

CHROM. 9500

Letter to the Editor

The compressibility effects in syringe pumps for liquid chromatography

Sir,

Achener *et al.*¹ present a refinement of our study of the effects of solvent compressibility in syringe pumps used for liquid chromatography² by taking into account the variation in solvent compressibility with pressure; we wish to make two comments on that paper.

First, we are pleased to see that the conclusions of this second-order approach agree qualitatively with those of our first-degree approximation, although, naturally, the quantitative agreement between calculated and experimental data becomes closer when using the equation derived by Achener *et al.*

We certainly agree, as mentioned previously², that compressibilities at atmospheric pressure cannot be extrapolated to high pressures without introducing significant errors, but it should be emphasized that *n*-pentane is an extreme case, the one chromatographic solvent for which both the compressibility, χ , and $d\chi/dP$ are most important: hence the difference between the predictions of the first- and second-order assumptions might be expected to be small in practice —less than 20% at 100 atm.

For completeness, however, we wish to mention that the expression governing variation in compressibility with pressure used by Achener *et al.* is a first approximation of the Tait equation³ and that an exact treatment of the problem would necessitate taking account of the variation in solvent viscosity with pressure, which can have important effects³.

Finally, our simplified approach gives reasonably good results, even at high pressures, if an average compressibility is used; this is important, because very few accurate data exist in the literature on the coefficients of the Tait equation, even data on the compressibilities of liquids are hard to find, and such data vary largely from one author to another^{1,2}.

These minor points should obscure neither the basic agreement between us and Achener *et al.* that a finite time is needed to achieve steady-state conditions of pressure and flow-rate (and that this time depends on the column characteristics, on the solvent and on the volume of the reservoir), nor our agreement on the order of magnitude of this time.

We are also glad to note that manufacturers have studied these problems and can offer some means for obtaining satisfactory results with syringe pumps under analytical conditions. One solution is to use, momentarily, a very high pumping speed, until the pressure corresponding to the desired steady-state flow-rate is attained. This, of course, requires that the pressure be known from previous measurements, which is usually so in routine analysis only. For this purpose, however, the pump motor must be quite powerful, and not all manufacturers offer pumps with a speed sufficiently high for this operation to be practical. Similarly, the good results described by Achener *et al.* in their study of stop-flow injection can be obtained only if the valve is close

to a low-volume injection port. It should be emphasized that, in both cases, the solutions suggested by Achener *et al.* do not seem to be easily applicable to preparative liquid chromatography, to say the least.

In practice, the judicious use of these refinements is possible only if the phenomenon to be minimised (and, perhaps, overcome) is well known and understood. That was the aim of our original paper; we are happy that it seems to have been achieved.

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(Received July 6th, 1976)