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Review

A Short Review of Simple Analytical Methods for the Evaluation of PAHs and PAEs as Indoor Pollutants in House Dust Samples

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Abstract: Studies on indoor air quality are indispensable when considering that people spend approximately 85% of their time in confined environments. This short review mostly takes into consideration research that uses passive samplers to evaluate the quality of indoor environments (houses, school, cars, etc.). This short review summarizes most analytical methods to detect and quantify PAHs and PAEs in house dust used as a passive sampler. The objective of house dust analysis is to identify the presence, amount and distribution of specific hazardous substances in confined spaces and, if possible, to identify their sources. Household dust and the compounds present in it can enter the human body by inhalation, non-food ingestion and absorption through the skin. The observed differences in concentrations of house dust may also indicate important differences in the chemical and physical nature of pollutants caused by air filtration and absorption during the migration of ambient air into the indoor environment.

Keywords: indoor air monitoring; PAHs and PAEs; indoor pollutants

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1. Introduction

In recent decades, the presence of numerous classes of hazardous organic compounds has been found in all environmental matrices (air, water, soil, etc.) and, at the same time, damage to health associated with exposure to these compounds has been reported [1–4]. Most of the population, especially those living in large urban areas, do not know that, in their indoor environments (homes, schools, cinemas, theaters, museums, buses, cars, trains, etc.), the concentrations of many pollutants are greater than in outdoor environments [5–7]. Indeed, the indoor environment has been recognized as one of the causes affecting human health [8–11].

Many hazardous air pollutants are produced in indoor environments from common activities such as cooking, cleaning, smoking, etc.

Some studies have identified house dust as an important route for toxicant exposure, and often the levels of pollutants found in house dust, including compounds banned long ago, are significant sources of exposure for the general population. Moreover, several researchers hypothesize that indoor pollutants may be closely linked with health effects, especially in children and adults with chronic lung disease [8–11]. Wang et al. [12] validated the health effects of polycyclic aromatic hydrocarbons (PAHs) from 15 indoor dust samples to test their mutagenicity. Their results showed that total PAHs were significantly correlated with the potency of their mutagenicity. Sonnette [13] proposed a method coupling automated thermal desorption (ATD) with in-tube derivatization, solid phase microextraction, and on-injector derivatization gas chromatography–tandem mass spectrometry (GC/MSMS) for the analysis of 100 different semi volatile compounds (SVOCs) (pesticides, PAHs, polychlorobiphenyls (PCBs), phthalates (PAEs) and alkylphenols) in indoor air and indoor particulates. Kadi et al. [14] reported the PAE and PAH profiles in settled dust collected from various mosques in Jeddah to evaluate the health risks associated with these chemicals via dust ingestion, inhalation and dermal contact for the public who attend mosques for prayers. In the investigated environments, phenanthrene (500–3000 ng/g), pyrene (40–1220 ng/g) and chrysene (95–4590 ng/g) were the major PAHs, and $\sum$12PAH concentrations ranged from 2550 to 9150 ng/g, whereas diethylphthalate and benzobutylphthalate were the major phthalates in the mosque dust.

Studies on indoor air quality are indispensable when considering that people spend approximately 85% [15] of their time in confined environments; thus, it is necessary to evaluate indoor contaminant concentrations and distributions in order to assess total human exposure to them. Exposure to house dust does not exclusively occur via inhalation; for instance, it can occur by ingestion of house dust particles adhering to food, objects, and hands or by direct absorption through the skin.

This review examines papers on substances of toxicological interest [16–19] in an unconventional environmental matrix: the dust [18–20] deposited on the surfaces of confined environments with which the population is really in contact (respiration, skin contact, etc.). By comparison, most literature in this field examines concentrations of pollutants in particulate matter dispersed in the air and sampled by suction pumps [6]. We discuss several methods to assess indoor air quality for the presence of PAHs and phthalates (PAEs) using passive samplers (domestic dust).

Samples referred to as "house dust" vary significantly because house dust may be of different origins, amounts and compositions, and the method used for sampling the dust influences the properties of the sample used for analysis [7,13,20].

Hazardous air pollutants are defined by the United States Environmental Protection Agency (EPA), and include, among others, polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), and heavy metals (lead, chrome compounds, etc.) [21–26]. Usually, these hazardous substances are deposited on surfaces in buildings located in anthropized areas [19,20]. Most studies focus on heavy metals, volatile organic compounds, and pesticides, while less attention has been paid to the potential health risks of exposure to persistent and semi-volatile endocrine-disrupting chemicals (EDCs) such as phthalic acid esters (PAEs), generally called phthalates, in the indoor environment [7,10,14].

Polycyclic aromatic hydrocarbons are semi-volatile organic compounds that are chiefly produced during the incomplete combustion of fossil fuels and biomass, domestic burning, power generation and pyrosynthesis of organic materials [27–39].

The most important PAHs investigated are reported in Figure 1.

PAHs enter into the environment both through natural processes [32] and from anthropogenic sources [40–42]. In the indoor environment, PAHs are formed from different activities such as the use of a wood or gas stove for heating and cooking [39,40], coal and candle burning [43,44], etc. Incense burning is a common practice in Gulf countries, and, as suggested by several authors, might be an important source of PAHs in the indoor environment of this region [37]. Infiltrating air and soil tracked in from outdoor with PAHs is also an important source of contamination [38].

Phthalate Acid Esters (PAEs) are widely used as plasticizers to give flexibility and resilience to materials [45–49]. In this context, plasticizers are important promoters in materials processing and are widely used in building materials, packaging materials, electronics, medical parts and many other necessities of life [49–51]. As the most widely used plasticizer, phthalate esters are ubiquitous in indoor environments and have become emerging organic pollutants in indoor air.

In most of the research described below, evaluation of the quality of indoor environments was carried out through the use of passive samplers (house dust, etc.), targeting the materials with which the occupants of different environments (houses, schools, means of transport, etc.) come into contact.

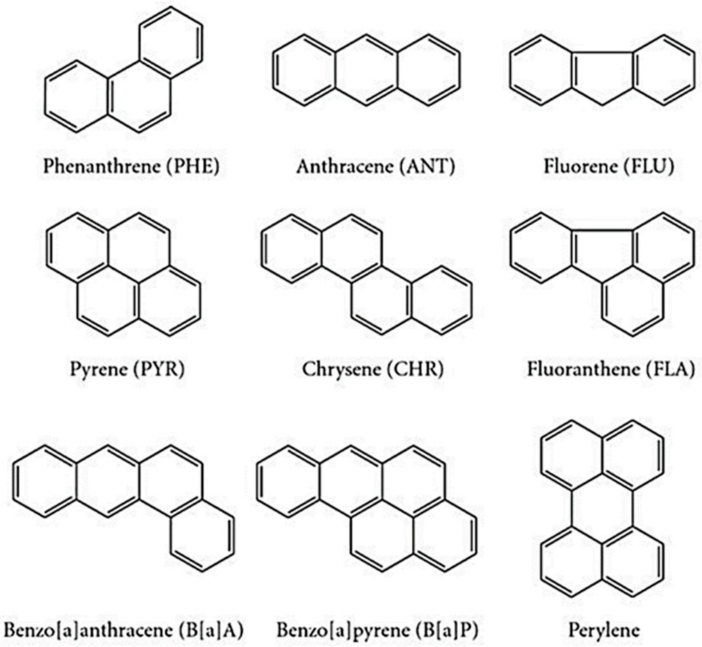

Figure 1. Most important PAHs investigated.

2. Polycyclic Aromatic Hydrocarbons (PAHs)

This class of compounds has received increased attention in recent decades due to the associated health problems. Indeed, several PAHs are classified as probable and possible carcinogenic substances for humans; in particular, benzo[a]pyrene (B[a]P) has been identified as highly carcinogenic [20–26].

Their presence is ubiquitous in common matrices (air, waters, soil, sediments, organisms, food, etc.) [52–59]. To understand the extent of human indoor exposure to B[a]P and other PAHs, reliable sampling and analytical methods are necessary.

Although various studies have reported on the determination of PAHs in different outdoor environment matrices, few studies have been conducted regarding indoor environments, especially when considering specific different indoor environments, characterized based on the profiles of their different pollutants, relative to work or living activities.

2.1. Polycyclic Aromatic Hydrocarbon Analysis in Indoor Dust

Passive accumulators supply information on the average variation in time and space in the concentrations of contaminants in a considered area, characterize real human exposure to pollutants in indoor areas, and compare indoor levels to corresponding outdoor levels [59,60].

Several researchers [40–42] conducted studies on different methods for PAH analysis in different matrices. Generally, dust samples were collected in metropolitan areas and were subjected to different analytical procedures (extraction, cleanup and analysis), as reported in Table 1.

Table 1. Different analytical procedures (extraction, cleanup and analysis) for PAHs.

Technique	Solvent Mixture	Cleanup
Accelerated Solvent Extraction	Dichloromethane/Acetone/Acetonitrile	Alumina, Florisil Silica gel
Soxhlet	Dichlorometane/Hexane/ Pentane	Alumina Florisil Silica gel
Ultrasonic	Acetone/Cyclohexane/Methanol/ Dichloromethane/Acetonitrile	Alumina Florisil Silica gel

Mannino [5] collected dust samples in areas of Palermo city, assessing concentrations in indoor environments in order to assess the possible origins of the considered substances. In this monitoring study, dust samples were collected from 45 indoor environments (bedrooms, living rooms, kitchens, laboratories, offices, market and a car). In order to establish the source of PAHs in dust, a station within a rural community (Cefalù) was chosen as a sampling area with negligible anthropogenic activities. The authors [5] estimated the recovery rates of the analytes in the samples throughout the whole analytical process by adding 250 μL of a standard solution of surrogate PAHs (anthracene-d_{10} and benzo(a)anthracene d_{12}) to samples. Dust samples were extracted in a Soxhlet apparatus for 24 h using dichloromethane–pentane as a solvent mixture. The extracts were dried with anhydrous Na_2SO_4 and concentrated in a rotary evaporator at T = 35 °C. The final volume was approximately 2 mL. The last stage in the procedure involved drying the PAH-containing solution under a weak inert gas flow at room temperature. The dry residue was dissolved in 1 ml of a solution containing perdeuterated internal standards (acenaphthene d_{10}, phenanthrene d_{10}, chrysene d_{12} and perylene d_{12}) in cyclohexane. Analysis was carried out using a gas chromatograph coupled with a mass spectrometer and equipped with a data acquisition system. The data were acquired via operating in selected ion monitoring mode (SIM). Total PAH (Figure 2) concentrations in dust samples ranged from 0.036 to 34.5 mg kg^{-1} d.w., with an average of 5.1 mg kg^{-1}. Rural and lightly urbanized areas had markedly lower PAH concentrations than urban/anthropized areas. Taking into account only all domestic environments, the highest total PAH concentrations were measured in kitchens (on average approximately 1.5 mg kg^{-1} d.w), while the lowest concentrations were measured in living rooms (on average approximately 0.750 mg kg^{-1} d.w) [5]. PAH concentrations in indoor dust in a smoking household where tobacco was burned were higher (from twofold higher, observed in the kitchen, to 16-fold higher in the bedrooms) than the others. The results suggest that most PAHs identified in residential indoor dust samples originated from combustion processes; in particular, the highest value was found in dust collected in the winter period in a living room where a fireplace was utilized, while in indoor dust collected at a petrol pump and in a car, PAHs originated from petroleum products. Moreover, results from five samples from offices and laboratories at the Departments of Chemistry (Inorganic and Organic), which had centralized systems of aeration, established that dust from offices and laboratories in the same structure had similar relative distributions of PAHs, while higher total concentrations of PAHs were observed in the office of the Inorganic Chemistry Department. In this case, the authors hypothesized that PAHs were transported inside by people.

Finally, the results showed that wood combustion for heating increased the emissions of PAHs in living rooms more than in bedrooms in the same building.

Generally, in environmental matrices, the molecular patterns generated by diverse sources resemble fingerprints, which make it possible to hypothesize which process generate PAHs by studying their distribution in samples [5,34,54,55,58]. Phenanthrene/anthracene, fluoranthene/pyrene, benzo[a]anthracene/chrysene and indenopyrene/benzo[g,h,i]perylene ratios are commonly used as a means of determining the main origins of PAHs. Orecchio et al. [61–64] found that the values of four considered isomeric ratios were not in agreement, and considering that the sources of PAHs in a matrix can have different and irregular results, we calculated a total index as the sum of all single indices normalized to the limit value (low-temperature sources–high-temperature sources) reported in the literature [61–63]. The authors considered PAHs in dust to originate predominantly from high-temperature processes (combustion) when the total index was >4, while lower values indicated predominantly low-temperature sources (petroleum product) (Figure 3).

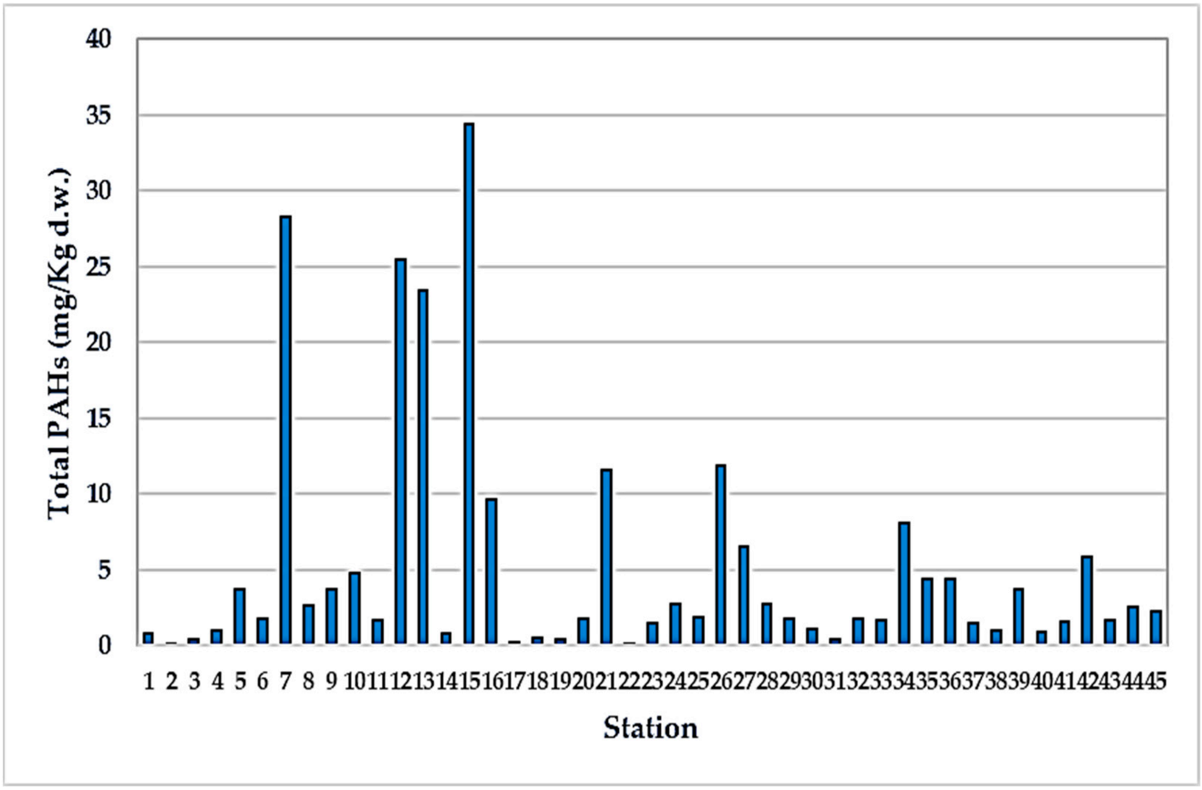

Figure 2. Total PAHs (mg kg^{-1}) in indoor dust samples [5].

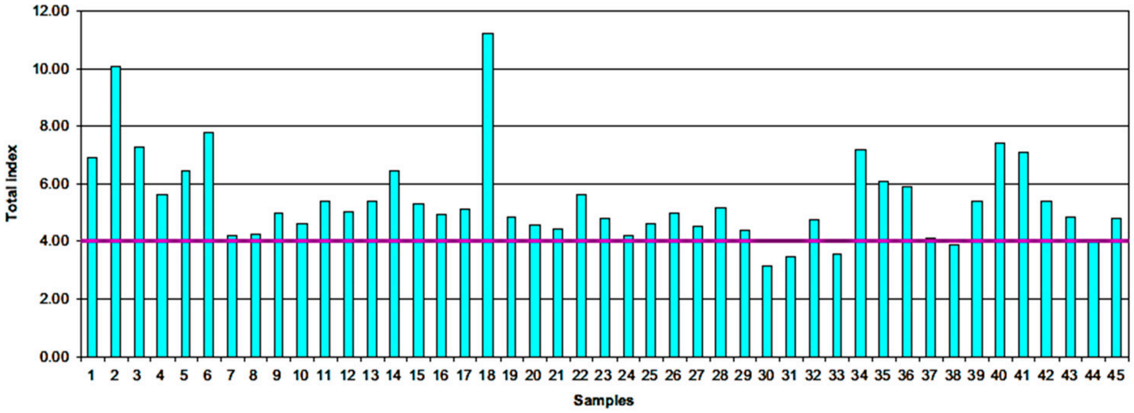

Figure 3. Total index for PAH source identification in indoor dust sample. Purple line indicates high temperature sources (Total index< 4) from low temperature sources (Total index > 4).

2.2. Polycyclic Aromatic Hydrocarbon Analysis from Candle Emissions

Another important source of PAHs as indoor pollutants can be indoor candle emissions [6,43,44]. Wax candles have been employed since the 5th–4th centuries BC as a source of light and are, in the present day, recurrently used for decorative and religious purposes in diverse indoor environments (homes, churches, temples, etc.). The smoke produced by wax candles is proven to contain Volatile Organic Compounds (VOCs) such as acetaldehyde, formaldehyde, acrolein, phenol, benzene, toluene, xylene, aromatic and aliphatic hydrocarbons, etc. [44]. According to the Ames test [43], candle smoke has been identified as mutagenic.

Because polycyclic aromatic hydrocarbons produced during the use of wax candles are emitted between the gas and particulate phases, a recent paper [6] describes a sampling and analysis procedure for 18 PAHs involving the use of a combination of cold traps, glass filters and sorbent cartridges with successive analysis via GC/MS. To sample the emitted PAHs, the filter holder was placed at a height of 10 cm from the candle. The time of sampling varied between 5 and 8 h. Emissions were collected using a gas sampler with a pump drawing air through a glass fiber filter to collect particulate matter containing PAHs, a cold trap to collect the PAHs contained in the vapor, and three glass cartridges containing XAD2 resin to collect the gas-phase analytes. After sampling, the volume of the sampled air was recorded. For particulate PAH analysis, glass filters were extracted in an ultrasound bath three times with dichloromethane. The extracts were dried using Na_2SO_4 and concentrated in a rotary evaporator. The final volume was approximately 1 mL. The last step in the analysis involved drying the solution containing PAHs under a weak inert gas flow at room temperature. The dry residue was dissolved in a solution containing the perdeuterated internal standards. The extraction of the aqueous phase from the trap was performed using liquid–liquid extraction with dichloromethane. Similarly, to the solution obtained from the particulate, the dried and concentrated extract was dissolved in a solution containing the internal standards. The elution of PAHs from the three cartridges was carried out using three fractions of dichloromethane and treated as before. The solutions obtained from the trap, filter and cartridges were separately quantified using GC–MS. The total PAH concentration (particulate + aqueous phase + gas phases) emitted by candles was between 2.3 and 50 $\mu g\ kg^{-1}$ and averaged 15 $\mu g\ kg^{-1}$.

Solid phase microextraction (SPME) of the gas phase components produced by wax combustion could also be a promising technique to sample and quantify PAHs. Solid phase microextraction is a very sensitive sample preparation technology that does not require the use of solvents. It is based on the adsorption/sorption and desorption principle and uses a fiber coated with an extracting phase to concentrate the volatile and semi-volatile compounds present in a sample [65].

2.3. Phthalate Acid Ester Analysis in Indoor Dust

Among substances dangerous to health, phthalate esters are considered hazardous pollutants due to their reproductive effects and carcinogenicity [10,11,48,65–68]. Generally, phthalates are odorless and colorless liquids with high boiling points from 228 to 380 °C, low volatility, low solubility in water and predominantly fat solubility.

With the exception of dimethyl phthalate, which is included on the list of VOCs, PAEs are generally categorized as Semi-Volatile Organic Compounds (SVOCs) Phthalates are imputed into the environment by human activities [69–74]. This compound class is usually introduced in the air in the form of small particles and gases [75]. Several compounds with great molecular mass are generally employed as plasticizers and/or additives for several materials, although PAEs with low molecular mass are generally used as constituents for industrial solvents, wax, drugs, adhesives, ink, pesticide formulates and body care products. These compounds do not form strong chemical bonds with polymers; instead, they are only physically deposited on the materials, and therefore can be released very easily into the surrounding environment and accumulated in different environmental matrices and in food. The scientific literature is rich in articles regarding the concentrations and physical and chemical properties of indoor particulates; in particular, many of them show correlations between their presence and concentration inside rooms and in the outdoor air [57,59] In order to evaluate their distribution and concentration in confined spaces to determine the probable sources of PAEs in the Palermo area, Orecchio et al. conducted a research study collecting 12 indoor dust samples from different sites [7]. The samples were extracted in an ultrasonic bath using hexane as solvent and analyzed via GC–MS.

In a study [7], researchers monitored six PAEs, dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), benzyl butyl phthalate (BBZP), bis (2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DnOP), in settled indoor dust (used as a passive sampler) collected from thirteen indoor environments in Palermo city.

The total concentrations of these compounds at the various sampling stations were in the range 269–4831 mg kg^{-1} d.w. The obtained results, with regard to concentration, indicated a good correlation between a single phthalate and total PAEs, with the exception of the two greatest volatile analites (DMP and DEP), which were measured in significant quantities only at two sampling stations. The data obtained by the researchers suggested that several pollutants in the settled dust from the studied confined spaces originated from similar kinds of materials. Indeed, in a specific indoor environment, generally only one compound is not present, but rather a mixture which over time develops comparable percentages of PAEs. Moreover, the authors also noted dissimilarities in concentrations of phthalates when comparing edifices from diverse building periods; total PAEs were higher in ancient homes compared to in those built later. The researchers hypothesized that these differences were due to an increasing interest by manufacturers in the environment and consumers. Finally, a good correlation between building age and total PAE concentration was observed (R = 0.71). Similar results were obtained by other researchers. In detail, in a study [67], the authors examined associations between the concentrations of different phthalate esters in the dust from selected bedrooms and various characteristics of the home. The study focused on BBzP and DEHP, since these were the phthalates associated with health complaints. For both BBzP and DEHP, associations were found between their concentrations in dust and the amount of PVC used as flooring and wall material in the home. Furthermore, high concentrations of BBzP (above median) were associated with self-reported water leakage in the home, and high concentrations of DEHP were associated with buildings constructed before 1960. Other associations, as well as an absence of associations, were reported. Both BBzP and DEHP could be found in buildings with neither PVC flooring nor PVC wall coverings, consistent with the numerous additional plasticized materials that are anticipated to be present in a typical home.

Compared to other research studies, the total PAEs determined by Orecchio et al. [7] (1289 mg/Kg) were smaller than those measured by other researchers in different nations (2352 mg/Kg), for example, in Bulgaria (8860 mg/Kg) [11,45,46]. This different trend could most likely be caused by the regular use of poly vinyl chloride in floor coverings in Bulgaria; in addition to what has been said, the differences in PAH concentrations in the dust in confined environments could also be caused by different climatic conditions (temperature, humidity, etc.), different daily habits, and the economic status of the owners. It should be emphasized that Italians, in the construction or renovation of their homes, prefer to use traditional materials (marble, ceramics, terracotta, etc.) rather than synthetic materials such as polymers [76]. Furthermore, especially in Southern Italy, where the researchers in [76] carried out their studies, the climatic conditions and the arrangement of doors and windows in houses allow for an excellent exchange of indoor air during all seasons. For this reason, the concentrations of pollutants in indoor dust in Palermo may be lower than those observed in other European areas. Consequently, Orecchio et al. doubted that data from different countries are comparable, due to the diverse sampling process.

In another study [77], the authors investigated dust samples randomly collected from 21 homes and analyzed eight phthalates. The concentrations of total phthalates were normally log-distributed and ranged from 470 to 7800 µg/g. Five phthalates, Di(2-ethylhexyl) phthalate (DEHP), Di-n-octyl phthalate (DnOP), Di-n-butyl phthalate (DBP), Benzyl butyl phthalate (BzBP), and Dicyclohexyl phthalate (DcHP), were routinely detected. DEHP was the major phthalate detected (median 2256 $\mu g\ g^{-1}$), accounting for 92% of the total phthalates measured. Using the measured concentrations and estimates of dust ingestion rates for children and adults, the authors estimated that the human non-dietary exposure, based on median phthalate concentrations, ranged from 938 ng/kg-bd/day for adults to 13,362 ng/kg-bd/day for toddlers. The difference in exposure estimates between children and adults in this study supports previous reports that children are at greater risk from pollutants that accumulate indoors.

Generally, in indoor environments, PAEs could be derived from plastic materials. However, several studies detected PAEs in some non-plastic products currently used in indoor environments. In this context, PAEs were found in mural paints and perfumes, used as softeners in water-based paintings and denaturant products, respectively. In the first case, in a study [78] conducted on mural paint samples collected from different buildings, the total concentrations of 15 PAEs ranged from 0.8 to 236 mg kg^{-1} with an average of 39 mg kg^{-1}. The highest concentrations were found in wall paint sampled in the living room of an apartment built approximately 50 years ago. Moreover, in 80% of tested samples, DEHP was detected as the predominant PAE (from 30 to 100% of total phthalates) with a range from 0.6 to 236 mg/Kg d.w. Occasionally, DiNP was used as an alternative to DEHP. Diisobutyl phthalate was detected in seven samples and ranged from 0.17 to 13 mg Kg^{-1}, while DEP, at appreciable concentrations, was detected in only three samples in the range from 0.013 to 1.1 mg/Kg^{-1}.

Regarding phthalates used in different products, PAEs with low molecular weight, such as dimethyl phthalate and diethyl phthalate and, prior to 2009, di-n-butyl phthalate, were widely used in cosmetics and personal care products [49–51]. The presence of DMP and DEP enabled perfume fragrances to evaporate more slowly and the scent to linger longer. Additionally, DEP is an ethanol denaturant (a substance added to ethanol for tax purposes to make it not suitable for food in Italy).

Several researchers quantified phthalates in cosmetics and personal care products purchased in different countries [29].

An environmental organization [72] found PAE in approximately 70% of tested cosmetic and personal care products. In addition, Greenpeace (2005) [73] testified that phthalates were present in perfumes available in the European market.

In a recent study [50], the quantification of phthalates was carried out directly with no sample preparation on 30 samples of commercial products using gas chromatography and mass spectrometry (GC–MS). The total concentrations of 15 investigated compounds ranged from 17 to 9650 mg L^{-1} with an average of 2643 mg L^{-1}. The highest total concentration was found in a cologne sample.

These examples regarding unconventional phthalate sources are very important when considering that most people regularly use perfumes or other personal care products. In this context, it is possible to suppose that most of these substances can accumulate in dust at different orders of magnitude in static indoor environmental conditions.

3. Conclusions

To meet the necessities of consumers, the number of substances used or produced in confined spaces is constantly growing; consequently, in order to assess the quality of indoor air, analytical chemists must be able to provide qualitative and quantitative information on substances (for which toxicological characteristics are often not known) with which the inhabitants are in contact for most of their day.

The quantification of pollutants in indoor environments using traditional methods is particularly difficult, both due to the high number of possible hazardous substances and, often, their very low concentrations (ppm, ppb, ppt). Furthermore, within the same building (home, school, etc.), there are environments in which the performed activities are different (kitchens, bathrooms, living rooms, schoolrooms, etc.) and consequently the types of substances produced vary both qualitatively and quantitatively. In many cases the effect on the environment of external sources of contaminants is decisive. Research should be extended to emerging pollutants (drugs, plasticizers, etc.). In this context, indoor dust can be used as a passive sampler in order to determine real human exposure over long time periods.

In this short review, simple analytical methods for the evaluation of PAHs and PAEs as indoor pollutants in house dust samples were discussed. The presence of polycyclic aromatic hydrocarbons and phthalate acid esters in indoor dust has been proven through many studies.

To satisfy the above considerations, we conclude that applying innovations (instruments, methods, etc.) to the ever changing, complex and diversified field of environmental chemistry is a big challenge for the modern analytical chemist. In particular, the use of bioaccumulators and/or passive samplers is beneficial because of their high selectivity and sensitivity and low expense. Unlike traditional methods employed to assess indoor air quality, dust deposited on domestic surfaces, for example, can be advantageous as a suitable passive sampler for several airborne pollutants (metals, PAHs, PAEs, etc.). Domestic dust analysis cannot replace traditional indoor air analysis methods, but rather provides additional information. Using dust as passive sampler, the need for protracted sampling times using complex and expensive equipment is avoided. In addition, the information obtained through investigation of settled dust samples gives mean data from the time of the last cleaning of the dust until final sampling, without introducing external influences, as could happen with traditional analysis due to the immediate conditions during the sampling time. Furthermore, ancient settled dust samples could be employed for retroactive pollutant analysis. Since this type of sampling is fast and therefore also economical, it can be used to evaluate the air quality in homes, cars, garages, and workshops of private citizens who wish to understand the environment in which they live and/or work.

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