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PERFORMANCE OF THE CAPACITANCE DETECTOR FOR LIQUID CHROMATOGRAPHY

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SUMMARY

The performance and applicability of a detector based on the measurement of the dielectric constant of the eluate were investigated. Variations of the dielectric constant (ε) are converted into frequency changes in the oscillator circuit and are further processed electrically. In the design described, the instrument is suitable for the detection of substances sufficiently soluble in the mobile phase, provided that the solution formed has no electrical conductivity and low dielectric losses. The basic frequency of the oscillators being 18 MHz and the stability $0.77 \cdot 10^{-6}$, the linear range of the responses is $1.38 \cdot 10^{4}$. When hexane was used as the mobile phase ($\varepsilon = 1.89$), the minimum detectable concentrations varied from $2.6 \cdot 10^{-2}$ % for *n*-octane ($\varepsilon = 1.948$) to $4.2 \cdot 10^{-5}$ % for acetone ($\varepsilon = 20.7$).

INTRODUCTION

The investigation of detectors for liquid chromatography has received considerable attention. A number of instruments have been described and many of them are commercially available. Little interest, however, has been aroused by the possibility of using the dielectric properties of substances characterized by the complex permittivity, $\varepsilon^* = \varepsilon' + \varepsilon_i''$. The real part of the complex permittivity (numerically equal to the quantity denoted also as the dielectric constant), ε', is the measure of the change of the capacitance of a capacitor if the substance serves as a dielectric. The imaginary part, ε_i'', characterizes the dielectric losses that occur when a.c. voltage of a defined frequency is put across this capacitor. Both components are dependent on the frequency, and for their measurement a number of static and dynamic methods have been developed, *e.g.*, refs. 1–8. The frequency range of hundreds of Hz to the region of centimetre waves (*e.g.*, refs. 9–11) is used.

Dielectric properties were first used for detection in liquid chromatography by GORDON *et al.*[12] in 1963 and their applicability was briefly reviewed by CONLON[13]. Recently, the theory of various methods for the measurement of both complex permittivity and their components was evaluated by HADERKA[14,15].

Of the possible methods for capacitance measurement, the measurement of

interference, which was applied to gas chromatography[16–19], was chosen by the authors of this paper. Unlike other methods (*e.g.*, bridge methods), this selected method allows the measurement only of changes in the real part of the complex permittivity. Dielectric losses, characterized by the imaginary part of the complex permittivity, cause damping of the resonance circuit which results in the deterioration of the detector properties. It is therefore necessary to work with liquids having minimum dielectric losses (non-electrolytes). The performance and applicability of the detector working at a basic frequency of $1.8 \cdot 10^7$ Hz using hexane as the mobile phase were examined.

DESCRIPTION OF THE DETECTOR

The actual sensing element is the flow capacitor D (Fig. 1), where the eluate of the chromatographic column acts as the dielectric. Changes in the eluate composition, followed by the variation of its dielectric constant, result in changes in the capacitance of the capacitor D, thus modifying the frequency of the measuring oscillation circuit 2. This variable frequency f_2 is compared with the constant frequency f_1 (fed from the comparative oscillator 1) in mixer 3. The signal, proportional to the absolute value of the difference of frequencies $|f_1 - f_2|$, is taken from the frequency meter 4.

The change in frequency of the measuring oscillation circuit (equal to $|f_1 - f_2|$), caused by the change in the dielectric constant of the eluate, is equivalent to the detector response. This response is a function of the dielectric constants of the mobile phase and the sample, of the volume concentration of the sample, the basic frequency

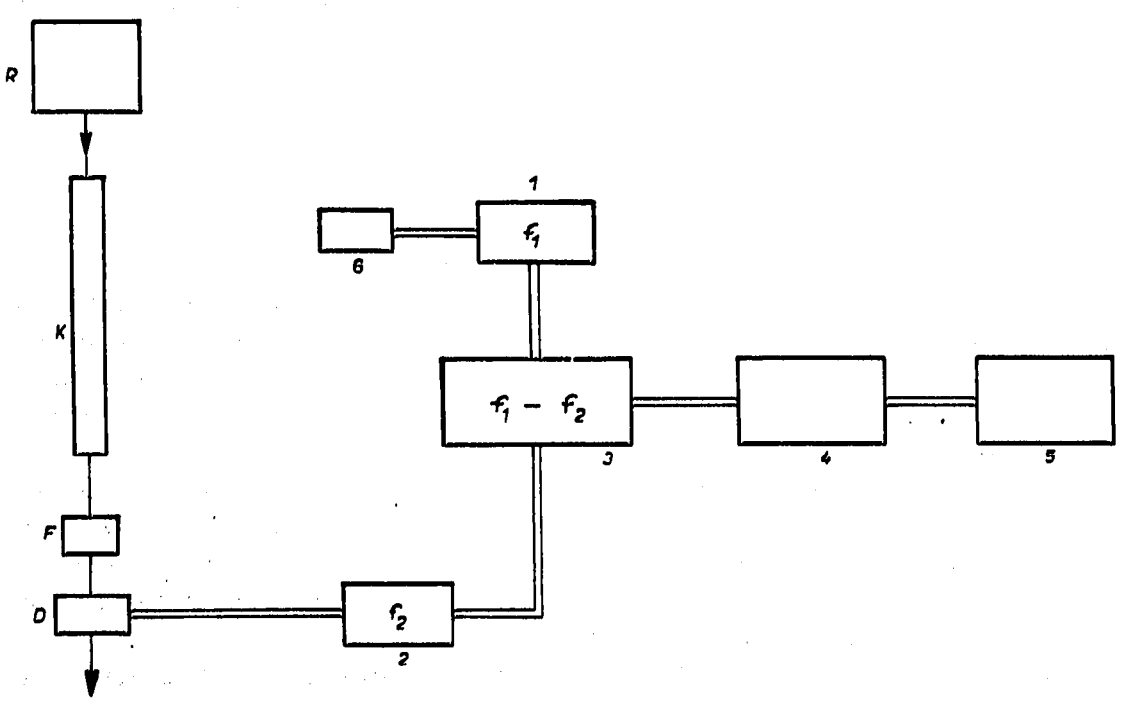

Fig. 1. Block diagram of the measurement of time variations of the dielectric constant of the eluate. R = Reservoir of the mobile phase; K = chromatographic column; F = inlet filter; D = detection cell; 1 = comparison oscillator with constant frequency f_1; 2 = metering oscillator with variable frequency f_2; 3 = mixer; 4 = frequency meter; 5 = recorder; 6 = tuning capacitor of the oscillator 1.

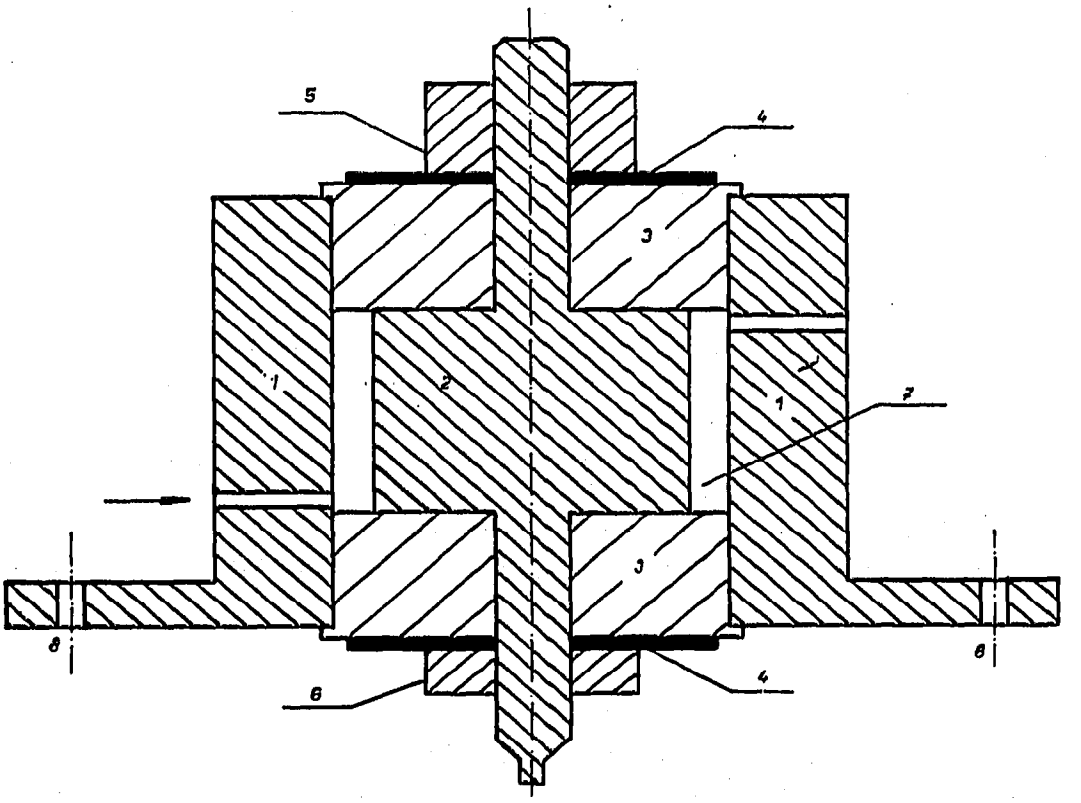

Fig. 2. Schematic section of the detector cell. 1 = Detector body serving as earthed plate of the capacitor; 2 = core serving as second capacitor plate; 3 = Teflon sealing; 4 = washer; 5, 6 = nuts; 7 = space for the dielectric; 8 = hole for tightening screw. All parts are made of brass. Eluate passage is marked with arrow.

of the oscillation circuit and the magnitude of the invariant capacities of the detection cell (see eqns. 4 and 5).

The capacitor used consists of two brass coaxial cylindrical electrodes (Fig. 2), which are fixed with Teflon. Perfect sealing of the cell space was attained by deformation of the Teflon sealing rings, lathed simultaneously with the central electrode. This technique also allows the exacting demands of perfect coaxial situating of the electrodes to be met, even in the case when the detection cell has a small volume. The detector size can be easily changed and electrode material taken as required. The outer jacket of the capacitor, provided with capillaries for the ingress and egress of the eluate, is screwed to the upper surface of the oscillator box and thus earthed. In this way, it forms, together with the oscillators, a compact unit. The height, external diameter and internal diameter of the free space of the capacitor are 0.496, 1.000 and 0.985 cm, respectively. The internal volume of the detection cell is 11.7 μl. The variable capacitance of the capacitor filled with hexane ($\varepsilon = 1.89$), calculated for the dimensions used, is 34.4 pF. The measured value was 49.7 pF. The difference caused by stray capacitance and the capacitance of the parts separated by Teflon does not change during the measurement.

The electronic part contains two oscillators, a mixer, a frequency meter and d.c. supplies.

Both oscillators are made geometrically as identical as possible so that their temperature dependences may be as close as possible and may compensate each other.

For good stability, Clapp's oscillators are used. They are placed, together with buffer stages, in an aluminium block, which is mechanically very stable. The block temperature is controlled in such a way that the detector, fixed on the top, may be maintained at the required constant temperature. It is therefore necessary to conduct away the heat produced by the electronic valves.

Cooling semiconductor thermocouples are used for cooling. A resistance thermometer is used for measuring the temperature of the block, including the detector, and also for controlling the operation of the thermocouples. The selected temperature is controlled with a precision better than 0.01°; its absolute value cannot be measured.

The signal from both oscillators is converted in the multiplication mixer and the intermediate frequency, which has a low frequency character, is amplified. The signal shape is modified to a square wave. This periodic signal having a variable frequency $|f_1 - f_2|$ is fed to the capacitor. The potential across the capacitor is then proportional to the difference of the frequencies $|f_1 - f_2|$.

The device was fed from an electronically stabilized supply, the stabilization factor of which, k_{stab}, was 5.000. The heating potential of the oscillator valves was also stabilized.

EXPERIMENTAL

In all measurements, *n*-hexane of analytical-reagent grade, dried with sodium, was used as the mobile phase. The hexane was kept in a reservoir and passed through the apparatus under the action of gravity (Fig. 3). The hexane was degassed on passing through a copper tube immersed in a water bath heated electrically to about 60°. Sample volumes of 0.05–40 μl were injected into the column with Hamilton and

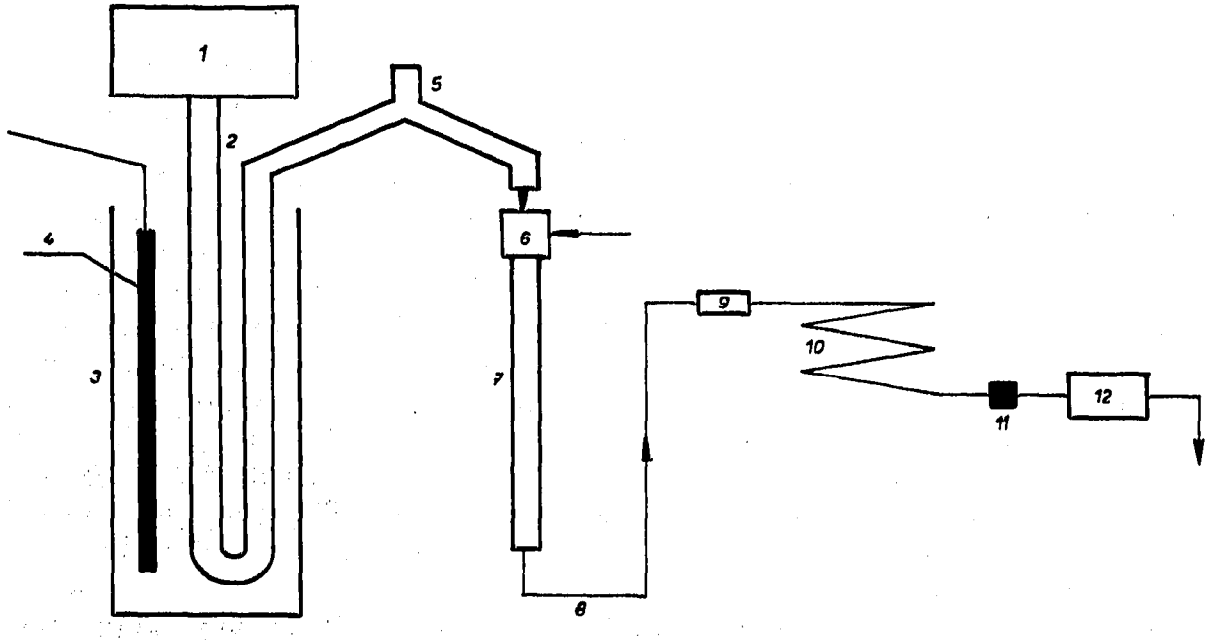

Fig. 3. Scheme of the experimental set-up. 1 = Reservoir containing pure *n*-hexane; 2 = degassing tube; 3 = water bath; 4 = heating element; 5 = T-fitting; 6 = injection block; 7 = column; 8 = connecting capillary; 9 = joint; 10 = heat exchanger; 11 = cotton-wool inlet filter; 12 = detection cell.

Chrominject syringes. The column was a 22-cm long copper tube of 0.2 cm I.D., packed with glass beads 0.125–0.160 mm in size. For measuring the flow dependence of the response, the column was replaced by a needle valve (Zimmermann, G.D.R.). The column was connected via a 15-cm capillary to a 30-cm W-shaped capillary that served as heat exchanger and which was fixed mechanically to the thermostatted aluminium jacket. In order to reduce zone broadening, the capillaries were shaped[20]. A cotton-wool filter was attached to the detector.

The thermocouples were cooled with water, but in the final stage a water thermostat was used. The temperature of the detector varied between 12° and 18° according to the temperature of the cooling water. For each series of measurements, the chosen temperature being kept constant.

On checking the detector performance and measuring the relation between the response and the volume sampled, a flow rate of 0.26 ml/min was used. The range of detector applicability was tested at a flow rate of 0.19 ml/min. Minimum detectable concentrations were measured using a 50-cm long stainless-steel column of 0.2 cm I.D., packed with glass beads (140–160 mesh), in the experimental set-up described by KREJČÍ *et al.*[21].

Spectroscopically pure benzene was used as both the standard and the basic testing compound. The eluates used to measure the relation between the response and the volume sampled were of the following grades: *n*-octane, chromatographically pure; diethyl ether, p.a.; pyridine, >99.5%; acetone, p.a. Other substances used were of the highest grades available, but the purities stated by the manufacturers were not checked and the substances were not purified further before use.

RESULTS

The relation defining the detector response during the measurement of interference has been given by HADERKA[14]. If, for the given mobile phase, the magnitude of the invariant capacitance, C_K, is expressed as the k-multiple of the variable capacitance, C_1, of the capacitor filled with mobile phase having dielectric constant ε_1, the total capacitance of the measuring capacitor, C, becomes

$$C = C_K + C_1 = C_1 (1 + k) \tag{1}$$

The magnitude of the response, $|\Delta f|$, is then given by

$$|\Delta f| = |f_2 - f_1| = f_1 \left| \frac{[(1 + k)C_1 + \Delta C_1]^{\frac{1}{2}} - [(1 + k)C_1]^{\frac{1}{2}}}{[(1 + k)C_1 + \Delta C_1]^{\frac{1}{2}}} \right| \tag{2}$$

where f_1 is the frequency of the measuring oscillator, on filling the detection cell with pure mobile phase of dielectric constant ε_1; f_2 is the frequency of the measuring oscillator, on filling the detection cell with sample solution, the dielectric constant of the solution being ε_2; and $\Delta C_1 = C_2 - C_1$, where C_2 is the capacitance of the measuring capacitor filled with sample solution.

Since the geometry of the detecting capacitor does not vary during measurements carried out at constant temperature, with respect to the relation of the capacitance of a capacitor, $C = \frac{\varepsilon \cdot S}{4\pi d}$, one can write

$$C_1 = \frac{\varepsilon_1 S}{4\pi d} \; C_2 = \frac{\varepsilon_2 S}{4\pi d} \; \Delta C_1 = C_2 - C_1 = (\varepsilon_2 - \varepsilon_1)\frac{S}{4\pi d} \tag{3}$$

When eqn. 3 is substituted into eqn. 2, one obtains

$$|\Delta f| = f_1 \left| \frac{[k\varepsilon_1 + \varepsilon_2]^{\frac{1}{2}} - [(1+k)\varepsilon_1]^{\frac{1}{2}}}{[k\varepsilon_1 + \varepsilon_2]^{\frac{1}{2}}} \right| = f_1|A| \tag{4}$$

When the additivity of the dielectric constants of solution components is assumed[14], the value ε_2 for a binary mixture is

$$\varepsilon_2 = V_1\varepsilon_1 + V_S\varepsilon_S = \varepsilon_1 + V_1(\varepsilon_S - \varepsilon_1) \tag{5}$$

where V_1, V_S, and ε_S are the volume fraction of the mobile phase, the volume fraction of the sample and the dielectric constant of the sample, respectively.

Eqns. 4 and 5 were used to evaluate the experimental results.

For the operation of the detector, the following basic assumptions should be fulfilled:

(a) The mobile phase passing through the detector must be sufficiently dry and must not contain gas bubbles which bring about abrupt changes of the capacitance of the detecting capacitor.

(b) It is necessary to prevent penetration of solid particles into the detection cell where, owing to their electrical conductivity, they may cause a short-circuit.

(c) The detector and the mobile phase must be thermostatted at the same temperature. The block, including oscillators, must be arranged in such a way that both the heat conduction through the metal jacket and the air convection inside the block may be of use.

The relation between the sample quantity and the response was measured for five substances: *n*-octane ($\varepsilon = 1.948$), benzene ($\varepsilon = 2.284$), diethyl ether ($\varepsilon = 4.335$), pyridine ($\varepsilon = 12.30$) and acetone ($\varepsilon = 20.7$)[22]. The range of the measuring device was set to allow reading of the responses up to 25 kHz. Responses higher than 15 kHz were read from the calibration graph because the frequency meter operated linearily only up to this limit of frequencies.

The substances measured were sampled either pure or in a hexane solution prepared by weighing. The syringes were calibrated. The over-all eluate concentrations ranged over seven orders of magnitude, and for each measured substance over approximately three orders of magnitude. The results are summarized in Fig. 4. Linear plots, having a slope of unity, were obtained for all substances measured. The response is therefore directly proportional to the sample quantity or to the volume concentration of the substance entering the detector. The results also confirm that the assumption of the additivity of dielectric constants in a solution holds satisfactorily.

During these measurements, the detector noise varied between 40 and 60 Hz. Minimum detectable concentrations (Table I) were established after the noise had been decreased to *ca.* 14 Hz (Fig. 5).

The dependence of the detector response on the flow rate was followed for flow rates ranging from 0.092 to 1.03 ml/min; it is possible, however, to use much higher flow rates[21]. The measurement was carried out without a column in order to estimate the zone extension due to joints and the detector. The peak areas were adjusted to the same sensitivity of the detection system and chart speed.

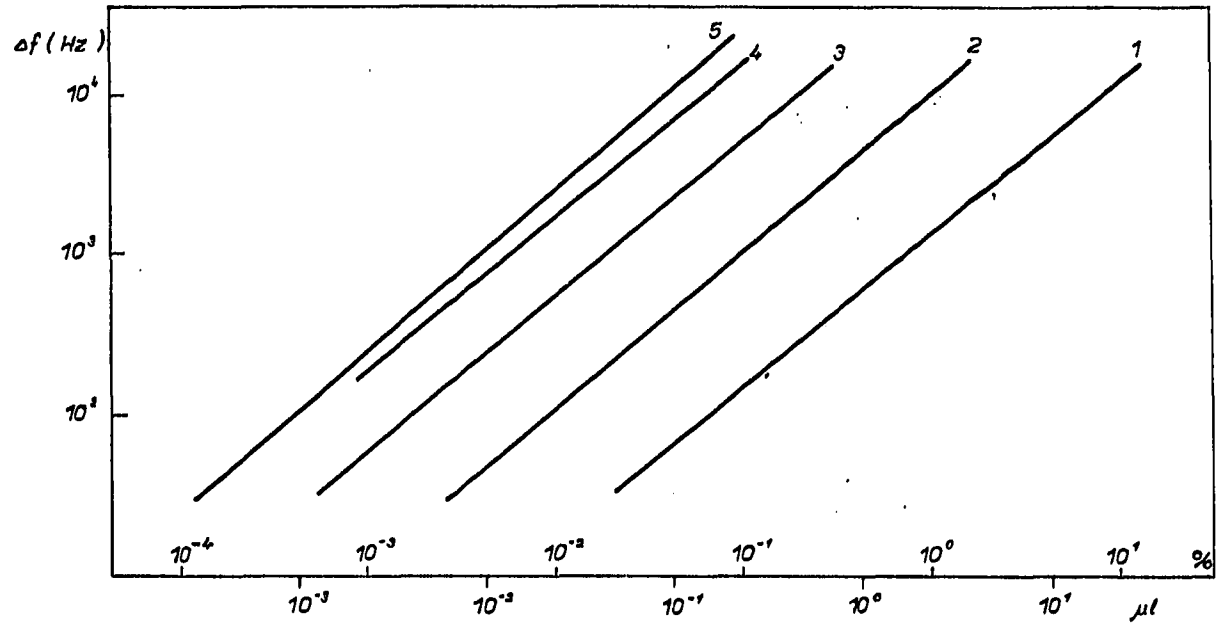

Fig. 4. Dependence of the response on the quantity of the sampled substance with various dielectric constants. 1 = *n*-Octane ($\varepsilon = 1.948$); 2 = benzene ($\varepsilon = 2.284$); 3 = diethyl ether ($\varepsilon = 4.335$); 4 = pyridine ($\varepsilon = 12.30$); 5 = acetone ($\varepsilon = 20.7$). Mobile phase = *n*-hexane ($\varepsilon = 1.89$).

The dependence of the peak area on the flow rate for the quantities sampled (0.1, 0.25, 0.5 and 1 μl of benzene) is illustrated in Fig. 6. Apart from the lowest measured flow rate, 0.092 ml/min, the product of peak area and flow rate can be considered to be constant within the limits of experimental errors. After reducing to equal sample volumes, the products of the peak areas with the corresponding flow rates, for 1.0, 0.5, 0.25, and 0.1 μl of benzene sampled are 9.4 ± 0.3, 9.2 ± 0.5, 9.7 ± 1.0 and 9.9 ± 0.8, respectively. The detector investigated can therefore be described as a concentration detector. This conclusion is supported also by eqns. 4 and 5, characterizing the magnitude of the response. Variables included therein are functions only of volume concentration. In agreement with this classification is the fact that the detector response does not change even when the flow of the mobile phase is stopped.

The evaluation of the potential of the detector was carried out by measuring the response of 39 organic substances representing various types of compounds (Table II). Organic acids were omitted because of the danger of their irreversible sorption in the brass detection cell.

The ratio of the experimental and theoretical responses, $\Delta f_{exp}/\Delta f_{th}$, was used

TABLE I

MINIMUM DETECTABLE CONCENTRATIONS

Substance	ε	$\Delta\varepsilon$	C_{th} (%)	C_{exp} (%)
n-Octane	1.948	0.058	$1.5 \cdot 10^{-2}$	$2.6 \cdot 10^{-2}$
Benzene	2.284	0.394	$2.1 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$
Diethyl ether	4.335	2.445	$3.4 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$
Pyridine	12.30	10.41	$8.0 \cdot 10^{-5}$	$7.8 \cdot 10^{-5}$
Acetone	20.7	18.8	$4.5 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$

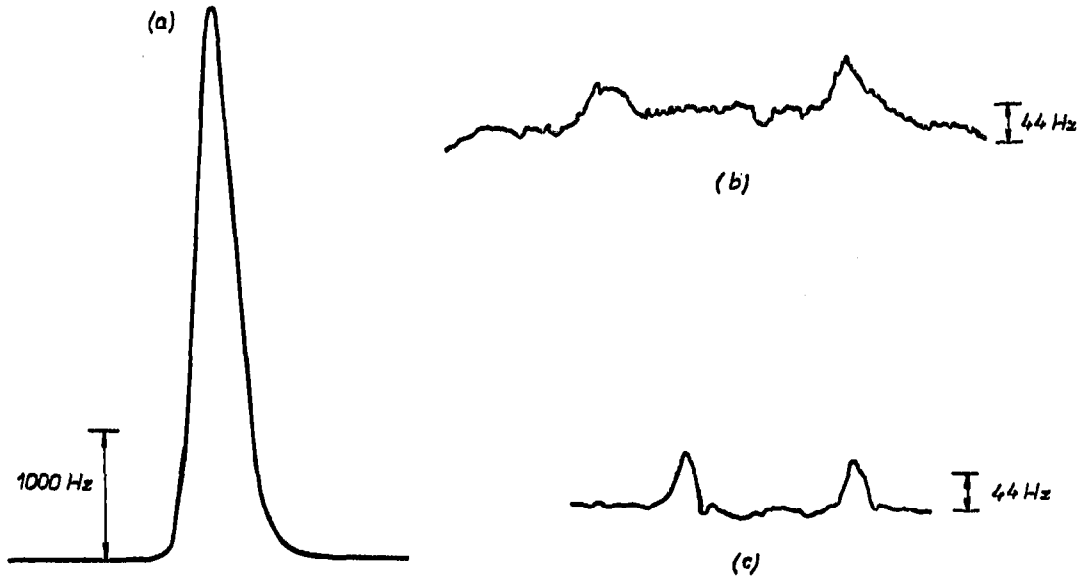

Fig. 5. Characteristic detector responses at different sensitivities and noise. (a) Benzene, 0.5 μl; n-hexane flow rate = 0.092 ml/min; sensitivity = 2; $\Delta f_{max.}$ = 4700 Hz; column length = 22 cm. (b) Benzene, 0.014 μl; n-hexane flow rate = 0.238 ml/min; sensitivity = 4; $\Delta f_{max.}$ = 66 Hz; higher detector noise; column length = 22 cm. (c) Benzene, 0.02 μl; n-hexane flow rate = 0.478 ml/min; sensitivity = 4; $\Delta f_{max.}$ = 48 Hz; lower detector noise; column length = 50 cm.

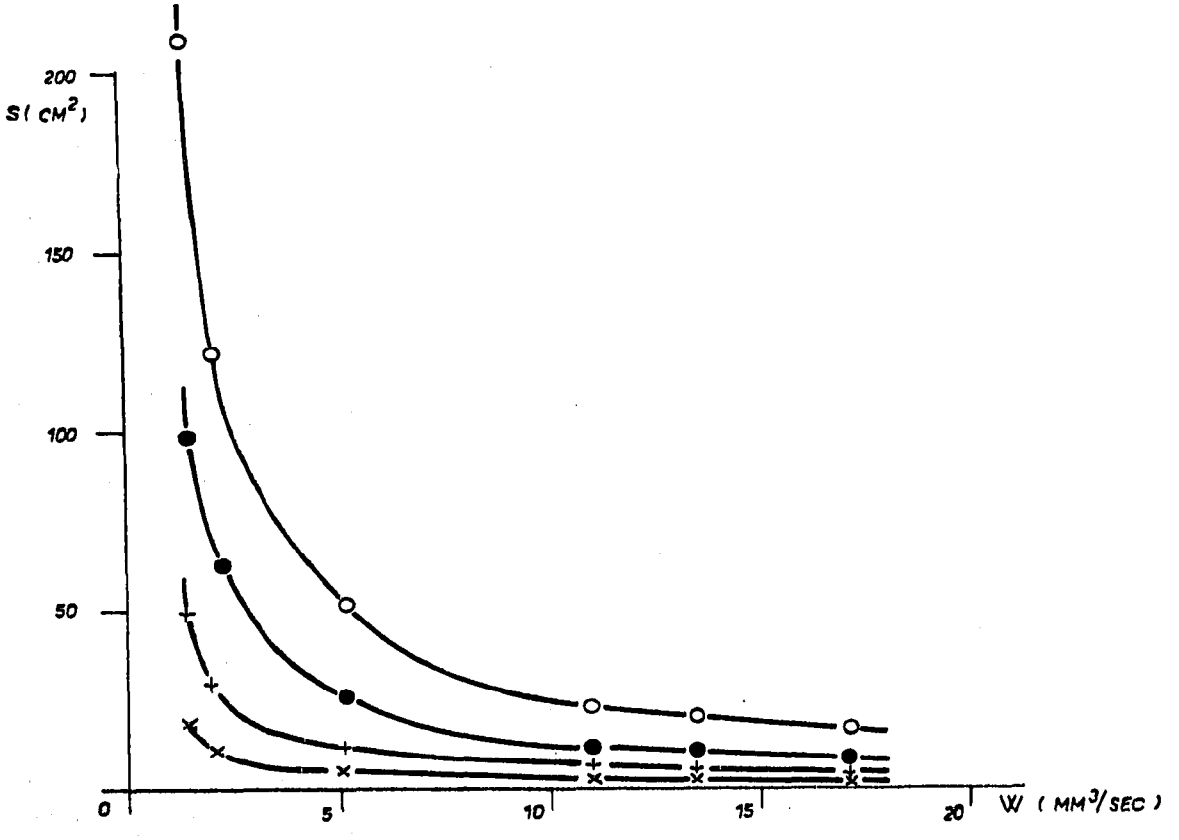

Fig. 6. Dependence of the peak area on the flow rate. Sample volume: ○, 1 μl; ●, 0.5 μl; +, 0.25 μl; ×, 0.1 μl.

TABLE II

RESPONSE OF DIFFERENT SUBSTANCES IN *n*-HEXANE

Substance	*Volume fraction of the substance in the eluate*	ε[a]	Δf_{exp}	Δf_{th}	$\Delta f_{exp}/\Delta f_{th}$	*Purity of the sample*
n-Octane	$4.322 \cdot 10^{-3}$	1.948 (20)	800	812	0.985	Chromatographically pure
n-Decane	$4.149 \cdot 10^{-3}$	1.991 (20)	1444	1395	1.035	Chromatographically pure
Cyclohexene	$2.714 \cdot 10^{-3}$	2.220 (25)	3435	3046	1.128	Chromatographically pure
Benzene	$2.394 \cdot 10^{-3}$	2.284 (20)	3205	3212	0.998	Spectrally pure
Toluene	$1.804 \cdot 10^{-3}$	2.379 (25)	3105	3009	1.047	Chromatographically pure
o-Xylene	$1.107 \cdot 10^{-3}$	2.654 (20)	2864	2795	1.024	p.a.
Diphenyl	$2.710 \cdot 10^{-4}$	2.53 (75)	666	592	1.125	Zonally pure
Naphthalene	$3.115 \cdot 10^{-4}$	2.54 (85) 2.52[b] (17–22)	843	671	1.256	Zonally pure
Phenanthrene	$1.152 \cdot 10^{-4}$	2.80[b] (17–22)	337	358	0.941	Zonally pure
Carbon tetrachloride	$2.746 \cdot 10^{-3}$	2.238 (20)	3750	3252	1.153	p.a.
Chloroform	$4.496 \cdot 10^{-4}$	4.806 (20)	3713	4495	0.826	Pure
Chloroform	$4.938 \cdot 10^{-4}$	4.806 (20)	4071	4937	0.825	p.a.
Bromoform	$6.102 \cdot 10^{-4}$	4.39 (20)	4532	5228	0.867	Pure
Bromobenzene	$3.625 \cdot 10^{-4}$	5.40 (25)	4561	4363	1.045	Pure
Piperidine	$2.510 \cdot 10^{-4}$	5.8 (22)	1103	3366	0.329	Impure[c]
Quinoline	$1.335 \cdot 10^{-5}$	9.0 (25)	1674	2227	0.735	Pure
Isoquinoline[b]		10.7 (25)	2787	—	—	No purity given
Furan	$2.877 \cdot 10^{-5}$	41.9 (20)	2005	3950	0.508	Laboratory preparation[d]
Dioxan	$1.978 \cdot 10^{-3}$	2.209 (25)	3395	2146	1.583	p.a.
Methanol[e]	—	32.63 (25)	—	—	—	p.a.
Ethanol	$1.088 \cdot 10^{-4}$	24.3 (25)	2568	8363	0.309	Spectrally pure
1-Propanol	$2.070 \cdot 10^{-4}$	20.1 (25)	3175	12,961	0.246	Chromatographically pure
1-Butanol	$2.347 \cdot 10^{-4}$	17.1 (25)	2943	12,238	0.240	Pure
2-Butanol	$2.160 \cdot 10^{-4}$	15.8 (25)	2691	10,331	0.260	Chromatographically pure
1-Pentanol	$2.235 \cdot 10^{-4}$	13.9 (25)	2220	9204	0.241	Pure
Cyclohexanol	$2.183 \cdot 10^{-4}$	15.0 (25)	2568	9813	0.262	Chromatographically pure
Benzyl alcohol	$1.759 \cdot 10^{-4}$	13.1 (20)	1673	6765	0.241	Pure
Diisopropyl ether	$4.397 \cdot 10^{-4}$	3.88 (25)	2266	2578	0.876	p.a.
Acetaldehyde	$6.829 \cdot 10^{-5}$	21.8 (10)	3092	4665	0.663	Chemically pure
Benzyl aldehyde	$8.750 \cdot 10^{-5}$	17.8 (20)	3425	4776	0.723	p.a.
2-Butanone	$6.034 \cdot 10^{-5}$	18.5 (20)	3505	5400	0.664	p.a.
Cyclohexanone	$1.153 \cdot 10^{-4}$	18.3 (20)	4400	6390	0.689	p.a.
Acetylacetone	$1.166 \cdot 10^{-4}$	25.7 (20)	3759	9526	0.395	p.a.
Ethyl acetate	$1.590 \cdot 10^{-4}$	6.02 (25)	3532	2252	1.568	p.a.
Tricresyl phosphate	$2.044 \cdot 10^{-4}$	6.9 (20)	3067	3513	0.873	Chromatographically pure
Carbon disulphide	$1.482 \cdot 10^{-3}$	2.641 (20)	3769	3804	0.991	Content exceeding 99.5%
p-Toluidine	$6.002 \cdot 10^{-5}$	4.98 (54)	596	636	0.937	Laboratory preparation
Diphenylamine	$1.041 \cdot 10^{-4}$	3.3 (52)	541	503	1.075	Impure[f]
Nitrobenzene	$3.938 \cdot 10^{-5}$	35.74 (20)	3190	4574	0.697	Pure
Acetamide	—	59 (83)	[g]			Pure

[a] Numbers in brackets give the temperature at which the tabulated value of the dielectric constant was measured.

[b] Value measured at the frequency $4 \cdot 10^8$ Hz.

[c] The sample contains a yellow-coloured fraction, insoluble in *n*-hexane.

[d] Black-coloured preparation contains an oily fraction, insoluble in *n*-hexane.

[e] The sample is adsorbed in the detection cell.

[f] The sample contains a brown insoluble fraction.

[g] The sample gives no response; the substance is insoluble in *n*-hexane.

[h] Saturated solution.

as the basic criterion for the evaluation. Experimental values of the response were read at the maxima of the elution peaks. Theoretical values were calculated for the corresponding concentrations from the relations for the response.

Except for methanol and acetamide, the ratio $\Delta f_{exp}/\Delta f_{th}$ was in the range 1.583 (dioxan) to 0.240 (1-butanol). The solubility of acetamide in *n*-hexane is so small that it cannot be detected even when 40 μl of saturated solution are injected. Methanol is probably strongly adsorbed in the brass detector because the duration of the response suggests that it is eluated very slowly from the detection cell.

The calculation of Δf was affected by the following factors.

(1) The hexane used as mobile phase was not absolutely pure and its dielectric constant was not the same as the theoretical value of 1.890. Direct determination of the actual value was not possible because no data on the dielectric constants of substances used as the mobile phase and standard, at the given frequency, were available.

(2) All the substances used were not pure enough, especially with respect to the admixtures with great deviations of the dielectric constant or those insoluble in hexane. Observed deviations are listed in Table II.

(3) The discrepancy between the experimental and calculated values of the response is especially evident in the case of substances with high dielectric constants. It can also be caused by neglecting the frequency or temperature dependence of the dielectric constant if the tabulated values, used in the calculation, were given for considerably different frequencies and/or temperatures than the ones used.

Totally exceptional is the case of the detection of alcohols which, disregarding the hydroxyl position and the structure of the carbon skeleton, give responses corresponding to 24–30% of the calculated values. This phenomenon cannot be explained either by deviations in purity or by the temperature or frequency dependence of the dielectric constant. It is possible that this phenomenon is related to the molecular state of alcohols in hydrocarbons (*e.g.*, dimer formation).

Though the calculation of Δf_{th} suffers from the above errors, it permits at least a relative comparison between the individual substances and groups of substances. From the results listed in Table II, it follows that the detector gives responses to all substances which are sufficiently soluble in hexane, regardless of the type, structure and substituents on the basic carbon skeleton; as far as the adsorption of the measured substance in the detector can be eliminated, the value of the response can be estimated in advance from tabulated dielectric constants and eqns. 4 and 5, at least semi-quantitatively. The responses given by alcohols, regardless of the structure of the carbon skeleton carrying the hydroxyl group, are extraordinarily low (about 24–30% of theoretical ones).

DISCUSSION

The capacitance detector belongs to the group of non-specific differential detectors, which are generally preferred[20]. In the design described, it can be applied to substances which are sufficiently soluble in a selected mobile phase if the solution formed has no electrical conductivity and low dielectric losses. The detector gives smooth differential chromatographic curves of the usual type (Fig. 5). As the dielec-

tric constant is an electrical analogue of the refractive index, it is useful to compare the results obtained by measuring changes in these physical quantities.

Before this comparison, the minimum and maximum detectable concentrations and the range of the linear response must be defined. The minimum detectable concentration is considered to be that concentration of the solute in the mobile phase such that its response is twice the noise level. The maximum detectable concentration is that concentration for which the deviation from the ideal linear response is 3%[24]. As the response Δf for the given basic frequency f_1 is proportional to the factor A (eqn. 4), the maximum detectable concentration is defined uniquely by the deviation of the curve for the numerical value of the factor A (depending on the volume fraction of the solute) from the tangent line plotted through the origin. The value $A_{max.} = 206.08461 \cdot 10^{-4}$ is independent of the basic frequency and oscillator stability. Also, it does not depend on the magnitudes of the dielectric constant of the mobile phase and of the solute, or on the magnitude of the invariant capacitance of the detecting capacitor. These values influence only the volume fraction of the sample, for which $A = A_{max.}$. The value of $A_{min.}$ (corresponding to minimum detectable concentration for the given basic frequency) is determined by the noise which, in fact, is given only by the stability of the oscillators used. In our case, at a noise of about 14 Hz and $f_1 = 1.8 \cdot 10^7$ Hz (oscillator stability $0.77 \cdot 10^{-6}$), $A_{min.} = 0.01537 \cdot 10^{-4}$.

The range of linear response is given by the ratio $A_{max.}/A_{min.}$. If it is supposed that the oscillator stability is constant, regardless of both the change of the mobile phase and the invariant capacitance of the detecting capacitor, the value of $A_{min.}$ does not change and the ratio $A_{max.}/A_{min.}$ equals $1.34 \cdot 10^4$. With an error of -3% (the accepted deviation from the ideal linear response), it is equal to the ratio of maximum and minimum detectable quantities, regardless of both the dielectric constant of the mobile phase and the magnitude of the invariant capacitance. After expressing it in terms of concentration, the range of the linear response $c_{max.}/c_{min.}$ is $1.38 \cdot 10^4$ for any detectable substance. For the refractometer, the ratio $c_{max.}/c_{min.}$ is usually equal to about 10^3.

The minimum detectable concentrations can be considered to be one of the most important characteristics when refractometric and capacitance detectors are compared.

Differences in the refractive indices of pure substances do not exceed 0.5. If the mobile phase is a liquid with an extreme value of the dielectric constant, *e.g.*, hexane ($\varepsilon = 1.890$), it is possible to work with substances the dielectric constants of which differ by tens of units.

The requirement is made for the liquid detector to detect 1–5 p.p.m. of substance in the mobile phase[25], which corresponds to the highest sensitivity of the refractometric detector produced by Waters Associates. When choosing hexane as the mobile phase, this sensitivity was obtained with substances having dielectric constants of about 5 ($\Delta\varepsilon = 3$). At a concentration of about $5 \cdot 10^{-4}$ %, these substances give responses between 30 and 40 Hz, which can be easily determined (Fig. 5). The same responses can be obtained for substances with $\varepsilon = 12$ ($\Delta\varepsilon = 10$), and $\varepsilon = 20$ ($\Delta\varepsilon = 18$) at concentrations of 8×10^{-5} % and 4.5×10^{-5} %, respectively.

When comparing the sensitivities obtained by the refractometric detector at numerically the same difference of the values measured, it is obvious that the sensi-

TABLE III

DECREASE IN THE RESPONSE OF THE CAPACITANCE DETECTOR WITH INCREASE IN THE INVARIANT CAPACITANCES OF THE DETECTION CELL

k	$k \cdot \varepsilon_1$	$(A/A_0)min.$	(A/A_0) $max.$
0.000	0.00000	1.000	1.000
0.250	0.47250	0.800	0.805
0.444[a]	0.83916	0.693	0.699
0.750	1.41750	0.572	0.579
1.000	1.89000	0.503	0.508

[a] Value estimated for the detection cell used. A_0 = factor A calculated from eqn. 4 for k = 0. Mobile phase, n-hexane; ε_1 = 1.890; $(\varepsilon_2)_{min.}$ = 1.89000581; $(\varepsilon_2)_{max.}$ = 1.97037600.

tivity of the device used is lower by about one order of magnitude. There are several reasons, as follows.

The magnitude of the response of the capacitance detector is reduced by the invariant capacitances of the detecting cell (see eqn. 4). The effect of the invariant capacitances for $0 \leqslant C_K \leqslant C_1$ ($0 \leqslant k \leqslant 1$) is illustrated in Tables III and IV. It can be seen that the response was decreased by tens of per cent, but the region of the linear response was not affected. The influence of invariant capacitances, although perceptible, is therefore not fundamental. As, in addition, their magnitude can vary according to the construction of the detection cell, the detection sensitivity and response region will be considered further under the assumption that $k = 0$.

From eqns. 4 and 5, it follows that the output signal of the capacitance detector is not directly proportional to the difference between the dielectric constants of the solute and that of the mobile phase, but is a function of the difference in the square roots of these quantities. Therefore, for the given difference in the number of units of the dielectric constant and the refractive index, the refractometric detector will give a higher response. In addition, the response of the capacitance detector for a given

TABLE IV

CONCENTRATION RANGE OF THE LINEAR RESPONSE OF SOME SUBSTANCES IN n-HEXANE AT DIFFERENT VALUES OF INVARIANT CAPACITANCES OF THE DETECTION CAPACITOR

Substance	ε	k							
		0.0		*0.250*		*0.444*		*1.000*	
		$c_{max.}$ (%)	$c_{min.}$ (%)	$c_{max.}$ (%)	$c_{min.}$ (%)	$c_{max.}$ (%)	$c_{min.}$ (%)	$c_{max.}$ (%)	$c_{min.}$ (%)
n-Octane	1.948	138	$1.00 \cdot 10^{-2}$	173	$1.25 \cdot 10^{-2}$	200	$1.45 \cdot 10^{-2}$	277	$2.00 \cdot 10^{-2}$
Benzene	2.284	20.6	$1.47 \cdot 10^{-3}$	25.5	$1.84 \cdot 10^{-3}$	29.5	$2.13 \cdot 10^{-3}$	40.8	$2.95 \cdot 10^{-3}$
Tricresyl phosphate	6.9	1.60	$1.16 \cdot 10^{-4}$	2.00	$1.45 \cdot 10^{-4}$	2.31	$1.67 \cdot 10^{-4}$	3.21	$2.32 \cdot 10^{-4}$
Acetyl chloride	15.8	0.577	$4.18 \cdot 10^{-5}$	0.722	$5.22 \cdot 10^{-5}$	0.834	$6.03 \cdot 10^{-5}$	1.16	$8.36 \cdot 10^{-5}$
Ethanol	24.3	0.371	$2.69 \cdot 10^{-5}$	0.448	$3.24 \cdot 10^{-5}$	0.518	$3.74 \cdot 10^{-5}$	0.717	0.352
Nitrobenzene	35.74	0.236	$1.71 \cdot 10^{-5}$	0.297	$2.15 \cdot 10^{-5}$	0.343	$2.48 \cdot 10^{-5}$	0.475	$3.43 \cdot 10^{-5}$
p-Nitro-aniline	56.3	0.148	$1.07 \cdot 10^{-5}$	0.185	$1.33 \cdot 10^{-5}$	0.213	$1.54 \cdot 10^{-5}$	0.295	$2.14 \cdot 10^{-5}$

TABLE V

CONCENTRATION RANGES OF THE LINEAR RESPONSE FOR MOBILE PHASES HAVING DIFFERENT DIELECTRIC CONSTANTS

$\Delta\varepsilon = \varepsilon_s - \varepsilon_1 = \text{const.} = 1$; $k = 0$; $A_{max.} = 0.020608461$; $A_{min.} = 0.000001537$.

ε_1	$c_{max.}$ (%)	$c_{min.} \cdot 10^4$ (%)	$c_{max.}/c_{min.} \cdot 10^{-4}$
1.890	8.02	5.81	1.38
2.00	8.49	6.15	1.38
4.00	17.0	12.3	1.38
6.00	25.5	18.5	1.38
10.00	42.4	30.7	1.38
15.00	63.6	46.1	1.38
20.00	84.6	61.3	1.38
30.00	127	92.2	1.38
40.00	170	123	1.38
60.00	213	154	1.38

$\Delta\varepsilon = \varepsilon_S - \varepsilon_1$ is not constant, but depends on the dielectric constant of the mobile phase (Table V).

From the analytical form of the factor A, the range of admissible values of A, and from eqn. 5, the dependence of both the minimum detectable concentration of different substances and of the linearity range of the detector response on the dielectric constant of the mobile phase can also be derived (Table VI). Tabulated values of dielectric constants were used in the calculations irrespective of the actual mutual solubility of the substance considered. It follows from Tables V and VI that the detection sensitivity expressed as concentration decreases with increasing ε_1 for the given value of $\Delta\varepsilon = \varepsilon_S - \varepsilon_1$. An increase in the minimum detectable concentration is followed by an equal increase in the maximum detectable concentration. Their ratio

TABLE VI

CONCENTRATION RANGES OF THE LINEAR RESPONSE FOR SUBSTANCES HAVING DIFFERENT DIELECTRIC CONSTANTS IN *n*-HEXANE AND FURAN

$k = 0$; $A_{max.} = 0.020608461$; $A_{min.} = 0.000001537$.

Substance	ε	*n-Hexane*			*Furan*		
		$c_{max.}$ (%)	$c_{min.} \cdot 10^5$ (%)	$c_{max.}/c_{min.} \cdot 10^{-4}$	$c_{max.}$ (%)	$c_{min.} \cdot 10^5$ (%)	$c_{max.}/c_{min.} \cdot 10^{-4}$
n-Hexane	1.890	—	—	—	4.44	32.2	1.38
n-Octane	1.948	138	1000	1.38	4.46	32.3	1.38
Benzene	2.284	20.6	147	1.38	4.49	32.5	1.38
Diethyl ether	4.335	3.28	23.8	1.38	4.75	34.3	1.38
Tricresyl phosphate	6.9	1.60	11.6	1.38	5.01	36.8	1.38
Isoquinoline	10.7	0.911	6.60	1.38	5.70	41.3	1.38
Pyridine	12.3	0.770	5.58	1.38	6.00	43.5	1.38
Acetyl chloride	15.8	0.577	4.18	1.38	6.82	49.4	1.38
Acetone	20.7	0.426	3.09	1.38	8.39	60.8	1.38
Ethanol	24.3	0.371	2.69	1.38	10.1	73.2	1.38
Nitrobenzene	35.74	0.236	1.71	1.38	28.8	209	1.38
Furan	41.9	0.200	1.45	1.38	—	—	—
p-Nitroaniline	56.3	0.148	1.07	1.38	12.3	89.4	1.38

for any case considered remains constant. Its value is $1.38 \cdot 10^4$ for the considered maximum deviation from the ideal linear response and oscillator stability. The increase in the dielectric constant of the mobile phase therefore generally causes a deterioration in the detection sensitivity expressed as concentration, but it does not change the usable ratio of solute concentrations. From the viewpoint of sensitivity, systems having a low ε_1 are preferred. The improvement in the detection sensitivity and the elimination of the ε_1 effect on the detection are not possible with the measuring method selected and the given stability of the oscillators.

Requirements for thermal stability are also important. While, for most liquids, the temperature coefficient of the refractive index, dn/dt, is about $3 \cdot 10^{-4}$, the temperature coefficient of the dielectric constant, $d\varepsilon/dt$, varies within the approximate range $1.0 \cdot 10^{-3}$ to $5.0 \cdot 10^{-3}$. At maximum sensitivity, with the device used and with hexane as the mobile phase, we detected changes of dielectric constant of about 10^{-6} units. To obtain this value, it is necessary to ensure that the temperature is stable to within about 10^{-3} °, *i.e.*, the same stability as required when working with a refractometric detector at maximum sensitivity.

We managed to attain this stability (Fig. 5). Temperature measurement by means of a resistance thermometer and cooling with thermoelectric elements facilitated both sufficiently sensitive measurement and fine control of the operating temperature and of the coolant input. Cooling of the thermoelectric elements with thermostatted water and thermal insulation of the whole detection block with a thick layer of polystyrene foam was also beneficial. The effect of the heat produced by the valves used in the oscillators and separation stages was unfavourable, however. This source of heat instability can be successfully eliminated by employing transistors.

The total temperature dependence of the detector response is a function not only of the temperature coefficients of the dielectric constants of the components present in the solution measured, but also of the material of the detection cell. It is affected also by the temperature dependences of the electronic components used in the oscillators.

An important detector characteristic, especially in the measurement of the dynamics of chromatographic procedures, is the minimum detectable width of the zone. It is affected by zone broadening inside the inlets and inside the detection cell and by the time increment of the detector.

The capacitance detector converts the input function (the time change of the dielectric constant of the eluate) directly into electric signals, which are then processed electronically. The time increment of the detector to the output function (time changes of the potential at the output from the frequency meter) is therefore negligible. The minimum detectable zone width is therefore given by zone broadening in the system injection block–connecting tube–heat exchanger–detection cell. Because of the small volume of the detection cell (11.7 μl), it can be assumed that its contribution to the total zone broadening will be small. In spite of this fact, considerable broadening was found in the system used, characterized for different flow rates by σ_v^2-values about ten times higher than those of commercial detectors, where σ_v^2 is a volume variance of the output function in the dependence on the flow rate[23]. As the injection block and the capillaries were not optimized from this aspect, it is possible that better results could be obtained.

In liquid chromatography, it is often difficult to measure the dead volume of the column because the detectors commonly used usually do not give sufficient response to solutes that are very similar to the mobile phase. As the dead volume is usually taken as the elution volume of the unretained sample, its minimum interaction with the column packing can therefore be assumed[26]. The capacitance detector, however, does give satisfactory response to substances as similar as hexane and octane, *e.g.*, Fig. 4. From the theory of liquid chromatography it follows that, in these cases, the interaction of the solute with the column packing is actually negligible[27]. The capacitance detector therefore facilitates the measurement of the dead volume.

In contradistinction to the refractometric detector, the detector investigated is less sensitive to changes in flow rate. When the flow rate was increased from 0.1 to 4.6 ml/min, the frequency of the detection oscillator changed by approximately 1000 Hz when the temperature of the detector was about 13° and the column was at room temperature. Hence the detector could be used when working with a flow programme. However, it will not be suitable for detection when a mobile phase with concentration gradients is used. In addition to the base-line shift, which cannot be fully eliminated even if comparative columns are used, detection sensitivity will also change owing to changes in the dielectric constant of the mobile phase during elution. When using a reference column, not only the magnitude of the factor A (Tables V and VI) but also the basic frequency f_1 will change.

When considering the possibilities of increasing the sensitivity of the capacitance detector, it is necessary to take into account eqn. 4, instrumentation potentialities and the temperature dependence of the dielectric constant.

Increasing the sensitivity allows experimental conditions to be attained that permit one to work with solutions characterized by values of the factor $A < 1.54 \cdot 10^{-6}$. It is theoretically possible, however, that serious experimental obstacles will arise.

It is necessary to use an instrument having a stability of the oscillators better than 10^{-6} and, if the response is expressed by the absolute value of the frequency change, a basic frequency higher than 10^7 Hz (it is not possible to measure a frequency change less than 1 Hz). The increase of detection sensitivity is directly proportional to the increase in the stability of the oscillators. The stability being 10^{-7} when $\Delta\varepsilon = \varepsilon_S - \varepsilon_1 = 0.394$, it would be possible to detect 4–5 p.p.m. of benzene in hexane, *i.e.*, at the same numerical differences of the refractive indices and dielectric constants to attain sensitivities comparable with the sensitivity of the refractometer.

When a mobile phase of low dielectric constant is used, it will probably be much more difficult to attain a temperature stability of the order 10^{-4} °, which, in this case, is necessary to detect changes of the dielectric constant of the order of 10^{-7} units. Besides the extremely precise design of the thermostatting system, certain possibilities are offered by the use of a reference column. On increasing ε_1, the magnitude of the minimum detectable change of the dielectric constant also increases and, therefore, the requirements for thermal stability are diminished. In these cases, oscillators with a more stable frequency could be used, even at a temperature stability of the order 10^{-3} °.

CONCLUSIONS

Properties and potential of the liquid chromatography detector, the opera-

tion of which is based on the measurement of time changes of the dielectric constant of the eluate leaving the column, were investigated. Changes of this quantity are converted into frequency changes of the oscillation circuit which are then processed electrically. The capacitance detector is a binary, unspecific type and its differential response is proportional to the actual mean concentration of the substance in the detecting cell.

The magnitude of the response, expressed as the change of frequency of the oscillation circuit, is a function of the basic oscillator frequency, f_1, the dielectric constant of the mobile phase, ε_1, the dielectric constant of the sample, ε_S, its volume fraction in the eluate, V_S, and the magnitudes of the invariant capacitance of the detecting capacitor (see eqns. 4 and 5).

After determining the basic assumptions for the operation of the detector, the relation between the response and the sampled volumes of *n*-octane ($\varepsilon = 1.948$), benzene ($\varepsilon = 2.248$), diethyl ether ($\varepsilon = 4.335$), pyridine ($\varepsilon = 12.30$) and acetone ($\varepsilon = 20.7$) was measured. The flow-rate dependence of the detector response was investigated for flow rates in the range 0.092–1.03 ml/min. For analytical use, the detector was operated at flow rates up to 4.6 ml/min[21]. The applicability of the detector was investigated by measuring the response of 39 organic compounds of various types. In all cases, *n*-hexane (p.a.) was used as the mobile phase. The results obtained and the properties of the detector were compared with the properties and parameters of the refractometric detector.

The detector, in the design used, is suitable for the detection of all substances which are sufficiently soluble in the mobile phase, provided the solution obtained is electrically non-conducting and shows low dielectric losses. The magnitude of the response can be determined, at least semi-quantitatively, from the tabulated dielectric constants of the components in question. A very low response, about 24–30% of theory, is given by hexane solutions of alcohols, regardless of the structure of the carbon skeleton carrying the hydroxyl group.

The minimum detectable concentrations found experimentally, change according to the dielectric constant of the sample, from $2.6 \cdot 10^{-2}$ % for *n*-octane ($\varepsilon = 1.948$) to $4.2 \cdot 10^{-5}$ % for acetone ($\varepsilon = 20.7$). They are in good agreement with the values derived theoretically from the stability of the oscillators, $0.77 \cdot 10^{-6}$ (noise = 14 Hz at a basic frequency of 1.8×10^7 Hz). At this stability of the oscillators, the range of linear response (defined by the ratio of the maximum and minimum detectable concentrations of the substance measured) is equal to $1.38 \cdot 10^4$, regardless of the system investigated, the magnitude of the invariable capacitances of the detecting capacitor and the basic frequency f_1. In order to reach these sensitivities, a temperature stability of the order of 10^{-3} ° is necessary.

In general, it is possible to conclude that the detector has the following advantages. It is versatile and can be used with all solutions having low dielectric losses. It has a sufficiently high sensitivity, in optimal cases even higher than the refractometer, and a wide range of linear response. The construction of the detecting cell is very simple and sufficiently small volumes can be easily obtained. The response of the detector is only slightly dependent on the flow rate. As it gives a sufficiently high response even to substances which are very similar to the mobile phase, it enables easy and accurate measurements of the dead volume of the column to be made.

The main disadvantage is that the detector imposes considerable requirements

on temperature stability. The magnitude of the response for the given difference of the dielectric constants of the mobile phase and the sample decreases with increasing dielectric constant of the mobile phase. The detector is therefore not very convenient for use in gradient elution.

In general, the capacitance detector is a further suitable type of detector for use in liquid chromatography.

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