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Sampling and analysis of emerging pollutants

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Hot topics and emerging contaminants for air monitoring

Microplastics

Formaldehyde

Particulate monitoring

PFAS

Hot topics and emerging contaminants for air monitoring

Microplastics

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Particulate
monitoring

PFAS

PFAS in air

Sources and monitoring sites

Production | Manufacturing | Paints | Non-stick products | Pesticides | Fire fighting foams | Food packaging

PFAS in air

Sources and monitoring sites

Production Manufacturing Paints Non-stick products Pesticides Fire fighting foams Food packaging

Ambient air Indoor air Industrial sites Workplaces Landfill Incineration plants

How can monitoring be approached?

Thermal desorption offers 3 main choices for taking a sample:

- Tube
- Canister/bag
- Online

For PFAS and PFAS breakdown products a combination approach is sometimes required

Re-collection

- Confirmatory analysis can be performed on exactly the same sample.
- Samples can be archived for investigation at a later date

Thermal Desorption for volatile PFAS compounds

- AFFFs are used in fire fighting and in the past contained PFOS and PFOA. Formulations have now been modified to contain different more volatile PFAS.

- Thermal desorption for PFAS sampling and analysis offers:
  - Fast sampling times ~ minutes (vs hours) for sample collection
  - Quantitative sampling of very volatile compounds > Capture volatile PFAS and breakdown products.
  - Compatibility with a wide analyte range > Untargeted analysis aid characterisation of new PFAS compounds and breakdown products.

JACOBS

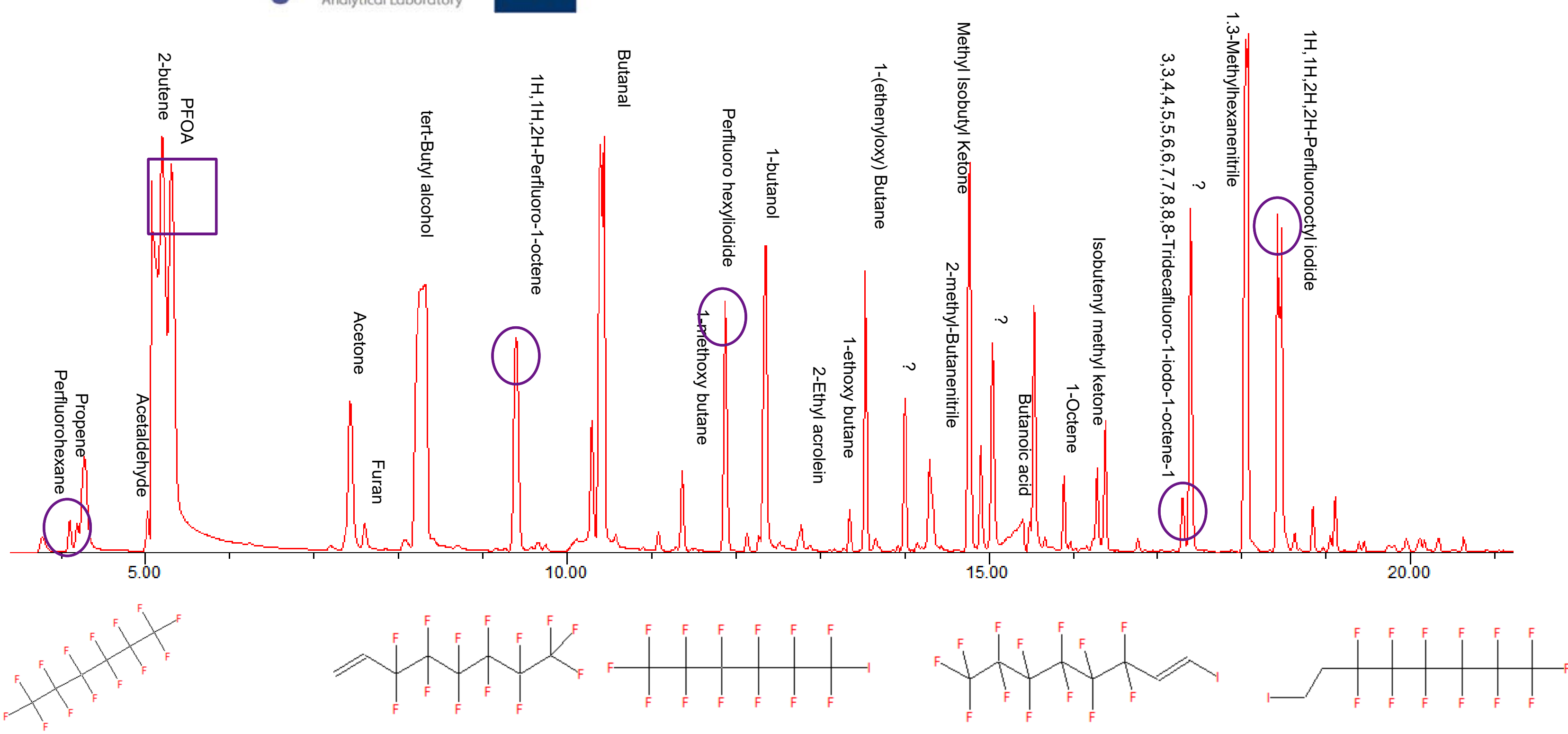
Vista Analytical Laboratory

University of Nevada, Reno

https://theintercept.com/2018/02/10/firefighting-foam-afff-pfos-pfoa-epa/

Thermal Desorption for volatile PFAS compounds

JACOBS | Vista Analytical Laboratory | University of Nevada, Reno



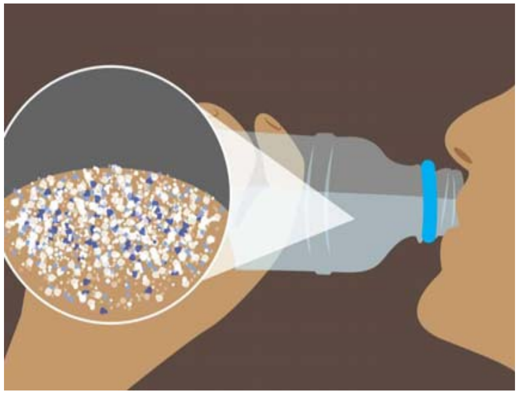
Microplastics

Microplastics already pose a global environmental problem.

Plastics are found throughout the environment

Microplastics are any type of plastic polymer less than 5 mm in length*

Due to their small size they can be easily ingested and accumulate in the human body.



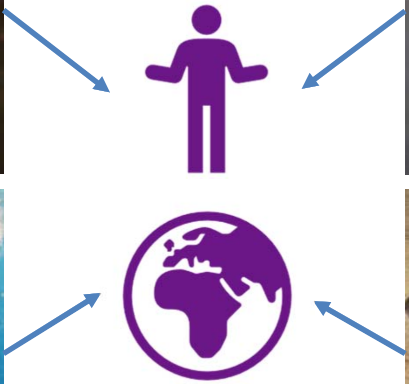
Microplastics have been reported in studies to potentially cause problems with human health, such as with immune and reproductive systems and have therefore been highlighted as cause for concern

*Source: NOAA

Where are they found in the environment

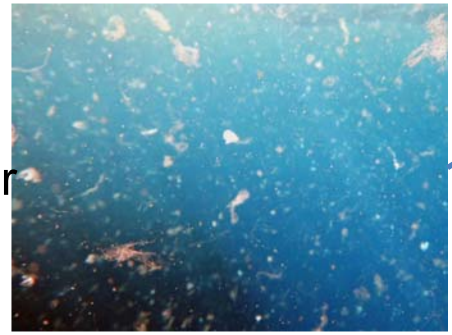
…are found in a variety of different matrices

in air



in soil

in water

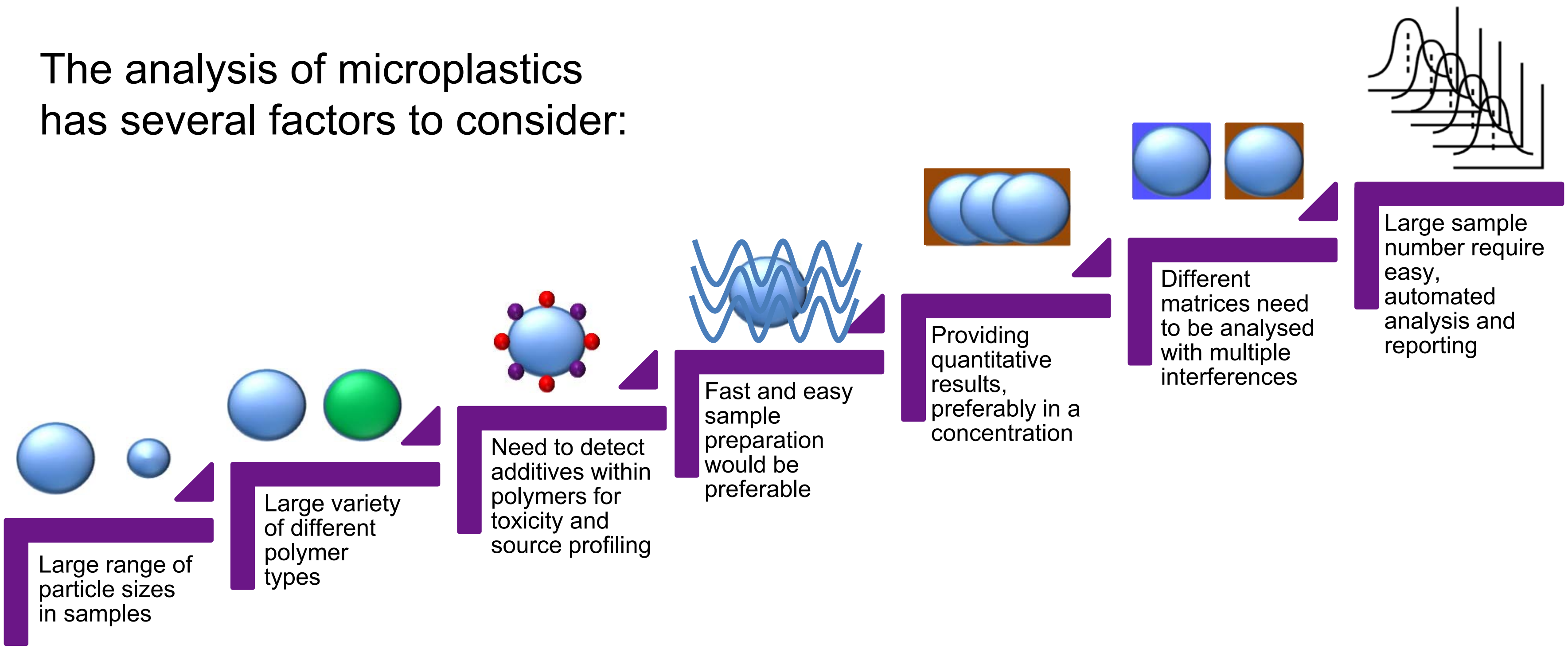


in food

→ each matrix provides a different opportunity to enter the human body and caus

Methodology considerations for analysis of microplastics

The analysis of microplastics has several factors to consider:



Microplastics by TD-GC-MS

Bottled beverages case study

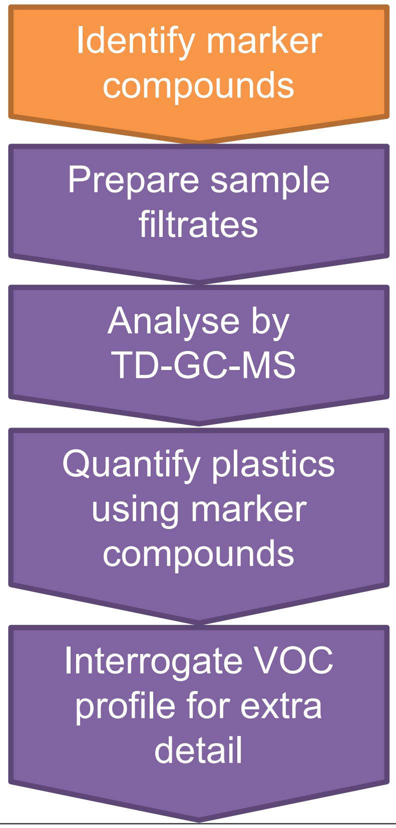
IPROMA

A company of the SCHAUENBURG International Group

Workflow overview

Microplastics analysis by TD-GC-MS

- Marker compounds for target compounds identified by TD-GC-MS analysis of standards.
  - Quantitation and qualification compounds required.
- Microplastics samples collected onto filters
- Filters are directly thermally desorbed
- Evolved VOCs are separated and analysed by GC-MS
- Marker compounds used to identify the presence, and measure the concentration, of specific plastics.
- VOC profiles also contain extra information useful in source apportionment and toxicity assessment.



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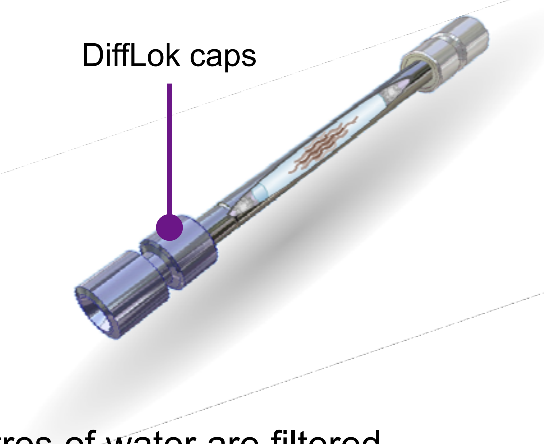
Workflow: Sample Preparation

Simplified using TD-GC-MS



- Hundreds of mL to litres of water are filtered
- The filter is then washed with multiple reagents to remove organic matter
- Dried filter is then placed directly into an empty thermal desorption tube for analysis

Filtering
0.2µm quartz filter

Washing
with reagents

Drying
30min at 100˚C

Quick Preparation
filter into TD-tube

1 h Sample preparation time

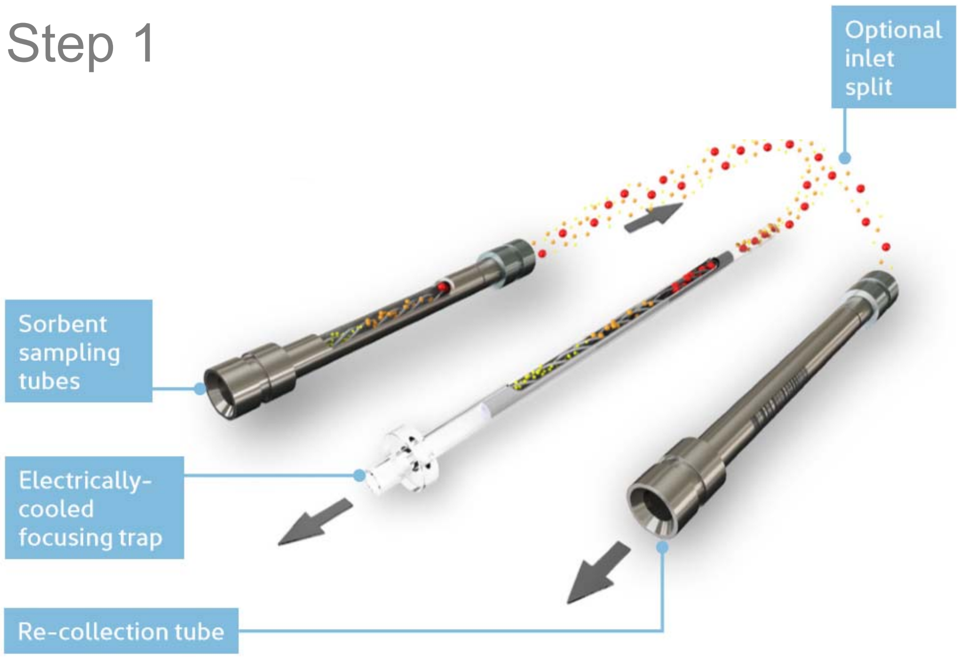
Direct Desorption
at 320˚C

30 mins analytical cycle

Workflow: Direct thermal desorption

Direct desorption of Microplastics

Step 1

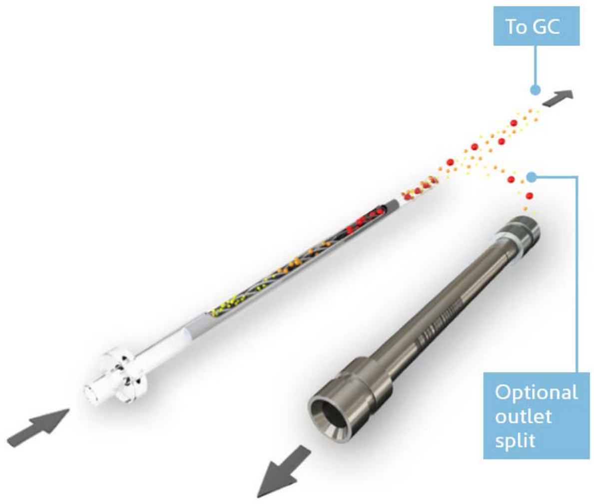


- Filter placed directly into empty thermal desorption tube and sealed with Difflok caps.
- Tube is placed in TD100-xr, automated thermal desorption system.
- Sample tube is heated, VOCs and SVOCs are emitted.
- Analytes are focused on the cryogen-free sorbent-packed trap.
- VOCs and SVOCs are concentrated, maximising the sensitivity for low level target compounds.

Workflow: Direct thermal desorption

Direct desorption of Microplastics

Step 2

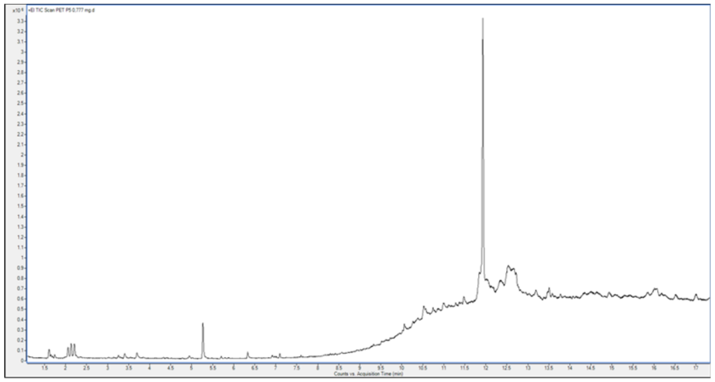


- Focusing trap rapidly heated (up to 100ºC/s) in a reverse flow of carrier gas (‘backflush’ operation)
- The analytes are transferred to the GC-MS (with an optional outlet split)
- Split flows can be re-collected onto sorbent tubes for future re-analysis.

Workflow: GC-MS analysis

Analysis using Gas Chromatography / Mass Spectrometry (GC/MS)

- After trap desorption the compounds separate within the GC column and are detected and identified with the MS.
- This produces a chromatogram which can be used as a chemical fingerprint
- Marker compounds are identified using standards and peak areas can be used to create a calibration curve
- If the same compounds are found in samples a concentration of the plastic found can be calculated in µg/L
- TD-GC-MS also facilitates identification of other compounds such as additives or unique identifiers that may be used to trace the source of the plastic and determine toxicity



Advantages of Markes TD for microplastics

Why use the TD-100-xr and Markes' trapping technology for microplastics

TD-100-xr

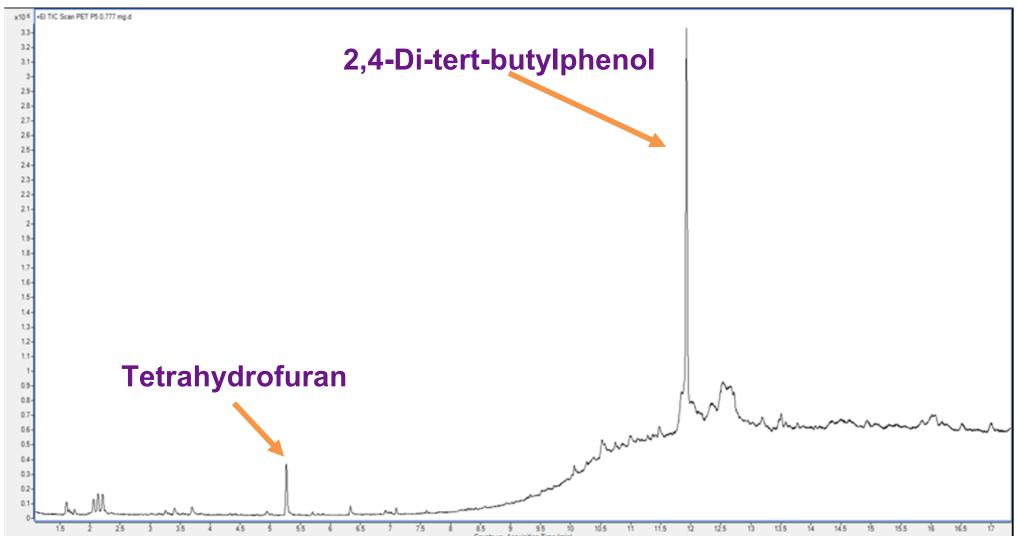
- 100-tube capacity — •Unattended, automated operation over an entire weekend
- Electrically-cooled focusing trap — •No safety or supply concerns associated with liquid cryogen, no risk of ice blockages. Low running costs.
- Overlap mode — •Maximise instrument productivity
- Diffusion locking — •No uncapping/re-capping of tubes, plastic free
- Leak test — •Guarantees sample integrity.
- Backflushed focusing trap — •simultaneous analysis of VOCs and SVOCs capturing marker compounds and contaminants
- Desorption temperature range — •35 – 450 °C in 1 or 2 stages for full sample characterisation
- Re-collection — •Sample archiving, automated repeat analysis & extended dynamic range
- Internal standard — •Added to focusing trap for analytical QC

Markes' trapping technology

Microplastics in beverages: Case study

Polyethylene terephthalate (PET) in beverages

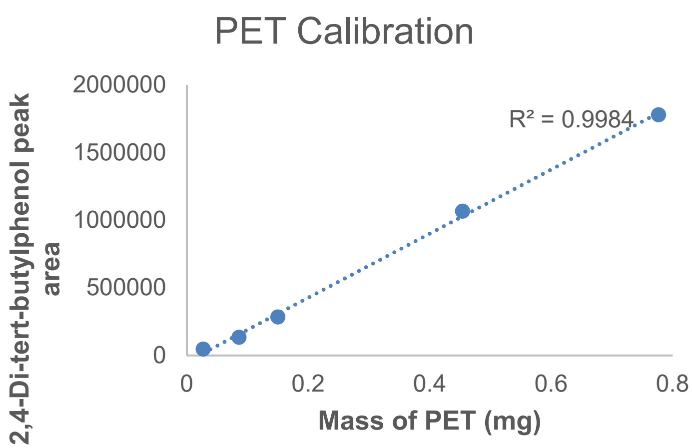
1. Identify marker compounds for PET by TD–GC–MS analysis of standard pellets.
   - 2,4-di-tert-butylphenol used as quantitation marker
   - Tetrahydrofuran is used to confirm presence of PET



Microplastics in beverages: Case study

Polyethylene terephthalate (PET) in beverages

1. Identify marker compounds for PET by TD–GC–MS analysis of standard pellets.
   – 2,4-di-tert-butylphenol (DTBP) used as quantitation marker
   – Tetrahydrofuran is used to confirm presence of PET
2. Create calibration curve to quantify PET in samples
   • Mass of PET vs DTBP peak area



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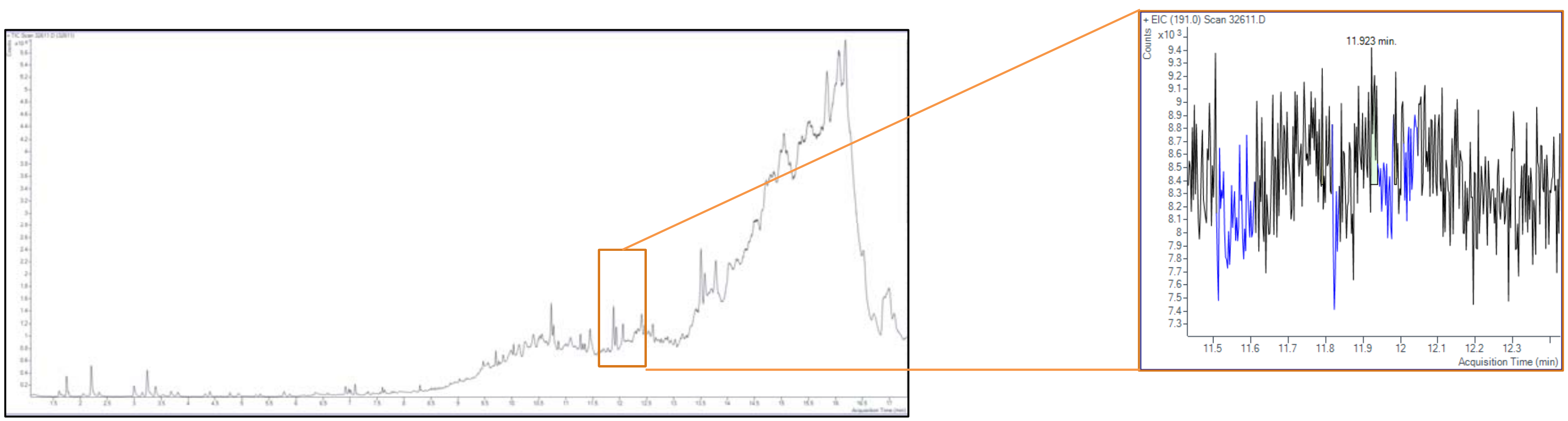
Microplastics in beverages: Case study

Polyethylene terephthalate (PET) in beverages

3. Check for false positives
   - Zero result sample showed plastic-free filtration and analysis process

EIC
2,4-Di-tert-butylphenol



Microplastics in beverages: Case study

Polyethylene terephthalate (PET) in beverages

3. Check for false positives
   - **Zero result** sample showed plastic-free filtration and analysis process
4. Spike plastic-free water with a known amount of PET to validate the full process
   - Spiked matrix (Water) showed **> 90% recovery for PET**

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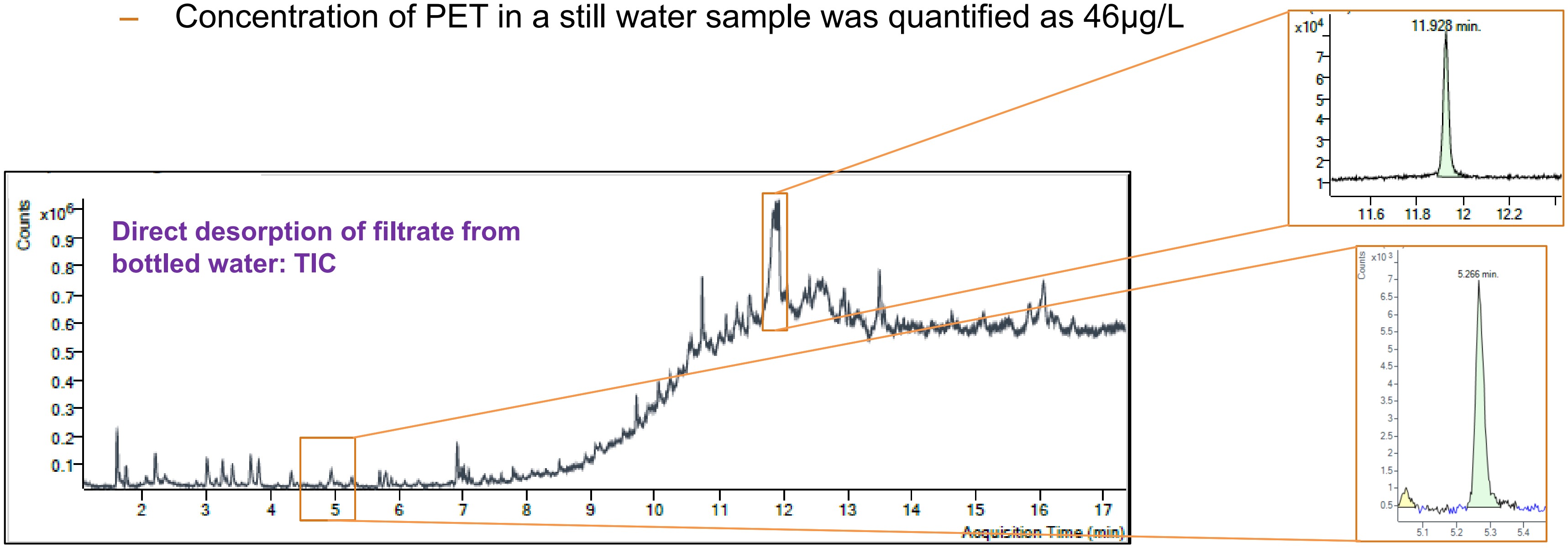
Microplastics in beverages: Case study

Polyethylene terephthalate (PET) in beverages

5. Bottled water sample analysis
   - Both the quantification and confirmation markers were identified
   - Concentration of PET in a still water sample was quantified as 46µg/L

EIC
2,4-Di-tert-butylphenol



EIC Tetrahydrofuran

Microplastics in beverages: Case study

Polyethylene terephthalate (PET) in beverages

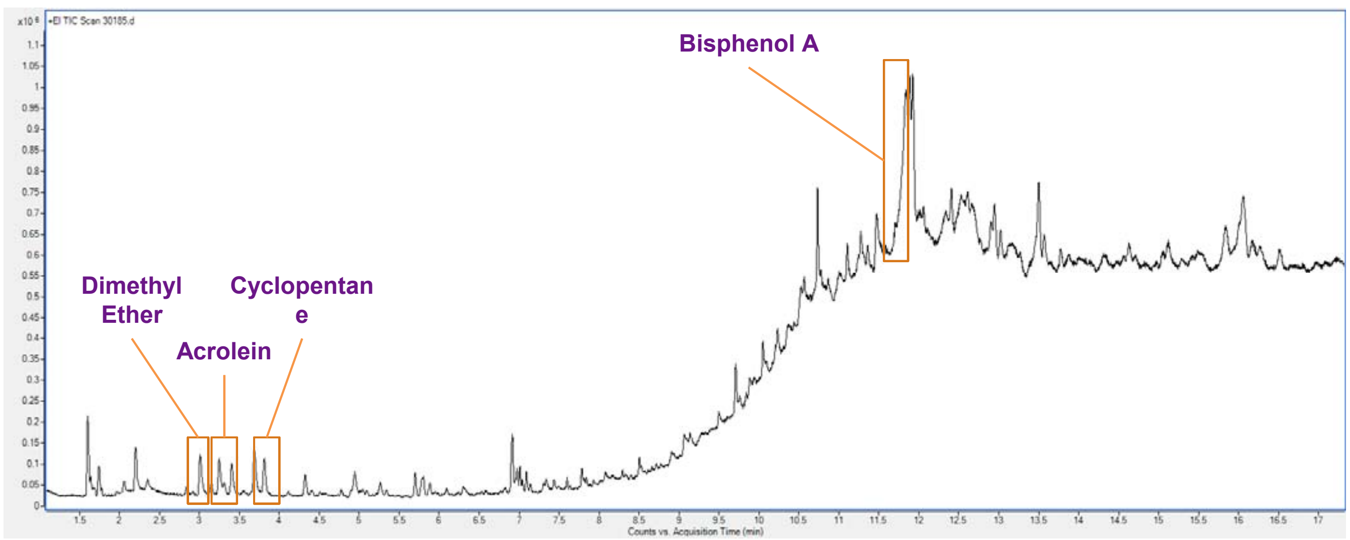
6. Analyse additional bottled beverages
   - Both the quantification and confirmation markers were identified in 3 / 4 beverages.
   - Concentration of PET from different beverages was compared

Sample type	Calculated concentration (ug/L)
Bottled water (still) (Brand A)	46.6
Bottled water (still) (Brand B)	Not detected
Bottled water (carbonated)	16.6
Bottled cola	22.1

Microplastics in beverages: Case study

Unknowns analysis: what else can be found? – Bottled water sample

- In addition to markers for PET, a number of compounds used in the process of manufacturing plastics have been tentatively found including dimethyl ether, acrolein and cyclopentene and could assist with source profiling.
- Bisphenol A (BPA) is an additive found in plastics to help with hardening. Research suggests this may be an endocrine disruptor so it is a compound of interest in assessing toxicity.



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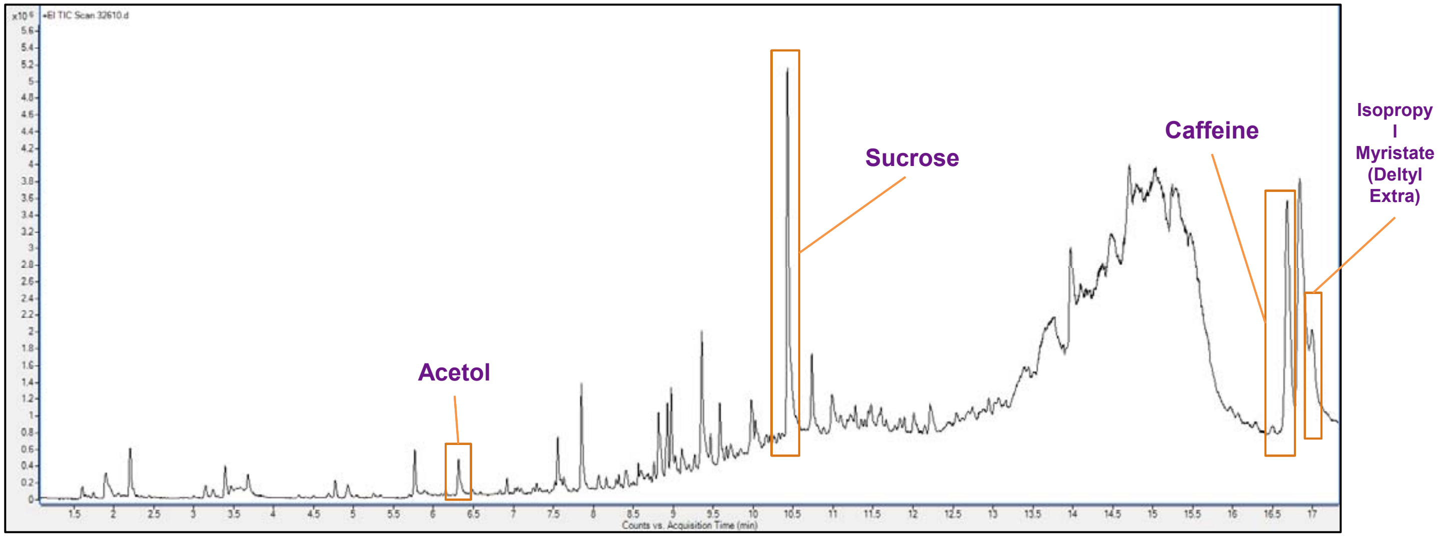
Microplastics in beverages: Case study

Unknowns analysis: what else can be found? – Bottled cola sample

- Beyond plastic, sucrose and caffeine were both detected with high responses and are known components of cola drinks
- Acetol and Deltyl Extra were also detected in this sample, both of these compounds are known for their use in the food and flavour industry and may help to identify the source of the plastic.



Microplastics in beverages: Case study

Conclusions

In this case study we have demonstrated:

- ✓ The use of direct desorption to Qualify **AND** Quantify microplastics from bottled beverages
- ✓ Plastic free preparation and analysis means no false positives
- ✓ Confident quantification with >90% recovery of test samples
- ✓ Provides simultaneous information on **targets and non-targets** compounds.
  - ✓ **Additional toxicity information** and source profiling.
- ✓ Able to sample from **whole filter** to ensure representative results
- ✓ Analyse down to **0.2 µm diameter particles** (micro and nano-plastics).
- ✓ **Time per sample** 1 h sample preparation and 30 mins TD-GC-MS run time
- ✓ Well-established, straightforward analytical techniques with simple, automated data processing.

Summary: TD-GC-MS for microplastics

TD-GC-MS has many advantages for micoplastics.

- Simple sample preparation workflows that can be applied to wide ranging sample types
- Particle size is only limited by the size of filter chosen
- Large sample sizes for enhanced repeatability and sensitivity
- Can be used for samples containing more than one plastic
- Deliver results as mass balance concentration in a simple automated fashion
- Provide extra information in VOC profiles for source profiling and toxicity evaluation
- Add to existing GC-MS for lower capital investment overheads
- Well established in both discovery workflows and high throughput routine analysis with in-built features for high quality data
  - Leak test & diffusion locking technology
  - Internal standard addition
  - Re-collection
  - Cryogen-free backflush trap technology