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Application News

No. L537

High Performance Liquid Chromatography

Increased Throughput with Nexera™ GPC system: Overlapped Injection and Simultaneous Determination of Polymer Additives

Measuring molecular weight distribution of polymer compound by size exclusion mode is one of the typical parts of HPLC and generally called gel permeation chromatography (GPC). Nowadays there is an increasing demand demand for high throughput analysis even in well-established GPC. Here we introduce a novel GPC analysis that affords both high throughput GPC results by overlapped injection using conventional size of columns and simultaneous determination of polymer additives.

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GPC Analysis by Overlapped Injection and Simultaneous Determination of Polymer Additives

A refractive index detector (RID) that gives a response to a sample weight is commonly employed for GPC to calculate average molecular weight and polydispersity. On the other hand, A UV detector is used for determination of polymer additives such as antioxidants. Consequently, serially connected those two detectors were used for this study. In GPC, there is hardly any eluates prior to exclusion limit. So if the sample elution band from previous injection is managed to be overlapped within this no elution interval in present analysis, short analysis cycle time can be obtained and it provides increased throughput in sequential analyses. When two or more polymer additives are contained, correct determination of those small additives is difficult because complete separation of additives is almost impossible even using GPC columns of small exclusion limit due to small difference of molecular weight among those polymer additives. To address this difficulty, a photodiode array detector (PDA) that affords spectrometric information as well as chromatographic results was employed to give increased separation of polymer additives by peak deconvolution function within a single GPC analysis.

Fig. 1 and Table 1 show obtained chromatogram of polystyrene containing three antioxidants and employed analytical conditions respectively.

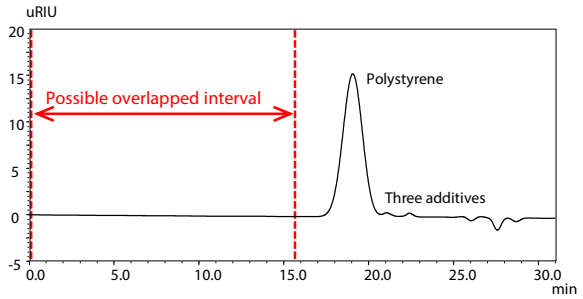

Fig. 1 Chromatogram of Polystyrene and Three Additives (RID)

Table 1 Analytical Conditions

Column	: Shim-pack™ GPC 805+GPC 801 (300 mmL. × 8 mmI.D. for each)
Mobile phase	: THF
Flow rate	: 0.8 mL/min
Column temp.	: 40 °C
Injection vol.	: 10 µL
Detection	: RID / PDA (220-400 nm)
Sample	: 0.5 % Polystyrene containing three additives
Cycle time	: 31 min
Overlap time	: 15.5 min

Increased Throughput by Overlapped Injection

Based on the chromatogram in Fig. 1, 0 to 15.5 term was assigned to overlapped interval due to no elution during it. Fig. 2 shows the comparison of sequential chromatograms obtained with/without overlapped injection. Almost 50 % of decreased analysis cycle time provided increased throughput of sequential GPC analyses.

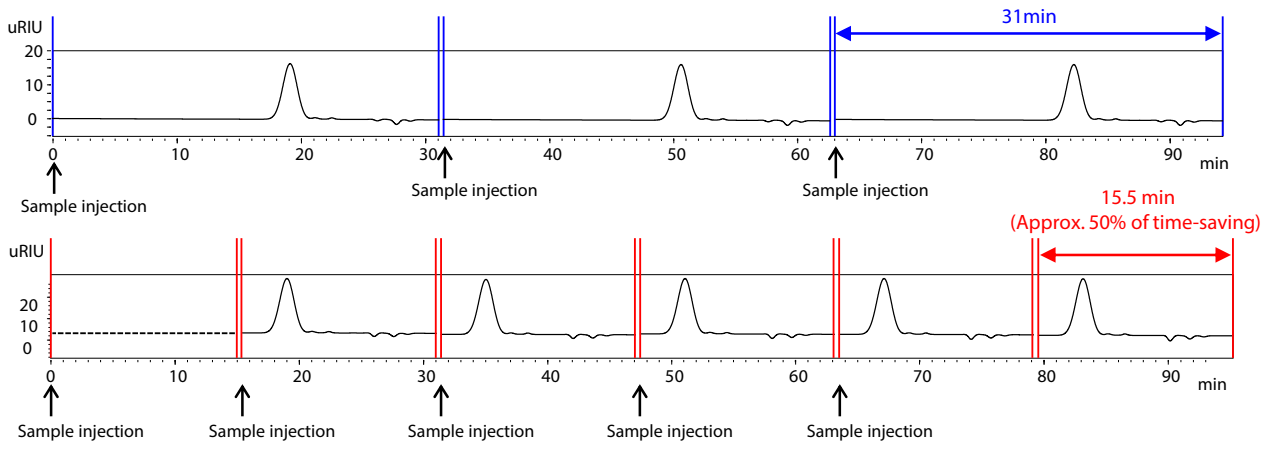

Fig. 2 Comparison of Sequential GPC Analyses With (Lower) / Without (Upper) Overlapped Injection (RID)

Peak Deconvolution by *i*-PDeA II*

LabSolution™ workstation software equips two types of peak deconvolution functions named *i*-PDeA and *i*-PDeA II, those attempt to improve incomplete separation using spectral information obtained with PDA. The former handles two components cases using derivative spectra to cancel the effect from the one. The latter handles two or more components cases using a computer simulation to obtain chromatographic approximate solution of isolated peaks based on three-dimensional information from PDA. In this study, we employed *i*-PDeA II because incomplete separation band consists of three components. Fig. 3 shows a schematic image of peak deconvolution process.

* Shimadzu Technical Report C191-E042

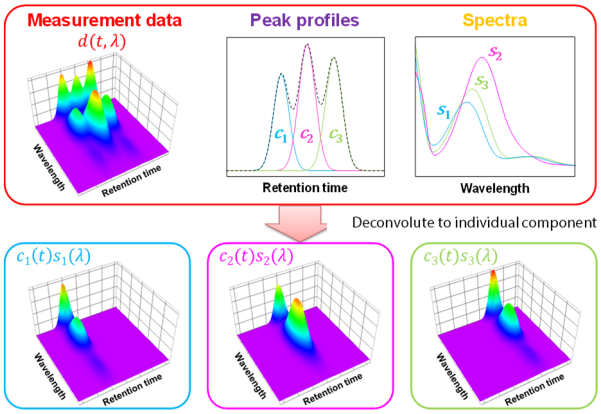

Fig. 3 Peak Deconvolution Process by *i*-PDeA II

Peak Deconvolution for Incomplete Separation of Polymer Additives

Fig. 4 shows the structural formulas of the three antioxidants added to the polystyrene. Fig. 5 shows the chromatogram at 240 nm and overlaid chromatograms of isolated respective compounds with *i*-PDeA II. Fig. 6 shows the UV spectra of three antioxidants after the peak deconvolution process. The original UV-chromatogram provides only two peaks, however three isolated peaks appeared after peak deconvolution process. Furthermore, the obtained peak areas can be applied to the quantitative determination because each peak area after the process directly comes from the original peak area contribution to incomplete peak separation band.

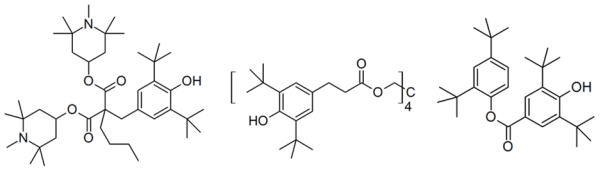

Fig. 4 Structural Formulas of Three Polymer Additives

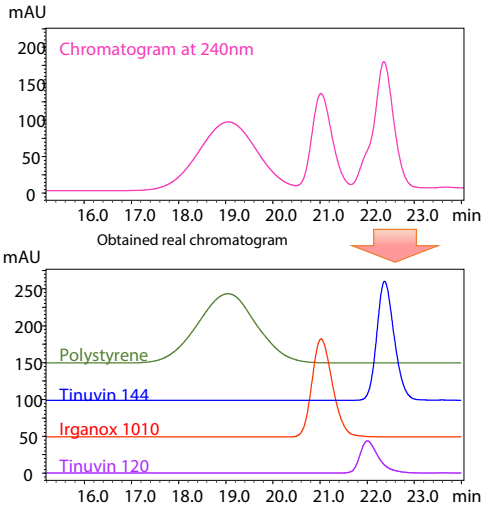

Fig. 5 Deconvolution Result of Three Polymer Additives (PDA)

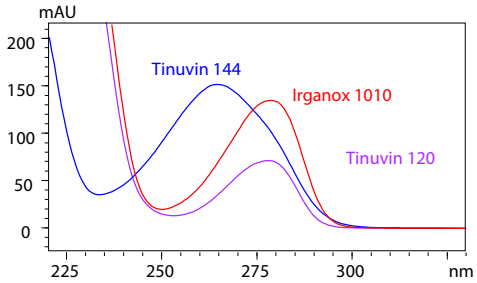

Fig. 6 UV Spectra of Three Additives Obtained After Peak Deconvolution

Determination After Peak Deconvolution

The calibration curves for the three additives were created in the range from 0.01 to 0.1 % (w/v) and applied to determination of the additives contained in the polystyrene. Linearity of calibration curve and determined result of each additive through consecutive six injections are summarized in Table 2. The GPC calculation results of the polystyrene based on RID chromatograms are shown in Table 3 as well. These results suggest that the value added high throughput GPC analysis can be performed using overlapped injection and *i*-PDeA II, which enhances separation performance of GPC column having small exclusion limit.

Table 2 Determination Results of Three Polymer Additives (n=6)

Additive	Irganox 1010	Tinuvin 144	Tinuvin 120
Linearity of calibration curve (r^2)	0.999	0.995	0.998
Determined content (mg/g)	49.2	23.1	27.4
%RSD	1.28	1.93	1.47

Table 3 GPC Calculation Results of Polystyrene (n=6)

	Number average molecular weight Mn	Weight average molecular weight Mw	Polydispersity Mw/Mn
Polystyrene	2.63×10^4	4.89×10^4	1.86
%RSD	1.41	0.89	0.52

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