

Determination of Volatile Organic Compounds in Ambient Air using Sorbent Tubes and Automated, Cryogen-Free Thermal Desorption

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Introduction

Volatile Organic Compounds (VOCs) are monitored in many industrial and urban environments as a measure of air quality. Several standard methods have been developed for this application including US EPA method TO-17⁽¹⁾. This monitoring procedure involves pulling a volume of air through a sorbent packing to collect VOCs followed by a thermal desorption (TD) capillary GC-MS analytical procedure.

This work presents a VOCs monitoring procedure with the use of a cryogen-free TD technology that offer an automated method compliant to TO-17.

Results and Discussion

The analytical system used in this study comprised a thermal desorber coupled to a GC-MS. The sorbent tubes were heated in a flow of carrier gas transferring the analytes to a cryogen-free, electrically-cooled (25°C), sorbent-packed focusing trap. Once the process of transferring vapors from the sample/sorbent tube to the focusing trap was completed (primary desorption), the trap was purged with dry carrier gas in the sampling direction to remove residual water. The flow of carrier gas was then reversed and the trap heated rapidly. At this point the retained organics were desorbed into the carrier gas stream and transferred/injected into the GC analytical column. The desorption of the focusing trap is so efficient that splitless analysis is possible without significant peak broadening, ensuring optimum sensitivity.

Tubes packed with Carbograph 1TD™ and Carboxen™ 1003 were used and the pumped air sampling flow rates were 50 ml/min. A 62 component 1 ppm gas standard in nitrogen was used in combination with an air actuated 6 port valve to inject 1 ml aliquots of standard gas into the sorbent tubes.

The quantitative re-collection of split flow, available in this system, facilitates repeat analysis and validation of TO-17 method/data. The repeat analysis of a sample equivalent to 1 L of 1 ppb air toxics standard, split 10:1, demonstrates quantitative recovery across the analyte volatility range. Six repeat analyses were carried out on samples equivalent to a 1 L volume of 1 ppb standard run under splitless conditions and typical RSDs were

less than 6%. Carryover for 1 L of 10 ppb standard splitless analysed was less than 0.5%. The system linearity under splitless conditions resulted in R² values of 0.99 for most analytes.

The Minimum Detection Limits were found to be below 0.1 ppb for all 62 components tested under both 10:1 split and splitless conditions, assuming a minimum 1 L air/gas sample volume and full scan mode. Measurement at lower concentrations could be achieved by using the MS in SIM mode.

Real air samples were collected at a flow rate of 50 ml/min for 20 min giving a total volume of 1 L each, in three different locations: office, laboratory and semi rural outside area. Each sample tube was analysed splitless in full scan MS from 10 - 300 amu. The chromatograms obtained are presented in Figure 1.

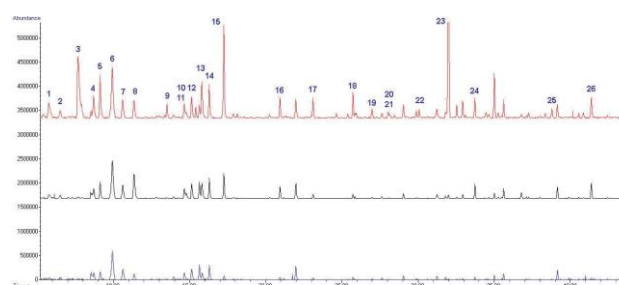


Figure 1. Chromatograms from three 1 L real air samples.

1 Methanol	10 2-Methyl hexane	19 Xylene
2 2-Methyl butane	11 Cyclohexane	20 Alpha-pinene
3 Ethanol	12 3-Methyl hexane	21 Cyclohexanone
4 Acetone	13 Heptane	22 Alpha-myrcene
5 Isopropyl alcohol	14 Acetic acid	23 D-limonene
6 2-Methyl pentane	15 1-Methyl-2-propanol	24 Phenol
7 3-Methyl pentane	16 Toluene	25 Menthol
8 Hexane	17 Hexanal	26 2-Phenoxy ethanol
9 Ethyl acetate	18 Xylene	

Conclusions

This work demonstrates the suitability of an automated, cryogen-free TD procedure to analyze VOCs in air, compliant to EPA TO-17 method. The system used permits repeat analysis for tubes, together with internal standard addition options. High sensitivity was achieved, with quantitative detection of 0.1 ppb on sorbent tubes and even less with the MS in SIM mode and/or sampling larger air volumes.

¹ EPA Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes.