NOTES

Adaptation of an Automatic Densimeter as Detector for Gel Permeation Chromatography

In the preceding paper,[1] a density cell of high accuracy adapted to an automatic digital densimeter DMA02 conceived by Kratky et al.[2] was described. The authors claim for liquid densities an accuracy of 2×10^{-6} g/cm^3. In the present communication, we shall describe the adaptation of this cell as a detector for gel permeation chromatography. For this technique, one usually uses as detector a differential refractometer, an UV or IR spectrometer, or an automatic viscometer.[3]

It was of interest to check the performances of this densimeter in order to see if they were comparable to those of the two other detectors or if this device could be used when the two other techniques fail (very small values of refractive index increment or no adsorption band in a region where the solvent is transparent).

PRINCIPLE OF THE DENSIMETER

The principle of the Kratky densimeter is based on the measurement of the vibration of a glass U-tube filled with a liquid of unknown density. This vibration period can be simply written

$$T = 2\pi \left(\frac{I_0 + vd}{C_1}\right)^{1/2}$$

where I_0 represents the inertia moment of the empty tube, v its inner volume, d the density of the investigated liquid or gas, and C_1 the elasticity constant of the tube.

Consequently, the square of the period is a linear function of the density of the liquid:

$$T^2 = A + Kd$$

A and K being constants depending upon the geometry of the tube. This law has been tested over a great range of densities[1] (between 10^{-3} and 2 g/cm^3). Usually, to know the absolute value of the density, it is necessary to determine A and K values starting from calibration of the apparatus with liquids of well-known densities. For the chromatographic detection, we are not usually concerned with this absolute value, but only with a parameter proportional to the polymer concentration of the eluted solution.

As the density d_{12} of a solution varies linearly with the concentration C of the solute (expressed in g/cm^3) following the relationship

$$d_{12} = d_1 + C(1 - \bar{v}_2 d_1) \tag{2}$$

(d_1 being the solvent density and $\bar{v}_2$ the apparent specific volume of the solute), we can deduce, from eqs. (1) and (2), that the difference of the squares of the periods corresponding respectively to the solution and to the pure solvent is directly proportional to the concentration C:

$$T^2 = K(1 - \bar{v}_2 d_1)C = K'C$$

Practically, since the ΔT values are small compared to T, it is sufficient to assume that T is proportional to C. Thus, if we plot T as a function of elution volume or time, we obtain a diagram similar to that registered with the refractometer in which the ordinate is proportional to the polymer concentration. It can be used exactly in the same manner as the classical refractograms. The analysis of the refractograms is based on the assumption that dn/dc does not depend on molecular weight and concentration.

We will assume, in the same manner, that $\bar{v}_2$ does not vary with these parameters even knowing that this assumption is not truly correct and is only a first approximation as has been shown by Barrall et al.[4] for dn/dc and François et al.[5] for $\bar{v}_2$.

EXPERIMENTAL

The vibrating tube is sealed in a well-thermostated brass cylinder. Its total length is 2.6 cm, its inner diameter 1 mm; this corresponds to a total liquid volume of 1.2 cm^3. But it is clear that only the part of liquid situated at the center of the U-tube participates effectively in the measurement of the period. This efficient volume is of the order 0.2 cm^3, which can be considered large for the chromatographic detection.

The frequency of the empty tube is 300 cycles/sec. The electronic measurement system compares its frequency with that of a reference quartz of 1 MHz. With such a system, and in order to obtain an accuracy of 2×10^{-6} g/cm^3 for the density (minimum precision for GPC), it is necessary to count the time of 4×10^4 periods of the tube, which corresponds, in our case, to 150 sec. This time is printed automatically, and measurements are made every 3 min.

For our test experiments, we used a Waters GPC 200 chromatograph equipped with five columns filled with Styragel of porosities 10^6, 10^5, 3×10^3, 10^3, and 60 Å and a refractometric detector. As a solvent, we used tetrahydrofuran (THF), and the densimeter was adapted according to Figure 1. The temperature of the cell, controlled with a Hewlett-Packard quartz thermometer, was selected as near as possible to the chromatograph temperature (21°C). The eluated liquid, before entering the cell (C), passes through a coil of capillary metal tubing (D) (2 m long, 1 mm in diameter) immersed in water thermostated with the same circuit than the cell. We used a relatively low flow rate (1 ml per min) for good temperature control and in order to obtain a sufficient number of points on the chromatogram, since we have only one point every 3 min.

With these precautions, we obtain stable values (10^{-6} g/cm^3) of the periods, for pure solvent, during hours of circulation. Drifts of this baseline are similar to those registered with the refractometer.

EXPERIMENTS WITH POLYSTYRENE SAMPLES

We studied four polystyrene samples prepared by anionic polymerization with low polydispersity indices (ratio of weight-average to number-average molecular weights lower than 1.3). Since the sensitivity of this detector is lower than that of the refractometer, we have injected 2 ml of a solution containing 0.25% of each sample. In order to avoid concentration effects, both calibration curve and experiments on unknown samples were made with the same polymer quantity.

In Figure 2, we report a peak obtained with the densimeter and the corresponding curve given by the refractometer. Unfortunately, it is impossible to compare them quantitatively since the units
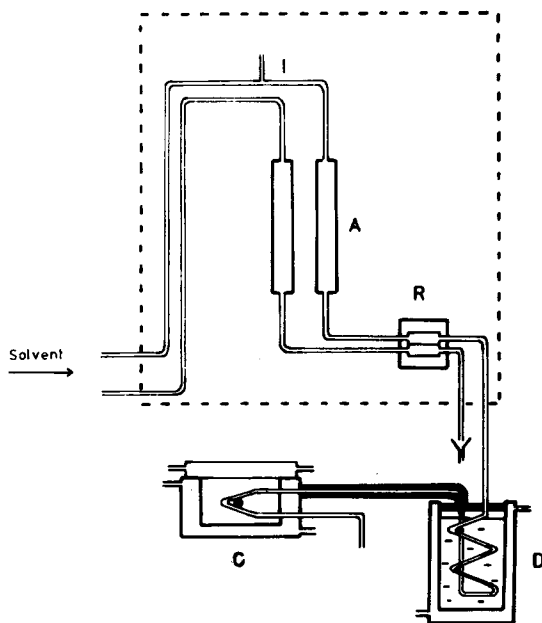

Fig. 1. Schematic of the adaptation of densimeter to the chromatographic apparatus: (A) columns; (C) density cell; (D) thermostated capillary; (I) insection; (R) refractometer.
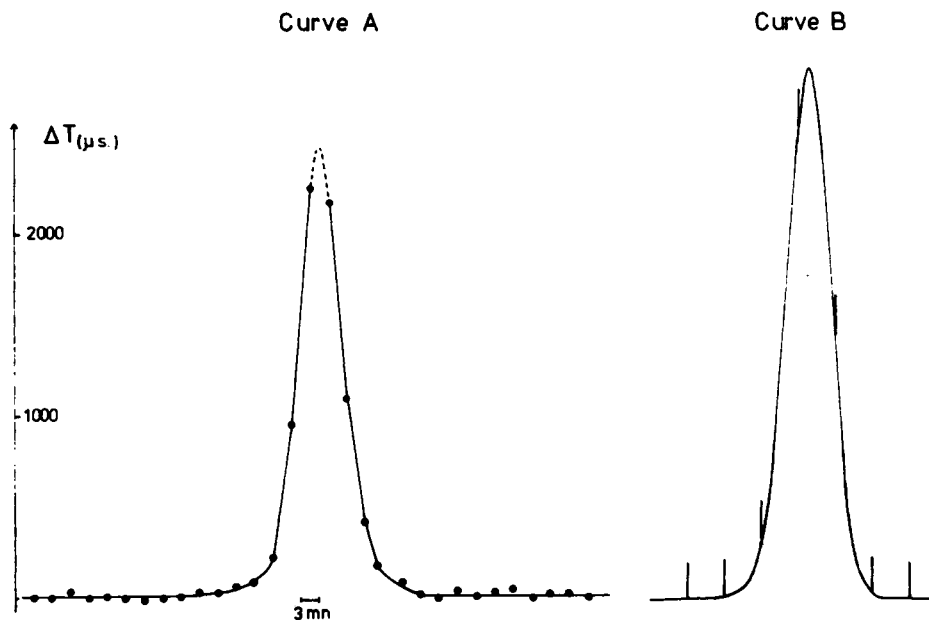
Curve A   Curve B

Fig. 2. Curves given by densimeter (curve A) and refractometer (curve B) for a polystyrene $(M_w = 98,200)$.

are not the same. For this narrow peak, corresponding to a polymer of low polydispersity, we have only nine points but, assuming that it is Gaussian, it is quite enough to draw the complete curve.

As we have said, the volume of the detector cannot be neglected. Therefore, it should introduce a broadening of the peaks and a diminution of the efficiency of the detection. Since direct comparison was not possible with our experimental setup, we tried to compare the results using the following method.

Having measured the elution volumes for four PS samples of known molecular weights, it was possible to draw a calibration curve log $(M_w M_n)^{1/2}$ versus retention time which was practically a straight line. Using the classical graphic integration technique, we did evaluate M_w, M_n, and the M_w/M_n ratios. The results are reported in Table I together with results obtained by the classical refractometric method on the same set of columns. The results are in surprisingly good agreement, except perhaps for the last sample. They show that the broadening we could introduce by the rather large volume (200 μl) of the detector can be neglected. This shows that this detector can be used in any cases since it is known that axial dispersion has a more important effect on narrow peaks than on broad fractions.

In order to show that in some cases this detector can be very useful, we have studied a sample of poly(dimethylsiloxane) in THF. We obtain a well-defined peak with our densimetric detector (Fig. 3) and no signal at all by refractometry since in this solvent the dn/dc of PDMS is practically zero.

The purpose of this note was to show the possibility of a detector based on the Kratky digital densimeter. It has some disadvantages: (a) It is not a differential apparatus but nevertheless has no more noise and drift than a refractometer if one correctly controls the temperature. (b) In many cases, its sensitivity is not as large as the sensitivity of a refractometer. (c) It provides digital results

TABLE I

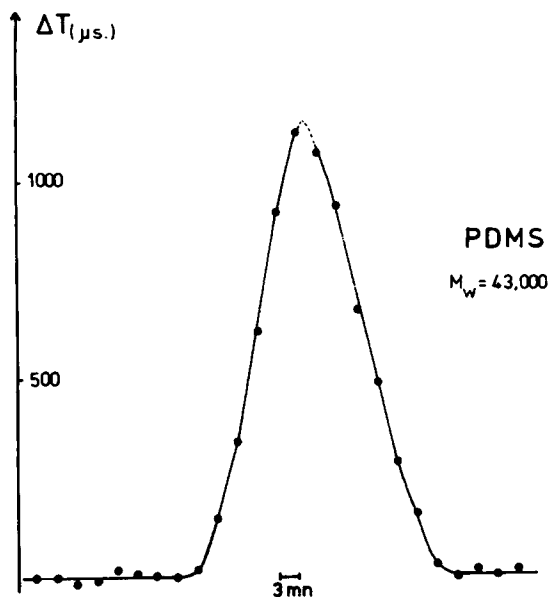| Sample	Refractometer			Densimeter		
	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n
1	10,700	9,950	1.08	10,700	9,915	1.08
2	52,900	48,100	1.10	61,600	57,000	1.08
3	101,700	94,000	1.10	118,500	106,500	1.11
4	426,000	375,000	1.13	499,000	407,000	1.23

Fig. 3. GPC curve of poly(dimethylsiloxane) $(M_w = 43,000)$ given by the densimeter.

at given time intervals and not a continuous curve. This last point could be an advantage if one wants to use a computer for the analysis of the results.

The main interest is that the detector can be used when dn/dc is near zero and when there is still an appreciable density difference between solvent and solute. In order to make this detector competitive, one should decrease the volume of the measuring tube, making it more suitable for chromatographic detection and shortening the measuring time.

References

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