

INFRARED EMISSION SPECTROSCOPIC IMAGING OF MICROPLASTICS USING LONG-WAVELENGTH INFRARED HYPERSPECTRAL CAMERA WITH IMAGING-TYPE TWO-DIMENSIONAL FOURIER SPECTROSCOPY

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ABSTRACT

We aim to realize a microplastic discrimination system, by using a hyperspectral camera that images in the longwave infrared (LWIR) band, which would be smaller, cheaper and faster than focal plane array-based Fourier-transform infrared spectroscopy (FPA-FTIR). We attempt to perform LWIR band (wavenumber range: 714–1250 cm^{-1}) emission spectroscopic imaging of 35- μm -thick polyethylene (PE) and polypropylene (PP) heated on an aluminum plate (surface temperature of aluminum plate: 103.7 $^{\circ}\text{C}$), in the hope for a consistent application to microplastics with a wide size range. It is confirmed that PE and PP exhibit a higher brightness than the aluminum plate. It is also confirmed that the infrared emission spectra of PE and PP produce characteristic peaks at the same positions as those in the reference absorption spectra, and the clustering results by the k-means++ method reveal the possibility for good discrimination among the aluminum plate, PE and PP.

Index Terms— Microplastic, Hyperspectral imaging, LWIR band, Emission spectroscopy, Fourier spectroscopy

1. INTRODUCTION

In recent years, marine pollution caused by microplastics has become an environmental issue. Fourier-transform infrared spectroscopy (FTIR) has been used in many cases to identify the plastic species in microplastics [1]. In particular, plane array-based Fourier-transform infrared spectroscopy (FPA-FTIR) using a two-dimensional array sensor can simultaneously acquire one spectrum per pixel of the two-dimensional array sensor for all pixels in a process known as spectral imaging. Therefore, FPA-FTIR is very useful for measuring small, numerous and sparsely-distributed samples such as microplastics. However, FPA-FTIR is very expensive

and requires a lot of space. In addition, because the number of pixels in the installed FPA is almost 128×128 pixels, even if the magnification is adjusted to make the field of view per pixel $20 \mu\text{m} \times 20 \mu\text{m}$, the measurement field of view will only be $2.56 \text{ mm} \times 2.56 \text{ mm}$, so it would take 9 hours to measure an area of $\phi 47 \text{ mm}$; therefore, a decrease in the measurement time would be beneficial [2].

We have constructed an inexpensive palm-sized longwave infrared (LWIR) band hyperspectral camera by combining a microbolometer and an imaging-type two-dimensional Fourier spectrometer to improve on the spectroscopic imaging of MPs [2]. The microbolometer is a general-purpose FPA in the LWIR band that has been commonly used in thermographic cameras in recent years. Although such FPAs are less sensitive than FPA-FTIR FPAs, such as HgCdTe (MCT), which require cooling, they are inexpensive and have a large number of pixels (e.g., 640×480 pixels). Imaging-type two-dimensional Fourier spectroscopy makes it possible to construct a hyperspectral camera with fewer optical components than a Michelson interferometer, which is mainly used in FPA-FTIR. In addition, because our hyperspectral camera involves near-common-path wavefront-division phase-shift interferometry, it is in principle more resistant to vibrations than Michelson interferometry, and there is no need to equip the hyperspectral camera with a vibration isolation mechanism.

As an example, we have reported the spectroscopic imaging results of black microplastics by reflection measurement using the LWIR band hyperspectral camera [2], but because microplastics (defined as plastics with a size of $<5 \text{ mm}$) have a wide range of particle sizes, transmission measurement and attenuated total reflection (ATR) measurement examples have also been reported.

In the reflection measurement, there are many ways to measure the specular reflection light and the diffuse reflection light. In the measurement of the specular reflected light, the

spectrum is distorted into a first-order differentiated waveform owing to the anomalous dispersion phenomenon of the refractive index, and it may be difficult to qualitatively evaluate the spectrum without Kramers-Kronig analysis [3]. There is also the problem where the amount of reflected light tends to fluctuate depending on the angle of incidence and the surface shape of the sample. Diffuse reflected light has a lower intensity than specular reflected light and so requires a highly sensitive spectrometer. It is generally difficult to apply the transmission method in the LWIR band to samples with thicknesses in the order of millimeters. In addition, the ATR method is not easily affected by the thickness of the sample, but if the sample and the ATR prism are not in close contact, the measurement will not be performed properly.

As an alternative to these methods, we have focused on infrared emission spectroscopy [4,5]. Fujioka measured the infrared emission spectra (wavenumber range: 500–4000 cm^{-1}) of polyethylene (PE) films and other materials using a point measurement type FTIR spectrometer equipped with an MCT detector [4]. His report foreshadows the hope that emission spectroscopy will eliminate the need to measure background spectra, to account for the difference in emissivity between the background and the object being measured, and that it will have consistent applicability to the measurement of microplastics with a wide range of sizes.

In this report, we measured the infrared emission spectra of microplastics (PE and polypropylene (PP)) with a palm-sized LWIR band hyperspectral camera by combining a microbolometer and imaging-type two-dimensional Fourier spectroscopy. We also report the clustering results of the

measured spectra using an unsupervised learning algorithm, the k-means++ method.

2. MATERIALS AND METHODS

2.1. Experimental setup

The experimental optical system used for microplastic measurements in this study is shown in Fig. 2(a),(b). The experimental optical system was composed of an imaging-type 2D Fourier spectrometer, a magnification lens (ϕ 50 mm, focal length: 25 mm), an aluminum plate (thickness: 1 mm) and a hot stirrer (CHPS-170DN, AS ONE Corporation., Osaka, Japan). The imaging-type 2D spectrometer (105 mm \times 90 mm \times 50 mm, 1.25 kg) was composed of an observation magnification lens (ϕ 50 mm, focal length: 50 mm), a multislit array (aperture: 24 μm , light shield: 24 μm), an objective lens (ϕ 25 mm, focal length: 17 mm), a fixed mirror, a movable mirror, an imaging lens (ϕ 25 mm, focal length: 17 mm) and a microbolometer-type FPA (Boson 320, FLIR Systems, Inc., Wilsonville, OR, USA). The movable mirror was adjusted by a piezo stage (PPS-20-11300, Micronix USA, LLC, Santa Ana, CA, USA) with a stage controller (MMC100-01010, Micronix USA).

SpectroCapture software (NISSIN KIKAI Co., Ltd., Kagawa, Japan) was used to control the movable mirror and FPA, and to acquire the image files (16-bit TIFF format) in which the interferograms were recorded by the spectrometer. The measurement conditions for the spectra were set to a measurement wavenumber band of 714–1250 cm^{-1} , a

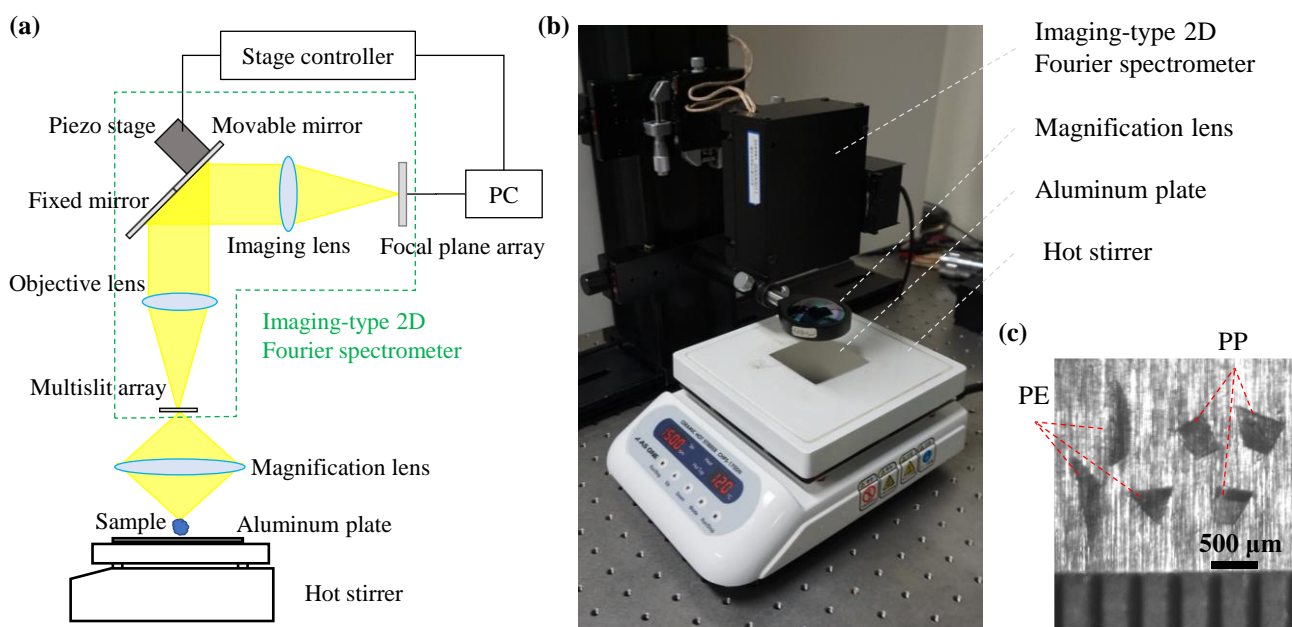


Fig. 1 Experimental optical system and samples. (a) Experimental optical system configuration. (b) Photograph of the experimental optical system. (c) Photograph of microplastics on an aluminum plate.

wavenumber resolution of 8 cm^{-1} , a field of view of $3.8 \text{ mm} \times 3.0 \text{ mm}$ (the field of view of one pixel was $12 \mu\text{m} \times 12 \mu\text{m}$) and a measurement time of 15 s. The number of scans was one. SpectroViewer (NISSIN KIKAI Co., Ltd.) was used to obtain the spectrum of each pixel from the interferogram, which was recorded in the direction of the number of images (16-bit TIFF format). The spectra were obtained by applying a fast Fourier transform (FFT) algorithm to the interferogram. Before FFT, the interferogram was multiplied by the 870-point Blackman window and zero-filled to obtain 1024 data points. The spectra of the focus pixel were obtained by averaging the spectra of 7×7 pixels centered on the focus pixel to reduce the noise.

The temperature setting of the hot stirrer was $120 \text{ }^\circ\text{C}$. The surface temperature of the aluminum plate at this time was $103.7 \text{ }^\circ\text{C}$, as measured by a thermocouple (306 DATA LOGGER THERMOMETER, CENTER Technology Corp., New Taipei City, Taiwan).

2.2. Materials

Fig. 2 (c) shows an image of the microplastics used for the measurements in the visible light range. The microplastics were prepared by cutting sections (thickness: $35 \mu\text{m}$) from the PE and PP products using a microtome (RM2035, Leica Biosystems, Nussloch, Germany), and then dividing the sections into pieces using a cutter so that the thickness was maintained.

2.3. Clustering

A clustering algorithm in unsupervised learning, k-means++, was used to discriminate among the aluminum plate, PE and PP. The k-means++ method automates the initial determination of cluster centers required by the k-means method [6]. In this study, the number of clusters was set to three, considering that there were three types of materials to be measured: the aluminum plate, PE and PP. We decided to use three features for clustering with the k-means++ method: the brightness of the binarized LWIR band image, the correlation coefficient with the PE reference spectrum and the correlation coefficient with the PP reference spectrum. The brightness of the binarized image of the LWIR band image was employed to determine the location of microplastics.

The binarized image was created by first creating a difference image between the image observed only on the aluminum plate and the image observed with the microplastic placed on the aluminum plate, applying a 5×5 averaging filter to the difference image, and then applying Otsu's binarization method [7]. In addition, the brightness after binarization was assigned to 0 or 255.

Correlation coefficients were employed because they are useful as a feature to discriminate between PE and PP. It is

known that the peak of the infrared emission spectrum and the wavenumber of the absorption spectrum are almost coincident [4,5]. Therefore, the absorption spectra (wavenumber range: $400\text{--}4000 \text{ cm}^{-1}$) provided by Primpke *et al.* were averaged for the reference spectra of PE and PP, and the spectra normalized to 0 for the minimum absorbance and 1 for the maximum absorbance were used as reference spectra [2,8]. To evaluate the spectra, correlation coefficients were calculated as follows:

$$r = \frac{\text{Cov}(y1(v), y2(v))}{\sigma y1 \cdot \sigma y2} \quad (1)$$

where r is the correlation coefficient; $y1$ and $y2$ are the intensity values in the sample spectrum and reference spectrum, respectively, for the wavenumber for v data points; and $\sigma y1$ and $\sigma y2$ are the standard deviations of all intensity values from the mean value of the sample spectrum and reference spectrum, respectively. r is a value in the range of -1 to 1 . In this study, as a result of the binarization of the LWIR band image, the correlation coefficient of the pixels that were determined to be the areas without microplastics were assigned a value of -1 . Because it is desirable to normalize the range of values for each feature during clustering, the correlation coefficient of -1 to 1 was treated by normalizing it to 0 to 255, matching the range to the binarized brightness.

3. RESULT AND DISCUSSION

3.1. Observed image and emission spectrum in the LWIR band

Figure 2(a) and 2(b) show the LWIR band images of the aluminum plate and the microplastic on the aluminum plate, respectively. The brightness of the pixels on the microplastic was higher than that on the aluminum plate (a higher brightness corresponded to a whiter image), which confirmed that the plastic emitted more LWIR band light than the aluminum plate, as reported by Fujioka [4]. Fig. 2(c) and (d) show the comparison among the LWIR band emission spectra of the aluminum plate, PE and PP, and the reference absorption spectra for the same pixels used in Fig. 2(a) and (b), respectively.

In the emission spectrum of PE, there was a peak at 722 cm^{-1} that was also seen in the reference absorption spectrum. This peak was not observed in the emission spectrum of the aluminum plate. The emission spectrum of PP showed peaks at $806, 841, 896, 974, 999$ and 1168 cm^{-1} that were observed in the reference absorption spectrum. These peaks were not observed in the emission spectrum of the aluminum plate. It was also confirmed that there was a clear difference in the shape of the emission spectrum between PE and PP, as the

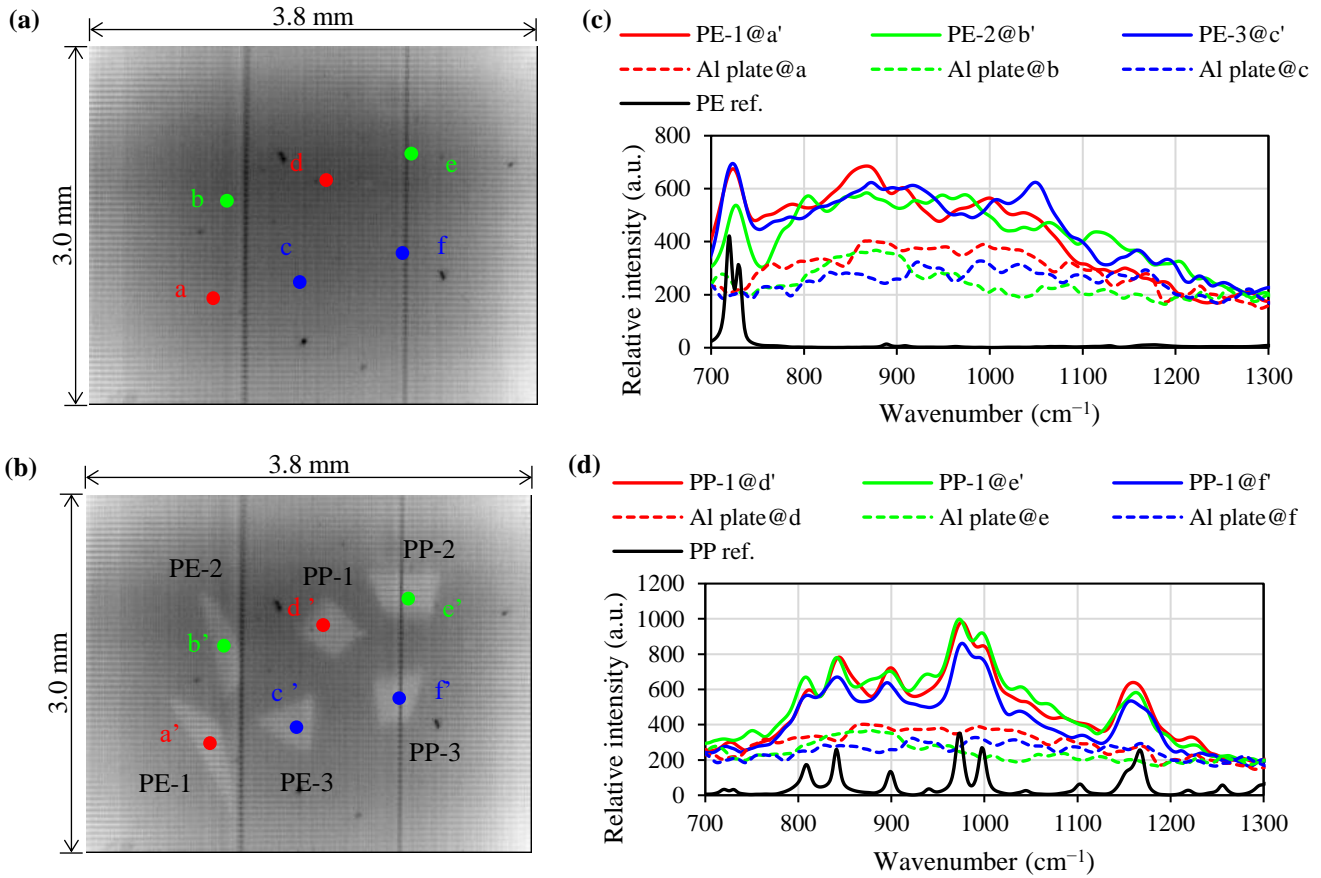


Fig. 2 LWIR band images and emission spectra of an aluminum plate and microplastics on an aluminum plate. (a) LWIR band image of aluminum plate. (b) LWIR band image of microplastics (PE and PP) on an aluminum plate. (c) Comparison of PE, aluminum plate emission spectra and PE reference absorption spectra at the same pixels shown in Fig. 2(a), (b). (d) Comparison of PP, aluminum plate emission spectra and PP reference absorption spectra at the same pixels shown in Fig. 2(a), (b).

722 cm^{-1} peak observed from PE was not observed in the spectrum of PP. In the infrared emission spectroscopy method, it is possible to use an object with low emissivity, such as an aluminum plate, as a background, which makes it relatively easy to detect spectral peaks specific to a material without having to collect a background spectrum. This is expected to reduce the time required for the identification of microplastics.

3.2. Clustering

Figure 3(a) shows the result of clustering by the k-means++ method, which plots the data distribution of each pixel in Fig. 2(b) using the binarized brightness and the correlation coefficients between emission spectra and the PE and PP reference absorption spectra. From Fig. 2(b) and Fig. 3(a) and (b), we see that the data classified into cluster 1, cluster 2 and cluster 3 were generally the same as those classified into the aluminum plate, PE and PP regions, respectively. These

results also suggest that it was relatively easy to discriminate among substances without measuring the background spectrum in the emission spectrum measurement when an object with small emissivity was used as the background.

Some of the pixels in the PE region were labeled with the same color as those in the PP region. In our spectrometer, the spectral response band was 714–1250 cm^{-1} , and the reason for this discrepancy was proposed to be that the sensitivity of the PE emission peak at 722 cm^{-1} was lower than that of the PP emission peak band. As a countermeasure, it is suggested that the discrimination performance can be improved by correcting the emission spectrum by accounting for the sensitivity characteristics of the spectrometer.

4. CONCLUSION

We attempted to measure and discriminate between the emission spectra of microplastics heated by an aluminum plate using a palm-sized LWIR-band hyperspectral camera

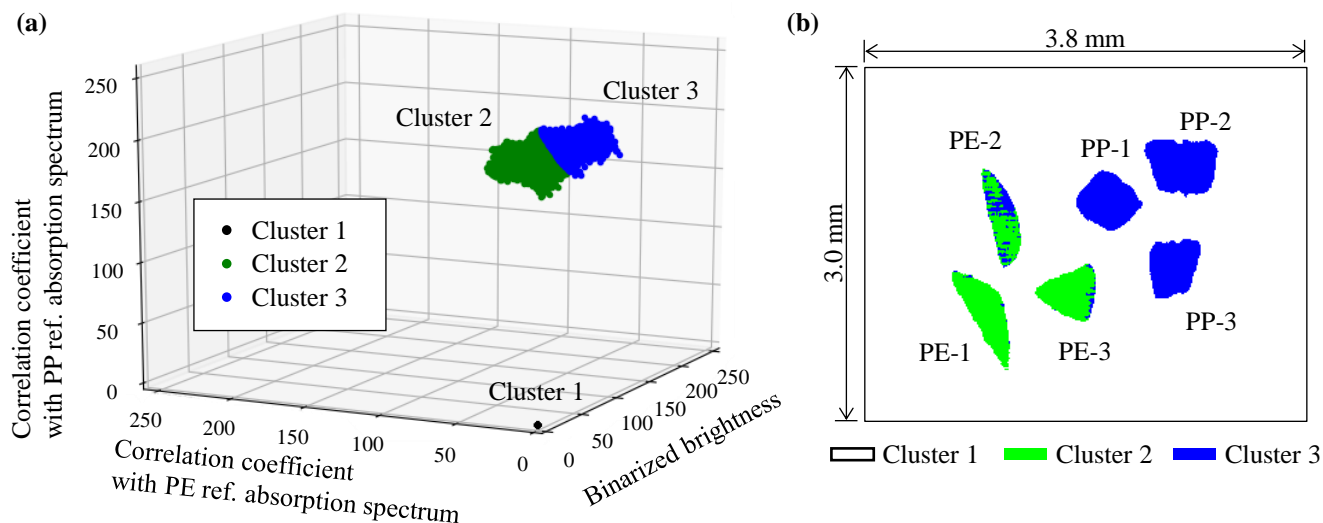


Fig. 3 Result of clustering each pixel shown in Fig. 2(b) based on three features: binarized brightness, correlation coefficient with PE reference absorption spectrum and correlation coefficient with PP reference absorption spectrum. (a) Data distribution and clustering results for each pixel in Fig. 2(b) in 3D space represented by binarized brightness, correlation coefficient with PE reference absorption spectrum, and correlation coefficient with PP reference absorption spectrum. (c) Clustering image drawn on the basis of Figure 3(a).

constructed by combining a microbolometer and imaging 2D Fourier spectrometer. It was confirmed that the microplastics could be detected as bright images by using a low emissivity object, such as an aluminum plate, as a background. In addition, the k-means++ method was used to verify the discriminability of the aluminum plate, PE, and PP using the emission spectra themselves without measuring the background spectra, which is necessary for calculating the absorbance, transmittance and reflectance, and good clustering results were obtained.

In the future, we will verify the effect of correcting the emission spectrum with and without accounting for the camera sensitivity characteristics, and the possibility of applying the correction to other types of plastics.

5. ACKNOWLEDGEMENTS

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