Measuring intraday and interday precision of GPC-SEC analysis data

Application

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Abstract

The daily (intraday) and day-to-day (interday) precision of M_n and M_w molecular weight data obtained by GPC-SEC has increased significantly over the past years. This Application Note describes what is possible nowadays in the area of intraday and interday precision of molecular weight data using state-of-the-art equipment. Typcial GPC conditions with organic eluents were chosen to obtain realistic-data.

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Introduction

Precision of molecular weight data obtained by GPC-SEC is of great interest to polymer chemists since the advent of the technique in the late 1960s.[1,2,3,4] Due to a special calibration procedure using a linear elution volume (retention time) on the x-axis versus a logarithmic molecular weight on the y-axis, each deviation of the elution volume has an exponential effect on the precision of the molecular weight data. Therefore, demands on the hardware are more stringent than in other HPLC modes.

Equipment

An Agilent 1100 Series GPC-SEC system consisting the following modules was used:

- Agilent 1100 Series vacuum degasser for efficient degassing of the mobile phase
- Agilent 1100 Series isocratic pump with large solvent cabinet
- Agilent 1100 Series autosampler with single valve design
- Agilent 1100 Series thermostatted column compartment for precise column temperatures
- Agilent 1100 Series refractive index detector with automatic recycle valve
- Agilent ChemStation Plus with GPC-SEC data analysis software

Results and discussion

Table 1 shows the strong influence of flow deviations on the weight average molecular weight M_w measured for a polystyrene sample. The system was calibrated at a flow rate of 1.0 mL/min. When analyzing the sample exactly at this flow rate the M_w value is 35400. Table 1 shows that, for example, for a flow deviation of only +0.60 % or +1.30 % errors of 11 % and even 23.6 % occur. The column temperature stability between calibration and sample run is also important. A 4 °C change, as it can easily occur if the column compartment is not thermostatted, will create an error of 2.6 %. Hardware and software parameter effects on precision of molecular weight data are discussed in references 4 and 5.

As outlined before an excellent inter- and intraday precision of the retention times (elution volumes) is a fundamental prerequisite. To measure the retention time precision we injected a technical poly(styreneacrylonitrile) (SAN) automatically every day over 20 days. Figure 1 shows the plot of the retention times versus the run number. Table 2 shows the calculated relative standard deviations for retention time, M_n and M_w. The very good interday (between days) precision from the 1st to the 20th day was 0.06 9%. The intraday (within day) precision was always below 0.05 % with

Flow [mL/min]	Flow deviation [%]	M_w	M_w deviation [%]
1.013	+1.30	43400	+23.6
1.006	+0.60	39300	+11.0
1.00	0	35400	-
0.992	-0.80	31100	-12.2
0.985	-1.50	27700	-21.80

Table 1
Influence of flow variations on M_w

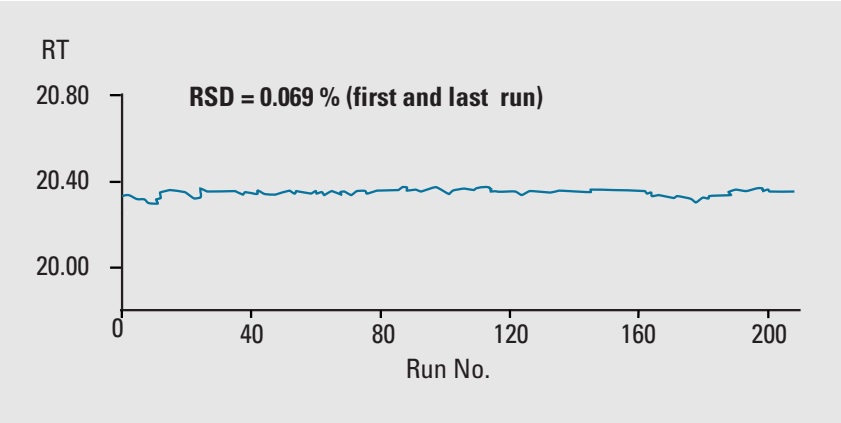

Figure 1
Intra-and interday precision of retention times for a poly(styreneacrylonitrile) copolymer (SAN) over 20 days

the exception of days 1, 2 and 15 but still below 0.08 %.

Figure 2 shows the precision of the styreneacrylonitrile analyses. It is an overlay of the injections made on days 1, 5, 10 and 20. The calculated relative standard deviations from day 1 to day 20 are shown for all injections. It should be pointed out that these very good data take almost all injections from day 1 to day 20 into account. Only about 10 injections had to be filtered out. They were stray points, for example, caused by a vial not filled correctly.

Conclusion

The intra- and interday precision of M_n and M_w molecular weight data obtained by GPC-SEC has increased significantly in recent years. With the Agilent 1100 Series GPC-SEC system intra-(within one day) and interday precision data (over 20 days) for M_n and M_w below 1.5 % were calculated in completely automated analyses for broad distributed polymers with THF as eluent. These results are mainly based on

- HPLC pumps with an intra- and interday flow stability better than 0.1 % (based on polymer retention time),
- column thermostats with a temperature precision better than 0.5 °C,
- automated eluent recycling after the analysis which results in a better conditioned system,

Day	% RSD retention time	% RSD for M_n	% RSD for M_w
1	0.071	1.16	1.12
2	0.075	1.43	0.78
3	0.020	0.92	0.72
4	0.032	0.82	0.83
5	0.030	1.18	0.97
6	0.038	0.95	0.78
7	0.037	1.13	1.08
8	0.030	0.58	0.81
9	0.043	0.91	0.66
10	0.025	0.73	0.32
11	0.022	1.43	0.43
12	0.021	0.81	0.35
13	0.016	0.89	0.59
14	0.029	0.88	1.19
15	0.065	1.08	1.27
16	0.002	0.68	0.70
17	0.045	0.99	0.85
18	0.038	0.94	0.78
19	0.041	0.95	0.80
20	0.009	0.70	0.71
Average %RSD per day	**0.035**	**0.96**	**0.78**

Table 2
Calculated relative standard deviations (intraday) for retention time, M_n and M_w

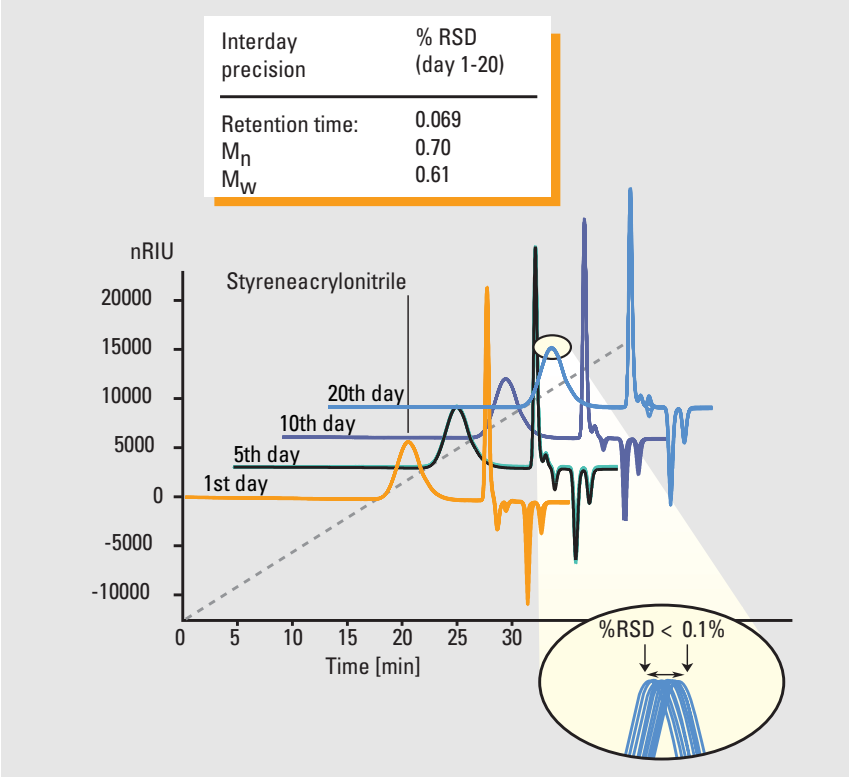

Figure 2
Overlay of all analyses of the poly(styreneacrylonitrile) sample on days 1, 5, 10 and 20. A zoom into the analyses of day 20 is shown in the bottom right.

- refractive index detectors with low noise (± 2.5×10^{-9} RIU)* and low drift (200×10^{-9} RIU/h)* for correct and repeat able baseline and integration window setting,
- software with flexible and repeatable integration and cal culation algorithms to adapt to broad polymer peaks, and
- full automation capabilities reducing human errors.

Good precision data not only improves the reliability of the results but also the productivity because less time-consuming recalibrations are needed.[5]

* According to ASTM E-1303-95 "Practice for Refractive Index Detectors used in Liquid Chromatography". Reference Conditions: response time 4 s, 35 °C, 1 ml/min water, restriction capillary

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