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Application News

No. A580

Spectrophotometric Analysis

Quantitative Analysis of Recycled Plastics Using FTIR – Individual Calculation Method –

Plastic bottles, containers, and packaging materials are commonplace items that can be found in various aspects of our everyday lives. In Japan, such items are discarded by consumers as waste plastic but are then collected and recycled into new raw materials and products according to the Container and Packaging Recycling Law in order to reduce and recycle waste plastic.
The main four components of recycled plastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET), which are all commodity resins. Quality standards are defined for recycled plastics and to determine the composition of components, generally a sample is dissolved in a solvent and then analyzed using a nuclear magnetic resonance (NMR) spectrometer. In place of this general method, this article introduces a screening analysis method using a Fourier transform infrared spectrophotometer (FTIR). Quantitation is possible by either the individual calculation method, in which the concentration of each component is calculated individually, or the mixing ratio calculation method, in which the concentration of each component is calculated by taking the sample as a whole as 100 %. This article studies the individual calculation method. A major feature of this method is that unlike the precision analysis using an NMR spectrometer, sample pretreatment is unnecessary and therefore speedy calculations of the composition of components are possible. For the mixing ratio calculation method, please refer to Application News No. A581.

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Analytical Conditions

The instrument used for analysis was the IRAffinity-1S Fourier transform infrared spectrophotometer combined with the Quest single-reflection ATR accessory as shown in Fig. 1. The principle of the ATR (attenuated total reflection) method is illustrated in Fig. 2 and the analytical conditions are listed in Table 1. The ATR method obtains a spectrum from a sample by first pressing the sample against the surface of a prism made of infrared transmitting material with a high refractive index and then detecting the reflected light beam that has penetrated the sample surface to a depth of a few microns.

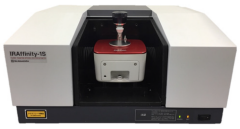

Fig. 1 The Instrument Used (IRAffinity-1S, Quest)

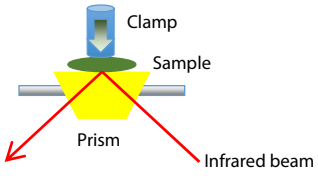

Fig. 2 The Principle of the ATR Method

Table 1 Analytical Conditions

Instrument	: IRAffinity-1S, Quest
Resolution	: 4 cm^{-1}
Accumulation Times	: 20
Apodization Function	: Happ-Genzel
Measurement Mode	: Absorbance
Detector	: DLATGS

Quantitative Analysis Using the Individual Calculation Method

By using samples with known concentrations, a calibration curve that indicates the relationship between concentration (wt%) and absorbance is created for each of the four plastics, PE, PP, PS, and PET. Then based on these calibration curves, quantitation values of PE, PP, PS, and PET can be calculated from the measurement results of a sample with unknown concentrations. The plastic-derived peak wavelengths used for quantitation are 719 cm^{-1} (PE), 841 cm^{-1} (PP), 698 cm^{-1} (PS), and 1721 cm^{-1} (PET) and the corrected peak height (the peak height from the baseline) is used.

Characteristics of the Method

- Since quantitation values are easily influenced by the degree of contact between the prism and the sample for ATR, the method is unsuited for samples in pellet form.
- The total concentrations of PE, PP, PS, and PET will not necessarily be 100 wt% and the quantitation values will reflect the existence of other components.

Samples for Analysis

The recycled plastics in sheet form shown in Fig. 3 were measured this time. Table 2 shows the composition of the five samples that were used to create the calibration curves.

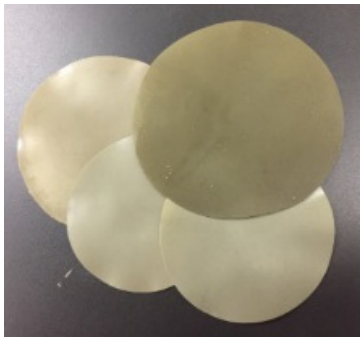

Fig. 3 Samples for Analysis

Table 2 Composition of Samples Used to Create Calibration Curves

	Composition (wt%)				
	PE	PP	PS	PET	Other
Sample 1	89	9	1	<1	1
Sample 2	74	14	3	2	7
Sample 3	21	65	4	4	6
Sample 4	20	68	10	1	1
Sample 5	14	79	4	1	2

Results of Quantitative Analysis Using the Individual Calculation Method

The samples 1 to 5 with known concentrations were measured four times each by changing the point for measurement each time. The calculated average infrared spectra are shown in Fig. 4. The calibration curves created for PE, PP, PS, and PET are shown in Fig. 5. The horizontal axis of the calibration curves indicates concentration (wt%) and the vertical axis indicates the corrected peak height values for the wavelengths 719 cm^{-1} (PE), 841 cm^{-1} (PP), 698 cm^{-1} (PS), and 1721 cm^{-1} (PET).

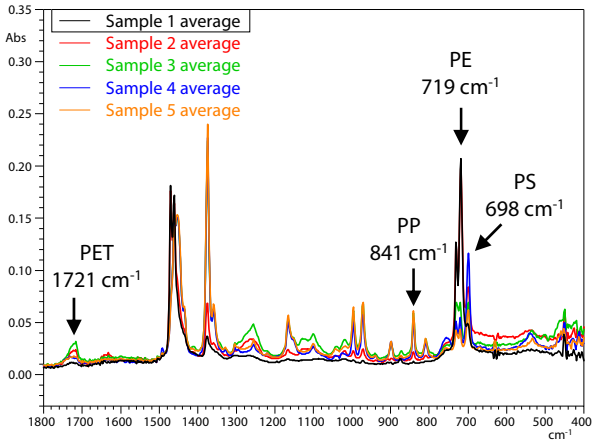

Fig. 4 Infrared Spectra of Samples 1, 2, 3, 4, and 5 (Average of four measurements)

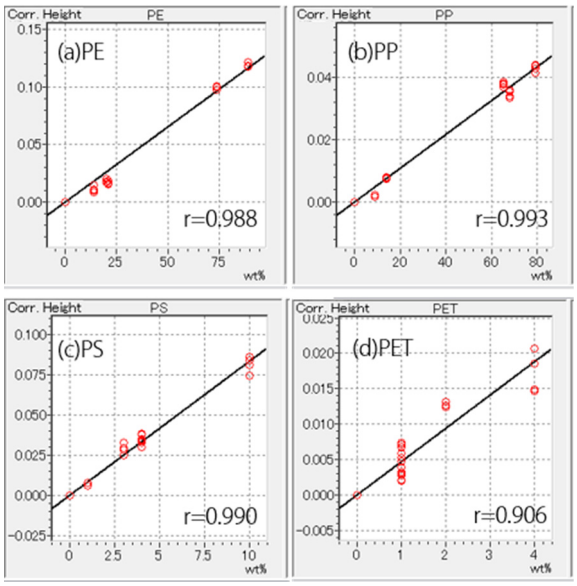

Fig. 5 Calibration Curves (a) PE, (b) PP, (c) PS, (d) PET

Next, two samples with unknown concentrations were measured and quantitated using the calibration curves shown in Fig. 5. Each sample was measured five times by changing the point for measurement each time. Table 3 shows the quantitative analysis results. To check the validity of the calculated composition based on measurements using FTIR, the table also lists the values calculated by using NMR as a reference.

Table 3 Results of Quantitative Analysis Using FTIR and Reference Values Using NMR Unit: wt%

Unknown 1	Measure-ment 1	Measure-ment 2	Measure-ment 3	Measure-ment 4	Measure-ment 5	Average	NMR Value
PE	59.0	59.0	59.0	56.9	55.5	57.9	56
PP	28.7	25.8	29.0	28.9	31.3	28.7	23
PS	8.3	8.9	8.5	8.5	8.1	8.5	10
PET	2.7	3.3	3.0	3.0	2.7	3.0	3
Unknown 2							
PE	89.1	89.9	87.9	90.7	91.1	89.8	89
PP	4.0	4.1	3.8	4.3	3.7	4.0	9
PS	0.8	1.1	1.2	1.1	1.1	1.1	1
PET	0.2	0.3	0.5	0.5	0.5	0.4	<1

There is a difference of up to 6 wt% between the quantitative analysis results using FTIR and the reference values obtained using NMR. Since the sample is measured directly without any pretreatment such as extraction when using FTIR, the variation in points on the calibration curve tends to increase in the low concentration range and this is also expected to affect the quantitation values. This means that the selection of the samples (concentration) for creating calibration curves is an important aspect.

Also, this study shows that samples in sheet form can achieve better contact with the ATR prism than samples in pellet form and thus variations between measurements tend to be small. However, measurements of trace components tend to result in greater variations.

Conclusion

This study examined simple methods for quantitative analysis of PE, PP, PS, and PET in recycled plastics using FTIR. The results suggest that for samples in sheet form, the individual calculation method described in this article may be able to obtain quantitation values that indicate a correlation with NMR values. Calibration curves were created using five samples with known concentrations in this study, but by increasing the number of samples, improvements in the accuracy of the calibration curves as well as the quantitative analysis results can be expected.

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