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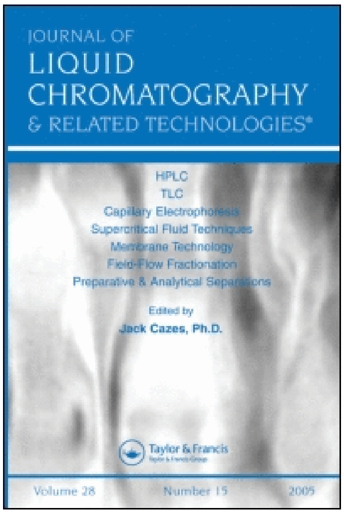

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GEL PERMEATION CHROMATOGRAPHY : PROBLEMS CAUSED BY POLYDISPERSITY IN THE APPLICATION OF THE BENOIT'S UNIVERSAL PARAMETER.

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ABSTRACT

The application of the Benoit's universal calibration $Ln[\eta].M = f\ (Ve)$ *in GPC is examined through the general problem of polydispersity, when an attempt is made to represent a mixture of different macromolecules by a single parameter* $[\eta].\overline{M}$. *The recently proposed* $[\eta].Mn$ *parameter leads to an ambiguous interpretation of universal calibration ; we try to classify the problems into three families. For the comparison of linear homopolymers of different polydispersities only by their peak apex, there is no general form of universal parameter. In the characterization of heterogeneous polymers, such as branched polymers or copolymers,* $[\eta]_i.\overline{Mn}_i$ *is the form to be used in the GPC calculations. It leads to* $[\eta]$ *and* $\overline{Mn}$ *when using the GPC-viscometer coupling but* $\overline{Mw}$ *can only be strictly obtained by the light scattering coupling. Finally, the apparent polydispersity caused by instrumental spreading cannot generally be represented by the* $[\eta]_i.Mn_i$ *parameter.*

INTRODUCTION

In the early days of Gel Permeation Chromatography (GPC) (1), it already appeared that macromolecule separation was not directly related to molecular weight, but was, rather, dependent upon molecular size. To take this effect into account, some parameters were successively proposed :

- *the extended chain length and the subsequent Q factor (2).*
- *the product* $[\eta]^{1/3}.M^{1/2}$ *(3) where* $[\eta]$ *is the limiting viscosity number and M the molecular weight. Besides their lack of theoretical*

basis, those parameters do not exhibit the universal character required for the interpretation of GPC data. In 1966, Benoit et al (4, 5) demonstrated the universality of the product $[\eta].M$ *as a calibration concept. Besides its simplicity, this parameter is the most suitable with regard to the basic support of the Flory's theory (6) for linear polymers :*

$$[\eta] = \phi'.\frac{R_G^3}{M}$$

where R_G *is the polymer radius of gyration in solution, and Einstein's equation (7) giving the viscosity of spherical particles in suspension :*

$$[\eta] = K.\frac{V}{M}$$

where V *is the particle volume. Analogously, Sadron (8) gave a definition of the macromolecule hydrodynamic volume* V_H *:*

$$[\eta].M = K.V_H$$

The parameter $[\eta].M$ *is therefore proportional to the equivalent volume of a macromolecule in a stream and assuming that the GPC separation is only based upon size exclusion, it can be directly linked to the elution volume by a "universal calibration curve". Except for some highly branched polymers (9, 10), this concept has been widely verified and is now unanimously accepted.*

Using this single assumption, we have examined the influence of polydispersity in the application of universal calibration. This parameter is not taken into account in the theory but often confuses the interpretation of GPC data. Problems related to polydispersity were encountered in three different ways we have successively examined :

- *comparison of polymers of different polydispersities*
- *polydispersity caused by structural or chemical heterogeneity*
- *polydispersity occuring from instrumental spreading.*

COMPARISON OF POLYMERS OF DIFFERENT POLYDISPERSITIES

General case.

This is the most frequent problem. It is encountered every time attempts are made to characterize the behaviour of a macromolecular sample by a single point of the curve $Ln[\eta].M = f(Ve)$. *It concerns the molecular weight standards required to establish the calibration curve but mainly the comparison of polymers with different polydispersities using the universal calibration concept. We will assume here that axial dispersion caused by instrumental spreading is negligible.*

Whereas a single molecular weight M *is expected, a set of molecular weights* M_j*, having a limiting viscosity number* $[\eta]_j$ *is practically considered, the chromatogram spreading out a certain range in elution volumes. As it is impossible to determine any set of values* $(M_j, [\eta]_j, Ve_j)$ *corresponding to the monodisperse fraction* j *for the application of the universal calibration concept, we have to use a set of mean values. Some are directly measured, such as :*

- *the number and weight-average molecular weights* $\overline{Mn}$, $\overline{Mw}$
- *the peak elution volume* Ve_p *and, very rarely, the weight-average elution volume* $\overline{Ve}_w$ *(11)*
- *the limiting viscosity number* $[\eta] = \dfrac{\sum_j [\eta]_j C_j}{\sum_j C_j}$

The average $[\eta]$ *being thus stated, the only coherent set of values is, accordingly (12) :* $[\eta]$*, the viscometric average molecular weight* $\overline{Mv}$ *and* Ve_v *elution volume of the molecules* j *such as* $M_j = \overline{Mv}$*. Unfortunately, this only valid solution :*

$$\ln[\eta].\overline{Mv} = f(Ve_v)$$

is inaccessible by experiment. It is, then, necessary to find the best approach. Some as :

$$\ln[\eta].\overline{Mw} = f(Ve_p)$$

or

$$\ln[\eta]\sqrt{\overline{Mn}.\overline{Mw}} = f(Ve_p)$$

are the most widely used. Recently, $[\eta].Mn$ *was proposed (13) as the general parameter of universal calibration ; that leads to the confusion of considering* $[\eta].\overline{Mn}$ *to represent the behaviour of a broad distribution. This form, as any form such as* $\ln[\eta].\overline{Mx} = f(Ve_p)$ *has no theoretical basis because no average molecular weight associated with the intrinsic viscosity and the peak elution volume can represent the universal calibration concept. However, we shall demonstrate that simple forms can be used for some models of molecular weight distribution : the Wesslau distribution, and the Schulz distribution.*

Case of the Wesslau distribution.

This simple model can be considered as a good approximation of the distribution curve of some macromolecular samples. It is expressed by :

$$W(LnM) = \frac{1}{\beta\sqrt{\pi}} . \exp\left(- \frac{1}{\beta^2} . \ln^2 \frac{M}{M_p}\right)$$

where $W(LnM)$ *is the weight fraction,* M_p*, the peak molecular weight* *and β, a function of the distribution width. Average molecular weights are easily obtained by :*

$$\overline{Mn} = M_p.\exp(-\frac{\beta^2}{4})$$
$$\overline{Mv} = M_p.\exp(a\frac{\beta^2}{4})$$
$$\overline{Mw} = M_p.\exp(\frac{\beta^2}{4})$$

where a is the exponent of the Mark-Houwink relationship :

$$(\eta) = K\overline{Mv}^a$$

Consequently, we obtain : $M_p = \sqrt{\overline{Mn}.\overline{Mw}}$

By using this peak molecular weight, M_p*, and the corresponding peak elution volume* Ve_p*, the viscosity to be used is :* $(\eta)_p = KM_p{}^a$ *, which is different from the limiting viscosity number :*

$$(\eta) = K\overline{Mv}^a = KM_p^a.\exp(a^2.\frac{\beta^2}{4}) = (\eta)_p.\exp(a^2.\frac{\beta^2}{4})$$

Accordingly, the simultaneous use of (η), M_p *and* Ve_p *is not suitable. In order to apply* (η)*, which is the only value available, we can write :*

$$(\eta)_p.M_p = (\eta).\exp(-a^2.\frac{\beta^2}{4}).M_p$$

which gives the expression of the average molecular weight $\overline{M}$ *to be used :*

$$\overline{M} = M_p.\exp(-a^2.\frac{\beta^2}{4})$$

or

$$\overline{M} = \overline{Mn}^{\frac{1+a^2}{2}}.\overline{Mw}^{\frac{1-a^2}{2}}$$

This expression can be simplified by introducing the polydispersity index $I = \frac{\overline{Mw}}{\overline{Mn}}$ *:*

$$\overline{M} = \overline{Mn}.I^{\frac{1-a^2}{2}} = \overline{Mw}.I^{\frac{-1-a^2}{2}}$$

Consequently, in the case of the Wesslau distribution, the correct form of the universal calibration is :

$$\ln((\eta).\overline{Mn}.I^{\frac{1-a^2}{2}}) = f(Ve_p)$$

As this equation is difficult to apply, we have examined the errors introduced when using the classical approximations $(\eta).\overline{Mn}$, $(\eta).\overline{Mw}$ *and* $(\eta).\sqrt{\overline{Mn}.\overline{Mw}}$ *plotted in Figure 1. The errors are :*

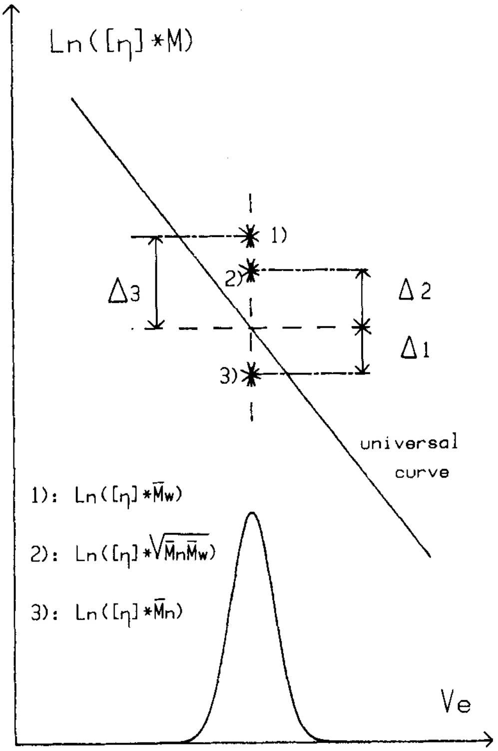

Figure 1 : Errors introduced by the classical approximations in the case of the Wesslau distribution.

for $[\eta].\overline{Mn}$: $\Delta_1 = -\frac{1}{2}\ \ln I.(1-a^2)$

for $[\eta].\sqrt{\overline{Mn}.\overline{Mw}}$: $\Delta_2 = \frac{1}{2}\ \ln I.a^2$

for $[\eta].\overline{Mw}$: $\Delta_3 = \frac{1}{2}\ \ln I.(1+a^2)$

The parameter $[\eta].\overline{Mw}$ *obviously appears to be the worst one. The best approach depends upon the Mark Houwink exponent value a.*
when $a < 0.7$ *it is* $[\eta]\sqrt{\overline{Mn}.\overline{Mw}}$
when $a > 0.7$ *it is* $[\eta].\overline{Mn}$

In addition, $[\eta].\overline{Mn}$ *is only strictly exact when* $a = 1$*, which is a limiting form rarely encountered. Finally, we notice that, for* *the classical value a = 0.7 (i.e.polystyrene in THF), the universal calibration parameter is :*

$$(\eta).\overline{Mn}.I^{0,25} \quad \text{or} \quad (\eta).\overline{Mw}.I^{-0,75}$$

As an example, let us consider the situation when two polymers of different polydispersities, $I \sim 1$ *and* $I \sim 2$*, having the same peak elution volume, are compared. In using the* $(\eta).\overline{Mn}$ *parameter, the* $\overline{Mn}$ *value is found to be approximatly 20% too high. Conversely, when applying the* $(\eta).\overline{Mw}$ *parameter, an incorrect value of* $\overline{Mw}$ *about 40% too small is obtained.*

Case of the Schulz distribution.

The Schulz distribution (15) is theoretically calculated in classical cases of polymerization or polycondensation. This model can represent the distribution curve of an important portion of macromolecular samples.

Its expression is :

$$W(M) = \frac{1}{\Gamma(1+\nu)}\,\gamma^{\nu+1}M^{\nu}.\exp(-\gamma M)$$

where: - Γ *is the classical gamma function :*

$$\Gamma(n) = \int_0^{\infty} e^{-x}x^{n-1}dx$$

- ν *and* γ *are parameters related to the average molecular weights as follows :*

$$\overline{Mn} = \nu/\gamma$$

$$\overline{Mw} = (\nu+1)/\gamma$$

$$\overline{Mw}/\overline{Mn} = 1 + 1/\nu$$

The viscosity-average molecular weight $\overline{Mv}$ *can be easily calculated (a is the Mark-Houwink exponent) :*

$$\overline{Mv} = \frac{1}{\gamma}\left[\frac{\Gamma(1+\nu+a)}{\Gamma(1+\nu)}\right]^{\frac{1}{a}}$$

In GPC, the logarithmic shape of elution chromatograms leads to the peak representation :

$$W(\ln M) = \frac{1}{\Gamma(1+\nu)}.\gamma^{\nu+1}M^{\nu+1}\exp(-\gamma M)$$

In this case, the weight-average molecular weight $\overline{Mw}$ *is located at the peak apex, whatever the values of the two parameters* ν *and* γ *may be.*

As we have the peak elution volume Ve_p *and the peak molecular weight* $M_p = \overline{Mw}$*, the intrinsic viscosity at the peak apex is :*

$$(\eta)_p = K.\overline{Mw}^a$$

When using the limiting viscosity number (η)*, the average molecular weight* $\overline{M}$ *to be used is then defined by :*

$$(\eta).\overline{M} = K\overline{Mw}^{\,a+1}$$

With the above mentioned $\overline{Mv}$ *value, it comes :*

$$\overline{M} = \overline{Mw}.(\nu+1)^a.\frac{\Gamma(1+\nu)}{\Gamma(1+\nu+a)}$$

Such a result is not practically easy to use, but calculation shows that the $(\nu+1)^a.\frac{\Gamma(1+\nu)}{\Gamma(1+\nu+a)}$ *factor remains, in the current cases, near unity. For example :*

- *when* $\nu = 1$*, the Schulz distribution is called the most probable distribution. The mean* $\overline{M}$ *to be used is :*

$$\overline{M} = \overline{Mw}.\frac{2^a}{\Gamma(2+a)}$$

where the $2^a/\Gamma(2+a)$ *parameter varying from 1 (for* $a = 1$*) to 1.06 (for* $a = 0.5$*).*

- $\nu = 2$ *corresponds to the vinyl polymerization when termination is only due to radical combination.*

Here : $\overline{M} = \overline{Mw}.\frac{2.3^a}{\Gamma(3+a)}$

with $1_{(a=1)} \leqslant \frac{2.3^a}{\Gamma(3+a)} \leqslant 1.04_{(a=0.5)}$

As a result, in the case of the Schulz distribution, the use of the relationship :

$$\ln((\eta).\overline{Mw}) = f(Ve_p)$$

is clearly the best one. It never introduces errors greater than a few percent, contrary to the Wesslau distribution.

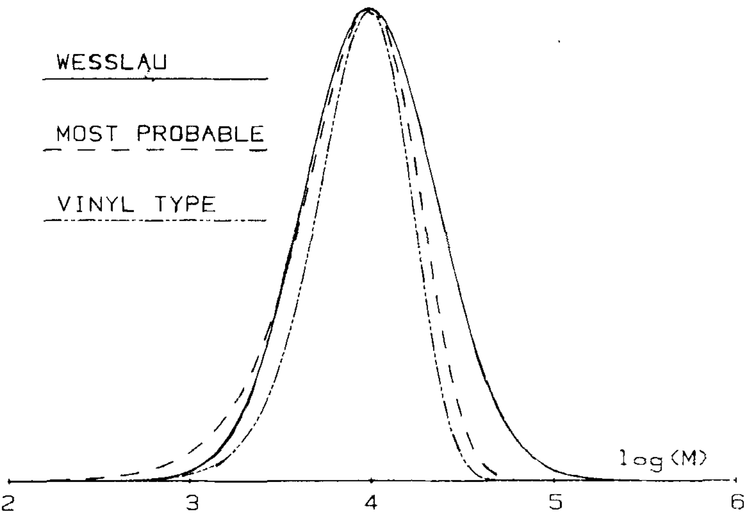

Figure 2 : Comparison of three model chromatograms with the same peak molecular weight.

As a conclusion of this first part, we have shown the importance of the molecular weight distribution in the use of the Benoit's calibration concept. Figure 2 is an example of the distributions we have developed here.

POLYDISPERSITY CAUSED BY STRUCTURAL OR CHEMICAL HETEROGENEITY.

The principle of macromolecule separation according to hydrodynamic volume leads to a separation of linear homopolymers by molecular weight. But in the other cases (branched polymers, copolymers, ...) many very different molecules can exhibit the same hydrodynamic volume.

Accordingly, each fraction in the detector cell has a polydispersity in molecular weight and one detector can only provide a mean value $\overline{M_i}$ *as a function of the elution volume* Ve_i*. To get more information on the molecular weight distribution, a second detector analyzing another polymer property must be coupled to the concentration detector.*

The GPC - viscometer coupling.

This is the case when an on-line viscometer (14) is added to the GPC instrument to provide the eluant viscosity continuously. We herein *mention the papers of Constantin (16) and Hamielec (13), related to branched polymer analysis. At the elution volume* Ve_i, *a mixture of different macromolecules* $M_{i1}, M_{i2} \dots M_{ij}$ *with the same hydrodynamic volume* $([\eta].M)_i$ *are present in the detector cell (band broadening is again neglected) :*

$$[\eta]_{i1}.M_{i1} = [\eta]_{i2}.M_{i2} = \dots [\eta]_{ij}.M_{ij} = ([\eta].M)_i$$

As the viscometer measures :

$$[\eta]_i = \frac{\sum_j [\eta]_{ij}.C_{ij}}{\sum_j C_{ij}}$$

that is :

$$[\eta]_i = ([\eta].M)_i . \frac{\sum_j \frac{C_{ij}}{M_{ij}}}{\sum_j C_{ij}}$$

we obtain :

$$([\eta].M)_i = [\eta]_i.\overline{Mn}_i$$

This particular result means that, when measuring continuously the viscosity $[\eta]_i$, *the universal calibration involves the number-average molecular weight of each fraction* $\overline{Mn}_i$. *Consequently, by integrating across the whole chromatogram, only the number-average molecular weight* $\overline{Mn}$ *can be strictly obtained. But practically, the other average molecular weights are calculated with a non-significant error compared to other experimental errors (16).*

Conclusively, $[\eta]_i.\overline{Mn}_i$ *and not* $[\eta].\overline{Mn}$, *appears to be the real parameter of the universal calibration in this case.*

The GPC - light scattering coupling.

The problem is different here, the weight-average molecular weight $\overline{Mw}_i$ *being continuously determined. The application of the universal calibration must lead to the determination of the limiting viscosity number (17).*

With $\overline{Mw}_i = \frac{\sum_j M_{ij}.C_{ij}}{\sum_j C_{ij}}$ *and* $M_{ij} = \frac{([\eta].M)_i}{[\eta]_{ij}}$

we see that :

$$([\eta].M)_i = \frac{\sum_j C_{ij}}{\sum_j \frac{C_{ij}}{[\eta]_{ij}}} .\overline{Mw}_i$$

That is, dividing $([\eta].M)_i$ *by* $\overline{Mw}_i$*, we arrive at an apparent viscosity :*

$$[\eta]'_i = \frac{\sum_j C_{ij}}{\sum_j \frac{C_{ij}}{[\eta]_{ij}}}$$

which is an unusual average viscosity, different from the classical limiting viscosity number $[\eta]_i$*. In replacing* $([\eta].M)_i$ *by its previously demonstrated value* $[\eta]_i.\overline{Mn}_i$ *and using the instantaneous polydispersity* $I_i = \overline{Mw}_i/\overline{Mn}_i$ *;*

We have : $[\eta]'_i = [\eta]_i/I_i$

This simple result shows that the GPC-light scattering coupling leads to the real intrinsic viscosity $[\eta]_i$ *for linear homopolymers* $(I_i = 1)$*, but that an apparent viscosity* $[\eta]'_i < [\eta]_i$ *is obtained for polymers exhibiting a polydispersity in branching or composition. The higher the heterogeneity, the greater the difference between the apparent and the real viscosity.*

Multidetection.

The above results lead to the conclusion (13) that the dual GPC-viscometer-light scattering coupling is the only way to strictly determine the different structural parameters of complex polymers such as low density polyethylene. The variations of $[\eta]_i$*,* $\overline{Mn}_i$*,* $\overline{Mw}_i$ *can then be measured as a function of the hydrodynamic volume allowing the determination of the instantaneous polydispersity and, therefore, the calculation of* $[\eta]$*,* $\overline{Mn}$ *and* $\overline{Mw}$ *by integrating across the whole chromatogram.*

POLYDISPERSITY OCCURING FROM INSTRUMENTAL SPREADING.

Finally, we examine the effects of instrumental spreading, hitherto neglected, that lead to an apparent polydispersity in the detector cell. In the simple case of a linear homopolymer, at the elution volume Ve_i*, although we would expect a single molecular weight* M_i*, a mixture of various macromolecules with close hydrodynamic volumes is present. For each macromolecule j, the hydrodynamic volume equation gives :*

$$[\eta]_{ij}.M_{ij} = K\, V_{Hij}$$

The limiting viscosity number $[\eta]_i$ *can then be written :*

$$[\eta]_i = \frac{\sum_j \frac{K\, V_{Hij}}{M_{ij}} \, . \, C_{ij}}{\sum_j C_{ij}}$$

and using the number n_{ij} *of macromolecules j :*

$$[\eta]_i = K \, \frac{\sum_j V_{Hij}\, n_{ij}}{\sum_j n_{ij}} \, . \, \frac{\sum_j n_{ij}}{\sum_j n_{ij} M_{ij}}$$

that can be expressed by :

$$[\eta]_i.\overline{Mn}_i = K(\overline{V_{Hn}})_i$$

where $(\overline{V_{Hn}})_i$ *is the number-average hydrodynamic volume. This relationship, previously demonstrated by Newman et al (18) could lead us to use the* $[\eta]_i.\overline{Mn}_i$ *parameter to take into account the instrumental spreading. Unfortunately, except for some particular shape of spreading distribution, the hydrodynamic volume* V_{Hi} *is different from the number average* $(\overline{V_{Hn}})_i$ *of the mixture. Consequently, the average molecular weight* $\overline{M}_i$*, deduced from universal calibration, is not the number-average* $\overline{Mn}_i$*, but a non-classical average near* M_i*, depending upon the spreading function that does not permit the correction of band spreading.*

CONCLUSION

We find a complex situation, especially for the simple comparison between polymers with different polydispersities in universal calibration. Using the experimental values of the intrinsic viscosity $[\eta]$ *and the peak elution* Ve_p*, there is no general rule that leads to a single average molecular weight* $\overline{M}$ *to point out a general universal parameter* $[\eta].\overline{M}$ *. In the Wesslau distribution :* $\overline{M} = \overline{Mw}.I^{\frac{-1-a^2}{2}}$ *rather different from* $\overline{Mw}$ *in practice, but in the Schulz distribution* $\overline{M} \simeq \overline{Mw}$*. Conclusively, the knowledge of the distribution shape and the Mark Houwink exponent are required to select the most suitable universal parameter.*

By contrast, in the analysis of heterogeneous polymers (branched or copolymers), $[\eta]_i.\overline{Mn}_i$ *is the real information provided by the* *universal calibration and must be used in the calculation of molecular weights. Viscometric coupling specifically gives* $[\eta]$ *and* $\overline{Mn}$*, whereas, with light-scattering coupling only* $\overline{Mw}$ *is correctly determined. Both detectors are required to achieve the complete characterization of complex polymers.*

Finally, $[\eta]_i.\overline{Mn}_i$ *cannot be used for the correction of the apparent polydispersity in the detector cell caused by instrumental spreading.*

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