Journal of Chromatography, 108 (1975) 243–254

CHROM. 8192

IMPROVEMENT OF THE PERFORMANCE OF THE CAPACITANCE DETECTOR FOR LIQUID CHROMATOGRAPHY

EFFECTS OF THE CELL VOLUME ON BAND SPREADING AND SENSITIVITY OF DETECTION

R. VESPALEC
Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 66228 Brno (Czechoslovakia)
(Received January 13th, 1975)

SUMMARY

Contributions to the zone width caused by band spreading in an injection block, connecting tubing and detection cell with volumes of 11.7–2.0 μl were measured at flow-rates of 0.03–0.85 ml/min. Cells that have the form of a flow capacitor do not contribute to the band spreading to a measurable extent if their volumes do not exceed 5.2 μl. Band spreading that is still acceptable can be obtained in an inlet tubing that has a total length of up to 62 cm if its internal diameter is 0.2 mm. The response of the capacitance detector was proved experimentally to be independent of the cell volume. If different mobile phases are used, the detector can be adapted by exchanging the detection cell or one of the plates. With noise corresponding to a change of $7.6 \cdot 10^{-7}$ unit of dielectric constant, the minimum detectable concentrations measured, expressed as volume per cent, varied from $3.2 \cdot 10^{-3}$ for *n*-nonane to $1.0 \cdot 10^{-5}$ for acetone in *n*-heptane as the mobile phase.

INTRODUCTION

Proportionality between the signal induced by a substance being detected, the response of the detection cell[1] and the output voltage of the auxiliary electronic equipment is necessary for good precision in recording changes of the solute concentration at a column outlet with time. If these conditions are fulfilled, any deviation between the recorded time course of the eluted zone and the course at the column outlet can be caused by only two effects: either by band spreading in joints between the column and the detection cell or by band spreading in the detection cell. In practice, both of these effects appear simultaneously and, in routine procedures, the joints with the column must be considered as integral parts of the detector.

It follows from the preceding paper[2] on band spreading in the inlets and in the detection cell that inlets made of capillaries with small diameters were the most suitable. The spreading was dependent not only on the dimensions but also on the shape of the free volume between the column outlet and the inlet of the detection

cell. The spreading of the leaving zones was independent of the flow-rate and was small in comparison with that with other detectors tested.

The contribution of the detector (*i.e.*, of the detection cell including the inlet and heat exchangers) to the total band spreading is a decisive aspect of the suitability of the detector for recording narrow zones. Band spreading can be derived from the values measured[2] only if the contribution of the column to the measured HETP is assumed to be negligible. Therefore, a series of measurements was carried out that enabled the detector contribution to be determined directly as a function of the flow-rate of the mobile phase and of the volume of the detection cell. The theoretical conclusion[3,4] that the volume of the detection cell has no effect on the sensitivity of the capacitance detector was studied experimentally.

EXPERIMENTAL

Measurements were carried out on a chromatographic apparatus of own construction[5] with a modified system of injection and connection of the detection cell. Analytical reagent grade *n*-heptane of greater than 99% purity (Lachema, Brno, Czechoslovakia), purified by perlocation through activated alumina, was used as the mobile phase. In order to measure the minimum detectable concentrations, *n*-nonane of 99% molar purity (Loba-Chemie, Wien-Fischamend, Austria), benzene for UV spectrophotometry, diethyl ether and acetone (both of analytical reagent grade) (Lachema) and pyridine purified in our laboratory (purity greater than 99.5%) were used as solutes. Benzene of spectral grade was used for measurements of the zone spreading. Samples of the compounds dissolved in the mobile phase were injected through a septum with a 1-μl Hamilton syringe. Concentrations of the solutions were selected such that a volume of 0.3 μl was injected when studying the band spreading and 0.4–0.6 μl in all other measurements.

The minimum detectable concentrations were measured at a flow-rate of 0.41 ml/min in a 500 × 1.8 mm stainless-steel column packed with glass beads with a mean particle diameter of 60 μm. When studying the band spreading at flow-rates of 0.03–0.85 ml/min, the inlet capillary of the detector was connected to the injection block by means of a joint with a dead volume of less than 1.5 μl. The details of newly designed connections of stainless-steel capillaries with internal diameters of 0.2 mm of the injection block according to Huber[6], which is equipped with a needle guide[7] in the measurements, and of the joint can be seen in Fig. 1.

Stainless-steel cells with volumes of 5.2 μl (cell II) and 2.0 μl (cell III) were used in addition to an original brass detection cell[4] with a volume of 11.7 μl (cell I, Fig. 2). The cells were designed so that their variable capacitances and outer dimensions differed from those of cell I as little as possible. Surfaces of the plates that came into contact with eluates were polished. The outer earthed plate of cells II and III was common, and virtually identical with that of cell I (Table I). The inlet opening of cell I was positioned under the centre of the outer plate, and the outlet opening over it. In cells II and III, both openings were positioned at half the height of the outer jacket. The cells were sealed with rugged Teflon rings that also centred the inner plate. Assembly and dismantling were easy and repetition of these operations had no influence on the performance of the cells. On exchanging cells, the frequencies of the measuring and reference oscillators could be tuned simply by a slight change in coarse

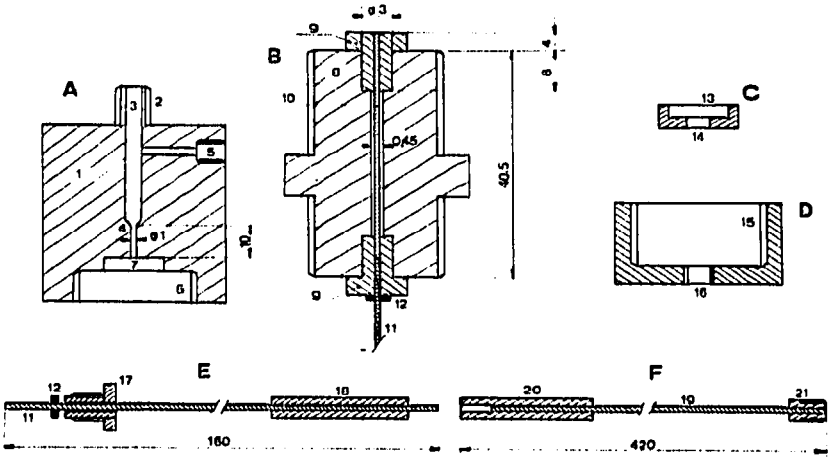

Fig. 1. Schematic sections through the parts used for the measurements of band spreading. A, Injection block: 1 = hexagonal body of the block; 2 = thread for screwing the needle guide to the sealing septum; 3 = inlet opening for the needle; 4 = capillary reduction; 5 = inner thread for fitting the inlet tubing; 6 = inner thread for joining the column or connecting part; 7 = counter-sink for the Teflon seal (9) in connecting part B. B, Connecting part: 8 = brass body of the joint with outer threads and hexagonal prism; 9 = Teflon seal; 10 = elongated injection capillary, 0.2 mm I.D.; 11 = capillary of the inlet tubing, 0.2 mm I.D.; 12 = supporting plate soldered to the capillary (11). C. Protecting ring: 13 = counter-sink for the head of the Teflon seal (9); 14 = opening for the supporting plate (12). D, Cap nut: 15 = inner thread for screwing to the connecting part or column 16 = inner thread for the sliding nut (17). E, Inlet tubing: 11 = metal capillary; 12 = supporting plate; 17 = sliding nut with outer thread; 18 = recess for the cap nut and barrel-shaped seal by which the capillary is fixed to a standard joint. F, Heat exchanger: 19 = stainless-steel capillary, 0.2 mm I.D.; 20 = recess with counter-sink for sliding in the capillary (11) protruding from recess (18) for cap nut and barrel-shaped seal by which the exchanger is fixed to the standard joint; 21 = recess with outer thread for screwing into the outer plate of the detection cell.

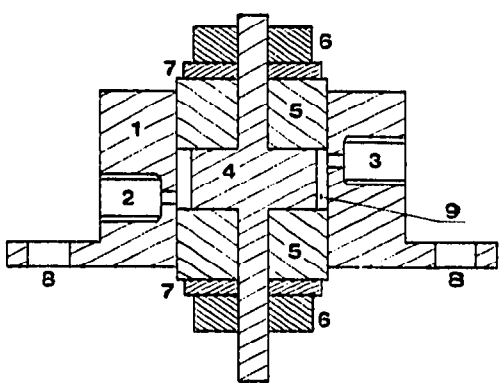

Fig. 2. Schematic section through the detection cell. 1 = Outer earthed plate; 2, 3 = openings with inner threads for screwing the heat exchanger and outlet tubing; 4 = inner plate; 5 = Teflon sealing ring; 6 = nut; 7 = support; 8 = openings for fixing screws; 9 = dielectric space.

TABLE I

CHARACTERISTICS OF THE CELLS USED

Cell No.	*Total diameter (mm)*	*Height of outer plate (mm)*	*Outer diameter (mm)*	*Inner diameter (mm)*	*Thickness of dielectric (mm)*	*Height of dielectric (mm)*	*Operating volume (μl)*	*Air capacity (pF)*	*Material of electrodes*
I	20	15	10.00	9.85	0.075	4.96	11.7	18.22	Brass
II	20	15	10.02	9.92	0.050	3.30	5.2	18.28	Stainless stee
III	20	15	10.02	9.96	0.030	2.16	2.0	19.98	Stainless stee

tuning[4]. Cell exchange did not cause any experimental difficulties. To start the operation, cells II and III did not require any additional adaptations.

A Kompensograph III recorder (Siemens, Karlsruhe, G.F.R.) with a sweep of less than 0.5 sec was used to record the output voltage from the auxiliary electronic equipment of the detector.

STUDY OF ZONE SPREADING

Theoretical

With the experimental arrangement used, the total band spreading measured is characterized by the square of the standard deviation, σ_V^2, expressed as a volume and given by the sum of contributions due to the injection block, σ_S^2, the connecting tubing, σ_T^2, and the detection cell, σ_C^2:

$$\sigma_V^2 = \sigma_S^2 + \sigma_T^2 + \sigma_C^2 \tag{1}$$

The square of the standard deviation of the zone leaving the column, σ^2, can be expressed as

$$\sigma^2 = \sigma_S^2 + \sigma_c^2 \tag{2}$$

where σ_c^2 characterizes the band spreading inside the column.

If a 5% increase in the standard deviation of the zone, σ, is assumed to be the maximum acceptable distortion of the zone during the detection, as in the paper by Scott and Kucera[8], then the following condition must hold:

$$\sigma_T^2 + \sigma_C^2 = 0.1\,\sigma^2 = 0.1\,(\sigma_S^2 + \sigma_c^2) \tag{3}$$

When evaluating the capability of the detector for following narrow zones in practice, subtraction of the contribution of the injection system, σ_S^2, from the total value measured, σ_V^2, is sufficient. Study of the band spreading in the tubing and in detection cells with various volumes necessitates a distinction being made for all contributions that characterize extra-column effects under consideration.

The contribution of the injection system, σ_S^2, is considered by Van Urk-Schoen

and Huber[9] to be independent of the flow-rate. If their assumption is valid, the value of the term σ_S^2 can be obtained by extrapolating the experimental dependence of σ_V^2 on the flow-rate towards zero flow-rate. According to the same authors, the contribution due to the tubing in the region of laminar flow can be determined by the following relationship:

$$\sigma_T^2 = 2\pi^3 r^6 LD/w + \pi r^4 L\, w/24\, D \qquad (4)$$

where r (cm) and L (cm) are the radius and the length of the tubing, respectively, w (ml/sec) is the flow-rate of the mobile phase and D (cm^2/sec) is the diffusion coefficient of the solute in the mobile phase used. The contribution of the longitudinal diffusion, characterized by the first term on the right-hand side of eqn. 4, can be neglected at higher flow-rates. Then the relationship is equivalent to the expression for the value of the standard deviation, σ_t^2, expressed as time, caused by the zone spreading in the tubing, reported by Scott and Kucera[8]. Design requirements (placing of columns and detectors in the chromatograph) are the most important for determining the length of the tubing, which can usually be shortened only slightly. The diffusion coefficient usually cannot be controlled as required as it is considerably affected by the size and structure of the molecules of the solute that is chromatographed. A change in the diameter of the tubing is the most effective means of influencing the value of the σ_T^2 term[8].

The contribution of the detection cell can be evaluated only from the difference

$$\sigma_C^2 = \sigma_V^2 - (\sigma_S^2 + \sigma_T^2) \qquad (5)$$

Eqn. 4 becomes invalid in the region of mixed flow ($2320 \leqslant Re \leqslant 10{,}000$) as well as in turbulent flow ($Re > 10^4$). The detection cell and the tubing must usually be evaluated in these regions as a compact unit. Turbulent flow disturbs the parabolic profile of the velocities in the tubing and therefore, with respect to laminar flow, it decreases the band spreading. The contribution of σ_T^2, calculated for these regions according to eqn. 4, gives the least suitable boundary values that should never be reached. The effect of turbulent flow is comparable to that of the tubing at the points where the parabolic velocity profile, originating in the region of laminar flow, is disturbed[10].

Results

The connecting tubes used, with a total length of 62 cm and I.D. 0.2 mm, consist of an extended injection capillary (4 cm), inlet capillary (16 cm) and heat exchanger (42 cm). It follows from the Reynolds criterion that the flow of *n*-heptane through this tubing is laminar up to a flow-rate of 0.134 ml/min. The diffusion coefficient of benzene at 20° (in *n*-heptane used as the mobile phase), $D = 3.34 \cdot 10^{-5}$ cm^2/sec, is given by the Wilke–Chang equation[11] if the data of Reid and Sherwood[12] are used. It follows from eqn. 4 that the contribution to the zone width due to the tubing, σ_T^2, varies in the range of the laminar flow from 1.2 μl^2 for a flow-rate of 0.03 ml/min to 5.4 μl^2 for a flow-rate of 0.134 ml/min. Even at a flow-rate of 0.850 ml/min, which

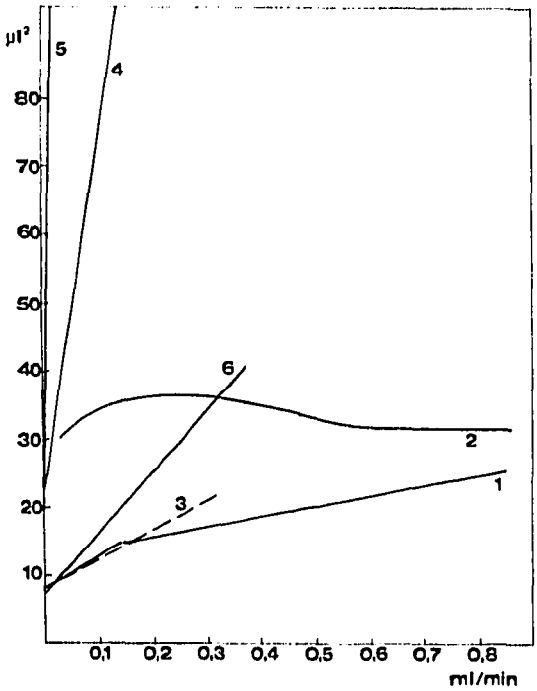

Fig. 3. Dependence of band spreading on flow-rate. 1, Dependence measured for cells II and III; 2, dependence measured for cell I; 3, course of the spreading in the tubing used calculated according to eqn. 4; 4, spreading in the cell of a Zeiss PMQ II spectrophotometric detector with a volume of 7.5 μl (ref. 13); 5, spreading in the cell of a Waters Associate R4 refractometer with a volume of 10 μl (ref. 13); 6, spreading in the cell of a microradiometric detector with a volume of 4.2 μl formed by a capillary, 0.38 mm I.D. (ref. 9).

lies in the range of turbulent flow ($Re = 10^4$ for a flow-rate of 0.587 ml/min), eqn. 4 gives the boundary value of $\sigma_T^2 = 35\,\mu l^2$. Therefore, the tubing is of high quality.

Flow-rates in the measurements were selected such that the widest possible range was covered. The upper limit was determined by the time required to pass the sample and by the chart speed of the recorder. The elution time was about 2 sec for the highest flow-rate used (0.850 ml/sec) and for a total volume of the inlet tubing of 31 μl. Zones eluted at higher flow-rates were recorded with a considerable distortion.

Fig. 3 summarizes the total spreading found experimentally in the system injection block–tubing–detection cell which is characterized by a value of σ_V^2 that depends on the flow-rate for the use of cells with varying volumes. Only the best results of those that were obtained earlier are given. Only such results as were obtained under similar experimental conditions are taken into consideration.

As far as the spreading of the zones being subjected to detection is concerned, it is advantageous to decrease the volume of the detection cell that has the same shape as that under study to 5.2 μl. A further decrease in this volume apparently has no effect on the extent of the band spreading for the procedure of measurement used and at the precision attained. However, very low cell volumes affect the influence of temperature on functioning of the detector, in that a shorter period of time is neces-

TABLE II

MINIMUM DETECTABLE ZONE WIDTHS AT VARIOUS MOBILE PHASE FLOW-RATES AND DETECTION CELL VOLUMES

Flow-rate (ml/min)	*Cell I*			*Cells II + III*		
	$\sigma_T^2 + \sigma_C^2$ (μl^2)	4σ		$\sigma_T^2 + \sigma_C^2$ (μl^2)	4σ	
		µl	*sec*		*µl*	*sec*
0.03	21.8	59.0	118	1.3	14.4	28.8
0.06	23.8	61.7	61.7	2.6	20.4	20.4
0.1	26.1	64.7	38.8	4.4	26.5	15.3
0.2	27.7	66.5	19.9	7.0	33.4	10.0
0.3	27.7	66.5	13.3	8.5	36.8	7.4
0.4	26.8	65.4	9.8	10.8	40.0	6.4
0.6	24.8	63.0	6.3	13.0	45.6	4.6
0.8	23.5	61.2	4.6	16.0	50.5	3.8
1.0	23.5	61.2	3.7	19.0	55.0	3.3
1.5	23.5	61.2	2.6	26.5	65.0	2.8
2.0	23.5	61.2	1.9	34.0	73.7	2.2
2.5	23.5	61.2	1.5	41.5	81.4	2.0
3.0	23.5	61.2	1.2	49.0	88.4	1.8
3.5	23.5	61.2	1.0	56.5	94.8	1.6
4.0	23.5	61.2	0.9	64.0	101	1.5

sary for the establishment of the detector temperature regime and smaller effects of temperature changes in both the measured liquid and laboratory on the stability of the baseline occur. For example, using a stainless-steel cell with a volume of 2 μl, the measurements can be carried out without thermostating or the use of a protective shield of polystyrene foam, giving a tenth of the maximum sensitivity of detection attainable.

The suitability of the cells tested (including the inlet tubing) for detecting narrow zones can be evaluated according to eqn. 3 on the basis of the values obtained by experimental measurements. Table II summarizes the results. The sums of the measured values of the flow-rate-dependent contributions of the tubing and the corresponding detection cell were used in the calculations for flow-rates up to 0.85 ml/min. For higher flow-rates, the minimum detectable zone widths were calculated from the extrapolated values of the zone spreading. The validity of eqn. 7 was assumed for cells II and III. Independence of the zone spreading from the flow-rate was assumed in the case of cell I in accordance with the results obtained by Krejčí and Pospíšilová[2]. The results calculated do not differ substantially (see Table II). Even in the most unfavourable instances and at flow-rates up to 4 ml/min, detection can be accomplished with the minimum distortion (up to 5%) of the zones the base widths of which are greater than 0.1 ml.

Discussion

The injection block and the connecting parts were kept unchanged in all measurements. Differences that were found in the band spreading in systems with different cells are due to the detector fitting to these cells. The results obtained show considerable dependence of the band spreading on the volume of the detection cell,

particularly at flow-rates up to 0.5 ml/min. The values measured with the 11.7-μl cell are greater over the whole range of measurements (Fig. 3) and pass through a maximum at flow-rates between 0.2 and 0.3 ml/min. The values obtained with cells II and III are lower and can be approximated by two straight lines. The relative error in the measurement of σ_V^2 value depends on the flow-rate and lies in the range $\pm$10–15%. The band spreading in the systems, including cells II and III, and thus also in the actual cells, is consequently identical within the limits of the precision of the measurements. Differences with regard to cell I can be caused by the character of the eluate stream through the detection cells or by the efficiency of the washing of the the cell space by the streaming liquid.

It can be considered that the space within the detection cell consists of two tubes of rectangular cross-section the ends of which are connected with one another. The dimensions of the rectangular tubing should be replaced with an equivalent diameter, $d_{equiv.}$ (ref. 14), in hydrodynamic calculations:

$$d_{equiv.} = 2\,ab/(a + b) \tag{6}$$

where a and b are lengths of the edges of the rectangular cross-section. The length of the tubing, equal to the half of the circumference of the bore of the outer plate, is 1.57 cm for all of the cells. The hydrodynamically stabilized flow occurs at 40 times the equivalent diameter of the tubing[14]. These diameters are 0.592 cm for cell I and 0.238 cm for cell III. Hence stabilized flow is established in all of the cells and the Reynolds criterion can be used in order to evaluate its character. The flow of the liquid is laminar ($Re < 2{,}320$) in all three cells within the range of flow-rates used, as is obvious from Table III. Changes in the character of the flow through the cells of various volumes must therefore be ascribed to the efficiency of the washing of the dielectric space by the streaming liquid.

On working with 5.2- and 2.0-μl cells, the dependence of σ_V^2 on the flow-rate (Fig. 3) can be described by the equation

$$\sigma_V^2 = A + B\,w' \tag{7}$$

where the flow-rate, w', is expressed in microlitres per second. In the range of laminar flow, the best approximation is obtained for $A = 8.5\,\mu l^2$ and $B = 2.6\,\mu l \cdot sec$. If the contribution of the injection block, σ_S^2, to the total zone spreading is independent of the flow-rate, according to Van Urk-Schoen and Huber[9], then it must be equal to A. The flow-rate-dependent contribution due to the spreading in the tubing and in the

TABLE III

REYNOLDS NUMBERS CHARACTERIZING FLOW THROUGH THE CELLS

Cell No.	*Flow-rate (ml/min)*	
	0.03	*0.850*
I	16.2	434
II	23.6	629
III	75.3	2050

detection cell is equal to $B \cdot w'$. The dependence of σ_V^2 has a slope $B = 0.9\ \mu l \cdot sec$ for flow-rates greater than 0.134 ml/min. However, for the $A = 12.5\ \mu l^2$, obtained by the extrapolation to zero flow-rate, a contribution of only $8.5\ \mu l^2$ (as with cell I) can be ascribed to the injection block.

Unambiguous distinction of the contributions of the tubing and detection cells is possible in the range of laminar flow only if the spreading in the tubing can be calculated according to eqn. 4. The design of the inlet capillaries provides close contacts among the individual parts and eliminates undesirable volumes in the joints. Therefore, the inlet tubing exhibits the behaviour of a compact unit for which eqn. 4 holds. At flow-rates of 0.03–0.134 ml/min, the calculated contribution of the tubing, σ_T^2, increases from 1.2 to $5.4\ \mu l^2$. The total measured contribution of the tubing and detection cell II or III varies, over the same range of flow-rates, from 1.3 to $5.8\ \mu l^2$. It follows from these values that the contributions of cells II and III are not detectable within the region of laminar streaming through the tubing with the use of the present measuring procedure and at the precision of measurements attained. The flow-rate-dependent contribution found is determined only by the band spreading in the inlets.

In the region of mixed and turbulent flow through the tubing, the extent of spreading in cells II and III can be anticipated on the basis of the course of the dependences measured and of the known influence of turbulence on the extent of band spreading. The flow-rate-dependent contribution to the spreading in the system when using cells II and III is the same also for flow-rates greater than 0.134 ml/min. Therefore, in this range, both cells provide identical contributions to the total band spreading. From the viewpoint of spreading, cell I is the worst. However, the flow-rate-dependent contribution of the system when using cell I decreases from a certain limit as the flow-rate increases. At the flow-rates under consideration, longitudinal diffusion does not play a role and a decrease in the band spreading with an increase in flow-rate in the joints is therefore not possible. Improved hydrodynamic behaviour found in the system when using cell I must be ascribed to this cell. The washing of cells II and III is perfect even at the lowest flow-rates used, at which they do not contribute to a measurable extent to the zone spreading. If the spreading in cells that have relatively large volumes improves as the flow-rate increases, there are no reasons for the worsening in cells with smaller volumes. The contributions of cells II and III to the total spreading are therefore negligible even at flow-rates above 0.134 ml/min and the flow-rate-dependent contribution is equal to the contribution of the tubing. The contribution of cell I to the total band spreading is obtained over the whole range of flow-rates studied from the difference between dependences 1 and 2 (Fig. 3).

The sensitivity of the detection sensing element to temperature changes is determined by two factors: temperature changes to the dimensions (and hence also the volume and air capacity) of the detection cell and changes in the dielectric constants of both the mobile phase and the solute. Changes in the dimensions of the detection cell can be suppressed by selecting materials with low dilatability (replacement of brass with stainless steel). The mass of the detection cell exceeds the mass and hence also the thermal capacity of the eluate in the detector by several orders of magnitude. The mass of the detection cell, with good thermal conductivity, operates as a heat exchanger that controls temperature changes in the dielectric. The rate of establishment of heat equilibrium at a given flow-rate increases with decreases in the total amount of the liquid in the detection cell and in the thickness of its layer (Table

l). Sturdiness of the detection cell is also advantageous not only from the viewpoint of good dimensional stability[15] and resistance to undesirable changes caused by repeated assembly and dismantling of the cell, but also from the viewpoint of thermal stability.

VOLUME OF THE CELL AND SENSITIVITY OF DETECTION

The response of the capacitance detector in the arrangement used is dependent on neither the dimensions nor the volume of the detection cell, as follows from the relationships derived earlier[3,4]. At a given basic frequency, f_1, the response, Δf, is a function of the dielectric constant of the solute, ε_s, of its volume fraction in the eluate, V_s, and of the value of the invariant capacitances of the detection cell[4]. The relationship between the invariant capacitance and the variable capacitance is represented by means of a coefficient, k.

$$\Delta f = f_1 \frac{(k\varepsilon_1 + \varepsilon_2)^{\frac{1}{2}} - [(1 + k)\,\varepsilon_1]^{\frac{1}{2}}}{(k\varepsilon_1 + \varepsilon_2)^{\frac{1}{2}}} \tag{8}$$

where

$$\varepsilon_2 = \varepsilon_1 + V_s\,(\varepsilon_s - \varepsilon_1) \tag{9}$$

In order to verify this conclusion experimentally, the minimum detectable concentrations of *n*-nonane ($\varepsilon = 1.972$), benzene ($\varepsilon = 2.284$), diethyl ether ($\varepsilon = 4.335$), pyridine ($\varepsilon = 12.30$) and acetone ($\varepsilon = 20.7$)[16] were measured with a detector equipped with cells of various volumes. The dielectric constant (ε_1) of *n*-heptane determined by interpolation of the tabulated values for *n*-paraffins with 5–10 carbon atoms[16], is 1.921.

In combination with modern recorders, the recorded noise of the detector equipped with cell I could be decreased to a value that corresponded to changes in the

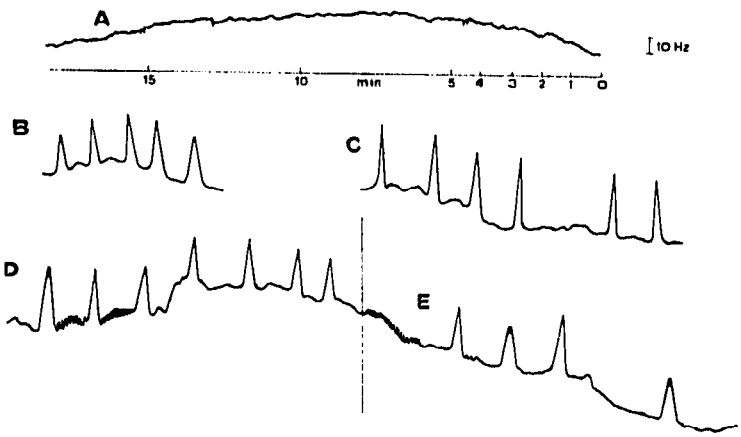

Fig. 4. Baseline and detector response at a noise of 3 Hz. A, Baseline, cell I. B, Detection of $2.5 \cdot 10^{-4}$ μl of diethyl ether, cell I. C, Detection of $2 \cdot 10^{-3}$ μl of benzene, cell II. D, Detection of $3.5 \cdot 10^{-5}$ μl of acetone, cell III. E, Detection of $7.0 \cdot 10^{-5}$ μl of pyridine, cell III. Flow-rate of the mobile phase: 0.4 ml/min.

TABLE IV

MINIMUM DETECTABLE CONCENTRATIONS AT A NOISE OF 3 Hz

Substance	ε	$\Delta\varepsilon$	$C_{theor.}$ (%)	$C_{exp.}$ (%)		
				Cell I	*Cell II*	*Cell III*
n-Nonane	1.972	0.051	$3.6 \cdot 10^{-3}$	$3.2 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$
Benzene	2.284	0.036	$5.1 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$
Diethyl ether	4.335	3.414	$5.4 \cdot 10^{-5}$	$6.4 \cdot 10^{-5}$	$8.6 \cdot 10^{-5}$	$4.4 \cdot 10^{-5}$
Pyridine	12.30	10.38	$1.8 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$
Acetone	20.7	18.8	$1.0 \cdot 10^{-5}$	$1.1 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$	$0.8 \cdot 10^{-5}$

frequency of oscillators of less than 3 Hz (Fig. 4). The same result was obtained with the detector equipped with cells II and III. Table IV summarizes the minimum detectable concentrations of the solutes tested, which were obtained experimentally with the use of 11.7-, 5.2- and 2.0-μl cells. Theoretical values were calculated on the assumption that the response equal to a change in frequency of 6 Hz will be evoked.

The values measured confirm the independence of the sensitivity of the detector from the volume and dimensions of the detection cell. Comparison with the values measured earlier at a noise of 14 Hz (ref. 4) shows that the decrease in the noise is followed by a directly proportional increase in the sensitivity of detection. The difference in the dielectric constants of the mobile phases used, *n*-hexane ($\varepsilon = 1.860$) and *n*-heptane ($\varepsilon = 1.921$), apparently has no effect on the sensitivity of the detection of benzene and particularly of diethyl ether, pyridine and acetone[4]. The dielectric constants of *n*-hexane and *n*-heptane are very similar and therefore the corresponding values of $\Delta\varepsilon = \varepsilon_x - \varepsilon_1$ differ only insignificantly.

CONCLUSION

This paper completes the information on the capacitance detector that was summarized in earlier papers[2,4] and describes a detailed study of the inlet tubing and cells with varying volumes and of their effects on the spreading of the detected zones.

Sufficiently low band spreading can be obtained in the inlets made of capillaries of 0.2 mm I.D. even with a total length of the tubing exceeding 50–60 cm. The flow coaxial capacitor that forms the detection cell is advantageous from the viewpoint of its shape. The contribution to the zone width caused by its spreading in the detection cell is virtually negligible at cell volumes of 5.2 μl and less. The detector tested is suitable for recording very narrow zones. The minimum detectable zone widths were calculated from the values measured, depending on the flow-rate.

The independence of the response of the capacitance detector from the detection cell volume[3,4] was verified experimentally. An approximately four-fold increase in the sensitivity of detection compared with the results published earlier[4] was obtained by decreasing the recorded noise from 14 to 3 Hz, which corresponds to a change of $7.6 \cdot 10^{-7}$ units in the dielectric constant. The minimum detectable concentrations of the tested solutes in *n*-heptane varied between $3.2 \cdot 10^{-3}$% by volume for *n*-nonane to $1.0 \cdot 10^{-5}$% by volume for acetone, and were in good agreement with the theoretical values. The minimum volume of the cell that was attained, $V = 2\ \mu$l, is three to five times smaller than the volumes of the common commercial cells of UV

and RI detectors. The independence of the response from the shape and dimensions of the cell suggests a means of overcoming one of the main experimental limitations of the capacitance detector, *viz.*, bad applicability to operations with mobile phases that have varying dielectric constants. Detection cells can be used with exchangeable plates the dimensions of which are selected such that both the volume of the cell and its capacitance may be kept within suitable limits after filling the cells with the mobile phase. The shape of the detection cell, its sturdiness and its resistance to repeated assembly and dismantling and the simplicity of the design and production are the main advantages of the detector.

REFERENCES

1 J. Novák, *Advan. Chromatogr.*, 11 (1974) 1.
2 M. Krejčí and N. Pospíšilová, *J. Chromatogr.*, 73 (1972) 105.
3 S. Haderka, *J. Chromatogr.*, 52 (1970) 213.
4 R. Vespalec and K. Hána, *J. Chromatogr.*, 65 (1972) 53.
5 M. Krejčí, R. Vespalec and M. Širec, *J. Chromatogr.*, 65 (1972) 333.
6 J. F. K. Huber, *J. Chromatogr. Sci.*, 7 (1969) 85.
7 A. Kroneisen, *Thesis*, J. W. Goethe Universität, Frankfurt am Main, 1969, p. 19.
8 R. P. W. Scott and P. Kucera, *J. Chromatogr. Sci.*, 9 (1971) 641.
9 A. M. van Urk-Schoen and J. F. K. Huber, *Anal. Chim. Acta*, 52 (1970) 519.
10 I. Halász, H. O. Gerlach, A. Kroneisen and P. Walkling, *Z. Anal. Chem.*, 234 (1968) 98.
11 C. R. Wilke and P. Chang, *AIChE J.*, 1 (1955) 264.
12 R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1966, pp. 88 and 549.
13 J. F. K. Huber, *J. Chromatogr. Sci.*, 7 (1969) 172.
14 A. G. Kasatkin, *Osnovnye Protsesy i Apparatury Khimicheskoi Tekhnologii (Fundamental Processes and Instrumentation of Chemical Technology)*, Gosudarstvennoe Nauchno-Tekhnicheskoe Izdatel'stvo Khimicheskoi Literatury, Moscow, Leningrad, 1948, pp. 44–51.
15 H. Poppe and J. Knuysten, *J. Chromatogr. Sci.*, 10 (1972) 16A.
16 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, Ohio, 46th ed., 1965, p. E-49.