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## COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL SAMPLING EFFICIENCIES ON TENAX GC

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### SUMMARY

Breakthrough curves for benzene on the polymeric adsorbent Tenax GC were recorded using a system for direct breakthrough measurement with effluent monitoring. A mathematical model was also designed which allows one to calculate theoretical collection efficiency as a function of sampling volume and number of theoretical plates of the adsorbent tube. Theoretical values correspond to sampling efficiency values derived from experimental breakthrough curves with a correlation coefficient of 0.98–0.99.

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### INTRODUCTION

As volatile organic air pollutants usually occur in concentrations far below the detection limit of the flame ionisation detector, samples should always be pre-concentrated. In general, three concentration techniques are used: cryogenic, absorptive and adsorptive trapping. Cryogenic methods have the disadvantage that considerable amounts of water are condensed together with the collected pollutants; this results in undesirable dilution and will cause interference problems during gas chromatographic-mass spectrometric (GC-MS) analysis<sup>1</sup>. Solvent absorption is applied mainly for the analysis of specific compounds, *e.g.* aldehydes<sup>2</sup>.

Adsorption is the most widely used method for the collection of trace compounds in air. It provides a powerful and non-selective concentration method that has been extensively reported. Activated charcoal is often used for occupational studies but requires solvent desorption, which results in possible interference in GC analysis<sup>3</sup>. Porous polymers do not have this disadvantage and are therefore chosen for most studies. A wide variety of synthetic adsorbents can be used: Amberlite-XAD, Ambersorb, Chromosorb, Porapak and Tenax GC are the most important<sup>4–9</sup>. In this study Tenax GC was chosen because of its following characteristics: high temperature stability up to 375°C, low affinity for water and inertness towards most pollutants<sup>10</sup>. Tenax GC proved to be a good compromise with adsorption and desorption characteristics, although it has a fairly low specific surface area of 18.6 m<sup>2</sup>/g<sup>7</sup>.

A lot of data on volatile organic compounds in air have been obtained using

solid sorbents<sup>11-26</sup>; nevertheless quantitative results are still open to discussion. When an air stream passes a sampling tube, an equilibrium between adsorption and desorption processes will be established quite soon. The more weakly a compound is adsorbed, the faster the equilibrium zone will move through the sorbent bed. The more volatile compounds can reach the sampler outlet before sampling is finished, impeding quantitative measurement. Especially for these substances, knowledge of the safe sampling volume is essential for analytical practice.

In the literature there are many different definitions of safe sampling volume and breakthrough volume. In most cases, breakthrough volume is defined as the volume sampled when the concentration at the sampler outlet,  $C_o$ , reaches 50%<sup>9,11,27,28</sup>, 10%<sup>29</sup>, 5%<sup>30</sup> or 1%<sup>31,32</sup> of the inlet concentration  $C_i$ , or when  $C_o$  attains the detection limit<sup>6,28,33</sup>. However a more realistic criterion is the fraction,  $f$ , of the total adsorbate collected, which is lost at the sampler outlet. This definition has been applied in few experimental studies<sup>34,35</sup>. On the other hand two theoretical models have been reported<sup>34,36</sup>, in which the fraction  $f$  is derived as a function of adsorbent number of theoretical plates,  $N$ , and adsorbate retention volume,  $V_R$ .

In order to deduce the breakthrough volume, several approaches have been adapted. A distinction should be made between direct and indirect techniques. The latter are based either on experimental methods using pulse chromatography<sup>4,37-40</sup> or on theoretical considerations that assume the distribution of a compound to be gaussian<sup>4,34</sup>. Cropper and Kaminsky<sup>34</sup> derived an equation that shows that at least 32 theoretical plates are necessary to obtain a collection efficiency — defined as  $(1 - f) \cdot 100$  — of 99% when the sampled volume  $V_s$  equals  $0.8V_R$ . A similar expression was used by Butler and Burke<sup>4</sup>, who proved that 30 plates are essential to retain 99% of a compound when sampling  $0.75V_R$ .

In the experimental technique the specific retention volume  $V_g^T$ , *i.e.* the retention volume per gram of adsorbent at sampling temperature  $T$  (in °K), is determined by a linear extrapolation based on the adapted Van 't Hoff equation<sup>41</sup>:

$$\log V_g^T = - \frac{\Delta H_{\text{ads}}}{2.3RT} + \text{constant}$$

The advantage of this method is that no experiment has to be performed at room temperature, at which extremely long retention times occur and where severe band-broadening can conceal the peak maximum. However, owing to errors in the  $V_g^T$  value at room temperature, which result from the extrapolation of data measured at higher temperatures, inconsistent  $V_g^T$  values have been reported, *e.g.* for benzene on Tenax GC: 83 (ref. 4), 67 (ref. 38), 62 (ref. 37), 77 (ref. 39) and 40 (ref. 40) l/g. The main reason is that linearity of the adapted Van 't Hoff equation is limited to an interval of 50°C because of the temperature dependence of the heat of adsorption  $\Delta H_{\text{ads}}$ <sup>42</sup>.

The conclusion is that direct measurement of breakthrough volumes, although technically more difficult to achieve, should be preferred to indirect techniques. In the direct approach, field sampling conditions are reproduced far better than in the indirect way, especially because experiments are carried out at ambient temperature. An atmosphere containing a constant concentration of the investigated compound is either passed through two sampling cartridges in series<sup>15,26,28,43</sup>, or passed through

a single tube while the effluent is continuously recorded by a flame ionisation detector<sup>1,6,8</sup>.

The first method involves the analysis of the second tube at regular intervals to check whether breakthrough has occurred or not. In spite of its simplicity, this procedure remains very time consuming. Thus, continuous effluent monitoring is the more useful technique. Nevertheless, preparation of an atmosphere containing a given concentration of a compound is complicated, especially when one aims concentrations of 1 ppm or lower. Pellizzari *et al.*<sup>1</sup> evaporated the compound and mixed it with pure air or nitrogen to atmospheric pressure, before introducing through a septum into an evacuated flask. The substance is loaded on the sampling tube by carrier gas. This technique has two disadvantages: continuous declining concentration and wall adsorption when used with low concentrations, even with deactivated glass surfaces.

Dynamic injection, as used by Sydor and Pietrzyk<sup>8</sup> is not applicable at low concentrations either. The lowest concentration they reached was 500 ppm, which is not realistic in comparison with ambient concentrations even in highly polluted areas.

The diffusion method is accurate for lower concentrations. The theory of the method of diffusion tubes and their application for dynamic generation of model mixtures has been described by Guiochon and co-workers<sup>44,45</sup>. The substance diffuses through a tube of known inner diameter into a stream of carrier gas. A very wide concentration range can be attained by varying the diameter of the diffusion tube and the gas flow-rate. However, the correct diffusion rate can only be determined by repeated gravimetric calibration, which is extremely time consuming, and requires sophisticated balances.

It was our purpose to derive the specific retention volume of benzene on Tenax GC, using a newly designed continuous monitoring system, by which complete breakthrough curves are recorded. Concentrations in the ppb range can be reached without gravimetric calibration. A mathematical model was also derived, based on the normal distribution concept in chromatography, which expresses the lost fraction  $f$  as a function of  $V_s/V_g^T$ , i.e. the ratio of sampled volume and specific retention volume; and the adsorbent number of theoretical plates. The experimental  $f$  values were calculated by computed plane geometry and compared with the model values. A high degree of concurrence was observed.

## EXPERIMENTAL

Breakthrough experiments were carried out at  $22 \pm 0.5^\circ\text{C}$ . Benzene was chosen as a test compound because of its volatility and toxicity, making it a pollutant of primary importance.

Glass adsorbent tubes had inner diameters of 4, 6, 8 or 10 mm. They were filled with 100, 150, 250 or 300 mg of Tenax GC (60–80 mesh), respectively, at an apparent density of  $0.21 \pm 0.01 \text{ g/cm}^3$  (Table I). With these amounts of adsorbent an acceptable breakthrough time was obtained. The adsorbent was purified by a 3-h Soxhlet extraction with acetone and conditioned overnight at  $220^\circ\text{C}$  under helium at a flow-rate of 10 ml/min. The linear velocity through the tubes was  $5.8 \pm 0.1 \text{ cm/sec}$ . This is approximately the optimum velocity in packed columns according to

TABLE I  
ADSORBENT TUBE SPECIFICATIONS

<i>Inner diameter (mm)</i>	<i>Amount of Tenax (mg)</i>	<i>Length of Tenax column (mm)</i>	<i>Apparent density (g/cm<sup>3</sup>)</i>
4	100	38	0.21
6	150	24	0.22
8	250	24	0.21
10	300	19	0.20

the Van Deemter equation<sup>41</sup>. Benzene concentrations were as low as possible in order to simulate field conditions: 250 ppb\*, 500 ppb, 750 ppb and 1 ppm.

A schematic diagram of the apparatus used for direct breakthrough measurement is shown in Fig. 1.

To prepare known concentrations of benzene in air, a stream at a concentration of 5.4 ppm in dry air from a pressurised reservoir —acquired from Matheson and calibrated with an accuracy of 5% (Certified Standard, Matheson, Oevel, Belgium)— was mixed with a purified air stream from a pressurised air tank. Flows were

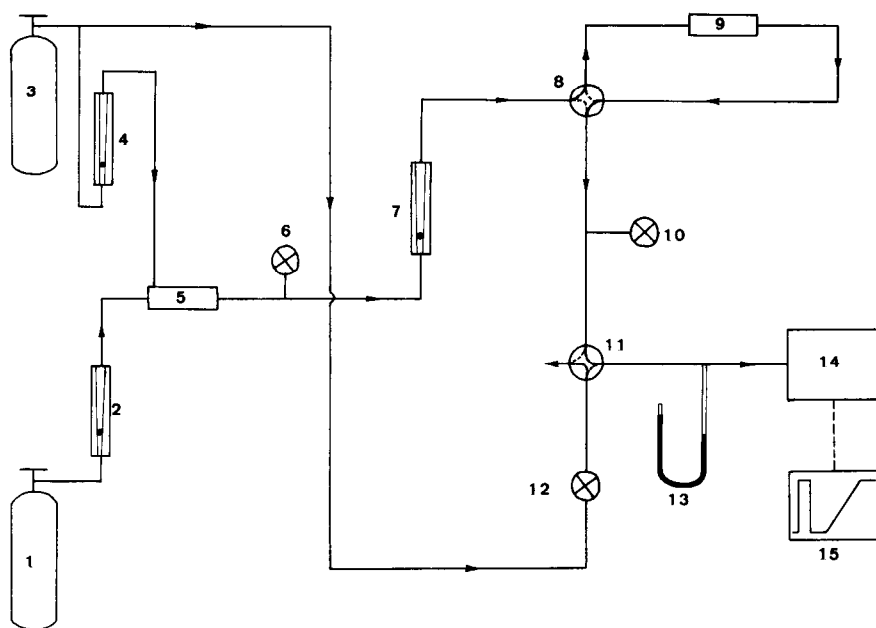


Fig. 1. Schematic diagram of the apparatus for direct breakthrough measurement. Components: 1 = pressurised benzene reservoir; 2 = rotameter type Matheson 600; 3 = pressurised air tank; 4, 7 = rotameters, Matheson type 602; 5 = mixing chamber; 6, 10, 12 = needle valves; 8, 11 = four-way valve; 9 = Tenax tube, passed through two septum rings and incorporated with Swagelock® nuts; 13 = water manometer; 14 = flame ionisation detector; 15 = recorder.

\* Throughout this article, the American billion (10<sup>9</sup>) is meant.

measured with flowmeters from Matheson (Types 600 and 602, respectively), previously calibrated with a soap-film bubble meter. A stream of pure dry air flowing to the flame ionisation detector, allows the baseline to stabilise on the recorder chart (flow from reservoir 3, through needle valve 12 and four-way valve 11). An air stream containing a given concentration of benzene can be fed directly to the detector, to determine the level of the curve at entire breakthrough, *i.e.*  $C_o = C_i$  (flow from mixing chamber 5, not passing through Tenax cartridge 9).

When the registration of a breakthrough curve is begun, valve 8 is switched and the effluent stream flows to the detector. Splitters provided with needle valves 6 and 10 were used to regulate the linear velocity through the tube and the flow-rate to the detector, respectively. The flow-rate to the detector is measured by a calibrated water manometer<sup>13</sup> and should be kept under 80 ml/min.

An example of an experimental breakthrough curve is shown in Fig. 2.

## RESULTS AND DISCUSSION

The specific retention volume for benzene on Tenax GC was determined by use of a direct measuring method. Ten different breakthrough curves were recorded, for different combinations of inner diameter and concentration. In order to ensure that adsorption phenomena could be described by the linear part of the Langmuir adsorption isotherm, concentrations below 1 ppm were used<sup>38</sup>. As a result, the curves showed the symmetrical sigmoid shape of the gaussian distribution. To eliminate recorder noise, every curve was drawn on normal probability paper. For different  $V_s$  values (l/g) in abscissa, the corresponding  $C_o/C_i$  ratio was calculated and plotted in ordinate. The best straight line was fitted to these points. According to the normal distribution theory, the breakthrough volume  $V_g^T$  is found using the abscissa value corresponding to 0.5 in ordinate (mean value), whereas  $V_g^T + \sigma$  corresponds to 0.84 (mean value plus standard deviation). The procedure also enables us to derive the number of theoretical plates from the standard deviation  $\sigma = V_g^T / \sqrt{N}$  (fig. 3)<sup>41</sup>.

The average specific retention volume for benzene on Tenax GC was found to be 59 l/g at 22°C. In practice, this means that, at an ambient temperature of 22°C, 59 l of air can be sampled on 1 g of Tenax GC before the benzene concentration at

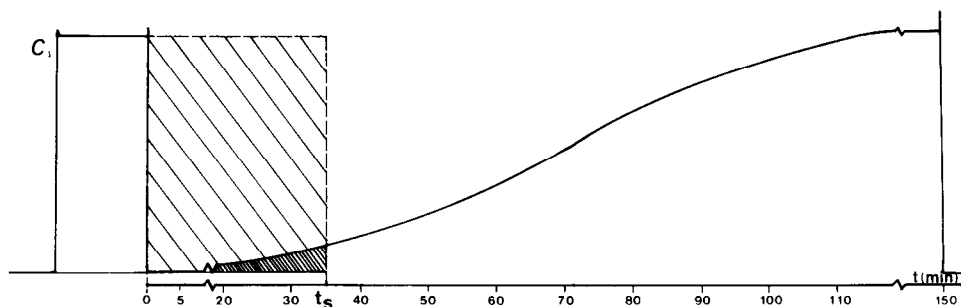


Fig. 2. Experimental breakthrough curve. Baseline and level at entire breakthrough are recorded initially, then the air stream with a given benzene concentration is allowed to flow over the adsorbent tube, while the breakthrough curve is continuously registered. Shaded areas were integrated by an electronic planimeter, for different  $t_s$  values. The results of these integrations yield experimental values for the non-retained fraction  $f$  by division of the integral of the dark shaded area by the total area  $C_i t_s$  (where  $t_s$  = sampling time).

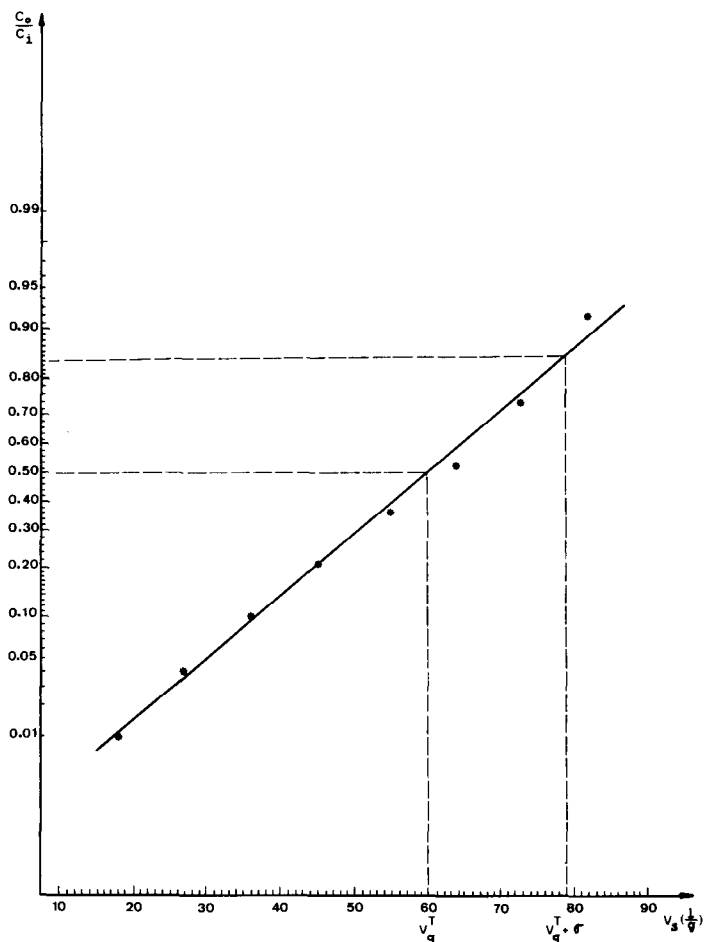


Fig. 3. Example of curve-fitting on normal probability paper. For different  $V_s$  values (in  $1/g$ ) the  $C_0/C_i$  ratio was calculated and plotted in ordinate. The best straight line was fitted to these points.  $V_g^T$  corresponds to 0.50 in ordinate (mean value),  $V_g^T + \sigma$  corresponds to 0.84 in ordinate (according to the normal distribution theory). From these values  $\sigma = 79 - 60 = 19$   $1/g$  is found, thus  $N$  equals 10 [ $N = (V_g^T)^2/\sigma^2$ ].

the sampler outlet reaches 50% of the inlet concentration. The average value was calculated from the ten experimental breakthrough curves and has a standard deviation of 8  $1/g$ . Although the value of  $\sigma$  is quite high, these results are acceptable when compared with the discrepancy between values obtained with the indirect method (see above).

As concentrations were lower than 1 ppm, the  $V_g^T$  value is independent of the concentration. The same is true for the inner diameter. For two tubes with inner diameters  $D_1$  and  $D_2 = 2D_1$  (inner cross-section  $A_2 = 4A_1$ ), filled with the same amount of adsorbent and used with the same linear velocity, one can calculate equal retention volumes ( $Q$  = flow-rate;  $t$  = retention time):

$$V_1 = Q_1 t_1 = \frac{Q_2}{4} \cdot 4t_2 = Q_2 t_2 = V_1$$

( $t_1 = 4t_2$  as the adsorbent length  $L_1 = 4L_2$ ). The theoretical independence is confirmed by experimentally obtained low standard deviations.

To evaluate sampling efficiency, a mathematical model was derived which allows one to calculate the fraction  $f$  of the total adsorbate collected, which is not retained on the sorbent, as a function of  $N$  and  $X_s = V_s/V_g^T$  (if the amount of adsorbent used differs from 1 g, then  $X_s = V_s/V_R$ ). The model is based on the standard gaussian distribution in frontal chromatography with mean value  $V_g^T$  and standard deviation:  $V_g^T/\sqrt{N}$ :

$$\frac{C_o(V)}{C_i} = \frac{1}{2} + \frac{1}{2} \operatorname{erf} \left[ \left( \frac{V - V_g^T}{V_g^T} \right) \frac{\sqrt{N}}{\sqrt{2}} \right] \quad (1)$$

where  $C_o(V)$  represents the adsorbate concentration at the sampler outlet—which is a function of the volume  $V$  sampled at each moment—and  $C_i$  the adsorbate concentration at the inlet (i.e. the ambient concentration).

The fraction  $f$  can be represented mathematically as:

$$f = \frac{\int_0^{V_s} C_o(V) dV}{C_i V_s} \quad (2)$$

Eqn. 1 is substituted in eqn. 2:

$$f = \frac{1}{2} + \frac{\int_0^{V_s} \frac{1}{2} \operatorname{erf} \left( \frac{V}{V_g^T} - 1 \right) \frac{\sqrt{N}}{\sqrt{2}} dV}{V_s} \quad (3)$$

This formula was transformed into the following numerically solvable equation, with  $X_s = V_s/V_g^T$ :

$$f = \frac{1}{2} + \frac{\sqrt{2}}{2 X_s \sqrt{N}} \left\{ \left[ (X_s - 1) \sqrt{\frac{N}{2}} \operatorname{erf} (X_s - 1) \cdot \right. \right. \\ \left. \left. \cdot \sqrt{\frac{N}{2}} + \frac{1}{\sqrt{\pi}} e^{-(X_s-1)^2 \frac{N}{2}} \right] - \left[ \sqrt{\frac{N}{2}} \operatorname{erf} \sqrt{\frac{N}{2}} + \frac{1}{\sqrt{\pi}} e^{-\frac{N}{2}} \right] \right\} \quad (4)$$

The expression is represented graphically in Fig. 4. From this diagram the collection efficiency  $(1 - f) \cdot 100$  can easily be calculated, for given  $X_s$  and  $N$  values.

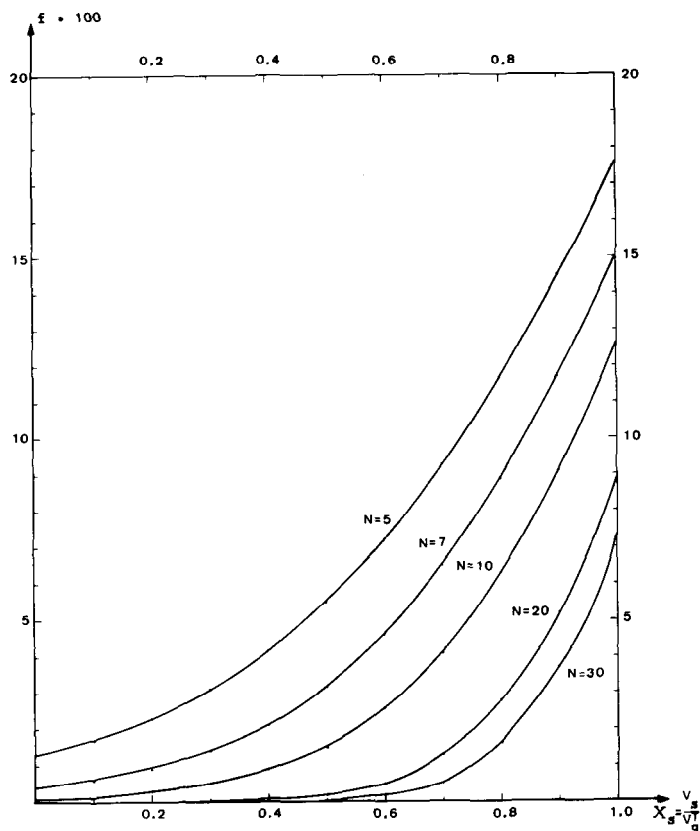


Fig. 4. Graphical representation of the relationship between  $f$ ,  $X_s$  and  $N$ .

For example, if 18 l of air are sampled on an adsorbent tube containing 1 g of Tenax GC (i.e.,  $X_s = V_s/V_g^T = \frac{18}{59} = 0.31$ ), with ten theoretical plates, one can estimate from Fig. 4 that benzene will be collected with an efficiency of 99.5% ( $f \cdot 100 = 0.5 \rightarrow (1 - f) \cdot 100 = 99.5$ ).

There is an initial loss as soon as sampling starts using a sampling cartridge with  $N > 10$  (cf. Fig. 4). This phenomenon is a result of the use of a gaussian model. As the sygmoid of the normal distribution starts from  $(-\infty, 0)$  going to  $(+\infty, 1)$ , the ordinate corresponding to an abscissa value of zero will always reach a value between 0 to 1, increasing with  $\sigma$  (mean value is supposed to be positive). As  $\sigma$  equals  $V_g^T/\sqrt{N}$ , the ordinate corresponding to  $X_s = 0$  in Fig. 4 will increase with decreasing  $N$  values.

In practice a detectable direct breakthrough was observed with  $N < 5$ . Thus, the model is acceptable from this point of view. At smaller  $\sigma$  values (i.e. larger  $N$ ) the area under the normal distribution function from  $-\infty$  to 0 (at the left of the origin, mean value still supposed to be positive) is completely negligible. So the model is a reliable reflection of reality for  $N \geq 10$ .

In order to examine agreement of the model with experimental results, the area



TABLE II

CORRELATION BETWEEN THEORETICAL AND PRACTICAL VALUES OF THE NON-RETAINED FRACTION

 $y = a + bx$ ;  $x$  = model value;  $y$  = experimental value.

$D$ (mm)	$C$ (ppb)	HETP (mm)	Equation	$r$
10	500	1.90	$y = 0.22 + 0.97x$	0.9994
10	750	1.58	$y = -0.51 + 1.13x$	0.9991
8	1000	3.43	$y = 0.25 + 0.90x$	0.9991
8	500	4.00	$y = 3.13 + 0.98x$	0.9994
8	1000	3.43	$y = -1.16 + 0.75x$	0.9767
6	500	4.00	$y = 0.14 + 1.14x$	0.9981

under the curve ( $\int_0^{V_s} C_o(V)dV$ ), as well as the total area  $C_i V_s$ , was integrated by a Summa Graphics electronic planimeter connected to a HP-9825 computer. These areas have been represented on the experimental breakthrough curve in Fig. 2 for an arbitrary value of  $t_s$  ( $V_s = Q t_s$ ). The procedure was repeated for at least twelve  $t_s$  values at regular intervals and was performed with six out of ten experimental breakthrough curves.

The other four curves were not taken into account because of their low  $N$  values. Correlation between theoretical and experimental values was calculated with the least-squares error method. A minimal correlation coefficient of  $r = 0.98$  was obtained (Table II). From these data it can be concluded that our model is in good agreement with experimental results.

Finally, we examined whether a significant difference exists between the model proposed here and the one developed by Senum<sup>36</sup>. This model is based on an equation derived from the CCD theory, first published by Reilley *et al.*<sup>46</sup>. It involves incorporation of a second term in the formula for  $C_o(V)$ . If the lost fraction  $f$  is defined as stated above, and not as the ratio between the unretained and the retained fraction, as originally proposed by Senum, we obtain his model in a slightly different form:

$$f = 1 + \frac{\sqrt{2}}{2 X_s \sqrt{N}} \left[ (X_s - 1) \sqrt{\frac{N}{2}} \operatorname{erf} \left( X_s - 1 \right) \sqrt{\frac{N}{2}} - (X_s + 1) \cdot \right. \\ \left. \cdot \sqrt{\frac{N}{2}} \operatorname{erf} \left( X_s + 1 \right) \sqrt{\frac{N}{2}} + \frac{1}{\sqrt{\pi}} e^{-(X_s-1)^2 \frac{N}{2}} - \frac{1}{\sqrt{\pi}} e^{-(X_s+1)^2 \frac{N}{2}} \right]$$

This can, subsequently, easily be compared numerically with the model explained above.

As an illustration, calculated results for  $N = 10$  and  $X_s = 0.1$ – $1.0$ , are compared in Table III. The most striking fact is that for  $N \geq 10$  and  $X_s \geq 0.3$  there is no more difference, if values are rounded to the first decimal. However, one can

TABLE III

COMPARISON OF THEORETICAL  $f \cdot 100$  VALUES FOR  $N = 10$  AND VARIOUS VALUES OF  $X_s$ 

$X_s$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
This paper	0.14	0.25	0.47	0.86	1.52	2.57	4.14	6.31	9.15	12.61
Ref. 36	0.18	0.28	0.49	0.88	1.54	2.58	4.15	6.32	9.16	12.62

calculate that even at very low  $N$  values, e.g.  $N = 5$ , the maximum difference in the  $f \cdot 100$  value is smaller than 1.00%, which means that collection efficiencies vary by less than 1%.

## CONCLUSION

Complete breakthrough curves for benzene on Tenax GC were recorded using a newly designed continuous monitoring system. From these data an average specific retention volume of 59 l/g was computed. This means that, using 1 g of Tenax GC, 59 l of air can be sampled before the outlet concentration of benzene reaches 50% of the inlet concentration.

A simple mathematical model was designed to calculate sampling efficiencies as a function of adsorbent number of theoretical plates and sampling volume. As a good agreement was shown to exist between theoretical values and experimental results, this model is useful in practice. The slight differences, at lower  $N$  values, from the model previously proposed by Senum<sup>36</sup>, are irrelevant, as in practice adsorbent samplers with at least 5 theoretical plates are used.

## APPENDIX

Transformation of eqn. 3 into the numerically solvable eqn. 4 was done as follows:

$u$  is introduced as a new variable:

$$u = \left( \frac{V}{V_s^T} - 1 \right) \sqrt{\frac{N}{2}}$$

$$\text{If } V = 0, u = -\sqrt{\frac{N}{2}}$$

$$\text{If } V = V_s, u = u_s = \left( \frac{V_s}{V_s^T} - 1 \right) \sqrt{\frac{N}{2}} = (X_s - 1) \sqrt{\frac{N}{2}}$$

Thus, eqn. 3 is transformed into:

$$f = \frac{1}{2} + \frac{\sqrt{2}}{2X_s\sqrt{N}} \int_{-\sqrt{\frac{N}{2}}}^{(X_s-1)\sqrt{\frac{N}{2}}} \operatorname{erf} u \, du$$

Integration by parts<sup>47</sup>:

$$\begin{aligned} \int \operatorname{erf} u \, du &= u \operatorname{erf} u - \int u \, d \operatorname{erf} u \\ &= u \operatorname{erf} u + \frac{1}{\sqrt{\pi}} e^{-u^2} \end{aligned}$$

This formula is applied to the transformed form of eqn. 3 and yields eqn. 4.

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