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Thermal desorption-gas chromatography–mass spectrometry method to determine phthalate and organophosphate esters from air samples☆

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ABSTRACT

A method based on thermal desorption-gas chromatography–mass spectrometry (TD-GC–MS) has been developed to determine four organophosphate esters, seven phthalate esters, and bis(2-ethylhexyl) adipate in the gas phase from harbour and urban air samples. The method involves the sampling of 1.5 L of air in a Tenax TA sorbent tube followed by thermal desorption (using a Tenax TA cryogenic trap) coupled to gas chromatography–mass spectrometry. The repeatability of the method expressed as %RSD ($n = 3$) is less than 15% and the MQLs are between 0.007 $\mu g\,m^{-3}$ (DMP, TBP, BBP, TPP and DnOP) and 6.7 $\mu g\,m^{-3}$ (DEHP). The method was successfully applied in two areas (urban and harbour) testing two and three points in each one, respectively. Some of these compounds were found in both urban and harbour samples. Di-(2-ethylhexyl)phthalate was the most abundant compound found in both areas at concentration levels between 6.7 $\mu g\,m^{-3}$ and 136.4 $\mu g\,m^{-3}$. This study demonstrates that thermal desorption is an efficient method for the determination of these semi-volatile compounds in the gas phase fraction of air samples

1. Introduction

Bis(2-ethylhexyl) adipate (DEHA), phthalate and organophosphate esters are a group of organic compounds frequently used as additives to modify physical properties (resistance and mouldability) of some polymeric materials and they are classified as semi-volatile due to their high boiling points and their low vapour pressure. Some phthalate esters such as dimethyl phthalate (DMP), diethyl phthalate (DEP), butyl benzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DnOP) are widely used as plasticisers in food wrappers, toys and facial and nail cosmetic products [1,2]. Moreover, DEHA and phthalate esters are mainly used as plasticisers in polymeric materials such as cellulose esters and vinyl chloride copolymers (PVC) [3]. In contrast, organophosphate esters are typically used as flame retardants, stabilisers and plasticisers in a variety of products such as tissues and materials for construction and furniture [4–6].

Some studies from the World Health Organisation (WHO) have demonstrated that this group of plasticisers has different biologic effects in humans and animals [7]. Organophosphate esters may cause skin irritation problems and phthalate esters could affect the mobility of human sperm and disturbing the reproduction function in humans [8]. Therefore, they are also considered as hormone disruptors [8,9], and the US Environmental Protection Agency (EPA) has also classified BBP and DEHP as possible human carcinogens [10]. The widespread use of phthalate and organophosphate esters and increasing public concern have stimulated the study of these compounds worldwide in a variety of environmental samples, including aerosols [11], particulate matter from indoor and outdoor air [12,13], dust [3,14–16], environmental water [17,18] and even in human matrices such as urine and blood [19].

The broad application range of these compounds may result in their volatilisation spreading diffusively into the environment [20]. Due to the physical properties of these plasticisers mentioned above, they can be found in the atmosphere attached on particulate matter or in the gas phase in different environments such as offices [21], workplaces [6], private homes [22], laboratories [22], newly-built houses [23] and others.

Organophosphate and phthalate esters are determined by liquid chromatography (LC–MS) [24–26] and gas chromatography coupled to mass spectrometry (GC–MS) [1–5,9,17–19,27]. Nevertheless, GC–MS is the most common technique used for the determination of both groups of compounds because this technique makes their determination easier due to their physical and chemical properties.

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To analyse air samples (particulate matter and/or gas phase), different sampling strategies were reported. Sampling of particulate matter is usually done by passing a high volume of air through to the glass fibre filter which retains the particulate matter depending on the porous size of the filter ($PM_{2.5}$ and PM_{10}). After collection, these filters may be extracted using pressurised liquid extraction [12], ultrasonic assisted extraction [29] and Soxhlet extraction [30], all of these with organic solvents. Moreover, some authors propose the use of thermal desorption for the analysis of filters containing particulate matter [11,13]. On the other hand, sampling techniques of gas phase from air were done passing air through to polyurethane foams (PUF) [6], SPE cartridges [3] or thermal desorption sorbent tubes [28,31]. PUF and SPE cartridges were used to determine organophosphate and phthalate esters, but thermal desorption sorbent tubes was only applied to determine phthalate esters from indoor and outdoor air samples.

Some studies about the determination of phthalate and organophosphate esters in air samples using thermal desorption have been previously reported. Ho et al. [11] evaluated an in-injection port thermal desorption-gas chromatography method for non-polar organic compounds in ambient aerosols samples and demonstrated the suitability of desorption technique to determine some phthalates using a quartz fibre filter inserted into a tube. Moreover, Tienpont et al. [28] have also evaluated a sorptive enrichment on sorption tubes packed with 5% polydimethylsiloxane (PDMS) coated support followed by on-line GC–MS for the analysis of phthalates in gas phase.

Some phthalates are ubiquitous compounds present in common laboratory equipment and then [14], to minimise contamination problems related to sample treatment, thermal desorption is a good option when these compounds are studied in air samples. This technique is environmentally friendly (organic solvent-free), rapid and simple to run, no dilution of the sample with a high desorption efficiency and it operates with an on-line process coupled to GC system. In recent years, a number of studies have demonstrated that this technique is very suitable for determining volatile compounds. However, this technique may also be useful for the determination of semi-volatile compounds because it is more sensitive than others techniques based on liquid desorption [32,33]. Thermal desorption application is limited depending on the compounds studied because in some cases, when the compounds studied do not have low vapour pressures or thermal stability it cannot be applied. Moreover, its does not allow a repetition of the analysis because TD is a destructive technique.

The presence of some organophosphate esters in particulate matter samples from indoor air collected on glass fibre filter was studied by Sanchez et al. [22] and Björklund et al. [21], being TPP and TEP the most frequently compounds determined at concentration levels between 0.494 ng m^{-3} and 35.3 ng m^{-3} [22] and between <LOD and 10 ng m^{-3} [21], respectively., Other studies have also reported the presence of some phthalates [12,23,27] and organophosphate esters [12,23] in indoor and outdoor air samples using glass fibre filters. The concentrations found in these studies show that the most abundant compounds were found in indoor air at maximum concentration levels of 2500 ng m^{-3} (DEP), 1700 ng m^{-3} (DiBP) and 1046 ng m^{-3} (DEHP). Moreover, phthalate esters were determined in particulate matter from indoor air in a semi-volatile multiresidue method based on thermal desorption of sampling glass fibre filter [13]. In this study, the highest concentration levels were for DiBP (115 ng m^{-3}) and DEHP (113 ng m^{-3}).

Sjödin et al. [6] and García-Jares et al. [14] reported the analysis of some phthalate and organophosphate esters associated to the particles in gas phase from indoor air using polyurethane foams (PUF). These studies show that one of the major organophosphate ester found was TPP at concentration values between 12 ng m^{-3} and 40 ng m^{-3}. Bergh et al. [3] and Toda et al. [34] studied both group of compounds in indoor air using SPE cartridges. Tri(2-chloroisopropyl) phosphate (TCiPP) (172 ng m^{-3}) and TBP (320 ng m^{-3}) were the compounds found at maximum concentration levels in each study, respectively. On the other hand, DBP was the most relevant phthalate ester found in both studies at concentration levels up to 780 ng m^{-3}. In addition, the presence of some phthalate esters was studied in gas phase from air [28,31]. Depending on the environment studied, the concentration values were from non detectable concentration in rural area to 1000 ng m^{-3} (DiBP and DEHP) in a laboratory or parking areas. Moreover, organophosphate esters have also been detected in snow and it has been suggested that these compounds are subject to long-range air transport [35].

Due to the fact that the occurrence of these compounds in particulate matter from indoor and outdoor air places [3,13,12] and the possibility of determining these kind of pollutants in gas phase supported by previous studies mentioned above, the aim of the present paper is to develop an analytical method to determine the presence of bis(2-ethylhexyl) adipate (DEHA) and phthalate and organophosphate esters in gas-phase air samples from a harbour and urban areas by thermal desorption-gas chromatography–mass spectrometry and to demonstrate the applicability of TD-GC–MS for the determination of semivolatile compounds. This is the first time that organophosphate esters have been determined in gas phase from outdoor air samples by thermal desorption-gas chromatography–mass spectrometry (TD-GC–MS).

2. Experimental

2.1. Reagents and solutions

The standards used were bis(2-ethylhexyl) adipate (DEHA), benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), dimethyl phthalate (DMP), di-*n*-octyl phthalate (DnOP), tributyl phosphate (TBP), triethyl phosphate (TEP), tri-iso-butyl phosphate (TiBP) and triphenyl phosphate (TPP) purchased from Sigma–Aldrich (St. Louis, USA). Chemical structures of target compounds are shown in Table 1. Each compound was dissolved in ethyl acetate (GC grade with >99% purity, supplied by Prolabo VWR, Llinars del Vallès, Spain) at a concentration of 1000 mg L^{-1}. A mixed solution of 10 mg L^{-1} was prepared freshly with ethyl acetate. All solutions were stored in the freezer at 4 °C.

Helium gas with 99.999% purity (Carburos Metálicos, Barcelona, Spain) was used for the chromatographic analysis.

2.2. Sorbent tubes and trap

Two kinds of stainless steel tubes (Markes International Limited, Llantrisant, UK, length 9 cm × 6.35 mm o.d × 5 mm i.d.) containing a sorbent bed of Tenax TA and multisorbent bed Tenax/Carbograph 1TD of about 350 mg were tested.

These cartridges were respectively used in combination with two kinds of cryogenic traps (also from Markes): a Tenax trap (filled with Tenax TA) and a general purpose hydrophobic trap (filled with Tenax TA and Carbograph 1TD).

Sampling tubes were cleaned before and after each use with 99.999% pure nitrogen gas at a flow of 100 mL min^{-1} at 335 °C, for 30 min, in line with the supplier's recommendations.

The clean tubes were capped with ¼ inch brass long-term storage caps with ¼ inch combined PTFE ferrules, stored in hermetically sealable glass jars in order to prevent any ambient contamination.