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Analysis of indoor air emissions: From building materials to biogenic and anthropogenic activities

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ABSTRACT

There is a clear relationship between indoor air quality, gaseous compounds (volatile and semi-volatile) and particles emitted by building materials, biogenic and anthropogenic activities, and human health. An increased interest in indoor air quality and emissions has raised during recent years. Nowadays, it is possible to find several analytical approaches based on a wide variety of sampling and analytical techniques. The main objective of this review is to clarify the different options available for the analyst by a critical evaluation of the different steps involved in these methods. In this way, a clear description and evaluation of the potential advantages and shortcomings for the different devices required in materials emission studies, the collection of total air samples using air canisters and particles by vacuum surface have been included in this review. In addition, the potential use of active and passive sampling techniques, for the efficient collection of different compounds from the air samples is described. Then, the selection of the most adequate analytical approach for the analysis of different compounds as a function of their physicochemical properties is evaluated. The latter will include not only traditional approaches such as gas or liquid chromatography but also more sophisticated ones such as proton transfer reaction or chemical ionization mass spectrometry. Finally, the application of these different analytical approaches to the evaluation of indoor air emissions, mainly from biogenic and anthropogenic activities but also from different building materials, are introduced.

1. Introduction

Modern lifestyle has led us to spend over 90% of our time indoors [1] – including homes, offices, stores, schools etc. In addition, in certain countries such as Finland, indoor air quality is generally worse than in outdoor environments [2]. It looks obvious that the different gas phase compounds (volatile and semi-volatile) and particles, emitted to indoor air by the building materials or as a consequence of biogenic and anthropogenic activities, can be absorbed by lungs and displace into the rest of the body by the breathing process. Some of these compounds, at above a certain concentration level, might be toxic for humans, affecting their health or at least their quality of life. Different health problems, most of them related with respiratory tract, have been widely reported when certain compounds are present in indoor air. Those include headaches, allergies, irritation of nose and throat, tiredness, lack of focus, vascular-nervous dysfunction and even cancer [3–5].

Building and construction materials are the main sources of volatile organic compounds (VOCs) in indoor sources. Hydrocarbons and their derivatives (polycyclic, aliphatic, aromatic, alkylbenzenes), phthalates, aldehydes, ketones, chlorinated compounds and terpenes [5–8] have been identified as potential indoor air emissions from a wide variety of building and construction materials, including wood-based surface materials (e.g. fibreboards, panels) [9–11], paints [12], floor material [7], adhesives and resins [10], plastics and polymeric materials [6], and even cement [13,14] Table 1. summarize these VOCs, the most usual emission sources and their potential effects on human health. Several reviews have been found in the literature covering in detail the emissions diverted from building and construction materials [5,15,16]. It looks noticeable that indoor air quality monitoring and VOCs emission studies are required to ensure safe concentrations indoors and to develop appropriate building materials [3,17]. Different studies have demonstrated a clear relation between the type of the building and the concentration of VOCs and aerosol particles, which tend to be higher in private homes than in public buildings or workplaces. This can be explained by the use of different building materials and ventilation systems, among others [18,19].

In this review, the emissions due to anthropogenic and especially biogenic activities will be discussed. In the case of the latter, it should keep in mind that microbes are living organisms. Synthesis and subsequent release of metabolites into indoor air might be affected by external environmental conditions. High humidity level and warm temperatures are needed to enlarge the production and emission of metabolites. On

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Table 1
Volatile organic compounds of interest for the evaluation of indoor air quality, common sources and potential human health effects.

Compound	Emission source	Health effect
Formaldehyde	Wood panels, adhesives, resins, fiberboards, particle boards, plywood	Irritation, cancer, asthma
BTEX	Wood materials, particle boards, paint, laminate, furniture	Anemia, cancer, immunological effects, irritation, nervous system effects, respiratory system, liver and kidney damage
Phthalates	Paints, plastics, vinyl flooring, wall coverings	Male reproductivity issues, male hormonal issues, issues in neurological development
Terpenes	Wood based materials	Irritation
Chlorinated compounds	PVC polymers	Irritation, toxicity, possibly carcinogenic

the other side, high temperatures might cause stress to microbes, limiting their metabolite production. Furthermore, air currents caused by air conditioning and ventilation may affect the mobilization of the non-volatile metabolites into the air. Finally, it should be considered that some microbes are able to regulate their metabolism according to other external factors such as time of the day and season [20]. Most of the compounds emitted by the microbes are not directly involved with their normal growth, development or reproduction. Therefore, these compounds should be considered as secondary metabolites [21].

Compounds emitted by microbes into the air can be divided into different groups according to their volatility. Microbial volatile organic compounds (MVOCs) comprise a large number of compounds produced and released into the environment by microbes, including fungi and bacteria. Alcohols, terpenes, esters, hydrocarbons, cyclohexanones and ketones among others can be included into this group. However, microbes should not be considered as an specific source for these compounds and other potential emission sources such as building materials or human activities, should not be discarded [22,23]. The emission of certain semi-volatile and non-volatile microbial secondary metabolites, might be considered as one of the principal causes for indoor air problems due to their hazardousness or toxicity for humans. Despite of their limited volatility, some of these compounds have been frequently detected in indoor air samples. Different studies have demonstrated their mobilization into the air by different mechanisms including small droplets, spores and/or parts of dead microbes [23,24].

Finally, the indoor air emissions generated through the activities of inhabitants such as cooking, smoking, and the use of electronic machines and consumer products, should not be discarded specially in the case of premises with an inadequate ventilation [25]. Within these anthropogenic emissions, it is possible to include aerosol particles, atmospheric gases and VOCs that can be easily mobilized into the different areas of the house causing adverse effects to the health of all the house occupants.

It should keep in mind that the potential toxicity of the different VOCs emitted by the different sources is just a part of the problem. The concentration these compounds in indoor air have also a relevant role in their health impact. As described before, this directly related to the use of ventilation systems. The use of proper systems, involving large enough ventilation rates [26] and/or catalytic nanomaterials [27], can be of a great help to reduce concentrations of VOCs; and therefore, their subsequent impact on the house inhabitants [8].

In general terms, it is possible to find several guidelines and directives, mostly just national, about the potential indoor air concentration limits for total VOC or specific compounds [28,29]. However, in some countries these limit are differentiated as a function of the exposure time between short term- and long-term emissions [30]. In addition, it is not possible to stablish a comparison between allowed in indoor air guidelines when different parameters such as surface emission rates or different test chambers are used for the determination of the maximum VOCs concentrations, emitted by building materials [31,32]. This great diversity in criteria might be problematic in a near future, and there is strong need for harmonization, and standardization of the different analytical techniques employed as well as a need for quality control procedures for routine laboratories performing indoor air analysis.

The main aim of this review is to describe and evaluate different approaches used for the determination of organic compounds emitted by materials and especially by biogenic and anthropogenic activities in indoor air. Different chambers, cells and samplers used for laboratory and field analysis will be introduced. Potential drawbacks and advantages of the multiple analytical techniques including a chromatographic step for the separation of the analytes will be represented. Furthermore, the application of these techniques and devices for the analysis of emissions from natural samples such as building materials, and due to anthropogenic and biogenic activities, will be summarized. Finally, future outlook and perspectives are given.

2. Analytical approaches for the determination of organic compounds from indoor air

Different sampling and analysis techniques have been developed for the evaluation of emissions from building materials and from anthropogenic and biogenic activities. Emission test chambers (ETC), field and laboratory emission cells (FLEC) are widely used to evaluate the indoor air emissions. Passive or active sorbent tubes, impregnated or not with a derivatization reagent, are the most popular sampling techniques followed by the proper desorption, individual separation, identification and quantitation of the analytes. Sophisticated sampling approaches such as solid phase microextraction (SPME) fibers and radial symmetry diffusive samplers (Radiello®) have been introduced as an alternative to the conventional ones [3,18,33,34]. The selection of the most appropriate experimental setup for indoor air quality evaluation is a key factor to achieve successful results. For example, it is well-known that conventional air sampling techniques might provide biased collection of the non-volatile metabolites emitted by the different microbes present in buildings. In addition, several studies have revealed that bioaerosol sampling techniques are prone to collect more small and dry spores instead of larger ones [35].

2.1. Emission test chambers, cells and sampling devices for laboratory and field analysis

Emission test chambers used in combination with suitable sampling can be considered as simplest and most robust approach for the evaluation of VOC-emission levels from indoor building materials and furniture. These devices, originally developed in 70 s of the last century, are still used in most of the studies. Laboratory made or commercial ETCs [5,7], are built with non-reactive materials such as steel and glass [13,14]. The size of the chamber, typically ranged between 3 dm^3 and 80 000 dm^3, is a key parameter of these devices allowing their subsequent classification into small- and large-scale emission chambers. Clear advantages and drawbacks are diverted from the use of these devices. In general, the cost of indoor air analysis using ETCs is high in terms of labor and time. In addition, large-scale emission chambers are not suitable for field sampling and analysis. In the case of small-scale chambers, the building materials must be deconstructed and reduced into smaller pieces before the analysis. However, the use of larger ones allows on-site analysis of materials without any modification. The ETC versatility allows the calculation of the chamber concentrations and surface emis-

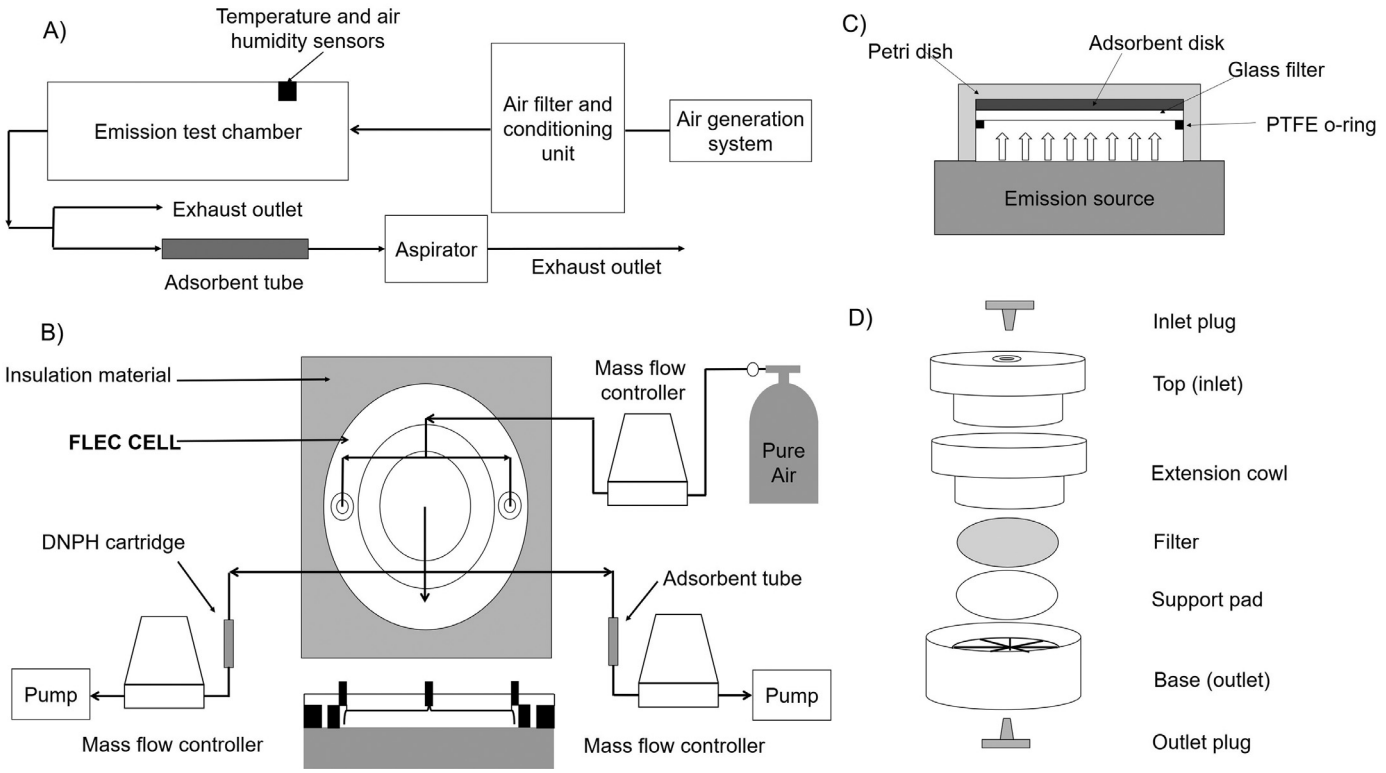

Fig. 1. Schematic representation of emission chambers, cells and sampling devices for laboratory and field analysis. Emission test chambers (A), field and laboratory emission cells (B), passive flux samplers (C) and microvacuum cassettes (D) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

sion rates from materials. The first one allows the potential estimation of VOCs concentration for certain building types and sampling conditions. However, the second one can be easily calculated using the air exchange rate, the loading factor and the measured chamber air concentration [36].

The ETC operation is relatively simple (Fig. 1a). A purified air flow is flushed trough the chamber under controlled conditions (temperature and relative humidity). At the same time, the released compounds are collected from the outlet air flow by an active sampling technique [5]. Nevertheless, the use of passive sampling techniques instead of the active ones has been introduced in the recent years [34]. These devices allow the *in-situ* VOCs screening from flat surfaces in recently built apartments, not interfering to their normal use.

Field and laboratory emission cells, used for first time in 1991, have become very popular in the recent years [5]. These stainless-steel disk shape devices might be considered as a miniaturized version of an ETC, similar performance with reduced operation and acquisition costs, to be used in flat surfaces [5,37]. Purified air is introduced into the chamber from both sides of the device and the outlet gas is collected by an active sampling from the middle of the device (Fig. 1b), passive sampling can be also used [38]. This miniaturized device is of special interest in the case of on-site analysis, allowing the evaluation of VOC emission rates without interfering with the normal activities in the sampling place [5].

Passive flux samplers (PFSs) are miniaturized and passive field sampling devices that are based on emission flux of target analytes from surfaces of building materials and their subsequent collection using a passive sampler inside the device. Collected analytes can be subsequent desorbed from the sampler via solvent extraction or direct thermal desorption (TD) [5,39]. As described before for FLEC, these devices are suitable for on-site emission analysis studies due to their simplicity [5]. In addition, PFS size, 2 cm of diameter, allow them to stablish emission profiles as a function of the position in large pieces of the material [5,39]. The disks are typically made of glass, steel or non-reactive plastic avoiding undesired reactions during the sampling. Furthermore, an absorbent disk placed at the bottom of the device, pointing away from the emission source, covered by a suitable filter frequently used as passive sampler (Fig. 1c). The adsorbent disk and/or the filter can be impregnated by a derivatization reagent to improve the collection, separation and detection of the target analytes [39]. Despite of PFS great potential due to its clear advantages over the traditional approaches (small size, passive use, low price simplicity and possibility of *in-situ* research), the application of PFS for the evaluation of potential emissions from building materials has been very limited. Just few studies can be found in the literature using this approach [39].

Alternative approaches will involve the use of air canisters or vacuum surface sampling which will allow the collection of total air and dust samples, respectively. The first one, a common outdoor air sampling technique, have been recently introduced to indoor air applications [40]. This technique is based on the use of evacuated inert steel canisters closed with a valve, which is opened to allow the collection of the air. Once ambient pressure is achieved inside the canister, the valve is closed again allowing the subsequent analysis of sampled gas phase compounds by gas chromatography mass spectrometry (GC-MS) [27]. The key advantages of canister sampling include that no electricity/pumping is needed at the field, safety for untrained users, possibility for multiple analyses from one canister sample and possibility of usage of real gas-phase standards for calibration. Despite the relative success of this approach the authors agreed in the study that active and direct sampling with an adsorption tube is the most suitable sampling technique in the evaluated scenarios [40]. However, the second, vacuum surface sampling, is one of the most common active sampling techniques used for the collection of fungal traces or secondary metabolites from dust samples [20]. Microvacuum cassettes, designed for the collection of asbestos and fungal spores are commercially available (Fig. 1d). These cassettes can be furnished with a microvacuum nozzle and filters for the collection of settled dust from surfaces providing a relatively high sampling flow-rate

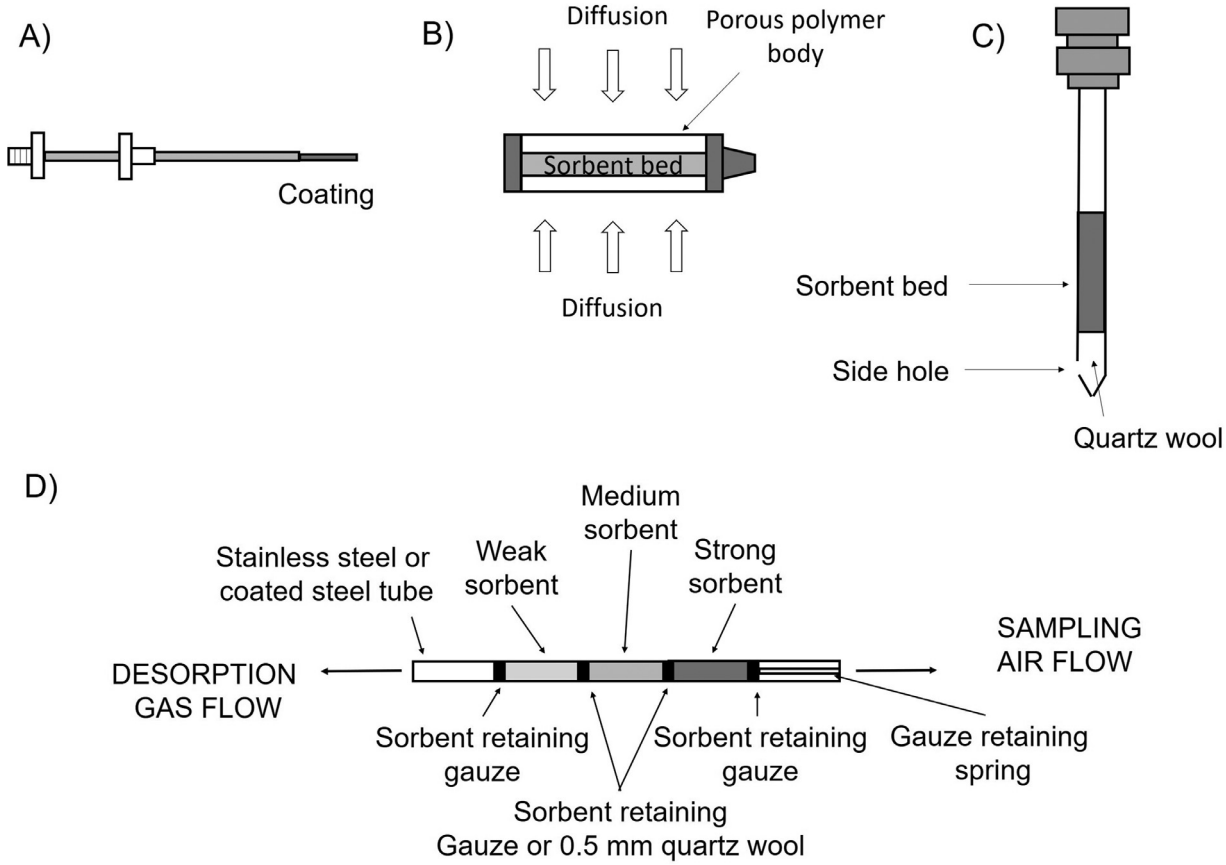

Fig. 2. Schematic representation of active and passive sampling techniques for the collection of gas phase and aerosol particles. Solid phase microextraction (A), radial symmetry diffusive sampler (B), needle trap microextraction device (C) and adsorption tubes (D) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

(10 L/min). This technique has clear limitations and can be used just for the identification of the different fungal species present in the building. Samples collected using this approach have been used for the elucidation of fungal species and secondary metabolites using high performance liquid chromatography mass spectrometry (HPLC-MS), viable culture and deoxyribonucleic acid (DNA) sequencing [41]. The main challenge of the research was the identification of a correlation between the concentration found for the potential secondary metabolites and the specific fungal species. In addition, the identification of potential contamination sources, as potential bias for the results, remained also unclear.

2.2. Active and passive sampling techniques

Passive sampling is one of the most common air sampling techniques. It can also be called diffusive sampling as it is based on Fick's law of diffusion. The different analytes pass onto the adsorbent material and are retained. After the sampling, analytes are desorbed from the material using solvents or temperature [42]. These systems have many advantages for field studies considering their design (small, light and silent), relative low price, commercial availability and the lack of requirements for external resources. Then again, they have clear limitations diverted from their sensitivity to external factors and their low sampling capacity. The relatively long sampling time required to collect the adequate amount of analytes for their subsequent determination might cause their back-diffusion into the air. Additionally, semi-volatile and non-volatile compounds have a poor diffusion into the medium thus decreasing the collection efficiency using these samplers [43,44]. Different approaches based on passive sampling, such as solid SPME and their different variants or radial symmetry diffusive samplers, have been used in indoor air studies, to study biogenic and anthropogenic activities, and material ETC/cell studies.

Solid phase microextraction has become popular as gas sampling device in the recent years. Thin steel rod is connected to the silica fiber, which is coated with a small volume ($< 1\,\mu$L) of suitable sorbent (Fig. 2a). The selection of the latter is the key parameter to improve the performance of the SPME sampler in terms of its suitability for different compounds and concentrations. Polydimethylsiloxane (PDMS) based material is frequently used for indoor air applications, sometimes alone but often in combination with carbon based or aromatic sorbents such as carboxen or divinylbenzene (DVB) [17,26,38]. In certain applications, such as the analysis of carbonyl compounds, the sorbent has been impregnated with a derivatization reagent [26]. The analysis of the collected compounds involves TD and GC. Mass spectrometry is commonly used for the identification and quantitation of the compounds but the use of other detectors should not be discarded [45]. Commonly used SPME fiber in indoor air studies has also been utilized in VOCs emission studies from several materials as an alternative sampling technique to active sorbent tube approach [26,38]. Emission rates and indoor air concentrations were calculated from equilibrium surface concentrations and no differences were observed for the latter in comparison with ISO 16,000 based standard methods.

The design of radial symmetry diffusive samplers, also called Radiello® (Fig. 2b), allows the relatively fast diffusion through the protective layer, avoiding the potential sampling artifacts formed under environmental conditions. Since the uptake of analytes towards the equilibrium is relatively fast, radial passive sampling are suitable for short-term sampling. After the sampling, the analytes can be removed with solvent extraction and analyzed, but also TD suitable variants exist [34,46,47]. These samplers have mainly been used for sampling of VOCs in indoor

air. Several applications of these samplers in emission and indoor air studies can also be found in the literature [34,47]. In addition, this sampling technique has been successfully applied for the identification of molds from damp housing materials using the MVOCs fingerprint patterns and statistical tools [48–50].

Radiello® samplers can be furnished with a wide variety of sorbent materials, including carbon based ones such as Carbograph and activated charcoal [19,34,47]. For the latter, carbon disulfide should be used for the solvent extraction of the retained compounds since this material is not compatible with TD [19]. Similar to other approaches based on active sampling, a derivatization reagent can be used to impregnate the sorbent in the samplers and improve the chromatographic properties of the target analytes during the sampling [40].

Active sampling is based on the use of an external pump or vacuum system to push the air sample through the collection media, filters or sorbent traps. In all the cases, air flow-rate through the system is controlled or at least measured, allowing the subsequent calculation of the concentrations for the analytes. These devices can be divided to three classes, low volume, medium-volume and high-volume samplers, according to their sampling flow-rate. Low and medium-volume samplers have usually flow rates less than 1.0 $m^3\ h^{-1}$. However, high-volume samplers allow air flows up to 60 $m^3\ h^{-1}$ [51]. Tenax, Chromopak and silica gel are the most common sorbents used in active sampling applications but other carbon-based sorbent materials, such as Carbograph 4, Carbotrap 202, Carbopack B and Carboxen 1000 have been also used. Additionally, most of the sorbents used for passive sampling might be applicable also for active sampling. The main advantage of the active sampling approaches in comparison with the passive ones is the collection of both gas phase compounds (volatile and semi-volatile analytes) and compounds in aerosol particles (semi- and non-volatile compounds) with a single device. Moreover, active samplers allow the collection of a relatively large volume of air in a short period of time, reducing the sampling time from several days or even weeks to few hours in comparison with passive sampling approaches. Finally, several studies have demonstrated the robustness of active sampling techniques to external environmental factors, such as relative humidity [52,53]. On the other side, the size of the samplers and the requirement of external facilities in the field such as a power supply, have been traditionally considered to have limitations for the application of active sampling devices. However, recent advances in miniaturization of pumps and the development of robust and powerful batteries have overcome these problems making active sampling devices ideal for the collection of particles (dust, particles, bioaerosol) and gases. Different approaches based on vacuum surface sampling or absorption tubes have been used for the evaluation of microbial emissions [54,55].

Adsorption tubes are widely used in the standard ISO 16,000 methods for sampling using ETC or FLEC to promote their use for the collection of VOCs from indoor and outdoor air. There is a wide variety of packed tubes commercially available with relatively affordable price. The structure of these devices is very simple (Fig. 2c). A metal tube, approximate dimensions of 90 mm long and 6 mm thick, is packed with fixed amount of sorbent material [46] whose careful selection allows the collection of different VOCs. The absorption efficiency can be increased by using multiple layers of different materials. In addition, impregnation of the tubes with any reagent is possible to improve the chromatographic characteristics of the collected compounds.

Different miniaturized air sampling (MAS) techniques such as micro traps and needle trap devices (NTME), modified from adsorption tubes have also been used for the collection of VOCs from indoor air (Fig. 2d). The systems can be employed independently as portable pen size-sampling devices as well. In both cases, the amount of sorbent inside these devices is much smaller than that used in conventional adsorption tubes resulting in shorter sampling times and flows rates. In addition, the desorption step in these devices is also simplified [45,56–60].

The desorption of the collected compounds will depend on their physicochemical characteristics. Thermal desorption is the most common approach for volatile and semi-volatile compounds, which can be directly introduced into GC system by increasing the temperature of the adsorption tube. It should be emphasized that most of modern sorbent tubes are compatible with this desorption approach, avoiding solvent extraction step before the injection. Additional advantages are reliability, sensitivity and efficiency.

2.3. Analytical techniques for the determination of volatile semi-volatile and non-volatile compounds

Gas chromatography–mass spectrometry is the main analysis technique for the separation and identification of VOCs due to its good sensitivity and separation efficiency allowing the separation of complex mixtures at relatively low concentrations. This approach can be used for the direct analysis of the samples collected in the field. However, the analysis of the air in the headspace vials used for growing of the microbes is the most common approach for *in-vitro* studies. In both cases, cryogenic analyte focusing at the beginning of the chromatographic column is frequently used to improve chromatographic separation of the MVOCs, especially those with the higher volatility, and the sensitivity of the method [61]. It should be kept in mind that GC can be also used for the determination of low-volatile or non-volatile compounds after derivatization. These compounds should have some functionalities in their structures, like –OH, -NH, COOH and –SH, allowing their subsequent derivatization, for example by silylation, acylation, alkylation or esterification. Although this approach permits the determination of low volatile or thermally labile compounds, a detailed overview of the literature has revealed that in most cases the molar mass of the derivatives is below 500 Da [62].

However, the most adequate approach for the determination of low- and non-volatile compounds involves the use of HPLC furnished with different detectors such as fluorometers or mass spectrometers. The combination of HPLC and fluorescence detection has been traditionally used for the determination of aflatoxin B_1, emitted as secondary metabolite, in samples contaminated by *Aspergillus flavus*. Sample preparation involved several steps including the simple lixiviation of the analytes from the sample media and their subsequent cleanup by solid phase extraction [63,64]. The results achieved by this approach were consistent with those obtained in other study [65]. HPLC-MS allowed the potential elucidation of multiple *Aspergillus flavus* biomarkers. The use of a high-resolution quadrupole time-of-flight mass spectrometer resulted in the reliable identification of these compounds [65,66].

Proton-transfer-reaction-mass-spectrometry (PTR-MS) and chemical ionization mass spectrometry (CIMS) have become important tools (Fig. 3) for the analysis of VOCs emitted by a wide variety of biogenic and anthropogenic sources [67,68]. It looks obvious that the combination of PTR and CIMS for *in situ* analysis (real-time, direct air sampling) is of great interest in the evaluation of emission signatures of VOCs in a wide variety of indoor air environments including building materials, biogenic and anthropogenic emissions [69–74]. The main limitation of these systems is the identification capacity in the case of isobaric ions, commonly associated with multiple isomers, cluster ions, or fragmentation products that have the same molecular formula [75]. However, these limitations might be partially circumvented by the combination of the results achieved for the VOCs collected using single stage adsorbent tubes and a portable GC-MS furnished with a TD unit, and those obtained by the PTR-MS and/or CIMS [76].

2.4. Official and reference methods for indoor air analysis

The international standard series (ISO 16,000 series) contains several chapters for indoor air and emission chamber testing scenarios. This includes the determination of formaldehyde and other carbonyl compounds in indoor air and test chambers using active sampling (ISO 16,000–3:2011); the determination of formaldehyde using a diffusive sampling (ISO 16,000–4:2011); the determination of VOCs in indoor air

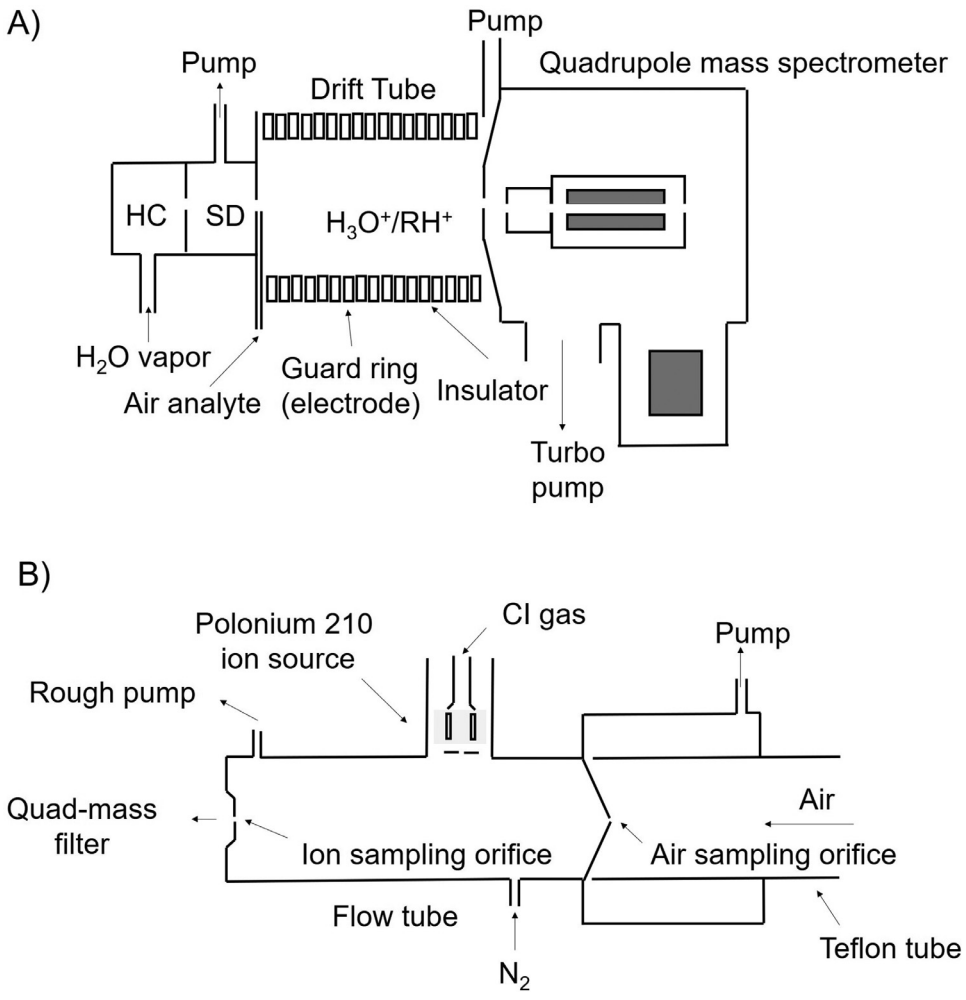

Fig. 3. Simplified representation of a proton-transfer-reaction-mass-spectrometer (A) and chemical ionization mass spectrometer (B). HC, hollow-cathode discharge source; and SD, source drift region (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

and test chambers by active sampling using Tenax TA as sorbent, TD–GC and MS or MS-FID as detector (ISO 16,000–6:2021); the determination of VOCs emission of from building products and furnishing using a ETC (ISO 16,000–9:2006/COR 1:2007) or a emission test cell (ISO 16,000–10:2006) [77–81].

In most of these active sampling methods, an adsorption tube packed with Tenax TA is used for VOCs active sampling and the analysis of the target analytes is carried out by TD-GC-MS. However, the standard methods for the determination of formaldehyde and other carbonyl compounds involves the use of DNPH impregnated cartridges for the simultaneous collection and derivatization of the target analytes. In this case, the individual separation and detection of the carbonyl derivatives is performed by HPLC-MS. The detailed evaluation of the literature showed that most of the standardized methods for indoor air analysis, or at least parts of them, have been directly transferred into the most recent studies, allows the intercomparison of the results.

3. Analysis of building materials emissions

A wide range of building materials are typically used in construction. Some of them such as wood, plastics, adhesives, paints, biomaterials and other low-emission materials, are able to produce indoor VOC emissions. The different analytical techniques applied to the analysis of their potential emissions will be discussed below in more detail Table 2. summarizes the different compounds identified and quantified from different building materials and/or from field studies using the techniques described in the previous section. The main limitation found in the evaluation of VOCs emissions from building materials is caused by the lack of reference materials for a reliable quality assurance. Some studies have been recently carried out to generate multi-VOC reference materials for the evaluation of the materials in interlaboratory studies [82,83].

Several factors such as temperature, humidity, air exchange rates and age of the building material can affect both the emission rates and VOCs concentrations in indoor air samples [33,84,85]. Different studies have shown that VOC-emission rates generally tend to increase when temperature and relative humidity are elevated [10,85]. However, several exceptions, such as TVOCs emitted by wood board materials [85], can be found in the literature. Briefly, emission temperature usually ranges between 20 ºC and 25 ºC and the relative humidity is setup around 50% [10,28,33,36,83,84]. Thus, emission conditions should be similar in natural and test chamber studies to achieve comparable results. In addition, emissions of VOCs tend to drop during the aging of materials [10] or the building [3,33]. Last but not least, potential contamination of the materials by the construction process or the outdoor air should not be discarded in the case of natural samples [3,18,33].

3.1. Wood and wood-based materials

Wood is one of the most common building materials use of which has been widespread in the recent years [11]. Wooden building includes plywood, wood-panels, particle boards (chip board) and fibreboards, as well as wooden furniture. Therefore, VOC emissions of these materials have been widely studied [10,11,17,33].

Typical wood-based materials emissions include terpenes and carbonyl compounds [11,17] and terpenes are directly emitted from unprocessed wood. In addition, wood additives, such as urea-formaldehyde

Table 2
Volatile organic compounds identified and quantified from different building materials and/or field studies.

Material	Sampling device	Analytical technique	Analytes	Ref
Medium density fiberboard, chipboard, fiberboard (no binder resin)	Glass ETC	AS with Tenax TA tube, GC-FID analysis	Linalool, alpha-pinene, toluene, cyclohexane	[10]
		AS with DNPH silica-gel cartridge, HPLC analysis.	Formaldehyde, acetaldehyde and 11 other carbonyl compounds	
Glass wool, several wood based materials, polyurethane adhesive, paint	ETC	AS, Carbograph 4 tube, GC-FID analysis	Hexanal, BTEX, styrene, α-pinene, 3-carene, δ-limonene	[33]
		AS, BPE/DNPH cartridge, HPLC analysis	Formaldehyde, acetaldehyde	
PVC flooring	Laboratory designed ETC	AS, Tenax TA tube, GC-MS analysis	Phthalates	[7]
Latex paints	ETC (0.25 m^3 and 55.06 m^3)	AS, Tenax TA tube, GC-MS analysis	Phthalates	[12]
Selected known emitters in a field study including paint, laminate and furniture	FLEC	AS, Tenax TA tube, GC-FID analysis	BTEX and terpenes	[18]
		AS, DNPH silica-gel cartridge, HPLC analysis	Formaldehyde and carbonyls	
Wood based materials	Small-scale FLEC	PS, Radiello® (Carbograph 4 sorbent), GC-MS analysis	Terpenes	[34]
Glass wool, several wood based materials, polyurethane adhesive, paint	Vacuum vial	PS, SPME fiber, GC-MS analysis	Formaldehyde, acetaldehyde, hexanal, BTEX, styrene, α-pinene, 3-carene, δ-limonene	[33]
Lab made cross laminated timber panels with different adhesives	ETC	AS, Tenax TA tube, GC-MS analysis	Acetic acid, toluene, terpenes	[36]
		AS, DNPH silica-gel cartridge, HPLC analysis	Formaldehyde, acetaldehyde and heavier carbonyl compounds	
Field study, real houses and public buildings with various materials	FLEC	AS, Tenax TA tube, GC-FID analysis	BTEX, terpenes	[18]
		AS, with DNPH silica-gel cartridge, HPLC analysis	Formaldehyde, carbonyl compounds	
		PS, Radiello® (Charcoal sorbent), GC-FID analysis	VOCs	
		PS, Radiello® (DNPH coating), HPLC analysis	Carbonyls	
Wood materials inside	IRINA model room	AS, Carbotrap 202 tube, GC-MS analysis	Terpenes	[11]
		AS, with DNPH silica-gel cartridge, HPLC analysis	Formaldehyde, carbonyl compounds	
Paint, floorings, wood-materials		PS, Radiello® impregnated with DNPH, HPLC analysis	Aldehydes	[3]
		AS, Waters Sep-Pack XPoSure with DNPH, HPLC analysis	Aldehydes	
		PS, Radiello® (Charcoal sorbent), GC-MS analysis	VOCs, BTEX, alcohols, halogenated hydrocarbons	
Paint, PVC-flooring, plasterboard, particle board, melamine resin, polyester, laminate, varnished bench	Vacuum vial and lab-made material surface/air equilibrium cylinder	PS, SPME fiber sampling, GC-MS analysis	Formaldehyde, acetaldehyde, toluene, p-xylene, styrene, 1,2-dichlorobenzene, tetrachloroethylene, hexanal, α-pinene	[26]

and phenol-formaldehyde resins, widely used as binding materials in the production of wood panels and boards, can release formaldehyde over the time [11].

Solid phase microextraction fibers have frequently been used for the collection and subsequent determination of VOCs in new timber frame buildings. The emission profile includes formaldehyde, acetaldehyde, hexanal, BTEX, styrene, alpha-pinene, δ−3-carene and D-limonene as the main compounds with concentrations ranging from < 0.5 $\mu g\ m^{-3}$ to 16 $\mu g\ m^{-3}$. Additionally, ETC and active sampling have been used for the evaluation of emission rates which ranged from 0.8 $\mu g\ m^{-2}\ h^{-1}$ to 134 $\mu g\ m^{-2}\ h^{-1}$ with formaldehyde typically having the highest value [33]. Similar results have been achieved in recent a study developed right away after a building renovation [10].

3.2. Plastic, polymers and adhesives

Plastics, adhesives, polymeric flooring materials and adhesives, widely used in buildings, can be regarded as one of the main indoor air VOCs emission sources. Although a high number of publications have been reported for the emissions of these materials, a recent review article [6] pointed the need for additional studies to better understand indoor air quality.

The list of released compounds includes BTEX, phthalates, styrene and phenols among others [6,12,38]. Two different pathways can be established as potential sources of these compounds, degradation products or the additives used in their production [6]. Additionally, some studies have reported a detailed evaluation of the VOCs emission rates [7,33,86–88].

PVC-flooring material-gas phase equilibrium concentration has been evaluated for selected phthalates by a laboratory made ETC [7]. The equilibrium concentration was achieved using a very short sampling time (2–5 days) in comparison with the traditional sampling techniques (1–5 months). In addition, the analysis of the emitted compounds required the use of Tenax TA adsorption tubes and TD-GC–MS. Emission rates for phthalates ranged between 0.1 $\mu g\ m^{-2}\ h^{-1}$ for di(2-ethylhexyl) isophthalate and 7.8 $\mu g\ m^{-2}\ h^{-1}$ for di-n-butyl phthalate. Even though high phthalate concentrations can be found in PVC products, their vapor pressures as heavy organic compounds are lower and therefore the emission rates are relatively low.

The emission products of adhesives have been evaluated as well, just after application, or after a certain period of time. A relatively large variety of VOCs can be emitted from adhesives including formaldehyde, BTEX, styrene, aliphatic hydrocarbons, aromatic hydrocarbons, ethers, alcohols and acetates [33,88]. The typical analytical procedure for these samples involves a drying step to stable weight, and the subsequent sampling and analysis using an ETC, active sampling and TD-GC-MS. It is common to evaluate the emissions from adhesives as TVOC, that in the study of Ahmed et al. ranged from 203 to 23,911 $\mu g\ m^{-2}h^{-1}$ as a function of the adhesive type [88]. However, in some cases these experiments were focused on the determination of the emission rates for individual compounds, where emissions ranged from 0.5 $\mu g\ m^{-2}h^{-1}$ (hexanal) to 2447 $\mu g\ m^{-2}\ h^{-1}$ (m- and p-xylenes) [33]. It can be assumed that adhesives have much higher emission rates than wood materials. However, wood materials are much more used in buildings by volume.

3.3. Paints

The relevance of paint as potential source of indoor air VOCs should not be underestimated. Its presence in indoor environments is almost ubiquitous covering both large surface areas and furniture. In this case, it looks obvious that emission rates drop significantly with the time. How-

ever, the number of studies reported in the literature is quite short in comparison with those devoted to wood materials [3,12,33,58,86,87].

The list of VOCs emitted by paints includes a relatively large number of compounds such as toluene, xylenes, aldehydes (including formaldehyde and hexanal among others), ethylbenzene, styrene, n-butanol, high molecular weight hydrocarbons, ethylene glycol and even terpenes [3,33,86,87]. However, the exact emission profile depends of the paint type. For example, phthalates are almost exclusively emitted by latex paints [12] and water-based paints emit significant amounts of toluene, xylenes, n-butanol and high molecular weight hydrocarbons [86]. On the other side, no-differences were detected for VOC-emission rates in the case of water and sorbent-based paints. However, the complete evaporation of VOCs is faster in the first. Typical VOC emission rates, calculated from the data obtained using a FLEC system, ranged between 2.1 $\mu g\ m^{-2}\ h^{-1}$ (ethylbenzene) and 107 $\mu g\ m^{-2}\ h^{-1}$ (acetaldehyde) [33]. In addition, emission rates of phthalates in latex paints ranged between 238 $\mu g\ m^{-2}\ h^{-1}$ and 918 $\mu g\ m^{-2}\ h^{-1}$ as a function of the time after the application [12].

3.4. Biomaterials and low emission materials

Bio-based and low emission materials have recently become interesting alternatives to traditional building materials [17]. The key idea is to reduce the emission rates from materials by improving the indoor air quality [3,10,36]. A successful application of low emitting building materials on the construction can be found in the study developed by Gallon et al. for VOCs [3]. Up to 46 semi-VOCs and 43 VOCs were determined in different premises through the different steps of the construction and once finished. Although elevated VOC emission levels were found during certain steps of the construction process (e.g. painting), they stayed below the emission limit values in all the cases. Additionally, the final indoor concentrations of VOCs during the delivery were at acceptable levels.

Typical low emission materials include resins, adhesives, low emission natural raw materials and low emission fiberboards [10,17,36,89,90]. Furthermore, analytical procedures used for the analysis of their emissions are the traditional ones. Carbonyl compounds and terpenes in fiberboard, chipboard and thermo-pressed binderless panels proved that the latter (biomaterial) provided the lowest emissions compared to the conventional ones [10], being especially significant for formaldehyde whose emission rate decreased from 42 and 84 $\mu g\ m^{-2}\ h^{-1}$ found for the commercial panels compared to 0.1 $\mu g\ m^{-2}\ h^{-1}$ for the biomaterial. However, in the case of cross-laminated timber panels, constructed using traditional and bio adhesives, the lowest formaldehyde emissions were achieved for those prepared with a traditional adhesive polyurethane [36].

4. Analysis of emissions due to anthropogenic activities

Recent studies have revealed that cooking, cigarette smoking and the use of cleaning and personal care products are the main VOC sources in indoor air [25]. The first one is especially remarkable in those countries where wood and oil are still used as main combustion source for cooking or heating, enabling the emission of large amounts of VOCs into indoor air [71,72,91–93]. Several hundreds of VOCs have been identified from biomass combustion including different hydrocarbons (unsaturated, saturated, polycyclic aromatic, aromatics, etc.), oxygenated compounds (aldehydes, alcohols, phenols, quinones, etc.) and chlorinated organics. These compounds can easily be mobilized from the kitchen or the living room to other areas of the house and they might cause adverse effects on the health of all the house occupants [94,95]. However, just 50 compounds were identified in liquefied petroleum or town gas, used as cooking fuel. Alkenes accounted for approximately 53% of the total measured VOCs collected from town gas devices, while alkanes contributed approximately to 95% of the VOCs from liquefied petroleum gas during the cooking periods. The concentrations of aromatic hydrocarbons such as benzene and toluene were also increased during the cooking periods. The total amount of carbonyls emitted from the town gas dwelling was three times higher than that at liquefied petroleum gas dwelling. Finally, acetaldehyde was just detected in town gas dwelling. This study was based on the U.S. EPA TO-14 method, which involves the use of air canisters for the collection of the samples followed by direct analysis of the collected compounds by cryogenic focusing and subsequent GC-MS analysis [91].

Tobacco smoke is a complex, dynamic and reactive mixture, including over 5000 VOCs according to the literature. It can be considered the most significant source of toxic chemical exposure and chemically mediated disease in humans [96]. The presence of multiple aromatic organic compounds, such as, BTEX, TMBs, styrene, and naphthalene in addition of α-pinene and D-limonene, should be expected at high concentrations in smoking areas [97]. However, all compounds have not been observed in the analysis of the indoor air from smoking houses. A study involving more than 60 smoking residences indicated relatively large concentrations of benzene, trimethylbenzene, 2-ethyl toluene, propylbenzene, butyl benzene and C_7–C_{11} n-alkanes in houses with an inadequate ventilation. The experimental setup employed in this study involved passive sampling followed by TD–GC–MS [98]. Strong carcinogens N-nitrosamines, were determined in a smoking room using a NTME sampler for the collection of the target analytes followed by subsequent analysis and GC-MS. The highest concentration of N-nitrosodimethylamine detected was 2954 ng L^{-1} which decreased to 470 ng L^{-1} when the room was not in use [57].

Oxygenated and aromatic VOCs have been identified in the indoor air of a classroom occupied by university students giving consistent correlations with the phenol concentration, used to be as human bioeffluent marker [71]. The results proved human activities in the classroom as the principal emission source for these compounds. In addition, the concentrations of some indoor VOCs, evaluated from a different classroom using positive matrix factorization, revealed a clear ‘human influence’ component, which might be explaining by the effect of the human breath and the ozonolysis of human skin lipids [71]. Moreover, large amounts of decamethylcyclopentasiloxane, a well-known major inactive ingredient in some personal care products, were found in another study made in university premises [72]. In all these studies, VOCs were determined using PTR-MS. This technique was also used for the evaluation of the variations in VOC profiles in cinema air as a function of the screenings and the audiences. Data mining tools and statistical algorithms, proved that specific film events, namely “suspense” or “comedy” caused audiences to change the emission of specific chemicals [69].

Perchloroethylene (PCE or PERC), determined in dry cleaning facilities using a NTME device packed with graphene and carbon nanotubes ranged between 0.05 and 96.7 ng m^{-3} depending on the sampling position. Small differences were observed between samples due to the selection of the packing material [59,60].

5. Analysis of emissions due to biogenic activities

It is well known that bacteria and fungi are ubiquitously present in indoor premises. Indoor air, for instance, contains between 10^2 and 10^9 microbes per dm^3 of air volume, and a similar number of microbes can be found coating every cm^2 of indoor surface [99]. Some of them can even grow in their inhabitants, both animals or humans. All these microbes are able to produce and emit into the air a large variety of volatile, semi- and non-volatile secondary metabolites affecting the chemical composition of indoor air.

Bacteria based biotechnology have become an important alternative to many physical and chemical techniques to remove or at least decrease the concentration of the VOCs present in indoor air. This technology, especially successful in the case of industrial pollutants removal, have been recently introduced to indoor air [100]. However, very little information have been reported in the literature about bacterial

Table 3
Common microbial organic compounds reported in indoor air and suggested as biological markers. F, Fungi; B, Bacteria.

Compound	Microbes	Species
1,2-dimethoxybenzene	*A. Versicolor*	F
1-octen-3-ol	*P. expansum, P. chrysogenum, A. versicolor, A. fumigatus, A. niger, C. cladosporoides*	F
2,4-pentandione	*A. fumigatus*	F
2-methyl-1-butanol	*P. expansum, P. chrysogenum*	F
2-methyl-1-propanol	*P. expansum, A.niger*	F
2-octanone	*A. candidus*	F
2-pentanone	*P. expansum, P. chrysogenum, A. versicolor, A. fumigatus*	F
3-cyclohepten-1-one	*A. candidus*	F
3-methyl-1-butanol	*P. chrysogenum, A. fumigatus, A. niger, C. cladosporoides*	F
Dimethyldisulfide	*P. expansum*	F
Limonene	*A. fumigatus, A. versicolor, P. crysogenum, P. glabrum*	F
Methyl benzoate	*A. fumigatus*	F
Methanol	*Staphylococcus, Caryophanon* spp., *Methylobacterium phyllosphaerae, Mycoavidus cysteinexigen, Mycobacterium iranicum, Pseudomonas oryzihabitans, Pseudomonas syringae, Serattia marcescens, Stachybotrys chartarum*	B
Methanethiol	*Staphylococcus, Caryophanon* spp., *Methylobacterium phyllosphaerae, Mycoavidus cysteinexigen, Mycobacterium iranicum, Pseudomonas oryzihabitans, Pseudomonas syringae, Serattia marcescens, Stachybotrys chartarum*	B
Butyric acid	*Staphylococcus, Caryophanon* spp., *Methylobacterium phyllosphaerae, Mycoavidus cysteinexigen, Mycobacterium iranicum, Pseudomonas oryzihabitans, Pseudomonas syringae, Serattia marcescens, Stachybotrys chartarum*	B

emissions [101]. Opposite fungal emissions have been widely studied due to their potential effect on human health. In order of relevance, *Penicilium, Apergillus, Stachybotrys, Trichodermas, Chaetomium globosum and Aternaria* are the most common fungal species identified in indoor spaces. Frequently, their presence is related with the damages produced by water in the buildings [35,102–104]. In addition, the highest concentrations of the different species can be found during warm months, through March to September in northern globe, with peaks in July and September [105,106]. The presence of these fungi is related, in most of the cases, to the decomposition of the cellulose materials, such as wood, wallpapers, carton-gypsum or insulation materials, in the buildings. However, some fungi as *Chaetomium globosum* has been detected also on linoleum, concrete and gypsum wallboards [103].

5.1. Microbial volatile organic compounds

A quick literature overview indicated different databases containing MVOCs information. The most remarkable is MVOC 2.0. This extensive database, containing over 2000 MVOCs from 1000 species, was launched by Lemfack et al [107].. Individual MVOCs have been used for the identification of microbes [23]. However, this approach has clear limitations due to the impossibility to identify the emission source (e.g., plant vs microbe vs pollutants). Thus, there is the need for measurement of more complete MVOC fingerprints to serve as specific tracers [108]. Common MVOCs emitted by specific fungi can be found in Table 3.

Misztal et al. have recently published an study based on the growing of different microbial species, including fungi and bacteria, under controlled conditions on nutrient media, or on residential structural materials, has demonstrated the presence of a relative large number of VOCs (over 400) emitted by the microbes using a high resolution PTR-MS for the detection of the compounds [109]. This study is of special relevance giving the relevant information about bacteria emissions including *Staphylococcus, Caryophanon* spp., *Methylobacterium phyllosphaerae, Mycoavidus cysteinexigen, Mycobacterium iranicum, Pseudomonas oryzihabitans, Pseudomonas syringae, Serattia marcescens*, and *Stachybotrys chartarum* among others. Well-known MVOCs emitted by bacteria, such as methanol and methanethiol (CH4S) were identified in this study. It should be emphasized, that methanethiol with a few other sources in the indoor environment seems to be more suitable biological marker for bacteria presence. Methanethiol and butyric acid were the largest VOCs emitted by plant isolated microbes. Large alcohols, fatty acids, and amino acid esters had dermal type of microbes as main emission sources, although these were also emitted by plant and building microbes at much smaller concentration. *Staphylococcus hominis*, a commensal dermal bacterium was the main source for aromatic compounds. In addition, the authors proposed the use of different ratios between compounds such as pyruvic acid to methanethiol, styrene to acetamide, and octenol to styrene, for identification of representative microbial species from indoor air.

Lorentzen et al. has demonstrated that chloroanisoles, a well-known by-product of chlorophenol microbial metabolism, may explain the characteristic odor found in the houses and premises contaminated with molds. However, these compounds should not be considered a potential tool for the evaluation of major problems with molds and dampness due to their extremely low human odor thresholds for these compounds [110]. The use of anisole as a potential mold biomarker has been confirmed using seven toxigenic strains of *Stachibotry chartarum*, a filamentous mold frequently identified among the mycobiota of water-damaged building materials [111]. In both cases Tenax TA tubes were used for the collection of the VOCs followed by TD-GC-MS.

Target and non-target analysis approaches have been used for the determination of MVOCs in indoor air. The first one allowed the successful identification of molds from damp housing materials using just 19 MVOCs related with fungal metabolism, and some statistical algorithms [48–50]. The later was used for the potential identification of MVOCs from natural samples. In the case of *Ganoderma boninense or Trichoderma atroviride* fungi, a total of 57 MVOCs (including alcohols, alkanes, volatile acids, ketones, aldehydes, esters, sesquiterpenes and polycyclic aromatic hydrocarbons) were identified using a two-parameter approach, which involved the comparison of the GC retention times and mass spectra obtained from the different peaks and those achieved by NIST database [112,113]. The strict selection criteria required a spectral match factor at least 90% and a maximum relative deviation of the linear temperature programmed retention index for hydrocarbons of ±2% from literature values. It should be emphasized, that aliphatic compounds with eight-carbons such as 1-octen-3-ol, 3-octanone and 1-octanol (commonly detected in actively growing microbes), were the most abundant metabolites in the samples [112]. Similar approach was used for the identification of volatile alcohols, ketones, alkanes, furanes pyrones and terpenes emitted by *Trichoderma atroviride* and *Penicillium roqueforti*. From all these compounds, the real presence of 11 MVOCs was confirmed by the use of authentic standards [114–116]. It should also be emphasized that adsorption tubes were used for the collection of MVOCs emitted by *Aspergillus fumigatus*. In this case, the selection of Tenax TA and Carbograph 5TD allowed the collection of a wide range of compounds avoiding the problems caused by water adsorption. The TD-GC-TOF-MS used for the separation and identification of the MVOCs allowed the identification of unique markers [88]. As discussed before, the main limitation of this approach is derived from the volatility and the thermal stability of the target compounds. In these cases, solvent extraction is still in use allowing their subsequent analysis by HPLC [5].

Table 4
Non-volatile secondary metabolites emitted by different fungal species and reported in indoor air after their mobilization.

Microbe family	Secondary metabolites, potential presence in air	Secondary metabolites, reported in air
Penicillium	Andrastin A, Brevianamide, Koninginin A, Koninginin E, Koninginin G, Meleagrin, Monoterpenoids, Micophenolic acid, Penicillin G, Penitrem A, Physcion, Roquefortine C, Secalonic acid D, Secalonic acid F, Skyrin, Xanthocillin X	Chaetoglobosins, Communesin A, Communesin B, Communesin D
Aspergillus	Auroglaucin, Epiheveadrides, Flavoglaucin, Fumonisins, Isotetrahydro auroglaucin, Neoechinulin A, Neoechinulin B, Zearalenone	Aflatoxin B_1, Aflatoxin B_2, Ochratoxin A, Trichothecenes
Stachybotrys	Drimanes, Trichothecenes,	Atranones, Roridins, Satratoxins, Verrucarins, Phenylspriodimanes
Trichodermas	Bisvertinol, Sorbicillin derivatives, Spirosobicillonol A, Trichotetronine, Vertinolide	
C. Globosum	Chaetoglobosin A, Chaetoglobosin C, Chaetoglobosin F, Chaetomugilin D, Chaetoviridin, Cochliodones	
Alternarias	Alternariol, Altenuene, Anternarion methyl ether,	

5.2. Microbial non-volatile secondary metabolites

The mobilization of non-volatile compounds into the indoor air can be explained by a couple of well identified mechanisms. The first one has been reported for *Penicillium* and *Trichoderma* fungi that are able to produce guttation liquids which contain volatile and non-volatile secondary metabolites, the latter can be easily mobilize into the air through dispersion of these fungal droplets [24]. The second mechanism, identified for *Aspergillus* or *Stachbotrys* fungi involves the participation of the indoor air dust in the mobilization of these mobilize non-volatile metabolites [66]. Non-volatile secondary metabolites emitted by different fungal species and detected in indoor air after their mobilization can be found in Table 4.

Penicillium is one of the most common fungi found in damp buildings. More than 350 Penicillium species has been identified each of them with their own metabolite profile influenced by the media and the growing conditions. For example, meleagrin, roquefortine C, xanthocillin X and secalonic acid D and F which were found as the main secondary metabolites in the case of *Penicillium rubens* [117]. However, just the last 3 were found in the case of *Penicillin G* [104,118]. Other common secondary metabolites emitted by *Penicillium* fungi include penitrem A, andrastin A, meroterpenoids, koninginin A, E and G, brevianamide and mycophenolic acid [119,120].

Aspergillus also exhibit clear variations on its secondary metabolite profile between different chemotypes. Briefly, flavoglaucin, auroglaucin, isotetrahydroauroglaucin, epiheveadride and neoechinulin A and B are well-known major metabolites [121]. However, Aflatoxins (AF) B_1 and B_2 and ochratoxins, poisonous carcinogenic and mutagenic compounds, are the most problematic ones from health and safety point of views. In addition, other compounds belonging to fumonisins and trichothecenes, in addition to zearalenone have been detected [122]. It should be emphasized that although aflatoxins and ochratoxins were detected in indoor air samples collected from industrial environments (grain mills), these compounds were not detected from domestic environments [106]. This observation fits well with the potential mobilization of these non-volatile compounds by the indoor air dust [66]. The elucidation of multiple non-volatile biomarkers from *Aspergillus flavus* was done using HPLC-MS. The list of identified compounds includes potentially toxic and non-toxic compounds for humans such as AF B_1, AF G_1, aspergillic acid, aspyrone, betaine, chrysogine, deacetyl parasiticolide A, flufuran, gregatin B, hydroxysodonic acid, nicotinic acid, phomaligin A, spinulosin and terrain. Even though concentrations were not reported in this study, some of these compounds might be emitted into air via spores and particles [65].

Different mycotoxins have been detected as secondary metabolites emitted to the indoor air in the case of *Stachybotrys.* These compounds can be divided into three groups according to their molecular structures: macrocyclic trichothecenes (MCTs), atranones and phenylspirodrimanes (PSDs). Most of the *Stachibotrys* secondary metabolites with the highest toxicity (Satratoxins, roridins, verrucarins, etc.) belongs to the group of MCTs [123].

Trichodermas are able to produce trilongins B_I-B_{IV} and trilongin AI as main secondary metabolites. These compounds are toxic, especially for gametes [124]. However, these fungi have an active metabolism proving a relatively large number of compounds into the air. Sorbicillin-derived compounds (i.e. vertinolide), spirosorbicillonol A-C, bisvertinol and trichotetronine are clear examples of *Trichodermas* emissions [125,126]. These fungi are well-known to produce guttation droplets. An exhaustive analysis of these droplets has demonstrated the presence of toxic peptaibols such as trichorzianines and trichostrigocins that can be easily mobilized into the air by the dispersion of the droplets.

Studies from Northern America and Europe have proved that chaetoglobosins A, C and F, chaetomugilin D, chaetoviridin A and cochliodones are the most common secondary metabolites of *C globosum* [103,120]. Last but not least, altenuene, alternariol and anternariol methyl ether were detected in building materials contaminated with *Alternaria* fungi [104].

6. Future outlook

During the last two decades, the development of active and passive MAS techniques, such as, capillary microtraps, needle trap devices, SPME fibers and thin-film microextraction devices have offered high performance alternatives to conventional sampling systems for indoor air researchers [45]. The main advantages of these techniques in comparison with the traditional sampling systems are their operational simplicity, automation capacity, high performance (short collection times and air sampling volumes) and a wide compatibility with thermal desorption, avoiding organic solvent consumption. However, not all these MAS techniques have been accepted or at least tested for the collection of VOCs from indoor air. As discussed before, multiple SPME fiber and NTD applications can be easily found from the literature, but very little information is available about the use of other MAS systems, most probably due to their potential drawbacks in terms of robustness, extraction capacity and efficiency. These limitations can be fortunately circumvented by SPME Arrow and in-tube extraction (ITEX) sampling systems. Both of these MAS techniques have been successfully applied for the determination of VOCs from outdoor air [127–131]. However, to our best knowledge, these high-performance MAS techniques have not yet been used for indoor air samples.

There is the need for the development of more accurate, affordable and reliable total analysis systems for the determination of VOCs from indoor air in a near future. Similar to the different sensors currently available in the market, these total analysis systems should be preferably miniaturized, portable and relatively simple to operate, even for a non-trained person. However, opposite to the sensors, the present systems available at the moment are able to give information about the concentration of the different individual VOCs in the air samples. Additional software or algorithms to provide information about the potential emission sources would be highly welcome.

Last but not least, the potential discrimination between species of microbes involved in the VOCs emissions will be improved by the use of

sophisticated artificial intelligence algorithms, allowing the elucidation of VOCs sets with microbial discrimination power in terms of precision and accuracy [132]. In this way, the reliable identification of the different microbial species present in the collected samples and their subsequent quantitation would be a key factor to enhance the performance of the artificial intelligence models. The use of DNA sequencing and quantitative polymerase chain reaction assays will contribute to minimize the variability, in terms of sensitivity and precision, associated with the traditional approaches based on the preparation of cultures and followed by microscopic cell count [101,133].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Jose Ruiz-Jimenez: Writing – original draft, Visualization. **Ilmari Heiskanen:** Writing – original draft. **Ville Tanskanen:** Writing – original draft. **Kari Hartonen:** Writing – review & editing, Supervision. **Marja-Liisa Riekkola:** Writing – review & editing, Supervision, Funding acquisition.

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