Recent Advances in Passive Air Sampling of Volatile Organic Compounds

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ABSTRACT

Volatile organic compounds (VOCs) are not only harmful to human health, but also important precursors of ozone and PM2.5, which cause severe air pollution. Therefore, it is critical to study these compounds, and monitor them by developing reliable and effective techniques. Passive air samplers (PASs) are small and uncomplicated, with the advantages of simple operation, easy transportation, and do not require external power; therefore, they are more economical and practical to monitor VOCs compared to active sampling techniques. As an alternative method, passive sampling is particularly suitable for long-term monitoring in remote regions and wilderness areas, simultaneous large-scale measurement, and recording of individual exposure. In recent years, commercial PASs have been improved continuously, while emerging samplers have been developed for new applications. The following main trends can be distinguished: (1) many novel PASs were specifically designed to monitor only one or few VOCs also including numerous redesigned commercial PASs; (2) the improvement of sorbents is still ongoing towards high efficiency, low cost, and multiple choices for more analytes; (3) structural improvement is another important aspect of PAS development mainly focusing on both sampler performances and applications; (4) the development of new technologies provides more sampling conveniences such as using unmanned aerial vehicles and sampling robots to special monitoring sites e.g., a stack or a ventilating duct.

Keywords: Volatile organic compounds; Passive sampling; Air monitoring; Passive sampler; Diffusive sampler.

INTRODUCTION

The term VOCs covers a range of chemical classes, including aliphatic, aromatic, amines, aldehydes, ketones, esters, ethers, alcohols, acids, and halogenated hydrocarbons. VOCs have a high saturated vapor pressure, low boiling point, small molecular mass in standard pressure, and high volatility at room temperature. The World Health Organization (WHO) categorized indoor organic pollutants as very volatile organic compounds (VVOCs), volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs), by the ease with which they are emitted (World Health Organization, 1989). VOCs are emitted into the atmosphere from natural and anthropogenic sources. Natural sources of VOCs are mainly from marine, vegetation, soils, volcanoes, and rainwater. Isoprene and monoterpenes, which are primarily emitted from woodlands, contributed over half of the global natural VOC flux (Guenther et al., 1995; Yaman, 2015). However, it is worth noting that natural sources have been strongly affected by human activities in the past two centuries (Guenther, 2000). For instance, decreasing isoprene and methanol emissions were mainly attributed to the tropical deforestation (Lathiere et al., 2006) and over fifty-percent global carbon disulfide emission was caused by industrial products such as rayon, pigment, and pulp (Lee and Brimblecombe, 2016). Anthropogenic sources of VOCs are more complicated mainly including industry, agriculture, transportation, and daily living. Most industrial processes can emit quantities of VOCs, such as coating and packaging processes, rubber fabrication, and manufacturing of petrochemicals and furniture (Environment Agency, 2014). Compared to fuelwood combustion and savanna burning for the last century (Piccot et al., 1992), emissions from transportation, coating process, oil and solvent use have become the main anthropogenic outdoor contributors for recent years (Klimont et al., 2002; Qiu et al., 2014; Mo et al., 2016). On the other hand, emissions from tobacco smoke, personal care products, cleaning products, perfumes, glues, and construction materials have been major anthropogenic indoor sources (D'Souza et al., 2009; Pandey and Kim, 2010).
Many VOCs are directly harmful to human health, causing skin irritation, toxic effects, carcinogenicity, teratogenicity, and mutagenicity (Woodruff et al., 1998; Morello-Frosch et al., 2000). A large group of VOCs has been included in Hazardous Air Pollutants (HAPs) listed by the United States Environmental Protection Agency (EPA), such as BTEX (benzene, toluene, ethylbenzene, and xylenes), which are also listed in the extremely hazardous class by the European Environment Agency (EEA) (Kelly et al., 1994). In addition, VOCs are the key precursors of ozone and PM$_{2.5}$, not only causing an increase in ozone concentrations, stratospheric ozone consumption, and the formation of photochemical smog directly, but also affect human health indirectly (Derwent et al., 1996; Atkinson and Arey, 2003; Carter, 2012).

Since the Los Angeles photochemical smog occurred in 1940, VOCs have gained attention gradually (Bertolotti, 2012). In 1952, Haagen-Smit first demonstrated the chemistry and physiology of the Los Angeles smog (Haagen-Smit, 1952). To date, VOCs have been studied for over half a century (Wang, 2014; Lo Vullo et al., 2016; Cheng et al., 2017; Choi et al., 2017; Zhang et al., 2017). Due to their characteristics of multiple components, high volatility, low and variable concentrations, and easy pollution, monitoring techniques of VOCs are required to be simple, quick, efficient, and pollution-free during the sampling and analyzing (Michulec et al., 2005). The monitoring techniques of VOCs are generally composed of sampling, pretreatment, separation, and detection processes. The active techniques usually automate the former processes, and directly separate analytes via gas chromatography (GC) prior to mass spectrometry (MS) (Sheehan et al., 2012; Gong et al., 2017), flame ionization detection (FID) (Santos and Galceran, 2002), electron capture detection (ECD) (Silva-Barni et al., 2017), photo-ionization detector (PID) (Francke et al., 2000), reduction gas detector (RGD) (Fisher, 2003), or atomic emission spectroscopy (AES) (Van Stee et al., 2002). For the class of carbonyls, it is usually desorbed by acetonitrile and analyzed via high-performance liquid chromatography (HPLC), coupled to an ultraviolet-visible detector or a photodiode array detector (Claeson and Sunessson, 2005; Uchiyama et al., 2006). In addition, there are certain techniques for direct analysis, skipping the separation process, such as proton transfer reaction MS (PTR-MS) (Blake et al., 2004; Kuster et al., 2004), atmospheric pressure chemical ionization MS (APCI-MS) (Aznar et al., 2004; Tsachaki et al., 2005), and membrane inlet MS (MIMS) (Lago et al., 2003; Jakubowska et al., 2005).

Undoubtedly, the active techniques have shortened both sampling and pretreatment processes, obtained continuous sampling data, enhanced monitoring temporal resolution, and reduced environmental and anthropogenic disturbances. Nevertheless, it should not be ignored that active analytical instruments generally have high prices, which limits large-scale simultaneous monitoring. In addition, due to the requirements of external power, appropriate operating temperature, professional operations and maintenance, the active analytical instruments cannot afford long-term monitoring in remote regions and wilderness areas. In summary, these factors have restricted the widespread application of active analytical instruments (Krupa and Legge, 2000). Fortunately, the passive sampling techniques have overcome these shortages. With their advantages of low-cost, small sizes, uncomplicated constructions, simple operation, easy transport, and do not require external power, passive sampling is particularly suitable for long-term monitoring in remote regions and wilderness areas, simultaneous large-scale measurement, and recording of individual exposure. In addition, the passive techniques provide a variety of sampling tools, e.g., sorbent-tubes (Kim et al., 2014), canisters (Lee et al., 2002), Tedlar bags (Yao et al., 2015; Saalberg and Wolff, 2016), and PASs.

This paper focuses on advances in passive air sampling for VOCs, specifically concentrating on recent years. Beginning with the theory of passive air sampling, we then discuss the critical factors of PASs. After that, the latest improvements and applications of PASs will be introduced by listing commercial and emerging samplers. Furthermore, we will present introductions and applications of passive air sampling by governments and organizations. Finally, based on the recent developments of PASs, the latest trends and future perspectives will be discussed.

**THEORY**

Due to the lack of external power, PASs depend on turbulent diffusion and/or molecular diffusion to sorb the analyte, which is transferred from the sampled medium (air) to the collecting medium (sorbent) depending on the concentration gradient between the media (McLagan et al., 2016a). The absorption process of the analyte can be divided into 3 steps by the two-film theory (Whitman, 1923): transport from ambient air to the internal airspace of the sampler, from internal airspace to the sorbent-air interface in the sampler, and from the sorbent-air interface into the sorbent (see Fig. 1). Zhang and Wania proposed a three-process assumption to describe the mass transfer through the passive sampling media (sorbents) which was ignored in the two-film theory (Zhang and Wania, 2012): the sequential molecular diffusion through the stagnant air-side boundary layer and the sorbent macro-pores, and the reversible sorption onto the sorbent (see Fig. 1). Depending on the way in which gas molecules enter the sorption layer, PASs can be classified into two categories: diffusion samplers and permeation samplers (see Fig. 2). The accumulation of the analyte by the sorbent in a PAS can be divided into 3 phases (Shoeib and Harner, 2002): linear uptake phase, curvilinear uptake phase, and equilibrium phase. In the linear uptake phase, the sampling rate (SR) (mL min$^{-1}$) of a diffusive PAS (same as the SR of a dynamic device) can be derived by Fick’s first law:

$$SR_d = \frac{M}{t \cdot C} = \frac{D \cdot A_d}{L_d}$$

(1)
Fig. 1. Schematic of mass fluxes between ambient air and PAS considering the two-film theory (Whitman, 1923) and three-process assumption (Zhang and Wania, 2012). The diffusive barrier and membrane are particularly for diffusive sampler and membrane sampler, respectively.

Fig. 2. Ideal concentration profiles for diffusion and permeation PASs. $C_m (C_m = K C)$ represents the concentration of the analyte on the surface of the membrane, $K$ represents the partition coefficient of the analyte between air and membrane, and $C$ is the concentration of the analyte in air.

where $M$ is the mass of sorbed analyte (µg), $t$ is the deployment time (min), $C$ is the concentration of the analyte in air (µg m$^{-3}$), $D_{aw}$ is the diffusion coefficient of the analyte in air (cm$^2$ min$^{-1}$), $A_d$ is the cross-section area of diffusion path (cm$^2$), and $L_d$ is the length of diffusion path (cm). Similarly, for permeation samplers the Eq. (1)
where $M$, $t$, and $C$ have the same meanings as in Eq. (1), $D_m$ is the diffusion coefficient of the analyte in the membrane (cm$^2$ min$^{-1}$), $A_m$ is the surface area of the membrane (cm$^2$), $K$ is the partition coefficient of the analyte between air and membrane (unitless), and $L_m$ is the membrane thickness (cm) (Seethapathy et al., 2008). Considering the tortuous path taken through the diffusive barrier, the length of diffusion path needs to be adjusted which was usually ignored during modeled SR assessments. McLagan et al. (2016b) proposed an equation to adjust the length of diffusion path, and the theoretical SRs after calibration compared favorably with the experimental values:

$$SR = \frac{V_{air}}{t} \times \left[ 1 - \exp\left( -\left( \frac{A_i}{V_s} \cdot \left( \frac{K_{avg}}{K_{s-a}} \right) \cdot \frac{t}{L_m} \right) \right) \right]$$

Equation (4)

where $V_{air}$ is the equivalent air sample volume that contains the same mass of the analyte sorbed by the PAS under equilibrium conditions (cm$^3$), $t$ is the deployment time (min), $K_{s-a}$ and $K_{avg}$ are the medium - air partition coefficient and the average medium partition coefficient of the analyte (cm min$^{-1}$), respectively, and $V_s$ (cm$^3$) and $A_i$ (cm$^2$) are the volume and planar surface area of the sampling medium, respectively. Harner et al. (2004) used this method to assess urban-rural spatial trends and seasonal variation for persistent organic pollutants (POPs) over 12 months in Canada (Motelay-Massei et al., 2005). Chaemfa et al. (2009) derived different SRs for polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) by PUF-PAS. In fact, PASs are deployed at various geographic scales and under different meteorological conditions to assess the distribution of VOCs in air. During the sampling period, SRs are strongly influenced by meteorological factors which are not considered in Eq. (4). Ockenden et al. (2001) and Farrar et al. (2005) used PCBs as the depuration compounds (DCs) or called performance reference compounds (PRCs) as well to determine SRs of POPs under various environments. DCs are usually the homologous compounds of the analyte which do not exist in the sampling environment and disturb the analysis. SR can be gained from the DCs as (Gouin et al., 2005):

$$SR = \frac{\ln(C_i / C_0)}{t} \cdot K_{s-a} \cdot V_s$$

where $C_0$ and $C_i$ are the concentrations of DCs before and after the deployment, and $t$, $K_{s-a}$ and $V_s$ are the same meanings as in Eq. (4). Ideally, the recoveries of DCs should between 20 to 80% in order to derive more precise SRs and lower uncertainty (Söderström and Bergqvist, 2004). Moeckel et al. (2009) presented guidelines for the use of DCs and the calibration of PASs. The concentrations of POPs derived
from PUF-PAS compared favorably with the values from active techniques (Farrar et al., 2005; Gouin et al., 2005). This method of DCs considered the effects of meteorological factors on individual PAS, but also increased the cost of analysis at the same time. However, addition of DCs was not helpful in correcting for possible site differences in SRs by the XAD-2 resin based passive air sampler (XAD-PAS) due to the high absorbability of XAD-2 resin (Zhang et al., 2011). The benefits of DCs for other PASs still remain uncertainties. According to the theory of PASs, the diffusion coefficient of the analyte in air is an important factor that affects SRs a lot. The $D_{\text{air}}$ in Eq. (1) can be expressed in detail as (Fuller et al., 1966):

$$D_{\text{air}} = 1.00 \times 10^{-3} T^{1.75} \left(1 / M_A + 1 / M_X\right)^{0.5} \left[P V_A^{1/3} + P V_X^{1/3}\right]$$

(6)

where $D_{\text{air}}$, $T$, and $P$ have the same meanings as in Eq. (1) and Eq. (3), $M_A$ (g mol$^{-1}$) and $V_A$ (m$^3$ mol$^{-1}$) are the average molecular weight and volume of air, respectively, $M_X$ (g mol$^{-1}$) and $V_X$ (m$^3$ mol$^{-1}$) are the molecular weight and volume of the analyte, respectively. Apparently, $D_{\text{air}}$ is affected by temperature and pressure in air, and molecular weight of the analyte. Previous studies also indicated that SRs and diffusion coefficients both varied by different analytes for a PAS. Zhang et al. (2011) observed that homolog-specific SR decreased from the lighter to the heavier PCBs for both PUF-PAS and XAD-PAS. Wang et al. (2010) used the calibration equation based on Eq. (6) to calculate SRs of POPs in the air of the Tibetan Plateau. Liu et al. (2010) observed that the amount of hexachlorobenzene (HCB) sorbed in XAD-PAS was constant with altitude and season in mountainous western China, and used HCB to derive SRs that were specific for individual PAS. This sampler-specific SR method was also successfully used to observe spatial variability of atmospheric SVOCs in Chile (Shunthirasingham et al., 2011). In the field test, SRs were observed decreasing during the sampling period (Bradshaw and Ballantine, 1995; Tolnai et al., 2000), and noticeably different from the theoretical values (Gelencsér et al., 1994; Woolfenden, 2011). This is possibly due to the neglect of the SR calibration particularly for the diffusive samplers e.g., Eq. (3). In addition, selecting an appropriate deployment time is also very important, e.g., overlong deployment time will cause back-diffusion of the sorbed analyte (Kilic and Ballantine, 1998). Moreover, the lower outdoor temperatures might cause slower molecular diffusion in air, thus, the SR. Finally, the addition of the sampler housing for outdoor deployments reduced the effect of wind speed on the SRs, particularly for higher wind speeds in the field (McLagan et al., 2016b).

CONSIDERABLE FACTORS OF PAS

Structure

According to the structure, PASs can generally be divided into badge-type and tube-type, and most designs of the current samplers are improved from these two types (see Fig. 3). Quite a number of publication have tested and compared the main performances of representative PASs with different types. Compared to the SKC sampler (badge-type), the Perkin Elmer sampler (axial-type), and the ATD-tube sampler (tube-type), the Radiello® sampler (radial-type) had the fastest SR, the largest cross-section area, and the shortest diffusion path (McAlary et al., 2015). The 3M™ Organic Vapor Monitors (OVM) 3500 (badge type) and the GABIE® sampler (badge type) were both suitable for assessing very low exposures (Oury et al., 2006). Except for the 3M™ OVM 3500, samplers of ATD-tube, SKC Ultra, WMS™, and Radiello® all had reliable SRs with low face velocity and high humidity (McAlary et al., 2014b). Zhang et al. (2012) observed that short cylindrical sorbent container of XAD-PAS had a higher SR, which was in line with the studies using PUF-PAS to sample SVOCs. The sampler housing with the cylindrical shape (XAD-PAS) had less influence from particulate phase POPs than two-bowl shape (PUF-PAS) in the field test (Schrlau et al., 2011; Zhang et al., 2011).

Sorbent

The PAS sorbent is considered to be tightly related to its sampling performance. If the sampling period is monthly or even longer, the large uptake capacity and stable chemical property of a sorbent ensure that it will not become saturated or reach its equilibrium uptake capacity during the sampling period. An ideal sorbent needs to have a strong ability to sorb the analyte during the sampling period and be efficiently desorbed in the analysis process (Woolfenden, 2010). Some commonly used sorbents are listed below: (1) The active carbon (active charcoal) as one of the most commonly used sorbents is suitable for most of VOCs. It is preferred by many PASs for a cheap price, stable performance, and large uptake capacity e.g., 3MTM OVM, Radiello® sampler, Analyst® sampler, etc. (Villanueva et al., 2013; Verriele et al., 2016; North et al., 2017). (2) Graphitized Carbon Blacks (GCBs), with high thermo-stability, can afford around 400°C to ensure efficient desorption; e.g., the Carbotrapp™ series products are able to trap a large range of VOCs of C4–C5 hydrocarbons and other macromolecules; the Carbopack® X series products are commonly used to monitor C4–C9 VOCs such as benzene and 1,3-Butadiene (Gustafson et al., 2007; Ballesta et al., 2016). (3) Carbon molecular sieves (CMS), recommended in method TO-2 by EPA, are particularly suitable for sampling small molecule compounds such as C1–C2 hydrocarbons. The Carbosieve® is suitable for methane, ethylene, and acetylene. It has a high sorption for V VOCs as an alternative to active charcoal. However, it might become irreversibly contaminated with compounds higher boiling than xylene (C8) (Woolfenden, 2010). The Carboxen® series products were widely used in SPME samplers for C2–C8 VOCs and chlorinated VOCs (CVOCs) (Ulanowska et al., 2011; Sheehan et al., 2012; Koziel et al., 2017). (4) Porous polymers have a wide application range for both VOCs and SVOCs. Tenax® recommended as a hydrophobic sorbent in method TO-1 by EPA is suitable for a little higher boiling compounds e.g., BTEX compared to Chromosorb® 106 which was used for
Fig. 3. Schematics of PASs types for VOCs. A: basic tube-type or axial-type sampler. B: basic badge-type sampler. C: modified badge-type WMS™ sampler (Sirelab). D: radial-type XAD-PAS (Wania et al., 2003). E: two-bowl type PUF-PAS (Wilford et al., 2004). F: radial-type Radiello® sampler (Sigma Aldrich). G: modified axial-type combined radial-type POD sampler (Ballesta et al., 2016). H: modified radial-type THPDS sampler (Du et al., 2013). Sampler images are not proportional and slight variations may exist from actual designs.

low boiling VOCs e.g., cis-1,2-Dichloroethylene and Trichloroethylene (McAlary et al., 2014a). (5) The resin, a styrene-divinylbenzene copolymer, is commonly used for monitoring atmospheric POPs e.g., resin XAD-2 for XAD-PAS. It has a very high capacity for POPs and well behavior at subzero temperatures and high moisture than other polymers (Wania et al., 2003). (5) The PUF disks is another widely used sorbent for both indoor and outdoor studies of a range of SVOCs, including polycyclic aromatic hydrocarbons (PAHs), PCBs and organochlorine pesticides, PBDEs, and polychlorinated naphthalenes (PCNs) (Chaemfa et al., 2008). It has a low specific surface area and thus has a lower capacity for gaseous SVOCs compared to the XAD-2 resin (Bidleman and Tysklind, 2018). The sampling efficiency of the PUF disks improved when the temperature declined as well as the resin (Wania et al., 2003). Shoeb et al. (2008) and Schuster et al. (2012) impregnated a PUF disk with XAD powder to increase the uptake capacity of the PUF-XAD as for legacy POPs e.g., PCBs and PBDEs. Furthermore, there are also other sorbents such as coconut shell activated carbon, purified carbon black, silicone, and multi-sorbent (see Table 1). More introductions can be found in relevant reviews (Harper, 2000; Woolfenden, 2010).

Sampling Rate

SR is a major element of a PAS and is a critical parameter for quantifying the analyte. An ideal SR remains constant in different sampling environments, while in fact, it needs to be calibrated depending on specific conditions (Tolnai et al., 2000; McLagan et al., 2016b). Due to variations of multiple orders of magnitude for VOC concentrations, SR is also required to be matched correspondingly. It needs less deployment time for a sampler with a fast SR under elevated VOC concentrations such as industrial regions (Bruno et al., 2008; Fenech et al., 2010; Colman Lerner et al., 2012). In contrast, a lower SR could prolong the sampling period to achieve long-term monitoring in remote areas as long as one year period (Thoma et al., 2011; Brown et al., 2012). The SRs of existing PASs for VOCs range over 6 orders of magnitude (see Table 1). The lowest SR of 0.0055 mL min⁻¹ was determined by a needle trap device for o-xylene (Gong et al., 2008). On the other hand, the Radiello® sampler provided a fast SR of 125 mL min⁻¹ for methanol. For all the samplers listed in Table 1, it is obviously that the tube-type samplers have relatively lower SRs ranging from 0.0055–0.60 mL min⁻¹, while the radial-type samplers have faster SRs ranging from 0.76–125 mL min⁻¹. Compared to the SRs for VOCs, SVOCs due to the lower volatility and concentrations in air need much faster SRs to be sorbed by samplers e.g., PUF-XAD with SRs ranging from 1.0–10.0 m³ d⁻¹ (Bohlin et al., 2010) and XAD-PAS with SRs ranging from 1.4–5.0 m³ d⁻¹ (Gong et al., 2017). Several
Table 1. Applications of PASs for VOCs from recently published literatures.

| PAS name | Sorbent material | Analytes | Analytical method | Deployment time | Sampling rate (mL min⁻¹) | Applications | References |
|----------|------------------|----------|-------------------|-----------------|--------------------------|--------------|------------|
| 3M™ OVM  | Activated carbon | BTEX     | Not reported      | 3 w             | 21.5–45.0 (3M)           | Biomonitor exposure of European starlings | (North et al., 2017) |
|          | Activated carbon | BTEX     | CS₂ desorption and GC-MS | 24 h            |                          | Investigate personal exposures of school children | (Demirel et al., 2014) |
|          | Activated carbon | 23 VOCs  | Dichloromethane: methanol (50:50) desorption and GC-FID | 30 d            |                          | Detect VOCs in indoor air in small enterprises | (Colman Lerner et al., 2012) |
|          | Activated carbon | 29 VOCs  | 2:1 v/v mix of acetone and CS₂ desorption, and GC-FID | 72 h and 96 h   |                          | Study hurricane impact on air quality | (Chung et al., 2009) |
|          | Activated carbon | 11 VOCs  | Acetone/CS₂ mixture desorption and GC-MS | 24 h and 48 h   |                          | Study spatial variation of air toxics in "hot spot" areas | (Zhu et al., 2008) |
| ACFL-SPMS| Activated carbon and florisil | BTEX     | Head-space GC-MS | 1, 3, 5, 7, 24, and 48 h | 0.01–0.13 L h⁻¹ | Determine BTEX in indoor air environments | (Esteve-Turrillas et al., 2009) |
|         | Active charcoal   | Formaldehyde | Acetonitrile desorption and HPLC with UV detection | 2 d             |                          | Measurement of formaldehyde in indoor and outdoor ambient air | (Mabilia et al., 2010) |
| | Graphitized charcoal | 63 VOCs | CS₂ desorption and GC-MS | 8 h             | 5.47–8.93                | Investigate BTEXs indoor and outdoor in Algeria | (Moussaoui et al., 2012) |
| | Active charcoal   | Formaldehyde and acetaldehyde | Acetonitrile desorption and HPLC with a photodiode array detector | 14-20 d         | 11.6 ± 3.0 and 11.4 ± 1.0 | Measure formaldehyde and acetaldehyde in indoor and outdoor ambient air | (Villanueva et al., 2013) |
| ATD      | Tenax® TA and Carbopack® B Chromosorb® 106 | 10 VOCs | TD GC-MS | 1–7 d | 0.28–0.60 | Laboratory testing of indoor VOCs | (McAlary et al., 2015) |
|          | cis-1,2-DCE and TCE |          | TD GC-MS | 2 h and 15 h | 0.47 and 0.50 | Quantitative passive soil vapor sampling for VOCs | (McAlary et al., 2014a) |
| DSD-DNPH | DNPH             | Aldehydes and acetone | HPLC with UV detector | 10 d | 24.1–71.9 (Sigma Aldrich) | Study indoor air concentrations of aldehydes and acetone | (Diodiu et al., 2016) |
|          | DNPH             | 20 VOCs | HPLC | 24 h |                          | Study seasonal variations of carbonyl compounds in urban area | (Xu and Gao, 2009) |
| PAS name | Sorbent material | Analytes | Analytical method | Deployment time | Applications | References |
|----------|------------------|----------|-------------------|-----------------|-------------|------------|
| FLEC®-SPME | Carboxen® | VOCs | TD GC-FID and TD GC-MS | 5 min and 20 min | Analyze VOCs emitted from solid building materials | (Nicolle et al., 2008, 2009) |
| GABIE® | Active charcoal | 50 VOCs | CS₂ desorption and GC-MS | 1 w | Measure VOCs from indoor Kerosene heaters | (Hanoune and Carteret, 2015) |
| | Methyl methacrylate (MMA) | | GC with infrared spectroscopic detector and GC-FID | 460 min | Monitor concentration of MMA indoor air | (Amoretti et al., 2013) |
| | Toluene | | dichloromethane desorption and GC-FID | 8–9 h | Monitor personal exposure to atmospheric toluene | (Ducos et al., 2008) |
| ORSA-5 | Carcoal | Toluene, isoflurane, and perchloroethylene | CS₂ desorption and GC-MS | 15 min, 1 h, and 4 h | Test VOCs under fluctuant concentration conditions | (Langlois, 2008) |
| | | | toluene desorption and GCMS | 2–3 h | Determine occupational exposure of carbon disulfide | (Kilo et al., 2015) |
| | | | | 5–10 (Draeger) | Monitor in indoor and outdoor air of public buildings and private homes | (Gallego et al., 2008) |
| PCB | Polypyrrole | Xylene and styrene | TD GC-FID | 8 h | Monitor the xylene and styrene in copy-print shops in Thailand | (Saelim et al., 2013) |
| Perkin Elmer | Tenax® TA | Styrene | TD GC-MS | 0.5–8 h | Determine styrene both in the laboratory and in the field | (Lindahl et al., 2009) |
| | Carbopack® X | Benzene | TD GC-MS | 2 w | Monitor concentration of benzene in ambient air | (Thoma et al., 2011) |
| | Tenax® TA | Toluene, isoflurane and perchloroethylene | TD GC-MS | 15 min, 1 h, and 4 h | Test VOCs under fluctuant concentration conditions | (Langlois, 2008) |
| | Carbopack® X | 1,3-Butadiene and Benzene | TD GC-FID | 1 w | Quantify personal exposure and indoor levels of VOCs | (Gustafson et al., 2007) |
| PFS | DNPH | 13 VOCs | Acetonitrile desorption and HPLC with a photodiode array detector | 0.5–24 h, 16 h | Measure VOCs emission rates and determine emission sources in indoor environments | (Shinohara et al., 2007, 2009) |
| | | | | 0.5–3 h | | (Yamashita et al., 2010) |
| PAS name | Sorbent material | Analytes | Analytical method | Deployment time | Sampling rate (mL min⁻¹) | Applications | References |
|----------|------------------|----------|-------------------|-----------------|--------------------------|-------------|------------|
| POD      | Carbopack® X     | VOCs (C5-C9) | TD GC-FID         | 24 h            | 1.50 ± 12.6%–8.88 ± 5.9% | Laboratory testing of indoor VOCs | (Ballesta et al., 2016) |
|          |                  |          |                   |                 |                          | Assess airborne PAHs in occupational environments | (Bohlin et al., 2010) |
|          |                  |          |                   |                 |                          | Investigate outdoor and indoor sources of PAHs in Pakistan | (Hamid et al., 2017) |
| PUF-PAS  | PUF disks        | PAHs     | Soxhlet extraction and GC-MS | 1 and 2 w      | 1.0–10.0 m³ d⁻¹          | Monitor selected POPs for nationwide dataset in Turkey | (Kurt-Karakus et al., 2018) |
| PUF disks | PUF disks        | PAHs     | Soxhlet extraction and GC-MS | 8 w             |                          | Assess airborne PAHs in indoor environments | (Hamid et al., 2017) |
|          | PUF disks        | PCBs, OCPs, and PBDEs | Soxhlet extraction and GC-MS | 3 months       |                          | Monitor selected POPs for nationwide dataset in Turkey | (Kurt-Karakus et al., 2018) |
| Radiello® | Carbograph® 4   | 27 VOCs  | TD GC-FID         | 2 w             | 8 ± 4.7%–125 ± 9.2% (Sigma Aldrich) | Study indoor and outdoor VOCs in school buildings in France | (Verriele et al., 2016) |
| Activated charcoal | 17 VOCs  | TD GC-FID | 1 w and 2 w |                |                          | Study seasonal variations of VOCs in a Spanish National Park | (Villanueva et al., 2014) |
| Carbograph® 4 | 20 VOCs  | TD GC-MS | 3 d, 4 d, 7 d, and 14 d |  |                             | Evaluates the performance of Radiello® for analysis of VOCs | (Gallego et al., 2011) |
| Activated charcoal | BTEX    | CS₂ desorption and GC-MS | 1 w             |                |                          | Determine the influence of the traffic artery on the concentration of VOCs | (Buczynska et al., 2009) |
| Charcoal | 10 VOCs         | TD GC-MS | 1–7d             | 49–72           |                          | Laboratory testing of indoor VOCs | (McAlary et al., 2015, 2016) |
|          | monoterpenes (α-Pinene, 3-Carene, D-Limonene) | TD GC-MS | 300 min | 6.4, 11.3, and 12.8 | Study the influence of the emission of monoterpenes on indoor air quality | (Marc et al., 2014) |
| Carbograph® 4 | 21 VOCs  | TD GC-MS | 24 h             | 12.3–28.8       | Identify the main VOCs source and in South Italy | (Bruno et al., 2008) |
|          | monoterpenes  | TD GC-MS | 1–30 d          | 42.2–54.8       | Analyze behavior and origin of VOCs in Kyoto City | (Yamada et al., 2004) |
|          | 1,3-Butadiene and Benzene | TD GC-FID | 24 h             | 14.9 and 16.0   | Laboratory testing of indoor VOCs | (McAlary et al., 2015) |
|          | SKC Ultra       | BTX      | CS₂ desorption and GC-FID | 1–7 d          | 4.7–15.0                  | Quantify personal exposure and indoor levels of VOCs | (Gustafson et al., 2007) |
|          | SKC Ultra       | 10 VOCs  | TD GC-MS | 1–7 d | 4.7–15.0 | Laboratory testing of indoor VOCs | (McAlary et al., 2015) |
|          | SKC Ultra       | 1,3-Butadiene and Benzene | TD GC-FID | 24 h | 14.9 and 16.0 | Quantify personal exposure and indoor levels of VOCs | (Gustafson et al., 2007) |
|          | SKC Ultra       | DNPH     | Acetonitrile desorption and HPLC with a dual-wavelength absorbance detector | 7 d | 20.4 | Monitor formaldehyde in libraries and archives and personal exposure | (Fenech et al., 2010) |
| PAS name          | Sorbent material | Analytes                                      | Analytical method                  | Deployment time | Sampling rate (mL min⁻¹) | Applications                                                                 | References                                                                 |
|-------------------|------------------|-----------------------------------------------|------------------------------------|-----------------|-------------------------|----------------------------------------------------------------------------|----------------------------------------------------------------------------|
| SPME              | Carboxen®        | DMDS, DMTS, pyrimidine, phenol, and p-cresol   | Thermal desorption(TD) GC-MS       | 10–60 min       |                         | Track mark VOCs emitted during aerobic digestion of biohazardous animal tissue | (Koziel et al., 2017)                                                       |
|                   | Carboxen®        | Benzene, toluene, ethylbenzene, and o-xylene  | TD GC-MS                           | 1–600 min       |                         | Quantify BTEX in vehicle exhaust gases                                     | (Baimatova et al., 2015)                                                   |
|                   | Carboxen®        | CVOCs                                         | TD and GC-ECD                      | 10 min          |                         | Determine CVOCs in planta                                                  | (Sheehan et al., 2012)                                                     |
|                   | Carboxen®        | Acetone, Ethanol, Isoprene, etc.              | TD GC-MS                           | 10 min, 1 h, and 2 h |                         | Determine lung cancer biomarkers by breath analysis                        | (Ulanowska et al., 2011)                                                   |
|                   | Carboxen®        | BTEX                                          | TD GC-MS                           | 1–95 h          | 0.0055–0.016            | Monitor VOCs in both occupational and community environments              | (Gong et al., 2008)                                                       |
| Tailor-made diffusive sampler | Activated carbon | 29 VOCs                                       | CS₂ desorption and GC-MS          | 24 h and 1 w    | 5.94 ± 2.17–10.08 ± 3.58 | Measure indoor air quality assessment in Turkey                            | (Can et al., 2015; Özden Üzmez et al., 2015)                                |
| THPDS             | Silica zeolites  | BTX                                           | TD GC-MS                           | 24 h            | 0.76 ± 0.22–5.44 ± 1.46 | Monitor indoor BTX in 43 homes in Guangzhou                                | (Du et al., 2013; Du et al., 2014)                                        |
| TOPAS             | Tenax®           | VOCs                                          | TD GC-MS                           | 5 h             | 0.5 ± 0.1–2.6 ± 0.2 L h⁻¹ | Determine the emission of a flooring material                              | (E et al., 2001)                                                          |
| TraceAir®         | Charcoal         | Benzene, n-hexane, and total hydrocarbons     | CS₂ desorption and GC-FID          | 72 h            | 30–90                   | Estimate spatial variability of VOCs in Toronto                             | (Su et al., 2010)                                                         |
| WMSTM             | Anasorb®        | 10 VOCs                                       | TD GC-MS                           | 1–7 d           | 2.4–14.0                | Laboratory testing of indoor VOCs                                          | (McAlary et al., 2015)                                                    |
|                   | Anasorb®        | cis-1,2-DCE and TCE                           | Solvent extraction and GC/MS       | 2 and 15 h      | 1.9 and 3.3             | Quantitative passive soil vapor sampling for VOCs                         | (McAlary et al., 2014a)                                                   |
|                   | XAD-PAS         | POPs                                          | Soxhlet extraction and GC-MS       | 2 months        | 1.4 ± 0.7–5.0 ± 5.2 m² d⁻¹ | Field calibration of XAD-PAS on the Tibetan Plateau                        | (Gong et al., 2017)                                                       |
|                   | XAD resin       | PCBs and pesticides                           | Soxhlet extraction and GC-ECD, and GC-MS/MS | 4 or 5 months |                         | Study the distribution of PCBs and pesticides in Argentina                  | (Silva-Barni et al., 2017)                                                 |
studies have compared the effects of meteorological factors on SRs by controlled chamber experiments such as temperature, relative humidity, and wind speed. The SRs of badge-type and tube-type samplers, as well as PUF-PAS and XAD-PAS without the diffusive barrier, may have more effects by wind speed in outdoor deployments due to the high susceptibility to turbulence (Brown, 2000; Wang et al., 2010), e.g., SRs of gas-phase SVOCs varied by about a factor of 2 from 1.5 to 5.5 m s⁻¹ by PUF-PAS (Klánová et al., 2008). For radial-type THPDS sampler, this effect is much less due to the diffusion body which decreased the analyte uptake in the sampler (Du et al., 2013). Furthermore, wind speed has different influences on different VOCs, e.g., the correlation of SR with wind speed was significant for toluene but not for styrene ( Özden Üzmez et al., 2015). Therefore, correction might be done depending on different VOCs. In addition, the effects of temperature on SRs should not be neglected. A 30.6% decrease of toluene SR was observed within the range of 25°C to 40°C by THPDS sampler (Du et al., 2013). Klánová et al. (2008) observed that SRs of gas-phase SVOCs also had a significant decrease from −6°C to 25°C by PUF-PAS. On the contrary, Ballesta et al. (2016) observed increasing trends of BTEX SRs by POD sampler. This result might due to the different sorbents used in the samplers, which have contrary influences by the temperature. For the effects of relative humidity on SRs, there was no significant variation between 10 to 80% for POD sampler as well as THPDS sampler, which might due to the high hydrophobicity of the sorbents (Du et al., 2013; Ballesta et al., 2016). Hayward et al. (2011) indicated that water did not form a strong barrier on XAD-2 resin at high relative humidity based on the little influence on 52 SVOCs.

Detection Limit

The detection limit of PASs is mainly determined by the method detection limit (MDL) and analytical detection limit (ADL). Based on Fick’s law, MDL can translate to a minimal deployment time for the PAS (McLagan et al., 2016b). Most of the existing PASs for VOCs rely on spectroscopic techniques for analysis (see Table 1). 24 studies including 10 samplers relied on thermal desorption followed by either GC-MS or GC-FID to quantify the analytes. 11 studies including 8 samplers used CS₂ or acetone/CS₂ mixture desorption instead of thermal desorption. The remaining analyzed VOCs by other solution desorption and techniques e.g., acetonitrile and followed by HPLC (see Table 1). For analyzing SVOCs, the Soxhlet extraction and GC-MS are commonly used by PASs e.g., PUF-PAS and XAD-PAS. In the field, different sampling sites will have corresponding requirements for the levels of detection limit. In contaminated environments, the ppb level is sufficient for the sampling demands. For instance, SPME sampler with the detection limits of BTEX ranging from 1.6–5.2 mg m⁻³, was used to qualify the concentrations of BTEX in vehicle exhaust gases (Baimatova et al., 2015). Corresponding to the low concentrations of SVOCs in air, the relative detection limits are much lower than VOCs e.g., ranging between 0.2 and 2 pg m⁻³ for PCBs by XAD-PAS (Silva-Barni et al., 2017). On the other hand, many samplers have low detection limits (i.e., on the ppb level) which are suitable for monitoring in remote areas. The MDLs of BTEX by Radiello® sampler ranging between 0.007 and 0.014 μg m⁻³ (Buczynska et al., 2009), which are capable for outdoor BTEX concentrations between 0.26 and 6.11 μg m⁻³ (Demirel et al., 2014). Nonetheless, PASs which are suitable for higher concentrations might not be able to monitor VOCs at lower concentrations due to the lower equilibrium uptake capacity of samplers (McLagan et al., 2016a).

Cost Effectiveness

A well-designed PAS should be inexpensive and made of common materials, which are inert to the analyte. It is required to be deployed and retrieved easily, stored and transported conveniently, and pretreated and analyzed efficiently (McLagan et al., 2016a). During the sampling period, it should generally be free of the need for daily care and maintenance.

EXISTING PASS FOR VOCs

The conceptual development of diffusive monitoring was initiated during the late 1960s to early 1970s. Since the passive sampling of sulfur dioxide by means of measuring its TWA exposure was introduced in 1973 (Palmes and Gunnison, 1973; Morello-Frosch et al., 2000) and the introduction of a commercially available product in 1974 (Gosselink et al., 1981), numerous studies focused on research and development of PASs have been published and new PASs have been continuously reported. With such a great effort, many samplers have been commercial successfully from laboratories, such as ORSA-5, 3M™ OVM, SKC, and Radiello®. The development of PASs has not stopped in the latest years, and both commercial and emerging PASs are selectively listed below.

Recent Improvements and Applications of PASs for VOCs

The 3M™ OVM, commercial badge-type samplers, which were introduced to the market in Jan 1978 (Gosselink et al., 1981), are widely used both for air quality and personal monitoring. The Formaldehyde Monitor 3720 and the Ethylene Oxide 3550 were recently reported to provide more choices for VOC monitoring (3M). The Analyst® sampler, a diffusive badge-type sampler, consists of a polyethylene cylinder, an anti-turbulence net, and a 2,4-DNPH coated adsorbent bed. It was designed to enable long-term sampling due to its large charcoal bed (Bertoni et al., 2001), and has been used to measure VOCs in indoor and outdoor air in recent years (Mabilia et al., 2010; Moussaoui et al., 2012; Villanueva et al., 2013).

The Passive ATD tube sampler includes a standard Automated Thermal Desorption (ATD) tube. The tube can be filled with a wide variety of sorbents, according to the analyte, and can directly be deployed onto a thermal desorption unit for GC/MS analysis. Therefore, it has been widely used both in the laboratory and ambient air (McAlary et al., 2014a, 2015).

The DSD-DNPH diffusive sampler is comprised of a porous polyethylene tube, a syringe, and DNPH as the
sorbent. It is versatile and has been used for indoor (Diodiu et al., 2016), outdoor (Xu and Gao, 2009), and personal sampling particularly for carbonyls, and is recommended by the Japanese government (Sigma Aldrich).

The Du Pont PRO-TEK™ G-AA and G-BB, badge-type diffusive samplers, were designed to monitor personal exposure due to its small size and weight (Rudling et al., 1984). A series of samplers were developed based on PRO-TEK™ for commercial applications; e.g., the TraceAir® monitor and the ChemDisk™ 546, 566 monitors (Assaytech).

The GABIE® sampler, a badge-type designed by INRS, was marketed by Arelco, France. It contains a geometric surface of 7 cm² and 550 mg of coconut charcoal sorbent (Delcourt and Sandino, 2001). It has been used for measuring VOCs in indoor air (Amoretti et al., 2013; Hanoune and Carteret, 2015), in laboratory conditions (Langlois, 2008), and for personal exposure (Ducos et al., 2008).

The ORSA-5 sampler, commercially produced by Dräger (Lübeck, Germany) (Wolfgang, 1989), is a tube-type sampler with low SR and high sorption capacity. It was used to measure airborne contaminants in workplaces to determine personal exposure (Rihs et al., 2008; Kilo et al., 2015), and was also suitable for indoor and outdoor monitoring (Gallego et al., 2008).

The Perkin Elmer sampler, an axial sorbent-base tube sampler, was specially developed for VOC monitoring in 1981. It consists of a steel tube, filled with sorbents like Tenax® TA, Carbopack® X, and Chromosorb® 106 (Brown et al., 1981). It was also widely used not only in indoor (Langlois, 2008; Lindahl et al., 2009) and outdoor air (Thoma et al., 2011), also for personal exposure (Gustafson et al., 2007).

PUF-PAS, a two-bowl type sampler, is suspended in the center of the two dishes between washers with the common size of 14 cm diameter, 1.35 cm thick, and 365 cm² surface area. It is often used for both indoor and outdoor SVOCs sampling (Wilford et al., 2004). A large-scale PUF-PAS deployment at over 50 sites under the Global Atmospheric Passive Sampling (GAPS) was in progress from Dec 2004 (Harmer et al., 2006), and Herkert et al. (2018) used the database of GAPS to predict the gas-phase SRs for PUF-PAS in global environment. Further, PUF was usually used for active high-volume sampling e.g., to observe seasonal trends of POPs in West Africa (Nost et al., 2018).

The Diffusive Radiello® sampler, a popular commercial PAS, had a notable SR compared to other commercial samplers (McAlary et al., 2015). It consists of a diffusive body that contains an adsorbing cartridge. With two types of sorbents (activated charcoal for CS₂ desorption and Carbograph® 4 for thermal desorption), separately packed in a stainless steel net, it provides an alternative choice for VOC monitoring. Numerous studies of VOC monitoring have applied the Radiello® sampler as a preference, including structural improvement such as small-scale passive emission chamber (SSPEC). It has a stainless steel container that contains a Radiello® sampler, which aims to determine the emission flux of monoterpenes from wood-based flat surfaces located indoors (Marc et al., 2014).

The Shibata gas-tube sampler (Shibata, Tokyo), is filled with 200 mg activated carbon inside porous polytetrafluoroethylene tubes (Yamada et al., 2004). It was developed and used for the determination of VOCs in Japan.

The SKC sampler, a plastic badge-type sampler, contains about 600 mg adsorbent such as Carbopack® X (Eriksson et al., 1994). With further development, there were UME® 100 passive sampler for formaldehyde, SKC 575 series for organic vapors, and SKC ULTRA III for SVOCs (Skcltd).

The Solid-phase microextraction (SPME), was designed to reduce the sample extraction and to shorten analysis process via thermal desorption and GC-MS directly (Arthur and Pawliszyn, 1990). Several studies have been reported on passive sampling by retracted SPME using the TWA method for quantifying VOCs concentrations. Two types of the needle trap device (NTD) (badgelike and penlike) were improved (Gong et al., 2008). Later, several structural improvements and new sorbents packed for the purpose of studying biogenic emissions were reported (Asl-Hariri et al., 2014).

TOPAS, a badge-type sampler, consists of a basic aluminum body with a cut groove, containing Tenax® as the sorbent (Kleine-Benner et al., 2001). TOPAS is suitable for a personal dosimeter and environmental monitoring. However, its further improvement has not been reported recently.

XAD-PAS contains XAD-2 resin as the sorbent packed in a stainless steel mesh cylinder, and a steel mesh shelter. It was designed for monitoring POPs over long-term sampling periods (Wania et al., 2003; Shen et al., 2004). Zhang et al. (2012) did several calibrations of sampler configuration to observe the influence on the SRs. Gong et al. (2017) modified the design of XAD-PAS to dampen the wind turbulence for sampling on Tibetan Plateau. Recently it was deployed in Argentina to evaluate the spatial and temporal variations of pesticides and PCBs in air (Silva-Barni et al., 2017).

Recent New PASs for VOCs

ACFL-SPMS contains a low-density polyethylene layflat tube, filled with a mixture of 50 mg florisil and 5 mg activated carbon using Head-Space(HS)-GC-MS for the fast determination of BTEX. Compared to the triolein-containing semipermeable membrane device (SPMD) and the Radiello® sampler, ACFL-SPMS decreased the cost and increased sampler versatility by combining different solid phases (Esteve-Turrillas et al., 2009).

The FLEC®-SPME sampler was designed for passive sampling of VOCs emitted from solid building materials. It consists of a standard FLEC® emission cell with SPME for rapid sampling and simple thermal desorption, which is directly performed in the GC injector. Compared to dynamic sampling, it better represented VOCs surface emissions and transfers in indoor air (Nicole et al., 2008, 2009).

A novel Printed circuit board (PCB) passive sampler was developed via chemical deposition of silver particles and electropolymerization of a polypyrrole sorptive layer on the surface of the PCB substrate. This sampler can be used up to four times (only cost 0.25 USD per sampling), which provided a better opportunity for developing countries to...
apply large-scale VOC monitoring (Saelim et al., 2013).

The Passive flux sampler (PFS) consists of a glass Petri dish, containing a DNPH-impregnated sheet (Shinohara et al., 2007, 2009). It was developed to measure emission rates of VOCs and to determine emission sources in indoor environments. A further PFS named the emission cell for simultaneous multi-sampling (ECSMS) is composed of a commercially available stainless steel container, fitted with a DNPH tube (Yamashita et al., 2010). It has a small size and is lightweight, cheap, and easy to handle. It is also suitable for simultaneous multi-sampling of VOCs, which emitted from building and furnishing materials.

The Pocket diffusive (POD) sampler is a novel diffusive sampler that combines both radial and axial types. It mainly consists of a support body, an adsorbent cartridge with a stainless steel cylindrical mesh, and a diffusive body made of stainless steel, bronze, or any other polymeric materials. VOCs (C5–C9) were measured under both laboratory and field conditions by the sampler which was possible to estimate SRs for a wider range of compounds (Ballesta et al., 2016).

A Tailor-made diffusive sampler, the Anadolu diffusive sampler, mainly consists of a sampler body, a stainless steel mesh barrier, a closed cap, pressed glass wools, a fixer ring, and activated carbon as its sorbent. Most parts of the sampler are made from plastic and can be reused many times after proper cleaning, which highly reduces its cost. It was developed for the sampling of atmospheric VOCs and its performance was comparable with other commercial samplers (Can et al., 2015; Özden Üzmez et al., 2015).

The Tsinghua passive diffusive sampler (THPDS), a cost-effective radial diffusive sampler, consists of a stainless-steel powder-sintered porous cylinder, containing about 60 mg silica zeolites. It provides an adequate and cost-effective alternative for indoor air BTX measurements in China (Du et al., 2013) and had been used to monitor indoor BTX in 43 homes in the city of Guangzhou (Du et al., 2014).

The Waterloo Membrane Sampler™ (WMS™), was developed from the permeation passive sampler prior to its commercialization (Seethapathy and Gorecki, 2011). It incorporates a polydimethylsiloxane (PDMS) membrane across the face of a vial, which filled with sorbent medium. In addition, it also provides a WMS™-LU sampler with a low uptake rate for soil vapor (Siremlab).

OFFICIAL INTRODUCTIONS AND APPLICATIONS

Since the 1970s, governments have started to study VOCs for their atmospheric chemical processes, sources of emissions, and effects on human health. With research progress, the VOCs analytical methods, techniques, and instruments have been significantly developed. (1) The US EPA gradually introduced 17 standards (TO-1 to TO-17) for toxic organic compounds in the ambient air since the 1980s. Passive sampling as an alternative method had been used many times for the monitoring of ambient air toxics (Chung, 2004–2009). (2) Further, the EEA advised a list of Technical Guidance Notes (TGN), including M8 (monitoring ambient air) and M16 (monitoring VOCs in stack gas emissions), which referenced VOCs monitoring methods. Among these references, passive sampling was recommended to monitor benzene, 1,3-butadiene, and other hydrocarbons (www.mcerts.net). (3) Moreover, the European Standards provided a diffusive sampling guidance for the determination of concentrations of gaseous pollutants in the ambient and indoor air, e.g., EN 14412 and EN 14662 (www.cen.eu). (4) Besides, ISO/FDIS provided a general guidance for the sampling and analysis of VOCs in the workplace and indoor air (ISO, 2000, 2004; Geiss et al., 2009, 2011). (5) Furthermore, the National Institute of Health Sciences (NIHS) in Japan conducted a study using the DSD-DNPH diffusive sampler from April 2000 to March 2004 to monitor carbonyls in the indoor air especially related to the “sick building syndrome”. It has now been specified in the OSHA 1007 method for the determination of aldehydes in the USA (Lee et al., 2017).

LATEST TRENDS AND FUTURE PERSPECTIVES

Based on the development of PASs in recent years, the following main trends and future perspectives can be distinguished:

Field Observation Combined with Model Research

There still have further research demands for the theory of the PAS as well as absorption dynamics. The influences on SRs by environmental and meteorological factors need to be calibrated and evaluated depending on more methods and techniques. An effective approach is a comprehensive study on field observation combined with model research. Zhang and Wanja proposed a three-process assumption to describe the mass transfer through the passive sampling media which was ignored in two-film theory (Zhang and Wanja, 2012). The model was limited by the lack of quantitative information of the sorption rate constant $K_{sorb}$ on sampling media for specific analytes. More experimental data need to be tested to close this knowledge gap in order to predict specific SRs for different analytes. On the other hand, these field data can verify and optimize the models to predict more precise results.

Specific Samplers for Target Analytes

Compared with those popular commercial samplers, many PASs were specifically redesigned to monitor only one or few VOCs. Such samplers include the UME® 100 and the 3M™ 3720 Monitor for formaldehyde, the SKC ULTRA III for SVOCs, the 3M™ 3550 Monitor for ethylene oxide, and the TraceAir® 580 Monitor for aldehydes. These samplers have higher sensitivities and lower detection limits, and are more accurate and reliable for the monitoring of target analytes. Furthermore, they are simpler to be commercialized and more customer friendly. It is highly possible that the samplers for target analytes will be continuously improving toward more subdivided areas for analytes and better performance.

Varieties and Combinations of Sorbents

A large and stable uptake capacity of the sorbent will prolong the ideal sampling period of a PAS. Including but
not limited to this purpose, the improvement of sorbents is still ongoing. (1) One type of sorbent can be used to monitor more than one type of analyte, e.g., activated carbon is able to sorb either VOCs or inorganic compounds such as gaseous elemental mercury (McLagan et al., 2016b). This helps to decrease the cost, making it possible to monitor different analytes with the same sampler. (2) To increase the absorption of target analytes, multi-sorbents are developed to sorb a wider volatility range of target analytes. The most common example is the packing of a tube with multiple sorbent materials, e.g., ATD sampler with sorbents of Tenax® TA and Carbopack® B (McAlary et al., 2015). Furthermore, the Radiello® sampler provided a mix of CMS for the sampling of anesthetic vapors, and ACFL-SPMS used a mixture of activated carbon and florisil for sorbing BTEX (Esteve-Turrillas et al., 2009). (3) Moreover, there are other materials than general sorbents like nano-particles (Valcárcel et al., 2008; Farhadi et al., 2014), metal-organic frameworks (MOFs) (a type of highly porous crystalline material) (Gu et al., 2010; Kim et al., 2017), molecularly imprinted polymers (MIPs) (Bunte et al., 2007), and polypyrrole (as a sorptive layer on a printed circuit board) (Saelim et al., 2013).

Continuous Improvement of the Structure

The structural improvement is another important aspect of PAS development. Among various designs, four common features have been listed in the following: (1) For the purpose of specific applications like SSPEC (a Radiello® diffusive passive sampler inside) (Marc et al., 2014), ECSMS (a DNPH tube inside) (Yamashita et al., 2010), and FLEC®-SPME (a standard FLEC® emission cell with SPME) (Nicolle et al., 2008, 2009), these PASs were specifically designed to monitor VOCs emitted from building and furnishing materials. (2) New prototype NTDs were constructed for increased user-friendliness (Gong et al., 2008) and higher desorption efficiency (Asl-Hariri et al., 2014) via modification of mechanical structures. (3) With regard to the sampling period and sampling rate, the Radiello® sampler with a large cross-section area and a short diffusion path was designed for a faster SR (McAlary et al., 2015). Zhang et al. (2012) did several calibrations of XAD-PAS configuration to enhance the sorption efficiency of analytes. In contrast, WMS™-LU with its very small size, has a low uptake rate, which is particularly useful for soil vapor monitoring (McAlary et al., 2014a). (4) Since environmental factors, such as turbulent airflow can affect sampler performance, a diffusive barrier is often required for a PAS; e.g., a modified design of air spoiler consisting of four metal sheets dampens the wind turbulence (Gong et al., 2017).

Tentative Combination of Advanced Technologies and External Devices

Bearing in mind that the SR value of a PAS depends on temperature, relative humidity, and wind speed, the measured concentration of the analyte will be more accurate if precise measurements of these environmental factors are performed during sampling. Taking temperature effects such as urban heat islands into account, it can make a difference of 4–5°C. The Radiello® sampler provides a thermometer, equipped with a data logger that is sufficiently small to be perfectly suitable for the sampler. It has a button battery that can afford to record one temperature value like every 15 min for 22 d, or every 30 min for 43 d, or every 60 min for 85 d, etc. without replacement (Magnusson et al., 2012). The comprehensive 2D gas chromatography with time-of-flight MS (GC × GC/ToF-MS) had a good separation of complex mixtures for individual analyte e.g., PAHs (Manzano et al., 2012). GC-isotope ratio mass analysis (GC-IRMS) (Wernig et al., 2018) and GC interface with multiple-collector inductively coupled plasma MS (GC-MC-ICPMS) (Renpenning et al., 2018) help to distinguish the resources and physiochemical process of analytes. With the expected development of the micro-electro-mechanical system (MEMS) and sensor technology, the terminal devices will be much smaller and lighter, and will have stronger integration, higher sensitivity, and lower energy, thus making it possible to have more reliable and precise environmental data compared to the data from nearby weather stations or manual measurements.

Samplers are often deployed and retrieved via manual operation in general indoor and outdoor sampling. However, it is not always easy and convenient to operate at some special monitoring sites; e.g., a stack or a ventilating duct. Through new intelligent devices such as unmanned aerial vehicles (UAVs) (Watts et al., 2012; Brady et al., 2016) and sampling robots (Nee et al., 2015; Rea and Ottaviano, 2018), it is much easier to bring the PASs to the destination via remote control. Although attention should be paid to the effect on samplers from the device itself, such as turbulent airflow from UAVs, these devices are considered as highly efficient assistant tools for PASs.

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