EVALUATION OF A TENAX GC SAMPLING PROCEDURE FOR COLLECTION AND ANALYSIS OF VEHICLE-RELATED AROMATIC AND HALOGENATED HYDROCARBONS IN AMBIENT AIR

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SUMMARY

A technique for the measurement of vehicle-related emissions of aromatic and halogenated hydrocarbons in ambient air has been evaluated in order to permit routine monitoring of these compounds. Aromatic and halogenated hydrocarbons present in air are concentrated on Tenax GC and subsequently thermally desorbed into either an electron-capture or flame ionization detector equipped gas chromatograph using packed columns. The study reported here was undertaken to assess the effects of the concentration of determinands, rate of sampling, humidity and temperature on the safe sampling volumes. It is concluded that the technique is sensitive, versatile and accurate and can provide useful data on changing ambient air concentrations of aromatic and halogenated hydrocarbons.

INTRODUCTION

Emissions of hydrocarbons from petrol-driven vehicles have been a matter of concern for a number of years, in particular aromatic[1] and polycyclic aromatic hydrocarbons (PAHs) because of the known carcinogenicity of certain compounds in these chemical groups, *e.g.*, benzene and benzo[*a*]pyrene[2]. In addition, the emission of lead from internal combustion engines, arising from the use of alkyl-lead compounds as anti-knock additives in petrol, has been a source of considerable concern[3]. As a result of the latter, a reduction in the alkyl-lead content of petrol, from a concentration of 0.4 g l^{-1} to 0.15 g l^{-1} by 1985, has been announced recently in Great Britain. This is in line with action taken in other countries[4]. The implementation of this reduction is likely to entail increases in the concentrations of aromatic hydrocarbons in petrol, in order to maintain the octane rating of the fuel[5]. These increases will result in elevated concentrations of aromatic hydrocarbons and PAHs in ambient air[6].

Accompanying the decrease in the alkyl-lead content of petrol will be a concomitant reduction in the lead scavengers 1,2-dichloroethane (EDC) and 1,2-dibromoethane (EDB), which are added to petrol on a mole to mole basis with lead. Both EDC and EDB are of environmental interest, not only because of possible

adverse health effects[7], but also because they can provide potentially useful data on emission sources when correlated with benzene and toluene concentrations in ambient air[8].

In common with other trace organics, the concentrations of aromatic and halogenated (EDC and EDB) hydrocarbons in air are relatively low, and therefore a preconcentration step is required when sampling prior to analysis by gas–liquid chromatography. Concentration procedures frequently used include cryogenic trapping, solvent scrubbing and adsorption onto a solid surface[9].

Cryogenic trapping can lead to analytical difficulties because freezing-out of water vapour occurs along with the organic content of air, whereas solvent scrubbing is insufficiently sensitive for the analysis of organics below the parts-per-million (ppm) range. Consequently, the use of solid adsorbents such as charcoal, porous polymers (Porapak P, Tenax GC, Chromosorb 102, etc.) and silica gel, is more popular when sampling for trace organics in air. Of the adsorbents available, porous polymers have the advantage of direct thermal desorption into a gas chromatograph as opposed to solvent desorption for charcoal and silica gel and the most frequently used of these polymers, Tenax GC, has been employed in this study because of its high thermal stability[10]. This study was undertaken to assess the effects of various sampling parameters, including determinand concentration, flow-rate, humidity and ambient temperature upon the chromatographic qualities and hence the safe sampling volumes and collection efficiencies of Tenax GC sampling tubes.

EXPERIMENTAL

Adsorption tubes

Stainless-steel sampling tubes (74 × 4.5 mm I.D.), cleaned by ultrasonication in Decon 90, were packed with 0.13 g of Tenax GC, 35–60 mesh (Chrompack, London, Great Britain) which had been previously preconditioned at 280°C with oxygen-free nitrogen (OFN) carrier gas at a flow-rate of 20 ml min^{-1} for 8 h in order to avoid heat shrinkage of the Tenax GC. The adsorbent was held in place by clean silanized glass wool and after packing was conditioned as described before.

Thermal desorption

Sampling tubes were thermally desorbed at 250°C in a Bendix flasher (Bendix, Milton Keynes, Great Britain) interfaced with a Hewlett-Packard 5700A gas chromatograph (Hewlett-Packard, Winnersh, Great Britain) equipped with either an electron-capture detector (ECD) or a flame ionization detector (FID).

The efficiency of desorption was examined by comparing direct column injections of standards of the individual compounds made up in hexane to similarly spiked sampling tubes which were thermally desorbed into the gas chromatograph.

Gas chromatographic conditions

Separation of halogenated hydrocarbons was achieved on a 2 m × 3.1 mm O.D. stainless-steel column packed with 5 % Carbowax 1500 on Chromosorb W HP (80–100 mesh) operated at 70°C. The detector (ECD) temperature was 250°C with a carrier gas flow-rate of 35 ml min^{-1}. Aromatic hydrocarbons were separated on a 2 m × 3.1 mm O.D. stainless-steel column packed with 10 % TCEP on Chromosorb P

HP (100–120 mesh) operated at 70°C. The detector (FID) temperature was 250°C with a carrier gas flow-rate of 40 ml min^{-1}.

Calibration procedures

It is desirable that the calibration method should reflect actual sampling procedures as closely as possible. Therefore, a permeation tube oven coupled to an exponential dilution flask[11] was adopted for the introduction of a known mass of organic vapour onto the sampling tubes, which on subsequent analysis provided values for construction of calibration graphs. A DuPont constant-flow sampling pump Model P-4000 (DuPont, Stevenage, Great Britain) was used to draw clean air through the permeation oven and into the exponential dilution flask until the atmosphere in the flask was saturated with the vapour of the calibration compound. The pump was then used to draw clean air through the flask and onto sampling tubes for known periods of time. The concentration of organic vapour decayed in the flask according to the equation

$$C = C_0\,e^{-Ft}/V \tag{1}$$

where

C	=	the concentration at time t (min)
C_0	=	the initial concentration
F	=	dilution flow-rate (ml min^{-1})
V	=	volume of the dilution flask (ml)

The vapour concentration in the flask was verified at intervals during the calibration procedure by direct injection of aliquots (0.05–1 ml) into the gas chromatograph.

Equal amounts of benzene and toluene were introduced by this method onto a number of tubes which were then capped and stored at 4°C for periods varying between 1 and 21 days in order to evaluate the effects of storage time on analysis.

Evaluation of sampling parameters

The sampling tubes can be regarded as short chromatographic columns operating at ambient temperatures. Therefore, chromatographic theory can be applied to evaluate whether a particular organic vapour can be sampled efficiently using Tenax GC sampling tubes under varying conditions.

A sampling tube was connected into the gas chromatograph oven with the outlet connected directly to the FID. Two forms of analysis were performed (frontal and elution), these differing primarily in the manner of sample introduction.

Organic vapour was introduced continuously during frontal analysis by diverting carrier gas through a permeation oven, containing either benzene or EDC permeation tubes and thence into the inlet of the sampling tube. The time taken for the concentration of determinand in the effluent carrier gas stream from the tube to equilibrate (monitored by the FID) and the shape of the breakthrough curve (Fig. 1) provided chromatographic data on retention volumes and the number of theoretical plates for these components.

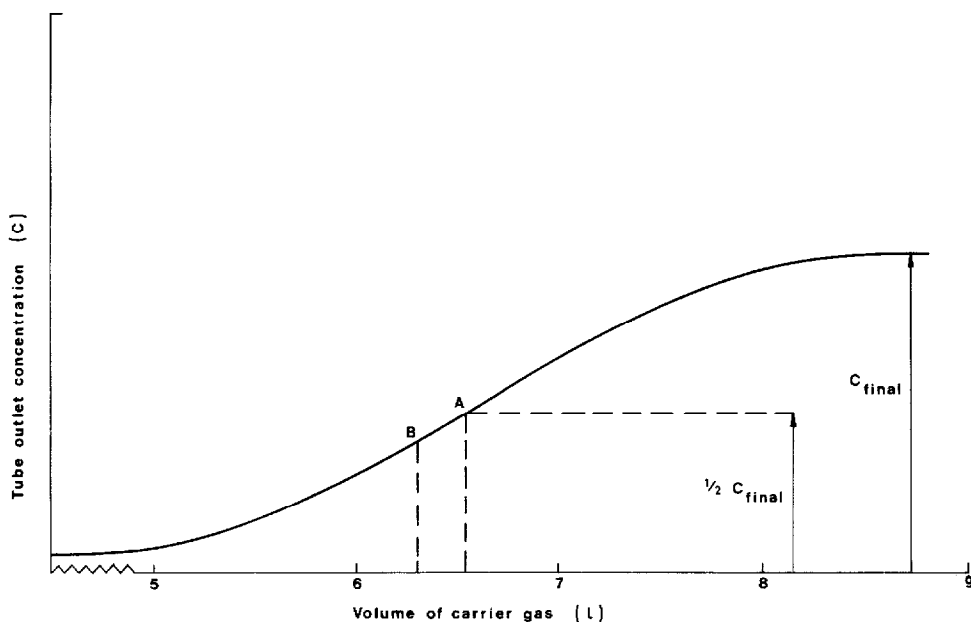In elution analysis, small amounts (0.01–0.5 ml) of organic vapour from a

Fig. 1. Frontal analysis for benzene on Tenax sampling tube. Carrier gas flow-rate, 50 ml min^{-1}. The retention volume of 6.6 l was determined at point A. The retention volume determined from elution data was 6.3 l (B).

static dilution flask were injected by gas syringe onto the sampling tube. The time taken to obtain peak maxima and the peak shapes were recorded for various operating temperatures. In this way data on retention volumes and the numbers of theoretical plates were obtained, thus permitting an evaluation of the effects of various sampling conditions.

The effect of humidity on the sampling efficiency of Tenax GC was evaluated by introducing a humidifier into the sampling stream. This consisted of a stainless steel cartridge (200 × 50 mm I.D.) filled with water and glass beads (3 mm diameter) and with this large surface area of water it was assumed that the carrier gas was saturated at room temperature. The compounds utilized in this study have been selected as representative of vehicle-related aromatic and halogenated hydrocarbon emissions[12].

RESULTS AND DISCUSSION

Calibration procedures

A comparison between direct injection of liquid standards and thermal desorption of spiked sampling tubes, using five replicates for each analysis, is presented in Table I for benzene, toluene and EDC. The flasher, operated at 250°C, demonstrates high desorption efficiencies for benzene (97.4%), toluene (103.6%) and EDC (101.1%).

The permeation tube oven–exponential dilution flask method of calibration proved to be accurate in loading a precise mass of organic vapour onto a sampling

TABLE I

COMPARISON BETWEEN DIRECT INJECTION OF STANDARD SOLUTIONS AND THERMAL DESORPTION OF SPIKED SAMPLING TUBES FOR BENZENE, TOLUENE AND 1,2-DI-CHLOROETHANE

Compound	Direct injection relative response		Thermal desorption relative response		Thermal desorption/direct injection (%)
	$\bar{x}$	R.S.D.(%)	$\bar{x}$	R.S.D.(%)	
Benzene	132.2	2.1	128.8	1.33	97.4
Toluene	89.7	2.37	93	1.26	103.6
1,2-Dichloroethane	64.7	2.5	65.4	1.4	101.1

TABLE II

COMPARISON OF EXPECTED AND ACTUAL BENZENE VAPOUR LOADINGS ON TENAX GC SAMPLING TUBES

Tube No.	Expected vapour loading (μg)	Actual vapour loading (μg)	Actual/ expected (%)
1	3.11	3.31	106
2	2.95	2.80	95
3	2.28	2.21	97
4	1.85	1.82	98.4
5	1.10	1.15	105
6	0.53	0.57	107.5
			Mean = 101.5%
			RSD = 4.8%

TABLE III

EXTRAPOLATED RETENTION VOLUME OF SELECTED AROMATIC AND HALOGENATED HYDROCARBONS AT 20°C DETERMINED BY ELUTION ANALYSIS

Compound	Constants*		Correlation coefficient	Retention volume (l)
	$A \cdot 10^3$	B		
Benzene	3.0076	6.4648	0.99	6.31
Toluene	3.759	7.0136	0.99	65.4
o-Xylene	3.7505	7.5234	0.97	189.2
Ethylbenzene	5.2846	2.8111	0.99	20.4
p-Ethyltoluene	4.375	8.7882	0.97	1391.6
o-Diethylbenzene	5.0	10.24	0.99	6680
1,3,5-Trimethylbenzene	4.1909	8.347	0.99	905
1,2-Dichloroethane	2.8676	6.1933	0.99	3.92
1,2-Dibromoethane	3.8991	7.6572	0.99	446.9

* A and B are constants in the equation $\log V_g = A \cdot T - B$.

tube. Calibration data for benzene are presented in Table II, which demonstrates a loading efficiency of 101 % with a relative standard deviation (R.S.D.) of 4.8 %. Storage of tubes, calibrated for benzene and toluene for up to 21 days, had no significant effect on the repeatability of analysis.

Comparison of frontal and elution analysis techniques for the determination of retention volumes and theoretical plate values

The retention volume, in both frontal and elution analysis, corresponds to 50 % breakthrough[13,14], *i.e.* the volume at peak maxima in elution analysis and the volume at which 50 % of the inlet adsorbate concentration (C) is detected in the effluent carrier gas stream from the sampling tube.

The result of a frontal analysis for benzene is presented in Fig. 1. With a carrier gas flow-rate of 50 ml min^{-1} the retention volume (V_g) for benzene was 6.6 l (after dead volume correction).

Retention volumes for the compounds of interest were determined by elution analysis at the same flow-rate (50 ml min^{-1}) by operating the sampling tubes at temperatures above ambient and extrapolating the log retention volumes against reciprocal absolute temperature using least squares regression. The results of these retention volume studies are presented in Table III, together with correlation coefficients and values for the constants (A, B) in the equation

$$\log V_g = A \cdot T - B \tag{2}$$

where T = reciprocal of temperature ($1/^\circ K$). No significant deviations from linearity occurred, which compares well with other published data[13,15].

The retention volumes presented in Table III have been determined by extrapolation of the data back to the expected ambient sampling temperature of 20°C. However, if ambient atmospheres are sampled above or below this temperature then the retention volumes will alter according to eqn. 2. For example, the retention volume for benzene is reduced to 4.24 l at 25°C from 6.3 l at 20°C and the safe sampling volume decreases correspondingly. The retention volume for benzene (6.3 l at 20°C) is in excellent agreement with the 6.6 l determined by frontal analysis. Similar agreement was found for toluene.

The number of theoretical plates (N) was determined from the slope of the line at the 50 % breakthrough volume from the equation

$$\text{slope} = C \, (N/2\pi)^{\frac{1}{2}}/V_g \tag{3}$$

N being equal to 34 plates for benzene. This compares well with the value of 35 determined by elution analysis using the equation

$$N = (4 \, t/w)^2 \tag{4}$$

where t is the elution time (or volume) and w is the distance between the points of intersection of the tangents to the inflection points of the peak[16].

The accurate measurement of hydrocarbons and halocarbons in ambient air is limited by the lowest retention volume of an individual compound of interest where a
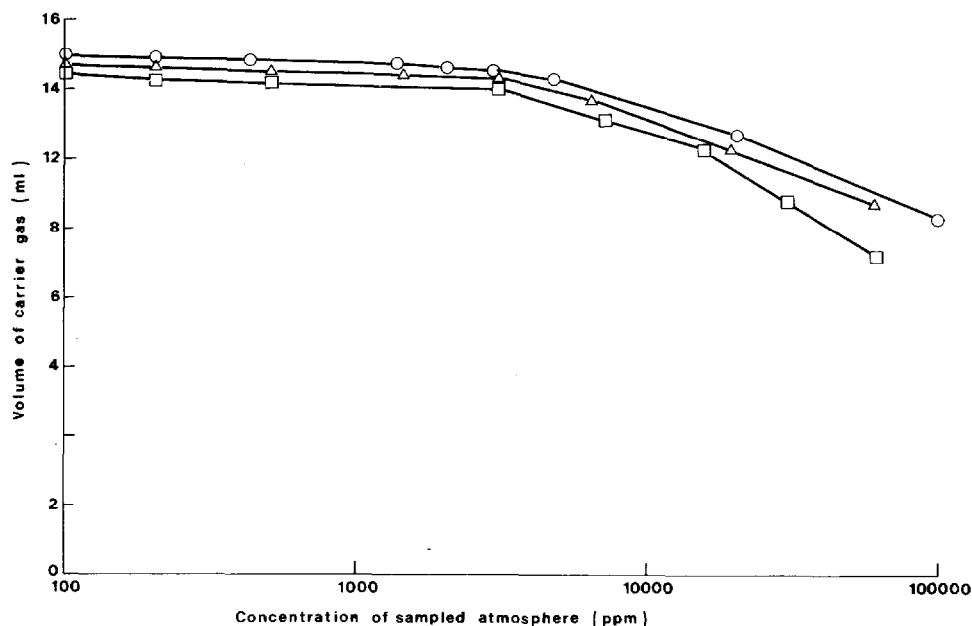
Fig. 2. Effects of vapour concentration on retention volumes at 120°C, 190°C and 116°C, respectively, for benzene (○), toluene (□) and 1,2-dichloroethane (△).

mixture is present. The two lowest retention volume values presented in Table III, determined by elution analysis, are for EDC and benzene (3.92 l and 6.31 l respectively) which are well below those of other compounds, e.g. toluene (65 l). Consequently, experiments to determine the effect of various sampling parameters have been performed using compounds with low retention volume values, as any demonstrable effect of sampling parameters will have the largest influence on the sampling volumes of these compounds.

Effect of adsorbate concentrations on retention volumes

It is known that peak asymmetry, retention time and the number of theoretical plates of Tenax GC chromatographic columns are affected by the column load[17]. Consequently, it is important to assess the influence of concentration on retention volumes of the Tenax GC sampling tubes.

High adsorbate concentrations of benzene, toluene and EDC were built up in a flask and single aliquots of the sample atmospheres were injected onto the sample tubes (at a carrier gas flow-rate of 50 ml min^{-1}). Because of the wide difference in retention volumes (6.3 l to 65.4 l for benzene and toluene, respectively, at 20°C), the sampling tubes were operated at 120, 190 and 116°C for benzene, toluene and 1,2-dichloroethane, respectively, in order to measure accurately the retention volumes at different concentrations. The results, presented in Fig. 2, indicate that no significant change in retention volumes occurred until the injected concentration approached 3000 ppm, and it is evident that these results agree closely with the findings of Brown and Purnell[18] for acetone using elution analysis. However, continuous introduction of 100 ppm of acetone vapour was shown by these authors to have a significant effect

on retention volume because of a more rapid overload of the Tenax GC column with a continuous atmosphere than with a single aliquot of the same concentration. Recent work by Vejrosta *et al.*[19], using direct measurements of sorption equilibria at varying gas-phase concentrations to determine distribution constants of acetone on Tenax GC, is in accord with these findings.

Further work by Vejrosta *et al.*[20], determining distribution constants of benzene on Tenax GC at various gas-phase concentrations by direct measurements of sorption equilibria, concluded that the retention volume was independent of benzene concentration only up to a concentration of *ca.* 1 ppm. The difference between the findings presented in Fig. 2 and by Vejrosta *et al.* for benzene compares well with the difference described by Brown and Purnell[18] between elution and frontal analysis techniques. It is suggested that the determination of retention volumes of distribution constants by direct measurement of sorption equilibria (frontal analysis) represents the more realistic sampling condition and therefore the retention volume for benzene is independent of concentration up to 1 ppm. However, ambient concentrations of this magnitude are extremely unlikely to occur and, in this range, a concentration step would not be required. At expected ambient concentrations, no discernable effect on retention volumes was detected.

TABLE IV

EFFECT OF HUMIDITY ON RETENTION VOLUMES AT 20°C OF BENZENE, 1,2-DI-CHLOROETHANE AND TOLUENE

Compound	Retention volume (l)		V_g (humid)/V_g(dry)
	High humidity	Dry	
Benzene	4.98	6.31	0.79
1,2-Dichloroethane	3.48	3.92	0.89
Toluene	53.42	65.0	0.82

Effect of humidity on retention volumes

Previous studies[21,22] have investigated the influence of water vapour on retention volumes of various compounds using Tenax GC sampling tubes and have concluded that the effect on retention volumes under conditions of high ambient humidity is dependent upon the polarity of the adsorbate. The work of Piecewicz *et al.*[22] indicates that ethyl bromide and 2-butanone (both Kiselev Group B compounds[23] — slightly polar) which have a similar polarity to aromatic and halogenated hydrocarbons, exhibit decreases in retention volumes of 22 % and 31 %, respectively, at high ambient humidity. This compares well with previous work[21] which found a 21 % decrease in retention volume for benzene (Group B polarity).

The effects of humidity on the Tenax GC sampling tubes used in this study are presented in Table IV for the adsorbates benzene, toluene and EDC. The decrease in retention volumes of 21 % is identical with the findings of Janák *et al.*[21] for benzene, and the smaller decreases of 11 % and 18 % for EDC and toluene are comparable with the decreases reported for more polar compounds and with the values reported by Piecewicz *et al.*[22]. This study also reported an additional 25 % decrease in retention
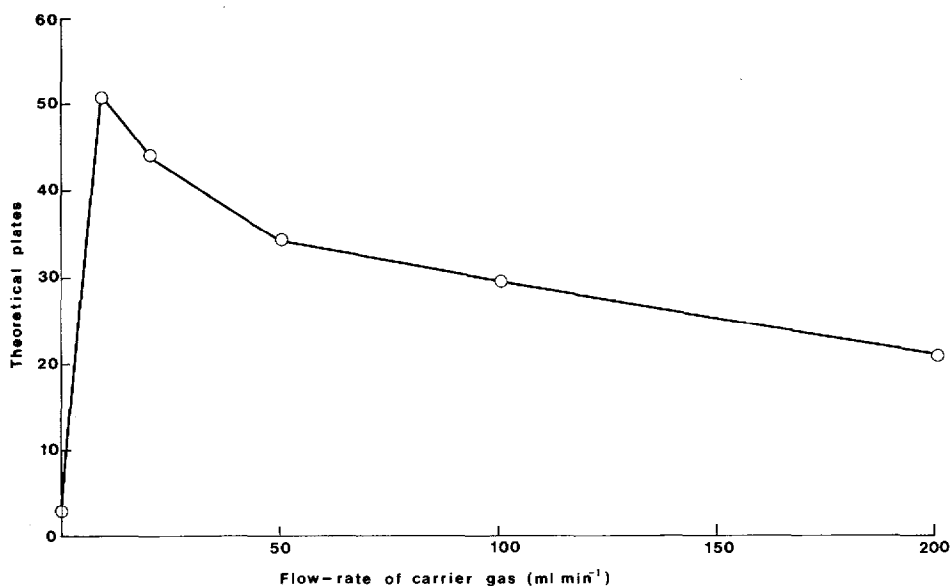
Fig. 3. Effects of flow-rate on theoretical plate numbers for benzene.

volumes in the presence of 10 % (v/v) carbon dioxide and high humidity, conditions typical of gaseous effluent from combustion processes.

Effect of flow-rate on the theoretical plate values and retention volumes

The numbers of theoretical plates for benzene were determined at different flow-rates up to 200 ml min^{-1} and are presented in Fig. 3. In order to prevent possible passive sampling and very low plate numbers, resulting in inaccurate sampling, flow-rates below 10 ml min^{-1} were avoided. The number of plates decreased with increasing flow-rates between 10 and 200 ml min^{-1}, from 51 to 22. No appreciable change in retention volumes was detected in the range of flow-rates between 10 and 200 ml min^{-1}.

Although the efficiency of an adsorbate sampler increases with increasing adsorbent theoretical plates, a compromise between theoretical plate numbers and the time taken to sample sufficient air for analysis exists. Therefore, the determination of a safe sampling volume must take account of this compromise.

Selection of a safe sampling volume

For the collection method to be quantitative, the volume of air sampled containing a particular compound (adsorbate) must not exceed a predetermined safe sampling volume. This safe sampling volume can be defined as the volume of air containing the adsorbate that may be sampled without a significant amount of adsorbate passing through the sampling tube without being collected[14]. The safe sampling volume is dependent not only on the retention volume, but also on the number of theoretical plates. An explicit expression for the adsorbate concentration at the outlet of the sampling tube as a function of the sampled volume, the adsorbate retention volume and the number of theoretical plates has been derived recently by Senum[14].

TABLE V

SAFE SAMPLING VOLUMES FOR BENZENE AND 1,2-DICHLOROETHANE AT VARIOUS FLOW-RATES AND SAMPLING EFFICIENCIES

Compound	V_g (l)	Flow-rate (ml min^{-1})	Safe sampling volume (l)		
			99.9%	99%	95%*
Benzene	6.3	10	4.35	5.17	6.10
		20	3.91	4.91	5.98
		50	3.72	4.72	5.86
		100	3.28	4.6	5.73
		200	3.02	4.28	5.48
1,2-Dichloroethane	3.92	10	2.70	3.21	3.80
		20	2.43	3.06	3.72
		50	2.31	2.94	3.64
		100	2.04	2.86	3.58
		200	1.88	2.66	3.41

* Sampling efficiency.

This expression has been used to calculate the safe sampling volumes over a range of flow-rates for benzene and EDC. This method is exact for all plate numbers, as it containes no approximations, unlike expressions derived in previous studies[15,18,24], which can be inaccurate when N is decreased below 30 (ref. 14). Safe sampling volumes for benzene and EDC are presented in Table V, for flow-rates between 10 and 200 ml min^{-1}, at 99.9%, 99% and 95% sampling efficiencies. These results demonstrate the versatility of approach that can be achieved by adopting different flow-rates according to the sampling time and efficiency that is required.

CONCLUSIONS

The retention volumes and numbers of theoretical plates for a selection of vehicle-related aromatic and halogenated hydrocarbons on Tenax GC sampling tubes have been determined by elution chromatographic analysis. This method has been evaluated by comparison with frontal analysis. Using an explicit expression, safe sampling volumes have been determined for a variety of sampling efficiencies and flow-rates. This provides adequate versatility in a sampling system for the measurement of vehicle-related aromatic and halogenated hydrocarbons in ambient air.

The effects of various sampling parameters on retention volumes and hence safe sampling volumes have been evaluated. High ambient humidity has been found to reduce retention volumes by 21% and 11% for benzene and EDC, respectively, the compounds with the lowest retention volumes and therefore the limiting cases. Ambient temperature has also been demonstrated to have a significant effect on retention volumes and application of the constants presented in Table III provides data to assess this change in retention volumes. At normal ambient concentrations of the compounds considered, no significant change in retention volumes with concentration has been demonstrated.

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