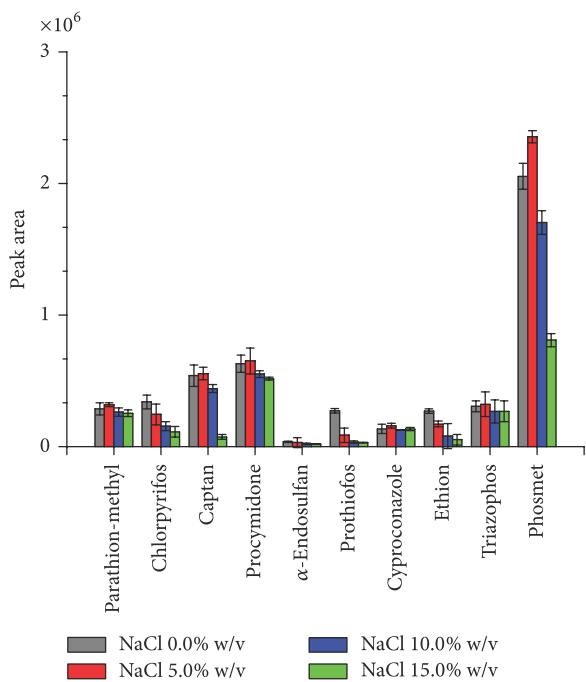


FIGURE 3: Influence of the aqueous phase ionic's strength on pesticides extraction efficiency. Extraction conditions of the donor phase: 15.0 mL of water spiked at  $100.0 \mu\text{g L}^{-1}$  of each pesticide with NaCl; extraction time of 60 min; stirring speed of 100 rpm; and ethyl octanoate in the acceptor phase. Error bars represented the standard deviation of the mean peak area for  $n = 3$  replicates.

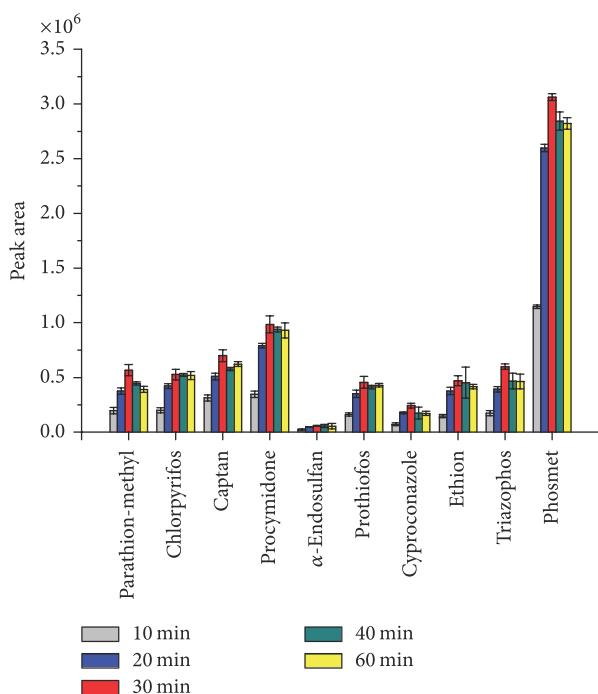


FIGURE 4: Effect exposure times on the extraction efficiency. Extraction conditions of the donor phase: 15.0 mL of water spiked at  $100.0 \mu\text{g L}^{-1}$  of each pesticide; stirring speed of 200 rpm; and ethyl octanoate in the acceptor phase. Error bars represented the standard deviation of the mean peak area for  $n = 3$  replicates.

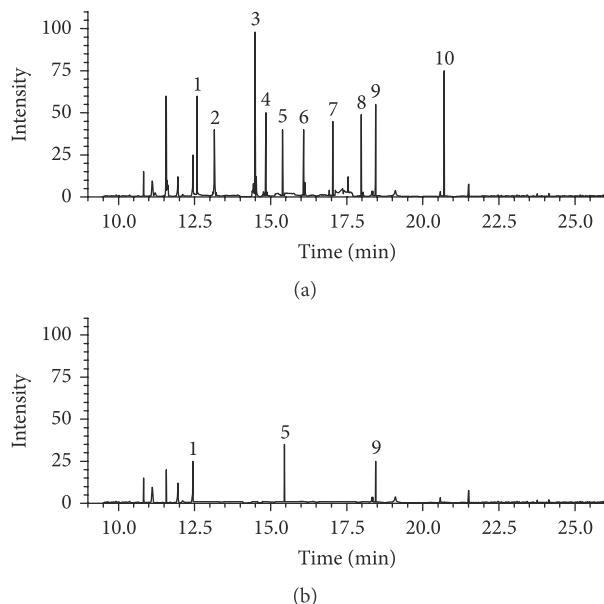


FIGURE 5: (a) Chromatogram of pesticides GC/MS analysis using HF-LPME extraction. Extraction for 30 minutes in aqueous donor solution spiked at  $50.0 \mu\text{g L}^{-1}$ ; stirring speed 200 rpm; and ethyl octanoate as acceptor phase. 1: parathion-methyl. 2: chlorpyrifos. 3: captan. 4: procymidone. 5:  $\alpha$ -endosulfan. 6: prothifos. 7: cyproconazole. 8: ethion. 9: triazophos. 10: phosmet. (b) Chromatogram of pesticides in real environmental water sample under same extraction conditions.

of ethyl octanoate, immersion in a vial containing 15.0 mL of sample for 30 min under stirring at 200 rpm, and injection of 1.0  $\mu\text{L}$  to the acceptor phase in the GC/MS system. Figure 5 shows chromatogram of pesticides GC/MS analysis using HF-LPME extraction in aqueous donor solution spiked at  $50.0 \mu\text{g L}^{-1}$  with standards (Figure 5(a)) and real environmental water sample (Figure 5(b)) under the same extraction conditions. Chromatographic separation was satisfactory for all target analytes in a short time.

Under the optimal extraction conditions ten pesticides were selected for the analysis. The parameters linearity, limits of detection (LOD), limits of quantification (LOQ), recovery, and precision were carefully investigated. The experimental results are presented in Table 2.

A linear range of  $0.14 \mu\text{g L}^{-1}$  to  $200.00 \mu\text{g L}^{-1}$  was used in the investigation. The linearity was assessed by the determination coefficient ( $R^2$ ) that was in the range of 0.9807–0.9990. The LOD ranged from  $0.04 \mu\text{g L}^{-1}$  to  $0.44 \mu\text{g L}^{-1}$ , and LOQ ranged from  $0.14 \mu\text{g L}^{-1}$  to  $1.69 \mu\text{g L}^{-1}$ . The recovery and precision studies were performed by three replicates of real water samples spiked with concentration of  $10.0 \mu\text{g L}^{-1}$  of each pesticide. Recovery ranged from 85.17% to 114.73%. Intraday precision (RSD,  $n = 3$ ) ranged from 0.90% to 15.16%. The merit parameters values of linearity and precision obtained in this study are consistent with other results reported in the analysis of pesticides in water [37, 57–61]. On the contrary, the limits of detection and quantification obtained in this study were better than those obtained in

TABLE 3: Comparative study for some parameters of HF-LPME-GC/MS developed method with other related methods.

Extraction method	Number of analytes	Multiclass <sup>a</sup>	LOD ( $\mu\text{g L}^{-1}$ )	Precision (%)	Recovery (%)	Extraction time (min)	Cost effective	Refer.
SPE	12	Yes	0.004–0.08	2.5–17.4	83–126	—	High	[28]
SPME	5	No	2.0–8.0	—	—	30	High	[31]
HF-LPME	9	No	0.002–0.012	4.2–18.4	69.4–122.7	360	Low	[35]
DLLME	18	No	0.001–0.025	5–15	75–101	0.5	Low	[39]
HF-LPME <sup>b</sup>	3	No	0.015–0.080	8.7–30			Low	[44]
SPME	6	Yes	0.003–0.145	4–12		60	High	[46]
SPME	16	Yes	0.015–0.13	1.9–9.6	82–114	60	High	[29]
SPME	7	Yes	0.006–0.600	2.7–23.5	60–121	80	High	[47]
SPME	16	Yes	0.02–0.30	6.3–16.9	70.2–104.6	30	High	[48]
HF-LPME	11	Yes	0.04–0.35	0.9–15.2	85.2–114.7	30	Low	This work

<sup>a</sup>Presence of different class of pesticides. <sup>b</sup>Sample extraction of 72 h.

TABLE 4: Analyses of pesticides in real environmental water samples (spring water, stream 1, and stream 2).

Pesticide	Average ( $n = 3$ ) concentrations ( $\mu\text{g L}^{-1}$ )			<sup>c</sup> Permitted value ( $\mu\text{g L}^{-1}$ )
	Spring water	Stream 1	Stream 2	
Parathion-methyl	<sup>a</sup> 0.06	<sup>a</sup> 0.08	0.15	35
Chlorpyrifos	<sup>b</sup> ND	ND	ND	<sup>d</sup> x
Captan	ND	ND	ND	x
Procymidone	ND	ND	ND	x
$\alpha$ -Endosulfan	<sup>a</sup> 0.16	ND	<sup>a</sup> 0.20	0.2
Prothiofos	ND	ND	ND	x
Cyproconazole	ND	ND	ND	x
Ethion	<sup>a</sup> 0.30	<sup>a</sup> 0.31	ND	x
Triazophos	<sup>a</sup> 0.17	<sup>a</sup> 0.14	<sup>a</sup> 0.16	x
Phosmet	ND	ND	ND	x

<sup>a</sup>Below LOQ. <sup>b</sup>ND: not detected. <sup>c</sup>Regulation 357/2005. Ministry of Environment: pesticide levels in surface water in Brazil. <sup>d</sup>x: not regulated by Brazilian legislation.

other works using HF-LPME [59, 62]. Besides, comparing other methods described in the literature (Table 3) to the multiclass pesticides analysis this HF-LPME method presents better precision and low cost.

**3.3. Analysis of Real Environmental Samples.** The application of the HF-LPME-GC/MS method for determination of pesticides of real samples was achieved through the analysis of three real samples of surface water (spring, stream 1, and stream 2) collected in a rural area of the state of Minas Gerais, Brazil.

Agriculture is the main activity in the region upstream. The concentrations determination for each pesticide in water samples are shown in Table 4.

Parathion-methyl was quantified in the sample of stream 2 and detected in spring water and stream 1. The value found for this pesticide in the samples analyzed is lower than the limit established by Brazilian legislation [63]. Triazophos was detected in all the samples analyzed.  $\alpha$ -Endosulfan was detected in the spring water and stream 2. Ethion was detected in spring water and stream 1. These results show the ability of the method for the analysis of ten pesticides of different chemical classes in real samples.

## 4. Conclusions

This study describes the use of a simple and quick method for the determination of pesticides in environmental water by two-phase HF-LPME-GC/MS. The main factors related to HF-LPME extraction method such as the extraction mode, solvents, agitation, salt addition, and extraction time were investigated and optimized before the validation tests. The proposed method showed good linearity, low detection and quantification limits, high selectivity, and good repeatability for the pesticides selected. This procedure is selective, simple, fast, and low cost; it has minimal use of solvents and does not require pretreatment of samples. The results obtained from the analyses of three environmental water samples (spring and streams) have demonstrated the ability of the method to measure trace levels of pesticides. This method has the potential for automation and capacity for integrated sampling.

## Competing Interests

The authors declare no conflict of interests.

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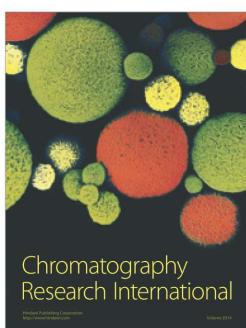
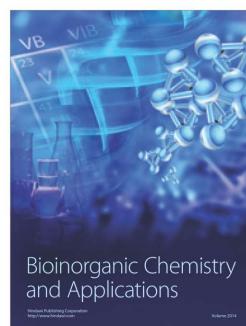
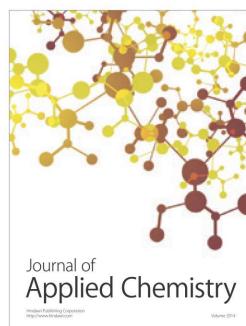
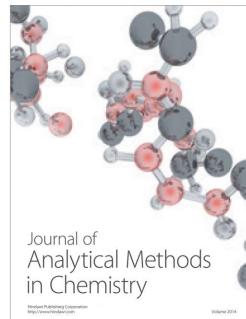
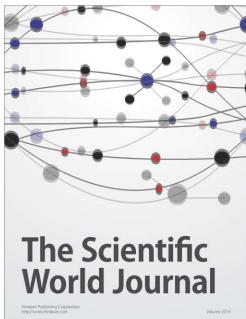
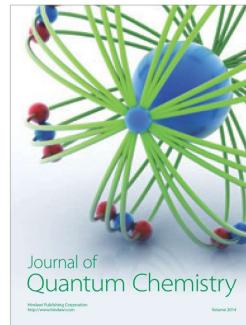
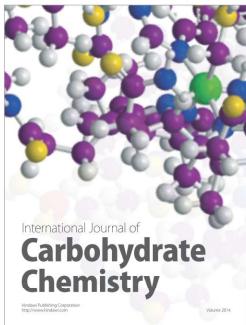
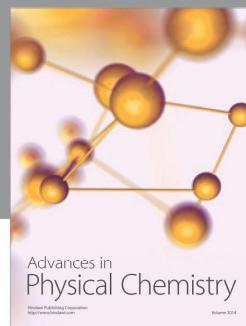
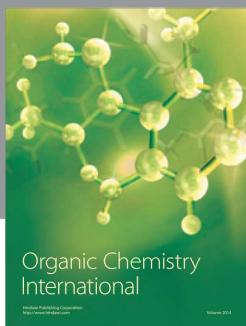
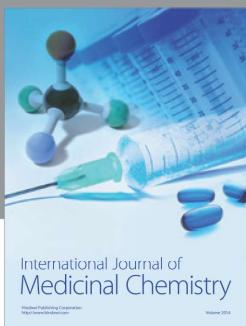
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## Review

# Liquid-phase microextraction with porous hollow fibers, a miniaturized and highly flexible format for liquid–liquid extraction

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**Abstract**

Since 1999, substantial research has been devoted to the development of liquid-phase microextraction (LPME) based on porous hollow fibers. With this technology, target analytes are extracted from aqueous samples, through a thin supported liquid membrane (SLM) sustained in the pores in the wall of a porous hollow fiber, and further into a  $\mu\text{L}$  volume of acceptor solution placed inside the lumen of the hollow fiber. After extraction, the acceptor solution is directly subjected to a final chemical analysis by liquid chromatography (HPLC), gas chromatography (GC), capillary electrophoresis (CE), or mass spectrometry (MS). In this review, LPME will be discussed with focus on extraction principles, historical development, fundamental theory, and performance. Also, major applications have been compiled, and recent forefront developments will be discussed.

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**Keywords:** Sample preparation; Liquid-phase microextraction; Hollow fibers; Review

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## 1. Principle of liquid-phase microextraction

In liquid-phase microextraction (LPME), a water immiscible organic solvent is immobilized as a thin supported liquid membrane (SLM) in the pores in the wall of a porous hollow fiber. This is easily accomplished by dipping the hollow fiber for a few seconds in the organic solvent, which immediately flows into the pores by capillary forces. The lumen of the hollow fiber is subsequently filled with a  $\mu\text{L}$  volume of an acceptor solution, and the whole assembly is placed in a sample solution for extraction of target analytes. The target analytes are extracted from

the sample (aqueous), through the SLM (organic), and trapped in the acceptor solution (aqueous or organic) in the lumen of the hollow fiber. After extraction, the acceptor solution is directly subjected to a final chemical analysis by liquid chromatography (HPLC), gas chromatography (GC), capillary electrophoresis (CE), or mass spectrometry (MS). The acceptor solution can be an organic solvent providing a 2-phase extraction system, which is directly compatible with GC. Alternatively, the acceptor solution can be an aqueous solution providing a 3-phase extraction system, which is compatible with HPLC or CE. The volume of sample in LPME ranges between 50  $\mu\text{L}$  and more than 1 L, whereas the volume of acceptor solution in most cases is in the range 2–30  $\mu\text{L}$ . Because of this high sample-to-acceptor volume ratio, very high analyte enrichments can be obtained by LPME without any need for evaporation and reconstitution. The vol-

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ume of the SLM is typically 5–30  $\mu\text{L}$ , resulting in an extremely low consumption of organic solvent per extraction. LPME may therefore be utilized as a green chemistry approach to reduce the consumption of hazardous organic solvents in the chemical laboratory. As a third point, LPME is a very efficient technique for sample clean-up, reducing or eliminating potential problems from matrix components. Especially in the 3-phase mode, excellent clean-up has been reported from complicated biological and environmental samples. Finally, LPME may easily be automated in commercially available robotic systems, providing a fully automated approach to sample preparation. In this review, focus will be directed to the historical development of LPME, and to fundamental theory, performance, and forefront applications.

## 2. Historical development of liquid-phase microextraction

The invention of solid-phase microextraction (SPME) by Pawliszyn and co-workers [1] basically initiated the interest for microextraction techniques in analytical chemistry. With the SPME technique, target analytes of low or medium polarity are extracted from aqueous or gaseous samples and onto a solid polymeric fiber attached to a thin needle on a syringe (SPME needle). Extraction occurs by passive diffusion and the extraction yield is essentially determined by the fiber to sample partition coefficient. After extraction, the analytes are thermally desorbed from the SPME needle in a hot injection port of a GC, and finally analyzed by GC. The target analytes can also be desorbed from the SPME fiber by elution with an organic solvent, which subsequently is injected into HPLC. SPME rapidly gained widespread interest, especially because it eliminated the use of organic solvents for sample preparation, and the technique has been commercially available for several years.

Following the development of SPME, similar research was conducted to miniaturize liquid–liquid extractions into LPME. In 1996, Dasgupta and co-workers [2], and Cantwell and co-workers [3] presented the first papers on LPME, and later also Lee and co-workers [4] and Andrews and co-workers [5] were involved in this early development. The LPME systems at that time were based on extraction of analytes from aqueous samples and into a small drop of an organic solvent. Typically, the small drop of organic solvent was suspended from the tip of a GC syringe, and placed in the aqueous solution for extraction. During extraction, target analytes were extracted from the aqueous sample and into this hanging drop based on passive diffusion, and extraction recoveries were essentially determined by the organic solvent to water partition coefficients. When finished, the drop of organic solvent was withdrawn into the syringe and subsequently injected in GC. Although hanging drop LPME is very simple and efficient, and reduces the consumption of organic solvents per sample to a few  $\mu\text{L}$ , it is still used only in a limited number of research laboratories. One reason for this may be the low stability of the hanging drop, which is easily lost into the sample during extraction.

As a solution to improve the stability and reliability of LPME, Pedersen-Bjergaard and Rasmussen introduced hollow-

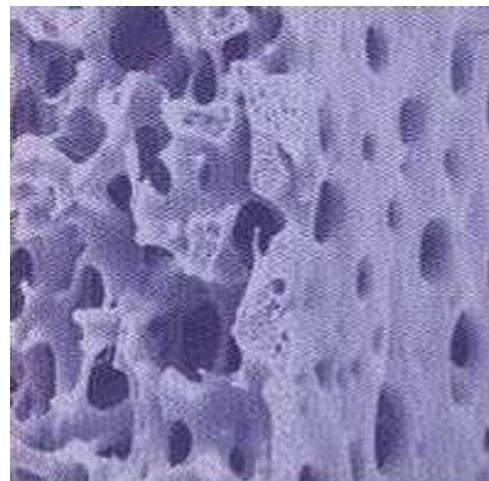


Fig. 1. Picture of cross-section of LPME hollow fiber.

fiber based LPME in 1999 [6]. In this concept the extracting phase was placed inside the lumen of a porous polypropylene hollow fiber. Fig. 1 shows a cross-section of the fiber wall. The fiber had a porosity of 70%; a pore size was 0.2  $\mu\text{m}$ , a wall thickness of 200  $\mu\text{m}$  and an internal diameter of 600  $\mu\text{m}$ . A supported liquid membrane was formed by dipping the hollow fiber into the organic solvent. The solvent penetrated the pores of the hollow fiber and was bound by capillary forces to the polypropylene network comprising the fiber wall. The high porosity enabled immobilization of a considerable volume of solvent as a thin film. A 1 cm length of the fiber was able to immobilize ca. 8  $\mu\text{L}$  of solvent as a 200  $\mu\text{m}$  film within the polypropylene network. The extracting phase (acceptor solution) which was placed in the lumen of the fiber was mechanically protected inside the hollow fiber and it was separated from the sample by the supported liquid membrane (organic solvent). This prevented dissolution of the extracting phase (acceptor solution) into the sample. In hollow fiber LPME, analytes are extracted from an aqueous sample, into the organic solvent immobilized as a SLM, and into the acceptor solution placed inside the lumen of the hollow fiber. Subsequently, the acceptor solution is removed by a micro-syringe and transferred to final chemical analysis.

The chemical principle of hollow-fiber LPME was essentially the same as the pioneering work of Jönsson and co-workers [7–13] with SLM extraction. In the latter, extraction was accomplished from aqueous samples through a SLM sustained in a flat sheet of porous polymeric membrane or in a hollow-fiber, and into an acceptor phase on the other side of the SLM. The technical set-up, on the other hand, differed considerably from hollow-fiber LPME. For SLM extraction, the sample was pumped with a syringe pump to the SLM, providing a flow system. On the other side of the membrane, the acceptor solution was pumped with another syringe pump. In total, the SLM extractions required substantial instrumentation. The first publication on hollow-fiber by Pedersen-Bjergaard and Rasmussen [6] was pioneering in the way that it was the first paper to show the use of SLM extractions with a small piece of hollow fiber in a stagnant system without the use of pumps to deliver the sample and the acceptor phase. In the period since 1999, the interest

for hollow-fiber LPME has increased significantly, and several research groups have been involved in the early development of the technique. This work is reviewed in the current paper, and the discussion has been limited to work including the use of porous hollow fibers to support the SLM.

### 3. Fundamental theory

The basic set-up for LPME is illustrated in Fig. 2. LPME can be performed either in the 2- or 3-phase mode. Prior to extraction, the sample is filled into a sample vial, and an internal standard may be added. For acidic or basic compounds, pH in the sample is adjusted in order to suppress the ionization of the target analytes. A short piece of a porous hollow fiber is used for LPME, and this may either be a rod configuration with a closed bottom [14] or a u-configuration [6] where both ends of the hollow fiber is connected to guiding tubes. First, a SLM is formed in the pores in the wall of the hollow fiber. This may be accomplished by dipping the hollow fiber into an organic solvent of low polarity (like *n*-octanol, dihexyl ether or toluene) for a few seconds. Alternatively, a small quantity of the organic solvent can be injected into the lumen of the hollow fiber and immobilized from the inside of the hollow fiber. After loading the SLM, the acceptor solution is filled into the lumen of the hollow fiber. This acceptor solution can be an organic solvent (same as used for the SLM) resulting in a 2-phase extraction system, or the acceptor solution may be an acidic or alkaline aqueous solution resulting in a 3-phase extraction system.

In the 2-phase LPME system, the target analytes are extracted from the aqueous sample and into the organic solvent (acceptor solution) present both in the porous wall and inside the lumen of the hollow fiber. This process may be illustrated with the following equation:



where  $A$  represents the target analyte. The partition coefficient for  $A$  is defined as

$$K_{\text{acceptor}/\text{sample}} = \frac{C_{\text{eq},\text{acceptor}}}{C_{\text{eq},\text{sample}}} \quad (2)$$

where  $C_{\text{eq},\text{acceptor}}$  is the concentration of  $A$  in the acceptor solution at equilibrium (organic phase) and  $C_{\text{eq},\text{sample}}$  is the concentration of  $A$  in the sample at equilibrium (aqueous phase). Based on Eq. (2) and a mass balance of the 2-phase LPME system, the recovery ( $R$ ) of  $A$  at equilibrium can be calculated by

the following equation [15]:

$$R = \frac{K_{\text{acceptor}/\text{sample}} V_{\text{org}}}{K_{\text{acceptor}/\text{sample}} V_{\text{org}} + V_{\text{sample}}} \times 100\% \quad (3)$$

where  $V_{\text{org}}$  is the total volume of organic phase in the system (sum of organic solvent present in the porous wall of the hollow fiber and in the lumen of the hollow fiber) and  $V_{\text{sample}}$  is the volume of the sample. From Eq. (3) it can be predicted that the recovery is dependant on the partition coefficient, the volume of organic solvent, and the volume of the sample. High recoveries are obtained for compounds with high partition coefficients. This can be accomplished by proper selection of the organic solvent, by proper selection of pH for acidic/basic analytes, and in some cases by addition of sodium chloride at high concentrations to the sample. In addition, small sample volumes are beneficial in order to obtain high recoveries for equilibrium extractions.

The extraction kinetics for a 2-phase LPME system can be described by the following equation [3]:

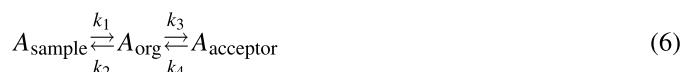
$$C_{\text{acceptor}} = C_{\text{eq},\text{acceptor}}(1 - e^{-kt}) \quad (4)$$

where  $k$  is the rate constant ( $\text{s}^{-1}$ ) defined by

$$k = \frac{A_i}{V_{\text{org}}} \beta_0 \left( K_{\text{acceptor}/\text{sample}} \frac{V_{\text{org}}}{V_{\text{sample}}} + 1 \right) \quad (5)$$

$C_{\text{acceptor}}$  is the concentration of  $A$  in the acceptor phase (organic phase) at time  $t$ ,  $A_i$  the interfacial area, and  $\beta_0$  is the overall mass transfer coefficient with respect to the organic phase. Eq. (5) reveals that for rapid extractions,  $A_i$  and  $\beta_0$  should be maximized and  $V_{\text{sample}}$  should be minimized. Also, the overall mass transfer coefficient should be maximized by strong agitation of the whole LPME device.

In 3-phase LPME, the analytes are extracted from the aqueous sample, through the organic SLM, and further into the aqueous acceptor solution present inside the lumen of the hollow fiber. This process may be illustrated by the following equation:



where  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are the first order extraction rate constants. To establish an equation for calculation of equilibrium recovery, partition coefficients both between the organic phase (SLM) and the sample as well as between the acceptor phase and the organic phase have to be considered:

$$K_{\text{org}/\text{sample}} = \frac{C_{\text{eq},\text{org}}}{C_{\text{eq},\text{sample}}} \quad (7)$$

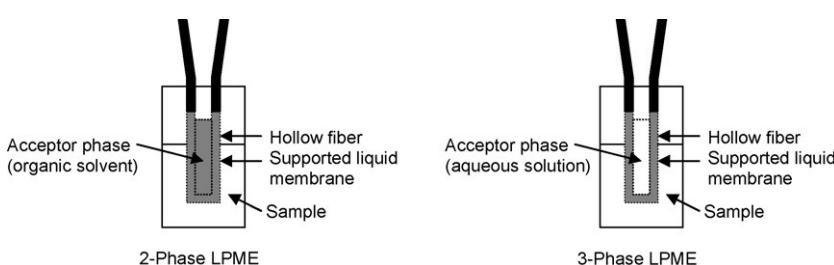


Fig. 2. Schematic illustration of 2- and 3-phase LPME.

$$K_{\text{acceptor/org}} = \frac{C_{\text{eq,acceptor}}}{C_{\text{eq,org}}} \quad (8)$$

Based on Eqs. (7) and (8), and based on a total mass balance for the 3-phase LPME system, the following equation can be derived for calculation of recoveries ( $R$ ) in 3-phase LPME [15]:

$$R = \frac{K_{\text{org/sample}} K_{\text{acceptor/org}} V_{\text{acceptor}}}{K_{\text{org/sample}} K_{\text{acceptor/org}} V_{\text{acceptor}} + K_{\text{org/sample}} V_{\text{org}} + V_{\text{sample}}} \times 100\% \quad (9)$$

where  $V_{\text{acceptor}}$  is the volume of aqueous acceptor solution and  $V_{\text{org}}$  is the volume of organic phase immobilized in the pores of the hollow fiber (SLM). From Eq. (9) it may be concluded that recoveries in 3-phase LPME are controlled by the two individual partition coefficients, and by the volumes of the sample, the organic phase and the acceptor phase, respectively. In general, high partition coefficients are beneficial, and this can be obtained by proper selection of the organic solvent (SLM) and by proper selection of the pH conditions in the aqueous solutions. For basic analytes, pH in the sample should be high (preferably 3 units higher than the  $pK_a$ -value of the analytes), whereas the acceptor phase should be acidic (preferably 3 units below the  $pK_a$ -value of the analytes), and vice versa for acidic analytes. Also, to ensure high recoveries, the volumes of sample and organic phase should be as small as possible.

Two practical aspects can be derived from the equations above; LPME can provide very high enrichments, and LPME extractions are relatively sensitive to the magnitude of the partition coefficients [15]. LPME is superior to traditional liquid–liquid extraction (LLE) for substances of low polarity, providing high enrichments and excellent discrimination of polar substances. On the other hand, LPME is relatively inefficient for the most polar substances, and for those, more efficient extractions may be accomplished by traditional LLE. The latter may explain the strong clean-up properties of LPME.

#### 4. Performance characteristics of liquid-phase microextraction

LPME is an equilibrium extraction technique, where the concentration of analyte in the acceptor solution increases to a certain level, and subsequently the system enters equilibrium and the analyte concentration in the acceptor phase remains constant versus time as illustrated in Fig. 3 [16]. Thus, LPME is not an exhaustive extraction technique like LLE and solid-phase extraction (SPE). The extraction recovery in LPME is determined by the actual partition coefficients, the sample volume, the volume of the SLM, and the volume of acceptor phase. Typically, LPME recoveries reported in the literature range between 10 and 90%. This is illustrated in Table 1 for 3-phase LPME of selected psycholeptics from human plasma [17]. Especially in the 3-phase mode, recoveries exceeding 80–90% are rare due to some analyte trapping within the SLM. The actual recovery for a certain application has to be measured and built into the calibration of the LPME method in a similar way as performed in SPME. Kinetic calibration, where the extracting phase

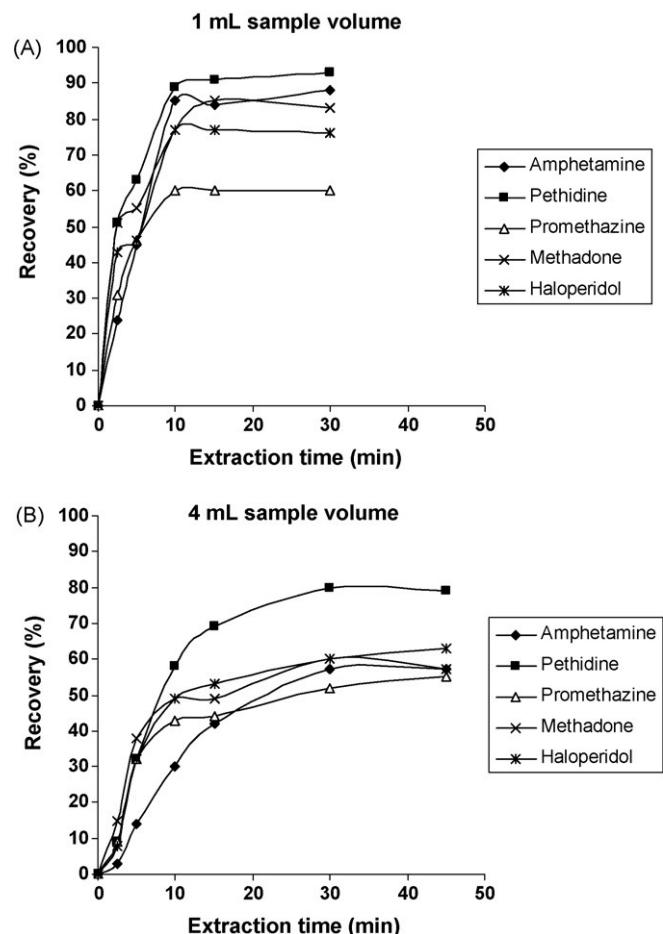


Fig. 3. Extraction time profiles for five model drugs in 1 mL (A) and 4 mL (B) aqueous solution. Data collected from [16].

has been preloaded with analyte to measure the release of analyte to the sample, has also been explored for LPME and may be an interesting future concept for exact calibration in LPME [18].

As analytes are extracted from relatively large sample volumes and into a very small volume of acceptor solution, most LPME applications provide substantial analyte enrichment. High enrichments are obtained directly without the need for solvent evaporation and re-constitution as required for high enrichment by LLE and SPE, and this is one of the major advan-

Table 1  
Recoveries obtained by 3-phase LPME of selected psycholeptics from human plasma [17]

Compound	Recovery (%)
Chlorpromazine	24
Levomepromazine	21
Dixyrazine	42
Fluphenazine	31
Perphenazine	29
Prochlorperazine	47
Haloperidol	65
Flupentixol	19
Chlorprothixene	24
Zuclopentixol	32

Table 2

Enrichments obtained by 2-phase LPME of triazine herbicides from water [19]

Compound	Enrichment
Simazine	42
Atrazine	141
Propazone	178
Secbumeton	165
Sebutylazine	190
Desmetryn	170
Simetryn	179
Prometryn	208

tages of LPME. The enrichment factor in LPME is basically determined by the analyte recovery and by the volume of the sample. As the volume of the sample increases, the enrichment factor also increases. Table 2 illustrates an example, where tri-

azine herbicides were extracted by 2-phase LPME from 3 mL samples and into 3  $\mu$ L of acceptor solution [19]. Enrichments up to 27,000 have recently been reported from 1100 mL samples [20] supporting the high potential of LPME for analyte enrichment.

In addition to recovery and enrichment, also sample clean-up is an important objective of sample preparation. Especially in the 3-phase mode, LPME provides very clean extracts from a variety of samples like environmental waters [21] and biological samples [22]. An example of the latter is illustrated in Fig. 4, where citalopram and methamphetamine were spiked to human urine, plasma, and whole blood [23]. In spite of the complex matrices of these samples, almost no other components than the two basic drugs were recovered in the acceptor solution. The high sample clean-up performance is a second major advantage of LPME.

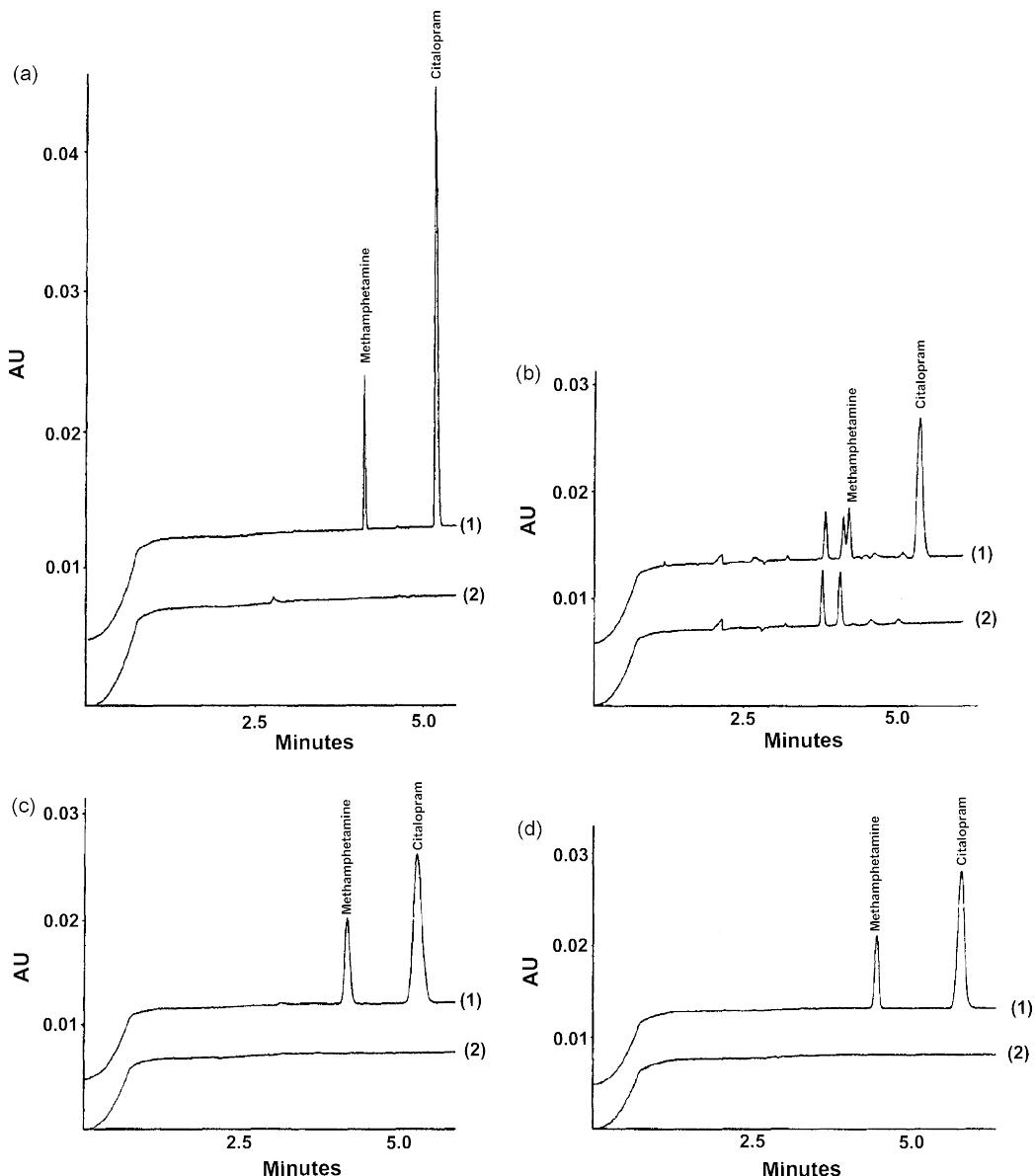


Fig. 4. CE-UV analysis of LPME extracts from (a) water, (b) urine, (c) plasma, and (d) whole blood. Samples spiked with 100 ng/mL methamphetamine and citalopram [23].

Table 3

Validation data for 3-phase LPME of aromatic amines from water samples [25]

	Compound			
	3-NA	4-CA	4-BA	3,4-DCA
Inter-day precision (RSD, %)	4.3	4.8	3.9	3.8
Intra-day precision (RSD, %)	5.6	7.3	5.1	4.9
Linearity range ( $\mu\text{g/L}$ )	1–500	1–500	0.5–500	1–500
Correlation coefficient ( $r^2$ )	0.9988	0.9998	0.9988	0.9917
Accuracy (surface water) (%)	96.6	97.3	101.5	98.1

In addition to high analyte enrichment and excellent sample clean-up, a major advantage of LPME is the low consumption of organic solvent per sample. Typically, the volume of organic solvent immobilized in the pores of a hollow fiber segment range between 5 and 30  $\mu\text{L}$ . In the 2-phase mode, also the acceptor solution inside the lumen of the hollow fiber is an organic solvent, with a volume typically ranging from 2 to 30  $\mu\text{L}$ . In other words, the total consumption of organic solvent per analysis normally ranges between 10 and 40  $\mu\text{L}$ . One recent paper even demonstrated that in the 3-phase mode, where the organic solvent only serves as an intermediate extraction medium, soy-bean oil or anise oil can be used as the SLM providing a totally “Green chemistry” approach to sample preparation [24].

From a technical point of view, LPME enables a high degree of flexibility. With the same extraction device, either 2- or 3-phase extractions can be performed, providing compatibility with both GC, HPLC, CE, and MS. Neutral substances can be extracted in a 2-phase system, and acidic and basic compounds can be extracted either in a 2- or 3-phase system. Recently, 2-phase LPME was even fully automated in a robotic system combined with GC [18]. In addition, validation data reported demonstrate acceptable repeatability, reproducibility, accuracy, linearity, and robustness, even though all reports until now have been accomplished with home-built equipment. An example of validation data are illustrated in Table 3 [25].

While enrichment, clean-up and low solvent consumption are the major advantages of LPME, relatively long extraction times is perhaps the major disadvantage of the concept. Normally, extraction times to equilibrium range between 15 and 45 min for sample volumes below 2 mL [16], whereas for 1 L samples even 2 h may be required to reach equilibrium [20]. On the other hand, when the LPME process is finished, the acceptor phase is directly subjected to the final analysis with no further sample preparation steps required. Also, many samples may be extracted in parallel to speed up the throughput, extractions may be carried out under non-equilibrium conditions [16], or extractions may be carried out by dynamic LPME [25]. Recently, a paper demonstrated that LPME extraction can be performed with increased extraction speed utilizing an electrical potential applied across the SLM [26], and this approach may eliminate the speed disadvantage of LPME in the future.

## 5. Applications and forefront developments

In Table 4, current applications of LPME reported in the scientific literature are summarized. As seen from the table, most

applications have been reported within the fields of environmental analysis and drug/pharmaceutical analysis. In addition, a few papers have been focused on food, beverages, and peptides. Typically, 2-phase LPME has involved the use of either toluene or *n*-octanol as the organic phase, whereas 3-phase LPME in most cases has been conducted with *n*-octanol or dihexyl ether as the SLM. For 3-phase LPME, HCl and NaOH have in most cases been used to make appropriate pH adjustments in the sample and in the acceptor solution. The majority of applications will not be discussed in detail in this review, but can easily be found in the literature based on the list of references. However, the text below will focus on selected applications demonstrating some of the LPME frontiers, where alternative extraction principles or specialized technical solutions have been addressed.

While many LPME papers have utilized static extraction systems, some environmental applications have been conducted with dynamic systems, both in the 2- and 3-phase modes. Dynamic LPME was claimed to provide better extraction efficiency and improved reproducibility as compared with the static mode. In one paper, dynamic LPME was conducted in the 2-phase mode for extraction of pesticides [25]. A conventional micro-syringe with a 1.3-cm length of hollow fiber attached to its needle was connected to a syringe pump to perform the extraction. The micro-syringe was used both as the microextraction device as well as the sample introduction device for GC-MS analysis. The attached hollow fiber served as the “holder” and “protector” of the 3  $\mu\text{L}$  of toluene used for extraction. The solvent was repeatedly withdrawn into and discharged from the hollow fiber by the syringe pump. The pesticides were extracted from 4 mL water samples into the toluene impregnated in the hollow fiber, and subsequently, the organic solvent was injected into GC-MS. Slurry samples of soil and water were extracted with this set-up, which provided excellent precision and linearity data. A similar set-up was utilized in the 3-phase mode for extraction of aromatic amines prior to CE [56].

The dynamic LPME approach has also been tested for headspace extractions [87], where selected PAHs were extracted from soil samples. Water was added to the soil samples in order to release the target analytes to the headspace, the sample was heated to 90 °C to support analyte volatilization, and extraction was accomplished with *t*-octanol as the organic phase. This solvent provided excellent extractions, it was directly compatible with the GC-MS system, and very importantly, the volatility of this solvent was low in order to avoid partial evaporation during LPME. The system was simple and inexpensive, and provided good analyte enrichment factors, linear range, limits of detection, and repeatability.

An interesting variant of the headspace LPME system was recently published under the name “liquid–gas–liquid microextraction (LGLME) [80]. In this technique, a small amount (6  $\mu\text{L}$ ) of aqueous acceptor solution (0.5 M NaOH) was introduced into the lumen of a 2.7 cm polypropylene hollow fiber. The hollow fiber was then immersed in an aqueous sample solution (70 °C). The aqueous acceptor solution in the channel of the hollow fiber was separated from the sample solution by the hydrophobic microporous hollow fiber wall with air inside its pores. Different phenols passed through the microporous hollow fiber membrane

Table 4  
Overview of LPME applications

Analytes	2-Phase/3-phase	Sample	SLM	Acceptor phase	Analytical method	Refs.
<b>Drug analysis/pharmaceuticals</b>						
Amino alcohols	3-Phase	Urine	1-Octanol	100 mM HCl	CE	[27]
Amphetamines	3-Phase	Blood, urine	Dihexyl ether	10 mM HCl	FIA-MS	[28]
Anabolic steroids	2-Phase	Urine	1-Octanol	1-Octanol	LC-MS	[29]
Antidepressants	3-Phase	Human breast milk	Polyphenyl-methylsiloxane	10 mM HCl	CE	[30]
Antidepressants	3-Phase	Blood, plasma	Dodecyl acetate	200 mM HCOOH	LC-MS	[31]
Antiinflammatory drugs	3-Phase	Urine	Dihexyl ether	10 mM NaOH	CE	[32]
Basic drugs	2-Phase	Plasma	1-Octanol	1-Octanol	GC	[33]
Basic drugs	3-Phase	Plasma, urine	1-Octanol	10 mM phosphate (pH 3)	CE, HPLC	
Basic drugs	3-Phase	Blood, plasma, urine	Dihexyl ether	100 mM HCl	CE	[23]
Basic drugs	3-Phase	Plasma	Dihexyl ether	10 mM HCl	CE	[16]
Basic drugs	3-Phase	Plasma, urine	1-Octanol	50 mM HCl	CE	[34]
Basic drugs	3-Phase	Water, plasma	Dihexyl ether	10 mM HCl	CE	[17]
Basic drugs	3-Phase	Hair	1-Octanol	10 mM HCl	HPLC	[35]
Basic drugs	3-Phase	Water	Dihexyl ether	Different acids	CE	[36]
Benzodiazepines	2-Phase	Plasma, urine	Dihexyl ether, 1-octanol, butyl acetate	Dihexyl ether, 1-octanol, butyl acetate	GC	[37]
Benzodiazepines	3-Phase	Blood	Nonanol	1 M HCl	HPLC	[38]
Cannabinol	2-Phase	Urine	BSTFA+1-octane	BSTFA + 1-octane	GC-MS	[39]
Chiral drugs	3-Phase	Plasma	Dihexyl ether	10 mM HCl	CE	[40]
Citalopram	3-Phase	Plasma	Dihexyl ether	20 mM phosphate (pH 2.8)	CE	[41]
Citalopram	3-Phase	Plasma	Dodecyl acetate	20 mM phosphate (pH 2.8)	CE	[42]
Cocaine	2-Phase	Urine	Chloroform	Chloroform	GC	[13]
Cocaine	2-Phase	Saliva	Chloroform	Chloroform	GC	[43]
Doping agents	3-Phase	Urine	1-Octanol	50 mM NH <sub>3</sub>	LC-MS	[44]
Methamphetamine	3-Phase	Plasma, urine	1-Octanol	100 mM HCl	CE	[6]
Mirtazapine	2-Phase	Plasma	Toluene	Toluene	HPLC	[45]
Polar drugs	3-Phase	Plasma	1-Octanol	50 mM HCl	LC-MS	[46]
Polar drugs	3-Phase	Plasma	1-Octanol	50 mM HCl	CE	[47]
Salbutamol, terbutaline	3-Phase	Tablets, urine	Dihexyl ether + Aliquat 336	1 M NaBr	LC-MS	[48]
Triphenylphosphine oxide	2-Phase	Pharmaceuticals	1-Octanol	1-Octanol	HPLC	[49]
<b>Environmental</b>						
Acidic drugs	3-Phase	Wastewater	1-Octanol	10 mM (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	LC-MS	[50]
Acidic herbicides	2-Phase	Water	1-Octanol	1-Octanol	GC-MS	[51]
Analgesics	2-Phase	Water	1-Octanol	1-Octanol	GC-MS	[52]
Antiinflammatory drugs	3-Phase	Wastewater	1-Octanol	10 mM NaOH	HPLC	[53]
Antiinflammatory drugs	3-Phase	Water	1-Octanol	100 mM NaOH	HPLC	[54]
Aromatic amines	3-Phase	Tap, surface water	Dihexyl ether	0.5 M HCl + 18-crown-6 ether	HPLC	[55]
Aromatic amines	3-Phase	Water	1-Octanol	500 mM HCl	CE	[56]
Aromatic amines	3-Phase	Water	Benzyl alcohol + ethyl acetate	10 mM HCl	HPLC	[57]
BTEX	2-Phase	Water	1-Octanol	1-Octanol	GC-MS	[58]
Carbamate pesticides	2-Phase	Water	1-Octanol	1-Octanol	GC-MS	[59]
Chlorophenols	3-Phase	Water	Ionic liquids	100 mM NaOH	HPLC	[60]
Dichlorophenol	2-Phase	Water, urine	1-Octanol	1-Octanol	GC-MS	[61]
Dinitrophenols	3-Phase	Water	Undecane	600 mM NaHCO <sub>3</sub>	HPLC	[62]
Fatty acids	2-Phase	Water	1-Octanol	1-Octanol	GC-MS	[63]
Fungicides	2-Phase	Farm water	Toluene	Toluene	GC	[64]
Haloacetic acids	3-Phase	Drinking water	Dihexyl ether + TOPO	10 mM NaOH	HPLC	[65]
Hydroxyaromatic compounds	3-Phase	River water	Nonanol + dihexyl ether	1 M NaOH	HPLC	[66]
Inorganic selenium	2-Phase	Water	Tetrachloromethane	Tetrachloromethane	ETV-ICP-MS	[67]
Insecticides	2-Phase	Water	Toluene	Toluene	GC	[68]
Nitroaromatics	2-Phase	Water	Toluene	Toluene	GC-MS	[69]

Table 4 (Continued)

Analytes	2-Phase/3-phase	Sample	SLM	Acceptor phase	Analytical method	Refs.
Nitrophenols	3-Phase	Seawater	1-Octanol	10 mM NaOH	HPLC	[70]
Organic pollutants	2-Phase	Rainwater	Toluene	Toluene	GC-MS	[71]
Organic pollutants	2-Phase	Marine sediments	Toluene	Toluene	GC-MS	[72]
Organochlorine pesticides	2-Phase	Seawater	Toluene	Toluene	GC-MS	[73]
Organochlorine pesticides	2-Phase	Water	Toluene	Toluene	GC-MS	[74]
Organophosphorus pesticides	2-Phase	Lake water	Cyclohexane	Cyclohexane	GC-MS	[75]
Pesticides	2-Phase	Pond water	Toluene	Toluene	GC-MS	[25]
Pesticides	2-Phase	Soil	Toluene	Toluene	GC-MS	[76]
Phenols	3-Phase	Tap water	1-Octanol	8 mM NaOH	CE	[77]
Phenols	2-Phase	Seawater	Toluene	Toluene	GC-MS	[78]
Phenols	3-Phase	Water	1-Octanol	100 mM NaOH	HPLC	[79]
Phenols	Gaseous diffusion	Water	Air	500 mM NaOH	HPLC	[80]
Phenoxyacetic acid	3-Phase	River water	1-Octanol	500 mM NaOH	HPLC	[81]
Phenoxy acid herbicides	3-Phase	Water	1-Octanol	10 mM NaOH	HPLC	[82]
Phthalate esters	2-Phase	Portable water	Toluene	Toluene	GC-MS	[83]
PAH metabolites	2-Phase	Water	1-Octanol	1-Octanol	Fluorescence, CE	[84]
PAHs	2-Phase	Water	1-Octanol	1-octanol	GC-MS	[85]
PAHs	2-Phase	Soil slurry	1-Octane	1-Octane	GC	[86]
PAHs	Headspace	Water	1-Octanol	1-Octanol	GC-MS	[87]
PAHs	2-Phase	Wastewater	Toluene	Toluene	GC-MS	[88]
PAHs	3-Phase	Water	n-Decane	n-Decane	HPLC	[89]
Polybrominated biphenyls	2-Phase	Water	n-Undecane	n-Undecane	GC-MS	[90]
Polychlorinated biphenyls	2-Phase	Plasma	Toluene	Toluene	GC-MS	[91]
Primary amines	2-Phase	River water	Toluene	Toluene	GC-MS	[92]
Salbutamol, terbutaline	3-Phase	Water	Dihexyl ether + Aliquat 336	1 M NaBr	LC-MS	[48]
Triazine herbicides	2-Phase	Soil slurry	Toluene	Toluene	GC-MS	[19]
Trihalomethanes	2-Phase	Water	1-Octanol	1-Octanol	GC	[93]
Vinclozolin	2-Phase	Natural water	Toluene	Toluene	GC	[94]
Warfare agents	2-Phase	Water	Chloroform	Chloroform	GC-MS	[95]
Warfare agents	2-Phase	Water	Trichloroethylene	Trichloroethylene	GC-MS	[96]
Food and beverages						
Carbaryl	2-Phase	Red wine	1-Octanol	1-Octanol	GC-MS	[18]
Ochratoxin A	2-Phase	Wine	1-Octanol	1-Octanol	HPLC	[97]
Organochlorine pesticides	2-Phase	Tea	1-Octanol	1-Octanol	GC	[98]
Pesticides	3-Phase	Vegetables	Dihexyl ether + TOPO	100 mM HCl + methanol	LC-MS	[99]
Phenoxy herbicides	3-Phase	Bovine milk	1-Octanol	100 mM NaOH	HPLC	[100]
Peptides						
Peptides	3-Phase	Water	1-Octanol	HCl	HPLC	[101]
Peptides	3-Phase	Water	1-Octanol	100 mM HCl	HPLC	[102]
Miscellaneous						
Octanol–water partition	2-Phase	Water	1-Octanol	1-Octanol	HPLC	[103]

BTEX: benzene, toluene, ethylbenzene and xylenes; PAH: polycyclic aromatic hydrocarbon.

by gas diffusion, and were trapped by the basic acceptor solution in the lumen of the hollow fiber. After extraction, the acceptor solution was withdrawn into a micro-syringe and injected into a small sample vial for CE analysis. This system, which was totally solvent-free, showed comparable results with traditional LPME with an extraction time of 20 min.

As seen from Table 4, GC or GC-MS has in most cases been used for the final analysis of extracts from 2-phase LPME, whereas HPLC, LC-MS, or CE has been used in combination with 3-phase LPME. Because LPME often provides very clean extracts, some papers have reported the direct coupling of LPME with different spectroscopic techniques, where the chromatographic or electrophoretic step has been eliminated.

In one paper, LPME was coupled directly to electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) for the determination of inorganic selenium in natural waters [67]. The organic chelating reagent ammonium pyrrolidine dithiocarbamate was used both as the extracting solvent in the hollow fiber and as chemical modifier for the ETV-ICP-MS determination. Following extraction, the organic phase was directly loaded into the ETV-ICP-MS system for quantification of inorganic selenium. In another paper, LPME was coupled directly to tandem MS through a flow-injection system [28]. Different amphetamines were extracted from whole blood and urine in a 3-phase LPME system utilizing dihexyl ether as the organic phase and 25  $\mu$ L 10 mM HCl as the acceptor

solution, and subsequently the acceptor solution was introduced directly into the mass spectrometer. Based on a combination of selected ion monitoring MS and selected reaction monitoring tandem MS, the different amphetamines were identified in human samples down to the low ng/mL level. With elimination of the chromatographic step, the system enabled a very high sample through-put analyzing one or two samples every minute.

Because LPME can provide very high enrichments, combinations with CE may be used to determine drugs and drug metabolites in human plasma although CE with UV detection is known to provide relatively poor detection limits. This may be especially interesting for chiral applications since CE is well known for excellent chiral selectivity. Thus, 3-phase LPME of both mianserin [40] and citalopram [42] was followed by chiral CE to monitor the chiral metabolism in humans. Although the CE analysis was conducted with UV detection, therapeutically relevant concentrations were easily measured due to the high enrichment obtained by LPME. In addition to chiral CE, also chiral HPLC has been utilized in combination with LPME [45].

As mentioned above (Section 3), ionic substances have typically been extracted under pH conditions where their ionization is suppressed in order to maximize partition coefficients. Alternatively, a couple of papers have discussed the possibility of implementing ion-pair or carrier-mediated extractions to the LPME format. Recently, long-chain fatty acids were extracted by 2-phase LPME from water samples as ion-pairs with tetrabutylammonium hydrogen sulfate [63]. The ion-pair complexes were extracted into *n*-octanol as the solvent, and were subsequently derivatized quantitatively to butyl esters in the injection port of a GC. This procedure was successfully applied to measure long-chain fatty acids in real water samples. A similar report on acidic herbicides has also been published [51] in the 2-phase mode. In the 3-phase mode, some focus has been devoted to ion-pair or carrier mediated LPME of drugs. Drugs of low polarity ( $\log P > 1.5$ ), like antidepressants and antiepileptic drugs, are normally extracted with medium (>30%) or high (>60%) recoveries in 3-phase LPME [17] based on their favorable partition coefficients. On the other hand, polar substances provide low recoveries (0–30%) due to their low partition coefficient between the organic SLM and the aqueous sample. In order to enhance the extraction of hydrophilic drugs, carrier-mediated LPME has been reported [34]. In carrier-mediated LPME, sodium octanoate was added to the sample (pH 7.0) to form ion-pairs with the hydrophilic basic drugs. The ion-pair complexes were easily extracted into the SLM, and at the interface between the SLM and the acidic acceptor solution, the hydrophilic drugs were released from the ion-pair reagent and extracted into the acceptor solution. From the acceptor solution, protons were back-extracted into the SLM to protonate the octanoate ions. Thus, the extraction was forced both by high partition coefficients of the drug-ion pair complexes, and by a high proton concentration in the acceptor solution. Several reports have investigated carrier-mediated LPME [46,47], and several hydrophilic drugs with  $\log P$  values below 1.0 were extracted from human plasma with recoveries exceeding 45%.

In addition to ion-pair or carrier-mediated LPME, several papers have focused on alternative approaches to enhance recoveries in LPME. Several reports have focused on optimization of the SLM utilizing binary solvent mixtures, and in several cases, combinations of different solvents was found to enhance extraction recoveries as compared to the more traditional LPME solvents like *n*-octanol, dihexyl ether, or toluene. [57,66]. Also, derivatizing reagents have been added to the organic phase like *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) to enhance partitioning of 11-nor- $\Delta^9$ -tetrahydrocannabinol-9-carboxylic acid into the SLM and simultaneous derivatization [39], and trioctylphosphine oxide (TOPO) was added to the SLM to enhance the extraction of haloacetic acids [65]. The acceptor solution has also been subject to implementation of more advanced chemistry. In one case, methanol was added to the acceptor solution (10 mM NaOH) to enhance the extractability of different non-steroidal anti-inflammatory drugs (NSAIDs) from human urine [32]. The addition of methanol to the acceptor solution was also shown to improve the extractability of pesticide residues in vegetables [99]. In another example, 18-crown-6 ether was added to the acceptor solution (0.5 M HCl) in order to increase the recovery of aromatic amines [25]. In the latter case, the level of crown ether was 500 mM.

One of the major advantages of LPME is the possibility of high analyte enrichments, as target analytes are extracted into a very small volume of acceptor phase. In two papers, LPME has been accomplished from large sample volumes in two individual steps to provide very high enrichment in a relatively short time [53,57]. In the former report, nonsteroidal anti-inflammatory drugs were extracted from a 100 mL sample, through *n*-octanol as the SLM immobilized in 10 individual hollow fibers, and into 10 mM NaOH as acceptor solution present in the lumen of each of the 10 hollow fibers. Following, the acceptor solutions were combined, acidified, and subsequently extracted with a single hollow fiber containing *n*-octanol as the SLM and 2  $\mu$ L 10 mM NaOH as the acceptor solution. In this system the analytes were transferred from a 100 mL sample to 2  $\mu$ L of acceptor solution, and enrichments exceeding 15,000 were reported. This was further refined in a very recent paper, where basic drugs in wastewater were extracted from 1100 mL samples, through dihexyl ether as SLM, and into 20  $\mu$ L 10 mM HCl as acceptor solution in a single step [20]. In the latter report, enrichments exceeding 27,000 were obtained after 2 h of extraction, and subsequently, the extracts were directly subjected to LC–MS without further sample preparation required. This enabled drug residues in municipal wastewater to be detected down to the low pg/L level.

A final interesting perspective of LPME is the possibility of performing “green chemistry”. In one LPME report, trace level drug analysis was conducted in human plasma sample without the use of hazardous organic solvents [24]. In the 3-phase mode, the SLM serves as an intermediate extraction medium, and in principle alternatives to pure synthetic organic solvents can be used. Thus, 3-phase LPME of basic drugs were accomplished with soy-bean oil or anise oil as the organic phase, and subsequently the extracts were analyzed by a totally aqueous CE system.

## 6. Future trends

The current paper has focused on hollow-fiber LPME, including historical development, fundamental theory, performance, applications and forefront development. Based on this, and combined with earlier reviews [21,22,104] and recent work on practical optimization [105], the technique is very well suited for extraction of non-polar and medium-polar substances from different types of aqueous samples. Also, several reports have demonstrated acceptable validation data for the technique, in most cases with home-built equipment. With all this information, LPME is in principle mature for implementation in routine analytical laboratories.

However, the implementation of LPME is currently limited by the unavailability of commercial equipment. Work is in progress in this area, and hopefully the near future will show commercial equipment for LPME. This equipment should be fully automated and compatible with the most abundant laboratory robotics and auto-samplers. Also, reports with this type of equipment, with special focus on robustness and validation, is mandatory for future general acceptance and implementation of the technique. Finally, development of generic methods for different type of analytes is important, to reduce the time required for individual laboratories to develop LPME methods. For this purpose, the applications and theory reviewed in this chapter will be of high value.

Based on the strong advantages of LPME, it is expected to be an important future sample preparation technique complementing existing techniques like liquid–liquid extraction, solid-phase extraction, and solid-phase microextraction. Most probably, the majority of applications will be within environmental chemistry and for pharmaceutical analysis. However, analysis of foods and beverages is an increasing application field and may also benefit from utilizing LPME. Finally, LPME may be used in more untraditional ways, e.g. for the rapid determination of log *P* values, for estimating transport properties of chemical entities through biological and artificial membranes, and for passive samplers in the environment to mention only a few alternative applications.

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## Hollow-fibre liquid-phase microextraction of phthalate esters from water

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### Abstract

A simple and efficient liquid-phase microextraction (LPME) technique using a hollow-fibre membrane, in conjunction with gas chromatography–mass spectrometry has been developed for the extraction and analysis of six phthalate esters in water samples. Parameters such as extraction solvent, agitation of the sample, salt addition and extraction time were controlled and optimised. The developed protocol was found to yield a linear calibration curve in the concentration range from 0.02 to 10  $\mu\text{g l}^{-1}$  for most target analytes and the limits of detection were in the low  $\mu\text{g l}^{-1}$  level, ranging between 0.005 and 0.1  $\mu\text{g l}^{-1}$ . The repeatability of the method varied between 4% and 11%. Under the present experimental conditions, the performance of the method was found comparable to that of solid-phase microextraction (SPME). The advantage of the proposed method over SPME was that it eliminated carry-over of analytes between runs. The applicability of the developed hollow-fibre LPME method and SPME was demonstrated for real water samples. The ability of both microextraction methods to concentrate many organic analytes was demonstrated as both methods allowed the confirmation of the presence of an extra contaminant (ethyl *p*-ethoxybenzoate) in bottled mineral water samples.

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**Keywords:** Hollow-fibre membranes; Liquid-phase microextraction; Extraction methods; Water analysis; Phthalates; Ethyl ethoxybenzoate

### 1. Introduction

The mechanical properties of rigid poly(vinyl chloride) (PVC) can be modified through the addition of low molecular mass compounds that mix with the polymer matrix. Addition of these so-called plasticisers (mainly phthalates and adipates) in various amounts generates materials with versatile properties that have led to the use of PVC in a vast range of applications [1].

Today, all the phthalates used as plasticisers in diverse applications are ubiquitous in the environ-

ment. Since they are not chemically but only physically bound to the polymer chains, they may be leached into food and beverages from the packaging material [2]. Likewise, penetration of phthalates from waste plastics into the ecosystem surrounding the waste disposal sites may occur. Certain phthalates, as well as their metabolites and degradation products, can cause adverse effects on human health (in particular on liver, kidney and testicles) [3]. Potential endocrine disrupting properties were also reported [4]. The most commonly used phthalates include bis-2-ethylhexyl phthalate (DEHP), di-*n*-butyl phthalate (DBP) and butylbenzyl phthalate (BBP). Due to their potential risks to human health and the environment [5], these phthalates are on the first three priority lists for risk assessment in accordance with

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the European Union's Regulation 793/93 on existing substances [6]. The US Environmental Protection Agency (EPA) has set the maximum contamination level (MCL) for DEHP in water systems at  $6 \mu\text{g l}^{-1}$  and recommended that concentrations above  $0.6 \mu\text{g l}^{-1}$  be closely monitored [7].

Determination of phthalates in aqueous samples commonly requires the use of different preconcentration techniques such as liquid–liquid extraction (LLE) or solid-phase extraction (SPE), followed by gas chromatography (GC) or high-performance liquid chromatography (HPLC) [8,9]. These sample pretreatment methods are considered expensive, time-consuming, and labour-intensive methods, which often result in high blank values. This is due to phthalates present in many laboratory products including glassware, chemicals and plastic accessories, which can easily migrate into the water samples destined for analysis [8,10].

Solid-phase microextraction (SPME) is an innovative sample preconcentration technique that has been used for a wide variety of organic contaminants in environmental samples [11,12]. Recently, several published reports dealt with the development and validation of SPME methods in phthalate analysis [9,10,13–15]. In these studies, several commercially available SPME fibres were compared and the influence of temperature, salt addition and sample agitation were examined. The results confirmed that SPME is a fast, simple, solventless and efficient preconcentration technique that enables determination of phthalates at low  $\mu\text{g l}^{-1}$  contamination levels in water samples. More importantly though, they concluded that the use of SPME reduced the risk of secondary contamination during sample handling, a major concern in phthalate analysis.

A recent trend in sample pretreatment techniques involves the miniaturisation of the LLE extraction procedure by greatly reducing the solvent to aqueous phase ratio, leading to solvent microextraction methodologies [16]. A technique that evolved from this approach is single-drop microextraction, where the extractant phase is a microdrop of a water-immiscible solvent suspended on the tip of a conventional microsyringe, immersed in a contaminated water sample [17]. Although single-drop microextraction proved to be a simple, inexpensive, fast, and virtually solvent-free sample pretreatment technique, prob-

lems of drop stability and low sensitivity were often encountered [16,18].

The quest for novel micro-LLE methods has never ceased and a new microextraction method, termed liquid-phase microextraction (LPME), using porous polypropylene hollow-fibres was recently introduced [19]. In one of the possible configurations, the fibre is connected at one of its ends to the needle tip of a microsyringe while the other end is left suspended in the sample solution [20]. This fibre configuration is considered an evolution of single-drop microextraction, because the organic microdrop is protected by the hollow-fibre.

The aim of the present study was to investigate the applicability of hollow-fibre LPME method for the determination of phthalates in water samples. Parameters such as extraction solvent, agitation speed, ionic strength of the aqueous sample and sampling time were controlled and optimised. The resulting method was validated and compared to SPME for the extraction of phthalates from real water samples. Overall, both techniques allowed the low  $\mu\text{g l}^{-1}$  level analysis of phthalates in aqueous samples and reduced the risk of secondary contamination. The advantages of hollow-fibre LPME over SPME included a low analysis cost per sample and elimination of sample carry-over between analyses due to the disposability of the polypropylene fibre.

## 2. Experimental

### 2.1. Chemicals and sample preparation

The Accurel Q 3/2 polypropylene hollow fibre membrane used here was obtained from Membrana (Wuppertal, Germany). The wall thickness of the fibre was 200  $\mu\text{m}$ , the inner diameter was 600  $\mu\text{m}$ , and the pore size was 0.2  $\mu\text{m}$ .

Methanol, hexane and acetonitrile were Suprasolv quality (for organic trace analysis) and were obtained from Merck (Darmstadt, Germany). Deionized water used for sample preparation was prepared on a water purification system (EASYPure RF) supplied by Barnstead/Thermolyne (Dubuque, IA, USA). Ethyl 4-ethoxybenzoate (>99%) was purchased from Eurolabs (Poynton, UK). Sodium chloride more than

99.5% pure was obtained from Merck. The six phthalates selected for investigation were purchased from Supelco (Bellefonte, PA, USA) in the form of a standard methanolic stock solution containing 2000 mg l<sup>-1</sup> of dimethyl phthalate (DMP), diethyl phthalate (DEP), DBP, BBP, DEHP and di-n-octyl phthalate (DOP). From this solution, working mixtures in methanol (100 mg l<sup>-1</sup>) were prepared weekly. Standard solutions in hexane were also prepared for direct injection calibration containing all phthalates in the range 0.1–50 mg l<sup>-1</sup>. All solutions were stored in the dark at 4 °C.

The spiked aqueous solutions were prepared daily at the concentration levels of interest. For extraction, a 5-ml spiked aqueous sample was placed each time in a 7-ml clear glass vial (Supelco). For the SPME experiments, the vials were fitted with aluminium foil and screw caps with a hole (Supelco). Unless otherwise stated, magnetic stirring at 1000 rev./min was applied at all times using a glass-coated flea micro spinbar (8 mm×3 mm).

## 2.2. Hollow-fibre liquid-phase microextraction

Before use, the hollow fibre membrane was sonicated in acetone for several minutes to remove any contaminants. The fibre was then removed from the solvent solution and allowed to dry completely. It was then cut, manually and carefully, into 1.3-cm pieces.

A 10-μl Hamilton gas-tight syringe (Hamilton, Bonaduz, Switzerland), Model 1701RNR, with a blunt needle tip (length, 5.1 cm; O.D., 0.071 cm; I.D., 0.015 cm), was used to introduce the acceptor phase, support the hollow fibre and act as the injection syringe. A 3-μl portion of a water immiscible organic solvent was withdrawn into the syringe followed by 3.4 μl of water. The tip of the microsyringe's needle was then inserted into the hollow fibre, which was then immersed into the organic solvent for 10 min, to ensure that the pores were filled with the extraction solvent. After solvent impregnation, water in the microsyringe was injected carefully into the hollow fibre, removing thus any excess of organic solvent from the inside. The fibre was then removed from the organic solvent and immediately immersed into the stirred water sample

destined for analysis. The plunger was depressed and the 3-μl portion of the organic phase was injected into the hollow fibre. The use of stands and clamps ensured reproducible and stable positioning of the hollow fibre. After extracting for a prescribed period of time (typically 20 min) at room temperature, the organic solvent was withdrawn into the microsyringe and then injected into the GC–MS for analysis. Due to the low cost, a new fibre was used for each extraction.

## 2.3. Solid-phase microextraction

SPME was performed using a manual 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) SPME fibre and an SPME fibre holder assembly, all purchased from Supelco. The fibre was initially conditioned according to the recommendations of the producer. Each day and prior to extracting any samples, the fibre was immersed for a few minutes in a stirred acetonitrile solution, and a blank analysis was then run to ensure that the fibre was free of contaminants. For extraction, the SPME fibre holder assembly was clamped at a fixed location above the 7-ml glass vial containing 5 ml of the spiked sample solution, stirred at 1000 rev./min. The SPME fibre was exposed to the aqueous phase and after sampling for 20 min at room temperature, the fibre was retracted and transferred to the heated injection port (260 °C) of the GC–MS where it remained for 5 min.

## 2.4. GC–MS analysis

All analyses were carried out on a Shimadzu GC-17A (Version 3) QP-5050A GC–MS system. The instrument was equipped with a 30 m×0.25 mm, 0.25 μm HP-5MS capillary column (Agilent Technologies). All analyses were performed in the splitless mode with the split closed for 5 min. An 8-min solvent delay time was used. The injector's temperature was 260 °C. Helium (>99.999% pure) was used as a carrier gas at a flow-rate of 1.2 ml min<sup>-1</sup>. The column oven was initially set at 60 °C for 1 min and then programmed to 300 °C at a rate of 10 °C min<sup>-1</sup>, where it was held for 5 min. The

interface temperature was set at 310 °C and the detector voltage at 1.40 kV. The ionization mode was electron impact (70 eV). Based on the literature, the selected ion monitoring (SIM) mode was used as a sensitive tool for quantitative measurements [15]. The esters were monitored according to the following target ions *m/z* DMP: 163, 194, DEP: 149, 177, DBP: 149, 223, BBP: 149, 206, 91, DEHP: 167, 149, 279, DOP: 149, 279. Prior to quantification in the SIM mode, the full scan mode (*m/z* 50–465) was used for identification of all target compounds based on their mass spectra and GC retention times. The limits of detection (LODs) were calculated from the calibration curves that defined linearity and the value of the Winefordner and Long criterion [23]. The value of the slope of the calibration curves (*b*) and the standard error of the independent term of the regression (*S<sub>b</sub>*) were substituted for each target analyte in:

$$\text{LOD} = \frac{3S_b}{b}. \quad (1)$$

The response of the mass detector in the SIM mode by direct injection of 1 µl of the different standard solutions was investigated and was found to be linear within the range of 0.1–50 µg ml<sup>-1</sup>. The correlation coefficients were above 0.99 and were comparable with previously reported values [15].

The linearity of each microextraction method was checked within the range of 0.2–10 µg l<sup>-1</sup> for most target analytes by using spiked deionised water. The concentration of phthalates in real water samples was calculated by using the calibration curves obtained for each microextraction method after subtraction of the blank analysis (deionised water) values.

Shimadzu GC instruments require a thick septum. Although thermo-resistant Thermogreen LB-2 septa (Supelco) were used here, the thick needle-protector of the SPME fibre as well as the thick needle of the 10-µl Hamilton microsyringe (Model 1701RNR) were damaging it irreversibly. This resulted in phthalate contamination due to the small polymer pieces introduced into the inlet liner of the GC injector and even carrier gas leaks and extraneous peaks. This problem could be overcome simply by drilling the septum prior to its use.

### 3. Results and discussion

#### 3.1. Optimisation of the hollow-fibre LPME method

##### 3.1.1. Extraction solvent

A crucial step in hollow-fibre LPME is choosing the most suitable extraction solvent [20]. As in LLE the principle “like dissolves like” is applied. The water immiscible solvent used should fulfil several requirements [19,20]. Firstly, it should be able to provide high solubility for the target analytes, and be compatible with direct injection into the capillary GC column. In addition, it should have a low solubility in water to prevent solvent dissolution during extraction, especially when faster stirring rates and extended extraction times are applied. Finally, it should have a polarity matching that of the polypropylene hollow-fibre, namely, the solvent must be able to impregnate and become immobilised within the pores of the hollow-fibre, in order to enhance transfer of analytes into the organic phase, as extraction occurs onto the surface of the immobilised organic solvent. For the purpose of the present experiments, three solvents were investigated: toluene, hexane and cyclohexane. Solvent selectivity was evaluated for 20-min extractions of 5-ml water samples spiked at 10 µg l<sup>-1</sup> of each target analyte and stirred at 1000 rev./min. The results showed that toluene was the most suitable extraction solvent as it resulted in an increased response of the analytical instrument. In addition, toluene combined low solvent loss during extraction and, compared to the other organic solvents tested, had the ability to be easily immobilised in the pores of the hollow-fibre within seconds [20].

##### 3.1.2. Agitation of the sample

Magnetic stirring enhances extraction and reduces the time required to reach thermodynamic equilibrium. Since the solvent here is protected by the hollow-fibre, faster stirring rates may be applied. This was not the case for single-drop microextraction where the solvent-drop was directly exposed to the aqueous phase and higher stirring rates usually resulted in drop displacement and/or drop dissolution [21]. The instrument’s response was examined

for several stirring rates ranging from 0 to 1250 rev./min for a 20-min extraction of 5-ml aqueous samples spiked at  $10 \mu\text{g l}^{-1}$  of each target analyte. As shown in Fig. 1, the results confirmed that agitation of the sample greatly enhances extraction. Although the instrument's response was at maximum at the highest agitation speed attainable by the magnetic stirrer (1250 rev./min), the results were difficult to reproduce due to solvent dissolution. Thus, the 1000-rev./min stirring rate was used for all subsequent experiments.

### 3.1.3. Salt addition

Increasing the ionic strength of the aqueous solution may have several effects upon extraction [12]. Usually, depending on the solubility of the target analytes, adding salt to the sample enhances extraction of the more polar analytes. In the case of single-drop microextraction, salt addition was generally found to limit or not to affect extraction of analytes. It was assumed, that apart from the salting-out effect, the presence of salt was causing a second effect, adverse for the extraction, whereby the physical properties of the extraction film were changed, reducing thus the diffusion rates of the analytes into the drop [16]. For the purpose of the present experiments, the effect of NaCl concentration (ranging from 0 to 30%) was investigated and the extraction efficiency was monitored. The results revealed that in hollow-fibre LPME, addition of salt restricted extraction of target analytes except in the case of the more polar DMP.

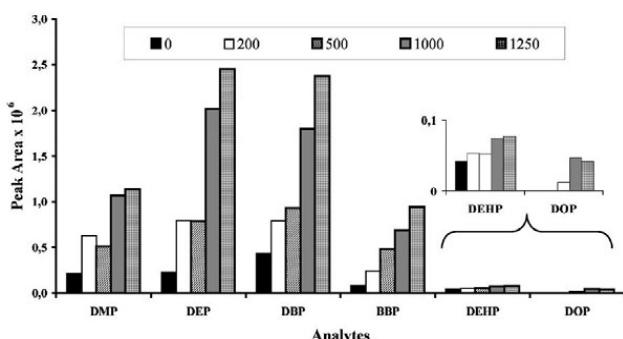


Fig. 1. Effect of sample agitation (rev./min) on hollow-fibre LPME extraction of phthalates from water samples: concentration  $10 \mu\text{g l}^{-1}$ ; 20 min extraction time.

During the SPME extraction of DEP from water samples, blank aqueous solutions of NaCl were found to contain DEP, possibly originating from the plastic containers in which the salt was stored, and it was found necessary to extract the salt twice with acetonitrile to remove any traces of DEP [13]. Taking into account all the above considerations and in accordance with Luks-Betlej et al. [15] who made similar observations concerning the effect of salt on the SPME analysis of phthalates, we decided not to alter the salt content of the sample solutions in the subsequent extractions as the sensitivity of the procedure was not poor.

### 3.1.4. Extraction time

The extraction time profile was then investigated. Standard aqueous solutions ( $10 \mu\text{g l}^{-1}$ ) were prepared and extracted by varying the exposure of the extraction solvent to the sample from 5 to 30 min. Extraction times longer than 30 min could not be investigated as they typically resulted in significant solvent dissolution. As shown in Fig. 2, extraction increased with increasing exposure times and it seems that only DEHP and DOP reached equilibrium after 20 min of extraction. For routine analysis however, it is not necessary to attain equilibrium if constant extracting conditions are maintained [13,15,16,20–22]. Therefore, a 20-min extraction was used for all subsequent experiments as it matched the chromatography run time and maximised sample throughput.

Based on the above data, the calibration curves and analyses of real samples were obtained under the following conditions: 3  $\mu\text{l}$  toluene, 5 ml water samples, 1000 rev./min stirring rate and 20 min sampling time.

## 3.2. SPME method

Previous studies dealing with the optimisation of the SPME procedure for the analysis of phthalates in water samples revealed that the SPME fibres containing a DVB phase were more suitable, as they yielded high extraction efficiency [15] and were less affected by the composition of the matrix since extraction with this type of fibre occurs via absorption [9]. When using the PDMS–DVB fibre, sam-

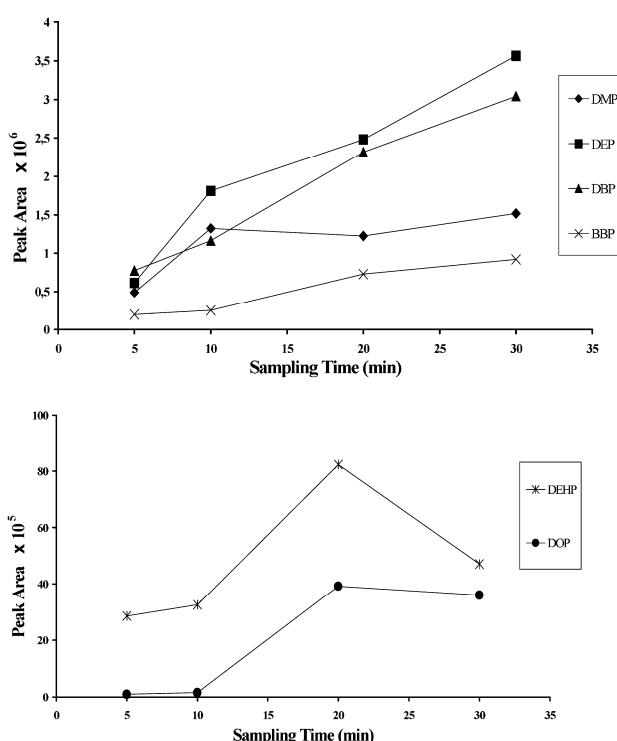


Fig. 2. Extraction time profiles for hollow-fibre LPME extraction of phthalates from water samples: concentration  $10 \mu\text{g l}^{-1}$ ; stirring rate 1000 rev./min.

pling time was reduced which maximised sample throughput [9,13]. The experimental conditions for the SPME procedure were comparable to the ones used for hollow-fibre LPME to allow direct comparison and were: PDMS–DVB fibre, 5 ml water

samples, 1000 rev./min stirring rate and 20 min sampling time.

The main drawback of SPME when compared to hollow-fibre LPME is the possibility of analyte carry-over between runs during phthalate analysis [10]. In order to eliminate such a possibility in the present studies, after desorption, the SPME fibre was immersed in a stirred solvent solution for 5 min and was subsequently transferred to the heated injection port of another GC system until the next extraction to avoid contamination between runs. In hollow-fibre LPME, since the price of each extraction unit was low, each hollow-fibre was used only for a single extraction. The disposable nature of hollow-fibre LPME eliminated the possibility of analyte carry-over.

### 3.3. Method validation and comparison with the SPME method

Calibration curves for most analytes were calculated in the concentration range from 0.02 to  $10 \mu\text{g l}^{-1}$ . As shown in Table 1, linearity for hollow-fibre LPME was very good with correlation coefficients  $r^2$  being greater than 0.9984 ( $n=5$ ) except in the case of DEHP and DOP where the  $r^2$  values were 0.9888 and 0.9875, respectively. For SPME, the  $r^2$  values were all greater than 0.9974 ( $n=5$ ). The repeatability of the method, expressed as relative standard deviation (RSD), was evaluated by extracting five consecutive aqueous samples spiked at  $1 \mu\text{g l}^{-1}$  with

Table 1

Main method parameters (linear range, correlation coefficients, limits of detection and repeatability) of phthalates in water when using hollow-fibre LPME and SPME

Analyte	Hollow-fibre LPME				SPME <sup>a</sup>			
	Linear range ( $\mu\text{g l}^{-1}$ )	Correlation coefficient ( $r^2$ )	LODs ( $\mu\text{g l}^{-1}$ ) <sup>a</sup>	RSD $n=5^c$ (%)	Linear range ( $\mu\text{g l}^{-1}$ )	Correlation coefficient ( $r^2$ )	LODs ( $\mu\text{g l}^{-1}$ ) <sup>a</sup>	RSD $n=5^c$ (%)
DMP	10–0.02	0.9992	0.01	12	10–0.05	0.9985	0.01	7
DEP	10–0.02	0.9991	0.01 <sup>b</sup>	19	10–0.02	0.9985	0.01 <sup>b</sup>	4
DBP	10–0.02	0.9999	0.005 <sup>b</sup>	4	10–0.02	0.9998	0.003 <sup>b</sup>	7
BBP	10–0.02	0.9984	0.01	5	10–0.02	0.9993	0.008	7
DEHP	10–0.1	0.9888	0.02 <sup>b</sup>	12	10–0.05	0.9974	0.01 <sup>b</sup>	11
DOP	10–0.5	0.9875	0.1	18	10–0.1	0.9989	0.04	10

<sup>a</sup> Calculated using the Winefordner and Long criterion [23].

<sup>b</sup> Estimated values (see text).

<sup>c</sup> Spiking level  $1 \mu\text{g l}^{-1}$ ; mean values for five determinations.

each target analyte. The RSD of the hollow-fibre LPME ranged from 4% to 19% with a mean value of about 12%. For SPME, the RSD values varied between 4% and 11% (8% mean value). Regarding the  $r^2$  and RSD values obtained here for the SPME method, similar values have been published elsewhere [9]. The LODs for DEP, DBP and DEHP under the MS-SIM conditions were calculated by using the calibration curves and the Winefordner and Long criterion [23]. Despite all precautions taken to avoid secondary contamination during extraction, the deionised water used for preparing the water solutions was found to contain trace amounts of the above-mentioned analytes. Similar observations have been previously reported [9,10]. The LODs when using hollow-fibre LPME and SPME techniques were found to be in the low  $\mu\text{g l}^{-1}$  level and ranged between 0.005 to 0.1  $\mu\text{g l}^{-1}$  and 0.003 to 0.04  $\mu\text{g l}^{-1}$ , respectively. Under the present experimental conditions, the two techniques seem to be comparable in terms of linearity and sensitivity. It should be noted however, that in the case of SPME better LODs are expected by prolonging the extraction time. Nevertheless, the wide linear range combined with the low detection limits obtained with the two extraction methods studied here, suggests a high potential for monitoring phthalates in water samples. The performance of hollow-fibre LPME reflects the fact that the extraction solvent is protected by the hollow-fibre, improving the stability and repeatability of extraction compared to that of the single-drop microextraction method.

#### 3.4. Application to real samples

The performance of hollow-fibre LPME and SPME was also tested by analysing potable water from the Chania water-supply network. As shown in Table 2, DEP, DBP, and DEHP were the principal

contaminants and found in low concentration levels. In the case of DEHP, the concentration was ca. 0.9  $\mu\text{g l}^{-1}$  when using both extraction methods. As stated earlier, the US EPA suggests that DEHP concentrations in potable water above 0.6  $\mu\text{g l}^{-1}$  be closely monitored [7].

In addition, two different brands of commercial bottled mineral water were analysed. They were both distributed in PET bottles having a push-pull closure, which enables consumers to drink straight from the bottle without removing the cap from the bottle. Analyses of the samples by using both microextraction techniques revealed that DEP, DBP and DEHP were also the principal contaminants (Table 2). Similar findings in PET bottles have been reported previously [10,14] and it was assumed that such levels of phthalate contamination corresponded to common background contamination during production.

The ability of these techniques to concentrate many organic analytes in aqueous samples was demonstrated in the case of brand B where an extra peak appeared at 13.04 min (Fig. 3). The mass spectrum of this peak (Fig. 3) in the full-scan mode corresponded to ethyl *p*-ethoxybenzoate (PEEB) with a 0.95 match factor. The identity of this compound was also confirmed in terms of retention time, by running a hexane solution of the commercially available analyte under the same chromatographic conditions. Detection of the above-mentioned analyte was also possible under the MS-SIM mode (194 ion in the ion set for the DMP). PEEB forms part of the fourth generation Ziegler–Natta catalyst in polypropylene production [24]. The European Union has recently set regulations for this compound and the maximum permitted concentration of this substance in materials intended to come into contact with foodstuffs is currently 3.6  $\text{mg kg}^{-1}$  [25]. In the present studies, it was assumed that

Table 2  
Concentration ( $\mu\text{g l}^{-1}$ ) of phthalates found in tap water and in two brands (PET A and PET B) of bottled mineral water

Analyte	Hollow-fibre LPME			SPME		
	Tap water	PET A	PET B	Tap water	PET A	PET B
DEP	0.30	0.05	0.13	0.11	0.12	0.07
DBP	1.04	0.32	0.51	0.44	0.08	0.14
DEHP	0.93	0.65	0.57	0.87	0.36	0.46

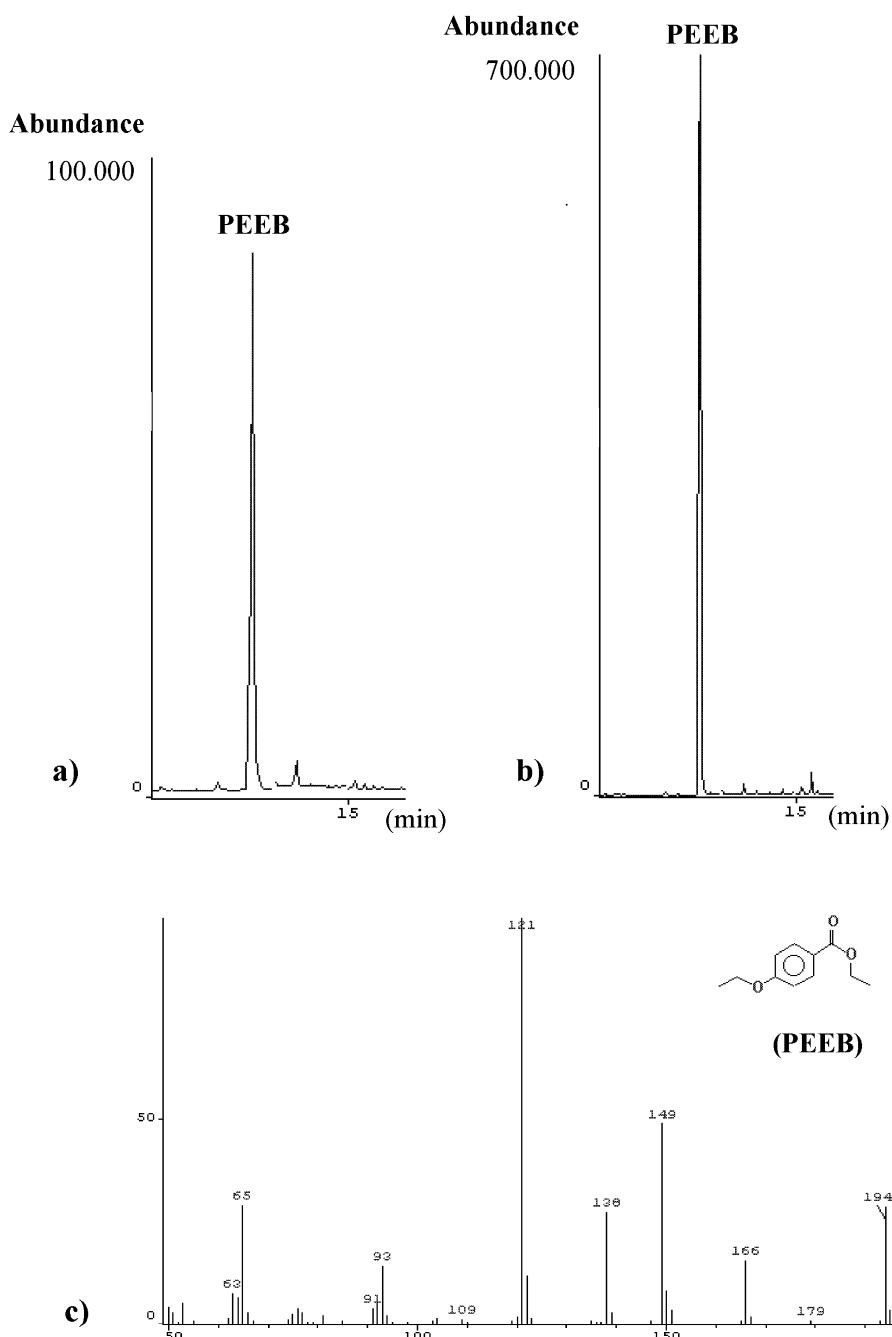


Fig. 3. Part of the SIM chromatogram of bottled mineral water (brand B) analysed by (a) hollow-fibre LPME and (b) SPME, revealing the presence of ethyl *p*-ethoxybenzoate (PEEB); (c) mass spectrum recorded at 13.04 min in the total ion chromatogram of mineral water brand B when using SPME–GC–MS, identified as PEEB.

PEEB originated from the push–pull closure of the particular brand. It should be mentioned here that caps are often responsible for phthalate contamina-

tion of bottled mineral water. For example, even commercially available mineral waters distributed in glass bottles are suspected of such contamination,

as it has been reported that metal caps may be sealed with PVC inserts contributing to a high level of DEHP contamination [10].

#### 4. Conclusions

Hollow-fibre LPME coupled to GC–MS was successfully applied for the analysis of trace levels of phthalates in water samples. The developed protocol proved to be a simple, rapid, inexpensive, precise and sensitive analytical procedure. The advantages of this extraction method over other microextraction methods follow from the presence of the hollow fibre, which protected the extraction solvent and allowed the use of high stirring rates without drop displacement and drop dissolution as in single-drop microextraction. The disposable nature of the hollow-fibre eliminated the possibility of carry-over effects seen in SPME. Hollow-fibre LPME and SPME minimise the risk of secondary contamination during analysis, a major problem in phthalate analysis. In addition, the performance of hollow-fibre LPME was comparable to that of SPME and, overall, both extraction methods can be recommended for trace analysis of phthalates in water samples.

Application to potable water samples suggested continuous monitoring of the water, as the DEHP concentration exceeded the  $0.6 \mu\text{g l}^{-1}$  limit set by the EPA. Analyses of bottled mineral waters indicated phthalate contamination possibly originating from production. However, in one brand both methods revealed the presence of an extra contaminant, demonstrating their ability to concentrate many organic analytes in aqueous samples.

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# Developments in liquid-phase microextraction

E. Psillakis, N. Kalogerakis

The development of faster, simpler, inexpensive and more environmentally friendly sample-preparation techniques is an important issue in chemical analysis. Recent research trends involve miniaturisation of the traditional liquid-liquid extraction (LLE) principle by greatly reducing the acceptor-to-donor phase ratio. One of the emerging techniques in this area is liquid-phase microextraction (LPME), where a hollow fibre impregnated with an organic solvent is used to accommodate or protect microvolumes of acceptor solution. This novel methodology proved to be an extremely simple, low-cost and virtually solvent-free sample-preparation technique, which provided a high degree of selectivity and enrichment by additionally eliminating the possibility of carry-over between runs. This article presents the different modes and hollow-fibre configurations of LPME, followed by an up-to-date summary of its applications. The most important parameters and practical considerations for method optimisation are also discussed. The article concludes with a comparison of this novel method with solid-phase microextraction (SPME) and single-drop microextraction (SDME).

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**Keywords:** Biological samples; Environmental samples; Extraction techniques; Hollow fibre; LPME; Membrane extraction; Solvent microextraction

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## 1. Introduction

In recent years, the development of fast, precise, accurate and sensitive methodologies has become an important issue. Despite the great technological advances, most analytical instruments cannot handle sample matrices directly and, as a result, a sample-preparation step is commonly introduced. For organic trace analysis, this step mainly comprises extractions, which serve to isolate compounds of interest from a sample matrix. Ultimately, the concentration of target compounds is enhanced (enrichment) and the presence of matrix components is reduced (sample clean up).

LLE is a versatile sample-preparation technique, prescribed in many standard analytical methods. Despite its wide-

spread use, it is considered to be a time-consuming, tedious, multistage operation [1], where problems of emulsion formation obstruct automation. More importantly though, the use of large amounts of toxic organic solvents influences trace analysis, poses a health hazard to laboratory personnel and results in the production of hazardous laboratory waste, thus adding extra operational costs for waste treatment. Driven by the need to overcome these drawbacks, new sample-preparation techniques have been developed over the last two decades, facilitating rapid and efficient sample preparation as well as eliminating the consumption of toxic organic solvents.

SPME, introduced by Arthur and Pawliszyn [2], successfully redressed the limitations inherent in the traditional LLE method. It rapidly gained high popularity, as it incorporated sampling, extraction, concentration and sample introduction into a single solvent-free step. With SPME, a small amount of extractant phase, dispersed on a solid support (fibre), is exposed to the sample. Target analytes partition between the sample matrix and the extractant phase and, after a well-defined period of time, the fibre is transferred to a gas chromatograph (GC) or to the SPME-high-performance-liquid-chromatography (HPLC) interface for analysis [3]. More than a decade after its introduction, the main problems commonly encountered with SPME include the limited lifetime of the SPME fibres, their relatively fragile nature and the possibility of carry-over between analyses [4,5]. Nevertheless, to date, SPME accounts for numerous reports in a wide range of applications, such as environmental, food, clinical and forensic analysis [3,6,7].

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The quest for novel sample-preparation techniques has never ceased, and one of the most recent trends is miniaturisation of the traditional LLE method. The general idea behind these novel techniques is a great reduction in the volumetric ratio of the acceptor-to-donor phase. This can be achieved by using either immiscible liquid phases (solvent microextraction) or a membrane to separate the acceptor-donor phases (membrane extraction).

The two main methodologies that evolved from the solvent microextraction approach are SDME [8–11], where the acceptor phase is a microdrop of a water-immiscible organic solvent suspended in an aqueous donor solution (two-phase system), and microextraction using immiscible liquid films including liquid-liquid microextraction (two-phase system) [11] and liquid-liquid-liquid microextraction using back-extraction (three-phase system) [12,13]. The term “liquid-phase microextraction” (LPME) was first introduced to describe two-phase systems in solvent microextraction [11]. Overall, solvent-microextraction techniques proved to be fast, effective and low-cost sample-preparation methods, which virtually eliminated the use of toxic solvents [9,11–13].

Another version of micro-LLE is membrane extraction and the techniques developed can be divided into two main categories [14]:

- *porous membrane* techniques, where the solutions on both sides of the membrane are in physical contact through the pores of a membrane; and,
- *non-porous membrane* techniques, where the membrane forms a separate phase (polymeric or liquid) between the donor and acceptor solutions.

One of the emerging techniques in non-porous membrane extraction was termed “supported liquid membrane” (SLM) that uses the pores of the polymeric membrane as a support for an organic solvent, thus creating a three-phase system, with the organic solvent layer sandwiched between the donor and acceptor aqueous solutions [15,16]. Where one of the phases (usually the acceptor) was also an organic solvent, a two-phase system was adapted and the resulting technique was (more commonly) termed “microporous membrane liquid-liquid extraction” (MMLLE) [14,17]. The use of membranes presents the advantages of high selectivity, clean extract formation and a high degree of enrichment. Trace analysis is thus facilitated by additionally reducing solvent consumption. The polymeric membrane units can be either flat or hollow fibres and most techniques involved some kind of on-line connection of the membrane extraction units to analytical instruments [14].

Despite the great advantages of automation, memory effects caused by the on-line configuration were reported and, for this reason, few examples of off-line devices have been developed [18–20]. One of these off-line devices, developed by Rasmussen and Pedersen-Bjergaard, was also termed LPME [20]. It utilised porous, hydrophobic, hollow fibres impregnated with an organic phase to create both SLM and MMLLE systems. The resulting method is also considered an evolution of the solvent microextraction methods, as it adds a protective feature to microdrop systems and/or aids the formation of immiscible liquid films [21,22]. This new extraction methodology proved to be an attractive alternative to other microextraction concepts because, apart from being simple, inexpensive, fast and virtually solvent-free, it resulted in increased sensitivity and, because of the disposable nature of the hollow fibre, it also eliminated the possibility of carry-over between analyses.

This review focuses for the first time on the developments in research on the off-line LPME method. It is divided into four sections:

1. the different modes and hollow-fibre configurations of LPME;
2. an updated discussion of the applications of LPME;
3. a summary of the most important parameters and practical considerations used for method optimisation and development of LPME protocols; and, finally,
4. a comparison of LPME with SPME and SDME, citing the advantages/disadvantages of each microextraction technique.

## 2. LPME sampling modes and hollow-fibre configurations

### 2.1. LPME sampling modes

There are two sampling modes that can be used with LPME: two phase; and, three phase.

In the two-phase LPME sampling mode, analyte  $i$  is extracted from an aqueous sample (donor phase) through a water-immiscible solvent immobilised in the pores of the hollow fibre into the same organic solvent (acceptor phase) present inside the hollow fibre (Fig. 1). The extraction process of the two-phase LPME for analyte  $i$  may be illustrated as follows:

$$i_d \leftrightarrow i_{org}$$

and is characterised by the distribution ratio  $K_{org/d}$ , which is defined as the ratio of the concentrations of analyte  $i$  in the organic and donor phase at equilibrium conditions.

Successful two-phase LPME requires large distribution ratios for target analytes. Such  $K_{org/d}$  values correspond to moderately or highly hydrophobic compounds containing acidic or basic groups, or neutral compounds of similar hydrophobicity [21].

It should be mentioned here that in two-phase LPME the final extract is an organic phase, compatible with analytical techniques, such as GC or HPLC [23].

In the three-phase LPME sampling mode, analyte  $i$  is extracted from an aqueous solution (donor phase) through the organic solvent immobilised in the pores of the hollow fibre (organic phase) into another aqueous phase (acceptor phase) present inside the lumen of the hollow fibre (Fig. 1). The organic phase in this case serves as a barrier between the acceptor and the donor aqueous solutions, preventing mixing of these two phases. The three-phase sampling mode is usually combined with a HPLC or a capillary electrophoresis (CE) system, as the acceptor phase is aqueous [23].

Overall, the three-phase LPME extraction process for analyte  $i$  may be illustrated as follows:

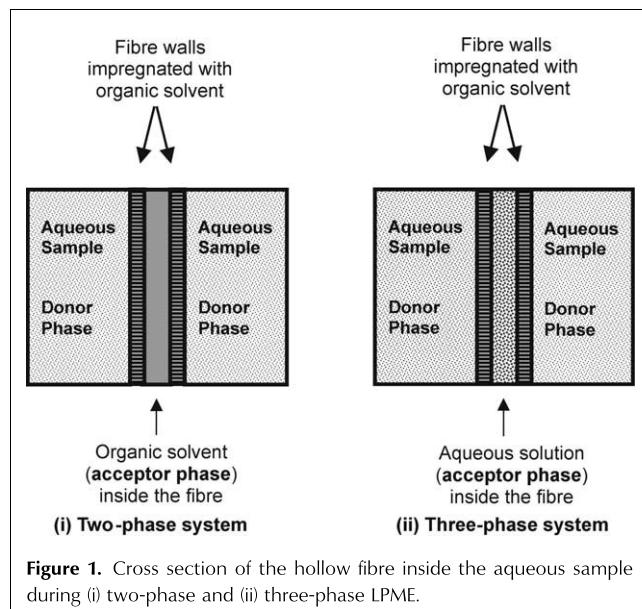
$$i_d \leftrightarrow i_{org} \leftrightarrow i_a$$

The three-phase LPME process is characterised by  $K_{org/d}$  and  $K_{a/org}$ , which are the distribution ratios at equilibrium between the organic phase and the donor phase, and the acceptor solution and the organic phase, respectively.

The overall distribution ratio  $K_{a/d}$  between the acceptor and the donor phase can be written as:

$$K_{a/d} = K_{org/d} \cdot K_{a/org}$$

Adjustment of the composition of the donor and acceptor phases is critical for successful three-phase LPME. Large  $K_{a/d}$  ( $\gg 1$ ) can be achieved when the analytes in



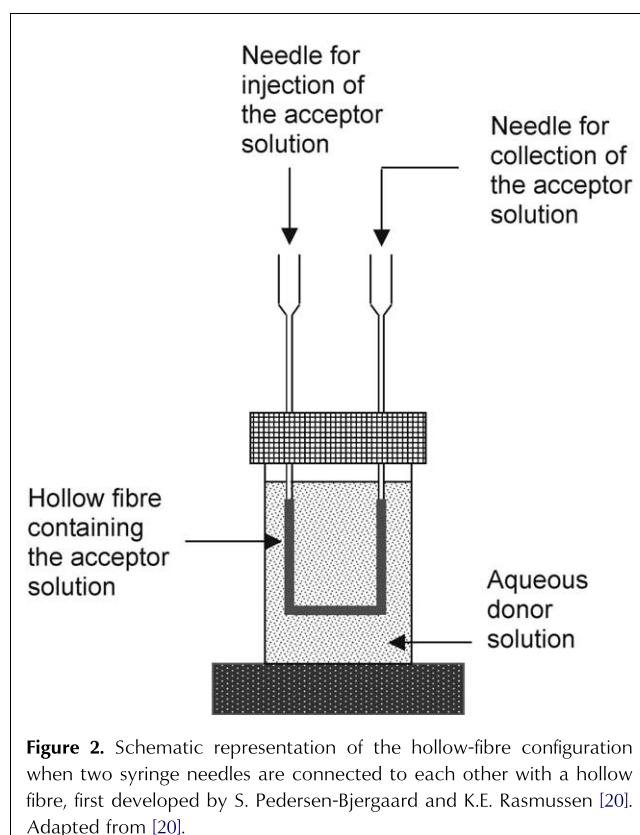
**Figure 1.** Cross section of the hollow fibre inside the aqueous sample during (i) two-phase and (ii) three-phase LPME.

the acceptor phase are converted by reactions, such as protonation [20] or complexation [24], to species that will have very small affinity for the organic phase. In this way, back extraction of analytes from the acceptor to the donor solution is prevented. Hence, the three-phase system will also extract acidic or basic compounds having a low  $K_{org/d}$ , as long as the  $K_{a/org}$  value is high, thus preserving the requirement for large overall distribution ratio [21]. This is very important, because the applicability range of LPME may be extended to ionisable analytes having a low  $K_{org/d}$  by simply changing from two-phase to three-phase LPME sampling mode [21].

## 2.2. Hollow-fibre configurations for the two-phase and three-phase LPME systems

There are essentially two different configurations (A and B, Fig. 2) of arranging the fibre during extraction with the two-phase or three-phase LPME sampling modes.

In configuration A, two conventional medical syringe needles are inserted through a septum and the two ends are connected with a piece of hollow fibre [20]. The length of the fibre usually varies from 4 cm to 8 cm. Longer fibre lengths (up to 27 cm) can be used and, in such cases, the hollow fibre is folded around a solid support [25]. When using either the two-phase or the three-phase technique, the hollow fibre is initially



**Figure 2.** Schematic representation of the hollow-fibre configuration when two syringe needles are connected to each other with a hollow fibre, first developed by S. Pedersen-Bjergaard and K.E. Rasmussen [20]. Adapted from [20].

immersed for several seconds in the organic solvent in order to immobilise the solvent in its pores. After impregnation, the hollow fibre is immersed in the donor solution. The acceptor solution is then injected in the lumen of the hollow fibre with the help of a microsyringe and, once extraction is completed, the acceptor solution is collected in microvials by applying a small head pressure on the inlet needle or withdrawn with the help of a microsyringe and submitted to analysis [23].

In configuration B, only one end of the hollow fibre is used for injection/collection of the acceptor solution and the other one is left suspended in the donor-sample solution. This is possible by using the tip of the needle of a microsyringe as a support for the fibre (Fig. 3). The microsyringe in this case serves to support the hollow fibre, introducing/collecting the acceptor solution, and as a sample-introduction device for subsequent analysis [26]. Another way of achieving this configuration is by using a septum-vial lid as a support for the hollow fibre. In this case, a metal tube is fitted in the centre of the septum to help introduce/lace the fibre in the septum [27]. Introduction/collection of the acceptor solution is effected with the help of a microsyringe. In general, when configuration B is used, the free end of the hollow fibre can be flame sealed [26,27]. Prior to

immersion in the donor solution, the fibre should be dipped in the organic solvent to impregnate it.

### 3. Applications of LPME

#### 3.1. Biomedical

A large number of applications using LPME involve the determination of several drugs in biological fluids (whole blood, plasma, urine and saliva). The micro-extraction method coupled to a GC, CE or HPLC analytical instrument has yielded detection limits in the low  $\mu\text{g/l}$  range, even when extracting small volumes of biological samples, because of the efficiency of analyte enrichment. The LPME-based methods were found to provide excellent sample clean up by excluding from the acceptor phase macromolecules and other compounds that could interfere with analysis. The two-phase LPME mode using configuration A [21,23,28] or B [27,35,36] was successfully used for these applications, but the majority of biomedical applications utilised the three-phase LPME mode (configuration A), as most drugs investigated had a low  $K_{\text{org/d}}$  value. Table 1 summarises all biomedical applications as well as their main experimental conditions.

#### 3.2. Environmental and food analysis

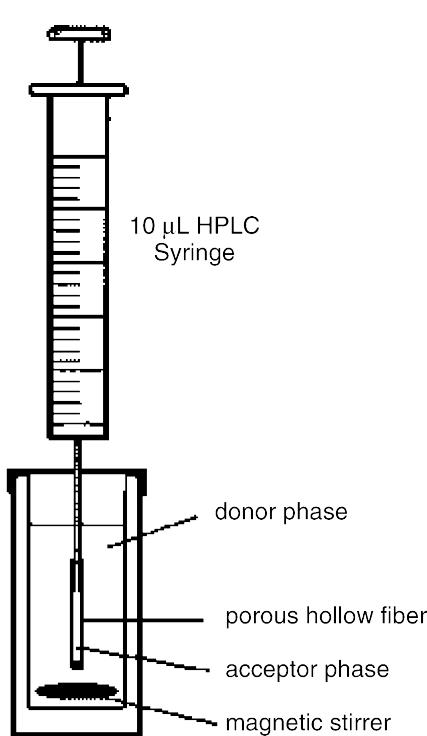
The application of LPME to the determination of pollutants in several matrices resulted in high enrichment factors of analytes in low concentration as well as selectivity because of the discriminatory nature of the hollow fibre preventing extraction of large molecules and/or suspended matter. All published reports in the environmental field so far have utilised configuration B for the hollow fibre. The two-phase [22,37–40] or three-phase [24,26] LPME modes may be used, depending on the chemical nature of the target analytes. In all reports, the developed protocols proved to be fast, accurate, sensitive and low-cost sample-preparation techniques that provided good enrichment factors and effective sample clean up even when dealing with complex matrices [22,40]. All published environmental applications as well as their main experimental conditions are also included in Table 1.

The applications of LPME are rapidly expanding. Recently, the technique was also applied in the field of food analysis [41] and more specifically for the detection of phenoxy herbicides in bovine milk (Table 1).

### 4. Method optimisation: parameters and practical considerations affecting LPME

#### 4.1. Hollow fibre

The hollow fibres employed in LPME should be hydrophobic as well as compatible with the organic solvent



**Figure 3.** Schematic representation of configuration B where a microsyringe is used for supporting the hollow fibre, introducing/collecting the acceptor solution, and serves as a sample introduction device for subsequent analysis. (Reprinted, with permission, from [26]. © 2001 Elsevier Science).

Application (Target analytes)	Sampling mode	Configuration <sup>a</sup>	Donor-solution composition	Organic solvent	Acceptor-solution composition	Analytical method	Limits of detection <sup>b</sup>	Refs <sup>c</sup>
<b>Drug analysis</b>								
Diazepam, N-desmethyl diazepam	Two-phase	A	3.5 ml urine pH = 7.5	<i>n</i> -octanol	3 µl butyl acetate: <i>n</i> -octanol (1:1 v:v)	GC/NPD	0.020–0.115 nmol/ml	[28]
Diazepam, Prazepam,	Two-phase	A	1.5 ml plasma pH = 5.5	<i>n</i> -octanol	15 µl <i>n</i> -octanol	GC/NPD	2 ng/ml (S/N = 2)	[23]
Methamphetamine,	Three-phase	A	2.5 ml plasma (made alkaline)	<i>n</i> -octanol	25 µl aqueous (acidic)		3 ng/ml (S/N = 2)	
Naproxen,			4 ml urine (made acidic)		25 µl aqueous (basic)	CE/UV	1 ng/ml (S/N = 2)	
Citalopram, N-desmethyl citalopram			1.5 ml plasma (made alkaline)	<i>n</i> -octanol	25 µl aqueous (acidic)	HPLC/RF	0.7 ng/ml (S/N = 2)	
<b>Drug analysis</b>								
Promethazine, Methadone, Haloperidol	Two-phase	A	1 ml urine or plasma (made alkaline)	Dihexyl ether	25 µl dihexyl ether	GC/FID	Not reported	[21]
Methamphetamine	Three-phase	A	2.5 ml urine or plasma (made alkaline)	<i>n</i> -octanol	25 µl aqueous (acidic)	CE/UV	5 ng/ml	[20]
<b>Drug analysis</b>								
Methamphetamine, Citalopram hydrobromide	Three-phase	A	2.5 ml urine, plasma or whole blood (made alkaline)	Hexyl ether	25 µl aqueous (acidic)	CE/UV	2 ng/ml (citalopram)	[25]

(continued on next page)

<b>Table 1</b> (continued)								
Application (Target analytes)	Sampling mode	Configuration <sup>a</sup>	Donor-solution composition	Organic solvent	Acceptor-solution composition	Analytical method	Limits of detection <sup>b</sup>	Refs <sup>c</sup>
<b>Drug analysis</b> Ibuprofen, Naproxen, Ketoprofen,	Three-phase	A	2.5 ml water samples (made acidic)  2.5 ml urine (made acidic)	Dihexyl ether	25 µl aqueous (basic)  25 µl aqueous (acidic) 25% MeOH	CE/UV	1 ng/ml (naproxen)	[29]
<b>Drug analysis</b> Citalopram hydrobromide, N-desmethylcitalopram hydrochloride	Three-phase	A	1 ml plasma (made alkaline)	Hexyl ether	25 µl aqueous (acidic)	CE/UV	5–5.5 ng/ml	[30]
<b>Drug analysis</b> Amphetamines and analogues	Three-phase	A	0.5 ml urine/whole blood (made alkaline)	Dihexyl ether	25 µl aqueous (acidic)	FIA/MS/MS CE/UV	Urine 2–100 ng/ml Blood 0.4–14 ng/ml	[31]
<b>Drug analysis</b> Methadone, Amphetamine, Haloperidol	Three-phase	A	0.25–1 ml plasma (made alkaline) 5–50% MeOH	Dihexyl ether	25 µl aqueous (acidic) HCl	CE/UV	Not reported	[32]
<b>Drug analysis</b> Basic drugs	Three-phase	A	4 ml water (made alkaline)	Dihexyl ether	25 µl aqueous (acidic)	CE/UV	Not reported	[33]
<b>Drug analysis</b> <i>R</i> - and <i>S</i> -Mianserin	Three-phase	A	0.5 plasma (made alkaline)	Dihexyl ether	25 µl aqueous (acidic)	CE/UV	4 ng/ml	[34]
<b>Drug analysis</b> 11-nor- $\Delta^9$ -tetrahydrocannabinol-9- carboxylic acid	Two-phase	B	8 ml urine (made alkaline)	Octane	20 µl derivatising reagent: octane	GC/PDHID	1 ng/ml	[27]
<b>Drug analysis</b> Cocaine and its metabolites	Two-phase	B	8 ml urine (made alkaline)	Chloroform	10 µl chloroform	GC/PDHID	11–48 ng/ml	[35]
<b>Drug analysis</b> Cocaine and its metabolites	Two-phase	B	2 ml saliva (made alkaline)	Chloroform	10 µl chloroform	GC/PDHID	6–28 ng/ml	[36]

(continued on next page)

<b>Table 1</b> (continued)								
Application (Target analytes)	Sampling mode	Configuration <sup>a</sup>	Donor-solution composition	Organic solvent	Acceptor-solution composition	Analytical method	Limits of detection <sup>b</sup>	Refs <sup>c</sup>
<b>Drug analysis</b>								
Amino alcohols	Three-phase	B	3.5 ml water or urine (made alkaline)	<i>n</i> -octanol	10 µl aqueous (acidic)	CE/UV	0.08–0.5 µg/l	[42]
<b>Environmental</b>								
Triazine herbicides	Two-phase	B	3 ml water or slurry 10% NaCl	Toluene	3 µl toluene	GC/MS	0.04–0.18 ng/ml (MS-SIM)	[22]
<b>Environmental</b>								
Organochlorine pesticides	Two-phase	B	5 ml seawater pH=2 3% NaCl	Toluene	5 µl toluene	GC/MS	0.013–0.059 ng/ml (MS-SIM)	[37]
<b>Environmental</b>								
Fluoranthene, Pyrene	Two-phase	B	3 ml water	<i>n</i> -octanol	3 µl <i>n</i> -octanol	GC/MS	Not reported	[38]
<b>Environmental</b>								
Phthalates	Two-phase	B	5 ml water	Toluene	3 µl toluene	GC/MS	0.005–0.1 ng/ml (MS-SIM)	[39]
<b>Environmental</b>								
Polycyclic Aromatic Hydrocarbons (soil)	Two-phase	B	1 g soil, 7 ml acetone, 15 ml water		8 µl octane	GC/FID	0.13–0.22 mg/kg	[40]
<b>Environmental</b>								
Aromatic amines	Three-phase	B	4 ml water (made alkaline) 20% NaCl 2% acetone	Dihexyl ether	4 µl aqueous (acidic) 18-crown-6 ether	HPLC/UV	0.05–0.1 ng/ml	[24]
<b>Environmental</b>								
Nitrophenols	Three-phase	B	2.5 ml water or seawater (made alkaline)	<i>n</i> -octanol	2 µl aqueous (acid)	cLC <sup>d</sup> /UV	0.5–1.0 ng/ml	[26]
<b>Food analysis</b>								
Phenoxy herbicides	Three-phase	B	8 ml bovine milk (made acidic)	<i>n</i> -octanol	7 µl aqueous (basic)	HPLC/UV	0.5 ng/ml	[41]

<sup>a</sup>Configuration of the hollow fibre.<sup>b</sup>Limits of detection for a signal/noise ratio of 3 (S/N), unless otherwise stated.<sup>c</sup>Reference number.<sup>d</sup>Conjoint liquid chromatography.

being used. Almost all published reports use polypropylene capillary membranes. The most common type of such fibres has an inner diameter of the order of 600 µm, compatible with the µl volumes of the acceptor solution required for microextraction. Its wall thickness (200 µm) provides excellent mechanical stability and simplifies the preparation of the extraction units [23]. Finally, the nominal and maximum pore sizes (0.2 µm and 0.64 µm, respectively) of these capillary membranes ensure efficient microfiltration, allowing penetration of only small molecules (target analytes) through the pores of the hollow fibre.

#### 4.2. Organic solvent

A crucial step in method optimisation for both the two-phase and the three-phase LPME modes is selection of the most suitable organic solvent to be employed. In general, several water-immiscible solvents differing in polarity and water solubility should be tested. It is also possible to use a mixture of organic solvents [28].

The final choice of the organic solvent should be based on several considerations. First, it should have a low solubility in water so as to prevent dissolution into the aqueous phase, and a low volatility, which will restrict solvent evaporation during extraction [20]. Where the two-phase LPME mode is used, the organic solvent should provide high solubility for target analytes [24] and, when coupled to a GC, it should also have an excellent GC behaviour [22]. As mentioned previously, in the three-phase LPME mode, the selected solvent should ensure high values for  $K_{org/d}$  and, more importantly, for  $K_{a/org}$ . Finally, the organic solvent should have a polarity matching that of the polypropylene fibre, so that it can be easily immobilised within the pores of the hollow fibre [20]. Solvent impregnation is of major importance in LPME, since extraction occurs on the surface of the immobilised solvent [39].

#### 4.3. Agitation of the sample

Agitation of the sample is routinely applied to accelerate the extraction kinetics. Increasing the agitation rate of the donor solution enhances extraction, as the diffusion of analytes through the interfacial layer of the hollow fibre is facilitated, and improves the repeatability of the extraction method [41].

In LPME, the acceptor solution is confined within the fibre, and it can tolerate very high agitation speeds. In both the two-phase and three-phase LPME modes, sample agitation, by using either vibration or magnetic stirring, dramatically increased extraction. Vibration of the sample had the advantage that it eliminated the possibility of sample contamination through the use of Teflon-coated magnetic stirrers [29]. Where magnetic stirring was used, application of the maximum stirring speed was found to promote the formation of air bubbles

that tended to adhere to the surface of the hollow fibre, thus accelerating solvent evaporation and introducing imprecision in the measurements [22].

#### 4.4. Salt addition

Depending on the nature of the target analytes, addition of salt to the sample solution can decrease their solubility and therefore enhance extraction because of the salting-out effect. In both the two-phase and the three-phase LPME methods, the effect of adding salt to the donor solution prior to extraction has been investigated. The results showed that, depending on the target analytes, an increase in the ionic strength of the aqueous solution may have various effects upon extraction: it may enhance [22,24,37], not influence [26,28,41], or even limit [22,39] extraction.

#### 4.5. Volumes of donor and acceptor solutions

The volumes of the donor and acceptor phases should be selected taking into account several considerations. In general, in both the two-phase and the three-phase LPME systems, the sensitivity of the method can be increased by decreasing the volume ratio of the acceptor-to-donor phase [12,22]. However, the volume of the acceptor solution used for extraction may also be adjusted, depending on the analytical technique coupled to LPME [23,27]. For example, in contrast to GC and CE, sample volumes in the range 10–25 µl are easily injectable into a HPLC instrument, so the whole acceptor phase may be analysed, potentially providing lower detection limits [23].

#### 4.6. Adjustment of pH

Adjustment of the pH can enhance extraction, as dissociation equilibria are affected together with the solubility of the acidic/basic target analytes. In two-phase or three-phase LPME, there are many reports where pH changes in the donor aqueous solution resulted in higher analyte pre-concentration.

As mentioned previously, in three-phase LPME, the adjustment of the composition of the donor and the acceptor phases is critical, since it results in large distribution ratios and ensures high enrichment factors and recoveries for target analytes [30]. This is usually done by adjusting the pH of the aqueous and donor solutions. For example, when investigating acidic analytes, the pH of the donor aqueous solution is adjusted in the acidic range so as to deionise the target compounds, reduce their solubility within the sample solution and ensure efficient transfer into the organic phase. Subsequently, in order to prevent trapping into the organic phase and ensure efficient extraction of analytes into the acceptor aqueous solution, the pH of the acceptor phase is adjusted in the basic range. This results in ionisation of target analytes and ensures higher solubility of target compounds into the acceptor

phase than into the organic one [23,26,34,35,41]. Analogous observations can be made for basic analytes [20,24,33].

#### 4.7. Extraction time

Mass-transfer is a time-dependent process and its rate is reduced the closer the system reaches equilibrium conditions. Whether extraction is exhaustive or works as a pre-concentration technique, equilibrium is attained only after exposing the acceptor solution to the sample for a "long" period of time. For method optimisation, it is therefore important to establish the extraction-time profiles of target compounds so as to configure the time after which equilibrium is attained in practice. Although longer exposure times of the acceptor solution generally result in increased extraction efficiency, it is not always practical to apply extended extraction times. Sampling times shorter than the total chromatographic time are often chosen so as to ensure high sample throughput [22]. However, it should be noted that, when working in the rising portion of the extraction-time profiles, consistent and precise timing is essential for good precision [43]. In studies where extended sampling times were imposed, simultaneous extraction of a large number of samples ensured high sample throughput [26,35].

### 5. Comparison of LPME with SPME and SDME

#### 5.1. Comparison of LPME with SPME

As mentioned in the introduction, SPME is a simple, solventless method that can be automated easily. It has been successfully applied to the determination of a wide variety of volatile and semi-volatile analytes using either immersion or headspace SPME sampling [3]. There are several types of SPME fibres, and selectivity of the method towards classes of compounds depends on the polarity and the film thickness of the coating phase. SPME fibres are rather expensive and have a limited lifetime, as they tend to degrade with increased usage. In addition, as the length and the coating character of each SPME fibre may differ from lot to lot, variations in analyte enrichment may be observed from fibre to fibre [5]. Before using a fibre for the first time, a thermal conditioning step is required. Even when this step is carefully done, partial loss of the coating may occur resulting into extra peaks during the chromatographic analysis, thus affecting the performance of the method [5]. In addition, sample carry-over between runs has often been reported with SPME and, unless an extra-cleaning step is introduced in the sampling protocol, the results are invalid [39].

A major advantage of LPME over SPME is that the range of compounds amenable to this technique can be extended by simply changing from the two-phase to the

three-phase LPME mode and by adjusting the composition of the different phases [21]. In addition, the low cost per unit allows the use of each fibre for only one extraction. The disposable nature of the hollow fibre totally eliminates the possibility of sample carry-over and ensures high reproducibility, as the chemistry of each extraction unit is not affected by its previous usage [29]. However, as the hollow-fibre segments are cut manually, variations in length are very likely. In addition, variations in wall thickness are possible and such fluctuations may alter analyte enrichment, especially when the two-phase approach is used [21].

Another advantage of LPME over SPME is that the small pore size ensures microfiltration, thus yielding very clean extracts [30]. On the contrary, when the SPME approach is used in complex matrices, a sample-pre-treatment step (such as filtration) or a modification of the sampling protocol (such as using membrane-protected SPME) is often required [22]. Damage to the SPME fibre, leading to imprecision in the measurements, has also been reported when high salt concentrations and/or pH adjustment are applied to the sample solution [3,5]. This is not the case for LPME, where the ionic strength of the sample solution and high or low pH values do not influence the repeatability of the method or the condition of the hollow fibre. However, in some cases, it appears that, in two-phase LPME, the presence of salt influences the extraction kinetics and does not yield a significant increase in the response of the analytical instrument seen with SPME [22].

#### 5.2. Comparison of LPME with SDME

The main sampling mode of SDME, (microdrop suspended from the tip of a microsyringe) is comparable to the two-phase LPME technique.

Although SDME is a simple, low-cost, fast extraction technique, applied even for headspace extraction [44,45], it requires careful and elaborate manual operations, given that problems of drop dislodgment/stability have often been reported [9]. When dealing with complex matrices, an extra filtration step of the sample solution is imposed. More importantly however, the sensitivity and the precision of the SDME methods developed are rather poor. This is because prolonged extraction times and faster stirring rates are not recommended, since they typically result in drop dissolution and/or dislodgment [9].

In LPME, the organic (acceptor) phase is protected by the fibre and it appears that the presence of the hollow fibre decelerates the process of organic solvent dissolution into the bulk solution [22,39]. Another factor contributing to the improved sensitivity of LPME is that the surface area for the rod-like configuration of the two-phase LPME system is larger than the spherical one adopted by the drop-based SDME method [22]. By increasing the contact area between the sample donor

solution and the organic acceptor phase, the rate of analyte extraction is increased.

## 6. Conclusions

LPME is a fast, effective, inexpensive, virtually solvent-free method, which provides a high degree of selectivity and enrichment. The disposable nature of the hollow fibre totally eliminates the possibility of sample carry-over and ensures high reproducibility. In addition, the small pore size prevents large molecules and particles present in the donor solution from entering the acceptor phase, thus yielding very clean extracts. Overall, the novel LPME methodology represents an emerging field of study for a wide variety of applications.

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# A Downhole Passive Sampling System To Avoid Bias and Error from Groundwater Sample Handling

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A new downhole groundwater sampler reduces bias and error due to sample handling and exposure while introducing minimal disturbance to natural flow conditions in the formation and well. This “*In Situ Sealed*”, “ISS”, or “Snap” sampling device includes removable/lab-ready sample bottles, a sampler device to hold double end-opening sample bottles in an open position, and a line for lowering the sampler system and triggering closure of the bottles downhole. Before deployment, each bottle is set open at both ends to allow flow-through during installation and equilibration downhole. Bottles are triggered to close downhole without well purging; the method is therefore “passive” or “nonpurge”. The sample is retrieved in a sealed condition and remains unexposed until analysis. Data from six field studies comparing ISS sampling with traditional methods indicate ISS samples typically yield higher volatile organic compound (VOC) concentrations; in one case, significant chemical-specific differentials between sampling methods were discernible. For arsenic, filtered and unfiltered purge results were negatively and positively biased, respectively, compared to ISS results. Inorganic constituents showed parity with traditional methods. Overall, the ISS is versatile, avoids low VOC recovery bias, and enhances reproducibility while avoiding sampling complexity and purge water disposal.

## Introduction

Two general approaches are used to collect water samples from wells or open boreholes: (i) *uphole sampling*, with water pumped from depth and collected at the surface and (ii) *downhole sampling*, with a sampling vessel lowered down the well and the water sample collected at depth. In the 1970s, Tate (1) and Frost et al. (2) reported some of the first downhole groundwater samplers, which were developed for investigation of inorganic groundwater chemistry and employed a sampling vessel open at both ends to allow water to flow through during descent in the well. At the appropriate depth, the vessel ends could be closed by messenger or remote control. In the 1980s, the need arose to detect volatile organic contaminants (VOCs; e.g., chlorinated solvents) and other constituents at very low levels (i.e.,  $\mu\text{g/L}$ ), and it was recognized that uphole sampling could cause sample chemistry to be unrepresentative of *in situ* chemistry (3, 4). Downhole samplers were further developed to minimize

escape of VOCs and dissolved gases (e.g.,  $\text{CH}_4$ ,  $\text{CO}_2$ ). Gillham (5) developed a technique for downhole sampling using modified low-cost polyethylene syringes. The syringe was lowered to sampling depth, and then the plunger (and sample) withdrawn by vacuum applied via a hand pump at the surface. The syringe was then raised to surface and immediately capped. A new syringe was used for every sample, thus avoiding the need for sampler decontamination. This device has been used for studies of redox parameters, metals, and radon (5). Other downhole samplers included small cylindrical cartridges filled with sorbent material (6–8). After lowering to sampling depth, water was drawn through the sorbent material for capture of the contaminant mass; the cartridges were then removed and transferred to the laboratory for analysis. Similar to the syringe sampler, this method avoided sample exposure between sampling and analysis but required a thermal desorption step in the analytical procedure that is not standard in commercial laboratories. Passive downhole dissolved gas sampling approaches have also included syringes as a means of collection (9, 10).

Regulatory guidance in the United States in the 1980s concurrently pushed the groundwater industry toward vigorous well purging prior to sampling (e.g., removal of 3–5 well volumes) (11). This caused uphole collection to become standard practice, based on the premise that purging removes “stagnant” water from the well prior to sampling (11). However, Robin and Gillham (12) and Powell and Puls (13), among others, have argued (and shown) aquifer water in the screened interval of wells is not stagnant. These investigators illustrated water flows naturally through the screen zone of the well under background gradients, given hydraulic communication between the well and aquifer. The screened interval itself functions as a relatively high permeability zone, as indicated by borehole dilution tests (14). Low flow purging and sampling techniques in many cases also rely on flow-through in wells because the method commonly removes only a portion of the water within the screen interval (15, 16). Passive sampling also generally relies on this phenomenon (17, 18). Overall, well purging has three negative aspects: it generates contaminated wastewater needing treatment or disposal, it creates hydrologic disturbance in the aquifer prior to sampling, and it requires labor. The perception that monitoring wells must be purged prior to sampling is losing its appeal, as the “nonpurge” method (i.e., passive sampling) regularly provides similar data sets (19–23).

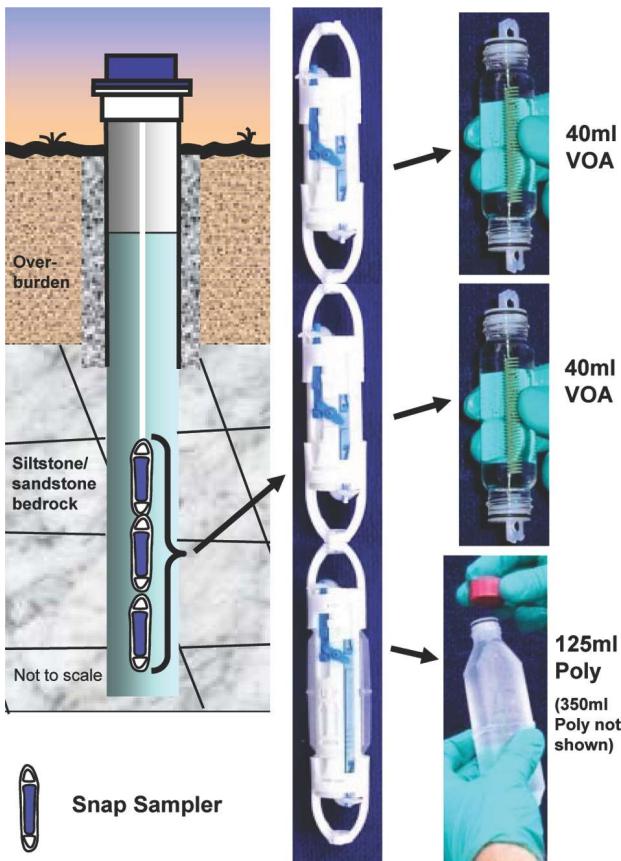
Development of passive samplers has more recently included the low-cost polyethylene diffusion bag (PDB) sampler. This flexible bag is filled with analyte-free water and positioned at the sampling depth to equilibrate with fresh formation water in the well screen (24, 25) under ambient/natural aquifer flow conditions. Samples are collected by retrieving the PDB from the well and transferring the water into a container. This method thus requires sample transfer and is limited to hydrophobic VOCs (e.g., benzene, tetrachloroethene) that readily diffuse across the polyethylene membrane.

Passive sampling approaches have since been further developed to increase the analytical capacity of this approach. This paper describes features and results of several field investigations of an “*In Situ Sealed*” (ISS) downhole sampler, or “Snap Sampler,” with direct comparisons with several standard and accepted alternative sampling approaches for various analyte types and hydrogeologic conditions. The ISS device seals samples downhole in the containers used to transport the sample to the laboratory. Thus, the sampler is

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**FIGURE 1.** “*In situ sealed*” (ISS) samplers deployed downhole, secured and locked at well head; inset shows loaded ISS/Snap samplers with caps set to open position; full bottles after collection and removal from samplers.

designed to minimize the alteration of groundwater samples from their *in situ* condition and allows the samples to arrive at the laboratory for analysis without exposure to external influences including: atmospheric air, tubing, or secondary containers.

## Methods

**Description and Operation of the ISS/Snap Sampler.** The ISS sampler holds specialized double end-opening sample bottles in series to allow collection of multiple sample bottles for laboratory analyses (Figure 1). Samplers can be stacked in different combinations of bottle size and separated vertically to collect samples from multiple depths if desired. The ISS sampler bottle is built with an internal Teflon-coated stainless steel spring retaining two Teflon end-caps (Figure S1). A release pin system holds the bottle caps open during a user-defined downhole equilibration period. The sampler is lowered downhole with a triggering line (polyethylene tube with an internal Teflon-coated stainless steel wireline, which is hung from the well head) that supports the sampler at a specific position and allows the user to close the sample bottles without a messenger system or movement of the sampler. The trigger system retracts the release pins on the sampler downhole, freeing the Teflon caps to close the bottle, thus sealing the sample *in situ*. Pneumatic and electric triggering systems are available for applications deeper than ~15 m.

Preparation for deployment and sampling consists of inserting sample bottles in the samplers, setting the bottle caps open onto the release pins, attaching the trigger line, and lowering downhole (Figure S1A-E). The samplers are left in the well in an open position to allow restabilization of undisturbed ambient flow in the well. This period can be

short if sampling objectives allow it (hours or days) or for the entire period between scheduled sampling events (3–6 months or more).

Deployment interval is largely a function of user logistics, but there are some minimum deployment limitations for certain VOCs. Parker and Mulherin (23) identify a 24 h “rule of thumb” minimum deployment period when sampling for most analytes, with longer periods (72 h) for some highly sorptive organics (e.g., m-xylene). Often times, a data quality objective requiring the well to physically restabilize after insertion of the device is longer than the time required for chemical equilibration. In most cases samplers are deployed for the entire interval between sampling events, avoiding concern about either problem. However, long deployment periods and certain well conditions may impact sampler function. Where ambient silting or substantial biofouling affect the physical function of the device, long deployment intervals may not be appropriate.

Once triggered to close, the sealed samples are retrieved. The bottles are designed to seal with no headspace, and in many cases can be sent to the laboratory without exposure to air. Surface preparation of the sample bottles consists of clipping the release pin tabs on the vial caps and securing a septa cap on each end of the bottle. If acid preservation is required, a cavity on each vial cap is sized to accept 0.5 mL of preservative (Figure S1F–H), which can be added without exposing the sample to air. A septa screw cap is then applied, similar to standard volatile organic analysis (VOA) vial preparation. After sample collection, bottles remain closed at all times in either preserved or unpreserved preparation and can be analyzed in standard laboratory autosampler equipment with no special considerations.

Limitations of the device primarily include sample volume and hydrogeologic or well conditions where communication between the well and aquifer are limited. Otherwise, the ISS sampler can be used for testing any analyte. Maximum sample volume is a limitation of the ISS sampler tested here and depends in part on well diameter. Fifty millimeter (2-in.) wells are a minimum requirement. In 50 mm wells, the maximum sample volume is approximately 750 mL. In larger diameter wells (100 mm or larger), potential sample volume increases to about 2 L. Long analytes lists requiring large sample volume may be problematic for this device, but as laboratory methods improve the volume limitation will diminish in importance. As described above, hydraulic exchange in the screen zone should generally be expected. However, if a well is very poorly yielding due to the geology encountered, or well condition, chemical exchange to the sampling device may be limited. In many cases, a pumped sample is also compromised by these conditions, so caution should be employed using either sampling approach where poor communication between the aquifer and well is present.

Sampling with this method is relatively rapid compared to purge sampling and is accomplished with little equipment. In dedicated applications, items brought to field site are minimal and include replacement bottles, a water level meter, a cooler, and documentation forms. No wastewater is generated from purging or extra sample waste; all water collected is submitted with the bottles to the laboratory. The method avoids the open air transfer step. Time to trigger, retrieve, and redeploy the ISS sampler is typically 10–20 min per well (Figure S2).

**Field Investigations.** Six field-based studies were conducted to compare the ISS sampler to traditional approaches, with data sets representing a wide range of chemical classes and hydrogeologic conditions (Table 1; detailed site and sampling information provided in the Supporting Information).

**TABLE 1. Site Information for Field Deployments**

site location	geology	sampling depth (m)	depth to water (m)	number of wells	sample intervals	analytes	compared to	notes
Chatsworth	fractured sandstone	24 to 52	6 to 35	3	1	VOC, gases	low flow	electric trigger 1 week deployment
Guelph	fractured dolostone	3 to 8	2 to 5	5	1–2	VOC	low flow, PDB	pull trigger 2 week deployment
Morgan Hill	silt/sand overburden	5 to 21	3 to 10	14	1–2	VOC, perchlorate	volume purge	pull trigger 2 week deployment
Hillside	silt/sand overburden	10 to 18	9 to 12	17	1–3	arsenic	volume purge	pull trigger 2 week deployment
McClellan	silt/sand/gravel overburden	33 to 52	29 to 33	10	3	VOC, anions 1,4-dioxane	low flow, vol. purge	multiple comparisons 1–3 week deployment
Los Angeles	silt/sand/gravel overburden	12 to 18	9 to 11	3	1	VOC	vol. purge	repeated long-term quarterly deployment

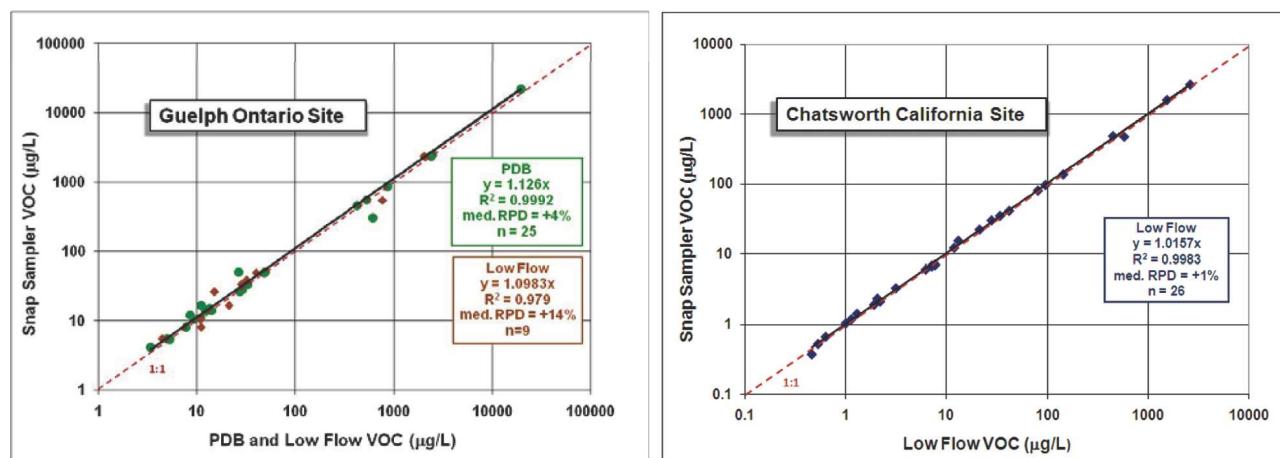
## Results and Discussion

Each field site yielded results illustrating one or more data-quality advantage of the sealed-*in situ* sampling approach. Overall, results from the ISS method and purge or alternate passive methods were very highly correlated. For the Guelph and Morgan Hill sites, PDB and purge sample VOC concentration data were, on average, slightly lower than from the ISS sampler ( $y > 1$ , positive relative percent difference [RPD]; Figures 2 and 3). At Chatsworth and Morgan Hill, y-slope and RPD are very close to neutral for VOCs and perchlorate, respectively. Across all sites, VOC concentrations were usually higher using the *in situ* approach (e.g., Guelph, Morgan Hill, McClellan sites); for nonvolatile constituents, concentration equivalence between the purge samples and ISS samples was very good (Hillside, Morgan Hill, McClellan). Figure S4 includes additional inorganic data.

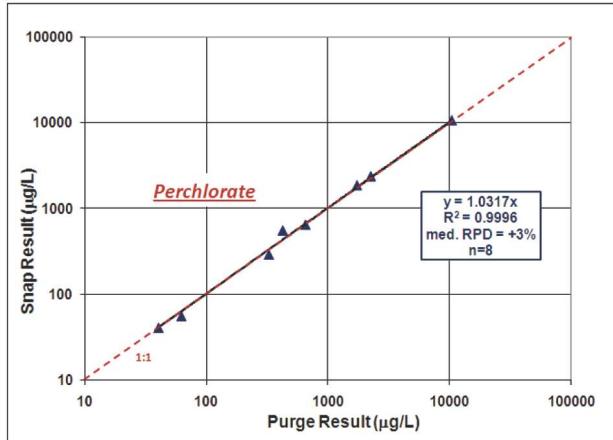
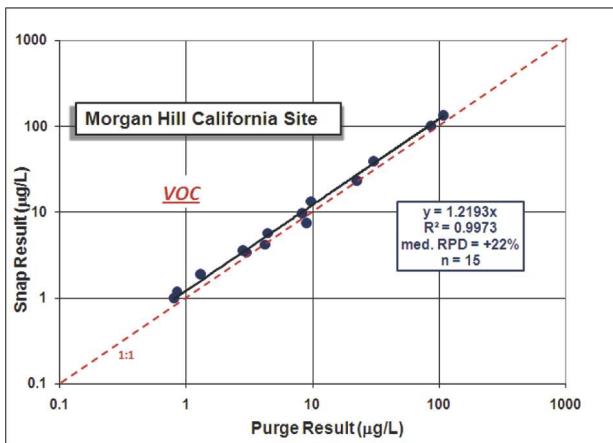
The passive approaches collect either a time-weighted sample in the case of the PDB or an instantaneous sample in the case of the ISS sampler. As such, the passive samples collect water at (or very near) the deployment position in the well at the time of collection. Early time purge samples (i.e., low flow/low volume purging) collect water from nearly the same position in the well when the pump is placed at the same position. Longer purge times and larger purge volumes interrogate larger portions of the well and eventually the formation adjacent to the well and beyond (Figure S3).

However, water delivered to the well under ambient flow-through conditions may be effectively the same in many cases, yielding similar results for this sampling approach (26). The comparisons highlight similarities and differences among methods and analyte type. For constituents not substantially affected by air or polymer exposure (e.g., perchlorate), or collected using low-bias methods (e.g., predeployed bladder pump using Teflon bladder and tubing), results are remarkably similar. In other cases, the purge method (e.g., peristaltic pump, bailer), and/or collection method (bailer, pouring), and/or exposure to unequilibrated plastics (tubing, bailer) contributed to the low bias for VOCs in the more traditional methods.

For the McClellan study site in Sacramento, CA, data previously reported by Parsons (22) were reanalyzed (27) to find additional clues about VOC recovery apparent in the data. The McClellan data are extensive and allow comparisons among a variety of sampling methods. The ISS/Snap sampler and low flow method consistently yielded the highest and lowest VOC concentrations, respectively (22, 27). The low bias of the low flow method compared to other methods at this site was attributed to multiple influences: an electric submersible pump was employed using new polyethylene tubing in each well; the tubing was not Teflon lined and was deployed immediately in advance of purging; and depth to sampling positions were often well over 100 ft (30 m) so



**FIGURE 2.** ISS/Snap sampler, diffusion sampler (PDB), and low flow comparison of VOCs at Guelph site (left panel); ISS/Snap sampler and low flow purge comparison at Santa Susanna Field Laboratory (SSFL) site (right panel). Slight positive offset of trendline ( $y > 1$ ) indicates y-axis comparator is slightly higher on average. Very good correlation coefficients relate tight correspondence among the methods. SSFL shows closer correspondence ( $y = 1.02$ ) with the use of a predeployed bladder pump rather than a peristaltic pump. Specific VOCs are listed in the Supporting Information.

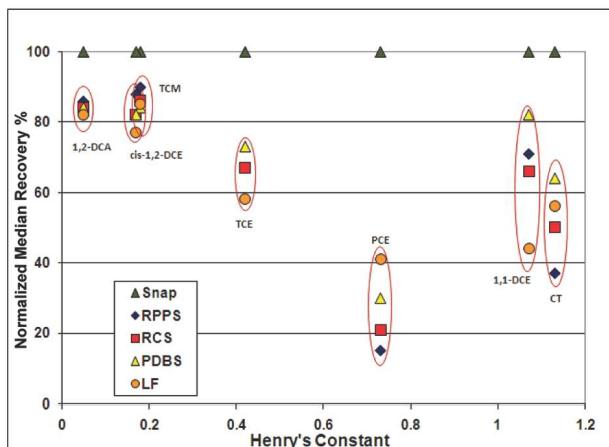
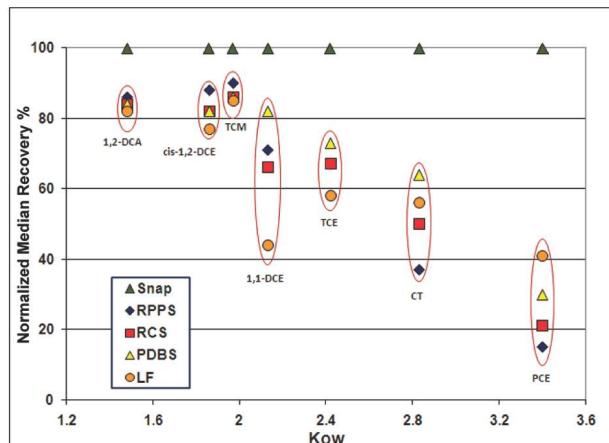


**FIGURE 3.** VOC (top panel) and perchlorate (bottom panel) comparative data plots from Morgan Hill site. These illustrate method recovery may differ more for volatile/sorptive chemicals than for nonvolatile/nonsorptive constituents from the same well(s). Volume purge based method used for “purge” samples. Specific VOCs are listed in the Supporting Information.

extensive exposure to the tubing occurred. Parker and Ranney (28) showed exposure to polymer tubing, especially at low flow rates, tends to promote sorptive VOC loss. Handling of the low flow and other passive samples in the study added to the low relative recovery as the ISS sampler experienced neither exposure to tubing nor any bottle-filling transfer steps.

Examination of the chemical-specific VOC recovery differentials among methods used at the McClellan site (22) supports the proposition that bias is due to exposure to air and exposure to sorptive polymer materials. In all comparisons, the Snap Sampler yielded the highest VOC recovery. Based on that observation, the ISS sampler results were treated as a baseline comparator (assumed 100% recovery), and all comparisons were normalized to the ISS.

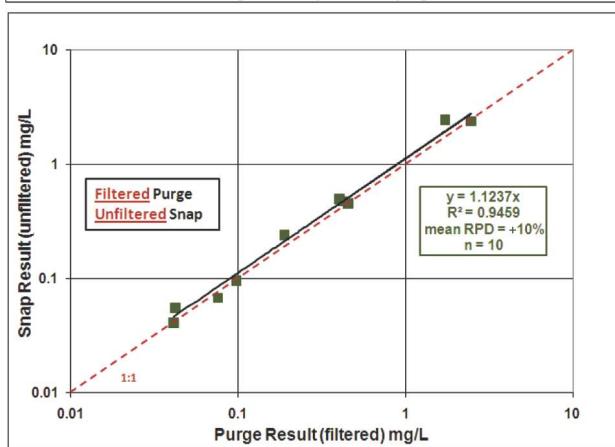
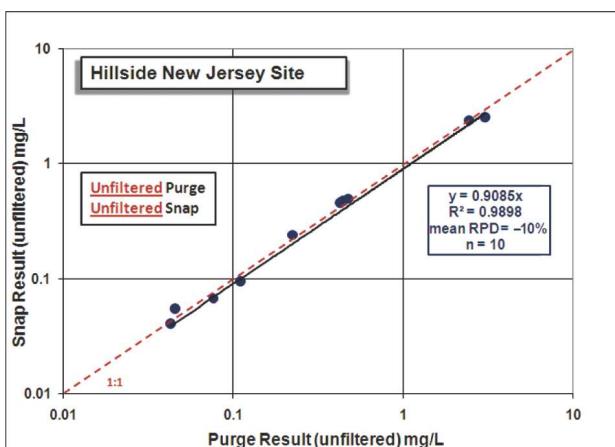
The plot of percent recovery vs octanol–water partitioning coefficient ( $K_{ow}$ ) of VOC components (Figure 4, top panel) indicates poorer VOC recovery percent is associated with higher  $K_{ow}$ , suggesting sorption contributed to the difference among methods. Similarly, a plot of percent recovery vs Henry's vapor partitioning coefficient suggests volatilization contributed to the difference among methods as poorer percent recovery was associated with a higher Henry's constant (Figure 4, bottom panel). To the authors' knowledge, this is the only data set to date that allows such chemical-specific analysis of field data. Differentials of this magnitude are rare, with these by far the largest identified. Chemical-specific associations could be developed due to the high differential recoveries and large size of the overall database. Differences are statistically significant at the 90% confidence level in 21 of the 28 comparisons; 11 of those were highly



**FIGURE 4.** Sorption and volatilization among passive and active sampling methods at the McClellan site. Data are from Parsons (19). This study showed relatively large VOC recovery differences among chemicals. The ISS/Snap sampler always had the highest recovery. Results were normalized using the ISS/Snap sampler as the baseline (100% recovery/control) comparator. Illustration shows device- and chemical-specific recoveries relative to (full) Snap sampler recovery. Recovery percent is strongly associated with  $K_{ow}$  (top panel) and moderately associated with vapor partitioning (Henry's constant; bottom panel).

significant at the 99% confidence level. For 6 of the 7 chemical/sampling method pairs where statistical significance was not demonstrated, few comparison pairs (4 or fewer) were available for the evaluation. Britt (27) spoke at length about individual constituent differences and the statistical tests employed. Tables S1 and S2 include statistical details.

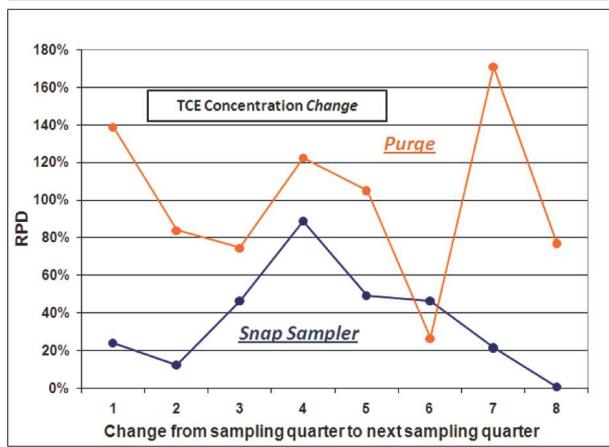
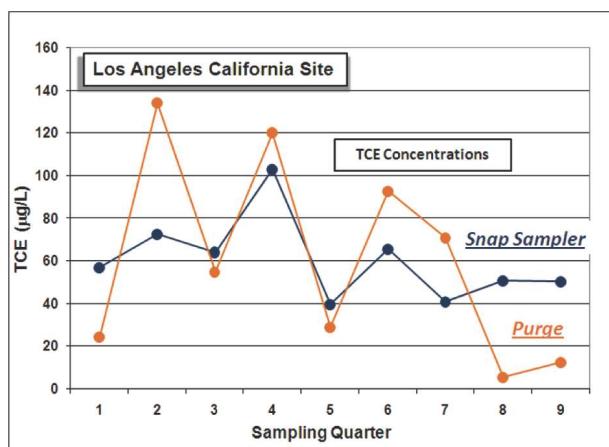
The primary contaminant of concern at the Hillside New Jersey site was arsenic. Sampling for metals in groundwater has been historically problematic due to entrainment of a nonmobile fraction (e.g., sediment) during purging (29), and samples are commonly filtered to remove the artifact solids. Unfortunately, filtration also removes the mobile colloidal fraction, and some regulatory jurisdictions prohibit this procedure. Multiple filtration methods have been employed to delineate the mobile fraction from artifact (30) but are rarely employed in the field. The closure action of the ISS sampler does not mobilize normally immobile formation particulates because no pumping is involved and therefore allows collection of naturally mobile colloidal contaminant load closer to that of ambient groundwater flow. Purge samples were collected, acidified, and analyzed in both filtered (0.45 µm) and unfiltered preparation; ISS/Snap samples were simply acidified after collection without filtration. Arsenic levels in filtered purge samples tended to



**FIGURE 5.** Arsenic concentration comparison from Hillside site. Unfiltered trendline slope ( $y < 1$ ) indicates  $x$ -axis comparator is higher concentration on average than  $y$ -axis comparator (top panel), while the filtered example shows the opposite (bottom panel). Comparison of sample differences suggests purge sample filtration eliminates a high bias, yet introduces a low bias.

be lower on average than unfiltered ISS samples, while unfiltered purge samples tended to be higher than unfiltered ISS samples (Figure 5). This is expected as the ISS sampler captures naturally mobile colloidal material, while unfiltered purge sample incorporates this colloidal material plus artifact particulates due to the disturbance caused by purging; a filtered purge sample removes (nearly) all particulates, including the mobile colloid fraction. Application to other colloid-borne or colloid-like constituents is implied by these findings; however, further work is required to test the applicability to bacteria, pathogens, or other colloidal constituents of concern.

The Los Angeles site data analysis compared long-term consistency of the sealed *in situ* method vs a traditional purge and bail-sample approach. Over two years, ISS sampling and traditional purge sampling yielded 181 comparators of individual VOC concentrations from one calendar quarter to the next. Overall, median purge results changed from one event to the next approximately 30% more than the ISS samples. Take, for example, a concentration of 100 that changes to 140 from one event to the next for the ISS, and a concentration of 100 changes to 152 for purge. That differential is a 30% greater change for the purge result ( $52/40=1.30$ ). However, the *actual* groundwater concentration underlying the *measured* concentration changed by an unknown amount. If the *actual* concentration changed from say, 100 to 135, the difference between 135 and 140 (or 152) is the real measure of error. This translates to a true error of 5 for the ISS vs 17 for purge ( $140-135=5$ ;  $152-135=17$ ): a



**FIGURE 6.** Illustration of TCE concentration changes with time, Los Angeles site. Direction of change is consistent between the methods (top panel), but the magnitude of event-to-event concentration change is lower with the ISS/Snap method (bottom p panel). On average, the RPD from event to event is reduced by about 2/3 for TCE with the ISS method. This includes the actual change in concentration contributed from the aquifer, which implies that the reduction in change attributed to the sampling error may be larger.

340% difference. Because the *actual* groundwater concentration cannot be isolated, the difference in concentration change is the closest proxy. This proxy is a *minimum* error estimate and reflects all factors influencing concentration, including the actual change in ambient contaminant concentration at the well plus any artifacts of either sampling procedure.

Changes in trichloroethene (TCE) concentration over the course of the comparison (Figure 6) were more pronounced than VOCs overall. Both sampling approaches result in event-to-event changes in the same direction, but the magnitude is reduced with the downhole *in situ* approach. The overall concentration range in the Figure 6 example was smaller for the ISS (0.0379–0.103 mg/L) compared to purging (0.0056–0.134 mg/L). The median RPD from event to event for purge sampling was 94% but only 35% for the ISS sampler, a substantial reduction indicative of an approach that reduces sources of data variability that are often unknown, uncontrolled, or uncontrollable.

These field investigation findings point to potential improvements in sampling methodology and data quality that can be achieved through *in situ* collection and sealing of samples. Data quality, which includes precision, accuracy, consistency, and repeatability, should be a controlling factor in selecting groundwater sampling methods. The evolution from strong-purge sampling to low flow sampling was prompted by the desire to improve data quality by reducing

mobilization of normally immobile particles into the pumped sample and to improve consistency in sampling methods (15, 29). Passive, nonpurge, ISS/Snap sampling minimizes mobilization of particles and adds consistency to the sampling procedure. It also avoids handling and disposal of contaminated waters and the time and costs associated with pumping and field parameter measurements. Moreover, given the overarching goal of groundwater sampling is to collect samples that are the closest feasible representation of *in situ* conditions in the aquifer (31), the ISS sampler improves data quality by limiting exposure of sample to air or multiple sample vessels. Indication of the importance of atmospheric exposure and exposure to plastics is evident in the field studies and shows VOC losses may be chemical-specific and dependent on Henry's vapor partitioning coefficient or  $K_{ow}$  (27, 32, 33). The method removes reliance on the operator for pump placement, purge times, purge parameter measurement, and bottle fill technique; avoids data quality problems due to tubing sorption loss and in-well mixing effects during purging; and limits the effect of uncontrollable aspects of field sampling, such as ambient temperature, humidity, or precipitation. Overall, the ISS approach retains many of the advantages while eliminating most of the disadvantages of diffusion-based sampling and can benefit nearly all categories of analytes, including field parameters, volatile organics, gases, metals, and dissolved inorganics.

Millions of monitoring wells are used worldwide to track temporal trends in natural groundwater and at contaminated sites; however, results are influenced by many factors associated with the sampling procedures themselves. These influential factors cause error in individual sample results and diminish the value of long-term trend monitoring. The *In Situ Sealed* sampler described here imparts the least degree of *differential* influence of any of these factors from one sampling event to the next through elimination of procedures and sample handling. As such, its use can most reliably focus interpretation of time-series data on the influences caused by the hydrologic system rather than the sampling process.

### Acknowledgments

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### Supporting Information Available

Details regarding field site geology, history, and sampling procedures as well as illustrations of the ISS/Snap sampler and steps for its deployment and retrieval and additional detail on the statistical significance of Figure 4 data are included as well as additional plots of inorganic constituent data comparisons of the ISS sampler and low flow purging and sampling techniques. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Semi-automated hollow-fibre membrane extraction, a novel enrichment technique for the determination of biologically active compounds in water samples

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### Abstract

An automated hollow fibre membrane extraction technique was developed for the GC–MS determination of pharmaceutical and endocrine disrupting compounds in water samples. Enrichment was carried out inside a porous polypropylene hollow fibre membrane, which separated the aqueous and organic phases and regulated the transfer of analytes. *n*-Octanol placed inside the hollow fibre was used as the acceptor solution. A water–solvent ratio of about 300:1 was used to concentrate the analytes. After 1 hour's extraction of the water sample under magnetic stirring, 1 µl of the *n*-octanol phase was automatically injected from the hollow fibre into the GC–MS. Development work included examining the influence of different sample matrices, volumes, extraction times and extraction solvents. The detection limits, linearity and standard deviations of the method were determined using drugs such as ibuprofen, phenazone and carbamazepine as well as the endocrine disrupting compounds, technical nonylphenols, bisphenol A, 17 $\alpha$ -ethinylestradiol and tonalide by way of example.

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**Keywords:** Hollow fibre membranes; Extraction methods; Water analysis; Endocrine disruptors; Drugs

### 1. Introduction

Monitoring the widespread presence of biologically active substances in aquatic systems is becoming increasingly important. They include pharmaceutical products and their metabolites as well as endocrine disrupting compounds. These compounds mainly enter the environment via municipal sewage plants. Water solubility and persistence prevent their complete degradation, allowing them to enter surface and ground water [1–3].

The polarity and low concentration levels of these compounds in the environment make them a serious challenge for analytical methods. Another major problem is their structural diversity. Therefore, universal methods are required which allow as many analytes as possible to be determined simultaneously.

The most common methods for determining biologically active compounds are liquid–liquid and solid-phase extraction (SPE) [4–11]. These methods are relatively robust and enable large sample amounts to be handled, resulting in detection limits in the lower ng/l range. However, they are rather time-consuming and often involve several clean-up and preconcentration steps. Solvent-free solid-phase microextraction (SPME) has also been used for

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endocrine disrupting compounds and drugs [12–14]. Although faster and simpler, SPME is not as sensitive as SPE. SPME is therefore more suitable for screening analysis at higher concentration ranges.

One promising way of determining organic compounds in water samples is to enrich them with hollow fibre membranes. Rasmussen et al. reported the application of a polypropylene hollow fibre for the liquid-phase microextraction (LPME) of several drugs and pharmaceutical compounds in urine and human plasma [15–18]. The authors obtained detection limits down to 2 ng/ml. For analyte enrichment they used a hollow fibre filled with a suitable solvent, usually *n*-octanol, and exposed it to the sample. After extracting the analytes under vibration, the acceptor solution was collected in inserts by using a small head pressure and analysed using capillary gas chromatography (GC), capillary electrophoresis (CE) or high-performance liquid chromatography (HPLC).

The high preconcentration factors obviously make hollow fibre extraction especially attractive for water analysis. It has already been used to extract nitrophenols with subsequent capillary liquid chromatography [19]. Enrichment is based on the pH gradient between the sample and the aqueous acceptor phase (HCl and NaOH, respectively) within the hollow fibre. Efficient analyte preconcentration is achieved by immobilizing *n*-octanol inside the pores of the hollow fibre, resulting in enrichment factors of up to 380.

The objective of our studies was to develop a hollow fibre extraction device which allows the enrichment of biologically active compounds from water samples and their subsequent automatic GC–

MS determination. We also investigated how various process parameters such as enrichment time and sample matrix affect extraction efficiency.

## 2. Experimental

### 2.1. Chemicals

Tonalide, ibuprofen, phenazone and carbamazepine were supplied by Promochem (Wesel, Germany). Bisphenol A, technical (t) nonylphenols and 17 $\alpha$ -ethinylestradiol were purchased from Sigma. Estradiol diacetate used as internal standard was obtained from ICN Biomedicals (Aurora, OH, USA) and 4-*n*-nonylphenol was supplied by Dr. Ehrenstorfer (Augsburg, Germany). All solvents for standard solutions as well as *n*-octanol (99%), sodium chloride, sodium hydroxide and hydrochloric acid were obtained from Merck (Darmstadt, Germany) and were used without further purification.

### 2.2. Hollow fibre extraction

The principle of hollow fibre extraction is shown in Fig. 1. The Q3/2 Accurel microporous hollow fibre membrane consisted of polypropylene (Membrana, Wuppertal, Germany). The fibre was cut into pieces 6 cm long with an internal diameter of 600  $\mu$ m and a wall thickness of 200  $\mu$ m. The pore size was 0.2  $\mu$ m. Before being used, the fibres were shaken in acetone for 2 h to remove polypropylene oligomers and other potential contaminants and air-dried. Afterwards, the hollow fibre was attached with one end to a funnel-shaped injection guide consisting

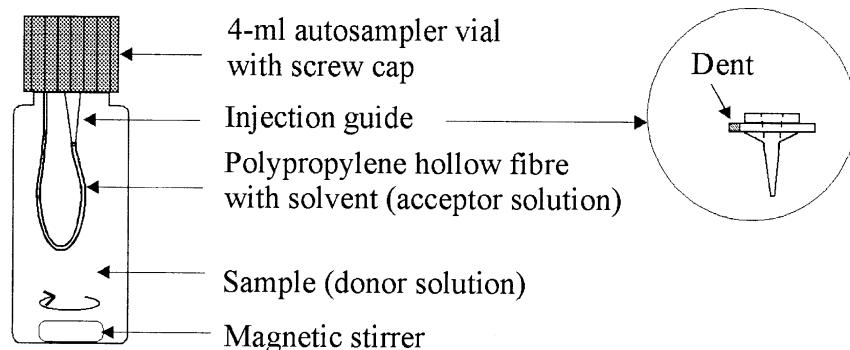


Fig. 1. Schematic set up of the hollow-fibre extraction.

of stainless steel. Additionally, in the injection guide a small dent is placed that holds the other end of the fibre unsealed. Thus, during injection the extraction solvent can move within the fibre and will not be partially pushed out by the intruding syringe needle. Furthermore, the advantage of such a hollow-fibre “loop” compared with a straight fibre is, that there are no problems with air bubbles when filling the autosampler syringe.

Before extraction the hollow fibre was filled with 40 µl of *n*-octanol using a microliter syringe. Subsequently, the solvent-filled fibre was immersed into a 4-ml autosampler vial with screw cap (Agilent Technologies, Palo Alto, CA, USA). The vial contained a 5-ml water sample, so that the fibre is completely immersed in the sample. The enrichment was performed under magnetic stirring (1000 rev./min).

### 2.3. Instrumental parameters

After extraction the sample vial was placed into a GC autosampler (7683 series, Hewlett-Packard, San José, CA, USA). One µl of the *n*-octanol phase was automatically taken from the hollow fibre and injected into the GC-MS system. GC was performed with a 6890 A series gas chromatograph equipped with a mass-selective detector 5973 (Agilent Technologies). Injections were carried out in pulsed splitless mode at a temperature of 280 °C. The injector was coupled to a retention gap (2.5 m×0.32 mm I.D.) and a 30 m×0.25 mm I.D., 0.25 µm HP-5MS capillary column (J&W). Helium was used as carrier gas at a column flow of 1 ml/min. The GC

oven temperature programme started at 120 °C. This temperature was maintained for 3 min and then increased at a rate of 10 °C/min to 300 °C.

The MS parameters were as follows: interface temperature 280 °C, source temperature 230 °C, electron impact (EI) ionization mode, 70 eV. Analysis was performed in the selected ion monitoring (SIM) mode using the characteristic ions given in Table 1.

## 3. Results and discussion

### 3.1. General considerations

Some of the compounds most frequently detected in aquatic systems were chosen as target analytes for these studies. They belong to different classes of pharmaceutical products and xenoestrogens, and are listed together with their range of application in Table 1.

Introducing an enrichment factor (EF) is useful in order to compare the experiments. It can be defined as a quotient between the final concentration of the analyte in the extraction solvent within the hollow fibre  $c_e$  and the initial concentration of the analyte within the aqueous sample  $c_s$ :

$$EF = c_e/c_s \quad (1)$$

The final concentration  $c_e$  was determined by calibration with standard solutions in *n*-octanol containing the corresponding analytes at concentrations up to 100 times higher than in the sample. Furthermore, extraction recoveries ( $R$ ) can be calcu-

Table 1

Investigated biologically active compounds with performance parameters of the hollow fibre extraction (sample: 5 ml distilled water, pH 7 for t-nonylphenols, bisphenol A, tonalide, 17α-ethinylestradiol; 5 ml saturated NaCl solution pH 7 for ibuprofen, phenazone, carbamazepine)

Analyte	Range of application/ effective as	Water solubility (µg/l)	$\log K_{ow}$	SIM target ions	LOD (µg/l)	Correlation coefficient ( $c=0.1\text{--}100\text{ }\mu\text{g/l}$ )	RSD ( $n=5$ ) (%)	Recovery, $R$ (%)
t-Nonylphenols	Industrial detergent/xenoestrogen	7	5.76	107, 135, 220	0.1	0.9989	11.0	20.1
Bisphenol A	Plasticizer/xenoestrogen	120	3.32	213, 228	0.3	0.9986	21.1	23.6
Tonalide	Musk/xenoestrogen	1.25	5.7	243, 258	0.02	0.9985	13.1	35.2
17α-Ethinylestradiol	Synthetic estrogen	11.3	3.67	160, 213, 296	0.02	0.9952	5.3	33.8
Ibuprofen	Analgetic, antirheumatic	21	3.97	161, 163	0.02	0.9996	11.1	48.7
Phenazone	Analgetic	51,900	0.38	173, 188	0.04	0.9995	9.3	1.8
Carbamazepine	Analgetic, antiepileptic	17.7	2.45	193, 236	0.02	0.9993	12.4	15.5

LOD, limit of detection.

lated as a percentage of the total analyte amount originally contained in the sample  $n_s$  and the amount enriched in the extract  $n_e$ :

$$R (\%) = (n_e/n_s) = (V_e/V_s) \cdot EF \quad (2)$$

where  $V_e$  is the volume of the extraction solvent and  $V_s$  the volume of the sample. Exactly observing the extraction time guarantees a reproducible loss of extraction solvent by diffusion through the membrane into water. An extraction volume of 13  $\mu\text{l}$  in mean ( $\pm 1 \mu\text{l}$ ) was defined. This volume of solvent remaining was determined by withdrawing the extract in a microlitre syringe. It was used to calculate the recoveries  $R$  in Table 1.

### 3.2. Selection of a suitable solvent (acceptor solution)

When selecting a suitable solvent, two factors need to be taken into account. First of all, for enrichment to be effective, the analytes should be well soluble in the solvent used. Another factor is the appropriate viscosity of the solvent applied to avoid diffusion through the porous hollow fibre membrane into the aqueous phase. Therefore *n*-octanol [15] and *n*-octanol mixed with butyl acetate or dihexyl ether [16] were used as acceptor solution. The application of octanol for the extraction of 11-nor- $\Delta^9$ -tetrahydrocannabinol-9-carboxylic acid [20] and chloroform for the extraction of cocaine and its metabolites [21] has also been described, although in these cases enrichment times of only 10 and 3 min, respectively, were used because of the leakage of the solvent. The sensitivity of this method was reported to be in the  $\mu\text{g/l}$  range.

To determine the bioactive analytes in this study, several organic solvents such as *n*-octanol, butylacetate, dihexyl ether, *n*-alkanes ( $C_8$ – $C_{11}$ ), xylene, mesithylene and *tert*.-butylbenzene were tested for usage with the hollow fibre technique. These experiments demonstrated that *n*-octanol yielded a reproducible enrichment associated with a reasonable amount diffused through the membrane into the aqueous phase. Dihexyl ether proved unsuitable owing to interference with some important target ions in the SIM mode. All the other solvents displayed greater leakage, and so only shorter extraction times could be applied. Due to the time

dependence of the extraction yields in this case, lower enrichment factors have to be expected. For example, the calculation of enrichment factors for extraction with *n*-octan and an enrichment time of 10 min resulted in EF values below 10 for the relatively polar compounds bisphenol A and 17 $\alpha$ -ethinylestradiol. In order to attain optimal detection limits on the basis of these results, *n*-octanol was chosen for all additional investigations.

Indeed, the usage of *n*-octanol with a boiling point of 178.5 °C has consequences for the subsequent GC–MS analysis. To accomplish tailing-free peaks, an initial column temperature of at least 120 °C is necessary. Hence only compounds with boiling points above 250 °C can be determined reproducibly in this way. Further investigations regarding the modification of the hollow fibres used are necessary for the utilization of GC common solvents.

### 3.3. Influence of the enrichment time

To determine the influence of the enrichment time, aqueous standard solutions were extracted within different times of between 5 and 90 min. Fig. 2 shows the extraction time profiles of all the compounds investigated at a concentration of 10  $\mu\text{g/l}$  in distilled water.

Despite the analytes belonging to different substance classes, the course of the curves for all analytes is comparable. Optimum extraction yields are obtained after an enrichment time of 60 min. Therefore, this time was selected for the subsequent enrichment experiments. The uniform behaviour of all the analytes allows their simultaneous determination within one analysis run.

### 3.4. Influence of the donor solution

The enrichment of organic compounds from water samples is significantly influenced by the properties of the sample solution. Depending on the substance class of the analyte, recovery can for example be increased by optimally adjusting the pH or adding sodium chloride.

In order to optimize the extraction yield for the individual compounds, the influence of various sample parameters was investigated. Table 2 shows the

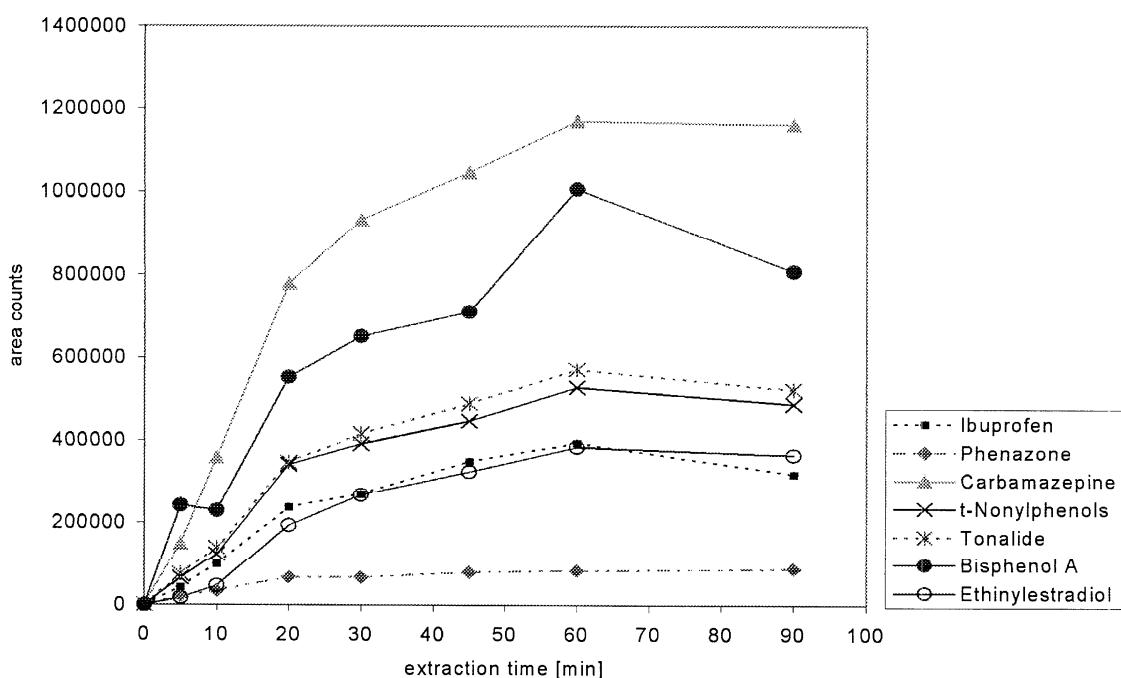


Fig. 2. Enrichment time profiles for the hollow-fibre extraction of the biologically active compounds at a concentration of 10 µg/l in distilled water.

correlation between sample matrix and enrichment factor.

The enrichment of the analytes within the fibre is significantly influenced by their hydrophobicity and their solubility in the extraction solvent. With *n*-octanol as the extraction solvent, the enrichment of the analytes according to their octanol–water partition coefficient ( $K_{ow}$ ) was to be expected. However, as can be seen from Table 2, the highest enrichment factors were achieved for ibuprofen, bisphenol A and 17 $\alpha$ -ethinylestradiol with  $\log K_{ow}$  values between 3.32 and 3.97. For example, ibuprofen in distilled

water with pH 7 provided an enrichment factor of 187. t-Nonylphenols and tonalide possess higher  $\log K_{ow}$  values of 5.7. Yet in both cases only enrichment factors below 100 were yielded. This indicates that not only the distribution equilibrium of the analytes between water and octanol but also the enrichment of the compounds within the microporous hollow fibre membrane has to be taken into account.

In order to assess adsorptive effects of the polypropylene material, empty hollow fibre membranes were shaken in aqueous standard solutions containing known amounts of all analytes. After drying,

Table 2  
Influence of various sample matrices on the enrichment factor of the bioactive compounds ( $c=10 \mu\text{g/l}$ )

Analyte	Enrichment factor			
	Distilled water pH 7	Distilled water pH 2	Distilled water pH 10	Saturated sodium chloride solution
t-Nonylphenols	77	82	114	29
Tonalide	91	111	118	35
Bisphenol A	135	151	9	189
17 $\alpha$ -Ethinylestradiol	130	144	101	125
Ibuprofen	187	254	0.3	415
Phenazone	7	2	1.8	13
Carbamazepine	60	39	30	166

these membranes were extracted with acetone. Analysing the obtained extract by GC–MS showed that nearly 75% of the t-nonylphenols and 90% of the tonalide was to be found in the extract whereas all the other compounds could not be detected. This means that in the case of analytes with a very high  $K_{ow}$  value and extremely low water solubility, adsorption within the hydrophobic polypropylene membrane plays an important role. More detailed investigations on these processes were not carried out because the main issue of this study was the liquid–liquid partition of the target analytes.

Lowering the pH to 2 only for ibuprofen led to a significant improvement in the extraction yield because of its carboxyl group. The influence on all the other compounds including bisphenol A and 17 $\alpha$ -ethinylestradiol, both containing two OH groups, was rather small. Using a pH of 10 did not significantly improve enrichment efficiency. However, the enrichment factors for bisphenol A and ibuprofen dropped markedly due to their OH and carboxylic groups, respectively.

The addition of sodium chloride increased extraction efficiency, especially for ibuprofen and carbamazepine. In both cases the EFs were more than doubled to values of 415 and 166, respectively. Interestingly, the extraction yields of t-nonylphenols and tonalide in the presence of salt markedly declined. The reduction of the water solubility due to the sodium chloride content probably led to the greater adsorption of these two compounds in the hollow fibre membrane.

Phenazone with the lowest log  $K_{ow}$  value (0.38) and the largest water solubility (51.9 g/l) of all the compounds investigated delivered an enrichment factor of just 13 for sodium chloride saturated samples. Nevertheless, because of its favourable signal-to-noise ratio for the target ions in GC–MS analysis, satisfactory detection limits were achieved (Table 1).

### 3.5. Evaluation of the hollow fibre technique

The performance parameters of the hollow fibre technique such as detection limits, correlation coefficients, relative standard deviations and recoveries are listed in Table 1. The specified values for the endocrine disrupting compounds, t-nonylphenols,

bisphenol A, tonalide and 17 $\alpha$ -ethinylestradiol were determined in distilled water with pH 7, while those of ibuprofen, phenazone and carbamazepine were achieved using sodium chloride-saturated sample solutions. In all cases a sample volume of 5 ml was used.

In particular the detection limits within the ng/l range demonstrate the capability of the method for determining organic compounds in water samples. If necessary the sensitivity could be further enhanced using larger sample volumes. However, longer extraction times must be applied to reach the distribution equilibrium. For example, by using sample volumes of 20 ml and extraction times of 120 min, the detection limits for the pharmaceutical compounds were lowered to values between 15 ng/l for phenazone and 7 ng/l for carbamazepine. The relatively high detection limits for t-nonylphenols and bisphenol A are due to blind values. In the case of t-nonylphenols they come from the hollow fibre. This was proved by heating up some fibres in the tube of a thermodesorber. In the GC–MS chromatogram obtained, t-nonylphenols were evidenced.

The standard deviations achieved were in the range of 5.3% for 17 $\alpha$ -ethinylestradiol and 21.1% for bisphenol A. Regarding the relatively polar nature of the compounds investigated, these values are acceptable. After all they are analyzed without derivatization, which requires an inert GC–MS system.

Hollow-fibre extraction had already been tested for the determination of bioactive compounds in real samples. Fig. 3 shows the GC–MS chromatogram of the influent of the tern-sewage plant in Grosslehn near Leipzig. 4-*n*-Nonylphenol, [ $^2\text{H}_{14}$ ]bisphenol A and estradiol diacetate were used as internal standards. The endocrine disrupting compounds, t-nonylphenols, bisphenol A, tonalide and in some cases 17 $\alpha$ -ethinylestradiol were thus detected and determined in concentrations between 0.03 and about 4  $\mu\text{g/l}$ . Hence, hollow-fibre extraction is also a useful tool for analysing very contaminated samples. Using the established methods of liquid–liquid or solid-phase extraction, the analysis of such polluted samples normally would take several clean-up steps.

One essential advantage of the hollow fibre technique is the relatively high enrichment factors, which can even be achieved with small sample and solvent volumes. This is attributable to the favourable

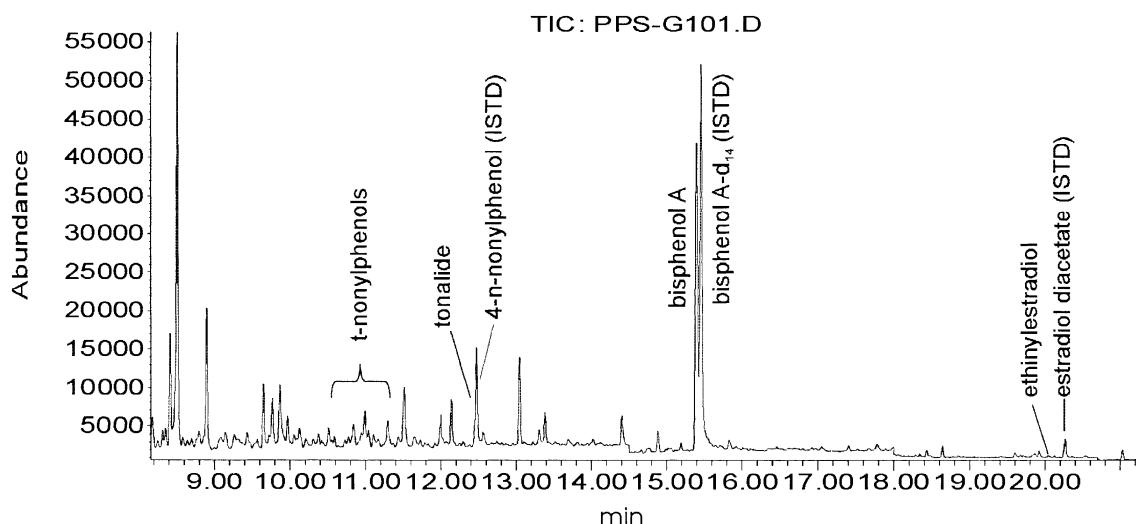


Fig. 3. GC-MS chromatogram of the hollow fibre extract for an influent of the tern-sewage plant in Grosslehna. The peaks correspond to 5 µg/l for the internal standards 4-n-nonylphenol, [ $^2\text{H}_{14}$ ]bisphenol A and estradiol diacetate. Analyte concentrations determined were 3.70 µg/l t-nonylphenols, 0.77 µg/l tonalide, 2.05 µg/l bisphenol A and 0.035 µg/l ethinylestradiol.

geometric dimensions of the hollow fibre. Assuming a hollow fibre with a length of 6 cm and an internal diameter of 600 µm, the resulting inner volume is ~17 µl. Hence applying just a 5-ml sample volume would result in a water/solvent ratio of about 300:1, while larger sample volumes increase this ratio. Due to the high enrichment factor the injection of 1 µl of the extract is usually sufficient to secure the required sensitivity. Large volume injections [22,23] often entailing the pollution of the liner and capillary column as well as additional optimization efforts are not required.

Furthermore, the automation facility should be underlined. After extraction, the sample vial can be placed directly into a GC autosampler. Using appropriate injection guides, the technique can be used with all commercial autosampler systems.

The polypropylene hollow fibres used are low-cost articles, thus allowing a new piece of hollow fibre to be used for each individual analysis to avoid carry-over effects of the analytes.

#### 4. Conclusion

This article introduces a new analytical method for biologically active compounds in water samples

based on enrichment with polypropylene hollow fibres. Advantages of the new method over established enrichment techniques such as liquid–liquid and solid-phase extraction are the small amount of solvent required and the low sample consumption. Although hollow fibre extraction cannot match either of these methods in terms of detection limit, limits in the ng/l range can be achieved if the right analysis conditions are chosen. Furthermore, no preconcentration or clean-up steps are necessary.

Other benefits of the hollow fibre technique are its low cost, the possibility of automation, and its simple handling, which requires only a negligible amount of material.

The investigations reveal the potential of hollow fibre extraction as a simple but nevertheless effective tool in water analysis. Its advantages make automatic hollow fibre enrichment especially suitable for screening analysis. Moreover, given appropriate sample volumes the technique is also a useful tool for trace analyses.

Further investigations are required for the use of solvents other than octanol. One way of keeping more suitable solvents in the fibre is probably to immobilize stationary phases within the pores of the hollow fibre. This could also improve selectivity for several classes of substances.

## Acknowledgements

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# Liquid–Liquid–Liquid Microextraction for Sample Preparation of Biological Fluids Prior to Capillary Electrophoresis

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Methamphetamine as a model compound was extracted from 2.5-mL aqueous samples adjusted to pH 13 (donor solution) through a thin phase of 1-octanol inside the pores of a polypropylene hollow fiber and finally into a 25- $\mu$ L acidic acceptor solution inside the hollow fiber. Following this liquid–liquid–liquid microextraction (LLLME), the acceptor solutions were analyzed by capillary zone electrophoresis (CE). Extractions were performed in simple disposable devices each consisting of a conventional 4-mL sample vial, two needles for introduction and collection of the acceptor solution, and a 8-cm piece of a porous polypropylene hollow fiber. From 5 to 20 different samples were extracted in parallel for 45 min, providing a high sample capacity. Methamphetamine was preconcentrated by a factor of 75 from aqueous standard solutions, human urine, and human plasma utilizing 10<sup>-1</sup> M HCl as the acceptor phase and 10<sup>-1</sup> M NaOH in the donor solution. In addition to preconcentration, LLLME also served as a technique for sample cleanup since large molecules, acidic compounds, and neutral components were not extracted into the acceptor phase. Utilizing diphenhydramine hydrochloride as internal standard, repetitive extractions varied less than 5.2% RSD ( $n = 6$ ), while the calibration curve for methamphetamine was linear within the range 20 ng/ $\mu$ L to 10  $\mu$ g/mL ( $r = 0.9983$ ). The detection limit of methamphetamine utilizing LLLME/CE was 5 ng/mL (S/N = 3) in both human urine and plasma.

During the last 10 years, capillary electrophoresis (CE) has been developed into a highly attractive separation technique for both ionic and neutral compounds. Owing to high separation efficiencies, low separation times, a low consumption of reagents, and relatively simple method development, CE has been implemented for research and routine analysis of pharmaceuticals, peptides, proteins, agrochemicals, raw materials, water, and DNA as well as for many other applications.<sup>1</sup> However, because most CE is performed with UV detection directly on the narrow fused-silica capillaries used for the separation and because only nanoliter volumes of sample are injected in traditional CE, most concentra-

tion detection limits obtained in CE are relatively high. Therefore, CE is principally used for compounds present at relatively high concentration levels, while the advantages of the technique are difficult to utilize for trace analysis applications in connection with biological and environmental samples.

Several attempts to improve concentration detection limits in CE have been published. A number of workers have developed advanced injection techniques including analyte stacking, field amplification, and transient isotachophoresis that facilitate the analysis of larger sample volumes.<sup>2–6</sup> All of these are based on voltage applied across the CE capillary, resulting in stacking or focusing due to variation of ion mobilities in various field strengths or chemical microenvironments. As a result, relatively large sample volumes can be analyzed with minimal loss of analyte resolution or separation efficiency. However, since the advanced injection techniques are carried out within conventional CE capillaries, injection volumes are normally limited to <1  $\mu$ L, and consequently, these are only a partial solution to the relatively poor concentration detection limits of CE. In addition, in most cases sample cleanup is required for complicated biological and environmental samples prior to the large-volume injections.

As an alternative to the advanced injection techniques, several workers have utilized an analyte concentrator<sup>7–11</sup> or a membrane preconcentration cartridge<sup>12–14</sup> within the CE capillary for large-volume injections. These devices usually consist of an adsorptive

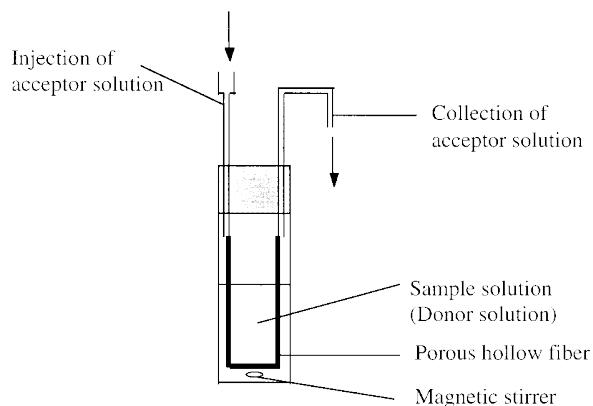
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phase at the inlet of the CE capillary and serve both to enrich trace level analytes and to clean up the sample prior to the component separation by CE. Injection of sample volumes in excess of 100  $\mu\text{L}$  have been reported into CE capillaries of <300 nL total volume,<sup>15</sup> and both specific materials based on antibodies<sup>7</sup> and nonspecific solid-phase adsorbents<sup>16</sup> have been used to trap the analytes. Unfortunately, although the technique is easily automated, the CE separation capillaries are filled with sample solution during the sample-loading process. Thus, for complicated samples such as human plasma, the chemistry on the surface of the fused-silica capillaries may be substantially deteriorated resulting in poor performance following injection of several samples.

Recently, sample workup of the basic drugs bambuterol and physostigmine in human plasma was reported for CE utilizing a supported liquid membrane (SLM).<sup>17–19</sup> With this technique, basic drugs were extracted from a stream of plasma sample (donor solution) into an organic solvent immobilized in a porous poly(tetrafluoroethylene) membrane or hollow fiber and subsequently back-extracted into a stagnant aqueous acceptor phase on the other side of the membrane (liquid–liquid–liquid extraction). Because the acceptor solution was acidic and the donor solution was alkaline, and since the volume of the acceptor solution was small compared with the volume of the donor phase, the basic drugs were enriched within the acceptor solution. In addition to this analyte enrichment, sample cleanup occurred in the SLM system because macromolecules, anionic compounds, and neutral components were not extracted into the acceptor solution. However, the experimental setup for this promising technique was relatively complex and required a peristaltic pump, a syringe pump, and a special SLM unit machined from blocks of PTFE.

In the present work, the basic principle of SLM has for the first time been integrated into simple, inexpensive, and disposable extraction units for liquid–liquid–liquid microextraction (LLLME) utilizing polypropylene hollow fibers as the membrane. The low cost of each extraction unit (comparable with the price of a column for solid-phase extraction) was important for two reasons: (1) a large number of different samples (5–20 in the present work) may be exposed to LLLME simultaneously providing a high sample capacity, and (2) each extraction unit is disposed of after a single extraction to avoid cross-contamination problems from sample to sample and to avoid the need for regeneration. The volume of the donor phase was 2.5 mL while the volume of the acceptor phase was 25  $\mu\text{L}$  in order to obtain high analyte enrichments. The basic setup for LLLME is discussed in the present paper, and the technique is optimized for methamphetamine as a model compound with respect to the type of organic solvent used for immobilization, pH of the acceptor and donor



**Figure 1.** Diagram of the LLLME extraction unit (not to scale).

solutions, and extraction time. In addition, LLLME is validated for quantitative purposes, and applications to humane urine and plasma are illustrated.

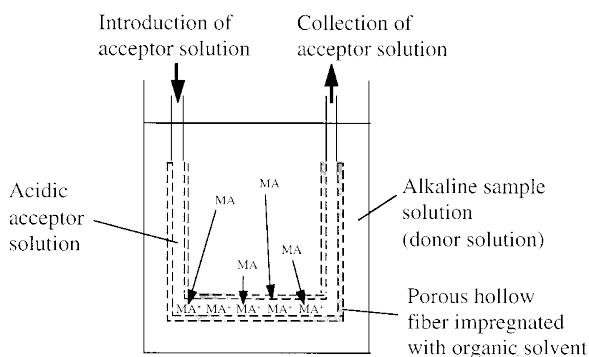
## EXPERIMENTAL SECTION

**Liquid–Liquid–Liquid Microextraction.** The experimental setup for the off-line LLLME is illustrated in Figure 1. The sample solution was filled into a 4-mL amber vial with a screw top/silicon septum (Supelco, Bellefonte, PA). Two 0.8-mm-o.d. syringe needles were inserted through the silicon septum; one served to introduce the acceptor solution into the hollow fiber prior to extraction while the second needle was utilized for collection of the acceptor solution after extraction. The end of the two needles were connected to a 8-cm piece of Q3/2 Accurel KM polypropylene hollow fiber (Akzo Nobel, Wuppertal, Germany). The inner diameter of the hollow fiber was 600  $\mu\text{m}$ , the thickness of the wall was 200  $\mu\text{m}$ , and the pore size was 0.2  $\mu\text{m}$ .

Extractions were performed according to the following scheme: A 2.5-mL aliquot of sample solution (pH adjusted with NaOH as described below) was filled into the vial, and a small magnet was placed in the solution to ensure efficient stirring during the extraction. A new 8-cm length of hollow fiber was placed between the two needle ends and subsequently dipped for a 5-s period into the organic solvent (typically 1-octanol) used for impregnation; the latter procedure served to fill the pores of the hollow fiber with the organic solvent. After impregnation, air was flushed through the hollow fiber with a 5-mL syringe to remove excess organic solvent from the inside of the fiber. After impregnation, 25  $\mu\text{L}$  of acceptor solution was injected into the hollow fiber with a microliter syringe, and subsequently, the fiber was placed in the sample solution. During extraction, the solution was stirred at 400 rpm. After extraction, the acceptor solution was flushed into a 200- $\mu\text{L}$  vial/insert (Beckman, Fullerton, CA) for the capillary electrophoresis instrument by applying a small pressure with a 5-mL syringe on the inlet needle for the hollow fiber. Each piece of porous hollow fiber was used only for a single extraction.

**Capillary Electrophoresis.** Capillary electrophoresis was performed with a MDQ instrument (Beckman, Fullerton, CA) equipped with a UV detector. Separations were accomplished in a 75- $\mu\text{m}$ -i.d. fused-silica capillary with a total length of 40 cm (Beckman). For standard solutions and human plasma samples, the separations were performed in the 10-cm length from the outlet of the capillary to the detector window (reverse direction),

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**Figure 2.** Principle of the LLLME.

while human urine samples were analyzed in the normal direction utilizing a 30-cm effective length. The running buffer was 25 mM phosphate adjusted to pH 2.75. The instrument was operated at 15 kV, which generated a current level of approximately 75  $\mu$ A. Samples were introduced by hydrodynamic injection at 0.5 psi for 5 s. Detection was accomplished at 200 nm utilizing a 100  $\times$  800  $\mu$ m slit.

**Chemicals.** HCl (37%) and NaOH of analytical grades were obtained from Merck (Darmstadt, Germany). Methamphetamine (>99%) and diphenhydramine hydrochloride (>99%) were purchased from Norsk Medisinaldepot (Oslo, Norway). 1-octanol (>99.5%) and 2-octanone (>97%) were obtained from Fluka (Buchs, Switzerland), hexyl ether (purity not reported) was purchased from Sigma (St. Louis, MO), and isoctane (>99.5%) was obtained from Merck.

**Standard Solutions and Biological Samples.** Standard solutions of methamphetamine was prepared in different concentrations of NaOH by dilution from a 0.2 mg/mL stock solution of methamphetamine in water. For the validation studies, diphenhydramine hydrochloride was added as an internal standard from a 0.2 mg/mL stock solution in water. The stock solutions of methamphetamine and diphenhydramine hydrochloride were stored at +5 °C and protected from light. Prior to LLLME, samples of human urine and plasma were prepared by the following procedure: 2.5 mL of sample was spiked with 3  $\mu$ L of the 0.2 mg/mL stock solution of methamphetamine and subsequently 125  $\mu$ L of 2 M NaOH was added.

## RESULTS AND DISCUSSION

**Basic Principle.** Metamphetamine was selected as a model compound (analyte) in the present work and was extracted from aqueous standard solutions, human urine, and human plasma. The basic principle of LLLME is illustrated in Figure 2. Prior to extraction, the sample solution was made strongly alkaline in order to deionize the analyte and consequently to reduce the solubility within the sample solution (donor solution). A small piece of a porous hollow fiber of polypropylene was treated with an organic solvent (typically 1-octanol) immiscible with water and filled with a small volume of diluted hydrochloric acid (acceptor solution). The exposure to the organic solvent served to fill the pores of the hollow fiber with the organic solvent. Subsequently, the hollow fiber was placed within the sample solution, resulting in a three-phase system that consisted of a large volume of an alkaline

sample solution (aqueous donor solution), a very small volume of organic solvent immobilized in the pores of the hollow fiber, and a small volume of diluted hydrochloric acid inside the hollow fiber (aqueous acceptor solution). Because the organic solvent in the pores of the hollow fiber was immiscible with water, it served as an effective barrier between the donor phase and the acceptor phase. Owing to the low solubility of the analyte within the alkaline donor phase and because of the correspondingly high solubility in the acidic acceptor solution, the analyte was extracted from the donor solution through the organic solvent in the pores of the hollow fiber and into the acceptor solution. Because the analyte molecules were ionized within the acceptor solution, they were prevented from re-entering the organic solvent in the pores of the hollow fiber. Since the volume of acceptor solution inside the hollow fiber was very small compared to the volume of the donor solution (sample), the analyte was preconcentrated within the acceptor solution with time. In addition to analyte enrichment, LLLME served as a method for sample cleanup. Large molecules (like proteins) were unsoluble in the immobilized organic solvent and remained in the donor solution (sample). Furthermore, anionic and neutral sample constituents were not extracted into the acidic acceptor phase; acidic compounds were ionized and were unable to penetrate the organic solvent in the pores of the hollow fiber, polar neutral components were also unsoluble in the organic phase, and hydrophobic neutral compounds principally were distributed within the organic phase and the donor solution.

**Equilibrium Considerations and Enrichment Factor.** As discussed above, the LLLME process involves a series of two reversible extractions. In the first step, the analyte is extracted from the sample solution (donor solution) and into the organic phase immobilized within the pores of the hollow fiber. In the second step, the analyte is back-extracted into the aqueous acceptor phase inside the hollow fiber. For an analyte *i*, the extraction process may be illustrated with the equation

$$i_{a1} \leftrightarrow i_o \leftrightarrow i_{a2} \quad (1)$$

where the subscript a1 represents the aqueous donor phase (sample solution), o the organic phase within the pores of the hollow fiber, and a2 the aqueous acceptor phase. At equilibrium, the distribution ratios for the analyte *i* in the three-phase system are

$$K_1 = C_{o,eq} / C_{a1,eq} \quad (2)$$

and

$$K_2 = C_{o,eq} / C_{a2,eq} \quad (3)$$

where  $C_{o,eq}$  is the equilibrium concentration of *i* in the organic phase,  $C_{a1,eq}$  is the equilibrium concentration of *i* in the donor phase, and  $C_{a2,eq}$  is the equilibrium concentration of *i* in the acceptor phase. At equilibrium, the mass-balance relationship

**Table 1. Enrichment Factor ( $E_e$ ) as a Function of the Donor/Acceptor Volume Ratio ( $V_{a1}/V_{a2}$ ) and the Acceptor/Donor Partition Coefficient  $K$**

phase ratio ( $V_{a1}/V_{a2}$ )	enrichment factor ( $E_e$ )			
	$K = 10$	$K = 100$	$K = 1000$	$K = \infty$
1000	9.9	91	500	1000
100	9	50	91	100
40	8	29	39	40
20	7	17	19	20
10	5	9.1	9.9	10
1	0.91	0.99	1	1

for  $i$  is given by<sup>20,21</sup>

$$C_{a1,\text{initial}} = (K_2 C_{a2,\text{eq}})/K_1 + (K_2 C_{a2,\text{eq}} V_o)/V_{a1} + (C_{a2,\text{eq}} V_{a2})/V_{a1} \quad (4)$$

where  $C_{a1,\text{initial}}$  is the initial concentration of  $i$  in the donor phase (sample),  $V_{a1}$  is the volume of donor solution (sample),  $V_o$  is the volume of organic solvent in the pores of the hollow fiber, and  $V_{a2}$  is the volume of acceptor solution inside the hollow fiber. The enrichment factor ( $E_e$ ), defined as the ratio  $C_{a2,\text{eq}}/C_{a1,\text{initial}}$ , may be calculated by rearrangement of eq 4 to

$$E_e = 1/[K_2/K_1 + (K_2 V_o)/V_{a1} + V_{a2}/V_{a1}] \quad (5)$$

In LLLME, the volume of organic solvent immobilized in the pores of the hollow fiber ( $V_o$ ) is small, and eq 5 may be simplified to

$$E_e = 1/[1/K + V_{a2}/V_{a1}] \quad (6)$$

where

$$K = C_{a2,\text{eq}}/C_{a1,\text{eq}} \quad (7)$$

Enrichment factors based on eq 6 were calculated for different  $K$  values and volume ratios between the donor and acceptor phase (Table 1). On the basis of these calculations,  $K$  values of 100 or more are required for the analytes of interest in order to obtain high enrichment factors ( $>50$ ). In addition, the donor/acceptor volume ratio should not be below 100 in order to obtain high enrichments and to ensure analyte preconcentrations attractive for practical work with biological samples. This information was of high importance during construction of the technical setup for LLLME.

**Technical Setup.** The porous hollow fiber used was commercially available and made of polypropylene. A polypropylene fiber was selected owing to the excellent compatibility with a broad range of organic solvents. With this material, no degradation of the hollow fiber was observed following impregnation. The inner diameter of the hollow fiber was 600  $\mu\text{m}$ . This was appropriate for the microliter volumes of acceptor solution utilized in the present work (discussed below). The wall of the hollow fiber was

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relatively thick (200  $\mu\text{m}$ ), which simplified the preparation of extraction units; the mechanical stability of the hollow fibers was excellent and the fibers were easily connected to the two syringe needles of the simple extraction unit prior to LLLME. A pore size of 0.2  $\mu\text{m}$  was selected to ensure efficient penetration of small molecules such as methamphetamine while blocking for larger matrix components (like proteins in plasma samples).

Following extraction, the extracts (acceptor solutions) were collected in small inserts placed in the vials for the CE instrument. For the instrumentation used in the present work (MDQ from Beckman), 200- $\mu\text{L}$  inserts were selected among the commercially available alternatives providing the lowest sample volume. From this type of insert, 25  $\mu\text{L}$  was found to be the minimum volume providing repeatable injections, and consequently, 25  $\mu\text{L}$  was selected as the acceptor volume. The volume of acceptor solution was measured exactly and introduced into the hollow fiber by a microliter syringe. With a 25- $\mu\text{L}$  acceptor volume and a desire to achieve enrichment factors in the range 50–100, LLLME was performed from sample volumes of 2.5 mL throughout the work (donor/acceptor volume ratio of 100; see Table 1).

Commercially available 4-mL vials with screw caps were utilized as extraction units. Two medical needles were penetrated through the screw cap and were connected to the ends of the porous hollow fiber; one served to guide the syringe for injection of the acceptor solution while the other was utilized for collection of the acceptor solution after extraction. In addition to the extraction unit, a microliter syringe was required to introduce the acceptor solution as described above, and an inexpensive 2.5-mL syringe filled with air was utilized for collection of the acceptor solution into the CE vials. This simple setup combined with the low price of the porous hollow fiber resulted in very low costs for each extraction unit; each in-vial extraction unit was a disposable device utilized only for a single extraction. This effectively prevented carry-over effects during large series of extractions.

**Impregnation.** The type of solvent immobilized within the pores of the hollow fiber was of high importance in order to achieve efficient analyte preconcentration by LLLME within reasonable time. The solubility of the analyte in the immobilized solvent should be higher than the solubility in the donor phase in order to promote analyte migration through the pores of the hollow fiber. In addition, the solvent should be immiscible with water to avoid dissolution during the extraction, nonvolatile to prevent evaporation during sample preparation, and effectively immobilized on surfaces of polypropylene to ensure a high quality of the intermediate phase. On the basis of these criteria, 1-octanol, 2-octanone, hexyl ether, and isoctane were evaluated as solvents for immobilization. Enrichment was accomplished by 45 min of LLLME from standard solutions of 100 ng/mL methamphetamine dissolved in 0.1 M NaOH. With 1-octanol, 2-octanone, and hexyl ether, methamphetamine was enriched by a factor of 62–70 (Table 2). These solvents were easily immobilized on the hollow fiber by a 5-s exposure, the volatility was low, and the solvents remained effectively immobilized during the extraction (no leakage to the sample). With isoctane in contrast, the highly nonpolar nature complicated immobilization within the porous polypropylene hollow fiber. On the basis of the immobilization experiments, 1-octanol was selected for the rest of the work.

**Table 2. Preconcentration of Methamphetamine Utilizing Different Solvents for Impregnation of the Porous Hollow Fiber**

solvent	preconcn factor <sup>a</sup>
1-octanol	70
2-octanone	65
hexyl ether	62
isooctane	— <sup>b</sup>

<sup>a</sup> Results varied within 20% RSD ( $n = 6$ ). <sup>b</sup> No signal was observed for methamphetamine.

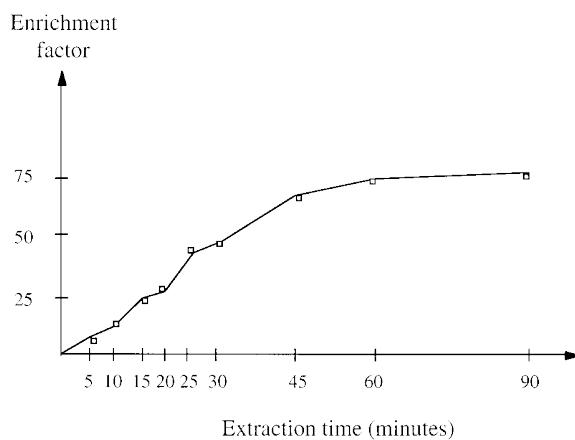
**Table 3. Preconcentration of Methamphetamine Utilizing Different Donor and Acceptor Solutions**

donor, NaOH (M)	acceptor, HCl (M)	preconcn factor <sup>a</sup>
1	$10^{-1}$	80
$10^{-1}$	$10^{-1}$	74
$10^{-2}$	$10^{-1}$	65
$10^{-3}$	$10^{-1}$	64
$10^{-4}$	$10^{-1}$	40
$10^{-1}$	1	— <sup>b</sup>
$10^{-1}$	$10^{-1}$	74
$10^{-1}$	$10^{-2}$	40
$10^{-1}$	$10^{-3}$	17
$10^{-1}$	$10^{-4}$	2

<sup>a</sup> Results varied within 20% RSD ( $n = 6$ ). <sup>b</sup> Problems related to high ionic strength of sample during capillary electrophoresis.

**Donor and Acceptor Solutions.** With the hollow fiber impregnated with 1-octanol, subsequent experiments were conducted to optimize the composition (pH) of both the donor and acceptor solutions. For all of the experiments, LLLME was accomplished for 45 min with NaOH in the donor solution (sample) and HCl in the acceptor solution. For the donor phase, the concentration NaOH was varied between  $10^{-4}$  and 1 M. As illustrated in Table 3, the enrichment factor for methamphetamine increased with increasing pH. With  $10^{-4}$  M NaOH, the pH of the solution was close to the  $pK_a$  value of methamphetamine ( $pK_a = 10.1$ ), but despite this the analyte was enriched by a factor of 40. While 1 M NaOH provided the highest enrichment factor for methamphetamine (approximately 80),  $10^{-1}$  M NaOH was selected for the rest of the work for both stability and practical reasons. In addition to  $10^{-1}$  M NaOH, NaCl was added to the donor solution in a subsequent experiment to evaluate the possibility of out-salting the analyte from the donor phase. However, although NaCl was added at concentration levels of 10, 20, and 30%, no further enrichment was obtained.

While the composition of the donor solution was not very critical, the enrichment was more sensitive to compositional (pH) variations of the acceptor solution. As illustrated in Table 3, the concentration of HCl in the acceptor solution was varied between  $10^{-4}$  and 1 M. With 1 M HCl, problems were observed during capillary electrophoresis of the extract; owing to the high ionic strength of the sample extract (acceptor solution) as compared with the 50 mM phosphate buffer (pH 2.75) utilized as separation medium, the methamphetamine peak was heavily distorted and defocused due to antistacking. With  $10^{-1}$  M HCl in contrast, the peak shape was significantly improved and methamphetamine was enriched by a factor of approximately 74. As the concentration of



**Figure 3. Preconcentration of methamphetamine versus extraction time.**

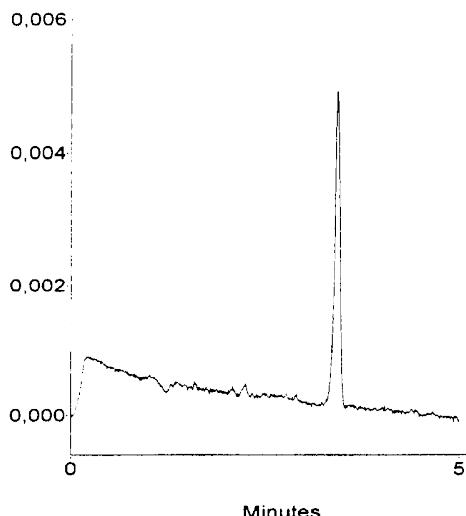
HCl was decreased below  $10^{-1}$  M, the enrichment factor for methamphetamine was dramatically reduced. Although the initial pH of the acceptor solution of  $10^{-4}$  M HCl was far below the  $pK_a$  value of methamphetamine ( $pK_a = 10.1$ ), no enrichment was observed because the absolute buffer capacity within the small volume of acceptor solution was low. Thus, on the basis of the results in Table 3,  $10^{-1}$  M HCl was selected as the acceptor solution for the rest of the work.

**Extraction Time.** With the hollow fiber impregnated with 1-octanol,  $10^{-1}$  M NaOH in the donor solution, and  $10^{-1}$  M HCl as the acceptor solution, the extraction time was optimized for methamphetamine in Figure 3. The amount of methamphetamine extracted by LLLME increased with increasing exposure time from 5 to 45 min, while the enrichment factor stabilized at about 70 utilizing extraction times above 45 min. On the basis of these results, 45 min was selected as the extraction time. Although the extraction time was relatively long, a large number of different samples (5–20) were extracted simultaneously resulting in a very high sample capacity.

**Extraction Efficiency and Distribution Ratio.** On the basis of the experiments discussed above, optimal LLLME of methamphetamine was obtained by utilizing a porous hollow fiber impregnated with 1-octanol, an acceptor solution of  $10^{-1}$  M HCl, a donor solution containing  $10^{-1}$  M NaOH, and an extraction time of 45 min. In this case, methamphetamine was typically enriched by a factor of 75 from aqueous samples (Figure 4). This corresponded to a 75% extraction efficiency. With  $V_{a2} = 25 \mu\text{L}$ ,  $V_{a1} = 2.5 \text{ mL}$ , and  $C_{a1,\text{initial}} = 100 \text{ ng/mL}$ , a value of 293 was obtained for the partition coefficient between the acceptor phase and the donor phase ( $K$ ) for methamphetamine by utilizing eq 6. This value effectively explained the significant enrichments obtained in the present work.

**Validation.** To evaluate the practical applicability of the proposed LLLME technique, repeatability, linearity, detection limit, and limit of quantification were investigated by utilizing standard solutions of methamphetamine in water. For this purpose, diphenhydramine was added as internal standard at the 50 ng/mL level. This compound was appropriate because it was enriched approximately by the same factor as methamphetamine ( $E_e \approx 75$ ) and it was easily separated from methamphetamine by the CE system.

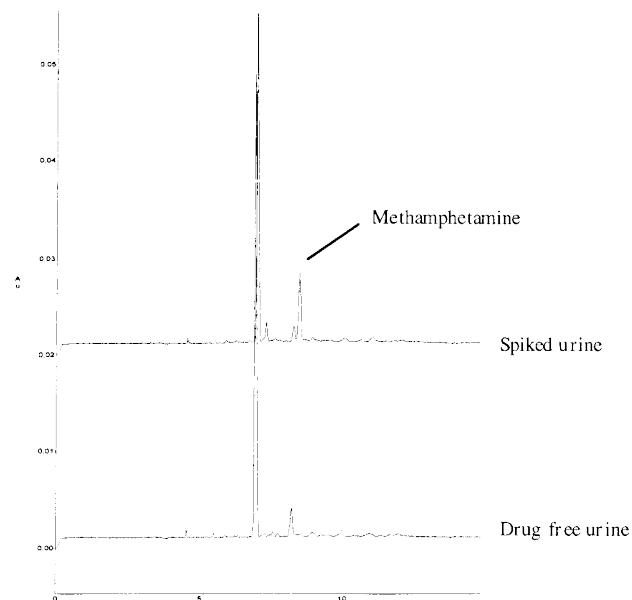
In a first experiment, six replicates of methamphetamine (100 ng/mL) and diphenhydramine (50 ng/mL) were treated by



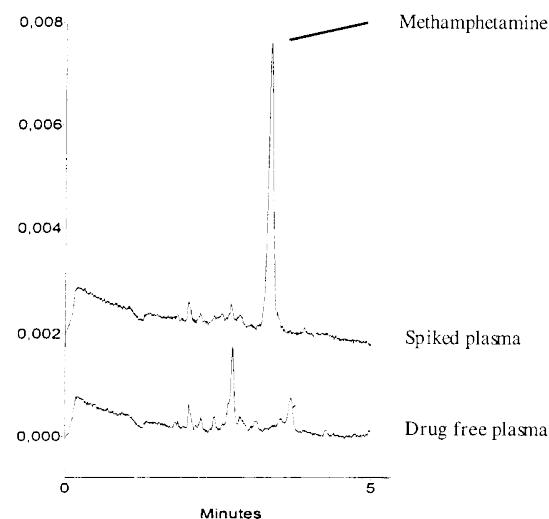
**Figure 4.** Preconcentration of 100 ng/mL methamphetamine from a standard solution in water: CE buffer, 50 mM phosphate pH 2.75; separation voltage, 15 kV; capillary, 10 cm (effective length)  $\times$  75  $\mu\text{m}$  i.d.; detection, UV at 200 nm.

LLLME/CE. The absolute peak areas for methamphetamine and the internal standard varied within 20% RSD, but the repeatability was significantly improved when the results for methamphetamine were corrected with the internal standard. In the latter case, the results varied within 6.8% RSD when peak areas were utilized and within 5.2% RSD based on peak heights. The repeatability was acceptable and comparable with other microextraction techniques reported in the literature.<sup>19</sup> In a subsequent experiment, the linearity was evaluated within the range 20 ng/mL to 10  $\mu\text{g}/\text{mL}$  where a linear regression coefficient of 0.9983 was obtained. The limit of detection ( $S/N = 3$ ) for methamphetamine was 5 ng/mL, and the limit of quantitation was 17 ng/nL ( $S/N = 10$ ). The broad linear range combined with the low detection limit suggests a high potential for monitoring methamphetamine in human urine and plasma by LLLME/CE.

**Preconcentration of Methamphetamine from Human Urine and Plasma.** To finish the evaluation of LLLME, methamphetamine was preconcentrated from both human urine and plasma. Aliquots (2.5 mL) of both samples were spiked with 100 ng/mL methamphetamine, and subsequently, 125  $\mu\text{L}$  of 2 M NaOH was added to each to provide an approximately  $10^{-1}$  M concentration in the donor solution. The low volume of a strong NaOH solution served to effectively reduce dilution of the sample prior to LLLME. LLLME was performed for 45 min by utilizing a  $10^{-1}$  M solution of HCl inside the porous hollow fiber. As illustrated in Figures 5 and 6, methamphetamine was effectively preconcentrated also from the biological samples. In both cases, an enrichment factor of approximately 75 was obtained, which provided a 5 ng/mL detection limit ( $S/N = 3$ ). The enrichment factors indicated that LLLME of methamphetamine was not influenced by the high ionic strength of urine or by the proteins present in human plasma. The concentration range available with LLLME/CE was highly relevant for the monitoring of methamphetamine in human urine and plasma. In addition to excellent enrichment, a high sample cleanup potential was observed for LLLME in connection with the biological samples. For drug-free plasma, only a few other peaks emerged in the electropherograms



**Figure 5.** Preconcentration of 100 ng/mL methamphetamine from human urine: CE buffer, 50 mM phosphate pH 2.75; separation voltage, 15 kV; capillary, 30 cm (effective length)  $\times$  75  $\mu\text{m}$  i.d.; detection, UV at 200 nm.



**Figure 6.** Preconcentration of 100 ng/mL methamphetamine from human plasma: CE buffer, 50 mM phosphate pH 2.75; separation voltage, 15 kV; capillary, 10 cm (effective length)  $\times$  75  $\mu\text{m}$  i.d.; detection, UV at 200 nm.

(Figure 6), which enabled very rapid CE runs in a 10-cm effective length capillary. For human urine, the drug-free samples were also very clean when exposed to LLLME (Figure 5), but a single peak present in the blanks comigrated with methamphetamine when analyzed in 10-cm CE capillaries. Thus, for urine samples, a 30-cm capillary was utilized to ensure sufficient separation of methamphetamine.

**Advantages of LLLME/CE.** The present work has demonstrated a high potential of LLLME/CE based on a porous polypropylene fiber. For methamphetamine present in both human urine and plasma, a 65–80 times enrichment and effective sample cleanup was accomplished with 45 min of LLLME. Owing to the off-line nature of the concept and the low costs of each extraction

unit, a large number of samples were prepared simultaneously. With LLLME in combination with the short CE runs, a large number of samples were analyzed within short time. The cost of each extraction unit was low and each unit was a disposable device utilized only for a single extraction. This was a major advantage because cross-contamination and carry-over effects were totally eliminated. Work is in progress to evaluate the concept for other

basic compounds and for acidic compounds and to fully automate LLLME as an attractive off-line sample preparation technique for CE.

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