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## ROLE OF THE MOBILE PHASE PERMITTIVITY IN THE USE OF THE CAPACITANCE DETECTORS IN LIQUID CHROMATOGRAPHY

STANISLAV HADERKA

*Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)*

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## SUMMARY

The influence of the mobile phase permittivity on the sensitivity and linearity of detection by the capacitance detectors has been investigated theoretically. Relations have been derived between the response and the concentration for the interference and bridge methods. A higher mobile phase permittivity in comparison to that of the substance detected results in greater linearity and a lower sensitivity.

## INTRODUCTION

The progress of modern liquid chromatography has been limited, to a great extent, by the parameters of the existing detectors. The detectors employed up to the present time have been critically evaluated recently<sup>1</sup>. There is no doubt that some new principles of detection will be studied. A detection method whereby a change in the real part of the complex permittivity

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (1)$$

is measured seems to be promising.

The aim of the present paper is to derive the dependence of the linearity and sensitivity of detection on the permittivity of the mobile phase.

The mobile phase acts as the dielectric of the measuring condenser of the capacitance detector, and the measuring circuit is arranged in such a way that the electrical signal is backed off to zero when pure mobile phase with a permittivity  $\varepsilon'_0$  flows through it. If a component of the mixture analysed, having a different real part  $\varepsilon'_x$ , occurs in the mobile phase, the reactance of the condenser,  $X = 1/\omega C$ , will be changed by  $\Delta X$  which results in a signal at the detector output.

A linear additivity relation for calculating the resultant permittivity,  $\varepsilon'_r$ , holds approximately,

$$\varepsilon'_r = c_x \varepsilon'_x + c_0 \varepsilon'_0 \quad (2)$$

where  $c_x$  and  $c_0$  are the volume fractions of the component under detection, with a permittivity  $\varepsilon'_x$ , and of the mobile phase of permittivity  $\varepsilon'_0$ , respectively.

## THE MEASURING CONDENSER

The measuring condenser has an invariable capacity  $C_k$ , given by the solid dielectric which keeps the electrodes in their respective positions, as well as by the stray capacity, and a variable capacity that is dependent on the permittivity of the liquid dielectric (*cf.* Fig. 1). Hence, the total capacity of the measuring condenser may be characterised by the equation

$$C = C_{\epsilon'} + C_k \quad (3)$$

It is obviously desirable that the capacity  $C_k$  be small in comparison to  $C_{\epsilon'}$ . A high capacity  $C_k$  decreases the sensitivity of the detection, but improves, to some extent, the linearity.

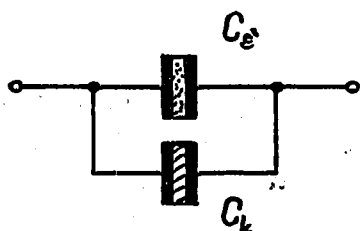


Fig. 1. An equivalent circuit for the measuring condenser of the capacitance detector.

THE RELATIONSHIP BETWEEN  $\epsilon'_x$  AND  $\epsilon'_0$ 

If the component under detection is to bring about a change in the resultant permittivity, it is necessary that the permittivity of the former,  $\epsilon'_x$ , be different from the carrier permittivity  $\epsilon'_0$ ; the greater the difference the larger the change at a given volume concentration. There are, in principle, two possible cases:

1. The mobile phase permittivity,  $\epsilon'_0$ , is much higher than that of the component detected,  $\epsilon'_x$ .
2. The permittivity of the component under detection is much higher as compared with that of the mobile phase.

Let us analyse the above cases with respect to the two groups of methods of measurement:

- A. Interference methods;
- B. Bridge methods.

*Interference methods*

The principle of the above methods is illustrated by the scheme shown in Fig. 2. A fixed frequency  $f_1$  from an oscillator driven by a piezoelectric resonator is mixed in a mixer, M, with the frequency produced by the oscillator with the detecting condenser, whose capacity is given by eqn. 3. The high frequency components of the spectrum are rejected by a low-pass filter, F, so that the frequency component

$$|f_1 - f_2| = f_t \quad (4)$$

enters the frequency meter FM. Its output voltage is proportional to the frequency.

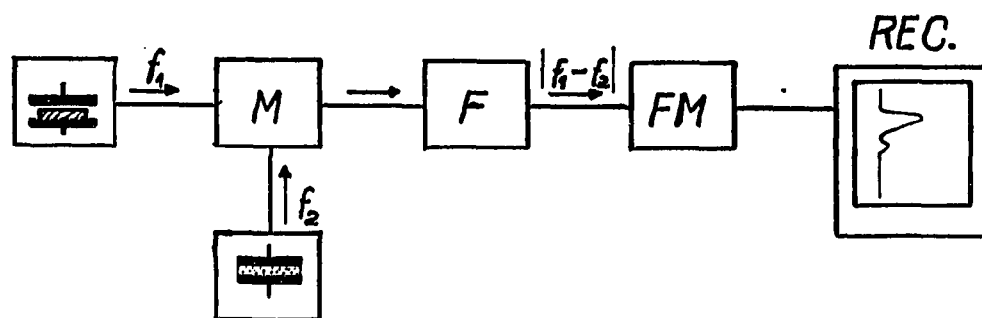


Fig. 2. Diagram of the measuring circuit used in the interference methods.

The relation between the frequencies  $f_1$  and  $f_2$  is chosen in such a way that the interference frequency equals zero when a pure mobile phase passes through the measuring condenser. Hence,

$$f_1 = f_{2(0)} = \frac{I}{2\pi\sqrt{L}\sqrt{C_{\epsilon'_0} + C_k}} = k_1 \frac{I}{\sqrt{C_{\epsilon'_0} + C_k}} \quad (5)$$

When the component detected occurs in the mobile phase, the permittivity of  $\epsilon'_r$  will change, in compliance with eqn. 2, and the frequency  $f_2$  will be:

$$f_{2(r)} = \frac{I}{2\pi\sqrt{L}\sqrt{C_{\epsilon'_r} + C_k}} = k_1 \frac{I}{\sqrt{C_{\epsilon'_r} + C_k}} \quad (6)$$

and the frequency meter FM will receive a frequency

$$f_i = |f_{2(0)} - f_{2(r)}| = k_1 \left| \left( \frac{I}{\sqrt{C_{\epsilon'_0} + C_k}} - \frac{I}{\sqrt{C_{\epsilon'_r} + C_k}} \right) \right| \quad (7)$$

In order to illustrate the role of the relation between  $\epsilon'_0$  and  $\epsilon'_x$ , the data for plotting the graphs in Figs. 3 and 4 have been calculated from eqn. 7. If the measuring condenser has a capacity  $C_{\epsilon'} = 4$  pF with air and the invariable capacity is  $C_k = 1$  pF, while the inductance  $L$  is chosen so that the frequency of the oscillator  $f_2$  was 100 MHz in case of an empty condenser, it is possible to write:

$$f_2 = \frac{I}{2\pi\sqrt{L}\sqrt{(4 + 1) \cdot 10^{-12}}} = k_1 \cdot \frac{10^6}{\sqrt{5}} \quad (8)$$

*i.e.*,  $k_1 = 223.607$ .

The plot in Fig. 3 illustrates the dependence of the interference frequency  $f_i$  on the volume fractions of the component within the range 0-0.10, for mobile phase and detected component permittivities of  $\epsilon'_0 = 10$  and  $\epsilon'_x = 2$ , respectively.

The basic frequency with the mobile phase is:

$$f_1 = f_{2(0)} = k_1 \frac{I}{\sqrt{C_{\epsilon'_0} + C_k}} = 34.921 \ 509 \text{ MHz} \quad (9)$$

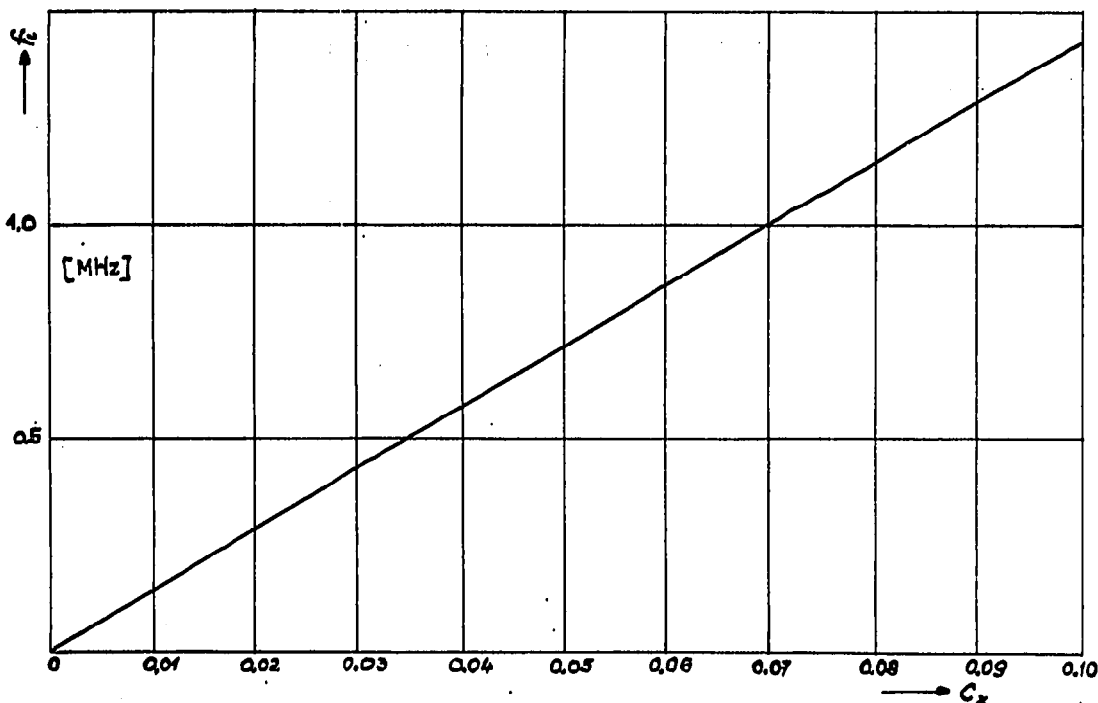


Fig. 3. Dependence of the interference frequency  $f_i$  on the concentration with  $\epsilon'_0 = 10$  for the mobile phase and with  $\epsilon'_x = 2$  for the detected component.

The plot in Fig. 4 represents the dependence of the interference frequency  $f_i$  on the volume fraction within the range 0–0.10 for a mobile phase permittivity  $\epsilon'_0 = 2$  and the permittivity of the substance detected  $\epsilon'_x = 10$ .

The basic frequency with pure mobile phase is:

$$f_1 = f_{2(0)} = k_1 \frac{1}{\sqrt{C_{\epsilon'_0} + C_k}} = 74.535\ 597 \text{ MHz} \quad (10)$$

It has been assumed in calculating the data for plotting the graphs that the same measuring condenser and inductivity  $L$  are employed, in both cases, while adjusting the fixed frequency  $f_i$ .

One can see on comparing the above diagrams that if the carrier permittivity  $\epsilon'_0$  is low in comparison to the permittivity of the component being detected,  $\epsilon'_x$ , both the absolute and the relative sensitivity is higher than in the opposite case by about one order.

However, the situation is the reverse from the point of view of linearity. Higher values of the permittivity  $\epsilon'_0$  in comparison to  $\epsilon'_x$ , results in a very good linearity being attained within a volume fraction range of 0–0.10. If a carrier liquid of low permittivity is used, the linearity may be regarded as satisfactory at very low concentrations. In the example given, *i.e.*,  $\epsilon'_0 = 2$  and  $\epsilon'_x = 10$ , satisfactory linearity may be expected within volume fraction limits of 0–0.03; at a concentration of 0.10 a correction, by adding about 0.013, would be necessary.

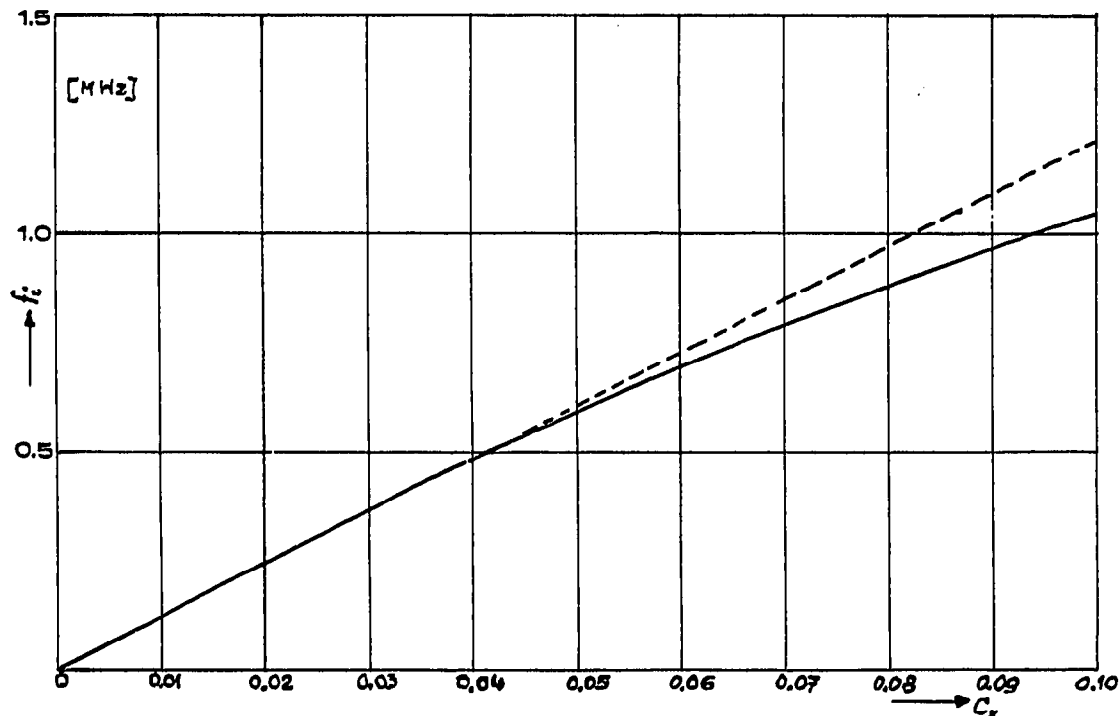


Fig. 4. Dependence of the interference frequency  $f_i$  on the concentration with  $\epsilon'_0 = 2$  for the mobile phase and with  $\epsilon'_x = 10$  for the detected component.

#### Bridge methods

If the impedance of the arm b-d in a balanced bridge as shown in Fig. 5 is changed by  $\Delta Z_4$ , the voltage occurring across the diagonal a-b is given by:

$$\Delta \vec{U} = \vec{U} \cdot \left( \frac{\vec{Z}_4 + \Delta \vec{Z}_4}{\vec{Z}_3 + \Delta \vec{Z}_4 + \vec{Z}_4} - \frac{\vec{Z}_2}{\vec{Z}_1 + \vec{Z}_2} \right) \quad (11)$$

After a simple mathematical rearrangement we obtain:

$$\Delta \vec{U} = \vec{U} \cdot \frac{\Delta \vec{Z}_4}{\vec{Z}_4} \cdot \frac{\vec{Z}_1}{\vec{Z}_2} \cdot \frac{1}{\left( \frac{\vec{Z}_3}{\vec{Z}_4} + 1 + \frac{\Delta \vec{Z}_4}{\vec{Z}_4} \right) \cdot \left( \frac{\vec{Z}_1}{\vec{Z}_2} + 1 \right)} \quad (12)$$

Let us introduce the presumption corresponding to maximum sensitivity of the bridge towards a change in the impedance of the arm  $Z_4$ :

$$\frac{\vec{Z}_1}{\vec{Z}_2} = \frac{\vec{Z}_3}{\vec{Z}_4} = 1 \quad (13)$$

Then, the voltage change  $\Delta U$  across the bridge diagonal is given by:

$$\Delta \vec{U} = \vec{U} \cdot \frac{\Delta \vec{Z}_4}{\vec{Z}_4} \cdot \frac{1}{\left( 4 + 2 \cdot \frac{\Delta \vec{Z}_4}{\vec{Z}_4} \right)} \quad (14)$$

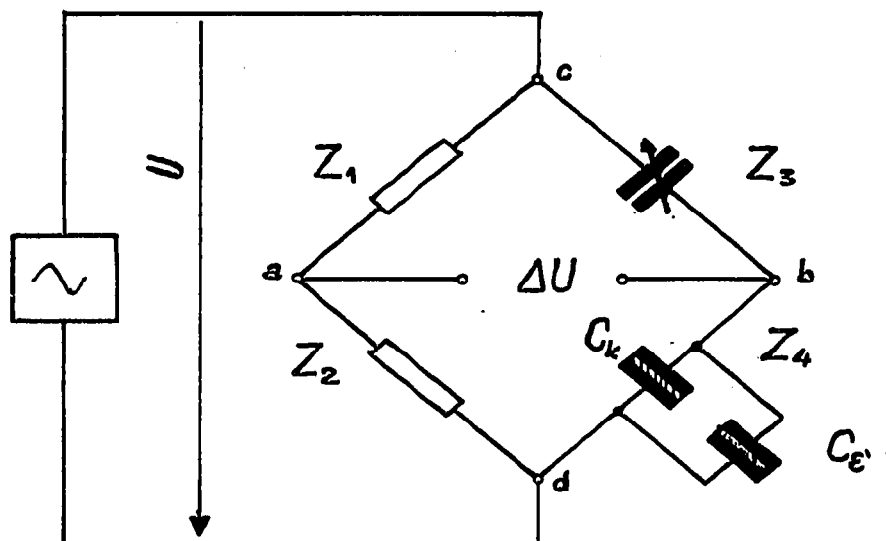


Fig. 5. Representative scheme of the measuring bridge.

If we assume that the impedance  $Z_4$  is only represented by the reactance of the measuring condenser:

$$Z_4 = j X_4 = \frac{j}{\omega \cdot (C_{\epsilon'_0} + C_k)} \quad (15)$$

and

$$\Delta Z_4 = j \Delta X_4 = \frac{j}{\omega} \cdot \left( \frac{1}{C_{\epsilon'_0} + C_k} - \frac{1}{C_{\epsilon'_x} + C_k} \right) \quad (16)$$

Then

$$\frac{\Delta X_4}{X_4} = \frac{C_{\epsilon'_x} - C_{\epsilon'_0}}{C_{\epsilon'_x} + C_k} \quad (17)$$

On substituting the relation into eqn. 14, we obtain:

$$\Delta \vec{U} = \vec{U} \cdot \frac{(C_{\epsilon'_x} - C_{\epsilon'_0})}{(C_{\epsilon'_x} + C_k)} \cdot \frac{1}{\left[ 4 + \frac{2(C_{\epsilon'_x} - C_{\epsilon'_0})}{C_{\epsilon'_x} + C_k} \right]} \quad (18)$$

for the voltage change across the bridge diagonal.

This formula has been used to calculate the data for the plots shown in Figs. 6 and 7. The plot in Fig. 6 represents the dependence of the voltage  $\Delta U$  for a bridge with an arm ratio  $\vec{Z}_1/\vec{Z}_2 = \vec{Z}_3/\vec{Z}_4 = 1$ , fed by a voltage  $U = 1$  V, with the measuring condenser quoted in the above examples at  $\epsilon'_0 = 10$  and  $\epsilon'_x = 2$ , on the concentration within volume fraction limits of 0-0.10.

Fig. 7 shows a plot for the same bridge, but for  $\epsilon'_0 = 2$  and  $\epsilon'_x = 10$ .

In the second case, at  $\epsilon'_0 = 2$  and  $\epsilon'_x = 10$ , the sensitivity is higher by a factor

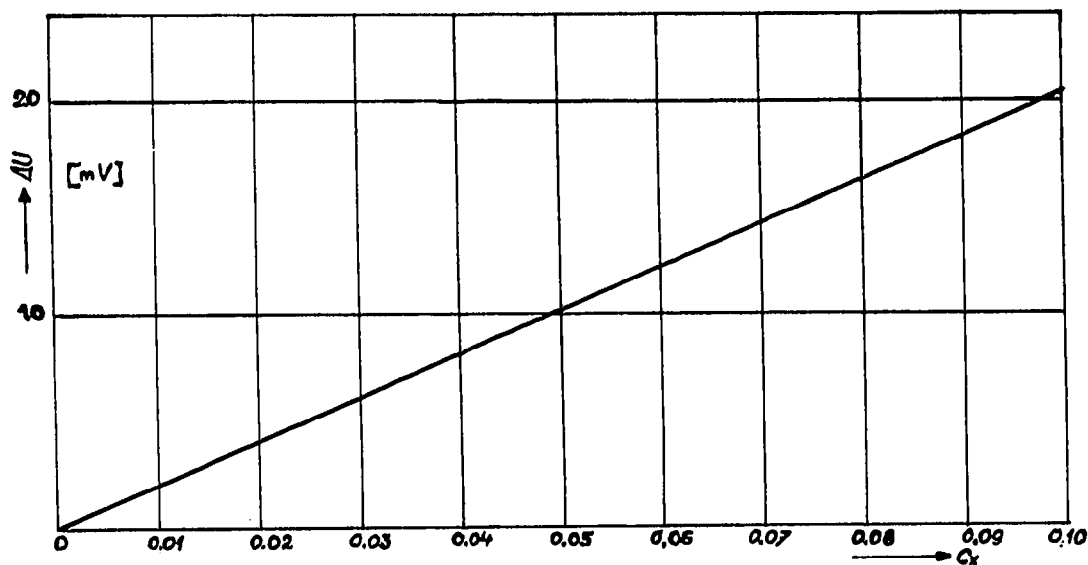


Fig. 6. Output voltage of the bridge with equal arms, fed by IV, showing the dependence on concentration ( $\epsilon'_0 = 10$ ,  $\epsilon'_x = 2$ ).

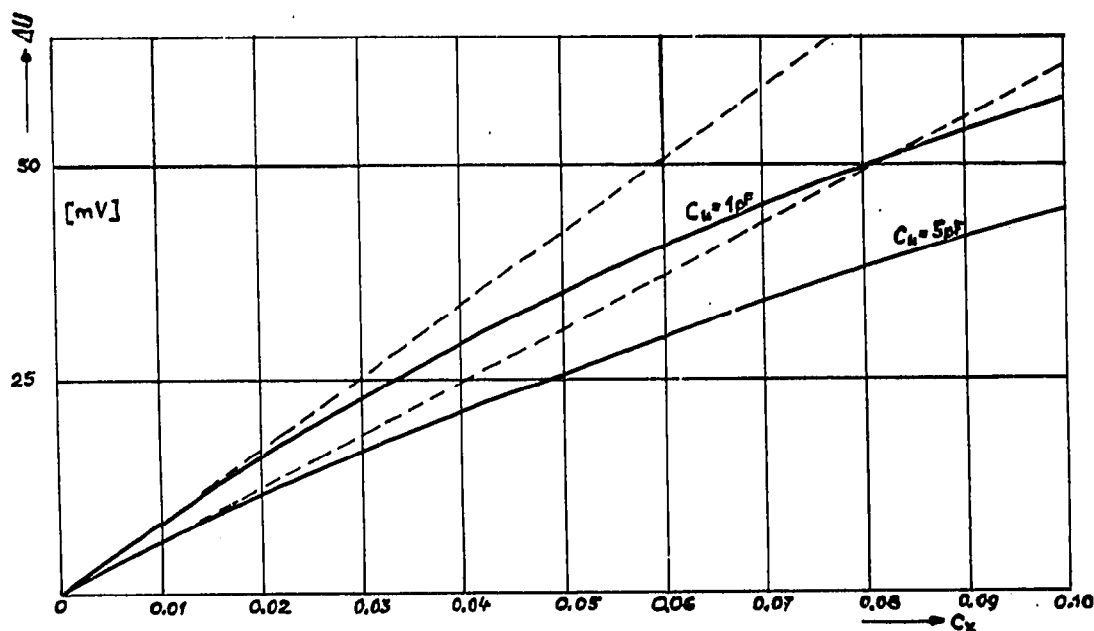


Fig. 7. Output voltage of the bridge with equal arms, fed by IV, showing the dependence on concentration ( $\epsilon'_0 = 2$ ,  $\epsilon'_x = 10$ ).

of 4 at concentrations up to 0.01. However, the linearity is substantially worse and may only be regarded as satisfactory up to a volume fraction of only 0.01.

When employing a mobile phase of high permittivity,  $\epsilon'_0$ , in comparison to the permittivity of the component detected,  $\epsilon'_x$ , excellent linearity may be attained, but at a somewhat lower sensitivity.

In Fig. 7 there is also a plot for the output voltage  $\Delta U$  for the case where the invariable capacity  $C_k = 5$  pF and the  $C_{\epsilon'}$  of the empty condenser is again 4 pF. It is apparent from the plot that although the sensitivity falls, the linearity increases.

## CONCLUSION

In virtue of the present theoretical study it would seem that detection based on the principle of permittivity changes is promising for the construction of sensitive and linear detectors for modern liquid chromatography in the case where the mobile phase having a very different permittivity to that of the substance detected is used. Excellent linearity is attained when the permittivity of the mobile phase is substantially higher than that of the detected components, but the sensitivity is lower. Higher sensitivity is attained in the case when a mobile phase with a lower permittivity relative to the permittivities of components detected is used, however, the linearity is poorer and may only be regarded as satisfactory up to volume fraction concentrations of about 0.01.

## REFERENCE

- 1 J. F. K. HUBER, *J. Chromatog. Sci.*, 7 (1969) 172.
- J. Chromatog.*, 52 (1970) 213-220