# Optimisation steps of an innovative air sampling method for semi volatile organic compounds

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## HIGHLIGHTS

- An innovative method for the measurement several groups of SVOCs in air has been optimised.
- As the method collects gaseous as well as particulate matter SVOCs, it avoids underestimating the total air concentration.
- The applicability of the method to sample PAHs, PCBs and PEs from different urban environments was confirmed.
- The presented strategy reduces the risk of contamination during sample preparation steps compared to more traditional techniques.

## ARTICLE INFO

## ABSTRACT

This work describes optimisation steps of an innovative method for the measurement several groups of semi-volatile organic compounds (SVOCs) in air, collecting both gaseous and particulate air fractions. It is based on active air sampling on sorption tubes (consisting of polydimethylsiloxane (PDMS) and Tenax TA), followed by thermal desorption and gas chromatography mass spectrometry analysis (TD–GC–MS). The optimised method was validated in the laboratory for the measurement of selected target compounds from the following chemical classes: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and phthalate esters (PEs). It was applied in different Belgian urban outdoor as well as indoor environments. The new method is characterised by limits of detection in the range of 0.003–0.3 ng m$^{-3}$ for PAHs, 0.004–0.2 ng m$^{-3}$ for PCBs, 0.113 –0.201 ng m$^{-3}$ for PBDEs and 0.002–0.2 ng m$^{-3}$ for PEs, a linearity of 0.996 and a repeatability of less than 10% for all studied compounds.

## 1. Introduction

According to the definition of the World Health Organisation (WHO), semi-volatile organic compounds (SVOCs) are organic chemicals with boiling points ranging from 240–260 °C to 380–400 °C (World Health Organization, 1989). This range covers a large number of compounds that are present in outdoor and indoor air (e.g. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), phthalate esters (PEs). These classes of compounds may occur in meaningful abundances both in the gas phase and on the surface of airborne particles, which recognises them as a human health concern. Although in recent years, the study of the occurrence, fate and

human exposure to these compounds has become an important research topic, SVOCs have not been so widely studied as certain other classes of air pollutants such as VOCs, airborne particles and inorganic gaseous pollutants (Weschler and Nazaroff, 2008). The high degree of analytical challenges in measuring SVOCs has impeded progress in studying them.

Sampling of SVOCs is mostly done by the collection of both the gas and the particle phase, using high volume samplers. In most cases the particulate phase is trapped on a filter (quartz or glass fibre) and the breakthrough of the gas phase is subsequently trapped on a sorbent (PUF or XAD) (EN ISO 16000–13, 2008; Batterman et al., 2009; Elflein et al., 2003). A widely used method for sample treatment after collecting several m$^3$ of air, is solvent desorption of the filters (Soxhlet extraction, accelerated solvent extraction, sonication) followed by analysing the compounds of interest by GC–MS (gas chromatography coupled to mass chromatography) or HPLC techniques. There are several limitations and

disadvantages related to this traditional method for sampling and detection of SVOCs. These include the lower sampling efficiency of compounds with higher vapour pressure (Bidleman et al., 1986) and the underestimation of the actual content caused by filter reactions with oxidative gases (Schauer et al., 2003). The method also implies the use of high-volume sampling pumps, which are not suitable for personal and indoor air sampling (due to dimensions and noise nuisance) and need electricity power supply, which is not always convenient when sampling outdoors. Another disadvantage is that the analysis method is time-consuming and requires the samples to be manipulated, which means that there is considerable risk of contamination and/or losing some of the compounds.

Several new methods, based on diffusion denuders (Temime et al., 2002), passive samplers (Wania et al., 2003; Namiesnik et al., 2005; Ni et al., 2007; May et al., 2011), sorbent-impregnated filters (Galarneau et al., 2006) or molecular imprinted polymers (Krupadam et al., 2010) have been developed as alternatives for the high-volume sampling method. These methods have advantages compared to the high-volume sampling method, such as more efficient sampling of the compounds with higher vapour pressure (diffusion denuders), elimination of pumping unit (passive samplers) and reduction in size, simplified sample handling and decrease in solvent consumption (sorbent-impregnated filters, molecular imprinted polymers). However, those methods have other disadvantages such as long sampling time (denuders and passive samplers), and possible losses due to photo degradation reactions (passive samplers) that are not excluded as well.

As an alternative for these methods, Wauters et al. (2008) have introduced another method for PAHs sampling, based on active sampling on sorption tubes consisting of polydimethylsiloxane (PDMS) foam, PDMS particles and a Tenax TA bed, followed by thermal desorption and analysis by GC–MS. The method is characterised by the advantages to only require low flow sampling (using quasi noiseless and portable sampling pumps), and to considerably reduce the risk of contamination during the sample preparation and analysis steps.

The main objective of this reported study is to explore the possibilities of using the mixed bed sampling method to sample and analyse different classes of SVOCs, by performing several optimisation steps. The optimised method was validated for measurement of the listed target compounds (see Table 1) in different Belgian urban outdoor as well as indoor environments.

## 2. Material and methods

High purity standards (98.0–99.9%) were used in this study. The standard calibration mix of PAHs in methylene chloride with a concentration 2000 μg mL$^{-1}$ was purchased from Restek, USA. Deuterated PAHs (d8-naphthalene, d10-fluorene, d10-fluoranthene, d12-benzo(a)pyrene and d12-benzo(g,h,i)perylene) and PCBs were purchased from Promochem/C.N. Schmidt, The Netherlands. PBDEs standards were purchased from Wellington Laboratories, Canada. All standard solutions were prepared by dilution in methanol. The solvents were GC grade with purity >99.9% (Merck, Germany). The standard reference material of PAHs (ERM-AC213) was purchased from Institute for Reference Materials and Measurements (IRMM, Belgium). Nitrogen gas of 99.999% purity was used for spiking the thermal desorption sorbent tubes and 99.999% pure helium gas was used for chromatographic analysis.

### 2.1. Sampling

Air samples were collected by active air sampling with a constant flow air sampling pump GSA SG350 (GSA Messgerätebau

**Table 1**
Target compounds and respective retention times and the quantification ion studied in air.

| Compound | RT, min | Q, m/z |
|---|---|---|
| **PAHs** | | |
| Naphthalene (cas no 91-20-3) | 8.20 | 128 |
| Acenaphthylene (cas no 208-96-8) | 10.15 | 152 |
| Acenaphthene (cas no 83-32-9) | 10.33 | 153 |
| Fluorene (cas no 86-73-7) | 10.88 | 166 |
| Phenanthrene (cas no 85-01-8) | 12.00 | 178 |
| Anthracene (cas no 120-12-7) | 12.07 | 178 |
| Fluoranthene (cas no 206-44-0) | 13.94 | 202 |
| Pyrene (cas no 129-00-0) | 14.40 | 202 |
| Benz(a)anthracene (cas no 56-55-3) | 17.63 | 228 |
| Chrysene (cas no 218-01-9) | 17.74 | 228 |
| Benzo(b)fluoranthene (cas no 205-99-2) | 21.20 | 252 |
| Benzo(k)fluoranthene (cas no 207-08-9) | 21.30 | 252 |
| Benzo(a)pyrene (cas no 50-32-8) | 22.28 | 252 |
| Dibenz(a,h)anthracene (cas no 53-70-3) | 26.01 | 276 |
| Benzo(g,h,i)perylene (cas no 191-24-2) | 26.68 | 278 |
| Indeno(1,2,3-cd)pyrene(cas no 193-39-5) | 25.88 | 276 |
| **PCBs** | | |
| 2,4,4′-trichlorobiphenyl (PCB-28) (cas no 7012-37-5) | 13.93 | 256 |
| 2,2′,5,5′-tetrachlorobiphenyl (PCB-52) (cas no 35693-99-3) | 14.20 | 292 |
| 2,2′,4,5,5′-pentachlorobiphenyl (PCB-101) (cas no 37680-73-2) | 14.99 | 326 |
| 2,3′,4,4′,5-pentachlorobiphenyl (PCB-118) (cas no 31508-00-6) | 15.67 | 326 |
| 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB-138) (cas no 35065-28-2) | 16.25 | 360 |
| 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB-153) (cas no 35065-27-1) | 15.90 | 360 |
| 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB-180) (cas no 35065-23-3) | 17.21 | 394 |
| **PBDEs** | | |
| 2,4,4′-Tribromodiphenyl ether (BDE-28) (cas no 41318-75-6) | 22.70 | 406 |
| 2,2′,4,4′-tetra-bromodiphenyl ether (BDE-47) (cas no 5436-43-1) | 24.86 | 486 |
| 2,2′,4,4′,5-penta-bromodiphenyl ether (BDE-99) (cas no 60348-60-9) | 26.83 | 406 |
| **PEs** | | |
| Dimethylphthalate (DMP) (cas no 131-11-3) | 12.61 | 163 |
| Diethylphthalate (DEP) (cas no 84-66-2) | 13.35 | 149 |
| Di-n-butylphthalate (DBP) (cas no 84-74-2) | 15.10 | 149 |
| Benzyl butyl phthalate (BBP) (cas no 85-68-7) | 17.55 | 149 |
| Bis(2-ethylhexyl)adipate (BEHA) (cas no 103-23-1) | 17.75 | 129 |
| Bis(2-ethylhexyl)phthalate (DEHP) (cas no 117-81-7) | 18.87 | 149 |
| Di-n-octyl phthalate (DNOP) (cas no 117-84-0) | 20.45 | 149 |

GmbH). The cartridges for sampling and thermal desorption were stainless-steel tubes (Markes International Ltd.) with the following dimensions: 9 cm length, 6.53 o.d. and 5 mm i.d. and packed with PDMS/Tenax sorbent material. Prior to each use, the sampling tubes were conditioned by thermal cleaning under a nitrogen flow rate of 75 mL min$^{-1}$ at 300 °C for 60 min, sealed with end caps and stored under nitrogen atmosphere to prevent any contamination of the sorbent.

After loading, the samples were immediately sealed again with the end caps and stored under nitrogen atmosphere until analysis. The samples were analysed within seven days after the collection.

### 2.2. Analysis

All the analyses were performed on a TD-GC-MS system, which consisted of a TD100 Thermal desorber (TD) equipped with a multi-