Journal of Chromatography A, 1217 (2010) 2674–2684

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Review

Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air

Part 1: Sorbent-based air monitoring options

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A R T I C L E I N F O

Article history:
Available online 11 January 2010

Keywords:
Air monitoring
Sorbent tubes
Sorbent traps
VOCs
SVOCs
Volatile organic chemicals
Semi-volatile organic chemicals
Thermal desorption

A B S T R A C T

Sorbent tubes/traps are widely used in combination with gas chromatographic (GC) analytical methods to monitor the vapour-phase fraction of organic compounds in air. Target compounds range in volatility from acetylene and freons to phthalates and PCBs and include apolar, polar and reactive species. Airborne vapour concentrations will vary depending on the nature of the location, nearby pollution sources, weather conditions, etc. Levels can range from low percent concentrations in stack and vent emissions to low part per trillion (ppt) levels in ultra-clean outdoor locations. Hundreds, even thousands of different compounds may be present in any given atmosphere. GC is commonly used in combination with mass spectrometry (MS) detection especially for environmental monitoring or for screening uncharacterised workplace atmospheres. Given the complexity and variability of organic vapours in air, no one sampling approach suits every monitoring scenario. A variety of different sampling strategies and sorbent media have been developed to address specific applications. Key sorbent-based examples include: active (pumped) sampling onto tubes packed with one or more sorbents held at ambient temperature; diffusive (passive) sampling onto sorbent tubes/cartridges; on-line sampling of air/gas streams into cooled sorbent traps; and transfer of air samples from containers (canisters, Tedlar® bags, etc.) into cooled sorbent focusing traps. Whichever sampling approach is selected, subsequent analysis almost always involves either solvent extraction or thermal desorption (TD) prior to GC(/MS) analysis. The overall performance of the air monitoring method will depend heavily on appropriate selection of key sampling and analytical parameters. This comprehensive review of air monitoring using sorbent tubes/traps is divided into 2 parts. (1) Sorbent-based air sampling option. (2) Sorbent selection and other aspects of optimizing sorbent-based air monitoring methods. The paper presents current state-of-the-art and recent developments in relevant areas such as sorbent research, sampler design, enhanced approaches to analytical quality assurance and on-tube derivatisation.

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doi:10.1016/j.chroma.2009.12.042

1. Introduction

Airborne organic vapours range in volatility from methane to n-C_{20} and above and include most chemical groups—alcohols, ketones, aldehydes, esters, glycol ethers, chlorofluorocarbons, hydrogenated chlorofluorocarbons, other halogenated organics hydrocarbons, amines, sulphides, volatile fatty acids, mercaptans, etc. The concentration of these vapours in air will vary depending on the source, ambient temperature, wind/air speed and type of location (indoor, outdoor, etc.). Levels can range from low percent in stack and fugitive emissions to low ppt in ultra-clean ambient locations such as the mid-Pacific or Arctic.

Moreover, as there is little toxicological data for many of the VOCs found in air and as the toxicity of compounds for which data does exist varies over 6 orders of magnitude, it is usually necessary to measure the concentration of each individual chemical. Overall or total VOC (TVOC) data – such as that generated by direct read-out detectors – does not give sufficient information to allow an accurate assessment of the potential health risks associated with a given atmosphere. In the case of individual organic components, only methane is quantitatively and routinely monitored using direct read-out detectors.

Given the complexity and variability of organic vapours in air, no one sampling approach suits every monitoring scenario. A variety of different sampling strategies have been developed to address specific applications with most options being based on some form of sorbent tube/trap. Key examples include pumped or diffusive (passive) sampling onto sorbent tubes and using sorbent focusing traps to selectively concentrate vapours from online air streams or whole-air containers (canisters/bags).

Once sampled, the best analytical technology for identifying and measuring individual compounds in the complex ‘cocktail’ of hundreds, even thousands, of organic chemicals present in air is gas chromatography (GC) combined with mass spectrometry (MS). There are two main options for extracting retained organics from sorbent tubes/traps and transferring them into the GC(/MS), namely thermal desorption (TD) and solvent extraction. Thermal desorption is a gas extraction process offering significant concentration enhancement and 100% transfer of desorbed analytes into the GC column if required. The TD process also lends itself to automation—be it online, or for the sequential analysis of canisters/bags via sorbent traps or the automated desorption of sorbent tubes. In contrast, solvent extraction methods are inherently more manual. They typically involve extraction/dilution of compounds in a few millilitres of solvent before 1 or 2 μl are injected into the GC/MS. Generally speaking, this translates to a 1000-fold reduction in sensitivity relative to TD.

The first stage of the thermal desorption process normally involves heating sampled sorbent tubes (or SP(M)E devices) in a reverse stream of carrier gas (That is the flow of carrier gas through the tubes during desorption is in the opposite direction to the air flow during sampling.) Alternatively, a metered flow of whole air/gas can be drawn from a container or online manifold. In either case organic vapours are transferred from the primary sampling device (sorbent tube, air sample container or online manifold) and into a sorbent focusing trap maintained at near ambient or sub-ambient temperatures, typically using electrical (Peltier) cooling. Once all the compounds of interest have been transferred to the focusing device and all unwanted volatiles (e.g. water) have been swept to vent, the focusing device is itself thermally desorbed in

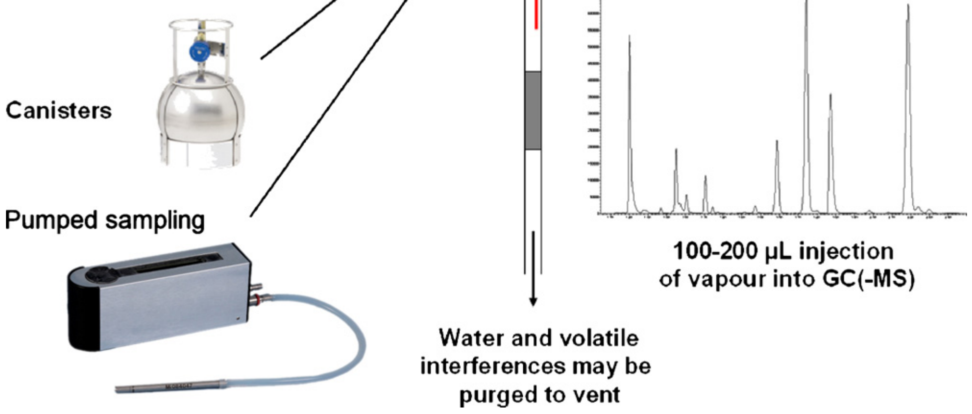

Fig. 1. Schematic overview of the two-stage thermal desorption process for sorbent-based air sampling.