

Study of Some Adsorbents for Sampling and Analysis of Several Volatile Organic Compounds

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In this study, the effect of concentration on some critical thermal desorption parameters such as desorption temperature, desorption time and cold trap temperature were evaluated and compared when using tenax TA and anasorb CMS for the sampling and analysis of acetone, benzene, toluene, methylethylketone, tetrachloroethylene and styrene at low and high concentration levels.

Key Words: Sampling, Adsorbents, Volatile compounds.

INTRODUCTION

Volatile organic compounds (VOC) can occur in non-industrial indoor and outdoor air as well as industrial workplaces and also in some food packing materials. The most widely used analytical method for the study of volatile organic compounds is sampling on to adsorbents and subsequent thermal desorption of trapped compounds on to a capillary gas chromatographic column and detection using generally flame ionization or mass spectrometric detection^{1,2}. Long term diffusive sampling, for one to four weeks sampling periods, is cost effective and easy to apply for measuring ambient VOC levels provided with appropriate uptake rates³. Recent developments in monitoring environmental air quality are about measurement of annual average concentrations. Passive sampling of VOC using adsorbent tubes for long-term exposure periods (14 weeks) is cost effective for this purpose, but appropriate uptake rates should be determined prior to sampling.

The need for pre-concentration of compounds in environmental samples to overcome the detection limit of detector used, particularly flame ionization detectors, leads to the extensive use of solid adsorbents in volatile organic compound analysis in headspace and environmental air. Solid adsorbents used for sampling of compounds present in headspace and ambient air are basically gas chromatography column packings.

Tenax TA is a traditional adsorbent trapping medium to high boiling compound, especially useful for low concentrations because of its low background. Anasorb CMS is a traditional carbon molecular sieve adsorbent for trapping low-boiling compounds. Both are suitable for use in EPA methods TO-2 or IP-IB.

Compounds trapped on adsorbents can be stripped subsequently by either solvent extraction or thermal desorption. Thermal desorption is a simple extension of the technique of gas chromatography (GC) and is most commonly used in combination with a GC analyzer. In the process of thermal desorption, heat and a flow of inert gas are used to extract volatile and semi-volatile organics retained

in a sample matrix or on a sorbent bed. Adsorbents are selected for their thermal stability in addition to their adsorptive qualities.

The aim of this study was to compare the suitability of two adsorbents for the collection and the analysis of several typical volatile organic compounds. Some critical thermal desorption parameters such as desorption time and cold trap temperature were evaluated for tenax TA and anasorb CMS for acetone, benzene, toluene, methylethylketone (MEK), tetrachloroethylene (TCE) and styrene at low and high concentration levels.

EXPERIMENTAL

Experiments were performed by loading the related compounds on the adsorbent tubes and analyzing them by thermal desorption gas chromatography and FID detector system for the optimization of analytical parameters and adsorbent selection for sampling of several volatile organic compounds. ATI Unicam 610 model gas chromatograph fitted with Tekmar AEROTrap 6000 thermal desorption cold trap injector and flame ionization detector was used for the subsequent analysis of the compounds.

Adsorbent Tube Loading

A mixture of acetone, benzene, toluene, methylethylketone, tetrachloroethylene and styrene were prepared by syringing 500 μL of each of these analytes into a vial fitted with a septum seal.

Total sixteen adsorbent tubes, eight tenax TA and eight anasorb CMS, were placed in an aluminium tube holder. Two replicates of each adsorbent tube were analyzed for each parameter set.

The tubes in the tube holder were placed inside the 5 L volume glass vessel with a septum fitted cap. A 1 μL aliquot of the standard mixture was syringed into the vessel through septum and the tubes were exposed to the vapour of this mixture for 1 h for loading compounds on the adsorbent tubes prior to the analysis to simulate the real sampling case⁴.

A 0.6 μL aliquot of the standard mixture was syringed into the vessel through septum of experiment and the tubes were exposed to the vapour of this mixture for 1 h to compare two adsorbents for the sampling of volatile organic compounds in air.

Adsorbent tubes were conditioned and kept in refrigerator in their vial capped glass containers before and after each sampling.

Thermal desorption parameters investigated

Trap cool down ($^{\circ}\text{C}$): Max. 100, Min. 180

Desorb time (min): Max. 10, Min. 5

Loading volume (μL): 1

The precision of the tube loading method was investigated for both high and low loading on tenax TA and anasorb CMS adsorbents by doing all experiments two times and desorbing them to obtain the % RSD between the tubes.

Automatic thermal desorber parameters

Desorption temperature: 250 $^{\circ}\text{C}$ (tenax TA)/300 $^{\circ}\text{C}$ (anasorb CMS); trap hold: 4 min; trap high: 250 $^{\circ}\text{C}$; split injection, split factor: (24.8% to GC).

GC conditions

Column: 25 m × 0.32 mm × 0.25 µm, polydimethyl siloxane WCOT capillary column.

Carrier gas: N₂ (10 psi), Make up/ref: 0, detector temperature: 250°C, injection temperature: 200°C, column temperature: 40°C, init time: 2 min, ramping: 100C/min, upper temperature: 200°C, temperature program: column temperature was held for 2 min at 40°C, then increased at 10°C/min to 200°C, which was not held at this temperature.

Identification of analytes

Retention times of analytes were determined by direct liquid injection (Table-1).

TABLE-1
PHYSICAL PROPERTIES AND RETENTION TIMES OF
VOLATILE ORGANIC COMPOUNDS

	b.p. (°C)	m.w. (g/mol)	Retention time (min)
Acetone	56	58.08	5.95
MEK	80	72	6.87
Benzene	80.2	77	7.21
Toluene	111	91	9.16
TCE	121	165.83	10.69
Styrene	146	104	11.01

RESULTS AND DISCUSSION

Mean area values obtained at the analysis of two replicates for each adsorbent were given in Table-2. The comparison of critical parameters in the analysis of VOC were shown for tenax TA in Fig. 1 and for anasorb CMS in Fig. 2.

TABLE-2
MEAN AREA VALUES ON TENAX TA AND ANASORB CMS

Adsorbent	Tenax TA				Anasorb CMS			
	10	10	5	5	10	10	5	5
Desorb time (min)	10	10	5	5	10	10	5	5
Trap cool down (°C)	-100	-180	-100	-180	-100	-180	-100	-180
Acetone	267.5	1845	1800	6363	244.5	2161.5	3215	9195
MEK	601	4895	4568	6702	488.5	5893.5	7051	7378
Benzene	118.5	1499	1644	1533	155.5	3105.5	7661.5	16622.5
Toluene	542.5	7971	7500.5	10762	478.5	10139.5	11228	8515
TCE	151	1810	1669.5	2397.5	123	2269.5	2520	2042.5
Styrene	6053.5	5416	5416	7427.5	6350	7301.5	7773	6464.5

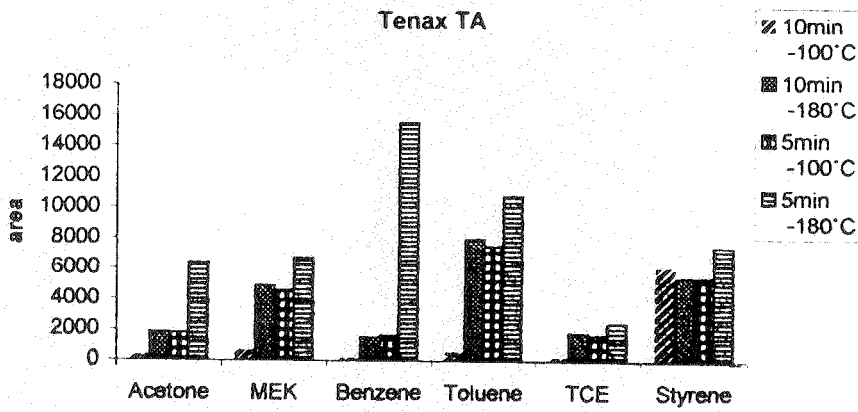


Fig. 1. Comparison of critical parameters for tenax TA in the analysis of VOC

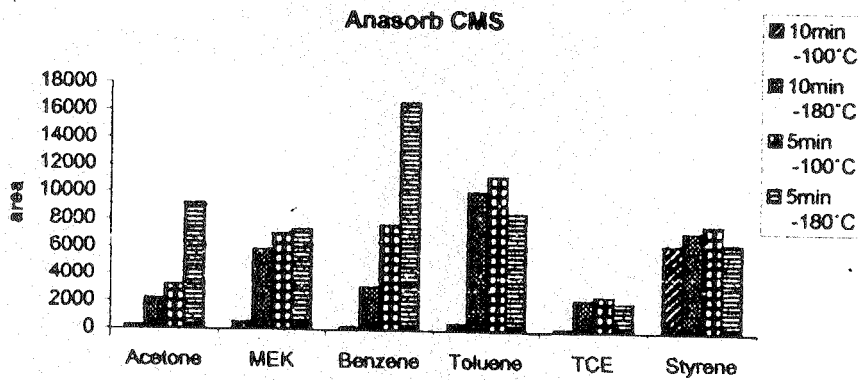


Fig. 2. Comparison of critical parameters for anasorb CMS in the analysis of VOC

Comparison of tenax TA and anasorb CMS for sampling of the volatile organic compounds is shown in Fig. 3.

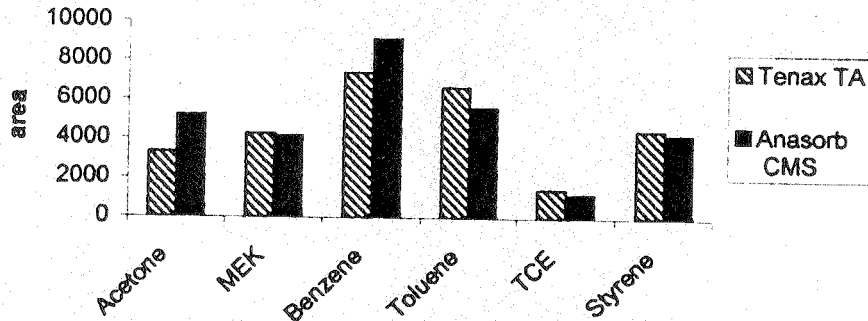


Fig. 3. Comparison of tenax TA and anasorb CMS (trap cool down: -140°C , desorp time: 7.5 min, loading volume: $0.6\ \mu\text{L}$)

The gaseous compounds are trapped on the adsorbent only by reversible physical sorption on the available surface; the surface area is a very important characteristic of adsorbents. The surface area of an adsorbent refers to the solid surface that is accessible for adsorption and specific surface area refers to the surface area per adsorbent mass unit and many of the adsorbents with large surface area are porous.

Prior to the sampling and analysis, selection of right adsorbent-adsorbate pair is the most important step of the sampling and analysis of volatile organic compounds using adsorbent tube sampling and thermal desorption gas chromatography.

The best conditions for all of the compounds when using tenax TA were 5 min desorption time and -180°C trap cool down temperature, while for anasorb CMS for high loading were 5 min desorption time and -180°C trap cool down temperature and were 10 min desorption time and -180°C trap cool down temperature for low loading.

The average % RSD for tenax TA was from 0.40–25.68 and 0.25–21.66 for anasorb CMS. It has been shown that anasorb CMS is better than tenax TA to collect acetone and benzene and comparable for toluene, MEK, tetrachloroethylene, styrene at this atmospheric concentration. Area values obtained for tetrachloroethylene were lower since the flame ionization detector is not sensitive for compounds with chlorine.

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