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FERRITE PRESSURE TRANSDUCER IN SYRINGE PUMPS USED IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A ferrite pressure transducer acting as a constant flow device was applied to a high-performance liquid chromatographic syringe pump, and permitted high stability and reproducibility of chromatographic results in isocratic elution to be obtained and a Y–t recorder to be applied.

INTRODUCTION

It is well known that syringe pumps used in high-performance liquid chromatography (HPLC) have many advantages in comparison with other types. Martin *et al.*[1] described the influence of the fluid compressibility on the chromatographic peaks recorded as a function of time. This problem cannot be neglected in the case of real fluids closed in a syringe pump with a volume of 250–500 ml and a back-pressure of up to several hundred atmospheres. Theoretical considerations[1] and experimental values[2] have been presented recently.

Such effects can be avoided when constant-displacement syringe-type pumps are used, by modifying the driving system. The ideal, but so far non-existing, solution would be to place a flow meter in the head of the pump and to feed its signals back to the motor. In others words, a flow meter should not be sensitive to the changes in the density of liquids caused by the back-pressure. Meanwhile, one can apply a pressure transducer based on Darcy's equation:

$$Q_0 = \frac{kS}{\bar{\eta}L} \cdot \Delta p_\infty$$

where k, S, $\bar{\eta}$ and L are constants when Δp_∞ is the pressure under steady-state conditions and Q_0 is the set flow-rate. Transducers of these types were recently described by Van Lenten and Rothman[3] and by Achener *et al.*[4].

TABLE I

TYPES OF PRESSURE TRANSDUCER

Type of transducer	*Example*	*Pressure range (atm)*	*Remarks*
Piezoresistive	Manganine	> 20,000	Large size, depending on temperature
Semiconductor junction	Zener diode	> 20,000	For high pressures
Ultrasonic propagator		⩾ 19,000	Large size
Magneto-elastic ferrite	Torroidal core	⩽ 2000	Chemically resistant, thermally stable, small size
Others	Bourdon tube, membrane[5]		Connected with other transducers, not expensive

EXPERIMENTAL

For electrical measurements of hydrostatic pressure, various methods can be used and a comparison of these methods is given in Table I. We believe that, for measurements of pressure and for the feed-back connection to the pump in HPLC, a ferrite transducer is the most suitable. A torroidal-shaped core (Fig. 1A) made from nickel–zinc ferrite as the pressure transducer was used. The chemical composition and specially developed technology enabled us to obtain a rectangular hysteresis loop and pressure sensitivity[6]. Rectangular and current pulses (Fig. 1B), which are necessary for magnetizing the core, induce the voltage pulses in the measuring coil (Fig. 1C). The amplitude, U_m, of these pulses can be described approximately as follows:

$$U_m = KAZ_p \cdot \frac{\Delta B}{t_s}$$

where K is a constant depending on the impulse shape, Z_p the number of coils in the measuring circuit, A the area of the cross-section, ΔB the change in magnetic induction of the core and t_s the response time of the transformer. Changes in the hydrostatic pressure acting on the ferrite core result in changes in ΔB and t_s, *i.e.*, changes in

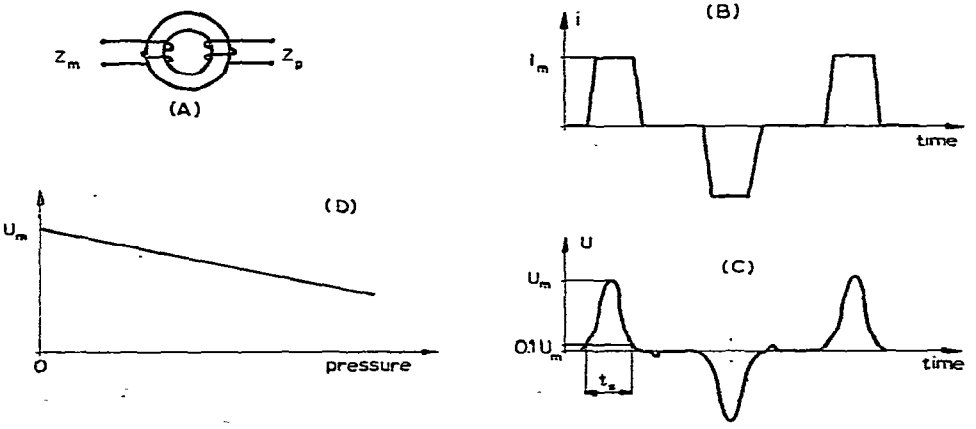

Fig. 1. (A) Ferrite core. (B) Magnetizing current pulses. (C) Voltage pulses in the measuring coil. (D) Pressure characteristics of the ferrite core.

the output amplitude due to the inverse magnetostrictive effect (Fig. 1D). When the hydrostatic pressure increases, the output voltage pulses, U_m, consequently decrease. The characteristic of the ferrite transducer is shown in Fig. 1D to be linear in the range 0–400 atm. A torroidal core with O.D. 2 mm, I.D. 1.3 mm and height 0.9 mm as a pulse transformer was used[7]. There are two coils for the input Z_m and the output Z_p.

A schematic diagram of the transducer connected with the syringe pump (driven by the stepping motor) is shown in Fig. 2. Rectangular pulses are generated by the generator and fed into the transformer. The amplitude of the output pulses U_m, depending on the pressure, is converted by the peak detector into the d.c. voltage U_p. Next, the characteristic of the ferrite transducer is reversed and for the pressure $\Delta p = 0$ the d.c. voltage $U_p = 0$. The signal U_p is compared with the reference voltage, U_{ref}, which can be derived from the potentiometer. When $U_p > U_{ref}$, the signal from the comparator causes the gate G to close, *i.e.*, the pulses from the voltage-to-frequency (V/F) converter used normally to drive the stepping motor are switched off. At this moment, the stepping motor stops, which is indicated by a light. When $U_p < U_{ref}$, the gate is open for pulses from the V/F converter. In this instance, the stepping motor is on and the light is off. The pressure which stops the motor can be adjusted according to U_{ref}. The potentiometer Q_r sets the piston speed. The voltage behind the peak detector permits the measurement and recording of the pressure. The transducer is placed in the head of the pump. A high-pressure valve is located between the column and the output of the pump and enables stop-flow injection to be used. When U_p reaches U_{ref}, corresponding to the steady-state pressure, the constant flow mode for the syringe pump is obtained.

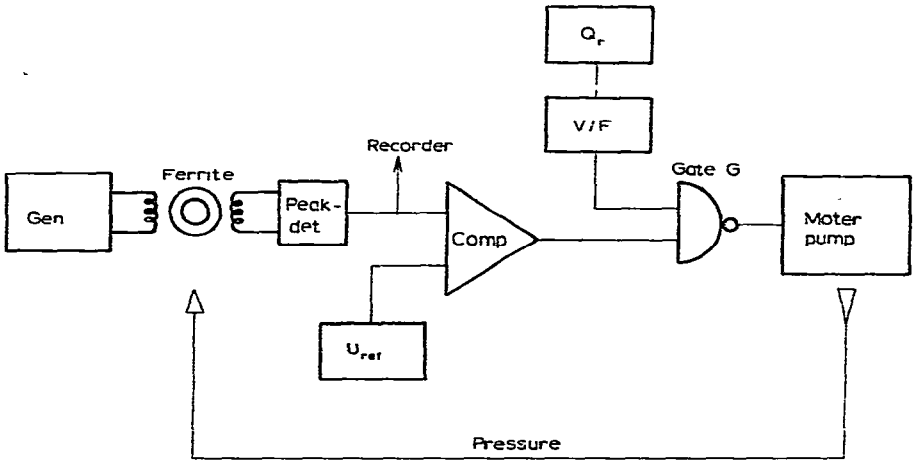

Fig. 2. Schematic diagram of the electrical and pressure feed-back connection of the ferrite transducer to the driving system.

The action of the transducer was examined on a home-made constant-displacement syringe pump liquid chromatograph fitted with a UV detector. The syringe volume was 250 ml, the highest back-pressure 400 atm and the highest flow-rate 6 ml/min. A column of length 250 mm and I.D. 3 mm packed with Merckosorb SI-60, particle diameter 5 μm, was used. The flow-rate was measured as a function of time using a recording balance.

The signals from the balance, the pressure manometer, the UV detector and the clock were recorded or printed out.

RESULTS AND DISCUSSION

The correlation between the flow-rate and the back-pressure was measured; according to the Darcy equation, this should be linear. The results obtained (100–300 points printed at 0.5- or 1-sec intervals) were analyzed using the least-squares method according to the equation

$$Q(t) = a\Delta p(t) + b$$

where $Q(t)$ is the flow-rate calculated from the mass flow and the density of *n*-hexane. The measurements were carried out with an initial pump volume of 50 ml and an initial pressure of zero. In the instance, when the set flow-rate is 2 ml/min, the pressure increased to about 150 atm. The mass of the *n*-hexane eluent was measured with an accuracy of 1 mg and the pressure with an accuracy of 0.1 atm.

The negative b values (Table II) can be regarded as a result of the difference in the input and the output flow-rates, because of the compressibility and viscosity of *n*-hexane in the column. In the simple form of the Darcy equation, this influence of the pressure on the flow-rate is neglected. The same discrepancy with the theoretical data was observed earlier[4] by measuring the time (t_{99}) needed for steady-state flow conditions to be attained.

TABLE II

CONSTANTS OBTAINED IN THE EQUATION $Q(t) = a\Delta p(t) + b$

Q_0 (ml/min)	$a \times 10^4$ (ml/min.atm)	$b \times 10^2$ (ml/min)
0.5	134.8 ± 6.7	−0.9 ± 1.5
1	130.4 ± 2.7	−1.4 ± 1.3
2	133.6 ± 2.3	−2.3 ± 2.9

The high-pressure valve and electronic feed-back of the pressure manometer to the motor were applied in order to give stop-flow injection and to obtain a constant flow-rate. When a new column and/or mobile phase is used and Q_0 is set, then a considerable time is needed in order to attain steady-state flow. To permit the use of the valve, U_{ref} has to be adjusted such that $U_{ref} = U_p$. The opening and closing of the valve in connection with stop-flow injection does not change the pressure in the syringe pump. The phenomena that occur during the closing and opening of the valve are represented in Fig. 3. The 3-sec delay is needed in order to obtain a constant flow-rate after opening the valve and no change in pressure is observed. The long-term drift of the pressure read on the manometer is not greater than 0.5 atm at a level of 150 atm and 0.2 atm at 40 atm.

It is important in chromatography to demonstrate the influence of the fluid compressibility in the pump on the chromatograms recorded as functions of time and volume. The signal from the UV detector, the mass flow-rate and time were recorded

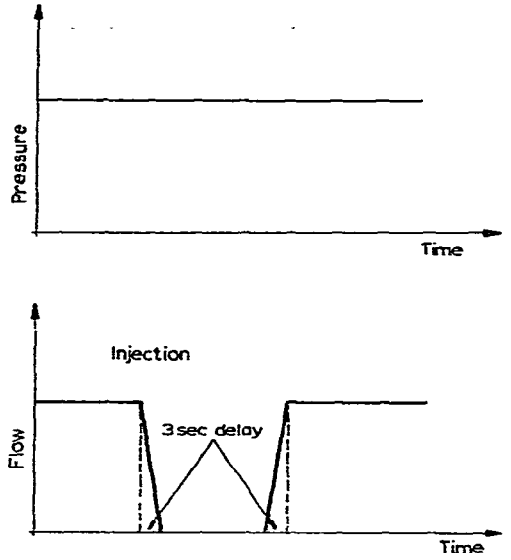

Fig. 3. Flow and pressure characteristics in the stop-flow injection mode.

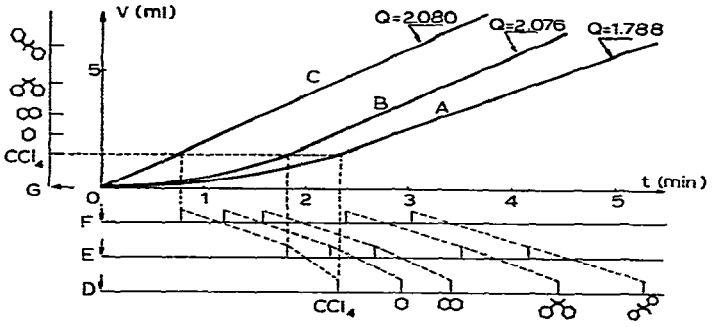

Fig. 4. A, B and C represent the effluent volumes on the time scale; C was obtained using the pressure device. D, E and F show the retention times of the substances analyzed under conditions A, B and C, respectively. G represents the true retention volume of the substances analyzed.

simultaneously. Fig. 4 shows the dependence of the effluent volume on time. Curves A and B were obtained for the initial volumes of the pump, $V_0 = 250$ and 50 ml, respectively, where Q_0 was set 2 ml/min and the starting pressure was zero. Curve C is a straight line and depicts the situation when the stop-flow injection mode is employed, using the constant-flow device.

Chromatographic analyses of a mixture of carbon tetrachloride, benzene, naphthalene and *cis*- and *trans*-stilbene were carried out and the retention data were recorded. These were always constant on the volume scale (*cf.*, G in Fig. 4). However, the retention times on chromatograms D, E and F were different and depended on the starting conditions (*i.e.*, initial volumes, pressures, etc.). The broken lines pass through the peaks of the same substances. The true capacity factors for all of the substances could be calculated only from plot C, which was obtained with the use of the

constant-flow device. This means that in the constant flow-rate mode, a Y–t recorder can be applied.

CONCLUSION

The equipment described enables one to obtain high stability and reproducibility of chromatographic results in isocratic elution and a Y–t recorder can be used. We consider that owing to the expansion of the liquid along the column, small differences between the set flow-rate (Q_0) and the flow-rate actually recorded (Q) can be observed even when the constant flow-rate device is used.

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