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Problems and challenges associated with estimating the emissions of organic compounds from indoor materials

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abstract

For several years intensive research has been carried out with the aim of developing a database of the types and amounts of pollutants released from indoor materials to the indoor environment. The paper discusses in detail basic problems and challenges encountered when estimating the emissions of chemical compounds released from of indoor materials. Factors affecting the validity of data obtained by using two different types of analytical devices operating in a dynamic mode (the ex-situ methods) or passive mode (the in-situ methods) for collecting the analytes samples from the gaseous phase were discussed. The main advantages and important limitations of specific analytical devices and aspects of the morphology of the studied indoor material that may influence the type and amount of chemical compounds released into the air were also highlighted. Attention has also been drawn to challenges encountered when developing candidate reference materials dedicated for measuring emissions from indoor matrices.

Keywords:Emissions, Emission test chambers, Passive flux samplers, Indoor materials, Small-scale passive emission chambers

1. Introduction

According to recent information provided in scientific literature, an adult person may breathe air of varying composition containing traces of pollutants in open spaces (atmospheric air, urban air) or in various enclosed spaces, referred to as the indoor environment or the indoor microclimate (residential rooms, workplaces, public utilities, etc.) [1,2]. The types of air that people breathe throughout their life are diagrammatically presented in Fig. 1. Artificial breathing mixtures (also might be defined as a “special type of atmosphere”) is a term referring to air of precisely defined composition and generated by specially designed devices. People can come in contact with such air inside rescue chambers, hyperbaric chambers, submarines or space stations. Different terms have been used in scientific literature for air inside various enclosed spaces, such as indoor environment, indoor air, and indoor microclimate. Indoor air quality (IAQ) is an issue directly linked with indoor air/indoor environment, and in the available literature it is defined as “*a multi-disciplinary phenomenon, determined by the many pathways in which chemical, biological and physical contaminants eventually become a portion of the total indoor environmental composition*” [1,3].

The presence of various types of chemical contaminants in the indoor environment strongly depends on four basic factors [4–7]:

(i) Migration of chemicals into the indoor air directly from the atmospheric air surrounding a room or building;
(ii) Emission of chemicals from a wide range of indoor furnishing materials in residential facilities, including building materials and structural elements;
(iii) Emission of biogenic chemicals (mainly volatile organic compounds) from green plants grown indoor (BVOCs);
(iv) Daily human activity in residential facilities, including a range of routine or spontaneous actions.

Among all the described factors the process of releasing various types of chemicals (mainly the volatile organic compounds – VOCs) into the indoor air from furnishing and finishing materials has a significant influence on the indoor air quality (defined by the type and amount of compounds present in it) [8–10]. The speed of the direct emission of chemical compounds from indoor materials to indoor air depends mainly on the temperature, relative humidity and air velocity in the indoor area [11–14].

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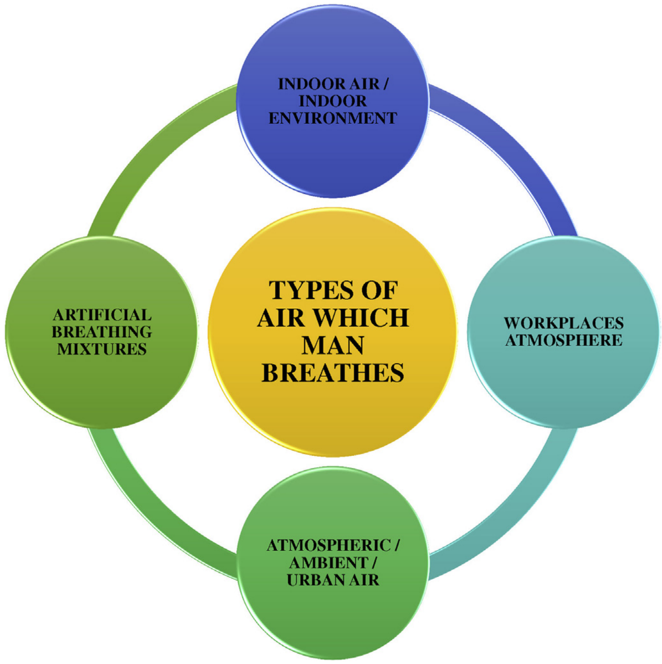

Fig. 1. Example types of air that people might breathe throughout their life.

Due to the complex nature of the process in which contaminants from indoor materials are released into the gaseous phase, the migration of compounds is analysed on a macroscopic scale. In this case the indoor material is defined as a solid body (a solid of a characterized internal structure) with chemical compounds (in a gaseous form) immobilized in the free spaces inside the material. In addition, in the macroscopic model describing emissions, chemical compounds may also be adsorbed directly onto the surface of a given indoor material [15–18].

The process of the emission of chemicals from furnishing or finishing materials is shown diagrammatically in Fig. 2. The transport of chemical compounds may be driven by the differences in concentrations, temperature and partial pressure. The mechanism of the emission of organic compounds into the indoor environment is much more complicated, and also depends on the internal structure of the material and on the type of coating used on the surface of the indoor material. The diagram in Fig. 2 shows a simplified (generalized) emission process, allowing for better understanding and visualization of processes taking place in the indoor environment and affecting its quality [19,20]. Detailed information and a precise description of the emission process, along with factors directly affecting changes in the transport of compounds from the indoor material into the gaseous phase (indoor air) has been provided in previous reports [21,22].

In addition, many research centres are conducting multidisciplinary studies aimed at explaining in detail the processes and phenomena related to the release of compounds from the surface of materials into the indoor environment, and some of them employ advanced mathematical tools (modelling studies using relevant databases) [14,23,24]. Han et al. [14] proposed model-based approach (double-exponential decay model; a power-law decay model and a mechanistic diffusion model) using advanced analytical technique - proton transfer reaction-mass spectrometry (PTR-MS) to predict with a significant accuracy the long-term so-called emission signatures (ES) of studied indoor materials. A specific type of so-called fingerprint which might define the type and amount of emitted specific chemical compounds from selected indoor materials was applied. As for another types of modelling studies in the field of emissions research, Liu e al. [23], describes in details physically-based mass-transfer models usually applied to assess and predict the emissions of volatile and semivolatile organic compounds (SVOCs) from building and constructing materials. Moreover, the information enclosed in this valuable review article concerns the mathematical modelling methods used in everyday laboratory practice, which were divided into three main groups: (i) models estimating the VOCs emissions from solid materials; (ii) models estimating the emission of VOCs from liquid materials; and (iii) models estimating the SVOCs emissions. Application of various types of a mass-transfer mathematical models in the field of assessment the emissions of organic compounds might be very good solution to support the laboratory emission research and gives an opportunity to reduce the costs of a single analysis of indoor material [24]. However, at this point it should be realized that conducting various type of model studies is necessary to have a basic knowledge as well as a suitable database on the process and

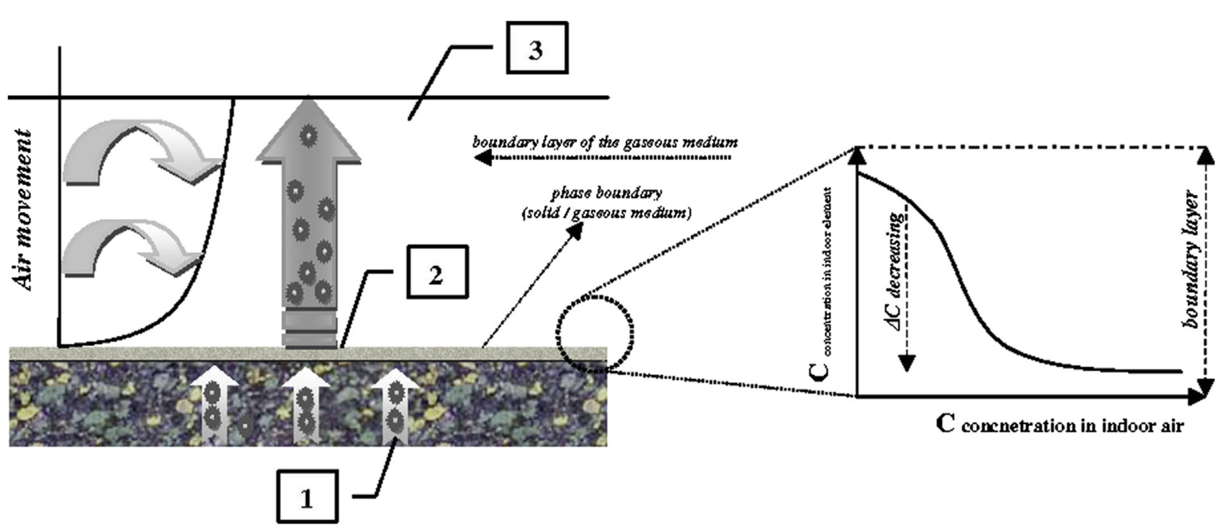

Fig. 2. Graphical scheme of the phenomenon of emission of chemical compounds from the surface of indoor material into the indoor environment (gaseous phase): 1 – diffusion inside the indoor material (internal); 2-desorption (release of the analyte from the surface of the indoor material); 3-convection (based on the literature information published in Refs. [19,20]).

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phenomena of release of chemical compounds from building and constructing materials (including various types of indoor equipment).

2. Major factors determining the appropriate choice of analytical devices dedicated for estimating the emissions of organic compounds from indoor materials

Indoor air quality in residential facilities and public buildings is significantly influenced by various aspects of human activity associated with lifestyle, occupation, leisure activities, personal behaviour, culinary and aesthetic preferences, etc. Other factors, such as the type and number of plants kept, number of occupants per room, or the presence of pets are also important for the quality of the indoor environment [25–27]. All of these factors can be grouped into a single category and defined as dynamic indoor factors determining the quality of the indoor environment. This term covers all sorts of everyday human activities (usually daily and short-term), which significantly affect the quantity of contaminants released into the indoor environment [28]. The second category of factors that significantly affect the type and quantity of chemicals present in the indoor air of residential and public buildings includes various furnishing and finishing materials, including a wide range of building and structural materials [8,29,30]. They can generally be termed as passive factors because their impact on the quality of the indoor environment is not directly related to human activity. In addition, these factors are a source of continuous/long-term emissions of contaminants into indoor air measured in days, months and even years. Contaminants from indoor materials are mainly and directly released into the indoor environment (emission of contaminants) by spontaneous molecular diffusion. The dynamics of this process depend on the environmental conditions inside the room, such as temperature, humidity or insolation of the material's surface, and the morphological characteristics of the indoor material [31,32].

Currently, many research centres use a number of devices and techniques to carry out studies estimating the emissions of chemical compounds from the surface of indoor materials. General information on devices used to determine the types and the amount of chemicals released into the indoor air is shown in Fig. 3.

The operation of analytical devices presented in Fig. 3 used for the conditioning of indoor materials and collecting the analytes samples from the gaseous phase in analytical protocols relies on two basic methods: (i) ex-situ methods – all operations and stages of the analytical procedure are performed in a laboratory, mainly using stationary analytical equipment – stationary environmental test chambers (ETCs) (small-scale or large-scale). Material sampled indoor also has to be transported to the place of analysis; (ii) – in-situ methods – chemical compounds emitted from the surface of indoor material are sampled directly in a residential room. Portable

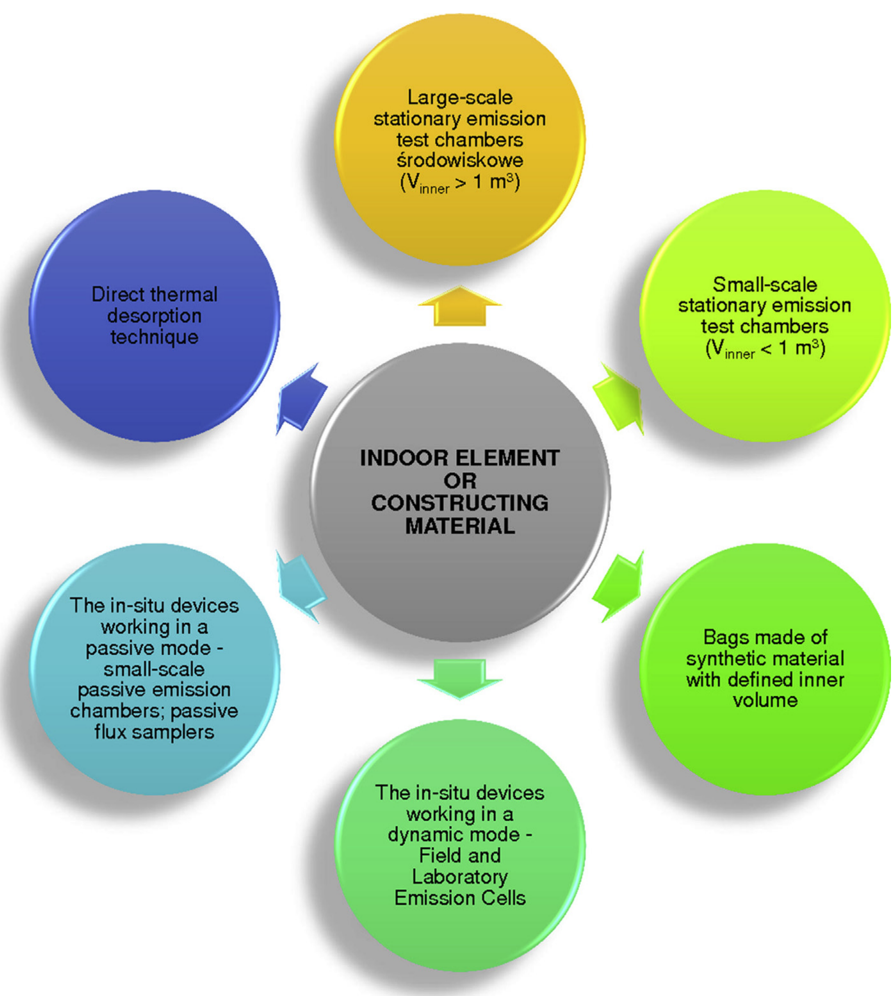

Fig. 3. Analytical devices used in laboratory practice for studies focused on the estimation of the emission of chemicals released into the gaseous phase from the surface of indoor materials.

small analytical devices sampling analytes from the gaseous phase in a passive mode are used for this purpose. Further stages of the analytical procedure take place in a laboratory on stationary analytical equipment. The group of analytical in-situ instruments also includes field and laboratory emission cells (FLECs). These instruments, however, collects the analytes samples from the gaseous phase in a dynamic mode, and their operation principle as well as analytical equipment used at the final stage of research is the same as for stationary ETCs [33–36].

In the mentioned analytical devices (working in a passive or dynamic mode) the key construction elements are containers or vessels filled with defined sorption medium dedicated for retaining chemical compounds present in gaseous phase. One of the most important physicochemical parameters that characterized selected sorption material are the specific surface area [m^2/g] and sorption strength. According to the literature data sorption materials (polymer or carbon type) applied to collect chemical compounds samples from gaseous phase (mainly volatile or semivolatile organic compounds) might be divided into the following general groups, differing in a sorption strength: (i) very weak sorption strength – graphitized carbon black sorbents like Carbotrap C or Carbopack C; (ii) weak sorption strength – porous organic polymers like Tenax TA (or GR); (iii) medium sorption strength - porous organic polymers like Chromosorb or Poropak and graphitized carbon black sorbents like Carbograph 1TD (or 5TD) or Carbopack X; (iv) strong sorption strength – carbon molecular sieves like Spherocarb or UniCarb; (v) very strong sorption strength - carbon molecular sieves like Carboxen 1000 or Molecular Sieve 5A and activated carbon/charcoal. At this point it is also worth mentioning that in almost every cases the selection of a sorption material defines the liberation technique, which should be applied to release the collected chemical compounds from the sorption medium. The most popular techniques used in laboratory practice and dedicated to liberate the organic compounds retained on the sorption medium are the thermal desorption (TD) and the solvent extraction using e.g. CS_2 or acetonitrile as an extraction medium [37–40]. All listed types of sorption medium might be applied not only in emission research, but also as a sorbents used at the stage of collecting organic compounds samples from air in indoor areas as one of the key step of studies concerning the quality of indoor environment.

Taking into account previously mentioned information, two main factors should be considered when planning research directly aimed at obtaining data on the type and amount of chemicals emitted from the surface of an indoor material into the indoor environment: (i) the economic and logistical aspects, mostly affected by operating costs of the equipment used at each stage of the analytical procedure, and the costs associated with the transport of the studied indoor material to the laboratory. In some cases adjustment of the size of the studied material to the operating capabilities of devices should also be considered (destructive methods to reduce the size of the sample to be studied); (ii) a factor defining the type and character of obtained analytical data, the interpretation of which allows for the qualitative and quantitative determination of a specific compound or group of compounds released into the gaseous phase from the studied indoor material. Fig. 4 shows in detail factors determining the choice of technique/approach for the measurement of emissions, the type of analytical information obtained with a chosen technique, and significant aspects influencing the costs of a single assay.

Nevertheless, when planning research to assess the emissions of chemical compounds from building materials, it is also necessary to take into account the opinion of occupants living in a particular residential facility, in addition to the aforementioned major factors. From the point of view of occupants (individual users), the most important thing is to obtain clear and simple (understandable to occupants) information about the major source of contaminant emissions and types of chemical compounds emitted in the largest quantity. Moreover, in many cases the priority for individual occupants of residential facilities is to carry out measurements in a short time using methods that are non-invasive to the indoor material and at the lowest possible cost. Taking into account the described preferences of occupants of residential facilities, the optimal solution would be one that relies on analytical instruments suitable for indoor installation (in-situ) and which provide the opportunity for screening studies and can give, in a relatively short time, information on chemicals and their potential effects on the occupants' well-being and health in the long-term perspective.

On the other hand, when full characterization of a specific indoor material is required, including detailed information on the emission profile of a defined compound or group of compounds, the best option is to conduct laboratory research using stationary emission chambers. Data obtained in this way help to create a relevant database on the emissions of contaminants from the studied indoor material, and to ascertain the very precise characteristics of the studied object. Nevertheless, for occupants/users of the facility this brings considerable financial expense, and sometimes they have to consent to the destructive manipulation of the indoor material (irreversible changes in the structure of the studied indoor material). Therefore, even at the stage of planning the emission research, the budget necessary for this purpose available to the occupants of the residential facility has to be discussed and agreed upon. On the other hand, the role of the analyst is to: (i) estimate the operating costs of analytical instruments; (ii) make a proper assessment of the capabilities offered by the laboratory; (iii) define the character of the analytical information to be tailored to the specific type of research and the preferences of the occupants of residential facilities.

3. Problems and challenges associated with the use of stationary emission test chambers

During the analytical procedure aimed at estimating emissions of chemical compounds, based on the use of stationary in-situ emission chambers at the stage of conditioning of sampled indoor material, all operations specified in the designed analytical procedure are carried out in a laboratory. The use of stationary emission chambers means that the indoor material to be studied has to be transported to the laboratory. Moreover, in some cases the size of the indoor material to be studied has to be reduced by cutting it into pieces of suitable length and width to fit the chamber dimensions. This operation causes irreversible changes in the structure of the indoor material and prevents its further use in the residential room in the way it was designed and constructed. From the occupant's point of view, this is a very inconvenient solution, which not only generates expenses associated with the transport of the furnishing material, but also removes it from the original installation site (residential room). Therefore, stationary emission chambers are mainly used for studying samples of indoor materials supplied directly by the company or consortium operating in the production of a wide range of building and finishing materials. In addition, studies employing stationary emission chambers are costly and time-consuming, since the chamber has to be prepared by washing and preheating, and a suitable technique for the extraction/isolation of analytes, as well as a relevant system of analytical instruments for qualitative and quantitative determination of compounds have to be selected. The example diagram of an analytical procedure for the assessment of the emission of contaminants from finishing and building indoor materials is presented in Fig. 5.

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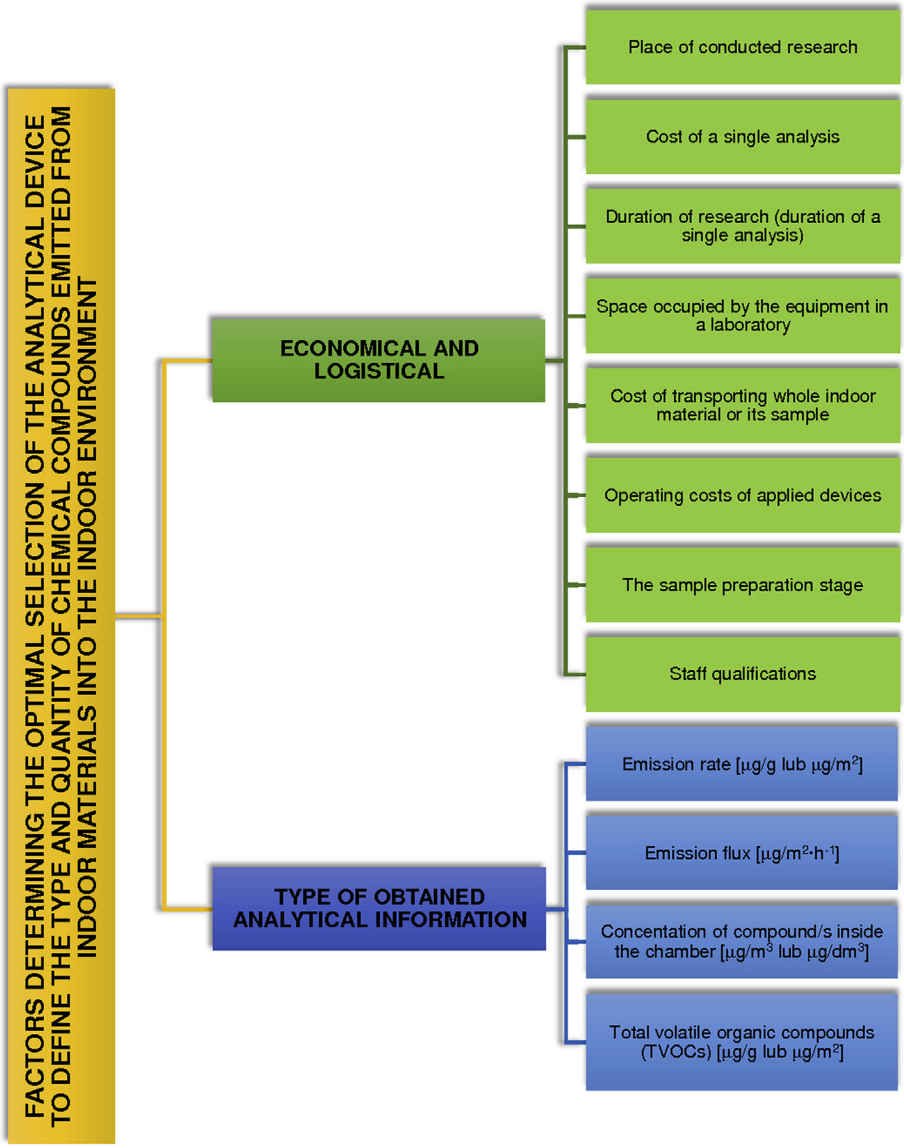

Fig. 4. Factors determining the optimal selection of the analytical device to assess the types and amounts of chemical compounds emitted from indoor materials into the indoor environment.

Nevertheless, if the economic and logistical factors are insignificant in the context of the entire analytical procedure, and if the occupants agree to fragment the indoor material into pieces, then the use of stationary emission chambers becomes an ideal solution for the assessment of the quality of indoor materials and estimating emissions of contaminants from their surface. Stationary emission chambers offer the precise measurement and control of research parameters such as temperature (from room temperature to 65°C), humidity (40–60%), the flow rate of purified and dried air or an inert gas (0.5–10 m^3/h), air exchange rate inside the chamber [number of exchanges/h], and loading factor (0.5–5.0 m^2/m^3) [36,41]. This allows for a number of studies in conditions almost perfectly reflecting the specific microclimate of the residential rooms. For this reason, after completing all stages of the analytical protocol, the obtained dataset is accurate and valid, or at least gives a very probable estimation of emissions of chemical compounds that are actually found under real/field conditions (indoor environment of the residential rooms). Another way to measure the emissions of contaminants released from the surface of indoor materials is to use large-scale ETCs with volumes much greater than 1 m^3, and which can accommodate and condition pieces of equipment used in residential rooms, or building and structural materials without their previous fragmentation. In addition, all fittings and finishing materials that are used in a given residential room can be installed inside a large-scale ETCs. This type of laboratory research provides very accurate real-life information on the effect of all furnishing elements present in a residential room on the indoor environment [42–44]. It should be noted, however, that research carried out using large-scale emission chambers are unable to clearly identify specific sources of emissions if many furnishing elements of different characteristics are installed inside the chamber.

If the budget and laboratory space are limited, the use of a small-scale stationary ETC is a good solution. Very often this type of analytical equipment is self-built by research centres using commercially available elements. Most often these are glass desiccators of a defined inner volume, suitably modified and adapted to research conditions, or polished stainless-steel cylindrical containers with a sealed lid. In addition, such instruments must also be equipped with a sensor monitoring temperature inside the

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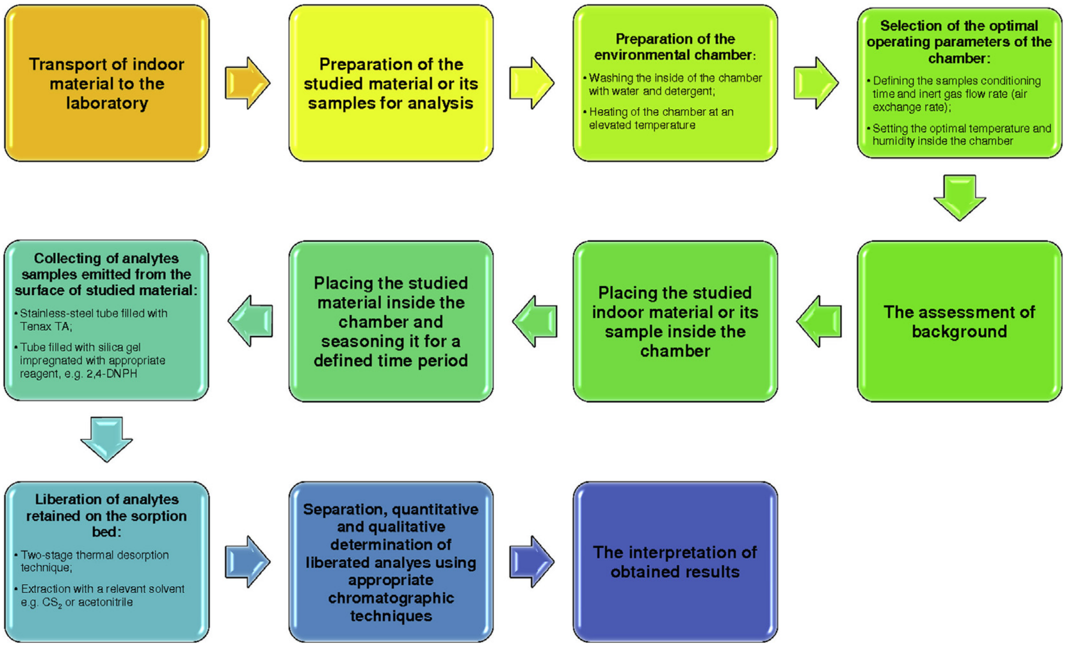

Fig. 5. The general scheme of the analytical procedure employing stationary ETCs for estimating the quality of furnishing and finishing materials.

chamber and a sensor measuring relative humidity [45,46]. Custom-made ETCs should be designed and built in a way ensuring the minimum number of joints between chamber walls. Consequently, research laboratories more often built cylinder-shaped small-scale ETCs than rectangular ones, since a cylindrical design significantly reduces so-called “dead volumes/spaces” inside the chamber. This aspect is quite important because each combining site between the walls that is not perfectly smooth can consequently cause the sorption of contaminants on their surface. As a result, the final measurement may be overestimated (if contaminants retained in the wall combining sites will be released during conditioning of the material) or underestimated (if contaminants emitted to the gaseous phase will be retained on the surface of combining sites between the chamber walls). Fig. 6 presents the main advantages and significant limitations to be considered when planning research and studying emissions of chemical compounds from indoor material using stationary ETCs.

4. Advantages and limitations associated with the use of portable analytical instruments collecting the analyte samples from gaseous phase in a passive way (estimation of in-situ emissions)

The group of instruments most often used for studying the quality of indoor materials directly in residential rooms includes small-scale passive emission chambers (SSPECs) and passive flux samplers (PFSs). These instruments do not require an external source of power, pumps or aspirators, or tubes to supply carrier gas. Moreover, they need no additional instrumentation such as temperature or humidity sensors. Chemical compounds emitted from the surface of indoor material to the gaseous phase are sampled in a passive mode, using an appropriately selected sorbent bed. Chemical compounds present in the studied material move to the sorbent bed consistently with Fick's law of diffusion. The speed at which chemical compounds are collected from the gaseous phase mainly depends on the concentration gradient between the surface of the studied indoor material and the surface of the sorbent bed placed inside the sampler [18,34,35].

Therefore, the use of portable analytical instruments for the estimation of the type and quantity of compounds released from the surface of indoor materials seems to be the right solution convenient for the occupants of residential rooms. SSPECs allow for non-invasive screening studies (non-destructive to the studied indoor material) without interfering with the normal activity of the occupants of a particular residential room. Passive emission chambers require no external source of power or forced flow of gas inside the chamber, and therefore can be installed inside a residential room without causing acoustic or aesthetic discomfort to occupants. Another important advantage comes from the fact that these portable instruments are very easy to operate, and are relatively inexpensive to design and build. Because of this, the occupants of premises (residents) can be engaged in conducting studies after having received brief training on the proper setting of the instrument for work and its installation in a residential room [47,48].

The use of PFSs under real/field conditions (setting directly in residential rooms) significantly reduces the costs of a single analysis and completely eliminates the need for the transport of indoor material to the laboratory (thus the effect of economic and logistical factors is minimized). However, the most important and time consuming factor is the precise understanding of the operating characteristics of a passive sampler, which are defined under laboratory conditions based on appropriately designed preliminary model studies. Therefore, in order to design and conduct the whole analytical procedure in a reliable manner, not only the advantages and benefits of a given instrumental solution have to be considered, but also its limitations, scope of applications and precise operating characteristics. In-situ measurements using portable analytical instruments appear to be a very good solution from the point of view of occupants of residential rooms. This is due to the fact that occupants only require general information which, after quick interpretation, can help identify the major sources of chemical compounds emissions in an indoor environment and identify the type and quantity of chemical compounds released from the surface of the studied material. Emission research employing portable passive sampling devices are carried out for screening purposes

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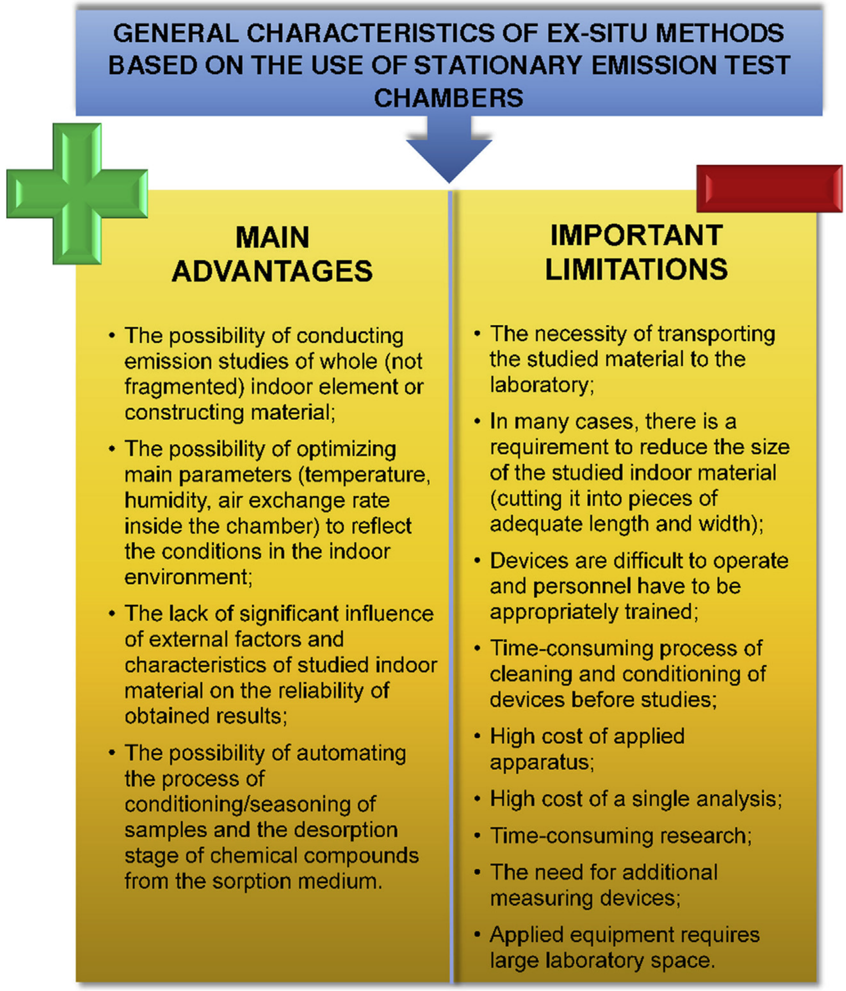

Fig. 6. Advantages and limitations of ex-situ methods for estimating the quality of indoor materials (to define the type and quantity of chemical compounds released from the surface of indoor materials).

and provide datasets on chemical compounds that have been emitted only from a fragment of the surface area of the studied indoor material [17,18,47,48].

The following aspects have to be considered in order to properly design and construct an instruments passively sampling analytes from the gaseous phase: (i) the choice of the appropriate type and form/shape of the sorbent bed – with a specific indication of the type of chemical compound for which the designed instrument is dedicated; (ii) the selection of suitable structural materials and their appropriate preparation; (iii) use of additional structural components such as weights or seals made of synthetic material to ensure proper tightness of the system during the studies. The designed and built portable analytical device has to be studied in a laboratory to determine all its performance parameters. Model studies performed under laboratory conditions are necessary to obtain data on the optimum operating/working time of the designed instrument under real/field conditions, to define the type of analytical data to be obtained in the course of its use, to clearly identify the group of chemicals to be sampled by the designed instrument, and to eliminate potential structural shortcomings affecting the final result of measurements [49].

Analytical devices from the group of SSPECs can operate in two modes: kinetic and equilibrium, allowing for a variety of analytical information to be obtained. It is important to specify the type of area/range in which the developed device can operate as early as at the stage of planning and performing model studies under laboratory conditions. If the passive device operates in the kinetic mode, than the obtained analytical information is expressed as the value of emission flux [$\mu g/m^2\ h^{-1}$]. This is determined using a formula taking into account the amount of chemical compound retained on the sorbent bed, the surface of exposed studied material (defined by the shape and size of the chamber) and the predefined exposure time of the device. If the designed SSPEC operates in the equilibrium mode, then the obtained analytical data are defined as the emission level [$\mu g/m^2$] and do not depend on the duration of sampling. The occurrence of this type of phenomena is possible only if the system reaches equilibrium in a relatively short period of time – rapid saturation of the applied sorption bed. Proper model research under laboratory conditions requires from the researchers first of all knowledge of the characteristics of the applied sorbent bed and the general laws and principles associated with passive sampling of analytes from the gaseous phase. The designed SSPEC can be used under real/field conditions - in the indoor environment – only if its parameters have been characterised in a time-consuming and laborious process. For this reason, the most important factor influencing the validity of the analytical result is the correct design and construction of the device and the correct determination of its

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performance characteristics in a laboratory. The analytical devices for the passive sampling of analytes from the gaseous phase are simple and easy to operate under real/field conditions, but require adequate knowledge and skills at the stage of their design, and full characterization of operating parameters [18,34,35,47,49].

Just like the previously described stationary emission chambers, SSPECs must also be washed with deionised water and detergent, and dried at elevated temperatures. When sampling of analytes from the gaseous phase by passive portable devices is completed, the further steps of the protocol and analytical instruments are the same as in the case of analytical procedures using stationary emission chambers. A summary of the discussed problems related to the in-situ measurement of emissions is presented in Fig. 7, which also shows major advantages and important limitations resulting from the development and use of SSPECs for estimating the emissions of chemical compounds directly in the indoor environment.

5. Main factors significantly affecting the final results of measurements when estimating the emissions of chemical compounds released from indoor materials

In studies aimed at the acquisition of a dataset providing information on the type and quantity of chemicals released from the studied indoor material the final result of measurements is influenced by three main factors: (i) characteristics of the study area - environmental conditions in the room; (ii) the character and operation mode of the device used for sampling analytes from the gaseous phase, and (iii) morphological characteristics of the intact material or its sample being studied [49]. These factors, which significantly affect the reliability of the analytical information obtained, are presented diagrammatically in Fig. 8.

The methodological approach related to the type of used analytical device plays a key role. It largely concerns the principle of the device's operation, including the conditioning of sampled indoor materials and the step in which samples of analytes are

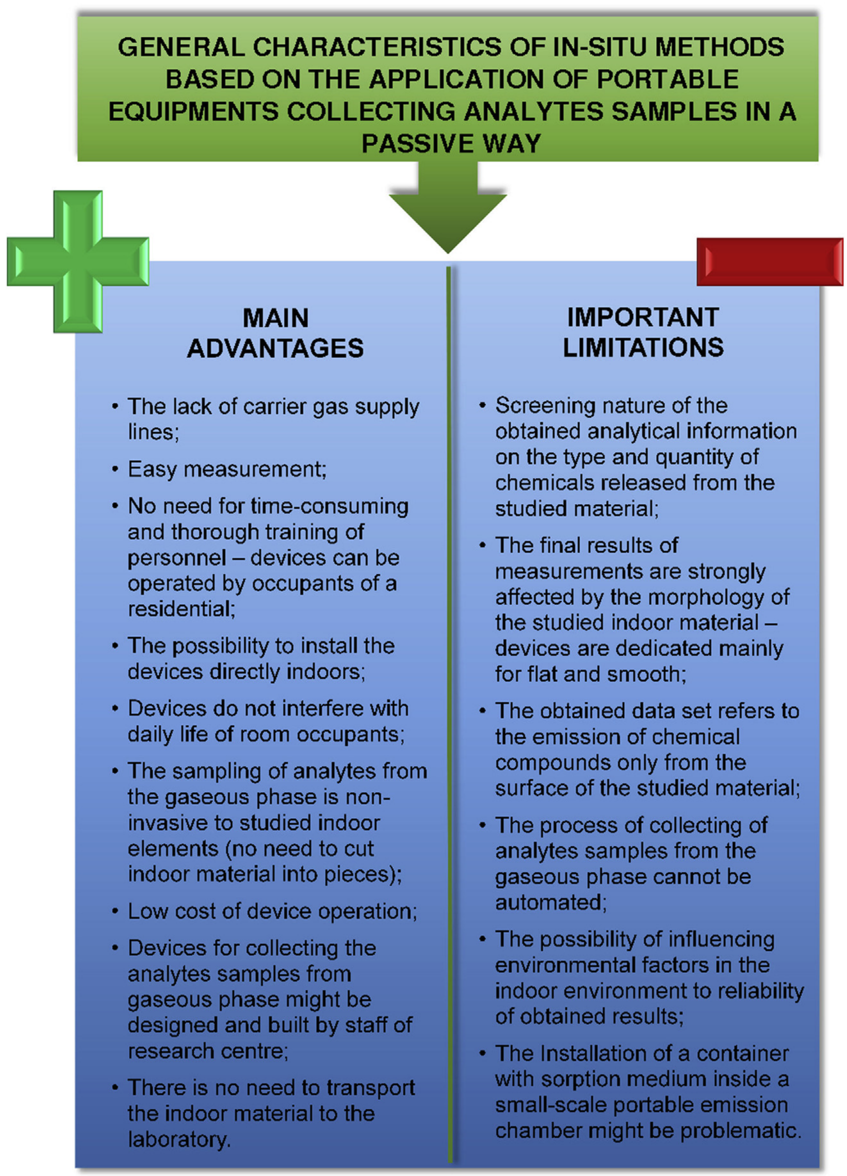

Fig. 7. Advantages and limitations associated with in-situ research conducted with the use of portable passive sampling devices to assess the emissions of chemical compounds released from the various types of indoor elements.

Fig. 8. Factors significantly affecting the reliability of data obtained when estimating emissions of chemical compounds released from indoor materials.

collected from the gaseous phase. When stationary emission chambers (large or small-scale) are used, analytes are sampled from the gaseous phase dynamically, sometimes at a slightly elevated temperature. Conducted research determine the type and amount of chemicals released from the whole indoor material or fragment thereof with defined dimensions. Due to the use of high-quality polished stainless steel or glass, the wall memory effect on the final analytical result is minimized. Because of all these factors the obtained analytical information is reliable and is likely to reflect the emission potential of the studied material. Furthermore, it should be noted that stationary chambers for emission studies do not operate in the equilibrium mode. Compounds released from the surface of the studied indoor material are passed from inside of the chamber directly onto the sorbent bed (where emitted analytes are retained) in a continuous process, until they are completely removed. The continuous release of compounds from the surface of the studied material is forced by a concentration gradient between the surface of the studied material and the gaseous phase in direct contact with the surface of this material [18,47,49].

Research conducted with the use of portable analytical devices installed directly in a residential room rely on passive sampling of analytes from the gaseous phase. The compounds present on the surface of the studied material move to the sorbent bed consistently with Fick's law of diffusion, and the flow is spontaneous [18,34,35,47,49]. Consequently, the transport of compounds is much slower than in the case of devices sampling analytes from the gaseous phase in a dynamic mode. Because studies are carried out directly in residential rooms, external factors in the indoor environment (air exchange in the room, temperature and relative humidity) and the appropriate preparation of the sampler for work can have a significant impact on the final result of measurements. In addition, the reliability of a dataset obtained when using SSPECs is strongly influenced by the characteristics of the studied indoor material. The biggest problem here is the tightness of the measuring system during the collecting of analytes samples from the gaseous phase, and potential migration of chemical compounds present in the indoor air into the interior of the passive emission chamber. For this reason, portable analytical devices based on the application of passive sampling technique should be installed indoors on furnishing elements having a flat, plain and uniform surface (rigid). If the object of in-situ studies has an irregular and flexible surface (e.g. floor coverings, carpets, wallpapers), a suitable mechanical pressure (causing be the appropriate stainless-steel weight) should be applied to stabilize the passive sampling device on the surface of the studied indoor material. Elastic fibres and an irregular surface of the material may cause leakage between the cover of the passive sampling device and the studied indoor surface. Consequently, there is a risk of migration of chemical compounds present in the indoor air into the chamber of the passive device, affecting the final result of measurements [18,47,49]. Nevertheless, from the point of view of the indoor air quality, the use SSPECs is a method that can better describe the impact of specific furnishing and finishing materials on the quality of the indoor environment. This is mainly due to the fact that the device works directly in indoor environmental conditions that are influenced by the daily use of the residential area.

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6. Problems and challenges encountered when comparing results obtained using two different types of devices at the stage of analytes sampling from the gaseous phase

A comparison of data obtained using two different analytical devices for determining the type and quantity of chemicals released from indoor materials is not an easy process. Factors described in the earlier sections show how many aspects can affect the final result of measurement depending on the type of analytical equipment used for collecting the analytes samples from the gaseous phase. Very often there is no clear statistically significant agreement between the emissions of contaminants released from the same studied material. Differences between the obtained results are primarily attributed to the fact that these devices operate in different modes (dynamic or passive) when sampling analytes from the gaseous phase. Little effect, in terms of the design of both analytical devices, can also be exerted by different ways in which cartridges packed with the sorbent bed, an element for sampling analytes from the gaseous phase, are installed. In stationary ETCs this is the commercially available and appropriately characterized Tenax TA – polymer sorbent bed placed inside a steel tube. On the other hand, in SSPECs the sorption medium is usually made of carbon (activated carbon or graphitized charcoal) placed inside a tube made of a stainless-steel net, or deposited uniformly on the surface of a net/strainer installed inside.

Differences between results may also be directly associated with the studied indoor material, its composition, and the superficial structure of the indoor material (homogeneity of structure and colour). In addition, very often in the course of this type of research the exact "service life" of the studied indoor material is unknown, namely its precise storage/conditioning time at the retailer's premises. Because most indoor materials are characterised by varying degrees of homogeneity, it is likely that by using two different analytical methods, statistically significant differences will be found for the obtained data.

One solution that would allow for the clear and unambiguous comparison of research results obtained by using the two different methodological approaches, and to show the potential differences is to apply a suitable reference material characterized by a constant predefined emission profile of selected chemical compounds. This option would allow for a detailed comparison and indicate the analytical device offering better precision and accuracy [49]. At present, many research centres are making intense efforts to develop this type of solution for estimating the emissions of chemical compounds. A suitably chosen reference material should meet specific criteria: (i) it has to represent one of the compound classes most commonly occurring in indoor materials; (ii) it should be neutral to structural elements of the sampling device; (iii) a compound or group of compounds has to be released from the reference material (or a tool serving this purpose) at a predefined rate in a predefined time interval – the quantity/mass of analytes released to the gaseous phase per defined time unit has to be known. Furthermore, a reference material must have optimal long-term stability during storage and transport to its destination point (to minimize the loss of chemicals emitted from it) and have a compact size suitable for placement inside the dedicated device for emissions assessment. So far, only a few such solutions are known in which the suitability of the designed and used analytical devices measuring emissions of organic compounds are studied with home-made reference materials (mainly based on a predefined quantity of toluene – representing VOCs) released into the gaseous phase. Cox et al. [50], and Howard-Reed et al. [51], described in details the new type of diffusion-controlled reference material for VOCs emission studies. In a developed reference material the thin film (thickness from 0.025 to 0.25 mm) of synthetic homogeneous material made of polymethylpentene (PMP) was used as a carrier medium. Then selected organic compound – toluene, was loaded to the PMP carrier medium structure through a diffusion process. Described analytical tool might be considered in the emission studies as a representative or a substitute of a "dry" building or constructing material. In addition, it should be noted, that diffusion-controlled reference material using PMP as a carrier medium was the main subject of pilot inter-laboratory research project, which contains four participating laboratories: (i) Air Quality Sciences, Inc. (Atlanta, GA); (ii) Berkeley Analytical (Berkeley, CA); (iii) National Institute of Standards and Technology (Gaithersburg, MD), and (iv) National Research Council of Canada (Ottawa, Canada) [50,51].

Different solution in the field of reference material for organic compounds emission research was proposed in a scientific literature by Wei et al., [52,53]. The authors developed and characterized an analytical tool defined as a liquid-inner tube diffusion-film-emission (LIFE). The LIFE reference material consists of the following elements: (i) a cylindrical contained made of Teflon; (ii) a thin diffusion film (membrane) made of aluminium oxide melamine-impregnated paper as a cover and (iii) liquid – a solution of a single purified organic compound representing VOCs. Mentioned device was designed to assess the working parameters (the performance) of stationary emission chambers (for both large-scale and small-scale chambers) applied to estimate the emission rate of organic compounds emitted from furniture materials. The main advantage of the use of LIFE reference material in analytical practise is the fact, that it is a reliable, fast, and easily-used analytical tool with a constant emission rate of selected organic compound (toluene) under defined temperature and relative humidity conditions [52,53].

An example of another new approach to the development and use of reference materials for estimating emissions of chemical compounds is the use of thermoplastic material (polyurethane) as a carrier for selected VOCs developed by Richter et al., [54]. Thermoplastic polyurethane (PTU) is a specific carrier, coated with VOCs. Coating is conducted under increased pressure to ensure optimal penetration of VOCs to deeper layers of the carrier material. Again, the challenge is to ensure the stability of the obtained reference material and repeatability in the process of release of the analytes from the surface of the reference material [54].

7. Summary

There is an urgent need to turn today's analysts' attention to the problems and limitations that might take place in everyday laboratory practice, regardless of the developing trend (according to green analytical chemistry philosophy) associated with miniaturization of analytical equipment and the continuous improvement of its applicability and functionality. This phenomenon is also related to many devices and analytical techniques used in the process of estimating emissions of chemical compounds from various types of indoor equipment, buildings or constructing materials.

In everyday laboratory practice, special attention should be paid to obtain reliable analytical information about the actual state of the studied sample or medium when using home-made analytical devices and the newest commercially available analytical equipment. It is particularly important that the laboratory staff handling analytical equipment have the appropriate qualifications and knowledge about the basic principles and phenomena's related to the applied technique or analytical devices.

In the process of estimating the quality of indoor equipment and building materials (defined by the type and amount of chemical compounds emitted to the gaseous phase), it is necessary to offer and implement such methodological solutions that allow to minimize the costs (financial inputs) of single analysis and reduce the number of steps in the applied analytical protocol. The special attention should be paid to the comfort and predisposition of the users of the indoor areas (premises, apartments, households); to search for such a constructional, design and methodical solutions, which allow for obtaining the optimum quality of the database. Moreover, it is important to achieve analytical information relatively fast and in a non-invasive way and using a reasonable amount of funding about the type and the amount of chemical compounds released from the indoor materials.

An additional challenge for today's analytical chemists is to develop and characterize the new reference materials in the field of chemical compounds emissions. Positive results in this field will allow for an optimal comparison of self-designed and home-made emission chambers and commercially available analytical devices. Furthermore, this would give an opportunity to conduct full characterization of the new type of devices used in the process of estimating emissions of chemical compounds from indoor materials. The challenge for the future is to develop such type of reference material (with its morphological characteristics and emission profile) that will reflect with a high probability the characteristics of a commercially available indoor materials, such as wood-based materials or floor coverings made of synthetic materials.

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