The influence of brominated flame-retardants on the pyrolysis behavior of plastics via TGA and Py-GC-MS

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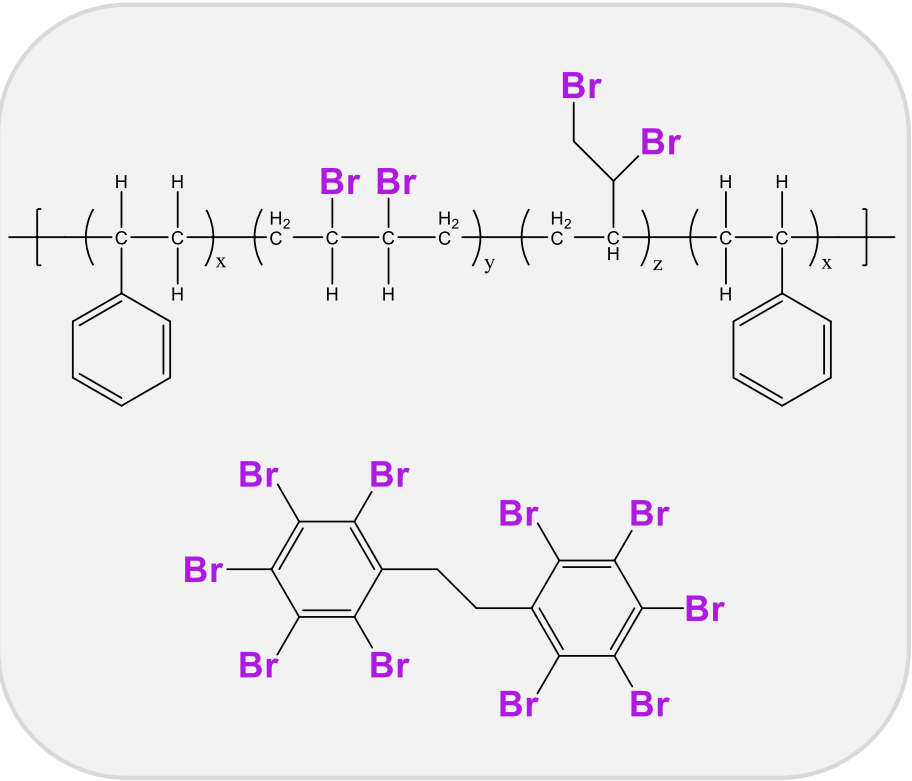
Background

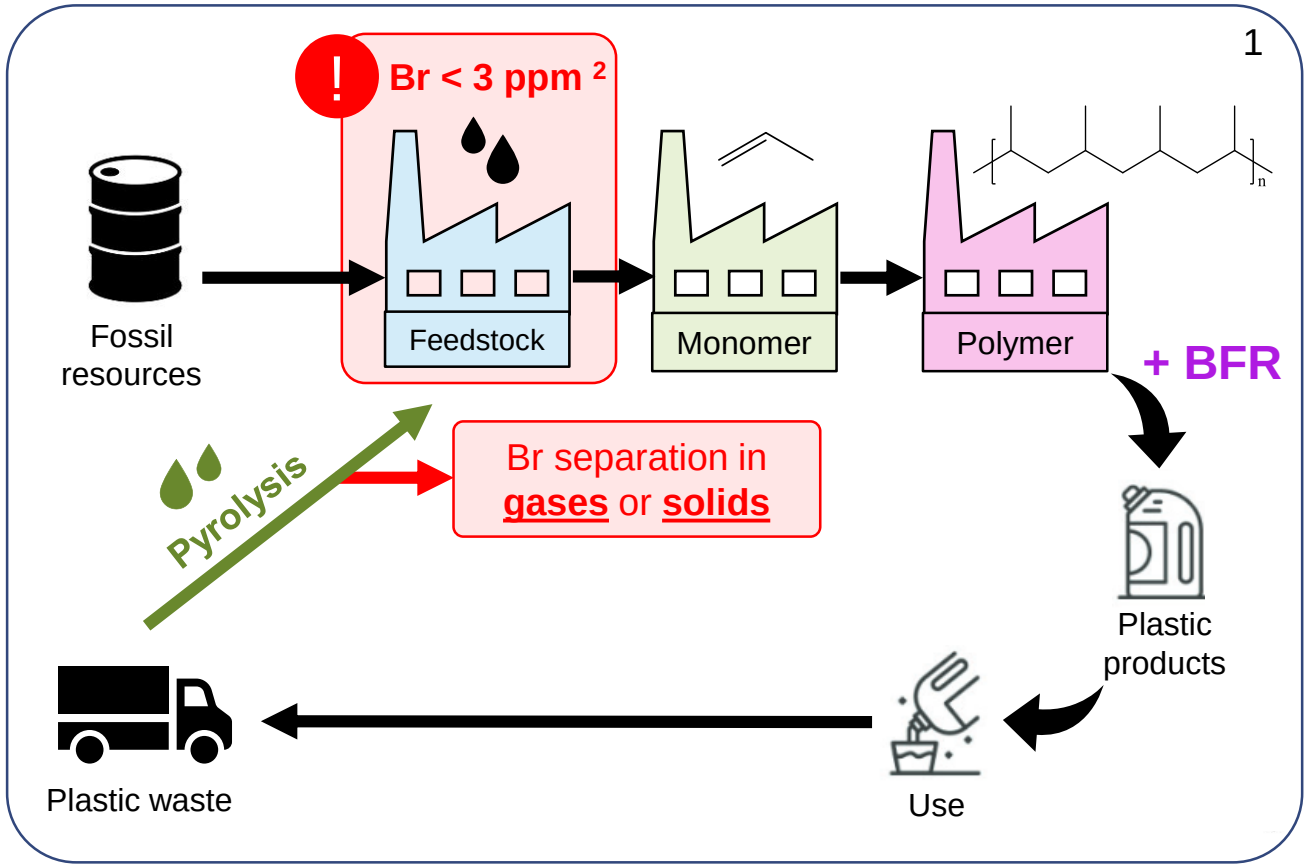
Examples of BFRs



BFRs: brominated flame retardants

Background

Goal: clean cycles, i.e. **bromine-free**

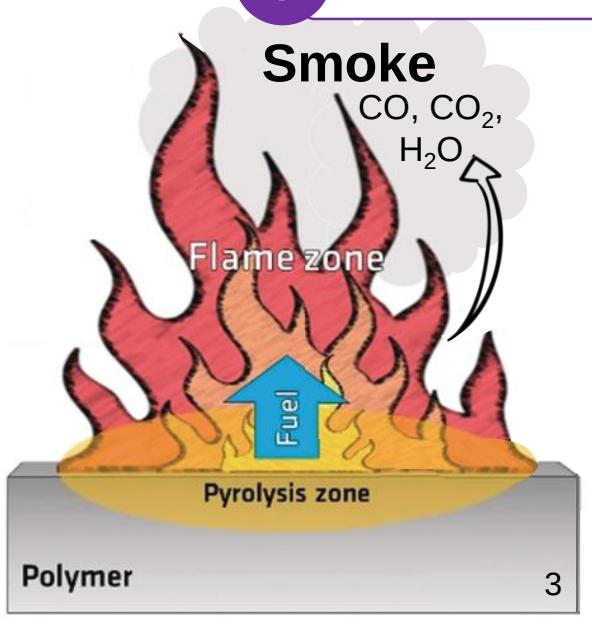


[1] Adapted and recreated from https://plasticseurope.org/knowledge-hub/chemical-recycling-mass-balance-explained/
[2] Cl threshold value for industrial steam crackers, from Kusenberg et al., 2022, DOI: 10.1016/j.wasman.2021.11.009

+ **HBr** forms in the pyrolysis zone

+ Literature: **temperature-staging** could lead to **Br separation** [5]

? Does this apply to **all BFRs**?



Radical scavenging flame inhibition [4]

HBr + OH· → **H2O** + Br·
HBr + H· → **H2** + Br·

Pyrolysis zone [4]

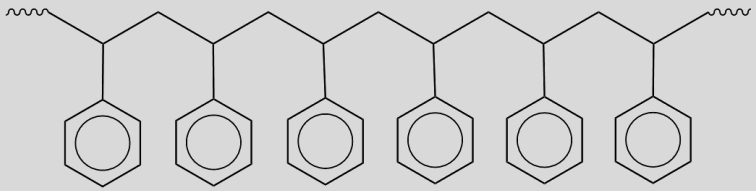
R-Br → R· + Br·
R-H + Br· → R· + **HBr**

[3] Adapted and recreated from Velencoso et al., 2018, DOI: 10.1002/anie.201711735
[4] Sai et al., 2022, DOI: DOI: 10.1002/sus2.73
[5] Barontini et al., 2006, DOI: 10.1016/j.jaap.2006.01.003

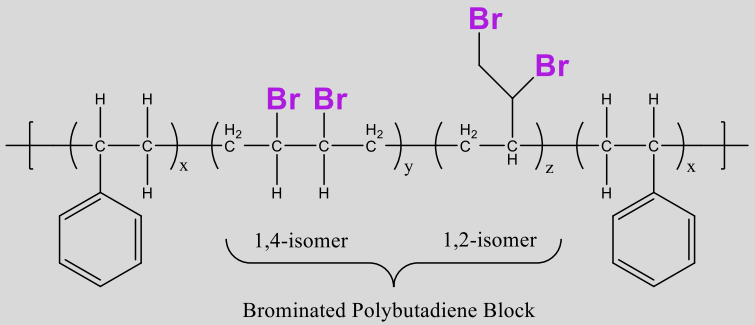
Test matrix

Model materials

System of compounds 1



Polystyrene (PS)

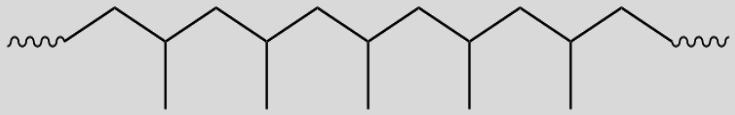


- 64 wt.-% Br
- Blended into PS
- 1 - 2 wt.-% in PS

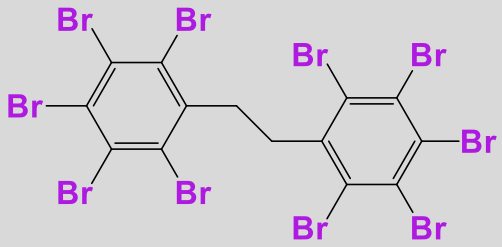
e.g. for **aliphatic** flame retardant (**ALIPH**)

PolyFR: block copolymer of polystyrene and brominated polybutadiene

System of compounds 2



Polypropylene (PP)



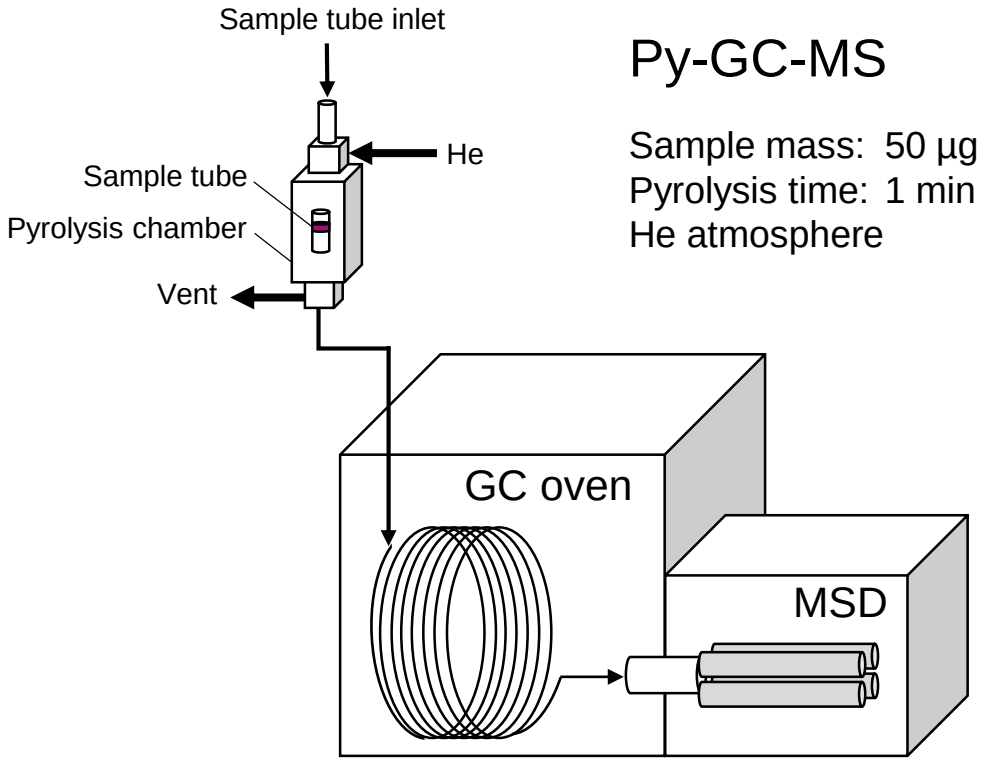
- 81 wt.-% Br
- Blended into PP
- 21 wt.-% in PP

e.g. for **aromatic** flame retardant (**AROM**)

DBDPE: decabromodiphenyl ethane

Test matrix

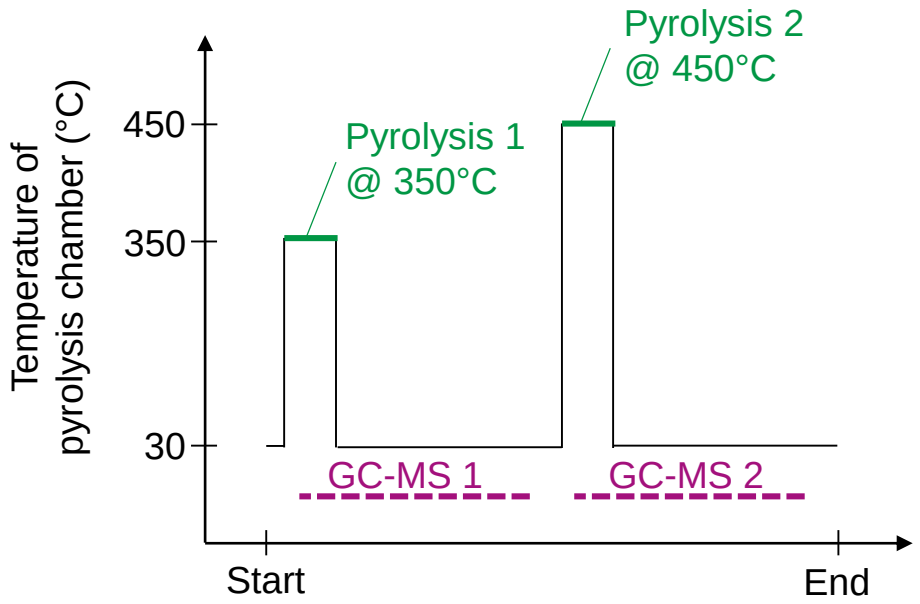
Analytical methods



Py-GC-MS

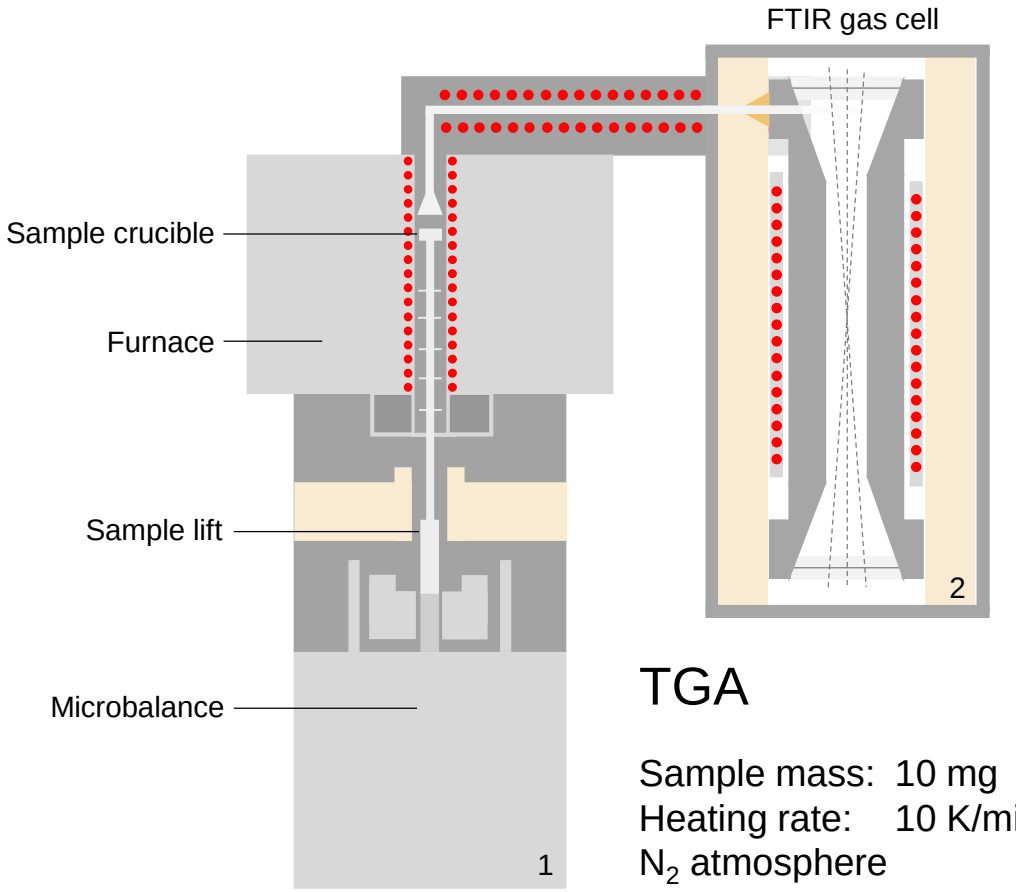
Sample mass: 50 µg
Pyrolysis time: 1 min
He atmosphere

Temperature-staged pyrolysis



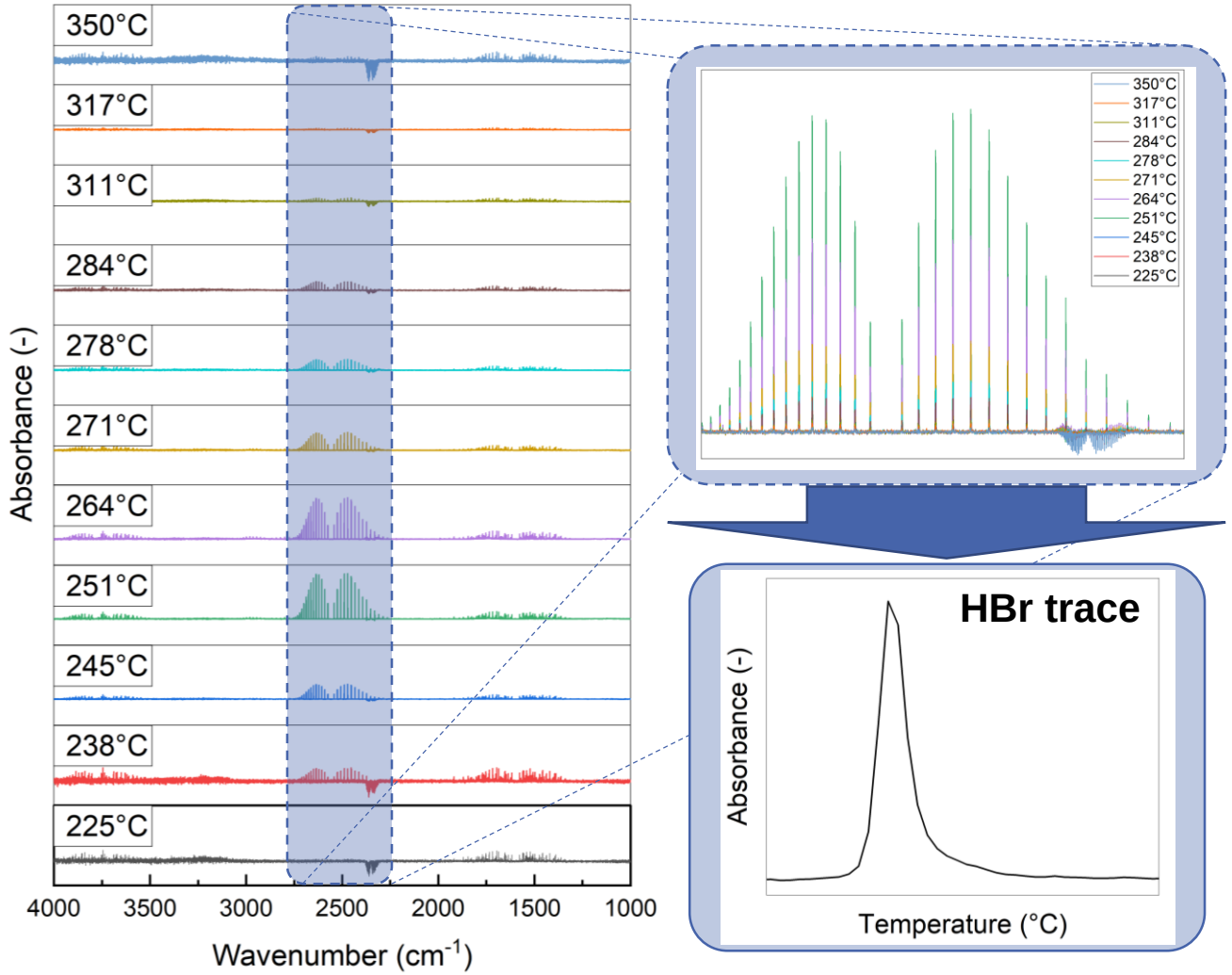
Test matrix

Analytical methods



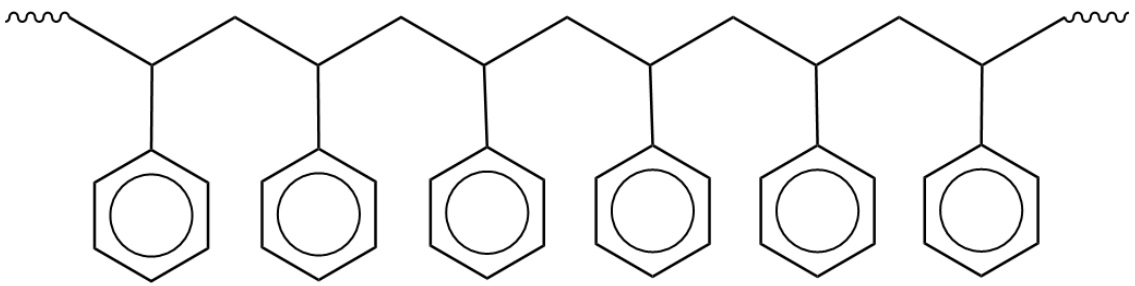
TGA

Sample mass: 10 mg
Heating rate: 10 K/min
N_2 atmosphere

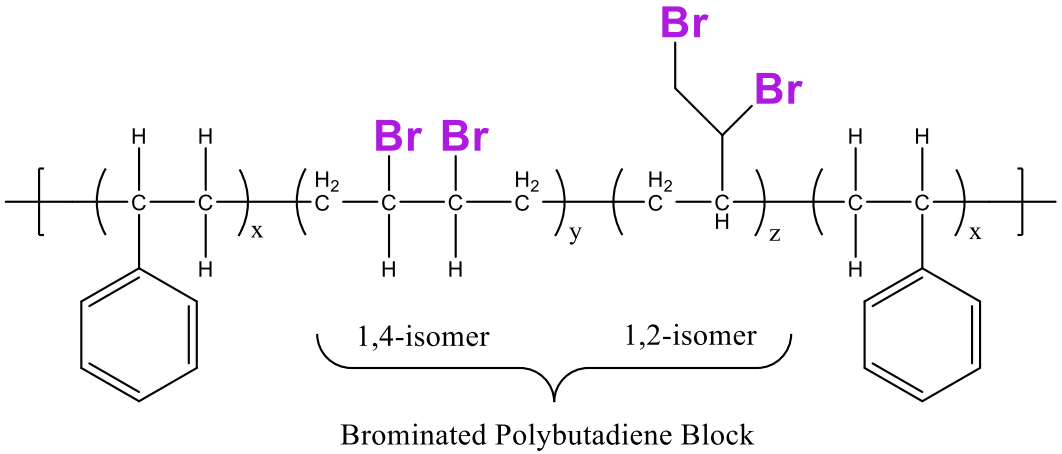


[1] Adapted and recreated from https://particletechlabs.com/analytical-testing/thermogravimetric-analysis/
[2] Adapted and recreated from https://www.azom.com/article.aspx?ArticleID=5951/

PS compounds



Polystyrene (PS)



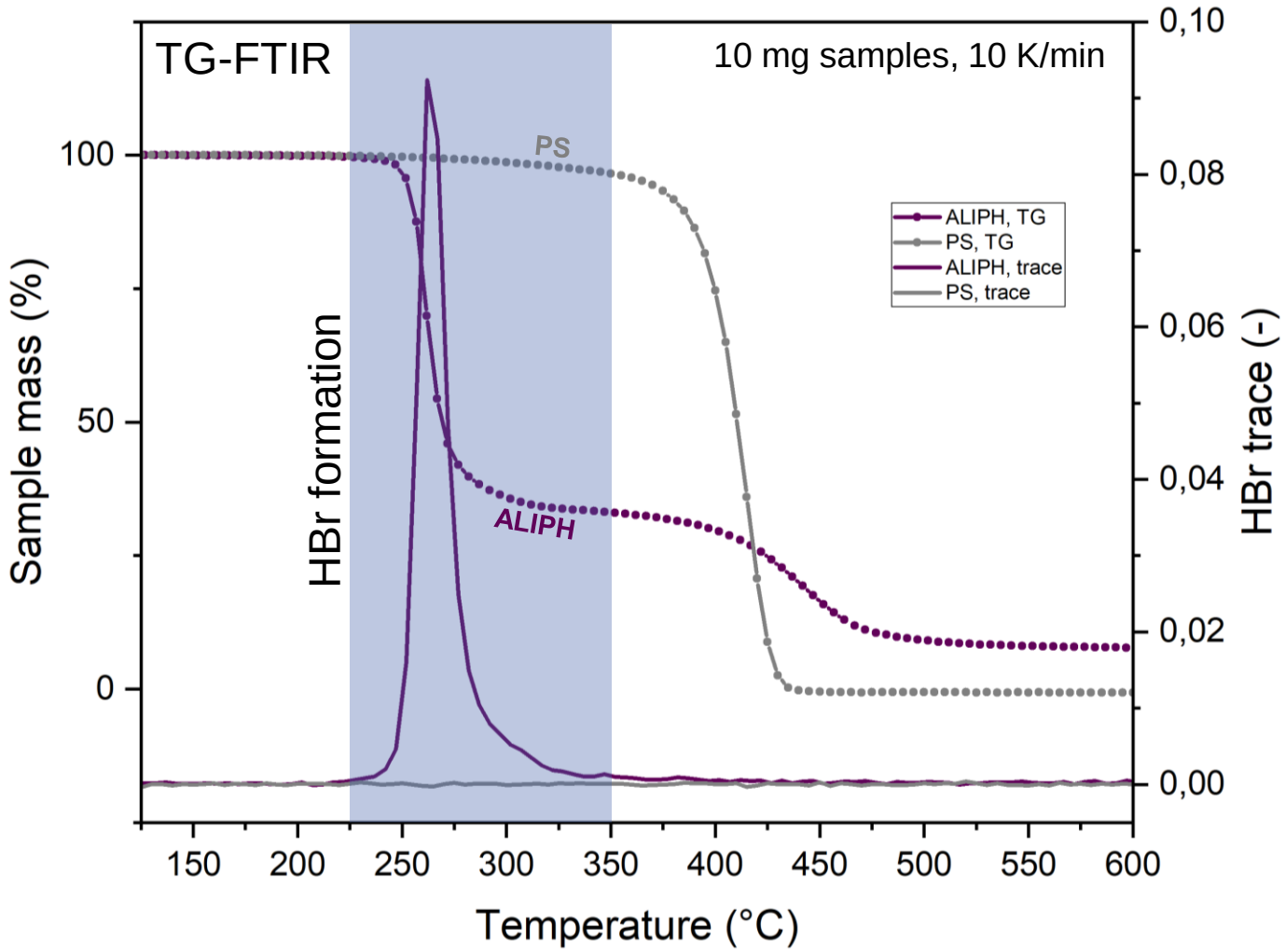
Aliphatic flame retardant (ALIPH)

PS compounds

HBr formation and tracing

Samples	Loading of ALIPH / wt.-%	Br content / wt.-%
ALIPH	100	64
PS	0	0
PS50ALIPH	50	32
PS26ALIPH	26	16.6
PS10ALIPH	10	6.4

Confirmed by Py-GC-MS:
HBr is detected only in **stage 1**
(@ 350°C)



PS compounds

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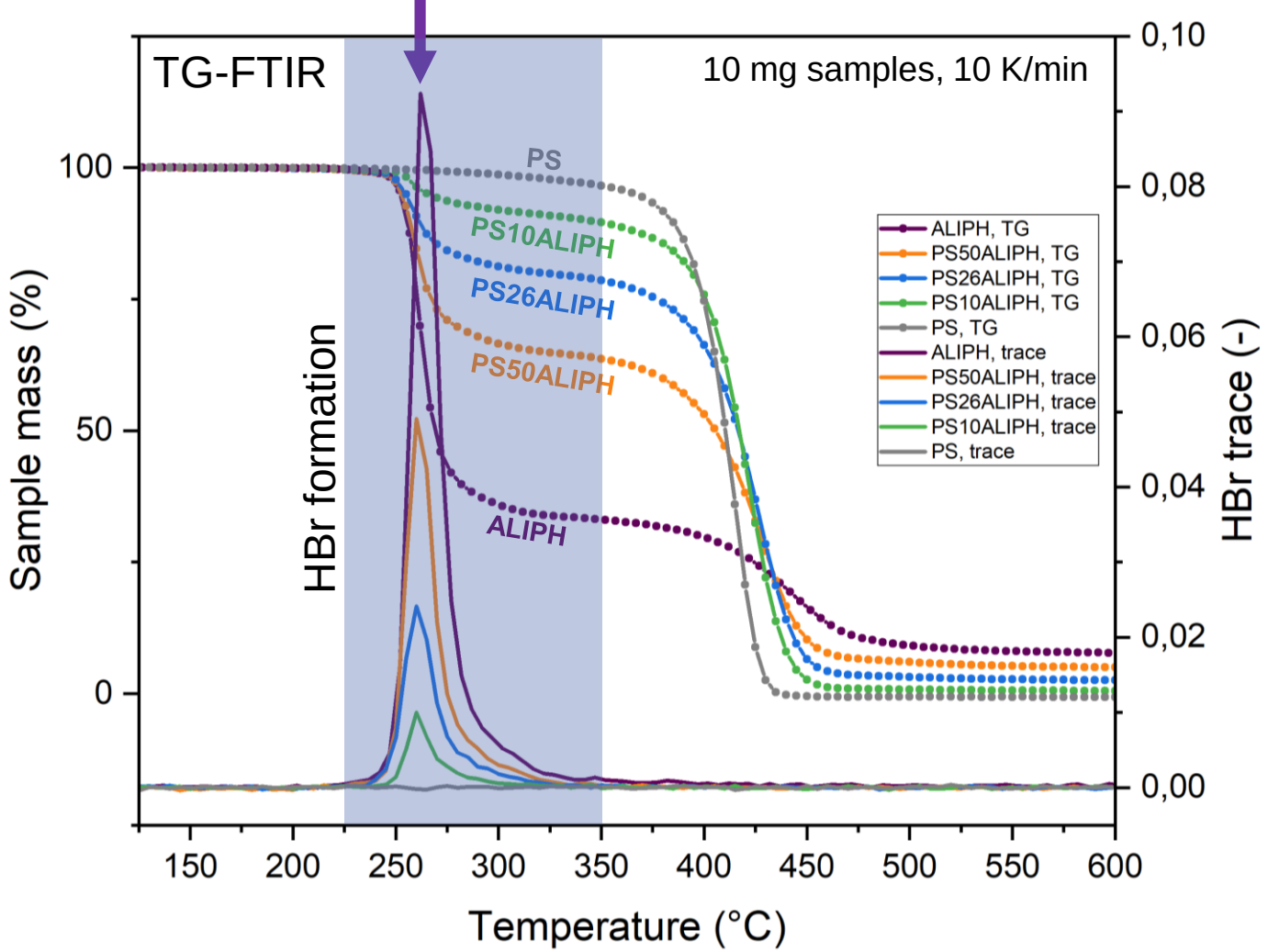
Samples	Loading of ALIPH / wt.-%	Br content / wt.-%
ALIPH	100	64
PS	0	0
PS50ALIPH	50	32
PS26ALIPH	26	16.6
PS10ALIPH	10	6.4

1 HBr trace max @ **260°C**

2 **Linear correlation** between ALIPH-loading & trace area

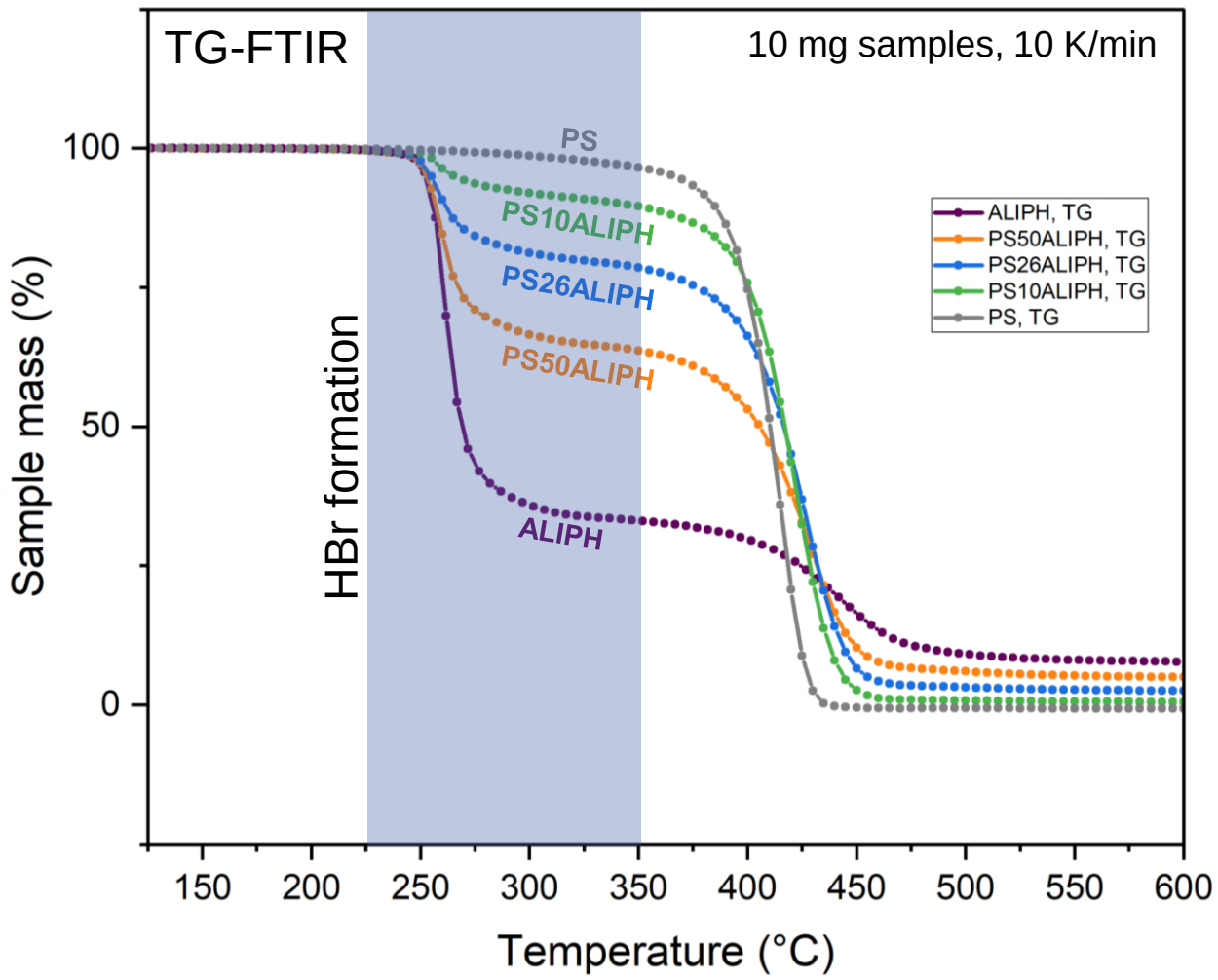


PS compounds

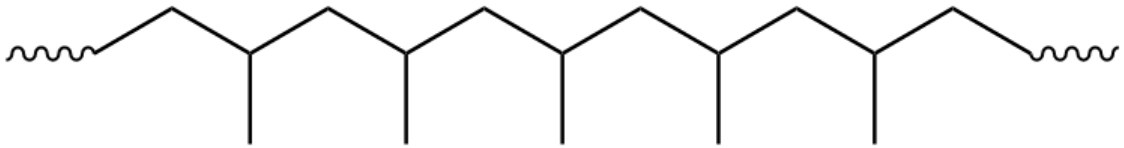
HBr formation and tracing

3 **Mass loss** in the 1st step (< 350°C) is close to **Br-levels** in the samples

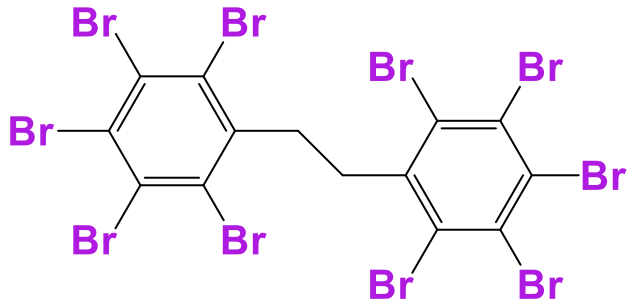
Samples	Br content / wt.-%	% sample mass loss @ 350°C
ALIPH	64	68
PS50ALIPH	32	34
PS26ALIPH	16.6	22
PS10ALIPH	6.4	10



PP compounds



Polypropylene (PP)



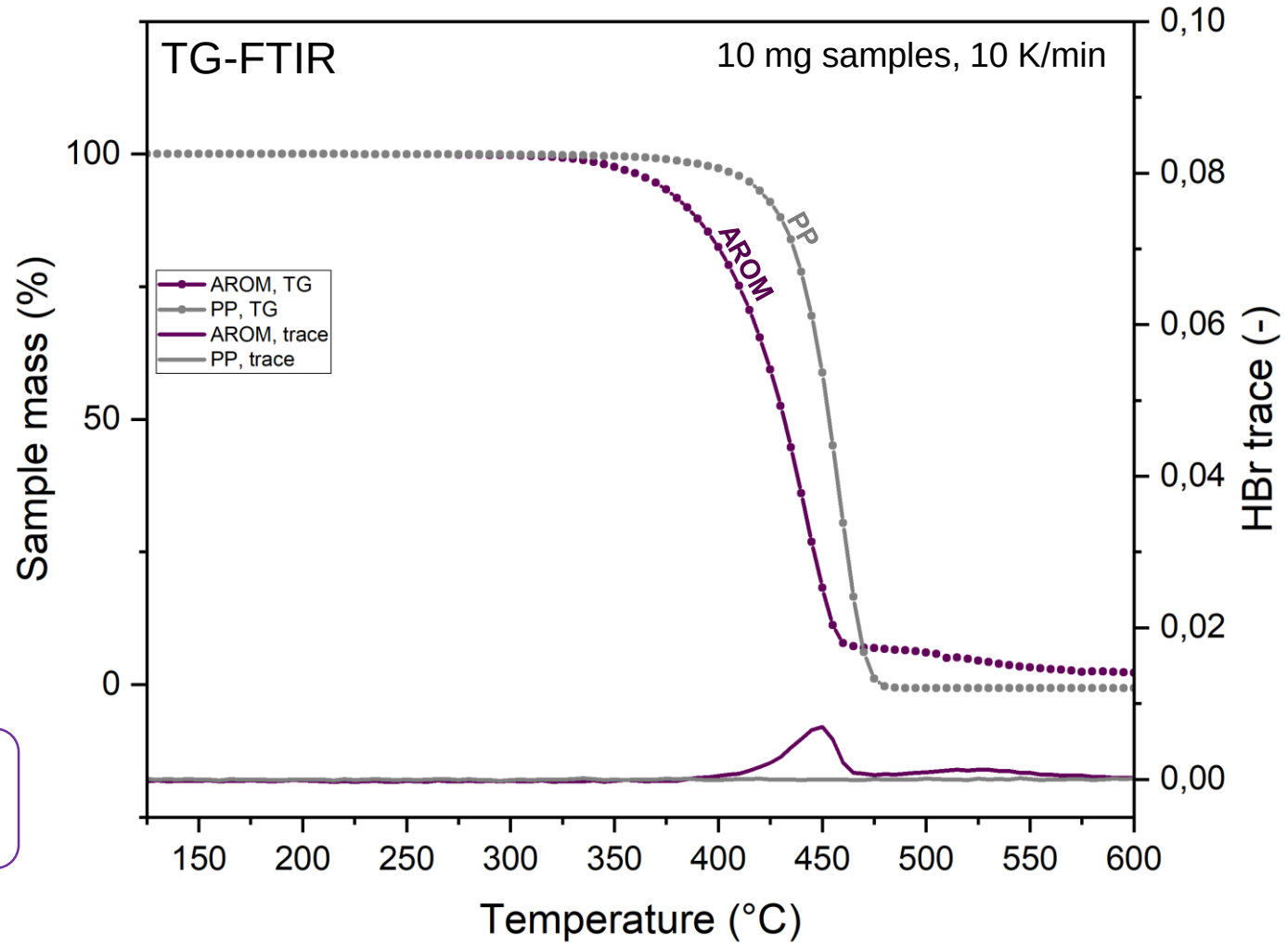
Aromatic flame retardant (AROM)

PP compounds

HBr formation and tracing

Samples	Loading of AROM / wt.-%	Br content / wt.-%
AROM	100	81
PP	0	0
PP50AROM	50	41
PP21AROM, compounded	21	17
PP10AROM	10	8.1

! Confirmed by Py-GC-MS:
AROM yields **aromatic Br-HCs** (C6+)

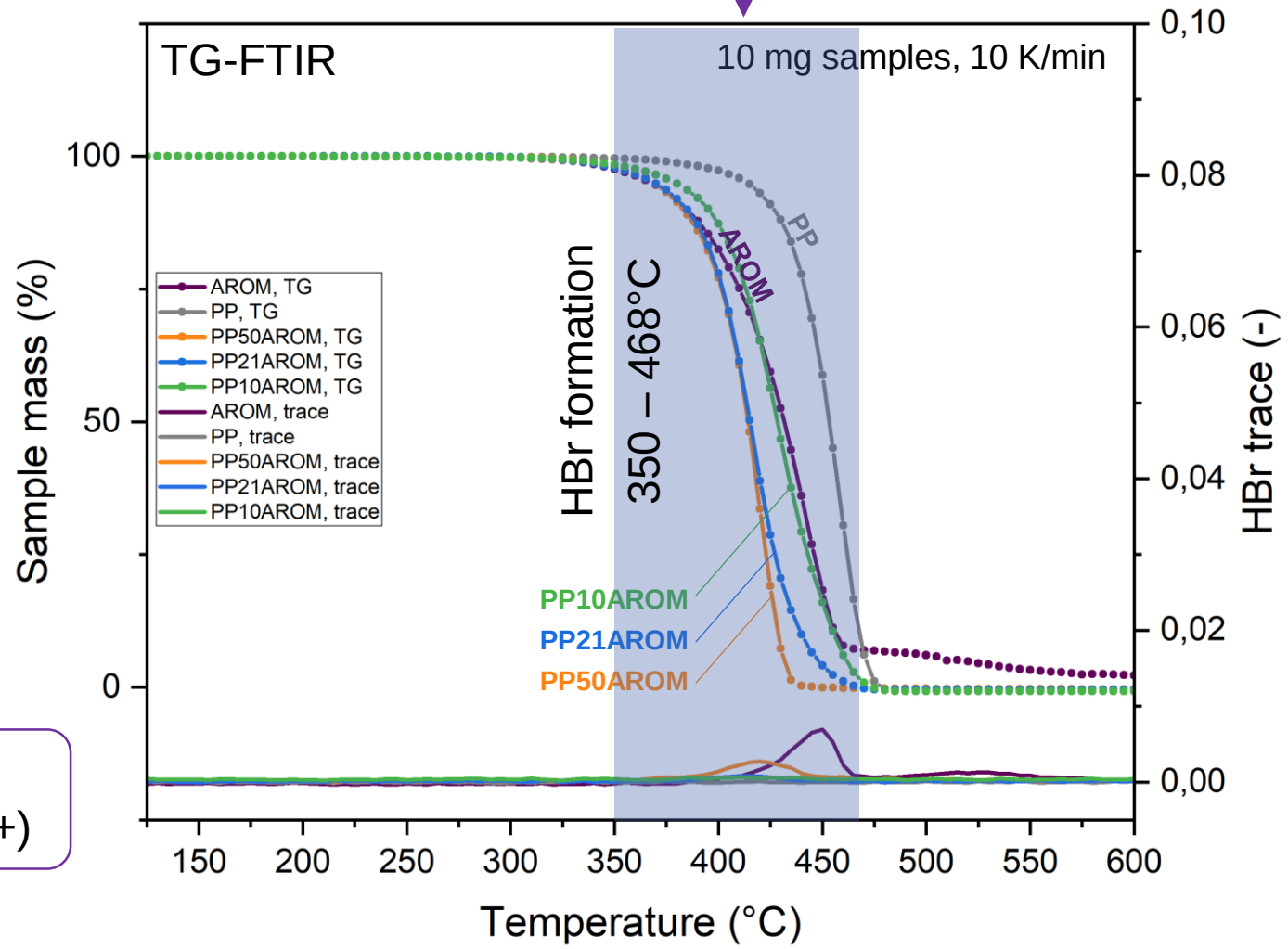


PP compounds

HBr formation and tracing

Samples	Loading of AROM / wt.-%	Br content / wt.-%
DBDPE	100	81
PP	0	0
PP50AROM	50	41
PP21AROM, compounded	21	17
PP10AROM	10	8.1

1 HBr trace max @ **410 – 420°C**



2 Confirmed by Py-GC-MS:
PP21AROM yields **aromatic Br-HCs** (C6+)

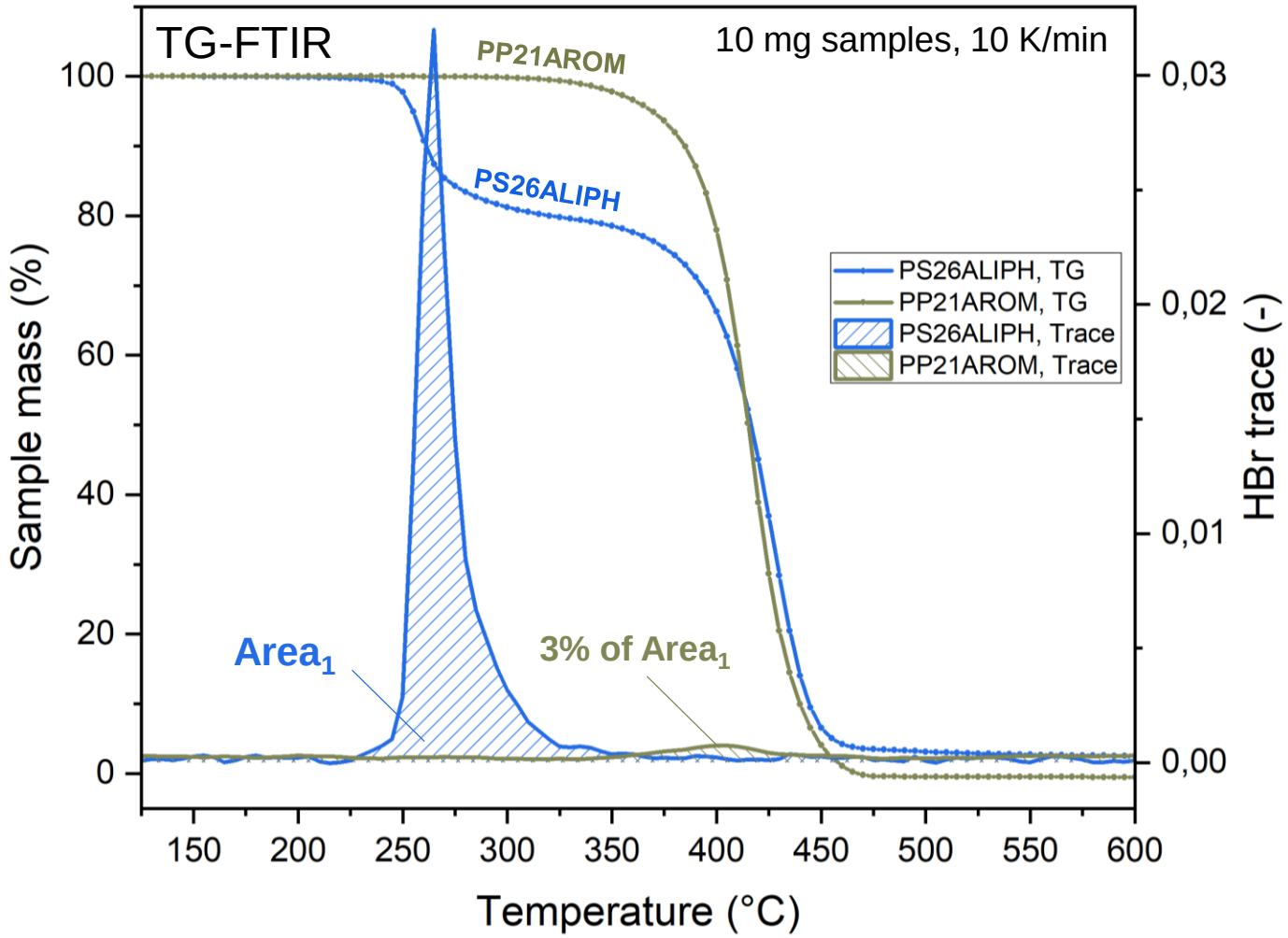
ALIPH vs. AROM flame retardants

HBr formation and tracing

Samples	Loading of BFR / wt.-%	Br content / wt.-%
PS26ALIPH, mixed	26	16.6
PP21AROM, compounded	21	17

+ ALIPH:
- **Non-overlapping** phenomena
- **High** release of **HBr**

! AROM:
- **Overlapping** phenomena
- **Low** release of **HBr**



Conclusion

Summary & Outlook

ALIPH – e.g. PolyFR in PS

Pyrolysis products:
- HBr-rich ≤ 350°C
- HBr-poor > 350°C

Br separation in the gas phase

[1] https://partner.sciencenorway.no/

AROM – e.g. DBDPE in PP

- Overlapping phenomena
- Formation of aromatic Br-HCs

Further treatment: Br separation in the solid phase

[2] https://www.wastepackgroup.co.uk/
[3] https://www.alldriveautoparts.com.au/

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Niklas Netsch

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Mixed plastics in pyrolysis

Razan Alsharqawi

Oral #52

Brominated flame retardants in pyrolysis

Malte Hennig

Oral #58

Value chain integration of **pyrolysis products**

Dr.-Ing. Salar Tavakkol

Group Leader Pyrolysis Technology

Prof. Dieter Stapf

Head of Institute for Technical Chemistry KIT