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Chemical Meaning of Near Infrared Spectra from a Portable Near Infrared Spectrometer for Various Plastic Wastes

Masanori KUMAGAI^{*,**}, Hideto SUYAMA^{*}, Tomoaki SATO^{*}, Toshio AMANO^{***}
Ryoei KIKUCHI^{*} and Nobuaki OGAWA^{*}

^{*}Faculty of Engineering and Resource Science, Akita University,
Tegata Gakuencho, Akita 010-8502, Japan

^{**}Akita Research Institute of Food and Brewing, Arayamachi, Akita 010-1623, Japan

^{***}OPT Research Inc., Akasaka, Minatoku, Tokyo 107-0052, Japan

E-mail : kumagai@arif.pref.akita.jp

We examined NIR spectra obtained from various plastic wastes using a portable near infrared spectrometer; herein, we discuss chemical implications of spectral characteristics. A barcode spectrum derived from the second-order derivatives spectrum provides effective alternatives to discriminate plastic types. Principal component analysis, which is applied to barcode spectra, reveals characteristics and similarity of NIR spectra among plastic samples. Chemical structure of plastic samples reflects NIR spectra. Spectral differences can be explained with reference to whether the plastic has some functional group (aromatic CH, CO and Cl) or not.

Key Words : portable NIR spectrometer, discrimination of plastic, barcode spectrum.

1. Introduction

The most important global problem is the promotion of more effective use of resources and prevention of waste materials. Recently, there has been growing interest in environmental protection. Local governments and corporations have engaged in promoting a recycling-oriented society. However, in 1997, of the total emissions of plastic wastes in Japan, about 53% were incinerated, while about 34% were buried as landfill.¹⁾ Only 12% of plastic wastes were reused as reprocessed plastics.¹⁾ For advancing recycling rates, it is absolutely essential to establish a plastic waste recycling system for detailed discrimination; moreover, development of an *in-situ*, low-cost, effective sorting method to separate plastics into original groups is attracting a global effort. Recent advanced technologies based on spectroscopic determinations, such as IR and Raman method, present the possibility of sorting plastic wastes.²⁾ Still, most noteworthy developments have used near infrared spectroscopy (NIRS).³⁾ The NIRS method is preferred for its speed and simplicity of operation compared to all other methods, including IR and Raman spectroscopy. A method to distinguish many kinds of plastics by combining near infrared spectra measurements and neural network analyses was proposed by Tanabe and colleagues.^{4,5)} We are also conducting a thorough investigation for NIRS feasibility; we have attained some positive results⁶⁾ for discrimination analysis of plastic wastes using a portable NIR spectrometer relying not only on a statistical and mathematical approach, but also on chemical interpretation of NIR spectra. Ozaki and his coauthors also reported discrimination of copolymers by near infrared spectroscopy; they pointed out the necessity to deepen fundamental

understanding of relations between spectral properties in the near infrared region and chemical and physical characteristics of investigated polymers.⁷⁾ Without a chemistry-based interpretation, a robust discrimination of analytes will not be significant in the field of spectroscopic science. This study attempts to further the investigation of plastic waste discrimination.

2. Experimental

Seventy-one kinds of plastics were collected and used as samples for measuring NIR spectra. The NIR diffuse reflection spectra were measured three times for each sample with a portable near-infrared spectrometer, PlaScan SH (OPT Research, Inc., Japan; Figure 1), which was equipped with an acousto-optic tunable filter (AOTF). Main specifications are: dimensions (250

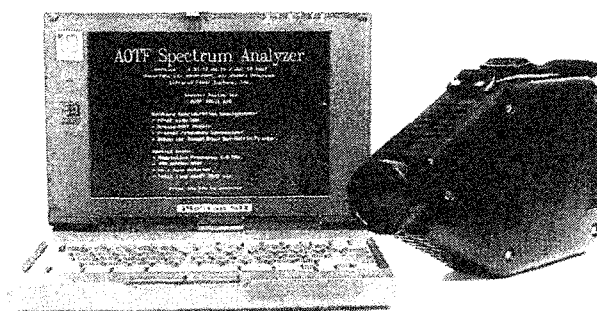


Figure 1 A portable near infrared spectrometer: PlaScan SH (OPT Research Inc., Japan).

mmL \times 150 mmW \times 55 mmD), weight (1.7 kg), wavelength range (1100 to 2500 nm), time required (0.1 to 1 sec, depending on data points and number of repetitions), data points (100, 200, 400, 500, 800, 1200, and 2400 points), radiation source (tungsten halogen lamp, 5 W), and detector (lead sulfide). Plastic samples were distinguished simply by the built-in software program with the standard model PlaScan into 15 sorts: ABS resin, acrylonitrile-butadiene-styrene resin; AS, acrylonitrile styrene; PA, polyamide;

PBT, polybutylene terephthalate; PC, polycarbonate; PC/ABS, PE, polyethylene; PET, polyethylene terephthalate; PMMA, polymethylmethacrylate; POM, polyacetal; PP, polypropylene; PS, polystyrene; PUR, polyurethane; PVC, polyvinyl chloride; PVDC, polyvinylidene chloride; and others. The program is based on discrimination analysis using a Mahalanobis Distance. A white ceramic disk was used as a reference in the diffuse reflection mode. In this work, the wavelength was re-corrected using a

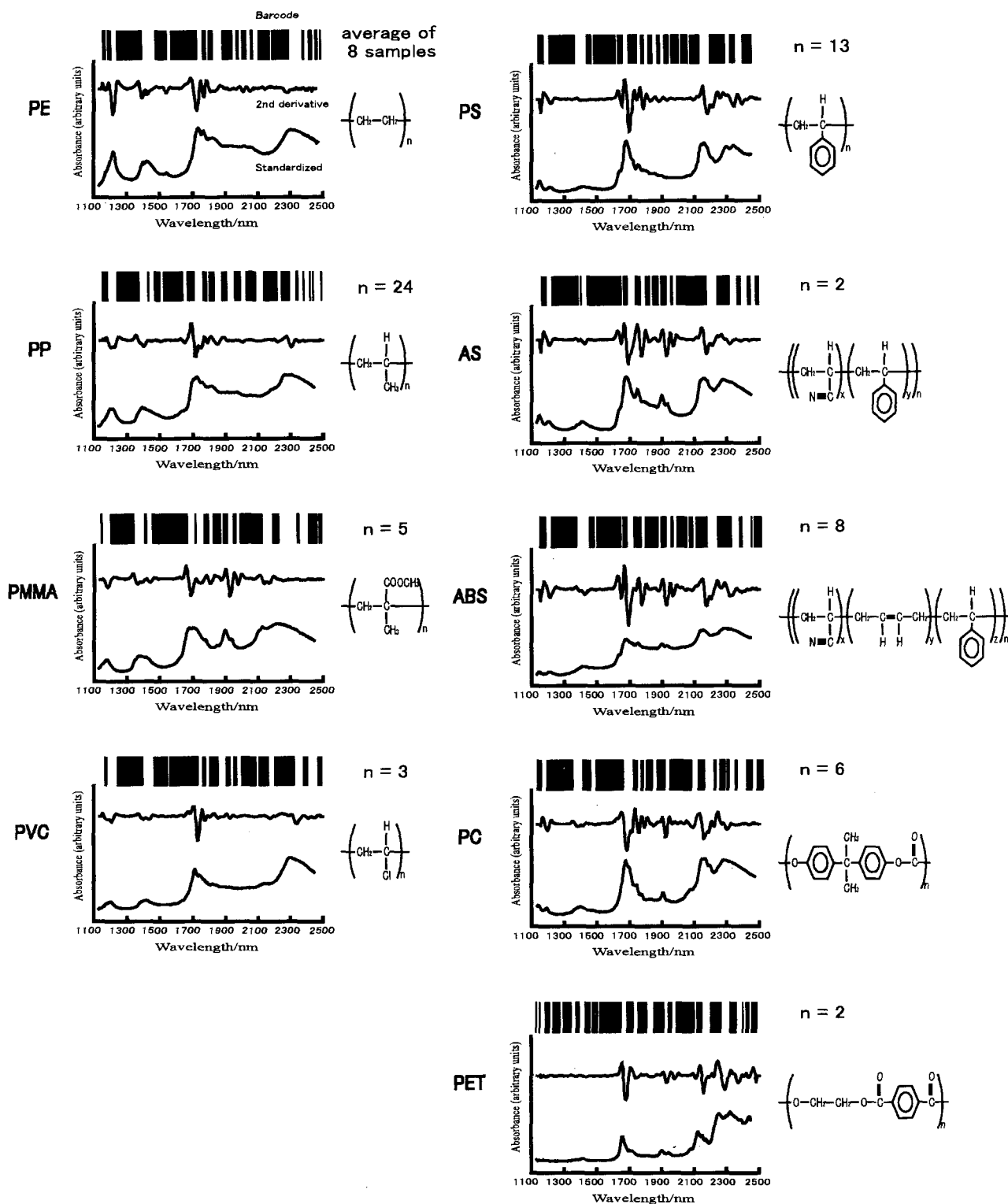


Figure 2 Standardized spectra, second-order derivative spectra, and barcode spectra for nine types of plastic samples. Each spectrum indicates the average for each type.

grating monochromator device (NIRS 6500, FOSS-NIRSystems) for apparent observed wavelength.⁸⁾ 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).

3. Results and Discussion

3.1 Standardized spectra, second-order derivative spectra and barcode spectra

Discrimination of samples was accomplished completely by built-in software of the PlaScan SH. Investigated samples were classified into nine types of plastics: polyethylene (PE), polypropylene (PP), polymethylmethacrylate (PMMA), polyvinyl chloride (PVC), polystyrene (PS), acrylonitrile styrene (AS), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), and polyethylene terephthalate (PET). This work presents more detailed characterization of NIR spectra to facilitate further discrimination. We acquired NIR spectra and performed the following spectral analyses.

First, because baseline differences of spectra were observed due to variation of individual constituents and optical properties, etc., a standardized normalization procedure⁹⁾ is applied to remove such systematic variation. It reduces the effect of baseline drift in original NIR spectra. This treatment centers each spectrum around zero by subtracting the mean and dividing each value by the standard deviation of the entire spectrum. 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 baseline 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 barcode spectrum.⁶⁾ 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 shows standardized NIR spectra, second-order derivative spectra, and barcode spectra for nine types of plastic samples. Each spectrum in Figure 2 shows an average for each of nine types of plastics. Accordingly, Figure 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.

3.2 Principal component analysis based on barcode spectra

Figure 3 shows two-dimensional score plots of the first two principal components (second principal component, PC2 vs. first principal component, PC1) for plastic samples based on barcode spectra. The PC1 accounted for 24.4% of total variance; PC2 accounted for 14.4% of total variance. Although separations of all samples are not complete in this figure, each kind of plastic was gathered.

The PC1 could be associated with discrimination among groups of PP, PE, and other. It seems that this result shows discrimination whether or not plastics have aromatic CH, or CO functional group. To reveal relations of chemical structure among plastics, we discounted the idea of wavelength contribution ratio spectrum⁸⁾, and showed it for PC1 (a) and PC2 (b) in Figure 4, respectively.

The contribution of absorbance at each wavelength to the principal component was considered using the following formula:

Contribution ratio (%) = (factor loading)² / (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 4(a) shows that wavelength contribution ratios assigned to the first overtone of aromatic CH (1667-1682 nm) and the second overtones of CO (1840-1910 nm and 1946 nm) are high for PC1. However, although the PVC does not have aromatic CH and/or CO functional groups, it is drawn near the groups including such functional groups. This would be indirectly attributable to existence of a Cl group, but we can not describe that attribution in this work.

Figure 4(b) shows wavelength contribution ratios assigned to

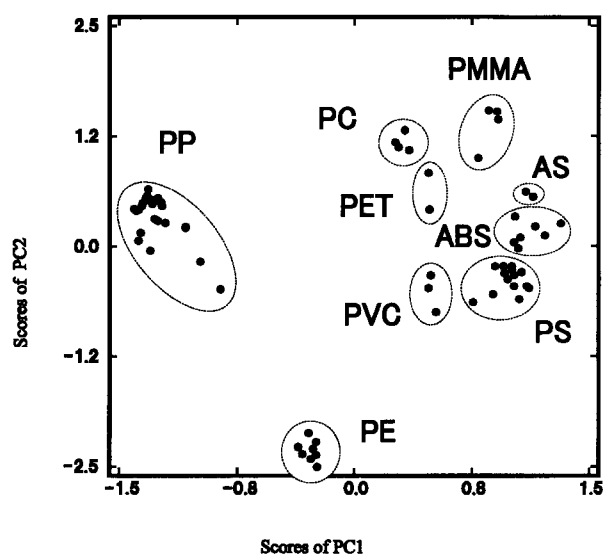


Figure 3 Score plots of PC2 vs. PC1 for plastic samples based on barcode spectra.

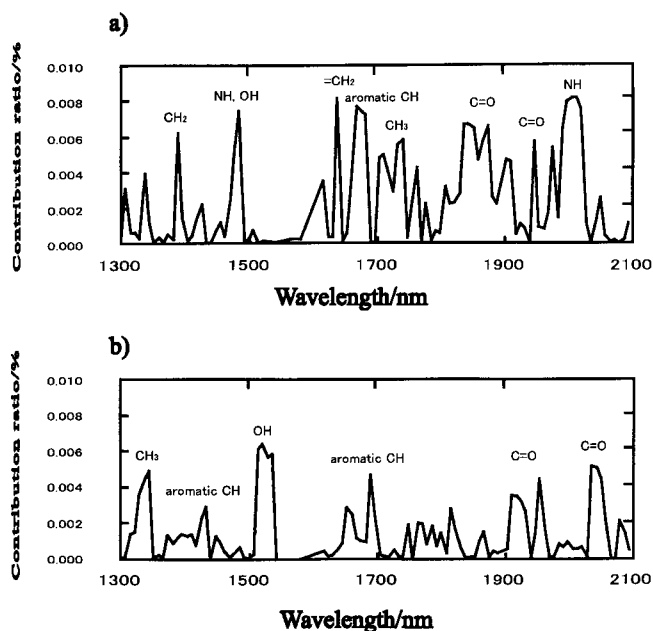


Figure 4 Wavelength contribution ratio spectra for PC1 (a) and PC2 (b).

the combination tone of CH_3 (1340 nm), the combination tone of aromatic CH (1440 nm), the first overtone of OH (1528 nm), the first overtone of aromatic CH (1690 nm) and the second overtone of CO (1910-1953, 2040 nm), which are high for the PC2. Addressing PC, PET, PVC, PMMA, AS, ABS, and PS, it is considered that PMMA, PC, and PET form a small cluster which involves the CO group. Also, AS, ABS, and PS have styrene structures in common; these can be gathered into one cluster. Therefore, PC2 would be attributable to structural existence of the CO group and aromatic CH in plastics.

3.3 Principal component analysis based on types of functional groups

PCA 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, CH_3 , 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 5 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. From this figure, we can see relative physical relationships among sample materials based on chemical structures. Although PS, AS, and ABS in cluster 1 involve styrene in the repeating structure, AS also involves the CN functional group and ABS involves the C=C functional group. Accordingly, these samples are discriminated by orientation of CN and C=C of factor loading vector. The PE, PP, PMMA, and PVC in cluster 2 involve ethylene in the repeating structure. In addition, PP involves CH_3 , PMMA involves CH_3 and COOCH_3 , and PVC involves Cl. These facts reflect discrimination among PE, PP and PMMA by the CH_3 group, and between PE and PVC by the Cl group. The PE and PMMA are also discriminated by orientation of the COO group. The PET and PC in cluster 3 are discriminated from others because they involve both the C-O and COO group. Moreover, while PET is separated from PC due to existence of CH_2 group, clusters 1 and 3 are separated from cluster

2 due to existence of the aromatic group.

Associating the above discussions with Figure 5 and Figure 3, although the PMMA is an analogue of PE, PP, and PVC in Figure 3, existence of the CO group, which affects the NIR spectrum strongly, results in the PMMA drawn near PET and PC. Influence of the CO group on the NIR spectrum has been shown in wavelength contribution ratio spectra in Figure 4. The Cl group also affects the NIR spectrum dramatically in Figure 3; 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.

5. Summary

In this article, we used a portable near infrared spectrometer to examine NIR spectra obtained from a variety of plastic samples; we discussed chemical implications of spectral characteristics.

Recently, there is a trend toward miniaturization of analytical instruments. Ochiai reported current technology of portable near infrared spectrometers.¹⁰⁾ Further development of a low-cost miniaturized instruments, like the PlaScan used here, may expand application of NIR spectroscopy tremendously.

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 either practically or scientifically.

We demonstrated that barcode spectra provide an effective alternative to discriminate types of plastics. 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. Principal component analysis, which is applied to barcode spectra, reveals the relationship of characteristics and similarity of NIR spectra among plastic samples. The PCA of barcode NIR spectra reflects plastic samples' chemical structure. Variation of functional groups, especially aromatic CH, CO group and Cl group, allows spectral difference of plastics.

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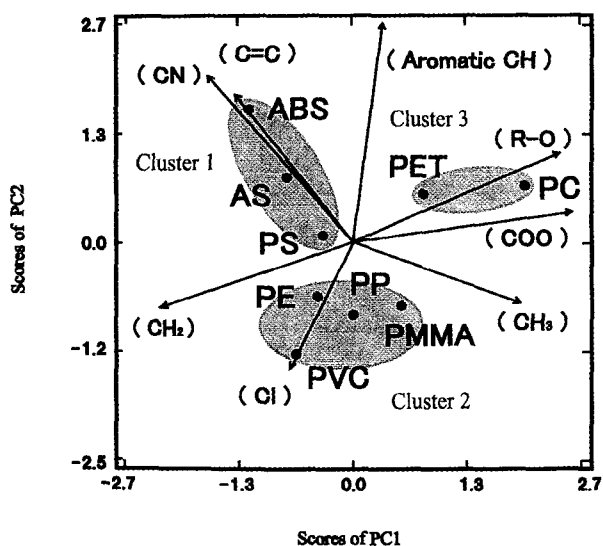


Figure 5 Score plots of PC2 vs. PC1 for plastic samples based on types of functional group.

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