CrossMark

FTIR spectroscopy supported by statistical techniques for the structural characterization of plastic debris in the marine environment: Application to monitoring studies

Mauro Mecozzi [a,*], Marco Pietroletti [a], Yulia B. Monakhova [b,c]

[a] *Laboratory of Chemometrics and Environmental Applications, ISPRA, Via di Castel Romano 100, 00128 Rome, Italy*
[b] *Spectral Service AG, Emil-Hoffmann-Straße 33, 50996 Cologne, Germany*
[c] *Institute of Chemistry, Saratov State University, Astrakhanskaya Street 83, 410012 Saratov, Russia*

A B S T R A C T

We inserted 190 FTIR spectra of plastic samples in a digital database and submitted it to Independent Component Analysis (ICA) to extract the "pure" plastic polymers present. These identified plastics were polypropylene (PP), high density polyethylene (HDPE), low density polyethylene (LDPE), high density polyethylene terephthalate (HDPET), low density polyethylene terephthalate (LDPET), polystyrene (PS), Nylon (NL), polyethylene oxide (OPE), and Teflon (TEF) and they were used to establish the similarity with unknown plastics using the correlation coefficient (r), and the crosscorrelation function (CC). For samples with $r < 0.8$ we determined the Mahalanobis Distance (MD) as additional tool of identification. For instance, for the four plastic fragments found in the *Carretta carretta*, one plastic sample was assigned to OPE due to its $r = 0.87$; for all the other three plastic samples, due to the r values ranging between 0.83 and 0.70, the support of MD suggested LDPET and OPE as co-polymer constituents.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The presence of plastic debris in the marine environment is a problem of increasing interest due to the related risk and consequences for living organisms (Moore, 2008; Cole et al., 2011). Polymeric materials are present as different structural compounds and dimensions, causing dangerous interactions with aquatic environment because many living organisms can be harmed or even killed by ingested plastics (Claessens et al., 2013; Farrel and Nelson, 2013). In addition, other emergences can derive by the invader effect of plastics like pellets and scrubbers (Derraik, 2002; Lavender and Thompson, 2014) which enter the trophic chain (Lazar and Gračan, 2011; Farrel and Nelson, 2013; Depledge et al., 2013; Galgani et al., 2014; Long et al., 2015). An updated review covering all the aspects of occurrence, fate and chemical methods of analysis for plastics in the environment is available (Rocha-Santos and Duarte, 2015).

The study of the effects and fates of plastic debris in the marine environment depends obviously on their distribution in the aquatic environment (Angiolillo et al., 2015) and on their chemical composition (Moore, 2015) and several studies describe analytical techniques to identify the polymeric composition of plastics. A specific

method for the quantitative determination of polyacrilamide polymers in water and wastewater applies UV–vis spectroscopy (Al Momanî and Örmeci, 2014). A recent study reports a classification method of plastics based on the presence and dimension of phatalate polymers determined by liquid chromatography (De Lucia et al., 2014). In a study focused to investigate the exposure of baleen whales to phatalate polymers, Fossi and co-workers applied reverse phase liquid chromatography with mass spectroscopy (Fossi et al., 2012). Elemental analysis has been applied to investigate the presence of low and high density polyethylene and polypropylene materials in plastic debris from the western North Atlantic Ocean (Morèt-Ferguson et al., 2010). Other techniques to identify plastic materials are optical microscopy (Song et al., 2015), electron scanning microscopy and FTIR spectroscopy (Srinivasa Reddy et al., 2006).

Recent studies show that the most reliable method to identify the composition of plastic debris in the marine environment is the Fourier transform infrared (FTIR) spectroscopy (Srinivasa Reddy et al., 2006; Frias et al., 2010; Hidalgo-Ruiz et al., 2012). In fact, FTIR spectroscopy can identify all the molecular and functional groups present in plastic polymers (www.thefreelibrary.com/Identification+of+polymers+by+IR+spectroscopy.-a0119376722; Stuart, 1996).

However, the FTIR spectrum of a complex molecular system such a polymer often shows several peaks and due to the high chemical heterogeneity so that their visual interpretation generally requires a skilled operator. The example of Fig. 1 shows the spectral complexity for some

* Corresponding author.
  E-mail addresses: mauro.mecozzi@isprambiente.it, mauromecozzi2004@libero.it
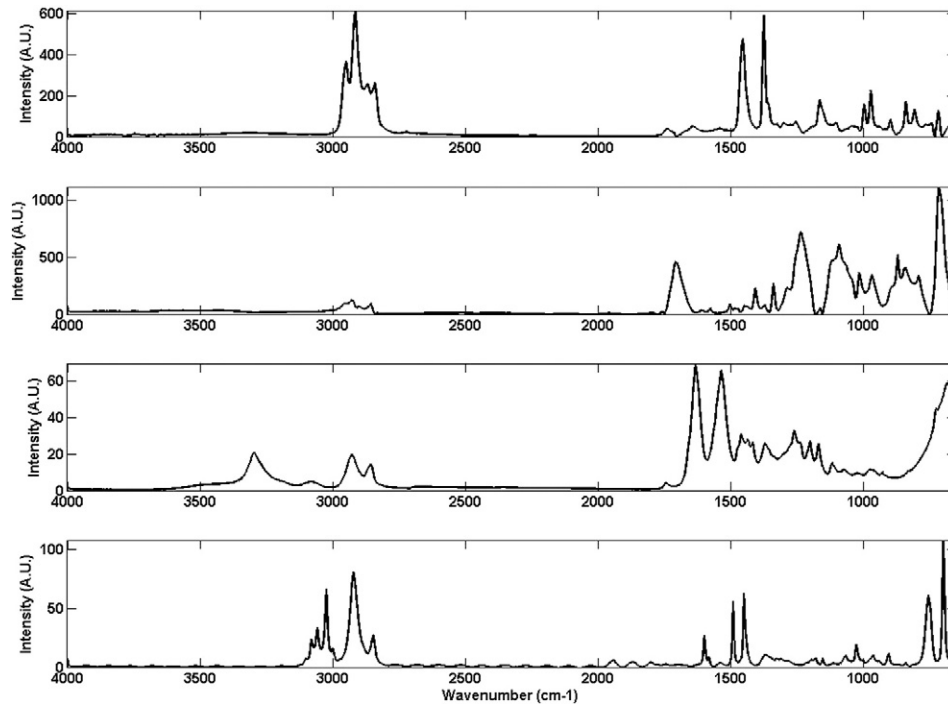 (M. Mecozzi).

Fig. 1. FTIR spectra of some plastic materials common in the marine environment. Starting from the top they are polypropylene, polyethylene phatalate, nylon and polystyrene. For the visualization of the specific bands of each plastic typology please see Table 1.

of the most common plastic materials observed in the marine environment such as PP, PE, PET and NL (Morèt-Ferguson et al., 2010; Andrady, 2011). In addition, external agents such as the interaction of the plastics with hydrological factors, living organisms and the natural ageing process of the polymer can modify its spectral features, making even more complex the identification of the plastic typology.

A support to the accurate identification of plastic is the comparison of the unknown FTIR spectrum with the FTIR spectra of well known samples present in specific spectral libraries. This comparison allows to estimate the structural similarity of the unknown spectrum with the spectra present in the library, supporting their chemical identification. This comparison is based on the determination of the correlation coefficient r which becomes a direct measure of the structural similarity among unknown and well known spectra (Miller and Miller, 1992; Clarck et al., 1993).

The use of a spectral library generally does not require a skilled operator of FTIR spectroscopy but in any case, due to the well known properties of the mathematic and probabilistic properties of r (Rodgers and Nicewander, 1988; Li et al., 2006), the estimation of the structural similarity by means r results requires some specific evaluations before assessing the polymer identity. In fact, the same plastic typology can give different spectral features depending on its molecular structure and conformational characteristics. This is the case of the common polyethylene materials which generally consist of crystalline and amorphous mixtures, having different spectral features (Zerbi et al., 1989). Fig. 2 reports the example of different polyethylene samples having different correlation coefficients with respect to a pure crystalline or a pure amorphous structure. Analogous cases are those of the terephthatalate and nylon based polymers; they can differ for the orientation of the aliphatic chains (Chen et al., 2012) and/or for the starting monomers present which produce different FTIR spectra (Sammon et al., 2000; Bodis et al., 2007; Galimberti et al., 2013). At last, the same type of plastic can show difference in its spectral characteristics depending on the already described interactions with the surrounding marine environment, interactions which determine fragmentations and modifications of the starting material (Fotopoulou and Karapanagioti, 2012; Claessens et al., 2013.). All these aspects could make the identification

of an unknown plastic samples not easy even in the case of the comparison with a well established spectral library (Song et al., 2015).

The approach presented in this paper consists in the construction of an ad hoc FTIR spectral library (i.e. 190 samples) of common plastic materials coming from different uses. Then these spectra were submitted to Independent Component Analysis to identify the individual spectral components (i.e. the single plastic typologies) present in the database (Hyvärinen and Oja, 2000; Mecozzi et al., 2012). Then the FTIR spectra of samples collected from the marine environment were compared with the "pure" individual typologies of plastic materials using as similarity measurements the conventional r measurement and the crosscorrelation (CC) function (Lewis, 1995). For the uncertain cases, we also propose the determination of the Mahalanobis (MD) distance (Manley, 1986; Brereton, 2003).

This proposed method has been applied to the identification of plastic debris sampled in three coastal sites and in a marine turtle.

2. Methods and materials

2.1. Sampling of polymer plastics for the digital database (library)

Plastic samples from several commercial, food and domestic uses were collected for the construction of the original spectral data set to be submitted to ICA. They were identified as 57 polyethylene terephthalate samples from bottles of mineral water, milks and beverages, 51 polyethylene samples from envelops, gloves and containers of food, 23 nylon samples from industrial and commercial uses, 20 polypropylene samples from envelops, gloves and food containers, 10 polyethylene oxide samples from envelops and domestic tools (forks, knives), 22 polystyrene samples from commercial boxes and envelops, and 7 teflon samples from several industrial tools. Within the same plastic typology, the samples had some differences in spectral features depending on their conformational characteristics and on the presence of plastic additives.

Marine plastic samples from three sites along the Tyrrhenian coasts (Sperlonga, Orbetello, Sant'Agostino, Central Italy) and four samples extracted by the stomach of a *Carretta carretta* turtle were