MARKES international

THE QUEEN'S AWARDS FOR ENTERPRISE: INNOVATION 2019

New Insights from TD-GC-MS data on Microplastics in salt samples

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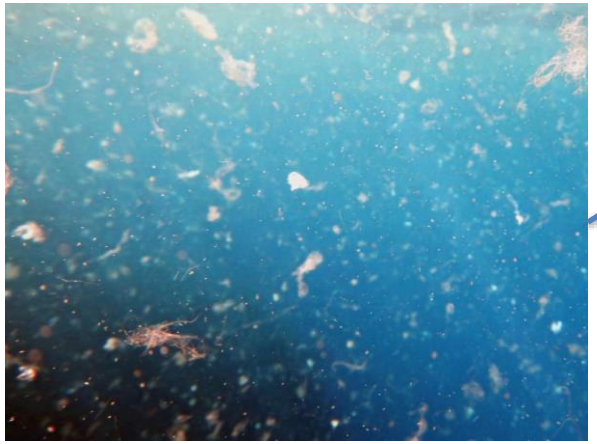
Where are MPs found in the environment

…are found in a variety of different matrices

in air

in soil

in water



in food

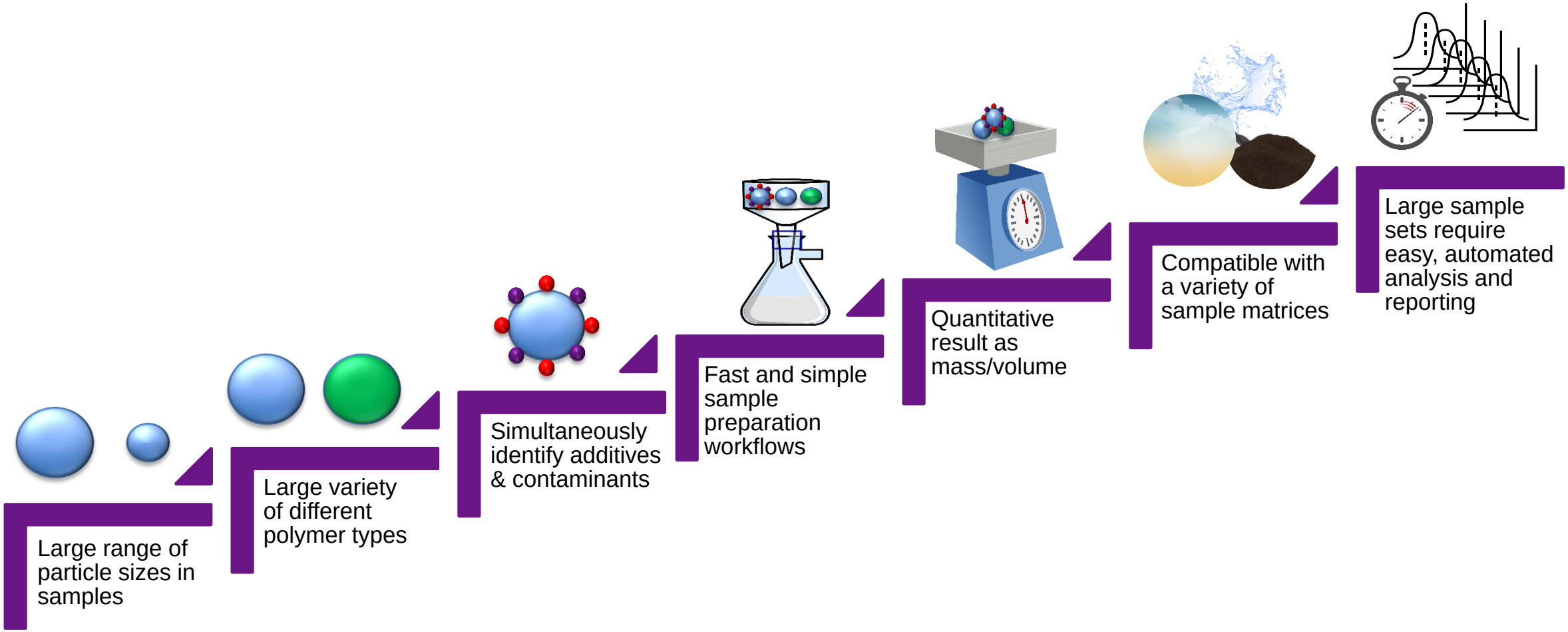
→ each matrix provides a different opportunity to enter the human body and cause harm

How can we measure microplastics?

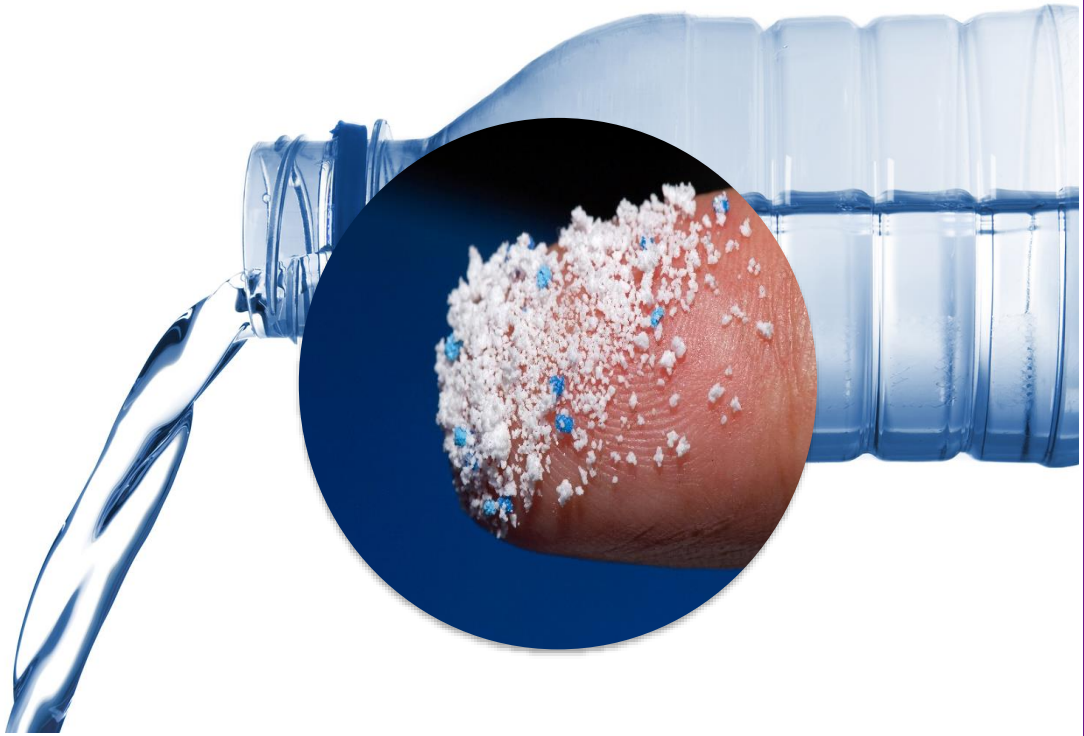
Spectroscopic techniques

Chemical analysis methods

Considerations for microplastics analysis



Microplastics in bottled beverages with TD-GC-MS



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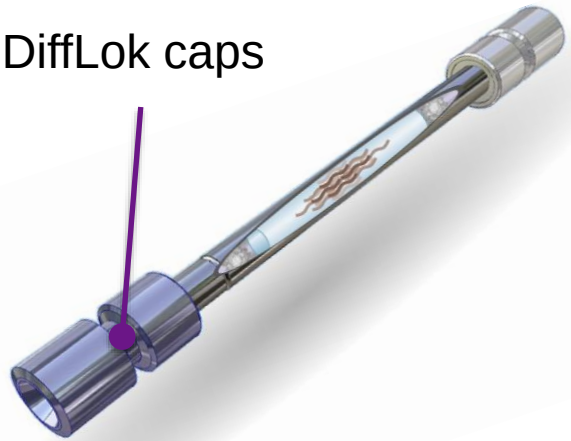
Workflow: Sample Preparation

Simplified using TD-GC-MS

DiffLok caps



- Hundreds of mL to liters 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
0.3µm quartz filter

Washing
with reagents

Drying
30min at 100˚C

Quick Preparation
filter into TD-tube

1 h
Sample
preparation
time

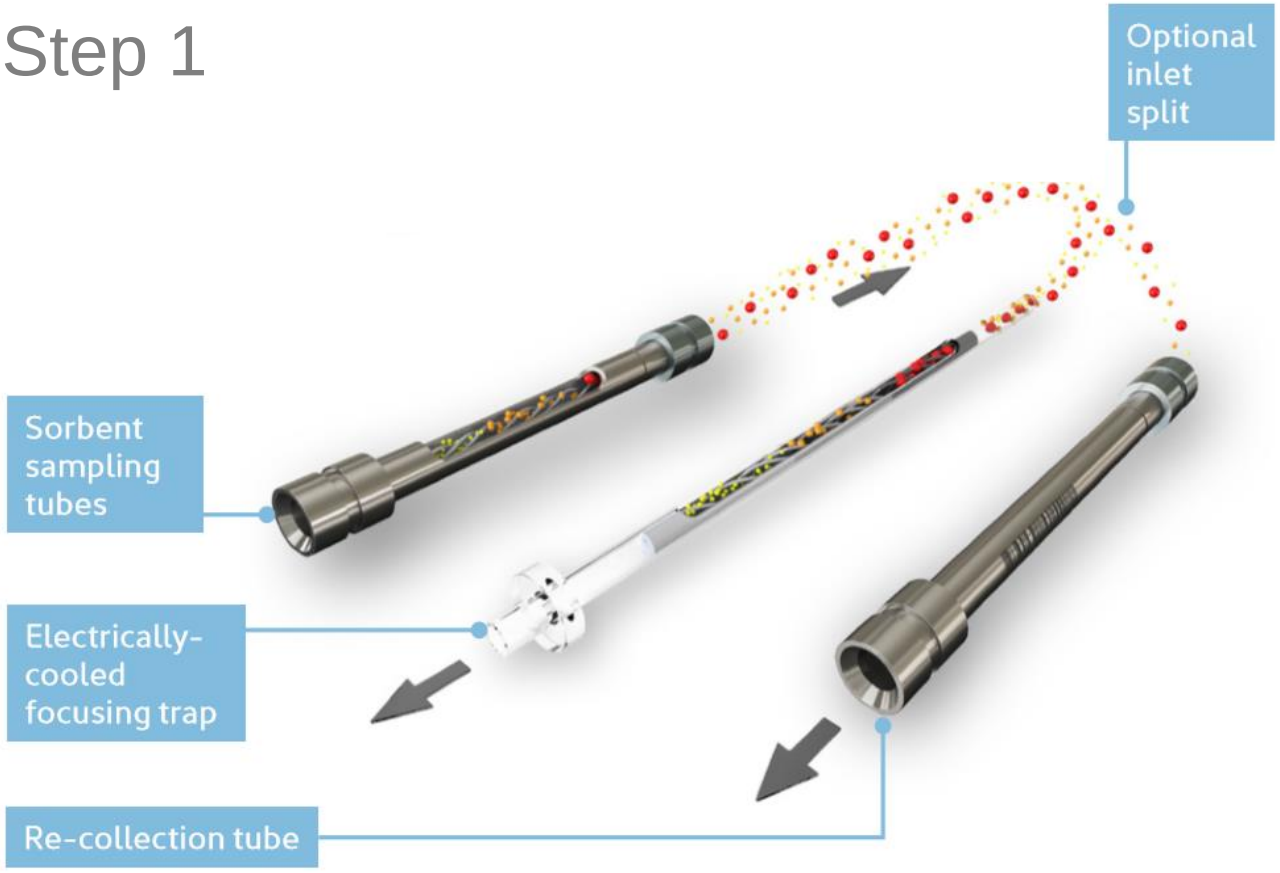
Direct Desorption
at 320˚C

30 mins
analytical
cycle

Workflow: Direct thermal desorption

Direct desorption of Microplastics

Step 1

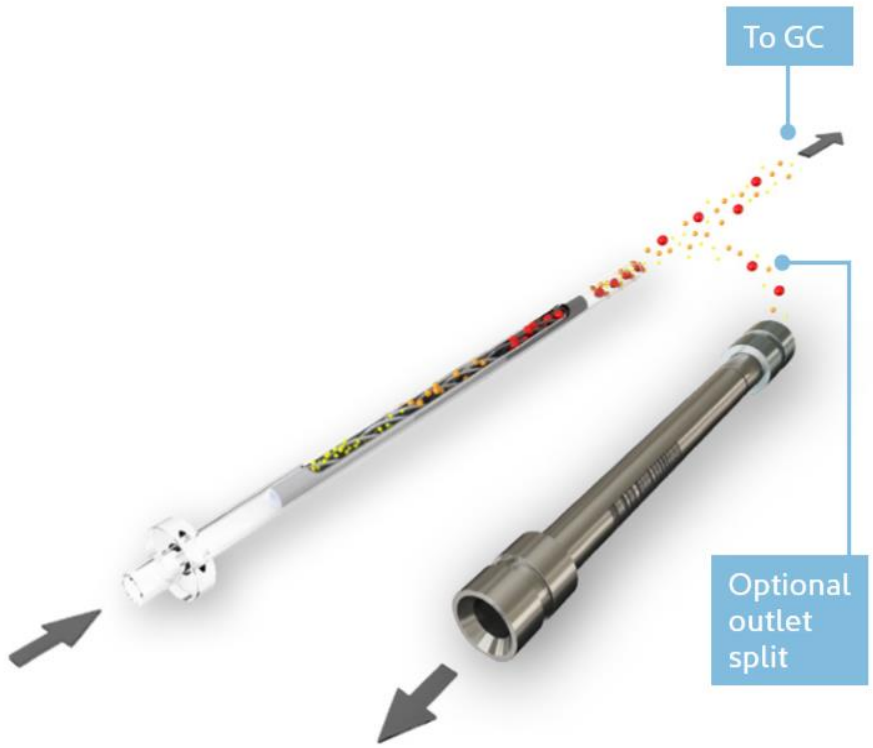


- Filter placed directly into empty thermal desorption tube and sealed with Difflok caps.
- Tube is placed in TD100-xr, automated thermal desorption system.
- Sample tube is heated, VOCs and SVOCs are emitted.
- Analytes are focused on the cryogen-free sorbent-packed trap.
- VOCs and SVOCs are concentrated,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

Workflow: Direct thermal desorption

Direct desorption of Microplastics

Step 2

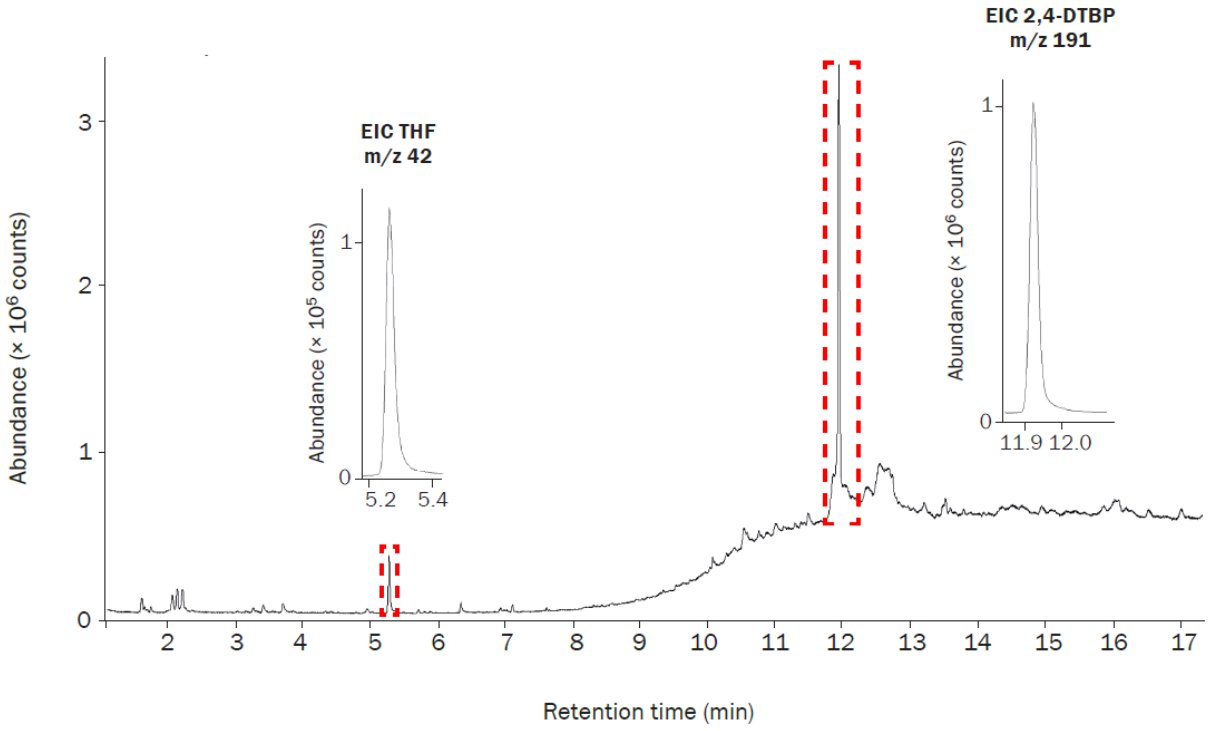


- Focusing trap rapidly heated (up to 100ºC/s) in a reverse flow of carrier gas (‘backflush’ operation)
- The analytes are transferred to the GC-MS (with an optional outlet split)
- Split flows can be re-collected onto sorbent tubes for future re-analysis.

Microplastics in beverages: Case study 1

Polyethylene terephthalate (PET) in beverages

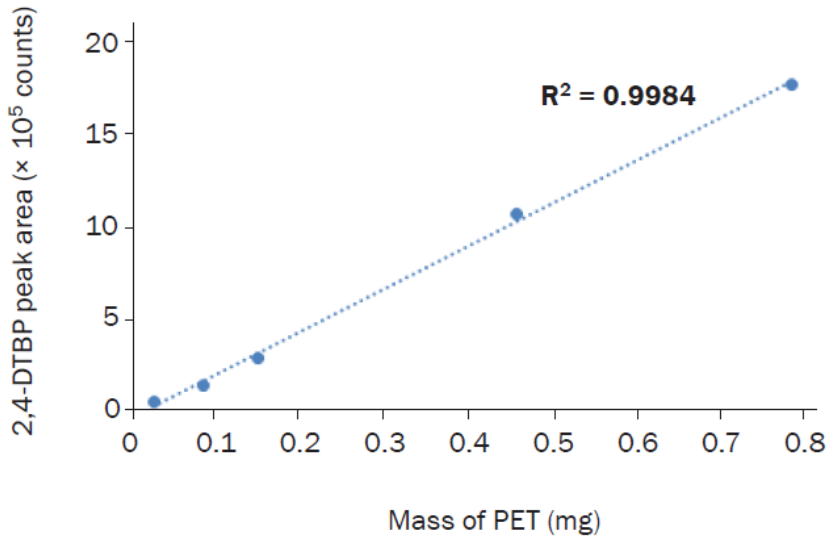
1. Identify marker compounds for PET by TD–GC–MS analysis of standard pellets.
   - 2,4-di-tert-butylphenol used as quantitation marker
   - Tetrahydrofuran is used to confirm presence of PET



Microplastics in beverages: Case study 1

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

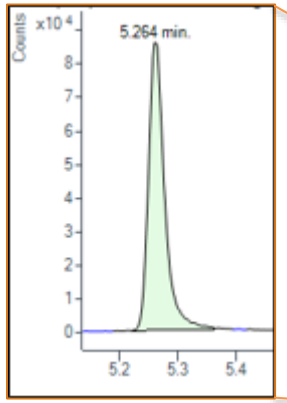


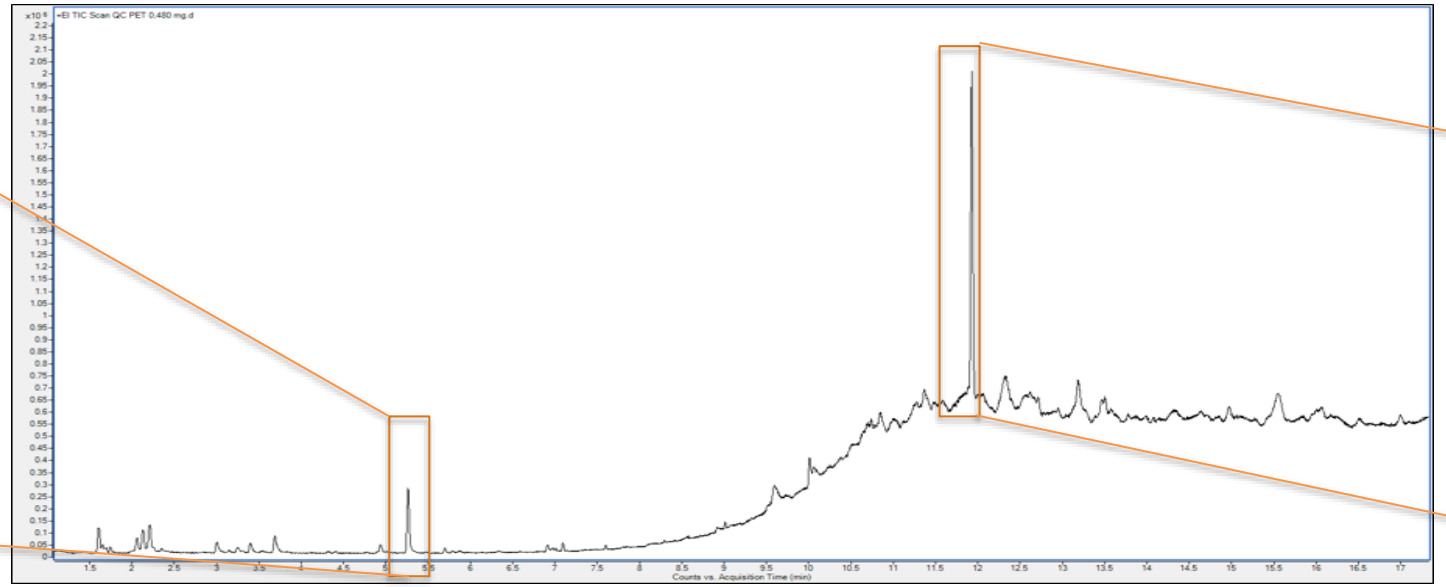
Microplastics in beverages: Case study 1

Polyethylene terephthalate (PET) in beverages

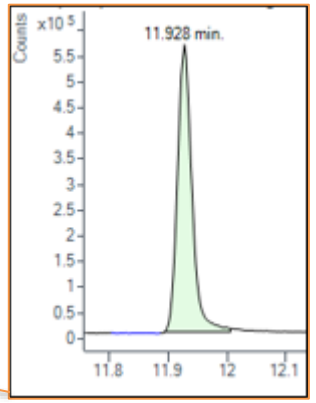
3. Check for false positives
   - **Zero result** sample showed plastic-free filtration and analysis process
4. Spike plastic-free water with a known amount of PET to validate the full process
   - Spiked matrix (Water) showed **> 90% recovery for PET**

EIC Tetrahydrofuran





EIC 2,4-Di-tert-butylphenol



Microplastics in beverages: Case study 1

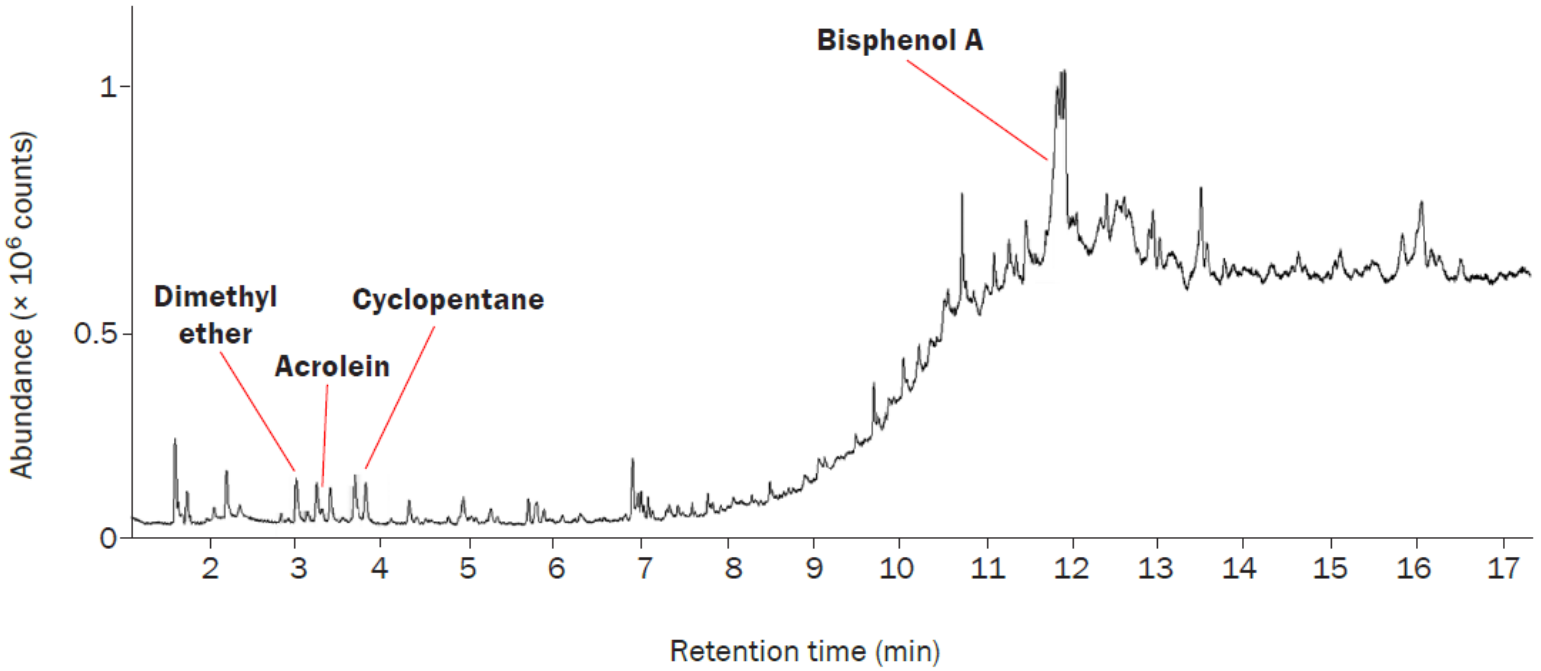
Polyethylene terephthalate (PET) in beverages

5. 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)	N. d.
Bottled water (carbonated)	16.6
Bottled cola	22.1

Microplastics in beverages: Case study 1

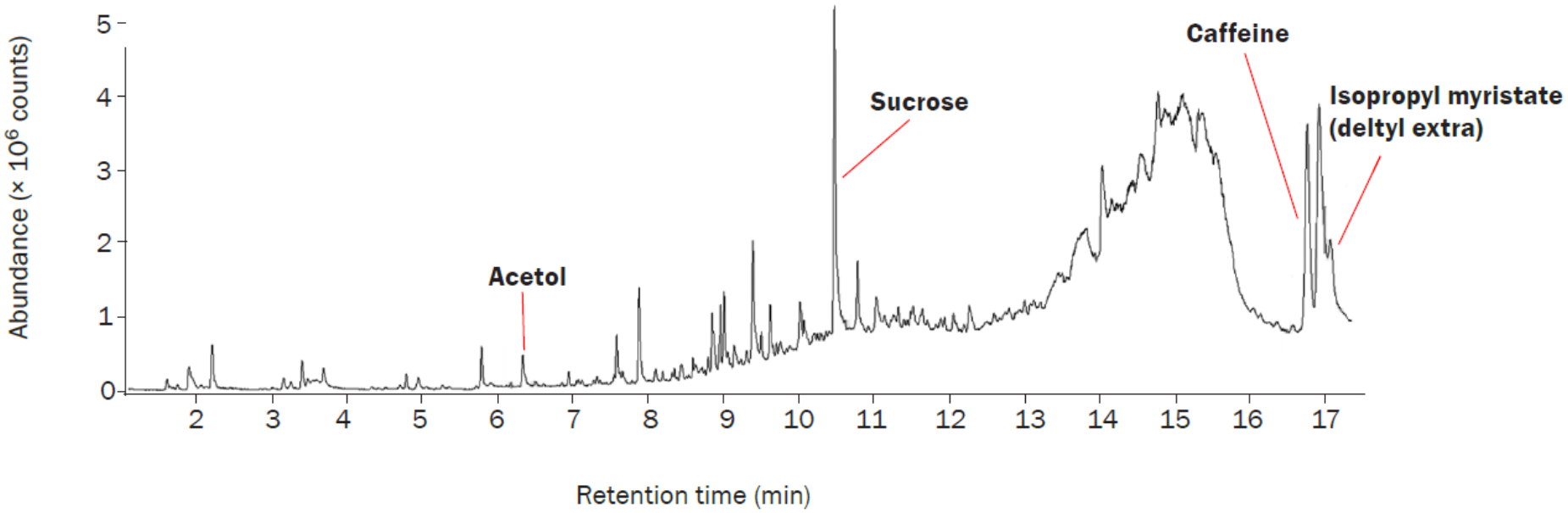
- Unknowns analysis: what else can be found? – Bottled water sample
- In addition to markers for PET, a number of compounds used in the process of manufacturing plastics have been tentatively found including dimethyl ether, acrolein and cyclopentene and could assist with source profiling.
- Bisphenol 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.



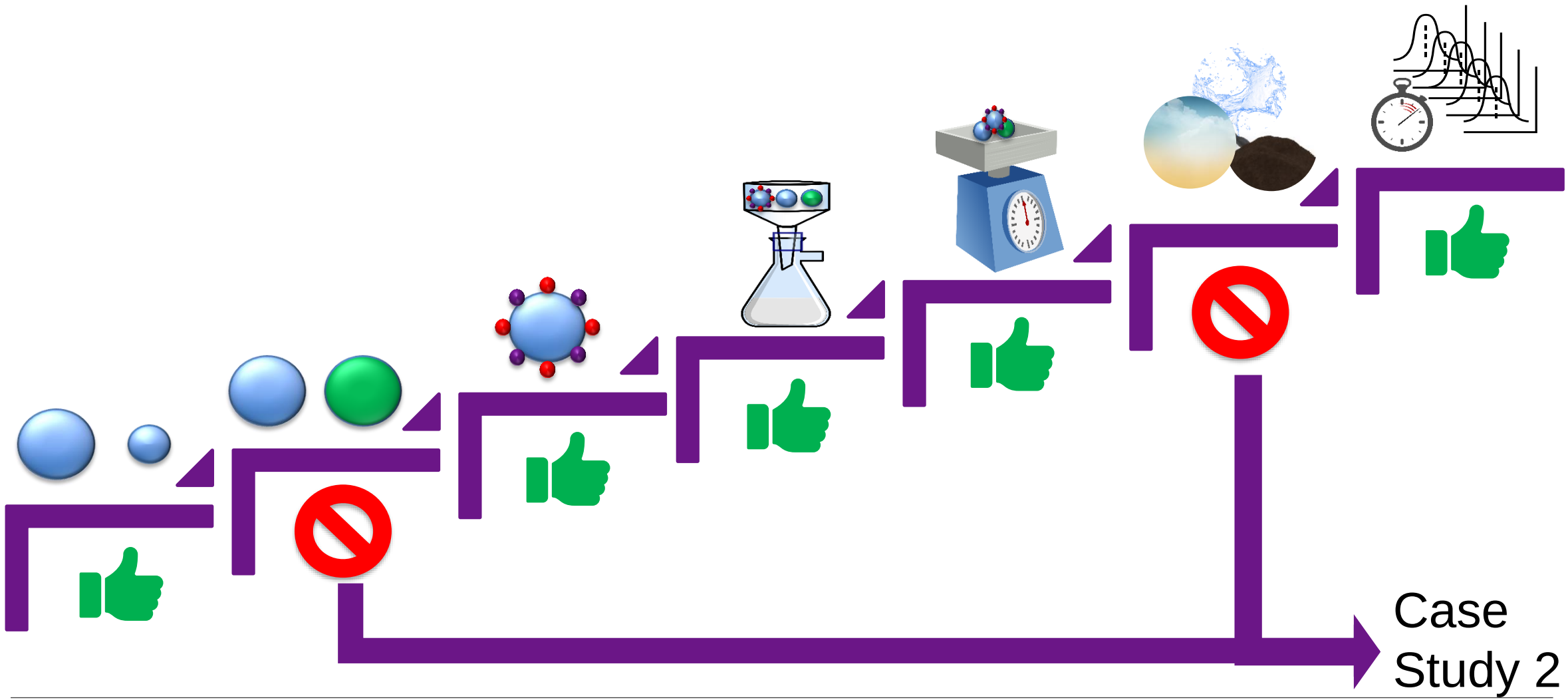
Microplastics in beverages: Case study 1

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.



TD-GC-MS for microplastics analysis



Microplastics in salt samples with TD-GC-MS

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Microplastics in Salt

Sea salt:
from today's seawater

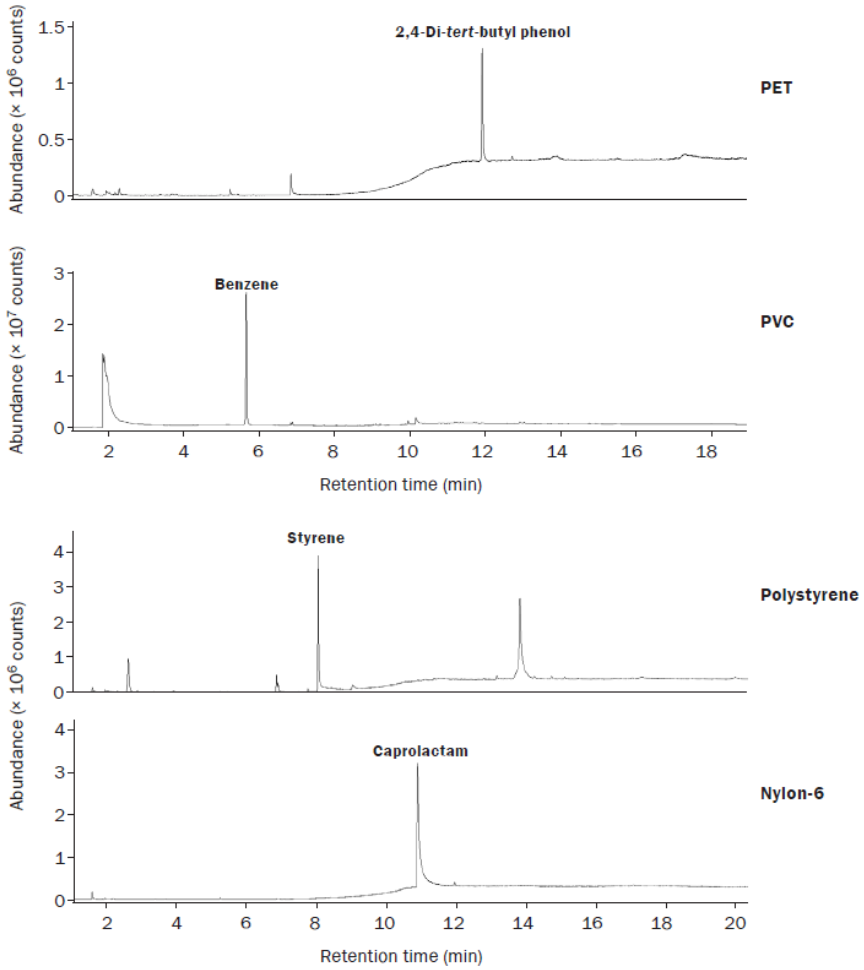
Rock salt:
from ancient water sources

Table salt:
from mostly unknown origin

Microplastics in Salt – Multiple polymers

Identification of marker compounds for the four polymer standards

Polymer	Marker compound	RT (mins)	Linearity	Degradation process
Nylon-6	Caprolactam	10.9	0.9961	Depolymerisation of caprolactam
PET	2,4-DTBP	11.9	0.9959	PET glass transition
PS	Styrene	8.05	0.9967	Depolymerisation of styrene
PVC	Benzene	5.67	0.9930	Dehydrochlorination process of PVC

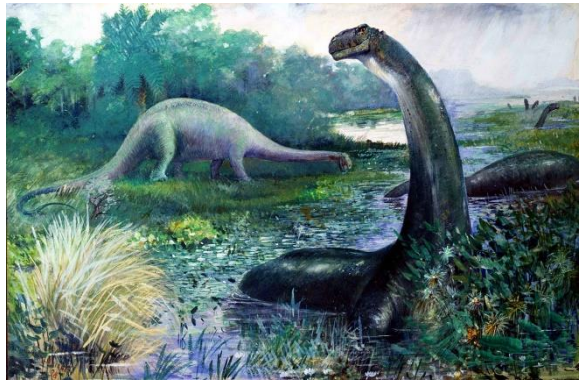


Microplastics in Salt - Results

The importance of density of polymers

- Microplastics from packaging were determined in all salt samples.

Salt type	PET µg/g	PVC µg/g	PS µg/g	Nylon-6 µg/g
Blanco NaCl	-	-	-	-
NaCl + 300 µg Nylon-6	-	-	-	330
NaCl Spiked with microplastcics	23.6	194	184	-
Himalayan RS	7.75	0.165	20.7	-



The *Himalayan Pink Salt* we use today was first formed over 350 million years ago when dinosaurs ruled the world in the Jurassic era.

Microplastics in Salt - Results

The importance of density of polymers

- Microplastics from packaging were determined in all salt samples.
- Microplastics from several polymers were found in a variety of sea salt samples in various concentrations
- Sea salts contained varying amounts of polymers (both PE and PS)

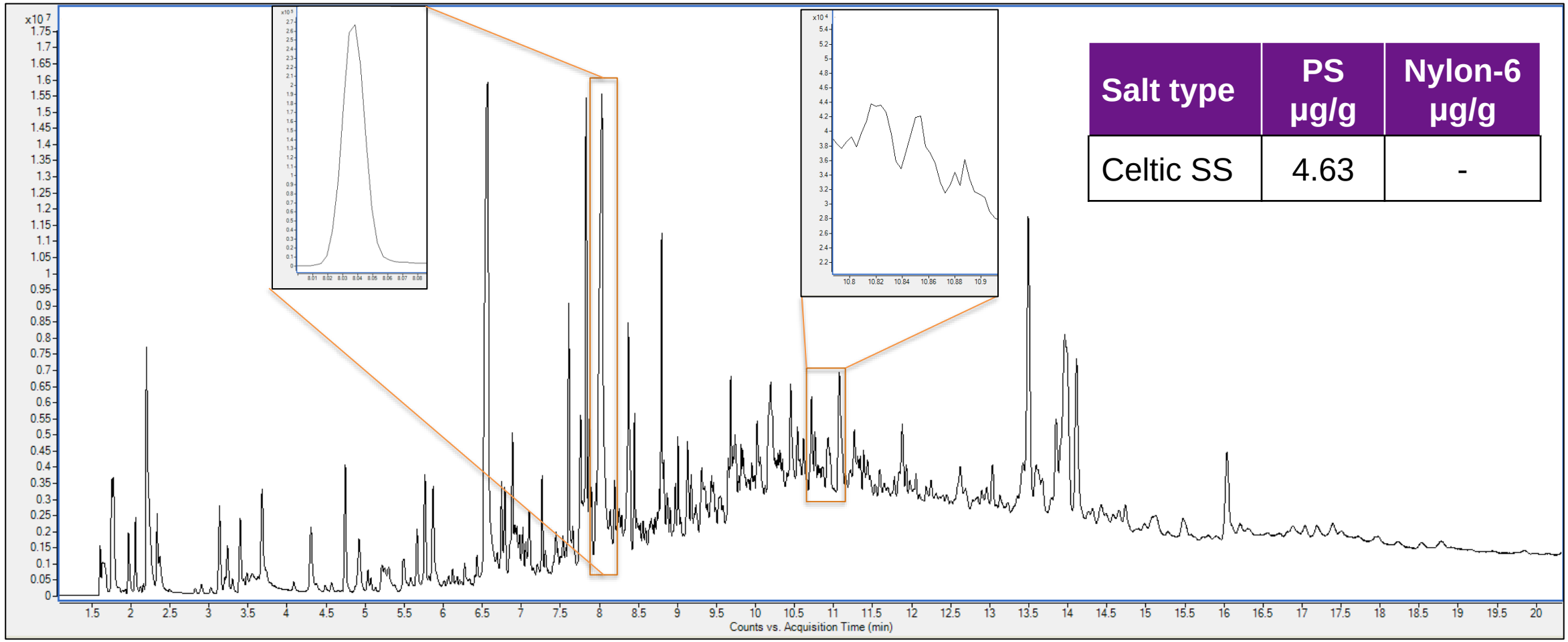
Salt type	PET µg/g	PVC µg/g	PS µg/g	Nylon-6 µg/g
Celtic SS	15.9	1.02	4.63	-
Sal 1	2.57	0.265	2.98	-
Sal 2	1.73	0.12	1.52	-

Luscher et al. (2013)

Microplastics in Salt - Celtic Sea Salt

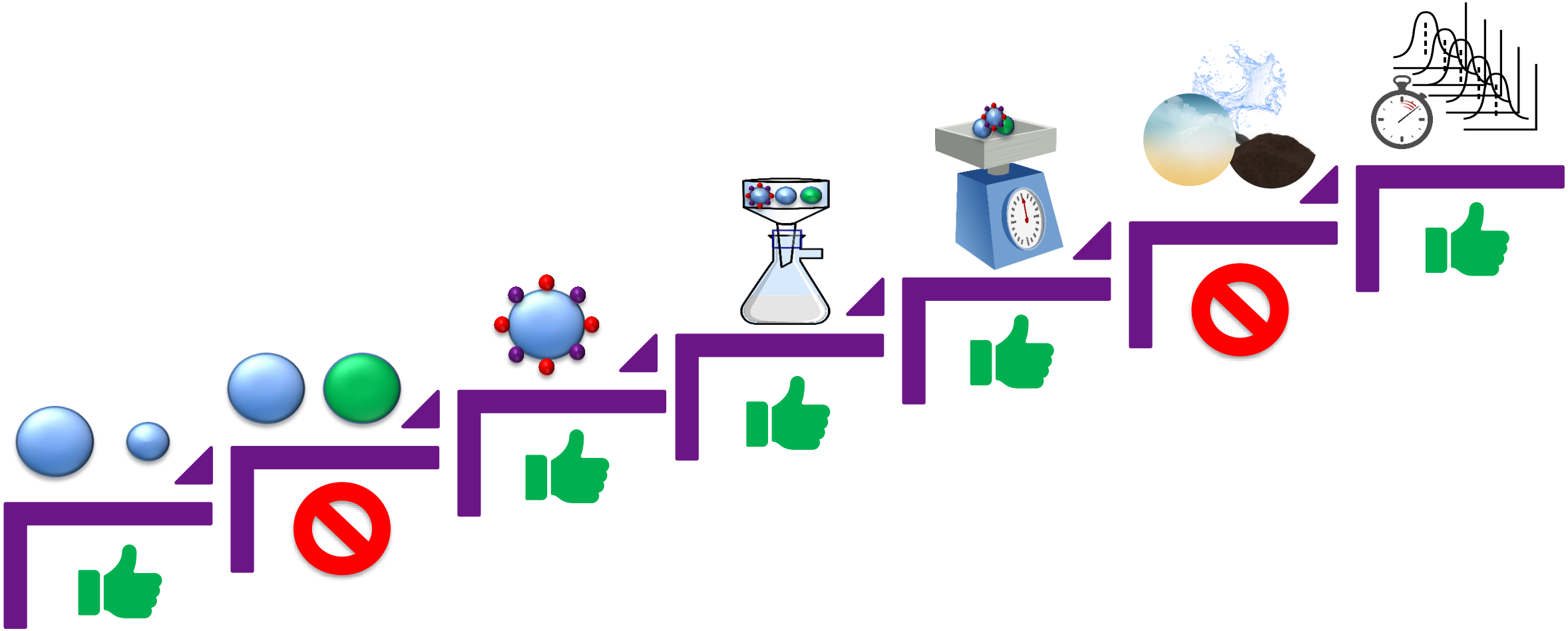
EIC Styrene (polystyrene)

Nylon 6

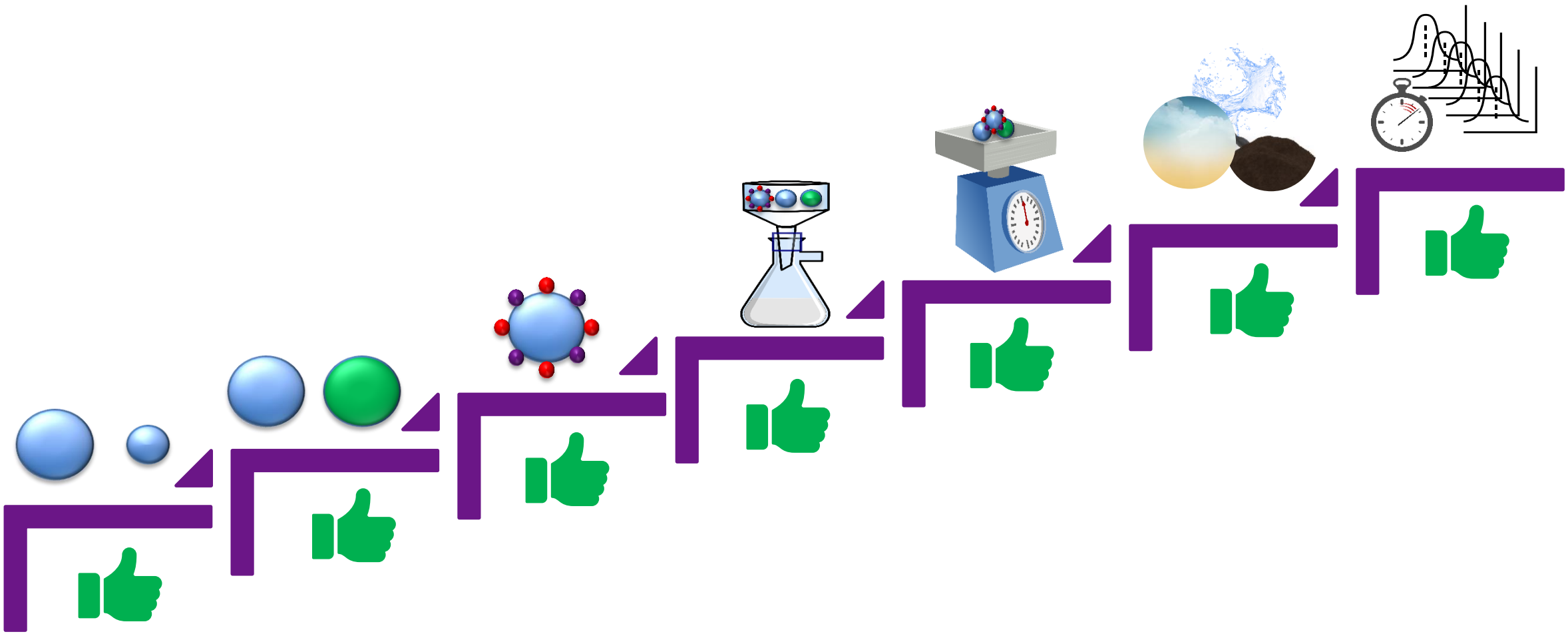


Salt type	PS µg/g	Nylon-6 µg/g
Celtic SS	4.63	-

TD-GC-MS for microplastics analysis



TD-GC-MS for microplastics analysis

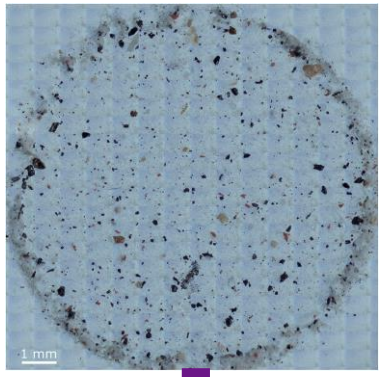


Outlook

Bringing together spectroscopy and thermal analysis

Spectroscopic techniques

Thermal analysis methods



Spectroscopic result

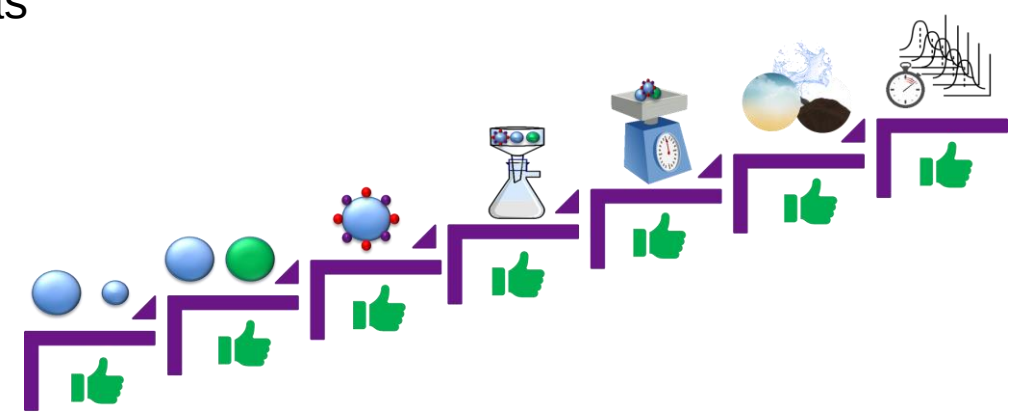
Thermal analytical result

Microplastics

Take home messages

Using TD-GC-MS we have:

- ✓ Qualify and Quantify micro- and nano plastics as small as 0.3 µm diameter.
- ✓ Provided simultaneous information on targets and non-targets compounds in a single run with rapid sample preparation and high degree of automation.
- ✓ Additional toxicity information and source profiling.
- ✓ Analysis of the whole filter to ensure representative results and allowing for easy implementation of complementary methods (e.g. spectroscopic techniques



Thank you for your attention!
Any questions?

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