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SIMPLE THEORETICAL DESCRIPTION AND PRACTICAL EVALUATION OF A PERMITTIVITY DETECTOR FOR FLOWING STREAM MONITORING

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SUMMARY

A simple theoretical model has been developed to describe the behaviour of a permittivity detector operating between 8 and 10 MHz and tested experimentally. The application of the detector to the monitoring of permittivity changes in media of high dielectric constant for the detection of phosphorus esters and sugar has been assessed and found to be useful, giving good linear response ranges and reasonable sensitivity.

INTRODUCTION

The measurement of changes in dielectric constant as a means of detecting alterations in the concentration of solutes in a solvent is well known. Haderka[1] outlined the possibilities of this approach if applied to liquid chromatography and particularly to high-performance liquid chromatography (HPLC) and went on[2,3] to predict behaviour and response of these detectors in practical situations. Krejčí and Pospíšilová[4] made a comparison of these devices with other detectors used for HPLC, ultraviolet (UV) absorption and a differential refractometer. Although not as good as the UV detector they conclude that the dielectric constant detector is usable both theoretically and practically. Poppe and Kuysten[5] describe a thermostated permittivity (dielectric constant) detector for HPLC using an impedance bridge measuring system and a high-precision thermostat. They claim detection limits corresponding to a permittivity change of *ca.* $5 \cdot 10^{-7}$.

The means of monitoring the dielectric constant variations employed has been mainly the impedance bridge[3,5], but others[4,6,7] have used detectors using the resonance principle[1].

The measurement of changes in dielectric constant through the influence of the capacitance change on the frequency of oscillation of a resonant circuit is well known[8] and the recent availability of low-cost rapid-response automatic frequency meters with analogue output has made detection in this way an attractive proposition.

The requirements of a detector for HPLC in particular but for any other flow-stream detector also, are sensitivity, long and short term stability, linearity of response, ease of operation, low cost, small size and versatility. Selectivity is not always a requisite in chromatography where the column makes that contribution. Permittivity measurements can fulfil most of these criteria and one of the simplest ways of achieving a useful detector is through frequency measurement.

This work describes a study of the performance of a permittivity detector operating at 10 MHz.

EXPERIMENTAL

The power supply used was an in-house built unit with better than 0.5 % voltage regulation. The circuit of the heterodyne frequency measuring device is given in Fig. 1 and was designed by B. Skilton in this department. The range of the device was ±10 kHz or ±100 kHz and the linearity of d.c. voltage out with frequency change over the range ±100 kHz was better than 0.2% with a minimum detectable change of *ca.* 25 Hz. The lock-in range of the detector about the zero beat frequency was ±3 kHz which limited the linear range on both the ranges. This pulling of the variable oscillator to the crystal oscillator is a design artifact which can be eliminated. For frequency measurement using a direct reading meter an AMF-Venner 7737A device was used with a digital–analogue converter (in-house built) giving d.c. output of the last three significant digits to 0.1 %.

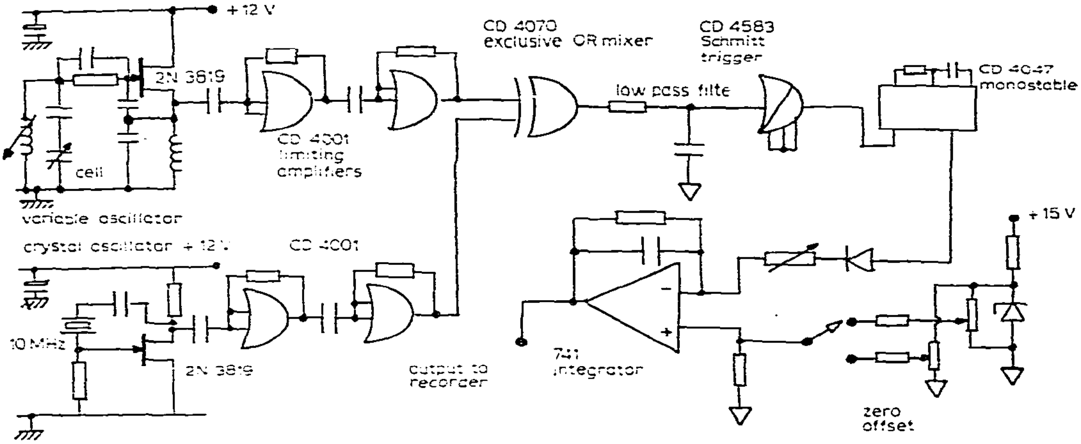

Fig. 1. Circuit diagram of heterodyne measuring system (schematic).

The pump used was a Masterflex (Cole-Palmer Inc.) with continuously variable pumping speed, or a Technicon AutoAnalyzer pump. Solvents used were of the highest purity obtainable and were degassed by vacuum heating or ultrasonic vibration prior to use to avoid degassing in the pump and cell. Even so it was found advantageous to operate the cell under a low pressure (about 50 cm water) to avoid bubble formation and the consequent "bubble noise".

THEORETICAL

Much of the work described here was carried out using a parallel plate capacitor (Fig. 2) although the theory applies just as well to the cylindrical capacitor also employed (Fig. 3) which was based on Vespalec's design[6,7].

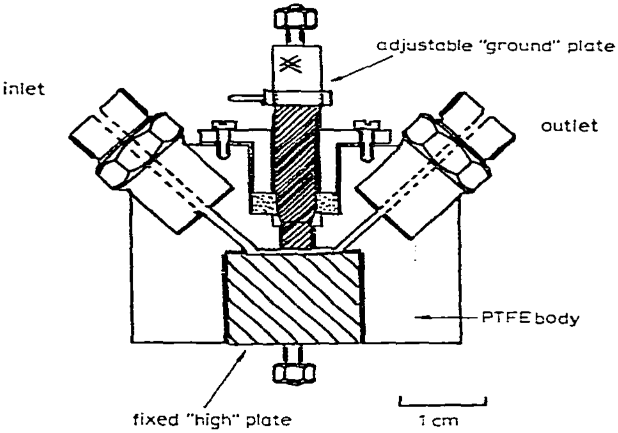

Fig. 2. The parallel plate capacitor.

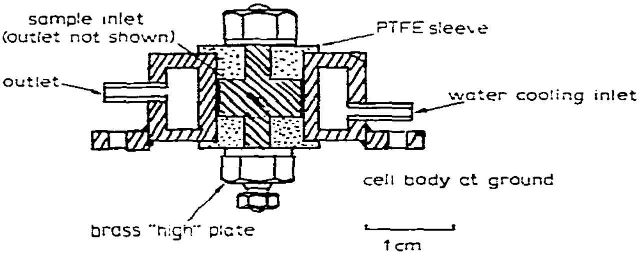

Fig. 3. The cylindrical capacitor.

The nature of permittivity and loss are well described in the literature[8]. The simplest treatment which can be considered results in Debye's equation which refers to low polarity solvents

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \times \frac{M}{\varrho} = 4\pi N(\alpha + \mu^2/3kT)/3\varepsilon \tag{1}$$

where ε_0 = the low frequency (static) dielectric constant, M = molecular weight, N = Avogadro's number, α = distortion polarisability, μ = electric dipole moment, ε = permittivity of free space, T = temperature, and k = Boltzmann constant.

The quantity

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \times \frac{M}{\varrho} \tag{2}$$

is called the "molar polarisation" (P) and in dilute solution

$$P_T = \Sigma P_i x_i \tag{3}$$

where x is the mole fraction of substance having molar polarisation P.

Abbreviating

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \text{ to } \varepsilon^* \tag{4}$$

and substituting eqns. 2 and 4 in 3 taking into account that $\varrho = MN/V$ one obtains

$$\varepsilon_T^* = \Sigma \varepsilon_i^* V_i \tag{5}$$

where V_i is the volume fraction of the ith component in the solution.

For a two-component system, as may be found in liquid chromatography, for example, eqn. 5 becomes

$$\varepsilon_T^* = \varepsilon_x^* V_x + \varepsilon_c^*(1 - V_x) \tag{6}$$

where the subscripts T, x and c refer to total, solute and solvent respectively. Eqn. 6 rearranges to

$$\varepsilon_T^* = \varepsilon_c^* + V_x(\varepsilon_x^* - \varepsilon_c^*) \tag{7}$$

which if expanded with eqn. 4 and assuming dilute solutions where $\varepsilon_T^* \approx \varepsilon_c^*$ gives

$$\varepsilon_{0T} = \varepsilon_{0c} + 3V_x \cdot \frac{(\varepsilon_{0x} - \varepsilon_{0c})}{\varepsilon_{0x} + 2} \tag{8}$$

These equations are similar to those given by Haderka[2] but differ because he assumes $\varepsilon_{0c} \approx \varepsilon_{0x} \approx \varepsilon_{0T}$ which is not valid in the experiments described here where ε_{0x} is often much greater than ε_{0c}.

Analysis of the oscillator circuit

Most of the commonly met oscillator circuits were designed for high frequency stability and lend themselves well to this sort of work. The circuit employed in this study was a Colpitts type modified for use with a field effect transistor. It is possible that other circuits will perform as well or better, for example the Franklin oscillator[9] but these have yet to be essayed. It is important that the cell capacitance should play a dominant role in the frequency determination of the circuit to yield maximum sensitivity, although some trade off must be made to assure low drift, noise and loss characteristics. Good power supply stability is essential and the effects of pulling due to load impedance changes or the presence of local oscillatory circuits, as in the heterodyne measuring device minimised.

The circuit of the oscillator used is shown in Fig. 1. The resonant part of the circuit can be simplified to Fig. 4 and the theoretical relationship between a change in the oscillation frequency caused by a change in the dielectric constant of the medium in the detector cell calculated.

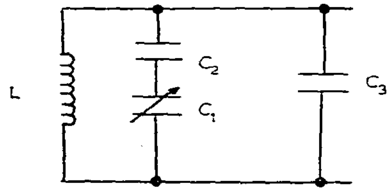

Fig. 4. Equivalent circuit of the oscillator.

The resonant frequency of this circuit is given by

$$f^{-2} = 4\pi^2 L C_T \tag{9}$$

where f is the frequency (Hz), L the inductance (H) and C_T the total capacitance (F) in parallel with L. From Fig. 4

$$C_T = C_3 + C_1 C_2/(C_1 + C_2) \tag{10}$$

and substituting eqn. 9 in 10 gives

$$f^{-2} = A + B\left(\frac{C_1}{C_1 + C_2}\right) \tag{11}$$

where $A = 4\pi^2 L C_3$ and $B = 4\pi^2 L C_2$.

Now where there is only the solvent in the detector cell (C_1) the capacitance will be C_c, with solute and carrier in let it be C_x. For small V_x, $f_x \sim f_c$ so

$$f_c^{-2} - f_x^{-2} \simeq \frac{2\Delta f}{f_c^3} \tag{12}$$

where Δf is the change in frequency due to V_x; $\Delta f = f_x - f_c$. Making the subtraction described in eqn. 12 gives:

$$\frac{2\Delta f}{f_c^3} = \frac{B C_2 (C_c - C_x)}{(C_c + C_2)(C_x + C_2)} \tag{13}$$

Now, the capacitance of the detector cell is, assuming it to be a parallel plate capacitor,

$$C = \frac{A\varepsilon \cdot \varepsilon_0}{d} \tag{14}$$

where A is the plate area and d its spacing. Now

$$\varepsilon_T = \varepsilon_{0c} + \frac{3\Delta\varepsilon}{\varepsilon_{0x} + 2} \cdot V_x \tag{8}$$

where ε_T is the permittivity of the solute and solvent mixture. So substituting eqn. 8 in 14 gives

$$C_x = \frac{A\varepsilon}{d}\left(\varepsilon_{0c} + \frac{3\Delta\varepsilon}{\varepsilon_{0x} + 2} \cdot V_x\right) \tag{15}$$

$$C_x = C_c + kDV_x \tag{16}$$

where $k = A\varepsilon/d$ and $D = 3\Delta\varepsilon/\varepsilon_{0x} + 2$ (note $A\varepsilon \cdot \varepsilon_{0c}/d = C_c$). Substituting eqn. 16 in 13 gives

$$\frac{-2\Delta f}{f_c^3} = \frac{B C_2 k D V_x}{(C_c + C_2 + kDV_x)(C_c + C_2)} \tag{17}$$

$$= \frac{B C_2 k D V_x}{(C_c + C_2)^2} \cdot \left(1 + \frac{kDV_x}{C_c + C_2}\right)^{-1} \tag{18}$$

As $kDV_x \ll C_c + C_2$, neglecting terms in V_x^2 and above we have

$$\frac{-2\Delta f}{f_c^3} = \frac{BC_2kDV_x}{(C_c + C_2)^2} \cdot \left(1 - \frac{kDV_x}{C_c + C_2}\right) \tag{19}$$

Re-substituting for B, k and D one obtains

$$-\Delta f = f_c - f_x = \frac{3}{2} f_c \cdot \frac{C_2^2 C_c}{C_T(C_c + C_2)^2} \cdot \frac{\Delta\varepsilon}{\varepsilon_{0c}(\varepsilon_{0x} + 2)} \cdot V_x \tag{20}$$

This formula has a circuit constant in it so it is apparent that there must be values of capacitance which give optimum sensitivity. Differentiation of eqn. 20 with respect to C_3 shows that $d\Delta f/dC_3$ is negative for all positive values of C_3. The value of C_3 is related to the feedback requirements of the oscillator and cannot be changed *ad lib.* This value should therefore be minimised, due regard being paid to circuit stability. The effect of C_2, the capacitance in series with the cell is rather complex. $d\Delta f/dC_2$ is positive for all positive values of C_2 being zero at $C_2 = 0$ and tending to zero for large values. (It must be remembered that f_c contains a C_2 term when evaluating the differential.) Numerical substitution of component values into the circuit capacitance term reveals that the ratio (R) when $C_2 = 5$ to $C_2 = 1$ pF of the capacitance term is $R(C = 1/C = 5) = 85$; $R(C = 10/C = 5) = 1.8$; $R(C = 30/C = 10) = 1.6$ and $R(C = 60/C = 30) = 1.1$. It can be seen therefore that a value of $C_2 \approx 30$ pF for a cell capacitance of *ca.* 7 pF is about optimum, there being neither advantage nor disadvantage of going to a higher series capacitance from the viewpoint of sensitivity.

Effect of plate spacing in the detector cell

There is a theoretical dependence of the slope of Δf *vs.* V_x with the plate spacing (d). Substituting in eqn. 20 for C_c the formula for a parallel plate capacitor eqn. 14 and performing the differentiation $d\Delta f/dd$ one can show that the curve continuously decreases towards a minimum at very low values of C_c (high values of d) and goes to a large, finite value when $d \rightarrow 0$. This is indeed observed for ethanol, ethyl acetate and nitrobenzene in cyclohexane *vs.* cyclohexane (Fig. 5). For solvents having high permittivities, however, a maximum is observed. Water in ethanol *vs.* ethanol and propan-1-ol in ethanol *vs.* ethanol both exhibit reproducible and well defined maxima at the sort of plate spacing normally employed (Fig. 5); the reason for this is not clear. The presence of a maximum for the polar mixtures and the different form of the curves means that if one operates the cell at the maximum for such mixtures there is much less of an effect of plate separation and consequently rather more thermal–mechanical stability. This propably accounts for the experimental observation of less drift when working with 60% methanol–40% water mixtures in the cell compared with cyclohexane solutions (*sic*).

It is a fact that the capacitance of the parallel plate capacitor used in this study does not vary as d^{-1} but as $d^{-0.31}$ (as measured with a 0.1% capacitance bridge with n-hexane in the cell). This is probably due to the construction design: unequal plates and the large PTFE mass. Although this influences the decay rate of the theoretical Δf *vs.* d curve it serves to lessen the gradient and does not alter the overall shape of the curve for positive values of d, compared to the theoretical dependency of a perfect parallel plate capacitor.

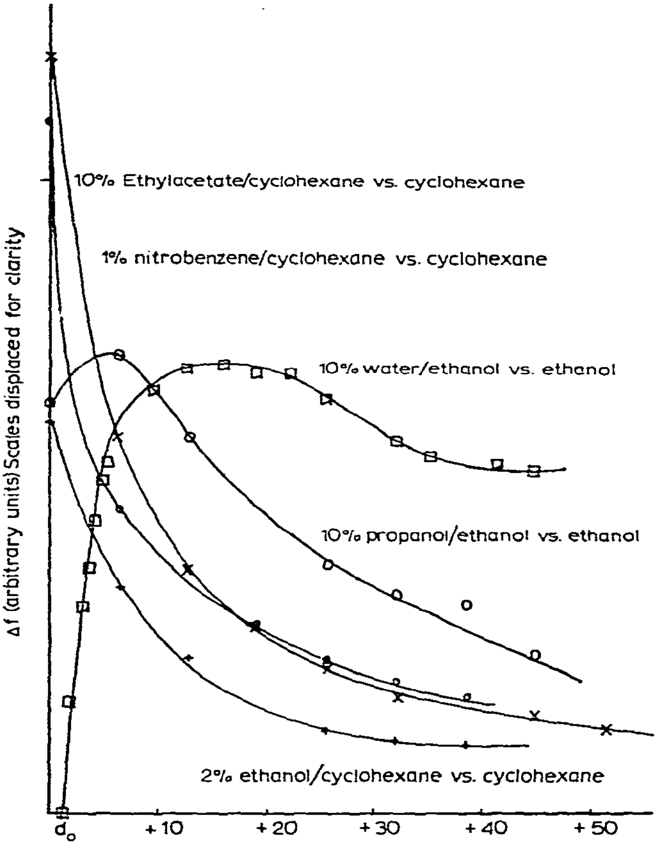

Fig. 5. Incremental plate spacing ($\times$ 10^{-6} m). d_0 = position of minimum spacing to permit oscillation after touching.

It can be seen, therefore, that for maximum response with low permittivity media, minimum plate spacing is desirable but, as this will impart more thermal–mechanical instability, a trade-off between sensitivity and stability will be required.

Effect of temperature on the frequency of the oscillator

Apart from altering the dielectric constant of the medium in the cell, temperature variations may alter the dimensions of the cell and the circuit component values. The latter part is not likely to be a major source of interference as the electronic circuitry is self-thermostatting to a large extent and short term variations in liquid or cell temperatures will not cause any temperature variation in it. Long term drift is however another matter and correct oscillator design is important. The cell dimensions will, however, be influenced by temperature due to contraction or dilation of the plate spacing in particular.

As a function of temperature therefore one can write the frequency response of the circuit as

$$\frac{df}{dT} = \frac{df}{d\varepsilon} \cdot \frac{d\varepsilon}{dT} + \frac{df}{dA} \cdot \frac{dA}{dT} \qquad (21)$$

where A is a cell dimension factor. The former part can be evaluated over small temperature ranges[8]

$$\varepsilon_T = \varepsilon_{T_0} - a\,(T - T_0) \tag{22}$$

where ε_0 is the permittivity at a temperature T_0. So

$$\frac{d\varepsilon}{dT} = -\,a \tag{23}$$

$$f = \frac{1}{2\pi\,\sqrt{LC_T}} = KC_T^{-1/2}$$

where $K = 1/2\pi\,\sqrt{L}$.

Substituting for C_T (eqn. 10) and evaluating $df/d\varepsilon$ one obtains

$$\frac{df}{d\varepsilon} = -\,\frac{1}{2}KBC_2^2\,(B\varepsilon + C_2)^{-1/2}\cdot[B\varepsilon(C_3 + C_2) + C_3C_2]^{-3/2} \tag{24}$$

where B is a cell parameter $C_{cell} = B\varepsilon$, ε being the permittivity of the medium in the cell. Multiplying eqn. 23 by 24 gives $df/dT\ [\varepsilon(T)]$ and it can be seen to be increasing positively towards an assymptote T', where T' is large ($\approx 10^3 C$). This is an imaginary value but serves to show that over a small temperature range (± 10°C) near to $T = T_0$, the gradient can be considered invariant.

The parameter B can be measured experimentally with air in the capacitor, in the case of the cylindrical fixed-plate cell this was found to be 19.9 pF; a is available from the literature for certain liquids[10] and the other circuit parameters are known.

Calculation of df/dT for cyclohexane at 20°C ($a = 16 \cdot 10^{-4}$; $\varepsilon = 2.02$)[10] using this equation yields a value of $df/dT = 1.1 + df/dA \cdot dA/dT$ kHz deg.$^{-1}$. Similar calculations for toluene ($a = 24.3 \cdot 10^{-4}$; $\varepsilon = 2.38$ at 25°C)[10] and carbon tetrachloride ($a = 20 \cdot 10^{-4}$; $\varepsilon = 2.24$ at 20°C)[10] give coefficients of 1.2 and 1.0 kHz deg.$^{-1}$ respectively. Measurements of df/dT for these three solvents over the range 17–25°C reveal coefficients of 0.3 ± 0.05 kHz deg.$^{-1}$ for all three solvents. It would seem therefore that, assuming the calculations to be valid. $df/dA \cdot dA/dt$ is about constant for the cell with each of the solvents in and, in fact, serves to increase the capacitance of the cell with increasing temperature. Observation of the formula for the capacitance of such a cylindrical capacitor supports this view

$$C = 2\pi\varepsilon_0\varepsilon h/\ln(b/a) \tag{25}$$

where a and b are the internal and external surface radii and h the cylinder height, one would expect a positive capacitance–temperature coefficient with such a design.

The effect of temperature on the dimensions of the parallel plate capacitor is much more difficult to estimate. The biggest proportional effect would be due to plate spacing change and this would be affected by both the expansion of the PTFE block and the plates themselves. One might also expect the proportional change to be inversely proportional to place spacing.

Measurements of temperature effect have not been made specifically with the parallel plate cell but in continuous laboratory use it has been found to respond to slow, gross changes in ambient temperature by drifting, although the effect is by no means large and does not seriously interfere with chromatographic detection measurements.

Effect of temperature on dilute solutions of low permittivity

Rearranging eqn. 1 and assuming the distortion polarisation (α) and the dipole moment (μ) to be temperature invariant over small temperature changes (ΔT) one obtains

$$\varepsilon^* = \left(A + \frac{B}{T}\right) \varrho \tag{26}$$

where $A = 4\pi N\alpha/3M\varepsilon$ and $B = 4\pi N\mu^2/9kM\varepsilon$. Now $\varrho(T)$ can be written

$$\varrho = \varrho_0(1 - \gamma\Delta T) \tag{27}$$

where ϱ_0 is the liquid density at $T = T_0$ and γ the temperature coefficient of density over the range ΔT from T_0. If one assumes $\Delta T \approx \pm 5°\mathrm{K}$ about an ambient 275°K, ΔT is only $2\%\ T$, so one can say to that approximation:

$$T_0 \pm \Delta T \sim T_0 \tag{28}$$

So substitution of eqns. 28 and 27 in 26 gives

$$\Delta\varepsilon^* = -\varepsilon^*\gamma\,\Delta T \tag{29}$$

where, in this case, ε^* is defined at T_0.

Substituting eqn. 29 in 7 one obtains, for a dilute solution of a low polarity liquid

$$\Delta\varepsilon_s^*[f(T)] = -\,\Delta T[\gamma_c\varepsilon_c^* + V_x(\varepsilon_x^*\gamma_x - \varepsilon_c^*\gamma_c)] \tag{30}$$

where s, x and c refer to solution, solute and solvent respectively. It is apparent that for small V_x eqn. 30 tends to eqn. 29 so one would expect similar temperature effects for dilute solutions as for the solvent, which makes any temperature compensation requirement much easier.

Frequency *vs.* temperature measurements on solutions of nitrobenzene in cyclohexane were made using the water-jacketed cylindrical capacitor. The liquid being pumped through the cell is first thermostatted in the same bath as the cell jacketing water to assure that cell and liquid are at the same temperature. The temperature is measured at the cell exit with a thermocouple previously calibrated against a 0.01° Beckman thermometer. The results are listed in Table I and agree well with the theoretical predictions and are in agreement with the findings of Slavík[11].

The results for ethanol and methanol also show that there is no significant temperature effect on the sensitivity for small values of V_x.

In obtaining these data slow heating rate (less than 7°C h^{-1}) was essential as more rapid rates (20°C h^{-1}) produced steeper gradients tending towards 1–1.5 kHz

TABLE I

OSCILLATOR FREQUENCY *vs.* SOLUTION/CELL TEMPERATURE FOR NITROBENZENE IN CYCLOHEXANE OVER THE RANGE 17–25°C AND FOR ETHANOL OVER THE RANGE 20–25°C

The response curves are straight lines over this range.

V_x	*Temperature response* $(kHz\ deg.^{-1})$
Nitrobenzene	
0	0.30 ± 0.05
$1 \cdot 10^{-4}$	0.30 ± 0.05
$2 \cdot 10^{-3}$	0.35 ± 0.05
$1 \cdot 10^{-2}$	0.7 ± 0.05
$2 \cdot 10^{-2}$	0.8 ± 0.05
Ethanol	
$1 \cdot 10^{-2}$	0.4 ± 0.05
$2 \cdot 10^{-2}$	0.7 ± 0.1

deg.$^{-1}$. The reason for this is as yet uncertain but may be due to the cell not being able to attain equilibrium sufficiently quickly and thus the compensating effect of the cell dimensional changes being lost.

RESULTS

Verification of the theoretical response of the detector

Using the water jacketed cylindrical capacitor of empty capacitance 19.9 pF (Fig. 3), calibration curves of Δf *vs.* V_x were obtained for a range of solutes in cyclohexane at an ambient temperature of *ca.* 22°C. It can be seen in Table II that the calculated and observed slopes are of the same order of magnitude and that the trend is the same, although there is a significant difference between the calculated and observed response of nitrobenzene and acetylacetone.

TABLE II

RESPONSE OF VARIOUS SOLUTES IN CYCLOHEXANE

All the calibration curves were obtained with a frequency around 8.22 MHz.

Compound	Δf *vs.* V_x			*Minimum detectable volume ratio*	*Dielectric constant of pure solute*
	Theoretical slope (Hz)	*Observed slope (Hz)*	*Linear range*		
Hexane	$1.5 \cdot 10^4$	$7.6 \cdot 10^4$		$3 \cdot 10^{-3}$	1.9
Ethyl acetate	$0.9 \cdot 10^6$	$1.1 \cdot 10^6$	0.15	$9 \cdot 10^{-6}$	6.02
Ethanol	$1.5 \cdot 10^6$	$1.3 \cdot 10^6$	0.05	$8 \cdot 10^{-6}$	25.0
Propan-1-ol	$1.5 \cdot 10^6$	$1.0 \cdot 10^6$	0.05	$4 \cdot 10^{-5}$	22.2
Nitrobenzene	$1.8 \cdot 10^6$	$6.0 \cdot 10^6$	0.03	$3 \cdot 10^{-6}$	35.5
Acetylacetone	$1.6 \cdot 10^6$	$3.7 \cdot 10^6$	0.04	$5 \cdot 10^{-6}$	25.7

Studies in polar media

The description of behaviour of the detector given above is derived from the Debye equation which is not truly applicable to polar media. Modifications of the theory to account for polarity results in rather complex relationships and it is not apparent what the response of the detector will be in practice[8]. Since, however, the majority of HPLC applications require polar eluents and, indeed, are for the separation of polar compounds, it is important to assess the detector's utility with these media.

A useful system to study is methanol–water and as solutes the phosphorus esters as these compounds are polar but have no significant visible or UV chromophore so are not amenable to detection by absorptiometric detectors using the mercury 253.7 nm line.

Triethyl phosphate solutions were made up in a 60% methanol–40% water (6040 MW) mixture and pumped through the cell at 1.8 ml min^{-1} and 25°C. The log Δf *vs.* log V_x curve was a straight line of gradient 1.1–1.2 over the range 10^{-3}–10^{-2} V_x. The linear plot had a gradient of *ca.* $2 \cdot 10^6$ Hz (assuming a straight line response) with a practically observed limit of detection of *ca:* $5 \cdot 10^{-4}$ V_x. Pumping noise due to degassing of the 6040 MW, which was a significant problem with this solvent in spite of careful degassing prior to pumping, degraded this limit of detection and some improvement could be anticipated if this were overcome.

Solutions of diethyl methylphosphonate were made up in 6040 MW and pumped through the cell at 1.0 ml min^{-1} at 25°C. The response with concentration was linear over the range $5 \cdot 10^{-4}$ to 10^{-2} V_x with a gradient of *ca.* 10^5 Hz. A practical limit of detection of $5 \cdot 10^{-4}$ V_x was obtained; the same comments as to bubble noise apply as to the previous compound.

Ethyl hydrogen methylphosphonate was also studied in the cell. It was made up in 6040 MW and pumped through the cell at 1.8 ml min^{-1} at 25°C. The response obtained was curious: the log log plot of Δf *vs.* V_x was linear over the range 2–$20 \cdot 10^{-6}$ V_x with a gradient of 1.4. An extrapolated limit of detection from the linear plot gives $\approx 10^{-6}$ V_x as the lowest detectable amount. Above $5 \cdot 10^{-5}$ V_x, however, the plot flattened off dramatically. This response behaviour is probably associated with the ester –OH group and the effect observed may be due to dissociation leading to increased conductance in the cell and subsequent lowering of the Quality factor, Q, of the tuned circuit, with the resultant frequency alteration and instability. Solutions of 10^{-3} M HCl at the 10^{-1}–10^{-5} V_x level in 6040 MW were pumped through the cell but gave erratic results which cannot confirm or deny the previous hypothesis. The effect is, however, being studied presently.

Another group of compounds not amenable to UV absorptiometric detection using the 253.7 nm mercury line is the sugars. A solvent typically employed for the HPLC of these species is ethyl acetate–propan-2-ol–water (50:35:25)[12] which has a calculated dielectric constant of *ca.* 15 at 22°C. In order to assess the performance of the detector for sugars, solutions of sucrose in this solvent were made up and pumped through the cell at *ca.* 1 ml min^{-1} and 24°C. The change in frequency compared to the solvent was measured as a function of sucrose concentration. Δf *vs.* concentration of sucrose revealed a straight line response between $1 \cdot 10^{-4}$ and $3 \cdot 10^{-3}$ g ml^{-1} sucrose and a slope of $1.5 \cdot 10^7$ Hz g^{-1} ml. The estimated limit of detection from the curve obtained was *ca.* 5 μg ml^{-1}. Further experiments varying the proportion of water in the solvent between 10 and 28% showed a reduction in sensitivity by a factor of two over that range, *ca.* 35% water resulting in an emulsion being formed.

CONCLUSION

The permittivity detector provides a simple means for the monitoring of changes in dielectric constant in flowing streams. The small cell size and high sensitivity make it suitable as a detector for HPLC work using solvent media of both high and low polarity. The effect of temperature on the frequency of the oscillator is both small and predictable and, for dilute solutions, is approximately that of the solvent. This means that temperature compensation will be straightforward by monitoring the eluent temperature and correcting the output frequency by a simple feedback circuit which need only be programmed to the solvent temperature coefficient. The fact that the polar solvents exhibit a broad maximum response with plate spacing makes the parallel plate cell more attractive because of the lessened apparent temperature effect due to mechanical variation, ease of fabrication and low cell volume.

The agreement of the theoretical predictions with the observed cell and circuit behaviour is reasonable and permits calculation of optimum circuit parameters and cell design. There is no doubt that the permittivity cell has a place in the range of solute detectors for HPLC and other flowing stream monitors, particularly for polar species not having appreciable UV chromophores.

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REFERENCES

1 S. Haderka, *J. Chromatogr.*, 54 (1971) 357.
2 S. Haderka, *J. Chromatogr.*, 57 (1971) 181.
3 S. Haderka, *J. Chromatogr.*, 91 (1974) 167.
4 M. Krejči and N. Pospíšilová, *J. Chromatogr.*, 73 (1972) 105.
5 H. Poppe and J. Kuysten, *J. Chromatogr.*, 132 (1977) 369.
6 M. Krejči, R. Vespalec and M. Širec, *J. Chromatogr.*, 65 (1972) 333.
7 R. Vespalec, *J. Chromatogr.*, 108 (1975) 243.
8 N. E. Hill, W. E. Vaughan, A. H. Price and M. Davies, *Dielectric Properties and Molecular Behaviour*, Van Nostrand-Reinhold, Princeton, N.J., 1969.
9 S. Garner, *Radio Commun.*, 55 (1979) 32.
10 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, CRC Press, Cleveland, Ohio, 52nd ed., 1971.
11 V. Slavík, *J. Chromatogr.*, 148 (1978) 117.
12 J. C. Linden and C. L. Lawhead, *J. Chromatogr.*, 105 (1975) 125.