

Discrimination of plastics based on the chemical structures using a portable near infrared spectrometer

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Introduction

We examined NIR spectra obtained from various plastic wastes using a portable near infrared spectrometer; herein, we discuss chemical implications of spectral characteristics. In this article, we propose the novel idea of utilizing a barcode spectrum, which is derived from the second-order derivatives spectrum and provides the effective alternatives to discriminate kinds of plastics.

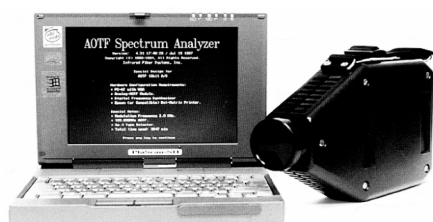
Methods

Samples

Seventy-one kinds of plastics were collected and used as samples for measuring NIR spectra.

NIR spectroscopy

The NIR diffuse reflection spectra in the 1100 - 2500 nm wavelength region (800 data points) were measured three times for each sample with a portable near-infrared spectrometer (Fig.1), PlaScan SH (OPT Research, Inc., Japan), equipped with an acousto-optical tunable filter (AOTF)¹⁻³.



Dimension	: 250mmL×150mmW×55mmD
Weight	: 1.7kg
Device	: acousto-optic tunable filter (AOTF)
Wavelength range	: 1100 to 2500nm
Measurement time	: 0.1 to 1 sec
Measurement point	: 100, 200, 400, 500, 800, 1200, 2400 points
Radiation source	: tungsten halogen lamp, 5W
Detector	: lead sulfide

Figure 1 Portable NIR Spectrometer PlaScan SH (OPT Research, Inc., Japan)

It is widely believed that the AOTF method theoretically caused a wavelength shift. In the case of PlaScan SH, because polystyrene film is used to correct the wavelength only at 1680 nm, the shift from an accurate wavelength increases as it departs from the corrected wavelength. In this work, the wavelength was re-corrected using a grating monochromator device (NIRS 6500, FOSS-IRSystems)

for the apparent observed wavelength. Plastic samples were distinguished simply by the built-in software program with the standard model PlaScan into 15 sorts (Table 1). The program s based on discrimination analysis using a Mahalanobis Distance. A white ceramic disk was used as a reference in the diffuse reflection mode. Spectra in the 1100-2500 nm regions were subjected to data analysis using the JUSE-Stat Works / V3.0 software program (The Institute of Japanese Union of Scientists & Engineers).

Table 1. Fifteen distinguishable plastics by the standard model of PlaScan SH

ABS : acrylonitrile-butadiene-styrene	PMMA : polymethylmethacrylate
AS : acrylonitrile styrene	POM : polyacetal
ABS : acrylonitrile-butadiene-styrene	PMMA : polymethylmethacrylate
PA : polyamide	PP : polypropylene
PBT : polybutylene terephthalate	PS : polystyrene
PC : polycarbonate	PUR : polyurethane
PC/ABS	PVC : polyvinyl chloride
PE : polyethylene	PVDC : polyvinylidene chloride
PET : polyethylene terephthalate	OTHERS

Barcode spectrum

First, second-order derivative treatment was applied to original spectra to abstract more characteristic features from NIR spectra of samples. The second-order derivative spectra can be very useful in spectral analysis because of the fact that peak positions in this form are maintained with those in the original spectral pattern where base line drift disappears or declines. Then, for each wavelength, second-order derivatives were replaced by zero or one: positive second derivative values are one, the remainder are zero. We call this a 0/1 value exchange spectrum as a barcode spectrum^{1,2}. Figure 2 demonstrates the barcode spectrum derived from second-order derivative spectra of PE. This 0/1 value exchange was performed to reduce systematic variation of the data set and to extract qualitative information from NIR spectra to discriminate investigated plastic samples.

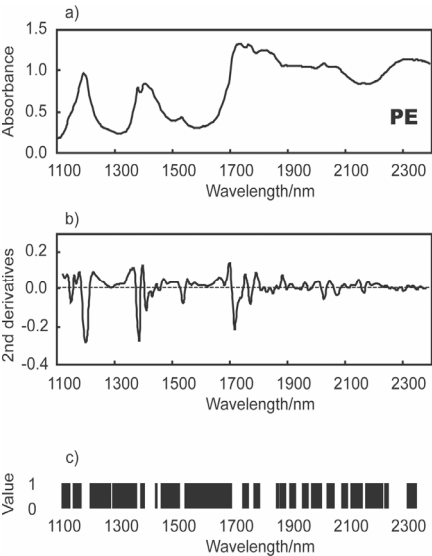


Figure 2 Barcode spectrum derived from second-order derivative spectra. (with permission from [1])

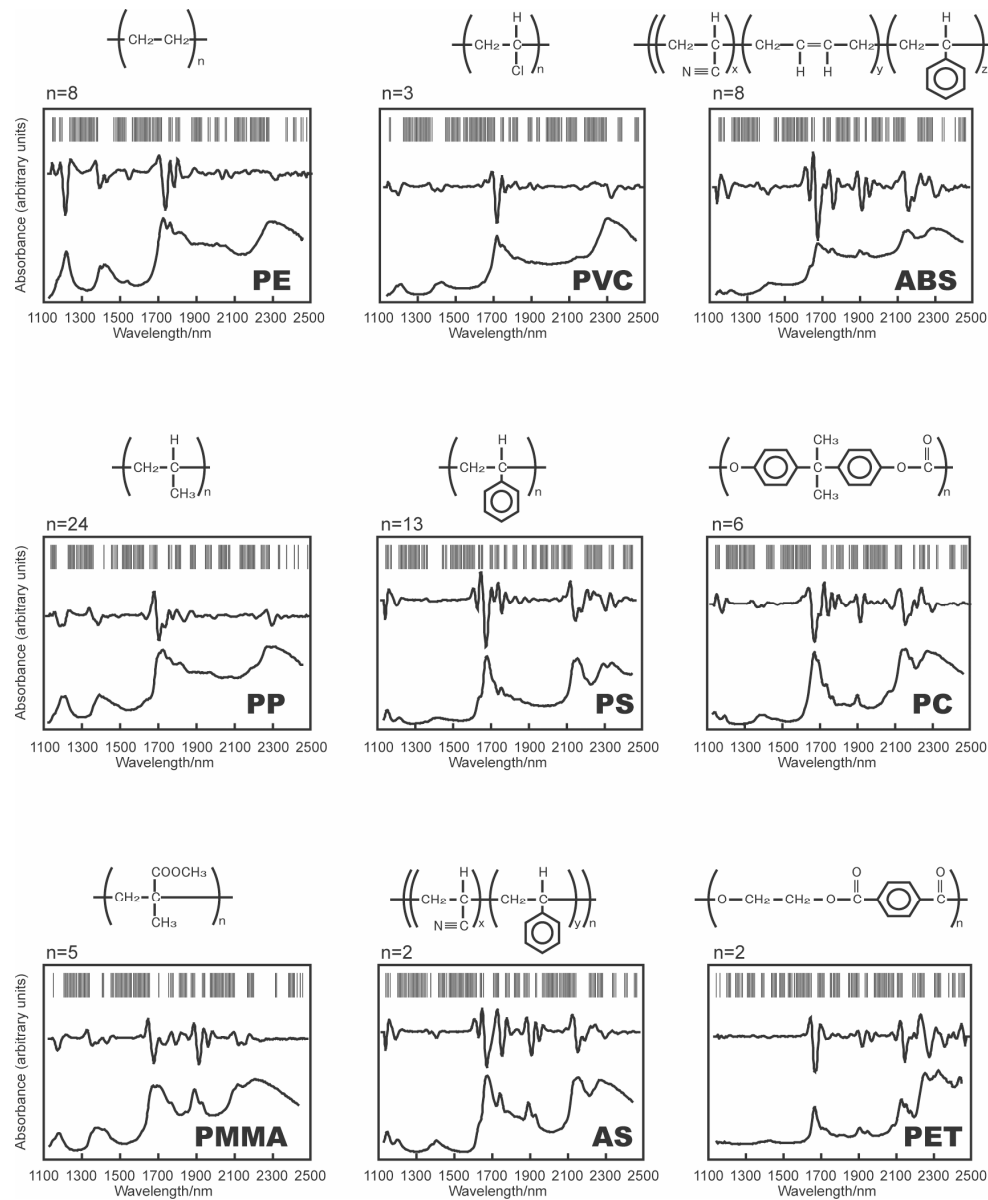


Figure 3 Standardised spectra, second-order derivative spectra and barcode spectra for nine types of plastic samples. (with permission from [2])

Result and discussion

Figure 3 shows standardized NIR spectra, second-order derivative spectra, and barcode spectra for nine types of plastic samples. Each spectrum in Fig. 3 shows an average for each of nine types of plastics. Accordingly, Fig. 2 is the representative spectrum of plastic samples; the shape differences of NIR spectra are based on sample composition chemical structure. One could use the barcode spectra as spectral databases for plastics, widely.

The barcode spectrum loses information of peak intensity and negative peaks; however, it presents the advantage of discriminating all kinds of plastic waste, including those which are dirty, colored, damaged, and so on. That is to say, it is important to extract qualitative information from NIR spectra rather than excess detailed information to discriminate investigated plastic samples.

Figure 4 shows two-dimensional score plots of the first two principal components (PC1, PC2) based on original spectra, second-order derivative spectra and barcode spectra for plastic samples. Although the discrimination of plastic types is not done completely in case of original spectra, the similarity of every type of plastics is on the improve rather than based on the original spectra, because the spread area of each samples gathered into groups. Figure 4 demonstrates the availability of barcode spectra for discriminating the types of plastics.

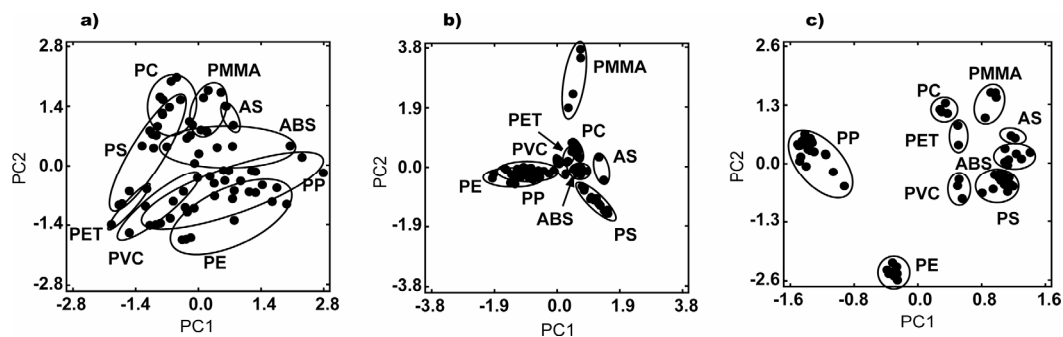


Figure 4 Score plots of PC2 vs. PC1 based on original spectra (a), second-order derivatives spectra (b), and barcode spectra (c).

In order to evaluate the real meanings of the PCA factor axes and associate with the chemical information to the NIR spectra, we introduced the idea of wavelength contribution ratio spectrum^{2,3}. We calculated the wavelength contribution ratio at every wavelength using the following formula:

$$\text{Contribution ratio (\%)} = (\text{factor loading})^2 / (\text{total number of measured wavelengths})$$

where factor loading indicates the correlation coefficient between the principal component and the original variable; both of them are for absorbance at corresponding wavelengths.

Figure 5 shows the three-dimensional score plots based on the barcode spectra and their contribution ratio spectra. Contribution ratio spectra could suggest the meanings of the principal component axis of the score plots. PC1 shows that wavelength contribution ratios assigned to the first overtone of CH_2 , aromatic CH and the second overtones of CO are high. PC2 shows that wavelength contribution ratios assigned to the combination tone of CH_3 , the combination tone of aromatic CH, the first overtone of OH, the first overtone of aromatic CH and the second overtone of CO are high. PC3 shows that wavelength contribution ratios assigned to the combination tone of CH

is high, respectively. In this manner, we can understand what is important wavelength for the variance of principal component axis more quantitatively.

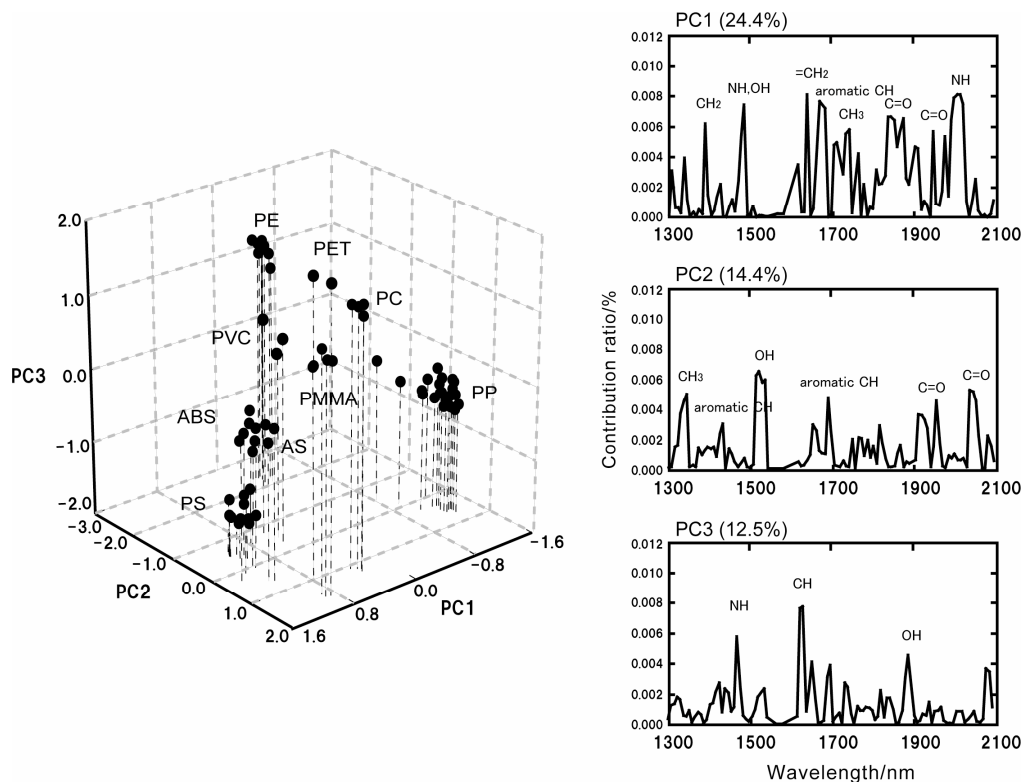


Figure 5 Three-dimensional score plots based on the barcode spectra and their contribution ratio spectra.

We tried further investigation to clarify the relations between the NIR spectrum and its chemical structure information, and principal component analysis was applied to 0/1-converted data based on types of functional groups. To put it concretely, if sample material contains aromatic CH, C=C, C-O, COO, CH₃, and Cl groups, then the values for the functional groups are one. If it does not contain them, then the values are zero. Consequently, the first two principal components obtained using 0/1-converted data based on types of functional groups accounted for 37.7% of total variance and 27.6% of total variance, respectively. Figure 6 shows score plots of PC2 vs. PC1 with orientation and amount of factor loadings. It is easy to signify dimensional space by overlapping factor loadings as a vector expression on score plots.

ABS, AS and PS involve styrene in the repeating structure, and AS also involves the CN group, and ABS involves the C=C double bond. These plastics make a cluster in both Fig. 4-c and 6.

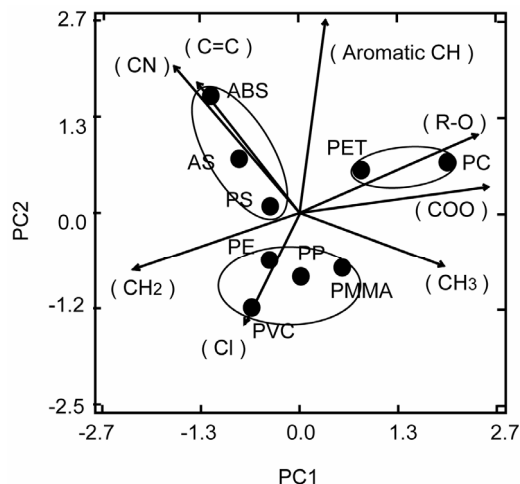


Figure 6 Score plots of PC2 vs. PC1 based on functional group. (with permission from [2])

Similarly, PET and PC are forming a cluster, due to the existence of CO and COO group. By the way, PMMA is an analogue of PE, PP, and PVC, so these are forming a cluster in Fig. 6. But, PMMA has the CO group, which affects the NIR spectrum strongly; therefore, PMMA was drawn near PET and PC in Fig. 4-c. Influence of the CO group on the NIR spectrum has been shown in wavelength contribution ratio spectra in Fig. 5. The Cl group also affects the NIR spectrum dramatically in Fig. 4- c; that is, PVC is far separated from PE and PP. Accordingly, we have a great deal of interest in the contribution of Cl group on the NIR spectrum. While we can hardly explain where the difference due to the Cl group lies on the NIR spectrum, the fact that PVC is separated far from PE and PP implies that a difference should be reflected in spectra. We will continue to study the relationship between PCA results and their chemical and structural interpretation of spectra.

In this article, we propose the novel idea of utilizing a barcode spectrum, which is derived from the second-order derivatives spectrum, and a contribution ratio spectrum for interpretation of principal component using a portable NIR spectrometer "PlaScan SH". We would emphasize that chemistry-based interpretation of NIR spectra is the most essential and important concept for development of NIR spectroscopy. Without this strategy, NIR spectroscopy can not become a useful and reliable analytical method practically and scientifically.

References

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