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Application of a Multiple Linear Regression Model to Fixed Bands IR Detector Data in GPC-IR Analysis of Polyolefins

A. Ortín, B. Monrabal, J. Montesinos, P. del Hierro*

Summary: An infrared detector based on a set of narrow band optical filters was coupled to a high temperature Gel Permeation Chromatograph (GPC) producing continuous chromatograms of absorbance after the molar mass fractionation. A multiple linear regression (MLR) model was established to relate the measured absorbance to the average octene weight percent in industrial ethylene-octene copolymer samples. This method is compared to univariate and multivariate band ratio models. The application of these models to produce molar mass compositional distributions is also outlined.

Keywords: infrared spectroscopy; gel permeation chromatography (GPC); microstructure; polyolefins

Introduction

High temperature gel permeation chromatography coupled to infrared detection (GPC-IR) is a powerful technique to investigate the chemical composition across the molar mass distribution in polyolefins. This can be accomplished by means of Fourier transform infrared detectors which scan and record full spectrum data,[1,2] or by fixed band IR detectors based on narrow optical filters, which continuously record absorbance at two or more IR bands.[3–5] In this work this second approach is explored and different data processing methods are implemented and compared.

The absorbance at four different bands in the C–H stretching mid-infrared region (2800–3000 cm^{-1}) are available from the detector, and so it was possible to apply more complex numerical methods. In order to compare the different data processing methods, the areas under the chromatograms from the four detector channels were calculated. This information, representing the sample absorption at the different bands, is correlated to the average octene weight percent in a set of ethylene-octene copolymer industrial samples.

Different regression models are established, including univariate and multivariate linear regression (MLR). These numerical approaches aim to take advantage of information contained in several IR bands simultaneously, compared to the classical band ratio which uses only two bands, and still without the complexity of dealing with full spectrum data as FTIR detector requires.

Experimental Part

A GPC-IR, high temperature gel permeation chromatograph (Polymer ChAR, Spain), was used to automatically dissolve, inject and separate according to molar mass the polymers studied. A multiple band infrared detector model IR5 with a thermoelectrically cooled MCT sensor (Polymer ChAR SA, Spain) was coupled to the instrument, after the separation columns, in order to detect and monitor the sample absorbance in different bands simultaneously.

Polymer Char, Valencia Technology Park E-46980 Paterna, Spain
E-mail: alberto.ortin@polymerchar.com

The IR5 detector was equipped with four narrow band optical filters in the region or 2800 to 3000 cm^{-1}, in which different absorption bands are observed due to the C-H stretching from the polymer backbone as well as the comonomer side chains (1), while at the same time the mobile phase used was transparent enough. The detector signals were designated as CH (broader band covering the spectral region from 2800 cm^{-1} to 3000 cm^{-1}), CH_3 (narrow band filter centered at 2959 cm^{-1}, absorption band due to methyl vibrations), CH_2 and CH_2-2 (both centered at 2928 cm^{-1}, absorption wavelength due to C–H stretching from methylene groups, the second one having a narrower band). Different sets among those absorbance signals were used by the different methods to obtain the copolymers octene weight percent as described below. Detector signals from the above described four bands are collected at 1 point per second scan rate.

Typical analytical conditions for high temperature analysis of polyethylene and copolymers were used: 1,2,4-TCB stabilized with 300ppm BHT as the mobile phase, three PLgel Olexis (Polymer Laboratories Inc, UK) columns kept at 150 °C, 200 μL injection loop and analysis pump flow rate of 1.0 mL/min. The samples were dissolved within the same instrument at 160 °C for 1 hour with gentle shaking, and automatically filtered through a 10 μm filter before injection.

One polyethylene homopolymer and three polyethylene-octene industrial copolymers with known weight percent of comonomer, ranging from about 3% to 31%, were used as calibration standards 1 to 4. The standards were injected twice, at different concentration level of 2.0 mg/mL and 1.0 mg/mL respectively.

Two additional industrial polyethylene copolymers were used as control samples A and B to evaluate the different data processing algorithms. The control samples were injected by duplicate at 2.0 mg/mL concentration.

Results and Discussion

In Figure 1 the four chromatograms collected from two of the samples analyzed as calibration standards are shown for illustrative purposes. The relative height differences among the chromatograms represent differences in sample absorbance measured at the different bands and can be translated into useful information about the sample chemical composition.

The continuous chromatograms representing these four absorbance signals are baseline corrected and the area between

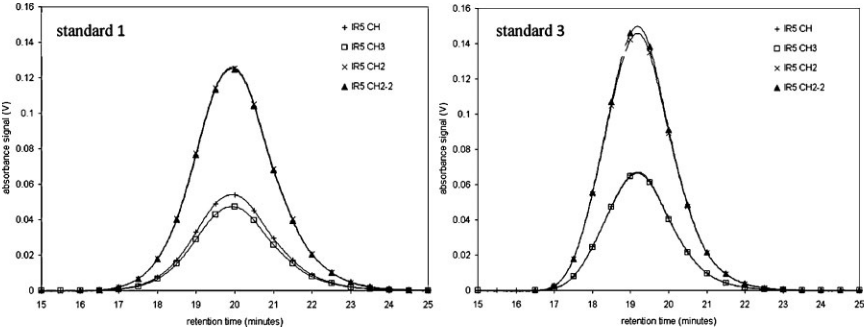

Figure 1.
Chromatograms acquired from the IR detector at the four different bands selected for standards 1 (homopolymer polyethylene) and 3 (ethylene-octene copolymer having 31.3 weight percent octene) It is interesting to notice that the relative height of the CH_3 chromatogram is higher in the standard sample having highest octene content.

Table 1.
Summary of chromatogram areas and area ratios from calibration set (standard 1-4) and control samples A and B.

Sample ID	conc mg/mL	octene Wt%	area CH	area CH_3	area CH_2	area CH_2 -2	IR ratio 1	IR ratio 2	IR ratio 3
std 1	2	0.0	0.1377	0.1219	0.3231	0.3184	0.4261	0.3773	0.9854
std 2	2	10.6	0.1426	0.1333	0.3262	0.3262	0.4371	0.4088	1.0000
std 3	2	31.3	0.1449	0.1440	0.3182	0.3241	0.4552	0.4524	1.0185
std 4	2	3.2	0.1345	0.1209	0.3115	0.3098	0.4319	0.3882	0.9947
std 1	1	0.0	0.0746	0.0655	0.1740	0.1717	0.4284	0.3765	0.9866
std 2	1	10.6	0.0730	0.0688	0.1681	0.1673	0.4342	0.4091	0.9954
std 3	1	31.3	0.0665	0.0668	0.1482	0.1500	0.4485	0.4505	1.0119
std 4	1	3.2	0.0699	0.0634	0.1638	0.1620	0.4270	0.3872	0.9890
A	2	*1.6*	0.1421	0.1264	0.3307	0.3279	0.4296	0.3821	0.9915
A	2	*1.6*	0.1542	0.1380	0.3587	0.3557	0.4298	0.3849	0.9916
B	2	*18.7*	0.1451	0.1388	0.3265	0.3287	0.4444	0.4250	1.0066
B	2	*18.7*	0.1557	0.1484	0.3477	0.3516	0.4480	0.4268	1.0114

proper integration limits quantified. Different ratios of bands are also generated, taking the methylene band (CH_2) as denominator and so producing three absorbance ratios, designated as IR ratio 1, 2 and 3. All this numerical information extracted from the raw data chromatograms is presented in Table 1.

For each of the data processing methods described below, suitable data from the calibration standards are taken from Table 1 in order to develop a calibration equation or model to relate the measured parameters (chromatogram areas or band ratios) to the comonomer content. This calibration model is subsequently applied to the data from the duplicated analysis of the control samples, also taken from Table 1. The results obtained for the octene content of control samples are summarized in Table 2, together with the average value of duplicated analysis. In order to compare the quality of the different data processing methods, the root mean square error (RMSE) for each method is calculated as:

$$RMSE = \sqrt{\frac{\sum (y_i - \bar{y})^2}{n}}$$

where data from the two duplicates of the two control samples are included in the summation.

Classical IR Bands Ratio Method

In this method, detector signals from only two IR bands are considered. The ratio of absorbance chromatogram areas from the methyl band (CH_3) over the methylene band (CH_2), designated as "IR ratio 2" in Table 1, is chosen given its higher variation range observed with the comonomer content in the calibration standards.

The values of this IR ratio are used together with the standards nominal comonomer content to obtain a calibration curve. A quadratic equation provides a better fit to

Table 2.
Summary of octene weight percent obtained by applying the three methods described to the control samples.

Sample ID		single IR ratio C8 Wt%	multiple IR ratio C8 Wt%	MLR direct absorbance total mass (mg)	C8 Wt%
sample A		1.48	1.54	0.403	0.94
sample A		2.27	2.30	0.438	2.06
	average	1.87	1.92		1.50
sample B		17.53	17.14	0.407	19.34
sample B		18.37	17.72	0.434	20.34
	average	17.95	17.43		19.84
RMSE*		0.41	0.34		0.53

the experimental data than a linear equation as can be seen in the calibration graph shown in Figure 1 and was therefore used in the data processing of the control samples.

Multiple IR Bands Ratio Inverse Calibration Method

This model is an extension of the simple IR ratio method to include additional terms from the other band ratios. Quadratic terms are included based on the previous single ratio calibration study, as well as a constant term. In this model the signals from the other three available bands are rationed over the methylene band signal, and an inverse calibration model[6,7] is established to the octene weight percent. The following equation is found to represent this model:

$$
\begin{aligned}
C8\% = {} & 1089.07 + 4411.05 \\
& \times \textit{ratio}\ 1 - 5247.32 \times \textit{ratio}\ 1^2 \\
& -1740.65 \times \textit{ratio}\ 2 + 2638.88 \\
& \times \textit{ratio}\ 2^2 - 3570.68 \times \textit{ratio}\ 3 \\
& + 1837.15 \times \textit{ratio}\ 3^2
\end{aligned}
$$

The above equation is applied to the experimental data in Table 1 for the two control test samples and the results shown in the summary Table 2. There is a slight reduction in the RMSE as compared with the single ratio method, possibly due to the additional information provided by the two additional IR bands used in this case.

MLR Method: "Classical" Calibration of Absorbance and Concentration of Sample Components

The main difference in this method is that absorbance chromatogram areas are used directly with no rationing. The fourth band (CH2-2) was discarded as it did not add significant information to that provided from the other three bands and only contributed to the system noise. The classical calibration equations[6,7] are written having the concentration of the ethylene (C2) and octene (C8) components as independent variables, and the absorbance at the three different bands (referred to as CH, CH_3, CH_2) as dependant variables:

$$
\begin{aligned}
& \text{Abs (band i)} = s_{i1} \cdot C8 \\
& \quad + s_{i2} \cdot C2; \quad \text{for i} = 1 \text{ to } 3 \\
& \text{Or, in matrix form}: \mathbf{A} = S \cdot \mathbf{C}
\end{aligned}
$$

In the calibration step, the S matrix (6 coefficients in this case) is found based on the known C2 and C8 and the measured absorbance chromatogram areas from the calibration standards (Table 1).

In the data processing, the S matrix is used together with the measured absorbance to obtain the individual components concentrations (C2 and C8) and from them, the total concentration and the octene percent (Table 2). It must be noticed that the total concentration is obtained in this

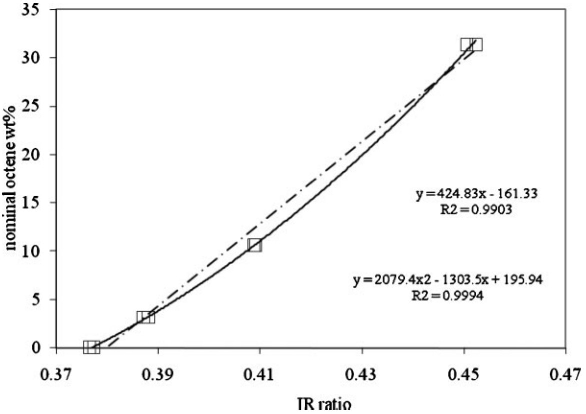

Figure 2.

Calibration curve IR ratio vs. octene weight %. Linear and quadratic fits are calculated. Based on the best correlation coefficient the second order fit is chosen.

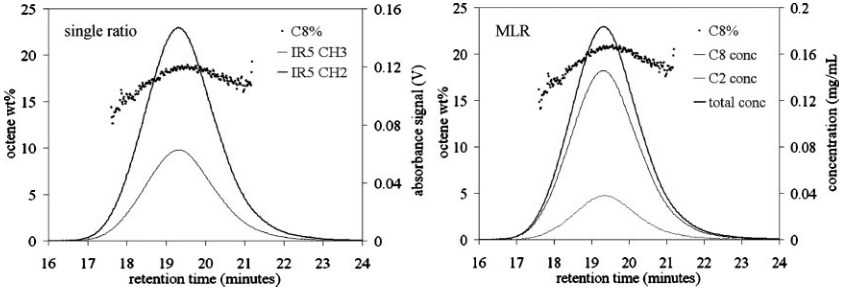

Figure 3.

Octene weight percent calculated at every retention volume slice for one of the injections of sample B. Comparison of single ratio of two bands to MLR using absorbance in three bands.

case which was not possible with the other two procedures described before. This becomes of great importance when using other on-line detectors such as viscometer or light scattering which require an accurate determination of concentration independent of compositional drifts.[2]

The error term resulted to be somewhat higher compared to the ratio-based methods and the predicted octene percent separated also from the ratio based methods. We can only speculate this is due to the very little data available to calculate the model and that larger data sets would result in improved accuracy or lower detection limits.

Comonomer Distributions

In addition to the determination of average comonomer content from the chromatogram areas, the above developed models were also applied on a slice by slice basis to obtain the comonomer level across all the retention time range. With proper GPC columns calibration this would result in a molar mass compositional distribution, provided the effect of chain ends is compensated for when the molar mass is not high enough to neglect it. In Figure 3 this comonomer distribution is shown as calculated from two of the models for one of the test samples studied. In all cases data is not reliable towards the tails of the main peak due to the low sample concentration, and in general all methods show consistent results.

Conclusion

A multiple linear regression model was established to relate the absorbance at a limited number of bands generated by a fixed band IR detector to the octene weight percent in industrial polyethylene copolymers. Results obtained were comparable to other simpler processing methods based on band rationing, with the advantage of delivering the concentration of the components as well as the total concentration.

Larger calibration and validation sets would be required to really quantify the precision and accuracy of the proposed methods, although the general agreement among them indicates that the application of this kind of multivariate methods on a small set of IR absorbance signals, in order to determine the comonomer content in polyethylene copolymers by on-line GPC-IR, seems to be reasonable. It is also an interesting technique from a practical point of view given the simplicity of the analytical setup required, compared to other existing methods. However it would be necessary to conduct a comprehensive work using larger data sets in order to assess the applicability and limitations of the technique.

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