

Headspace Gas Analysis: Comparison of the Efficiency of Thick Film, Ultra Thick Film, and Activated Charcoal Open Tubular Capillary Traps for the Concentration of Volatile, Airborne, Organic Compounds

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Summary

Determination of the rate at which volatile organic molecules diffuse through the wall of a polysiloxane rubber tube, shows that the full depth of the rubber lining of ultra-thick film open tubular traps is utilized for the retention of volatile organic compounds in headspace gas analysis. Small apolar molecules migrate rapidly through the rubber, but larger molecules and polar compounds diffuse relatively slowly into the rubber. Neither traps with a thick film of an apolar stationary phase, nor those with an ultra thick polysiloxane rubber lining retain highly volatile compounds very effectively. Traps containing activated charcoal particles fused into their inside glass surface have a much higher capacity than those with activated charcoal particles embedded in a layer of stationary phase.

1 Introduction

A headspace analytical technique in which organic compounds are trapped off-line on short capillary traps containing either a thick film of an apolar phase (FTs) or a monoparticulate layer of activated charcoal particles embedded in the inside glass surface of the capillary tube (COTs), was introduced by *Grob* and *Habich* in 1985 for trapping of volatile, airborne, organic compounds [1]. The volatile compounds are desorbed from a trap in the injector of the gas chromatograph and transported to the capillary column by the carrier gas. The technique requires very little expertise and could be an ideal method for the collection of, for example, the volatile compounds implicated in air pollution or produced by industrial fires.

COTs have capacities far exceeding those of FTs; they do, however, suffer from two disadvantages. The first is the high temperatures required for rapid and complete desorption of the trapped volatiles: the high adsorptive power of activated charcoal and its catalytic activity at elevated temperatures result in thermally labile compounds undergoing rearrangement, decomposition, or polymerization [1, 2].

A second disadvantage is the preferential adsorption of some compounds which, if they are present in a high concentration in the gas sampled, may exclude some of the minor constituents from the activated charcoal surface. If, furthermore, a gas sample has a high moisture content, water may condense on the activated

charcoal surface (a situation associated with a change in the color of the activated charcoal from dull greyish black to shiny black) causing retention of molecules in the trap to be governed, to a large extent, by their solubility in the water layer: small polar molecules are then retained preferentially [3]. It is, therefore, advisable to use an FT in the exploratory stages of an investigation or to obtain qualitative information.

Because of the high viscosity of the stationary phase solution necessary for the production of thick film traps, it is difficult to produce a film more than 15 μm thick. The capacity of such traps can be augmented by increasing the length of the trap or by developing techniques to increase the film thickness.

A serious disadvantage of increasing the length of a trap beyond about 70 mm, is that desorption of the volatiles cannot be performed in the injector of the gas chromatograph, and the analysis has either to be performed on a dual-oven instrument or the longer traps have to be ohmically heated. Both of these possibilities have been successfully explored [4–8].

An ingenious but technically exacting technique for producing traps with very thick films was recently developed by *Blomberg* and *Roeraade*: a thick prepolymer film was formed by dynamic coating [6] and immediately fixed by polymerization.

Burger et al. [9] recently developed a simple method for inserting polysiloxane rubber tubing into fused silica tubing of 0.53 mm i.d. to produce ultra thick film traps (UFTs) with a film or lining thickness of ca. 145 μm . Such traps were used in a few headspace gas determinations and appeared to perform satisfactorily. Although the very thick rubber lining was expected to produce large quantities of siloxane decomposition products during thermal desorption of the trapped volatiles, the traps proved to be remarkably stable at elevated temperatures.

Organic molecules are known to pass very rapidly through the polysiloxane membranes which used to be employed in GC-MS interfaces, and most organic volatiles might, therefore, be expected to penetrate to the full depth of the rubber lining of the UFTs. Comparison of the capacity of these traps with that of other open tubular capillary traps was, however, needed in order to form any idea of their efficiency.

2 Material and Methods

Breakthrough volumes for a number of volatile organic compounds on different types of trap were determined at 28 °C by using a syringe to push headspace gas samples through traps coupled to the FID of a Carlo Erba 5300 gas chromatograph via a short length of fused silica capillary tubing. Breakthrough curves similar to those shown in a previous publication [10] were recorded and used to calculate the breakthrough volumes of the compounds on the different types of trap.

It was found to be necessary to heat traps containing activated charcoal to ca 200 °C after each determination to restore the activity of the adsorbent. With the UFTs this was performed only after experiments with the heavier alkanes such as hexadecane.

Because of the compressibility of gases, the volume of gas flowing through a trap in unit time lags behind the volume displaced by the plunger of the syringe. In these experiments the flow rate was, therefore, calibrated at different infusion pump settings by using a bubble flow-meter connected to the trap.

A device for the simultaneous determination of the breakthrough volume and the diffusion rate of different organic compounds was constructed according to the schematic drawing given in **Figure 1**. Headspace gas samples were pushed through the central polysiloxane rubber tube at 28 °C using a gas-tight syringe installed in an infusion pump. The outlet end of the rubber tube was connected to one of the two FIDs on the gas chromatograph.

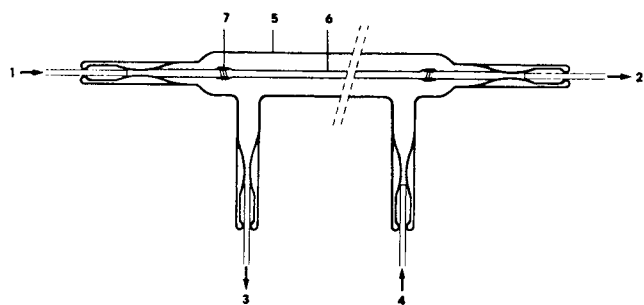


Figure 1

Device for determining the rate at which various volatile organic compounds diffuse through the wall of a polysiloxane rubber tube: 1, gas sample containing 1 ppm of an organic compound in purified nitrogen; 2, FID to detect breakthrough; 3, FID to detect the presence of volatile organic compounds in the coaxial jacket of the device; 4, carrier gas at 11 ml/min; 5, borosilicate glass body of device, 2.5 mm i.d.; 6, polysiloxane rubber tubing, 70 mm × 0.30 mm i.d. × 0.64 mm o.d.; 7, rubber tubing fastened to glass capillaries with thin copper wire.

Carrier gas was passed through the coaxial jacket of the device, in the opposite direction to the flow through the rubber tubing, at a flow rate of 11 ml/min. The outlet port of the coaxial jacket was connected to the other FID. All connections were made with deactivated fused silica tubing and press-fit connectors. COTs and FTs were produced using methods described in detail elsewhere [3] and UFTs by inserting polysiloxane rubber tubing into 0.53 mm fused silica capillary tubing [9].

FTCOTs, *i.e.* capillary traps containing a monoparticulate layer of activated charcoal particles embedded in a film of stationary phase, were made by sucking the activated charcoal particles (28–38 μm) into long (300 mm) lengths of capillary tubing

statically coated with PS-255. A layer of the activated charcoal was retained by the tacky stationary phase which was subsequently cross-linked with dicumyl peroxide by heating the closed tubes from 160 to 200 °C at 0.3°/min: the charcoal particles were thus permanently embedded in the stationary phase. The finished product was divided into shorter lengths suitable for desorption in the injector of a gas chromatograph.

3 Results and Discussion

The determination of the efficiency with which material is retained on a trap at different gas flow rates usually requires a series of measurements, the results of which can be used to plot a breakthrough curve of the amount of the compound retained against sample volume. A second trap, connected in series to the first, can also be used to detect breakthrough. More rigorous detection of breakthrough can, however, be achieved by using direct FID detection of any organic material passing through a trap. To use this method, the trap has to be connected to the detector with, for example, a short length of fused silica tubing. The results of experiments in which the efficiency of different types of trap was compared by this method, are given in **Table 1**.

The COT had much the largest capacity for all the compounds investigated and if quantitative retention is required, this is clearly the trap type to use. It is, nevertheless, remarkable that methanol has a relatively low breakthrough volume on the COT used in this investigation. In this regard it must be borne in mind that for this method of determining breakthrough volume the purity of the test compounds and the gas in which the gas samples are prepared is of the utmost importance. Depending on its volatility and concentration, an impurity could reach the detector before the compound under investigation breaks through, resulting in the measurement of breakthrough volume being too low. Although care was taken to use only highly pure compounds, it is possible that an impurity could have been responsible for the low breakthrough volume of methanol on the COT. Another possibility is that interaction of methanol with the activated charcoal surface could have either desorbed or produced another volatile substance which was detected by the FID.

In view of the problems involved in the production of COTs in laboratories which do not have access to a capillary drawing machine, attempts were made to produce fused silica traps with activated charcoal particles embedded in a layer of a stationary phase, similar to the long traps used in an earlier investigation [4]. It was found that these traps, containing the same activated charcoal used for the production of the COTs, have only a limited capacity. They were, however, conditioned for several days at 270 °C and it is possible that the activated charcoal became irreversibly deactivated by the decomposition products of the supporting layer of polysiloxane stationary phase.

Contrary to expectations, highly volatile compounds such as pentane and dichloromethane were not retained more effectively by the UFT than by the FT. As the volatilities of the compounds decrease, they are retained more effectively by the UFT, but not to the extent which would be expected from the large difference in film thickness. No information is yet available about the type of polysiloxane rubber used for the production of the UFTs. The very low bleed rate of these traps seems to indicate a high degree of cross-linking and it is possible that other siloxane monomers or other cross-linking procedures could produce rubber tubes with which higher breakthrough volumes could be attained.

Table 1
Breakthrough volumes obtained with different types of open tubular trap at 28 °C.

Compound ^{a)}	Trap	Flow rate [ml/min]	Breakthrough volume [ml]
Pentane	FT	1	0.15
	UFT	1	0.1
	FTCOT	10	1.5
	COT	10	> 200
Hexane	FT	1	0.2
	UFT	1	0.17
	FTCOT	10	1.5
	COT	10	> 200
Heptane	FT	1	1.0
	UFT	1	1.3
Octane	FT	1	2.4
	UFT	1	6.0
	COT	10	> 200
Nonane	FT	1	5.3
		10	4.7
	UFT	1	15
		10	4.5
Dichloromethane	FT	1	0.2
	UFT	1	0.2
	FTCOT	1	> 15
		10	3.0
COT	1	> 20	
	10	104	
Chloroform	FT	1	0.4
	UFT	1	0.4
	FTCOT	10	3.0
	COT	10	> 200
Benzene	FT	1	0.5
	UFT	1	0.9
Toluene	FT	1	1.4
	UFT	1	4.5
	FTCOT	10	10
	COT	10	> 200
Methanol	FT	1	0.1
	UFT	1	0.3
	FTCOT	10	1.4
	COT	10	14.5

^{a)} Gas samples were prepared by adding 5 μ l of the compound to 5 l of purified nitrogen (activated charcoal) in a 5 l flask.

The question arises as to whether the unexpectedly low capacity of the UFT might not be because the organic molecules do not penetrate the rubber beyond the first few μ m of the lining, *i.e.*, the extreme thickness of the lining is not fully utilized. In order to investigate the rate of diffusion of different organic molecules into the polysiloxane rubber used for the production of UFTs, a device was constructed (**Figure 1**) which enabled the headspace gas to be passed through a short length of the polysiloxane rubber tubing. The volatile organic compounds emerging from the outlet of the tube and those diffusing through its wall were detected by separate FIDs.

In order to restrict any possible time-lag in the detection of breakthrough, the device was constructed such that the carrier gas used to purge the volatile organic compounds from the outer coaxial jacket, left the jacket at the position where the first molecules are expected to emerge from the rubber tube. In test runs with methane diluted with nitrogen, the methane could be detected in the purge gas line within 1.5 s. Breakthrough was almost instantaneous.

Examples of the FID response curves obtained in experiments with somewhat heavier molecules are shown in **Figure 2**. The traces in Figures 2A and C were obtained from the detector coupled to the coaxial jacket of the device and thus indicate that the volatile organic compound has diffused through the rubber tubing. The time elapsed between introduction of the headspace gas into the rubber tube and the first indication of an increase in the detector response is a measure of the time it takes for a specific organic compound to diffuse through 170 μ m of the polysiloxane rubber. The traces in Figures 2B and D were obtained from the detector coupled to the outlet of the rubber tube; here an increase in detector response indicates that breakthrough is taking place.

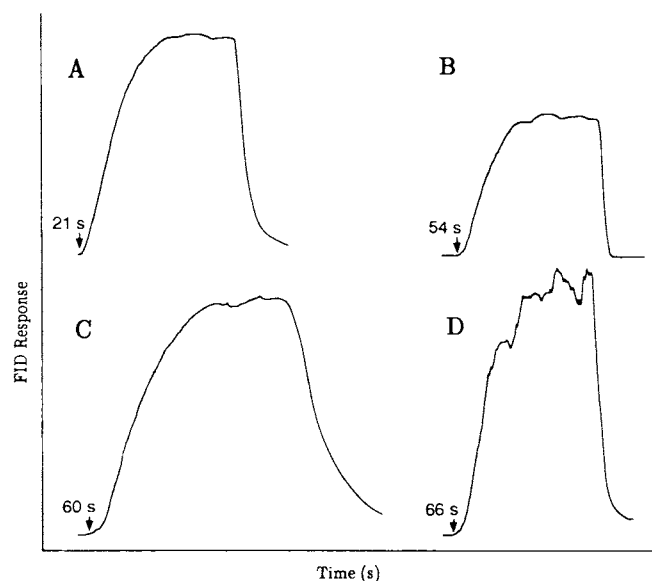


Figure 2

Diffusion rate and breakthrough curves for 1.0 ppm hexane or methanol in nitrogen, determined at 28 °C with a dual FID instrument for simultaneous detection of diffusion of compounds through the wall of a rubber tube and breakthrough at a flow rate of 1 ml/min: A, diffusion of hexane; B, breakthrough of hexane; C, diffusion of methanol; D, breakthrough of methanol.

The breakthrough volumes calculated from these FID response curves are, however, only very rough approximations: the headspace gas is stripped of organic molecules as it passes through the tube, resulting in an increasingly leaner mixture moving towards the outlet and the detector. This effect could possibly be responsible for the large differences in the breakthrough volumes of the more volatile compounds in determinations using the coaxial device (**Table 2**) and direct coupling of the UFT to the FID (**Table 1**). In compounds with slower diffusion in the rubber, smaller quantities of material are purged from the system before breakthrough is detected, resulting in smaller differences being observed in breakthrough volumes determined by the two methods.

Table 2

Rate of diffusion of volatile organic compounds through the wall of a rubber tube^{a)} and the accompanying breakthrough volumes of the gas samples^{b)} flowing through the tube (temperature 28 °C).

Compound	Flow rate [ml/min]	Time required for diffusion through 170 µm of poly-siloxane rubber [s]	Time required for breakthrough [s]	Approximate breakthrough volume [ml]
Pentane	1	13	24	0.4
	10	12	8	1.3
Hexane	1	21	54	0.9
	10	10	11	1.9
Heptane	1	25	90	1.5
	10	11	21	3.5
Octane	1	30	150	2.5
	10	17	37	6.1
Nonane	1	43	300	5.0
	10	30	88	14.6
Dichloromethane	1	11	48	0.8
	10	9	12	2.0
Chloroform	1	19	78	1.3
	10	13	16	2.7
Methanol	1	60	66	1.1
	10	52	15	2.5
Toluene	1	28	> 1500	> 25
	10	14	32	5.3

^{a)} 70 mm × 0.3 mm i.d. × 0.64 mm o.d. Silastic medical grade tubing (Dow Corning); ^{b)} prepared as described in Table 1.

It is, however, also possible that other effects are involved. For example, methanol, which moves very slowly through the rubber, also has a breakthrough volume in the coaxial device which is higher than expected. In addition, toluene which diffuses through the rubber about as fast as octane, also has an exceptionally high breakthrough volume in this device.

According to the results given in Table 2, the diffusion of the organic molecules through the wall of the rubber tube appears to be promoted by a higher headspace gas flow rate. This phenomenon is, however, most unlikely to be the result of the increased flow rate itself, but rather of the higher pressure used to achieve the higher flow rate through both the tube and the connecting lengths of fused silica capillary tubing. Although there does not seem to be a simple relationship between the flow rate (or pressure) of the headspace gas, the rate with which the molecules diffuse through the rubber, and the accompanying breakthrough volumes, the higher breakthrough volumes obtained at a higher flow rates might arise because an increase in the pressure in the rubber tube will promote the diffusion of organic molecules into the rubber and their removal from the gas flowing through the tube.

For some inexplicable reason which was not further investigated, toluene gave an exceptionally high breakthrough volume at a low flow rate in these experiments.

Summarizing the results in Table 2, it appears that the breakthrough volumes determined using the coaxial device are not as reliable and informative as those given in Table 1. It was,

nevertheless, clearly established that the full thickness of the polysiloxane rubber lining of UFTs is utilized in retaining volatile organic compounds.

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