

## Application Note 079

# Air monitoring – The advantages and applications of canisters and tubes

### Summary

This Application Note discusses the application areas of canister-based and sorbent-tube-based sampling for volatile organic compounds (VOCs), and the advantages and limitations of each approach.



### Introduction

Volatile (vapour-phase) organic 'air toxics' or 'hazardous air pollutants' (HAPS) are monitored in many industrial and urban environments as a measure of air quality. They range in volatility from methyl chloride to hexachlorobutadiene and trichlorobenzenes, and include some polar as well as non-polar compounds. Several national and international standard methods have been developed for air toxics and related air monitoring applications. Key examples include:

- **US EPA Method TO-17:** Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes.
- **US EPA Method TO-15** (and its predecessor TO-14): Determination of volatile organic compounds in air collected in SUMMA canisters and analyzed by GC-MS.
- **ASTM D-6196-03:** Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for volatile organic compounds in air.
- **ASTM D-5466:** Standard test method for the determination of volatile organic chemicals in atmospheres (canister sampling method).
- **ISO EN 16017:** Air quality – Sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/capillary gas chromatography.  
Part 1: pumped sampling; Part 2: diffusive sampling.
- **ISO EN 16000-6:** Determination of VOCs in indoor and chamber air by active sampling on Tenax TA, thermal desorption and gas chromatography MS/FID.

All these standards specify air sampling using either canisters or sorbent tubes with subsequent analysis by thermal desorption (TD-)GC-MS.

In response to increasing demand for ambient air toxics monitoring around the world, cryogen-free TD technologies have now been developed that offer an automated, method-compliant analytical platform for both canisters and tubes. The latest systems typically feature innovations such as repeat analysis for sorbent tubes, together with internal standard addition options for both canister and tube operation. Figure 1 shows splitless analysis of an air toxics standard using the TD system shown, in conjunction with GC-MS and using a capillary column specifically designed for US EPA 624 (VOCs in water).

### Air monitoring applications of tubes and canisters

As evidenced by US EPA Methods TO-15 and TO-17, both canisters and sorbent tubes are compatible with air toxics in typical ambient concentrations, *i.e.* 0.1–25 ppb. However, for compounds outside the volatility range of methyl chloride to hexachlorobutadiene, and for other air monitoring applications, there are differences between the two sampling methods that can make one more suitable than the other in a particular situation. The result of this is that, in effect, canisters and sorbent tubes complement one another, allowing analysts equipped with both to address a larger range of air monitoring applications than either method on its own.

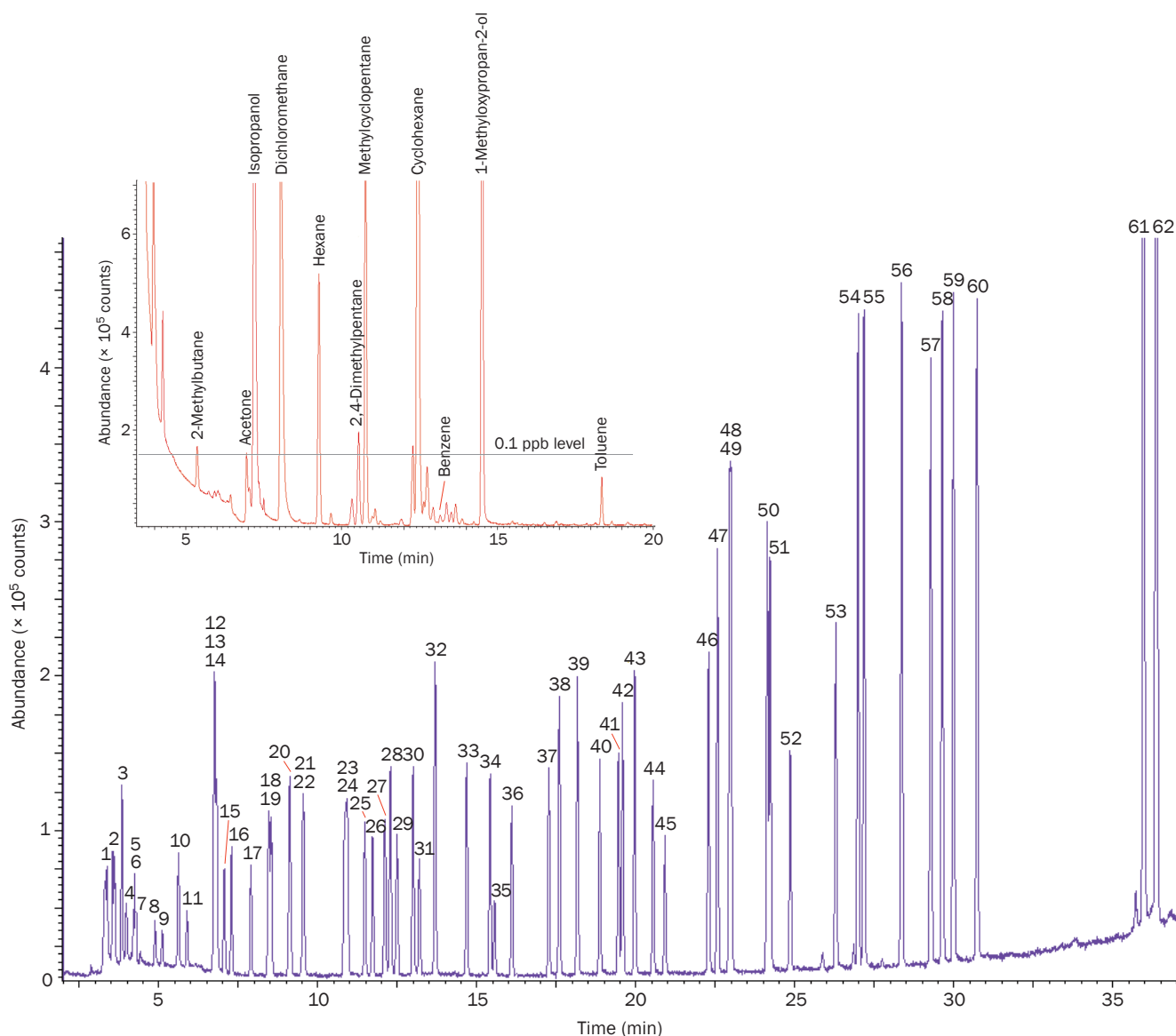
#### Analyte compatibility

Canisters are most useful for very volatile, non-polar compounds, key examples including C<sub>2</sub> hydrocarbons and some of the most volatile freons such as CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>. These compounds are of key interest in environmental research – for example global pollution mapping – but they are too volatile to be quantitatively retained by sorbent tubes at ambient temperatures. However, such compounds are very stable in canisters and are not prone either to adsorption on inner surfaces or to partitioning with the film of water adsorbed on its inner surface.

In contrast, sorbent tubes are better suited for less volatile analytes (polar or non-polar), which tend to condense on the inner walls of canisters, or to be subject to partitioning. Applications that would not work well with canisters, and that are better suited to sorbent tubes, include fuel gases (*e.g.* for soil gas surveys), most material emissions studies, and odour/fragrance profiling.



- |  |                                      |                                      |
|--|--------------------------------------|--------------------------------------|
| 1 Propene  | 21 1,1-Dichloroethane                | 42 Tetrachloroethene                 |
| 2 Dichlorodifluoromethane                                | 22 Vinyl acetate                     | 43 Methyl n-butyl ketone             |
| 3 1,2-Dichlorotetrafluoroethane                          | 23 <i>trans</i> -1,2-Dichloroethene  | 44 Dibromochloromethane              |
| 4 Chloromethane  | 24 Methyl ethyl ketone               | 45 1,2-Dibromoethane                 |
| 5 Chloroethane   | 25 Ethyl acetate                     | 46 Chlorobenzene                     |
| 6 Butadiene  | 26 Tetrahydrofuran                   | 47 Ethylbenzene                      |
| 7 Bromomethane   | 27 Chloroform                        | 48 ] <i>m</i> - and <i>p</i> -Xylene |
| 8 Chloroethene   | 28 1,1,1-Trichloroethane             | 49 ]                                 |
| 9 1,2-Dichloroethene                                     | 29 Cyclohexane                       | 50 <i>o</i> -Xylene                  |
| 10 Trichlorofluoromethane                                | 30 Carbon tetrachloride              | 51 Styrene                           |
| 11 Ethanol   | 31 Benzene                           | 52 Tribromomethane                   |
| 12 1,1-Dichloroethene                                    | 32 <i>n</i> -Heptane                 | 53 1,1,2,2-Tetrachloroethane         |
| 13 1,1,2-Trichloro-1,2,2-trifluoroethane<br>(Freon® 113) | 33 Trichloroethene                   | 54 1,2,4-Trimethylbenzene            |
| 14 Acetone   | 34 1,2-Dichloropropane               | 55 1,3,5-Trimethylbenzene            |
| 15 Carbon disulfide                                      | 35 1,4-Dioxane                       | 56 1-Ethyl-4-methylbenzene           |
| 16 Isopropanol   | 36 Bromodichloromethane              | 57 1,2-Dichlorobenzene               |
| 17 Dichloromethane                                       | 37 <i>cis</i> -1,3-dichloropropene   | 58 1,3-Dichlorobenzene               |
| 18 <i>tert</i> -Butyl methyl ether                       | 38 Methyl isobutyl ketone            | 59 (Chloromethyl)benzene             |
| 19 <i>cis</i> -1,2-Dichloroethene                        | 39 Toluene                           | 60 1,4-Dichlorobenzene               |
| 20 <i>n</i> -Hexane                                      | 40 <i>trans</i> -1,3-Dichloropropene | 61 1,2,4-Trichlorobenzene            |
|  | 41 1,1,2-Trichloroethane             | 62 Hexachlorobutadiene               |



**Figure 1:** Gas-phase TO-15 air toxic standard (1 ppb in 1 L) analysed splitless using Markes' UNITY™-CIA 8 system with GC-MS. The inset shows analysis of a whole-air sample collected from a semi-rural/semi-industrial environment, and analysed on the same system.

## Mode of sampling

Practical/operating differences between the two technologies also tend to favour specific applications. Evacuated canisters, for example, lend themselves to simple grab-sampling. The operator needs only to open a valve and then shut it again a few seconds later to collect a sample.

In contrast, sorbent tubes are more suited to time-weighted-average (TWA) monitoring – either with pumps (active sampling) or as passive (diffusive) monitors (see ISO EN 16017-2 and ASTM D6196-03). This fulfils the requirements of many workplace and environmental air regulations, which use TWA data for comparison with limit levels.

Similarly, the small size of sorbent tubes favours their application as unobtrusive personal/human exposure monitors that can be worn near the breathing zone without interfering with normal activities.

## Cleaning

Simpler cleaning procedures can also make it more convenient to use sorbent tubes in atmospheres where there is potential for high vapour concentrations. Examples of applications that can feature high-ppb or ppm levels of organic vapours include workplace air, some indoor environments, car cabin air (see Figure 2) and the exhaust from material emissions test chambers.

Canisters exposed to high vapour concentrations can require extensive cleaning after analysis, particularly if the contaminants are polar or higher-boiling than toluene. Canister cleaning typically involves a sequence of evacuations and air purges, often at elevated temperatures, followed by analysis of zero air from the cleaned canister to confirm that all contamination has been removed. If artefact levels remain high, the sequence of evacuation, purging and TD-GC-MS blank analysis is repeated until the appropriate level of cleanliness is achieved.

In contrast to this, the process of thermal desorption of sorbent tubes cleans the tube automatically. Typical desorption efficiencies are >99.95%, which means that desorbed/analysed tubes can usually be sent straight back out for field monitoring without any additional conditioning. In the worst case, tubes used for ppm-level monitoring may require one additional thermal cycle, after analysis, if they are to be re-used immediately for trace-level work. Moreover, even when such additional conditioning is required, it can be cost-effectively carried out on- or off-line, with negligible impact on the analytical apparatus or lab productivity. Cleaning costs and time considerations alone can mean that sorbent tubes are better suited than canisters to monitoring atmospheres containing higher levels (>100 ppb) of vapour.

A summary of the respective advantages of canisters and sorbent tubes for different air monitoring applications is provided in Table 1.

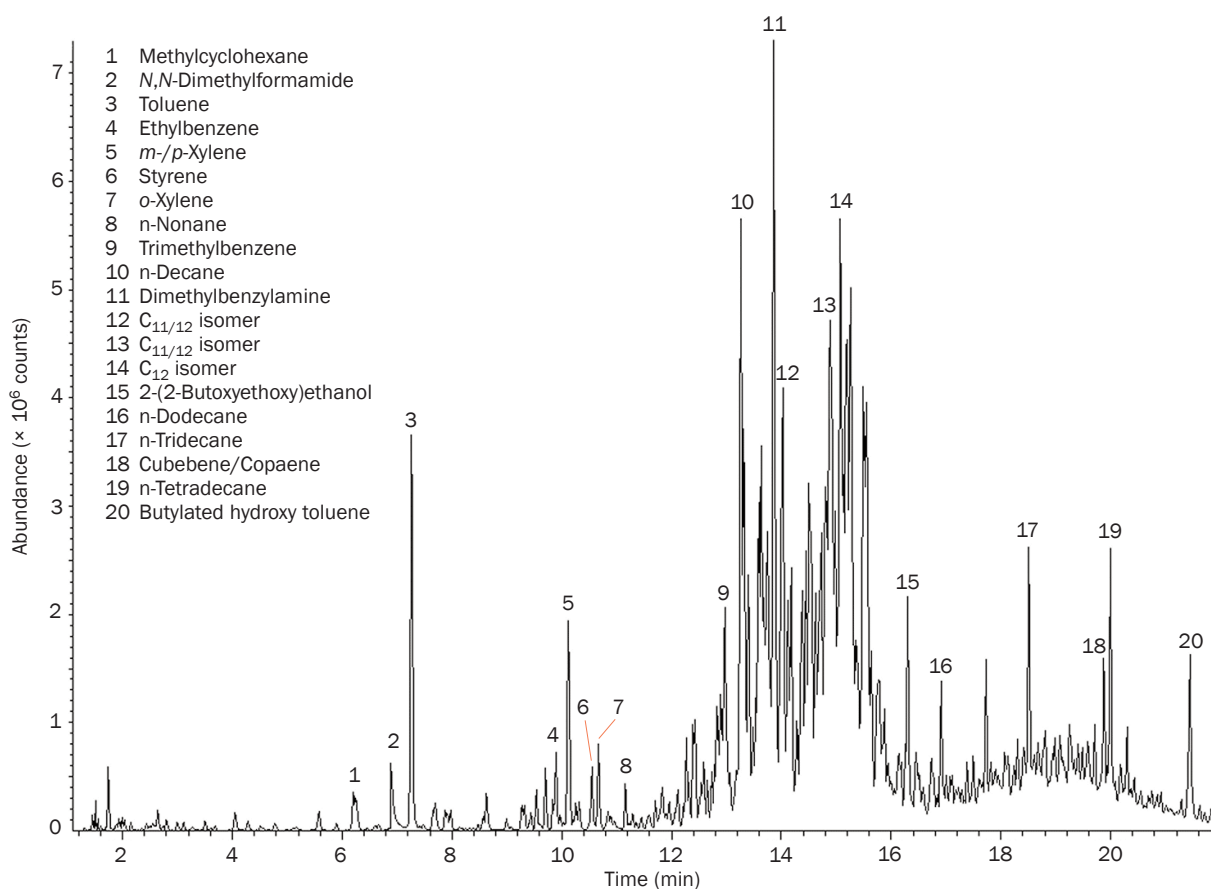


Figure 3: Air sampled from inside a passenger car at 40°C. Total VOC level: 9.7 ppm.

Sorbent tubes are:	Canisters are:
Well-supported by international standard methods for monitoring vapour-phase organics in workplace, indoor and ambient air and for material emissions testing. (ISO 16017, ASTM D6196, EN ISO 16000, etc.). Well validated for 'air toxics' (US EPA Method TO-17).	Well-validated for volatile 'air toxics' (methyl chloride to hexachlorobutadiene) in ambient air (US EPA Method TO-15). Well validated for ozone precursors (C <sub>2</sub> to C <sub>10</sub> hydrocarbons) in ambient air.
Small and unobtrusive for wearing in the workplace or ambient environment to monitor personal exposure	
Suitable for quantitative retention and recovery of compounds ranging in volatility from C <sub>3</sub> to n-C <sub>30</sub> and above Suitable for analytes over a wide range of polarity (including alcohols, esters, ketones, halocarbons, aldehydes and aromatics) and concentration range (from ppt to percent levels). Even milligram levels of analyte can be completely removed from a tube in one run.	Ideal for ultra-light compounds such as C <sub>2</sub> hydrocarbons and freons that are too volatile for quantitative retention by sorbent tubes at ambient temperature.
Easy to clean – the analytical process automatically cleans tubes, with no additional conditioning required, saving time and money.	
Relatively low-cost to buy, transport and store. Re-usable almost indefinitely.	
	Suitable for rapid transfer (not storage) of ultra-volatile reactive compounds such as H <sub>2</sub> S.
Suitable for diffusive and pumped sampling.	Ideal for simple grab-sampling.
Free from partitioning/poor recovery issues when analysing polar compounds in humid air.	Not prone to artefacts if stringently cleaned
Repeatable (if using a split, as is typical for all but the cleanest rural air samples, modern TD systems such as Markes' UNITY™ and TD-100™ offer quantitative re-collection for repeat analysis).	Repeatable (if analysis of a portion of the canister air sample offers sufficient sensitivity, canisters allow repeat analysis).
Compatible with large-volume sampling (>100 L in some cases). In combination with 100% transfer to the GC via TD, this offers optimum sensitivity.	
The simplest way of collecting time-weighted-average (TWA) samples, as required by many clean air and industrial hygiene regulations	
Well-validated with respect to storage stability (up to 30 days for multi-bed sorbent tubes; 1–2 years for stable compounds on single-bed sorbent tubes).	Well-validated for long-term storage of very light compounds.

**Table 1:** Comparison of the advantages of tubes and canisters.

## Conclusions

Cryogen-free, method-compliant thermal desorption technology is now available, offering high sensitivity measurement of air toxics in both canisters and tubes on a single analytical platform.

Both canisters and sorbent tubes have been extensively validated for monitoring air toxics in ambient indoor and outdoor air. Outside this specific application, canisters and tubes offer complementary air monitoring technology. Canisters offer ideal sampling technology for monitoring trace levels of very volatile and volatile organic compounds in ambient air, particularly if grab-sampling is an option. Canisters are not normally used for TWA monitoring, personal exposure assessment, higher-boiling compounds (>n-C<sub>9/10</sub>) or higher-concentration atmospheres, and they do require sophisticated cleaning apparatus/procedures.

Sorbent tubes are best suited to workplace, indoor and ambient air monitoring of analytes ranging from n-propane through to semi-volatiles; phthalates, PCBs, jet fuel, diesel, etc. They suit TWA monitoring and can be used in trace- or high-level atmospheres such as soil gas/vapour intrusion studies. Tubes are not suited for the most volatile freons or C<sub>2</sub> hydrocarbons, but provide an unobtrusive solution to personal exposure monitoring and are universally specified for material emissions testing.

## Trademarks

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