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Air sampling with Empore solid phase extraction membranes and online single-channel desorption/liquid chromatography/mass spectrometry analysis: Determination of volatile and semi-volatile organophosphate esters

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Abstract

A method for determining organophosphate esters in air samples using C8 Empore solid phase extraction (SPE) membranes has been developed. After the sampling the analytes trapped in the membrane are completely desorbed with methanol, using an extraction cell connected online to the organic modifier channel of a HPLC gradient pump. The addition of water to the mobile phase prior to analytical chromatography ensures that the analytes are refocused and efficiently separated. Sampling with Empore SPE membranes enables the collection of analytes in both the vapour phase and particulate matter. During the air sampling procedure no losses were observed after 24 h of sampling, yielding a total volume of 14.4 m^3, even for the most volatile compound used in this investigation (trimethylphosphate). Complete desorption was observed for all the organophosphate esters and recoveries were greater than 95%, with a relative standard deviation of less than 8%. The limits of detection ranged between 0.4 and 19 pg/m^3. The effect of particulate matter on the extraction efficiency was investigated in detail by spiking the membranes with reference standard material. It was also found that the SPE membranes could be stored for at least 5 days at room temperature without any evidence of loss. The efficacy of the method was verified using real samples from different common indoor environments. Interestingly, significant quantities of several phosphate esters were found in a NIST standard reference material (urban dust, SRM 1649a).

Keywords: Air sampling; Air analysis; Online; Single-channel desorption; Dynamic solvent extraction; Extraction methods; LC-MS; Volatile; Semi-volatile; Organophosphate esters; Empore disk; Solid phase extraction; SPE; Membranes; Particulate matter; Urban dust; Environmental analysis; Organophosphorus compounds; Phosphate

1. Introduction

Solid phase extraction (SPE) membranes are most commonly used for the extraction of liquid samples [1]. Just recently the use of SPE membranes in air sampling has been reported [2–4]. The use of SPE cartridges in air sampling has been described in several publications [5–7]. The main advantage of using SPE membranes, as opposed to the conventional SPE cartridges, is the higher permeability of the former due to their higher surface area to volume ratio, which allows higher sampling flow rates.

The Empore SPE membrane consists of polytetraflouroethylene (PTFE) fibrils impregnated with small particles of a solid sorbent e.g. C8. Airborne analytes are absorbed in the C8 phase and thus trapped, giving the membrane a high sampling capacity and simplifying the storage of the samples. The filtering efficiency of Empore membranes, which have 0.5 μm pores, was recently evaluated using a scanning mobility particle sizer (SMPS) [8]. The cited study, in which the test particles had sizes ranging from 8 to 500 nm, demonstrated that even particles as small as 8 nm are retained in the membrane at pumping rates of up to 20 l/min.

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SPE membranes are suitable for online coupling with HPLC (in a fashion analogous to conventional online SPE-HPLC). Online desorption of the analytes greatly simplifies sample preparation and reduces analysis time. Furthermore, the risks of contamination and non-reproducible sample losses are minimized, and the injection of the entire extracted sample decreases the limit of detection. However, desorbing the analytes directly with the mobile phase requires a more retentive stationary phase in the analytical column in order to refocus the analytes. The possibility of performing the desorption of vapour phase samples on C18 SPE membranes online with LC-MS was investigated in a previous study in which analytes were refocused using a porous graphitic carbon analytical column [3].

Organophosphate esters (OPEs) are a heterogeneous group with large structural variations among their substituents; these differences give rise to widely varying chemical and physical properties. For example, the vapour pressure of trimethyl phosphate is 0.86 mmHg, whereas that of triphenyl phosphate is 6.28×10^{-6} mmHg. These differences make the organophosphate esters ideal target compounds for assessing the utility of the Empore disk as an air sampling device for both volatile and semi-volatile compounds.

OPEs are considered to be ubiquitous priority pollutants in indoor air. These compounds are used as additive flame retardants and plasticizers in numerous products, notably plastics and electronic goods. Because they are not covalently bonded to the other constituents of these materials, they can migrate from the material to the surrounding air and thus pose potential risks [9–11]. OPEs have been sampled using glass fibre filters [12,13], SPE cartridges [14] or SPME [15–17]. Several accounts of investigations into the occurrence of organophosphate esters in indoor environments have been published previously [18–20]. Weschler [21] have identified tris(2-butoxyethyl) and tris(2-chloroethyl) phosphate in office building air, and Wilkins et al. [22] reported the presence of tri(*n*-butyl) and tris(2-chloroethyl) phosphates in dust from office floors. Nine different organophosphate esters were identified and studied in air samples collected in common indoor work environments by Carlsson et al. [11]. Furthermore, it has been shown that the plastic material in the outer covers of computer video display units (VDUs) is a significant source of triphenyl phosphate in indoor environments housing computers [23].

Several biological effects of exposure to organophosphate esters have been reported, including contact allergy to triphenyl phosphate [24], which has also been shown to be a powerful inhibitor of the monocyte carboxylase in human blood [25]. In studies of rats and mice, tri(2-chloroethyl) phosphate has shown neurotoxic and carcinogenic properties [26]. Furthermore, tri(2-chloroethyl) phosphate and tri(chloropropyl) phosphate have exhibited gonadotoxic effects when tested on rats [27,28].

The aim of the study reported here was to develop a fast and efficient method for determining volatile and semi-volatile organic compounds in air samples, expanding the analysis range up to the most volatile trimethylphospate and taking into account the possible effects of particulate matter (PM). A novel setup for online desorption, the single-channel, that solves problems related to the refocusing of the analytes on the analytical column, was also developed. The method was used for determining OPEs in real air samples from different indoor environments.

2. Experimental

2.1. Chemicals

Trimethyl (TMP, 99%), triethyl (TEP, 99%), tri-*n*-propyl (TPP, 99%), tri-*n*-butyl (TBP), tris(2-chloroethyl) (TClEP 97%) and triphenyl phosphate (TPhP) were all purchased from Sigma–Aldrich (Milwaukee, WI, USA). Tris(chloropropyl) phosphate (TClPP, 100%) was provided by Akzo Nobel (Herkenbosch, the Netherlands), as a mixture of three isomers. Deuterated triphenyl phosphate was used as an internal and volumetric standard and was synthesized in the laboratory [29]. HPLC grade methanol was purchased from BDH (Poole, U.K.), acetone from Merck (Darmstadt, Germany) and trifluoroacetic acid from Riedel-de Haën (Seelze, Germany).

2.2. Air sampling

Air sampling was performed using a previously described [3] sample holder made of anodized aluminium containing a 47 mm Empore C8 solid phase extraction membrane made by 3 M (St. Paul, MN, USA). The membrane was supported by a stainless steel net and kept in place by two Teflon rings. Prior to use, the membranes were washed in a glass frit Büchner funnel, first with 5 ml × 5 ml of acetone and then with 5 ml × 5 ml of methanol, after which they were air-dried. The pump used for the sampling was a VDE 0530 KNF (Neuberger, Freiburg, Germany) with a flow rate of 15 l/min.

For breakthrough experiments a vial containing TMP was placed inside a dessicator and the atmosphere in the headspace was pumped through a silicon rubber tube connected to the membrane holder. In order to allow a small continuous release of TMP, a GC syringe needle was inserted in the vial cap. For recovery and desorption experiments the membrane was placed in the holder and spiked with a standard solution using an HPLC syringe while the air pump was operating.

In the storage experiments, the most volatile phosphate esters (TMP, TEP and TPP) were collected from the dessicator over a 12 h period, after which the membrane was cut into four pieces. Two pieces were individually weighed and extracted by sonication in 4 ml of methanol for 20 min, while the other two were stored in darkness at room temperature for 5 days prior to weighing and extraction.

2.3. Online desorption

After sampling, each SPE membrane was folded twice and cut into six small pieces that were inserted into a stainless steel extraction cell (45 mm × 4.6 mm). The cell was connected to the LC-MS system via the switch valve of the LC-MS detector, as illustrated in Fig. 1, and filled with water using a Shimadzu