Trends in Analytical Chemistry 91 (2017) 77–90

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Determination of phthalate esters in air with thermal desorption technique – Advantages and disadvantages

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ARTICLE INFO

Article history:
Available online 7 April 2017

Keywords:
Phthalate esters
Thermal desorption
Indoor air
Outdoor air
Air samples

ABSTRACT

Phthalate esters are widely used in production of polymer materials (approximately five millions tones annually), therefore they occur in final products (food packages, cosmetics, vinyl products) and undergo emission into the environment. Phthalates have a negative impact on living organisms (e.g. disturbing function of endocrine/reproductive systems) and some of them are restricted (REACH, U.S. CPSC). Investigating their occurrence in the environment, especially indoor/outdoor air, is very important. After several improvements in recent years (e.g. heating/cooling efficiency), sorption of analytes on sorbent followed by thermal desorption (TD) and GC–MS seems to be the best suited protocol to determine phthalates in air samples. It is a straightforward technique, without dilution of samples and use of toxic solvents. However, it cannot be applied to compounds which are thermally unstable and have a low vapor pressure. Overall, TD it is one of the best available technique for desorption of phthalates from a sorbent.

1. Introduction

Phthalates esters are a group of synthetic chemical compounds (Table 1) that are commonly used in a variety of consumer products. The annual global consumption of phthalates is estimated to be around five millions tones and they consist 87% of all used plasticizers [3]. Long chain phthalates are added as plasticizers in polyvinyl chloride (PVC) plastics, adhesives, food packaging, medical products (blood transfusion bags, intravenous fluid bags, tubing, gloves), pharmaceutical coatings, automotive parts, children's toys, vinyl products (e.g. flooring, shower curtains, rain coats), shoes, table cloths, floor tiles, furniture upholstery.

Phthalates are added as plasticizers (up to 50% by weight of them in PVC) to increase flexibility and durability of synthetic polymers. Short-chain phthalates are used in formulation of perfumes, creams, nail polishes, baby lotions and house fragrances. Phthalates are also used as solvents to hold fragrance, reduce cracking of nail polish, reduce stiffness of hair spray, make products more effectively penetrate and moisturize the skin. Phthalate esters are linked non-covalently to the polymer chains; hence, they may be leached into the environment and are ubiquitously found in air (from <LOQ to few thousands ng/m^3; up to 7 × 10^6 ng/m^3 in industrial areas – detailed data are presented in Section 5. Concentration of phthalates in air samples and Table 6), water (from <LOQ to tens μg/L; up to 0.5 × 10^6 μg/L), soils (from <LOQ to few hundred mg/kg d.w.), sediments (from <LOQ to tens mg/kg d.w.), food (from <LOQ to ten mg/kg – vegetables; from <LOQ to tens μg/L – alcohol drinks) and living organisms (from <LOQ to few hundred mg/kg – fish muscles; from <LOQ to few hundred μg/L – human fluids as monophthalates) [4–14].

Phthalates are classified as semivolatile and low volatile chemical compounds. Due to the fact that phthalates are only physically bound to the polymer, which are used in wide ranges of temperature conditions, pressure and humidity, and also during contact with other substances, it causes their release from

Abbreviations: BBP, Butylbenzyl phthalate; BEP, Butyl-2-ethylhexyl phthalate; CIS, Temperature programmable cooled injection system; CPSC, Consumer Product Safety Commission; CS_2, Carbon disulfide; DAP, Diamyl-phthalate ester; DBP, Dibutyl-phthalate ester; DDP, Didecyl-phthalate ester; DEHP, Bis(2-ethylhexyl)-phthalate ester; DEHA, Di(2-ethylhexyl)adipate; DEP, Diethyl-phthalate ester; DiBP, Di-isobutyl phthalate; DiDP, Di-isodecyl phthalate; DiNP, Di-isononyl phthalate; DMP, Dimethyl-phthalate ester; DNP, Di-*n*-nonyl-phthalate ester; DOP, Di-*n*-octyl-phthalate ester; DPHP, bis(2-propylheptyl) phthalate; EI, Electron ionization; FID, Flame ionization detector; GC, Gas chromatography; IT, Ion trap; LOD, Limit of detection; MS, Mass spectrometry; MTBE, Methyl-*tert*-butyl ether; PDMS, Polydimethylsiloxane; PTV, Programmed temperature vaporizing; PUF, Polyurethane foam; RSD, Relative standard deviation; SE, Solvent extraction; TD, Thermal desorption; TDS, Thermodesorption system; TIGF, Teflon impregnated glass-fiber filters.

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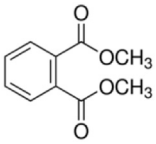
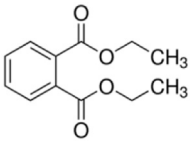
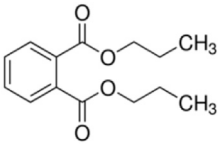
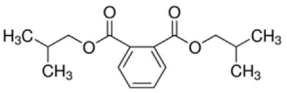
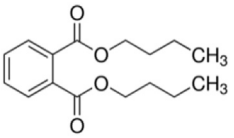
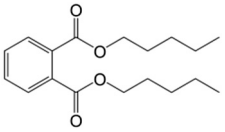
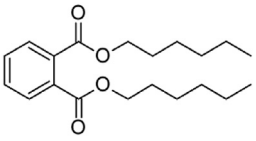
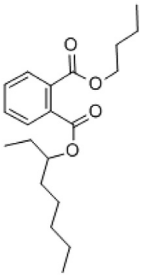
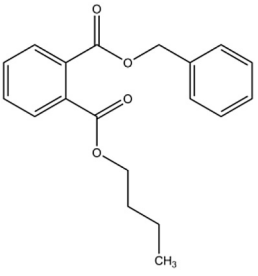
http://dx.doi.org/10.1016/j.trac.2017.04.002
0165-9936/

Table 1
Basic information on compounds from the group of phthalates [1,2].

Compounds	Acronym	Molecular formula	Molecular structure	Molecular weight [g/mol]	Vapor pressure, t = 25°C [Pa]	Boiling point [°C]
Dimethyl phthalate	DMP	$C_{10}H_{10}O_4$		194	2.63×10^{-1}	282
Diethyl phthalate	DEP	$C_{12}H_{14}O_4$		222	6.48×10^{-2}	298
Di-*n*-propyl phthalate	DPRP	$C_{14}H_{18}O_4$		250	1.75×10^{-2}	317
Diisobutyl phthalate	DiBP[c]	$C_{16}H_{22}O_4$		278	4.73×10^{-3}	327
Di-*n*-butyl phthalate	DBP[a,c]	$C_{16}H_{22}O_4$		278	4.73×10^{-3}	340
Di-*n*-pentyl phthalate	DPP	$C_{18}H_{26}O_4$		306	1.28×10^{-3}	342
Di-*n*-hexyl phthalate	DHP	$C_{20}H_{30}O_4$		334	3.45×10^{-4}	350
Butyl-2-ethylhexyl phthalate	BEP	$C_{20}H_{30}O_4$		334	2.36×10^{-5}	359
Butylbenzyl phthalate	BBP[a,c]	$C_{19}H_{20}O_4$		312	2.49×10^{-3}	379