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NEW RESULTS IN THE APPLICATION OF A TORSION BALANCE TO LIQUID CHROMATOGRAPHY

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ABSTRACT

New results are given in the application of a torsion balance as a dielectric constant detector.
Response and reproducibility are firstly tested by introducing polar liquids into an apolair main stream which was led directly into the detector. Dips in the recorded peakshape are explained by a maximum in the responsion curve of the detector. Chromatographic separations are achieved on a silicagel column and n-hexane as eluent. A separation of some benzene derivatives is shown.

INTRODUCTION

Detection of small variations of the dielectric constant is the object of a cooperation between the Universities of Berlin and Eindhoven. In this cooperation special attention is paid to force measurements as an alternative to the usually applied impedance measurements. This is of special importance when macromolecular polar liquids are concerned. Considering that proteins have relaxation times as high as 10^{-5} s, and that asymmetrical bio-molecules may tend to even higher values, we conclude that, when measuring the capacitance, the impedance would have inconvenient high values when using frequencies below 10^{8} Hz. The apparatus we used for the pondoromatic measurements has been described earlier (1-3).

RESULTS AND DISCUSSION

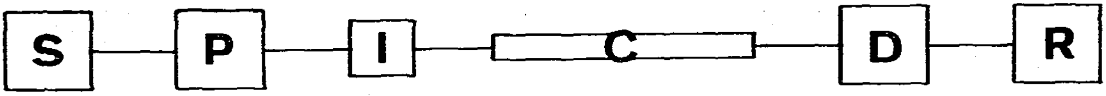


Fig.1: Schematic representation of the experimental arrangement S = solvent reservoir, P = pump, I = injection valve, C = column, D = detector, R = registration

In the work reported here we used the set-up shown in Fig.1. In the first experiments the column was by-passed. Reproducable amounts of several liquids were introduced into the mainstream by means of an injection valve. When the sample included in the eluent arrived at the detector both its front and rear boundary were blurred because of diffusion and mixing effects.

When introducing an effective diffusion constant covering all possible disturbances leading to this blurring we may use eqn. 1 for the concentration measured by the detector as a function of time.

$$C(t) = \tfrac{1}{2}\, C(0) \left[\operatorname{erf}\left(\frac{x_o - Vt + b}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(\frac{x_o - Vt - b}{2\sqrt{Dt}}\right) \right] \qquad (1)$$

where x_o = the distance between detector and the middle of the injection loop

V = the velocity of the eluent flow

$2b$ = the length of the injection loop

D = the effective diffusion constant

The asymmetrical shape of the detectors signal, following from equation 1 can be noticed in Fig.3. This asymmetry is mainly due to mixing in dead volumes and in the great cell-column in the preliminary detector design. Another drawback of the detection system is that as yet no feet-back coupling was used. This brings along a maximum in the responsion curve (V versus ε_r) due to the use of a resonance circuit. When this maximum is passed, a dip in the recorded peak-shape will occur. An example of this effect is given in Fig.2.

The reproducibility of the detector proved to be in the order of a percent as shown in Fig.3.

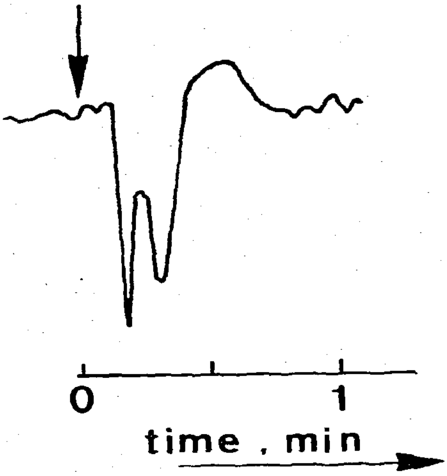


Fig.2: Detection signal of 10% v/v ethanol in n-hexane with n-hexane as eluent, showing the effect of a maximum in the response curve of the detector.

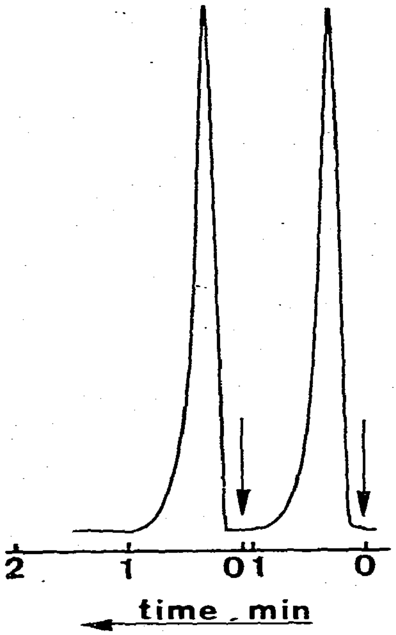
To check the performance of our detector in a liquid chromatographic set-up a column was placed between the injection valve and the detector (see figure 1). As the best sensivity will be obtained when the eluent has a low dielectric constant and a low dipole moment apolar liquids are optimal as mobile phase; therefore a polar silicagel column can be used as it gives a good selectivity in combination with apolar to moderately polar mobile phase mixtures. A separation of sample components will be obtained due to differences in affinity to the silica surface.

An example of these measurements is shown in Fig.4, where three benzene derivatives were separated.

The detectibility achieved so far proved to be in the order of 100 μg.

The authors have the impression that this limit could easily be improved by a renewed design.

An improvement by some orders of magnitude does not seem impossible.



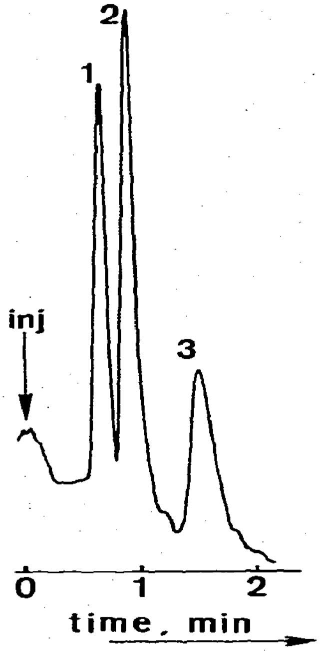


Fig.3: Reproducibility of the detection signal. 7.5 nitrobenzene, solved in 200 µl eluent, is injected; flow 1 ml min^{-1}*; measurement is performed without column.*

Fig.4: Separation of 3 benzene derivatives.
Column: Lichrosorb Si-60, d_p *= 5 µm, L = 150 mm, Dinw = 4.6 mm; Mobile phase = n-hexane; flow 2 ml min*$^{-1}$*,*
ΔP = 90 atm, injection volume 60 µl.
Compounds: 1 = 0-dichlorobenzene (6 mg), 2 = nitrobenzene (2 mg), 3 = dinitrotoluene (3 mg).

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