

Pyro-GC-MS as a strong analytical tool for the identification and quantification of remaining (non-) intentionally added substances in polymer waste

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Introduction

Plastics are an important element in our everyday life, and the prospective is that plastic demand will still grow for future years to come. To allow this, and to lower the impact of plastics on the environment, the European Union has increased its plastic recycling targets (Ragonnaud, 2023). However, nowadays, there is not enough 'clean plastic waste' (e.g. post-industrial waste) to allow recycling to high quality products. Important issues of conventional mechanical recycling plants are remaining odour, colour and additives, therefore leading to downcycling of the 'dirty plastic waste' (e.g. post-consumer waste) (Horodytska et al., 2018). Hence, to assure compliance with these recycling targets, innovative recycling technologies are needed. Moreover, classic analytical techniques such as GC-MS are not able to measure high molecular weight additives, such as brominated flame retardants often used in polystyrene waste. Next to flame retardants, this will also be important to identify treatment technologies that could be used to recycle plastics to food contact material grade. For example, as opposed to PET, polyolefins have a lower polarity, therefore allowing higher molecular weight compounds up to 800 g/mol (Palkopoulou et al., 2016). Although this is currently not included in the EFSA challenge test, future updates should include these high molecular weight compounds to assure health safety. In the 10th meeting of the EFSA network on the cooperation and harmonisation of risk assessment of food contact materials in October 2023, it was stated that currently only a very limited number of substances is focused on in the challenge test, and that novel analytical approaches should be considered in the future (Briggs, 2023). Consequently, there is an urgent need for an analytical technique that allows for a quantitative analysis of additives remaining on plastics.

A promising technique that allows for the identification and quantification of these compounds is pyrolysis gas chromatography mass spectrometry (pyro-GC-MS). Using this technique, high molecular weight compounds are fragmented into lower molecular weight compounds, which can be analysed using GC-MS. Interestingly, the fragmentation pattern of these compounds acts as a fingerprint for the molecule under investigation. Therefore, this technique shows a high potential for the analysis of remaining (non-) intentionally added substances after sorting and pre-treatment. In addition to additives, this technique can also be used to assess the polymer itself. The challenge, however, is that there are currently no commercial libraries available that allow for the identification of these fragmentation patterns. Therefore, the goal of this research is to start creating know-how on the fragmentation pattern of often used additives and polymers. As a starting point, two case-studies are presented. The first case focuses on the identification and quantification of often used brominated flame retardants in polystyrene waste. The second case focuses on the identification and quantification of polyvinyl chloride (PVC) and plasticizers.

Results and discussion

Regarding the flame retardants, a thorough literature review revealed four important ones: hexabromocyclododecane (HBCD), FR-122P, tetrabromobisphenol A (TBBPA) and triphenyl phosphate (TPHP). To set the initial pyrolysis temperature, thermogravimetric analyses (TGA) were performed (table 1). For HBCD, mass loss was found in two stages: about 93% of the total mass was lost at about 250°C, and the remaining mass at about 480°C. FR-122P showed mass loss over three stages: 60% mass loss at 250°C, 7% mass loss at 330°C, and 22% at 480°C. For TBBPA, one main peak was found at about 350°C, corresponding to 75% of the total weight. The remaining TBBPA was then gradually lost when increasing temperature. TPHP revealed one main peak at 350°C, comprising 99% mass loss. Overall, based on the TGA results, it was decided to use 370°C as pyrolysis temperature for all flame retardants. This temperature should allow to see fragmentation products of the flame retardants but still avoid interference of polystyrene.

Table 1: Main mass losses observed in TGA for flame retardants

	Stage 1		Stage 2		Stage 3	
	T (°C)	Mass loss (%)	T (°C)	Mass loss (%)	T (°C)	Mass loss (%)
HBCD	250	93	480	7		
FR-122P	250	60	330	7	480	22
TBBPA	350	75				
TPHP	350	99				

Pyro-GC-MS of TBBPA and TPHP indicated that both compounds were not degraded and could be measured and identified by the NIST 2020 library. HBCD and FR-122P were degraded but both brominated compounds could be quantified by using the H-Br peak observed at a retention time of 1.5 minutes. Interestingly, both compounds had differences in their fragmentation pattern, therefore allowing identification of both of them when being present in an unknown sample. Calibration curves ranging from 130 mg/kg – 2500 mg/kg yielded R² values larger than 0.91. The final method was validated by analyzing two waste samples made from extruded polystyrene (XPS) obtained from a company. The first sample comprised an old XPS foam from construction which should still contain HBCD, while the second sample comprised recent XPS insulation boards which should contain FR-122P. Both samples were analyzed with the newly developed method. Based on the fragmentation pattern, the flame retardant in the first sample was identified as HBCD. Using the calibration curve, concentrations of 2.85±0.9 wt% were obtained. The flame retardant in the second sample was identified as FR-122P, with a concentration of 0.85±0.15 wt%. These results confirm that the developed method is able to identify and quantify different flame retardants in real waste samples. This method can now be used for screening purposes to test whether companies comply to the strict regulations regarding flame retardants, but also for recycling companies to verify input and output materials. Concerning the latter, as a next step, this method will be used to identify and quantify polystyrene samples obtained from waste from electrical and electronic equipment (WEEE).

Regarding PVC, relatively pure samples with only di(2-ethylhexyl)phthalate (DEHP) as plasticizer were assessed. Extraction of DEHP was done using different solvents. DEHP could be identified and quantified using both standard liquid injection GC-MS and pyro-GC-MS. However, to close the mass balance, both the amount of PVC had to be determined as well as other additives which are often added in small amounts. For this, a pure PVC sample was directly analyzed using pyro-GC-MS. Pyrolysis temperature was set at 400°C as TGA analysis revealed a 70% mass loss at 260°C (related to HCl). Quite similar to the brominated flame retardants, a H-Cl peak was observed at a retention time of 1.8 minutes. A calibration curve ranging from 0.06 to 0.18 mg PVC yielded a R² value of 0.989. Using the calibration curve, PVC samples containing DEHP were analyzed. The results indicated that 55.6±0.1 wt% consisted of PVC and 26.3±1.8 wt% of DEHP. When closing the mass balance, 18% is still not accounted for. This can be explained by the presence of stabilizers which can hinder HCl losses (Jiménez et al., 1997), and the presence of other additives such as triphenyl phosphate and stearic acid, which were identified as well (although not yet quantified). Given the strict regulations regarding plasticizers in PVC, these results show that pyro-GC-MS is a promising technique to identify and quantify them, making it a useful and easy technique (in terms of lack of sample preparation) to assess compliance.

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