

## Accepted Manuscript

Title: Analysis of industrial contaminants in indoor air. Part 1. Volatile organic compounds, carbonyl compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls

Authors: Ruth Barro, Jorge Regueiro, María Llompart, Carmen Garcia-Jares



PII: S0021-9673(08)01936-5  
DOI: doi:10.1016/j.chroma.2008.10.117  
Reference: CHROMA 349438

To appear in: *Journal of Chromatography A*

Received date: 8-4-2008  
Revised date: 27-10-2008  
Accepted date: 31-10-2008

Please cite this article as: R. Barro, J. Regueiro, M. Llompart, C. Garcia-Jares, Analysis of industrial contaminants in indoor air. Part 1. Volatile organic compounds, carbonyl compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, *Journal of Chromatography A* (2008), doi:10.1016/j.chroma.2008.10.117

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1 **Analysis of industrial contaminants in indoor air. Part 1.**  
2 **Volatile organic compounds, carbonyl compounds, polycyclic**  
3 **aromatic hydrocarbons and polychlorinated biphenyls**

4  
5 **Ruth Barro<sup>a</sup>, Jorge Regueiro<sup>b</sup>, María Llompart<sup>b</sup>, Carmen Garcia-Jares<sup>b\*</sup>**

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7 *<sup>a</sup>CIEMAT (Centro de Investigaciones Energeticas, Medioambientales y Tecnologicas),*  
8 *Ministerio de Ciencia e Innovacion, CEDER-CIEMAT, Carretera Nacional 111*  
9 *Madrid-Soria, km 206, Lubia 42290, Soria, Spain*

10 *<sup>b</sup>Departamento de Quimica Analitica, Nutricion y Bromatologia, Instituto de*  
11 *Investigacion y Analisis Alimentarios, Universidad de Santiago de Compostela,*  
12 *Santiago de Compostela 15782, Spain*

13  
14  
15 \*Corresponding author. Phone: +34-981563100, ext. 14394, fax: +34-981595012

16 E-mail address: carmen.garcia.jares@usc.es

17  
18 **Abstract**

19 This article reviews recent literature on the analysis of industrial contaminants in  
20 indoor air in the framework of the REACH project, which is mainly intended to  
21 improve protection of human health and the environment from the risks of more than 34  
22 millions of chemical substances. Industrial pollutants that can be found in indoor air  
23 may be of very different types and origin, belonging to the volatile organic compounds  
24 (VOCs) and semivolatile organic compounds (SVOCs) categories. Several compounds  
25 have been classified into the priority organic pollutants (POPs) class such as  
26 polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans  
27 (PCDD/PCDFs) and related polychlorinated compounds, and polycyclic aromatic  
28 hydrocarbons (PAHs). Many of these compounds are partially associated to the air gas  
29 phase, but also to the suspended particulate matter. Furthermore, settled dust can act as  
30 a concentrator for the less volatile pollutants and has become a matrix of great concern  
31 for indoors contamination. Main literature considered in this review are papers from the  
32 last ten years reporting analytical developments and applications regarding VOCs,  
33 aldehydes and other carbonyls, PCBs, PCDDs, PCDFs, and PAHs in the indoor  
34 environment. Sample collection and pretreatment, analyte extraction, clean-up  
35 procedures, determination techniques, performance results, as well as compound

1 concentrations in indoor samples, are summarized and discussed. Emergent  
2 contaminants and pesticides related to the industrial development that can be found in  
3 indoor air are reviewed in a second part in this volume.

4  
5 *Keywords:* Indoor air; dust; industrial contaminants; air analysis; VOCs; aldehydes;  
6 PCBs; PAHs; review

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## 1 **1. Introduction**

2 The concern about the uncontrolled production, emission and use of many  
3 chemical substances lacking information on their environmental and health effects has  
4 increased in the European Union (EU) during the last years. In this way, the aim of the  
5 Registration, Evaluation and Authorisation of CHEmicals (REACH) system that came  
6 into force in June 2007 is to protect human health and the environment from the impact  
7 of more than 34 millions of chemical substances registered to the Chemical Abstract  
8 Service (CAS) [1]. REACH places a great responsibility on industry to manage the  
9 risks that chemicals may pose to the health and the environment. Consequently,  
10 REACH needs to be based on solid analytical methods to identify the most harmful  
11 chemical compounds enabling their progressive elimination [2].

12 Industrial contaminants may be broadly considered to include those compounds  
13 produced, manufactured and emitted by the industry, or appearing into the environment  
14 because of the industrial development. In such broad sense, among industrial pollutants  
15 that can be found in air volatile organic compounds (VOCs) have been extensively  
16 studied, as well as other SVOCs compounds such as PCBs, PCDD/PCDFs and related  
17 compounds, and PAHs, belonging to the priority organic pollutant (POPs) category.  
18 POPs are characterized by their persistence, bioaccumulation and sub-chronic toxicity  
19 potential, as well as their tendency to undergo long-range atmospheric transport.

20 Most people in developed countries spend up to 90% of their time indoors [3,4].  
21 Taking into account that each person inhales about 22 m<sup>3</sup> air per day [5], inhalation of  
22 indoor air is potentially the major determinant of human exposure to many pollutants  
23 [4]. Exposure to pollutants in the indoor environment has increased with improved  
24 insulation and reduced ventilation making many indoor environments act as  
25 concentrators of emissions from plastics, paints, and other building materials, while  
26 protecting from outdoors contaminants. Inadequate ventilation can increase indoor  
27 pollutant levels by not bringing in enough outdoor air to dilute emissions from indoor  
28 sources and by not carrying indoor air pollutants out of the home. High temperature and  
29 humidity levels can also increase concentrations of some pollutants. On the other side,  
30 in many other communities, indoor pollution may be dominated by the outdoor levels of  
31 contaminants. Apart from specific point sources, outdoor pollution is mainly due to  
32 mobile sources (traffic) emitting high levels of PAHs and VOCs, among many other  
33 compounds.

34 The purpose of this review is to present an overview of the recent developments  
35 and methodologies for the analysis of industrial contaminants of concern in indoor air.  
36 This review focuses on VOCs, PCBs and related compounds, and PAHs, while

1 compounds such as phthalates, flame retardants, synthetic musks, pesticides, and other  
2 emergent contaminants, are object of other review in this volume. Given the extensive  
3 literature published on the analysis of the considered compounds in air, the literature  
4 basis for this review had to be properly defined. In order to identify the latest  
5 developments and trends, research literature from the latest ten years has been reviewed.  
6 Occasionally, a few of significant earlier articles have been included. This review  
7 focuses on indoor air analysis and hence, methodology developed or applied to  
8 atmospheric or ambient air analysis has been excluded. Only procedures that have been  
9 developed for indoor analysis, or those that can be indistinctly applied for both indoor  
10 and outdoor analysis, have been taken into consideration. Main attention has been paid  
11 to the analysis of the gas phase indoor. In addition, the importance of domestic dust and  
12 suspended particulate matter as vehicles of indoor pollutants have not been neglected  
13 and as such, the last part of the review is devoted to the analysis of these solid samples.

14 International agencies have published analytical methods, which are available  
15 for all users to determine organic pollutants in air. Occupational Safety and Health  
16 Administration (OSHA) has published evaluation guidelines for air sampling methods  
17 utilizing chromatographic analysis or spectroscopic analysis [6]. The National Institute  
18 for Occupational Safety and Health (NIOSH) Manual of Analytical Methods is a  
19 collection of methods for sampling and analysis of contaminants in workplace air, and  
20 in the blood and urine of workers who are occupationally exposed [7]. These methods  
21 have been developed or adapted by NIOSH or its partners and have been evaluated  
22 according to established experimental protocols and performance criteria. US  
23 Environmental Protection Agency (EPA) has also published numerous methods relating  
24 to environmental monitoring, stack testing, and indoor air quality [8]. Many of these can  
25 find application in evaluating occupational exposure. Others can be used to supplement  
26 information during specific evaluations.

27 Growing emphasis on environmental monitoring has encouraged the  
28 development of more rapid and less expensive methods of analysis for toxic pollutants.  
29 Sampling techniques for air analysis have been considered in several comprehensive  
30 revision articles. Among them, it is worth highlighting those of Demeestere *et al* [9] and  
31 Dewulf and Van Langenhove [10] on sample preparation for VOC analysis in air and  
32 water matrices; passive air sampling advantages and trends have been fully studied by  
33 Harner *et al* [11], Seethapathy *et al* [12], Krupa and Legge [13] and Partyka *et al* [14].  
34 The use of sorbent materials for air enrichment has been reviewed by Harper [15], and  
35 Dettmer and Engewald [16]. Sampling and sample preparation strategies for air analysis  
36 based on solventless techniques like solid-phase microextraction (SPME) have been

1 studied by Koziel and Novak [17]. The determination of air pollutants performed by gas  
2 chromatography (GC) has been the object of the paper by Helmig [18]. Other employed  
3 techniques have been referenced in the corresponding sections.

## 5 **2. Volatile organic compounds**

6 Volatile organic compounds (VOCs) comprise an important group of chemicals  
7 that evaporate easily at room temperature, and are commonly present in indoor air.  
8 Some of them may cause short- and long-term adverse health effects. It has been  
9 demonstrated that some VOCs induce cancer in animals, and some of them are  
10 suspected or known to cause cancer in humans, even at very low concentrations. Key  
11 signs or symptoms associated with exposure to VOCs include eye irritation, nose and  
12 throat discomfort, headache, allergic skin reaction, nausea, fatigue, or dizziness. VOCs  
13 are emitted from a wide array of products used indoors as paints and lacquers, cleaning  
14 supplies, organic solvents, cosmetic products, pesticides, building materials and  
15 furnishings, office equipment such as photocopiers and printers, correction fluids,  
16 graphics and materials including glues and adhesives, permanent markers, and  
17 photographic solutions. VOCs are related to the sick building syndrome. Studies have  
18 found that levels of these chemicals average 2 to 5-fold higher indoors than outdoors.  
19 During and for several hours immediately after certain activities, such as paint stripping,  
20 levels may be 1,000-fold the background outdoor levels.

21 The purpose of this paper is not to review all the extensive bibliography  
22 published on the VOCs issue up to now. Several papers reviewed sampling, extraction  
23 and determination methods to collect VOCs in air [19-25]. Table 1 summarizes some of  
24 the last studies devoted to the determination of VOCs in indoor air.

### 26 *2.1. Sampling*

#### 27 *2.1.1. Active air sampling*

28 VOCs have been actively sampled, pumping air through a solid adsorbent or  
29 mixtures of adsorbents, where the compounds are retained. Different US EPA Methods  
30 (TO-1, TO-2 and TO-17), where VOCs have actively collected have been published [8].  
31 Several comprehensive reviews on adsorbent materials for VOCs were published [103-  
32 105,15,16]. Charcoal [42,53,101] or organic porous polymers as Chromosorb [26] or  
33 XAD-2 resin [63], and graphitized carbon blacks as Carbotrap [37,40], are some of the  
34 adsorbents recently used to retain VOCs from air. Mixtures of adsorbents based on  
35 carbon or porous polymers, as Carbo-pack and Carboxen [28,58] or Carbosieve [74,95],  
36 Carbotrap and Carbosieve [72], two types of Carbograph [106] or Tenax with Carboxen

1 [32], Carbopack [55] or Carbotrap [95] have also been utilised to actively collect these  
2 volatile compounds.

3 Tenax has been extensively used for the recovery of VOCs from contaminated  
4 air, due to its hydrophobic nature, thermal stability, and rapid desorption kinetics  
5 [29,35,39,66,96]. The storage stability of VOCs has been investigated on Tenax TA,  
6 Chromosorb 106, and Carbotrap using thermally desorbable tube type samplers [52].  
7 Tenax TA and Carbotrap yielded lower recoveries and were more influenced by  
8 variation in storage time, storage temperature and analyte loading, showing no signs of  
9 artefact development over time. Nevertheless, Chromosorb contained more artefacts, in  
10 spite of its excellent storage capability, which may limit its use in field studies where  
11 long storage times are normal. Tenax TA, Tenax GR, Carbosieve SIII, and Chromosorb  
12 106 were tested to monitor monoterpenes from dynamically generated atmospheres [87],  
13 being Tenax GR and TA the sorbents giving the best yields. In addition, Jurvelin *et al.*  
14 compared Tenax TA with Carbotech as a part of EXPOLIS (Air Pollution Exposure  
15 Distributions within Adult Urban Populations in Europe) study [93]. Carbotech method  
16 allowed to quantify only 14 of the 30 target compounds, and showed lower precision  
17 and accuracy. Additionally, it systematically determined lower levels than Tenax TA.  
18 Peters and Bakkeren compared the stability of Chromosorb 106, Carboxen 569, Tenax  
19 GR and Carbosieve S-III charged with chlorinated and non-chlorinated hydrocarbons  
20 over periods from months to years [107]. Especially Tenax showed good results  
21 whereas some other sorbents were found to be unsuitable for storage over a prolonged  
22 time.

23 Several adsorbents can be combined in multisorbent traps, which allows  
24 collecting compounds of a wide volatility range. Ribes *et al* have developed a dynamic  
25 method to trap gas and vapour VOCs for air-quality and nuisance odours on multi-  
26 sorbent tubes filled with 70 mg Carbotrap, 100 mg Carbopack X, and 90 g Carboxen  
27 [36]. Triple sorbent traps were also utilised to collect VOCs from diluted sidestream  
28 tobacco smoke, which contributes to increase lung cancer and risks of respiratory and  
29 cardiopulmonary diseases [72]. Air samples from two semiconductor factories were  
30 collected too on multisorbent tubes, including Carbopack B, Carbopack C and  
31 Carbosieve SIII with a 24-h automatic active sampling system [74]. Volatile  
32 hydrocarbons were also collected in thermal desorption tubes containing a triple sorbent  
33 (two beds of Carbopack followed by Carboxen) in diesel exhaust from the trucking  
34 industry [28]. Analysis of volatile amines is difficult because of their high volatility and  
35 polarity, basic character and high solubility in water. For this reason, derivatization  
36 reactions are usually included. For example, XAD-2 resins impregnated with

1 naphthylisothiocyanate can be employed to actively sampling primary and secondary  
2 amines in workplace air [63]. Active methods were also used for measuring emissions  
3 from materials for indoor use. Known volumes of air from stainless-steel cylindrical  
4 chambers where several materials were introduced were passed through a tube packed  
5 with 300 mg of Tenax TA [39].

#### 6 7 2.1.2. Whole air sampling

8 The simplest way to collect air samples is the whole air sampling, using bags or  
9 canisters [103]. Total air sample is collected, avoiding breakthrough problems. However,  
10 and derived of the limited sample collected, air contained within this type of samplers  
11 needs to be preconcentrated to achieve acceptable sensitivity, using either a cold trap or  
12 a cryofocusing device.

13 8-h time-integrated samples were obtained by using mass flow controllers and  
14 canisters according US EPA method TO-14A to measure VOCs from burning of  
15 incense in temples [31]. US EPA method TO-15 and OSHA Method PV2120 collects  
16 VOCs in canisters too [6,8]. A canister-based method was also used to collect whole air  
17 in fused silica-lined mini-canisters (1.4 L) following passage through a calcium chloride  
18 drying tube [34]. The method developed was applied for quantifying volatile sulphur  
19 compounds from animal feeding operations. BTEX concentrations were measured using  
20 passive sampling badges type OVM 3500 and ORSA, which were tested for their use  
21 for environmental indoor exposure assessment in epidemiological studies in homes [62].  
22 Using organic vapour monitors (OVMs; badge-type samplers consisting of a permeable  
23 membrane and an activated-charcoal pad) occupational and non-occupational exposures  
24 to VOCs were monitored for days [30,61] or weeks [67,68]. Another badge-type  
25 sampler (SKC Ultra Passive Sampler) containing about 600 mg Carbopack X was also  
26 used to quantify personal exposure and indoor levels of four VOCs in a town where  
27 wood burning for heating is common [38]. This sampler was also compared to Radiello  
28 (a diffusive sampler with a cartridge filled with Carbopack or Carbograph), showing  
29 results which agreed with those obtained for active samplers [46]. It has been  
30 demonstrated that fused-silica-lined canisters show superior inertness compared to  
31 traditional SUMMA canisters [108]. Recently, significant interest has arisen in using  
32 evacuated canisters for personal breathing zone sampling. A flow control device  
33 combined with an evacuated canister was evaluated against charcoal tubes and diffusive  
34 badges [69]. The designed system was found to be more accurate for the 6 VOCs  
35 evaluated, as well as easier to use and analyze than charcoal tubes and passive  
36 dosimeter badges. A similar method was used by Buckley *et al.* to determine VOCs in

1 alveolar breath [109]. The subjects breathed through one-way valves such that  
2 inhalations were purified through an activated charcoal filter and exhalations passed  
3 into a Teflon tube. After that, the sample was drawn from the tube through a critical  
4 orifice into 1.8 L Summa polished canisters over an 80 seconds period. The entire  
5 breath sampling procedure required approximately 2 min and limits of detection (LODs)  
6 ranged from  $2.5 \mu\text{g m}^{-3}$  for vinylidene chloride to  $3.5 \mu\text{g m}^{-3}$  for p-dichlorobenzene.

7 Several authors have combined whole sampling with adsorbent tubes. For  
8 example, Destailats *et al.* identified indoor secondary pollutants from household  
9 product emissions collecting 80-L air in Tedlar bags, and trapping VOCs onto Tenax  
10 sorbent tubes [41]. A canister-based sampling technique was combined with solid  
11 adsorbents for the determination of 52 VOCs in air by Tolnai *et al.* [110]. A 200-mL  
12 sample was drawn through a multilayer adsorbent bed containing Carbosieve and two  
13 sections of Carbotrap. Another possibility is the collection of the air sample using a  
14 canister [111] or a badge and the extraction of analytes by exposing a SPME fiber.  
15 Lestremau and co-workers collected air samples into homemade 100-L Tedlar bags at a  
16 poultry factory suffering from severe odor problems [73]. After that, a SPME syringe  
17 needle was exposed to the sample with the fiber retracted and the volatile sulphur  
18 compounds were diffused to the fiber. Other authors have also sampled VOCs from  
19 workplace air using a combination of a Tedlar bag and SPME [85,112].

### 21 2.1.3. Passive air sampling

22 In passive sampling, the transport of the analytes to the sampling medium is  
23 caused by diffusion. Passive samplers have become increasingly important in the last  
24 few years. Because of their simplicity, low prize and their ease of use, diffusive  
25 sampling devices become also popular for workplace measurements as well as for  
26 sampling campaigns that have to be performed by non-experienced personal.  
27 Nevertheless, their use is limited; their low sampling rates necessitates long sampling  
28 times at low concentrations and meteorological conditions influence the quantification  
29 significantly.

30 Passive samplers containing Tenax in a tube type configuration have been used  
31 to measure VOCs present in residential garages due to emissions from vehicles [27] or  
32 personal exposures in homes [84]. Chien *et al.* compared passive sampling using Tenax  
33 to active sampling with charcoal tubes [75]. Concentrations obtained for some VOCs  
34 were mostly less than those given by active protocols, concluding that the use of a fixed  
35 uptake rate constant for diffusive applications in complicated field conditions could  
36 result in errors. However, another study compares passive samplers with silicone

1 membranes and active charcoal to dynamic samplers using active charcoal or Tenax  
2 tubes, obtaining no significant differences [23]. A simple and cheap homemade passive  
3 sampler was also developed by Thammakhet and his group, using common glass bottles,  
4 packed with only 75 mg of activated Tenax TA [47]. It was successfully tested for the  
5 monitoring of BTEX at petrol stations. Other passive samplers used charcoal [50,71] or  
6 Carbopack [57] as the sorption phase. Analyst diffusive sampler (VOCs are sampled on  
7 an active charcoal bed) has also been used since it was designed in 2000, for example  
8 for monitoring the air quality around an oil refinery [113]. Just as active samplers,  
9 passive ones can contain several adsorbents; for example Tenax and Carbosieve [114].  
10 Zabiegala *et al* [54] designed a homemade box-type passive sampler equipped with a  
11 polydimethylsiloxane (PDMS) foil membrane filled with active carbon. It was used to  
12 estimate time-weighted average (TWA) concentrations in homes for a period of 4-5  
13 weeks.

14

#### 15 2.1.4. Solid-phase microextraction

16 It is worth a mention all the papers focused on VOC sampling using Solid-Phase  
17 Microextraction (SPME) [17,115-119]. SPME provides some advantages over  
18 traditional extraction methods. It offers solvent-free operation, and in spite of the  
19 limited amount of analyte extracted, all is introduced into the GC injection port,  
20 allowing for good sensitivity, with cost effectiveness and operational simplicity. In  
21 addition, SPME quantitation is feasible in non-equilibrium conditions once  
22 experimental parameters are held constant, which considerably reduces sampling time  
23 [120]. Larroque and co-workers have compared two SPME methods, under non-  
24 equilibrium (1-45 min) and equilibrium (3 h) conditions for sampling VOCs in indoor  
25 air [45]. The non-equilibrium method, involving short extraction time, can be used for  
26 detection of pollution peaks whereas equilibrium extraction is preferable for  
27 measurement of sub- $\mu\text{g m}^{-3}$  ground concentration levels. Dynamic versus static  
28 sampling was also studied with several fibres [121,122]. Competitive sorption was  
29 observed for the fibres ruled by adsorption processes i.e. polydimethylsiloxane-  
30 divinylbenzene (PDMS-DVB) and Carboxen-polydimethylsiloxane (CAR-PDMS)  
31 fibres, which may lead to calibration problems [122]. When sampling was performed  
32 with CAR-PDMS fibres in the dynamic mode, compounds with lower affinity for the  
33 coating showed a very narrow linear range, meaning that competition for adsorption  
34 was quickly discriminative [121]. Adsorption fibres such as CAR-PDMS [33,43, 49, 59,  
35 64, 91], PDMS-DVB [100,102] as well as those based on absorption processes like  
36 polyacrylate (PA) [86] have been tested for measuring indoor VOC concentrations.

1 Calibration is the main obstacle for applying SPME to the indoor air monitoring.  
2 Nevertheless, great efforts have been made to overcome this problem [123,64,78,124-  
3 127]. Bartelt and Zilkowski [124,125] quantified volatiles in air streams by SPME in a  
4 dynamic mode and under non-equilibrium conditions. Tested analytes evaporated  
5 slowly from a rubber septum entering in the air stream. The air stream flowed past the  
6 SPME fiber, which was positioned along the central axis of the sampling port. Sampling  
7 times ranged from 30 min to 3 days. For calibration, Mangani and Cenciarini exposed a  
8 Carboxen coated fiber to a flask where permeation tubes containing the target analytes  
9 were placed [128]. At the same time, a stream of nitrogen flowed through the system.

10 SPME offers multiple alternatives, as an example, it has been proposed to  
11 quantify emissions of biogenic VOCs from plants [124,129] or pine forests [130].  
12 Augusto *et al.* [98] designed two portable dynamic air sampling devices based on  
13 diffusion calibration for rapid field sampling. One sampler consists of a household hair-  
14 dryer modified to invert the air flow direction and to force the passage of the air through  
15 a slit where the fiber is inserted. The second is designed in a sandwich shape, where a  
16 Teflon spacer separates two stainless steel sheets which allowed the exposition of the  
17 fiber. The use of the proposed samplers resulted in greater adsorbed VOCs mass for  
18 qualitative screening of live plant aromas and contaminants in indoor air compared to  
19 the conventional SPME extraction in static air. PA fibres were also used to estimate  
20 emissions of formic and acetic acids from several materials at a museum [86]. Another  
21 application of dynamic air sampling with SPME can be the extraction of odour-causing  
22 VOCs present in swine building environments [82]. Davoli *et al.* [131] has  
23 demonstrated the suitability of a three phase fiber, DVB-CAR-PDMS, to rapidly  
24 individuate emission sources of olfactive nuisances. Several needle trap devices with  
25 different sorbents immobilized inside a needle were applied to extract organic  
26 components from gaseous samples [60]. Jia *et al.* have presented a fast field method  
27 using very short sampling times (1 min) combined with portable GC, providing a near-  
28 real-time measurement of target VOCs [102].

29 Fiber storage before and after sampling was also studied. Larroque *et al.*  
30 developed a homemade assembly, consisting of a tube hermetically closed by stainless  
31 steel plugs and with internal walls treated with Silcosteel for inertness [44]. Under this  
32 condition, fibres can be stored up to two days before use. Although many coatings are  
33 already commercially available, new coatings are being continuously proposed, some  
34 examples are ethoxy-PDMS, polyurethane acrylate, 50% phenyl-PDMS [79] or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>  
35 [65].

1 Other alternative is the use of membranes with sorbent interface (MESI) to  
2 monitor, for instance, plant fragrances emitted into indoor air [88] or VOCs in  
3 laboratory air [70].

#### 4 5 2.2. Sample treatment

6 Thermal desorption techniques are used as a first attempt to characterize  
7 potential contaminants in workplace [83]. The main advantage of thermal desorption is  
8 that all the trapped analytes can be chromatographed in a single chromatographic run;  
9 sample can be completely transferred into the gas chromatographic system without  
10 dilution of the analytes, ensuring minimum detection limits [104,132]. VOCs have been  
11 widely extracted from adsorbents by means of thermal desorption [26-29,32,35-  
12 39,48,51,52,56-58,72,75,84,93-95]. Anyway, there are multiple options. Analytes can  
13 be trap at the head of the column, kept at ambient temperature during the process.  
14 Another possibility is their trapping on another adsorbent bed (microtrap) from which  
15 analytes can be quickly desorbed in the form of a narrow band. Grote and Kennedy [83]  
16 desorbed VOCs collected in the workplace using an automated thermal desorber with an  
17 internal focusing trap containing Carboxen 1000. A small multi-  
18 adsorbent preconcentration / focusing module for a portable GC with microsensor-array  
19 detector was designed to determine complex mixtures of VOCs and SVOCs  
20 encountered in indoor working environments [89]. Short-path thermal desorption  
21 (SPTD) can also been applied to the determination of VOCs in different  
22 microenvironments as office buildings, residential houses and petrol stations [55]. It  
23 provides maximum sensitivity by minimizing artefacts, losses and carry-over effects.  
24 Batterman *et al.* [114] evaluated the use of thermal desorption techniques for low flow  
25 active and passive sampling configurations, employing Tenax GR and Carboxieve SIII.  
26 VOCs, collected in tubes at a lithographic printing facility, were desorbed by means of  
27 an automated SPTD/cryofocusing system. The method provided good performance and  
28 tremendous flexibility that facilitates their use in many applications, including  
29 workplace settings. Other authors have constructed a simple but effective thermal  
30 desorption device [47]. A brass block acts as a heating plate and it is calibrated and  
31 monitored by a thermocouple-multimeter. Cryothermal focussing traps analytes at the  
32 head of the column, which is kept at very low temperature, decreased with the use of  
33 vapour of liquid nitrogen or carbon dioxide. Thermal desorption and cryogenic  
34 enrichment was also carried out to desorb VOCs from several traps, collected in parked  
35 motor vehicle indoor air [40], dweelings [87], or semiconductor and electronics  
36 industries [74]. Ochiai *et al.* [108] extracted VOCs by thermal desorption concentrating

1 them in a glass bead cryogenic trap. The trap was then heated to 20°C and was held  
2 there while slowly passing helium to transfer these compounds to a secondary Tenax  
3 trap. Nevertheless, thermal desorption techniques are expensive, not rapid processes,  
4 and required complex instrumentation.

5 When VOCs are too strongly adsorbed, for example with adsorbents such as  
6 activated carbon, thermal desorption is useless to recover the compounds, due to the  
7 very high temperature needed [15,103]. The most common solvent used for solvent  
8 desorption is carbon disulfide [23,49,50,54,62,67,69,75,81,93], because of its good  
9 solubilisation properties for many analytes [104]. However, other solvents can also be  
10 used as methanol [42], toluene [71] or acetone [30]. VOCs can be extracted from a  
11 charcoal pad using ultrasound-assisted solvent extraction. Some examples are the  
12 extraction of benzene [53], or ethylbenzene, indan, indene and acenaphthene collected in  
13 the breathing zone of the workers of a coke plant [101].

14 Apart from being used as a sampling/extraction technique, SPME can be  
15 combined with a sampling method and utilized only as an extraction technique to  
16 achieve higher sensitivity. Saba *et al.* placed solutions of high volatile VOCs (benzene  
17 and toluene) [96,133] in a U-shape glass tube. Pumped air forced the transfer of analytes  
18 to Tenax. After that, desorption of the adsorbent was performed by headspace (HS)-  
19 SPME. The addition of solutions with known concentrations of VOCs allowed an easy  
20 calibration of the procedure. Some years later, Barro *et al.* applied a similar combination  
21 of solid phase extraction (SPE) using only 25 mg of Tenax and HS-SPME for the  
22 determination of several chlorinated VOCs and SVOCs (chlorobenzenes) in indoor air  
23 [66]. Elke *et al.* combined passive sampling using a charcoal pad with two extractive  
24 techniques; solvent extraction and SPME [134]. Applications such as the determination  
25 of BTEX in indoor air of buildings, a train or a car were presented, although the  
26 proposed extraction process is tedious and time-consuming.

27 In order to verify the occurrence of volatile organic peroxides in indoor air,  
28 Hong and co-workers [97] developed a method based on sampling into Carbotraps and  
29 extraction by supercritical fluid extraction (SFE) using CO<sub>2</sub> with methanol as modifier.

### 31 2.3. Determination

32 GC is by far the most common technique applied to determine VOCs in air. It is  
33 usually coupled to FID or MS detectors. Some examples are given in Table 1. It can  
34 also be combined with electron capture detection (ECD) [67,71] or pulsed flame  
35 photometric detection (PFPD) [34,73]. If higher sensitivity is needed, GC/MS/MS  
36 [42,53] or HRGC/MS [110] can be applied.

1 Fast separation and speciation of common indoor air pollutants is also possible  
2 with the use of a modified, portable GC instrument, equipped with a photoionization  
3 detector (PID), FID, and a dry electrolytic conductivity detector in series [102].  
4 Combination of the fast, portable GC with short SPME sampling time can provide a  
5 near-real-time measurement of target VOCs. High-speed analysis of complex indoor  
6 VOC mixtures can also be achieved by vacuum-outlet GC with pressure-tunable column  
7 selectivity, and PID [92]. The capillary column ensemble consists of a segment of non-  
8 polar PDMS followed by a segment of polar trifluoropropylmethyl polysiloxane. The  
9 entire mixture of 42 compounds was analyzed in less than 7 min, with minimal overlap  
10 in eluting peaks. Another possibility includes the determination of complex vapour  
11 mixtures of VOCs and SVOCs using multi-adsorbent preconcentration/focusing module  
12 for a portable GC with microsensor-array detectors; surface-acoustic wave sensors  
13 [89,94]. When enantioselective separation is required, specific columns can be utilized  
14 as, for example,  $\beta$ -cyclodextrin capillary columns [129].

15 Compared to conventional one-dimensional GC, comprehensive two-  
16 dimensional GC (GCxGC) greatly increases the separation capability, improves  
17 resolution and enhances mass sensitivity, generating two-dimensional chromatograms  
18 [135]. The most important application of GCxGC was reported by Lewis *et al.* [136],  
19 who illustrated the separation of more than 500 chemical species of VOCs from urban  
20 air samples in one run. Schwarz and Heumann coupled inductively coupled plasma –  
21 mass spectrometry (ICP/MS) to a gas chromatographic system with ECD to characterize  
22 and quantify halogenated (brominated and iodinated) VOCs in air samples [137]. The  
23 hyphenated GC/ECD-ICP/MS system provides high selectivity and sensitivity for  
24 monitoring individual halogenated VOCs under fast chromatographic conditions.

25 For more polar VOCs, some examples of using liquid chromatography can be  
26 found. Organic peroxides can be determined by HPLC using post-column derivatization  
27 and fluorescence detection [97]. Anyway, GC/MS was employed to check for the  
28 possible presence of compounds interfering with the determination. Volatile primary  
29 and secondary amines were analyzed by means of LC/MS/MS with a triple quadrupole  
30 equipped with electrospray ionization (ESI) [63]. Nitroaromatic compounds were  
31 separated onto a porous graphitic carbon HPLC column and analyzed by an LC/MS/MS  
32 with a triple quadrupole detector, equipped with an atmospheric pressure chemical  
33 ionization (APCI) interface [77]. Another alternative is direct spectrometry on a PMDS  
34 solid sorbent for detecting benzenic pollutants [90]. Although results as precise as those  
35 given by chromatographic methods can not be expected by this method, it might have  
36 valuable applications, particularly for “on site” pollution monitoring.

1 Another promising technique is the ion mobility detection. Liu and Pawliszyn  
2 determined p-xylene together with four PAHs by means of an on-line method using  
3 MESI with ion mobility spectrometry system with a preheated carrier (stripping) gas  
4 [138]. The method was shown to be capable for on-site measurements of emissions  
5 from cigarette smoke.

#### 6 7 2.4. Concentration in indoor air

8 Some VOCs are mutagenic and/or carcinogenic, and many of them found  
9 indoors have the potential to cause sensory irritation and central nervous system  
10 symptoms. In addition, indoor total VOC (TVOC ) has been used as an indicator of  
11 building healthiness because the prevalence rate of sick building syndrome symptoms or  
12 complaints was suggested to correlate with TVOC concentration [139]. For all these  
13 reasons, VOC concentrations in different environments have been extensively reported  
14 in recent years [3,4,139-152]. Taking into account the extensive literature on this topic,  
15 only some brief comments are remarked in this epigraph, making special emphasis on  
16 indoor or workplace air. Table 2 lists several VOC concentrations measured in indoor  
17 environments during last years, or in ambient air with clear workplace implications, for  
18 example for agricultural workers.

19 VOCs have been measured in a wide range of indoor environments, i.e. several  
20 parts of homes [27,35,54-56,62,81], garages [27], kitchens during the use of biomass  
21 fuels in cooking time [38,42,53], during evaporating essential oils [32], offices [55,156],  
22 schools [81], vehicles [27,37,40], petrol stations [55] museums [59,86], temples [31],  
23 semiconductor foundries [74], different stores [157], photocopy centres [29], restaurants,  
24 bars and theatres [26], a furniture factory [161], and a tollbooth [58]. In an interesting  
25 study carried out by Park and Ikeda, VOC levels were continuously monitored during 3  
26 years in new and older homes [50]. Practical implications include that the initial levels  
27 of VOCs in new homes decreased dramatically and were close to the mean values for  
28 older homes after one year. Besides, decreasing tendency of indoor air VOC levels in  
29 new homes did not appear to show any dependency upon the ventilation systems over  
30 the whole period. Zhang *et al.* [162] measured concentrations of benzene, toluene,  
31 xylenes and formaldehyde in the microenvironments of parked new cars. As it was  
32 expected, newer vehicles exhibited higher concentrations than older ones. Moreover, it  
33 seemed to be a connection between the types of interior materials used in the passenger  
34 cabin and the concentration of certain air pollutants. Namiesnik *et al.* [79] estimated  
35 volatile aliphatic amine concentrations in a pharmaceutical plant, a chemical storeroom,  
36 a car paint shop and a city market, finding triethylamine concentrations up to 148.2 mg

1 m<sup>-3</sup> in the pharmaceutical plant. Kim *et al.* [95] measured 15 VOCs in a wide range of  
2 urban microenvironments; homes, offices, restaurants, pubs, department stores, coach  
3 and train stations, cinemas, libraries, laboratories, perfume shops, heavily trafficked  
4 roadside locations, buses, trains and automobiles. Mean concentrations of most VOCs  
5 were elevated in transportation microenvironments. Of the public microenvironments  
6 monitored, pubs and train stations were shown to have the highest concentrations of  
7 most target VOCs. Another paper estimates occupational exposure to diesel exhaust in  
8 the trucking industry, e.g. in buses, cars, etc. [28].

9 Schlink *et al.* [67] proved that seasonality is the most dominant pattern of  
10 indoor-VOCs, founding the highest concentration during the winter months, which  
11 decrease from three to four times during summer. Rehwagen also elucidated the spatial  
12 and temporal variation of VOC concentrations obtaining similar results [68].

13 Indoor air halogenated VOC concentrations resulting from the use of four  
14 selected household products were measured before, during, and 30 min after bathroom,  
15 kitchen, and floor cleaning applications [163]. Chloroform (2.9-24.6 µg m<sup>-3</sup>) and carbon  
16 tetrachloride (0.25-459 µg m<sup>-3</sup>) concentrations significantly increased during the use of  
17 bleach containing products, indicating that the bleach use can be important in terms of  
18 inhalation exposure to these chemicals and several other halogenated VOCs.

19 VOC concentrations are usually higher in indoor environments than in outdoor  
20 air [56,68,95]. Sexton *et al.* [61] evaluated differences in personal exposures, outdoors  
21 in urban neighbourhoods and in indoor air in homes. Results showed a clear pattern for  
22 the VOCs monitored, with personal concentrations higher than those measured indoors  
23 and these clearly higher than outdoors. Indoor and outdoor samples were also collected  
24 in offices, obtaining TVOC concentrations from 304.3 to 1679.9 µg m<sup>-3</sup> indoors and 22  
25 to 643.2 µg m<sup>-3</sup> outdoors [155].

26 In addition, some papers, which estimated VOC concentrations in ambient air,  
27 should be emphasized due to their workplace possible implications. For example,  
28 measurements made to determine VOCs emitted from landfills [131], around an oil  
29 refinery [113], or from animal feeding operations [34].

### 31 **3. Carbonyl compounds**

32 Carbonyls present in ambient air are directly discharged by primary sources such  
33 as incomplete combustion of many organic substances as biomass and fossil fuels used  
34 in industrial processes. They can also be formed from secondary sources such as  
35 photooxidation of hydrocarbons [164]. In occupational and residential indoor  
36 environments, predominant carbonyls are aldehydes, mainly formaldehyde and

1 acetaldehyde. Although aldehydes can also be released from indoor ozone reactions  
2 with unsaturated VOCs [165], the major sources of indoor carbonyls are building  
3 materials and furniture. Indoor aldehyde concentrations are 2-13-fold higher than the  
4 outdoor ones [155,166]. Formaldehyde, acetaldehyde, benzaldehyde and acrolein are  
5 suspected carcinogens and mutagens, as well as other low-molecular-mass aldehydes,  
6 which reactivity and possible mutagenicity are similar to those of acetaldehyde [167-  
7 169]. These compounds are also related to other health problems and are the essential  
8 cause of odour problems [164]. Table 3 summarizes some analytical procedures recently  
9 published for the determination of aldehydes and other carbonyls in indoor air.

10

### 11 3.1. Sampling

12 Collection methods for carbonyls in air are usually based on a simultaneous  
13 sampling/derivatization process using sorbents coated with the derivatizing agent.  
14 Sorbents can be used in diffusive samplers or for active sampling. Most popular  
15 methods use 2,4-dinitrophenyl-hydrazine (DNPH) [155,175,166,176] to form coloured  
16 dinitrophenylhydrazones suitable for UV detection. Also, 5-dimethylaminonaphthalene-  
17 1-sulfohydrazide (dansylhydrazine, DNSH) [171,177], pentafluorophenylhydrazine  
18 (PFBH) [168,172], and 3-methyl-2-benzothiazolinone hydrazine (MBTH) [170] have  
19 been described to be used in indoor sampling methods. Most of the collection methods  
20 are common for both outdoor and indoor sampling. Passive techniques present some  
21 advantages in occupational environments but require long sampling times. To reduce  
22 sampling time, especially when aldehyde concentrations are at trace level, SPME has  
23 been proposed as an alternative [168,172]. Very recently, Saito *et al* [175] developed an  
24 in-needle sample preparation device designed for the GC analysis of aldehydes and  
25 ketones commonly found in typical house environments. A simultaneous  
26 derivatization/collection process is performed using DNPH included in a needle  
27 longitudinally packed with a bundle of polymer-coated filaments. Using 30  $\mu\text{L}$   
28 acetonitrile for desorption of the derivatized compounds in the injection port of the GC,  
29 the LOD achieved are in the range 1.2-11.7  $\text{ng L}^{-1}$ . A novel method has been recently  
30 reported by Saitoh *et al* [179] and it is based on the thermo-responsive precipitation of a  
31 water-soluble polymer such as poly(N-isopropylacrylamide). Aliphatic aldehydes from  
32 an air sample collected in a Tedlar bag are solubilized in an aqueous solution of  
33 dimedone and form fluorescent derivatives by the Hantzsch reaction. These derivatives  
34 are extracted by precipitation with the polymer. Since the precipitates condense in a  
35 small gum-like glob, LODs  $<20 \text{ ng m}^{-3}$  are achieved. Other non-conventional method  
36 has been described by Sritharathicun *et al* [178] for the collection and concentration of

1 traces of formaldehyde in air by using flow injection analysis (FIA) coupled to a  
2 chromatomembrane cell, which allows an on-line operation.

3 For all methodologies, it is mandatory to assure suitable blanks, especially for  
4 the analysis of formaldehyde and acetaldehyde, the predominant carbonyls found in air  
5 samples. Thus, collection devices must be thoroughly cleaned before sampling [170].  
6

### 7 3.2. Sample treatment

8 Derivatized carbonyls are usually extracted by solvent extraction, with the  
9 exception of SPME-based methods using thermal desorption in the injection port of the  
10 GC. Since most procedures for aldehyde analysis imply the use of HPLC, acetonitrile is  
11 the solvent of choice, and sometimes desorption is assisted by sonication [173,176]. In  
12 general, clean-up procedures previous to the analysis are not described.  
13

### 14 3.3. Determination

15 Determination of aldehydes and other carbonyls are performed by detection of  
16 the coloured or fluorescent derivatives formed with the above indicated reagents. When  
17 only formaldehyde is the target, just a spectrophotometric measure at 628 nm of the  
18 color obtained after the oxidation of the azine formed by reaction of formaldehyde with  
19 MTBH allows for its determination in the sample [170]. When various carbonyls are  
20 separated by HPLC, absorbance or fluorescence changes are used for their detection  
21 [155,166,171,173, 176,179,180]. Capillary electrophoresis (CE) with UV or laser-  
22 induced fluorescence has also been used for the determination of aldehydes [177]. The  
23 use of a chromatomembrane cell coupled to a continuous FIA system with UV or  
24 fluorescence detection allowed LODs of  $60 \text{ ng m}^{-3}$  and  $30 \text{ ng m}^{-3}$ , respectively, for a 40  
25 mL diluted air sample. Enhanced selectivity and sensitivity can be achieved with MS  
26 detection. Recently, Chi *et al* [181] developed a method for quantitative analysis of 32  
27 carbonyls in air using DNPH derivatization and LC-ESI/MS/MS detection. With this  
28 technique, the reported LODs were  $<10 \text{ ng m}^{-3}$  assuming a sample volume of 180 L air.  
29

### 30 3.4. Concentration in indoor air

31 Very recently, Marchand *et al* [166] performed a comprehensive study to assess  
32 domestic aldehydes concentrations and identify possible associations between those  
33 concentrations and the indoor environment characteristics. In this study concerning 162  
34 residential homes at Strasbourg, the formaldehyde mean concentration was  $32.2 \mu\text{g m}^{-3}$ ,  
35 which is in agreement with formaldehyde concentrations previously found in homes all  
36 around the world [155,166,167,179] (see Table 2). Koziel *et al* [172] applied a SPME

1 device to the determination of formaldehyde in various indoor environments, including  
2 an apartment, a residential house, an elementary school, and various workplaces. The  
3 highest value were found at the residential house especially in the master bedroom (376  
4 ppbv) whereas at the other emplacements formaldehyde levels ranged between 10 and  
5 36 ppbv. Regarding acetaldehyde, concentrations in homes are similar or lower than  
6 those found for formaldehyde [155,166,167]. Nevertheless, Saitoh *et al* [179] found  
7 30.9-49.6  $\mu\text{g m}^{-3}$  of acetaldehyde, and 12.7-23.2  $\mu\text{g m}^{-3}$  of formaldehyde. C3 to C6  
8 aldehydes are found at concentrations 2-100-fold lower than the major formaldehyde  
9 and acetaldehyde [166,167,179]. In hospitals, Lu *et al* [182] found similar  
10 concentrations of several carbonyls indoors and outdoors. Among aldehydes,  
11 formaldehyde and acetaldehyde were predominant, with concentration ranges of 5.3-  
12 13.4  $\mu\text{g m}^{-3}$  and 7.9-21.4  $\mu\text{g m}^{-3}$ , respectively. Predominant ketones were acetone, 2-  
13 butanone, and cyclohexanone with concentrations ranging from 2.2 to 49  $\mu\text{g m}^{-3}$ . The  
14 relationship between indoor and outdoor levels of carbonyls, as well as their sources,  
15 has been pointed out by Santarsiero and Fuselli [183], who applied principal component  
16 analysis to elucidate correlations between both compartments.

17

#### 18 **4. Polycyclic aromatic hydrocarbons**

19 PAHs are among the most concerning classes of POPs in all industrialized  
20 countries. They are formed during the incomplete combustion of organic matter at high  
21 temperatures, and major sources include industrial processes, vehicle exhausts, waste  
22 incineration, and domestic heating emissions, as well as other natural sources such as  
23 forest fires.

24 The presence of PAHs in the indoor environment has been related to a  
25 combination of sources. Tobacco smoke, cooking, and domestic heating have been  
26 reported as main PAHs indoor sources, whereas the emissions of road traffic showed  
27 the highest impact on urban indoors air quality. Indoor environment in non-smoker  
28 residences was dominated by 2-3-rings PAHs, resulting mainly from cooking and wood  
29 stoves heating; whereas the presence of 4-7-rings PAHs has been attributed to  
30 infiltration by outdoor air [184-187]. Relationships between indoor/outdoor  
31 concentration levels of PAHs have been the focus of an important number of studies  
32 throughout the world [58,184,186-193]. Because of their carcinogenic and mutagenic  
33 activity in addition to their ubiquity and persistence, the US EPA has listed 16 PAHs as  
34 priority pollutants. This list includes benzo[a]pyrene (BaP), the usual marker for  
35 carcinogenic levels of PAHs in environmental studies, although its suitability as cancer

1 risk indicator as well as many other aspects related to the cancer risk assessment has  
2 been the content of a comprehensive report conducted by Boström *et al* [194].

#### 3 4 4.1. Sampling

5 Most of the methodologies for the analysis of PAHs in air and particulate matter  
6 are based on the active enrichment of the compounds on a sorbent, and the  
7 simultaneous collection of the particulate matter in a glass fiber filter (GFF) [195] or in  
8 a quartz fiber filter (QFF) [184,186,187,190,192,196-198]. Polyurethane foam (PUF)  
9 appears to be the most used adsorbent for the collection of PAHs in the gas phase  
10 [187,192,195]. Also, several commercial and homemade devices include polystyrene-  
11 divinylbenzene XAD-2 resin alone or sandwiched between two PUF plugs  
12 [184,186,190,196-201]. PAHs in occupational settings are sometimes 2-3 orders of  
13 magnitude higher ( $\mu\text{g m}^{-3}$ ) than in non-occupational settings ( $\text{pg m}^{-3}$ ). High volume (hi-  
14 vol) samplers working at rates of about  $200 \text{ L min}^{-1}$  for approx. 24 h are employed to  
15 collect more than  $300 \text{ m}^3$  of indoor and outdoor air samples [190,196,199,202-207],  
16 although low volume (lo-vol) samplers [184,186,189,190,192,195,197,198] are  
17 currently selected for indoor or personal sampling, with sampling rates of a few  $\text{L min}^{-1}$   
18 during 12-24 h to collect total air volumes of a few  $\text{m}^3$  per sample (see Table 4). The  
19 use of surrogate standards directly spiked to the sorbent before sampling is usually  
20 recommended for recovery calculations. Best surrogate standards for MS detection are  
21 isotopically labelled congeners such as deuterated compounds [190,192].

22 There is a lot of work dealing with the passive sampling of organic pollutants  
23 including PAHs in all environmental compartments. A comprehensive study on passive  
24 sampling in environmental analysis has been recently conducted by Seethapathy *et al*  
25 [12], which includes different designs of passive samplers mainly based on SPME, PUF  
26 samplers and disposable devices based on PDMS membranes. Focused on air analysis,  
27 Harner *et al* [11] have underlined the advantages and trends of passive air samplers for  
28 POPs in the frame of the new requirements that national and international controls are  
29 introducing on the production and use of POPs. Namiesnik and Zygmunt [132] have  
30 contributed to the development of a number of passive sampling devices based on  
31 different mechanisms. Passive samplers are becoming of increasing interest to monitor  
32 semivolatile organic compounds in air and have mainly been used for outdoor ambient  
33 long-term monitoring [213,214]. A recent example is the paper of Daly *et al.* [201], who  
34 describe the use of a passive air sampler design extensively used throughout North  
35 America to measure PAHs concentration in tropical environments [215]. The sampler  
36 consists in a stainless-steel mesh cylinder, filled with XAD-2 resin and suspended in a

1 steel can with an open bottom. The applicability of XAD-based passive samplers in  
2 terms of volatility is not exactly established, but covers a log octanol–air partition  
3 coefficient ( $K_{OA}$ ) range from approximately 8 to 11 [202]. Polymers can be an  
4 alternative to resins. Very recently, Kennedy *et al* [216] conducted a field comparison  
5 of ethylene vinyl acetate and low-density polyethylene (LDPE) thin films for  
6 equilibrium phase passive air sampling of the 16 PAHs listed by the US EPA. The  
7 results of their work showed that both polymers are useful for equilibrium phase  
8 sampling of predominantly vapour phase PAHs with  $\log K_{OA} \leq 8.7$  (pyrene). In addition,  
9 theoretical predictions indicated that the chemical nature of the polymeric films may be  
10 of critical importance when used as thin-film passive samplers.

11 A full discussion on the advantages, limitations, and trends of passive samplers  
12 for indoor air monitoring of PAHs and other industrial contaminants has been recently  
13 conducted by Bohlin *et al* [217]. In this extensive revision dealing with occupational  
14 and indoor air exposure to POPs, the convenience of selecting adequate tracer  
15 compounds is underlined, as well as of establishing protocols including parameters such  
16 as minimum sampler exposure time, instrumental detection limits, typical blank levels,  
17 uptake rates, and typical atmospheric concentrations for the target compounds. It should  
18 be taken into account that photosensitive compounds such as PAHs can undergo  
19 photodegradation due to reflected light even in controlled light-exposition conditions as  
20 demonstrated by Bartkow *et al* [218]. Thus, a photosensitive high  $K_{OA}$  deuterated PAH  
21 is proposed as a performance reference compound to account for differences in  
22 exposition [214].

23 The use of SPME fibres has been demonstrated to be a simple and cost-effective  
24 alternative for passive sampling of compounds such as VOCs. But, in the case of PAHs,  
25 their low vapour pressure and their high sorption ability hamper the preparation of  
26 gaseous standards. Therefore, the applications of SPME has been restricted to the  
27 identification of PAHs in diesel exhaust [219–221], the measurement in a static mode  
28 calibration [222], and to estimate the distribution coefficients  $\log K$  (air/PDMS) of the  
29 PAHs based on the use of a linear relationship between  $\log K$  and linear temperature–  
30 programmed retention indexes of the compounds without necessity of calibration [223].  
31 In this last case, the established distribution coefficients were used for approximate  
32 quantification of low molecular weight PAHs in both indoor and outdoor air samples.

33

#### 34 4.2. Sample treatment

35 PAHs from the gas phase air can be extracted from the sorbents using one of the  
36 extraction techniques described below. Filters with the PAHs from the aerosol or

1 particulate matter phase samples are usually extracted and analyzed separately, although  
2 in some cases the extracts from particulate and gas phases are combined for the analysis.  
3 For recovery studies the addition of surrogates, mainly deuterated congeners, is  
4 sometimes reported [198].

5 Soxhlet extraction is the most common extraction technique for PAHs retained  
6 in filters and sorbents. Different solvent mixtures have been tried for best polarity  
7 adjustment and quantitative recovery of the PAHs [195,196,198,212]. Rudel *et al* [197]  
8 used Soxhlet extraction for 16 h in 150 mL of 6% ether in hexane solution,  
9 concentration of extracts to 2mL and volume adjusting with 10% diethyl ether in hexane.  
10 Good recoveries have been also obtained by combining two Soxhlet extractions  
11 changing the solvent. In this way, Li *et al* [190] used hexane-DE 90:10 for 24 h  
12 followed by other 24 h extraction with dichloromethane (DCM). Chuang *et al* [199]  
13 extracted XAD-2 or XAD-4 cartridges with DCM for 16 h followed by ethyl acetate for  
14 8 h. In the procedures described by Naumova *et al* [187,188], PUF was statically  
15 extracted at 50°C with hexane-DCM (4:1 by volume) and finally the extracts were  
16 concentrated to 4 mL by rotary evaporation.

17 Ultrasounds are commonly used to accelerate mass transfer in solvent  
18 extraction. In indoor air analysis of PAHs, ultrasounds have been successfully applied  
19 among others by Sanderson and Farant [184], and Liu *et al* [186] to obtain PAH extracts  
20 from XAD-2 sorbents suitable for HPLC analysis achieving quantitative recovery  
21 values.

22 Sorbent extraction by pressurized liquid extraction (PLE) was selected by authors  
23 such as Menichini *et al* [192], who used an n-hexane-acetone 1:1 mixture at 100 °C and  
24 100 bar. The extracts were finally concentrated to ca. 500 µL before the clean up step.  
25 PUF and XAD-2 were extracted by PLE with DCM by Iavicoli *et al* [200]. DCM was  
26 also the extractant solvent selected by Albinet *et al* [207] for PLE desorption of PAHs  
27 from the PUF sorbent.

28 Microwave-assisted thermal desorption has been optimized by Wei *et al* [209] as  
29 an in-situ one-step sample preparation procedure to help desorption of PAHs collected  
30 on XAD-2 resin into a sorbent solution (10-mL ethylene glycol -1M NaCl 7:3)  
31 irradiated with 120 W for 40 min. Analytes were collected by a SPME fiber  
32 (PDMS/DVB) at 35°C. Results of more than 80% recovery and LODs ranging from  
33 0.02 to 1.0 ng are reported.

34 Dialysis has been proposed by Söderström and Bergqvist [210], and Strandberg  
35 *et al* [211] to extract PAHs and PCBs from semi-permeable membrane device (SPMD)  
36 passive samplers. Compounds are dialyzed in cyclopentane-DCM (95:5) for 24 h and

1 further 24 h with fresh solvent mixture. In this way, recoveries of 70-126% are achieved.  
2 The use of deuterated surrogate standards to correct the recovery of PAHs is  
3 recommended.

4 Almost all procedures described for PAHs analysis imply a chromatographic  
5 separation of the compounds and thus, the clean-up of the extracts is usually a step  
6 preceding this separation. Clean-up is mostly performed by column chromatography on  
7 alumina [192], silica gel [187,190] or a combination of both sorbents [205,224],  
8 followed by concentration of eluates. However, Karthikeyan *et al* [203] found that no  
9 clean-up of the MAE extracts was necessary for the GC/MS analysis of the 16 PAHs  
10 listed in the US EPA priority list, as well as other authors, which directly concentrate  
11 the organic extracts prior to GC separation [195-199].

12

### 13 4.3. Determination

14 In the last ten years, determination of PAHs in air and particulate matter is  
15 mainly performed by GC, although some examples of methods based on HPLC are also  
16 reported. The popularity of capillary GC for the determination of PAHs is based on a  
17 favourable combination of greater selectivity, resolution and sensitivity compared to  
18 HPLC [225]. Conventional GC methods use a 5% phenyl substituted  
19 methylpolysiloxane column of 30 m×0.25 mm I. D. and 0.25 µm film thickness, which  
20 allows separation of most PAH compounds of concern in air and particulate matter [18].  
21 Fast GC with a short, wide-bore column coupled to a deactivated capillary at the inlet  
22 has been compared to conventional GC by Ravindra *et al* [206]. This method allowed a  
23 reduction of the separation time by a factor of three with the preservation of the  
24 chromatographic resolution for the low-molecular mass PAHs, which are the prevalent  
25 compounds in the gas phase of the ambient air. Programmable temperature vaporizer  
26 (PTV) inlets allow the injection of higher volumes of the PAH solution and thus, the  
27 improvement in sensitivity over the splitless injection can be 1-2 orders of magnitude.  
28 Norlock *et al* [212] reported LOD values ranging from 0.04 to 0.31 ng mL<sup>-1</sup> for most of  
29 the 16 individual PAHs analyzed by injecting a volume of 60 µL.

30 MS is the generalized detection technique, usually in the electron impact (EI)  
31 mode with selective ion monitoring (SIM) to enhance sensitivity [187,190,195,197,198].  
32 Chemical ionization has also been used in the positive mode (PCI) [199], as well as the  
33 negative mode (NICI) in the analysis of nitrated PAHs and oxygenated PAHs found in  
34 outdoor air [207].

35 Deuterated compounds are usually employed as internal standards. Some  
36 methods for PAH analysis in air use HPLC with fluorimetric detection as the

1 determination technique [184,186], although UV detection can also be used. PAH  
2 measurements were performed by both detection techniques in samples obtained inside  
3 a car and a subway train by Fromme *et al* [191]. UV detection at 254 nm has been  
4 reported by Pandit *et al* [226]. Resolution can be enhanced using ternary gradients and  
5 two reversed-phase columns connected in series for the analysis of parent PAHs and  
6 their nitrated and oxygenated derivatives as described by Albinet *et al* [207].

7 Non-chromatographic techniques have been used for certain environmental  
8 studies implying particulate matter. In this way, Sharma *et al* [227] proposed a method  
9 based on synchronous fluorescence to characterize a mixture of six PAHs finding  
10 concordance with GC/FID results.

11 Data on LODs as well as on recovery and repeatability achieved for PAHs  
12 analysis in indoor air samples are summarized in Table 4. LOD values usually account  
13 for the presence of the target compounds in blank samples, and range from about 0.1 to  
14 100 ng m<sup>-3</sup>, depending on the sample volume and the specific compound.

#### 16 4.4. Concentration in indoor air

17 A summary of PAH concentration levels found in different indoor environments  
18 is shown in Table 2. PAH concentrations in indoor air are dependent of both indoor and  
19 outdoor sources. A number of studies deal with the identification of these sources.  
20 Comprehensive assessment of indoor PAH concentrations in urban areas with different  
21 climates and their relationship to different types of outdoor emission sources would  
22 significantly contribute to the understanding of people exposure to industrial pollutants.  
23 In this way, Naumova *et al* [187] reported the results obtained from the subset of  
24 samples collected within the Relationship of Indoor, Outdoor, and Personal Air study  
25 (RIOPA). The goal of RIOPA was to gain a quantitative understanding of the impact of  
26 ambient sources of air pollutants such as VOCs, aldehydes, PM<sub>2.5</sub>, and PAHs on indoor  
27 air quality and human exposure by examining the relationships of concentrations of  
28 these pollutants in indoor, outdoor, and personal (breathing zone) air. RIOPA included  
29 homes in three different climate zones and with a variety of housing characteristics such  
30 as house types, air exchange rates, household appliances, and activities that can  
31 influence indoor air quality. Results of indoor-to-outdoor ratios indicated that indoor  
32 sources had a significant effect on indoor concentrations of 3-rings PAHs but a smaller  
33 effect on 4-rings PAHs, whereas the outdoor sources dominated the indoor  
34 concentrations of 5-7-rings PAHs. Similar results have been reported by Li *et al* [190],  
35 who demonstrated that indoor sources of PAHs are not negligible when activities such  
36 as cooking are considered, even in non-smoking homes. In a study conducted in

1 Chicago (USA) homes, they found that total concentrations of 15 PAHs in indoor air  
2 ranged from 2 to 147 ng m<sup>-3</sup>, with an average of 36 ng m<sup>-3</sup>. Similar concentrations were  
3 found outdoors (4 to 180 ng m<sup>-3</sup>) with the exclusion of naphthalene, which presented the  
4 highest mean among the 16 PAHs considered. It is well known that indoor naphthalene  
5 emissions are largely associated with mothball usage. In addition, the distribution of  
6 PAHs is dependent on altitude and thus, different human exposures through breathing to  
7 PAHs in air or in respirable particulate matter could be demonstrated [189].

## 9 **5. Polychlorinated biphenyls**

10 PCBs are considered hazard air pollutants (HAPs) under the Clean Air Act  
11 published by the US EPA in 1990 [228]. PCBs as well as some of their related  
12 compounds such as PCDDs and PCDFs, are included in the list of POPs of the United  
13 Nations Environment Programme. Therefore, PCBs remain intact in the environment  
14 for long periods, become widely distributed geographically, accumulate in the fatty  
15 tissue of living organisms, and are toxic to humans and wildlife. The Stockholm  
16 Convention is a global treaty to protect human health and the environment from POPs  
17 [229]. In implementing the Stockholm Convention, Governments will take measures to  
18 eliminate or reduce the release of POPs into the environment. The International Agency  
19 for Research on Cancer (IARC) and the US EPA classify PCBs as probable human  
20 carcinogens. The National Toxicology Program has concluded that PCBs are reasonably  
21 likely to cause cancer in humans. In addition, the NIOSH has determined that PCBs are  
22 potential occupational carcinogens.

23 PCBs have been detected in indoor air at concentrations of an order of  
24 magnitude higher than ambient air. It has been suggested that certain electrical  
25 appliances and devices, such as fluorescent lighting ballasts, which have PCB-  
26 containing components, may emit PCBs to indoor air. Also, PCBs were used as  
27 plasticizers in joint sealants, which can contain up to 30% PCBs. The American  
28 Conference of Governmental and Industrial Hygienists (ACGIH)-Threshold Limit  
29 Value (TLV) expressed as a TWA is 0.5 mg m<sup>-3</sup> for PCBs with a 54% of chlorine, and it  
30 is corresponded with the concentration of a substance to which most workers can be  
31 exposed without adverse effects. This value agrees with the The OSHA-PEL, expressed  
32 as a TWA too, which represents the concentration of a substance to which most workers  
33 can be exposed without adverse effects averaged over a normal 8-h workday or a 40-h  
34 workweek. The NIOSH recommended exposure limit (REL) is 0.001 mg m<sup>-3</sup>, for an 8-  
35 or 10-h TWA exposure and/or ceiling [230]. OSHA numbers are regulatory, whereas  
36 NIOSH and ACGIH numbers are advisory. Inhalation is an important route of

1 exposition to PCBs, especially for the less chlorinated ones. Recent findings suggest  
2 that indoor air is a major source of PCBs [231] contradicting the prevailing theory that  
3 soil volatilization is the primary source of PCBs in the atmosphere. Therefore, indoor  
4 air monitoring is a task of major concern. Some recent papers where PCBs were  
5 analyzed in indoor air are listed in Table 5.

### 6 7 5.1. Sampling

8 Active air sampling is by far the most common method used today for sampling  
9 PCBs. These methods are recommended for rapid and punctual measurements.  
10 Furthermore, they are very accurate and easy to calibrate. As US EPA Methods TO-4A  
11 and 10A [8] involve the use of PUF plugs in high and lo-vol air samplers, respectively,  
12 this adsorbent have been extensively used to actively collected PCBs in outdoor  
13 atmospheres [247-259]. Moreover, polychlorinated, polybrominated and  
14 brominated/chlorinated dibenzo-p-dioxins and dibenzofurans are determined by the US  
15 EPA Method TO-9A [8]. The method uses a Hi-Vol air sampler equipped with a QFF  
16 and PUF adsorbent for sampling 325-400 m<sup>3</sup> ambient air in a 24-h sampling period.  
17 High [244,246] or low [192,245] volume air samplers containing PUF plugs have also  
18 been used to trap PCBs present in the gas-phase of indoor atmospheres. Hi-vol samplers  
19 operate at about 1 m<sup>3</sup> min<sup>-1</sup>, while lo-vol samplers use pumps which typically operate at  
20 several L min<sup>-1</sup>. Apart from PUF plugs, other adsorbents may also been successfully  
21 utilised, especially if it is necessary to simultaneously collect some other volatile  
22 analytes. Less chlorinated PCBs are better retained in PUF combined with other  
23 adsorbents as Chromosorb, Tenax, Florisil, XAD resins or Porapak [260]. Florisil  
24 [7,232,237,241,261], a functionalized styrene-divinylbenzene (Oasis HLB) [242] or  
25 such small amounts as 25 mg of Tenax TA [238,239] have been demonstrated to be  
26 suitable adsorbents to collect PCBs in indoor air samples. In order to sample the PCBs  
27 fraction bound to the particulate matter, quartz [192,232,242,245] or glass [244,246]  
28 fiber filters are placed in front of the adsorbent. The adsorbent can also retain those  
29 compounds that volatilize from the filter during sampling. NIOSH Method 5517 [7]  
30 collects PCBs in a polytetrafluoroethylene (PTFE) filter and XAD-2 resin (100 mg/ 50  
31 mg). The sensitivity of the method is highly dependent on the volume of air collected.  
32 For this reason, breakthrough volumes should be determined in order to know the  
33 maximum volume of air that could pass through the adsorbent. In the case of PCBs,  
34 several m<sup>3</sup> of air can usually be sampled without significant losses. Ramil *et al.*,  
35 compares three different adsorbents to collect PCBs from indoor air, obtaining that  
36 OASIS exhibited higher breakthrough volumes than XAD-2 (>50 m<sup>3</sup>) [242].

1 Furthermore, the functionalized adsorbent is better than PUF cylinders in terms of  
2 solvent consumption and rapidity. When active samplers are used, some authors have  
3 reported sampling and analysis artefacts caused by elevated indoor air PCB  
4 concentrations or the presence of foam gasket near the main air flow path [246,262]. To  
5 avoid contamination sources, they strongly recommend measuring the background  
6 levels, a thoroughly cleaning of the sampler, as well as collecting blanks during field  
7 sampling, preparation and analysis.

8 The use of passive air samplers for indoor and workplace air is not as common  
9 as active sampling. Passive air samplers are increasingly employed for monitoring POPs  
10 due to their ideal applicability for long-term monitoring providing TWA estimations.  
11 They have a long operation time, from days to even several weeks, but its low cost  
12 facilitates simultaneous deployment in a large number of locations. Although these  
13 samplers have been sparingly used to monitor outdoor PCBs all around the world  
14 [210,263-276], there are only few reports on their use to monitor PCBs in indoor  
15 environments [211,231,234-236,243]. SPMDs [211] or PUF disks [231,234-236] have  
16 been successfully applied to indoor monitoring of PCBs. PUF disks are particularly  
17 attractive for POPs in indoor/outdoor air due to its high retention capacity [234]. In  
18 addition, their potential undersampling of particulate phase compounds is  
19 counterbalanced by the potential underestimation of indoor airborne concentrations if  
20 hi-vol active samplers are deployed for excessive periods [244]. In a study performed by  
21 Shoeib and Harner [243] three passive sampling media (SPMDs, PUF disks and an  
22 organic-rich soil), which were exposed to contaminated indoor air over a period of 450  
23 days, were tested and compared in terms of their functionality and versatility as passive  
24 samplers of POPs, including PCBs and polychlorinated naphthalenes (PCNs). A recent  
25 study sampled the contaminated air with burning plastic floor and electronic scrap using  
26 SPMDs and fresh unpolluted spruce needles, finding that above mentioned membranes  
27 can absorb much more PCDDs/Fs and PCBs than spruce needles [277]. Two novel  
28 promising passive devices based on LDPE membrane tubings have also been developed  
29 [278,279]. The first type (a spiral-rod sampler) consists of a low-density polyethylene  
30 membrane acting as a permeation film and a silicone elastomer as the receiving  
31 material; the second (a stir-bar sampler) has the same membrane material but a PDMS-  
32 coated stir bar acting as the collector phase. The first sampler is cheaper and it showed  
33 higher sensitivity compared to the second one. Anyway, both samplers have been  
34 successfully tested for the long-term air monitoring of SVOCs, including PCBs, in a  
35 polluted area over an exposure period of up to 28 days [278]. As it is well known, one  
36 of the drawbacks of passive samplers is the fact that they are very influenced by

1 sampling rates, among other factors. In the case of PCBs, several studies found variable  
2 congener-specific sampling rates [234], suggesting that sampling rates derived from a  
3 specific sampler configuration deployed under specific environmental conditions,  
4 should not be extrapolated to different sampler configurations.

## 5 6 5.2. Sample treatment

7 Soxhlet extraction is normally used to desorb PCBs from PUF plugs/disks and  
8 filters. It takes long periods of time (8-24 h) and uses large volumes of solvents, for  
9 example hexane [231,234-236,245], petroleum ether [243], DCM [244], toluene [232]  
10 or a mixture of hexane:acetone 1:1 [192]. US EPA Methods TO-4A and TO-10A  
11 recommended PUF extraction using a mixture of hexane:diethyl ether at 5% for a  
12 minimum of 16h, followed by concentration with nitrogen [8]. In a recent paper, PUF  
13 plugs were extracted by PLE in a pressurised solvent system with an n-hexane:acetone  
14 1:1 mixture at 100 °C and 100 bar, and filters were ultrasonically extracted with DCM  
15 [192]. When other adsorbents are used, solvent extraction with a few milliliters of  
16 hexane is often carried out [7,237,241,242]. Barro *et al* extracted PCBs from 25 mg of  
17 Tenax by ultrasound-assisted solvent extraction. Adding only 500 µL of n-hexane,  
18 recoveries ranging from 72.3-97.9% were achieved [239]. Miao and co-workers [261]  
19 extracted PCBs and PAHs from Florisil by supercritical fluid extraction with CO<sub>2</sub> or  
20 N<sub>2</sub>O. When high sensitivity is needed, PCBs can be extracted from Tenax using head-  
21 space SPME [238]. Previous to SPME, the addition of 100 µL of acetone is convenient  
22 to favour PCBs transfer towards the fiber. Limits of detection from 11 to 96 pg m<sup>-3</sup> were  
23 reached sampling only 2.5 m<sup>3</sup> indoor air. This method have the inherent advantages of  
24 SPME, including direct thermal desorption of the fiber into the injection port of a gas  
25 chromatograph. Tobias *et al.* [280] have also thermally desorbed into a PTV inlet  
26 several PCBs, among other SVOCs, previously collected into diffusion denuders. This  
27 procedure virtually provides complete transfer of analytes collected from ambient air  
28 into the GC, evidenced by recoveries of 90.7-120%. Passive samplers based on LDPE  
29 membrane tubing can be thermally extracted as well [278,279].

30 Processing of the SPMDs generally involves long and tedious stages as exterior  
31 cleaning and at least two consecutive organic solvent dialysis with hexane [243] or  
32 repeated rinsing/soaking with organic solvents, for example mixtures of cyclopentane  
33 and DCM [211]. An attractive alternative based on accelerated solvent extraction has  
34 been published by Wenzel *et al.* [281] to desorb PCBs from SPMDs. This procedure  
35 reduces the solvent consumption by two-thirds and it is up to 70 times faster, taking  
36 only 40 min. Yusá *et al.* [282] improved SPMDs treatment extracting some water-borne

1 hydrophobic contaminants, including several PCBs from membranes, by means of  
2 microwave-assisted extraction (MAE). The solvent mixture hexane-water (10:1) gave  
3 the highest extraction yields using an irradiation power of 500 W. The MAE procedure  
4 reduces extraction time to 9 min and solvent consumption to 99 mL hexane.

5 After extraction, size-exclusion chromatography, chemical class-specific  
6 fractionation using Florisil [234,244], silica gel [245] and/or alumina  
7 [192,242,245,246] sorption chromatography or reversed-phase chromatography is  
8 normally required. When large volumes of solvents are used for the extraction and/or  
9 clean-up processes, unavoidable additional steps are required to achieve the desirable  
10 sensitivity. Drying of extracts adding anhydrous sodium sulphate to remove any  
11 residual water content, filtration, or concentration are common procedures. Extraction  
12 from PUF disks often involves a treatment with concentrated sulphuric acid, liquid-  
13 liquid extraction with dimethyl sulfoxide, elution through a Florisil column,  
14 concentration, and solvent exchange to nonane [231,235,236].

### 16 5.3. Determination

17 GC is the selected technique for the analysis of PCBs using ECD  
18 [242,243,245,246], or low-resolution mass spectrometry (MS) working either in the EI  
19 [211,231,234-237,241] or chemical ionization (CI) mode [243]. When higher selectivity  
20 is required, tandem mass spectrometry can be used for the analysis [238,239]. Detection  
21 limits under  $\text{pg m}^{-3}$  can be obtained using GC/MS in the SIM mode [231,235]. High-  
22 resolution GC/MS provides detection limits as low as  $0.05\text{-}0.5 \text{ pg m}^{-3}$  [232]. Real-Time  
23 PCB monitoring using time of flight mass spectrometry (TOF/MS) with picosecond  
24 laser ionization has also been applied [283]. Not very elevated sensitivity ( $0.01 \text{ mg N}^{-1}$   
25  $\text{m}^{-3}$ ) but short measuring times of 1 min makes it suitable for measuring PCB  
26 concentrations in high polluted atmospheres as exhaust gas.

### 28 5.4. Concentration in indoor air

29 The total PCB content for an indoor air sample must be estimated as the sum of  
30 the 6 congeners PCB-28, 52, 101, 138, 153 and 180 multiplied by a factor of 5.  
31 According to the standard procedure given by World Health Organization (WHO)  
32 (updated in 2005), the toxicity equivalency for dioxins and dioxin-like compounds must  
33 be calculated as the sum of the products of the concentration of each congener with its  
34 toxicity equivalency factor (TEF) [284].

35 A study performed by Jamshidi *et al.* use chiral signatures in an innovative way  
36 to distinguish between PCB sources, which demonstrates that indoor air ventilation

1 releases far more PCBs to the atmosphere around Birmingham (UK) than does the soil  
2 [231]. Menichini *et al.* found indoor PCB concentrations higher than outdoors by an  
3 approximate factor of 2-50 [192]. These results indicate that indoor air may contribute  
4 to the overall exposure to PCBs more than the urban air, which it is consistent with the  
5 previous mentioned findings. For that reason, and taking into account the well known  
6 adverse effects that these chemicals can cause to the human health, PCB monitoring  
7 have become a priority issue. Table 2 lists some papers in which an estimation of PCB  
8 concentrations in diverse indoor microenvironments is presented. When clear workplace  
9 exposures could be involved, outdoor measurements were also included.

10 Several authors have estimated PCB concentrations in homes [211, 235, 236,  
11 244, 245]. A complete studied carried out by Harrad and co-workers measured PCB  
12 levels in 31 homes, 33 offices, 25 cars and 3 public microenvironments [235]. Cars  
13 were the least contaminated microenvironment with average concentrations of 1391 pg  
14 m<sup>-3</sup>. However, they found that inhalation makes an important contribution (between 4.2  
15 and 63%) to overall UK exposure to PCBs. Average concentration of PCBs (8920 pg m<sup>-3</sup>)  
16 was an order of magnitude higher than those previously reported for outdoor air.  
17 Currado and Harrad [236] also found higher PCB levels in indoor air (mean of 9.0 ng m<sup>-3</sup>)  
18 than in outdoor air (0.31 ng m<sup>-3</sup>) [244]. Unlike VOCs, PCB concentrations in older  
19 buildings seem to be higher than in newer ones. In addition, Hazrati and Harrad [236]  
20 found that seasonal variability in indoor contamination appears less significant than  
21 observed outdoors, although concentrations in warmer months usually exceeded those  
22 in colder ones. Kohler *et al.* [237,241] performed the first large-scale nationwide  
23 analysis in Switzerland on the issue of PCB-contaminated joint sealants. Other authors  
24 found similar levels (1 µg m<sup>-3</sup>) in buildings with known PCB sources as permanent  
25 elastic sealants [232]. In 42 cases where joint sealants containing PCBs were present,  
26 clearly elevated PCBs indoor air concentrations above 1 µg m<sup>-3</sup> were encountered. In a  
27 5% of cases, levels were higher than 3 µg m<sup>-3</sup> [237].

28 Hazrati and Harrad [234] derived TWA concentrations of 14 PCBs congeners  
29 using PUF disks exposed in an office microenvironment for periods ranging from 10 to  
30 50 days. TWA concentrations for an exposure of 10 days varied from 5 for PCB-136 to  
31 529 pg m<sup>-3</sup> for the less chlorinated PCB studied (PCB-18). In polluted schools, two  
32 different reports found similar PCB levels between 0.7 and 20.8 µg m<sup>-3</sup> [285,286]. PCB  
33 indoor air concentrations were measured in highly contaminated schools and control  
34 schools [287]. Total PCB concentrations were beyond 12 µg m<sup>-3</sup> in some rooms of the  
35 contaminated schools, being the less chlorinated PCBs the prevailing congeners. Data

1 supported the finding that heavy indoor air contamination with low chlorinated PCBs  
2 causes an increase of PCB-28 and PCB-52 blood levels.

3       Regarding outdoor urban/industrial areas showing possible occupational  
4 implications, Mari *et al.* [288] measured concentrations of PCBs, PCDDs/Fs and PCNs  
5 using active and passive air samplers at two zones of Barcelona near a municipal solid  
6 waste incinerator and a combined cycle power plant. Concentrations of the less  
7 chlorinated PCBs studied were up to 66 pg m<sup>-3</sup>. The contaminated air with burning  
8 plastic floor and electronic scrap was monitored using SPMDs, finding concentrations  
9 ranging from 9 to 25 ng of total PCBs per membrane [277]. Hu *et al.* [240] measured  
10 PCDD/Fs concentrations in four sites of municipal waste incinerators; a fly ash  
11 solidification facility, a slag bunker, a slag conveyor, and an ash conveyor. Results of a  
12 three-day workplace air monitoring in the incineration plants revealed total PCDD/Fs  
13 concentrations ranging from 0.87 to 136.67 pg m<sup>-3</sup>, which are equivalent to 0.06-7.11 pg  
14 m<sup>-3</sup> international toxicity equivalent concentration (TEQ). The presence of chlorinated  
15 and brominated compounds in electronic waste also results in the formation of  
16 PCDD/Fs and PBDD/Fs during the electronic waste dismantling process. Li *et al.* [233]  
17 found PCDD/F abundances between 64.9 and 2365 pg m<sup>-3</sup> in an electronic waste  
18 dismantling area.

## 20 **6. Industrial contaminants in indoor suspended particulate matter and dust**

21       Some of the industrial chemicals potentially affecting human exposure are  
22 mainly or partially associated to particulate matter. This is the case of PAHs, phthalates,  
23 polybrominated diphenyl ethers (PBDEs) and other flame retardants, PCBs and related  
24 compounds, as well as synthetic fragrance compounds or pesticides. PM<sub>2.5</sub> (fine  
25 particulate matter with a diameter of <2.5 μm) is closely associated with health negative  
26 effects since it acts as concentrator of many SVOC pollutants. Among the pollutants  
27 associated with indoor suspended particulate matter, PAHs are important owing to their  
28 carcinogenicity. Li *et al* [189] conducted a study to assess the content of PM<sub>2.5</sub> and  
29 PM<sub>2.5</sub> related PAHs in residential buildings in an industrialized region of China. Using  
30 a procedure summarized in Table 6 these authors found that indoor and outdoor  
31 concentrations of PM<sub>2.5</sub> largely exceeded the daily average concentration of 65 μg m<sup>-3</sup>  
32 proposed by the US EPA. Among PAHs, mainly contributors were the 5-7 ring PAHs  
33 (from benzo[b]fluoranthene to coronene, MW= 252-300). In addition, a high correlation  
34 was found between indoor and outdoor concentrate ions indicating that the indoor  
35 pollution was dominated by outdoor sources, mainly traffic. Analytical procedures for  
36 the analysis of pollutants associated to particulate matter usually imply the retention of

1 compounds in GFFs, QFFs, or in a combination of a filter and a polymeric cartridge  
2 followed by their extraction with a proper solvent, and the analysis by GC or HPLC.  
3 Pandit *et al* [226] used Soxhlet to extract samplers of GFF combined with PUF with 50  
4 ml of benzene for 8 h at 12 cycles h<sup>-1</sup>. The extract was filtered, dried under nitrogen  
5 flow and redissolved in 1 ml of acetonitrile for HPLC-UV analysis of PAHs. They  
6 found that although concentrations of PAHs could be two to ten-fold higher during a  
7 cooking period, the effective total daily exposure was only two-fold higher than that  
8 from ambient air. Ott and Siegmann [193] used an alternative analytical approach that  
9 takes advantage of the photoemission physics of PAHs adsorbed on the surfaces of fine  
10 particles to characterize several indoor and outdoor sources of PAHs. At ambient  
11 temperatures, the PAHs with less than four benzene rings remain in the gas phase, and  
12 hence they are not adsorbed on the surface; PAHs with four or more rings are  
13 predominantly adsorbed when in equilibrium with the carrier gas and in this way can be  
14 detected with great efficiency. With the light energy chosen, the particles by themselves  
15 are capable of only weak photoemission, but if they have PAH molecules condensed or  
16 adsorbed on the surface, the surface-bound flat PAH molecules absorb UV light with  
17 high efficiency. While neither the PAH molecules in the gas phase nor the particles by  
18 themselves are photoionized, the combination of a particle with an adsorbed PAH is  
19 ionized. Two continuous particle monitors are simultaneously used, one operating on  
20 photo-charging mode, that is on the principle ionization of fine particles that responds to  
21 surface particulate PAHs; and the second, on diffusion charging calibrated to measure  
22 the active surface area of fine particles. The result is the photo/diffusion charging ratio,  
23 which its physical interpretation is the amount of PAH mass per unit area of the active  
24 surface of the particles. Some workplaces such as tollbooths are more sensitive to  
25 pollution by airborne contaminants. To evaluate this hazard, Sapkota *et al* [58]  
26 measured the concentrations of VOCs and particulate matter-bound PAHs, finding a  
27 reduction of PAH levels from outdoors (50 ng m<sup>-3</sup>) to indoors (15 ng m<sup>-3</sup>) due to the  
28 positive pressure control ventilation system of the tollbooth.

29 Particle-bound PCBs can be simultaneously determined with the gas phase using  
30 GFFs [243,244,246] or QFFs [192,242,245]. Ramil *et al.* [242] collected the airborne  
31 particulate matter in a QFF and extracted the PCBs by MAE using a mixture of hexane  
32 and acetone.

33 Although VOCs are not usually studied in indoor particulate matter, in a recent  
34 study performed by Cai and co-workers [289], VOCs and odorants associated with  
35 swine barn particulate matter were determined using SPME and multidimensional  
36 GC/MS-olfactometry. Their findings indicated that a significant fraction of swine odor

1 could be carried by the suspended particulate matter. The majority of VOCs and  
2 characteristic swine odorants were preferentially bound to smaller-size particulate  
3 matter.

4 Concentrations of industrial pollutants found in indoor suspended particulate  
5 matter in homes are shown in Table 7.

6 House dust is a complex mixture of biologically-derived material, particulate  
7 matter deposited from the indoor aerosol, and soil particles brought in by foot traffic  
8 [293]. Many contaminants adsorbed onto suspended particulate matter are later settled  
9 out in homes because of PM deposition as house dust. Furthermore, these compounds  
10 have the potential to persist and accumulate in indoor dust, as they are not subjected to  
11 the same degradation processes that occur outdoors [294]. Since equilibrium  
12 concentrations on dust particles generally far exceed those found in the gas phase, dust  
13 and its associated fine particulate matter tends to become a sink for semivolatile organic  
14 compounds [295]. In addition, adsorbed compounds are not subjected to the same  
15 degradation processes that usually occur outdoors, and thus, contaminants persist and  
16 accumulate in indoor dust.

17 Inhalation, dermal adsorption and inadvertent ingestion of indoor dust have been  
18 recognized as important exposure pathways for organic contaminants [295], especially  
19 in the case of crawling children exhibiting hand-to-mouth behaviour [296]. Hence,  
20 analysis of organic contaminants in house dust should be performed in an effort to  
21 characterize human exposure in the indoor environment.

22 In most of reported methods for the analysis of organic contaminants in indoor  
23 dust, samples are collected from conventional vacuum cleaners equipped with paper  
24 dust bags. The content of the bags is passed through a suitable sieve to remove large  
25 pieces and to obtain a high degree of homogeneity. Dust samples are then weighed and  
26 solvent extracted using the techniques summarized in Table 8, and the target  
27 compounds usually determined by GC/MS. Recently, a standard reference material  
28 (SRM) has been developed to determine organic compounds in house dust. The SRM  
29 2585 is intended for use in the validation of methods for the analysis of PAHs, PCBs,  
30 chlorinated pesticides, and PBDEs [299].

31 Literature on measuring VOC concentrations in dust is scarce. It is worth a  
32 mention the study carried out by Nilsson *et al.* [291] in which 28 VOCs were analyzed  
33 in indoor dust from a large number of homes using a novel technique, GC/UV  
34 spectrometry. The compounds found in highest concentrations were saturated aldehydes  
35 (C5-C10), furfuryl alcohol, 2,6-di-tert-butyl-4-methylphenol, 2-furaldehyde, and  
36 benzaldehyde. Results demonstrated the presence of a number of VOCs in indoor dust,

1 and provide, for the first time, a quantitative determination of these compounds in a  
2 large number of dust samples from residences. Determination of PCBs in dust samples  
3 is not very common, although an example must be emphasized. PCBs, PCDDs and  
4 PCDFs were determined by Aries *et al* [298] in a waste dust sample collected in the  
5 electrostatic precipitator of a sinter plant from steel-making processes, finding  
6 concentrations between 0.4 and 285.6 ng kg<sup>-1</sup>. Regarding PCBs, PCB-128 was the  
7 major congener contributing to the WHO-TEQ (96%). The contribution to the overall  
8 TEQ of the waste dust sample was mainly attributed to PCDFs followed by PCDDs,  
9 which accounted for 86.6% and 8.7% to the overall TEQ, respectively. Concentrations  
10 of VOCs, PAHs and PCBs found in homes dust are shown in Table 7.

11

1 **7. References**

2

3 [1] E.P. Council, Regulation (EC) No 1907/2006 of the European Parliament and of the  
4 Council of 18 December 2006 concerning the Registration, Evaluation, Authorization  
5 and Restriction of Chemicals (REACH), establishing a European Chemicals Agency,  
6 amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93  
7 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC  
8 and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC, Off.  
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Table 1  
Analytical procedures for the determination of VOCs in indoor air

Ref	Analyte	Sampling	Desorption	Determination	Recovery (%)	RSD (%)	LOD
26	40 VOCs	Active with a cartridge containing 800 mg Chromosorb (20 mL min <sup>-1</sup> )	Thermal desorption (TD)	GC/MS	NR	NR	ng m <sup>-3</sup>
27	29 VOCs	Passive with Tenax in a tube-type configuration	TD	GC/MS	97	NR	0.024 µg m <sup>-3</sup>
28	20 VOCs	TD tubes with 430 mg Carboxen followed by 170 mg Carboxen (10-40 mL min <sup>-1</sup> , 8-10 h, 6-24 L)	TD	GC/MS (SIM)	83-91	NR	NR
29	BTEX	Active with stainless steel tubes packed with 250 mg Tenax (140-150 mL min <sup>-1</sup> , 2 h)	TD	GC/MS, GC/FID	NR	NR	0.5-0.8 µg m <sup>-3</sup>
30	32 VOCs	Organic Vapors Monitors 3M 3500 (badge-type passive sampler consisting of a permeable membrane and an activated-charcoal pad)	Solvent extraction (SE) with 1 mL acetone-carbon disulfide 2:1	GC/MS	NR	NR	1-49 µg m <sup>-3</sup>
31	38 VOCs	Canisters (8 h, US EPA Method TO-14)	TD	GC/MS	NR	NR	0.2 ppb
32	5 VOCs	Active with stainless steel tubes filled with Tenax and Carboxen (70 mL min <sup>-1</sup> , US EPA Method TO-17)	TD	GC/MS	NR	NR	NR
33	Toluene	Static sampling (stagnant air) using 1 L cylindrical glass bulbs equipped with Teflon stopcocks and a septum in the middle to introduce a SPME fiber (CAR-PDMS, 450 min)	TD	GC/FID	NR	16	0.11 µg m <sup>-3</sup>
34	7 Volatile sulfur compounds	Whole sampling using fused silica-lined mini-canister followed by a calcium chloride drying tube (1.4 L)	TD-cryofocussing	GC/MS, GC/PFPD	NR	17	LOQ= 0.300 µg m <sup>-3</sup> (PFPD), 0.048 µg m <sup>-3</sup> (MS), 600 mL
35	12 VOCs	Active using sorbent tubes containing Tenax (100 mL min <sup>-1</sup> , 3-300 min, 0.1-0.8 L)	TD	GC/MS	NR	NR	NR
36	57 VOCs	Active trapping of gas and vapor on multi-sorbent glass tubes containing 70 mg Carbotrap, 100 mg Carboxen and 90 mg Carboxen	TD	GC/MS	19-82	≤25	0.001-97 ng
37	12 VOCs	Active using multi-bed sorbent tubes containing Carbotrap (150 mL min <sup>-1</sup> , 45 min). SPME fiber exposition for interior parts and adhesives (PDMS, 40°C, 30 min)	TD	GC/FID, GC/MS	NR	NR	NR
38	4 VOCs	SKC Ultra Passive sampler: badge-type sampler containing 600 mg Carboxen (24h) Perkin Elmer passive sampler: steel tube filled with 300 mg Carboxen (1 week)	TD	GC/FID	NR	NR	NR

39	4 VOCs	Active using stainless steel tubes packed with 300 mg Tenax ( $10 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ ) in a Microchamber-Thermal Extractor ( $\mu\text{CTE}$ )	TD	GC/MS	NR	NR	NR
40	VOCs	Active using a Carbotrap tube ( $0.5\text{-}1.0 \text{ L}$ , $100 \text{ mL min}^{-1}$ )	TD-cryofocussing	GC/MS, GC/FID	NR	NR	NR
41	VOCs	Gas-phase delivered to a reaction chamber from an 80-L Tedlar bag ( $20\text{-}100 \text{ mL min}^{-1}$ ). The air freshener was continuously electrically powered inside an 80-L stainless steel drum ( $100 \text{ mL min}^{-1}$ ). VOCs were sampled onto Tenax sorbent tubes	TD-cryofocussing	GC/MS	NR	2-20	NR
42	Benzene, toluene	Active using charcoal sampling tubes ( $500 \text{ mL min}^{-1}$ )	SE with 1 mL methanol	GC/EI-MS/MS	NR	NR	NR
43	10 VOCs	The air sample is enclosed in a 250 mL glass bulb where the SPME fiber (CAR-PDMS) is exposed until equilibrium	TD	GC/FID, GC/EI-MS (SIM)	NR	6-12	$0.05\text{-}0.5 \mu\text{g m}^{-3}$
44	10 VOCs	SPME fiber exposition (CAR-PDMS). After sampling, the fibers were hermetically closed in a stainless steel tube with stainless steel plugs. For inertness, the internal walls of the tubes were Silicosteel treated	TD	GC/FID, GC/EI-MS	NR	NR	NR
45	9 VOCs	Air was aspirated through bulbs and the sampling chamber was then closed for extraction in static mode (stagnant air, 3 h for equilibrium conditions and 1-45 min for the non-eq method) by SPME	TD	GC/FID, GC/EI-MS	NR	4-20 (non-eq) 8.4-10.2 (eq)	$0.05\text{-}0.5 \mu\text{g m}^{-3}$ (eq, 0.25 L) and $0.38\text{-}5.26 \mu\text{g m}^{-3}$ (non-eq, 1 L, 4 min)
46	Benzene, 1,3-butadiene	2 diffusive samplers: SKC-ULTRA (badge-type sampler with a diffusion barrier) and Radiello (radial symmetry-type: a microporous polyethylene cylindrical diffusive body containing a stainless steel net coaxial cylindrical cartridge filled with Carbo-pack or Carbograph). Sampling time: 6 h-1 week	TD	GC/FID	NR	<10 (Carbo-pack) 15-30 (Carbograph)	NR
47	BTEX	Passive using a home-made sampler with common 10-mL bottles packed with 75 mg Tenax	TD	GC/FID	NR	NR	$0.24\text{-}0.73 \mu\text{g m}^{-3}$
48	11 VOCs	Diffusive: using a set of stainless steel, tube-type diffusive samplers consisting of tube shells filled with Carbo-pack (24 h) Active: combination of a 6-L passivated, stainless steel canister with a flow controller ( $3.75 \text{ mL min}^{-1}$ , 24 h)	TD	GC/MS	NR	6-29	30-298 pptv
49	10 Very Volatile Organic Compounds	SPME fiber exposition (10 min), HS-SPME (CAR-PDMS, 0.5-20 min) for emissions from materials. Comparison with active sampling using active charcoal (4 h, 600 L)	TD (for fiber) and SE with carbon disulphide (for charcoal)	GC/FID, GC/MS	NR	NR	NR

50	25 VOCs	Passive sampling with a charcoal tube (24 h)	SE with 3 mL carbon disulfide	GC/EI-MS (SIM)	NR	<5	LOQ = 3-11 $\mu\text{g m}^{-3}$ (24 h)
51	94 VOCs	Stainless steel thermal desorption tubes containing 160 mg Tenax and 70 mg Carbosieve, separated by glass wool plugs (2 L)	TD	GC/EI-MS (SIM or scan)	NR	<10	0.003-0.273 $\mu\text{g m}^{-3}$ (SIM)
52	10 VOCs	Stainless steel sampling tubes filled with 240 mg Tenax, 390 mg Carbotrap or 270 mg Chromosorb	TD	GC/EI-MS (SIM)	NR	<12	0.01-0.07 $\mu\text{g m}^{-3}$ (0.75 L)
53	Benzene	Active using a personal sampler fitted with activated charcoal tube (500 mL min <sup>-1</sup> , 45-60 min)	Sonication with 1 mL methanol	GC/EI-MS/MS	88-92	2	0.002 $\mu\text{g/mL}$
54	VOCs	Passive using a home-made box sampler with a PDMS membrane filled with active carbon (4-5 weeks)	SE with 1 mL carbon disulfide	GC/FID	NR	NR	LOQ = 0.2 $\mu\text{g m}^{-3}$
55	98 VOCs	Active using stainless steel glass-lined tubes filled with 100 mg Tenax and 50 mg Carbopack separated by glass wool (5-500 mL min <sup>-1</sup> )	SPTD-cryofocussing	GC/EI-MS (SIM)	65-100	<22	0.01-0.14 ppbv
56	37 VOCs	Active using tubes packed with Carbopack and Carboxen (10 L, 100 mL min <sup>-1</sup> , 100 min)	TD	GC/MS	72-139	<25 (in general)	$\leq 1.2 \mu\text{g m}^{-3}$ (10 L)
57	42 VOCs	Passive using tube-type diffusive sampler containing 650 mg Carbopack (24 h)	TD	GC/FID, GC/MS	NR	<20 (in general)	22-375 pptv
58	VOCs	Active using a sequential sampler with Air Toxic Tubes packed with Carbopack and Carboxen (every 3 h for 24 h, 25 mL min <sup>-1</sup> )	TD	GC/EI-MS (SIM)	NR	NR	NR
59	Acetic acid	SPME fiber exposition (CAR-PDMS, 30 min)	TD	GC/EI-MS (ion trap detector, ITD)	NR	4.7	5.7 $\mu\text{g m}^{-3}$
60	BTEX and n-alkanes	Two different needle traps: NT1, sealed tip in which sorbents were packed layer by layer with PDMS, DVB and Carboxen particles and quartz wool packed between the tip of the needle and the side port. NT2: a blunt tip in which the sorbent (Carboxen) was packed near the tip of the needle. During sampling, the needle was exposed to the sample, and the side hole was sealed with a septum. Active sampling required that the needle be connected with a pump or syringe	TD	GC/FID	NR	4	0.23-1.12 $\text{ng L}^{-1}$ (25 mL)
54,61	14-15 VOCs	Passive using 3500 Organic Vapor Monitors (samplers based on charcoal, 48 h)	SE with acetone:carbon disulfide 2:1	GC/MS	NR	NR	NR
62	BTEX	Two different sampling badges: OVM 3500 and ORSA (1-28 days)	SE with 2 mL carbon disulfide	GC/FID	NR	NR	NR
63	Volatile amines	Active using XAD-2 impregnated with NIT (18-208 L)	SE with 1 mL acetonitrile (ACN) and shaking, 30 min	LC/MS-MS (tripleQ)	NR	NR	0.12-0.25 $\text{ng L}^{-1}$
64	BTEX	SPME fiber exposition (CAR-PDMS, 30 min, non-equilibrium conditions)	TD	GC/EI-MS	NR	4.4-9.3	0.028-0.116 $\mu\text{g m}^{-3}$

65	8 VOCs	SPME fiber exposition with a new fiber coated with $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (20 min, 26 °C)	TD	GC/FID	4.59-109.6	4.1-9.2	<0.714-7.14 ng L <sup>-1</sup>
66	10 Chlorobenzenes	Active using a glass tube filled with 25 mg Tenax kept in place using a glass wool plug (2.5 m <sup>3</sup> , 100 L min <sup>-1</sup> , 25 min)	HS-SPME (PDMS-DVB, 15 min, 100°C)-TD	GC/EI-MS (ITD)	82-126	≤12	0.004-0.108 ng m <sup>-3</sup> (2.5 m <sup>3</sup> )
67,68	30 VOCs	Passive using OVM 3500 (4 weeks)	SE with 1.5 mL carbon disulfide with 1% methanol, and shaking, 30 min	GC/FID/ECD, GC/EI-MS	98-102	<10	0.01-1.0 µg m <sup>-3</sup> (FID/ECD, 4 weeks) and 0.01-0.05 µg m <sup>-3</sup> (MS, 4 weeks)
69	6 VOCs	A flow control device (500 mL min <sup>-1</sup> ) combined with an evacuated canister is compared against 600 mg charcoal tubes and diffusive badges (OVM)	Canister connected directly to the six-position valve that was connected to the GC injection port. SE with carbon disulfide	GC/FID	97-101 (canister)	<25 (in general)	NR
70	VOCs	The exterior of a hydrophobic hollow fiber membrane (part of a MESI system) is exposed directly to the air, while the carrier gas flowed continuously through the centre core of the membrane	TD-cryofocussing	GC/FID	NR	NR	NR
71	6 Chlorinated VOCs	Passive gas tube packed with activated charcoal (24 h)	SE with toluene	GC/ECD	NR	<9	0.02-0.21 µg m <sup>-3</sup> (24 h)
72	VOCs	Active using triple sorbent traps with 170 mg Carbotraps and 140 mg Carbosieve (80 mL min <sup>-1</sup> , 2h)	TD	GC/MS	NR	NR	NR
73	5 VSCs	Samples were collected into a home-made 100-L Tedlar bag using a pump. For TWA sampling (static mode), a SPME syringe needle was inserted through the septum of a sampling tube and the fiber (CAR-PDMS) was left retracted during sampling	TD	GC/PFPD	NR	NR	NR
74	11 VOCs	Active using multibed collection tubes custom-made of glass containing 400 mg Carbopack and 200 mg Carbosieve (1 L, 1 h, 10-20 mL min <sup>-1</sup> )	TD-cryofocussing	GC/MS	94-101	≤6.5	0.31-0.89 ppb (1L)
75	6 VOCs	Active (using ORBO-32 tubes containing 150 mg charcoal, 100 mL min <sup>-1</sup> , 5 h) / Passive (stainless steel tubes packed with 150 mg Tenax)	TD (Tenax) and SE with 1 mL carbon disulfide (charcoal)	GC/MS (Tenax), GC/FID (charcoal)	88.5-92.8 (Tenax) 99.5-112 (charcoal)	NR	NR

76	BTEX	SPME fibers (CAR-PDMS) and ORBO charcoal tubes connected or inserted into a cylinder	TD	GC/Carbon dioxide-cooled-Septum-equipped programmable injector (SPI)-FID	NR	<11	NR
77	11 Nitroaromatic compounds	Active using an anodized aluminium holder containing a Empore C <sub>18</sub> solid-phase extraction membrane kept in place by 2 Teflon rings (15 L min <sup>-1</sup> , 9.2 m <sup>3</sup> )	Direct on-line membrane desorption by the LC mobile phase	APCI-LC/MS-MS (triple Q)	0.5-600 ng	1-9	0.2-14.3 ng
78	BTEX	A long sampling cylinder with three different diameters is used. Air is pumped through the cylinder and a CAR-PDMS fiber with the fiber coating withdrawn into the needle is deployed at a section of the cylinder to determine TWA concentrations. Another CAR-PDMS fiber is used to monitor the real-time concentration by exposing the fiber to the moving air for 2 min at another section of the cylinder	TD	GC/SPI-FID, GC/EI-MS (ITD)	NR	NR	NR
79	6 Volatile aliphatic amines	SPME fiber exposition: PDMS-DVB (15-20 min)	TD	GC/FID	NR	NR	0.19-0.67 mg m <sup>-3</sup>
80	BTEX	Active with charcoal (100/50 mg) and GFF (3-4 h)	SE with 1 mL carbon disulfide (2-3 h)	GC/FID	NR	NR	NR
81	BTEX	2 Passive diffusive samplers : Analyst (for long-term, 1 month, charcoal-based type) and a home-made tube-type sampler (for a 12 h experiment, filled with graphitized carbon black)	SE with 2 mL carbon disulfide (charcoal) and TD (graphitized carbon black)	GC/FID, GC/MS (SIM)	NR	3-13.1	NR
82	11 VOCs	Dynamic field sampling: a SPME fiber (CAR-PDMS) was inserted in a 100-mL sampling vial. Air was pumped through the vial at a flow-rate of 100 mL min <sup>-1</sup> (60 min). A Teflon filter was placed at the inlet to filter out any dust particle that might damage the SPME fiber	TD	GC/SPI-FID, GC/MS	NR	4.24-17.26	NR
83	VOCs	Stainless steel sampling tubes with 3 beds of sorbents : 90 mg Carbopack (front), 115 mg Carbopack (middle) and 150 mg Carboxen (back)	Automated TD with internal focusing trap containing Carbopack and Carboxen	GC/MS	NR	NR	NR
84	18 VOCs	Passive using stainless steel tubes containing 279 mg Tenax (24 h)	TD	GC/MS	NR	NR	NR

23	7 VOCs	Passive samplers with silicone membranes and active charcoal as the sorption medium (4-5 weeks) / Active using active charcoal tubes (20 L h <sup>-1</sup> , 12 h) or Tenax tubes (0.5 L, 1 h)	SE with 1 mL carbon disulfide for 30 min (for charcoals) and TD (for Tenax)	GC/FID	NR	NR	NR
85	40 VOCs	Tedlar bag	SPME-TD	GC/MS	NR	NR	10 pptv - 0.93 ppbv
86	Acetic acid and formic acid	SPME fiber exposition (PA, < 4 L)	TD	SPI-GC/MS	NR	<11	5.3-28.9 µg m <sup>-3</sup>
87	11 Monoterpenes	Active trapping on 300 mg Tenax, Carbosieve or Chromosorb between two silanized glass wool plugs (60 min, 10 mL min <sup>-1</sup> , 0.6 L)	TD-cryofocussing	GC/MS	NR	7.7-20.9	LOQ = 0.96-14.22 µg m <sup>-3</sup>
88	Biogenic VOCs	MESI on-line system: a PDMS membrane and two different traps (PDMS and Tenax) in an extraction chamber. Quartz wool is placed at the ends of the sorbent bed to retain the packing	TD	GC/MS	NR	≤9	NR
89	43 VOCs	Portable analyzer with a capillary packed with 12.3 mg Carbopack and Carboxen as preconcentrator focuser (1 L)	TD	Portable GC/ Surface-acoustic wave sensors	NR	<9	100 ppt (1 L)
90	BTEX	Passive sampling using PDMS phase (OV1 type) shaped into parallelepiped blocks (6 mm x 10 mm) as absorptive surface		Spectroscopy (fluorimetry, absorptiometry)	NR	NR	2-20 mg m <sup>-3</sup>
91	3 VOCs	SPME fiber exposition (CAR-PDMS, 5 min)	TD	GC/MS	NR	<20	NR
92	42 VOCs	Field portable dual-stage preconcentrator and a microsensor array as the detector	TD-cryofocussing	GC/PID	NR	NR	NR
93	30 VOCs	Stainless steel tube containing 250 mg Tenax (2-3 L) / Glass tube containing two stacks of active charcoal (Carbotech) stabilized with 4 silver nets (30-50 L)	TD (for Tenax) and SE with carbon disulfide (for Carbotech)	GC/MS, GC/FID	NR	NR	0.7-5.2 µg m <sup>-3</sup> (Tenax) and 0.9-3.2 µg m <sup>-3</sup> (Carbotech)
94	20 VOCs	Air is drawn through a glass capillary tube packed with 3.4 mg Carbopack and 1.2 mg Carboxen (1 L)	TD	Portable GC/ Surface-acoustic wave sensors	NR	NR	NR
95	15 VOCs	Active with adsorbent tubes packed with 1g Carbopack and 150 mg Carbosieve or 300 mg Tenax followed by 600 mg Carbotrap (40 mL min <sup>-1</sup> )	TD	GC/MS	NR	<7.6	<0.32 µg m <sup>-3</sup>
96	Benzene	ORBO 402 cartridges filled with Tenax (2 beds: 100 and 50 mg), 200 mL min <sup>-1</sup> , 3.6 L	HS-SPME (PDMS-DVB, 10 min)-TD	GC/MS-ITD(µSIS)	NR	3-5	NR

97	5 Volatile organic peroxides	A supercritical fluid extraction cells (stainless steel tubes) filled with 2 Carbotraps (300 mg) separated by a QFF was used as sampling tube (120-140 L, 1 L min <sup>-1</sup> )	SFE using CO <sub>2</sub> and methanol (modifier)	HPLC/UV, GC/MS	83-97	NR	NR
98	6 VOCs	2 Portable Dynamic Air Sampling Devices (PDAS) using a PDMS-DVB fiber: Sampler 1: Household hair-dryer modified with air flow reverted. The fiber is exposed between the slit formed by 2 plain cardboard sheets where the air flow passes. Sampler 2: Sandwich design: the air passes through an orifice made in a device formed by 2 assembled stainless steel sheets separated by a Teflon spacer where the fiber is inserted	TD	SPI-GC/MS (ITD)	NR	NR	NR
99	6 VOCs	Passive using membrane extraction (hollow fiber silicon membrane and a section of another membrane inside a deactivated fused-silica tubing)	TD (electrical pulses with heating of the sorbent interface of the MESI)	GC/FID	NR	NR	NR
100	n-Alkanes	SPME with the fiber retracted during sampling (PDMS or PDMS-DVB, 1 min – 24 h)	TD	SPI-GC/FID	NR	NR	NR
101	4 VOCs	Active using charcoal tubes (0.5 L min <sup>-1</sup> , 6 h, 180 L)	Sonication (15 min) with carbon disulfide-methanol (60:1)	GC/FID	50.6-102.3	3.3-22.5	1.8-3.4 µg m <sup>-3</sup>
102	BTEX and hexane	SPME fiber exposition (PDMS-DVB, 1 min)	TD (30 s)	SRI portable GC/PID-FID-ELCD	NR	NR	1.3-8.6 ppb

NR: Not reported data

Table 2  
 Concentration of industrial organic contaminants in indoor air

	<b>Home</b>	<b>Office</b>	<b>School, kindergarten and daycare center</b>	<b>Store, market and shop</b>
VOCs ( $\mu\text{g m}^{-3}$ )	3-987 [32] 0.5-22.4 [61] 0.19-1226 [153] 0.31-28 [38] 0.2-159.0 [42] 0.035-3.8 [46] 1-269 [50] 0.01-231 [51] 6.6-114 [53] 1.59-13.91 [55] 0.005-455.87 [56] up to 1326 [62] 2.5-10.9 [64] 0.0156-12.8 [65] 0.5-58.6 [67] 0.03-4.96 [71] 0.90-2496 [68] 1.5-43.1 [81] 0.1-99.3 [95] 60-376 [154] 0.058-0.78 <sup>a</sup> [100]	2-1541 [32] 0.01-1252 [26] Total VOC=304.3-1679.9 [155] 1.5-3441 [156] 550-4600 [49] 0.59-9.83 [55] 0.1-22.0 [95] 14-112 [154]	0.34-33 [45] 0.3-48.0 [43] 1.8-11.8 [81] 11-22 [154] 0.067-0.084 <sup>a</sup> [100]	76 [157] 2200-140100 [79]

<p>Carbonyls (ng m<sup>-3</sup>)</p>	<p>Formaldehyde (FA): 40.0 (12.2-121.7), Acetaldehyde (AA): 20.5 (2.4-48.5) [155]  FA: 23-462 [172]  FA: 21.6, AA: 22.9, Propionaldehyde (PrA): 1.9, Hexaldehyde (HA): 4.6, Benzaldehyde (BA): 3.0 [167]  FA: 32.2, AA: 14.3, PrA: 2.1, HA: 8.6, BA: 1.2 [166]  FA: 2.7, AA: 1.2 [177]  FA: 4.39-9.27 [178]  FA: 12.7-23.2, AA: 30.9-49.6, PrA: 0.5-3.3, Valeraldehyde (VA): 0.5-2.1, HA: 1.0-2.9 [179]</p>	<p>FA: 17-24 [172]</p>	<p>FA: 14-16 [172]</p>	<p>FA: 17-29 [172]</p>
<p>PAHs (ng m<sup>-3</sup>)</p>	<p>PhA: 29-46, NaP: 697-1178 [208]  NaP: 860-1160, PhA: 210-240, BaP: 0.16-0.25 [196]  PhA: 9.1-330, BaP: 0.0027-1.1 [187]  NaP: 122-4813, PhA: 90-1358, BaP: 116-365, Σ12 PAHs: 1418-7974 [186]  NaP : ~2000, PhA : 80 [199]  NaP : 177, PhA : ~0.8, BaP : ~0.1, Σ15 PAHs without NaP: 2-147 [190]  BaP : 0.1-4.6 [192]  ΣPAHs: 14.18-77.9, NaP: 0.82-3.60, PhA: 0.19-1.00  BaP: 0.57-7.33 [189]  BaP: 0.09, 5.28 (median, max), ΣPAHs: 2.08, 15.8 (median, max) [191]  NaP: 6, PhA: 4.05 [209]  NaP: 271, PhA: 14.78, BaP: 0.177 [184]  PhA: 15, BaP: 0.19 [185]  NaP: 2.5-48, PhA: 13-190, BaP: &lt;0.01-0.27, 30-350 ° [211]</p>	<p>NR</p>	<p>NR</p>	<p>NR</p>

PCBs (ng m <sup>-3</sup> )	$\sum$ PCBs = 1.9-33 [192] $\sum$ PCBs = 0.0465-0.588 [231] $\sum$ PCBs = <0.01-5.5 <sup>c</sup> [211] $\sum$ PCBs=0.487-9.764 [235] $\sum$ 5PCBs=0.589-2.56 [236] <100 - >6000 [237] $\sum$ 6PCBs=720-4200 [241] $\sum$ PCBs = 0.001-1.25 [244] $\sum$ PCBs = 5.2-61 [245] 3.6-25 [197]	0.004-0.529 [234] $\sum$ PCBs = 0.816-102 [235] $\sum$ 5PCBs = 1.319-1.605 [236] 0.002-14.8 [244]	$\sum$ PCBs = 6-310 [246]	NR
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Table 2 (continued)

Concentration of industrial organic contaminants in indoor air

	Laboratory, hospital	Restaurant, bar, pub, cinema, theatre, museum	Car, truck, garage, petrol station, mechanic shop, public transport, station, airport, tollbooth	Greenhouse	Other workplaces and indoor environments
VOCs ( $\mu\text{g m}^{-3}$ )	0.1-8.3 [95]	7-110 [158] 0.5-150 [31] 0.01-4342 [26] 24-98 [59] 62-930 [86] 0.3-75.4 [95]	<0.01-115 [27] 0.3-494 [28] 6.3-11000 [37] 3.7-1571 [40] 2.0-198 [47] 9.41-54.9 [55] 0.10-95.7 [58] 35.0-131 [64] 4300 [79] 0.4-494.0 [95] 17-249 <sup>b</sup> [98] 0.46-0.72 <sup>a</sup> [100] 154.2-1265.5 [80]	NR	0.9-893 [159] 0.50-11500 [29] 1-2135 [30] 0.9-8327 [34] 2500-148200 [79] 0.04-1.85 <sup>b</sup> [85] 1-66714 [114] 14-57 [154] 0.019-0.032 <sup>a</sup> [100] 21.6-61.2 <sup>b</sup> [160]
Carbonyls ( $\text{ng m}^{-3}$ )	FA: 5.3-13.4, AA: 7.9-21.4, PrA: 1.8-6.1, VA: 1.0-7.0, HA: 1.3-3.5, BA: 1.3-2.7 [182]	NR	NR	NR	FA: 26.6-75.1 [172]
PCBs ( $\text{ng m}^{-3}$ )	NR	NR	$\sum\text{PCBs}=0.392\text{-}6.018$ [235]	NR	$\sum 6\text{PCBs}=13000$ [241]

NR: Not reported data

<sup>a</sup>  $\mu\text{g L}^{-1}$ <sup>b</sup> ppbv<sup>c</sup>  $\text{ng day}^{-1}$

Table 3  
Analytical procedures for the analysis of carbonyl compounds in indoor air

Ref	Analytes	Sampling	Extraction/Desorption	Extract treatment	Determination	Recovery (%)	RSD (%)	LOD
170	FA	Diffusive sampler with a semipermeable membrane and a coated collection filter with MBTH (~26.3 mL min <sup>-1</sup> )	Extraction with 5 mL MBTH, agitation (150 rpm, 35°C, 1 h)	Oxidation reaction of 4-mL MBTH extract with 1-mL FeCl <sub>3</sub> -sulfamic acid, 20 min	Spectrophotometry (628 nm)	93	4.0-7.5	9.7 ng m <sup>-3</sup> (24 h)
171	FA, AA, PrA, butanal, HA, crotonaldehyde (CA), BA, acrolein, acetone	Passive Aldehydes and Ketones Samplers (PAKS) diffusive sampler: C18 cartridge treated with DNSH (3.3-7.5 mL min <sup>-1</sup> ). After sample collection, cartridges were heated (60 °C, 60 min)	Elution with 2 mL ACN	NR	HPLC/Fluorescence (λ <sub>ex</sub> = 240 nm, λ <sub>em</sub> = 470 nm)	60.3-107.5	20	5-26 pg
155	FA, AA	Active collection on C18 cartridges pretreated with 2,4-DNPH (360 L, 6 h)	SE with DCM	Addition of 2,4-DNPH-cyclohexanone as internal standard (IS)	HPLC/UV (365 nm)	NR	<10	NR
172	FA	On-fiber derivatization (PFBHA) SPME (PDMS/DVB)	TD in SPI (45-250°C, 300°C min <sup>-1</sup> )	-	GC/FID	NR	NR	~1.22 µg m <sup>-3</sup>
173	FA	Diffusive sampler with a 2,4-DNPH impregnated filter	Sonication with ACN, 30 min	NR	HPLC/UV (355 nm)	>90	3	4.2 µg m <sup>-3</sup> (3 days)
174	FA	Diffusive sampler with a semipermeable membrane and a triethanolamine coated collection filter (~1.52 L h <sup>-1</sup> )	Extraction with 2 mL pure water	Addition of NaOH, acidic AHMT and potassium peryodate	Spectrophotometry (550 nm)	NR	5.8 (2.3-8.8)	1.48 µg m <sup>-3</sup> (7 days), 10.4 µg m <sup>-3</sup> (1 day)
168	VA	A modified PDMS SPME device used as a time-weighted average sampler. On-fiber derivatization with PFBHA	TD (250°C)	-	GC/FID	NR	NR	27 ng
175	FA, AA, PrA	A fiber-packed extraction needle with 2,4-DNPH for simultaneous derivatization and sampling	Desorption with 30 µL ACN at the injection port (170°C)	-	GC/EI-MS (total ion monitoring, SIM)	NR	NR	1.2-11.7 ng L <sup>-1</sup>
166	FA, AA, PrA, BA, HA	Active collection using two cartridges in series filled with silica impregnated with an acidified solution of 2,4-DNPH (30-95 min, 132-409 L).	20 mL ACN	NR	HPLC/UV (360 nm)	NR	NR	0.12-2.0 µg m <sup>-3</sup>
176	FA, AA, BA	Diffusive samplers with GFFs coated with 2,4-DNPH	Sonication with 4 mL ACN, 1 min	NR	HPLC/UV	NR	NR	NR

177	FA, AA, PrA, acrolein	Active collection with C18 cartridges pretreated with DNSH-trichloroacetic acid in methanol (1.0 L min <sup>-1</sup> , 2 h and 15 min). After sample collection, the cartridges were heated at 60 °C for 10 min	Elution with 2 ml methanol	Evaporation to dryness at 50 °C under reduced pressure, redissolution in 200 µL 95% methanol solution	Capillary electrophoresis/UV, Capillary electrophoresis /Laser-induced fluorescence	NR	NR	1.1-9.5 µg L <sup>-1</sup> (UV), 0.29-5.3 µg L <sup>-1</sup> (Fluorescence)
178	FA	On-line collection-FIA using a chromatomembrane cell with water as an absorbing solution (6 mL min <sup>-1</sup> , 20 mL)	-	Derivatization with acetylacetone and ammonium acetate at pH 5.6-5.8.	FIA/Spectrophotometry, FIA/Fluorescence	NR	1.5	0.06 µg m <sup>-3</sup> (Spectrophotometry), and 0.03 µg m <sup>-3</sup> (Fluorescence) for a 40 mL diluted air sample.
179	FA, AA, PrA, HA, butanal, heptanal	Air collection at 50 mL s <sup>-1</sup> in a 1-L Tedlar bag. Hantzsch reaction with dimedone and polymer-mediated extraction in thermo-responsive PNIPAAm polymer	Dissolution of polymer precipitates with the adsorbed aldehyde-dimedone derivatives in ACN	-	HPLC/Fluorescence.	NR	2.0-7.7	<20 ng m <sup>-3</sup>
180	FA, AA, PrA, butanal, pentanal, HA, CA, BA, acrolein, methacrolein, <i>p</i> -TA	Personal sampling pump cartridges (0.5 L min <sup>-1</sup> , 1.5 L)	Elution with 10 mL ACN	Derivatization with trideuterated 2,4-DNPH	HPLC/APCI-MS HPLC/UV (diode array, 190-500 nm).	88-103	4-10	0.1 µmol L <sup>-1</sup>

NR: Not reported data

Table 4  
Analytical procedures for the analysis of PAHs in indoor air

Ref	Analytes	Sampling	Desorption/Extraction	Extract treatment	Determination	Recovery (%)	RSD (%)	LOD
208	4 PAHs	Passive, Carbopack C	2 mL toluene	-	GC/EI-MS	NR	NR	NR
196	15 PAHs	QFF and XAD-2 cartridge in series (224 Lmin <sup>-1</sup> , 22 h)	Soxhlet with DCM, 16h	Concentration to 1 mL (Kuderna-Danish, K-D)	GC/EI-MS	NR	NR	NR
209	7 PAHs	Active, XAD-2	Microwave-assisted thermal desorption (10 mL ethylenglycol-1M NaCl)	Headspace SPME (PDMS-DVB fiber, 35°C) and TD (290°C, 5 min)	GC/EI-MS	>80	3-14	0.02-1 ng
197	2 PAHs	URG personal pesticide sampling cartridges (impactor inlet followed by a cartridge fitted with QFF, XAD-2 resin and PUF plugs) (8-9 L min <sup>-1</sup> , 10-14 m <sup>3</sup> )	Soxhlet with 150 mL of 6% diethyl ether/hexane, 16 h	Addition of sodium sulphate and concentration to 2 mL 10% ether-hexane.	GC/EI-MS (SIM)	40-220	15-25	2-75 ng m <sup>-3</sup>
187	55 PAHs	QFF and PUF	Statically extraction with 40 mL hexane-DCM 4:1 at 50°C, 1h	Rinse twice with 20 mL hexane-DCM 4:1 at 50°C, concentration, clean-up on silica, elution with 8 mL hexane-DCM, addition of deuterated IS, concentration to ~0.01 mL	GC/EI-MS (SIM)	62-91	7.3-16	NR
184	PAHs	Low noise indoor sampler provided with QFF and XAD-2 (0.018 m <sup>3</sup> min <sup>-1</sup> , 24 h)	Sonication with 6 mL (XAD-2) and 2 mL (QFF) cyclohexane	-	HPLC/UV-Fluorescence	73-130	3-9	0.01-30 ng m <sup>-3</sup> (26 m <sup>3</sup> sample)
210	<i>d</i> -PAHs (performance reference compounds)	Passive, SPMD	Dialysis with ciclopentane-DCM	-	GC/EI-MS (Selected ion recording)	NR	NR	NR
195	PAHs	Active/passive, GFF and PUF (2 L min <sup>-1</sup> )	Soxhlet with hexane-cyclohexane 1:1, 4 h	Concentration to ~1 mL and addition of IS	GC/EI-MS (SIM)	66-114	22	0.85-6.8 ng mL <sup>-1</sup>

186	12 PAHs	Low noise sampler provided with QFF and XAD-2 (1 L min <sup>-1</sup> , 12 h)	Sonication with 20 mL DCM-ACN 3:2, 30 min, avoiding water bath overheating	Addition of 30 µL dimethylsulfoxide to 10 mL raffinate, evaporation under N <sub>2</sub> , redissolution in 970 µL methanol, filtration with 0.2 µm filter	HPLC/Fluorescence	>90	<2.64	0.53-29.13 pg
199	PAHs	Indoor air samplers with XAD-2 or XAD-4 (230 L min <sup>-1</sup> , 24 h)	Soxhlet with DCM 16h and ethyl acetate 8h	Concentration to 1 mL (K-D) and addition of deuterated IS	GC/PCI-MS (SIM)	85-100	NR	0.1 ng m <sup>-3</sup>
211	28 PAHs	Passive with SPMD, two weeks	Dialysis in cyclopentane-DCM 95:5 24h and further 24h with fresh solvent	Addition of deuterated surrogate standard (SS), evaporation of solvent excess, clean-up on HR-gel permeation chromatography, enrichment	GC/EI-MS (Selected ion recording)	70-110	NR	NR
190,212	16 PAHs	QFF and modified ORBO-1000 PUF-XAD2-PUF cartridge with deuterated SS (10 L min <sup>-1</sup> , 46-48 h, 28 m <sup>3</sup> )	Soxhlet, with hexane-diethyl ether 90:10 for 24 h followed by other 24 h with DCM	Concentration to ~5 mL (K-D) and to ~2mL under N <sub>2</sub> ; clean-up on silica gel and anhydrous sodium sulphate; elution with hexane- diethyl ether 90:10 and DCM, concentration to ~2mL	PTV-GC/EI-MS (SIM)	70-126	2-25	3-145 pg m <sup>-3</sup> (497 pg m <sup>-3</sup> for the sum of 16 PAHs)
192	9 PAHs	Portable lo-vol sampler with QFF and PUF cartridge spiked with deuterated SS (25 L min <sup>-1</sup> , 24h)	PSE with hexane- acetone 1:1 at 100°C, 100 bar	Concentration to ~500 µL, clean-up on alumina, concentration to 50 µL	PTV-GC/EI-MS	NR	NR	NR
198	PAHs	Personal sampling pump coupled to a QFF and PUF-XAD-2-PUF cartridge (3.8 L min <sup>-1</sup> , 76-1545 min, 0.29-5.9 m <sup>3</sup> )	Soxhlet with 200 mL hexane-ether 94:6, 16 h after addition of a deuterated surrogate	Treatment with anhydrous sodium sulphate, concentration to 1 mL hexane-ether 90:10	GC/EI-MS (SIM)	60-145	3-45	0.0036-0.0127 µg mL <sup>-1</sup>
200	PAHs	QFF and PUF-XAD2-PUF cartridge spiked with deuterated SS (120 L min <sup>-1</sup> for about 24 h)	PSE with DCM	Concentration and addition of deuterated IS	GC/EI-MS-ITD	NR	NR	0.1 ng m <sup>-3</sup>

NR: Not reported data

Table 5  
Analytical procedures for the determination of PCBs in indoor air

Ref	Analyte	Sampling	Desorption/Extraction	Extract treatment	Determination	Recovery (%)	RSD (%)	LOD
232	PCBs, PCDDs/PCDFs	Active with Florisil (1000 L, 2 L min <sup>-1</sup> for PCBs or PUF plugs and QFF (PCBs, PCDDs/Fs)	Addition of isotopically-labelled SS. 1) Florisil: SE with hexane-DCM 80:20. 2) PUF: Soxhlet with toluene, 24 h	Column with acid silica (44% H <sub>2</sub> SO <sub>4</sub> conc), followed by separation and fractionation (PUF)	GC/ECD (Florisil), GC/HRMS (PUF)	NR	NR	0.3-1 ng m <sup>-3</sup> (Florisil), 0.05-0.5 pg m <sup>-3</sup> (PUF)
192	62 PCBs	Lo-vol portable samplers (ORBO 2000 tubes; PUF with QFF, 25 L min <sup>-1</sup> ). PUF spiked before sampling with <sup>13</sup> C-labelled PCBs.	ASE with hexane:acetone 1:1 (PUF)	Concentration to 500 µL, column chromatography on alumina and concentration to 50 µL (PUF)	GC/MS	NR	NR	NR
233	PCDD/Fs	Active using PUF and GFF (1.05 m <sup>3</sup> h <sup>-1</sup> , 24 h)	SE with toluene (48 h)	Cleaned through an acid silica gel bed, a multilayer silica gel column, and a Florisil column. Concentration to 20 µL (N <sub>2</sub> ). Addition of IS	HRGC/HRMS/EI (SIM)	NR	NR	NR
234	51 PCBs	Lo-vol passive sampler with PUF disks (10-12 days)	Addition of SS. Soxhlet with 200 mL hexane, 8 h	Concentration to 2 mL, addition of 2 mL H <sub>2</sub> SO <sub>4</sub> . Liquid-liquid back extraction using dimethylsulfoxide. Elution with 20 mL hexane through a column containing 1 g Florisil column and 1 g anhydrous sodium sulphate. Reduction to dryness and reconstitution with 20 µL nonane and IS	GC/EI-MS (SIM)	NR	≤21.8	NR
231	9 PCBs	Passive with PUF disks (3.5 m <sup>3</sup> day <sup>-1</sup> )	Addition of SS. Soxhlet with hexane, 12 h	Treatment with H <sub>2</sub> SO <sub>4</sub> , solvent exchange to hexane and elution through a column with 2 g of Florisil with 20 mL hexane. Concentration and solvent exchange to nonane	GC(β-cyclodextrin column)/EI-MS (SIM)	75-95	≤6.5	0.03 pg m <sup>-3</sup>
211	19 PCBs	Passive with SPMD (2 weeks)	Washing in a solvent mixture and drying with Kleenex tissue. SE with cyclopentane:DCM 95:5	Dialysis (2x24h). Addition of <sup>13</sup> C-PCB as IS	GC/MS-EI (SIM)	70-110	NR	NR

235,2 36	PCBs	Passive with PUF disks (28 days)	Soxhlet with hexane, 48 h	Desiccation and addition of SS, concentration to 2 mL and treatment with H <sub>2</sub> SO <sub>4</sub> conc, SE with dimethylsulfoxide and elution through a Florisil column (1 g). Drying with sodium sulphate (1 g) and elution with 20 mL hexane, concentration to dryness, and addition of 20 µL nonane containing an IS	GC/EI-MS (SIM)	75-95	NR	0.1 pg m <sup>-3</sup>
237	6 PCBs	ORBO-60 tubes containing 150 mg Florisil (180L)	Addition of <sup>13</sup> C-labelled PCBs as IS, SE with hexane	Silica gel column chromatography	GC/EI-MS (multiple ion detection, MID)	NR	5-25	NR
238	7 PCBs	Active with a glass tube containing 25 mg Tenax (100 L min <sup>-1</sup> , 2.5 m <sup>3</sup> )	Addition of 100 µL acetone followed by HS-SPME (PDMS fiber, 100°C, 30 min)	TD (270°C) in the injection port of the GC	GC/ ITD-MS/MS	92-108	≤12	11-96 pg m <sup>-3</sup> (2.5 m <sup>3</sup> )
239	7 PCBs	Active with glass tube containing 25 mg Tenax (100 L min <sup>-1</sup> , 2.5 m <sup>3</sup> )	Sonication with 500 µL hexane, 10 min	None	GC/ ITD-MS/MS	75.2-96.2	4.4-12.7	0.12-0.40 ng m <sup>-3</sup> (2.5 m <sup>3</sup> )
240	15 PCDD/PCDFs	Active with PUF samplers and a QFF (0.225 m <sup>3</sup> min <sup>-1</sup> , 900 m <sup>3</sup> , 72 h)	Spiked with <sup>13</sup> C <sub>12</sub> -labeled IS. Soxhlet (16h)	Sulphuric acid washing followed by clean-up on columns of silica gel, alumina, and carbon. Concentration to 1 mL. Further concentration to near dryness (N <sub>2</sub> )	HRGC/HRM S/EI	NR	NR	NR
241	6 PCBs	ORBO-60 tubes containing 150 mg Florisil (180L)	Addition of <sup>13</sup> C-labelled PCBs as IS, SE with hexane	Silica gel column chromatography	GC/EI-MS (MID)	NR	5-25	NR
242	6 PCBs	Active with SPE cartridge containing 60 mg functionalized styrene-divinylbenzene (Oasis HLB) and a QFF (6 m <sup>3</sup> h <sup>-1</sup> )	SE of Oasis with 2 mL hexane	Filtration through a Pasteur pipette filled with 0.25 g anhydrous sodium sulphate, 0.25 g florisil and 0.5 g alumina. Elution with 5 mL hexane and reduction to 1 mL	GC/ECD	89.0-98.2 (5 m <sup>3</sup> )	≤7.2	LOQ <sub>s</sub> = 3-40 pg m <sup>-3</sup> (50 m <sup>3</sup> )

243	17 PCBs	Passive sampling with SPMD, PUF disks and an organic-rich commercial topsoil	1) PUF disks: Addition of <sup>13</sup> C-labelled PCBs as SS, Soxhlet for 24 h with PE. 2) SPMD: dialysis with hexane. 3) Soil: Drying with anhydrous sodium sulphate and Soxhlet with DCM, 24 h	1) PUF disks: Concentration by rotary evaporation (N <sub>2</sub> ) to 1 mL and solvent exchange into isoctane, concentration and solvent exchange into isoctane. 2) SPMD: concentration to 0.5 mL (N <sub>2</sub> ), filtration through sodium sulphate, gel permeation chromatography using DCM, and solvent exchange into hexane. Further cleanup and fractionation	GC/ECD, GC/NI-MS	79.7-95.2 (SPMDs) 87.8-110 (PUFs) 61.8-88.4 (soils)	≤24	NR
244	37 PCBs	Hi-vol samplers modified to hold a GFF and a PUF plug (2-24 h, 0.7-0.9 m <sup>3</sup> min <sup>-1</sup> , 80-1300 m <sup>3</sup> )	Soxhlet with DCM	Acid washing, florisil column chromatography, solvent exchange between dimethylsulfoxide and hexane and concentration	GC/EI-MS (SIM)	47-89	≤22	NR
245	26 PCBs	Lo-vol samplers containing PUF plugs and QFF (5-10 L min <sup>-1</sup> , 24 h)	Addition of SS and Soxhlet with hexane, 24 h	Reduction with K-D, evaporation to 1 mL (N <sub>2</sub> ), clean-up in a chromatographic column packed with anhydrous sodium sulphate, 3% silica gel and 2% aluminium oxide. Concentration to 200 µL and addition of IS solution up to 3 mL	GC/ECD	83-98	2.2-6.1	NR
246	30 PCBs	Hi-vol samplers containing PUF plugs and GFF (24h, 1 m <sup>3</sup> min <sup>-1</sup> , 800-1200 m <sup>3</sup> )	Addition of PCBs and endosulfan-d <sub>4</sub> as SS. Soxhlet with acetone-hexane 50:50, 24-48 h	Clean-up on silica or alumina column and concentration by rotary evaporation to 0.1-1 mL	GC/ECD	NR	NR	NR

NR: Not reported data

Table 6

Analytical procedures for the determination of industrial organic contaminants in indoor air suspended particulate matter

Ref	Analytes	Sampling	Desorption/Extraction	Extract treatment	Determination	Recovery (%)	RSD (%)	LOD
289	VOCs	Tapered Element Oscillating Microbalance (TEOM) samplers	TEOM filters were placed in vials in a water bath (24 h, 25°C). After that, HS-SPME (CAR-PDMS, 3 h, 25°C). TD	None	Multidimensional GC/MS-olfactometry	NR	NR	NR
187	55 PAHs	Modified MSP samplers provided with QFF (10 L min <sup>-1</sup> , 29 m <sup>3</sup> )	Spike with deuterated SS, Sonication extraction with 25 mL DCM, 35 min (x2)	Concentration on rotary evaporator and N <sub>2</sub> , clean-up on silicic acid microcolumn, rinsing with 2 mL hexane-DCM 9:1, elution with 8 mL hexane-DCM 9:1, addition of deuterated IS, concentration to ~0.01 mL	GC/EI-MS (SIM)	62-91	7.3-16	NR
190	16 PAHs	QFF and modified ORBO-1000 PUF-XAD-2-PUF cartridge with deuterated SS	Soxhlet with hexane-diethyl ether 90:10 for 24 h followed by other 24 h with DCM	Concentration to ~5 mL (K-D) and to ~2mL under N <sub>2</sub> ; clean-up on silicagel and anhydrous sodium sulphate; elution with hexane-diethyl ether 90:10 and DCM, concentration to ~2mL	PTV-GC/EI-MS (SIM)	70-126	2-25	NR
192	9 PAHs	Portable lo-vol sampler with 47 mm QFF and PUF cartridge with deuterated surrogates (25 L min <sup>-1</sup> , 24 h)	Sonication with DCM, spike with labelled PAHs mixture and clean up by thin-layer chromatography on silica gel	Concentration to ~500 µL, clean-up on alumina, concentration to 50 µL	GC/EI-MS	NR	NR	NR
200	PAHs	QFF and PUF-XAD2-PUF cartridge spiked with deuterated SS (120 L min <sup>-1</sup> , ~24 h)	Sonication with DCM in a bath at room temperature for an hour	None	NR	NR	NR	NR

203	16 PAHs	Hi-vol and mini-vol sampler using QFFs of different dimensions	MAE with 20 mL acetone-hexane (1:1) at 150W of microwave energy (20 min)	Filtration through a PTFE membrane filter (0.45µm), concentration to 3 mL (rotary evaporator), and to near dryness with N <sub>2</sub> under low temperature. Redissolution in 1ml of 1:1 acetone:hexane. Clean-up was not found to be necessary	GC/EI-MS (SIM)	79-122	7-16	0.001-1.150 ng m <sup>-3</sup> (hi-vol), 0.041-1.224 ng m <sup>-3</sup> (mini-vol)
226	PAHs	Portable air sampling pumps with GFF and PUF plugs (~30 L min <sup>-1</sup> , 6-7 h total time collection in 4 sessions)	Soxhlet extraction with 50 ml benzene for 8 h at 12 cycles h <sup>-1</sup>	Filtration, evaporation under N <sub>2</sub> and redissolution in 1 ml ACN	HPLC/UV (254 nm)	NR	NR	0.01-0.03 ng m <sup>-3</sup>
227	6 PAHs	Hi-vol sampler (1.5 L min <sup>-1</sup> , 24 h) using GFF papers. After collection, papers are demoiristurized in a dessiccator for 24 h	Sonication with DCM-hexane (50:50) in a bath (20 Hz, 10-15°C) for 30 min	Centrifugation (30 min) and filtration through Whatman-1 filter, concentration to 1-2 mL (rotary evaporator, <40°C), redissolution in hexane	Synchronous fluorescence	NR	NR	NR
212	PAHs	Two air samplers with GFF (8h, 36 m <sup>3</sup> )	Sonication with 50 mL cyclohexane (x2) in an ultrasonic bath.	Cyclohexane evaporation and solvent exchange to ACN	HPLC/diode array, HPLC/Fluorescence	70-100	NR	40 pg m <sup>-3</sup> (BaP)
198	PAHs	Personal sampling pump coupled to a QFF and PUF-XAD-2-PUF cartridge	QFF: Soxhlet with 200 mL hexane-diethyl ether 94:6, 16 h, after addition of deuterated SS	Treatment with anhydrous sodium sulphate, concentration to 1 mL hexane- diethyl ether 90:10	GC/EI-MS (SIM)	60-145	3-45	3.6-12.7 ng mL <sup>-1</sup>

NR: Not reported data

Table 7  
 Concentrations of VOCs, PAHs and PCBs in indoor suspended particulate matter and dust in homes

<b>Particulate matter</b>	
	<b>Concentration (<math>\mu\text{g m}^{-3}</math>)</b>
VOCs	12-10530 [290]
PAHs	Total suspended particulates: 24-71 (airtight), 100-1500 (non airtight); BaP: 0.00034-0.0035 (airtight), 0.013-0.370 (non airtight) ; Total PAHs: 0.031-0.140 [193]
<b>Dust</b>	
	<b>Concentration (<math>\mu\text{g g}^{-1}</math>)</b>
VOCs	0.01-1000 [291]
PCBs	3.40-35.3 [197] 0.0001-0.0092 [292]
PAHs	BaP : 2.9 (0.455-10.6) [198] 0.0169-0.275 [153]

Table 8

Analytical procedures for the determination of industrial organic contaminants in indoor dust

Ref	Analytes	Sampling	Desorption/Extraction	Extract treatment	Determination	Recovery (%)	RSD (%)	LOD
291	28 VOCs	Conventional vacuum cleaner and a mouthpiece with a dust filter (5-10 mg)	Dust was desorbed in a glass tube (150°C, 4 min) and collected onto a SPME fiber (Carboxen-PDMS) in an unheated zone assisted by a N <sub>2</sub> flow (1 mL min <sup>-1</sup> ). TD	None	GC/diode array	NR	NR	NR
297	Phthalates, PCBs, PCDDs, PCDFs, PBDEs, PFCs	Collection in special filter bags by slowly vacuum-cleaning the floor of the room during 10 min	NR	NR	GC/FID, GC/ECD	NR	NR	NR
198	PAHs, phthalates, PCBs, pesticides	Dust (1.4-12.1 g) collected in a cellulose thimble	Soxhlet with 200 mL hexane- diethyl ether 94:6, 16 h, after addition of a deuterated surrogate	Treatment with anhydrous sodium sulphate, concentration to 2.5 mL cleanup with florisil, concentration to 2 mL in 10% diethyl ether in hexane and silylation	GC/EI-MS (SIM)	110-378	12-175	NR
298	6 PCDDs, 9 PCDFs, 12 PCBs	NR	ASE (150°C, 12 min, 2000 psi)	Concentration (N <sub>2</sub> ) using a Turbovap. Clean-up with multi-layered silica chromatography column and microcolumns packed with Florisil. Elution with DCM-hexane (1:49) for PCBs and with DCM for PCDD/Fs. Solvent exchanged with nonane and addition of IS. For PCB fractions collected after Florisil clean-up, concentration to 0.5 mL, additional clean-up on alumina (16 h, 200°C), elution with 25 mL DCM-hexane (3:7), solvent exchanged with nonane and addition of IS	GC/MS (SIM), HRGC/HRMS/positive ion mode (SIM)	58-112	≤41	1.0-12 pg g <sup>-1</sup>

NR: Not reported data