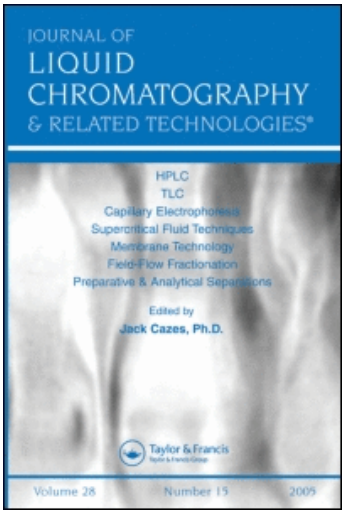

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Viscosity Detection with a Pulseless PUMP for Liquid Chromatography

Purnendu K. Dasgupta[a]
[a] Department of Chemistry, Box 4260 Texas Tech University, Lubbock, TX

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VISCOSITY DETECTION WITH A PULSELESS PUMP FOR LIQUID CHROMATOGRAPHY

Purnendu K. Dasgupta
Department of Chemistry Box 4260
Texas Tech University
Lubbock, TX 79409

ABSTRACT

The performance of a differential pressure transducer as a viscosity detector in conjunction with a pulseless high pressure syringe pump designed for the purpose is described. The detector, although relatively insensitive, is inexpensive and extremely rugged. Because it is non-destructive and introduces very little dispersion, serial coupling ahead of other detectors is possible. Response behavior is demonstrated.

INTRODUCTION

The differential refractometer is the only commonly used universal detector in the current practices of HPLC (1). Although optical absorption detectors dominate analytical HPLC, overloading of such detectors (especially fixed wavelength types) are frequent in preparative applications and therefore necessitate unusual designs. Viscosity is a bulk property, analogous

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to refractive index. The viscosity of a chromatographic effluent changes accompanying solute elution. Viscosity of a chromatographic effluent is most easily monitored by measuring the pressure drop across a capillary as the column effluent is made to flow through it as a constant rate. The pressure drop P across a capillary of radius r and length L is given by the Hagen-Poiseuille equation (2):

$$\Delta P = 8FnL/\pi r^4$$

where a fluid of viscosity n is flowing through the capillary at a constant flow rate F. Since F, L and r are constants for a given experimental condition, the pressure drop is related directly to the effluent viscosity. Ouano (3-5) first conceived the design and application of a flow through continuous viscometer, based on a pressure transducer, as a detector in HPLC. Such detectors are of particular utility in size exclusion chromatography, both because macromolecules cause significant changes in effluent viscosity and also because intrinsic viscosity values can be used for molecular weight determinations. By using a differential refractometer in tandem, the sample concentration may be independently evaluated and be used in conjunction with the viscosity detector output to calculate the intrinsic viscosity and thence the MW (3-7).

As the Hägen-Poiseuille equation indicates, a capillary pressure drop type viscosity detector is sensitive to flow fluctuations and as demonstrated by Lesec et al. (7), may in fact be used as a highly sensitive flow meter. The applications of a viscosity

detector have thus far been limited to size exclusion chromatography. To minimize flow pulsations common to high pressure reciprocating pumps, various types of pulse dampening systems have been used.

In this communication, the design and construction of a simple pulseless high pressure syringe pump, of particular utility with a capillary pressure drop based viscosity detector, is described. The response behavior of small solutes with such a detector is demonstrated.

MATERIALS AND METHODS

The Detector was based on a variable reluctance type differential pressure transducer (model DP 45) coupled to a carrier demodulator (model CD 15) both from Validyne Engineering Corporation, Northridge, CA. This transducer translates the pressure induced mechanical displacement of a flexible diaphragm into an electrical signal. The particular transducer-demodulator combination used in this work produced a 0-10V adjustable output with a differential pressure input equal to 1 inch of water column (0.035 psi). The voltage output is linearly related to the differential pressure input and could be offset up to 15 psi in either direction.

The detector was used generally in the true differential mode, as in the configuration depicted in Figure 1a. The capillary tube (316 stainless steel, 5-15 cm long, 0.05-0.015 cm internal diameter) was connected to the transducer inputs via zero dead volume tees (Valco) and universal couplings (Alltech). The latter fittings are not essential, but facilitate rapid

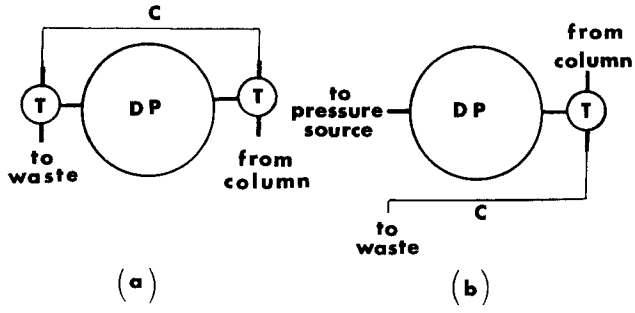

Figure 1. Two modes of detector configuration. T : zero dead volume tee; C : capillary; DP : differential pressure transducer.

exchange of different capillaries for experimental purposes. In this configuration the output can be offset only to the extent allowed by the detector electronics and thus sets a limit on the length of the capillary and/or flow rate (which together govern the pressure drop across the transducer) if baseline signal is to be adjusted to zero.

The alternative configuration depicted in Figure 1b utilizes the capillary connected to one side of the transducer, the capillary effluent being allowed to drain into a waste beaker. The other side is pressurized with a suitable source (e.g. cylinder gas with two-stage regulator) to obtain a zero or near zero differential pressure with the eluent flowing through the capillary at the desired rate. In this configuration, there are no restrictions on the capillary bore/length or flow rate, up to the maximum absolute pressure limit of the transducer.

Initial experiments with this detector used in a chromatographic system with a single piston

reciprocating pump equipped with a hydraulic capacitor type pulse dampener (Altex model 110 A) revealed that the attainable sensitivity is limited by the baseline noise (sawtooth type) induced by the pump pulsation. A high pressure syringe pump therefore was designed and built.

A stainless steel (type 316) cylinder, 15 inches in length, 1.5 inch in diameter and 0.25 inch wall thickness was inside polished to a mirror-finish (3-4 rms, Miether Machine Works, Odessa TX). If non-corrosive eluents are used, the hydraulic shock-absorber housing of a truck is an inexpensive alternative for this purpose. A stainless steel end cap, provided with a 1.5 mm diameter 0.75 mm bore stainless steel outlet tube was welded onto one end of the cylinder. Piston movements in this cylinder was accomplished via a worm-driven screw jack of 2 ton capacity (screw diameter 1 inch, screw lift 15 inches, model no. NKM-1802-15, Duff-Norton Company, Charlotte, NC). The lifting screw of this jack is keyed such that the lifting screw does not rotate during ascent/descent. The gear ratio produces 1 inch translational movement of the screw for 100 turns of the worm. The worm shaft was coupled to a 1/8 H.P. shunt wound D.C. bidirectional motor with 40:1 gear reduction (drive model 589 with type 916 speed control unit, Bodine Electric Company, Chicago, IL). Except for replacing the single turn potentiometer used for speed control by a 10-turn vernier readout potentiometer, no changes were made. The worm rotation speed could be reproducibly adjusted from 1-56 rpm.

The jack and the motor were firmly mounted on a 1.5 inch thick wooden base with the housing for the lifting screw protruding beneath the base through a suitably accomodating hole. The piston is attached to the top of the lifting screw (described in more detail below) and fits within the cylinder. The cylinder is held in place by two 0.75 inch thick aluminum plates containing holes of appropriate size and are aligned in position by four all-thread (0.5 inch diameter, 13 threads to the inch) steel supports. The pump may be used in the horizontal or vertical position. The latter position is preferable since it occupies little bench space and in this case, C-clamps are recommended for securely clamping the pump to the benchtop. The pump assembly is shown in Figure 2.

The piston was fabricated from stainless steel; a 3 inch length was machined to closely fit inside the cylinder. Approximately 1.5 inch length of this piece was further shaved to a diameter of 1 inch and threaded with 20 threads/inch. The threaded portion accomodated a set of cup shaped nylon V-rings in position. Neither the stainless steel body of the piston, nor the teflon disc contacts the cylinder wall during operation; the sealing is provided only by the rings. The top 0.75 inch poriton of the threaded lifting screw was shaved to a diameter of 0.75 inch. The stainless steel piston piece was machined to accomodate this portion of the screw at the end opposite from the teflon disc. With the lifting screw head tightly butting against the piston body, a recessed and somewhat loosely fitting retaining screw was put in to attach the two pieces. The retaining screw plays a role only during the withdrawal of the piston. The piston design is shown in Figure 3.

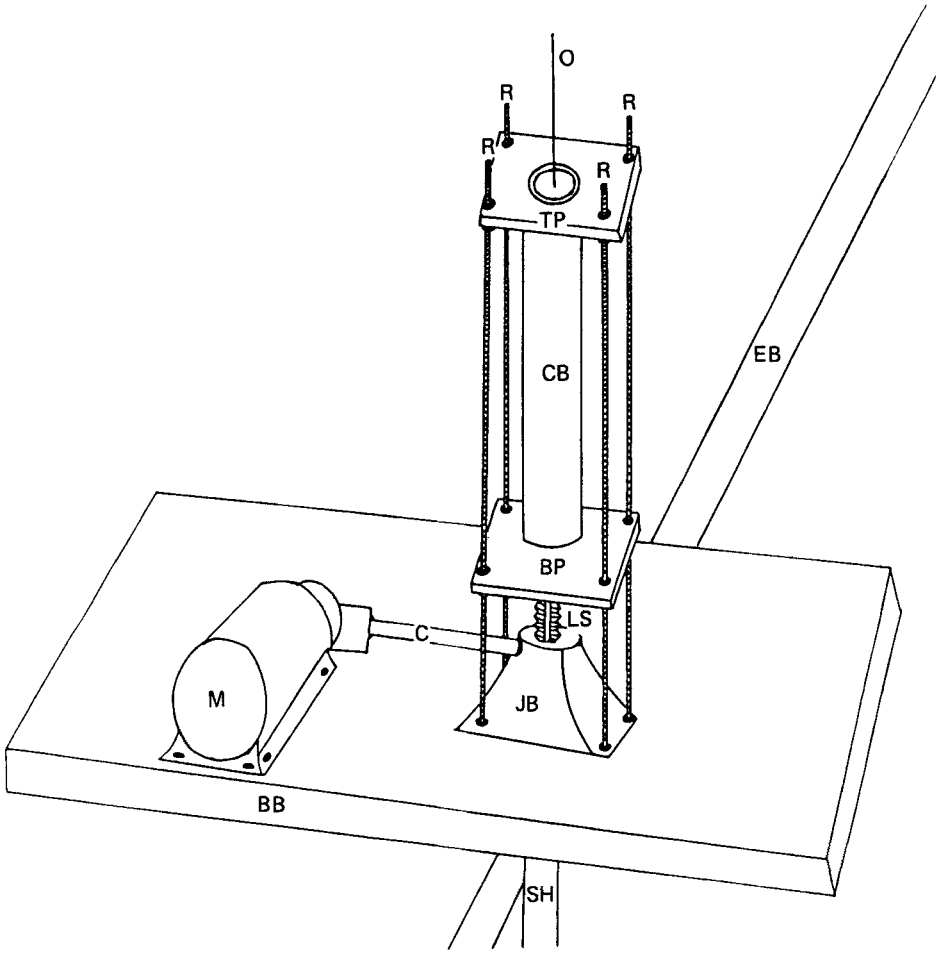

Figure 2. High pressure syringe pump. M : motor; C : coupling, motor shaft to worm shaft; JB : jack body; LS : lifting screw; SH : lifting screw housing; BB : baseboard; EB : edge of workbench; CP : syringe barrel; BP : bottom retaining plates; TP : top retaining plate; R : threaded support rods; O : pump outlet.

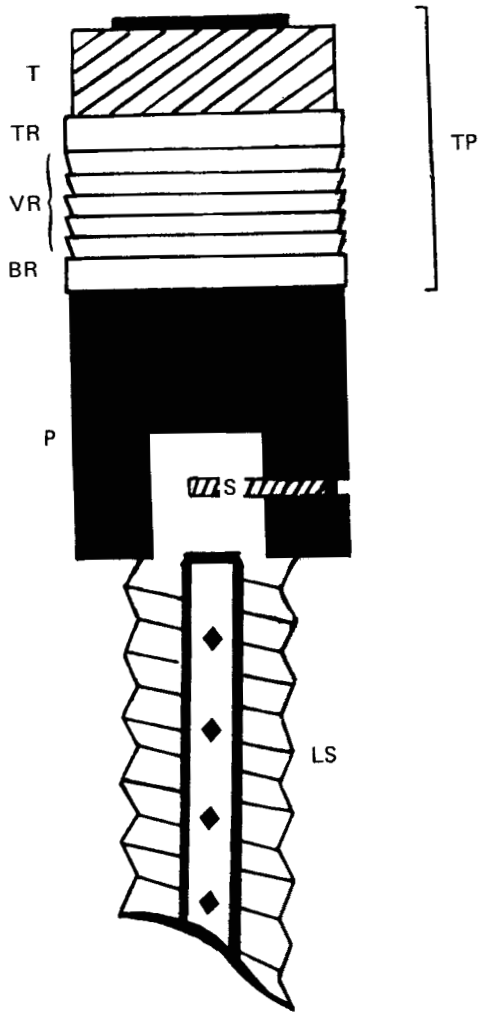

Figure 3. Details of the piston. T : teflon disc; TR : top, V-ring set; VR : v-rings (5); BR : bottom, V-rings set; P : stainless steel body of piston; TP : threaded portion of P: LS : lifting screw; S : retaining screw attaching lifting screw to piston. Diamonds in the lifting screw key slot indicate where numerals are engraved.

The pump outlet is connected via a 0.5 μm line filter (SSI) to a 3-way high pressure valve (SSI) which connects it either to an injection valve (Rheodyne type 7000) or a solvent reservoir. These connections are made with 0.75 mm bore tubing, to avoid cavitation during pump filling. To fill the pump (capacity 350 mL), the motor is run maximum speed in reverse with the inlet/outlet connected to the solvent reservoir, which should ideally be placed a level above the pump head to avoid cavitation. Less than 25 min are required for complete filling. Since the piston itself is not visible, it is necessary to provide a means to judge the position of the piston at any time. To accomplish this, numerals were engraved every 0.5 inch on the keying slot of the lifting screw (See Figure 3) and could be inspected between the cylinder bottom plate and the top of the jack housing. This allows one to avoid driving the piston beyond either of its intended limits. As a matter of convenience and further safeguard, especially to permit unattended filling and operation, two pairs of photoelectric sensors (infrared emitter-detector pair, Radio Shack 276-142), coupled to requisite electronics, may be mounted in the lifting screw housing which protrudes beneath the pump base. Obstruction of the light path in the bottom pair by the descending screw indicates complete filling of the pump and is configured to prevent further reverse movement of the motor. Lack of obstruction of the light path in the top pair by the ascending screw indicates the piston is at the end of its travel and is configured to prevent further forward movement of the motor. The control circuitry is shown in Figure 4.

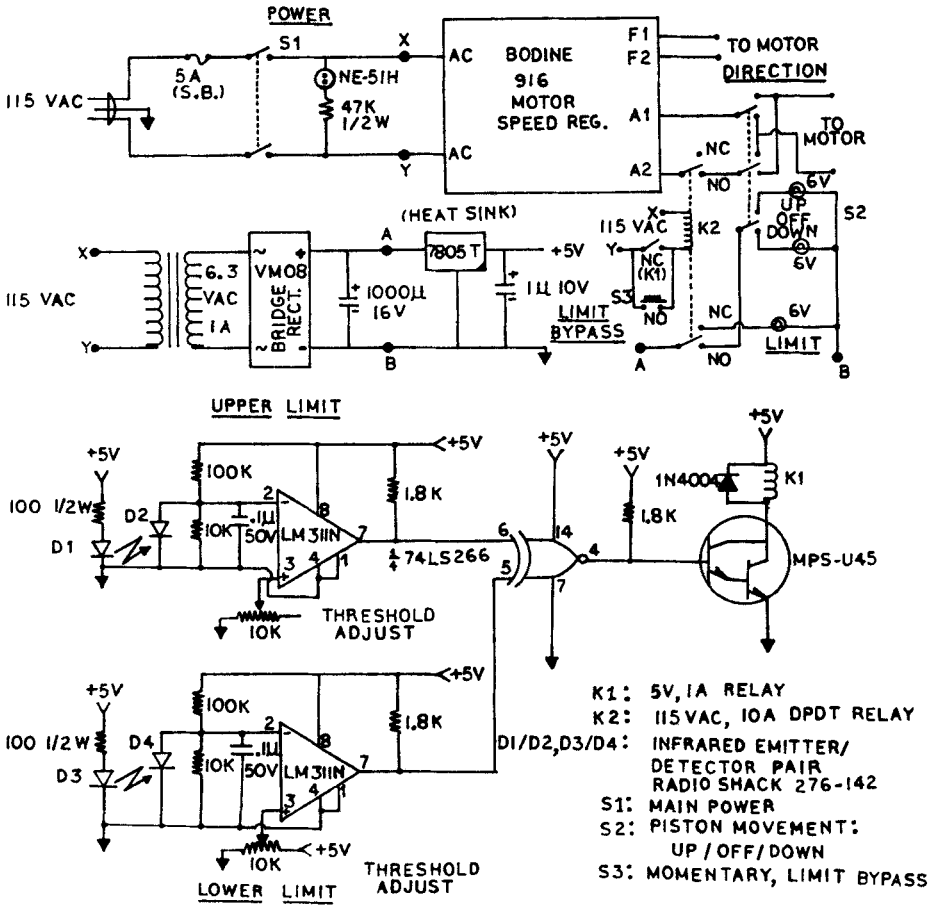

Figure 4. Control circuitry for pump. All resistors are 1/4 W, 5% unless otherwise specified.

RESULTS AND DISCUSSION

Pump Performance. The attainable flow rate of the pump is 0.4-16 mL/min and was primarily designed for conventional analytical and preparative work. Smaller flow rates may be obtained with a slower revolving motor although fill time will increase proportionally. A simple scaling down of the cylinder size and choosing a

slower motor easily permits a pump that delivers pulseless flow at flow rates down to 1 μL/min. Unattended pump filling is easily achieved by a suitable turn-off timer whether or not photocontrols are incorporated. The design pressure for this pump was 3,000 psi, primary limit being the rating of the jack. The pump has, however been used routinely at 3,500 psi without any observable ill effects. On a number of occasions, a partially blocked column had inadvertently led to the pump operating at 5,000-5,500 psi head pressure which caused leakage at the injection valve but was seemingly without effect on the pump itself. A pressure relief valve (Rheodyne 7037) set at 5,000 psi was subsequently incorporated ahead of the injector for safety measures. The long term effect of operating at pressures higher than 3,500 psi is not known however. No detectable pulsation or any other flow aberration was noticeable when a rotameter was connected directly to the pump output for flow measurements. Baseline noise levels, when directly coupled to a Schoeffel 770 optical detector set at 190 nm were two orders of magnitude below that obtained with an Altex 110 A reciprocating pump and its associated pulse dampener while reagent grade methanol was pumped through either system. At all but the maximum operating speed (e.g., during filling) the opertion of the pump is inaudible. The pump was built at a cost under $1,200.

Detector Performance. The directionality of a signal on such a detector is not predictable a priori. This is unlike refractive index detectors where a knowledge of the R. I. of the pure solute (or that of a

concentrated solution) and that of the eluent generally permits prediction of signal directionality. Viscosity of a mixture of two substances A and B may often be greater than that of A or B, such as for methanol and water. Because in a chromatographic situation a solute elutes from the column as a solution in the eluent and the peak concentration in that effluent band is determined by amount/concentration of the solute injected as well as the column efficiency and other chromatographic parameters, the viscosity behavior (or the detector response) is impossible to predict based solely on viscosity data of the eluent and pure solute (or that for one specific concentration of the solute in the eluent). Further, for the same solute-solvent combination, the viscosity of the solution may change from a value less than that of the solvent to a value greater than that of the solvent (or vice-versa) as a function of the solute concentration. With water/methanol or water/acetonitrile eluent systems in conjunction with conventional reverse phase (C-18) silica columns and small organic molecules as solutes, I find for most solutes that at higher concentrations, the peak response is indicative of a viscosity lower than that of the eluent. At low concentrations however, the eluted solutes generally produce a viscosity greater than that of the eluent. Because concentrations of the solute in the chromatographic band changes continuously as the solute elutes, the injection of a high concentration solute generally elicits not only a peak (decreasing viscosity) but is also commonly followed by a dip (increasing viscosity) formed by the low

concentration tailing portion of the solute band, before the signal returns to baseline. That the phenomenon is not a detector induced artifact is confirmed by the fact that the peak/dip ratio continually decreases with decreasing solute concentration injected until the peak disappears altogether. This behavior is demonstrated in Figure 5 with toluene as the test solute and 80/20 acetonitrile/water as eluent. The lack of a dip preceeding the peak, as may be expected for an eluted band of Gaussian symmetry, is not presently understood.

The response, whether measured in peak height, dip height, peak to dip height, peak and/or dip areas is not a linear function of injected concentration/amount, as may be expected. The departure from linear behavior increases with increasing solute concentration. Also, detection by viscosity measurement is relatively insensitive. A separation of benzene (5 mg) and Toluene (5 mg) on an analytical column (5 μ-ultrasphere-ODS, 250 x 4.6 mm) is demonstrated in Figure 6. Benzene produces a peak and dip, while the toluene produces a dip only. At higher acetonitrile/water ratios, which causes faster elution (and thus less dilution), the same mixture yields two peaks.

When the detector is operated in the experimental arrangement depicted in Figure 1b, a greater pressure drop across the capillary is feasible by using a longer or narrower capillary. Consequently, detection sensitivity is substantially increased. A long term drift or slow oscillatory behavior of the baseline under these conditions has however been noted. This may be due to thermally induced viscosity changes or gas

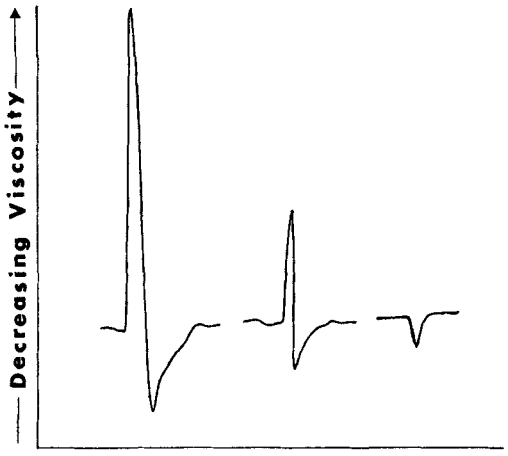

Figure 5. Detector response to toluene. The second and third sample are four- and sixteenfold dilutions of the first sample, respectively. Eluent 80/20 acetonitrile/water, 1 mL/min.

sorption/desorption on the gas pressurized side of the transducer. The results reported in this paper pertain to work carried out at room temperature with the experimental setup insulated by styrofoam blocks. Under these conditions, the experimental arrangement in Figure 1a produces a baseline noise equal to 2×10^{-4} times the total pressure drop experienced by the capillary. More elaborate thermostatic control will be necessary to attain lower baseline noise levels.

Bearing in mind that the transducer used in this work is not optimum for this application, the sensitivity can be potentially much better. Remarkable advances have been made in recent years towards fabricating miniature pressure transducers on silicon wafers. The accuracy and low cost of such devices open

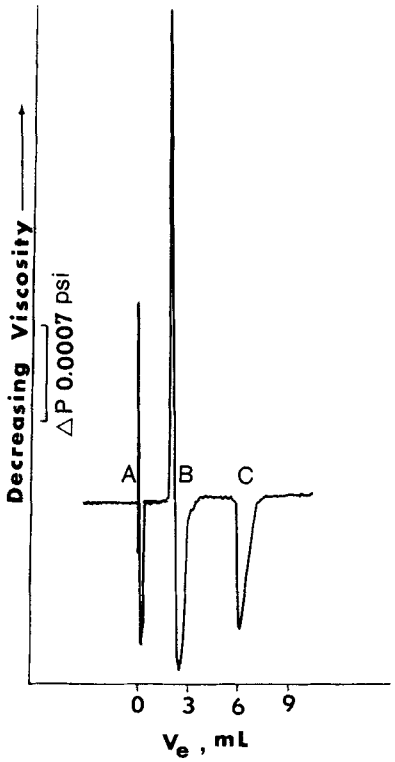

Figure 6. Separation of benzene and toluene. A : this is caused by actuation of the injection valve. Depending on the exact technique of actuating the valve, this spike can be smaller or greater. B : benzene peak and dip. C : toluene dip. Eluent 60/40 acetonitrile/water, 1 mL/min. Capillary : 0.25 mm bore, 10 cm length. Detector sensitivity : 1 Volt/0.0035 pounds/sq. in.

up new vistas for viscosity detectors in HPLC. Transducers that are both higher in sensitivity as well as tolerate a higher absolute pressure are commercially available with approximate cost less than $1,000. While such detectors are not likely to be attractive for the more common analytical applications, certain advantages

are worthy of consideration. Low costs, extreme ruggedness, lack of overloading at high concentrations, all make them good candidates for process chromatography. The fact that the detector is nondestructive and can be configured to introduce essentially no dispersion, makes it possible to use it in series with other detectors following it. For gradient applications, signal processing (e.g., differentiation) will be necessary however.

ACKNOWLEDGEMENT

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