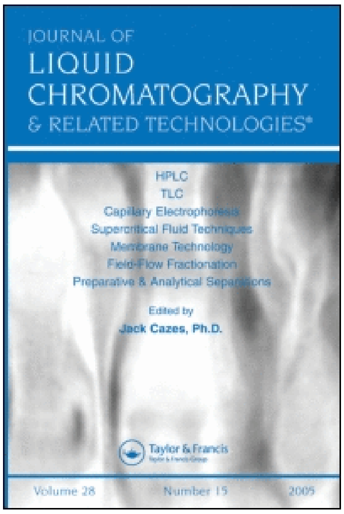

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Theoretical and Experimental Study of Radial Concentration Profiles Originating from a Non Punctual Injection Source

Claude Eon[a]; Patrick Sharrock[a]
[a] Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada

To cite this Article Eon, Claude and Sharrock, Patrick(1979) 'Theoretical and Experimental Study of Radial Concentration Profiles Originating from a Non Punctual Injection Source', Journal of Liquid Chromatography & Related Technologies, 2: 4, 485 — 497
To link to this Article: DOI: 10.1080/01483917908060078
URL: http://dx.doi.org/10.1080/01483917908060078

JOURNAL OF LIQUID CHROMATOGRAPHY, 2(4), 485-497 (1979)

THEORETICAL AND EXPERIMENTAL STUDY OF RADIAL CONCENTRATION PROFILES ORIGINATING FROM A NON PUNCTUAL INJECTION SOURCE

Claude Eon et Patrick Sharrock
Département de chimie
Université de Sherbrooke
Sherbrooke, Québec   Canada   J1K 2R1

ABSTRACT

Radial concentration profiles originating from non delta plug flow injection functions can be theoretically accounted for in terms of a Bessel function series. Results related to axial injections of various diameters relative to the column I.D. are described. They are in food agreement with the theory.

INTRODUCTION

The infinite diameter concept, as introduced by knox et al (1,2), is by now familiar to anyone involved in L.C. It states that, because of the packing heterogeneity at the wall vicinity, optimum column performances are obtained when the migration of the solute into the wall region is minimal. Hence best columns should have a large enough I.D. to ensure that the centrally injected solute hardly reaches the wall. When this is not so, the solute concentration builds up at the wall and performance deterioration occurs to a degree which can be appreciated from the radial concentration profile (3).

Strangely enough, radial dispersion, unlike its axial contrepart, does not seem to be greatly affected by the anisotropy of the medium; therefore, the theoretical radial concentration function, calculated as if the column were isotropic is a good indicator of the actual solute exposure to the wall region and, consequently, of the column efficiency. The model developed by Klinkenberg et al (4) and tested by Eon (3) seems to be reliable for a plug delta injection function. It is however unsuitable for prepscales systems as the injection then usually occupies a finite fraction of the column cross section. Hence an extension of the work of Klinkenberg et al (4) is needed so that it accounts for prepscale chromatography as well. This is the aim of the present contribution which is purposely restricted to the introduction and testing of a radial concentration function. At this stage no attempt will be made to underline any possible practical implications in terms of column and injection design. Those are presently being investigated in our laboratory.

THEORETICAL

The system being investigated is pictured in Figure I. The column is supposed to have a length L, an internal radius R, the injection is made centrally over a circular section of radius r* by means of an appropriate device (i.e.: a secondary pump). It was experimentally convenient to consider a plug flow injection as in frontal chromatography; hence, the theory has been developed accordingly. Nevertheless, it is believed that the radial concentration profiles so defined are also suitable for classical chromatography providing that relative concentrations rather than absolute ones are contemplated.

As the solute moves downward, it spreads radially and axially. To a first degree of approximation, the resulting broadening, can be regarded as a diffusion like process characterized by two pseudo diffusion coefficients Da and Dr which are respectively related to the axial (Ha) and radial (Hr) plate heights through:

$$Da = \frac{uHa}{2} \qquad Dr = \frac{uHr}{2} \qquad [1]$$

where u is the carrier linear velocity.

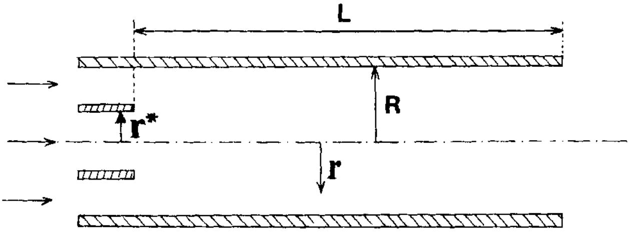

FIG. 1. Basic set up showing the definition and symbols of the pertinent parameters.

The problem is to find the solute concentration $C(r,\ell,t)$ at any radial distance r, any absissa ℓ and time t after the injection. This very difficult task can be greatly simplified by considering only abscissae related to the time through

$$\ell = u_s t \qquad [2]$$

where u_s, the solute linearvelocity is function of the capacity factor (k'):

$$u_s = u/(1+k') \qquad [3]$$

The advantage of this procedure is that it eliminates the time dependence. Hence the radial concentration profile as half the height of the break through curve takes the form $C(r,\ell)$.

The system mass balance equation is

$$\frac{\partial C}{\partial t} + u_s\frac{\partial C}{\partial \ell} = Dr\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right) + Da\,\frac{\partial^2 C}{\partial \ell^2} \qquad [4]$$

with the boundary conditions:

$$\frac{\partial C}{\partial r}(R,\ell,t) = 0,\ t > 0 \qquad [5]$$

$$\frac{\partial C}{\partial r}(o,\ell,t) = 0,\ t > 0 \qquad [6]$$

$$C(R,\infty,t) = \text{bounded} \qquad [7]$$

$$\begin{aligned} C(r,o,t) &= C_o \text{ for } r \leqslant r^* \\ &= 0 \text{ for } r > r^* \end{aligned} \qquad [8]$$

Because of the restriction imposed by eq. 2, the system can be solved as follows. Let's suppose that $C(r,\ell)$ can be expressed as the product of two functions $\Phi(r)$ and $\phi(\ell)$ as:

$$C(r,\ell) = \Phi(r)\ \Psi(\ell) \qquad [9]$$

Then eq. 4 reduces to

$$\frac{\partial^2\Psi}{\partial\ell^2} - \frac{u_s}{Da}\frac{\partial\Psi}{\partial\ell} - \frac{\alpha^2\Psi}{Da} = 0 \qquad [10]$$

$$\frac{\partial^2\Phi}{\partial r^2} + \frac{1}{r}\frac{\partial\Phi}{\partial r} + \frac{\alpha^2}{Dr}\Phi = 0 \qquad [11]$$

where α is to be found.

Eq. 11 has the form:

$$\Phi'' + \frac{a}{r}\Phi' + b\ \Phi = 0 \qquad [12]$$

whose solution is (5):

$$\Phi = r^{\left(\frac{1-a}{2}\right)} Z_{\frac{1-a}{2}}\ (r\sqrt{b}) \qquad [13]$$

or because a = 1

$$\Phi = A\ J_o\left[\frac{r\alpha}{(Dr)^{\frac{1}{2}}}\right] + B\ Y_o\left[\frac{r\alpha}{(Dr)^{\frac{1}{2}}}\right] \qquad [14]$$

where Jo is the zeroth order Bessel function. Next is should be noted that B = 0 by virtue of eq. 6. As for eq. 5, it implies (key $J'o(z) = -J_1(z)$(5)) that:

$$-A\ J_1\left[\frac{r^*\alpha}{(Dr)^{\frac{1}{2}}}\right] = 0 \qquad [15]$$

hence:

$$\alpha_{a_1} = \frac{a_1\ (Dr)^{\frac{1}{2}}}{r^*} \qquad [16]$$

where a_1 represent the roots of the first Bessel function. Combining eqs 14 and 16 leads to

$$\Phi a_1(r) = A\ Jo\left(\frac{a_1 r}{r^*}\right) \qquad [17]$$

As for eq. 11, which also involves α_{a_1}, it has a solution of the form

$$\psi_{a_1}(\ell) = K\ a_1 \exp\left[\frac{\ell}{2}(La_1)\right] + Pa_1 \exp\left[\frac{\ell}{2}(Ma_1)\right] \qquad [18]$$

La_1 and Ma_1 can be expressed from eq. 16:

$$La_1 = \left[\left(\frac{us}{Da}\right)^2 + 4\frac{a_1{}^2}{(r^*)^2}\frac{Dr}{Da}\right]^{\frac{1}{2}} + \frac{us}{Da} \qquad [19]$$

$$Ma_1 = -\left[\left(\frac{us}{Da}\right)^2 + 4\frac{a_1^2}{(r^*)^2}\frac{Dr}{Da}\right]^{\frac{1}{2}} + \frac{us}{Da} \qquad [20]$$

Eq. 7 imposes Ka_1 to be zero; hence combining eqs 17 and 18 as in 9 leads to a solution for the system

$$C(r,\ell) = \sum_{a_1=0}^{\infty} Qa_1\ Jo\left(\frac{a_1\ r}{r^*}\right) \exp\left(\frac{\ell}{2} Ma_1\right) \qquad [21]$$

where Qa_1 is to be calculated. One way of doing so is to consider the function $C(r',o) = f(r')$ where r', the reduced coordinate, is defined as r/R. According to eq. 8 f(r') becomes:

$$f(r') = \sum_{a_1}^{\infty} (Qa_1\ Jo\ (a_1\ r')) \qquad [22]$$

Because of the orthogonality of the system the coefficients Qa_1 can be calculated via the classical procedure as:

$$Qa_1 = \frac{\int_0^1 r' f(r')\ Jo\ (a_1 r')\ dr'}{\int_0^1 r'\ Jo^2\ (a_1 r')\ dr'} \qquad [23]$$

Note that the normalization integral N.I. becomes:

$$\text{N.I.} = \tfrac{1}{2}\left[Jo'^2\,(a_1) + Jo^2\,(a_1)\right] = \tfrac{1}{2}\,Jo^2\,(a_1) \qquad [24]$$

Then because of eqs 8 and 24, eq. 23 can be rewritten as:

$$Qa_1 = \frac{2\,Co \int_o^{r^{*\prime}} r\ \ Jo\,(a_1 r')\,dr'}{Jo^2\,(a_1)} \qquad [25]$$

This eq. can be solved by making use of the classical relation ship (5):

$$\int_{z_o}^{z} Z^{\nu}\ J_{\nu-1}(z)\ dz = \left[Z^{\nu}\ J\nu\ (Z)\right]_{z_o}^{z} \qquad [26]$$

The coefficients Qa_1's which result are:

$$(Qa_1)a_1 = Co\ r^{*\prime 2} = Co\left(\frac{r^*}{R}\right) \qquad [27]$$

$$(Qa_1)a_1 > 0 = \frac{2\ Co\ r^*\ J_1\ (a_1\ (r^*/R))}{R\ a_1\ J_0^2\ (a_1)} \qquad [28]$$

Hence by combining with eq 21, the final result is obtained

$$C(r,\ell) = Co\left[\left(\frac{r^*}{R}\right)^2 + \sum_{a_1>0}^{\infty} 2\left(\frac{r^*}{R}\right)\ \frac{J_1(a_1 r^*/R)\ Jo\ (a_1 r/R)}{a_1 J_o^2\ (a_1)}\ \exp\left[\frac{\ell}{2}\ Ma_1\right]\right] \qquad [29]$$

where Ma_1 is given by eq. 20. As previously mentionned, $a_1 > 0$ are the non zero roots of the first Bessel function (3.8317, 7.01559, 10.1734 ...). It should be noted that eq. 29 bears some resemblance with that derived by Fakien and Smith (6); it is however more accurate since Fahien and Smith Ignore axial dispersion.

Because of the complexity of eq. 29 it is illustrative to compute some $C(r,\ell)$ functions related to some typical cases. As reported in (3), it is first convenient to express the column length as a multiple of an arbitrary length L_1 defined in such a way that it normalizes the system with respect to the radial concentration function. If L_1 is the length for which the peak variance is one quarter of the column radius then

$$L_1 \equiv \frac{R^2}{dp^2} \frac{1}{16 [(B/\nu) + C]} \qquad [30]$$

where dp is the particle diameter and B and C the radial plate height coefficients if

$$h_r = \frac{B}{2} + C \qquad [31]$$

with ν, the reduced velocity. Note that eq. 31 supposes k' = 0 for the sake of simplification.

Figure II gives some theoretical radial concentration profiles for a column of lenght L_1 as a function of r*'. As expected, the larger r*', the more the solute is exposed to the wall. Also note that the profile for r* = 0 (punctual injection) is consistent with the one described previously (3). As for figure III, it displays some concentration profiles for r*' = 0.5 as a function of the column length.

The larger L, the more significant the wall effect.

Since these profiles are theoretical an experiment has been designed to check their ability to account for real chromatographic systems. This is the object of the next section.

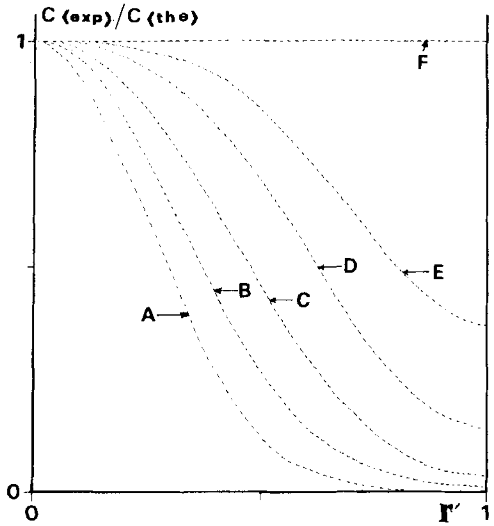

FIG. 2. Theoretical radial concentration profiles at the reduced length 1 ($L = L_1$) as a function of $r^{*'}$ ($r^{*'} \equiv r^{*}/R$)

A) $r^{*'} = 0$

B) $r^{*'} = .33$

C) $r^{*'} = .5$

D) $r^{*'} = .66$

E) $r^{*'} = .8$

F) $r^{*'} = 1.0$

EXPERIMENTAL

The basic set up is the same as in reference (3). An inert probe, p-nitrophenol in solution in a 0.1 M aqueous potassium chloride, freed from oxygen, was injected into a carrier of the same composition but free of nitrophenol. The local concentration at the column outlet was recorded by means of a dual polarographic detector as described

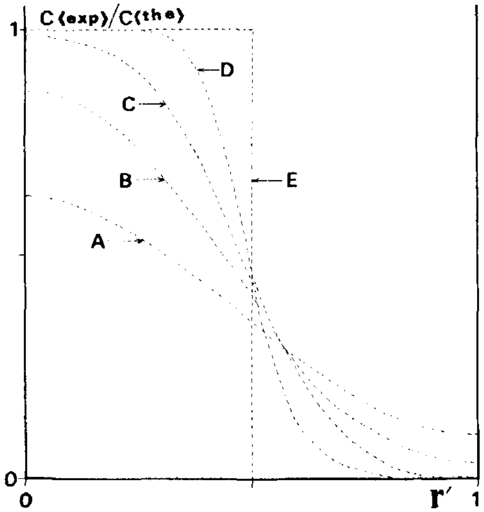

FIG. 3. Theoretical radial concentration profiles for $r^{*\prime} = 0.5$ as a function of the column length.

A) $L = 2\ L_1$

B) $L = L_1$

C) $L = 0.5\ L_1$

D) $L = 0.125\ L_1$

E) $L = 0$

by Knox et al (2). Because it proved to be much less sensitive to the wall effect than regular columns, the second column studied in reference (3) has also been investigated in the present study. It consists of an 1.58 cm I.D. teflon column, 60 cms in length, dry packed with glass beads of 76 µm average diameter. The soft wall column was radially compressed as in (3, 7); the latteral pressure was usually kept at least 50 bars higher than the column operating pressure. The only difference between this experiment and the previous one (3) is in the injection device. In this experiment a plug flow injection was made. By using pieces of thin tubings of various I.D's, pludged concentrically into the column inlet, the diameter (r^*) over which the injection took place could be changed at will. The linear velocity of the injected plug was matched to that of the carrier by means of an auxiliary pump.

Since the goal of the experiment was to check eq. 29, it was experimentally convenient to carry out the measurements at relativelly large reduced velocity (even so the tendency is to use now moderate reduced velocity in L.C.). This had the advantage of minimizing the role of molecular diffusion as a broadening factor as well as to appreciably reduce the duration of the experiment.

The results reported here are related to a reduced velocity of 20 ($\nu = 20$); this corresponds to $Dr = 1.45 \times 10^{-5}$ $cm^2.s^{-1}$ and $Da = 1.23 \times 10^{-4}$ $cm^2.s^{-1}$ (see (3) for more on the Column's performance).

At this velocity the column length expressed in terms of L_1, is 1.75 ($L = 1.75\ L_1$).

Figure 4 displays the results for various r^*/R ratios. It can be seen that excellent agreement is obtained between calculated and experimental results for the error never exceeded 7%; this warrants the use of eq. 29 in prepscale L.C. conditions. Furthermore,

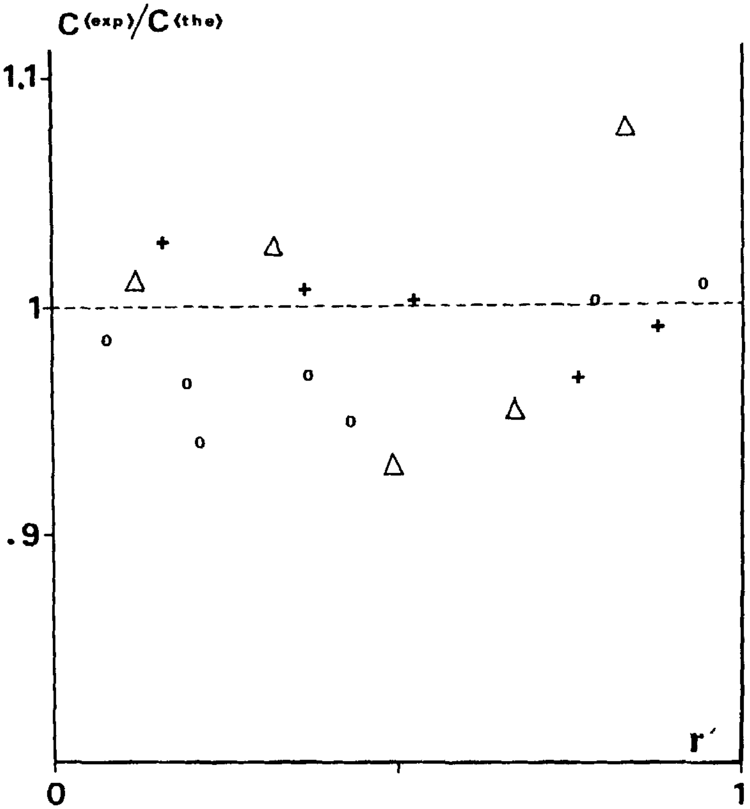

FIG. 4. Comparison of theoretical versus experimental local radial concentration for various r*' as a function of r'.

+ r*' = 0

Δ r*' = .25

0 r*' = .6

..... is the plot that should be obtained were theoretical and experimental in perfect agreement.

the wall effect is found not to affect the radial concentration profile as had been previously reported.

CONCLUSIONS

A priori computations of radial concentration profiles have proven to be feasible by means of equation 29. This is the first, but necessary, step toward optimisation of the injection mode prep-scale systems based on a compromise between injection size and wall-induced performance deterioration. This second phase is currently being investigated in our laboratory and will be reported shortly.

REFERENCES

1. Knox, J. H. and Parcher, J. F., Anal. Chem. 41, 1599 (1969).
2. Knox, J. H., Laird, G. R. and Raven, P. A., J. Chromatogr. 122, 129 (1976).
3. Eon, C. H., J. Chromatogr. 149, 29 (1978).
4. Klinkenberg, A, Krajenbrink, H. J. and Lauwerier, H. A., Ind. Eng. Chem. 45, 1202 (1953).
5. Angot, A., "Compléments de mathématiques", Masson Edt. Paris (France) 1972, chapter 7.
6. Fahien, R. W. and Smith, J. M., Amer. Inst. Chem. Eng. J. 1, 28 (1955).
7. Little, J. N., Cotter, R. L., Prendergast, J. A. and McDonald, P. D., J. Chromatogr. 126, 439 (1976).