

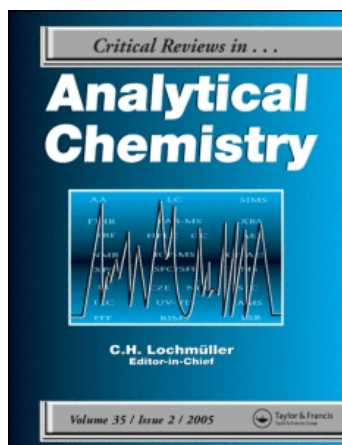
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Application of Passive Samplers in Monitoring of Organic Constituents of Air

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The principles of passive dosimetry, which has been known for over 100 years, are finding an ever increasing use in analytical practice and are being used as a convenient technique for isolation and enrichment of analytes from various environmental media. Due to its simplicity, a variety of designs, as well as the possibility of using a number of different final determination techniques, passive dosimetry has been applied in the analysis of organic and inorganic air pollutants, both in the outdoor and the indoor and workplace atmospheres, as well as in the monitoring of water and soil pollution. This paper is an attempt to review the designs of existing passive samplers, the media used to trap analytes and the techniques used for the release of the trapped analytes and their final determination.

Keywords passive sampling, dynamic sampling, air pollutants, organic compounds, air monitoring

INTRODUCTION

The control of air quality is an essential problem, whose theory and practice are being dealt with by a large number of scientists all over the world. Due to the fact that air pollutants, in both outdoor and indoor air, are present at very low concentrations, their isolation and enrichment is an important step in the analytical procedures for their determination. The existing isolation/enrichment techniques can be classified into three main categories (1):

1. Dynamic enrichment—based on forced (by means of pumps or aspirators) passing of a gas stream through a properly designed container filled with a solid or liquid sorbent. The desired components of the gas are retained (enriched) in the container due to physical or chemical sorption. Thus trapped analytes are next released and determined. The exact volume of the gas passed through the container and the sampling time have to be known to calculate the concentration of the analyte in the gas. Hence, the setup for dynamic enrichment has to be equipped with the device measuring the volume of the gas passed (2–4);

2. Denudation enrichment—is a combination of dynamic passing of a gas sample through a tube (or set of tubes) and diffusion of analytes from the gas stream to the surface of the wall coated with a trapping medium (5, 6); and
3. Passive enrichment—analyte enrichment in a passive sampler results from diffusion (diffusive samplers) or permeation (permeation samplers) of analytes from the immediate surroundings to the inside of the sampler and trapping them on the surface or in the bulk of a suitable trapping medium. In this case, the movement of molecules is effected by diffusion and, therefore, no additional devices for collecting air samples or measuring their volume are necessary. After releasing the analytes, their concentration can be calculated from a known exposure time and a previously determined calibration constant, characteristic of a given sampler and analyte (2, 7, 8).

The use of passive dosimetry during the sample collection step offers a number of advantages when compared with dynamic techniques. These include elimination of portable pumps and aspirators and their power supplies as well as gas meters or flow meters. Passive enrichment is suitable for the determination of average long-term concentration, and relatively small and simple passive samplers can be left unattended for the entire exposure period. The applicability of passive sampling is illustrated in Figure 1, while Table 1 compiles its advantages and shortcomings. The scope of this paper is limited to the

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TABLE 1
Advantages and shortcomings of passive dosimetry

Passive dosimetry	
Advantages	Shortcomings
• small, simple and light devices • elimination of pumps and power supplies • possibility of determination of time-weighted average concentration based only upon exposure time, without knowledge of sample volume • suitability for long-term collection of samples of analytes	• unsuitable for monitoring of short-term variations in analyte concentration • lower enrichment efficiency compared to dynamic techniques • sensitivity of enrichment efficiency to temperature fluctuations and air movement in the vicinity of a sampler • the need to determine enrichment factors for individual analytes • “historical” nature of results • impossible (in most cases) to automate

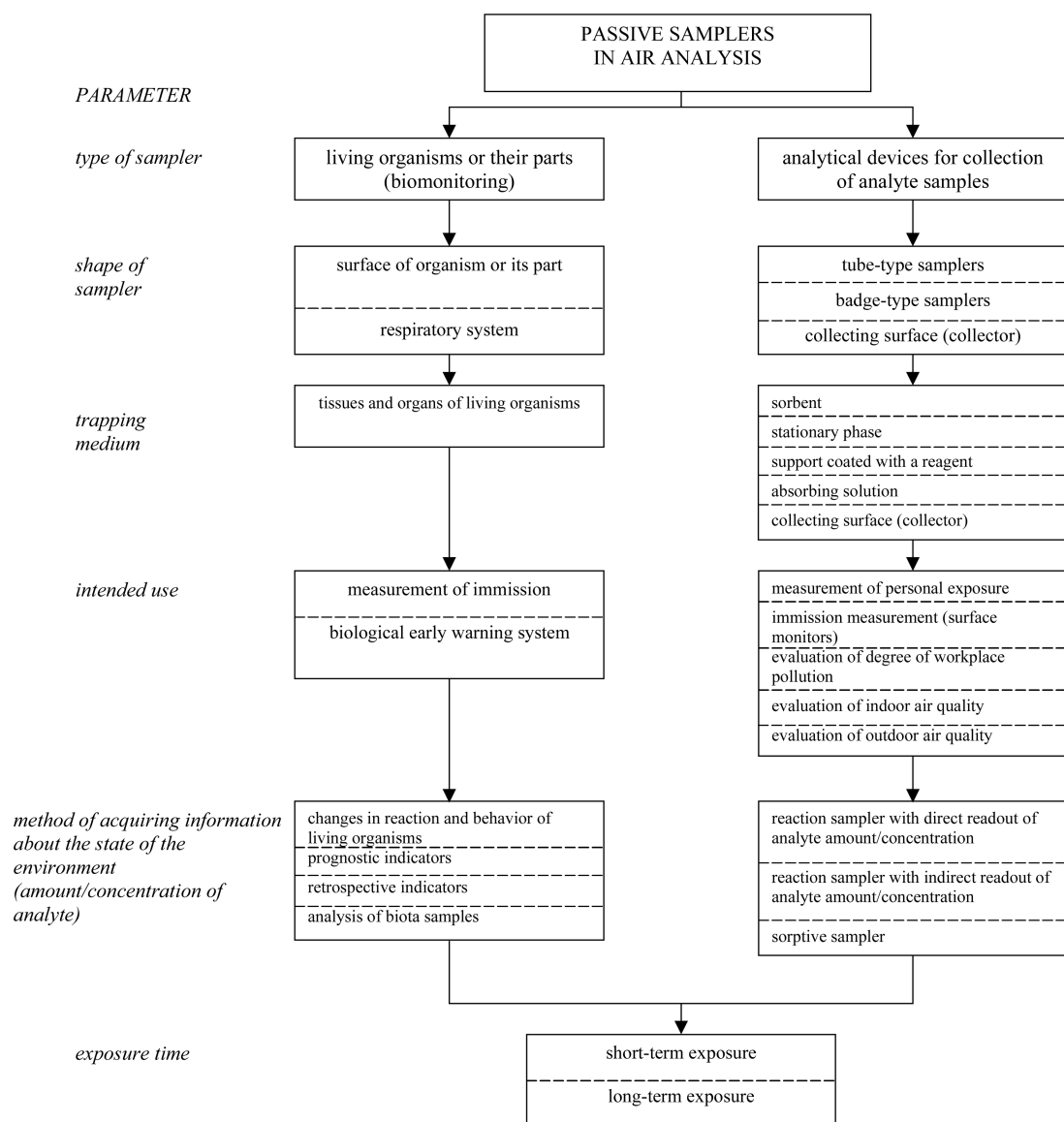


FIG. 1. Applicability of passive dosimetry in air monitoring.

application of passive samplers as a specific group of devices used for the collection of a variety of air components.

The problem of using living organisms both as components of Biological Early Warning Systems (BEWS) and as so-called integrated samplers for the collection of outdoor air components has been discussed in a number of reviews and monographs (9–14).

THEORY OF PASSIVE DOSIMETRY

The principle of operation of passive samplers is based upon mass transport, described by Fick's first law of diffusion. Passive samplers fall into one of the two categories, depending on the type of diffusion barrier used: diffusive passive samplers or permeation passive samplers.

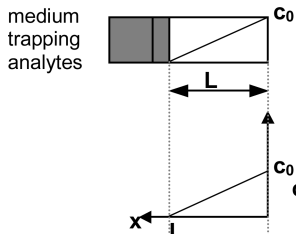
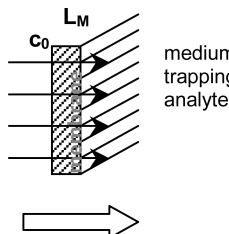
In diffusive passive samplers the transport of analytes takes place by way of free diffusion of the analyte through a gas layer whereas in permeation devices the transport of analytes takes place by way of permeation of the analyte through a semipermeable membrane. A detailed description of the operation of passive of passive samplers can be found in the available literature (7, 15–18), while a brief summary is compiled in Table 2.

To calculate the airborne concentrations of analytes in a real environment using passive devices on the basis of the amount

of analyte trapped in the sorption bed, the knowledge of parameters responsible for the rate of analyte collection from the gaseous phase is necessary. In the case of diffusive sampling, this parameter is sampling rate (*SR*), whereas in the case of permeation passive sampling this parameter is calibration constant (*k*). There are two approaches to the problem of calibration of passive devices. The first one is theoretical, based on finding the values of diffusion coefficient of the analyte (in case of diffusive sampling) or the permeability coefficient of the analyte and Henry's law constant (in the case of permeation sampling) in the literature (tables and physicochemical data) and accurately determining geometrical parameters of a sampler (cross-sectional area of the sampler and length of the diffusion path) or membrane thickness and area. The experimental approach involves experimental determination of sampling rate or calibration constants based on the exposure of the sampler to standard gas mixtures in exposure chambers.

Passive dosimetry was first used in 1853 by the Swiss chemist Schönbein. He tried to detect the presence of ozone in outdoor air using a strip of filter paper saturated with potassium iodide (19). The next application of passive dosimetry took place in 1927, when a passive sampler was used to determine carbon monoxide in air. However, these attempts were at best semi-quantitative (20). The true growth of passive dosimetry as an

TABLE 2
Comparison of principle of operation of diffusive and permeation passive samplers

	Diffusive passive sampler	Permeation passive sampler
Phenomenon used for mass transport of analytes	Diffusion	Permeation
Principle of operation of passive sampler		
Equation describing the rate of transport of analyte toward the trapping medium in a sampler	$U = \frac{DA}{L}(C_0 - C)$	$U = SA \frac{(p_1 - p_2)}{L_M}$
Equation describing the amount of analyte retained in the trapping medium in a sampler (for a given exposure time— <i>t</i>)	$M = \frac{DA}{L}C_0t$	$M = U \cdot t$ $M = \frac{SAa}{L_M}C_0t$
Expression describing the rate of collection of analyte from the air by a passive sampler	$\frac{DA}{L} = (SR)$	$k = \frac{L_M}{SAa}$
Equation allowing to calculate the analyte concentration in the air during the sampler exposure	$C = \frac{(SR)M}{t}$	$C = \frac{kM}{t}$

c—analyte concentration inside diffusion zone of a sampler [mol·cm⁻¹]; *A*—cross section of diffusion zone [cm²];

*c*₀—ambient concentration of analyte [mol·cm⁻¹]; *L*—length of diffusion zone [cm];

S—analyte permeability coefficient dependent on the membrane material [cm²·min⁻¹]; *U*—diffusional mass-transfer rate of analyte [mol·s⁻¹]; (*p*₁–*p*₂)—difference in partial pressure of the analyte on both sides of the membrane;

*L*_{*M*}—membrane thickness [cm]; *SR*—sampling rate [cm³·min⁻¹]; *k*—calibration constant [cm³·min⁻¹].

analyte enrichment technique dates back to 1973 (15). Since then, a number of reviews and monographs have been published and a variety of designs allowing isolation and/or enrichment of numerous organic as well as inorganic analytes have been proposed.

During this period of rapid development many sampler designs were proposed. Some of them have only been used in laboratory experiments; others are used by the designers of the sampler alone. Still other samplers have been patented and are now available commercially.

The primary problem in practical use of passive dosimetry for the isolation and enrichment of analytes from the gaseous medium is the selection of an appropriate trapping medium, which ensures complete retention of the analytes from the gas matrix. The following criteria should be taken into consideration in the selection of a trapping medium (3, 7): strength of interactions between the trapping medium and the analyte, affecting both the sorption and release of the analytes from the trapping medium in order to carry out the final determination; and cost and ease of utilization of the sorptive medium used.

The process of analyte enrichment from the gaseous phase, i.e., the efficiency of a passive sampler, can be influenced by a number of physicochemical factors. This interference can take place at every step of use of samplers, including sampler storage, exposure, storage after exposure and release of the retained analytes. Consequently, passive samplers are calibrated in specially designed exposure chambers under conditions simulating real exposure. Exposure chambers are used to test samplers under simulated field conditions, such as different temperature, variable concentration of the analyte, different wind velocity and relative humidity to evaluate the effects of these parameters on the performance of passive samplers (15, 21, 22).

DESIGN OF SAMPLERS AND THE USE IN MONITORING OF VOLATILE ORGANIC COMPOUNDS

The trapping medium is the most important element of the sampler, determining its suitability for the monitoring of air pollution by organic compounds. It should be emphasized, however, that the use of each of the medium type mentioned here entails both advantages and shortcomings at both the enrichment and the analyte release step. Due to its excellent adsorption properties for hydrocarbons and its high adsorption capacity, charcoal is the most frequently used adsorbent in passive sampling. Different types of passive samplers packed with charcoal as adsorbent are commercially available and have been used for the determination of environmental VOC concentrations in indoor and outdoor air such as OVM 3500 (by 3M), ORSA 5 (by Drägerwerk), PRO-TEK G-AA (by Dupont), PRO-TEK G-BB (Dupont) and Gasbadge (National Mine Service).

Depending on the type of trapping medium used, the release of trapped analytes is carried out either by solvent extraction or by thermal desorption. It should be pointed out that in some designs the body of sampler is at the same time an extraction

vial, which eliminates losses associated with the transfer of a trapping medium to the extraction container.

The design of samplers, the techniques used at the isolation and enrichment steps, and the techniques of release of compounds trapped in a sampler prior to their final determination are summarized in Table 3. We realize that the information on the various types of samplers is very variable with regard to the amount of detail given. As in any review based upon the published literature, there are omissions of relevant data, and we could only abstract the information given on the design and procedure for using samplers.

SPME fibers have also been used as passive samplers (37), but their application is limited to a short time of exposure under real conditions, sometimes to a few seconds. Samplers intended for dynamic sampling of analytes from gas samples have also found use in passive sampling with slight modifications only; such an approach was taken by Shinohara et al. (86) in 2004. The authors used a commercially available active carbonyl cartridge, which was originally and exclusively designed as an active sampler.

Passive sampling technique is used for different gaseous environments such as indoor, outdoor and workplace for different types of volatile organic compounds. Table 4 summarizes application of those devices for different environments and monitored analytes.

COMPARISON OF THE PERFORMANCE OF PASSIVE SAMPLERS WITH OTHER TECHNIQUE USED FOR VOLATILE ORGANIC COMPOUNDS IN MONITORING VARIOUS ENVIRONMENTS

The theory states that many of the factors that influence the performance of a diffusive sampler are functions of the sampler design, and affect the sampling of all chemicals. The data obtained from passive samplers have to be reliable and credible. The simplest way of verification of the obtained results involves comparing the data obtained using passive devices with those obtained by a reference method. The most common reference technique for passive sampling is the dynamic technique in which a specific volume of air to be sampled is pumped through sorption tubes (filled with an appropriate sorption medium). The validation criteria are published by NIOSH, Health & Safety Executive (HSE) (103) and Comité Européen de Normalization (CEN) European protocol (EN 838) (104). The criteria are as follows:

- (1) analytical recovery,
- (2) sampling rate and capacity,
- (3) reverse diffusion,
- (4) temperature effects,
- (5) factor effects,
- (6) storage stability, and
- (7) precision and accuracy (105).

The NIOSH protocol calls for a combined precision and accuracy within 25% of true value, 95% of the time. The European

TABLE 3
Passive samplers used in air monitoring and methods of desorption and final determination of compounds trapped

Type of passive sampler	Design and remarks	Analytes	Desorption	Method of final determination/Remarks
Group of OVM Samplers 3520 [21, 23–25], 3500 [26–36], 3551 [37]	The organic vapor monitor (OVM) (introduced by 3 M, Neuss, Germany) is a badge-type passive permeation sampler consisting of a permeable membrane and an activated-charcoal pad (180 mg) assembled in a disk-shaped plastic holder. The cross-sectional area through which diffusion occurs is $\sim 7.07 \text{ cm}^2$, the diffusion distance (length) is $\sim 1 \text{ cm}$. The sampler is also the extraction vessel—following exposure the protective membrane can be removed and replaced by a septum through which a solution extracting the analytes can be injected. Model 3520 contains a backup section of the sorbent.	A wide variety of volatile organic pollutants	– aliquot of 2:1 v/v acetone/ CS_2 . Extraction was completed by sonication – CS_2 containing 1% methanol – CS_2 added to vial; capped vials, placed in an ice water bath and sonicated for 40 minutes – acetonitrile/mixed solvent of 95:5 (v/v) dichloromethane and methanol – 10% methylene chloride in methanol	GC-MS with capillary column (Rtx-1— $60 \text{ m} \times 0.25 \text{ mm}$, Rtx-1— $60 \text{ m} \times 1 \text{ mm} \times 0.25 \text{ }\mu\text{m}$, Rtx-1— $60 \text{ m} \times 0.32 \text{ mm} \times 1.0 \text{ }\mu\text{m}$, HP #19091R-319— $90 \text{ m} \times 0.32 \text{ mm} \times 1.8 \text{ }\mu\text{m}$, Rtx-1— $60 \text{ m} \times 0.25 \text{ mm} \times 1 \text{ }\mu\text{m}$, DB-225— $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) GC-FID/ECD with two capillary columns: PVM5/5 ($50 \text{ m} \times 0.32 \text{ mm} \times 1.0 \text{ }\mu\text{m}$) and DMS ($50 \text{ m} \times 0.32 \text{ mm} \times 1.0 \text{ }\mu\text{m}$); GC-FID/FID connected via a Y-connector at a ratio 1:1 onto two columns of different polarity: DB-1701 ($60 \text{ m} \times 0.32 \text{ mm} \times 1 \text{ }\mu\text{m}$) and DB-5 ($60 \text{ m} \times 0.32 \text{ mm} \times 1 \text{ }\mu\text{m}$) GC-FID using aluminum oxide column PLOT $\text{Al}_2\text{O}_3/\text{KCl}$ ($50 \text{ m} \times 0.32 \text{ mm}$) or with megabore column DB-WAX ($30 \text{ m} \times 0.53 \text{ mm} \times 1 \text{ }\mu\text{m}$) GC with tandem FID-ECD system equipped with two capillary columns: DB-5 ($60 \text{ m} \times 0.32 \text{ mm} \times 1 \text{ }\mu\text{m}$) and DB-1701 ($60 \text{ m} \times 0.32 \text{ mm} \times 1 \text{ }\mu\text{m}$) GC with tandem FID-ECD system equipped with two capillary columns: DB-5 ($60 \text{ m} \times 0.32 \text{ mm} \times 1 \text{ }\mu\text{m}$) and DB-1701 ($60 \text{ m} \times 0.32 \text{ mm} \times 1 \text{ }\mu\text{m}$) HS-GC-FID (or ECD), fused silica capillary column SE 30-30 m GC-MS, Rtx-volatiles ($30 \text{ m} \times 0.32 \text{ mm} \times 1.5 \text{ }\mu\text{m}$) capillary column
ORSA-5 [28, 38–42]	Diffusive, tube-type sampler, open on both sides, commercially produced by National Dräger. The sorbent is granulated active charcoal (300–400 mg). Small value of sampling rate and high sorption capacity of the sorbent used indicate that the sampler could be utilized for exposure under conditions of high concentrations of compounds and longer sampling times. The sampler is suitable for: – personal monitoring – indoor air quality control – atmosphere monitoring It can also be used for the active enrichment of pollutants.	CH_2Cl_2 , CHCl_3 , CCl_4 , benzene, toluene, ethylbenzene, m-, o-, p-xylenes	– CS_2 , – benzyl alcohol	

(Continued on next page)

TABLE 3
Passive samplers used in air monitoring and methods of desorption and final determination of compounds trapped (*Continued*)

Type of passive sampler	Design and remarks	Analytes	Desorption	Method of final determination/Remarks
TOPAS—badge-type sampler [43]	Prototype of sampler combines the advantages of the passive sampling of badge-type passive samplers with thermal desorption for sample transfer to the gas chromatography system. The TOPAS system consists of basic aluminum body with its spiral-shaped groove. This groove contains the adsorbent (Tenax). The entire surface of the groove represents the diffusion cross section and is thus used for sampling. A microporous Teflon membrane assures a pure diffusion-controlled enrichment of the analytes. A diffusion cross section is about 5.25 cm². With this new badge geometry, high sampling rates equivalent to 3 L/h for volatile aromatic and halogenated hydrocarbons were achieved. For thermal desorption, the badge is set membrane-side down in the holder. Desorption gas inlet and outlet are located on the reverse of the badge. Only the narrow cross-section of the groove is used for desorption, ensuring a complete flow-through of the adsorbent bed and thus a complete sample transfer.	Toluene, propylene glycol, butyl acetate, chlorobenzene, ethylbenzene, m-,p-xylene, o-xylene, butyl glycol, benzothiazole, 2,2,4,6,6-pentamethylheptane, 2,2,6,6,6-tetramethyl-4-methyleneheptane, 2,2,4,6,6-pentamethyl-3-heptene, limonene, 2-ethylhexanol, butylbenzene, butyl glycol acetate, dodecane, butyl diglycol, tridecane, phenoxyethanol, tetradecane, butyl-diglycol acetate, longifolene, caryophyllene, cyclohexanone,	Thermal desorption system	GC-MS with HP-642 (30 m × 0.25 mm × 1.4 μm)
Pro-Tek G-AA, G-BB sampler [42, 44]	Diffusive sampler; badge-type, is manufactured by Du Pont. It is equipped with two diffusion elements (perforated plates with 1-mm diameter and 3.5-mm depth holes) placed on each side of the sorbent pad. This design of sampler minimizes convective air flow inside the sampler. Two tight covers are protecting the sampler. Sampler has a high sampling rate due to its wide cross-section area—can be opened on one or both sides. Active charcoal is used in the form of pressed stripes (approximately 300 mg). The rate of diffusion can be adjusted to some extent by removing one or both covers.	CH₂Cl₂, CHCl₃, CCl₄	benzyl alcohol	HS-GC-FID (or ECD), fused silica capillary column SE 30-30 m

G-BB is suitable for exposure at high analyte concentrations. It is designed similarly to charcoal tubes—the analyte diffuses through a diffusive layer to a charcoal layer, which in turn is separated by another diffusion layer from a second, backup charcoal layer.

Sampler is commercially available. High sampling rates for the analytes and relative low adsorption capacity of the sampler indicate that the sampler should be used for short-term sampling.

Sampler is suited for:

- personal monitoring
- area monitoring

Analyst [45–51]

Sampler is commercially available from Marbaglass (Marbaglass s.n.c., Rome, Italy). The diffusive, badge-type sampler consist of a glass cylinder (20 mm ID × 20 mm diffusive path length)

closed at the base and threaded near the opening for the plastic screw on top, which is perforated in the center with the rubber-Teflon septum. The adsorbent situated on the bottom within a stainless steel viewing ring, is active charcoal in grains with a high surface (1000 m²/g).

Due to the large amount of the charcoal bed (about 400 mg) the sampler can be used for long-term monitoring. A removable stainless-steel mesh grid, placed in an aluminum ring, is screwed on the top end of device during the sampling to avoid additional effects of eddy diffusion. It was subjected to a clean-up treatment in order to eliminate interferences. The device has been planned to be used also as an “extraction vial”, so that further transfer and manipulation of the adsorbent would be not necessary.

Due to the large amount of the charcoal bed (about 400 mg) the sampler can be used for long-term monitoring.

Benzene, toluene, ethylbenzene, xylenes

– CS₂
– benzyl alcohol

GC-FID with a capillary column HP FFAP (50 m × 0.32 mm × 0.25 μm)
GC-FID with SPB-5 (30 m × 0.32 mm × 0.25 μm)

GC-FID capillary column “Vocol” (30 m × 0.32 mm × 3 μm); 10% of samples was analyzed by GC-MS

GC-FID no data about capillary column
Extracted with benzyl alcohol

(Continued on next page)

TABLE 3

Type of passive sampler	Design and remarks	Analytes	Desorption	Method of final determination/Remarks
Radiello [22, 46, 52–59]	Diffusive sampler with radically changed diffusive path geometry. The diffusive surface is a synthesized, microporous, high-density polyethylene cylinder, 50 mm long; 1.75 mm wall thickness, 20–30 μm pore size, 37–45% void volume. In the center of the bottom cap are two seats, one concave and other convex, to facilitate centering sorbing cartridges. The top cap is tube-shaped to allow introduction of the sorbing cartridge and insertion into the sealing of a supporting plate. This is a plane cellulose acetate equilateral triangle, equipped with an attaching clip.	Benzene, butanol, butyl acetate, 2-buthoxyethanol, 2-buthoxyethyl acetate, cyclohexane, cyclohexanone, decane, dichloromethane, 1,2-dichloropropane, 2-ethoxyethanol, 2-etoxyethyl acetate, 1-ethoxy-2-propanol, ethyl acetate, ethylbenzene, heptane, n-hexane, isobutanol, isobutyl acetate, isooctane, isopropanol, isopropylbenzene, methyl ethyl ketone, methyl isobutyl ketone, 1-methoxy-2-propanol, octane, pentane, styrene, tetrachloroethylene, toluene, 1,1,1-trichloroethane, trichloroethylene, xylenes, formaldehyde, acetaldehyde, pentanal, hexanal	- dichloromethane - CS_2	GC-MS, 6 column tested: CP-Sil 8 (10 m $\times$ 0.53 mm $\times$ 1 μm), CP Wax 52 (10 m $\times$ 0.53 mm $\times$ 1 μm), CP Wax 52 (10 m $\times$ 0.53 mm $\times$ 2 μm), CP Wax 57 (10 m $\times$ 0.53 mm $\times$ 1 μm), CP Wax 57 (15 m $\times$ 0.53 mm $\times$ 1 μm), ChiraSil Dex (10 m $\times$ 0.53 mm $\times$ 1 μm) GC-FID, capillary column SP-Octyl (60 m $\times$ 0.24 mm $\times$ 1 μm)
Perkin-Elmer tubes [60–74]	The adsorbing cartridges are stainless steel net cylinders, 60 mm long, 100-mesh size, and 0.1 mm wire diameter, sealed at the ends by two stainless steel net cups. The sorbent is usually active charcoal (530 $\pm$ 30 mg, 35–50 mesh), but could be modified and use DNPH-coated cartridges (for aldehyde determination). One advantage of this type of sampler is that it can also be used for active sampling.	Benzene, toluene, o-, m-, p-xylene, styrene, ethylbenzene, propylbenzene, ethyltoluenes, trimethylbenzenes, methyl <i>tert</i> -butyl ether	Thermal desorber Automatic thermal desorption injector, desorption temperature 250°C for 10 min with a desorption flow of 30 ml/min (helium)	GC-MS with HP-1 capillary column (60 m $\times$ 0.25 mm) GC-FID with HP-5 (30 m $\times$ 0.32 mm $\times$ 0.25 μm), HP Ultra 2 (50 m $\times$ 0.2 mm $\times$ 0.33 μm), BP 10 (25 m $\times$ 0.22 mm $\times$ 0.25 μm) or CP-Sil 5CB (50 m $\times$ 1.2 μm)

GABIE sampler [75–76]	Sampler designed by INRS, manufactured and marketed by Arelco, France. Badge-type, diffusive sampler has geometric surface of 7 cm ² and contains 550 mg of coconut charcoal sorbent.	Volatile organic compounds	CS ₂ , shaken for 30 min	GC-FID with silica column SPB-TM1 (60 m × 0.53 mm × 1.5 μm)
SKC 575 sampler [59, 77–80]	Diffusion type sampler, commercially available. It is made in such a way that the desorbing solvent can be added directly to the sampler when analysis starts.	α-pinene, β-pinene, δ-carene, benzene, toluene, xylenes	CS ₂ ,	GC-FID, capillary column SE-30 (25 m × 0.32 mm) or capillary column DB-624 (30 m × 0.318 mm × 1.8 μm)
Shibata glass-tube sampler [81–84]	Tubes available commercially (Shibata Scientific Technology, Tokyo) consisting of granular activated carbon (20–40 mesh) packed inside of porous polytetrafluoroethylene tubes. The net collection length and the amount of adsorbent are standardized at 30.30 ± 0.37 mm and 1944 ± 3.8 mg, respectively.	Benzene, toluene, m-p-xylene, o-xylene, dichloromethane, chloroform, bromodichloromethane, bromoform, 1,1-dichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, 1,2-dichloroethane, trichloroethylene, tetrachloroethylene, o-, m- and p-dichlorobenzene, hexachloro-1,3-butadiene	– CS ₂ – toluene – distilled water	GC-FID, with DB-VRX capillary column (75 m × 0.45 mm × 2.55 μm) GC-ECD, the chromatographic column for p-dichlorobenzene was 10%PEG20M (3.1m × 3.2 mm), for other chlorinated VOC was 20% silicone DC550 (3.1m × 3.2 mm) GC-EDC, VOCOL fused silica capillary column (60 m × 0.32 × 3 μm) Spectrophotometry after specific reaction
LiPS (Liquid Passive sampler) [85]	Prototype of diffusive type sampler. The collection part (3.5 cm length, 0.9 cm diameter) and the diffusion layer (3.2 cm length, 0.59 cm diameter) are made of Teflon. 2 ml of distilled water is placed in the sampler before sampling. Organic vapors diffuse through the diffusion layer, pass the Teflon filter, and are absorbed by the water. After sampling is completed, the distilled water in the sampling port is collected in a vial for a gas chromatographic analysis. By using liquid as the absorbent, the problem with desorption of enriched analytes is omitted.	N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC)	—	GC-MS for N,N-dimethylformamide GC-FTD ¹ for N,N-dimethylacetamide; capillary column DB-WAX (30 m × 0.26 mm × 0.5 μm)

(Continued on next page)

TABLE 3
Passive samplers used in air monitoring and methods of desorption and final determination of compounds trapped (*Continued*)

Type of passive sampler	Design and remarks	Analytes	Desorption	Method of final determination/Remarks
Sampler constructed in Sep-Pak XpoSure active DNP cartridges [56, 86]	Active Sep-Pak XpoSure cartridges (commercially available, Waters Ltd.) are used as passive devices without any modification. The sampler is composed of adsorption material, gas inlet tube (20.8 mm length $\times$ 2 mm ID) and gas outlet tube (8.2 mm length $\times$ 4 mm ID), and polyethylene filters. DNP-coated silica gel, a specific adsorbent for carbonyl substances, is packed in the cartridge (10 mm $\times$ 10 mm) as an adsorption material. The net amount of DNP in the cartridge is 1mg. Both sides of the cartridge are connected to plastic tube for sampling.	Formaldehyde, acetaldehyde, acetone, propionaldehyde	Acetonitrile	HPLC with a photo diode array detector and packed column of XBD-C18 (250 mm $\times$ 4.6 mm $\times$ 5 μ m)
DSD-DNP [87–89]	The sampler, commercially available from Supelco, consists of three parts: porous polyethylene tube, reservoir made of polyethylene tube and DNP-coated silica gel. The porous tube is made of sintered polyethylene particles with 34.4% of porosity and works as a diffusion filter. The polyethylene tube is used for the reservoir of the adsorbent when eluting DNP derivatives by passing extraction solvent (acetonitrile). Amount of DNP is 1mg (2mg) per sampler. The modification of this sampler is using two porous polyethylene tubes, serially connected. Amount of DNP is 2mg per sampler in this case.	Glutaraldehyde, formaldehyde	Acetonitrile	HPLC with UV-VIS detector and column Intertsil ODS-8A (150 mm $\times$ 4.6 mm $\times$ 5 μ m)
	Sampler developed by Swedish Institute for Working Life, commercially available from SKC is designed for sampling of reactive compounds using reagent-coated filters. The diffusive-type sampler with the housing (with dimensions of 86 $\times$ 28 $\times$ 9 mm) made of polypropylene. Two impregnated filters are placed beneath a 2.9 mm thick screen. The part of the screen covering		Acetonitrile	HPLC with UV-VIS detector and column Discovery RP Amide C16 (250 mm $\times$ 4.6 mm $\times$ 5 μ m)
GMD sampler, later UME $\times$ 100 Sampler [90–94]		Methylamine, allylamine, isopropylamine, n-butylamine, dimethylamine	Acetonitrile	HPLC/fluorescence detection or LC-LC-MS analysis LC-MS/MS HPLC-UV, Zorbax ODS C18 (25 m $\times$ 4.5 mm)

the sampling filters comprises 112 holes

within a total area of 20×20 mm and

with a diameter of 1.0 mm for each hole.

A sliding cover was used to seal the holes

when the sampler was not in use. The

second filter is a control filter (as blank).

Above the screen is a sliding cover, used

for sealing the holes when the sampler is

not in use. Filters are impregnated with

proper sorption medium—depending on

type of sampled analyte.

Badge-type sampler equipped with PDMS

membrane protected on the outside from

mechanical damage by stainless steel

screen. The sorbent bed used is active

charcoal (20–40 mesh, about 200 mg),

which is placed directly behind the

membrane. The sampler is sealed on the

side of real atmosphere with a tight

polyethylene cap.

The new diffusive badge-type sampler,

designed to have a large exposure area

and compatible with thermal desorption.

As the sampler holder in this study, the

OVM 3500 cartridge was used. The

cross-sectional area through which

diffusion occurs is 7.07 cm^2 and the

diffusion distance is 1 cm. The new

adsorbent disk for thermal desorption

was made by packing of Carbopack B

(60–80 mesh, 50 mg) between two glass

fiber filters.

Prototype of sampler consists of a 2 ml

capacity, amber glass vial containing a

200 ml capacity glass insert, which in

turn contained a carbonaceous adsorbent

disk at bottom of insert. The adsorbent

disk ($6.67 \pm 0.15 \text{ mg}$, $3.5 \pm 0.1 \text{ mm}$ in

diameter, $0.7 \pm 0.05 \text{ mm}$ in thickness) is

cut from the activated charcoal cloth.

Permeation type sampler
[15, 16, 95–98]

Thanks to new approach
to the calibration

problem—wide spectrum

of volatile organic

compounds

GC-FID with DB-1 ($30 \text{ m} \times 0.32 \text{ mm} \times$
 $1 \mu\text{m}$)

Diffusive sampler for
thermal desorption [99]

Benzene, toluene,

ethylbenzene, m-,

p-xylene, o-xylene,

styrene

Thermal desorption apparatus

of special (badge)

construction, temperature of

desorption 250°C , 20 min at

50 ml/min (Helium)

GC-MS, DB-624 ($60 \text{ m} \times 0.25 \text{ mm} \times$
 $3 \mu\text{m}$)

Sampler developed by
Otson [100]

n-hexane, chloroform,

benzene,

trichloroethylene,

toluene,

tetrachloroethylene,

ethylbenzene,

(p,m)-xylene, o-xylene,

m-dichlorobenzene,

GC-MS, DB-624 ($60 \text{ m} \times 0.32 \text{ mm} \times$
 $1.8 \mu\text{m}$)

$30 \mu\text{l CS}_2$ added *in situ* to vial

(Continued on next page)

TABLE 3
Passive samplers used in air monitoring and methods of desorption and final determination of compounds trapped (*Continued*)

Type of passive sampler	Design and remarks	Analytes	Desorption	Method of final determination/Remarks
STB diffusive sampler [101]	One advantage of the prototype method is its lower cost compared to other commercially available passive samplers. In addition, the amount of potentially hazardous CS₂ used for the method is considerably less than that required for the OVM3500 method, and sample preparation is limited to the addition of CS₂ to the sampler. Use of the prototype sampler would be most practical and cost-effective for large air quality surveys, especially for exposure/workplace monitoring. Although detection limits can be improved by increasing the sampler exposure time, the potential for adsorbent saturation should be considered if VOC concentrations are too high. A standard stainless steel tube badge (STB), (6.3-mm o.d. $\times$ 0.5-mm i.d. $\times$ 90 mm length), packed with Carbopack X (650 mg). The STB is designed for a low diffusive sampling rate that is consistent with a small exposed adsorbent area, and a long diffusion channel (1.5 cm). Specially designed PTFE caps were used to seal the STBs during storage prior to analysis in the laboratory. Swagelok fittings with Teflon ferrules are used to seal the tubes during long storage times (days to weeks).	<i>p</i>-dichlorobenzene, naphthalene, 1,2-dichloroethane, styrene, α-pinene, 1,1,2,2-tetrachloroethane, <i>n</i>-decane, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, pentachloroethane, δ-limonene, <i>p</i>-cymene, hexachloroethane, 1,2,4-trichlorobenzene	Thermal desorption	GC-MS
TK-200 [102]	Sampler is commercially available (Zambelli, Barante, Milan). The mean recovery at three different styrene concentrations ranged from 94 to 103%. The coefficient of variation based on 10 determinations was 4.2%.	Styrene	CS ₂ and kept at room temperature (20°C) for 1 h, during which time it was periodically shaken	GC-MS, capillary column cross-linked 5% phenyl methyl silicone (25 m $\times$ 0.2 mm)

¹FTD—Flame Thermionic Detector.

TABLE 4
Semivolatile organic compounds monitored in air using passive samplers for the analyte collection

Sampler type and description	Group of analyte	Desorption mode	Monitoring site and time	Method of final determination
Tristearin-coated fiberglass sheets [113] The fiberglass cloth (200 g/m ²) was cut into 250 mm × 500 mm rectangles (=0.125 m ² interfacial surface area for each side). Adjustable stainless-steel frames (0.5 m × 0.5 m) were made and a container with open sides but which sheltered the samplers from rain and direct sunlight was designed. The container had a capacity of four frames, and thus could hold eight samplers at a time. Tristearin was selected as the sorption phase since it was readily available as a pure compound, is a solid at ambient temperature (as are cuticular waxes), yet can be readily applied to the fiberglass. Stir bar sampler [139, 140] Prototype of sampler was prepared from LDPE membrane tubing (4.0 mm × 4.5 mm; wall thickness of 250 μm) enclosing a Twister bar acting as solid medium. The Twister is a stir bar (14 mm length) consisting of a glass-coated magnetic core with a layer of PDMS. The PDMS sorptive layer is 500 μm thick with a volume of about 24 μl. The length and effective membrane surface areas of the LDPE tubing were 20 mm/2.8cm ² . The LDPE tubing with the receiving medium inside was heat-sealed at each end. Silicone tubing sampler [139, 140] Prototype of sampler was prepared from LDPE membrane tubing (4.0 mm × 4.5 mm; wall thickness of 250 μm) enclosing silicone tubing (3.0 mm × 3.6 mm, wall thickness 300 μm, 80 mm length and volume about 250 μl) acting as a solid medium. The length and effective membrane surface areas of the LDPE tubing were 85 mm/12.08 cm ² . The LDPE tubing with the receiving medium inside was heat-sealed at each end.	PAHs	Extraction with hexane	1-40-day exposure, September 1995–June 1996, Australia and Germany, outdoor air	GC-ITD1, DB-5 (30 m × 0.25 mm × 0.25 μm) GC-MS, DB-5MS (30 m × 0.25 mm × 0.25 μm)
	Pesticides, PCBs, PAHs	Thermal desorption at 250°C for 4 min at helium flow rate 50 ml/min	Laboratory evaluation and field tests (on-site exposure September-October 2001 in a disused waste dump for chemical industry (Germany))	GC-MS, HP-5 MS capillary column (30 m × 0.25 mm × 0.25 μm)
	Pesticides, PBBs	Thermal desorption	November 2002, atmospheric air, landfill “Grube Antoine”	GC-MS, HP-5 MS capillary column (30 m × 0.25 mm × 0.25 μm)
	Pesticides, PCBs, PAHs	Thermal desorption at 250°C for 4 min at helium flow rate 50 ml/min	Laboratory evaluation and field tests (on-site exposure September-October 2001 in a disused waste dump for chemical industry (Germany))	GC-MS, HP-5 MS capillary column (30 m × 0.25 mm × 0.25 μm)
	Pesticides, PBBs	Thermal desorption	November 2002, atmospheric air, landfill “Grube Antoine”	GC-MS, HP-5 MS capillary column (30 m × 0.25 mm × 0.25 μm)

(Continued on next page)

TABLE 4
Semivolatle organic compounds monitored in air using passive samplers for the analyte collection (*Continued*)

Sampler type and description	Group of analyte	Desorption mode	Monitoring site and time	Method of final determination
PUF sampler [116–118, 120] Polyurethane foam discs (14 cm × 1.35 cm diameter), suspended in the center of the two dishes between washers using solvent-rinsed tweezers, could be used in indoor and outdoor sampling. During outdoor deployment, a low-wind environment is preserved by housing samplers in protective chambers.	PBDE	Soxhlet extraction (21 h in petroleum ether)	3-week exposure, between December 2002 and March 2003, 74 randomly selected homes and at 7 outdoor sites in Ottawa (Canada)	GC-MS with DB-5 (60 m × 0.25 mm × 0.25 μm)
	PCB	Soxhlet extraction (21 h in petroleum ether)	450-day period exposure, April 2000–June 2001	GC-ECD, DB-5 (60 m × 0.25 mm × 0.25 μm)
	PDBEs	No data	4 four-month periods (February 2000–July 2001), urban-rural transect	GC-MS
	PCB, PDBE, organohalogen pesticides	18-h extraction with dichloromethane in a Bunchi extraction unit	71 samplers were deployed over a 6-week period (June–July 2002) across 22 countries	GC-MS
SPMD [117, 127, 128, 130, 131] Sampler consists of layflat polyethylene tubing cut into pieces, which are heat-sealed at one end. The tubes are filled with ~1ml (0.915g) of triolein. The dimensions of tubes could be different (for different authors and purposes) and are for example as follows:	PCBs	Extraction with hexane	Time-course experiments in the summer of 1995 and in winter 1995/1996—samples were collected after 15, 29, 45, 59, 71 and 88 days (14, 26, 39, 61 and 84, respectively) at a semirural meteorological field station site (UK) and two-month deployment study in the summer 1996	HPLC/variable wavelength detector
75 μm thickness, 28 mm × 104 cm pieces [130]	PAHs	Dialysis in n-hexane for 48 h with solvent exchange after 24 h	Two sampling campaigns during autumn 2002, exposure time varying from 1 to 4 weeks.	HPLC with DAD ² and programmed fluorescence detector with
75 μm thickness, 28 mm × 80–90 cm pieces [127]			Monitoring station in District Hygienic Station building at a very busy street (Czech Republic)	Supelguard column (2.1 × 250 mm) protected by a pre-column Supelguard (2.1 × 20 mm)
50 μm thickness, 28 mm × 82 cm pieces [128]			32-day exposure, in April 2002 at a residential suburb and urban site (Australia)	Adsorption chromatography
After squeezing out the air and forming a smooth lipid layer, the other end of tubing is heat-sealed.	PAHs	Extraction using hexane for 4 h at room temperature with solvent exchange after 24 h		
Samplers could be protected with a protection chamber to minimize the effect of direct sunlight, rain and wind.	PCB	Soxhlet extraction (21 h in petroleum ether)	450-day exposure, April 2000–June 2001	GC-ECD, DB-5 (60 m × 0.25 mm × 0.25 μm)
	PDBEs	No data	4 four-month periods (February 2000–July 2001), urban-rural transect	GC-MS
Analyst II [133, 134]	PAHs	2 ml of toluene	Laboratory tests and outdoor/indoor evaluation	GC-MS, DB-5 (25 m × 0.2 mm × 0.33 μm)

Analyst 2 consists of a glass cylinder (20 mm × 10 mm); it differs from the previous device because it is open at both ends and holds the adsorbent in the middle.	PAHs	1.5 ml toluene	Indoor/outdoor stations in Italy, during spring 2000	GC-MS, DB-5MS (25 m × 0.2 mm × 0.33 μm)
PAS [121, 122] Passive Air System based on the polymeric resin XAD-2. Sampler consists of a resin-filled stainless mesh cylinder that is suspended in an inverted galvanized steel can with the open bottom. The sampling container is a long thin cylinder made of a fine stainless steel mesh held in shape by two end caps. The mesh cylinder minimized potential contamination and adsorptive wall loss. The upper end has a loop attached to it. The entire cylinder is filled with a sampling medium (XAD-2). The shelter with an opening at the bottom is designed to minimize the effect of wind velocity and to prevent exposure of the sampling medium to precipitation and large aerosol particles subject to gravitational settling. It consists of a lid and a bottom part, which fit snugly and are able to withstand severe weather conditions. The cylinder is hanging on a carbine hook that is attached on the inside of the lid. This arrangement allows the repeated opening and closing of the shelter and the transfer of the cylinder into a shipping container without the operator ever touching the resin-filled containers. Spokes fitted into the steel shelter prevent the dangling and accidental unhooking of the cylinder. Air exchange in the shelter is through the bottom opening and a number of small holes in the top of the shelter. A grid with very wide	α-HCH, γ-HCH	Extraction with MeOH/DHM mixture	40 network stations, 1-yr deployment	GC-ECD

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TABLE 4
Semivolatile organic compounds monitored in air using passive samplers for the analyte collection (*Continued*)

Sampler type and description	Group of analyte	Desorption mode	Monitoring site and time	Method of final determination
mesh is fitted into the bottom opening to keep larger animals away from the sampling cylinder while maintaining sufficient air exchange. A double-lid design prevents rain or snowmelt water from the entering through the holes on the top. POG sampler [131] Sampler consisting of thin films of ethylene vinyl acetate on glass that was used to measure the chemical fugacity in fish tissues and other solid substrates. This is referred to as a Polymer-coated Glass (POG) sampler. The high surface-to-volume ratio that can be achieved with POGs allows rapid equilibration (hours/days) of target analytes, while varying the surface area or coating thickness offers the opportunity to vary the sensitivity and sampling time for different analytes and to meet different study objectives. POGs consist of a thin film of ethylene vinyl acetate coated onto the inside and outside surfaces of a hollow glass cylinder. A coating solution was prepared by dissolving EVA pellets in dichloromethane. The solution was magnetically stirred for approximately 3 h or until there was no visible sign of pellets. The solution was transferred to a 500 mL glass vessel. The POG cylinders were dipped in the solution covering all but the top 10 mm of the cylinder, resulting in a total coated surface of 300 cm². As the glass cylinder was withdrawn from the solution, the DCM quickly evaporated leaving a microlayer of EVA. For application of multiple coats of EVA, the dipping steps were repeated at interval ~30 s. The mean EVA film thickness was calculated as the mass of EVA divided by the surface area of the	PCB	Extraction with 35 ml dichloromethane	Laboratory investigations	GC-ECD, DB-5 (60 m × 0.25 mm × 0.25 μm)

sampler, recognizing that some variability between samplers and within the same sampler may exist. Prior and after the exposure, POG cylinders were stored in sealed 500 ml glass jars having Teflon-lined lids. This sampler was used for measuring elevated concentration of POPs in indoor ambient air

Polyethylene PSD [132]
A sampler consisted of approximately 30 cm by 30 cm of low-density polyethylene film.

Passive sampler [141]
Sampler consists of a PTFE tube, filled with adsorbing resin (0.75 g, Supelpack TM-2). The sampling rate is 0.0859 m³/day

PAHs	Extraction with hexane	30-, 60- and 90-day exposure, April 2002, Australia outdoor air	GC-MS, BD-1 (20 m × 0.2 mm × 0.33 μm)
Pesticides	3 ml toluene	46 dwellings, October 2000	GC-MS, DB-5MS (30 m × 0.32 mm × 0.25 μm)

¹ITD—Ion Trap Detector.
²DAD—Diode Array Detector.

TABLE 5

Application of passive samplers to air monitoring: comparison of the results obtained by passive samplers with those obtained by a reference method under laboratory conditions and for real atmosphere

Type of sampler	Analyte	Application of sampler	Comparison with a reference technique
Diffusive sampler for thermal desorption [99] GMD sampler [91, 92]	VOCs Volatile amines Methyl isocyanate	Laboratory measurements under different conditions and for different times of exposure Laboratory analysis, samplers were exposed for sampling periods ranging from 15 min to 8 h Laboratory evaluation in a paint spray box for 35 min	Comparison with OVM 3500 and active sampling—good agreement between obtained data Pumped sampling; good agreement of the results Pumped filter method—good agreement of the obtained data
Pro-Tek G-AA sampler [42]	Chlorinated hydrocarbons	Laboratory test	Active sampling technique—adsorption tubes (type SKC-charcoal tubes) were used. Correlations between active and passive methods are as follows: CH_2Cl_2 : 0.86; CHCl_3 : 1.2; CCl_4 : 0.80 Tubes designed for thermal desorption (dynamic technique), good agreement of results
OVM 3520, OVM 3550 [23, 24, 26–31, 33]	VOCs VOCs	1 sampling site (US), Outdoor air monitoring—routine monitoring in El Paso, Texas. Sampling periods were three time intervals (3-day week, 4-day week and 7-day week) for three consecutive weeks Two inner-city schools in Minneapolis (USA), children and children's homes. Indoor, outdoor and personal sampling. VOC measurements were obtained in winter (January–February) and spring (April–May) 2000. Personal and home samples were collected continuously for 48 h, in school samples were collected each day by capping samplers after school day, outdoor measurements were collected at each school continuously from Monday to Friday (~103 hr) 2103 dwellings in Germany. Indoor air quality monitoring, outdoor 4-week air sampling—in the time period between 1994 and 2001 Printmakers in a mixed-use university art school (US), personal sampling and area monitoring. September–October, for personal sampling samples were collected on nine occasions over a 6-week period (typically twice a week); area samplers were collected each sampling day	No data available No data available No data available
	VOCs	Indoor/outdoor sampling. Comparison of different types of passive samplers to the evaluation of indoor/outdoor air quality	Compared with Orsa-5 sampler, the ratio OVM/ORSA for indoor measurements are as follows: benzene 1.10, toluene 1.07, <i>m</i> , <i>p</i> -xylene 0.99, <i>o</i> -xylene 0.96, ethylbenzene 1.13, trichloroethene 0.89, tetrachloroethene 1.14, ethyl acetate 0.95, nonane 1.04; for outdoor measurements the ratios are as follows: benzene 1.25, toluene 1.24, <i>m</i> , <i>p</i> -xylene 1.06, <i>o</i> -xylene 1.2, ethylbenzene 1.26, trichloroethene 1.16, tetrachloroethene 1.23, ethyl acetate 1.11, and nonane 1.08.

Methoxyethanol		Copper laminate circuit board manufacturer—8 h workplace monitoring (personal and fixed-points samples),	Active sampling (coconut shell charcoal tubes)—no statistical difference was found between the techniques. Linear regression showed the correlation to be high ($r = 0.992$, slope $= 0.973$, $n = 93$) over the range of 0.17–163 ppm. The mean concentration difference was -0.34 ppm and the mean relative error was 3.5% No data available
VOCs		Ambient air in three urban neighborhoods, air inside the residences of participants and personal air of 71 healthy non-smoking persons in the Minneapolis/St. Paul metropolitan area. Indoor, outdoor, personal monitoring, 2-day sampling time (approximately 48-hour), over three seasons (spring, summer and fall) in 1999	
VOCs		Laboratory measurements under different conditions and for different times of exposure	Sorbent tubes—good agreement of obtained data
OVM 3500 [32]	Microbial VOCs	Children rooms in 132 dwellings, between February, and May 1997, 4-week exposure	Active sampling—difference was in the range $\pm 30\%$ (except fenchone—the differences was 62.3%) SPME device $r > 0.9699$, slope $\approx 1.12 \pm 0.07$
OVM 3551 [31]	Ethylene oxide	Laboratory evaluation and medical device company (Taiwan)—workplace monitoring. Sampling time was around 30 min	
ORSA-5 [28, 38–41]	VOCs	Indoor/outdoor sampling, comparison of different types of passive samplers for the evaluation of indoor/outdoor air quality	Compared with Orsa-5 sampler, the ratio OVM/ORSA for indoor measurements are as follows: benzene 1.10, toluene 1.07, <i>m</i> , <i>p</i> -xylene 0.99, <i>o</i> -xylene 0.96, ethylbenzene 1.13, trichloroethene 0.89, tetrachloroethene 1.14, ethyl acetate 0.95, nonane 1.04; for outdoor measurements the ratios are as follows: benzene 1.25, toluene 1.24, <i>m</i> , <i>p</i> -xylene 1.06, <i>o</i> -xylene 1.2, ethylbenzene 1.26, trichloroethene 1.16, tetrachloroethene 1.23, ethyl acetate 1.11, and nonane 1.08. Active sampling—sorption tubes with Tenax TA—good agreement of the results
VOCs		115 private houses, outdoor and personal sampling, Germany. Sampling was carried out from February 1995 until June 1997, indoor exposure duration was 2 weeks, outdoor 4 weeks	
BTX		20 monitoring sites in a residential area in the vicinity of cookery (Germany). Samplers were exposed over periods of approximately 15 days (October 1996 to April 1999)	Pumped sampling, correlation between both techniques was very good ($R^2 \geq 0.95$), the slopes of the regression lines ($\text{CORSA} = b \times c_{\text{Active}}$) $b = 0.96$ (0.98)
Analyst [45–51]	Aromatic hydrocarbons	Field test—9 sampling sites, area monitoring and indoor air monitoring. Sampling periods of time 1, 2, 4, 6 and 12 weeks (December 1998—February 1999) and eleven month period (June 1998—April 1999)—monthly sampling time	Automatic BTX analyzer. The obtained results are in very good agreement.

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TABLE 5

Application of passive samplers to air monitoring: comparison of the results obtained by passive samplers with those obtained by a reference method under laboratory conditions and for real atmosphere (*Continued*)

Type of sampler	Analyte	Application of sampler	Comparison with a reference technique
TOPAS [43] Perkin-Elmer tubes [60, 62–67]	Aromatic hydrocarbons	31 sampling points in four types of urban and suburban sites in Italy (area monitoring). Campaign took about six weeks, first sampling period was in May 1999, the second in June 1999	Intercomparison with Radiello sampler (in mode “short-time”—one a day, and “long-time”—the whole period). The data obtained was in good agreement.
	Volatile aromatic compounds	10 different sites, outdoor air monitoring. Two month sampling time from October 2001 up to March 2002	No data available
	BTX	2 schools in Italy (13 classrooms and the outdoors) and 13 homes, monthly sampling	12-hours home-made diffusive (tube-type) samplers/ No data available
	BTX	15 classrooms and 17 homes (indoor/outdoor monitoring). Monthly sampling, carried-out from December 2001 to April 2002	No data available
	BTEX	Indoor site (shop), Rome (Italy). 2-monthly sampling during 12-months (from July 1999 to June 2000)	No data available
	BTEX	56 sites (roadside, residential and background) near oil refinery, period from March to October 2001, monthly sampling	No data available
	VOCs	Laboratory experiments in environmental chamber, 5h sampling time	Active sampling—sampling tubes filled with Tenax TA; very good agreement of results
	BTEX	Parking garage, outdoor air monitoring—8 h sampling	Dynamic sampling (tubes filled with Tenax GR); good agreement of data obtained by both techniques
	Monoterpenes	Field test (sawmill), personal exposure and stationary sampling, ~8 h (working day) for field monitoring	Dynamic sampling (sorption tubes and pumps)—all personal samplers taken by diffusive sampling gave lower results than the pumped samples.
	Benzene	Chamber experiments in laboratory, 2-week-period test, 6 determinations, in controlled atmosphere test facility	Continuous on-line monitoring performed by gas chromatography and pumped sampling: good agreement found between benzene concentrations.
	BTEX	Chamber experiments in laboratory, 30 minutes exposure	Dynamic sampling (tubes filled with Tenax GR); good agreement of data obtained by both techniques
	Monoterpenes	Laboratory evaluation, exposure time varied from 15 min to 8 h	Dynamic sampling (sorption tubes and pumps)—no discrepancy between obtained results.
	Volatile compounds	Laboratory evaluation in chamber. The reconstituted atmospheres contained various concentrations of compounds ($20\text{--}90\ \mu\text{g m}^{-3}$) for exposure durations ranging from 4 to 16 hours to cover a wide range of possible ambient atmosphere scenarios.	Active sampling—sorption tubes filled with the same kind of sorbent (Carbotrap 20–40, approximately 140mg)—good agreement of obtained data
Aromatic hydrocarbons and MTBE	Toluene	Laboratory evaluation in chamber for different sampling times	Active sampling—sorption tubes. No clear differences were perceived between diffusive and pumped tube results.
	Aromatic hydrocarbons and MTBE	4 sites in Helsinki (urban air monitoring) 2-week periods during the year 2000	Active sampling—the diffusive/pumped concentration ratio is approximately 1 for most compounds, but the ratio decreases substantially for trimethylbenzenes

VOCs	44 homes in Southampton and 4 outdoor locations (indoor/outdoor air monitoring). 4-week exposure, samplers were exposed during March 1994 to November 1995	Active sampling—no significant differences between obtained data was observed
VOCs	Laboratory tests. The exposure time can range from 30 minutes to 24 hours depending on the environmental concentration	No data available
BTEX	340 samplers in Madrid and surrounding area. Sampling periods were 7 days every two months, during a year	No data available
BTEX	5 sampling sites, 7-day sampling	No data available
Benzene	Nardones street in Naples (area monitoring). 48-hour sampling (and 6-day sampling) during 6-day campaign in December 2002 and January 2003	No data available
VOCs	Paint-manufacture, personal exposure. Average sampling time was 420 min	Active sampling on charcoal tubes (SKC); the results reveal good agreement between obtained data (except for methyl ethyl ketone)
Toluene, trichloroethylene, methylene chloride, benzene and its derivatives	Workplace monitoring for four substances in four distinct sectors of activity: photogravure printing (toluene), screw cutting (trichloroethylene), manufacture of polyurethane foam (methylene chloride), filling stations (benzene and its derivatives). Two campaigns—first monitoring period was on average 413 min, the second—on average 419 min	Sorbent tubes with active charcoal—dynamic sampling—the results highlight a close correlation between the data obtained with the badge and those obtained using the reference method
Monoterpenes	Saw mill, personal sampling (sampling time was approximately 4 h), and area sampling (the sampling time was 8 h) and chamber experiments in laboratory	Active sampling, correlation coefficient = 0.997
BTEX	2 cities in Italy, personal sampling. Samplers were exposed three times during summer (July 1998) and three times during winter (January and February 1999)	No data
Methyl isocyanate	Laboratory tests. Sampling period varied from 15 min to 8 h	Coated filters for pumped sampling
BTEX	18 sampling sites, outdoor air monitoring. Samplers were exposed for 7–14 days at 5 sites since March 2001 and 13 stations since November 2002	Dynamic sampling—sorbent tubes with carbon molecular sieves; for short-term exposure (2 and 4 days) the relative standard deviation was 16.9% and 9.1%, respectively, for benzene, and less than 5% for other VOCs; for short term exposures RSD was between 3.0% and 10.5%.
Volatile organohalogen compounds	Indoor/outdoor pollution in 70 residences in Shizuoka, Japan, 24-hour sampling period during summer season of 1996	Active sampling (charcoal tubes)—the relation between logarithms of the amount collected and those of concentration in the air was: $y = 0.917x - 1.20$ ($r^2 = 0.9974$) for trichloroethylene and $y = 0.905x - 1.23$ ($r^2 = 0.9970$) for tetrachloroethylene

(Continued on next page)

TABLE 5

Application of passive samplers to air monitoring: comparison of the results obtained by passive samplers with those obtained by a reference method under laboratory conditions and for real atmosphere (*Continued*)

Type of sampler	Analyte	Application of sampler	Comparison with a reference technique
	Chlorinated VOCs	37 urban dwellings in Japan and 27 in Sweden (indoor air quality evaluation). Sampling was carried out in February 1998 in Japan and in February through May 1998 in Sweden. Sampling time was approximately 24 h.	No data available
Shibata diffusion sampler packed with silica gel containing triethanolamine [83]	Formaldehyde	37 urban dwellings in Japan and 27 in Sweden (indoor air quality evaluation). Sampling was carried out in February 1998 in Japan and in February through May 1998 in Sweden. Sampling time was approximately 24 h.	No data available
LiPS [85]	N,N-dimethylformamide, N,N-dimethylacetamide	Spandex fiber and polyurethane products manufacture, personal sampling for 8-hour period	Silica gel tubes (active sampling)—correlation between two techniques was obtained $C_{LiPS} = 0.912C_{Active}$ ($r = 0.932$, $p < 0.01$)
Sep-Pak XpoSure DNPH cartridges [86]	Carbonyl compounds	5 locations—two in apartment and three in detached house. Sampling period ranged from 12 hrs to 14 days	Sep-Pak XpoSure DNPH active cartridges: $y = 0.00412 + 1.48$
DSD-DNPH [87, 88]	Glutaraldehyde	Laboratory evaluation and field tests—model laboratory at university and dental clinic in Kanagawa, Japan. 1-hour sampling time in chamber test, field exposure time July 2003-January 2004, 8-hour sampling time	Active sampling—cartridges coated with DNPH—the relationship between air concentration measured by the active sampling and collected amount of GA by passive sampling per hour in chamber test was $y = 9.7 \times (R^2 = 1.0)$
GMD sampler [93]	Formaldehyde	Field tests in some newly erected buildings and a laboratory of university, 30-min exposure time	Active sampling—the relationship $C_{passive} = 1.0 \times C_{active}$ ($R^2 = 0.99$)
Prototype sampler developed by [100]	Carbonyl compounds other than formaldehyde VOCs	Laboratory experiments in environmental chamber of different volumes and field investigation in 57 smokers and non-smokers homes. 72-hour monitoring Laboratory test, 8h exposure time	Active sampling—good agreement of data
TK-200 personal passive monitor [102]	Styrene	Group of fiberglass-reinforced plastic workers, personal monitoring	Comparison with OVM 3500 sampler, for dichlorobenzene, <i>n</i> -decane, 1,2,4-trimethylbenzene, <i>m</i> , <i>p</i> -dichlorobenzene the prototype sampler values were quite similar to those obtained with the OVM3500. For naphthalene, styrene, and 1,2,4-trichlorobenzene, prototype values were lower than OVM3500 values.
			No data available

standard (EN 482) has different criteria depending on the usage of the sampler, but for compliance purposes the corresponding figure is 30% (106).

Laboratory tests of samplers generally revealed a good agreement between the results obtained using passive samplers and the results obtained by a dynamic method. The results of laboratory and field test of passive samplers are presented in Table 5.

APPLICATION OF PASSIVE DEVICES IN MONITORING OF SEMIVOLATILE ORGANIC COMPOUNDS IN AIR

In contrast with a wide spectrum of uses of passive samplers to monitor volatile organic compounds in indoor, outdoor air or workplace atmospheres, the application of passive devices to monitor the atmosphere for SOC is relatively novel and uncommon. Similarly to VOC monitoring, living organisms or fragments of their bodies, such as pine or spruce needle (107–109) moss and lichen (110) are used as passive samplers for SOC.

According to the literature, a few media have been tested for the passive sampling of semivolatile compounds, such as beeswax-coated filter paper (111), butter-coated glass plates [112], and tristearin-coated fiberglass sheets (113). (In this case we can speak about “natural” —biological passive samplers and “synthetic” samplers for air monitoring.) Progress in this field has been achieved using semipermeable membrane devices (SPMDs). The SPMD sampler consists of lay-flat polyethylene (LDPE) tubing enclosing a thin film of triolein, a high molecular weight neutral lipid. SPMDs (114, 115) originally developed for the monitoring of waterborne lipophilic contaminants, also proved to be highly effective passive samplers for semivolatile compounds in air. The utility of SPMDs has been demonstrated for monitoring gaseous pollutants, such as polychlorinated biphenyls, organochlorine pesticides and polycyclic aromatic hydrocarbons.

Passive samplers used for the sampling of SOC in air (both indoor and outdoor) contain the same types of sorption media as those used in dynamic sampling. The exposure time must be long enough to ensure the desired enrichment factor. The most common samplers used in outdoor air quality monitoring are:

- filled with polyurethane foam (PUF) (116–120),
- filled with XAD resins (121, 122),
- SPMDs (semipermeable membrane devices) (116, 123–130),
- polymer-on-glass (POG) (polymer-coated glass samplers) (116, 131),
- tristearin-coated fiberglass sheets (113),
- and samplers in which polyethylene foil was used as a trapping medium (116, 132).

The existing samplers used for the monitoring of volatile compounds in air are often modified and adapted to collect semivolatile organic compounds from air (e.g., the sampler *Analyst* has been modified and adapted for the monitoring of SOC as *Analyst 2*) (133, 134). SPME fibers are also sometimes used

as passive samplers (135, 136). The passive sampling theory for semivolatile organic compounds present in air was recently described in detail (137).

Similar to volatile organic compound monitoring, the analytes trapped on/in the sorption medium must be released for quantitative analysis. A common disadvantage of passive samplers extracted by solvent extraction or dialysis is the tedious recovery of analytes, and the need for the expensive cleanup of the extracts prior to chromatographic analysis. These problems do not appear when solvent-free techniques, such as thermal desorption, are used. Solid phase microextraction devices can act as diffusive samplers if the fiber is retracted a defined distance into its needle housing during the sampling period. For the Stir Bar Sorptive Extraction (SBSE)—developed in 1999 (138) the stir bars (consisting of a glass-coated magnetic core used with a layer of PDMS as the receiving organic phase) are commonly thermally desorbed by thermal desorption-gas chromatographic methods. Some authors (139, 140) have examined the performance of two passive samplers for long-term monitoring of semivolatile organic compounds in air. They consisted of a PDMS-coated stir bar or silicone tubing as solid organic receiving phase, enclosed in heat-sealed LDPE membrane tubing. A compilation of the data on design of samplers and semivolatile organic compounds monitored in air is given in Table 5.

SUMMARY

Ever since the first report on passive sampling, a large number of papers and monographs have been published, which discussed the following topics: theoretical basis of passive sampling; various designs of passive samplers; laboratory evaluation using different types of environmental chambers; field application of passive sampling technique to monitoring of various matrices; comparison of passive sampling techniques with reference techniques; influence of different parameters on sampling process of analytes in the sampler; and mode of calibration of samplers.

The available literature also discusses in detail the effects of physicochemical parameters, such as relative air humidity, temperature variations, fluctuations in concentration of the analytes and ambient air velocity on the enrichment process in passive devices. The wide applicability of passive techniques allows their use not only for organic compounds, but also for airborne inorganic pollutants.

The limiting factor in practical applications of passive dosimetry is a tedious and time-consuming calibration process of the samplers. Recent work on a novel calibration procedure (142, 143) will undoubtedly extend the applicability of passive dosimetry to air monitoring.

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