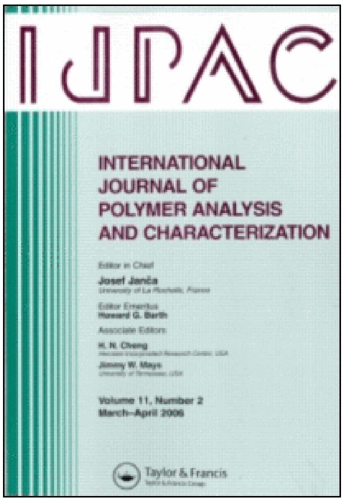

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# Discussion on Round-Robin Testing in Size Exclusion Chromatography Using Polyamides as an Example

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# Discussion on Round-Robin Testing in Size Exclusion Chromatography Using Polyamides as an Example

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The results of the validation of a high-temperature steric exclusion chromatography (HTSEC) method using benzyl alcohol for the characterization of polyamides 6, 11 and 12 are given. The validation consists of the statistical evaluation of the method in term of repeatability and of intralaboratory reproducibility from a collection of data on one commercial PA11. The need of a further step for validation of this method is discussed to examine different technical aspects and, to validate the method through round-robin testing.

*Keywords:* Polyamides, HTSEC, validation, round-robin testing

## INTRODUCTION

Size exclusion chromatography (SEC) is a useful tool for the basic characterization of polymeric materials in terms of the molecular weight distribution. There is a need to access the true molecular weight distribution and, in general, the universal calibration approach (UC) can be use [1] with the necessity that Mark-Houwink constants (M-H) of standards and samples in the solvent and at the temperature of the SEC experiment. In case of UC failure or unknown M-H constants, coupling of SEC with light scattering or with a viscometer enables one to derive true molecular weights without calibration or the need to

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know M-H constants. However, in spite of the interest of multidetection, most routine analyses are performed simply with a concentration detector.

Although SEC is widely used, for example, in macromolecular synthesis, production control, and polymer ageing studies, little effort has been given, to our knowledge, for standardization of methods [2,3], that is, for interlaboratory validation. This is probably due to two factors. Apart from classical room temperature SEC in THF, most methods are specific to a class of polymers or to individual ones. These methods are developed and used as internal company methods by polymer manufacturers who have a good knowledge of their polymers. However, as these methods need expensive chromatographic systems or specially trained operators, and are, in general, difficult to apply by customers. Round robin tests, however, require much planning.

In regard to polyamides, various solvent systems [4–9] or even derivatization methods [10] have been proposed and a review was recently published [11]. The main problem analysts have with this class of polymers is that a "universal" solvent can only be found using hazardous or/and expensive solvents and insofar the chromatographic systems have to be specially adapted [9]. However, benzyl alcohol, was proposed by Marot and Lesec [7,8] for the SEC characterization of polyamides 6, 11 and 12 (PA6, PA11 and PA12) at 130°C. From our experience, polyamides 6-6 and 6-12, for instance, are not soluble in this solvent without adding a cosolvent.

At IFP (Institut Français du Pétrole), benzyl alcohol is used for the characterization of PA6, PA11 and PA12. This paper describes the statistical evaluation of this solvent for internal validation and discusses briefly interlaboratory validation that could be used for thoroughly testing this method.

## EXPERIMENTAL

The chromatographic system was a Waters 150C equipped with PLgel Mixed B columns of 60-cm length (Polymer Lab., UK); optionally PLgel 500Å of 30-cm length was added. The eluant as well as the solvent for polymers was benzyl alcohol (Prolabo, France) stabilized with 2,6-di-*tert.*-butyl-4-methyl-phenol of purity 99% *m/m* (Merck, Darmstadt, Germany). The operating conditions were as follows: flow rate 1 mL/min, temperature 130°C, injection volume 180 µL, concentration of samples 1 to 1.5 mg/mL. The polyamide 11 sample was obtained from ATOCHEM (France). The following standards were used: PS, PEO, PEG, PTHF.

The acquisition of raw data was done using a HP1000 (Hewlett Packard, Avondale, USA). Data treatment was done using SEC software developed at IFP. The statistical analysis was done using the software Statgraphics (Manugistic, Rockville MA, USA).

## RESULTS AND DISCUSSION

The Mark-Houwink constants were obtained from Marot's work [7] and are reported in Table I. They were used to obtain a calibration table for PA6, PA11 and PA12 according to Equation (1) (see example in Table II).

$$\mathrm{LogM_{PA}} = \frac{1}{1 + a_{PA}} \cdot \mathrm{Log}\frac{K_S}{K_{PA}} + \frac{1 + a_S}{1 + a_{PA}} \cdot \mathrm{LogM_S} \qquad (1)$$

Where the following values are known:

a and K M-H constants
M molecular weight
S: standard
PA polyamide

An example of PA11 calibration curve is shown in Figure 1.

### Statistical Evaluation

For established analytical methods, the precision can be estimated through ring tests and two extreme values are determined: the repeatability (r) and the reproducibility (R). The repeatability describes the precision obtained at the

TABLE I Mark-Houwink constants used for universal calibration [7]

| *Polymer* | *K* *(mol cm$^3$ g$^{-2}$)* | *a* |
|---|---|---|
| PS | 0.0288 | 0.61 |
| PEO | 0.0135 | 0.78 |
| PTHF | 0.02 | 0.77 |
| PEG | 0.0238 | 0.75 |
| PA6 | 0.0745 | 0.63 |
| PA11 | 0.095 | 0.63 |
| PA12 | 0.071 | 0.64 |

Table II Example of calibration table. Molecular weights in g/mol. Polyamides molecular weights are obtained from universal calibration using both molecular weights of standards and Mark-Houwink constants in Table I

| *Retention time (min)* | $M_{PS}$ | $M_{PEO}$ | $M_{PTHF}$ | $M_{PEG}$ | $M_{PA11}$ | $M_{PA6}$ | $M_{PA12}$ |
|---|---|---|---|---|---|---|---|
| 12.53 | 3840000 | | | | 1533020 | 1779560 | 1678590 |
| 12.77 | 2650000 | | | | 1062770 | 1233680 | 1166280 |
| 13.56 | 980000 | | | | 397850 | 461830 | 439230 |
| 13.73 | 770000 | | | | 313520 | 363940 | 346630 |
| 14.25 | | 112300 | | | 98920 | 114820 | 110130 |
| 14.46 | 330000 | | | | 135770 | 157610 | 150880 |
| 14.90 | | 50400 | | | 41240 | 47870 | 46160 |
| 14.98 | | | 74600 | | 75180 | 87170 | 83850 |
| 15.17 | | 36000 | | | 28558 | 32038 | 33150 |
| 15.22 | 120000 | | | | 49990 | 58030 | 55890 |
| 15.49 | | | 37600 | | 35730 | 41470 | 40030 |
| 15.60 | | | | 23000 | 20610 | 23920 | 23170 |
| 15.70 | 66000 | | | | 27700 | 32150 | 31080 |
| 16.09 | | | | 12600 | 10800 | 12540 | 12190 |
| 16.46 | 30300 | | | | 12840 | 14900 | 14470 |
| 16.77 | | | 9500 | | 8020 | 9310 | 9070 |
| 17.13 | | | 6000 | | 4870 | 5650 | 5520 |
| 17.16 | | | | 4250 | 3360 | 3900 | 3820 |
| 17.60 | 9200 | | | | 3950 | 4590 | 4490 |
| 18.07 | | | | 1470 | 1080 | 1230 | 1250 |
| 18.51 | | | 1300 | | 925 | 1060 | 1074 |
| 18.71 | 3100 | | | | 1350 | 1570 | 1540 |
| 18.92 | | | | 600 | 410 | 470 | 480 |

best possible conditions, that is in the same laboratory, by the same operator with the same apparatus and in a short time-interval. The reproducibility describes the precision obtained in the most adverse conditions, that is, in different laboratories, by different operators with different apparatus and at different times. However, as indicated by Hartmann [12], and also considered in ISO5725 [13], intermediate conditions do exist. As a matter of fact, the dispersion of measurements in one laboratory can also be estimated in non repeatability conditions and, in such a case, the precision value must be intermediate between $r$ and $R$. This precision is called between-runs precision or factor-different intermediate precision as a number of factors can vary within a laboratory (time, calibration, operators, apparatus performances, etc.).

This factor-intermediate precision is of great interest for laboratories using internal method (not subjected to the ring test) as it gives an estimation of the precision of the method in the most adverse internal conditions.

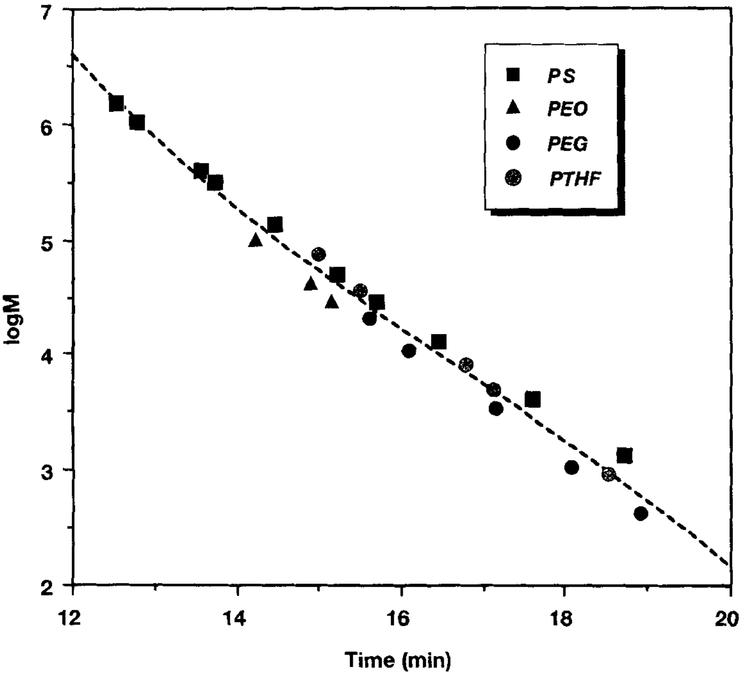

FIGURE 1 Calibration curve for PA11 using one PLgel mixed B column.

For the HTSEC method, we have estimated both the repeatability and the factor-intermediate precision that we called intralaboratory reproducibility ($R_L$). These values have been determined using a commercial polyamide 11 as a reference sample that was, in general, injected twice at each run. The data were collected during a long period of time (three years) and corresponding box and wiskers plots are shown in Figure 2a and 2b. Figure 2a shows an increase in $M_n$ values over time (test number); since no reason was found to explain this observation, all original data were taken into account for the analysis. The statistical treatment was done by an analysis of variance (ANOVA) in the same way as for the ring tests. The ANOVA extracts two contributions of the dispersion of measurements. First, the within-run dispersion which directly gives the repeatability; second, the between-runs dispersion from which is derived the intralaboratory reproducibility. The outliers were eliminated according to ref. [13].

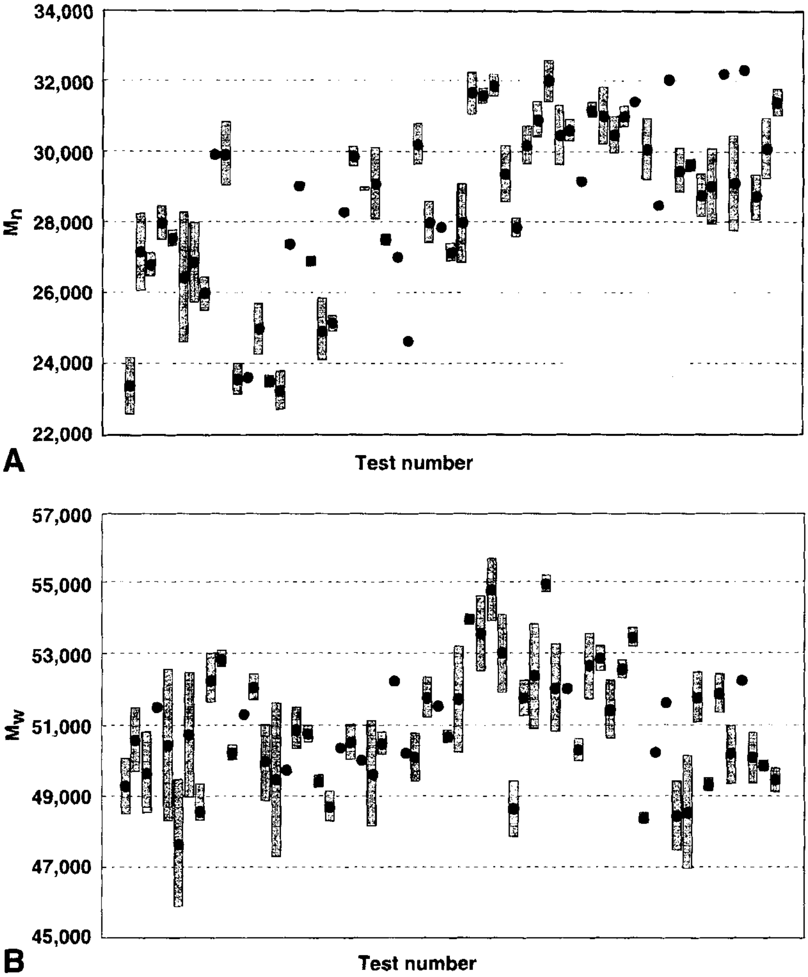

FIGURE 2 Box and wiskers plots for molecular weights averages of PA11 reference sample. a) $M_n$ and b) $M_w$.

TABLE III Repeatability and intralaboratory reproducibility

| *Molecular weight average* | $r$ | $R_L$ |
|---|---|---|
| $M_n$ | $0.09 \times M_n$ | $0.24 \times M_n$ |
| $M_w$ | $0.07 \times M_w$ | $0.10 \times M_w$ |

The precision for the determination of $M_n$ and $M_w$ in terms of $r$ and $R_L$ are reported in Table III. Repeatability and intralaboratory reproducibility are quite satisfactory for $M_w$. However, for $M_n$ the precision is poorer and a factor of three is found between $R_L$ and $r$ which is probably too large for one laboratory. A ratio of two to five between reproducibility and repeatability is considered acceptable from ring tests and consequently the ratio between $R_L$ and $r$ should be lower.

## Requirements of Round-Robin Testing

The internal validation of the method shows that the proposed method for characterizing three types of polyamides is acceptable. However, for comparison of data from different laboratories and for eventual standardization, the following study is required:

- The basis of the method is universal calibration and consequently an agreement on the values of Mark-Houwink constants should be found. That step could imply a new viscometric measurement on samples of different origins, and multidetection SEC experiments both on standards and polyamides samples.
- The calibration curve should be re-examined both in term of choice of standards and of curve fitting.
- The nature of the columns and performance criteria should be examined and defined either according to ref. [2] or ref. [14].
- The method should be validated for the three types of polymers and in a wider range of molecular weights.
- For low-molecular-weight fraction, the effect of dn/dc variation should be examined.
- Finally, the statistical evaluation of repeatability and reproducibility should be done.

## CONCLUSION

The internal validation of an SEC method used at IFP for the characterization of polyamide 6, 11 and 12 has been presented. Since this method uses a nontoxic solvent and is applicable to three polyamides, it could be used as the basis for round-robin evaluation. This paper could constitute a basis for round-robin testing which could be organized within the IUPAC Working Party IV.2.2. At least eight laboratories would be required for statistical evaluation.

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