DETERMINATION OF THE VOLUMES OF VOID ZONES IN PACKED CHROMATOGRAPHIC COLUMNS

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SUMMARY

In gas chromatography there is a pause in flow when sorbable material enters the packing and is absorbed by the stationary phase. There is a complementary surge in flow when the band of sorbed material leaves the packing. When a band passes a void zone, these effects combine to produce a doublet relative to the base-line on a recording of flow-rate against time. Such fluctuations can be measured by using a sensitive differential capillary flow meter. A theory is developed that enables the volumes of void zones in packed chromatographic columns to be found by measuring fluctuations in flow-rate observed when bands of sorbable material pass through the void zones. The theory is confirmed by experiment. The volume of a 0.06-cm^3 void zone was estimated to within about 3%.

INTRODUCTION

Gas chromatography is a widely used analytical technique. Very many publications have appeared that deal with its theory and practice. The practical side has now reached such a level of sophistication that chromatographic equipment manufacturers can offer very compact and versatile packages. However, the selection and sometimes the preparation of the chromatographic column itself, the key component which separates the sample species, is still the task of the analyst. It is important that the column be properly prepared if it is to accomplish the desired analytical results. Excellent practical manuals are available[1,2] that discuss how column parameters determine efficiency. For packed columns, homogeneity of the packing is extremely important. Unfortunately, no simple method is available to check the homogeneity of a conventional analytical or preparative column and to determine the volume(s) of void zones that may be present. Patton and Langer[3] studied thermal decomposition reactions in gas–liquid chromatographic reactors and proposed a method of estimating void-zone volumes from chromatograms obtained when using

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reactive species. Their method required understanding the kinetics of the reactions and thus has had very limited practical use.

We have previously reported[4] how the *position* of a void zone can be located by measuring the flow-rate fluctuation caused by desorption and resorption as a band of sorbable material traverses the void zone. In this paper we present a theoretical treatment that allows the *sizes* of void zones to be estimated from measured flow-rate fluctuations; experiments that confirm the theory are reported.

Sorption-effect chromatography

The sorption effect in gas chromatography was first described by Bosanquet and Morgan[5] who showed that the gas velocity is greater in a region of the column where gas is sorbed than it is in regions where there is no sorption. Another way of looking at the sorption effect is to think in terms of the changes in the inventory (that is to say, the molar quantities) of the several species present in a chromatographic column as analysis proceeds[4,6]. Suppose that a two-column chromatograph is equipped with a sensitive differential molar flow meter downstream from the columns in addition to the usual composition detector. When a sample band leaves a column, there is an increase in flow-rate caused by the desorption; both the conventional detector and the flow meter respond together because the effluent flow-rate and composition change together. However, the sorption-effect chromatogram (the differential flow-rate record) will show additional features that do not appear in a conventional chromatogram[4,6]. This is because the flow meter responds to flow rather than to compositional transients, and so can indicate changes in the amount of sorption anywhere in the system. Most of the molecules of a sorbable species in contact with the column packing are sorbed. Sorbed molecules occupy less volume than non-sorbed molecules and so adsorption or desorption produces a change in the volume that the sorbable molecules occupy in the column. This causes a pause or surge in the gas flow that can be detected by the downstream flow meter. Fig. 1 shows a sorption-effect chromatogram for a band of a single sorbable species injected upstream into an inert carrier passing through a properly packed column. The first peak is the surge in flow caused by injection; the second (negative) peak is the pause in flow as the sample is sorbed when it enters the column. There is then a delay as the peak migrates through the column followed by a surge in flow as net desorption occurs when the band leaves
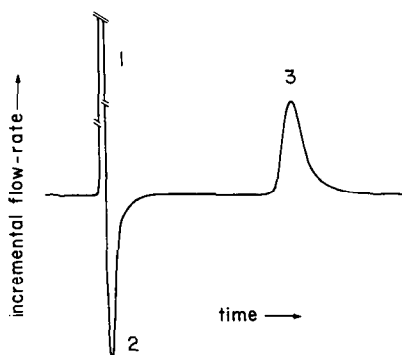

Fig. 1. A sorption-effect chromatogram for a single sorbed band. Responses: 1 = injection; 2 = sorption; 3 = desorption.

Fig. 2. A packed chromatographic column with a void zone.

the column. For a mixture that can be resolved by the column, there is a desorption peak for each resolved species.

Void detection and location

If a void zone is present in one of the packed columns, as shown schematically in Fig. 2, desorption occurs as a band of sorbable species leaves the packing and enters the void zone, followed by resorption as the band leaves the void zone and enters the packing downstream from the void. The position of the void zone can be found from the times at which the flow-rate changes caused by desorption and resorption occur[4]. Fig. 3 shows a sorption-effect chromatogram for a single sorbable component injected into non-sorbed carrier gas passing through a column with a single void zone. Desorption and resorption have combined to give a doublet on the chromatogram in addition to the peaks already present. The relative position of the void zone in the column is given by the time at which the doublet occurs relative to the main peak caused by desorption when the band leaves the column[4]. Times are measured from the sorption peak caused by sorption when the band enters the column.

We shall now show how the size of the void zone can be deduced by considering how the desorption and resorption phenomena at the void zone combine to affect the flow-rate and give the doublet in Fig. 3.

ESTIMATION OF VOID-ZONE VOLUME

It must be stressed that the flow-meter response in sorption-effect chromatography measures a flow transient and not a composition transient. Changes in amount of sorption are seen almost immediately they occur whereas composition changes are not seen until they reach the detector. This gives us a choice of emphasis in analyzing sorption-effect responses: in the present application, our main concern is to estimate
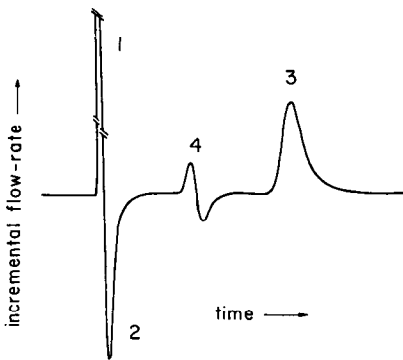

Fig. 3. A sorption-effect chromatogram for a single sorbed band passing through a column with a void zone (schematic). Responses: 1 = injection; 2 = sorption; 3 = desorption; 4 = doublet caused desorption–resorption at void zone.

the volume of a void zone. It does not matter whether the column is of uniform cross-section. The portion of column downstream from the void zone acts as a transmission line that conducts a flow-rate signal. We shall first show how the molar capacity of a void zone can be found from the flow-rate response (the sorption-effect chromatogram) and then show how this is related to a more general column-response function. The latter formulation is more appropriate when the objective is to study the chromatographic process rather than to measure the size of void zones. These analyses are in terms of molar flow-rates and a notional molar flow meter. We then show how the void-zone volume can be found by means of experiments with gases and a differential capillary flow meter.

Effluent flow-rate response analysis
        Fig. 4a is a schematic representation of a large void zone located in an otherwise properly packed column through which a test band of sorbed material is driven by a carrier. Passage of a band of sorbable material causes the downstream flow-rate to fluctuate. Let the deviation in the molar flow-rate of the effluent from the column caused when the sorbed material passes the void zone be $w(t)$ and the deviation in molar flow-rate when the sorbed material leaves the column be $n(t)$. If the test band of sorbed material is narrow and the void zone not too near either end of the column, the response $w(t)$ is separate from $n(t)$ as shown in Fig. 3. A molar flow meter at the column outlet can be used to find $w(t)$ and $n(t)$, because they make distinct contributions to
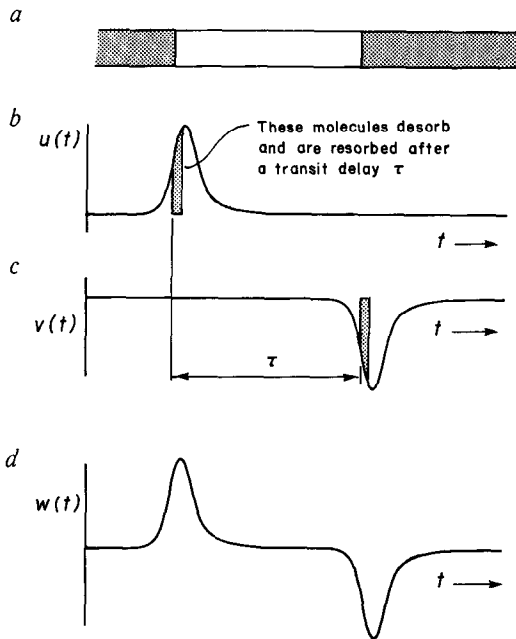

Fig. 4. A sorbable band passing a void zone. (a) The void zone; (b) the effluent flow-rate deviation as the band desorbs into the void zone; (c) the effluent flow-rate deviation as the band is resorbed after a transit delay τ; (d) the total effect caused by the void zone on the effluent flow-rate.

the chromatogram. Should the deviations $w(t)$ and $n(t)$ overlap, then neither can be determined from a flow-rate chromatogram.

The response w(t) is made up of two parts. During the time that the test band crosses the upstream face of the void zone, the amount of sorption decreases, giving an increase in the effluent flow-rate (Fig. 4b); a little later, at the downstream face, the test sorbate will be resorbed causing a decrease in the effluent flow-rate (Fig. 4c). Let $u(t)$ be the deviation in effluent molar flow-rate caused by desorption at the upstream face and $v(t)$ be the effluent molar flow-rate deviation due to resorption at the downstream face. The total response, $w(t)$, will be the sum of these two deviations (Fig. 4d):

$$w(t) = u(t) + v(t) \tag{1}$$

If there is piston flow in the void zone, then no mixing takes place there. The gain in inventory as a batch of molecules is resorbed by the packing downstream from the void zone is the same as the loss in inventory that occurred when those molecules were desorbed from the upstream section. $v(t)$ will be related to $u(t)$ but with a delay as the carrier gas transports the sorbable material through the void. Let this transit time be τ. Then $v(t)$ is the mirror image of $u(t)$ displaced by the time τ (Fig. 4c):
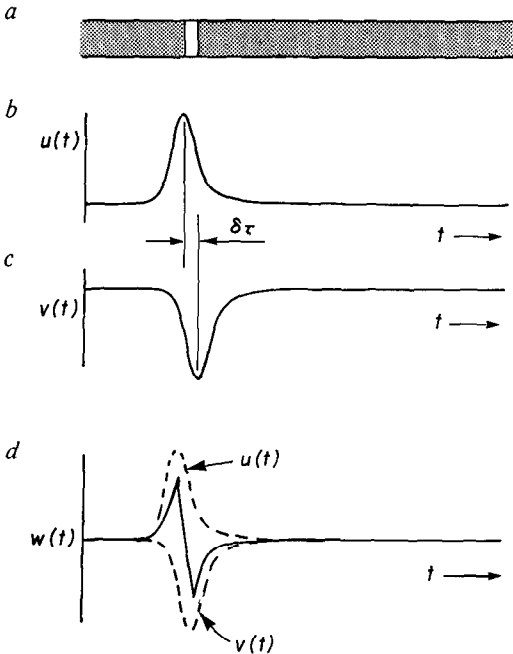
$$v(t) = -u(t - \tau) \tag{2}$$

Fig. 5. A sorbable band passing a small void zone (a). The desorption effect (b) and resorption effect (c) combine to give a doublet on the sorption-effect chromatogram as shown in (d).

Combining eqns. 1 and 2, eliminating $v(t)$, gives

$$w(t) = u(t) - u(t - \tau) \tag{3}$$

Note at this point that $u(t)$ is not constrained in any way and may be a very narrow peak, as it would be if caused by a void zone near the beginning of the column, or broad, as it would be when the void zone is near the column exit or when the injected pulse is wide. When the void zone is long, the time displacement τ is long enough for the two contributions to $w(t)$ to be seen separately on the chromatogram, as in Fig. 4d, and so $u(t)$ can be found. If the void zone is short, then the two contributions overlap and a doublet is produced (Fig. 5). Finally, as τ becomes zero the two contributions exactly cancel and, as would be expected if there were no void, $w(t)$ equals zero.

If the void zone is small but finite, then let the transit time be $\delta\tau$ (Fig. 5). For this case, eqn. 3 becomes

$$w(t) = \frac{\mathrm{d}}{\mathrm{d}t}[u(t)]\,\delta\tau \tag{4}$$

If eqn. 4 is integrated from 0 to some arbitrary time, using t' as a dummy variable, then one obtains

$$\int_0^t w(t')\,\mathrm{d}t' = \delta\tau\int_0^t \frac{\mathrm{d}}{\mathrm{d}t'}[u(t')]\,\mathrm{d}t' = \delta\tau\int_0^t \mathrm{d}u$$

$$= \delta\tau\,[u(t) - u(0)] \tag{5}$$

At $t = 0$ there is no flow-rate deviation (Fig. 5), and so $u(0) = 0$. Let this first integration of $w(t)$ yield $W(t)$, as shown in Fig. 6:

$$W(t) = \int_0^t w(t')\,\mathrm{d}t' = \delta\tau\,u(t) \tag{6}$$

The function $w(t)$ is known from the flow-rate chromatogram so, by integrating from the start to different times t, the function $W(t)$ can be found from the chromatogram. This is not the normal integration to find the area under a peak but a series of integrations until the whole doublet $w(t)$ is passed. An idea of how the functions $w(t)$ and $W(t)$ will generally look is shown in Fig. 6. $W(t)$ is shaped like the chromatographic peak $u(t)$.

A further integration over the peak $W(t)$ gives

$$\int_0^\infty W(t)\,\mathrm{d}t = \delta\tau\int_0^\infty u(t)\,\mathrm{d}t \tag{7}$$
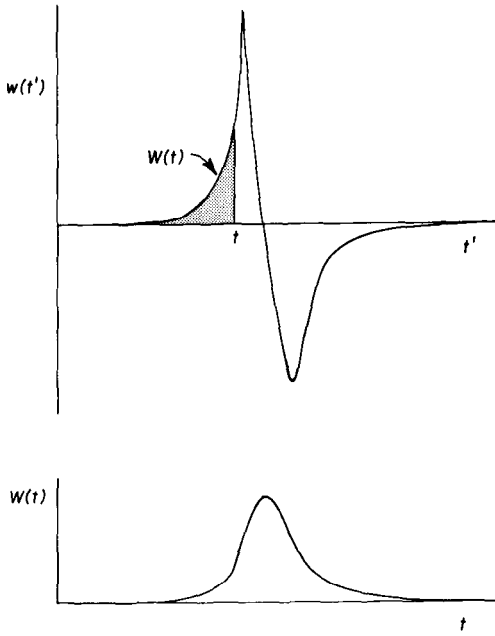
Fig. 6. Integrating the doublet $w(t)$ to find $W(t)$.

Now $u(t)$ is the deviation in the downstream flow-rate caused by the change in volume when sorbed molecules are released into the gas phase when the test band desorbs into a large void zone somewhere in the column. The integral of $u(t)$ over $0 < t < \infty$ represents the total molar amount of material in the test band that desorbs, N_{desorb}. Provided that the partition of the sample between the phases remains constant, this same amount later desorbs at the end of the column; the consequent flow-rate deviation is $n(t)$. Since the same amount is desorbed in both cases:

$$\int_0^\infty u(t) \, dt = N_{desorb} = \int_0^\infty n(t) \, dt \qquad (8)$$

Even though the chromatogram does not show $u(t)$ directly, its integral over $0 < t < \infty$ can be obtained by measuring $n(t)$. Eqns. 7 and 8 give the transit time across the small void zone:

$$\delta\tau = \frac{\displaystyle\int_0^\infty W(t) \, dt}{\displaystyle\int_0^\infty n(t) \, dt} \qquad (9)$$

If the concentration of sorbable material in the carrier gas crossing the void zone is small, then the total molar flow-rate, M, is almost constant and the transit time across the void zone is the ratio of the molar capacity of the void zone, N_{void}, to the molar flow-rate:

$$\delta\tau = N_{void}/M \tag{10}$$

From eqns. 6, 9 and 10 it follows that the molar capacity of the void zone is
E

$$N_{void} = \frac{M \int_{0}^{\infty} \int_{0}^{t} w(t')\, dt'\, dt}{\int_{0}^{\infty} n(t)\, dt} \tag{11}$$

The significance of terms here is that $w(t)$ is the effluent molar flow response as the test band passes the void zone and $n(t)$ is the molar flow response as the test band finally leaves the column. Both flow responses are available from the flow-rate chromatogram as responses at different times and so both the integrals in eqn. 11 can be evaluated from a chromatogram such as that shown in Fig. 3. The flow response doublet $w(t)$ has to be integrated over different times to give the peak response $W(t)$ and this peak response has to be further integrated over its range.

Column-response analysis

Much attention has been paid in the literature to developing theories and models that aim to explain how the mobile and stationary phase concentrations evolve spatially and temporally during a chromatographic transient. This topic is of interest in the current literature[7], but is so well developed that the principal ideas are discussed in textbooks on chromatography[8] and related fields[9,10]. Our analysis can be cast into this form in the following way. If we had a column of otherwise uniform properties, the downstream flow-rate deviation for desorption of a band into a large void at axial position z_v would be the same as the flow-rate deviation that would be observed in the void itself or when desorption occurs from a column of length z_v. It would also be the flow-rate deviation at position z_v within a long column. Let $n(t,z)$ be the flow-rate deviation within a long column at position z and time t. For concreteness, suppose that this is the response to instantaneous injection at $t = 0$. The $n(t,z)$ can be thought of as a family of spatial flow-rate profiles [$n(t,z)$ *versus* z for a set of values of t], or as a family of temporal profiles [$n(t,z)$ *versus* t for a set of values of z]. A sorption-effect chromatogram is an experimental recording of the effluent flow-rate deviation $n(t,L)$ observed from a column of length L. The $n(t,z)$ can be related to the composition transients of conventional chromatography theory because the flow velocity depends on composition[5,11].

Consider a column with packed length L that contains a void zone at $z = z_v$ (Fig. 7). Our previous functions may all be put in terms of $n(t,z)$:
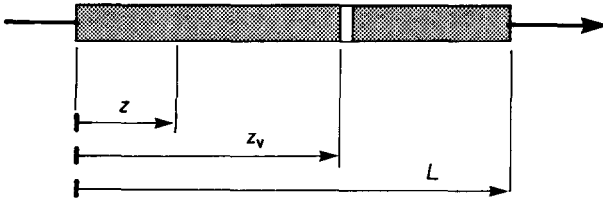
Fig. 7. Spatial coordinates.

$$u(t) = n(t, z_v) \tag{12}$$

$$n(t) = n(t - \tau, L) \tag{13}$$

$$w(t) = n(t, z_v) - n(t - \tau, z_v) \tag{14}$$

for a large void zone and

$$w(t) = \frac{\partial n}{\partial t} \delta\tau \tag{15}$$

for a small void zone. The integrations to find $\delta\tau$ and N_{void} follow as before.

The main potential use of the $n(t,z)$ formulation is the theory of the mechanism of chromatography. This is because theories of the chromatographic process that do not ignore the sorption effect involve spatial concentration and flow-rate profiles evolving in time. Conventional and sorption-effect chromatograms are concentration and flow-rate histories recorded at a fixed position. The $n(t,z)$ formulation connects these ideas.

Experimental principles

In practice, it is necessary to use a real flow meter. The flow-rate deviations, $w(t)$ and $n(t)$, in eqn. 11 are parts of the same chromatogram measured by a single molar flow meter. Any meter whose reading is proportional to molar flow-rate could be used without calibration, because the calibration constant, k, would cancel upon substitution of

$$\text{flow-rate} = k \times \text{reading} \tag{16}$$

in eqn. 11. In particular, if the effluent gas flow is measured at a fixed temperature and a low enough pressure for the gas to be ideal, then the molar flow-rate is proportional to the volumetric flow-rate, Q_{out}, at the downstream measuring point:

$$M = \frac{P_{out}Q_{out}}{RT} \tag{17}$$

The molar capacity of the void zone is related to the volume of the void zone by

$$N_{void} = \frac{P_{void}V_{void}}{Z_{void}RT} \tag{18}$$

where Z_{void} is the compressibility factor of the gas in the void zone. The volume of the void zone is found by substituting eqns. 17 and 18 into eqn. 11:

$$V_{void} = \frac{Z_{void} \left(\dfrac{P_{out}}{P_{void}}\right) Q_{out} \displaystyle\int_0^\infty \int_0^t w(t') \, dt' \, dt}{\displaystyle\int_0^\infty n(t) \, dt} \tag{19}$$

where volumetric flow-rates may replace the molar flow-rates, $w(t)$ and $n(t)$, directly in order to calculate V_{void}.

EXPERIMENTAL

The experimental apparatus and technique used to test this theory for finding the size of void zones were similar to those previously reported[4] for finding the location of void zones and are based on experience of using sorption-effect measurements to study adsorption equilibrium[12] and as an analytical tool[6].

The experimental arrangement is shown in Fig. 8. A standard Pye Model 104 isothermal katharometer chromatograph was fitted with two 4-mm diameter glass columns. One column had a glass-wool plug to create a void in the 500–710 μm Linde 5A molecular sieve packing. As before[4], a common, precision oil-damped pressure regulator [Negretti and Zambra (Aviation)] and thermostatted matched capillary chokes were used to maintain the carrier gas flow-rates. Capillary flow restrictors (70 cm × 0.5 mm diameter) fitted to the column outlets and a differential pressure transducer (Furness FCO 40, ±0.5 mm water) connected between the restrictor inlets were used to detect changes in the flow-rate.

During the final desorption, the composition of the gas flowing in the flow-sensing restrictor changes slightly. The resulting viscosity changes were not large enough to have a substantial effect on our results. The ratio of the pressure drop across the upstream chokes, the columns, and the downstream restrictors was about 100:10:1.
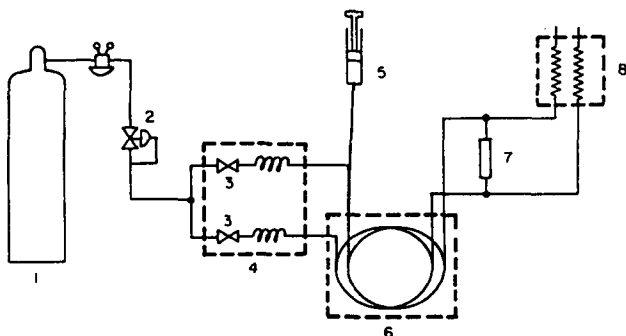

Fig. 8. Apparatus. 1 = Carrier gas reservoir; 2 = precision pressure regulator; 3 = trimming needle valves; 4 = thermostatted flow-setting chokes; 5 = injector; 6 = Pye 104 oven with packed adsorption columns; 7 = pressure transducer; 8 = flow-sensing capillary restrictors.
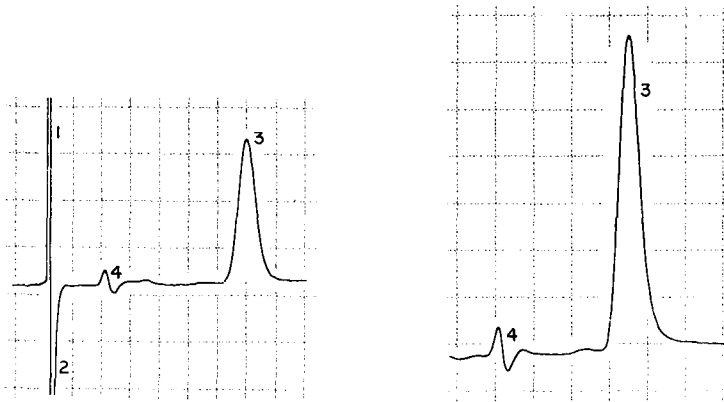
Fig. 9. Sorption-effect responses for injection of (left) 0.04 cm³ nitrogen (30 s grid) and (right) 0.02 cm³ argon (20 s grid) into a column with a void zone. Responses: 1 = injection; 2 = sorption; 3 = final desorption; 4 = passing the void zone. Injection (1) and sorption (2) were not recorded for argon injection.

Samples of adsorbable gas (a few hundredths of 1 cm³) were injected into a helium carrier flowing at 25 cm³/min. The oven temperature was maintained at 40°C.

RESULTS

Experimental chromatograms show the expected doublet flow-rate response as the sample passes the void zone in addition to the response as the sample is desorbed when it leaves the column. Fig. 9 shows chromatograms for experiments in which the injected species were nitrogen and argon. The results are typical of many runs carried out to check the feasibility of the method.

The void-zone volume was estimated from eqn. 19, with the integrals being evaluated graphically from the response curves. Table I reports the values obtained.

The estimated value of the void volume was reproducible to within about 3% and agreed with this accuracy with the actual value. Patton and Langer[3] claimed an accuracy of about 27% for their reaction-kinetic method.

CONCLUSION

The technique demonstrated here is simple and accurate. With a suitable probe

TABLE I

ACTUAL AND EXPERIMENTAL DETERMINED VALUES OF THE VOID ZONE VOLUME

System	Carrier gas flow-rate (cm³ min⁻¹)	Estimated residence time in void (s)	Estimated void zone volume (cm³)	Actual void zone volume (cm³)
Nitrogen–helium	25.0	0.249	0.0624	0.0628
Argon–helium	25.0	0.244	0.0611	0.0628

gas, it can be used to estimate the volumes of void zones in chromatographic and other packed columns.

LIST OF SYMBOLS

k	calibration constant
L	total length of packing
M	molar flow-rate
$n(t)$	molar flow-rate deviation as band emerges from column
$n(t,z)$	local molar flow-rate at time t and position z in response to instantaneous injection at $t = 0$.
N_{desorb}	loss in molar inventory when band desorbs
N_{void}	molar capacity of void zone
P_{out}	pressure at column exit
P_{void}	pressure in void zone
Q_{out}	volumetric flow-rate of effluent stream
R	universal gas constant
t,t'	time
T	absolute temperature
$u(t)$	effluent molar flow-rate deviation caused by desorption into a void zone
$v(t)$	effluent molar flow-rate deviation caused by resorption from void zone
V_{void}	volume of void zone
$w(t)$	$u(t) + v(t)$
$W(t)$	$\displaystyle\int_0^t w(t')\,dt'$
z	axial position
z_v	position of void zone
Z_{void}	compressibility factor of gas in void zone
τ	transit time across void zone

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