Quantitative analysis of microplastics in bottled drinks

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Introduction

There is a growing concern that the accumulation of microplastics in the environment could have an adverse effect on human health, so identifying and quantifying them is important. Microplastics are particles or polymeric fibres equal to or smaller than 5 mm and originate from sources such as plastic bottles, food packaging, toys and clothing.

Image source: https://www.conserve-energy-future.com/ongoing-plastic-invasion-across-deep-oceans-includes-food-chain.php

Microplastics can be found in many different types of environmental samples, so techniques to measure samples should:

- Be applicable to many sample types, *e.g.*, water, air, soil, sediment and biota
- Be capable of analysing a broad range of plastics and additives
- Require minimal sample preparation
- Produce quantitative results with ease, preferably providing concentration data.

Many current analytical methods rely on imaging techniques, such as FTIR or Raman microscopy, to identify the polymer type. However, they require lengthy sample preparation processes, are limited to particles >10 µm and do not provide information on concentration.

Here, we describe the use of direct thermal desorption (TD) of filtrates coupled to gas-chromatography mass spectrometry (GC–MS) to analyse microplastic samples, providing simultaneous polymer identification and quantitative results in a simple, time-efficient workflow.

This poster details the analysis of bottled beverages to measure the leaching of polyethylene terephthalate (PET) from the plastic bottle into the beverage.

Direct desorption TD–GC–MS workflow

Sample preparation

A beverage sample, such as bottled water, was filtered through a 0.2 µm quartz fibre filter (Figure 1). The filter was then washed with reagents to completely remove all organic matter, leaving only microplastics.

The filter was dried in an oven for 30 minutes, then the whole filter (or a section of it) was folded and placed inside an empty TD tube. The tube was then loaded into a TD100-xr™ automated thermal desorber coupled to a GC–MS for analysis. This sample preparation process is straightforward, typically takes <1 hour and can be applied to filters used for a wide range of sample types.

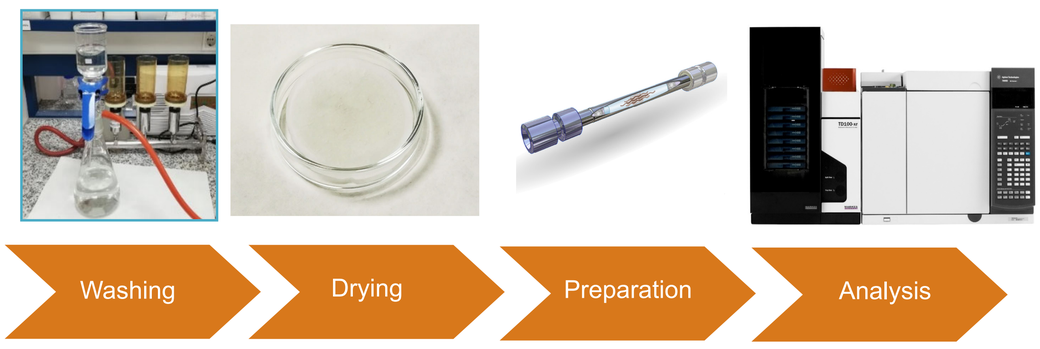

Figure 1: Sample preparation and analysis stages for the bottled beverage study.

Thermal desorption GC–MS

With Markes' thermal desorption instruments, there are two stages (Figure 2). First, the sample tube is heated to enable volatile organic compounds (VOCs) to be emitted. A carrier gas sweeps the VOCs to an electrically-cooled focusing trap, where the compounds are concentrated – this maximises the sensitivity to enable the detection of low levels of target compounds.

At the second stage, the focusing trap is heated rapidly in a reverse flow of carrier gas – known as backflushing – to transfer the VOCs to the GC column in a narrow band of vapour for separation and detection. Backflushing enables a wide range of compounds to be analysed in a single run, which is essential for environmental samples in which the compounds are unknown.

This technique is well established for direct desorption of materials and combines sample preparation, desorption, preconcentration and GC injection into a single automated process.

Split flows can be applied at both stages of desorption to improve the desorption efficiency and manage wide concentration ranges. Also, re-collection of a split flow onto a clean sorbent tube allows a portion of the sample to be archived for re-analysis, saving time spent re-preparing the filters and avoiding the need to store large volumes of liquid samples.

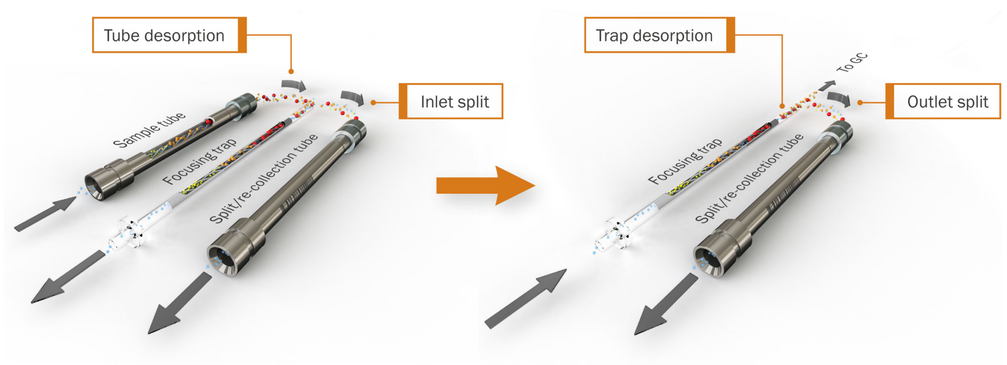

Figure 2: Two-stage thermal desorption and split flows.

TD coupled with GC–MS enables the identification of the polymer using a 'fingerprint' chemical pattern and quantitative results for the mass of each polymer – so a concentration can be provided in µg/L.

TD–GC–MS also facilitates identification of other compounds present in samples such as additives or unique compounds that may be used for source profiling and toxicity calculations.

Results and discussion

Marker identification and quantification

Powdered plastic standards were weighed onto filters and analysed by TD–GC–MS to identify marker compounds that could then be used to identify and quantify each microplastic. For PET, 2,4-di-*tert*-butylphenol (DTBP) was used as the quantitation marker and tetrahydrofuran (THF) was used as the confirmation marker. Both compounds must be present to confirm the presence of PET.

A calibration of mass of PET against DTBP peak area was used for quantitation and shows excellent linearity (Figure 3).

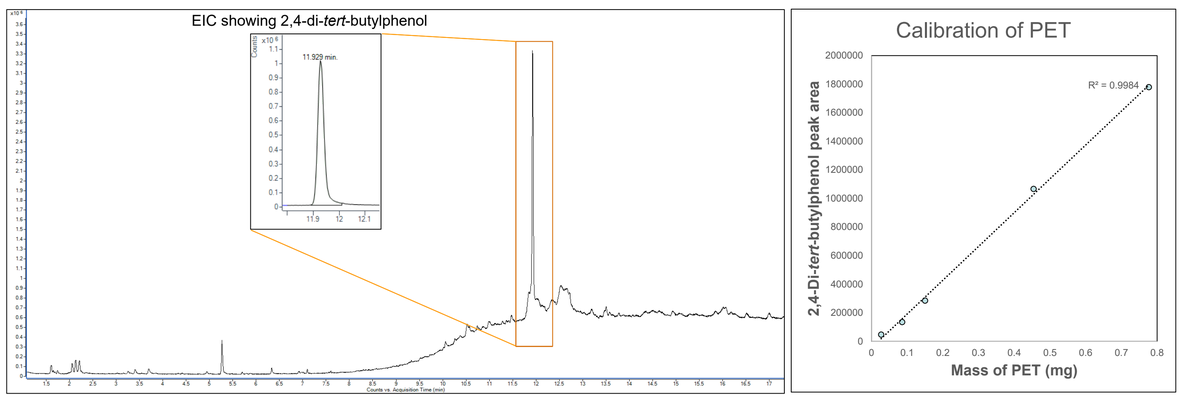

Figure 3: Total ion chromatogram (TIC) of a PET standard.

Recovery validation

To test the recovery obtained with the method, a 2 L volume of verified microplastic-free water was spiked with a known amount of PET and shaken vigorously. This was then subjected to the full sample washing and preparation method and analysis by TD–GC–MS. The results confirmed the presence of PET with DTBP and THF and showed >90% recovery, validating the analytical process.

PET levels in bottled drinks

Two brands of still water, one carbonated water and a cola were chosen at random to determine the levels of PET present. One still water sample (Brand A) contained both marker compounds (Figure 4) and the concentration of PET was quantified as 46 µg/L (Table 1).

With a different brand of still water (Brand B), no DTBP was detected, indicating that bottles from different manufacturers may leach differently. This also demonstrates the lack of plastic contamination in the full analytical workflow, ensuring no false positives. Carbonated water and cola also gave positive results for PET.

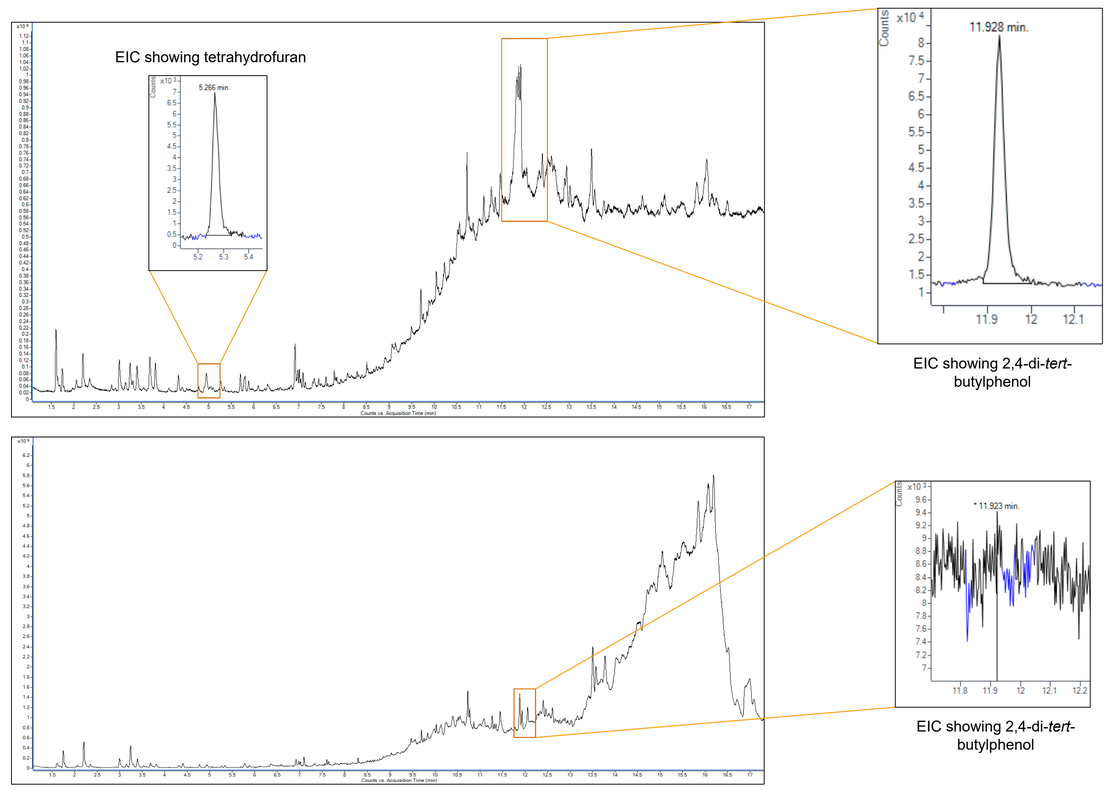

Figure 4: TICs showing the direct desorption of filtrate from bottled water. Brand A (above) shows a positive result for PET with the detection of DTPB and THF, whereas Brand B (below) shows no detectable levels of PET.

Sample type	Calculated concentration (ug/L)
Bottled water Brand A (still)	46.6
Bottled water Brand B (still)	n.d.
Bottled water (carbonated)	24.8
Cola	22.1

Table 1: Concentration of PET in four bottled drinks.

The initial data presented in this study indicates that people may be exposed to microplastics such as PET as a result of drinking beverages from plastic bottles. The origin of the PET is as yet unclear and may be the result of leaching from the bottle walls or residues left in the bottle as a result of the manufacturing process. Further work will explore this in more detail and could investigate the correlation between storage duration and temperature on PET levels.

Conclusions

- This study presents initial results for the analysis of microplastics using direct desorption TD–GC–MS with straightforward sample preparation steps that require minimal sample handling and are applicable to a range of sample types.
- TD–GC–MS enables the confident identification of marker compounds for automated concentration calculations and also facilitates identification of other compounds present in samples, such as additives and stabilisers used in the manufacturing process, that may be used for source profiling and toxicity calculations.
- TD facilitates split flow at two stages, enabling re-collection of samples for archiving and future re-analysis with alternative method conditions.

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