BAM
Bundesanstalt für Materialforschung und -prüfung

Sicherheit in Technik und Chemie

29.08.2019

UNDERSTANDING DEGRADATION MECHANISMS OF MICROPLASTICS IN ENVIRONMENTAL SAMPLES

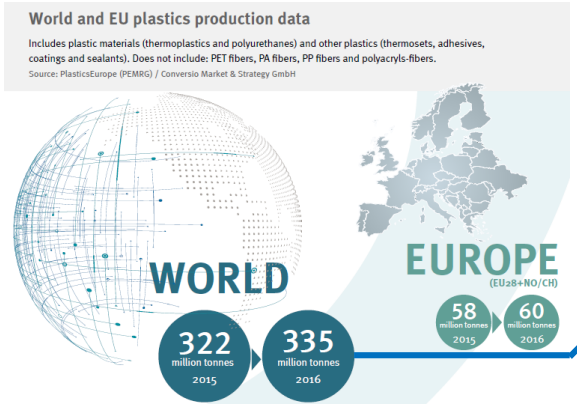
Ulrike Braun, Paul Eisentraut, Yosri Hassanein, Anna-Maria Elert

www.bam.de

Outline

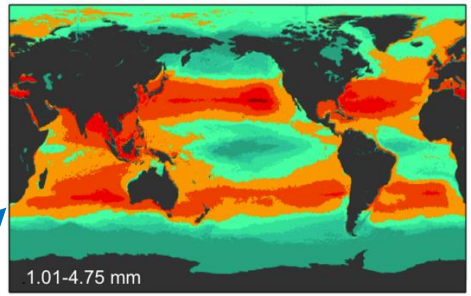
- Plastic in the oceans – introduction
- Tara sampling campaign
- Results so far
- Polymer aging
- New method: TED-GC-MS
- More results
- Outlook

Plastic in the oceans -introduction



Plastics – the facts Plastic Europe 2017

x%

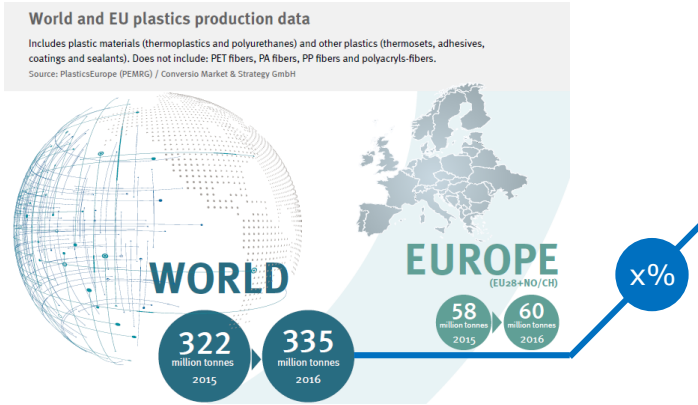


Eriksen et al. (2014) Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea. PLoS ONE 9(12): e111913. doi:10.1371/journal.pone.0111913

- High input

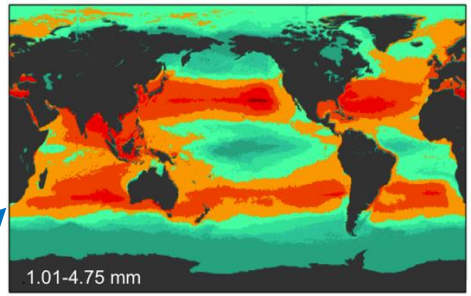
Zweifel, Maier, Schiller: Plastics Additives Handbook 6th edition, 2008

Plastic in the oceans -introduction



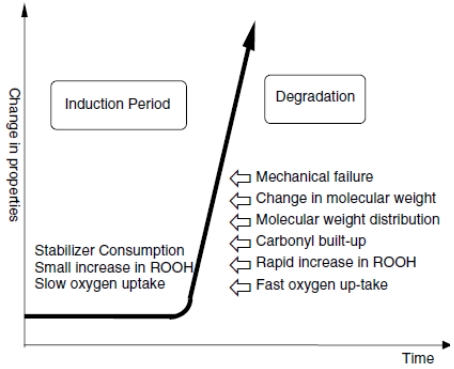
Plastics – the facts Plastic Europe 2017

x%



Eriksen et al. (2014) Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea. PLoS ONE 9(12): e111913. doi:10.1371/journal.pone.0111913

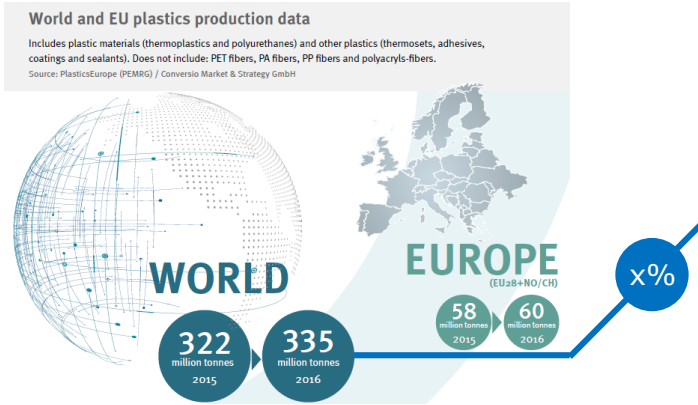
- High input
- Breakdown into particles < 5 mm



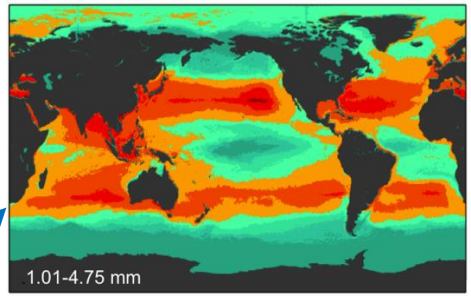
Scheme 1.3 Changes in material properties during aging of polymers

Zweifel, Maier, Schiller: Plastics Additives Handbook 6th edition, 2008

Plastic in the oceans -introduction

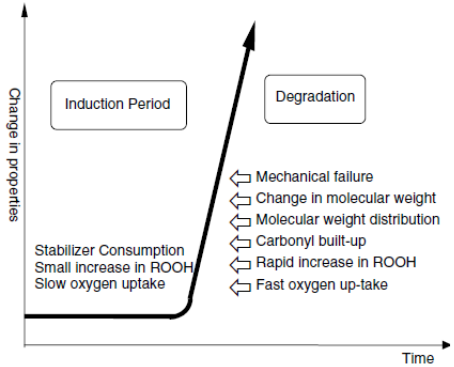


Plastics – the facts Plastic Europe 2017



Eriksen et al. (2014) Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea. PLoS ONE 9(12): e111913. doi:10.1371/journal.pone.0111913

- High input
- Breakdown into particles < 5 mm
- Risks unclear
- Need for high-troughput analytical protocol

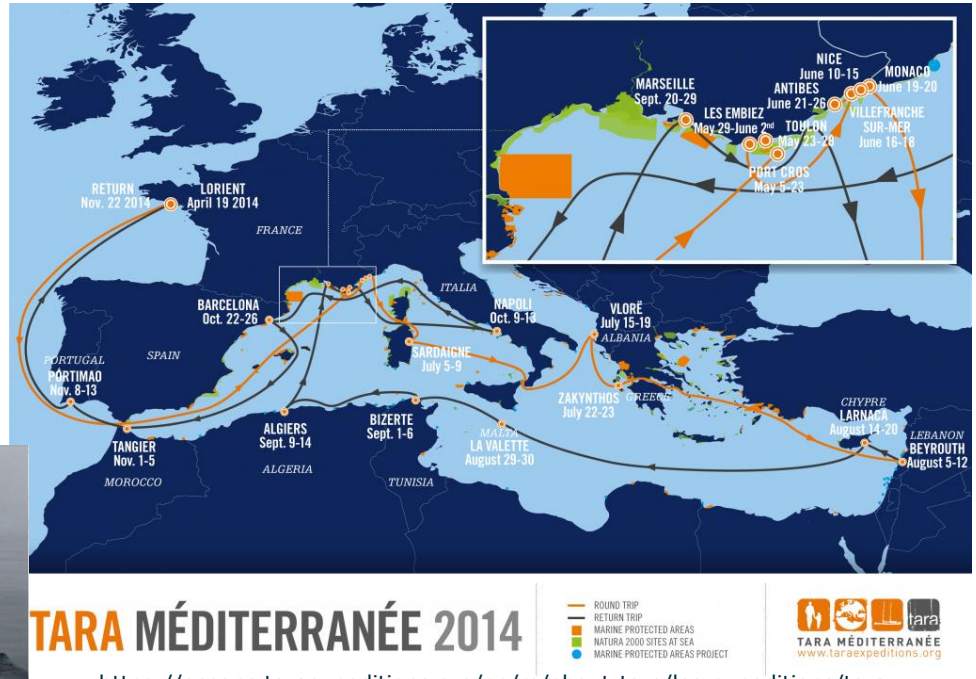


Scheme 1.3 Changes in material properties during aging of polymers

Zweifel, Maier, Schiller: Plastics Additives Handbook 6th edition, 2008

Sampling campaign

- Starting point:
  Tara-Mediterranean Expedition 2014



https://oceans.taraexpeditions.org/en/m/about-tara/les-expeditions/tara-mediterranee/

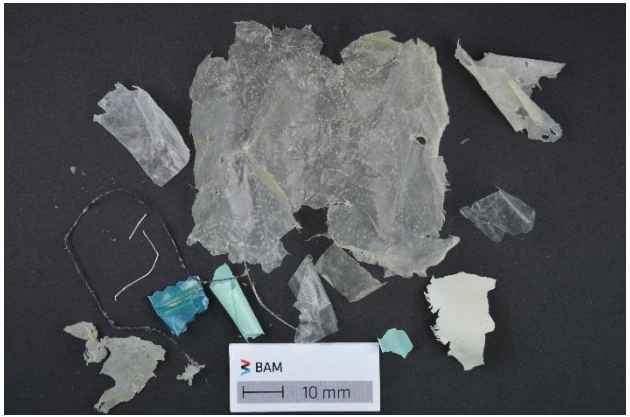
BAM sample set

- Sample set for BAM,
- Three size fractions
- Sampled around Corsica

< 5 mm

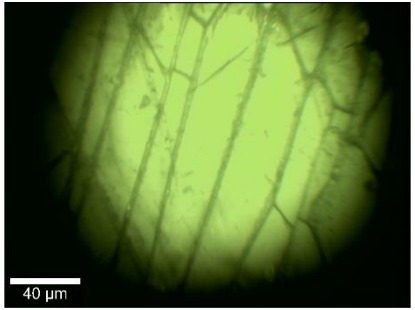
5 mm < X > 20 mm

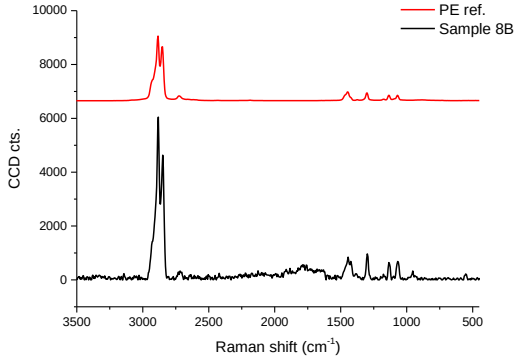
> 20 mm

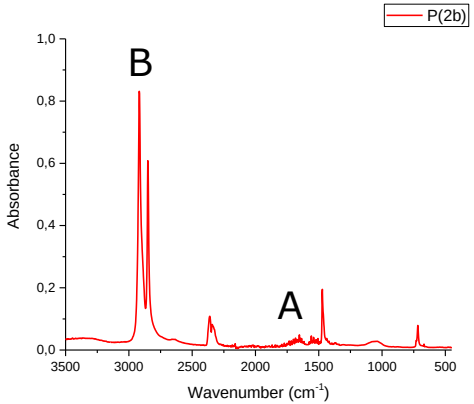


First results

- Polymer identification
  Via Raman & ATR-IR

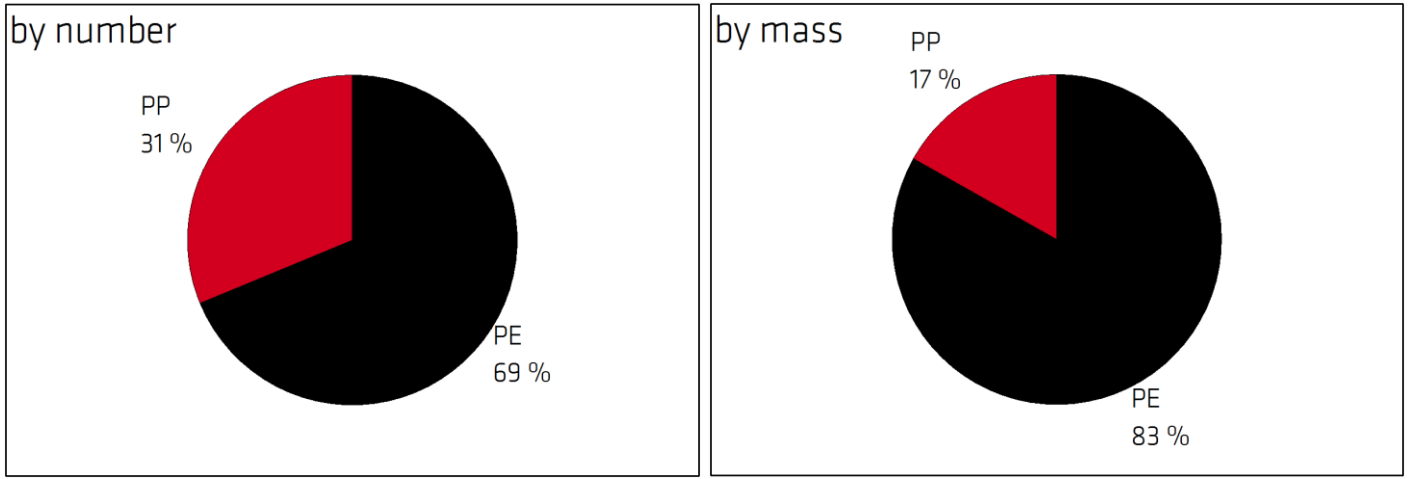






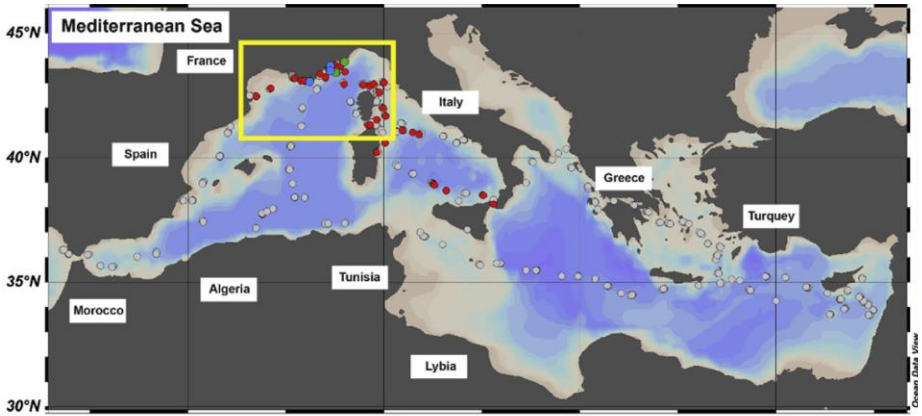
Sample set composition

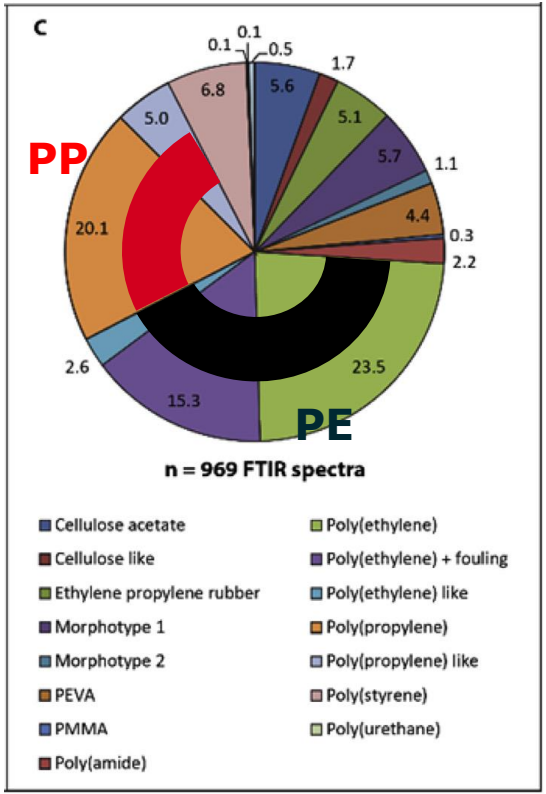
- Polymer identification:
  PE & PP only



Recently published

- Larger sample set with similar polymer composition
- Main focus: PE

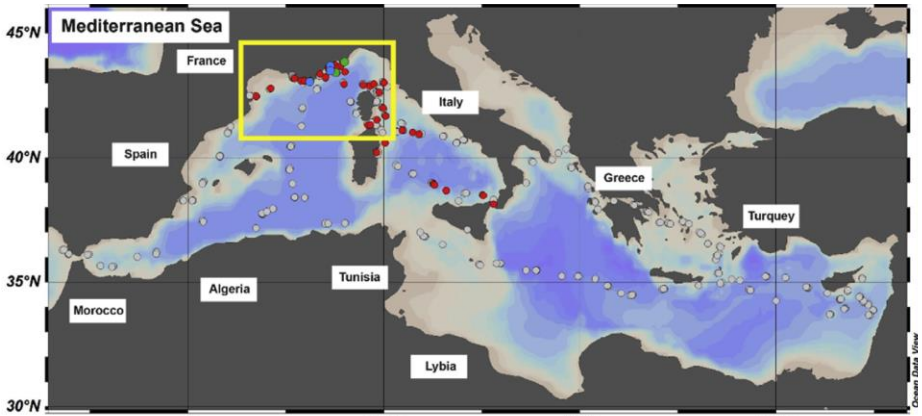




Kedzierski, M.; Falcou-Préfol, M.; Kerros, M. E.; Henry, M.; Pedrotti, M. L.; Bruzaud, S., A machine learning algorithm for high throughput identification of FTIR spectra: Application on microplastics collected in the Mediterranean Sea. *Chemosphere* **2019,** *234*, 242-251.

Sources and polymer age

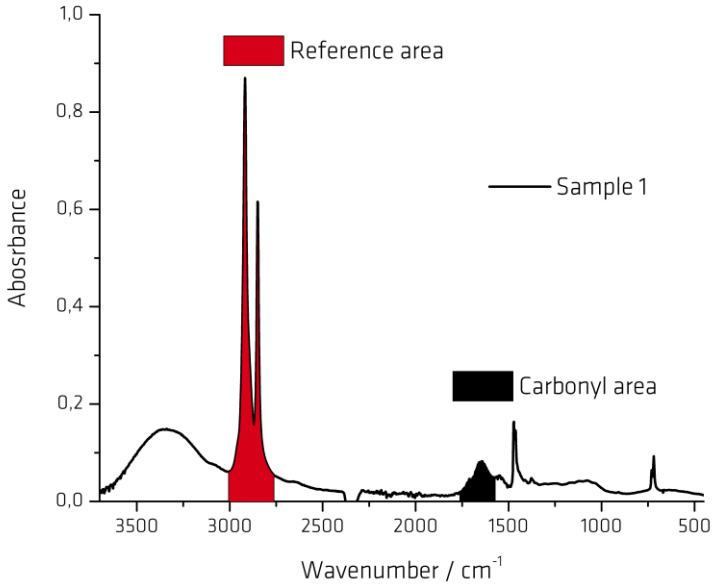
- Polymer aging status
- Knowledge about local currents



Kedzierski, M.; Falcou-Préfol, M.; Kerros, M. E.; Henry, M.; Pedrotti, M. L.; Bruzaud, S., A machine learning algorithm for high throughput identification of FTIR spectra: Application on microplastics collected in the Mediterranean Sea. *Chemosphere* **2019,** *234*, 242-251.

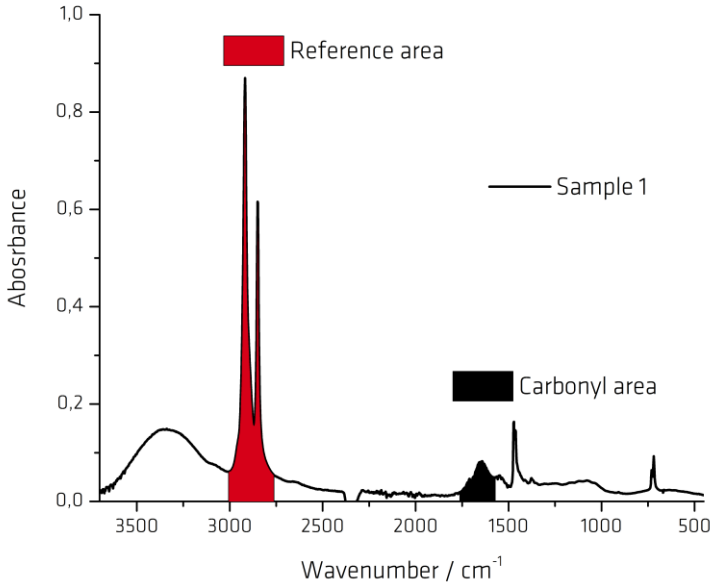
First hint: carbonyl index

- Polymer aging status: carbonyl index



First hint: carbonyl index

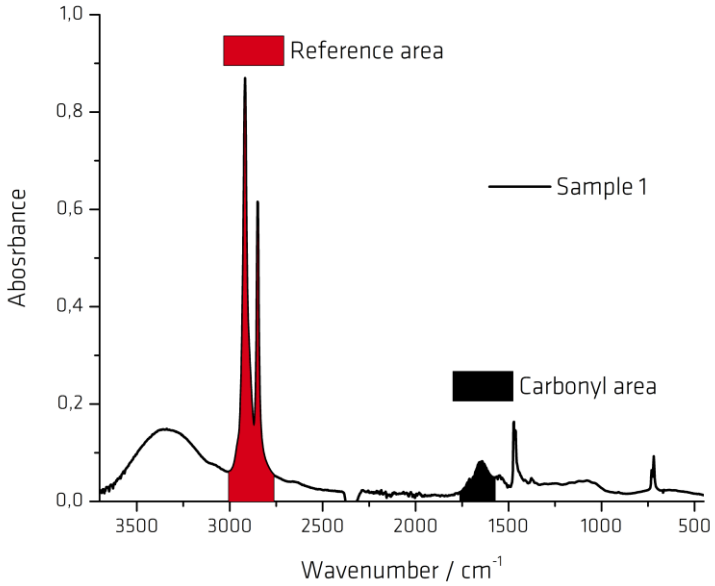
- Polymer aging status: carbonyl index



$$\text{Carbonyl index} = \frac{\text{Carbonyl area}}{\text{Reference area}}$$

First hint: carbonyl index

- Polymer aging status: carbonyl index



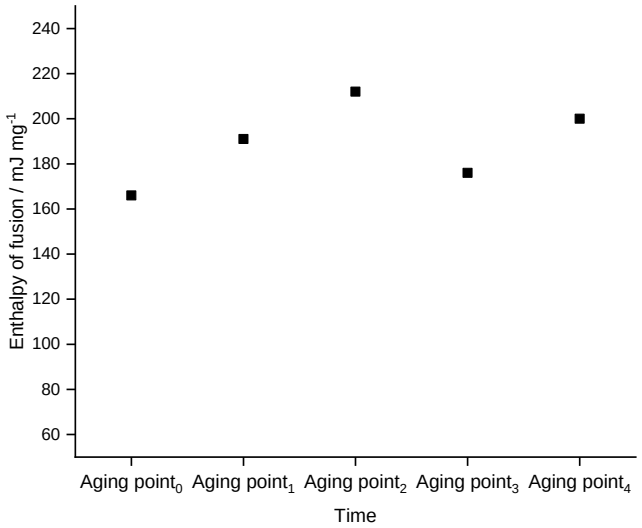
Sample Nr. 5-20 mm	Polymer	Carbonyl Content
1B	?	?
2B	PE	0.08
3B	PE	0.07
4B	PE	0.08
5B	PE	0.15
6B	PE	0.08
7B	PE	0.13
8B	PE	0.64
9B	PE	0.07
10B	PP	0.91
11B	?	0.21
12B	PE	0.13
13B	PE	0.38
14B	PE	0.05
15B	PP	0.16
16B	PE	0.06
17B	PP	0.09
18B	PP	0.07
19B	PE	0.14
20B	PE	0.20

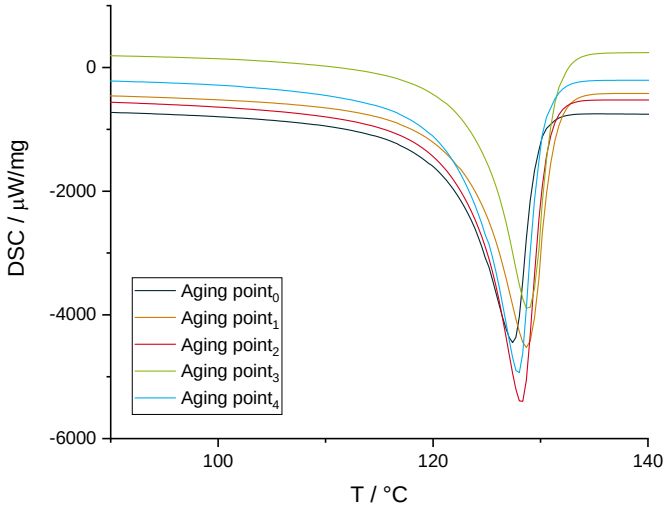
Lab aging studies

- Artificial aging of PE
- Sheets with 30 µm thickness
- UV-irradiated
- Elevated temperature

Lab aging studies -fusion enthalpy

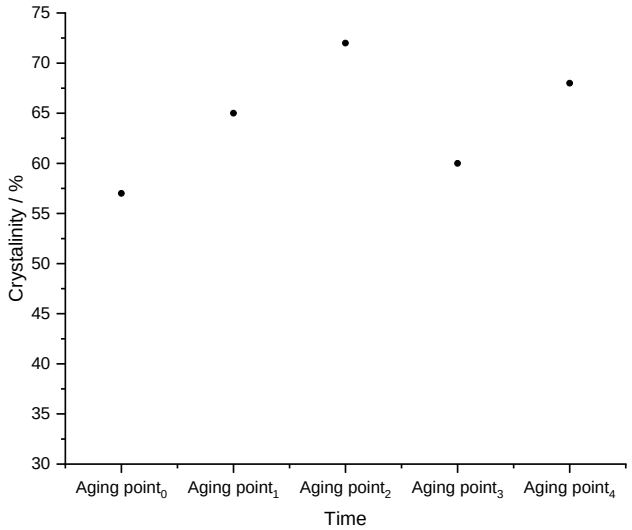
Characterisation: DSC

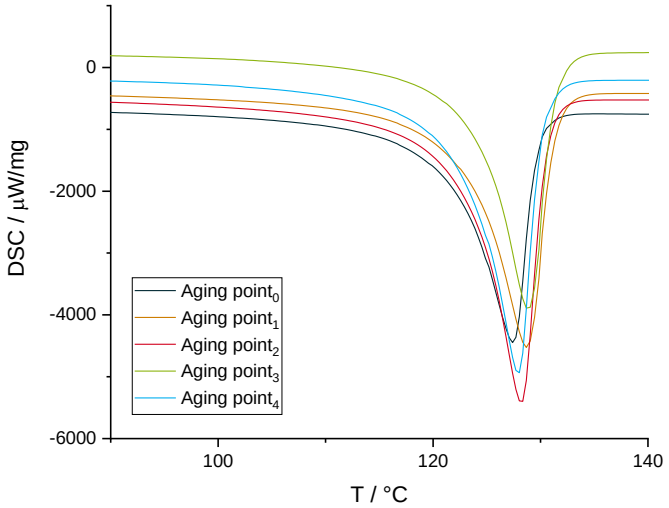




Lab aging studies -cristallinity

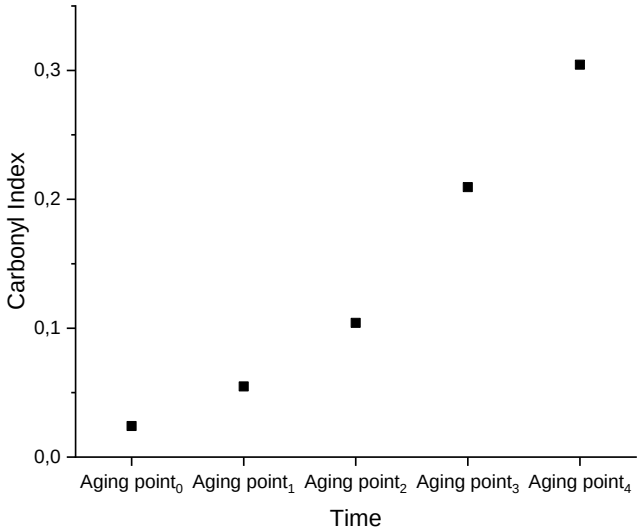
Characterisation: DSC





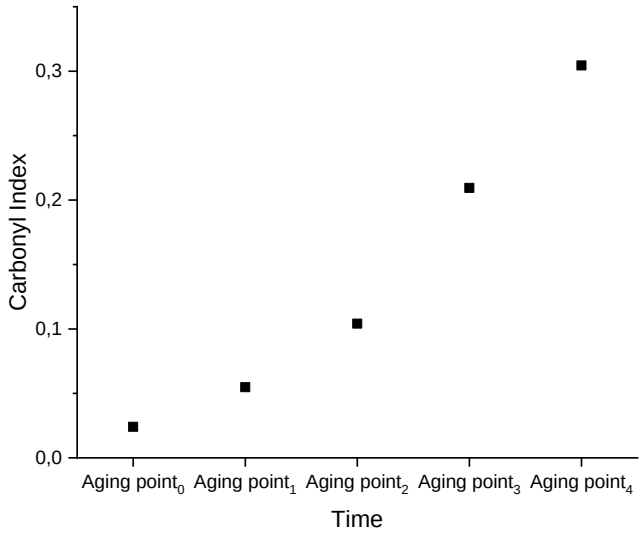
Lab aging studies -carbonyl index

Characterisation: ATR-IR, carbonyl index



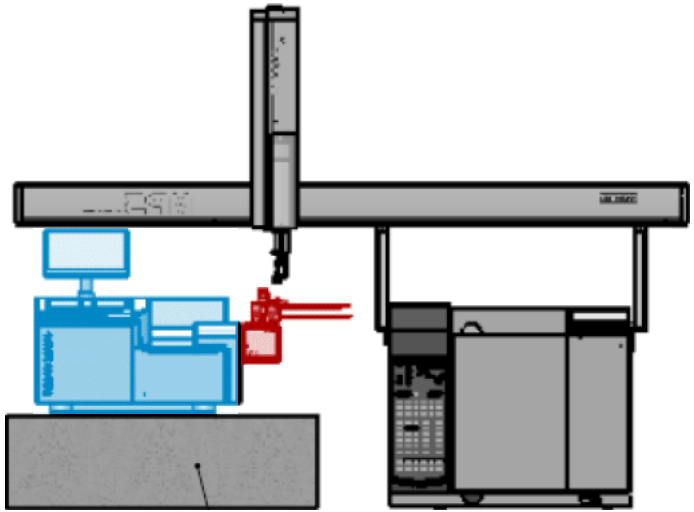
Lab aging studies -limitations

- ATR-IR surface-sensitive
- Surface biofilm causes high carbonyl signal
- Aging scenario inadequate
- Need for better (bulk) method



TED-GC-MS

Thermal **E**xtraction-**D**esorption **G**as **C**hromatography **M**ass **S**pectrometry
TED-GC-MS



- fully automated 2-step method
- 2.4 h/run
- main focus: Microplastics in environmental samples

TED-GC-MS
-working principle

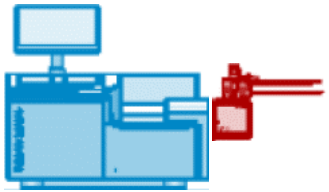
1st step

Thermo-balance (TGA)

- 500 µL (500 mg) sample
- heat to 600 °C
- 10 K/min
- N_2-atmossphere

TED-GC-MS
-working principle

connection

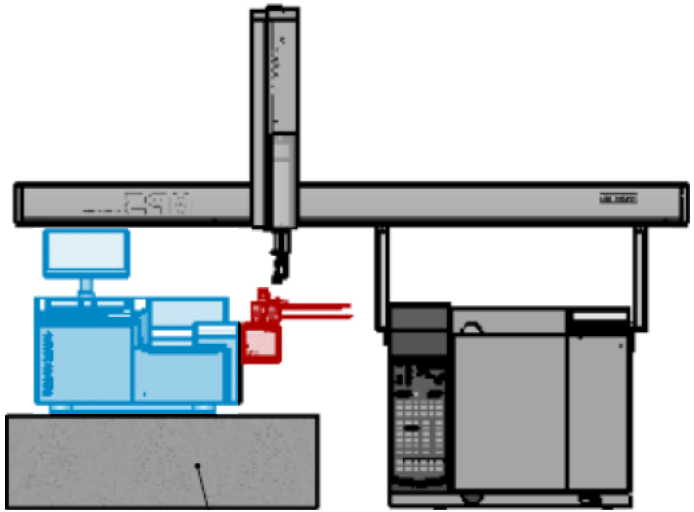


coupling device

- transfer &
- sorption of decomposition products
- on PDMS-bar
- time-controled selection of sampling window

TED-GC-MS
-working principle

2nd step

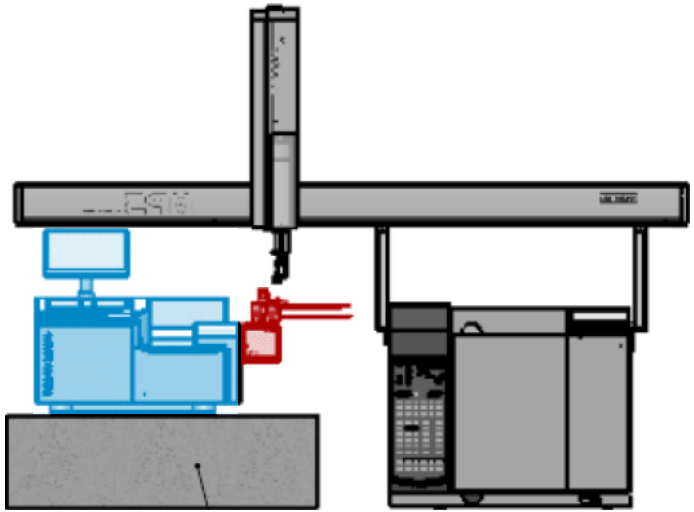


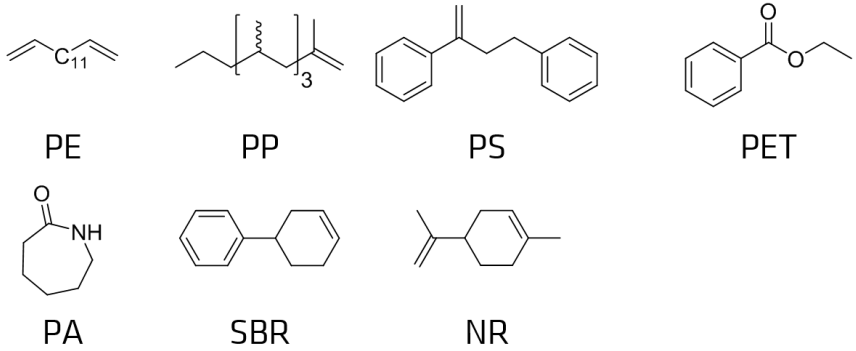
Thermodesorption-GC-MS

- remobilisation,
- separation &
- detection of decomposition products

TED-GC-MS -applications

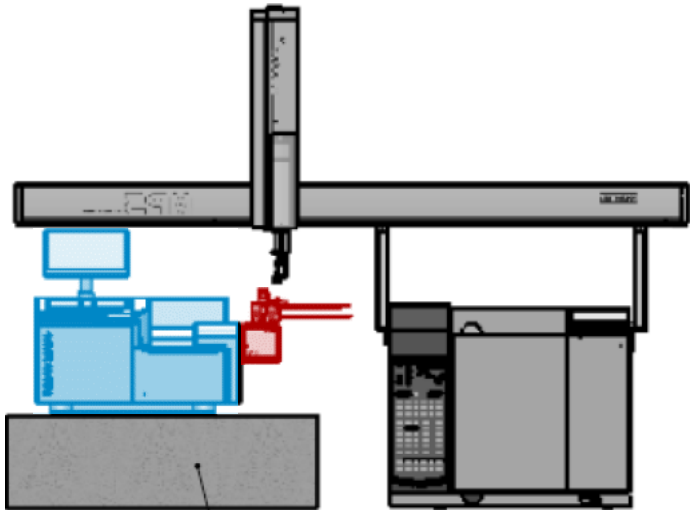
Decomposition products

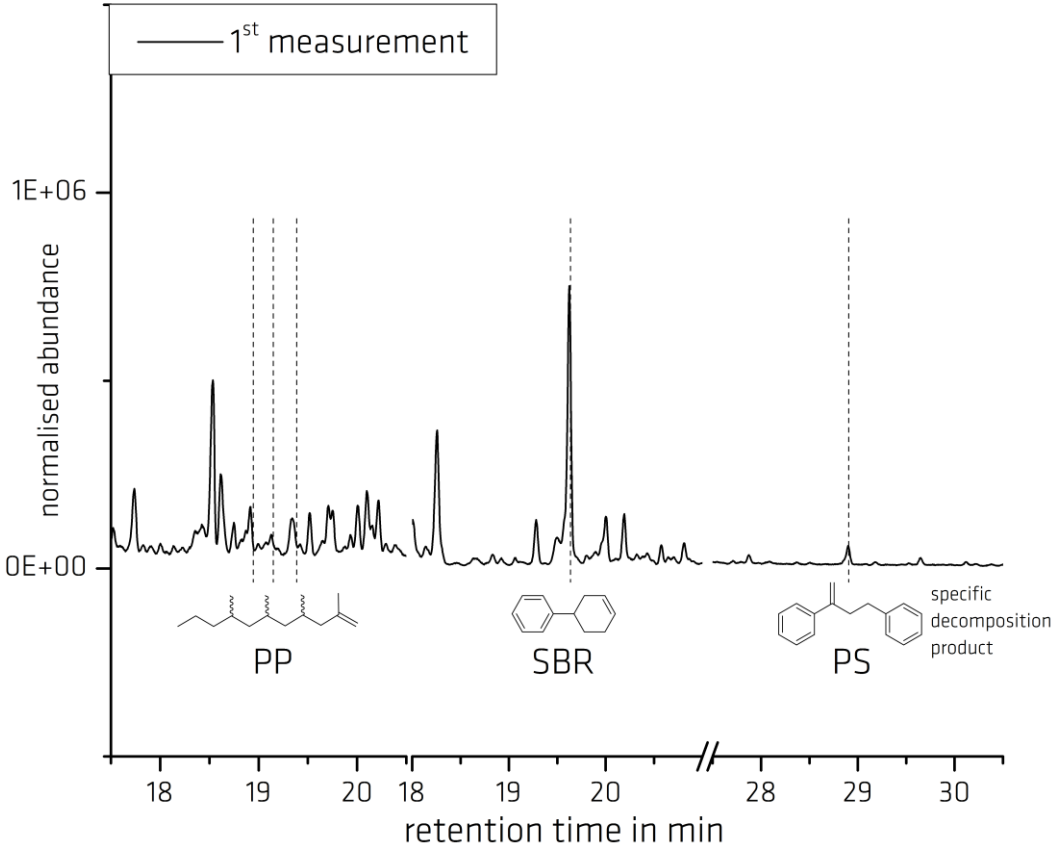




TED-GC-MS -applications

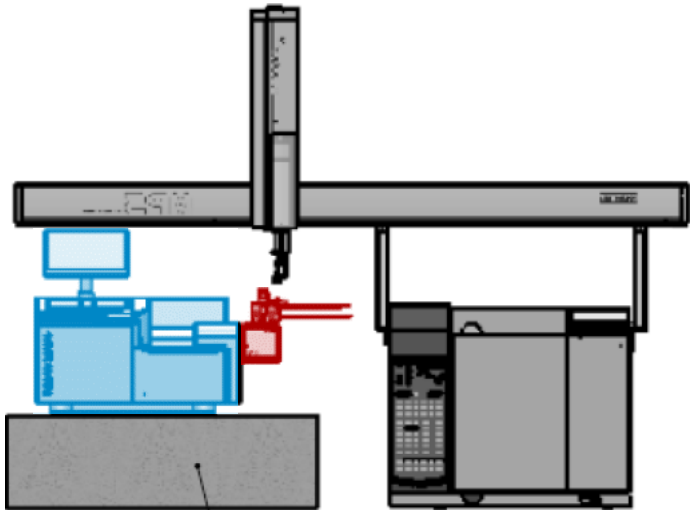
Environmental sample

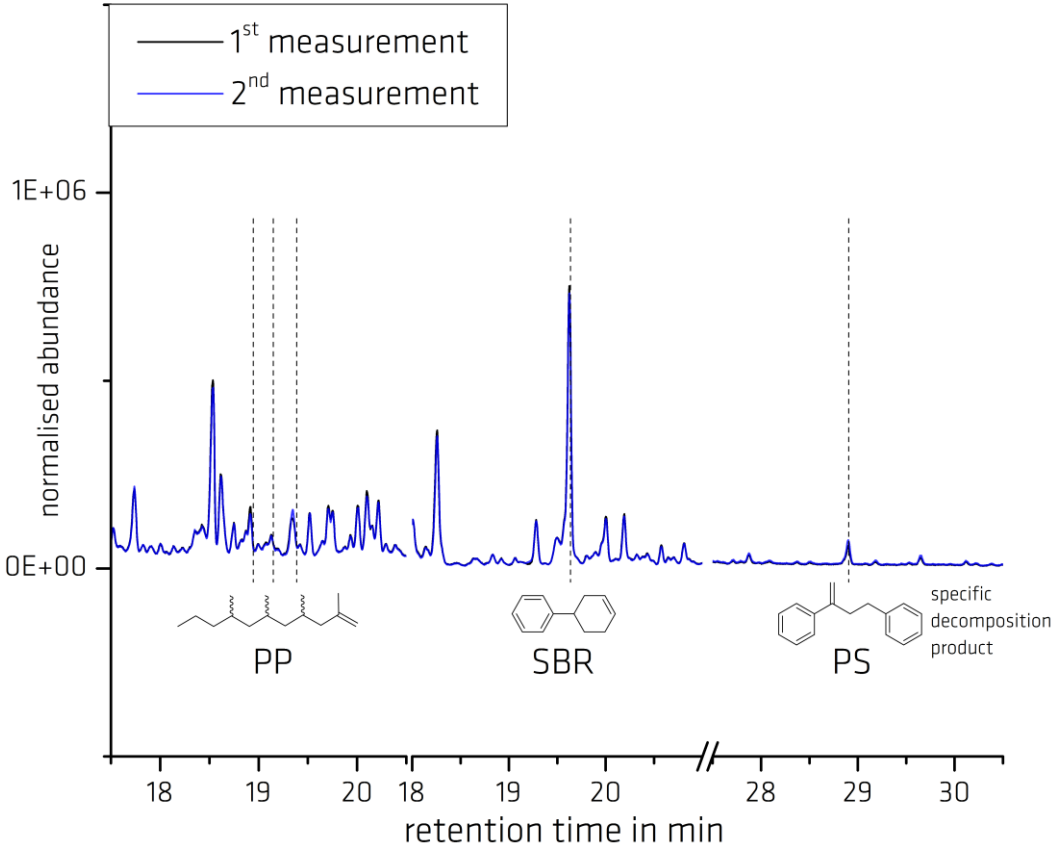




TED-GC-MS -applications

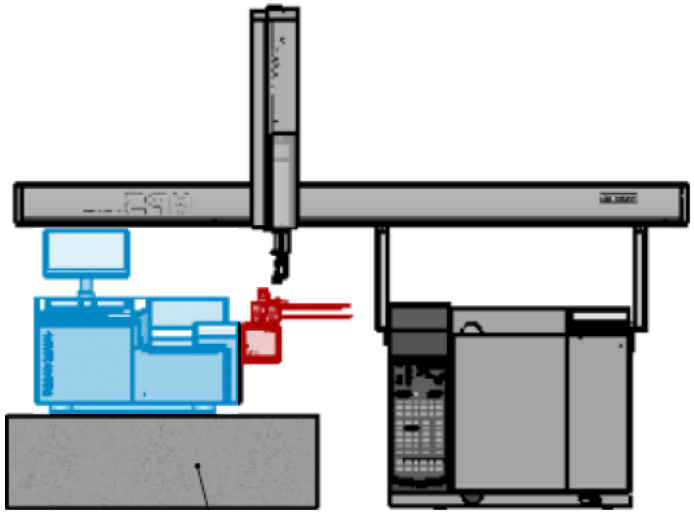
Environmental sample

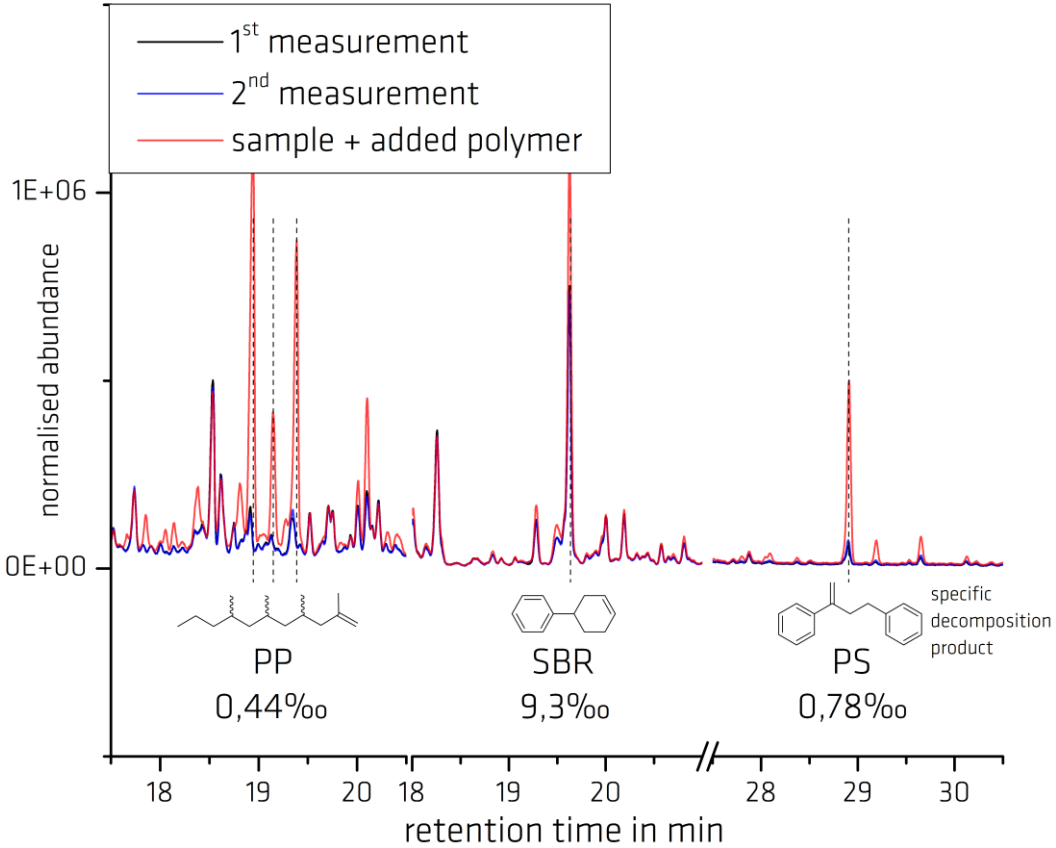




TED-GC-MS -applications

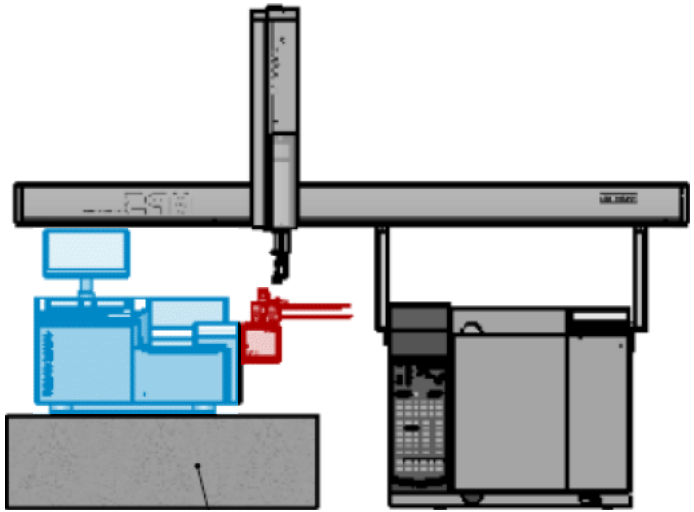
Environmental sample

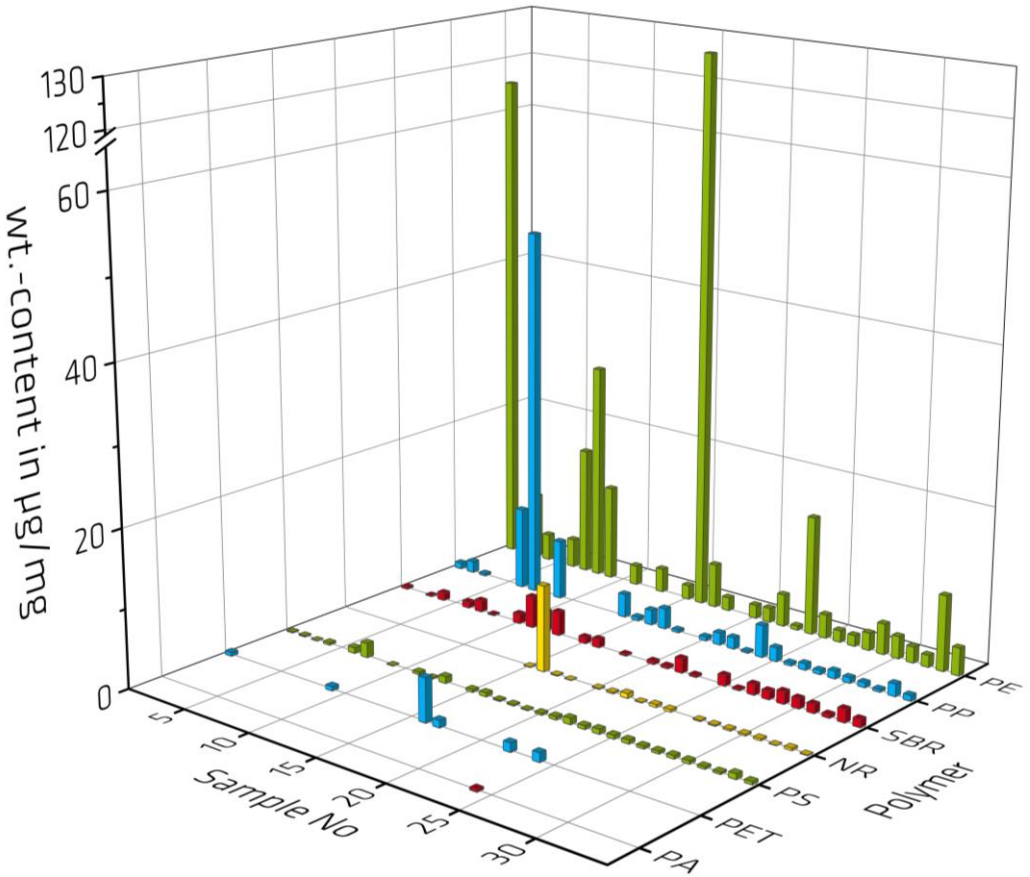




TED-GC-MS -applications

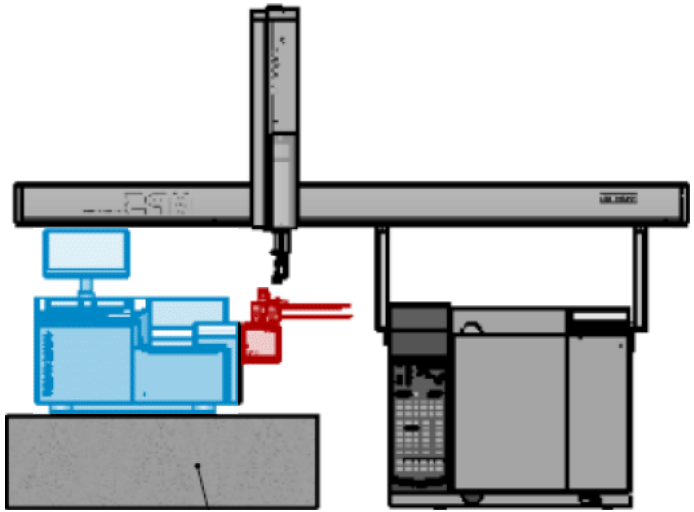
Environmental samples





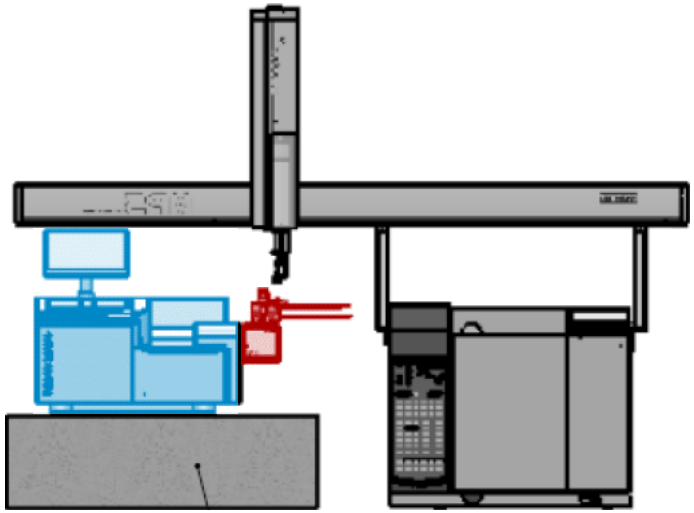
TED-GC-MS
-award winning method

Mülheim Water Award

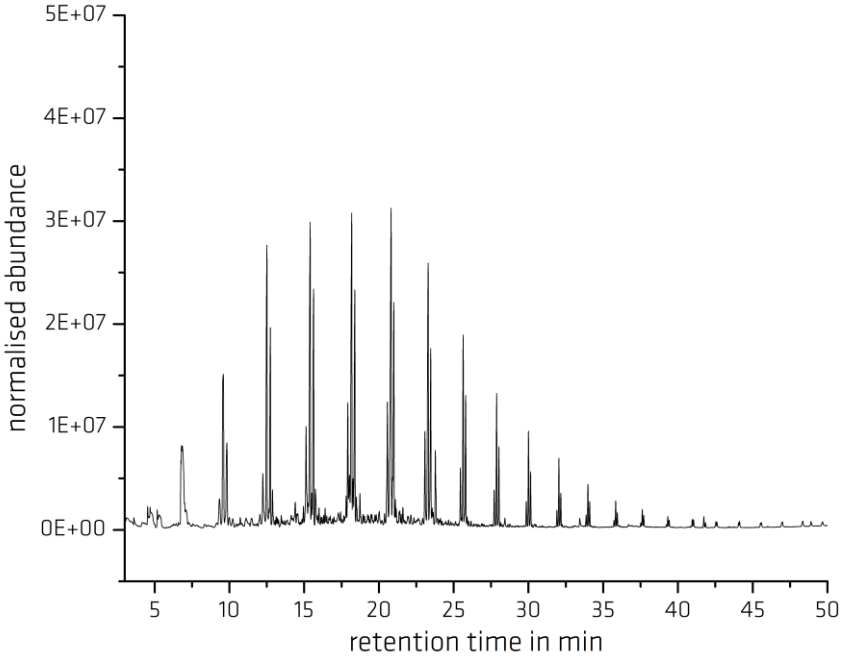


TED-GC-MS
-award winning method

Sold copies

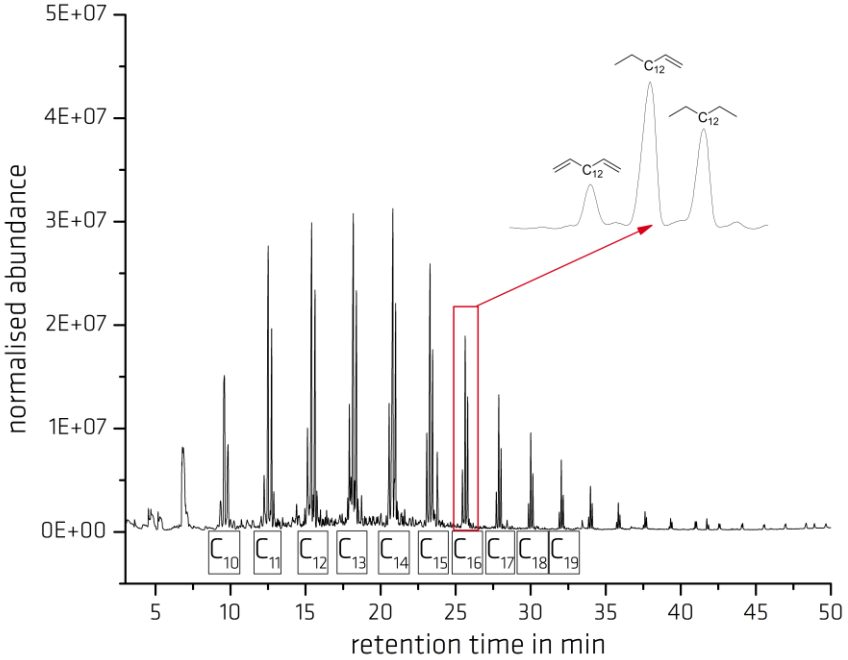


TED-GC-MS and PE

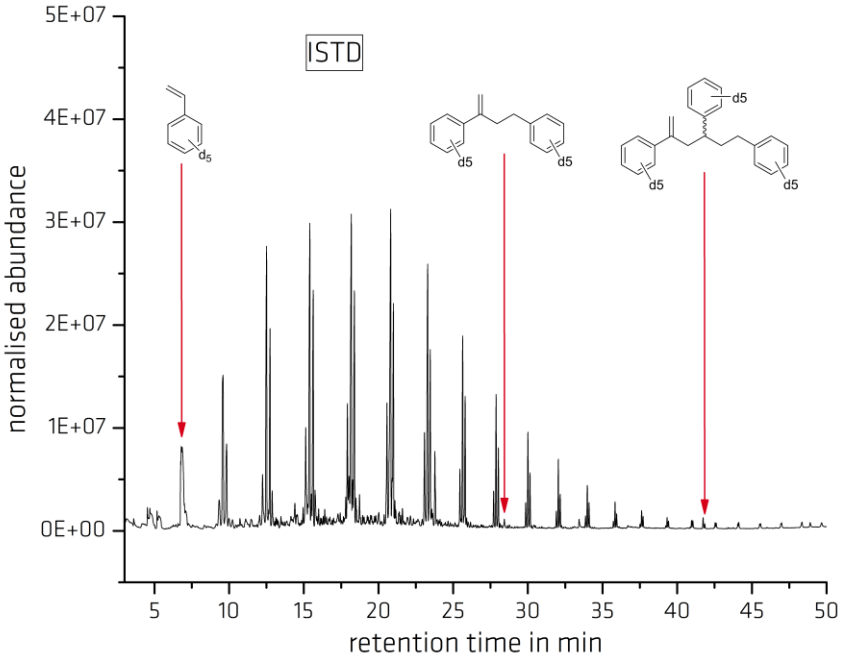


TED-GC-MS
Main decomposition products

- Main decomposition products of PE

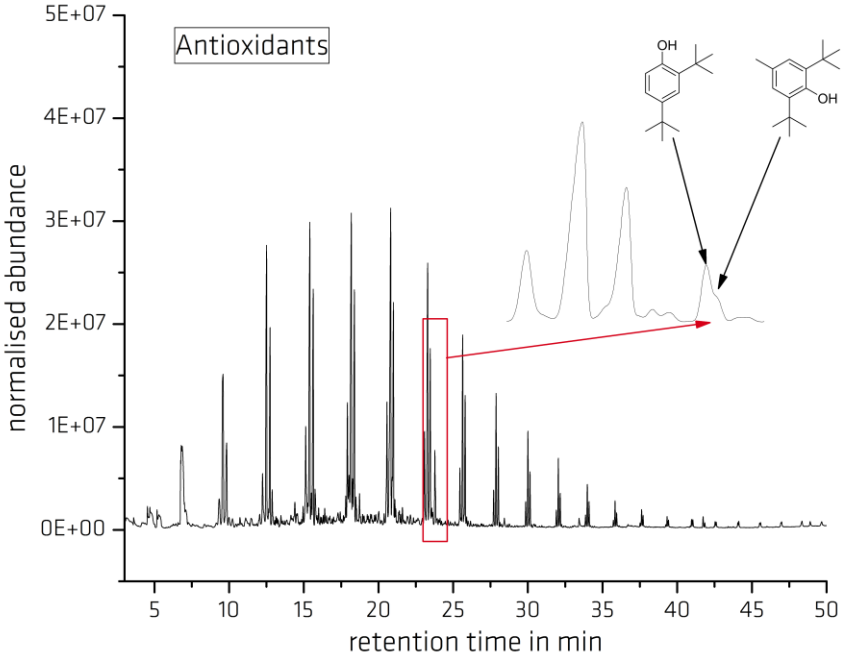


TED-GC-MS
Internal standard



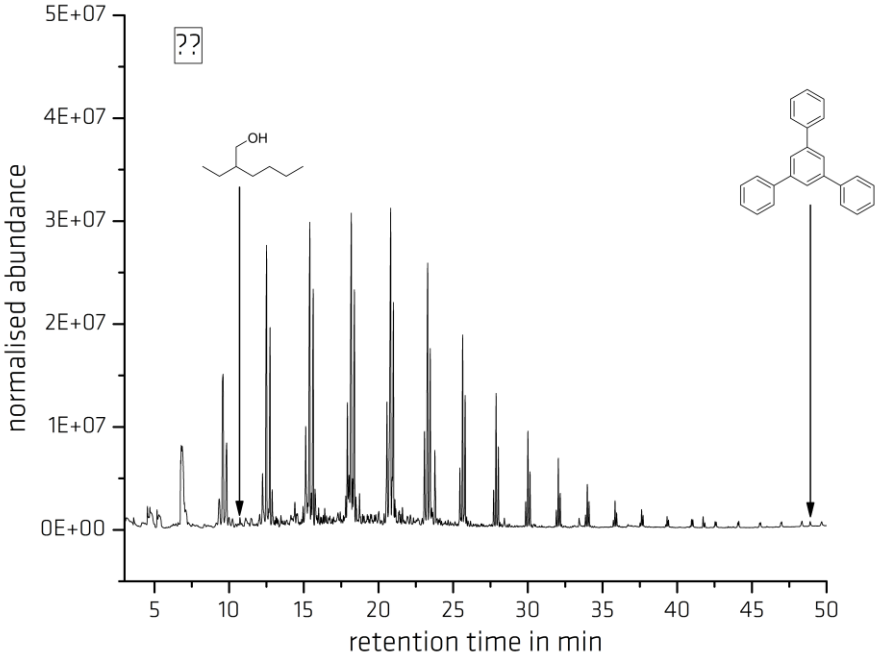
- Main decomposition products of PE
- Internal standard

TED-GC-MS
Antioxidants



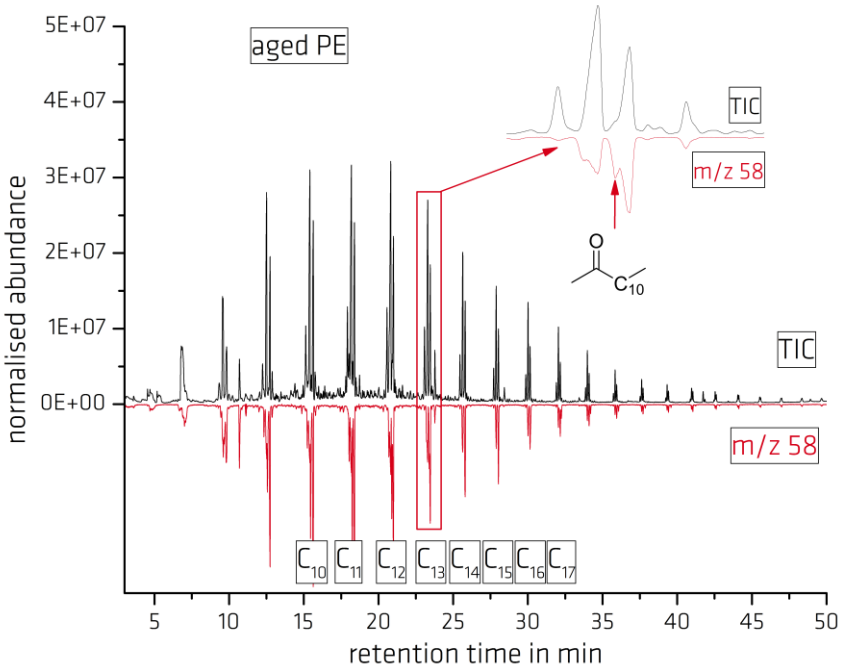
- Main decomposition products of PE
- Internal standard
- Anti-oxidants

TED-GC-MS
Auxiliary agents



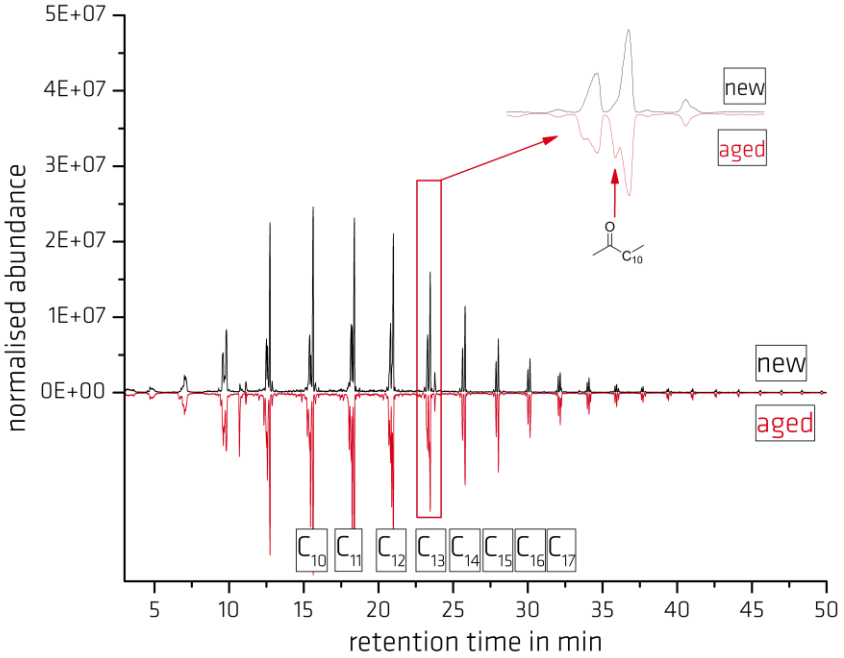
- Main decomposition products of PE
- Internal standard
- Anti-oxidants
- Auxiliary agents?

TED-GC-MS
Oxidation products



- Main decomposition products of PE
- Internal standard
- Anti-oxidants
- Auxiliary agents?
- Oxidation products: Ketones

TED-GC-MS
Oxidation products

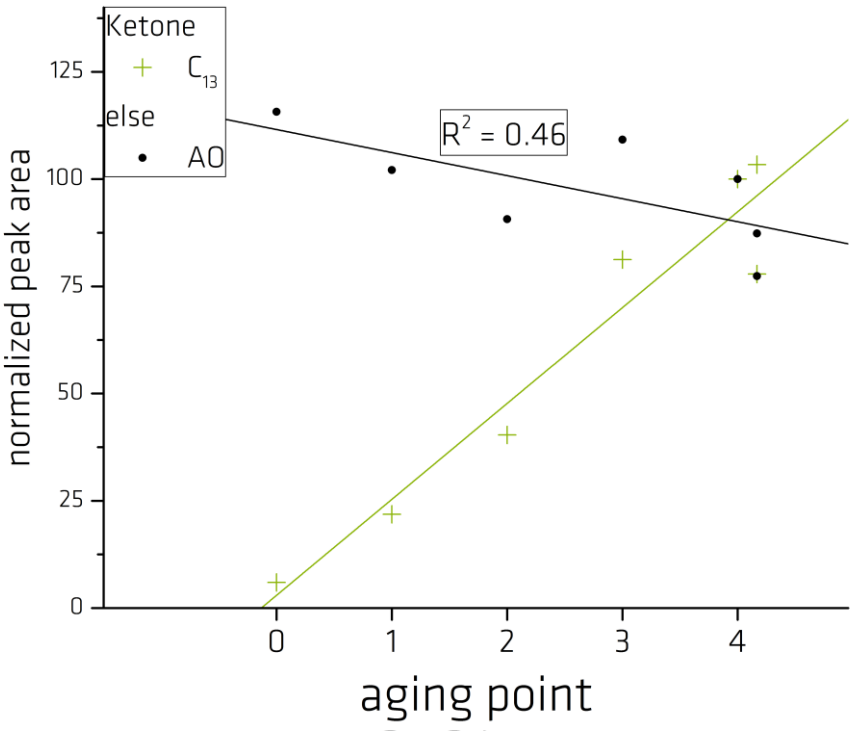


- Main decomposition products of PE
- Internal standard
- Anti-oxidants
- Auxiliary agents?
- Oxidation products: Ketones in
- increasing concentrations

TED-GC-MS
Oxidation products

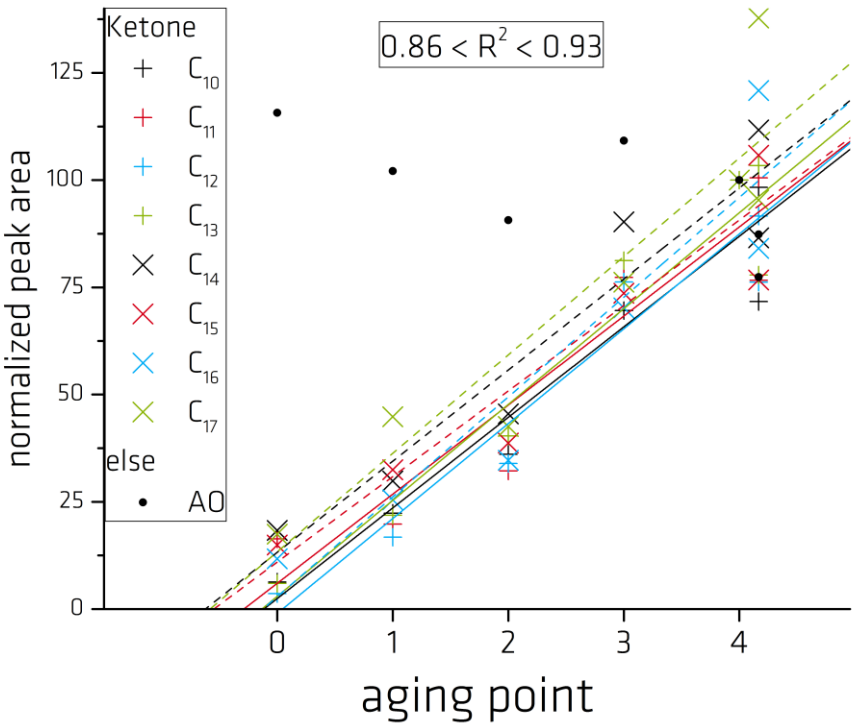
- Main decomposition products of PE
- Internal standard
- Anti-oxidants
- Auxiliary agents?
- Oxidation products: Ketones in
- Increasing concentrations &
- With good correlation to aging

TED-GC-MS
Oxidation products & Antioxidants



- Main decomposition products of PE
- Internal standard
- Anti-oxidants
- Auxiliary agents?
- Oxidation products: Ketones in
- Increasing concentrations &
- With good correlation to aging

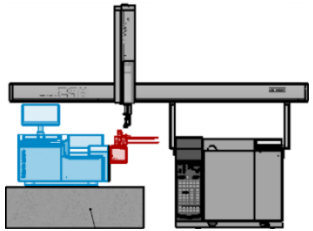
TED-GC-MS
Oxidation products

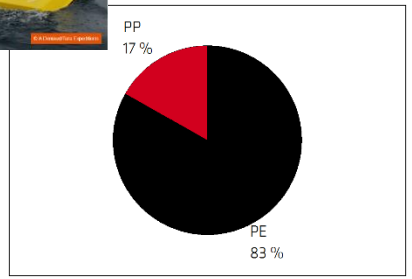


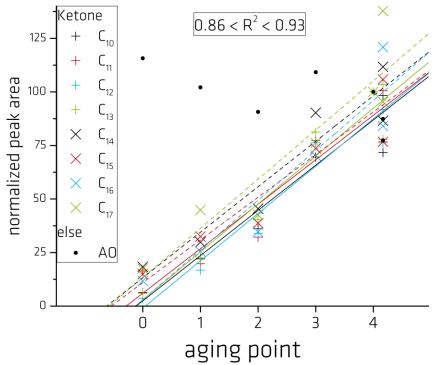
- Main decomposition products of PE
- Internal standard
- Anti-oxidants
- Auxiliary agents?
- Oxidation products: Ketones in
- Increasing concentrations &
- With good correlation to aging

Summary & Outlook

- Tara-Mediterranean Expedition 2014
- PE & PP most abundant
- Investigation of sources
  - Aging status
- First lab experiments: photooxidative
- Next lab experiments: marine aging
  - Both beyond the point of mech. failure
- Assessment of environmental samples

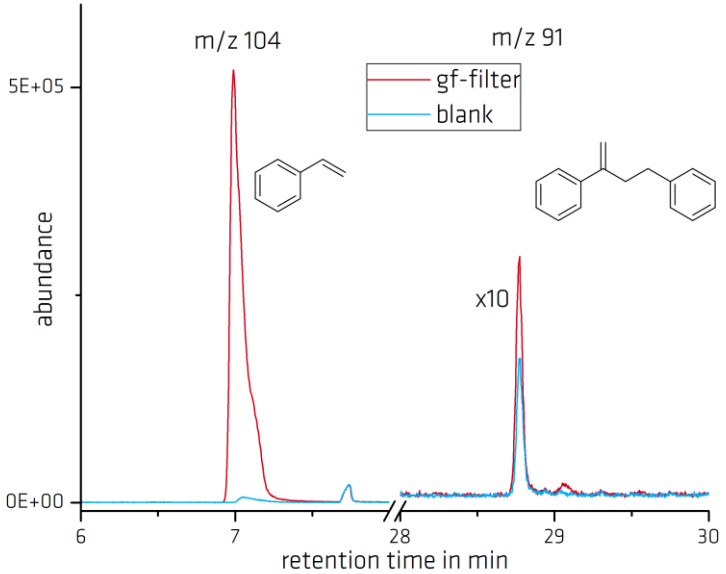




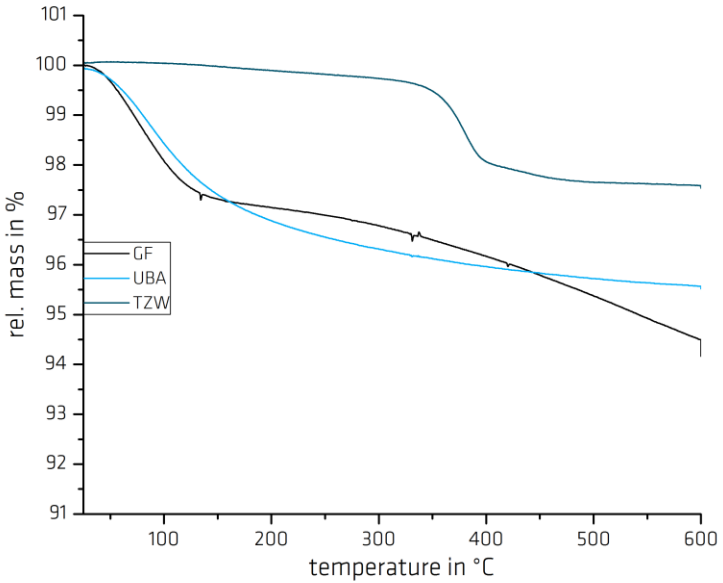


TED-GC-MS

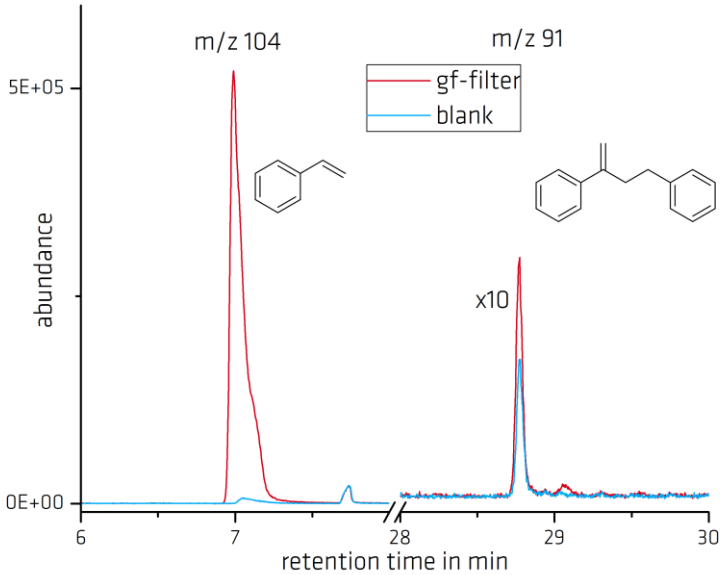
- Sampling campaign river Elbe
- Cellulose & glass fibre filter



TED-GC-MS
Sizing



- Sizing on glass fibre filter
- PS, PA, PET?



Thanks for your attention

Federal Ministry
of Education
and Research

Thanks to
Funding projects &
Colleaques