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**Direct screening of food packaging materials for post-polymerization
residues, degradation products and additives by liquid extraction
surface analysis nanoelectrospray mass spectrometry (LESA- nESI-MS)**

**Ambre Issart, Simon Godin, Hugues Preud'homme, Katarzyna Bierla, Ahmed Allal and
Joanna Szpunar**

IPREM- UMR 5254 CNRS- UPPA – Université de Pau et des Pays de l'Adour – Hélioparc – 2av. du president Angot 64053 Pau
Cedex, France.

Corresponding author: Joanna.szpunar@univ-pau.fr

Abstract:

Materials in direct contact with food should be monitored for the presence of species able to migrate into food. A direct method based on liquid extraction surface analysis nanoelectrospray mass spectrometry (LESA-nanoESI-MS) was developed for the analysis of the migrating species from a polymer film. Different types of molecules: post-polymerization residues, degradation products (oligomers resulting from polymer recycling, products of polymer oxidative degradation) and anti-oxidant additives (vitamin E) were demonstrated to be detected and identified, and determined quantitatively if relevant calibration standards are available. The method was validated by a comparison a standard method based on with bulk extraction mass spectrometry. It offers considerable advantages over the latter in terms of drastically reduced analysis time and solvent consumption. Also, LESA-nanoESI-MS produced simpler spectra (limited to compounds able to migrate into food) than Direct Analysis in Real Time (DART).

Key words: liquid extraction surface analysis (LESA), nanoelectrospray mass spectrometry (ESI MS), food packaging, polymer additives, polymer degradation products

1 Introduction

Polymer packaging plays a fundamental role in food industry protecting products from the environment and enhancing their shelflife. Polymers, usually polyethylene terephthalates or polyolefins are thermoformed to minimize the amount of oxygen to extend the shelf life of food. However, the high contact surface between the food and its package can provoke the contamination of the packed food in case of a low-quality plastic (migration phenomenon) ¹. The massive use of plastics for this purpose has been resulting in raising concerns about the associated health risks.

Plastics are mainly petroleum-based ²⁻⁵ and most of them contain additives which not only provide good mechanical properties and attractive look, but also improve their life time and lower processing costs. These additives as well as post-polymerisation residues or degradation products formed during recycling can migrate into food. The migration of constituents of polymer packaging into food has therefore two aspects. The additives, post-polymerization or degradation residues, and non-intentionally added species (NIAS) are a risk for the consumers but, at the same time, “intelligent” packaging releasing natural antioxidants improve food shelf life ⁶.

In order to evaluate the safety and functionalization of polymers in direct contact with food, they should be monitored for the presence of species able to migrate into food. The analysis and the characterisation of the mobile polymer fraction is necessary to evaluate the risk they can represent for food consumers.

Different methods for the mapping of polymer additives have been described, usually requiring extraction followed by chromatographic analysis coupled with mass spectrometry⁷⁻¹¹. The

preparation step can degrade the sample itself; for example, solvents used to extract specific species could also remove polymer chains, additives or other untargeted molecules, thus degrading the sample and increasing the complexity and noise in the analysis. Also, batch extraction is solvent and time consuming. Its tediousness stimulated interest in direct methods such as matrix assisted laser desorption analysis (MALDI), desorption electrospray ionisation (DESI) or direct analysis in real time (DART) mass spectrometry (MS)¹²⁻¹⁶. However, MALDI and DESI require a matrix addition or a sample swelling before the analysis whereas DART uses relatively harsh desorption conditions negatively affecting the method's selectivity (compounds other than those being able to migrate into food can be ionized).

Recently, liquid extraction surface analysis (LESA)^{17,18} was introduced for microvolume metabolomics, lipid analysis, protein analysis, carbohydrate analysis and enzyme monitoring¹⁹⁻²². Also, its potential for the detection of pesticides in sliced fruit and vegetables leaves was tested. LESA requires a minimum amount of solvent applied directly to the sample surface and is rapid and eco-friendly. The choice of extraction conditions can be optimized to focus on species able to migrate into food which results in simpler mass spectra²³. LESA works well on homogeneous hydrophobic surfaces making it highly compatible for many synthetic polymers used for food packaging²⁴. The applications of LESA in polymer science are scarce^{17,23,25-27}; to date, it has never been used for the quality control of food contact materials.

The objective of this work was the development of a method based on LESA for automated extraction of polymer additives and contaminants able to migrate into food and to combine it with nanoESI-MS analysis for the extracted compounds identification and quantification. We demonstrate the optimisation of LESA-MS parameters for the analysis of food contact polymer films for rapid screening for the presence of post-polymerization residues, oligomers resulting from polymer recycling, products of polymer oxidative degradation and polymer additives. We validate the method

by the classical in-batch extraction protocol. We also show that, when suitable solid phase standards with guaranteed additive's concentration are available, LESA-MS can be used for quantitative analysis.

2 Experimental

2.1. Materials

2.1.1. Reagents:

Methanol and acetonitrile (Chromasolv, Honeywell), chloroform and propanol (Chromasolv Plus, Honeywell) and formic acid were LC-MS grade (Optima, Fischer Chemicals). Alpha-tocopherol, linseed oil and ascorbic acid, used as additives in polymer films, were both HPLC grade (Sigma Aldrich, France).

2.1.2. Samples:

PolyEthylene Terephthalates (PET) samples come from a commercial packaging purchased in a local supermarket. Polyethylene and polypropylene films made of additive-free Low-Density PolyEthylene (LDPE) and isotactic PP (iPP) were provided as pellets by Repsol (Repsol, Madrid, Spain). The polymers blends containing different contents of additives were realized thanks to a double-screwed extruder (LabTech, Samutprakarn, Thailand) at 160 °C. The obtained blends were then shaped as films using a hydraulic heated press.

2.2. Procedures

LESA of the polymer constituents able to migrate into food. The principle of the LESA is outlined in **Fig. 1**. The extraction solvent (methanol/chloroform 1:1 v/v containing 0.1 % of formic acid) drop is applied to analysed plastic material. A microjunction is created between the solvent drop and the plastic resulting in the diffusion of plastic impurities into the drop. Then, the drop is sprayed using a

nanoESI silicon-based chip. The polymer samples were analysed directly after having been cut to the appropriate size and put into the instrument holder. The robotic system allowed a nanoESI infusion of the extract. The measurements were done in the positive ionization mode with a scan range from m/z 100 to 2000 at a resolution of 500,000 (FWHM at m/z 200). The automatic gain control (AGC) was set to 1.0×10^5 ions and a maximum injection time of 100 ms. Care was taken not to touch and contaminate the surface to be analysed.

Validation by the batch extraction method. The extraction consisted of 8 different steps: first about 0.25 g of the film was cut in small pieces, the sample was extracted 3 times with 2 mL of hexane, the latter extraction being carried out in the presence of 0.5 mL of 10% NaCl. Then, pooled extracts were salted out with NaCl. The organic layer was taken and dried. After drying, 1 mL of acetonitrile was added and the solution was warmed up to 37° and centrifuged. The supernatant was separated and dried again. Finally, the obtained residue was re-dissolved in 0.1 mL of acetonitrile and analysed by ESI-MS.

Comparison with DART MS. Helium was used as the reagent gas at flow rate of 3 mL min^{-1} , between 200 and 300°C. Positive ion mode was used for a mass range between 150 and 1000 m/z with helium for the analysis and nitrogen gas in standby mode. The grid electrode voltage used value was 350 V in both positive and negative mode. The detector voltage was 1.8 kV with a maximum value of 2.3 kV. The mass spectra were recorded every second with a resolution of 60,000 at m/z 400.

2.3. MS instrumentation

LESA MS spectra were acquired using a TriVersa NanoMate robotic system (Advion, Ithaca, NY) coupled to an Orbitrap Fusion LUMOS mass spectrometer (Thermo Scientific, Waltham, MA) with Thermo Scientific Xcalibur software. The instrument was calibrated daily and optimized for sensitivity by infusing the manufacturer's standard calibration solution employing TriVersa NanoMate chip-based nanoESI ion source. DART MS analyses were performed using a VELOS Orbitrap (Thermo)

Electrospray Ionization (ESI) mass spectrometer equipped with an IonSense DART source (Danvers, MA).

3. Results and discussion

3.1. Method optimization

The optimization was carried out using a commercial PET plastic film known to contain oligomeric degradation products. The method was validated by a comparison to classical in-bulk extraction mass spectrometry.

Extraction solvent. Solvent mixtures reported in the literature: 0.1% formic acid in (i) (4:1) methanol – water ²⁷, (ii) (2:1) methanol – chloroform ²⁶, (iii) (4:2:1) propanol – methanol – chloroform ²⁵ were tested and compared with (iv) 0.1% formic acid in (3:1) acetonitrile – water. The results show the evolution of the intensities of the families of peaks as a function of the solvent used (**Fig. 1 SI**). The highest sensitivity was obtained for 0.1% formic acid in (2:1) methanol – chloroform for all the series and this mixture was used throughout the study.

Instrumental parameters. The dispersion and aspiration height depends on the hardness and composition of the surface and the micro junction creation depends on the surface wettability. The number of repetitions and the time of the extraction were optimized accordingly with this concentration phenomenon explained above. The spray voltage and the pressure were chosen based on the supplier guidelines for individual solvents. **Table 1** below summarized the optimum parameters.

Consecutive extractions. A concentration effect was checked by carrying out LESA-MS analysis five times on the exact same point and under the exact same conditions (**Table 1**). The aim was to evaluate if there is any concentration change in the extracted species after several extractions. It was done twice for reproducibility reasons; the clear trend of decreasing of the peak intensity in the second and third extraction and then the stabilization of the signal was observed. In terms of

repeatability, the spectra obtained for consecutive extractions contained 89, 86, 82 and 74 peaks common with the first spectrum for the 2nd, 3rd, 4th and 5th extractions, respectively. In this situation it was decided to avoid repetitions and the time was optimized and set at 8 s (as a compromise between acceptable extraction and a stable micro junction).

Homogeneity. The first step in the study was to evaluate the homogeneity of the plastic sample (transparent part of a commercial food packaging). This information was considered to be essential as the size of the drop is tiny in comparison with the size of plastic samples. To do so, five points were chosen all over the plastic sample and analysed by LESA-MS under the conditions given in **Table 1**. The evaluation of the spectra obtained consisted of comparing the number of common peaks and their intensities (and relative intensity). The statistical analysis proved that 78.4% peaks are common between the five analyses with a slight deviation in terms of peaks intensities. These results allow one to consider the plastic sample as homogeneous and the results obtained as representative for the whole film surface.

3.2. Identification of polymer species able to migrate into food from polyethylene terephthalate (PET)

Polyethylene terephthalate (PET) is a common thermoplastic polymer of the polyester family used in containers for liquids and foods. **Fig. 2a** shows a LESA – nanoESI mass spectrum showing a series of small ($M < 700$) molecules which are likely to migrate from the polymer into food. These molecules have molecular masses separated by a regular interval of 44 Da (**Table SI 1**) which corresponds to polyethylene oxide (PEO, aka polyethylene glycol, PEG). PEO is used for PET synthesis; its presence can thus originate from polymerization residues or polymer degradation residues. Also, PEO is also often used as an additive for its plasticizing properties²⁸. The presence of PEO on the surface of the polymer creates a risk of its migration into food.

Note that the complexity of the mass spectra results from the fact that the $[M_n+H^+]$ series is accompanied by adducts including: $[M_n+Na^+]$, $[M_n+NH_4^+]$ and $[M_n+K^+]$ and by the presence of isotopic isomers of the detected compounds (for the sake of the clarity of the figure, only some peaks have been labelled). The actual distribution of the intensity of the individual degradation products can vary with the extraction solvent (**Fig. SI 1**).

Validation by the batch method. A mass spectrum (**Fig. 2b**) obtained using batch extraction from bulk (0.25 g) of the material using a multistep procedure outlined above is shown in Fig. 2b. In spite of the differences in the extraction processes, the obtained mass spectrum shows striking similarities in the $m/z > 300$ range; the same series of species can be observed. This type of mass spectrum can be used as a fingerprint of PET migration into food. Note that even if the mass spectrum of the batch extract shows a higher signal-to noise ratio, the same species are detected which validates the LESA procedure which is much shorter (minutes instead of several hours) and consumes much less solvent.

Comparison with DART-MS. The method was compared with another ambient ionisation method – DART-MS. The obtained mass spectrum is more complex as it represents the PET polymer itself and not the migrating PEO. Actually, the use of a heated gas stream and no solvent provokes degradation of the plastic thus making it impossible to see residual PEO. The latter brings about the risk of the occurrence of false positives suggesting the migration of other molecules that would have migrated during the contact with food. LESA-MS offers a soft extraction method and thus is more adapted for studies of migration from the polymer surface than DART-MS. However, DART-MS offers other possibilities for polymer analysis allowing access to different data sets as compared to LESA-MS.

3.3. Identification of polymer species able to migrate into food from low-density polyethylene (LDPE)

Low-density polyethylene (LDPE) is a thermoplastic produced by polymerisation of ethylene. Its most common use is in plastic bags and films. Being a polyolefin, it readily undergoes oxidation (**Fig. 3a**). The mass spectrum shows different degradation products including alcohols and esters but the formation of a carboxylic group on the polymer chain is the most systematic. For example, the major peak (m/z 554.5506 Da) corresponds to the oxidised molecule shown in the inset (Fig. 3a). Note that different adducts can also be identified.

This oxidation can be prevented by the addition of an antioxidant such as Vitamin E (**Fig. 3b**). The mass spectrum shows the absence of the degradation product and a predominant peak of vitamin E (m/z 429.37272)

3.4. Monitoring of the formation of species able to migrate into food during recycling of polyethylene and polypropylene

As recycling requires the polymer treatment at high temperature, the polymer is prone to oxidation. The method developed allows the monitoring of the formation of degradation products during polymer recycling (**Fig. 4**). The mass spectra are composed of peaks separated by 14 Da, corresponding to the methylene group. The intensity of the peaks from clusters of oligomers increases with the number of recycling cycles. Fig. 4 clearly shows polymer degradation as a result of the extrusion and the creation of small molecules potentially able to migrate into food. The risk of the formation of undesirable molecules able to migrate into food increases with the increasing number of the recycling cycles. This phenomenon is even more visible when analysing polypropylene as it is extruded at higher temperatures (180 °C instead of 150 °C for PE) and degrades by chain-scissions (whereas polyethylene suffers both from chains reticulation and chain scissions), creating clusters of oligomers. Nevertheless, both polymers show similar spectra throughout the recycling cycles.

3.5. Assessment of the efficiency of antioxidants used to stabilize polymers

As mentioned above, antioxidants (such as e.g. vitamin E) are used to stabilize the polymers. **Fig. 5** demonstrated that LESA MS allows a fast assessment of the efficiency of antioxidants used to stabilize polymers. Two samples of polypropylene modified by the addition of the same amount of natural antioxidants: vitamin E and linseed oil were compared. The result shows a weak efficiency (although higher than in the case of linseed oil) of vitamin E in protecting the polymer from the degradation. The peak intensity was normalized to the signal m/z 338.341 present in all the samples. Note that in the sample of polypropylene stabilized with vitamin E, a clear signal of this species was detected (at m/z 429.373) documenting its potential for migration from the polymer which is considered beneficial as means of the protection of food.

3.6. Linearity of the LESA – MS signal in polymer films as a function of concentration

In addition to its potential for qualitative analysis, the developed LESA – MS procedure can be useful for the quantitative determination of vitamin E in the polymers and, potentially, in food. A series of polyethylene doped with different amounts of vitamin E were produced to construct a calibration curve showing a linear response of the m/z 429.373 peak (vitamin E) intensity in LESA-MS as a function of the concentration of the antioxidant in the polymer. Note that the additive's concentration in the standard produced by the extrusion process may be different from that in the initial mixture. Therefore, in order to assure the accuracy of the quantitative method, the composition of the standards used for quantification has to be confirmed by another method. This observation demonstrates the possibility of direct quantitative analysis of polymer films by LESA – nanoESI MS provided that standards with the guaranteed additive's concentration are available.

Conclusions

LESA combined with nanoESI ionisation - MS was demonstrated to be a convenient method for the direct analysis of polymer packing materials. It was optimized to monitor (i) the release of residual polymerisation or polymer degradation residues, (ii) the degradation of additive-free low-density

polyethylene during recycling, and (iii) the efficiency of antioxidants additives to stabilize the polymer. Moreover, the release of additives, such as vitamin E, could be quantified using external calibration with solid state standards. The method was validated by the currently used method based on the extraction from the bulk followed by ESI-MS. LESA-nanoSI MS does not require sample preparation, is fast, eco-friendly and highly reproducible. It also compares favourably with ambient ionisation DART-MS in terms of selectivity producing simpler spectra limited to the mobile compounds of interest. It has to be mentioned that the sensitivity of LESA MS is inversely size dependent due to higher solubility and thus easier extraction from the surface of smaller species. At the same time, the potential migration into food is also facilitated in the case of small molecules.

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References

- (1) Hernandez R. J.; Giacin J. R.: Factors affecting permeation, sorption, and migration processes in package-product systems. In *Food Storage Stability*; CRC Press, 1997.
- (2) Standnes, D. C.; Skjevraak, I.: Literature review of implemented polymer field projects. *Journal of Petroleum Science and Engineering* **2014**, *122*, 761-775.
- (3) Breddermann, K.; Drescher, P.; Polzin, C.; Seitz, H.; Paschen, M.: Printed pressure housings for underwater applications. *Ocean Engineering* **2016**, *113*, 57-63.
- (4) Smith, C. A.: Thermochemical and physical properties of printed circuit board laminates and other polymers used in the electronics industry. *Polymer Testing* **2016**, *52*, 234-245.

- (5) Fuchs Erica; Roth Richard; Field Frank; Kirchain Randolph: Strategic materials selection in the automobile body: Economic opportunities for polymer composite design. *Composites Science and Technology* **2008**, *68*, 1989-2002.
- (6) Dobrucka, R.; Cierpiszewski, R.: Active And Intelligent Packaging Food – Research And Development – A Review. In *Polish Journal of Food and Nutrition Sciences*, 2014; Vol. 64; pp 7.
- (7) Marcato, B.; Guerra, S.; Vianello, M.; Scalia, S.: Migration of antioxidant additives from various polyolefinic plastics into oleaginous vehicles. *International Journal of Pharmaceutics* **2003**, *257*, 217-225.
- (8) Shahidi, F.; Zhong, Y.: Novel antioxidants in food quality preservation and health promotion. *European Journal of Lipid Science and Technology* **2010**, *112*, 930-940.
- (9) Moreta C.; Tena M.: Determination of plastic additives in packaging by liquid chromatography coupled to high resolution mass spectrometry. *J Chromatogr A*. **2015**, *77-87*.
- (10) Lin, Q. B.; Li, B.; Song, H.; Wu, H. J.: Determination of silver in nano-plastic food packaging by microwave digestion coupled with inductively coupled plasma atomic emission spectrometry or inductively coupled plasma mass spectrometry. *Food Additives & Contaminants: Part A* **2011**, *28*, 1123-1128.
- (11) Coulier, L.; Kaal, E. R.; Tienstra, M.; Hankemeier, T.: Identification and quantification of (polymeric) hindered-amine light stabilizers in polymers using pyrolysis–gas chromatography–mass spectrometry and liquid chromatography–ultraviolet absorbance detection–evaporative light scattering detection. *Journal of Chromatography A* **2005**, *1062*, 227-238.
- (12) Fouyer, K.; Lavastre, O.; Rondeau, D.: Direct Monitoring of the Role Played by a Stabilizer in a Solid Sample of Polymer Using Direct Analysis in Real Time Mass Spectrometry: The Case of Irgafos 168 in Polyethylene. *Analytical Chemistry* **2012**, *84*, 8642-8649.
- (13) Gross, J. H.: Direct analysis in real time--a critical review on DART-MS. *Anal Bioanal Chem.* **2013**, *406*, 63-80.

- (14) Haunschmidt, M.; Klampfl, C. W.; Buchberger, W.; Hertsens, R.: Rapid identification of stabilisers in polypropylene using time-of-flight mass spectrometry and DART as ion source. *Analyst* **2010**, *135*, 80-85.
- (15) Hintersteiner, I.; Sternbauer, L.; Beissmann, S.; Buchberger, W. W.; Wallner, G. M.: Determination of stabilisers in polymeric materials used as encapsulants in photovoltaic modules. *Polymer Testing* **2014**, *33*, 172-178.
- (16) Ackerman L. K.; Noonan G.; Begley T.: Assessing direct analysis in real-time-mass spectrometry (DART-MS) for the rapid identification of additives in food packaging. *Taylor & Francis* **2009**.
- (17) Paine, M. R. L.; Rae, I. D.; Blanksby, S. J.: Direct detection of brominated flame retardants from plastic e-waste using liquid extraction surface analysis mass spectrometry. *Rapid Communications in Mass Spectrometry* **2014**, *28*, 1203-1208.
- (18) Walworth, M. J.; ElNaggar, M. S.; Stankovich, J. J.; Witkowski, C.; Norris, J. L.; Van Berkel, G. J.: Direct sampling and analysis from solid-phase extraction cards using an automated liquid extraction surface analysis nanoelectrospray mass spectrometry system. *Rapid Communications in Mass Spectrometry* **2011**, *25*, 2389-2396.
- (19) Eikel, D.; Vavrek, M.; Smith, S.; Bason, C.; Yeh, S.; Korfmacher, W. A.; Henion, J. D.: Liquid extraction surface analysis mass spectrometry (LESA-MS) as a novel profiling tool for drug distribution and metabolism analysis: the terfenadine example. *Rapid Communications in Mass Spectrometry* **2011**, *25*, 3587-3596.
- (20) Menezes, R. C.; Kai, M.; Krause, K.; Matthäus, C.; Svatoš, A.; Popp, J.; Kothe, E.: Monitoring metabolites from *Schizophyllum commune* interacting with *Hypholoma fasciculare* combining LESA-HR mass spectrometry and Raman microscopy. *Analytical and Bioanalytical Chemistry* **2015**, *407*, 2273-2282.
- (21) Parson, W. B.; Koeniger, S. L.; Johnson, R. W.; Erickson, J.; Tian, Y.; Stedman, C.; Schwartz, A.; Tarcsa, E.; Cole, R.; Van Berkel, G. J.: Analysis of chloroquine and metabolites directly

from whole-body animal tissue sections by liquid extraction surface analysis (LESA) and tandem mass spectrometry. *Journal of Mass Spectrometry* **2012**, *47*, 1420-1428.

(22) Sarsby, J.; Martin, N. J.; Lalor, P. F.; Bunch, J.; Cooper, H. J.: Top-Down and Bottom-Up Identification of Proteins by Liquid Extraction Surface Analysis Mass Spectrometry of Healthy and Diseased Human Liver Tissue. *Journal of The American Society for Mass Spectrometry* **2014**, *25*, 1953-1961.

(23) Martin R. L. Paine; Philip J. Barker; Shane A. Maclaughlin; Todd W. Mitchell; Blanksby, S. J.: Direct detection of additives and degradation products from polymers by liquid extraction surface analysis employing chip-based nanospray mass spectrometry. *Wiley Online Library* **2012**.

(24) Martin R.L. Painea, P. J. B., Stephen J. Blanksbya: Ambient ionisation mass spectrometry for the characterisation of polymers and polymer additives: A review. **2014**.

(25) Brown, S. H. J.; Huxtable, L. H.; Willcox, M. D. P.; Blanksby, S. J.; Mitchell, T. W.: Automated surface sampling of lipids from worn contact lenses coupled with tandem mass spectrometry. *Analyst* **2013**, *138*, 1316-1320.

(26) Paine, M. R. L.; Barker, P. J.; Blanksby, S. J.: Characterising in situ activation and degradation of hindered amine light stabilisers using liquid extraction surface analysis-mass spectrometry. *Analytica Chimica Acta* **2014**, *808*, 190-198.

(27) Eikel, D.; Henion, J.: Liquid extraction surface analysis (LESA) of food surfaces employing chip-based nano-electrospray mass spectrometry. *Rapid Communications in Mass Spectrometry* **2011**, *25*, 2345-2354.

(28) Rezaei Kolahchi, A.; Ajji, A.; Carreau, P. J.: Enhancing hydrophilicity of polyethylene terephthalate surface through melt blending. *Polymer Engineering & Science* **2014**, *55*, 349-358.

Table 1. LESA-MS parameters used

Solvent	Solvent aspired, μL	Air aspired, μL	Solvent dispensed, μL	Dispense height, mm	Aspiration height, mm	Time, s	Spray Voltage, kV	Pressure, psi
2:1 MeOH – CHCl_3 + 0,1% FA	2	0.8	1.8	3	2.8	8	1.4	0.35

Table SI 1. Example of the identification of the species in LESA MS spectrum of a PET commercial sample.

ion	experimental molecular mass, m/z	theoretical molecular mass, m/z	formula	Number of monomer units (n)	Relative intensity, %
[M+H ⁺]	319.2838	319,2848	C ₁₈ H ₃₉ O ₄	4	33.45
	363.3104	363,3110	C ₂₀ H ₄₃ O ₅	5	100
	407.3367	407.3372	C ₂₂ H ₄₇ O ₆	6	61.5
	451.3630	451,3634	C ₂₄ H ₅₁ O ₇	7	39.08
[M+NH ₄ ⁺]	468.3890	468.3900	C ₂₄ H ₅₄ NO ₇	7	71,76
[M+Na ⁺]	429.3184	429.3192	C ₂₂ H ₄₆ NaO ₆	6	78,29
[M+K ⁺]	489.3187	489.3193	C ₂₄ H ₅₀ KO ₇	7	65,49

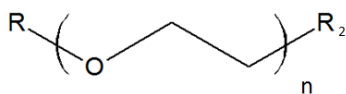


Figure 1. Identification of different series of peak.

Captions to Figures:

Figure 1. LESA-MS principle.

Figure 2. Mass spectra obtained for the analysis of a candidate packing materials (a) by LESA MS accompanied by the identification of the signals and (b) after a classical batch sample preparation method. For the sake of clarity only 13C peaks were labelled.

Figure 3. LESA-MS spectrum of (a) an oxidized LDPE and (b) LPDE stabilized with Vitamin E.

Figure 4. LESA-MS analysis on recycled bare polyethylene: (a) one cycle, (b) 9 cycles.

Figure 5. LESA-MS analysis of polypropylene stabilized with different antioxidants: (a) Vitamin E, (b) linseed oil

Figure 6. LESA MS of a polyethylene stabilized with vitamin E (m/z 429.373)

Supplementary information:

Figure SI 1. Example of the evolution of the intensity of the signals in the function of the solvent used for the analysis of a PET commercial sample.

Table SI 1. Example of the identification of the species in LESA MS spectrum of a PET commercial sample.

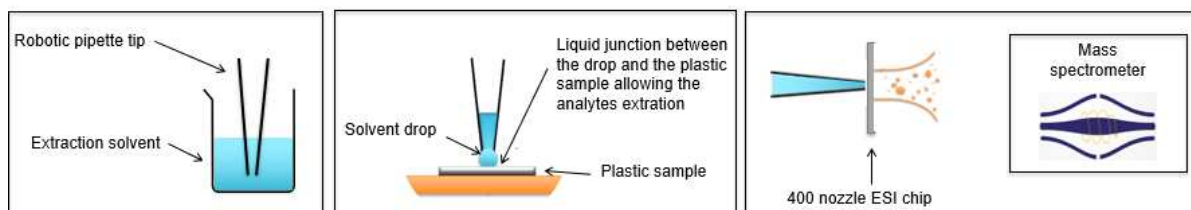


Figure 1. LESA-MS principle.

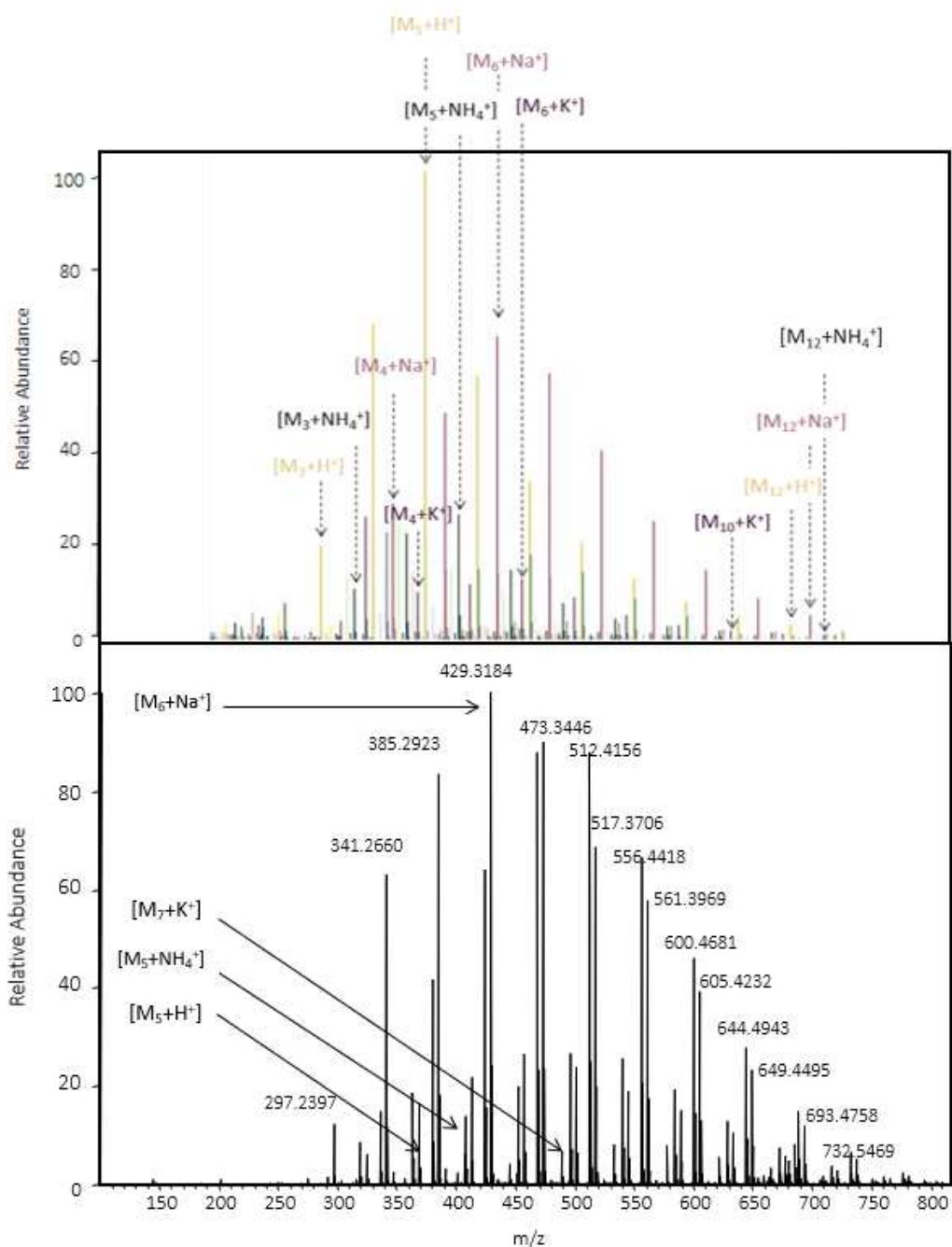


Figure 2. Mass spectra obtained for the analysis of a candidate packing materials (a) by LESA MS accompanied by the identification of the signals and (b) after a classical batch sample preparation method. Note: for the clarity of presentation only some species have been labelled, examples of the identification of M_n species (where n denotes the number of monomer units) are given in Table 1 SI.

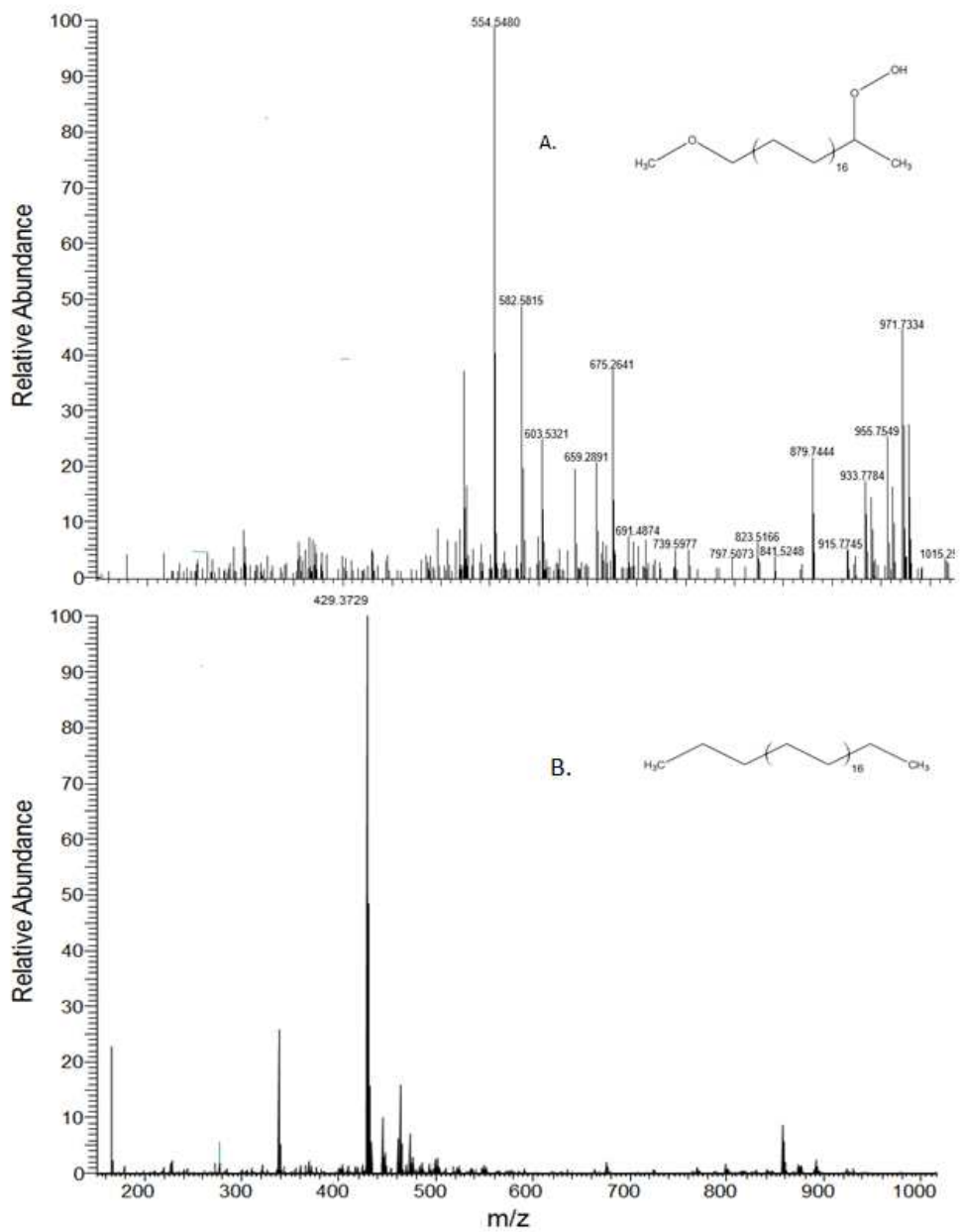


Figure 3. LESA-MS spectrum of (a) an oxidized LDPE and (b) LPDE stabilized with Vitamin E.

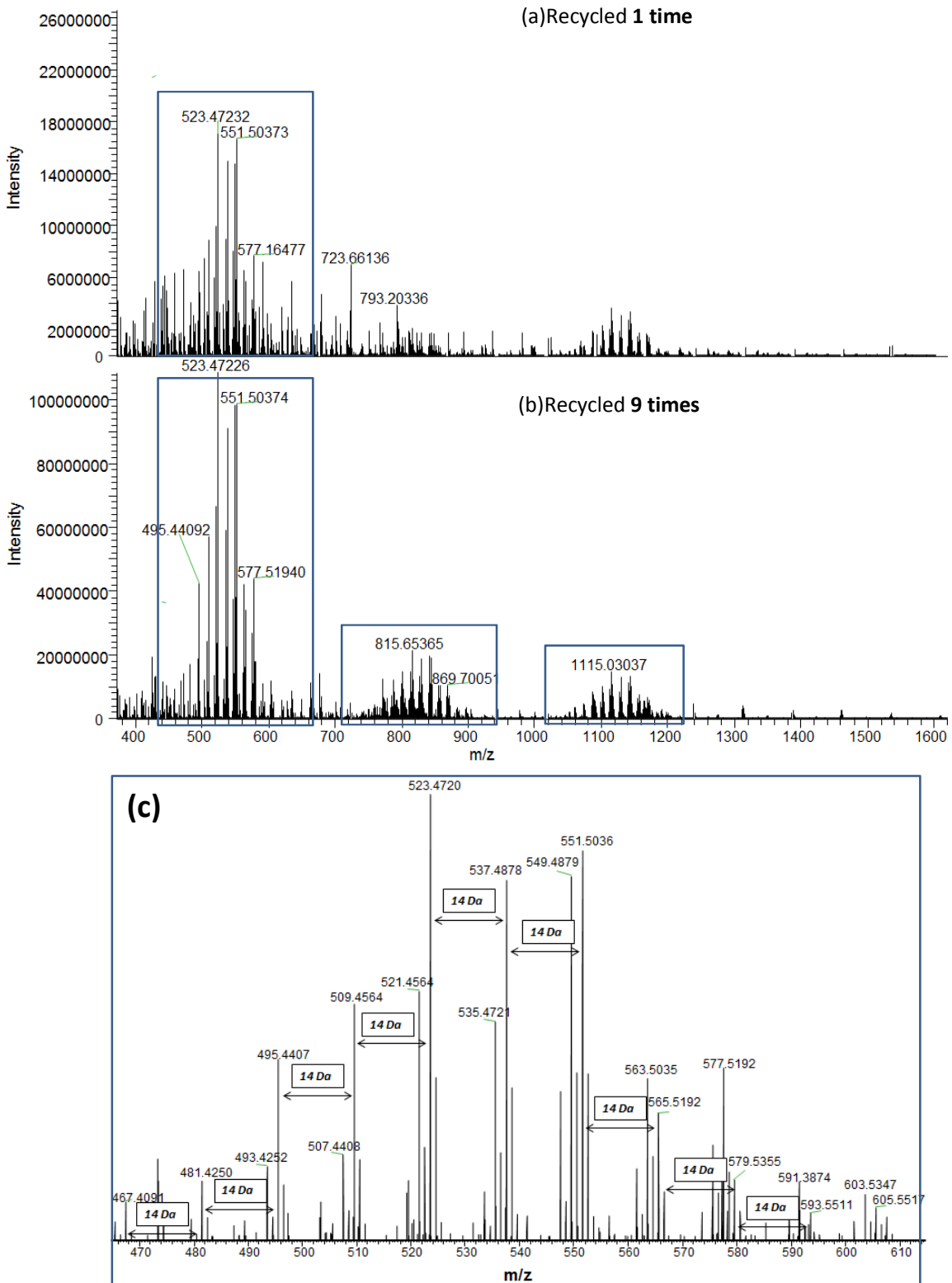


Figure 4. LESA-MS analysis on recycled bare polyethylene: (a) one cycle, (b) 9 cycles, (c) detail spectrum of the first oligomers' cluster of figure 4(b).

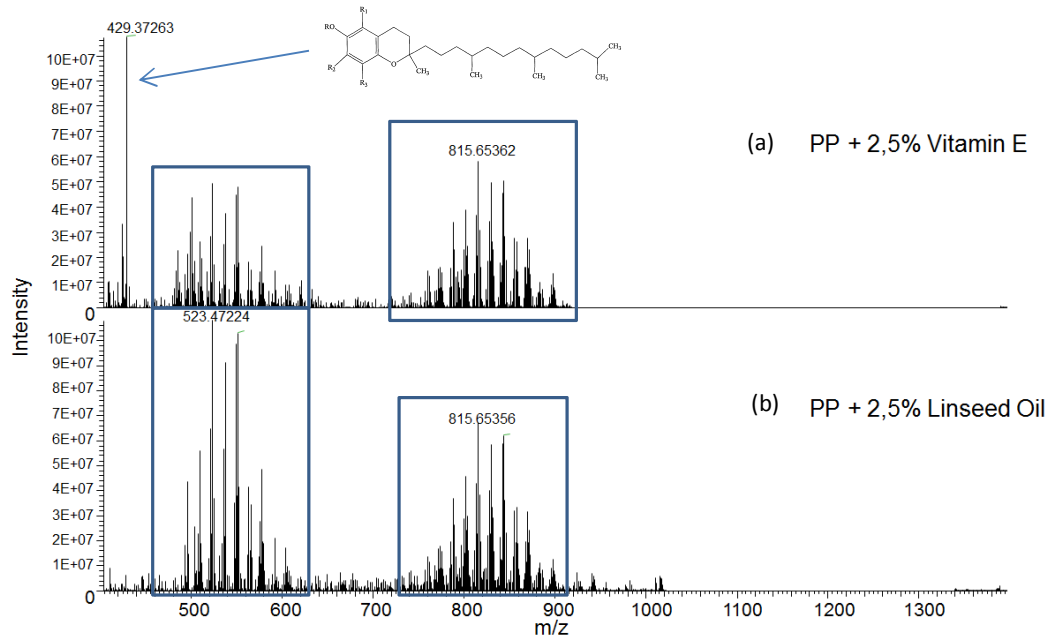


Figure 5. LESA-MS analysis of polypropylene stabilized with different antioxidants: (a) Vitamin E, (b) linseed oil

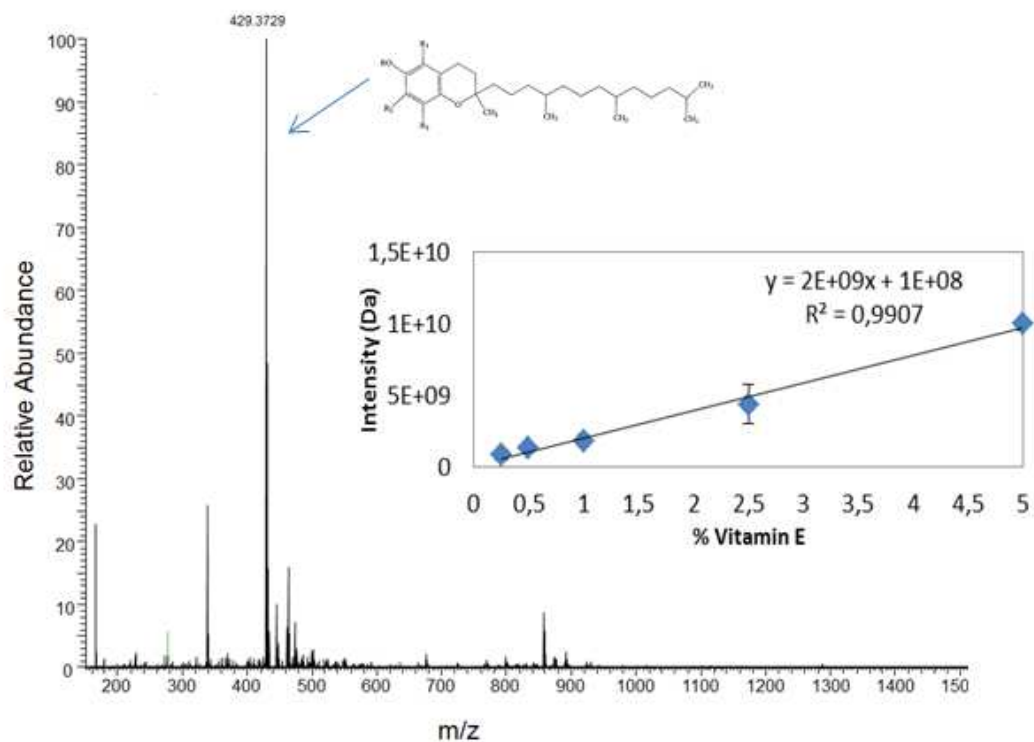


Figure 6. LESA MS of a polyethylene stabilized with vitamin E (m/z 429.373)

Supplementary information:

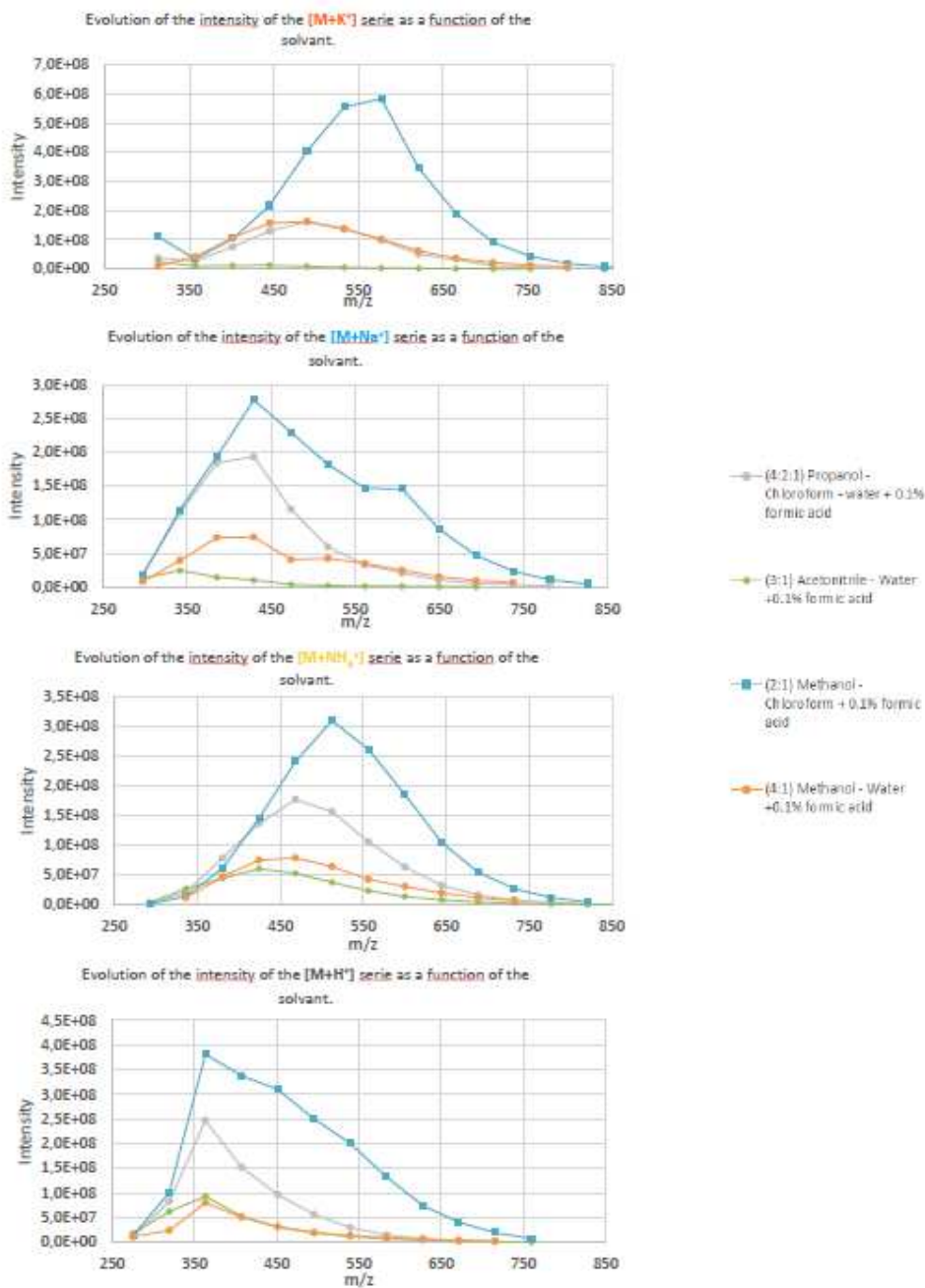


Figure SI 1. Example of the evolution of the intensity of the signals in the function of the solvent used for the analysis of a PET commercial sample.

