GC/MS-Orbitrap: an application for the characterization of organic plastic additives

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FATE AND IMPACTS OF MICROPLASTICS: KNOWLEDGE AND RESPONSIBILITIES

*Given the current uncertainty about the COVID-19 pandemic for this coming November 2020, our biannual international conference will be held during the originally planned dates 23-27 Nov. 2020. It will be substantially online-based with several in-person meeting nodes.

Introduction

- The analysis of organic plastic additives (OPAs) has shown a growing importance since the use of some of them has become controversial. In order to have a better understanding of their chemical toxicity, it is important to identify and, ideally quantify the OPAs included in plastic polymers.
- This is an analytical challenge due to the diversity of molecules, the complexity of polymeric matrices, and the fastidious sample preparation using traditional analysis technique, such as solvent extraction, which can bring biases. In order to integrate these biases and simplify the analysis approach, pyrolysis coupled to a gas chromatography mass spectrometer (Py-GC/MS) can be used.

Aim & Objective

- So far, a **common method in GC/MS-Orbitrap has been developed for the analysis of various plastic additives**.
- An additive **database** has been built.
- The final goal is to apply this method with **Py-GC/MS** for the **identification of the OPAs** in polymeric samples.

Steps & Methods

Additives selection

- Based on their use and toxicity (bibliography, ECHA list (2019), EFSA list (2020))
- 64 molecules candidates

Function (number of molecules)	Details
Plasticizers (24)	Phthalates (20)
	Adipate (2)
	Others (2)
Plasticizers/Antioxidants (6)	Nonylphenols (6)
	Bisphenol A
Antioxidants (6)	Irganox (3)
	Others (3)
UVs stabilizer (5)	Phenols (5)
Flames retardants (21)	Phosphorous (7)
	Phosphates (3)
	Phenols & PBDE (10)
	Citrate (1)
Monomers-intermediates (2)	BPS & BPF

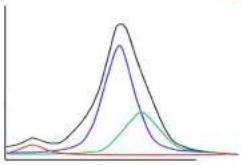
GC/MS Orbitrap analysis with a single method

- Preparation of stock solutions (from 0.05 to 100µg/mL)
- Liquid injection for GC/MS analysis

Analysis parameters	
Instrument	GC/MS-Orbitrap – TRACE 1300 - DB-5 like column
Injection T°	300°C
Oven program	80°C (0.5 min) → 10°C/min → 330°C (1 min)
Transfer line T°	300°C
Ion source T°	300°C
Scan ranges	33-750 m/z
Injection volume	1 µL
Injected [C]	0.32 µg/mL to 5 µg/mL
Cut-Off	5 min

Creation of our own library

- Deconvolution (TraceFinder software)
- Selection of quantitative and qualitative ions

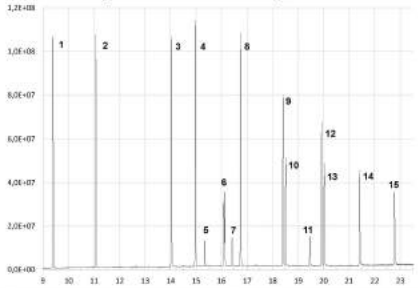


Results

Identification of OPAs

Phthalates

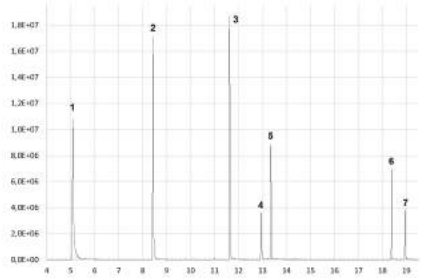
1 µg/mL – split 15



N° Pic	Molecules	N° Pic	Molecules
1	Dimethyl phthalate (DMP)	9	Di-n-hexyl phthalate (DHP)
2	Diethyl phthalate (DEP)	10	Benzyl butyl phthalate (BBP)
3	Diisobutyl phthalate (DIBP)	11	Bis(2-n-butoxyethyl) phthalate (DBEP)
4	Di-n-butyl phthalate (DBP)		
5	Bis(2-methoxyethyl) phthalate (DMEP)	12	Dicylcohexyl phthalate (DCP)
6	Bis(4-methyl-2-pentyl) phthalate (*DMPP isomers*)	13	Bis(2-Ethylhexyl)phthalate (DEHP)
7	Bis(2-Ethoxyethyl) phthalate (DEEP)	14	Di-n-octyl phthalate (DIOP)
8	Dipentyl phthalate (DPP)	15	Di-nonyl phthalate (DNP)

Phosphorous Flames retardants

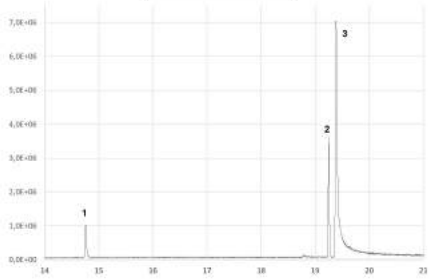
0.32 µg/mL – split 5



N° Pic	Molecules
1	Triethyl phosphate (TEP)
2	Tripropyl phosphate (TPP)
3	Tributyl phosphate (TBP)
4	Tris(2-chloroethyl)phosphate (TCEP)
5	Tris(2-chloro-iso-propyl)phosphate (TCPP)
6	Tris(1,3-dichloro)phosphate (TCP)
7	Triphenylphosphate (TPhP)

Antioxidants – Irganox®

0.64 µg/mL – split 5



N° Pic	Molecules
1	Irganox 1010
2	Irganox 1076
3	Irganox 1081

Conclusion

- A **single method** in **GC/MS-Orbitrap** showed its performance to analyze multiple additives used for plastic production. A **high resolution** mass spectra **database** of about **sixty additives** was created and provide help to characterize the chemical compounds contained included in plastic.
- GC/MS-Orbitrap coupled with pyrolysis was successfully used to identify several phthalates with the same method directly from plastic samples. These preliminary result are promising for the ability of Py-GC/MS to analyze plastic additives with simple sample preparation.

Further work

- A method using GC/MS-Orbitrap coupled with pyrolysis is under development and will be widely applied to identify the main plastic additives.
- Quantitative development should also be implemented.

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