

Thermal Desorption Technical Support

Note 79: Air monitoring - the respective advantages and applications of canisters and tubes

Key Words:

Environmental, Air toxics, Canisters, On-line sampling

Introduction

Volatile (vapor-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 methylchloride to hexachlorobutadiene & trichlorobenzenes and include some polar as well as apolar 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 GCMS
- 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 or 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 (Figure 1) with subsequent analysis by thermal desorption (TD)–GC/MS.



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

In response to increasing demand for ambient air toxics monitoring around the world, cryogenic TD technologies have now been developed which offer an automated, method compliant analytical platform for both canisters and tubes (see Figure 1). The latest systems typically feature innovations such as repeat analysis for

adsorbent 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).

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

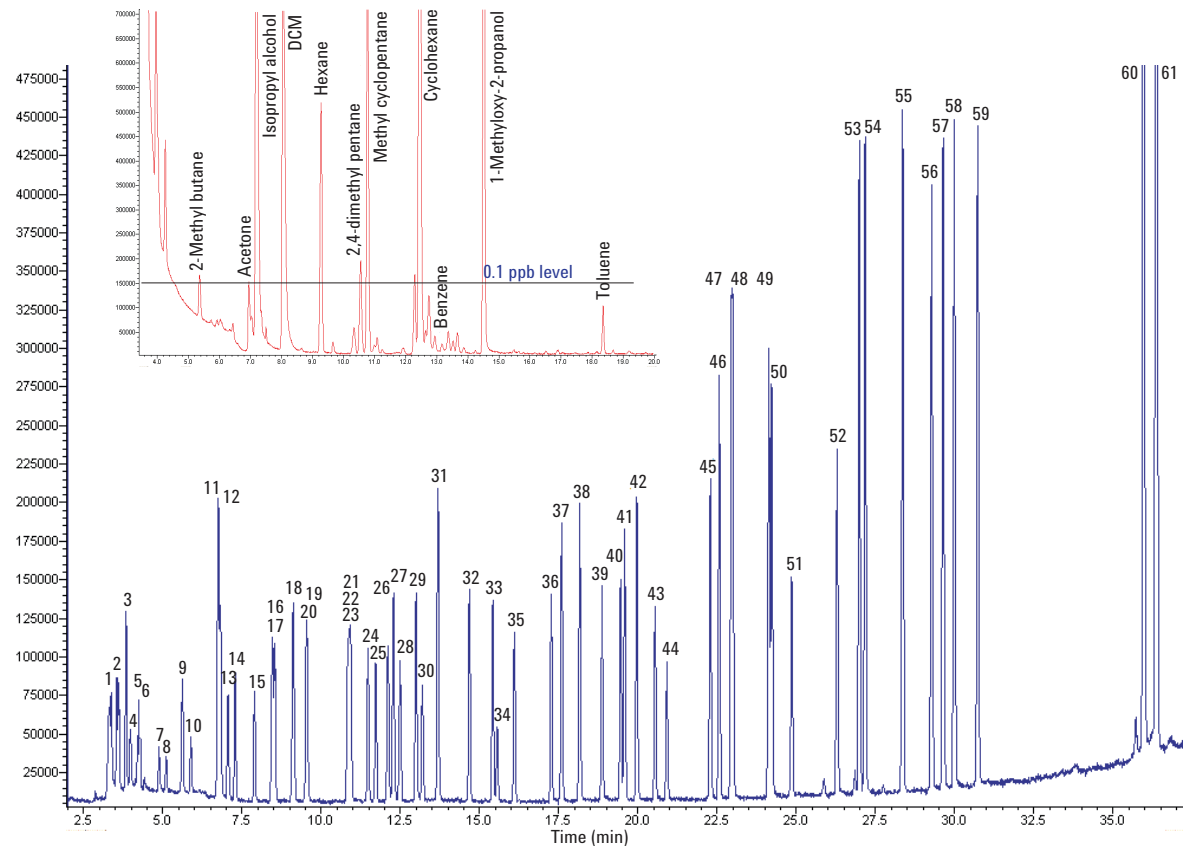


Figure 2: Gas-phase TO-15 Air Toxic standard (1 ppb in 1 L) analysed splitless using the Markes Series 2 UNITY-CIA 8 TD system with GC/MS. Inset shows measurement of a whole-air sample collected from a semi-rural/semi-industrial environment and analyzed on the same system

Tubes and canisters – respective air monitoring applications

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.* at 0.1 to 25 ppb levels. However, for compounds outside the methylchloride to hexachlorobutadiene 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 allowing analysts equipped with both to address a larger range of air monitoring applications than either method on its own.

Canisters are most useful for very volatile, nonpolar compounds. Key examples include; C₂ hydrocarbons and some of the most volatile freons *e.g.* CF₄ and C₂F₆. 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.

In contrast, sorbent tubes 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. Example applications that would not work well by canisters and that are better suited to sorbent tube sampling include: 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. 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 D 6196-03.) 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 favors their application as unobtrusive personal/human exposure monitors that can be worn near the breathing zone without interfering with normal activities.

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 (see Figure 3) 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. In the worst case, tubes used for ppm-level monitoring may require one additional thermal cycle, post analysis, if they are to be

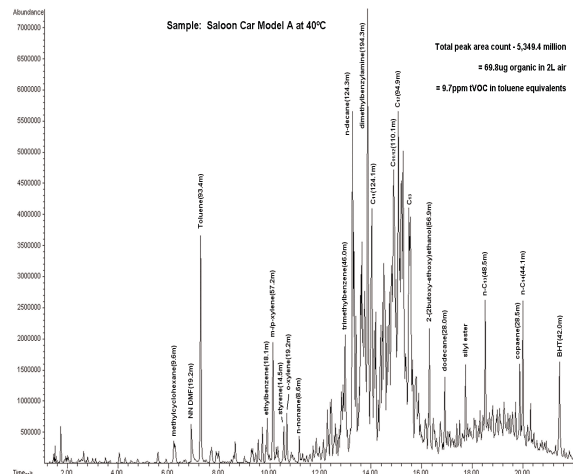


Figure 3: Air sampled from inside a saloon car at 40°C. Total VOC level: 9.7 ppm

re-used immediately for trace level work. Moreover, even if 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/time considerations alone can mean that sorbent tubes are better suited

than canisters to monitoring atmospheres containing higher levels (>100 ppb) of vapor.

A summary of the respective advantages of canisters and sorbent tubes for different air monitoring applications is tabulated below.

Sorbent tubes are:	Canisters are:
<p>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)</p> <p>Well validated for 'air toxics' (US EPA Method TO-17)</p> <p>Small and unobtrusive for wearing in the workplace or ambient environment to monitor personal exposure</p> <p>Suitable for quantitative retention and recovery of compounds ranging in volatility from n-C₃ to n-C₃₀ and above</p> <p>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.</p> <p>The analytical process automatically cleans tubes – No additional conditioning required. Saves time/cost.</p> <p>Relatively low cost to buy, transport and store. Re-usable almost indefinitely</p> <p>Suitable for diffusive and pumped sampling</p> <p>Free from partitioning/poor recovery issues when analyzing polar compounds in humid air.</p> <p>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.)</p> <p>Compatible with large volume sampling (> 100 L in some cases.) In combination with 100% transfer to the GC via TD – this offers optimum sensitivity</p> <p>The simplest way of collecting time weighted average (TWA) samples as required by many clean air and industrial hygiene regulations</p> <p>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</p>	<p>Well validated for volatile 'air toxics' (methyl chloride to hexachlorobutadiene) in ambient air (US EPA Method TO-15)</p> <p>Well validated for ozone precursors (C₂ to C₁₀ hydrocarbons) in ambient air.</p> <p>Ideal for ultra-light compounds such as C₂ hydrocarbons, and freons which are too volatile for quantitative retention by sorbent tubes at ambient temperature.</p> <p>Suitable for rapid transfer (not storage) of ultra-volatile reactive compounds such as H₂S</p> <p>Ideal for simple grab sampling.</p> <p>Not prone to artifacts if stringently cleaned</p> <p>Repeatable (If analysis of a portion of the canister air sample offers sufficient sensitivity, canisters allow repeat analysis).</p> <p>Well validated for long term storage of very light compounds.</p>

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 (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 ($>n\text{-C}_9/\text{C}_{10}$) 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 semivolatiles; 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 C_2 hydrocarbons but provide an unobtrusive solution to personal exposure monitoring and are universally specified for materials emissions testing.

Applications were performed using the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

Agilent Technologies
Published July 23, 2013
5991-2826EN