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STYRENE COPOLYMERS AS POLLUTANT ADSORBENTS

SAFE SAMPLING VOLUME DETERMINATION

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SUMMARY

The determination of safe sampling volumes of benzene and acetone on air samplers filled with Porapak Q, Chromosorb 101, 102 and 103 is described. Two direct methods are employed; one method is based on frontal chromatography, while the second one is a concentration method followed by thermal desorption. The results are compared to those determined by the indirect pulse chromatographic method. The safe sampling volumes determined by the direct methods were in accordance. The indirect method gives slightly different values; however, this procedure is carried out at "infinite dilution". The effect of the pollutant concentration on the safe sampling volumes was also examined. The values decrease with increasing pollutant concentration.

INTRODUCTION

Adsorption on solids is the most widely used method for the collection of traces of organic compounds in air. In particular, there has been increasing use of porous polymers due to their inertness towards adsorbed molecules. Previously^{1–4}, some styrene copolymers (Porapak Q, Chromosorb 101, 102 and 103) were studied as air samplers. It was pointed out that thermal clean up at the characteristic limit temperature of the polymer must be carried out for almost 6 h to obtain reproducible retention parameters, linear fittings of $\ln V_g$ vs. $1/T$ and satisfactory "blanks" during thermal desorption.

The aim of the present study was to characterize such polymers as pollutant adsorbents by determining the safe sampling volumes (SSVs) of benzene and acetone. Two different direct methods are used. In the first, the SSV is evaluated from frontal chromatograms. In the second method, the traps are loaded with atmospheres containing a constant pollutant concentration for different lengths of time, *i.e.*, different volumes, at a constant flow-rate. Recovery of the adsorbed organics is achieved by thermal desorption. The desorption peak areas are then plotted against the sampled volumes according to Lökvist and Jönsson⁵.

Data obtained with these methods are compared to those derived by the in-

direct pulse chromatographic method. This comparison is of interest since all these methods are widely employed but only a few authors⁶⁻⁸ have carried out such a test, especially on the same polymer batch. Moreover, in the literature there is disagreement as to the choice of SSV determination methods and at times this choice is not well justified. For example, Van der Straeten *et al.*⁹ prefer direct methods because of the quite different V_g values reported in the literature for benzene on Tenax GC; these variations were attributed only to the errors in the extrapolation at room temperature, but they may also be due to differences between polymer batches^{10,11} or to differences in polymer preconditioning¹.

EXPERIMENTAL

Materials and apparatus

Benzene and acetone were analytical grade products (Merck) and were chosen as test molecules owing to their volatility and toxicity. Chromosorb 101 (CH 101), 102 (CH 102) (60–80 mesh), 103 (CH 103) and Porapak Q (PQ) (80–100 mesh) were supplied by Supelchem (Milan, Italy). They were packed in stainless-steel columns (100 mm × 5.3 mm I.D.) between two glass-wool plugs. About 0.2 g of each polymer were used. The adsorbents were heated in a pure nitrogen stream (25 ml/min) at their limit temperatures³ for almost 6 h.

An Hewlett-Packard Model 5730 gas chromatograph equipped with a flame ionization detector (dual differential electrometer Model 5706) and a Model 8380S integrator was used. A 3% OV-101 on Supelcoport (80–100 mesh) glass column (6 ft. × 2 mm I.D.) for benzene and a 10% Carbowax 20M on Supelcoport glass column for acetone were employed.

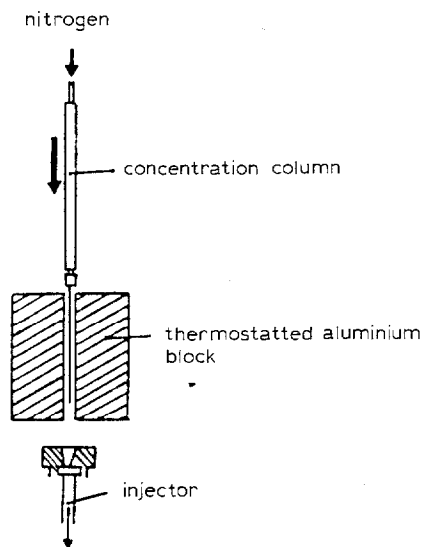
The gas mixtures were prepared by passing a stream of pure nitrogen into a diffusion cell according to Devaux and Guiochon¹². The diffusion rate was determined by gravimetric calibration. The system gave reproducible results with approximately 40 min between two repeated measurements.

Direct methods

The safe sampling volumes were evaluated at room temperature ($20 \pm 0.5^\circ\text{C}$). All experiments were made at least in triplicate.

Method 1 (M-1). In the determination of SSV by the frontal method (M-1), an atmosphere containing a constant concentration of the investigated compound was passed via a four port Valco valve through a trap directly connected to a flame ionization detector. Before each measurement, the system was conditioned with pure nitrogen at 40 ml/min until a stable baseline was achieved on the chart recorder. Subsequently, the sampling valve was switched to the adsorption position. The polluted atmosphere then flowed through the traps, advanced as a frontal zone and a frontal chromatogram was recorded. The SSV was determined when the baseline showed a drift equal to twice the noise. The standard deviation of the SSV data was smaller than 10% at a confidence level of 95%.

Method 2 (M-2). An apparatus (Fig. 1) similar to the one described by Lövkvist and Jönsson⁵ was employed for the second method (M-2). The SSV was evaluated by sampling a gas mixture of constant concentration for different lengths of time, *i.e.*, different volumes, at flow-rate of 40 ml/min. The sampling tube was fitted with



to analytical column

Fig. 1. Apparatus used for thermal desorption and to perform the direct method M-2.

a needle (Hamilton syringe Model 7105) and, before desorption, was connected to a gas chromatograph injector and inserted through a thermostatted aluminium block (250°C). During desorption, a nitrogen flow-rate of 60 ml/min was maintained in the trap, and 20 ml/min in the analytical column. It was observed that a minimum flow-rate ratio of about 3:1 is necessary for rapid transfer of the pollutant from the sampling column to the analytical column.

The desorption peak areas were plotted against the volumes sampled. Pollutant recovery was not quantitative when the plot deviated from linearity. Therefore, the SSV is the volume which corresponds to the extreme linear domain, and may be evaluated according to the statistical procedure of Liteanu *et al.*¹³. The SSV errors and the standard deviation were about 6% at a confidence level of 95%. In Figs. 2 and 3, examples of the curves obtained for benzene (on PQ) and acetone (on CH 103) are reported.

Indirect method

According to Raymond and Guiochon¹⁴ the safe sampling volume may be calculated by

$$SSV = V(1 - 2/\sqrt{N})$$

where V is the retention volume and N the plate number of the sampling column at the working temperature. These volumes are derived from chromatographic theory assuming a gaussian response to a narrow pulse injection of a trace concentration of pollutants.

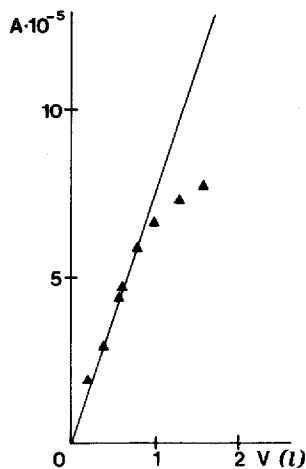
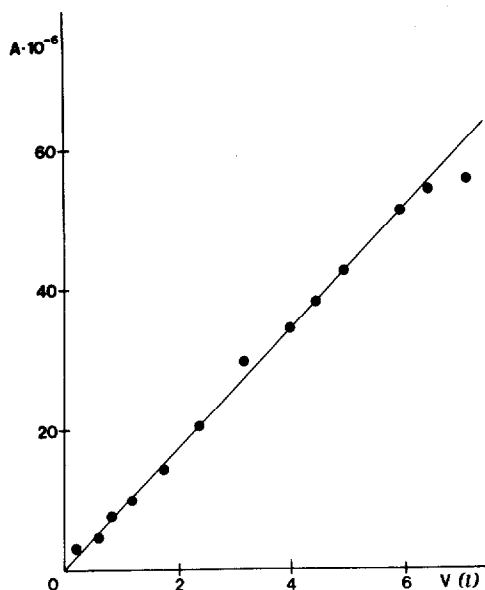


Fig. 2. Plot of benzene (60 ppm) peak desorption areas (arbitrary units) vs. volumes (l) sampled on PQ.
 Fig. 3. Plot of acetone (3 ppm) peak desorption areas vs. volumes sampled on CH 103.

In previous papers¹⁻³ the specific retention volumes of benzene and acetone on copolymer columns were determined. A good linear fit of $\ln V_g$ vs. $1/T$ was obtained in the measurement temperature range. The data extrapolated at 20°C are reported in Table I. A 20% error was estimated depending on the measurement precision and extrapolation errors. The efficiency of the sampling columns is reported in the same Table. The plate numbers were obtained with a small pulse of pollutant vapours at temperatures as near 20°C as feasible. However, the effect of temperature on trap efficiency is negligible^{6,15}. The measurements were carried out at a flow-rate of 40 ml/min, providing good column efficiency and satisfactory analysis time.

RESULTS AND DISCUSSION

The safe sampling volumes (l/g) obtained by direct methods are reported in Tables II and III for benzene at 60 ppm (v/v) and acetone at two slightly different concentrations. These methods gave similar results for the two adsorbates examined. Sometimes there were some differences, but these were within the limits of measurement reproducibility. Therefore these methods can be considered equivalent. It may be observed that both are time consuming, particularly the second (M-2). However M-2 has the advantage of being more sensitive than M-1. In fact, the sensitivity of M-1 is dependent on the detector's minimum detectable level, while in M-2 a pollutant concentration occurs before detection.

In Tables IV and V are reported the safe sampling volumes calculated by the indirect method and those determined by method M-1. At the lowest concentration (3 ppm) the SSV values are in good agreement. On CH 102 a difference exists for

TABLE I
EXTRAPOLATED RETENTION VOLUMES (l/g) AT 20°C AND COLUMN PLATE NUMBERS

<i>Adsorbent</i>	<i>Benzene</i>		<i>Benzene</i>	
	<i>V</i>	<i>N</i>	<i>V</i>	<i>N</i>
CH 101	41	13	6	19
CH 102	69	10	28	13
CH 103	43	18	9	18
PQ	87	20	10	19

TABLE II
BENZENE SAFE SAMPLING VOLUMES (l/g) AT 60 ppm (v/v)

<i>Adsorbent</i>	<i>Method</i>	
	<i>M-1</i>	<i>M-2</i>
CH 101	9	12
CH 102	11	16
CH 103	15	12
PQ	33	31

TABLE III
ACETONE SAFE SAMPLING VOLUMES (l/g) AT 3 AND 7 ppm (v/v)

<i>Adsorbent</i>	<i>3 ppm</i>		<i>7 ppm</i>	
	<i>M-1</i>	<i>M-2</i>	<i>M-1</i>	<i>M-2</i>
CH 101	3.5	3.5	2.9	2.7
CH 102	3.9	5.1	1.1	—
CH 103	5.2	6.1	4.0	3.6
PQ	5.6	5.8	4.6	3.7

TABLE IV
CALCULATED AND EXPERIMENTAL BENZENE SAFE SAMPLING VOLUMES (l/g) AT 20°C

<i>Adsorbent</i>	<i>SSV</i> (<i>calc.</i>)	<i>SSV (exptl.)</i>	
		<i>3 ppm</i>	<i>60 ppm</i>
		CH 101	18
CH 102	25	16	11
CH 103	23	21	15
PQ	48	> 40	33

TABLE V

CALCULATED AND EXPERIMENTAL ACETONE SAFE SAMPLING VOLUMES (l/g) AT 20°C

Adsorbent	SSV (<i>calc.</i>)	SSV (<i>exptl.</i>)	
		3 ppm	7 ppm
CH 101	4	3.5	2.9
CH 102	13	3.9	1.1
CH 103	5	5.2	4.0
PQ	5	5.6	4.6

benzene and acetone, and also for benzene on CH 101. However, it should be borne in mind that the specific retention volumes and the calculated SSVs are determined at "infinite dilution", while experimental safe sampling volumes are evaluated at finite concentration. Thus the differences between the calculated and experimental SSV values are even larger for benzene at 60 ppm.

Furthermore, it is well known that the breakthrough volume is expected to vary with sample concentration. To clarify this problem, the influence of the vapour concentration on SSV was evaluated. In Figs. 4 and 5 the SSV values (M-1) are

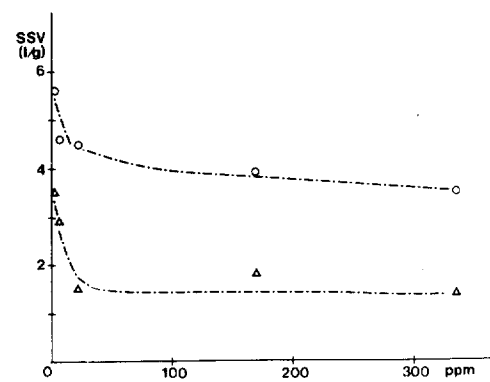
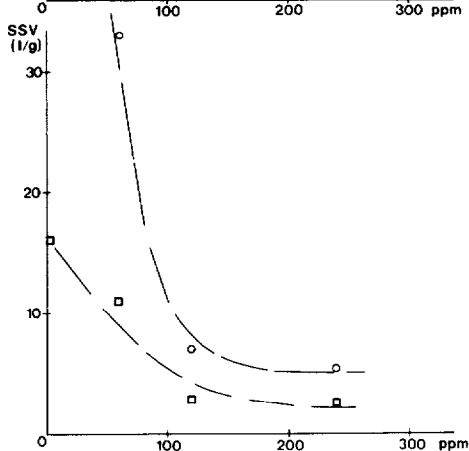
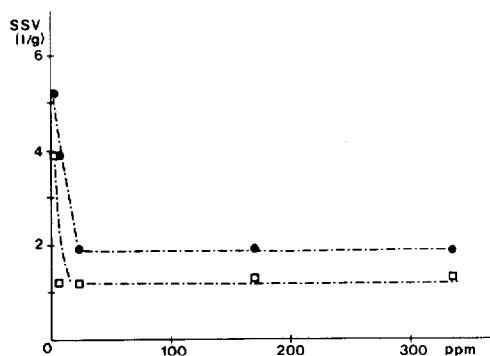
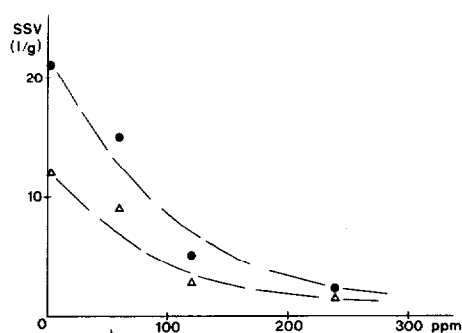


Fig. 4. Plots of SSV (l/g) vs. benzene concentration in the gas mixture. Adsorbents: CH 101 (Δ); CH 102 (\square); CH 103 (\bullet); PQ (\circ).

Fig. 5. Plots of SSV vs. acetone concentration in the gas mixture. Adsorbents as in Fig. 4.

shown as a function of the benzene and acetone vapour concentrations. Both adsorbate SSVs decrease as the concentration increases. While the acetone volumes vary noticeably up to about 20 ppm, with benzene this effect is observed up to approximately 100 ppm.

The experimental results show that both direct and indirect methods can be usefully employed for SSV determination. The indirect method is preferable; as previously observed, this method is referred to as "infinite dilution". Moreover the SSV may be determined in less time, the errors are high but acceptable for this type of analysis¹⁶.

However, the calculated safe sampling volumes must be employed with care as they may be larger than those evaluated at finite concentrations; this risk is highest for very polluted atmospheres.

In conclusion, using these data, it is advisable to sample different volumes, lower than the SSV determined by the indirect method, and to check whether the same ratio exists between the volumes sampled and the corresponding desorption peak areas.

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