Accepted Manuscript

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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

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

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Abstract

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

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

Keywords: Indoor air; dust; industrial contaminants; air analysis; VOCs; aldehydes; PCBs; PAHs; review

Contents

1. Introduction

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

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

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

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

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

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

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

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

2. Volatile organic compounds

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

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

2.1. Sampling

2.1.1. Active air sampling

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

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

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

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

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

2.1.2. Whole air sampling

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

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

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

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

2.1.3. Passive air sampling

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

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

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

2.1.4. Solid-phase microextraction

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

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

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

Fiber storage before and after sampling was also studied. Larroque *et al*. developed a homemade assembly, consisting of a tube hermetically closed by stainless steel plugs and with internal walls treated with Silcosteel for inertness [44]. Under this condition, fibres can be stored up to two days before use. Although many coatings are already commercially available, new coatings are being continuously proposed, some examples are ethoxy-PDMS, polyurethane acrylate, 50% phenyl-PDMS [79] or γ-Al_2O_3 [65].

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

2.2. Sample treatment

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

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

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

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

In order to verify the occurrence of volatile organic peroxides in indoor air, Hong and co-workers [97] developed a method based on sampling into Carbotraps and extraction by supercritical fluid extraction (SFE) using CO_2 with methanol as modifier.

2.3. Determination

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

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

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

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

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

2.4. Concentration in indoor air

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

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

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

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

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

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

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

3. Carbonyl compounds

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

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

3.1. Sampling

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

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

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

3.2. Sample treatment

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

3.3. Determination

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

3.4. Concentration in indoor air

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

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

4. Polycyclic aromatic hydrocarbons

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

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

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

4.1. Sampling

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

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

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

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

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

4.2. Sample treatment

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

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

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

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

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

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

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

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

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

4.3. Determination

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

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

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

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

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

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

4.4. Concentration in indoor air

A summary of PAH concentration levels found in different indoor environments is shown in Table 2. PAH concentrations in indoor air are dependent of both indoor and outdoor sources. A number of studies deal with the identification of these sources. Comprehensive assessment of indoor PAH concentrations in urban areas with different climates and their relationship to different types of outdoor emission sources would significantly contribute to the understanding of people exposure to industrial pollutants. In this way, Naumova *et al* [187] reported the results obtained from the subset of samples collected within the Relationship of Indoor, Outdoor, and Personal Air study (RIOPA). The goal of RIOPA was to gain a quantitative understanding of the impact of ambient sources of air pollutants such as VOCs, aldehydes, PM2.5, and PAHs on indoor air quality and human exposure by examining the relationships of concentrations of these pollutants in indoor, outdoor, and personal (breathing zone) air. RIOPA included homes in three different climate zones and with a variety of housing characteristics such as house types, air exchange rates, household appliances, and activities that can influence indoor air quality. Results of indoor-to-outdoor ratios indicated that indoor sources had a significant effect on indoor concentrations of 3-rings PAHs but a smaller effect on 4-rings PAHs, whereas the outdoor sources dominated the indoor concentrations of 5-7-rings PAHs. Similar results have been reported by Li *et al* [190], who demonstrated that indoor sources of PAHs are not negligible when activities such as cooking are considered, even in non-smoking homes. In a study conducted in

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

5. Polychlorinated biphenyls

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

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

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

5.1. Sampling

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

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

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

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

5.2. Sample treatment

Soxhlet extraction is normally used to desorb PCBs from PUF plugs/disks and filters. It takes long periods of time (8-24 h) and uses large volumes of solvents, for example hexane [231,234-236,245], petroleum ether [243], DCM [244], toluene [232] or a mixture of hexane:acetone 1:1 [192]. US EPA Methods TO-4A and TO-10A recommended PUF extraction using a mixture of hexane:diethyl ether at 5% for a minimum of 16h, followed by concentration with nitrogen [8]. In a recent paper, PUF plugs were extracted by PLE in a pressurised solvent system with an n-hexane:acetone 1:1 mixture at 100 ºC and 100 bar, and filters were ultrasonically extracted with DCM [192]. When other adsorbents are used, solvent extraction with a few mililitters of hexane is often carried out [7,237,241,242]. Barro *et al* extracted PCBs from 25 mg of Tenax by ultrasound-assisted solvent extraction. Adding only 500 µL of n-hexane, recoveries ranging from 72.3-97.9% were achieved [239]. Miao and co-workers [261] extracted PCBs and PAHs from Florisil by supercritical fluid extraction with CO_2 or N_2O. When high sensitivity is needed, PCBs can be extracted from Tenax using head-space SPME [238]. Previous to SPME, the addition of 100 µL of acetone is convenient to favour PCBs transfer towards the fiber. Limits of detection from 11 to 96 pg m^{-3} were reached sampling only 2.5 m^3 indoor air. This method have the inherent advantages of SPME, including direct thermal desorption of the fiber into the injection port of a gas chromatograph. Tobias *et al*. [280] have also thermally desorbed into a PTV inlet several PCBs, among other SVOCs, previously collected into diffusion denuders. This procedure virtually provides complete transfer of analytes collected from ambient air into the GC, evidenced by recoveries of 90.7-120%. Passive samplers based on LDPE membrane tubing can be thermally extracted as well [278,279].

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

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

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

5.3. Determination

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

5.4. Concentration in indoor air

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

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

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

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

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

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

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

6. Industrial contaminants in indoor suspended particulate matter and dust

Some of the industrial chemicals potentially affecting human exposure are mainly or partially associated to particulate matter. This is the case of PAHs, phthalates, polybrominated diphenyl ethers (PBDEs) and other flame retardants, PCBs and related compounds, as well as synthetic fragrance compounds or pesticides. PM2.5 (fine particulate matter with a diameter of <2.5 μm) is closely associated with health negative effects since it acts as concentrator of many SVOC pollutants. Among the pollutants associated with indoor suspended particulate matter, PAHs are important owing to their carcinogenicity. Li *et al* [189] conducted a study to asses the content of PM2.5 and PM2.5 related PAHs in residential buildings in an industrialized region of China. Using a procedure summarized in Table 6 these authors found that indoor and outdoor concentrations of PM2.5 largely exceeded the daily average concentration of 65 μg m^{-3} proposed by the US EPA. Among PAHs, mainly contributors were the 5-7 ring PAHs (from benzo[b]fluoranthene to coronene, MW= 252-300). In addition, a high correlation was found between indoor and outdoor concentrate ions indicating that the indoor pollution was dominated by outdoor sources, mainly traffic. Analytical procedures for the analysis of pollutants associated to particulate matter usually imply the retention of

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

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

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

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

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

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

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

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

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

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

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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^{-1})	Thermal desorption (TD)	GC/MS	NR	NR	ng m^{-3}
27	29 VOCs	Passive with Tenax in a tube-type configuration	TD	GC/MS	97	NR	0.024 µg m^{-3}
28	20 VOCs	TD tubes with 430 mg Carbopacks followed by 170 mg Carboxen (10-40 mL min^{-1}, 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^{-1}, 2 h)	TD	GC/MS, GC/FID	NR	NR	0.5-0.8 µg m^{-3}
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^{-3}
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^{-1}, 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^{-3}
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^{-3} (PFPD), 0.048 µg m^{-3} (MS), 600 mL
35	12 VOCs	Active using sorbent tubes containing Tenax (100 mL min^{-1}, 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 Carbopack 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^{-1}, 45 min). SPME fiber exposition for interior parts and adhesives (PDMS, 40ºC, 30 min)	TD	GC/FID, GC/MS	NR	NR	NR
38	4 VOCs	SKC Ultra Passive sampler: badge-type sampler containing 600 mg Carbopack (24h) Perkin Elmer passive sampler: steel tube filled with 300 mg Carbopack (1 week)	TD	GC/FID	NR	NR	NR

39	4 VOCs	Active using stainless steel tubes packed with 300 mg Tenax (10 m^3 m^{-2} h^{-1}) in a Microchamber-Thermal Extractor (µCTE)	TD	GC/MS	NR	NR	NR
40	VOCs	Active using a Carbotrap tube (0.5-1.0 L, 100 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 (20-100 mL min^{-1}). The air freshener was continuously electrically powered inside an 80-L stainless steel drum (100 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 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	0.05-0.5 µg 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 aspired 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)	0.05-0.5 µg m^{-3} (eq, 0.25 L) and 0.38-5.26 µg 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 Carbopack or Carbograph). Sampling time: 6 h-1 week	TD	GC/FID	NR	<10 (Carbopack) 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	0.24-0.73 µg m^{-3}
48	11 VOCs	Diffusive: using a set of stainless steel, tube-type diffusive samplers consisting of tube shells filled with Carboopack (24 h) Active: combination of a 6-L passivated, stainless steel canister with a flow controller (3.75 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 µg 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 µg 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 µg m^{-3} (0.75 L)
53	Benzene	Active using a personal sampler fitted with activated charcoal tube (500 mL min^{-1}, 45-60 min)	Sonication with 1 mL methanol	GC/EI-MS/MS	88-92	2	0.002 µg/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 µg 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^{-1})	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^{-1}, 100 min)	TD	GC/MS	72-139	<25 (in general)	≤1.2 µg 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^{-1})	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 µg 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 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 ng $µL^{-1}$
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 µg m^{-3}

65	8 VOCs	SPME fiber exposition with a new fiber coated with γ-Al_2O_3 (20 min, 26 ºC)	TD	GC/FID	4.59-109.6	4.1-9.2	<0.714-7.14 ng L^{-1}
66	10 Chlorobenzenes	Active using a glass tube filled with 25 mg Tenax kept in place using a glass wool plug (2.5 m^3, 100 L min^{-1}, 25 min)	HS-SPME (PDMS-DVB, 15 min, 100ºC)-TD	GC/EI-MS (ITD)	82-126	≤12	0.004-0.108 ng m^{-3} (2.5 m^3)
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^{-3} (FID/ECD, 4 weeks) and 0.01-0.05 µg m^{-3} (MS, 4 weeks)
69	6 VOCs	A flow control device (500 mL min^{-1}) 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^{-3} (24 h)
72	VOCs	Active using triple sorbent traps with 170 mg Carbotraps and 140 mg Carbosieve (80 mL min^{-1}, 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^{-1})	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^{-1}, 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_{18} solid-phase extraction membrane kept in place by 2 Teflon rings (15 L min^{-1}, 9.2 m^3)	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^{-3}
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^{-1} (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^{-1}, 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^{-3}
87	11 Monoterpenes	Active trapping on 300 mg Tenax, Carbosieve or Chromosorb between two silanized glass wool plugs (60 min, 10 mL min^{-1}, 0.6 L)	TD-cryofocussing	GC/MS	NR	7.7-20.9	LOQ = 0.96-14.22 µg m^{-3}
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^{-3}
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^{-3} (Tenax) and 0.9-3.2 µg m^{-3} (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^{-1})	TD	GC/MS	NR	<7.6	<0.32 µg m^{-3}
96	Benzene	ORBO 402 cartridges filled with Tenax (2 beds: 100 and 50 mg), 200 mL min^{-1}, 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^{-1})	SFE using CO_2 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 of PDMS-DVB, 1 min – 24 h)	TD	SPI-GC/FID	NR	NR	NR
101	4 VOCs	Active using charcoal tubes (0.5 L min^{-1}, 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^{-3}
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

	Home	**Office**	**School, kindergarten and daycare center**	**Store, market and shop**
VOCs ($\mu g\ m^{-3}$)	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 [a] [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 [a] [100]	76 [157] 2200-140100 [79]

Carbonyls (ng m^{-3})	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]	FA: 17-24 [172]	FA: 14-16 [172]	FA: 17-29 [172]
PAHs (ng m^{-3})	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: <0.01-0.27, 30-350 [c] [211]	NR	NR	NR

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

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 (µg 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 [b] [98] 0.46-0.72 [a] [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 [b] [85] 1-66714 [114] 14-57 [154] 0.019-0.032[a] [100] 21.6-61.2 [b] [160]
Carbonyls (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 (ng m^{-3})	NR	NR	∑PCBs=0.392-6.018 [235]	NR	∑6PCBs=13000 [241]

NR: Not reported data
[a] µg L^{-1}
[b] ppbv
[c] 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^{-1})	Extraction with 5 mL MBTH, agitation (150 rpm, 35ºC, 1 h)	Oxidation reaction of 4-mL MBTH extract with 1-mL $FeCl_3$-sulfamic acid, 20 min	Spectrophotometry (628 nm)	93	4.0-7.5	9.7 ng m^{-3} (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^{-1}). After sample collection, cartridges were heated (60 ºC, 60 min)	Elution with 2 mL ACN	NR	HPLC/Fluorescence (λex= 240 nm, λem= 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 (45-250ºC, 300ºC min^{-1})	-	GC/FID	NR	NR	~1.22 μg m^{-3}
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^{-3} (3 days)
174	FA	Diffusive sampler with a semipermeable membrane and a triethanolamine coated collection filter (~1.52 L h^{-1})	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^{-3} (7 days), 10.4 μg m^{-3} (1 day)
168	VA	A modified PDMS SPME device used as a time-weighted average sampler. On-fiber derivatization with PFBHA	TD (250ºC)	-	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 (170ºC)	-	GC/EI-MS (total ion monitoring, SIM)	NR	NR	1.2-11.7 ng L^{-1}
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^{-3}
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 metahnol (1.0 L min^{-1}, 2 h and 15 min). After sample collection, the cartridges were heated at 60 ºC 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^{-1} (UV), 0.29-5.3 μg L^{-1} (Fluorescence)
178	FA	On-line collection-FIA using a chromatomembrane cell with water as an absorbing solution (6 mL min^{-1}, 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^{-3} (Spectrophotometry), and 0.03 μg m^{-3} (Fluorescence) for a 40 mL diluted air sample.
179	FA, AA, PrA, HA, butanal, heptanal	Air collection at 50 mL s^{-1} 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^{-3}
180	FA, AA, PrA, butanal, pentanal, HA, CA, BA, acrolein, methacrolein, *p*-TA	Personal sampling pump cartridges (0.5 L min^{-1}, 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^{-1}

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 $Lmin^{-1}$, 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, 35ºC) and TD (290ºC, 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^{-1}, 10-14 m^3)	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^{-3}
187	55 PAHs	QFF and PUF	Statically extraction with 40 mL hexane-DCM 4:1 at 50ºC, 1h	Rinse twice with 20 mL hexane-DCM 4 :1 at 50ºC, 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^3 min^{-1}, 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^{-3} (26 m^3 sample)
210	*d*-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^{-1})	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^{-1}

186	12 PAHs	Low noise sampler provided with QFF and XAD-2 (1 L min^{-1}, 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_2, 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^{-1}, 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^{-3}
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^{-1}, 46-48 h, 28 m^3)	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_2; 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^{-3} (497 pg m^{-3} 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^{-1}, 24h)	PSE with hexane- acetone 1:1 at 100ºC, 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^{-1}, 76-1545 min, 0.29-5.9 m^3)	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^{-1}
200	PAHs	QFF and PUF-XAD2-PUF cartridge spiked with deuterated SS (120 L min^{-1} for about 24 h)	PSE with DCM	Concentration and addition of deuterated IS	GC/EI-MS-ITD	NR	NR	0.1 ng m^{-3}

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 $Lmin^{-1}$ 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% $H_2SO_{4\ conc}$, followed by separation and fractionation (PUF)	GC/ECD (Florisil), GC/HRMS (PUF)	NR	NR	0.3-1 ng m^{-3} (Florisil), 0.05-0.5 pg m^{-3} (PUF)
192	62 PCBs	Lo-vol portable samplers (ORBO 2000 tubes; PUF with QFF, 25 L min^{-1}). PUF spiked before sampling with ^{13}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 $m^3\ h^{-1}$, 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_2). 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_2SO_4. 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 $m^3\ day^{-1}$)	Addition of SS. Soxhlet with hexane, 12 h	Treatment with H_2SO_4, 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^{-3}
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 ^{13}C-PCB as IS	GC/MS-EI (SIM)	70-110	NR	NR

235,236	PCBs	Passive with PUF disks (28 days)	Soxhlet with hexane, 48 h	Desiccation and addition of SS, concentration to 2 mL and treatment with $H_2SO_{4\ conc}$, 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^{-3}
237	6 PCBs	ORBO-60 tubes containing 150 mg Florisil (180L)	Addition of ^{13}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^{-1}, 2.5 m^3)	Addition of 100 µL acetone followed by HS-SPME (PDMS fiber, 100ºC, 30 min)	TD (270ºC) in the injection port of the GC	GC/ ITD-MS/MS	92-108	≤12	11-96 pg m^{-3} (2.5 m^3)
239	7 PCBs	Active with glass tube containing 25 mg Tenax (100 L min^{-1}, 2.5 m^3)	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^{-3} (2.5 m^3)
240	15 PCDD/PCDFs	Active with PUF samplers and a QFF (0.225 m^3 min^{-1}, 900 m^3, 72 h)	Spiked with $^{13}C_{12}$-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_2)	HRGC/HRMS/EI	NR	NR	NR
241	6 PCBs	ORBO-60 tubes containing 150 mg Florisil (180L)	Addition of ^{13}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^3 h^{-1})	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^3)	≤7.2	LOQs= 3-40 pg m^{-3} (50 m^3)

243	17 PCBs	Passive sampling with SPMD, PUF disks and an organic-rich commercial topsoil	1) PUF disks: Addition of ^{13}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_2) to 1 mL and solvent exchange into isooctane, concentration and solvent exchange into isooctane. 2) SPMD: concentration to 0.5 mL (N_2), 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^3 min^{-1}, 80-1300 m^3)	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^{-1}, 24 h)	Addition of SS and Soxhlet with hexane, 24 h	Reduction with K-D, evaporation to 1 mL (N_2), 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^3 min^{-1}, 800-1200 m^3)	Addition of PCBs and endosulfan-d_4 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, 25ºC). After that, HS-SPME (CAR-PDMS, 3 h, 25ºC). TD	None	Multidimensional GC/MS-olfactometry	NR	NR	NR
187	55 PAHs	Modified MSP samplers provided with QFF (10 L min^{-1}, 29 m^3)	Spike with deuterated SS, Sonication extraction with 25 mL DCM, 35 min (x2)	Concentration on rotary evaporator and N_2, 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_2; 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^{-1}, 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^{-1}, ~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_2 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^{-3} (hi-vol), 0.041-1.224 ng m^{-3} (mini-vol)
226	PAHs	Portable air sampling pumps with GFF and PUF plugs (~30 L min^{-1}, 6-7 h total time collection in 4 sessions)	Soxhlet extraction with 50 ml benzene for 8 h at 12 cycles h^{-1}	Filtration, evaporation under N_2 and redissolution in 1 ml ACN	HPLC/UV (254 nm)	NR	NR	0.01-0.03 ng m^{-3}
227	6 PAHs	Hi-vol sampler (1.5 L min^{-1}, 24 h) using GFF papers. After collection, papers are demoisturized in a dessiccator for 24 h	Sonication with DCM-hexane (50:50) in a bath (20 Hz, 10-15ºC) for 30 min	Centrifugation (30 min) and filtration through Whatman-1 filter, concentration to 1-2 mL (rotary evaporator, <40ºC), redissolution in hexane	Synchronous fluorescence	NR	NR	NR
212	PAHs	Two air samplers with GFF (8h, 36 m^3)	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^{-3} (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^{-1}

NR: Not reported data

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

Particulate matter	
	Concentration (µg m^{-3})
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]
Dust	
	Concentration (µg g^{-1})
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 (150ºC, 4 min) and collected onto a SPME fiber (Carboxen-PDMS) in an unheated zone assisted by a N_2 flow (1 mL min^{-1}). 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 (150ºC, 12 min, 2000 psi)	Concentration (N_2) 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 alumnia (16 h, 200ºC), 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^{-1}

NR: Not reported data