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Role of photooxidation on the abiotic transformation of microplastics

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Marine and Coastal Systems Master

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UNIVERSIDADE DO ALGARVE

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Declaration of Authorship of Work

ROLE OF PHOTOOXIDATION ON THE ABIOTIC TRANSFORMATION OF MICROPLASTICS

Declaro ser a autora deste trabalho, que é original e inédito. Autores e trabalhos consultados estão devidamente citados no texto e constam da listagem de referências incluída.

I declare to be the author of this work, which is original and unpublished. Authors and works consulted are duly cited in the text and are included in the list of references.

Maria Carolina Melo de Sousa

Faro, 30 September 2024

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ABSTRACT

Plastic pollution poses a significant threat to terrestrial and aquatic ecosystems worldwide, largely arising from inadequate recycling and waste management practices. This results in the accumulation of microplastics and nanoplastics, which can harm marine organisms and pose potential risks to human health. In this study, polyethylene (PE) and polyethylene terephthalate (PET), two of the most prevalent plastic polymers in circulation, were studied with a focus on their photodegradation in coastal environments, which is a critical abiotic process driven by sunlight radiation exposure. An advanced analytical technique, Liquid Chromatography coupled with High-Resolution Mass Spectrometry (LC-HRMS), was implemented with Atmospheric Pressure Chemical Ionization (APCI) and Electrospray Ionization (ESI) to analyze the released molecules after photooxidation. APCI enhances the detection of moderately polar compounds, whereas ESI provides greater sensitivity for polar compounds containing carboxylic acid functional groups. PET readily degrades and produces a wide range of molecules that are potential environmental contaminants. In contrast, PE is more stable because the absorbance of radiation by its structure is much lower than PET. LC-HRMS allowed the identification of compounds uniquely correlated with each polymer's chemical structure and were therefore considered markers of these polymers in the environment. For PET the identified compounds were benzoic acid (m/z 121.030), terephthalic acid (m/z 165.019), and *4-((2-((4-carboxybenzoyl)oxy)ethoxy)carbonyl)benzoate* (m/z 357.062) while for PE, dicarboxylic acids were identified, such as hexadecanedioic acid. Many other compounds were annotated. These results indicate that the identified and annotated compounds are being released from plastics and microplastics and are potential environmental contaminants. On the other hand, by promoting the photochemical reaction on sand surfaces, the presence of microplastics and nanoplastics can be detected, specifically for PET.

Keywords: Plastic pollution, microplastics, photooxidation, polyethylene, polyethylene terephthalate, environmental contaminants.

SUMÁRIO

A poluição por plásticos representa uma ameaça significativa para os ecossistemas terrestres e aquáticos a nível global, principalmente devido a práticas inadequadas de reciclagem e gestão de resíduos. Este cenário resulta na acumulação de microplásticos e nanoplásticos, que prejudicam a vida marinha e representam potenciais riscos para a saúde humana. Neste estudo, foram analisados o polietileno (PE) e o polietileno tereftalato (PET), dois dos polímeros plásticos mais prevalentes em circulação, com foco na sua fotodegradação em ambientes costeiros, um processo abiótico crítico impulsionado pela exposição à radiação solar. Foi implementada uma técnica analítica avançada, Cromatografia Líquida acoplada a Espectrometria de Massa de Alta Resolução (LC-HRMS), com Ionização Química à Pressão Atmosférica (APCI) e Ionização por Electrospray (ESI) para analisar as moléculas libertadas após fotoxidação. O APCI melhora a deteção de compostos moderadamente polares, enquanto o ESI proporciona maior sensibilidade para compostos polares que contêm grupos funcionais de ácido carboxílico. O PET degrada-se facilmente e produz uma ampla gama de moléculas que são potenciais contaminantes ambientais. Em contraste, o PE é mais estável porque a absorção de radiação pela sua estrutura é muito inferior à do PET. O LC-HRMS permitiu a identificação de compostos que podem estar correlacionados de forma única com a estrutura química de cada polímero e, por isso, foram considerados marcadores destes polímeros no ambiente. Para o PET, os compostos identificados foram o ácido benzóico (m/z 121,030), ácido tereftálico (m/z 165,019) e *4-((2-((4-carboxibenzoil)oxi)etoxi)carbonil)benzoato* (m/z 357,062). Enquanto que para o PE, foram identificados ácidos dicarboxílicos, como, por exemplo, o ácido hexadecanedióico Muitos outros compostos foram anotados. Estes resultados indicam que os compostos identificados e anotados estão a ser libertados dos plásticos e microplásticos e são potenciais contaminantes ambientais. Por outro lado, ao promover a reação fotoquímica em superfícies de areia, nomeadamente no caso do PET, é possível detetar a presença de microplásticos e nanoplásticos.

Palavras-chave: Poluição por plásticos, microplásticos, fotoxidação, polietileno, polietileno tereftalato, contaminantes ambientais.

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LIST OF ABBREVIATIONS

PE	Polyethylene
PET	Polyethylene terephthalate
LC-HRMS	Liquid Chromatography-High Resolution Mass Spectrometry
MPs	Microplastics
UV	Ultraviolet
EG	Ethylene glycol
TPA	Terephthalic acid
LDPE	Low-density polyethylene
HDPE	High-density polyethylene
LLDPE	Linear low-density polyethylene
UHMWPE	Ultra-high-molecular-weight polyethylene
$\mathbf{S_0}$	Ground state
$\mathbf{S_1}$	Singlet state
$\mathbf{T_1}$	Triplet state
$\boldsymbol{\varepsilon}$	Absorption coefficient of transition
$\mathbf{E_S}$	Energy singlet
$\mathbf{E_T}$	Energy triplet
K	Reaction rate constant
$\mathbf{{}^1I}$	Singlet products
$\mathbf{{}^3I}$	Triplet products
F	Fluorescence
P	Phosphorescence
IC	Internal Conversion
ST	Intersystem Crossing
•OH	Hydroxyl radicals
$\mathbf{{}^1O_2}$	Singlet oxygen
ROS	Reactive oxygen species
ESR	Electron spin resonance
$\mathbf{O_2}$	Molecular oxygen

PH	Plastic polymer
Δ	Heat
$h\nu$	Radiation
POOH	Peroxides
PO•	Polymer-oxy radicals
IR	Infrared
GC-MS	Gas Chromatography-Mass Spectrometry
RT	Retention time
HPLC	High-Performance Liquid Chromatography
ESI	Electrospray Ionization
APCI	Atmospheric Pressure Chemical Ionization
m/z	Mass-to-charge ratio
API	Atmospheric pressure ionization
-COO-	Carboxyl groups
FWHM	Peak full width at half maximum
DAD	Diode array detector
AM-XIC	Accurate Mass Extracted Ion Chromatogram
DCM	Dichloromethane
MeOH	Methanol
ACN	Acetonitrile
CID	Collision-Induced Dissociation
HCD	High-Energy Collisional Dissociation
-OH	Hydroxyl group
MS/MS	Mass spectrum

1 Introduction

1.1 Background and Content

This study was focused on understanding the qualitative significance of photooxidation processes in the microplastics abiotic transformations. Polyethylene (PE) and polyethylene terephthalate (PET) were photochemically transformed on solid substrates, by capturing and characterizing their photodegradation products that are produced in simulated environment. Advanced analytical techniques such as chromatography coupled to mass spectrometry (LC-HRMS) were utilized in accordance with the aim of the study to provide a more complete understanding of the picture with regard to the factors that lead to the photooxidative processes of these microplastics.

This work focuses on the annotation and identification of degradation products with a particular attention to the comparative analysis of PE and PET microplastics sandwiched between various surfaces. Satisfying these targets, the study seeks to broaden the knowledge on the impact of photooxidation on the behavior of microplastics in different environmental scenarios which are crucial for ecosystem health and addressing aspects of plastic pollution.

1.2 Significance of the study

This study seeks to understand the nature plastics in the context of the environment with an emphasis on PET and PE (Figures 1.1A and 1.1B, respectively). In furthering the concept of photooxidation and studying the by-products in the context of a LC-HRMS in positive and negative modes, the propellant is to improve existing knowledge on alteration of behavior of plastic materials upon exposure to environmental elements. More particularly, this work focuses on how these polymeric materials suffer degradation with respect to their specific photooxidation and thermal oxidation.

Of utmost importance, this work goes to great lengths to show how these polymers are responsive to environmental stress, as the end products of photodegradation may be toxic in nature and may have the potential of contaminating the environment. Specifically point out that unlike PET, PE does not easily get damaged by light which affects its use to structures and differs between the two due to bonding. The reason that PE does not break down is simple; it does not absorb certain wavelengths of light and within strong limits: PET, on the other hand, does absorb these wavelengths which allows PET to absorb sunlight and ultraviolet radiation. (Fechine *et al.*, 2002; Jiao *et al.*, 2022; Zaki *et al.*, 2013).

In summary, this study seeks to deepen the understanding of the dynamic interactions between plastics (PE and PET in particular) and their behavior in natural environments, such as beach sand surfaces. The goal is to clarify the factors influencing degradation and emphasize the importance of context in addressing this critical environmental issue.

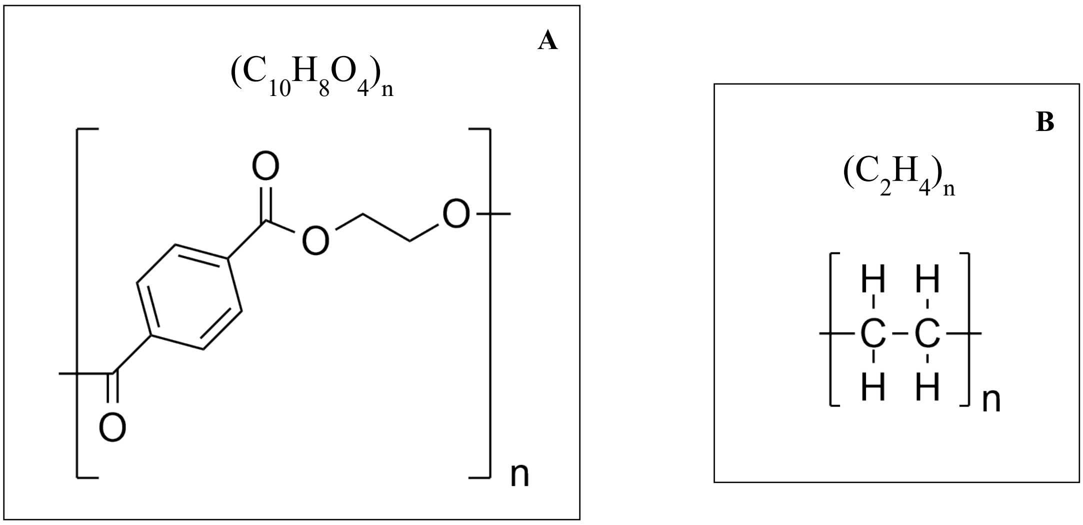


Figure 1.1. Structures of the studied polymers. A- Polyethylene Terephthalate (PET); B- Polyethylene (PE).

1.3 *Objectives and Questions*

The first objective for this study was to assess the release of molecules after the photodegradation of microplastics in coastal regions. Aiming to recreate these conditions, a xenon arc lamp is used, designing a spectrum very close to the sun's spectrum that is useful for the microplastics characterization. Dealing with two common plastics, polyethylene (PE) and polyethylene terephthalate (PET), the aim of this research was to reconstruct the photodegradation pathways, annotate and, if possible, identify some of the released compounds. The aim was to focus on their interaction with the natural sand to explore possible degradation markers. Such markers may be helpful in determining the ecotoxicological impact of microplastics.

- What molecules can be released during the photodegradation of microplastics (PE and PET) under simulated sunlight conditions?
- To what extent does the spectrum produced by the xenon arc lamp aid the simulation of environmental conditions?

- What are the possible pathways of the microplastics in terms of photodegradation and what measures can be taken to retrieve information on the released compounds?
- What are the roles played by other matrices, in this case natural sand, in relation to the released compounds in terms of their interaction?
- Are there any degradation markers that make it easier to understand the environmental impacts of microplastics?

2 Literature review

2.1 Plastics and Microplastics

Plastics, which are associated with enhanced durability, flexibility, and longevity, are defined as synthetic organic polymers made with a variety of additives (Cai *et al*., 2023; Derraik, 2002; Lee *et al*., 2013; Rios *et al*., 2007). These characteristics have led to them being used in diverse sectors and daily activities due to their exceptional mechanical characteristics, low weight and relatively inexpensive manufacturing processes (Birley, 2012; Pilapitiya & Ratnayake, 2024). Consequently, plastics have emerged as a principal form of marine litter around the world being 50 % to around 80 % of the world's debris (Fotopoulou & Karapanagioti, 2019).

Over the last 50 years, plastics have become increasingly used with annual production reaching millions of tons (Boucher & Friot, 2017). This trend is expected to reach approximately 1800 million tons by 2050 (Plastics–the Facts, 2019). Alarmingly, plastic consumption reached 100 kg per person per year in Western Europe and North America and 20 kg per person in Asia (UNEP, 2016). According to the framework of the United Nations and the European Union, it has been estimated that at least 50% of plastics are harmful materials as defined by their monomers, additives and by-products (Cai *et al*., 2023; Lithner *et al*., 2011). A substantial number of polymeric products find their way to the ocean through various routes. These include indiscriminate disposal of litter and illegal dumping (Moore, 2008), being blown into the atmosphere from landfills (Leslie *et al*., 2011), fibers from washing (Browne *et al*., 2011), scrubbers and abrasives in cosmetics and commercial cleaning applications, as well as unintentional release during manufacture and transport (Mato *et al*., 2001). Therefore, the increasing production of plastics is accompanied by the accumulation of plastic litter in marine environments (Barnes *et al*., 2009; Thompson *et al*., 2004). Plastic litter of terrestrial origin contributes to approximately 80 % of marine litter, and marine sources, such as fishing vessels, nets, lines, and other items contribute between 20 – 30 % (Andrady, 2011).

Over time, plastics degrade into microplastics (MPs), defined by the first international MPs workshop (2008) organized by the National Oceanographic and Atmospheric Administration (NOAA) as particles with a diameter of less than 5 mm (Arthur *et al*., 2009). While microplastic fragments can be visible to the naked eye at sizes approaching 5 mm, many of these particles, particularly those less than 1 mm, are truly microscopic in nature. Such small plastic particles become available after the plastic residues have been subjected to atmospheric exposure and physical weathering (Benke *et al*., 2022; Ding *et al*., 2022; Santhoskumar & Palanivelu, 2014). Their small size and chemical structure allow for the ability to adsorb contaminants and leach out hazardous plasticizers (Cole *et al*., 2011).

They arise in primary (intentionally introduced by anthropogenic factors) and secondary forms (fragments smaller than 5 mm originating from polymer degradation) depending on the sources and formation mechanisms (Geambulat *et al*., 2022). Primary MPs are manufactured to be microscopic and used in consumer products such as cosmetics, ship-breaking industry, and as industrial abrasives in synthetic 'sandblasting' media (Fendall & Sewell, 2009). Whereas secondary MPs derive from weathering and breakdown of meso and macroplastics both in marine and terrestrial environments (Babaghayou *et al*., 2016; Ryan *et al*., 2009; Thompson *et al*., 2004), ranging in size from 5 mm to 1 µm size, they are a byproduct of plastic fragmentation affected by processes such as photo, biological, thermal, and mechanical degradation (Fechine *et al*., 2004; Ferreira *et al*., 2021; Jiang *et al*., 2023). MPs are widely distributed throughout the oceans of shallow and surface waters (Browne *et al*., 2011; Hidalgo *et al*., 2012) as well as in deep-sea sediments (Fischer *et al*., 2015; Van *et al*., 2013; Woodall *et al*., 2014). As a result, the adverse impacts of plastic pollution are becoming more apparent as MPs permeate aquatic environments, posing a threat to the marine environment and potentially disrupting biota throughout the food web (Öborn *et al*., 2022).

Various environmental conditions affect the behavior and fate of MPs in the ocean, including currents, horizontal and vertical mixing, temperature, wind, biofilm formation, and ultraviolet (UV) exposure (Barnes *et al*., 2009; Lusher, 2015; Zeghoud *et al*., 2024). MPs in the sea are harmful to a wide range of marine organisms (Fendall & Sewell, 2009; Thompson *et al*., 2004), planktonic organisms (Cole *et al*., 2013), fish species (Phillips & Bonner, 2015), and large whales (Fossi *et al*., 2012). Recent studies have demonstrated that particle size influences the impact of MPs on bivalves (González *et al*., 2019). MPs are a threat not only because of their physical stress but also because of their ability to adsorb extraneous pollutants (Cao *et al*., 2022; Islam *et al*., 2021). Plastic particles, as noted by Hong *et al.* in 2024, also come about as a result of other chemicals or additives such as those manufactured and the ones incorporated at the sea, thereby performing a variety of functions once incorporated in the debris. It has also been explored that the sorption behavior that occurs on microplastics is influenced by the size and types of plastic micro particles (Wang *et al*., 2021). Therefore, adherence to MPs, ingestion through gills, and potential sources of bioaccumulation can be vectors for other contaminants (Endo *et al*., 2005; Teuten *et al*., 2009).

Persistent organic pollutants (POPs) are a group of chemicals that can adsorb on microplastics (MPs), increasing their bioavailability and posing a critical ecological risk by potentially entering the marine food web (Andrady, 2011; Wang *et al.*, 2021). Nonetheless, very little, if any, research has addressed in-field effectiveness studies of the mechanical, chemical and biological methods for microplastic degradation (Hurley & Leggett, 2009). The methods for microplastics degradation include implantation, targeted photodegradation, facilitated catalytical oxidation, electrochemical facilitated oxidation and biological methods (Dadsetan *et al.*, 1999; Pablos *et al.*, 2010; Xiang *et al.*, 2023; Yuwendi *et al.*, 2022).

PE and PET were selected because they are common nonbiodegradable thermoplastics (Thachnatharen *et al.*, 2021), particularly in single-use plastic bags and beverage bottles (Babaahmadi *et al.*, 2022; Hadiuzzaman *et al.*, 2022). PET is a commonly used plastic due to its advantageous properties, including low cost, high strength, lightweight, transparency, and gas barrier characteristics (Aziz & Angeline, 2010). These features make it widely utilized in diverse applications, such as apparel and food packaging (Aziz & Angeline, 2010; Dhaka *et al.*, 2022). However, with increasing concerns about the environmental impact and toxicity of plastic pollution, pernicious macro-meso-micro- and nanoplastics will create severe challenges to our management of PET materials (Abboudi *et al.*, 2016; Sang *et al.*, 2020). These plastics are formed owing to the polymerization processes of ethylene glycol (EG) and terephthalic acid (TPA) which facilitate the global mass consumption of PET due to its exceptionally high strength-to-weight ratio and flexibility (Li *et al.*, 2022; Sagong *et al.*, 2021).

As a result of its prevalent presence, consuming plastic has been associated with numerous health hazards (Dhaka *et al.*, 2022). More so troubling, annual production of PET soared to more than 70 million tons in 2020 (Eugenio *et al.*, 2021), with 90 % post-consumer PET waste. Consequently, this substantial volume of PET waste presents a considerable risk to environmental health and human well-being (Dai *et al.*, 2021; Nimchua *et al.*, 2007). Even though recycling systems are in place (e.g., for the PET bottle market), over half of the PET produced globally escapes collection and instead ends up in landfills or is released into the environment and is projected to persist for hundreds of years (Carr *et al.*, 2020; Liu *et al.*, 2021). Therefore, there is an urgent demand for cost-effective green approaches development to control PET pollution and protect global ecosystems (Dai *et al.*, 2021; Moshood *et al.*, 2022).

Currently, PET recycling is considered the best approach to resolve PET waste problems (Ghasemi *et al.*, 2021). To recover the utilized PET, multiple methods have been employed, including biochemical, biological and chemical methods (Ellis *et al.*, 2021; Hou *et al.*, 2021; Wojnowska *et al.*, 2022). Through cutting, heating, or extrusion, physical recycling transforms PET into new products. Carr *et al.* (2020) reported this method as being especially efficient, but also quite cost-effective. In an industrial context, PET can be depolymerized into its constituents via chemicals that can cleave ester bonds (Carniel *et al.*, 2021; Martín *et al.*, 2021; Sinha *et al.*, 2010). However, the deployment of chemical recycling solutions has been hindered primarily by the high processing costs compared to the relatively low cost of virgin PET (Forrest, 2019). There are challenges, however, with chemical recycling methods since this economic disadvantage provides difficulty competing to using new material in making virgin products (Burgess *et al.*, 2021). Moreover, the intricate nature of chemical recycling processes only pushes the price further upwards (Li *et al.*, 2022), causing a delay in both the commercialization and development of the given tech (Singh *et al.*, 2021). Mechanical processes are therefore the primary option for reprocessing reclaimed PET. Such methods are effective but they usually lead to the degradation of the material and a loss of its value (Demets *et al.*, 2021). Because of this lack of natural degradation, the estimate of landfilled PET plastic or one littered on the environment is said to remain for over hundreds of years (Austin *et al.*, 2018).

On the other hand, PE is one of the most common thermoplastics and is very cheap. It is also a lightweight and very durable material useful in a diverse range of industries including manufacturing and medical devices or even pharmaceutical packaging (Awad, 2021; Gardette *et al.*, 2013). It includes several low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and ultra-high-molecular-weight polyethylene (UHMWPE), with each having its unique properties that are used for various purposes. For instance, LLDPE is used in stretch films because of its applications in offering tensile strength and flexibility (Patel *et al.*, 2020), however, UHMWPE is used where wear resistance is a requirement in medical applications or high performed applications (Faruk *et al.*, 2023).

However, the use of PE has a downfall as it poses environmental threats due to the fact that it inflicts microplastics and never fully be decomposed in organisms' bodies and environments as a whole (Wong *et al.*, 2020). The presence of PE microplastics discovered in ocean sediment calls for better improvements in management practices due to the shocking levels found (Ahmed *et al.*, 2024). In search of finding a solution to this problem, some researchers have suggested the use bio-based polyethylene made from sugarcane which will lower dependence on fluctuating fossil resources and promote a more environmentally feasible lifecycle management (Ali *et al.*, 2023; Moshood *et al.*, 2022). Moreover, the use of certain additives that promote biodegradation and are reported to increase the rate at which PE breaks down in certain environmental settings is also attracting growing attention (Cai *et al.*, 2023; Martins *et al.*, 2022; Retnadhas *et al.*, 2024).

State-of-the-art developments have been made but the recycling of PE still remains one of the most complex processes because of varying polymer grades and better market resources contamination by food wastes (Gazeau *et al.*, 2024). In order to help increase the amount of recyclables, new sorting methods are being created using near-infrared spectroscopy (Lubongo *et al.*, 2024). In addition, the shift toward a circular economy is also placing attention on chemical recycling processes that could depolymerize PE that can then be used to produce feedstock similar to virgin material (Chawla *et al.*, 2022; Liu *et al.*, 2024). To meet the requirements of the consumers who demand for sustainable packaging products, this development is in tandem with the rationalization and availability of bio-based or recycled PE by the manufacturers (Eissenberger *et al.*, 2023). On the other hand, statutes and policies enforcing bans or restrictions on disposables also affect how plastics are disposed of by the companies (Ahmadi *et al.*, 2024).

2.2 Degradation of Microplastics

Abiotic degradation encompasses certain chemical processes including alteration of polymers color, chain conformation, molecular mass, molecular mass distribution, degree of crystallinity, chain flexibility, degree of cross linking, and branching (Jiang *et al.*, 2007; Venkatachalam *et al.*, 2012; Vilensky *et al.*, 2003). In general, biological contamination of water causes the greatest risk to humans in most countries (Lin *et al.*, 2022); however, pollution with chemicals is also an issue (Morin *et al.*, 2022).

The chemical industry and human activities have liberated vast amount of chemicals which can alter many ecosystems (Bratovčić, 2023). Chemical, physicochemical (including photo, thermal, and mechanical degradation), and biological processes can lead to the degradation of plastics (Fotopoulou & Karapanagioti, 2019; Liu *et al.*, 2022; Zhang *et al.*, 2021). Oxidation and hydrolysis are the primary processes involved (Asadi *et al.*, 2021; Bonyadinejad *et al.*, 2022; Fotopoulou & Karapanagioti, 2019).

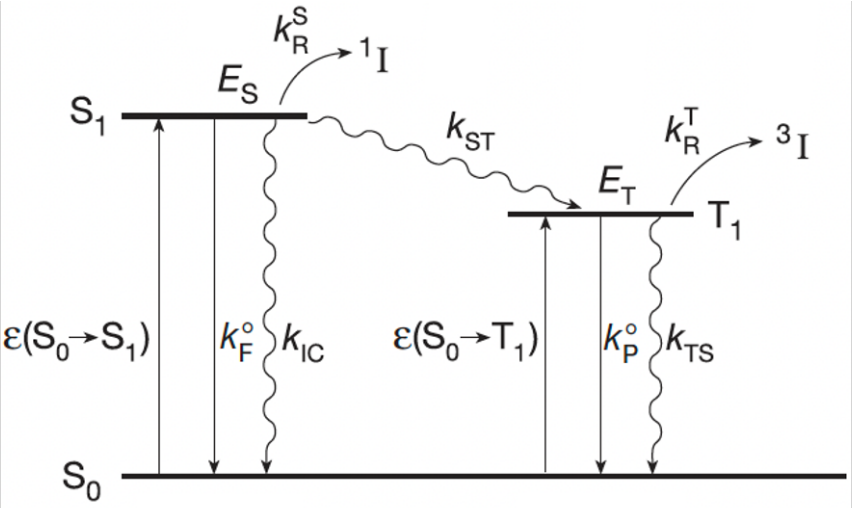
In addition, in order to ascertain likely effects on the environment and put on watch those that are of greater concern, it is important to assess the (eco)toxicological and environmental properties of the end products of the degradation process (Termopoli *et al.*, 2022). Photodegradation, the process in which materials are broken down by ultraviolet (UV) and visible light, in particular sunlight's near UV rays, poses one of the threats to polymeric materials as it enables the disintegration of synthetic polymers (Molokanova *et al.*, 2017; Pablos *et al.*, 2010; Smith *et al.*, 1989; Watanabe *et al.*, 2023).

2.3 Photodegradation

Photodegradation is a branch of chemistry that involves chemical reactions initiated by the absorbance of radiation (Rohatgi, 1978). These reactions occur when a compound absorbs radiation and the ability of the compound to absorb radiation is determined by the presence of chromophores (Turro *et al.*, 2009). The absorption of radiation results in the change of compounds from a ground-state energy level to an excited-state energy level, which matches the energy of the incident quantum radiation, as described by the equation $E = h\nu$, where h is Planck's constant, and ν is the frequency of the radiation absorbed (Turro *et al.*, 2009).

Electronic excitation caused by the absorption of radiation leads to the promotion of an electron from bonding to an antibonding or nonbonding orbital (Coxon & Halton, 1987). Most organic photochemical reactions are initiated by $\pi - \pi^*$ or $n - \pi^*$ transitions (Coxon & Halton, 1987; Turro *et al.*, 2009). In environmental photochemistry, the effect of radiation energy on organic compounds is primarily influenced by the solar spectrum, which has the highest energy between 300 – 750 nm (Remucal, 2014). The rate at which a molecule absorbs radiation depends on its structure and on the wavelength of the radiation (Suppan, 1994). Many organic compounds have maximum absorption sensitivity within the UV-visible wavelength range of the solar spectrum (Zhong & Jang, 2011). For instance, plastic polymers such as PET absorb radiation at wavelengths between 290 – 400 nm, which are entirely within the UV region of the solar spectrum (Kelen, 1983).

After a molecule absorbs a photon and undergoes a transition from the ground state (S_0) to an excited state, it can exist in two arrangements: an excited singlet state (S_1), where electrons are paired, and an excited triplet state (T_1), where electron spins are unpaired (Figure 2.1) (Turro *et al.*, 2009). A series of relaxation stages in aromatic or conjugated molecules can convert electrons from S_1 to T_1 via intersystem crossing (Coxon & Halton, 1987; Turro *et al.*, 2009). Eventually, relaxation returns the molecule to its ground-state energy level by losing energy through various transitions (Turro *et al.*, 2009).



Legend:

ε: Absorption coefficient of transition

E_S: energy singlet

E_T: energy triplet

K: reaction rate constant

^1I: singlet products

^3I: triplet products

Figure 2.1. Jablonski diagram. Adapted from Turro *et al.* (2009). The diagram illustrates the energy levels of a molecule and the transitions between them. S_0 represents the ground state, while S_1 and T_1 are excited states (singlet and triplet, respectively). Key transitions include Absorption: The molecule absorbs radiation to move from S_0 to S_1 or T_1; Fluorescence (F): Radiation emission when the molecule returns from S_1 to S_0; Phosphorescence (P): Radiation emission when returning from T_1 to S_0; Internal Conversion (IC): Energy is released as heat without radiation emission when moving from S_1 to S_0; Intersystem Crossing (ST): The molecule switches between S_1 and T_1 without emitting radiation; Photochemical reactions from S_1 or T_1 may lead to reactive intermediates. The intersystem-crossing rate constants k_{ST} and k_{TS} are sometimes referred to as k_{ISC}.

Photochemical reactions involve direct or indirect photodegradation (Vione, 2016). Direct photodegradation occurs when a chromophoric material directly absorbs radiation, causing chemical structure changes, such as bond cleavage, chain scission, or fragmentation (Steinberg & Paul, 2008). Indirect photodegradation occurs when a reaction is initiated due to radiation absorption by other chromophores distinct from the substrate of interest (Zafiriou *et al.*, 1984). In this process, reactive intermediates can initiate chemical changes in the substrate of interest through a series of reactions (Steinberg & Paul, 2008; Zafiriou *et al.*, 1984).

2.4 Environmental Phototransformations

Some formulations, even though they do not necessarily contain chromophores, do tend to possess additives or other contaminants in their structure which have a tendency of absorbing radiation, thus aiding the photo oxidation chemical reaction (Cai *et al.*, 2023; Feldman, 2002; Gangadoo *et al.*, 2020; Yousif & Haddad, 2013). Kaplan and Cory (2016) postulate that there must be some chromophores embedded within these polymers as otherwise it would have been impossible for them to absorb UV radiation and undergo photodegradation. Understanding the mechanisms of plastic degradation through photooxidation involves the monitoring of reactive species such as hydroxyl radicals (·OH) and singlet oxygen ($^1O_2$) using chemical probes (Haag & Hoigné, 1985; Page *et al.*, 2011). These probes allow researchers to gather insights into the oxidation process, assess the impact of these radicals on plastic degradation, and verify photodegradation products (Steinberg & Paul, 2008; Zhou & Mopper, 1990; Zito & Tarr, 2014).

According to Feldman's work in 2002, the molecular oxygen exists in a triplet configuration when plastic polymers are absorbed, this leads to the formation of new reactive species through various mechanisms. When a polymer interacts with photons, it is possible for an electron to get excited which later can interact with molecular oxygen creating superoxide which is a reactive substance that will then be further involved in chemical reactions (Andrés *et al.*, 2023). Other reactive oxygen species (ROS) can also be caused by superoxide, including hydroxyl radicals (Khan, 1978; Wu *et al.*, 2023). These ROS then participate as reactants in the process of indirect photodegradation of polymers and are crucial parts of the degradation stages of plastics (Pospíšil *et al.*, 2019).

2.4.1 *Role of Hydroxyl Radical*

The hydroxyl radical (·OH) is a highly reactive oxygen species (ROS) and is well known to be an aggressive chemical that is prone to oxidation and has a high turnover rate species (Duan *et al.*, 2022; Zhou & Mopper, 1990). Due to its unstable nature, ·OH has the tendency to interact with a range of chemical compounds and usually is at a low equilibrium count, this has been associated with the difficulties present in direct monitoring of the compounds through the analysis of electron spin resonance (ESR) due to the concentration low bias the readings. These difficulties were addressed by Zhou & Mopper who used spin trapping methods which enable the indirect detection of hydroxyl radicals in micro- and nanosized plastic particles exposed to ultraviolet light (Zhou & Mopper, 1990). This method is based on the formation of stable radical adducts which can be measured and thus provide information on the presence of hydroxyl radicals on the radical without the necessity of locating the radical itself.

From the thermally generated hydroxyl radicals from the plastic polymer, several pathways are initiated. A primary mechanism indicates that, plastic polymers, when exposed to molecular oxygen (O_2) interact with ultraviolet (UV) radiation. In short, this process can be represented by the following reaction (Figure 2.2):

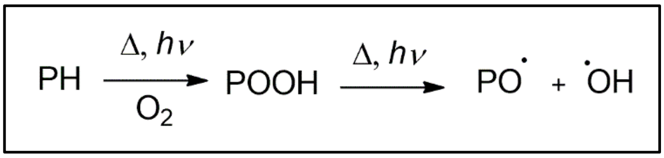


Figure 2.2. Formation of alkoxy (PO•) and hydroxyl (•OH) radicals. Adapted from Costa *et al.* (2024).

In this reaction pathway, PH significates the plastic polymer which when subjected to heat (Δ) and UV radiation (hv), interacts with O_2. This exposure to UV radiation leads to the formation of a peroxide (POOH). The peroxide along this process decomposes into polymer-oxy radical species (PO•) and a hydroxyl radical (•OH). The generation of hydroxyl radicals is critical as they are involved in several degradation processes of plastic polymers such as fragmentation, chain scission and cross-linking (Gangadoo *et al*., 2020; Yousif & Haddad, 2013).

Other sources of hydroxyl radicals include firstly the generation of a superoxide after the reduction of O_2 which then, through dismutation, yields hydrogen peroxide, which eventually yields hydroxyl radicals. Such pathways have already been studied and pathways by Feldman (2002) and Yousif & Haddad (2013) have been previously documented on. The arguments of Coxon & Halton (1987) as well as Steinberg & Paul (2008) are also relevant. Recent works by Duan *et al.* (2022) and Shi *et al.* (2022) have further elucidated the mechanisms underlying these reactions, underscoring the role of hydroxyl radicals in the photooxidation of hydrocarbon polymers (Kaing *et al*., 2024).

Coxon & Halton (1987) point out that photochemical and thermal oxidation of polymers are radical processes that are catalyzed off by exposure to radiation or simply thermal exposure of the polymer matrix. As stated above, photochemical oxidation does occur but to only the surface of the polymer because of the outstanding strength of radiation that a certain area has, but thermal overload happens to all areas of the substrate, (Hawkins, 1984). Photochemistry can also help in breakdown of polymers through external forms such as ozone and singlet oxygen as sources (Hawkins, 1984). Essentially, both photochemical and thermal oxidation exhibit similar intermediates and propagation mechanisms. One of the major features of the process includes the formation of hydroperoxides, which could further be converted into the polymer oxy radical (PO•) (Rabek, 1995). These radicals are very important to chain scission and provide a wide range of degradation products, such as aldehydes, ketones in the chain, and hydroxyl groups (Ferry *et al.* 2023; Gewert *et al*., 2015).

PET microplastic photodegradation is mainly initiated through certain photo-reaction pathways, leading to the formation of specific degradation products (Figure 2.3). According to the literature, carboxylic acid moieties are likely to be the main compounds produced from photodegradation (Ding *et al.*, 2022; Shi *et al.* 2022). Given their chemical nature, these compounds should show enhanced sensitivity under negative ESI (Zhang et al., 2019).

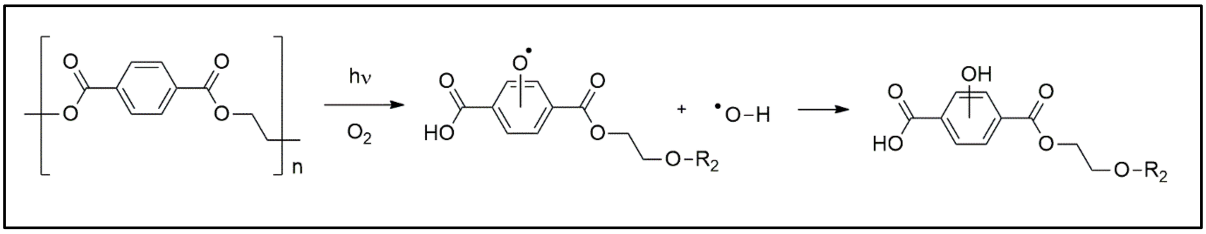


Figure 2.3. Main photoreaction pathways and some potential products from PET microplastic photodegradation.

2.4.2 Role of Singlet Oxygen

Singlet oxygen ($^1O_2$) is another important ROS that plays a significant role in photo-oxidative pathways, generated by reactive interactions with molecular oxygen (Steinberg & Paul, 2008). Absorption of radiation by an organic compound promotes it to an excited triplet state (Turro et al., 2009). The triplet state, through energy transfer to ground-state molecular oxygen, forms singlet oxygen and quenches the excited triplet state of the sensitizer compound. Like hydroxyl radicals, $^1O_2$ can be monitored indirectly using chemical probes (Haag & Hoigné, 1985). Elucidation of its generation and action in degradation processes will enrich knowledge of plastic degradation pathways.

2.4.3 Role of Ozone

Ozone (O_3) is one of the most significant ROS, which accelerates the photodegradation of plastics through different types of oxidative processes. It reacts with unsaturated bonds in polymer chains and chromophores, leading to oxidative cleavage and smaller degradation products (Shi *et al.*, 2022; Singh & Sharma, 2008). When exposed to UV radiation, O_3 generates excited singlet oxygen that initiates further radical reactions, intensifying plastic degradation (Beltrán, 2003; Singh & Sharma, 2008).

Moreover, ozone contributes to the formation of hydroxyl radicals and other secondary ROS, amplifying the oxidative stress on plastic materials (Hu *et al.*, 2023). This heightened stress can result in the fragmentation of polymer chains, compromising their integrity and contributing to environmental pollution (Ferrante *et al*., 2022). While being far less discussed than other ROS, O_3 is among the most important factors which influences the kinetics of photooxidation in variable environmental conditions (Figueredo *et al*., 2020). In general, monitoring of ozone and its degradation products is very necessary in relation to their ecological effects since some recent studies have been indicating an increase in toxicity from such products within aquatic ecosystems (Neale *et al*., 2023; Williamson *et al*., 2019). In conclusion, ozone is a strong oxidant that may have an impact on certain of the more complicated plastics degradation pathways and relates to very important ecological issues: plastic pollution.

2.5 Analytical Techniques for Analysis of Microplastics

There are generally two major ways to analyze microplastics: the first is direct analysis and the second is indirect by degradation products of polymers (Srinivasan & Leigh, 1982). In direct analyses, researchers have directly analyzed the particles using advanced techniques: for example, Infrared (IR) microscopy and Raman microscopy among other techniques (Cowger *et al*., 2020; Ivleva, 2021). The nature of the microplastics can be deduced from the gathered IR absorbance or Raman spectra (Ribeiro *et al*., 2017). Indirect analysis, conversely, is performed by detecting the degradation products of polymers usually obtained after thermal degradation (Dierkes *et al*., 2021). This approach correlates the original microplastic matrix and the identified chemicals (Hale *et al*., 2022). Gas Chromatography-Mass Spectrometry (GC-MS) is an analytical method used to analyze microplastics indirectly (Estévez *et al*., 2024). Recently, Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS) has been proposed for detecting microplastics in environmental samples (Costa *et al*., 2024).

GC-MS has been one of the most documented techniques for microplastic analysis (Ainali *et al*., 2021; Velimirovic *et al*., 2021). In this technique, the microplastic samples are thermally degraded, and the vaporized chemical components are analyzed using chromatography and mass spectrometry (Matilainen *et al*., 2011; Medhe, 2018). In product-based analyses, microplastic samples undergo specific treatments or environmental exposures to promote the release of degradation products, which can then be analyzed (Gazal & Gheewala, 2020; Pires *et al*., 2022). LC-HRMS techniques have proven effective in identifying microplastic components, including potential chain scission products from the breakdown of the polymeric fibers (Costa *et al*., 2024). Recent development in these techniques has further improved their sensitivity and precision in the detection of microplastics (Estévez *et al.*, 2024; Falandysz *et al.*, 2024). In this respect, it is crucial to identify compounds that can be uniquely correlated with targeted polymers. Within this analytical framework annotation involves the systematic comparison of detected compounds with established chemical libraries, facilitating the association of these compounds with degradation products induced by specific treatments (Wolfender *et al.*, 2018). The process of identification, which is equally critical, focuses on elucidating the molecular structure of the detected compounds, thereby contributing to a comprehensive understanding of their environmental impacts and associated risks (Quang *et al.*, 2023).

Chromatographic separation is a powerful technique used to separate and analyze complex mixtures of compounds based on their chemical properties (Rouessac & Rouessac, 2022). The fundamental principle involves the distribution of molecules between a stationary phase and a mobile phase, with diverse components interacting differently with the stationary phase (Abraham *et al.*, 1999). Consequently, the components migrate at different rates (RTs), leading to their separation (Ismail & Nielsen, 2010). Following this separation, the analytes can be introduced into a mass spectrometer for further examination (Trufelli *et al.*, 2011). In analytical practice, chromatography and mass spectrometry are often coupled to develop powerful hybrid techniques (Wille *et al.*, 2012). Although chromatography facilitates separation, it may not independently detect compounds, it generally requires supplementary techniques, such as UV detection or MS (Donato *et al.*, 2012).

High-Performance Liquid Chromatography (HPLC) (Figure 2.4) is a specific chromatographic technique that plays a critical role in analyzing the degradation products of microplastics (Ainali *et al.*, 2021). The coupling of HPLC with MS is pivotal to detecting the separated compounds (Forcisi *et al.*, 2013). As the eluted molecules arrive in the mass spectrometer, they are converted into ions for analysis, typically requiring an ion source where the analytes undergo ionization, a critical step before entering the mass analyzer (Garg & Zubair, 2023). Common ionization techniques include Electrospray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI) (Shi *et al.*, 2022). Once ionized, the ions go into the mass spectrometer and reach the analyzer, which could be an Orbitrap analyzer, which provides the measurement of mass-to-charge ratio (m/z) (Banerjee & Mazumdar, 2012). This process allows for the annotation of compounds based on their molecular weight and structural characteristics (Eliuk & Makarov, 2015).

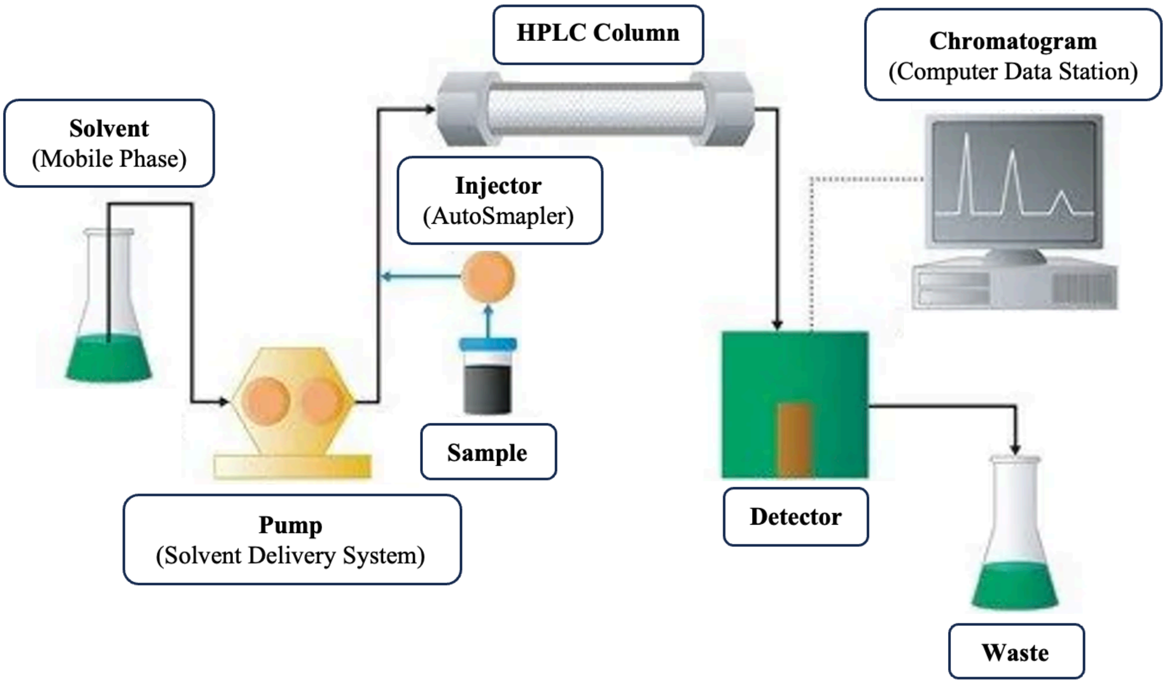


Figure 2.4. High-Performance Liquid Chromatography (HPLC) System. Adapted from Waters Corporation (2024). Available at: https://www.waters.com/nextgen/us/en/education/primers/beginner-s-guide-to-liquid-chromatography/how-does-high-performance-liquid-chromatography-work.html.

To ensure effective integration between Liquid Chromatography (LC) and Mass Spectrometry (MS), the eluent from the LC column must undergo a process that allows analyte molecules to be vaporized and ionized for MS detection (Donato *et al*., 2012). This transformation occurs through atmospheric pressure ionization (API), where the liquid phase is evaporated and the analytes are prepared for analysis in the mass spectrometer (Trufelli *et al*., 2011). ESI is considered the most effective and one of the most widely used ion sources for LC-MS because of its good performance based on polar and aqueous mobile phases; it possesses the capability to ionize compounds with certain functional groups such as carboxyl groups (-COO-). For less polar compounds, APCI is normally used as a complement and permits the quantification of a wider range of analytes by liquid chromatography (Figure 2.5). This step is crucial because the efficiency of ionization of the compounds will affect the sensitivity and selectivity of the LC-MS analysis (Gallagher *et al*., 2003).

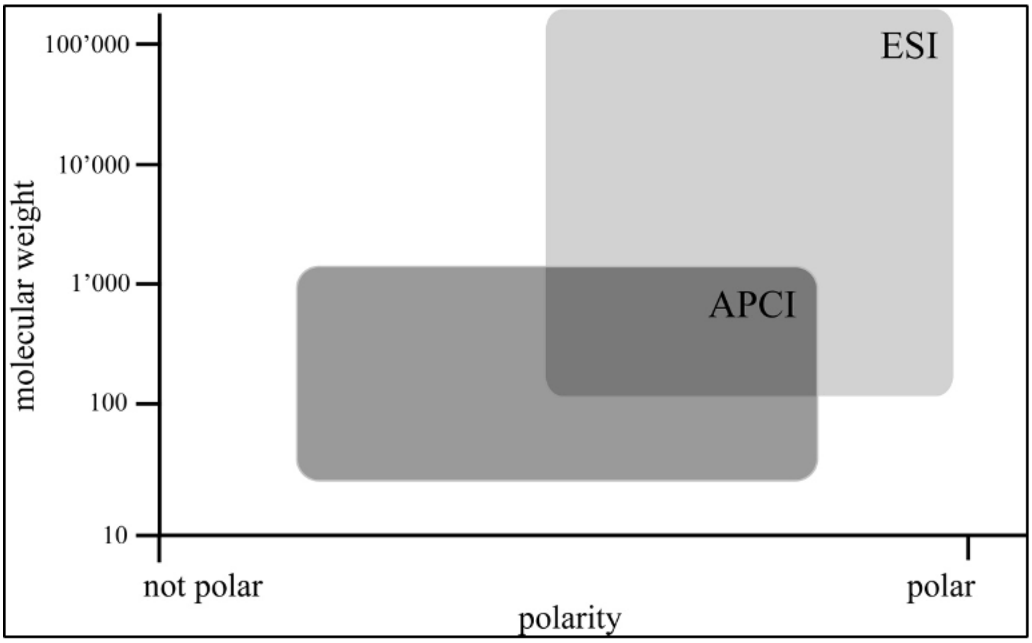


Figure 2.5. Comparison of Electrospray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI) based on molecular weight and polarity. ESI is more suitable for high-polarity and high-molecular-weight compounds, while APCI is typically used for lower-polarity and lower-molecular-weight compounds. The overlapping areas demonstrate the complementary application ranges of these ionization techniques. Reprinted from Bigler, L. 2009, Doctoral dissertation, University of Zurich.

According to Brenton and Godfrey (2010), precision in mass is achieved by comparison of the experimentally measured mass of a compound with its theoretically correct, true mass value. Such a comparison would provide a judgement on the accuracy of the mass spectrometric measurement, the accuracy itself expressed as a difference of these two. Identifying or characterizing compounds accurately is really related to the accuracy in their measured masses, particularly important in high-resolution mass spectrometry. The degree of this deviation is commonly expressed in parts per million (ppm), and the lower the ppm, the higher the mass accuracy. This is a critical value to describe the reliability of the analytical measurement by mass spectrometry, especially when detecting trace compounds from complex matrices (Balogh, 2004). Whereas the resolution is quantified as peak full width at half maximum (FWHM) and this factor depends upon the capability of an instrument in differentiating ions having very similar mass-to-charge ratios (Figure 2.6). The high resolution provided by mass spectrometry in identifying various types of analytes with accuracy, particularly in complicated analytical scenarios with overlapping peaks, is indispensable. These may provide a problem during analysis, especially in environmental samples as observed by Balogh (2004) and Schymanski *et al.* (2014).

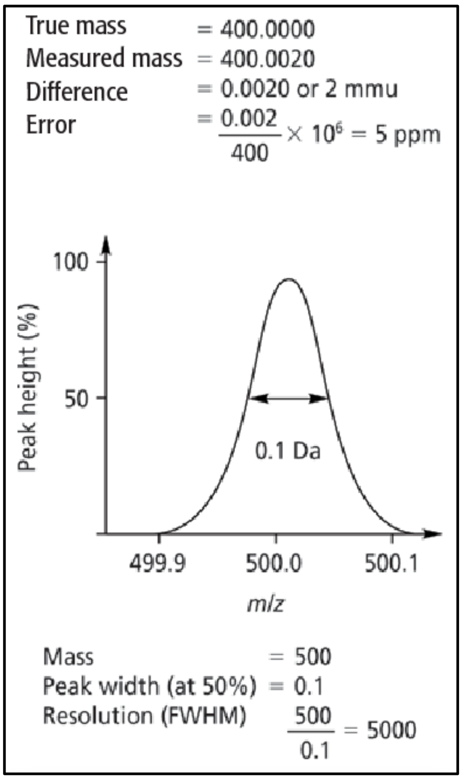


Figure 2.6. Mass accuracy determination (top) and the resolution for a mass spectrometer measured at a given ion (bottom). Reprinted from Balogh (2004).

In summary, LC-MS is a cutting-edge analytical technique that offers a reliable and sophisticated method for precise quantification of minor quantities in a wide range of sample matrices (Pérez *et al*., 2017; Perez *et al*., 2021). The sophisticated fusion of LC and MS not only solves the problems presented by complicated matrices but also provides analytical labs with unmatched accuracy and productivity as they look toward the future (Vaughan *et al*., 2012).

3 Materials and methods

3.1 Materials

In this study, various high-purity chemicals and materials were utilized to ensure the accuracy and reproducibility of the experiments. LC-MS grade solvents, including water, methanol, and acetonitrile, were purchased from Carlo Erba. Washing water was obtained using a Milli-Q system (18 MΩ cm). Benzoic acid, terephthalic acid, and hexadecanedioic were from Sigma Aldrich. *4-((2-((4-carboxybenzoyl)oxy)ethoxy)carbonyl)benzoate* was from BLDpharm. Suberic acid was from Alfa Aesar (Thermo Fisher Scientific, Heysham, UK). Sebacid acid was purchased from Sigma-Aldrich (St. Louis, MO, USA). Dodecanedioic acid and tridecanedioic acid were obtained from TCI (Tokyo, Japan). The polyethylene (PE) particles (with a size range of 10 − 45 μm) and polyethylene terephthalate (PET) granules were obtained from Cospheric and Sigma-Aldrich, respectively. The PET particles were further processed by cryogenic grinding using a Cryo-MM400 cryogenic sample grinding apparatus (details provided in Appendix A). This process involved operating at 30 rpm for 1 minute per cycle across six cycles.

Additionally, standard sand and silica, which were used as substrates for adsorption studies involving PE and PET, were acquired from Sigma-Aldrich. Natural sand, specifically collected from the coastal region of Faro Beach (N 37° 0' 29.4546", W 7° 59' 41.265"), was thoroughly washed with Milli-Q water before use. Filtration of the sample extracts was performed using a 0.45 μm syringe filter from Alwsci Corporation, specifically the 13 mm PTFE Hydrophilic Syringe Filter with Outer Ring.

3.2 Sample preparation

The PE and PET microplastics described above were used as pure materials and adsorbed on the surfaces of silica, standard sand, and natural sand. Natural sand was first washed with Milli-Q water. Adsorption of the PE and PET microplastics on the surfaces of the mentioned matrices was performed as follows: first, silica, standard sand, and natural sand were placed in an oven at 100 °C for 12 h and then removed from the oven and allowed to cool while covered with aluminum foil. Subsequently, a solution with a concentration of 10 mg/g of PE and PET was prepared. The solid samples were accurately weighed and placed in 20 mL vials, and the solid powder was covered with dichloromethane (DCM). Vials containing 3 – 4 g of sand and 2 g of silica were sealed and gently stirred for 30 min. After this stirring period, the vial caps were removed, and the mixture was evaporated at room temperature with continuous gentle stirring. Once the solid components were completely dry, a final thermal treatment of 40-minute duration at 70 °C was applied. Irradiation experiments were carried out employing a 150 W xenon lamp (obtained from Horiba) and/or a 16 W mercury lamp (from Applied Photophysics).

3.3 Experimental

3.3.1 Photodegradation

Pure microplastic particles

Samples of pure microplastic particles were subjected to irradiation experiments. Non-volatile compounds released from plastics during irradiation were analyzed. For this purpose, the samples were spread on glass microscope slides. Then they were positioned 5 cm from the lamp's surface and irradiated for 24 h. To prevent undesired heating effects, a quartz container filled with water was placed between the lamp and the surface. Subsequently, these samples underwent extraction procedures utilizing methanol, and the resulting extracts were analyzed using Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS). Control samples, which were stored at room temperature in the dark, were also subjected to the same analytical procedures for comparison.

Microplastics adsorbed on the surfaces

Photodegradation of the microplastics on the surfaces was also performed as described above. Non-volatile compounds released from the plastics during irradiation were analyzed to evaluate their composition. For this purpose, the samples were spread on glass microscope slides and positioned 5 cm from the lamp's surface, where they were irradiated for 24 h. To prevent any undesired heating effects, a quartz container filled with water was placed between the lamp and the surface. Following irradiation, the samples underwent extraction procedures utilizing methanol. During the extraction process, the system was purged with nitrogen gas to create an inert atmosphere and facilitate the removal of oxygen, thereby minimizing the oxidation of the non-volatile compounds. The resulting extracts were subsequently analyzed using LC-HRMS. For comparison, control samples stored at room temperature in the dark were subjected to the same extraction and analysis process, ensuring that observed changes were due to irradiation effects rather than environmental factors.

3.3.2 Thermal degradation

The thermal degradation was performed to compare the released photoproducts with those formed after chemical reaction (non-photochemical).

Pure microplastic particles

Samples of pure microplastic particles were added to glass tubes that fit into the aluminum blocks of an apparatus. The thermal degradation was performed at 250 ºC and the heating was achieved using a VELP Scientifica REC Digital ceramic hot plate and the temperature was monitored using a thermocouple thermometer (NESLAB instruments 1-800-258-0830). The samples were then heated for 10 min (250 ºC). Control samples kept at room temperature in the dark were also analyzed in the same way, without subjection to thermal degradation. After each thermal treatment, samples were extracted with methanol, filtrated, and analyzed by LC-HRMS. Then the tubes were cooled to room temperature. Subsequently, 0.5 – 1 mL of methanol was added to each tube, followed by a 10-second sonication to promote the release of formed compounds into the solvent. The supernatant was collected after allowing the particles to settle, ensuring the maximum volume without particles. Thereafter, the supernatant was collected, filtrated, and analyzed by LC-HRMS.

Microplastics adsorbed on the surfaces

Thermal degradation of the microplastics on the surfaces was performed in the same way described above. Control samples of 0.5 g of silica/sand (without microplastics) were thermally decomposed. The tubes containing the powdered samples were then subjected to thermal degradation for 10 minutes. Then the tubes were cooled to room temperature. Subsequently, 1 mL of methanol was added to each tube, followed by a 10-second sonication to promote the extraction process. The supernatant was collected, filtrated, and analyzed by LC-HRMS. Before further processing, the same amount of unprocessed sand was extracted, and a similar volume of extract was used for the extraction process. Finally, the extracts were collected, filtrated, and analyzed.

3.4 Analytical Techniques: LC-HRMS Analysis Method

3.4.1 Chromatographic Conditions

Column Selection

The chromatographic separation was performed on a Thermo Scientific Ultimate 3000 UHPLC (Appendix A). For the stationary phase, a Thermo Scientific Accucore RP-18 column with dimensions of 2.1 × 100 mm and a stationary phase particle size of 2.6 µm was used.

Mobile Phase Composition

For APCI ionization, the mobile phase consisted of water (solvent A) and methanol (solvent B), both containing 0.1% formic acid. The mobile phase gradient started with 20% of solvent B for 1 minute, followed by a linear increase to 60% over 7 minutes. The composition then increased to 100% of solvent B over an additional 14 minutes and was maintained at 100% for 6 minutes. The gradient returned to 20% of solvent B in 1 minute, where it was held for 4 minutes before the next run. For ESI ionization, the same gradient was used, but solvent B was replaced with acetonitrile containing 0.1% formic acid (Table 3.1). The flow rate of the mobile phase was 0.3 mL/min, and the sample injection volume was 20 µL.

Table 3.1. Solvent Gradient table for the LC.

Time (min)	% Solvent B	Flow rate (mL/min)
0	20	0.3
1	20	
8	60	
22	100	
28	100	
29	20	
33	20	

3.4.2 Mass Spectrometric Conditions

- *APCI Ion Source*

  Mass spectrometry was conducted using an APCI ion source in both positive and negative polarity modes. The APCI ionization parameters were as follows: vaporizer temperature 380 ºC; sheath gas flow 30 arbitrary units; auxiliary gas flow 20 arbitrary units; capillary temperature 350 ºC; source current 5 µA; and S-Lenses RF level 69%.

- *ESI Ion Source*

  For the ESI ionization, the following parameters were applied: heater temperature 350 ºC; sheath gas flow 35 arbitrary units; auxiliary gas flow 5 arbitrary units; capillary temperature 350 ºC; spray voltage 3.2 kV; and S-Lenses RF level 69%. The scan range for both ionization methods was 100 – 1500 m/z.

3.4.3 LC-HRMS Analysis

Studying the chromatographic behavior of targeted compounds is essential for developing a method that achieves good selectivity. In this study, High-Performance Liquid Chromatography (HPLC) was selected for its effectiveness in separating non-volatile compounds. Samples were analyzed using a Thermo Scientific Ultimate 3000 UHPLC system equipped with a diode array detector (DAD) for preliminary UV detection and a Thermo Scientific Orbitrap Elite mass spectrometer for advanced analysis. The high resolution and accuracy of the Orbitrap mass analyzer facilitated the extraction of peaks corresponding to each analyte based on their exact mass, Accurate Mass Extracted Ion Chromatogram (AM-XIC).

Data acquisition was performed in positive and negative polarities with full scan and data-dependent modes. Analyzing both positive and negative polarities provided a comprehensive overview of the detected substances, with notable compounds characterized by high identification confidence. APCI, specifically with positive polarity, was particularly effective in detecting smaller, moderately polar molecules. Additionally, the ESI mode allowed for a higher sensitivity in detecting polar lower molecular weight compounds (see Appendix B).

To determine the retention times (RTs) of the compounds selected for identification, a mixed solution containing 50 μM of each analyte in methanol (MeOH) was prepared. Solvent selection is a critical factor affecting the signal intensity during mass spectrometric analysis. Initially, acetonitrile (ACN) was utilized; however, it significantly suppressed the signals in the APCI mode compared to ESI. To enhance the signal strength during APCI analysis, ACN was replaced by MeOH, which provided more efficient ionization and improved analyte detection.

For data-dependent analysis, the three most intense ions were selected based on dynamic exclusion and subjected to Collision-Induced Dissociation (CID) activation, which is a soft fragmentation method. Additionally, the High-Energy Collisional Dissociation (HCD) method was also evaluated, which is characterized by its higher energy for ion formation, resulting in fragments with lower m/z values. This approach provides further insight into the fragmentation behavior of the molecules. LC-HRMS (Figure 3.1) data was processed using Xcalibur 4.1 software, and data-dependent profiles were analyzed with Compound Discoverer 3.3 (Thermo Fisher Scientific) to annotate the main signals. The compound identification workflows included access to local and online databases such as mzCloud, Extractables, and Leachables HRAM.

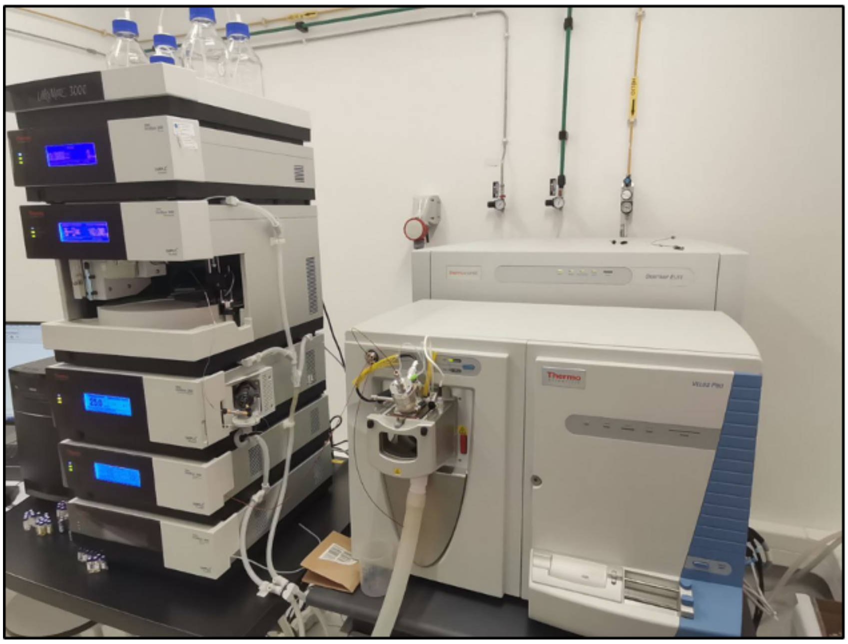


Figure 3.1. Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS) Instrument used in the present work.

4 Results and Discussion

4.1 LC-MS profiles

Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS) is a powerful technique used to separate and detect degradation products from microplastics. Liquid Chromatography (LC) separates the sample components, and High-Resolution Mass Spectrometry (HRMS) determines their molecular masses. In this study, a xenon lamp was utilized for irradiation because its spectrum closely mimics the sunlight spectrum at ground level, providing a relevant simulation of environmental conditions. Non-irradiated and irradiated microplastic samples were analyzed to assess the impact of these irradiation treatments on degradation. This method allows the detection of specific breakdown products, helping to link them to the polymer structure. The chromatograms of the non-irradiated and irradiated polyethylene terephthalate (PET) samples (Figure 4.1) highlight the differences in product formation after irradiation.

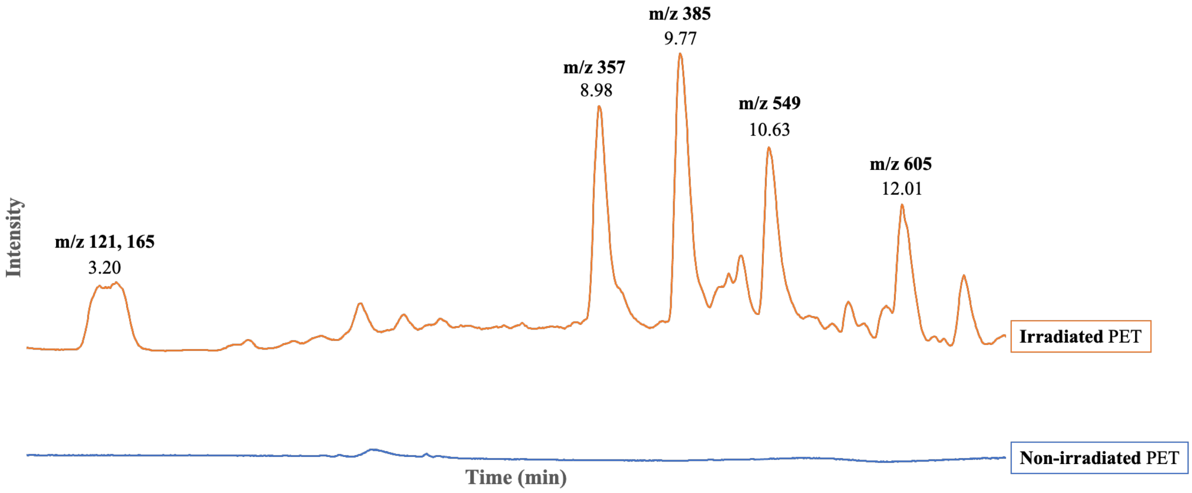


Figure 4.1. Full scan total ion chromatograms of MeOH extracts of PET particles obtained under negative polarity using ESI. The blue profile was obtained for non-irradiated PET particles. The orange profile corresponds to the profile of compounds released from PET after exposure to irradiation with a 150 W xenon lamp for 24 h. The m/z values of the main signals are the following: 121.030 (RT 3.20 min), 165.019 (RT 3.20 min), 357.062 (RT 8.98 min), 385.093 (RT 9.77 min), 549.109 (RT 10.63 min), and 605.177 (RT 12.01 min).

The above profiles were obtained under ESI ionization. Under these conditions, acetonitrile was used in the mobile phase. The solvent selection was critical because it directly influences the signal intensity during mass spectrometric analysis. ACN was initially employed for solvent in the mobile phase in APCI mode. It should be noted that APCI is expected to perform better for less polar compounds (see Figure 2.5) However, ACN significantly suppressed signals as compared to ESI. ACN was therefore replaced with MeOH to enhance the signal intensity, which proved to be a superior solvent for APCI analysis, resulting in more robust ionization and improved analyte detection.

The PET particles exposed to irradiation, using a 150 W xenon lamp for 24 hours, reveal more pronounced peaks (Figure 4.1), indicating the formation of degradation products as expected due to the behavior of PET, which absorbs UV radiation and undergoes polymer degradation (Kelen, 1983). Several major products characterized by their mass-to-charge ratios (m/z) were detected, including ions corresponding to m/z values 121.030, 165.019, 357.062, 385.093, 549.109, and 605.177. These m/z values correspond to specific chemical compounds and were first annotated based on their mass spectral properties and using Compound Discoverer 3.3. For further identification of some annotated degradation products, standards were acquired when not available in the laboratory. By following meticulous analysis and comparison of spectral profiles obtained in PET extracts and for the standards, we confirmed the presence of benzoic acid (m/z 121.030) and terephthalic acid (m/z 165.019) degradation products. Their identification supports the anticipated degradation pathways associated with the chemical structure of PET.

4.2 Ionization sources selection

Mass spectrometric analysis was conducted using Atmospheric Pressure Chemical Ionization (APCI) and Electrospray Ionization (ESI) ion sources. The selection of the appropriate ionization method depends on factors such as analyte properties, sample matrix, and required selectivity and sensitivity (Gallagher *et al.*, 2003). APCI is generally more effective for ionizing non-polar and weakly polar compounds, whereas ESI is more suitable for polar compounds (see Figure 2.5). In this study, APCI was particularly effective in detecting smaller, moderately polar molecules, but ESI provided greater sensitivity, especially in the negative ion mode, owing to the presence of carboxylic acid functional groups in the degradation products (see Appendices C and D). Negative ESI is crucial for accurate detection since it provides more detailed and comprehensive data, which aligns with literature findings, indicating that compounds with carboxylic acid groups ionize more effectively in this mode (Ding *et al.*, 2022; Shi *et al.*, 2022; Zhang *et al.*, 2019). Additionally, positive-ion mode analysis was conducted to detect different products formed under varying reaction conditions. This dual-polarity approach enabled comprehensive analysis, providing a more complete characterization of the degradation profile.

4.3 Detailed Fragmentation Study

In addition to the smaller identified degradation products, namely benzoic acid and terephthalic acid, the chromatographic analysis revealed more intense peaks corresponding to the larger compounds. These compounds are considered to be more specific to the PET polymer, as they better reflect the structure. Unlike benzoic acid, which might originate from various sources, the presence of larger degradation products, particularly the compound exhibiting an m/z value of 357.062, is a strong indicator, a potential marker, of PET degradation. This correlation underscores the specificity of these larger fragments for the polymer itself. We therefore proceeded to further mass spectrometry studies of this compound.

The compound with m/z 357.062 (Figure 4.2) showed a complex fragmentation pattern with major fragments at m/z values 313.072, 269.082, 225.056, and 121.030, suggesting multiple transformation pathways. These observations suggest that many of the detected compounds share structural features, such as aromatic rings and carboxyl groups, with compounds identified earlier, providing insight into their possible degradation mechanisms.

The fragmentation pattern obtained from MS/MS analysis of m/z 357.062 also revealed significant neutral losses, which refers to the removal of neutral fragments (molecules) during the ionization and fragmentation processes. Neutral losses can indicate the structural features of a compound, providing insight into the molecular transformations that occur during degradation in the gas phase. This way, the signal observed at m/z 313.072 corresponds to a neutral loss of 43.990, which is the release of CO_2, while the signals at m/z 269.082 correspond to the release of two CO_2 molecules. On the other hand, the difference between m/z 269.082 and m/z 255.056 corresponds to 44.026, which can be assigned to a C_2H_4O. Finally, the signal at m/z 121.030 is the benzoate ion. Based on the structure of PET and the spectral data the compound with m/z 357.062 was annotated as *4-((2-((4-carboxybenzoyl)oxy)ethoxy)carbonyl)benzoate*. However, owing to the complexity of the fragmentation pattern observed, we could not conclusively rule out other potential candidates for this mass. To confirm the identity of the compound, a standard reference compound was used.

Upon analyzing both the standard and the sample under identical conditions, we observed matching retention times, isotopic distributions, and fragmentation patterns. This comprehensive comparison led to the conclusive identification of a PET degradation product corresponding to the molecular formula $C_{18}H_{14}O_8$. This detailed fragmentation pattern provides valuable insight into the molecular structure of other related compounds facilitating their annotation. The presence of these specific neutral losses of the compound with m/z 357.062 allowed us to propose structures for many other products.

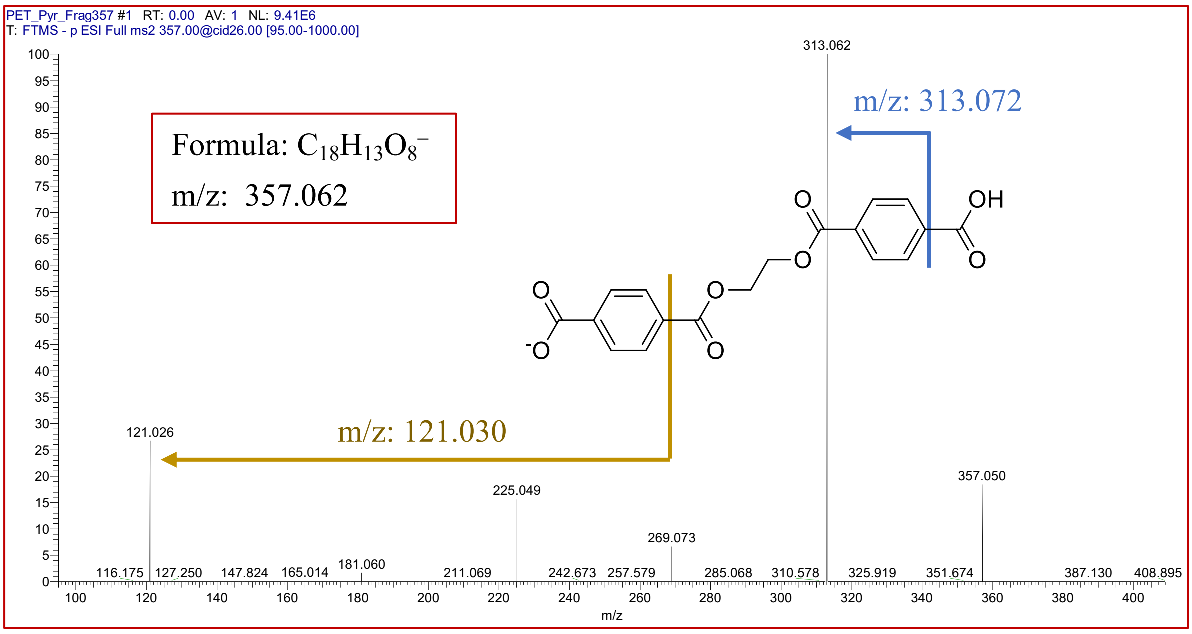
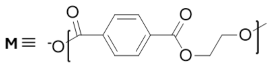
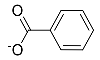
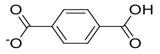
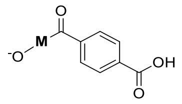
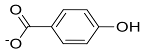
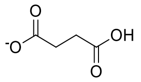
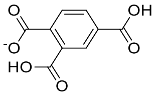
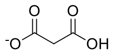
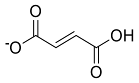
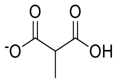


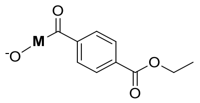
Figure 4.2. Mass spectrum (MS/MS) with the proposed structure for the ion m/z 357.062 obtained under negative polarity using ESI. The arrows represent possible fragmentation sites.

4.4 Identified or Annotated Compounds

The compounds identified in this study (see Table 4.1) are critical for understanding the degradation processes of polyethylene terephthalate (PET). These compounds consistently appeared under various experimental conditions. Their presence is indicative of the pathways through which PET degrades under irradiation conditions. Furthermore, the identification of these compounds will aid in elucidating the underlying mechanisms of PET degradation and contribute to a broader understanding of their stability and durability under UV exposure.

Table 4.1. Identified or Annotated Compounds of PET released compounds during photooxidation and thermal oxidation processes.

RT (min)	**m/z**	**Formula**	**MS/MS**	**Structure** 
3.20	121.030 (-)	$C_7H_6O_2$	77 (C_6H_6)	
3.20	165.019 (-)	$C_8H_6O_4$	121 ($C_7H_5O_2$)	
8.98	357.062 (-)	$C_{18}H_{14}O_8$	313 ($C_{17}H_{13}O_6$) 225 ($C_{14}H_9O_3$) 181($C_9H_{10}O_4$)* 121 ($C_7H_5O_2$)	
Annotated compounds (mzCloud > 90%)				
1.44	137.024 (-)	$C_7H_6O_3$	93	
0.85	117.019 (-)	$C_4H_6O_4$	99, 73	
0.83	209.009 (-)	$C_9H_6O_6$	165, 121	
0.86	103.004 (-)	$C_3H_4O_4$	85, 75, 59	
0.64	115.004 (-)	$C_4H_4O_4$	107, 71	
0.85	117.019 (-)	$C_4H_6O_4$	99,73	

8.92	385.093 (-)	$C_{20}H_{18}O_8$	341, 297, 225, 181, 121	

* In reference to the analysis of compound of m/z 181, it was not possible to draw any definitive conclusions regarding its structure due to the absence of a satisfactory fragmentation spectrum.

Based on the fragmentation study of m/z 357.062, we applied similar analytical logic to deduce and annotate the structures of other compounds detected during the experiments (Appendix E). For example, the compound with m/z 121.030 (Figure 4.3) displayed a fragmentation pattern producing a m/z 77 fragment (C_6H_6), which is consistent with benzene-like structures and shows the release of CO_2. Similarly, the compound with m/z 165.019 (Figure 4.4) exhibited a key fragment at m/z 121 ($C_7H_5O_2$), which also shows the release of CO_2, indicating a structural similarity to previously identified degradation products. The structure assigned to the compound with m/z 385.093 (Figure 4.5) was also based on the fragmentation behaviour of the ion observed at m/z 357.062.

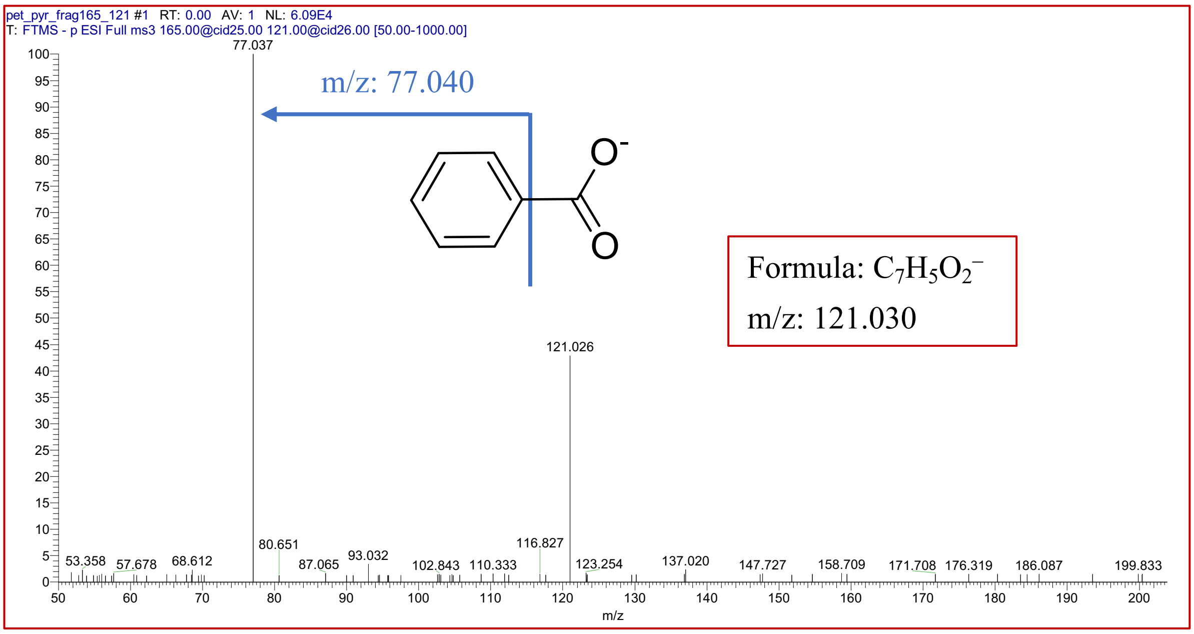


Figure 4.3. Mass spectrum (MS/MS) with the proposed structure for the ion m/z 121.030 obtained under negative polarity using ESI. The arrows represent possible fragmentation sites.

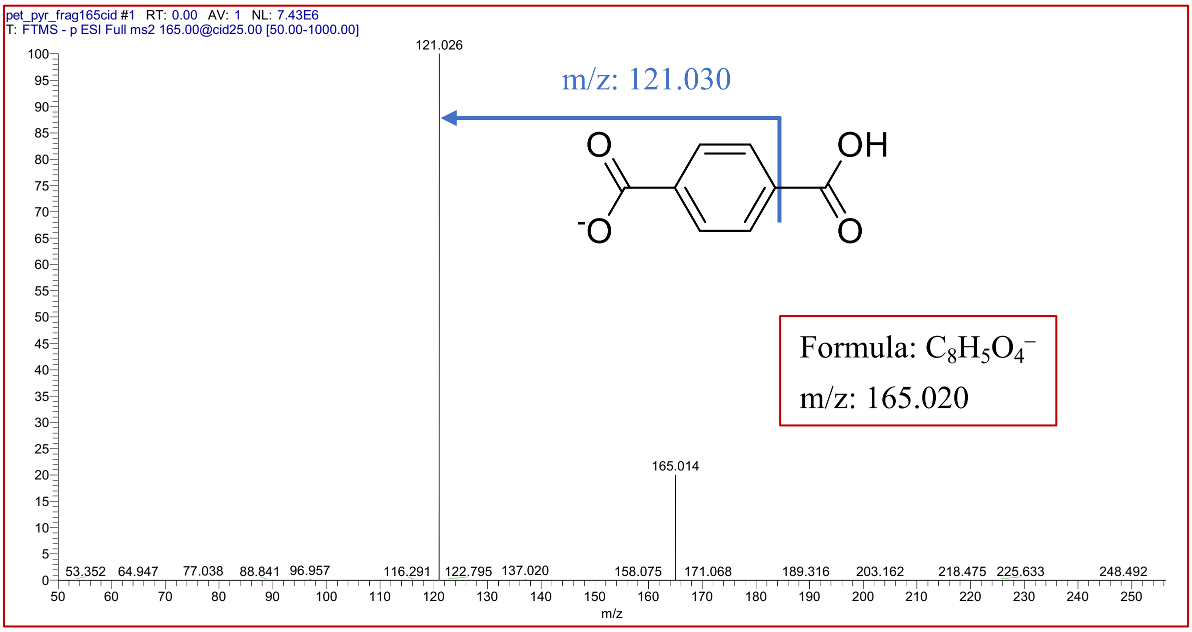


Figure 4.4. Mass spectrum (MS/MS) with the proposed structure for the ion m/z 165.020 obtained under negative polarity using ESI. The arrows represent possible fragmentation sites.

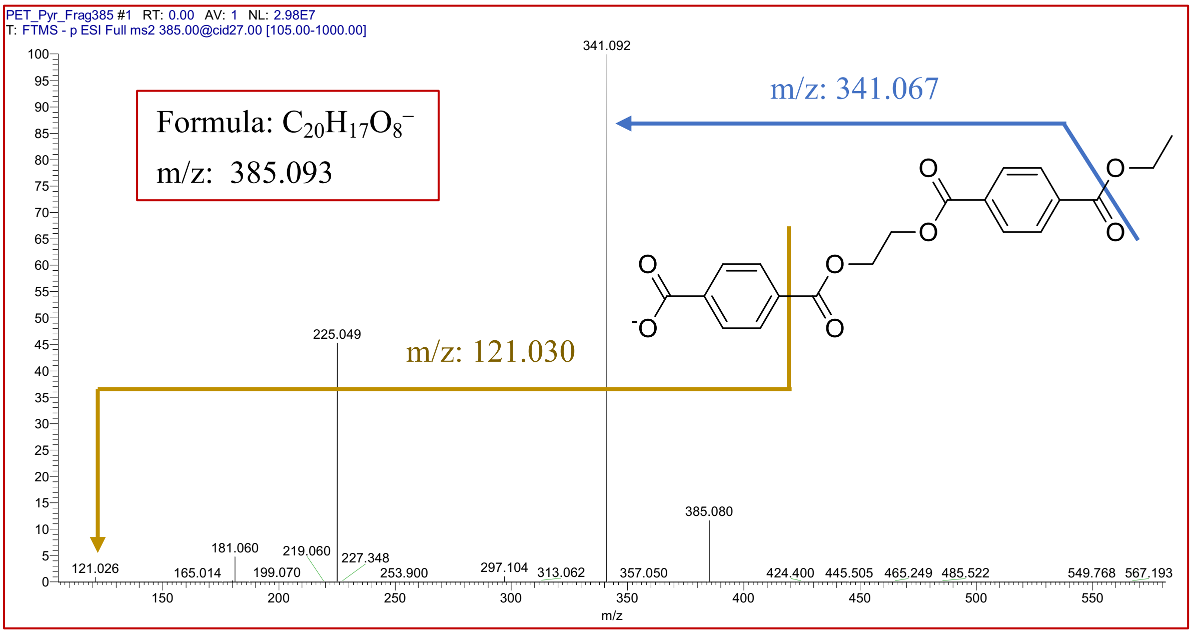


Figure 4.5. Mass spectrum (MS/MS) with the proposed structure for the ion m/z 385.093 obtained under negative polarity using ESI. The arrows represent possible fragmentation sites.

4.5 Role of the surface

To evaluate the role of the surface, we followed six of the major compounds detected in Figure 4.6. The selected compounds were the ones showing m/z values 121.030, 165.019, 357.062, 385.093, 549.109 and 605.177. This evaluation aims to deepen our understanding of how different conditions and surfaces influence the degradation of PET. A comparative analysis of degradation products from samples on surfaces versus those in bulk is presented in Figure 4.6. As can be seen from the profiles of the selected compounds for PET particles in different surfaces, the surface has little or no effect on the photoproduct distributions.

The detected compounds are likely to be released from PET plastics and microplastics under various environmental conditions, including interactions with inorganic surfaces such as beach sand. These results indicate that *4-((2-((4-carboxybenzoyl)oxy)ethoxy)carbonyl)benzoate* is a component of the PET polymer structure and serves as an effective environmental marker for assessing the contamination levels of these polymer materials. Figure 4.6 demonstrates that the distribution of primary photoproducts released from irradiated pure PET particles and those adsorbed on different surfaces remains largely unaffected by the surface type, which indicates that similar compounds are emitted from both pure PET materials and those in contact with natural inorganic surfaces like beach sand, it was confirmed through the analysis of natural sand samples, that plastics transform into diverse molecular forms, contributing to environmental contamination.

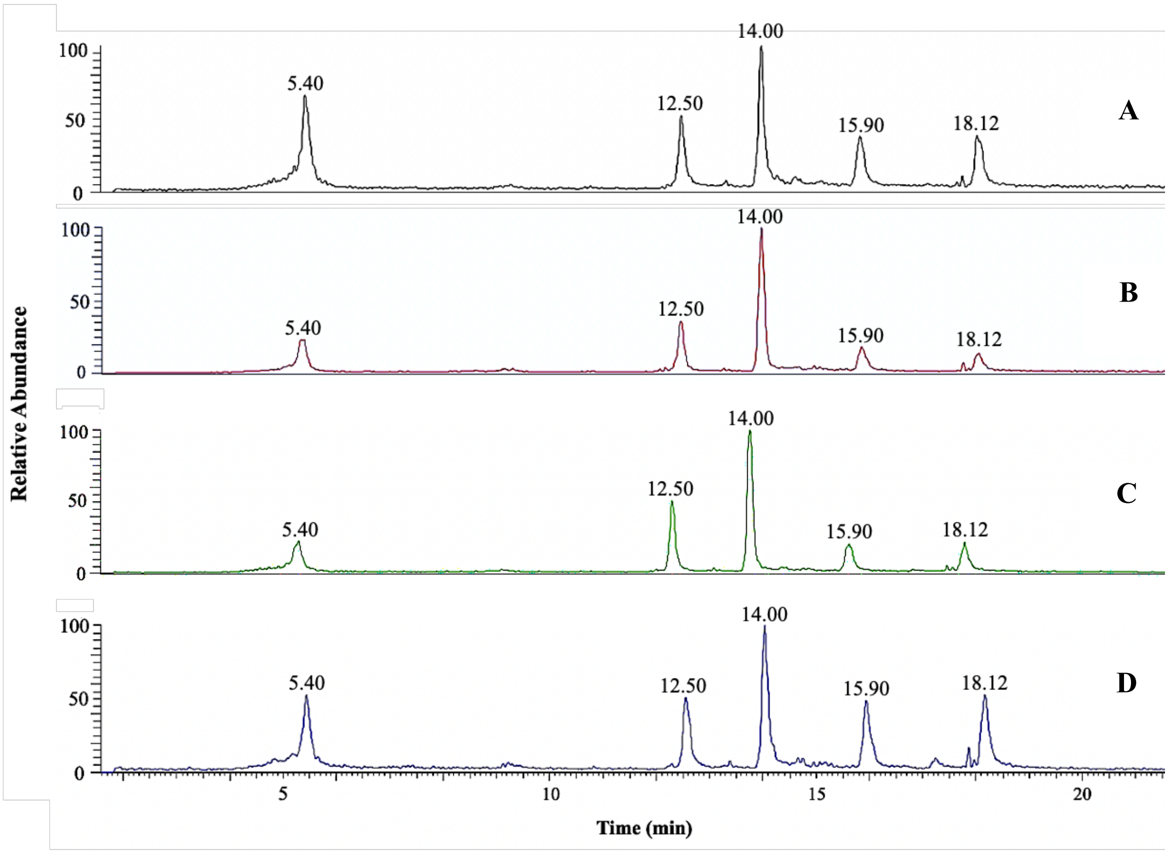


Figure 4.6. Accurate mass-extracted ion chromatograms (AM-XIC) (± 5 ppm) were obtained under negative polarity using APCI, with a 16 W mercury lamp for 24 h. The m/z values of the main signals are the following: m/z 121.030 (RT 5.40 min), 165.019 (RT 5.40 min), 357.062 (RT 12.50 min), 385.093 (RT 14.00 min), 549.109 (RT 15.90 min), and 605.177 (RT 18.12 min) from extracts of photo-oxidized PET particles. (A) Pure PET particles; (B) PET particles adsorbed on silica; (C) PET particles adsorbed on standard sand; (D) PET particles adsorbed on natural sand.

4.6 Role of oxygen

As oxygen is always present under environmental conditions, the influence of oxygen on the degradation process was also investigated. A comparative analysis of chromatograms obtained in the presence and absence of oxygen revealed some differences. However, from the literature, we expected the hydroxylation of the molecules released from the polymer structure. In the case of the compound with m/z 357.062, hydroxylation results in the formation of another compound containing one additional oxygen atom (Figure 4.7); this compound can be detected under negative polarity at m/z 373.057. The addition of an oxygen atom can occur in the following way:

- *Hydroxyl Group Addition*: A hydroxyl group (–OH) is introduced into one of the aromatic rings by replacing one of the hydrogen atoms. In Figure 4.7, the reaction between the compound with m/z 357.062 and a hydroxyl radical (•OH) leads to a product containing the –OH group at some position on the aromatic ring.

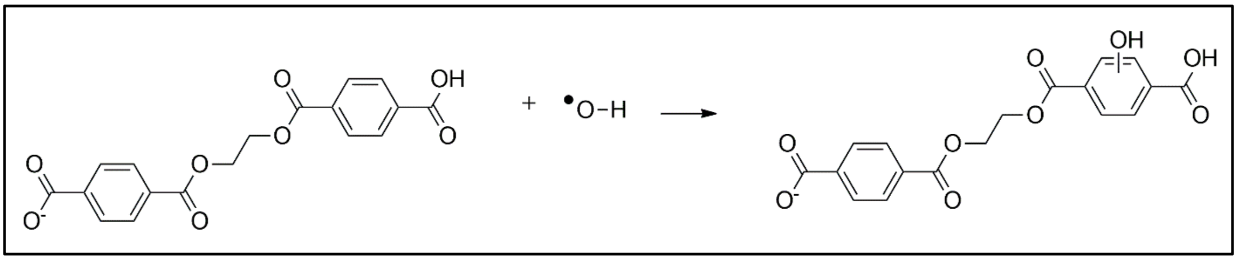


Figure 4.7. Reaction of a PET product with hydroxyl radicals (•OH). This figure illustrates a specific example of structural modification for the compound with m/z 357.062 after a reaction with hydroxyl radicals, resulting in aromatic rings containing carboxyl groups. A hydroxyl group (–OH) is added to one of the aromatic rings, replacing a hydrogen atom. The resulting compound is predicted to have an m/z value of 373.057 when analyzed under negative polarity.

The extraction of the exact m/z value of the hydroxylated product (m/z 373.057), as mentioned above, from profiles of extracts of irradiated PET particles under air (with oxygen) and nitrogen (without oxygen) atmospheres is presented in Figure 4.8. The observed signals reveal a strong increase when the irradiation is performed in the presence of oxygen, and therefore, the observed signals should correspond to hydroxylation products of the compounds observed at m/z 357.062. Moreover, more than one signal is observed, indicating the presence of isomers. Therefore, more than one compound is being formed. This suggests that hydroxylation can occur at different sites on the molecule, specifically at the benzene moiety or the ethyl moiety. Generally, oxygen availability enhanced the yields of primary degradation products. The generation of PET's hydroxylated derivatives can also be attributed to hydroperoxide formation, which is also linked to the presence of oxygen (Jamalzadeh & Sobkowicz, 2022).

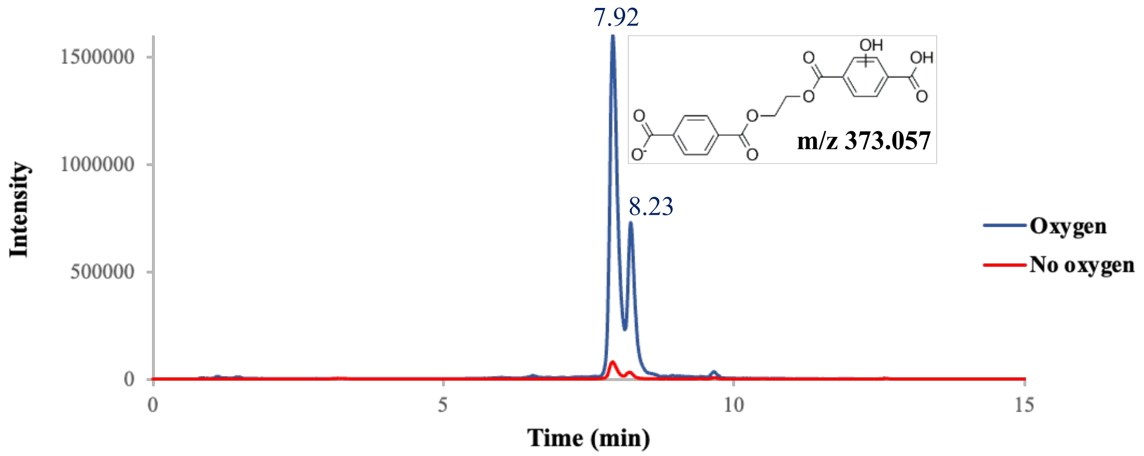


Figure 4.8. Accurate mass-extracted ion chromatograms (AM-XIC) (± 5 ppm) taken at m/z 373.057 of MeOH extracts of irradiated PET. The blue profile was obtained in the air atmosphere (presence of oxygen). The red profile corresponds to a nitrogen atmosphere (absence of oxygen).

4.7 Irradiation of PE

Compared to polyethylene terephthalate (PET), polyethylene (PE) exhibits remarkable stability under photoirradiation. This distinction arises from the structural differences between these polymers. While PET can absorb solar radiation at ground level (wavelengths above 290 nm), PE does not possess this capability, making it inherently photostable (Fechine *et al.*, 2002; Jiao *et al.*, 2022; Zaki *et al.*, 2013). However, when subjected to irradiation under a 150 W xenon lamp for 48 hours, signals of dicarboxylic acids can be observed (Figure 4.9). Dicarboxylic acids were also detected after thermal degradation.

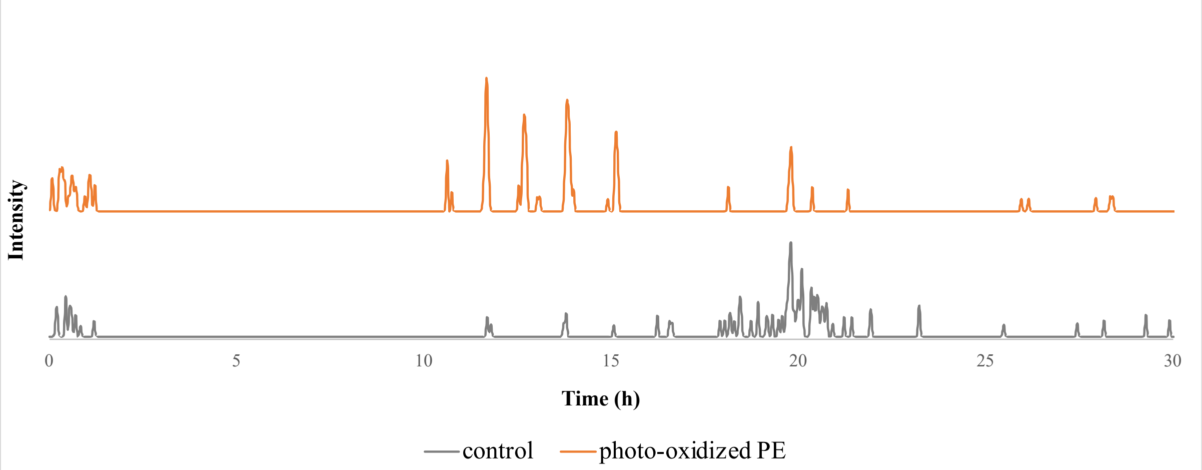


Figure 4.9. Accurate mass-extracted ion chromatogram (AM-XIC) (± 5 ppm) of dicarboxylic acids $HO_2C{-}(CH_2)_n{-}CO_2^-$, n = 14 to 17, obtained after PE photooxidation, under negative polarity using ESI, with a 150 W xenon lamp for 48 h. The orange profile corresponds to photo-oxidized PE on silica surface (10 mg/g). The grey profile corresponds to the control.

The generation of dicarboxylic acids, which act as markers for the degradation of PE, results from reactions at two distinct locations along the polymer chain: initial oxygen interactions followed by the cleavage of hydroperoxides (Costa *et al.*, 2024). The hydroperoxides can further react to form dicarboxylic acids (Figure 4.10). The process was reported under photoreaction and also under thermal degradation. Under the latter process, a set of dicarboxylic acids was reported to be formed from PE particles (Table 4.2). The results suggest that the same products are formed after photooxidation and thermal oxidation of PE.

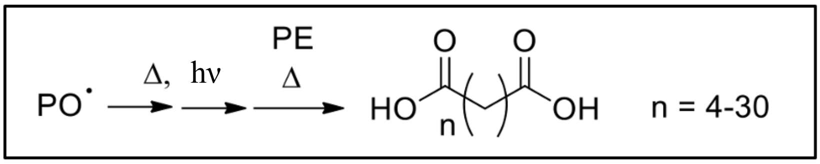


Figure 4.10. Reaction scheme of PE on surfaces. Adapted from Costa *et al.* (2024).

Table 4.2. Identified or annotated degradation compounds of Polyethylene (PE) during thermal/photochemical degradation.

RT (min)	Compound	Formula	m/z (polarity)	Annotation/ Identification
1.85	Adipic acid	$C_6H_{10}O_4$	145.051 (-)	Chemspider
6.87	Suberic acid	$C_8H_{14}O_4$	173.082 (-)	Identification
10.60	Sebacic acid	$C_{10}H_{18}O_4$	201.114 (-)	Identification
11.88	Undecanedioic acid	$C_{11}H_{20}O_4$	215.129 (-)	Chemspider
13.17	Dodecanedioic acid	$C_{12}H_{22}O_4$	229.145 (-)	Identification
14.49	Tridecanedioic acid	$C_{13}H_{24}O_4$	243.161 (-)	Identification
17.07	Pentadecanedioic acid	$C_{15}H_{28}O_4$	271.192 (-)	Chemspider
18.25	Hexadecanedioic acid	$C_{16}H_{30}O_4$	285.208 (-)	Identification
19.28	Heptadecanedioic acid	$C_{17}H_{32}O_4$	299.223 (-)	MS Data
19.57	2-Hydroxymyristic acid	$C_{14}H_{28}O_3$	243.197 (-)	mzCloud, match 99.4%
20.22	Octadecanedioic acid	$C_{18}H_{34}O_4$	313.239 (-)	MS Data
21.03	Nonadecanedioic acid	$C_{19}H_{36}O_4$	327.254 (-)	MS Data
21.55	16-Hydroxyhexadecanoic acid	$C_{16}H_{32}O_3$	271.228 (-)	mzCloud, match 87.7%

21.74	Eicosanedioic acid	$C_{20}H_{38}O_4$	341.270 (-)	MS Data
22.35	Heneicosanedioic acid	$C_{21}H_{40}O_4$	355.286 (-)	MS Data
22.90	Docosanedioic acid	$C_{22}H_{42}O_4$	369.302 (-)	MS Data
23.37	Tricosanedioic acid	$C_{23}H_{44}O_4$	383.317 (-)	MS Data
24.20	Pentacosanedioic acid	$C_{25}H_{48}O_4$	411.349 (-)	MS Data
25.96	Heptacosanedioic acid	$C_{27}H_{52}O_4$	439.380 (-)	MS Data
25.31	Octacosanedioic acid	$C_{28}H_{54}O_4$	453.396 (-)	MS Data
25.63	Nonacosanedioic acid	$C_{29}H_{56}O_4$	467.412 (-)	MS Data
25.97	Triacontanedioic acid	$C_{30}H_{58}O_4$	481.427 (-)	MS Data
26.40	Hentriacontanedioic acid	$C_{31}H_{60}O_4$	495.442 (-)	MS Data
26.75	Dotriacontanedioic acid	$C_{32}H_{62}O_4$	509.458 (-)	MS Data

5 Conclusion and Future Research Directions

This study provides an important contribution in the knowledge about the degradation products of two important used polymers namely polyethylene terephthalate (PET) and polyethylene (PE). The liquid chromatography high-resolution mass spectrometry (LC-HRMS) analysis provided with photo and thermal degradation enables to find many of the described breakdown products. Key findings revealed the characteristic markers released by the PET polymer: benzoic acid (m/z 121.030), terephthalic acid (m/z 165.019), and 4-((2-((4-carboxybenzoyl)oxy)ethoxy)carbonyl)benzoate (m/z 357.062) which can be utilized in microplastic and nanoplastic detection in environmental samples. The findings suggest that PET undergoes more extensive degradation under irradiation, the result is a wide range of smaller molecules, many of which pose potential environmental threats as contaminants. These products were formed across the studied surfaces indicating little surface effect.

On the other side, PE was more resistant towards photodegradation. The products detected were dicarboxylic acids that can only be detected under high-power irradiation conditions. The thermal degradation of PE also produces these degradation products that were seen during photodegradation. While PE photodegradation is slower and less extensive, its persistence in the environment allows it to function as a sink for other pollutants due to its adsorptive properties, resulting in distinct environmental challenges. The difference in photodegradation of PET and PE has significant consequences on the environment in the long run.

In particular, whereas the immediate risk posed by PET relates to numerous coastal degradation products that can be harmful, it is evident that PE will cause chronic problems because of its slow rate of degradation. It seems therefore that these two polymers contribute to environmental pollution in many ways. In addition, the above studies ought to focus on other plastic polymers in order to investigate their possible toxic effects.

Further research is necessary to develop mitigation strategies aimed at reducing the environmental footprint of these plastics, with particular focus on their degradation products and interactions with pollutants in different environments. As millions of microplastics and nanoplastics can be generated from a single macroplastic piece, the removal of macroplastics from coastal areas is the most direct way to prevent increased contamination by microplastics. It is important to note that while macroplastics can be effectively removed from coastal areas, the presence of microplastics and nanoplastics is far more challenging to address and is often practically irreversible (MacLeod *et al.*, 2021).

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Note: DeepL Translator (https://www.deepl.com/en/translator) was used to assist with translations.

Appendixes

Appendix A: Overview of Cryogenic Milling Equipment.

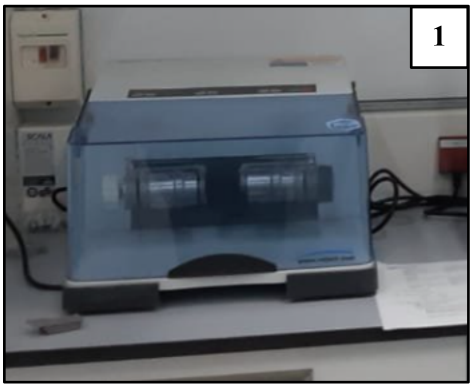

Figure A1. The Cryo-MM400, a cryogenic mill designed for efficient sample preparation, operates at low temperatures to minimize the thermal degradation of sensitive materials.

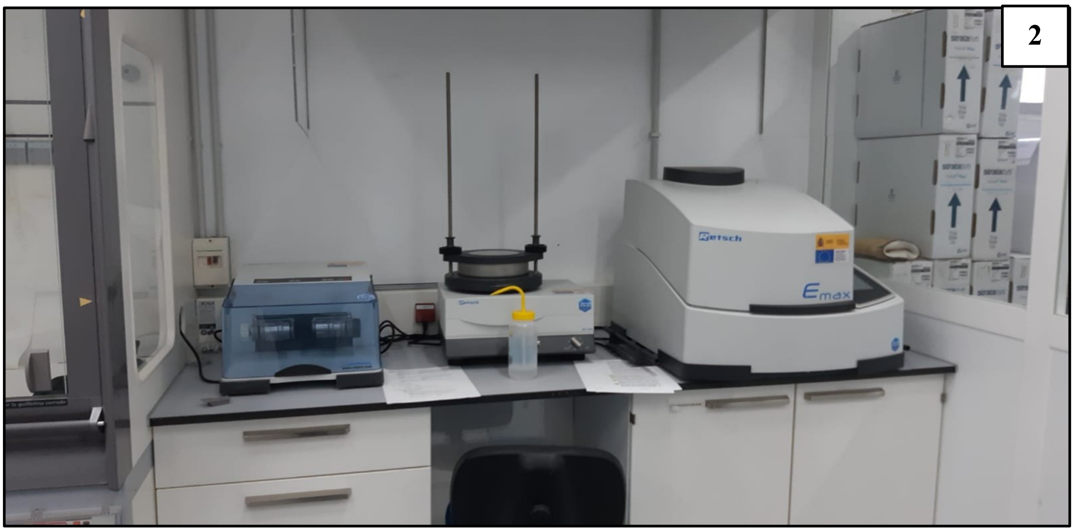

Figure A2. Cryogenic sample grinding setup, detailing the components and arrangement of the equipment used to achieve optimal grinding conditions for various samples.

Appendix B: Examples of Released Products Detected Through LC-HRMS Analysis.

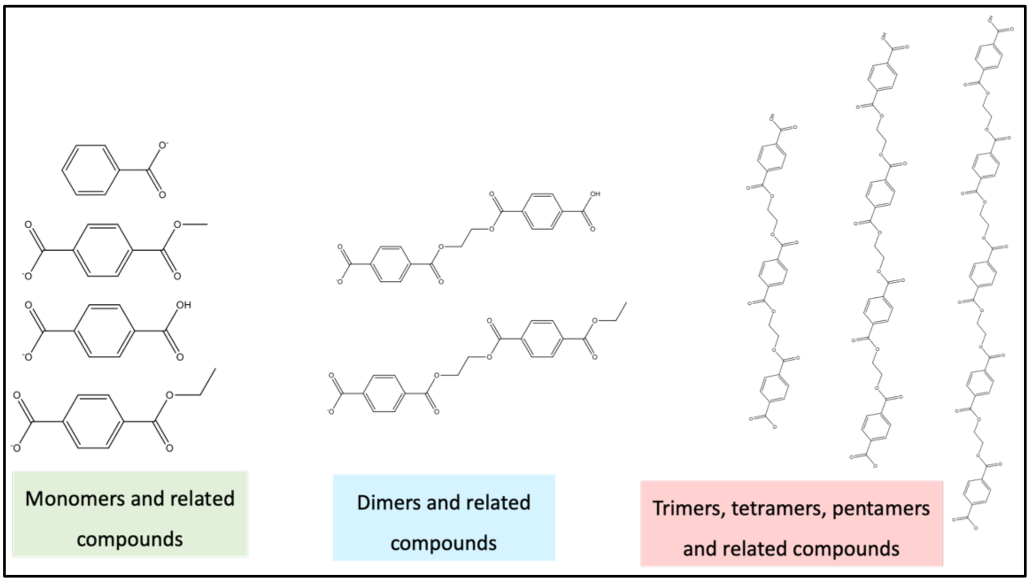

Figure B1. PET photodegradation products identified during the analysis, including low molecular weight compounds, dimers, oligomers, and related structures. The detected products highlight the structural diversity and potential environmental impact of these degradation products.

Appendix C: Abstract related to a short talk presented at a national Chromatography conference held at the Faculty of Pharmacy, University of Lisbon.

13° ENCONTRO NACIONAL DE CROMATOGRAFIA
17-19 DE DEZEMBRO DE 2023
FFUL - LISBOA

Identification of Polyethylene terephthalate (PET) photodegradation products by LC-MS

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A good chromatographic separation of unknown compounds is always a challenge. The need of mass spectrometry for identification also requires compatibility between the mobile phase and the ion source. Electrospray ionization (ESI) is commonly used with liquid chromatography (LC) because it works well with polar and aqueous mobile phases[1]. Atmospheric pressure chemical ionization (APCI) is also used with LC but for less polar compounds[2].

In this work, we evaluate combinations of two mobile phases, water/methanol, and water/acetonitrile, and two ion sources, ESI and APCI, to study the products released from PET after photoreaction. The study was performed under both positive and negative polarities.

The obtained products were annotated using Compounds Discoverer 3.3 and some were identified after injection of standards. The negative polarity gave more information than the positive polarity, which is related to the presence of carboxylic moiety in the structure of compounds. However, the positive polarity is complimentary as different products were detected. Acetonitrile strongly decreases the signals observed under APCI when compared with ESI. However, the use of methanol instead of acetonitrile improves the APCI signals but changes the retention times. As some compounds are more readily detected under APCI than ESI and *vice-versa*, the identification of unknowns should be made using the two ionization types.

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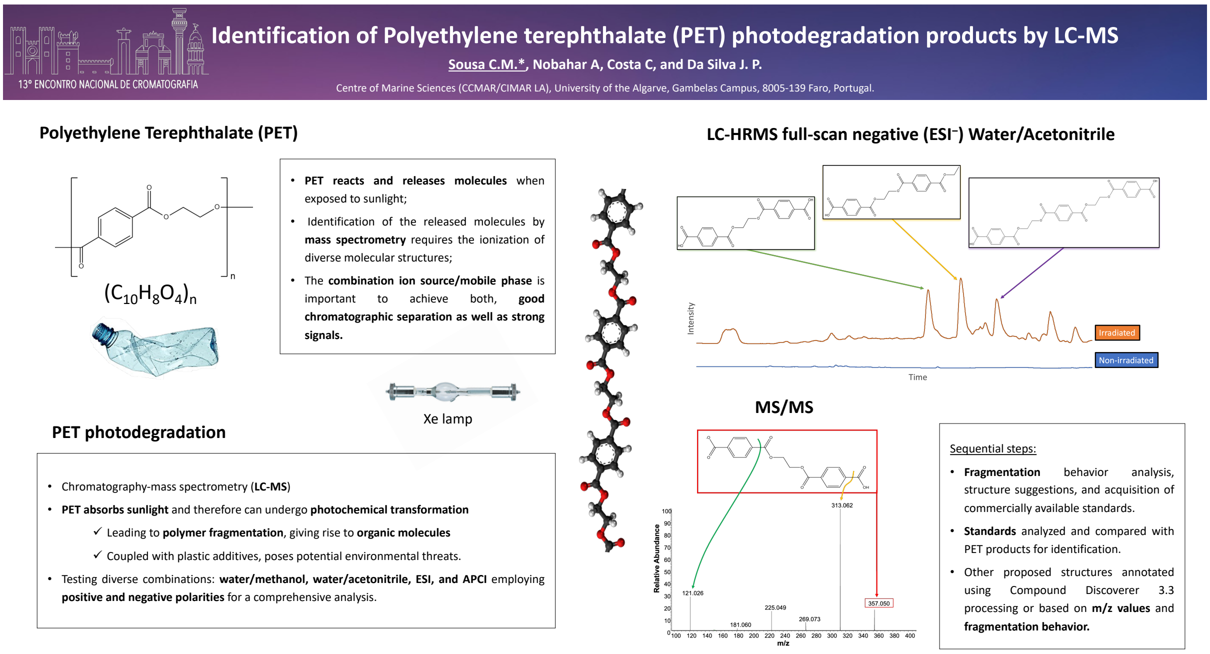
2. Thomas, S. N; French, D; Jannetto, P. J; Rappold, B. A; Clarke, W. A. Nature Reviews Methods Primers (**2022**). 2(1), 96.

Appendix D: Poster related to a short talk presented at a national Chromatography conference held at the Faculty of Pharmacy, University of Lisbon.



13° ENCONTRO NACIONAL DE CROMATOGRAFIA

Identification of Polyethylene terephthalate (PET) photodegradation products by LC-MS

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Polyethylene Terephthalate (PET)

$(C_{10}H_8O_4)_n$

- **PET reacts and releases molecules** when exposed to sunlight;
- Identification of the released molecules by **mass spectrometry** requires the ionization of diverse molecular structures;
- The **combination ion source/mobile phase** is important to achieve both, **good chromatographic separation as well as strong signals.**

Xe lamp

PET photodegradation

- Chromatography-mass spectrometry (**LC-MS**)
- **PET absorbs sunlight** and therefore can undergo **photochemical transformation**
    - ✓ Leading to **polymer fragmentation**, giving rise to **organic molecules**
    - ✓ Coupled with plastic additives, poses potential environmental threats.
- Testing diverse combinations: **water/methanol, water/acetonitrile, ESI, and APCI** employing **positive and negative polarities** for a comprehensive analysis.

LC-HRMS full-scan negative (ESI⁻) Water/Acetonitrile

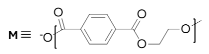
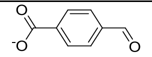
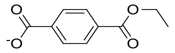
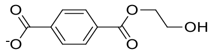
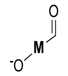
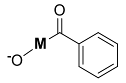
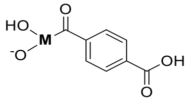
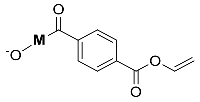
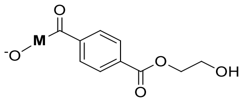
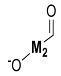
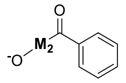
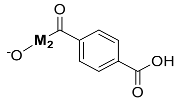
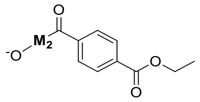
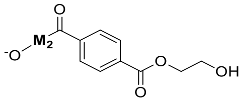
MS/MS

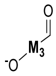
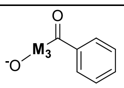
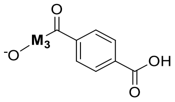
Sequential steps:

- **Fragmentation** behavior analysis, structure suggestions, and acquisition of commercially available standards.
- **Standards** analyzed and compared with PET products for identification.
- Other proposed structures annotated using Compound Discoverer 3.3 processing or based on **m/z values** and **fragmentation behavior.**

Appendix E: Expected compounds containing a benzoic acid moiety of PET particles.

Table E1. Expected photo-products containing a benzoic acid moiety.

RT (min)	**m/z**	**Formula**	**MS/MS (CID)**	**Structure** 
2.10	149.024 (-)	$C_8H_6O_3$	121, 105	
6.84	193.051 (-)	$C_{10}H_{10}O_4$	121, 149	
1.64	209.046 (-)	$C_{10}H_{10}O_5$	121, 165	
4.55	237.040 (-)	$C_{11}H_{10}O_6$	209, 193, 165, 121 209, 193, 179, 165, 121	
7.87 9.38	313.072 (-)	$C_{17}H_{14}O_6$	269, 165, 121 269, 165, 121	
7.92 8.23	373.057 (-)	$C_{18}H_{14}O_9$	329, 311, 285, 165, 163, 121, 119 329, 285, 207, 165, 121	
8.88	383.077 (-)	$C_{20}H_{16}O_8$	339, 295, 225, 181, 165, 121	
6.70 7.83 9.30	401.088 (-)	$C_{20}H_{18}O_9$	383, 357, 313, 235, 225, 181, 165, 121 357, 313, 265, 225, 121 357, 313, 235, 165, 163, 121	
9.37	429.083 (-)	$C_{21}H_{18}O_{10}$	401, 357, 179	
11.50	505.114 (-)	$C_{27}H_{22}O_{10}$	461, 417, 383, 357, 313, 225	
10.06	549.104 (-)	$C_{28}H_{22}O_{12}$	505, 417, 383, 357, 313, 165	
10.84, 12.29	577.135 (-)	$C_{30}H_{26}O_{12}$	533, 519, 505, 471, 411, 385, 357, 165 549, 509, 489, 383, 385, 357, 165	
10.07	593.130 (-)	$C_{30}H_{26}O_{13}$	549, 505, 383, 357, 209	

11.23	621.125 (-)	$C_{31}H_{26}O_{14}$	563, 533, 237, 179	
13.18	697.156 (-)	$C_{37}H_{30}O_{14}$	575, 549, 341, 313, 225	
11.45	741.146 (-)	$C_{38}H_{30}O_{16}$	575, 549, 357, 313, 225	
12.77	933.188 (-)	$C_{48}H_{38}O_{20}$	767, 741, 549, 401, 357, 313