Investigation of fluorescence spectra of various types of plastics for the purpose of sorting and further processing

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Abstract. Excitation-emission matrices of various plastic package samples were studied. A tuneable 210-310 nm laser was used as an excitation source. The samples of polyethylene terephthalate, polypropylene, and high-density polyethylene of various colour and transparency showed multiplex wideband fluorescence spectra dependent on the excitation wavelength. Principal component analysis demonstrated that the excitation-emission matrices of most samples are well described by two principal components, individual for their types and colorant additives. Despite complex structure of the excitation-emission matrices of different types of the plastic, appropriate linear combinations of the principal components allowed finding a characteristic component for each of them.

1. Introduction

The problem of efficient recycling of plastic packages in order to reduce the environmental pollution rate is extremely urgent nowadays. The most common types of the plastic packaging include polyethylene terephthalate (PET), polypropylene (PP), polyvinyl chloride (PVC), high-density polyethylene (HDPE), etc. Currently, a significant amount of PET packaging is recycled by separating it from lighter fractions (labels and other types of plastic) by grinding and washing. In practice, however, it is extremely inefficient, since it also leads to the appearance of by-products consisting of various types of light fractions plastics. Such mixtures are difficult to sort and recycle.

Obviously, it is more efficient to separate the plastic packages before the grinding and washing stage. This can be done using machine vision and image recognition of the known packaging types, UV and IR spectroscopy. In particular, it is possible to effectively separate PET and PVC objects based on differences in reflectivity in the near-IR spectrum [1], [2]. An alternative method is the fluorescence spectroscopy with the ultraviolet excitation [3]. It is less sensitive to dyes in plastic products and the presence of contaminants, which significantly affect the reflectance. Each fluorescent substance, present in plastic samples, exhibits wideband fluorescence. Usually, the profile of the spectrum of the specific fluorophore does not significantly depend on the excitation wavelength. This makes the fluorescence spectrum a fingerprint of the specimen. Due to a wideband nature of the fluorescence of plastics it might be difficult to analyze the measured spectra, since the spectra of individual fluorophores may
significantly overlap. This makes the separation of individual fluorophores’ contributions a tricky task. Statistical approach might be effective in this case.

Using principal component analysis (PCA) has already proved its perceptiveness [3]. PCA provide independent (orthogonal) principal components (PC), which are linear combinations of fluorophores’ spectra and are sorted according to the maximum correlation with the measurements. Additional data processing using physically reasonable assumptions might provide additional data [4]. By varying the excitation radiation wavelength, one could change the contributions of different fluorophores to the observed spectra, providing additional degree of freedom. Thus, measuring the excitation-emission matrices also extends the possibilities of finding individual fluorescent components, building multi-excitation recognition algorithms.

The purpose of this work is to study the fluorescence excitation-emission matrices for various types of plastics in order to determine the possibility of sorting them (especially separating PET from PP and HDPE) for further processing and recycling.

2. Materials and methods
Excitation-emission matrices of the plastic waste samples were measured using OPO pulsed laser system “Vibrant HE 355 II +UV” (Opotek, USA), and “Action SP2300” monochromator (Princeton Instruments, USA) with “Pixis 256” CCD camera (Princeton Instruments, USA). More details are described elsewhere [5].

A total of 58 samples of plastic used for the manufacture of various consumer goods were examined: 20 – HDPE, 18 – PP, 20 – PET. The size of the plastic pieces was about 6x4 cm. Each sample had its own color, from fully transparent to black. Spectral measurements were made for a randomly selected part of the sample. For each sample the laser radiation wavelength was scanned in the 210-310 nm range with 10 nm steps. The fluorescence signal was accumulated during 20 laser pulses. Each pulse energy density did not exceed 200 μJ/cm² to avoid non-linear effects [6]. Each spectrum was measured five times, normalized to the laser pulse energy and device relative spectral sensitivity, and then it was averaged.

3. Results
The examples of the specimen excitation-emission matrices are shown in figure 1. As it is seen each sample exhibits wide-band fluorescence. The spectral shape depends on the excitation wavelength. This means that the samples contain various fluorophores, which have individual excitation curves. Characteristics of the excitation-emission matrices were determined by the plastic type and dye, used to give it the desired colour. The latter could show its own fluorescence, as well as affect the optical properties of the media: the depth of laser radiation penetration, reabsorption of fluorescence. Thus, the excitation-emission matrix of each sample has its own features. The wide-band spectra of individual fluorophores overlap, making comparison of fluorescence intensities of various samples at individual wavelengths unproductive, since several fluorophores may contribute to it simultaneously. Reduction to model spectra of known substances is also impossible in this case, since the composition of each waste sample could not be predicted.

To analyze such complex excitation-emission matrices various statistical algorithms might be used. Knowing that the spectra in each excitation-emission matrix correlate, modifications of PCA may recover spectra of individual fluorophores [7]. But such algorithms need a dataset of the excitation-emission matrices of similar nature, but of different composition. In the case of plastic package, various samples have own individual properties, making such approach impossible. Each matrix needs to be analyzed individually – they are decomposed into PCs using nonlinear iterative partial least squares algorithm. Most spectra for all excitation wavelengths are well described by the sum of 2 components. PCs are alternating, because they are the linear combinations of the real fluorophores’ spectra best describing the statistical differences of the specific data set. Thus, any positively defined linear combination of PCs can claim to be a fluorophore spectrum. Therefore, some additional considerations are needed find such combination. We use the approach applied in [4] and [5]. The wideband spectra of
the plastic samples are the result of individual vibrational lines broadening. So positive linear combinations of PCs with the narrowest peak width (characterized by the ratio of the maximum of the function to its integral) should be the closest to the original ones. Using brute force method such linear combinations are found for each of the sample types. The results for the examples from figure 1 are shown in figure 2.

Figure 1. Examples of package plastic excitation-emission matrices. Arrows show excitation wavelength scan direction on waterfall plot.

Figure 2. Narrow peak components for the examples of waste plastic excitation-emission matrices form figure 1.
For each type of sample, pairs of components are analyzed. Each type of plastic has a component common in some approximation for each of the samples and a variable one, depending on the type of dye used. Typical peaks for each type of plastic are averaged and shown in figure 3. HDPE has a fluorescence peak at 332 nm, common for all studied samples. In the same way PET has a characteristic peak at 377 nm, and PP at 432 nm.

Figure 3. Fluorescence spectral peaks, typical for the given types of plastic.

Conclusions
Laser-induced fluorescence spectra of various types of plastics have been studied. Each sample shows wideband multipeak fluorescence. Laser radiation, tuned in 210-310 nm range, allowed investigating the features of the independent samples using the principal component analysis. A criterion that the fluorophores spectra are the narrowest ones among the linear combinations of the principal components was used. Although the excitation-emission matrices had a complex structure, this criterion served to find a characteristic component for each type of the plastic. The comparison of the fluorescence intensities at the wavelengths corresponding to the maxima of these components can be used to identify the type of plastic.

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