

Sampling and preconcentration techniques for determination of volatile organic compounds in air samples

Maria Rosa Ras, Francesc Borrull, Rosa Maria Marcé

Because air is complex and heterogeneous, continuously evolving in time and space and being influenced by atmospheric and geographical conditions, sampling is crucial in air analysis. Moreover, due to the low levels of pollutants present in the atmosphere, enrichment is often required.

This review deals with the most common techniques for sampling and preconcentration of volatile organic compounds (VOCs) in air samples (e.g., whole-air collection in containers, which is usually combined with preconcentration step, and solid-sorbent enrichment methods). We also describe solid sorbents used to trap VOCs in air, and subsequent desorption techniques.

In recent years, there have been many efforts to improve on-line analysis methods, which offer real-time data and are useful in providing rapid results. We examine the application of sorbent trapping to on-line analysis and other techniques for on-line analysis (e.g., membrane extraction and selected-ion-flow-tube mass spectrometry).

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Maria Rosa Ras,
Francesc Borrull*,
Rosa Maria Marcé
Departament de Química
Analítica i Química Orgànica,
Universitat Rovira i Virgili,
Campus Sescelades,
Marcel·lí Domingo, s/n, 43007
Tarragona,
Spain

1. Introduction

Interest in the trace analysis of volatile organic compounds (VOCs) in ambient air has grown considerably. Hydrocarbons comprise the main group of atmospheric VOCs. They play an important role in physico-chemical processes of the troposphere, as they contribute significantly to the formation of ozone and other photochemical oxidants. They can also pose a serious hazard to human health and the environment due to the well-known toxicity of several compounds (e.g., benzene and 1,3-butadiene). Table 1 shows some of the most common VOCs determined in ambient air, distinguished by their capacity as ozone precursors [1].

Determining individual components is preferable to finding the sum of total VOCs because of the importance of individual constituents, so the analytical method of choice is gas chromatography (GC) coupled with flame ionization detection

(FID), electron capture detection (ECD) or mass spectrometry (MS).

Air has complex characteristics. It is a heterogeneous system composed of gases, liquids and solid particles and its composition can be affected by meteorological conditions, diffusion, and reactivity, so sampling is crucial in air analysis. This procedure must allow representative samples to be taken, avoiding any variation in their composition. It should also be as simple as possible to enable field sampling. Moreover, due to the low levels of pollutants in the atmosphere, enrichment is often required in order to reach acceptable limits of detection (LODs).

The most common techniques used to sample and to preconcentrate VOCs in air are sampling of whole air in special recipients, collection onto solid adsorbents, and continuous sampling and on-line analysis. Some of these require combination with another enrichment technique (e.g., cryogenic trapping). Selecting the

*Corresponding author.
Tel.: +34 977 55 95 60;
Fax: +34 977 55 84 46;
E-mail:
francesc.borrull@urv.cat

Table 1. More frequent volatile organic compounds (VOCs) determined in environmental air samples

VOCs with significant photochemical ozone-creation potential		Other VOCs	
1-Pentene	Ethylbenzene	1,1-Dichloroethylene	Dibromochloromethane
2- <i>cis, trans</i> -Pentene	Styrene	Methylene chloride	1,2-Dibromoethane
Isoprene	<i>o</i> -Xylene	<i>cis, trans</i> -1,2-Dichloroethylene	Tetrachloroethene
<i>i</i> -Hexene	Isopropylbenzene	1,1-Dichloroethane	Chlorobenzene
<i>m,p</i> -Xylene	<i>n</i> -Propylbenzene	2,2-Dichloropropane	1,1,1,2-Tetrachloroethane
1,3,5-Trimethylbenzene	<i>sec, tert</i> -Butylbenzene	Bromochloromethane	Bromoform
1,2,4-Trimethylbenzene	<i>p</i> -Isopropyltoluene	Chloroform	1,1,2,2-Tetrachloroethane
1,4-Dichlorobenzene	<i>n</i> -Butylbenzene	1,1,1-Trichloroethane	1,2,3-Trichloropropane
<i>i</i> -Octane	<i>i</i> -Pentane	1,2-Dichloroethane	Bromobenzene
<i>n</i> -Heptane	<i>n</i> -Pentane	1,1-Dichloropropene	2-Chlorotoluene
Toluene	<i>n</i> -Hexane	Benzene	4-Chlorotoluene
<i>n</i> -Octane		Carbon tetrachloride	1,3-Dichlorobenzene
		Trichloroethylene	1,2,3-Trimethylbenzene
		1,2-Dichloropropane	1,2-Dichlorobenzene
		Dibromomethane	1,2-Dibromo-3-chloropropane
		Bromodichloromethane	1,2,4-Trichlorobenzene
		<i>cis, trans</i> 1,3-Dichloropropene	Naphthalene
		1,1,2-Trichloroethane	Hexachlorobutadiene
		1,3-Dichloropropane	1,2,3-Trichlorobenzene

right method or combination of methods may depend on the compounds of interest, expected concentration range, required sensitivity, accuracy and precision, selectivity, presence of interferences, type of sample (grab, time integrated, or real time), portability and cost.

We aim to provide an overview of sampling and enrichment techniques for VOCs in air samples, their characteristics, and their main advantages and disadvantages. We also cover the latest advances in the application of sorbent trapping and other techniques [e.g., membrane extraction and selected ion flow tube mass spectrometry (SIFT-MS) to on-line analysis].

2. Whole-air collection techniques

Collecting air samples in a container is the simplest way to collect them. The samples are usually analyzed later using GC, by direct injection or, more frequently, in combination with a preconcentration step. This technique presents some advantages over sorbent methods (e.g., whole-air sampling, avoiding the breakthrough of target compounds and eliminating the need for thermal or solvent desorption). It also provides multiple aliquots for replicate analysis, and time-integrated samples can be obtained using controlled-flow pumps with bags or metal containers. Several types of containers can be used (e.g., gas-tight syringes, glass bulbs, bags, or metal containers), although plastics bags and stainless-steel containers are the most widely used [2]. The U.S. Environmental Protection Agency (USEPA) adopted two evacuated-canister methods to determine VOCs (TO-14A [3] and TO-15 [4], which includes polar compounds).

These sampling methods have been widely used for monitoring toxic substances in air [5,6].

Plastics bags (e.g., Tedlar, Teflon or aluminized Tedlar) are simple to use, inexpensive and available in various sizes, normally from 500 mL to 100 L. Plastics bags are reused after cleaning by repeatedly filling them with pure nitrogen or ultrahigh-purity air, and evacuating them with slight negative pressure. A disadvantage of using Tedlar bags is that compounds may not remain stable for more than 24–48 hours [2]. Some bags are also permeable to certain chemicals, and losses of significant amounts of sample have been observed when they have been stored for prolonged periods [7]. Moreover, Tedlar bags can allow humidity to diffuse when relative humidity levels differ between inside and outside. A double-layer Tedlar bag has been designed with a drying agent between the two films to limit the impact of external humidity on a low-humidity sample [8].

Unlike the plastics bags, metal canisters have a high initial cost. Wang et al. [9] reviewed evacuated-canister methodology to determine VOCs in ambient air. In order to minimize internal surface reactivity, every canister is treated either by Summa passivation, which coats the surface of the canister with a pure chrome-nickel oxide layer, or by chemically bonding a thin fused-silica layer to the stainless steel surface. Prior to use, canisters must be carefully cleaned and evacuated in order to avoid contamination [2,7]. Samples are collected using two sampling methods (i.e. grab or time-integrated). They can also be collected with sub-atmospheric pressure (passive) or pressurized with a pump (active). The active method allows the sample to be pressurized and the collection of larger sample volumes, which are not

limited by the volume of the container. However, the pump does represent a potential source of contamination or air leaks [6,7]. The use of pressurized and sub-atmospheric pressure canisters for sample collection is described in US EPA method TO-14A [3].

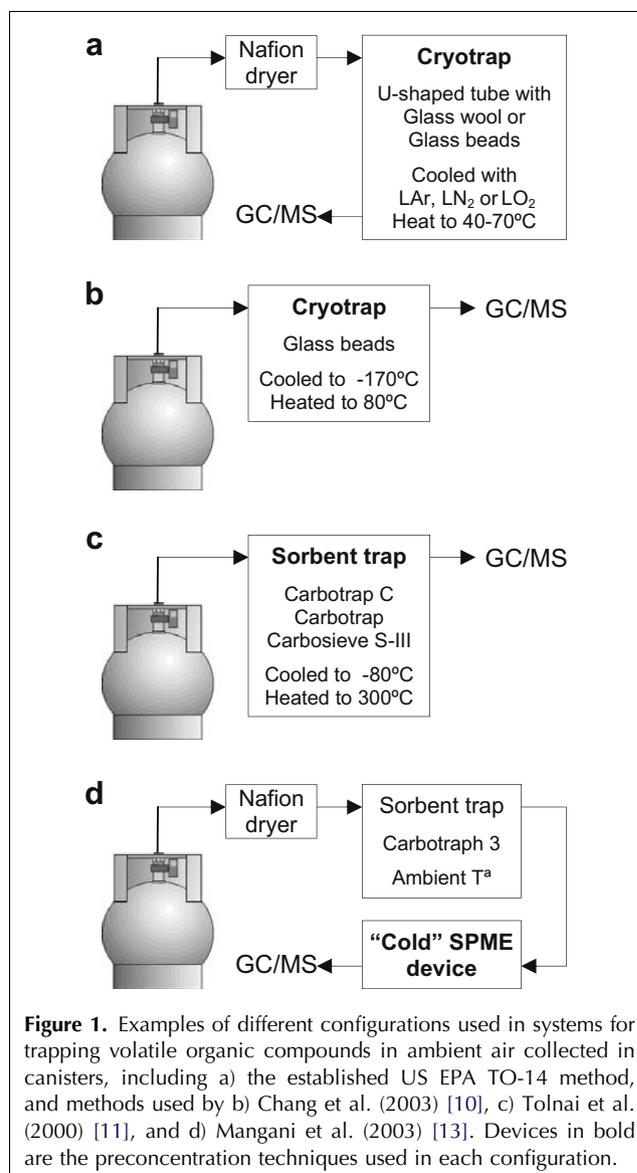
In whole-air sampling, VOC preconcentration is usually necessary prior to analysis. Sorbent or cryogenic trapping can be used to do this [2,7,9]. USEPA methods TO-14A [3] and TO-15 [4] use a cryogenic trap, and, e.g., Chang et al. [10] drew aliquots of canister-collected samples to a cryogenic trap packed with fine glass beads cooled at -170°C for preconcentration. On heating the trap to 80°C , trapped VOCs were flushed into a stream of high-purity helium gas in the chromatographic column.

Tolnai et al. [11] used a multilayer adsorbent bed packed with Carbosieve S-III, Carbotrap and Carbotrap C. It was kept at -80°C , and then heated for desorption and injection of analytes onto the column.

Solid-phase microextraction (SPME) has been used to preconcentrate analytes from air collected in containers [12]. Also, Mangani et al. [13] used "cold" SPME to preconcentrate compounds from air samples collected into stainless-steel canisters using sub-ambient temperatures to enhance the retention capability of the SPME fiber.

A big challenge is removing water from the sample. Although water is an advantage in the case of Summa canisters, where water enhances the stability of VOCs collected, it can also interfere with subsequent analytical techniques. Problems resulting from humid air streams include loss of VOCs in condensed water, blockage of cryogenic traps through the formation of ice, variability in GC retention time by overloading and damaging the stationary phase, and deterioration of the MS ion source due to ionization of water.

There are several techniques for removing water vapor from gas streams. These include drying using desiccants, adsorbents, cryocondensation and permeation [9]. Some of the most popular desiccants used to dry ambient air are $\text{Mg}(\text{ClO}_4)_2$, MgCO_3 , CaCl_2 , LiCl and K_2CO_3 . The desiccant should not cause contamination or lead to the loss of compounds. The adsorbents used for drying are silica gel, Al_2O_3 and zeolites. Irreversible adsorption of analytes along with water may occur with very polar and heavy compounds. When this happens, the adsorbent trap is heated to release the adsorbed analytes. Cryocondensation is performed by passing the gas stream through a cooled trap (-80°C) to condense the water. Specially-designed condensers can also be used at moderate sub-ambient temperatures (-10°C) on glass beads prior to sample elution in a GC column. Permeation drying is done by flushing the gas stream through a Nafion tube, which is an ionic copolymer of tetrafluoroethylene (Teflon) and a fluorosulfonic acid group. Water diffuses through the tubing to an external surface and evaporates in a highly selective process that prevents contamination of the sample and loss of



analytes [9]. US EPA method TO-14A calls for use of a Nafion dryer upstream from the trap. Fig. 1 shows different combinations.

The influence of ozone on sampling and storage of VOCs in canisters has been studied by Palluau et al. [14]. They observed a decrease in concentration of many vinyl group compounds (e.g., ethylene and propene) in the presence of ozone. Chemical reactants (e.g., NaCO_3 , Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and KI) have been used to remove O_3 [9].

Table 2 summarizes advantages and disadvantages of the whole-air collection technique.

3. Enrichment into solid sorbents

Adsorptive enrichment on solid adsorbents is a technique often used to combine preconcentration with

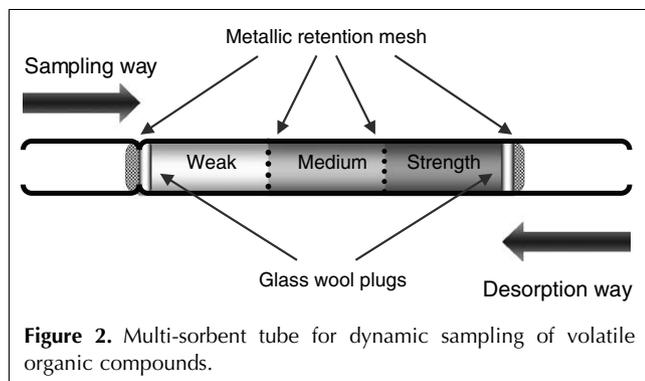
Technique	Advantages	Disadvantages
Whole-air collection	Simple technique. Whole-air collection. No analyte breakthrough. Desorption not needed. Multiple aliquots of the sample.	Initial cost of canisters Careful cleaning of the container is required Sample instability and loss of analytes in plastics bags Passivation treatment is required for canisters Preconcentration step needed (e.g., SPME)
Sorbent enrichment	Preconcentration of analytes allowed Lower method detection limits. A number of different sorbents are commercially available.	Loss of analytes due to interferences of ozone and humidity Sorbent must be conditioned Inertness of some sorbents Possible interferences in blank analysis and artifact formation
<i>Active sampling into solid sorbents</i>	High preconcentration efficiency Possibility of multi-sorbent beds, allowing the preconcentration of a wide range of volatilities Easy calibration in comparison with passive sampling Possibility of automated analysis Moisture traps can avoid interference from water Use of cryogenic traps and microtraps	Sampling pumps and flow-meters are needed Breakthrough of analytes
<i>Passive sampling into solid sorbents</i>	Small and simple devices Sampling pumps and flow-meters not needed Time-weighted-average concentration can be determined Radial passive samplers can be thermally desorbed Wide range of commercially available sampling devices	Not suitable for short-term variations of analyte concentration Low preconcentration capacity in comparison with active sampling Efficiency influenced by design of sampler Enrichment factors for individual analytes must be determined Automated analysis is not always possible Sensitive to temperature fluctuations and air movement Problems of contamination and artifact formation are more pronounced than those in active sampling
Membrane extraction	High enrichment power Great selectivity in enrichment Solvent use is avoided High automation potential Good capabilities for automated and on-line analysis	Time needed to complete the permeation due to boundary-layer effects

sampling (active or passive), which is a well-established sample preparation technique for VOCs in air [15]. The VOC portion of the air sample can be collected exclusively by trapping it using solid-phase extraction (SPE), through adsorption or reaction of the VOCs with a solid substrate.

3.1. Active methods

Active sampling consists of pumping a defined volume of air through a bed of sorbent(s) in a tube where analytes

are retained. Active sampling with sorbents is the most versatile option, and several official methods have been established based on this technique (e.g., EPA TO-17, ASTM D-6196-97, NIOSH 2549 and ISO 16017-1,2). Standard tube characteristics have also been defined: 3.5 in. long and 1/4 in. external diameter, which can sample efficiently at flow-rates in the range 10–200 mL/min. Moreover, stainless-steel sorbent tubes (Fig. 2) are adapted to thermal desorption (TD) (see Section 3.4. below). In active sampling, flow rates can vary in the



range 10–1000 mL/min, collecting sample volumes of 0.1–150 L [7].

Tubes filled with only one sorbent have been used to monitor some VOCs in ambient air (e.g., Rao et al. [16] determined benzene in workplace and ambient air using activated coconut shell charcoal, based on ASTM Method D3686). Charcoal beds have been used by other authors [17,18]. Tenax has been widely used for air monitoring (e.g., Baroja et al. [19] determined 42 volatile aromatic and chlorinated hydrocarbons in ambient air by active trapping in Tenax TA tubes). Srivastava et al. [20] used tubes filled with Chromosorb 106 to trap VOCs in indoor air, and tubes filled with Anasorb CSC were used by Gariazzo et al. [21] to trap VOCs in ambient air.

However, if analytes in a broad volatility range are determined, it is often useful to select more than one adsorbent and to arrange them in order of increasing adsorbent strength weakest to strongest sorbent, so as to keep less volatile compounds from being irreversibly retained in the strongest sorbent. If TD is used, it must be done in the opposite direction, as indicated in Fig. 2.

A widely used sorbent combination is Tenax and Carboxen 1000. However, carbon-based sorbents are not completely inert, and some labile analytes (e.g., sulfur compounds) can be degraded. Kuntasal et al. [22] used Tenax TA and Carboxen 1000 to collect 102 individual VOCs ranging from C₅ to C₁₂. Tubes filled with Carboxen 1000, Carboxen X and Carboxen-569 were used by Ribes et al. [23] to trap isocyanates, isocyanatocyclohexane and isothiocyantocyclohexane, among other VOCs.

Adsorbents may also be cryogenically cooled during sampling to enable the collection of volatile analytes. This helps to maintain sufficient sorption capacity and reduces the amount of sorbent, allowing on-line injection into the GC (see Section 4.1. below)

The presence of ozone and humidity can interfere in sorbent trapping. Interference caused by ozone can result in significant analyte loss, especially for reactive, unsaturated compounds. This effect is also influenced by the adsorbent used for sampling, as in the case of Tenax.

However no significant ozone interferences have been observed, if carbon-based adsorbents are used [24].

Interference caused by water must be also avoided, and moisture traps should be used, mainly when activated carbon is the chosen sorbent. Rao et al. [16] trapped benzene in active coconut charcoal using a silica-gel trap attached to the sampling tube. Elbir et al. [18] collected ambient VOCs using a moisture trap of calcium chloride attached to sampling tubes filled with activated carbon.

3.2. Passive methods

Analyte enrichment in passive samplers results from the diffusion of analytes from the immediate surroundings to the inside of the sampler. There, they are trapped on the surface or in the bulk of a trapping medium. Since the adsorbent has a strong affinity for the contaminant, a concentration gradient can be established to favor diffusion of the contaminant from the air to the adsorbent. The layer of adsorbent is covered with a barrier material, whose outer surface is exposed to the contaminated air. The barrier is a semi-permeable membrane or a layer of plastics drilled with many small parallel holes. Fick's law of diffusion describes the principle of passive-sampler operation, which is detailed in the literature [25]. Briefly, Fick's first law can be explained by the Equation (1) [7]:

$$m/(t A) = D(C_a - C_f)/L \quad (1)$$

where m is the mass of substance that diffuses (μg), t is the sampling interval (s), A is the cross-sectional area of the diffusion path (cm^2), D is the diffusion coefficient for the substance in air (cm^2/s), C_a is the concentration of substance in air ($\mu\text{g}/\text{cm}^3$), C_f is the concentration of the substance above the sorbent, assumed to be 0, and L is the diffusion path length (cm).

Assuming that adsorbents act as a perfect sink ($C_f = 0$), Equation (1) can be simplified to:

$$m/(t C_a) = DA/L \quad (2)$$

The term " $m/t C_a$ " is uptake rate or sampling rate. Theoretically, this is constant for an analyte and a type of sampler. Once it has been determined, it can be used to calculate ambient concentration C_a from a measured mass of analyte. Fig. 3a shows the process of diffusion.

One initial way to determine uptake rates is to use the theoretical values of diffusion coefficients and accurate geometrical sampler parameters (cross-sectional area and length of diffusion path). The experimental approach involves experimental determination of uptake-rate coefficients based on exposure of the sampler to standard gas mixtures in exposure chambers [25]. Uptake rates have been studied by many authors (e.g., Strandberg et al. [26] evaluated the uptake rates of two types of diffusive samplers [i.e. SKC-Ultra (badge type) and Radiello (radial type)], using Carboxen X or Carboxen 5 to measure 1,3-butadiene and benzene. With

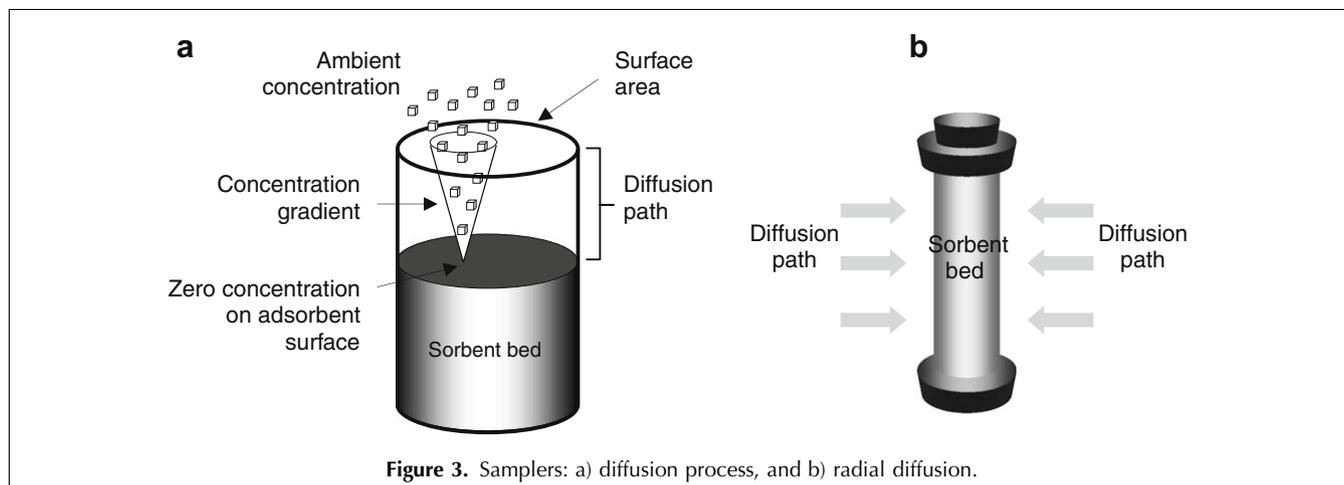


Figure 3. Samplers: a) diffusion process, and b) radial diffusion.

Carbopack, they found these diffusive samplers to be independent of atmospheric concentrations of compounds.

Different types of passive samplers are commercially available and have been used for the determination of environmental VOCs, (e.g., OVM 3500 by 3M (Two Harbors, Minnesota, U.S.A.), ORSA 5 by Drägerwerk AG (Lübeck, Germany), Gasbadge by National Mine Service (Saskatchewan, Canada), SKC-Ultra by SKC Inc. (Eighty Four, U.S.A.) or Radiello, patented by Fondazione Salvatore Maugeri-IRCCS (Padova, Italy) and distributed by Supelco (Bellefonte, U.S.A.).

Compared with dynamic techniques, passive samplers offer some advantages (e.g., elimination of portable pumps and flow-meters). Relatively small and simple, passive samplers can be left unattended for long-time exposures. Moreover, they are suitable for the determination of time-weighted-average concentration based on exposure time only, without knowing the sample volume. However, passive sampling is unsuitable for monitoring short-term variations in analyte concentration due to:

- the “historic” nature of the results;
- the lower enrichment efficiency compared to dynamic techniques;
- the need to determine enrichment factors for individual analytes; and,
- the impossibility of automating analysis in most cases.

Passive enrichment is sensitive to temperature fluctuations and air movement, and the efficiency of a passive sampler can be influenced by not only factors such as sampler storage, exposure, storage after exposure and desorption of analytes, but also sampler design [25]. The limitations of passive samplers include problems of contamination and artifact formation. These are more pronounced than for active samplers because longer sampling periods are required, due to the very low uptake rates. Blank levels of unexposed monitors have to be considered to correct data from exposed samplers.

Artifacts may also form during storage. Due to the characteristics mentioned above, diffusive sampling is mainly used to monitor indoor atmospheres [27] although it has also been used for outdoor ambient atmospheres [28].

Conventional passive samplers fall into two main geometrical categories:

- **axial** (Fig. 3a) which are characterized by a long axial diffusion path and a low cross-sectional area; and,
- **radial** (Fig. 3b), which have a diffusion path parallel to the cartridge radius and a greater cross-sectional area, allowing higher uptake rates.

Radial passive samplers are commercially available as Radiello (FSM, Padova, Italy). Radiello samplers have 100 times more area than axial samplers. This, combined with a shorter diffusion path, reduces sampling times. They are also compatible with TD. Radiello samplers have been widely evaluated for use in monitoring benzene, toluene, ethylbenzene, and xylenes (BTEX) and VOCs by many authors (e.g., Pennequin-Cardinal et al. [29], who found the blank values and analytical recovery of a mixture of 37 VOCs trapped in Carbograph 4 and released by TD to be in accordance with European Standard EN 13528-2 requirements, and uncertainty for benzene to be 20%).

However, radial diffusive samplers frequently reach sorbent saturation with analytes, with an associated risk of inverse diffusion. This was suggested as the probable reason of the decline in uptake rates for 1,3-butadiene over longer periods (1 week) found by Strandberg et al. [26] using Radiello with Carbopack X, the effect being less pronounced with SKC-Ultra.

Data obtained from passive samplers are often verified by comparison with data obtained by a reference method, which is most commonly a dynamic technique. Bruno et al. [30] evaluated Radiello for its potential for BTEX monitoring and subsequent TD. They found low blank values, good storage stability of sorbent cartridges

Table 3. Characterization of adsorbent materials commonly used for adsorptive enrichment in ambient air analysis [7,24,31,44]

Sorbent	Strength	Volatility range	Surface area (m ² /g)	Maximum T (°C)	Composition	Example of analytes
Porous organic polymers						
Tenax TA	Weak	Bp 100-400°C n-C ₇ to n-C ₂₆	~35	350	Poly(2,6-diphenyl-p-phenylene oxide)	Aromatics except benzene, non-polar compounds (bp > 100°C), and less volatile polar compounds (bp > 150°C)
Tenax GR	Weak	Bp 100-450°C n-C ₇ to n-C ₃₀	~35	350	Poly(2,6-diphenyl-p-phenylene oxide) + 23% graphitized carbon	Alkyl benzenes, PAHs, PCBs and as above for Tenax TA
Chromosorb 106	Medium	Bp 50-200°C n-C ₅ to n-C ₁₂	~750	225–250	Styrene-divinylbenzene co-polymer	Wide range of VOCs including volatile oxygenated compounds
Chromosorb 102	Medium	Bp 50-200°C	~350	250	Polystyrene	Wide range of VOCs, including volatile oxygenated compounds and haloforms less volatile than methylene chloride
Porapak N	Medium	Bp 50-150°C n-C ₅ to n-C ₈	~300	190	Polyvinylpyrrolidone	Specific for volatile nitriles: acrylonitriles, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from ethanol, and MEK (methyl-ethyl-ketone).
Porapak Q	Medium	Bp 50-200°C n-C ₅ to n-C ₁₂	~550	250	Ethylvinylbenzene-divinylbenzene co-polymer	Wide range of VOCs including oxygenated compounds
Graphitized carbon blacks						
Carbotrap C, Carbopack C, Carbograph 2TD	Very weak	n-C ₈ to n-C ₂₀	~12	>400	Graphitized carbon black, in which surface area depends on the extent of graphitization	Hydrocarbons to C ₂₀ , alkyl benzenes
Carbotrap, Carbopack B, Carbograph 1TD	Medium-weak	n-C _{5/6} to n-C ₁₄	~100	>400		Wide range of VOCs including ketones, alcohols and aldehydes (bp > 75°C), and all polar compounds within the volatility range specified, and perfluorocarbon tracer gases
Carbopack X Carbograph 5TD	Medium	n-C _{5/6} to n-C ₈	~240	>400		Hydrocarbons, BTEX
Carbograph 5TD	Medium	n-C ₅ to n-C ₈	~560	>400		Hydrocarbons
Carbon Molecular Sieves						
Sphercarb, UniCarb	Strong	Bp (-60)-80°C n-C ₃ to n-C ₈	~1200	>400	Produced by pyrolysis of organic polymers, commonly polyvinylidene chloride, poly(vinyl chloride) or corresponding co-polymers, which eliminate hydrogen chloride at temperatures of about 180°C, leaving the porous carbon backbone	Very volatile compounds [e.g., VCM (vinyl chloride monomer), ethylene oxide, CS ₂ , CH ₂ Cl ₂ and CH ₃ Cl]. Also for volatile polar compounds (e.g., MeOH, EtOH and acetone)
Carbosieve SIII	Very strong	Bp (-30)-150°C Ethane to n-C ₅	~800	>400		Ultravolatile compounds such as C ₂ , C ₃ and C ₄ hydrocarbons
Carboxen 1000	Very strong	C ₂ -C ₃	>1200	>400		Ultravolatile hydrocarbons
Molecular Sieve 5A	Very strong	Bp (-60)-80°C	>1200	350–400		Nitrous oxide
Molecular Sieve 13X	Very strong	Bp (-60)-80°C	>1200	350–400		1,3-Butadiene
Active charcoal	Very strong	Bp (-80)-50°C	>1000	400		Produced by low-temperature oxidation of vegetable charcoal

and a high level of correlation between BTEX measurements with Radiello and conventional BTEX analyzers. Other authors have tested and compared different types of diffusive samplers for their applicability to VOC monitoring [26], and a review of passive sampling of air was recently published by Partyka et al. [25].

Table 2 summarizes advantages and disadvantages of sorbent enrichment, as well as active and passive sampling.

3.3. Types of sorbents

In general, passive and active sampling can employ the same adsorbent material and desorption techniques. The following criteria should be taken into consideration in the selection of a trapping medium: strength of interactions between the sorbent and the analyte (this affects both the sorption and release of the analytes from the trapping medium); cost; and, ease of use. An ideal sorbent for preconcentrating VOCs should also have infinite breakthrough volume for the compounds of interest, complete desorption of them at moderate temperatures, no generation of artifacts and no retention of water vapor. However, no single available sorbent material meets all of these criteria, and there is a tendency, as mentioned in Section 3.1. (below), to use multiple sorbents in order to focus on a wider range of VOCs. In order to avoid contamination of the adsorbent, it should be conditioned, air should be prevented from diffusing into it, and it should be stored in a purified atmosphere at low temperatures [31]. The nature and the properties, and the advantages and the disadvantages of commercial sorbents for air monitoring have been widely discussed [24].

The main types of solid adsorbents used in air monitoring are porous organic polymers, graphitized carbon blacks, carbon molecular sieves (CMSs) and activated charcoal. Porous organic polymers have medium surface areas and are hydrophobic. A serious drawback is the limited temperature stability of several adsorbents, restricting the application of TD.

In the case of Tenax, artifacts tend to be generated by degradation of sorbent after exposure to O_3 and NO_2 , or by conversion of compounds. Tenax is a very hydrophobic material, characterized by high thermal stability. A mixture of Tenax and a graphitized carbon black, Tenax GR, offers the advantages of both materials (see Table 3).

Chromosorb 106 has a higher specific surface area than Tenax, but also lower temperature stability and higher blank levels, which makes it impractical for trace analysis.

Graphitized carbon blacks are non-specific, non-porous adsorbents, with high levels of surface homogeneity and hydrophobic properties. The graphitization process eliminates specific adsorption sites, and hinders the formation of hydrogen bonds. As a consequence,

very polar and small molecules (e.g., water) are not strongly adsorbed.

CMSs are micro-porous adsorbent materials with a narrow pore-size distribution and a high temperature limit ($>400^\circ C$). They are designed for the enrichment of small molecules (e.g., light hydrocarbons). They are often used in combination with weaker adsorbents for sampling, with a sequential adsorbent arrangement that prevents high-boiling compounds from entering the CMS tube where high boiling analytes would be strongly adsorbed, making complete desorption difficult. CMSs have higher water uptake relative to graphitized carbon blacks.

Activated charcoal, which is one of the most common sorbents used in solvent desorption, is characterized by broad pore-size distribution, high specific surface area ($800\text{--}1500\text{ m}^2/\text{g}$) and high temperature stability. The drawbacks of activated carbon include adsorption of water, irreversible adsorption of analytes and high desorption temperature. Activated carbons are mainly applied for workplace-air monitoring with passive samplers [31].

There are a number of adsorbents available commercially (Table 3, which includes their nature and characteristics). These sorbents have been evaluated by several authors for their ability to trap and to release

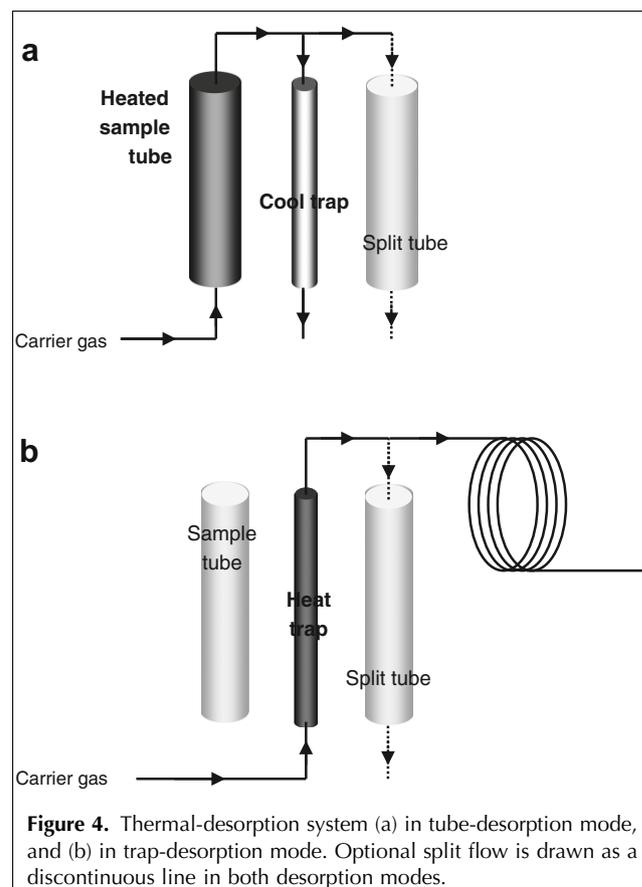


Figure 4. Thermal-desorption system (a) in tube-desorption mode, and (b) in trap-desorption mode. Optional split flow is drawn as a discontinuous line in both desorption modes.

organic compounds [32] (e.g., Volden et al. [33] studied the stability of frequently occurring indoor VOCs in Tenax TA, Chromosorb 106 and Carbotrap for 28 days. Chromosorb 106 showed the highest level of stability, while Tenax TA and Carbotrap were more influenced by variations in storage time, temperature and analyte loading).

Water uptake by CMSs and graphitized carbons was investigated by Fastyn et al. [34]. CMSs (e.g., Carboxen 1002, Carboxen 1003 and Anasorb CMS) adsorb higher amounts of water than graphitized carbons (e.g., Carbograph 5TD and Carbopack X and Carbopack Y), which had lower water-trapping levels. Two different water-adsorption mechanisms were in operation: adsorption on polar centers; and, micropore-volume filling. Adsorption on polar centers occurs at a low percentage of relative humidity (%RH). At high %RH, micropore-volume filling becomes predominant for CMS. The dry-purging technique is suggested to remove adsorbed water. While Carbograph 5TD and Carbopack X require only a few hundred ml of dry air, much larger volumes are needed for CMS.

Some new sorbents have recently been developed (e.g., Wu et al. [35] synthesized and assessed mesoporous silica MCM-41 for its applicability to VOC trapping). While it exhibited very uniform adsorption for C_8 – C_{12} compounds, it showed little sorption for smaller molecules (C_3 – C_7). In terms of TD of VOCs, C_8 – C_{12} compounds could be easily released at moderate temperatures of about 150°C, much lower than those needed in the case of CMSs. Two new generations of poly(styrene-divinylbenzene) resin (i.e. Bond Elut ENV and LiChrolut EN), commonly used in SPE, were evaluated by López et al. [36] as sorbents for gas-phase sampling followed by TD, and compared with Tenax TA. LiChrolut EN showed stronger retention, but poorer chromatographic behavior, giving asymmetric elution profiles. The two new sorbents decreased their retention with temperature much faster than Tenax.

Carbon nanotubes (CNTs), which can be visualized as a sheet of graphite that has been rolled into a tube, with either single walled or multi-walled structures, have attracted great attention because of their properties. Due to their porous graphite structure, it is possible to use CNTs as adsorbent to preconcentrate VOCs in environmental samples. Li et al. [37] evaluated a type of purified multi-walled CNT (PMWCNTs) as an adsorbent trapping for VOCs in gaseous samples. On PMWCNTs, all tested compounds presented breakthrough volumes two to three orders larger than those showed on Carbopack B, and recovery rates from 80 to 110%, which were not affected by humidity. Hussain et al. [38] studied the adsorptive behavior of single and multi-walled CNTs (SWCNTs and MWCNTs) either packed or self-assembled onto a micro-sorbent trap. The CNTs showed highly favorable adsorption as well as desorption, with rela-

tively large breakthrough volumes and narrow desorption bandwidth.

3.4. Desorption techniques

The adsorption of VOCs on solid sorbents is one of the most common sampling techniques. Once analytes are trapped, they must be released for analysis. The most common extraction techniques are solvent extraction and TD.

3.4.1. Solvent desorption. Solvent extraction allows longer sorbent beds, higher flow rates and larger total-sample volumes than TD. It is often used for processing passive samplers, and is the best technique for thermally-labile compounds. Furthermore, samples can be analyzed repeatedly, and no expensive equipment is required. However, the sample is diluted, and can be contaminated by the solvent. Trace analysis may require solvent evaporation, which can lead to losses of the most volatile compounds.

Analytes are extracted from the adsorbent with a low-boiling solvent [e.g., dichloromethane or carbon disulphide (CS_2)]. CS_2 is the most common solvent used for solvent desorption. It has good solubilization properties for many analytes, and a very low response on a flame-ionization detector (FID). However, it poses a serious risk to human health and the environment. Also, low boiling compounds can evaporate due to the adsorption heat released during desorption.

Elbir et al. [18] extracted VOCs trapped in activated carbon by adding 1 mL of CS_2 , using an ultrasonication bath and then centrifugation to obtain a clear phase at the top. Martins et al. [17] desorbed BTEX from coconut-shell charcoal by transferring the sorbent bed to vials and adding 1 mL of CH_2Cl_2 and agitating. Recently, pressurized liquid extraction (PLE) has been applied by Campos-Candel et al. [39] to extract BTEX from activated charcoal using acetonitrile as extraction solvent, obtaining recoveries >90% for all the compounds. This technique allowed the use of closed stainless-steel vessels that avoid the risk of airborne contamination, thus eliminating worker exposure to the solvent.

3.4.2. Thermal desorption. Due to the low concentrations of analytes, samples taken from relatively unpolluted environments cannot normally be analyzed using solvent desorption without additional sample concentration, and a procedure involving concentration, dilution and re-concentration is unwieldy in practice and prone to errors [40]. TD is a solvent-free method that works excellently with GC separation.

TD offers the advantage of lower LODs. This is because the sample can be completely transferred to the chromatographic column, and because it avoids the presence of a solvent peak, which can mask analyte peaks. It also

prevents analyte losses by minimizing sample manipulation and risks of contamination due to solvents.

The main disadvantage of TD is the initial cost of the equipment [41]. Another drawback is sample consumption in a single analysis, although modern TD equipment incorporates design modifications to allow re-collection of split samples in a fresh tube. This technique is commonly used for volatile chemical analysis, being the method of choice to determine VOCs in several studies of urban and industrial air [1,19,23,41], indoor and workplace atmospheres [20,27,33] and other atmospheres (e.g., those influenced by waste emissions [42]).

In some cases, analytes can be too strongly adsorbed [this occurs frequently with polar solutes and strong adsorbents (e.g., activated carbon)]. The analysis of thermally-unstable compounds is critical because of the risk of degradation. Furthermore, the adsorbents used in TD must be thermally stable to avoid artifact formation. The sorbents used in TD are Tenax TA, Chromosorb 106, and graphitized carbons (e.g., Carbotraps and CMSs). Activated charcoal and silica gel are not suitable for TD, since their high surface activity can lead to sample degradation at high temperatures.

Kornacki et al. [43] observed that graphitized carbons [e.g., Carbopack X, Carbograph 5TD and Carbotrap B (used to enrich samples of C₃ and C₄ alcohols)] produced experimental artifacts, and, after TD, recoveries were low, with the appearance of aldehydes and ketones in the chromatograms. However, polymeric adsorbents (e.g., Tenax TA and Chromosorb 106) do not exhibit such oxidative properties. The adsorbents commonly used in TD of VOCs have been reviewed [44].

When sampling with sorbent tubes, the sorbent may be thermally desorbed directly into the GC. However, this is not a rapid process and it would create a broad initial band in the capillary GC column, drastically reducing resolution. Consequently, a two-stage TD process with a focusing step is necessary. Analytes are desorbed and re-collected on the same kind of cooled secondary sorbent trap. This, in turn, is rapidly heated to inject the analytes into the column in a narrow plug. Oxygen and water are also purged from the sorbent tube before desorption, using dry carrier gas at ambient temperature. Fig. 4 shows a TD system. Packed and capillary traps are most commonly used as cold traps. Capillary traps have the same characteristics as columns, and they are usually constructed with fused silica with 0.2–0.53-mm ID and 40 cm long. Their main advantage is that the flow required to desorb analytes is fully compatible with GC capillary-column flows. Packed traps usually need split valves to adapt both flows, but they can take a greater load of analytes. These traps are usually quartz tubes that are filled with a sorbent or a mixture of them, and their common dimensions are 10 cm length and 2–3 mm ID.

The low-flow cold trap, which is a Perkin-Elmer (Waltham, Massachusetts, USA) modification of packed

traps, allows suitable concentration and subsequent desorption of the compounds at flows more compatible with capillary columns. This reduces the split ratio, and also the amount of analytes vented, which leads to improved LODs. Fernández-Villarrenaga et al. [41] compared the desorption of VOCs from two kinds of cold trap: standard packed and low flow. In the low-flow trap, they observed high significance of the desorption flow of tube and trap. The use of the low-flow cold trap enhanced sensitivity and improved LODs by more than 50%.

Short-path TD, patented by Scientific Instrument Services, Inc. (Ringoos, N.J., U.S.A.), is a TD system that sits directly on top of the GC injection port. Due to the short path of sample flow, these systems eliminate transfer lines, which are easily contaminated by samples, and optimize delivery of samples to the GC injector via the shortest path possible. The liquid-N₂-cooled cryo-focus trap is mounted in the GC oven, just below the injection port and around a short (5 cm) section of the capillary column. A small outboard power supply and controller unit is mounted alongside the GC [22].

Temperature-programmed desorption (TPD) has also been applied. In this case, organic compounds trapped in a solid adsorbent are released into the analytical instrument for detection. This uses a controlled temperature gradient that is slower than that of other trapping techniques. This makes the solid sorbent act as an analytical separation column. The adsorbent can be of any different type of solid adsorbent used to trap organic compounds from air samples [e.g., Ketola et al. [45] used TPD with a mixture of Tenax TA and HayeSep D to analyze in the same run polar compounds (e.g., methanol and ethanol) and non-polar compounds (e.g., benzene and toluene)].

Although TD is routinely used in conjunction with GC (TD-GC), this technique has been combined with SIFT-MS (see Section 4.3. below) to quantify volatile compounds (specifically xylene and toluene) more quickly than TD-GC and with no need for calibration standards. Due to the robustness of SIFT-MS analysis in the presence of water vapor and other major components of air, it is not necessary to purge the tubes to remove these constituents during the TD cycle, so reducing TD-cycle time [46].

4. On-line sampling

On-line chemical analysis is becoming increasingly important due to growing knowledge of the toxicity of VOCs and continual increase in environmental legislation driven by increasing public awareness of environmental problems. On-line analysis is useful to study variations in the levels of atmospheric pollutants, and for real-time detection of occasional high levels. It

provides rapid results that can be beneficial for speedy, appropriate response to a problem when one is detected. It is therefore the most widely used analytical technique in fixed and remote air-quality-control stations.

There is a critical need for instrumentation that can be used to carry out automated and on-line or on-site analysis rapidly and provide accurate information on a continuous basis. In general, spectroscopic techniques are ideal for on-line process monitoring because of their short analysis times. Currently, Fourier-transform infrared spectrometry (FTIR), X-ray fluorescence spectrometry (XRF), and MS are used for continuous, on-line monitoring [45]. Furthermore, band overlap requires a separation step, and, for this purpose, GC is an excellent technique for on-site environmental monitoring. Portable GCs have also been developed as a simpler and less expensive alternative to laboratory models.

Interference from moisture that commonly exists in air samples, the presence of interferences in complex matrixes, and the low levels of VOCs in environmental air require preconcentration, whereby analytes are first separated from the environmental matrix. In a continuous, on-line application, separation also has to be carried out continuously. In the following paragraphs, we describe the most common techniques for on-line extraction and preconcentration of VOCs in air samples.

4.1. On-line sorbent trap

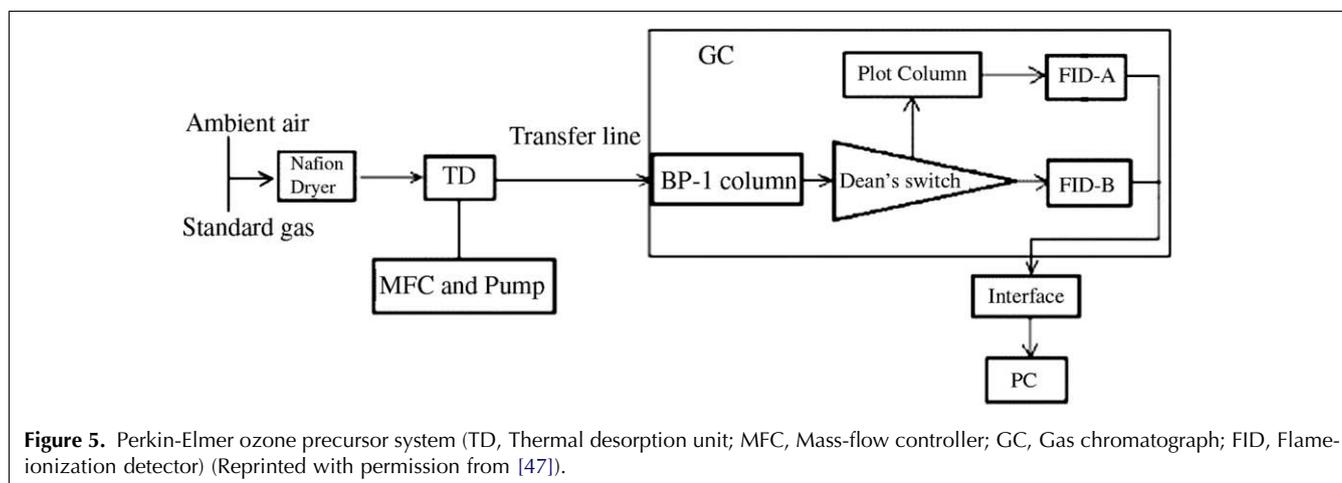
A sorbent trap is typically used off-line, as a second preconcentration step is necessary to refocus the analytes on the analytical column. This is frequently done by cryogenic trapping (see Section 3.4.2). There has been much effort to develop an on-line sorbent trap system that allows near-real-time measurements in ambient air and gaseous samples. On-line sorbent preconcentration has the advantage of reducing errors resulting from reactions that degrade the samples during storage of adsorbent tubes.

Cryogenic traps have been used to concentrate trace organic compounds in air analyses. Qin et al. [47] used a Perkin-Elmer system to monitor VOCs at unattended stations. The Perkin-Elmer system couples a GC with an adapted standard TD unit. Ambient air is pumped into the TD via a Nafion dryer at a controlled flow rate over a predetermined period of time and the analytes are retained in a trap cooled by a Peltier device. The trapped hydrocarbons are desorbed and injected into a GC. Typically, a dual chromatographic system is used, where the sample enters the first column, which separates the hydrocarbons in order of their boiling points from C₂ to C₁₀. The first eluting period of the C₂–C₅ species is cut by a Dean's switch to a plot column, where they are separated and detected by a FID. The C₆–C₁₀ compounds eluted from the first column are detected by another FID. Fig. 5 shows the Perkin-Elmer on-line sorbent trap system [47].

Cryotrapping is not suitable for samples with high humidity, because frozen moisture can appear in the cryotrap. The use of a microtrap for continuous on-line monitoring, as an alternative to cryotrapping, has been reported [48]. A microtrap is a short length of narrow-bore tubing that is packed with adsorbent. It can be used to concentrate the analytes by passing the sample stream through it. Then, the analytes can be thermally desorbed by electrical heating. Because the microtrap has low heat capacity, rapid heating is possible to desorb the organics as a narrow injection band.

Breakthrough of volatile compounds and quantitative desorption of large molecules are the major issues for microtraps, which are prone to low breakthrough volume as they contain a small quantity of adsorbent. A larger diameter trap with more adsorbent reduces breakthrough, but generates broad injection bands that reduce chromatographic resolution.

Sánchez et al. [49] evaluated an on-line multibed sorption trap, where a capillary-dimension, on-line sorption trap was used, packed with four different carbon-based adsorption materials that were graded



from weakest to strongest in the direction of the sample gas flow during sample preconcentration. The flow direction was then reversed for sample injection, in order to prevent the higher-boiling-point compounds in the sample from reaching the strongest adsorbing material during TD, from which they would be difficult to desorb as a sufficiently narrow vapor plug. This was applied to determine a mixture of 42 volatile compounds with volatility in the range C_5 – C_{12} .

On-line BTEX analyzers are special, automatic, portable GCs designed to measure selected organic compounds in situ. Air is pumped through a cold trap filled with a sorbent to trap BTEX. The trap is then heated and the VOCs are transferred by carrier gas to the GC with an FID or photoionization Detector (PID) for analysis [7].

One advantage of the BTEX analyzer is the high time resolution, typically obtaining time series of 15–30 min, so data can be compared and interpreted in real time. Moreover, it is possible to establish on-line data transmission as well as check the status of the instrument.

The disadvantages are high cost and the need for a monitoring hut with air conditioning, because a constant working temperature and carrier gas supply are required.

Commercial BTEX analyzers are commercially available, e.g.:

- Syntech Spectra GC955 series 600 BTEX Analyzer from Synspec B.V. (Groningen, The Netherlands), which focuses BTEX in a pre-column filled with Tenax TA, and is equipped with a PID;
- Model 8900GC BTEX Analyzer from Baseline-Mocon, Inc. (Lyons, Colorado, U.S.A.), equipped with a PID; and,
- GC 5000 BTX-2 from AMA Instruments (Ulm, Germany), with a pre-column filled with a combination of graphitized carbons and an FID.

4.2. Membrane extraction

Membranes are used for a number of diverse applications (e.g., microporous filtration, reverse osmosis, dialysis, and gas separation). Typically, analytes are transferred from a donor to an acceptor phase through a single membrane or a multi-membrane, where distinction can be made between non-porous and porous (solvent-impregnated) membranes. When determining VOCs in air samples, membrane extraction is particularly attractive for continuous monitoring applications due to its improved selectivity and the enrichment power of the membranes, minimized solvent use, and the automation potential (since the membrane allows continuous, on-line extraction and stripping of trace VOCs from the environmental matrix). The sample can continuously flow through or over the membrane, and the analytes can selectively permeate through the membrane while the bulk matrix of air and other interferences are

eliminated; near-quantitative removal of VOCs from the feed stream is possible [15].

4.2.1. Membrane introduction mass spectrometry (MIMS). In membrane-introduction MS (MIMS), one side of a thin membrane [typically polydimethylsiloxane (PDMS)] is directly exposed to the vacuum of the ion source of the MS. Exposing the other side of the membrane to the sample allows organic compounds to permeate the membrane wall. This is followed by diffusion in the gas phase to the ion source. Because the flow of the analyte matrix through the membrane is proportionally smaller than the flow of the desired organic analytes, analyte enrichment is obtained. This provides very sensitive levels of detection, as low as ng/m. Fig. 6 shows a MIMS set-up. The principles and recent developments of MIMS have been reviewed by Ketola et al. [50].

Membrane inlets do not offer direct sampling because of the enrichment step they provide. However, there are important advantages offered by MIMS (e.g., speed, lack of need for sample pre-treatment, low cost per sample, and the possibility of using it for long-term continuous monitoring). Different methods have been developed for MIMS air analysis [e.g., Ketola et al. [45] designed a new TPD device (see Section 3.4. above) to be used with MIMS]. The thin silicone membrane was kept at a high temperature, allowing most organic compounds to diffuse rapidly through the membrane. It was possible to measure low-molecular-weight compounds at sub-ng levels, with a total analysis time of 3–4 min. The development of low-power-consumption field instruments also enhances the on-site capabilities of MIMS (e.g., Hou et al. [51] developed a membrane inlet interface coupled to single-photon ionization (SPI) miniature time-of-flight mass spectrometer (TOF-MS) for on-line rapid measurement of VOCs in air).

4.2.2. Membrane extraction with a sorbent interface (MESI). Membrane extraction with a sorbent interface (MESI) was developed and later improved by

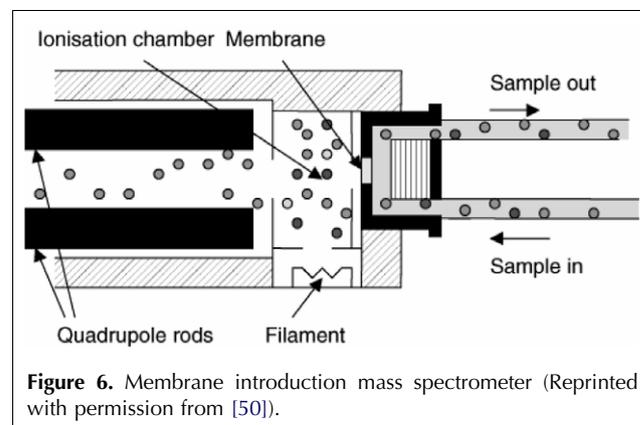


Figure 6. Membrane introduction mass spectrometer (Reprinted with permission from [50]).

Pawliszyn et al. [52]. This combines a hollow-fiber membrane module, a cryofocusing and TD sorbent interface, and capillary GC. The membrane is in direct contact with the sample. Analytes of interest diffuse across the membrane and are collected in the cryogenic trap. A heat pulse desorbs analytes to the GC column using a narrow concentration pulse.

This technique, using a sorbent microtrap of Tenax and Carboxen, was later combined with a portable micro-GC system [53] for on-site monitoring. A PDMS non-porous membrane was selected, providing rapid transport of analytes due to the high rate of diffusion, and preventing water and other polar matrices from entering the system. The sorbent trap replaced the GC injector, and the design of the trap was modified to enhance preconcentration of analytes.

The system allowed semi-continuous monitoring of samples, and increased the sensitivity of the micro-GC system by a factor of more than 100 by adding the MESI

system. In order to eliminate the inconvenience of concentrating water on the sorbent trap, a water trap was placed in the system between the membrane module and the sorbent interface. This system was also used to monitor acetone, benzene, toluene and ethylbenzene in laboratory air.

Fig. 7 shows the MESI extraction procedure and the major components of a MESI device.

4.3. SIFT-MS

SIFT-MS is a new technique that is increasingly being used for real-time VOC analysis. It is being used in on-line monitoring of environmental air [54]. SIFT-MS quantifies trace volatile compounds by reacting them with precursor ions (H_3O^+ , O_2^+ or NO^+) within a fast-flowing stream of helium gas. The precursor ions, generated using a microwave source and selected using a mass filter, are injected into the carrier gas where they warm to the carrier-gas temperature and react with the

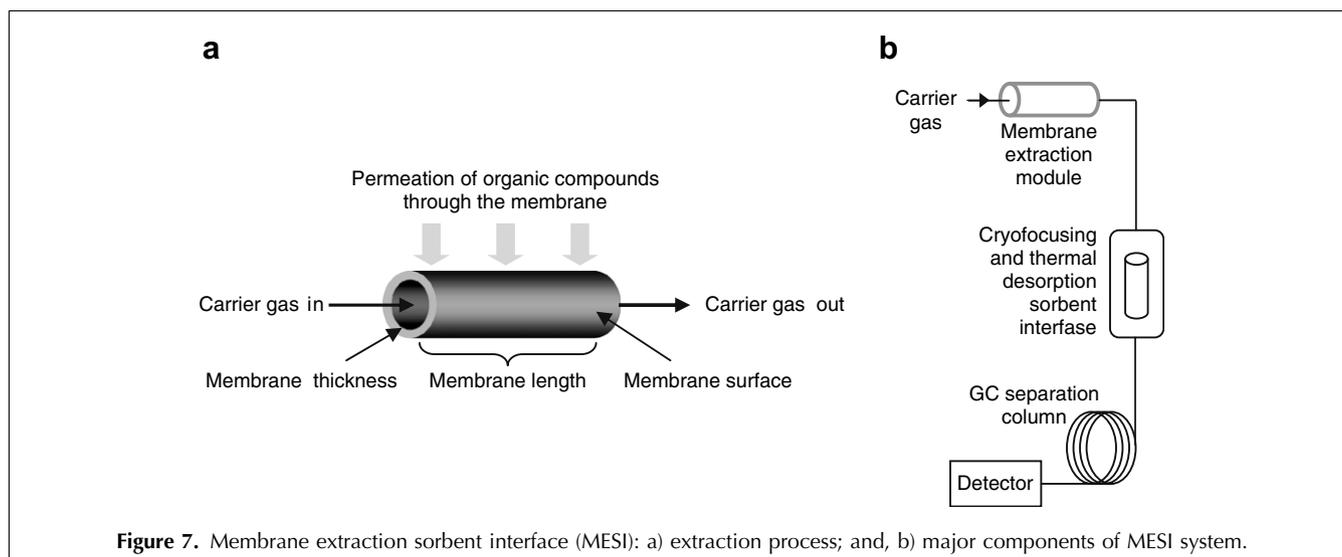


Figure 7. Membrane extraction sorbent interface (MESI): a) extraction process; and, b) major components of MESI system.

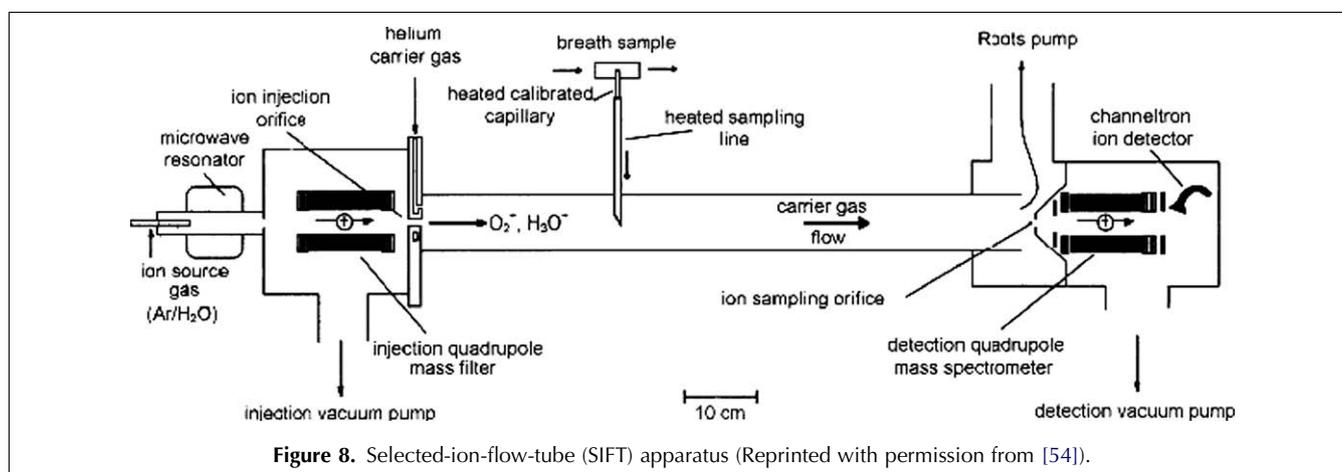


Figure 8. Selected-ion-flow-tube (SIFT) apparatus (Reprinted with permission from [54]).

trace gases introduced via a capillary at a known flow rate. The reaction produces characteristic product ions that are then analyzed using a differentially pumped quadrupole MS-ion-counting system [54]. Fig. 8 shows the SIFT apparatus.

If the kinetic constant of the reaction rate is known for the reaction between the trace compound of interest and the precursor ion, absolute quantification for the VOCs can be achieved in real time without using calibration standards [55].

The latest SIFT-MS instruments are capable of real-time quantification of trace gas levels in humid air with a sensitivity of $\mu\text{g}/\text{m}^3$. Although SIFT-MS lacks the chemical resolution of GC, it is a much faster analytical technique and is capable of significantly increasing the rate of sample throughput [46].

5. Conclusions

Whole-air collection with enrichment and trapping by active and passive sorbents are well-established techniques for collecting and preconcentrating air samples, which have been proposed by official organizations as standard methods for VOC monitoring.

For sorbent trapping, a great variety of sorbents are commercially available, although new sorbents recently been applied to gas-phase sampling showed significant advantages over the most commonly used sorbents in some cases.

As for desorption techniques, TD presents a useful, simple way to release adsorbed compounds. It is perfectly compatible with GC. In recent years, there have been some modifications (e.g., a low-flow cold trap, short-path TD and TPD), which have improved some capabilities of the analytical method.

Due to the growing interest in monitoring individual VOCs and to meeting the need for real-time data, great improvements in on-line methods have been reported in recent years. On-line sorbent trapping and membrane extraction coupled with GC can offer semi-continuous monitoring of VOCs. Moreover, SIFT-MS provides real-time data with no need for calibration standards, although this technique lacks the chemical resolution of GC.

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