Identification of Shredded Plastics in milliseconds using Raman Spectroscopy for Recycling

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Abstract - **Raman Spectroscopy is able to identify plastic components, similar to infrared absorption. This paper shows the potential application of Raman spectroscopy to post-consumer plastic recycling when massive and accurate sorting processes are required. We developed a high-speed Raman apparatus for scanning with an appropriate wavelength region of less as 1.5 milliseconds, and an analyzing methodology that uses a discrimination function. We successfully implemented this technique in a shredded plastic recycling plant. The online sensing system successfully carried out more than three hundred cycle decisions per second.**

I. INTRODUCTION

Plastics are used everywhere in daily life. Large amounts of them either become waste or are used as a fuel for thermal recovery at the end of their useful life. However, it is possible to double or triple the useful lifetime for plastics and so greatly reduce the use of fossil fuels if there are ways to repeatedly recycle plastics. This is called chemical or material recycling and many techniques have been introduced for this purpose. The classification of each kind of post-consumer plastic is the crucial technology for the type of material recycling that is most the effective for saving natural resources and energy.

Most plastic identification techniques now used in industrial recycling of massive amounts make use of various properties of plastics such as specific gravity, electrification, and heat conductivity. We also have developed an identification system for high-density polyethylene (HDPE) or low-density polyethylene (LDPE) that uses a photo-thermal conversion process [1]. Such techniques are well applicable to sub-ton per hour quantities; however, the quality of the sorted plastics is not so good for their reuse. Similarities in the properties of various plastics produce a mixture of the different plastics and this leads to a downgrading of the purity of the sorted plastics for material recycling.

On the other hand, in laboratory analyses, inferred (IR) and Near-IR (NIR) reflectance measurements are common methods used to identify kinds of plastics [2]. This spectroscopic analysis provides information about the molecular structures and can definitively classify plastics. In this paper, we present the applicability of Raman spectroscopy with multivariate analysis to industrial level plastic identification and show its advantages over IR and NIR measurements [3]. Figure 1 presents a scheme of the plastic sorting system in which Raman spectroscopic identification was implemented. In this system, the shredded post-consumer plastics are first feed into a preprocess line to remove metals, wire, labels and similar contaminations from the plastic mixture. The plastics are then moved under a spectrometer by a conveyor for analysis. In the last stage, an air gun is used for sorting the identified pieces of plastic. This system is being successfully operated in a factory, where pure polymer is recovered from shredded dust originating from waste household electronic appliances. In Japan, a law encourages the reuse of electronic household appliances. This law states that used electronic household appliances (air-conditioner, refrigerator, TV and washing machine) should be collected by their distributers and sent to recycle plants as a mass resource. In such facilities, large plastic parts are removed from electronic household appliances for reuse in new products. Other plastic parts are shredded and then carried through a classification system.

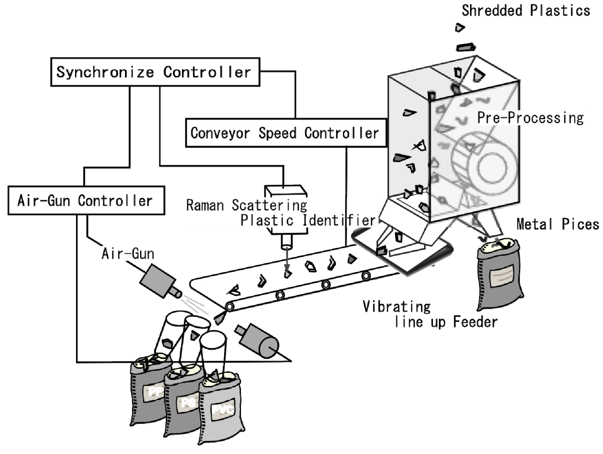

Figure 1. Scheme of the plastic sorting system with Raman spectroscopy.

II. RAMAN IDENTIFICATION

Raman spectroscopy also identifies the plastics from the molecular structure. In the recycling industry where accurate sorting of massive amounts is required, the application of Raman spectroscopy has great advantages compared with IR and NIR. For example; (1) no reference signal is required; (2) surface conditions and H2O and CO2 in the air or on the surface have less effects; (3) the signal to noise ratio (SNR) is easily achieved by a pumping laser. These advantages make Raman measurements more robust to changes of sample characteristics.

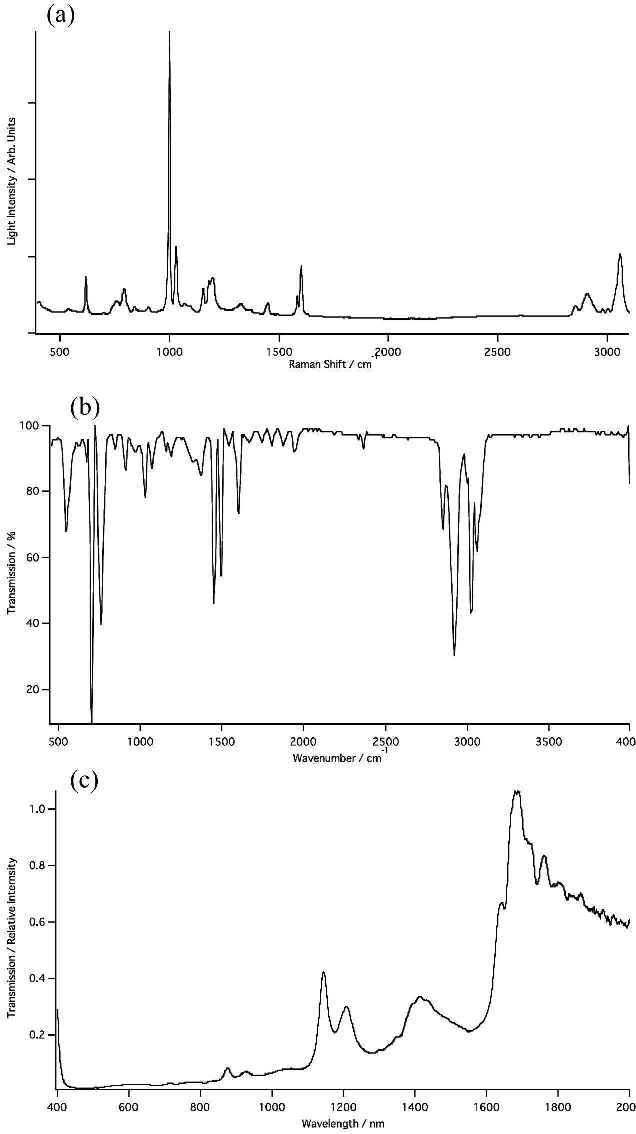

Figure 2. Spectra of polystyrene in (a) Raman, (b) IR and (c) NIR

Raman, IR and NIR spectra of polystyrene (PS) are shown in Fig.2. The IR and Raman spectra have sharp peaks whereas the NIR spectrum is broad. The reason for this broadness is that NIR spectrum consists of complicated harmonics of IR spectra. This broadness leads to degradation in SNR. Even with the problem of low SNR, the NIR system is still applied to the identification of plastics. This probably tells us that identification with Raman spectroscopy would be able to improve the purity and sorting speed compared to that done using NIR.

IR and Raman spectra demonstrate the rule of alternatively missing lines; a symmetric vibration such as ring breezing in benzene structure is known to be active in Raman whereas it is not active in IR. This phenomenon is shown in Fig. 2; there is sharp peak around 1000 cm^{-1} in the Raman spectrum, but not in the IR. However IR detection in a thermal energy region takes a long time, the order of a second at least regardless of the accuracy of the plastic identification in Raman and NIR.

III. EXPERIMENTAL

A. *Samples*

In electronic household appliances, 3 main kinds of plastics are used; polypropylene (PP), polystyrene (PS) and acrylonitrile-butadiene-styrene (ABS) resin. Some may contain additives. We collected 125 spectra from 120 test pieces of shredded post-consumer plastics from electronic home appliances. For references, 3 types, a total of 15 pieces of virgin pellet (raw material) from a plastic recycling factory in Saga, Japan and a local industrial technology center in Fukuoka, Japan, were used. For validation purposes, test samples are categorized into 4 groups (i.e. PP, PS, ABS, and unknown) depending on each spectrum.

B. *Instrument*

The spectra are gathered by a self made Raman spectrometer consisting of spectroscopic detection and data-analysis components. This optical part consists of a 785-nm high-power diode laser operated at 2 watts and a backside incident FFT-CCD of 1024 x 58 pixels. The optical system is designed to achieve high optical throughput with the appropriate resolution of ca.20 cm-1.The small laser focusing spot could deal with shredded plastic pieces of less than 1cm. The accumulated charges produced by photons in the longitudinal pixels are binned further into the last pixel line to improve sensitivity. The final output charges are feed into a 16-bit analog-to-digital converter. The data analysis part is able to be embedded in Field Programmable Gate Array (FPGA) circuits. This IC made for editable digital circuitry for the signal process algorithm and to replace the CPU to reduce processing time.

The spectra are measured at a photon accumulation time of 70 ms with the wave-number range of around 300 to 3500 cm-1 in 1024 data points. These data are saved in CSV files for further analysis. Calculations for the multivariate analysis are carried out on the free software "R" [5] for statistical computing, instead of being embedded in FPGE.

The whole apparatus fits into a unit of 32cm x 55cm x 4cm. This size reduction makes possible to the deployment of a number of Raman spectrometers at reduced cost. Increasing the number of the apparatus could directly increase amounts processed.

C. *Data Processing Flow*

In Raman spectra, a molecular vibration known as a normal vibration is observed as each peak. These peaks present information on the molecule structure, each of which is unique. This makes general identification possible by checking for the existence of a few distinctive peaks in the Raman spectra. Furthermore, modified plastics have extra peaks from the normal vibrations of additives. For more precise identification, multivariate analysis was used in this experiment.

Figure 3 presents the data processing flow of this experiment. Spectra data are taken into R, and preprocessed. Then, this data is feed for multivariate analysis (i.e. discrimination analysis) based on Mahalanobis' generalized distance. Finally, we were able to identify the plastics from the resulting values.

Peak extraction and baseline subtraction are considered in the preprocessing method. We determined the five points of the top of the peaks and both-side base points for each peak; employed for multivariate analysis. The area in the triangle from these five points is used as the peak signal intensity for the analysis. This simple method greatly reduced the calculation load.

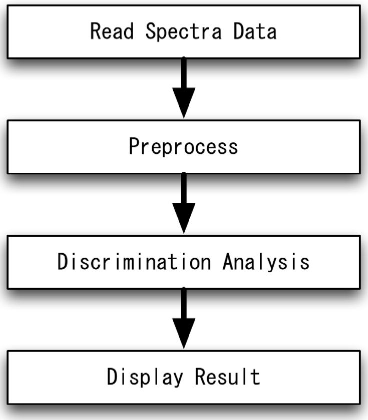

Figure 3. data processing flow used in this experiment

IV. RESULT AND DISSCUSSION

A. Raman Spectra of waste plastics

Figure 4 shows the robustness of the Raman spectra of PP, PS and ABS with characteristic peaks with good SNR, even with a measurement time of 6ms. In all spectra there are peaks around 3000cm-1, which are attributed to the stretching of CH or OH bonds that all plastic has. Styrene's (PS and ABS) and PP are distinct by the peak for ring breezing in benzene structure, and the peak around 1000cm-1. For Styrene, the apparent peak of CN-stretching around 2250cm-1 makes it possible to decide on PS or ABS that are not distinguishable in the commonly used NIR.

As shown in the PS and ABS spectra, the gradual slope can be attributed to Rayleigh scattering from the pumping laser, which shows how the Raman scattering is weak; the probability is 10-4 to 10-5 comparing to Rayleigh scattering.

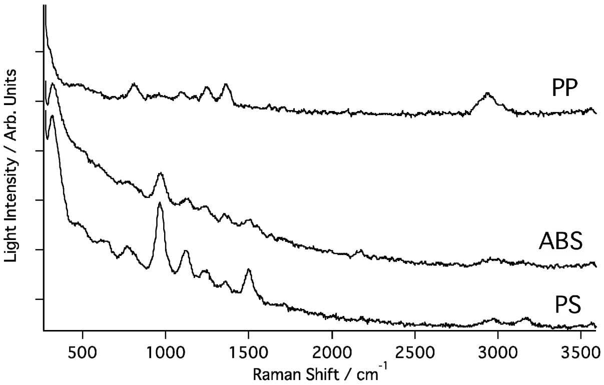

Figure 4. Raman spectra for PP, PS and ABS measured in 6ms. Good SNR is obtained in such a short period of time.

These spectra were obtained after several improvements to the optical components of the spectrometer. No optical fiber was used to reduce the loss of optical transmittance; though optical fiber is very useful for the optical system implementations. Another modification was broadening the slit width to be greater than those usually used in laboratory equipment. This makes it much brighter but broadens the peak on the other hand. We found the optimized slit width for the peak height and broadness.

B. Preprocessing for Raman spectra

Preprocessing of the signal has an important role to reduce of calculation load and to increase accuracy. Figure 5 shows comparisons of identification accuracy when a preprocessing method is applied. This result shows that accuracy of identification could increase by up to 94% by extracting unique peak intensities from the spectrum [5] to feed into the analysis. Some adjustments of spectrum such as complicated baseline subtraction and/or peak fitting, however, could not improve the accuracy. For down sampling, spectra data are folded up to equal widths of 127 to 8 channels each. Its accuracy was highest when 16 data channels are added and averaged.

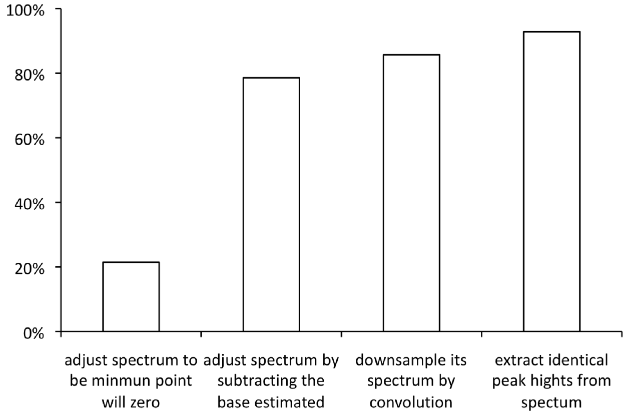

Figure 5. Accuracy depend on preprocess method.

C. *Identification with Discrimination analysis*

With discrimination analysis calculations are performed for each of the selected target. At first, a first order polynomial is generated by using a reference sample. Then, this set of the values is applied to calculate the resulting value of each candidate in the discrimination function. Figure 6 presents the distribution of the resulting values obtained from PP's equation for 61 pieces of PP confirmed by human eye for Raman and IR spectra. The frequency of the resulting value is plotted on a section width of 1000.

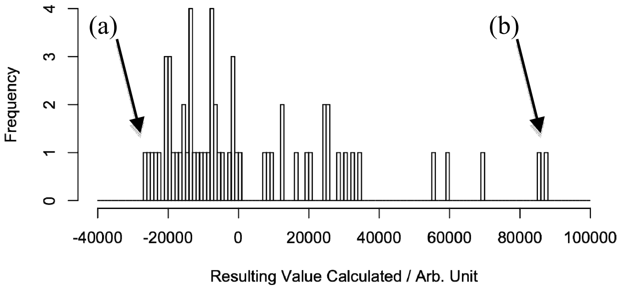

Figure 6. Histogram of resulting value for calculated for PP.

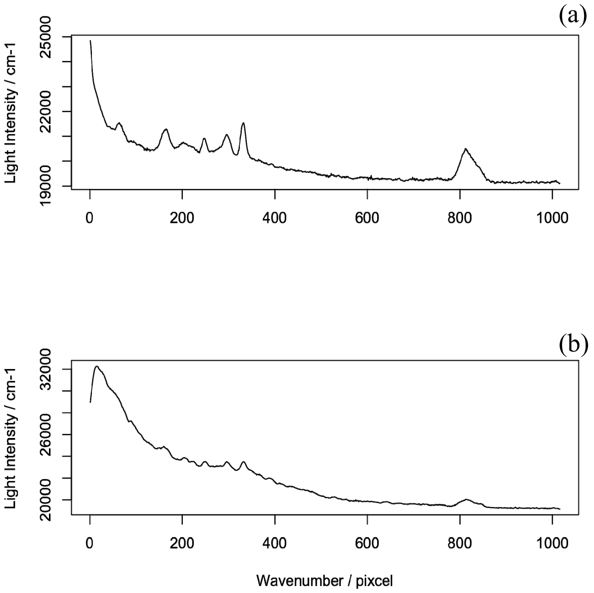

Figure 7. Difference of typical Raman spectrum (a) when the calculated value is less than zero, (b) when the calculated value becomes highest.

The resulting values are accumulated mainly in the region from minus forty thousand to zero. Figure 7 presents Raman spectra for the resulting value of the minimum (a) and the maximum (b) in a histogram. Raman spectrum of (a) clearly shows the peaks and less Rayleigh scattering baseline compared with (b).These features are typical for spectra with the resulting values of more than 50000. Such degradation of the spectral quality in the Raman spectrum of (b) may provide information of additive content or a degree of plastic quality decay.

D. *Implementing to on-line sensing*

The high-speed Raman apparatus developed in this work could measure the appropriate SNR spectrum and identify plastics with multivariate analysis in less as 1.5 milliseconds. Twenty-five of the apparatus could be installed in a plastic recycling plant utilizing a 50-cm width and 100-m/minute speed belt conveyor. This facility is able to process sub-ton per hour amounts of shredded plastics.

V. CONCULUTION

New identification techniques for post-consumer plastic components have been developed for the recycling industry where massive and accurate sorting processes are required. High-speed Raman spectroscopy with multivariate analysis was successfully implemented into an online sensing system in a shredded plastic recycling plant. The equipment could make more than three hundred cycle decisions per second. Multivariable analysis successfully distinguishes plastic components and made it possible to classify quality from the resulting values of discrimination analysis.

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