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Relationship Between Apparent and True Molecular Weight in GPC

Part 1. A New Analytical Solution of the Tung's Axial Spreading Integral

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Summary

The analytical relationship between the molecular weight averages obtained from an experimental GPC elution curve and the true ones is calculated by use of one integration method in order to solve the convolution integral. The knowledge of these relationship signifies an useful tool to carry out critical considerations on the operation of different methods existing for the calculation of the spreading correction and for the elaboration of the calibration function.

In the calculation of the molecular weight and its distribution from a GPC elution curve, the determination of the calibration function and the correction necessary because of the instrumental spreading are the most relevant aspects which must be taken into account. To this purpose, several procedures use eq. (1), and the aim of this note is to analyse its applicability under different conditions which are known to prevail in the GPC method.

$$\begin{aligned}\overline{M}_{k,\text{apparent}} &= \int f(v).M(v)^k.dv \\ &= R \int W(y).\ M(y)^k.dy = R.\ \overline{M}_k\end{aligned} \qquad (1)$$

where

f(v) is the experimental elution curve.

M(v) is the experimental relationship between molecular weight and elution volume, i.e. the calibration function.

W(y) is the elution curve corrected for the instrumental spreading.

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$\overline{M}_{k,\text{apparent}}$ and $\overline{M}_k$ are the apparent molecular weight average calculated directly from the experimental elution curve, and the true one respectively.

R is the relationship betwen the apparent and the true molecular weight which includes characteristic parameters of the spreading and the calibration function. The limits between which all the integrals in this note are to be performed are the limits of the domain of definition of f(v) or W(y).

Eq. (1) had been used, explicitly or implicitly, with different purposes, f.e. :

a.- To correlate the apparent molecular weight average with the concentration (BERGER and SCHULZ 1970).

b.- To compare different correction methods for Gaussian and not-Gaussian spreading functions (HAMIELEC and RAY 1969, BALKE and HAMIELEC 1969).

c.- To obtain a calibration function using the concept of an "universal calibration" (AMBLER 1973, CANE and CAPACCIOLI 1978, SAMAY et al. 1978).

d.- To make possible the use of polymer samples having broad distributions in order to elaborate the calibration function by means of an iterative method (VRIJBERGEN et al. 1978).

etc.

The different uses of eq. (1), however, are depending on the "well behaviour" character of R, that means that R should contain terms which arise only from the calibration and from the spreading function. In order to ilustrate this point we make use of the formalism (TUNG 1966) which relate the experimental elution curve f(v) with the true one W(y) and with the spreading function g(y-v) by means of the convolution integral (2)

$$f(v) = \int W(y).g(y-v).dy \qquad (2)$$

Inserting eq. (2) into eq. (1) and using the Leibnitz's rule we obtain the following general expression for the apparent molecular weight average

$$\begin{aligned} \overline{M}_{k,\text{apparent}} &= \iint W(y).g(y-v).M(v)^k.dy.dv = \\ &= \int W(y).\ I_v(y)\ .\ dy \end{aligned} \qquad (3)$$

where

$$I_v(y) = \int g(y-v).M(v)^k.dv$$

The requirement for a "well behaviour" of R is full-filled when

$$I_v(y) = M(y)^k .L \qquad (4)$$

where L is independent from y.

Eq. (4) is, however, not a general one but depends on the type of the calibration and of the spreading function. To show this, let us consider a non-linear calibration function (5) and an asymetric spreading function (6) which are of sufficient generality to account for the most frequently founded situations in GPC analysis:

$$g(y-v) = \frac{1 + T\,\frac{(y-v)}{S}}{(2\pi)^{0,5}S} \exp[-(y-v)/S]^2/2 \qquad (5)$$

$$\ln M = A - Bv + C\,v^2 \qquad (6)$$

Substituting the eqs. (5) and (6) in the eqs. (3) and (4) results in the expressions

$$I_v(y) = F4.M(y)^{kZ}.\exp F3 \qquad (7)$$

and

$$\overline{M}_{k,\mathrm{apparent}} = (F1 + F2.\int y.W(y).M(y)^{kZ}.dy)\mathrm{Exp}\ F_3 \,(8)$$

where

$$F1 = Z^{0,5}((1+ZBkTS).\overline{M}_{kZ})$$

$$F2 = Z^{0,5}.T(1-Z)/S$$

$$F3 = Zk^2S^2(-2AC + B^2/2)$$

$$F4 = Z^{0,5}.(1+ T(\frac{y(1-Z)}{S} + SZkB))$$

$$Z = (1 - 2kCS^2)^{-1}$$

For a better understanding of these results, we discuss the different cases on which they can be applied:

1.- The chromatographic columns do work ideally (S=T=0):

$$\overline{M}_{k,\mathrm{apparent}} = \overline{M}_k$$

2.- The dispersion is Gaussian and the calibration linear (T=C=0):

$$\bar{M}_{k,\text{apparent}} = \bar{M}_k \cdot \exp\,(S^2k^2B^2/2)$$

This result was formerly derived by HAMIELEC and TAY (1969) using the bilateral Laplace transform.

3.- The dispersion is Gaussian and the calibration function is not linear (T=0):

$$\bar{M}_{k,\text{apparent}} = Z^{\,0,5}\ \bar{M}_{kZ}\ \exp(Zk^2S^2(-2AC+B^2/2))$$

In this case, the apparent and the true molecular weight average are of different types. This means that it is not possible to define R properly because the relationship $\bar{M}_{kZ} / \bar{M}_k$, necessary to know in order to correlate $\bar{M}_{k,\text{apparent}}$ with $\bar{M}_k$, is a function of the molecular weight distribution.

4.- Not-Gaussian dispersion and linear calibration (C=0):

$$\bar{M}_{k,\text{apparent}} = \bar{M}_k(1+TSkB).\exp(S^2k^2B^2/2)$$

For the particular case that the exponential factor may be approximated by a linear expression, HAMIELEC and BALKE (1969) derived this equation by an euristic approach. Their skewing factor sk (Eq.(21) of HAMIELEC and BALKE 1969) is given by

$$sk = -2BTS$$

5.- Not-Gaussian dispersion and not linear calibration function:

In this case, eq. (8) shows that there is no relationship between the apparent and the true molecular weight average which is simultaneously independent from the details of the molecular weight distribution W(y).

The above shown results demonstrate that the relationship between apparent and the true molecular weight average are not only governed by the calibration and the spreading function, but may depend also on distinctive features of the molecular weight distribution. The method elaborated in the present communication allow to analyse each case and to decide which procedure must be used when eq. (1) is applied for calibration or spreading correction purposes.

As an example of such an analyse we can examinate in greater detail the case of a Gaussian spreading function and a not linear calibration function where the apparent and the true molecular weight average are not of the same type (Case 4 above). Experimentally we can obtain only two molecular weight averages which are able to be used as true averages, namely $\bar{M}w$ and $\bar{M}n$ which correspond to $\bar{M}_{kZ}$ with kZ=1 and to $(\bar{M}_{kZ})^{-1}$ with kZ = -1 respectively. Therefore, in order to correlate with $\bar{M}w$ we must calculate $\bar{M}_{k,\mathrm{apparent}}$ from the experimental elution curve where $k=Z^{-1} = 1-2kCS^2$ or $k=(2CS^2-1)^{-1}$, and in order to correlate with $\bar{M}n$ it is necessary to calculate $\bar{M}^{-1}_{k,\mathrm{apparent}}$ where $k = -Z^{-1}= 2kCS^2 -1$ or $k=(1+2CS^2)^{-1}$.

The equation (3) can, of course, be applied to any calibration or spreading function other than the considered here.

References

AMBLER M.R.: J.Polym.Sci. Polym.Chem.Ed. 11,191 (1973)
BALKE S.T. and HAMIELEC A.E.: J.Appl.Polym.Sci., 13, 1381 (1969)
BERGER K.C. and SCHULZ G.V.: Makromol.Chem. 136, 221 (1970)
CANE F. and CAPACCIOLI T.: European Polym.J. 14, 185 (1978)
HAMIELEC A.E. and RAY W.H.: J.Appl.Polym.Sci. 13,1319 (1969)
SAMAY G., KUBIN M. and PODESVA J.: Angew.Makromol.Chem. 72, 185 (1978)
TUNG L.H.: J.Appl.Polym.Sci. 10, 375 (1966)
VRIJBERGEN R.R., SOETEMAN A.A. and SMIT J.A.M.: J.Appl. Polym.Sci. 22, 1267 (1978)

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