Air Monitoring - The Respective Advantages and Applications of Canisters and Tubes

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Introduction

Volatile 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 methylchloride (CH_3Cl) to hexachlorobutadiene (HCBD) & trichlorobenzenes (TCB) and include some polar as well as apolar compounds. Several international standard methods have been developed for air toxics and related air monitoring applications that specify air sampling using either canisters or sorbent tubes (Figure 1) 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 which offer an automated, method compliant analytical platform for both canisters and tubes (see Figure 1).

Figure 1: Markes Series 2 (ULTRA-) UNITY-Air Server/CIA TD systems. Cryogen-free, method compliant analysis for sorbent tubes and canisters.

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 2 shows splitless analysis of an air toxic 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).

Tubes and canisters – respective air monitoring applications

As evidenced by US EPA Methods TO-15 and TO-17 (1, 2), both canisters and sorbent tubes are compatible with air toxics in typical ambient concentrations i.e. at 0.1 to 25 ppb levels. However, for compounds outside the CH_3Cl to HCBD range and for other air monitoring applications there are differences between the two sampling methods which can make one technology more suitable than the other for a particular situation. In effect, canisters and sorbent tubes provide complementary sampling technology.

Canisters are most useful for very volatile, nonpolar compounds. Examples: C_2 hydrocarbons and some of the most volatile freons e.g. CF_4 and C_2F_6. These compounds are of key interest in environmental research – for example global pollution mapping – yet they are too volatile to be quantitatively retained by sorbent tubes at normal ambient temperatures. Such compounds are very stable in canisters and are not prone to adsorption on inner surfaces or partitioning effects.

Sorbent Tubes, in contrast, are more applicable for less volatile analytes (polar or apolar), which would tend to condense on the inner walls of canisters or partition into the film of water adsorbed on its inner surface. Examples: fuel gases (e.g. for soil gas surveys), most material emissions studies and odor/fragrance profiling.

Practical/operating differences between the two technologies also tend to favour specific applications. With evacuated canisters 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 (3, 5).

Simpler cleaning procedures can also make it more convenient to use sorbent tubes in atmospheres where there is potential for high vapor concentrations. Examples of applications which can feature high ppb or ppm levels of organic vapors include workplace air, some indoor environments, car cabin air and the exhaust from material emission test chambers. Canisters exposed to high vapor concentrations can require extensive cleaning post-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 can to confirm that all contamination has been removed. If artifact 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.

1 Propylene
2 Dichlorodifluoromethane
3 1,2–Dichlorotetrafluoroethane
4 Methyl chloride
5 1,2-Dichloroethane
6 1,3–Butadiene
7 Methyl bromide
8 Chloroethane
9 Trichlorotrifluoroethane (Freon 113)
10 Ethanol
11 1,2,-Dichloroethlyene
12 1,1,2-Trichloro trifluoroethane
13 Isopropyl alcohol
14 Carbon disulfide
15 Methylene chloride
16 Tert-butyl methyl ether
17 Cis-1,2-Dichloroethylene
18 n-Hexane
19 Vinyl acetate
20 1,1-Dichloroethane
21 Methyl ethyl ketone
22 Trans-1,2-Dichloroethylene
23 Ethyl acetate
24 Tetrahydrofuran
25 Chloroform
26 1,1,1-Trichloroethane
27 Cyclohexane
28 Carbon tetrachloride
29 Benzene
30 Vinyl chloride
31 n-Heptane
32 Trichloroethylene
33 1,2–Dichloropropane
34 1,4-Dioxane
35 Bromodichloromethane
36 Trans-1,3-dichloropropene
37 Methyl isobutyl ketone
38 Toluene
39 Cis-1,3-Dichloropropene
40 1,1,2-Trichloroethane
41 Tetrachloroethylene
42 Methyl n-butyl ketone
43 Dibromochloromethane
44 1,2–Dibromoethane
45 Chlorobenzene
46 Ethylbenzene
47 Xylene
48 Xylene
49 Xylene
50 Styrene
51 Tribromomethane
52 1,1,2,2-Tetrachloroethane
53 1,2,4-Trimethylbenzene
54 1,3,5-Trimethylbenzene
55 1-Ethyl-4-methyl benzene
56 1,2-Dichlorobenzene
57 1,3-Dichlorobenzene
58 Chloromethylbenzene (alpha)
59 1,4–Dichlorobenzene
60 1,2,4–Trichlorobenzene
61 Hexachloro-1,3-butadiene

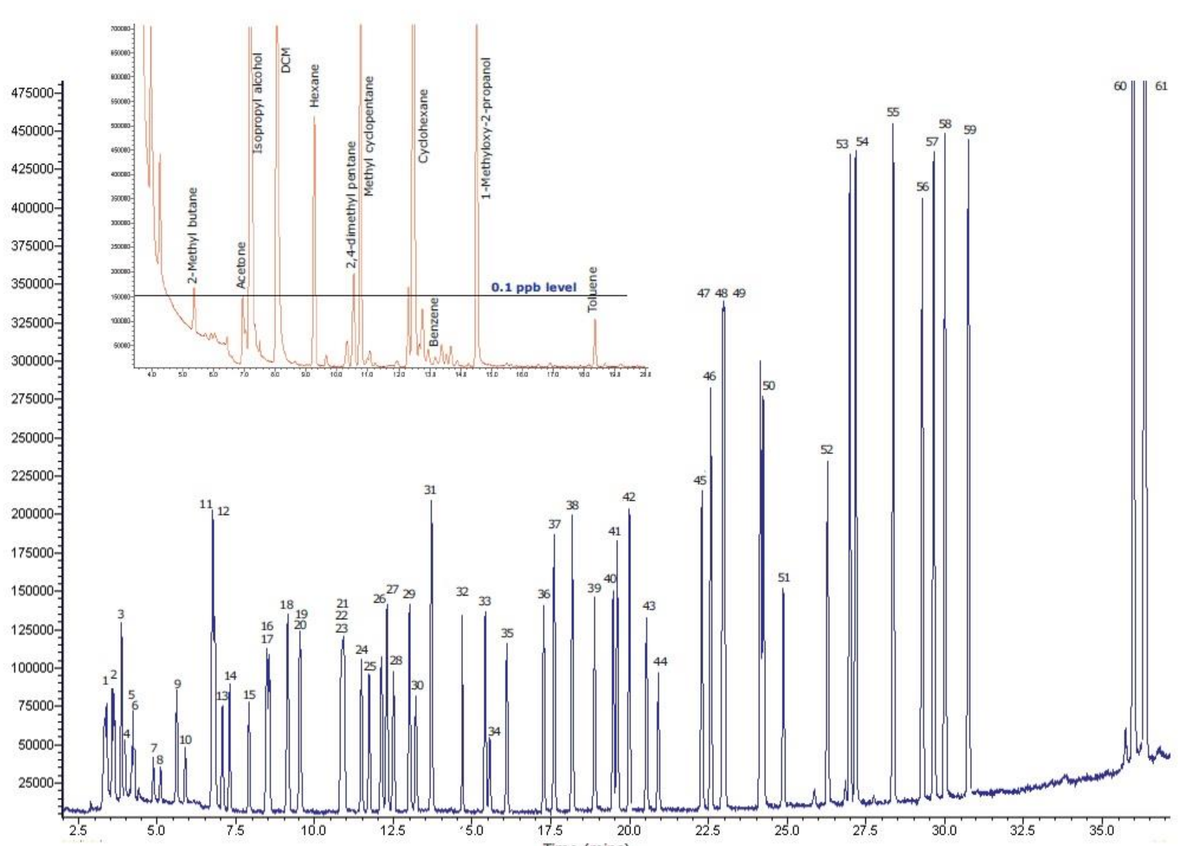

Figure 2: Gas-phase TO-15 Air Toxic standard (1 ppb in 1 L, Restek) analysed splitless using the Markes Series 2 UNITY-CIA 8 TD system with GC/MS.
Inset shows measurement of a whole-air sample collected from a semi-rural/semi-industrial environment and analyzed on the same system.

Advantages of canisters and sorbent tubes

Sorbent tubes are:	Canisters are:
Well supported by international standard methods for monitoring vapor-phase organics in workplace, indoor and ambient air and for materials emissions testing. (ISO 16017, ASTM D6196, EN ISO 16000, etc).	Well validated for volatile 'air toxics' (methyl chloride to hexachlorobutadiene) in ambient air (US EPA Method TO-15).
Well validated for 'air toxics' (US EPA Method TO-17).	Well validated for ozone precursors (C2 to C10 hydrocarbons) in ambient air.
Small and unobtrusive for wearing in the workplace or ambient environment to monitor personal exposure.	Ideal for ultra-light compounds such as C2 hydrocarbons, and freons which are too volatile for quantitative retention by sorbent tubes at ambient temperature.
Suitable for quantitative retention and recovery of compounds ranging in volatility from n-C3 to n-C30 and above.	Suitable for rapid transfer (not storage) of ultra-volatile reactive compounds such as H_2S.
Suitable for analytes over a wide polarity and concentration range – alcohols, esters, ketones, halocarbons, aldehydes, aromatics, *etc.* and from ppt to % levels. Even mg levels of analyte can be completely removed from a tube in 1 run.	Ideal for simple grab sampling.
The analytical process automatically cleans tubes – No additional conditioning required. Saves time/cost.	Not prone to artifacts if stringently cleaned.
Relatively low cost to buy, transport and store.	Repeatable (If analysis of a portion of the canister air sample offers sufficient sensitivity, canisters allow repeat analysis).
Re-usable almost indefinitely.	Well validated for long term storage of very light compounds.
Suitable for diffusive and pumped sampling.	
Free from partitioning/poor recovery issues when analyzing polar compounds in humid air.	
Repeatable. (If vapor levels are such that tube analysis can be carried out with a split (includes all but the cleanest rural air), modern TD systems such as Markes UNITY 2 and ULTRA *50:50* offer quantitative re-collection for 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-sorbent tubes, 1-2 years for stable compounds on single sorbent tubes.	

Conclusion

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 (hazardous air pollutants ranging in volatility from methyl chloride to hexachlorobutadiene) 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- C9/10) 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/vapor intrusion studies. Tubes are not suited for the most volatile freons or C2 hydrocarbons but provide an unobtrusive solution to personal exposure monitoring and are universally specified for materials emissions testing.

References

1. US EPA Method TO-17 Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes

2. US EPA Method TO-15 (and its predecessor TO-14) Determination of volatile organic compounds in air collected in SUMMA canisters and analyzed by GCMS

3. ASTM D-6196-03 Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for volatile organic compounds in air

4. ASTM D-5466 Standard test method for the determination of volatile organic chemicals in atmospheres (Canister sampling method).

5. 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 or Part 2: diffusive sampling

6. 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.

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