



A green approach for organophosphate ester determination in airborne particulate matter: Microwave-assisted extraction using hydroalcoholic mixture coupled with solid-phase microextraction gas chromatography-tandem mass spectrometry

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ARTICLE INFO

Keywords:

Organophosphate flame retardants
Experimental design
Microwave-assisted extraction MAE
Solid-phase microextraction SPME
Gas chromatography
Particulate matter

ABSTRACT

Particulate matter (PM) is among the most dangerous air pollutants, and there is a growing concern related to the effects of airborne particles on human health. Their harmful effects can be derived directly linked to the size of particles themselves and the associated pollutants after they have been taken up by inhalation. In this work was developed a new analytical method for the quantification of organophosphorus esters (OPE) bound to airborne PM. The proposed protocol provides for the microwave-assisted extraction (MAE) of the analytes from the PM followed by solid-phase microextraction gas chromatography-tandem mass spectrometry determination (SPME-GC-MS/MS). Unlike to the traditional protocol, which provides for the use of tedious Soxhlet extraction with environmentally damaging organic solvents, the proposed method allows for a reliable quantification by using an eco-friendly hydroalcoholic mixture (water/ethanol; 50:50, v/v). The method was developed using as target compounds ten organophosphate esters, namely tripropyl phosphate (TPP), tri-n-butyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tributoxyethyl phosphate (TBEP), triphenyl phosphate (TPhP), 2-ethylhexyl-diphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP) and tricresyl phosphate (TCP). The extraction performance of five SPME fibers was evaluated and the DVB/CAR/PDMS coating demonstrated to be the most suitable for the extraction of the target analytes. Experimental Design was used for the multivariate optimization of the parameters affecting the MAE process as well as the SPME extraction, and the optimal working conditions were determined by using Derringer's desirability function. The developed method was validated in terms of linearity, sensitivity (LLOQ values of 0.5 ng/mL for TDCPP and 0.1 ng/mL for the other analytes), matrix effect (81–117%), intra and inter day accuracy (83–115% and 80–115%, respectively), and precision (repeatability and reproducibility in the range 1.0–12.4% and 2.3–15.2%, respectively). The satisfactory performances reached make the proposed protocol a green and high-throughput alternative for OPE quantification in particulate matter.

1. Introduction

Organophosphate esters (OPEs) are synthetic derivatives of phosphoric acid with different substitutes including alkyl chains, aromatic functions, as well as partly halogenated alkyl chains. Due to the varying nature of the substituents, OPEs have a wide range of physical-chemical properties and several applications. Non-halogenated OPEs are widely applied as plasticizers, antifoaming agents, additives in rubber, textiles,

and lacquers, while halogenated OPEs are mainly used as flame retardants (FRs) to prevent ignition of materials such as furniture and electric and electronic instruments [1,2]. As a result, in recent years global consumption of OPEs has increased sharply. They are used as semi-volatile additives that are not covalently bound but just mixed to polymer matrices; consequently, they could easily leak into the environment via volatilization, abrasion, and dissolution, depending on the vapor pressure of the compound and the temperature. Moreover,

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<https://doi.org/10.1016/j.talanta.2018.07.077>

Received 22 April 2018; Received in revised form 19 July 2018; Accepted 23 July 2018

Available online 24 July 2018

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OPEs are relatively stable toward biodegradation, especially the chlorinated ones, such as tris(1-chloro-2-propyl) phosphate (TCPP) [3], and several studies report that once in the environment, OPEs may undergo long-range atmospheric transport to even remote regions of the world. This environmental behavior has resulted in their presence in almost every environmental compartment including wastewater and sludge [4–6], groundwater [7], sediment and soils [8,9], fish and biota [10–12], air and dust [13–18], and human plasma [19]. Their ubiquitous distribution in both indoor and outdoor environments has motivated the development of various analytical procedures to understand the fate and risk of this class of emerging pollutants. Many studies have been reported for the determination of OPEs in various environmental matrices including waters [20–22], soils [23], air [20,21,24], biota, and sediments [22]. In this context, we have recently proposed a method for the analysis of organophosphate flame retardant in environmental waters by using microextraction by packed sorbent (MEPS) coupled with gas chromatography-tandem mass spectrometry detection [25].

The main toxic effects of OPEs include eye and skin irritation, carcinogenicity, dermatitis, and neurotoxicity [1,14,26,27] and, in particular among the chlorinated OPEs, tri(2-chloroethyl) phosphate (TCEP), tri(dichloropropyl) phosphate (TDCPP) and TCPP are suspected of being carcinogenic [20,28]. Exposure through inhalation is directly dependent on the concentration of OPEs in the air, which can be in the form of gas-phase particles or bounded to particulate matter (PM). Several studies reported that OPEs are mostly associated with the airborne particles [14,29,30].

The analysis of OPEs in solid matrices has usually been carried out by combining an extraction step, often followed by a clean-up procedure, with a final determination using gas or liquid chromatography coupled to tandem mass spectrometry [31–33], nitrogen-phosphorous detector (NPD) [34] or inductively coupled plasma mass spectrometry [8]. Most of the studies about organophosphate esters used Soxhlet [29,30,35] or ultrasonic [2,36] extraction as sample preparation techniques, with hexane, acetone or chlorinated solvents (e.g., methylene chloride) as extraction solvents. More recently, microwave-assisted extraction has been proposed as a suitable alternative for the extraction of organophosphorus esters from solid matrices [8,9] because of its advantages over the traditional extraction modes such as the reduced solvent volume and extraction time as well as the improved reproducibility and recovery of analytes. In this regard, Ericson et al. proposed a lab-made dynamic microwave-assisted extraction system for OPE analysis in indoor air [37], whereas more recently a commercial MAE equipment was used for OPE extraction from indoor dust providing fewer contamination problems than Soxhlet [38].

In the work herein presented, we propose an optimized MAE approach for the extraction of OPEs from particulate matter followed by a solid-phase microextraction (SPME) analysis. Our work reports for the first time the use of MAE as a convenient approach for the OPE extraction from PM. The key point of the method is the use of an eco-compatible hydroalcoholic mixture, instead of the traditional organic solvents, which is compatible with the use of the direct immersion solid-phase microextraction (DI-SPME) and can be analyzed without any other clean-up step. SPME is an established sample preparation technique that has many advantages over the traditional approaches including the simultaneous extraction, pre-concentration, and direct introduction of analytes into the gas chromatographic system [39,40]. As a result, SPME has demonstrated to be a simple, solvent-free, reliable and flexible tool to analyze molecules with different physicochemical properties in various matrices [41–43]. Furthermore, analyses were performed using a GC-QqQ-MS system which represents a powerful analytical set-up because the high separation efficiency and reliability of gas chromatography are supported by the high selectivity and sensitivity of tandem mass spectrometry [44,45]. The variables affecting the microwave-assisted extraction and the solid-phase microextraction were optimized by multivariate approaches (i.e., Experimental design) to seek for the best value for each parameter by better exploring the

experimental domain, and taking into account the possible interactions between variables. The developed method was finally tested on particulate matter (PM10) samples collected at the monitoring station of the CNR-Institute of Atmospheric Pollution Research (CNR-IIA) located in a suburban area close to the CNR Research Institute.

2. Experimental

2.1. Chemicals and materials

All analytes [tripropyl phosphate (TPP), tributyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tris(2-butoxyethyl) phosphate (TBEP), triphenyl phosphate (TPHP), (2-ethylhexyl)-diphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP), tricresylphosphate (TCP) (technical mixture of isomers)] were purchased from Sigma–Aldrich (Milan, Italy) (see [Supplementary material; Fig. S1, Table S1](#)). The isotopically labeled compounds tris(2-chloroethyl)phosphate-d12 (TCEP-d12) and tributylphosphate-d27 (TBP-d27) were provided by Cambridge Isotope Laboratories, Inc. (Andover, MA, USA) whereas the triphenylphosphate-d15 (TPHP-d15) was bought from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). Ethanol (EtOH) and acetone were purchased from Fluka (Buchs, Switzerland), acetonitrile (ACN) from VWR Chemicals (France) and dichloromethane (DCM) from Riedel-de-Haën (Seelze, Germany). Strata C18-E cartridge (500 mg) was provided by Phenomenex (Torrance, CA, USA). Tissuquartz™ filters 2500 QAT-UP (47 mm dia) were purchased from Pall Life Sciences (Port Washington, NY; distributed by VWR Chemicals). The tested solid-phase microextraction fibers (polydimethylsiloxane 100 μm (PDMS), polyacrylate 85 μm (PA), polydimethylsiloxane/divinylbenzene 65 μm (PDMS/DVB), carboxen/polydimethylsiloxane 85 μm (Car/PDMS) and divinylbenzene/carboxen/polydimethylsiloxane 50/30 μm (DVB/Car/PDMS)) were purchased from Supelco (Bellefonte, PA, USA) and conditioned prior to use as recommended by the manufacturer. Aqueous solutions were prepared using ultrapure water obtained from a Millipore Milli-Q plus system (Bedford, MA).

2.2. Sampling

Particulate matter with aerodynamic diameter < 10 μm (PM 10) was collected on quartz fiber filters (QFFs) of 47 mm in diameter using a Tecora Echo PM (TCR Tecora, Italy) device provided with a PM10 size-selective inlet head according to the European Standard UNI EN 12341:2014. A sampling flow of 2.3 m³ h⁻¹ (38.33 L min⁻¹) and a sampling time of 24 h were used providing a total volume of filtered air approximately of 55 m³. Prior to sampling, filters were first pre-cleaned by overnight soaking in acetone and, after dried, they were conditioned according to EN 12341:2014 standard, at the temperature and the relative humidity of 20 ± 1 °C and 50 ± 5%, respectively, for at least 48 h. Later, each filter was weighted using a microbalance Crystal Micro (Gibertini, Novate, Italy) and stored in an aluminum foil. PM 10 samples were collected in a suburban site close to the CNR-IIA, located in Rende, near to Cosenza's city great urban area (Italy, 39°21'27.2"N 16°13'53.7"E). Immediately after collection, the quartz filters were wrapped in aluminum foil and stored at -20 °C until analysis, in order to prevent changes in the sample composition or the OPE concentration.

2.3. Analytical procedure

2.3.1. MAE conditions

The extraction of organophosphate esters was carried out using an Ethos-Up Microwave Extraction System (Milestone, Leutkirch, Germany), equipped with 50 mL volume PTFE vessels. Before analysis, each filter was spiked with 100 μL of a mixture of internal standards

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