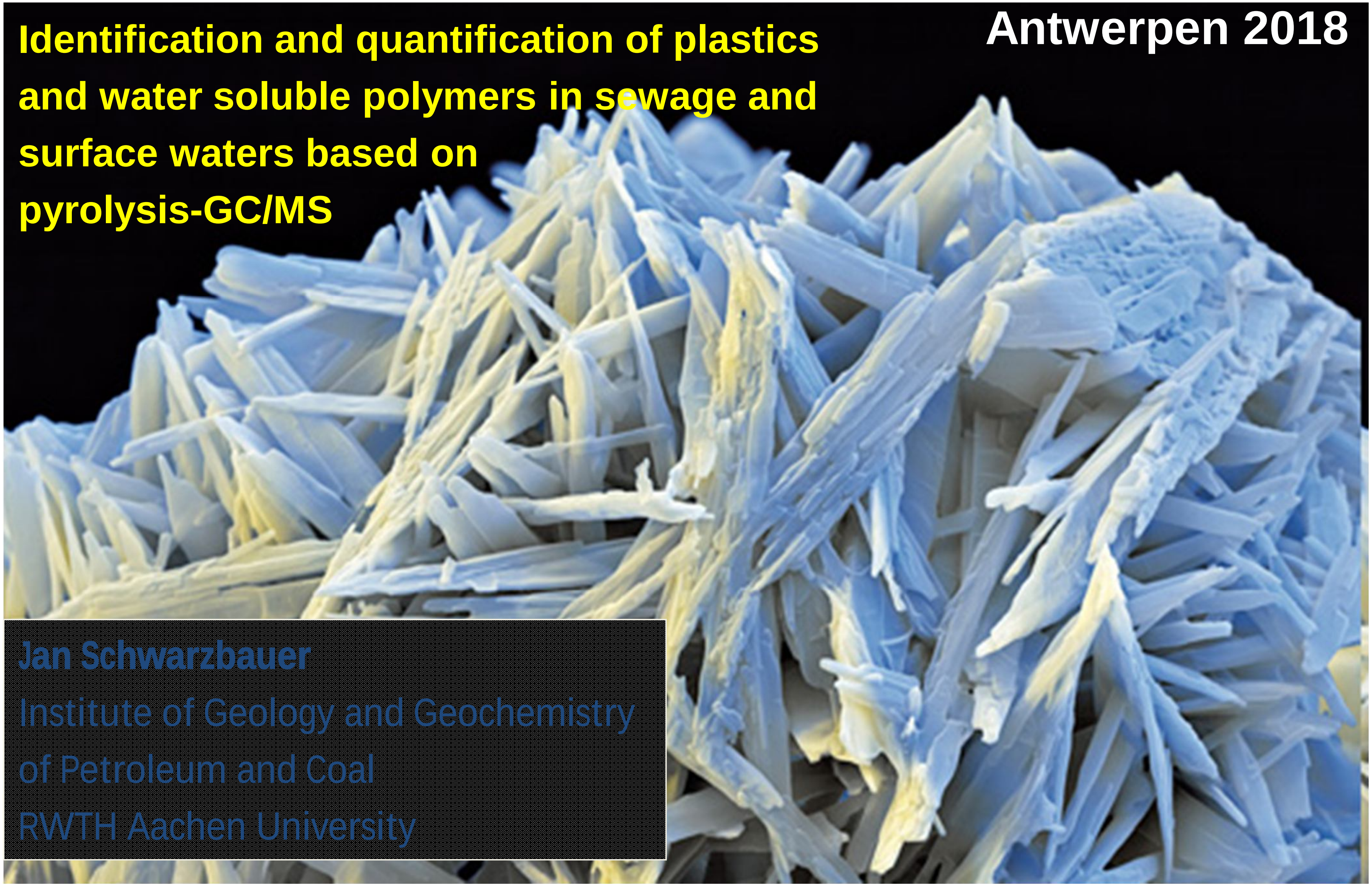
Mass spectrometry in support of the environment, food, and health interaction and desease



Antwerpen 2018

Identification and quantification of plastics and water soluble polymers in sewage and surface waters based on pyrolysis-GC/MS

Jan Schwarzbauer

Institute of Geology and Geochemistry of Petroleum and Coal

RWTH Aachen University

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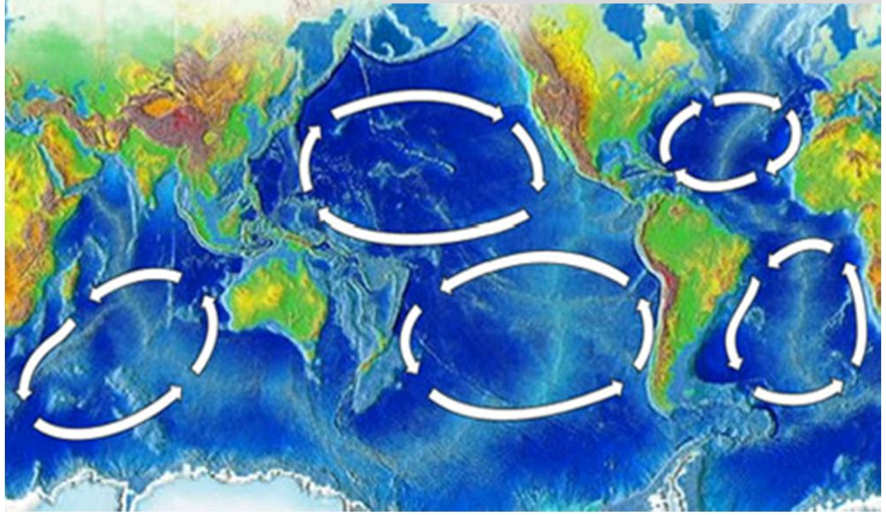
Waste Beaches

Kamilo-Beach at Hawai
(waste removal rate: 52 tons per year)

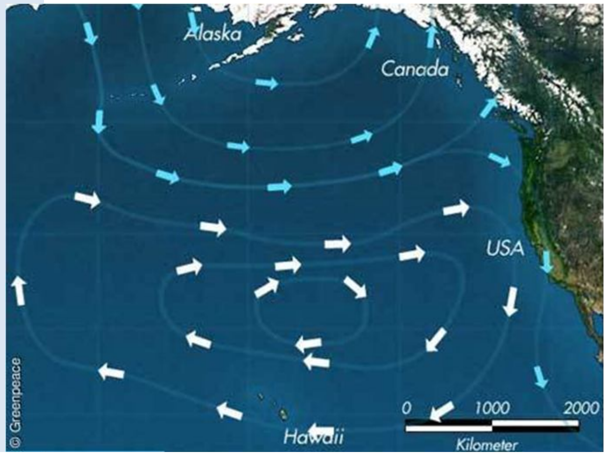
Very small (down to microscopic scale) plastic particles can account for up to 25% of weight in beach sands

Waste in Los Angeles River collected after a storm event


The 5 biggest oceanic gyres

Oceanic Garbage Patches

- Great Pacific Garbage Patch (Pacific Trash Vortex): Area of 7000.000 to 1.500.00 km^2, contains 100 Mio. tons of dominantly plastic waste
- According to an UNEP-study the average particle frequency on the oceans surface is approx. 18.000 plastic particles/km^2
- A rough calculation indicated a particle frequency on the oceans floor of approx. 11.000 plastic particles/km^2
- Plastic parts in oceanic travel with approx. 7cm/s for ca. 16 years resulrting in a distance of ca. 10.000 km (circulation time 2 - 4 years for one round)



Impact on marine organism

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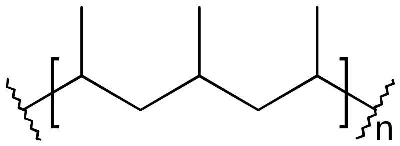
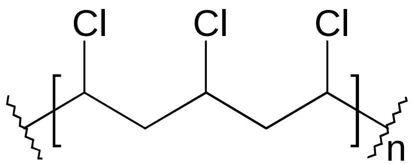
Structural diversity of synthetic polymers

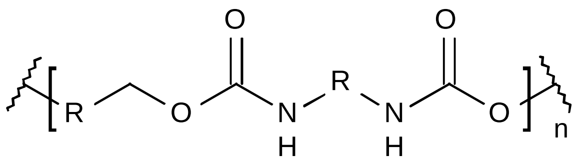
Polypropylene PP



Polyvinylchloride PVC

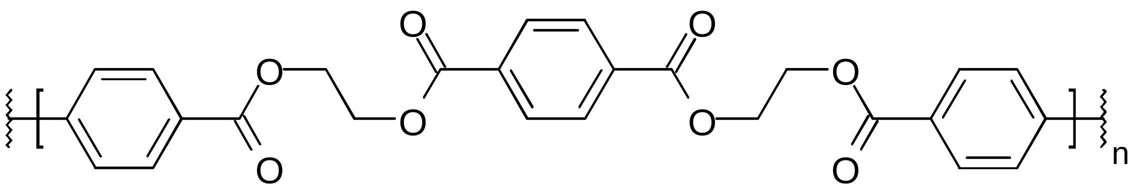


Polyamides PA



Polymer	Applications
Polyethylene (PE)	Wide application: plastic wrap, bin liner …
Polypropylene (PP)	Ropes, helmets …
Polystyrene (PS)	Insulant, packaging …
Polyethylene terephthalate (PET)	Bottles, textile fibers …
Polyvinylchloride (PVC)	Tubes, flooring …
Polymethyl methacrylate (PMMA)	Plexiglas, transparent plates ..
Polyamide (PA)	Stockings, fibres ….
Polyurethane (PUR)	Foams, membranes
Polyacrylamide (PAA)	Flocculants, absorbers ..

Polyethylene terephthalate PET



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Density

will float on water, available for uptake by filter feeders or planktivorous

?

will sink, accumulation in sediments

Plastic class	Acronym	Specific Density (g/cm³)	Main Use
Foamed polystyrene	XPS	0.028-0.045	House building, floats, foam cups
Polypropylene	PP	0.905	Folders, fod packaging, car bumper etc.
Low-density polyethylene	LDPE	0.92	Films for food packaging, reusable bags, etc
High-density polyethylene	HDPE	0.96	Toys, milk bottles, and pipes
Polyvinyl chloride	PVC	1.35-1.39	Window frames, flooring and pipes, clothes, etc.
Polyurethane	PUR	1.2	Mattresses and insulation panels
Polystyrene	PS	1.05-0.07	Spectacle frames, plastic cups, packaging, etc.
Polyethylene terephthalate	PET	0.96-1.45 (av. 1.38-1.41)	Plastic beverage bottles and packaging
Acrylonitrile butadiene styrene	ABS	1.01-1.08	Pipe systems, automotive components, medical devices, musical instruments, etc.
Polyamide (nylon)	PA	1.02-1.06	Textile, automotive applications, carpets and sportswear, etc.
Polycarbonate	PC	1.20-1.22	Electronic components, construction materials, dates storage, automotive components, etc.
Polymethyl methacrylate (acrylic)	PMMA	1.09-1.20	Transparent glass substitute, medical technologies and implants, etc.
Polytetrafluoroethylene (teflon)	PTFE	2.1-2.3	Industrial applications, coating on kitchen saucepans, frying Pans

.... for detecting/determining microplastic in particulate matter samples (soils & sediments)

Pyrolytic analyses

Pyrolysis-GC/MS

- Destructive method
- Specific pyrolyses products are needed
- Quantification using external calibration
- Matrix interfere
- Particle separation/isolation is partly needed

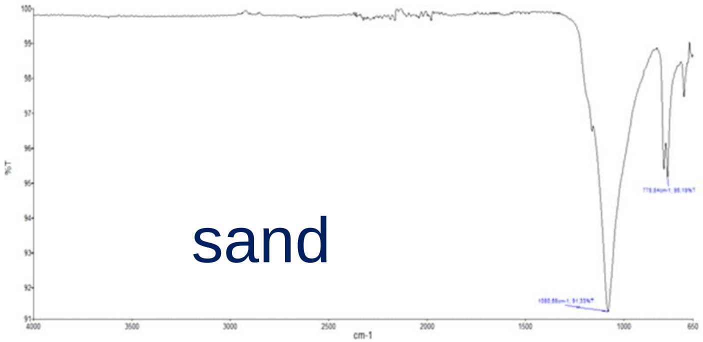
Spectroscopy

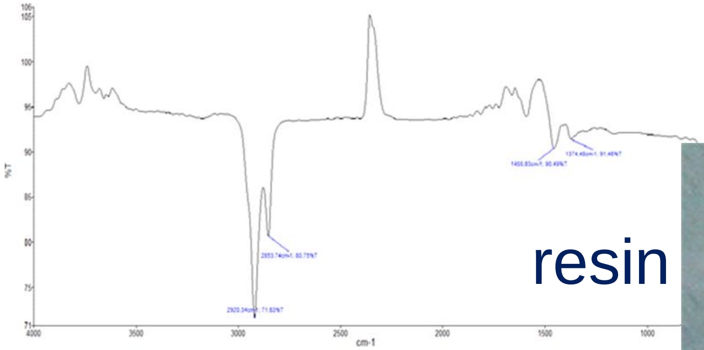
µFTIR, µRaman

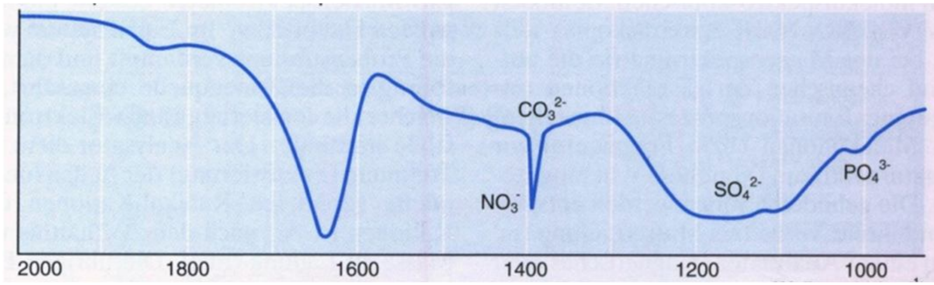
- Non-destructive method
- Specific absorption bands are needed
- 'Eliminates' matrix
- Fast measurement
- No quantification
- Extensive sample (pre)treatment

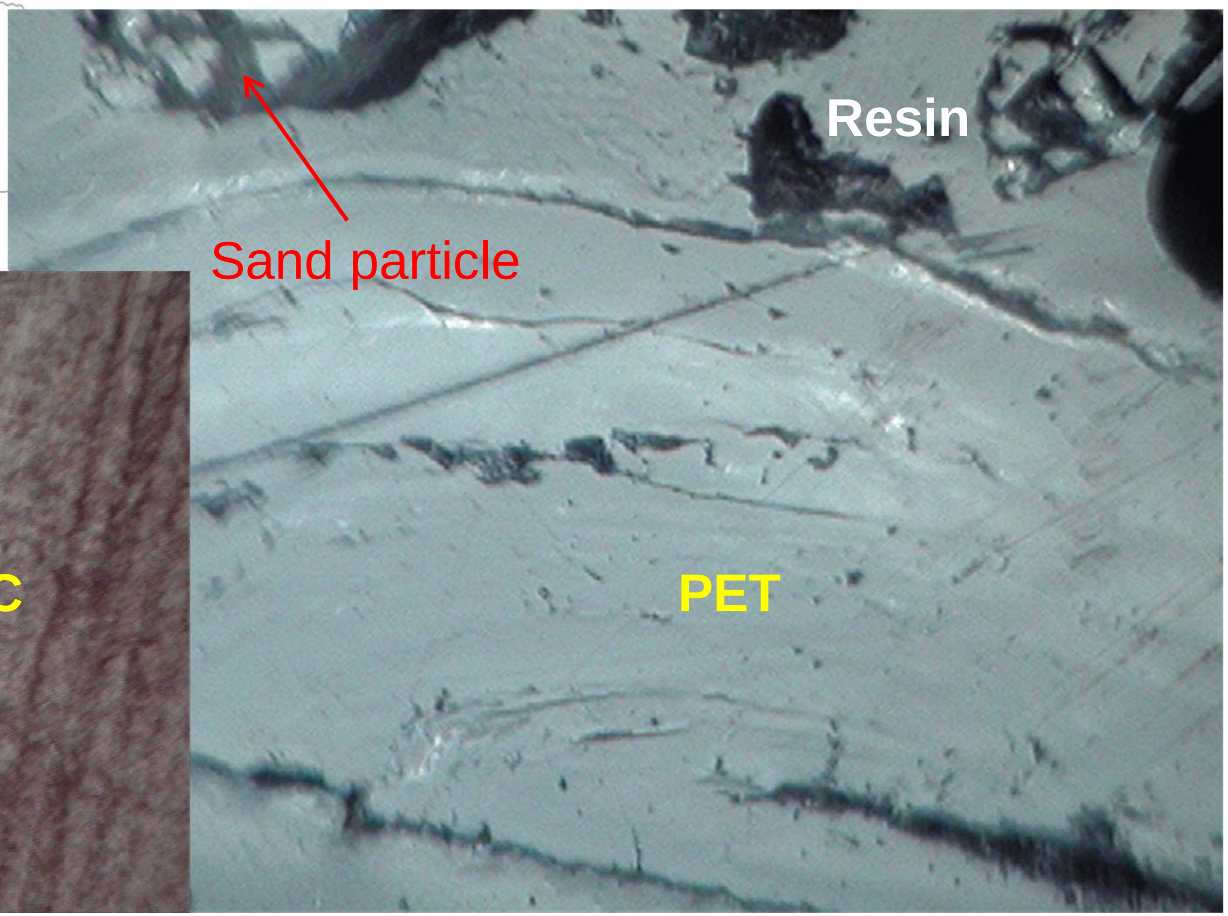
Complementary approaches with individual Pro's and Con's

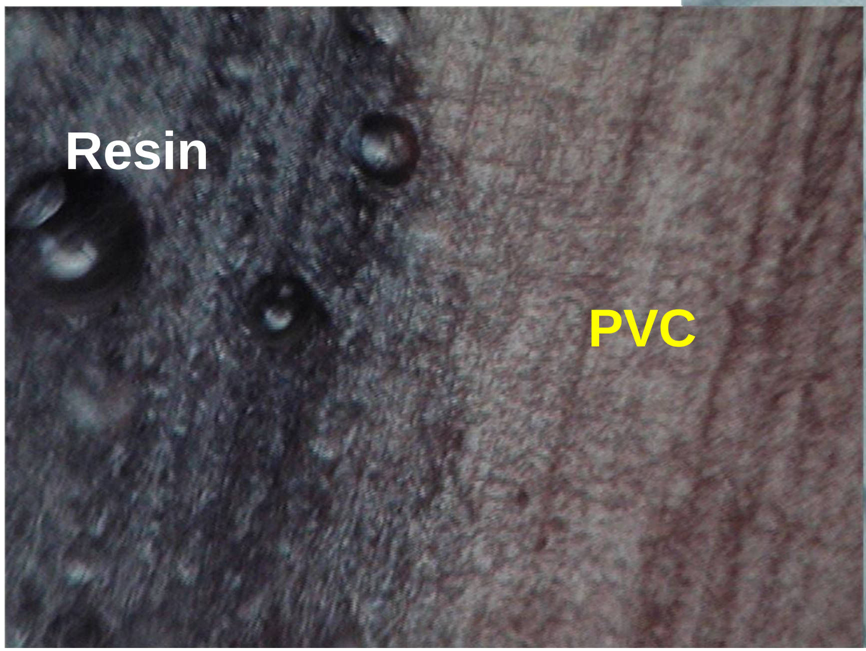
µFTIR as analytical alternative





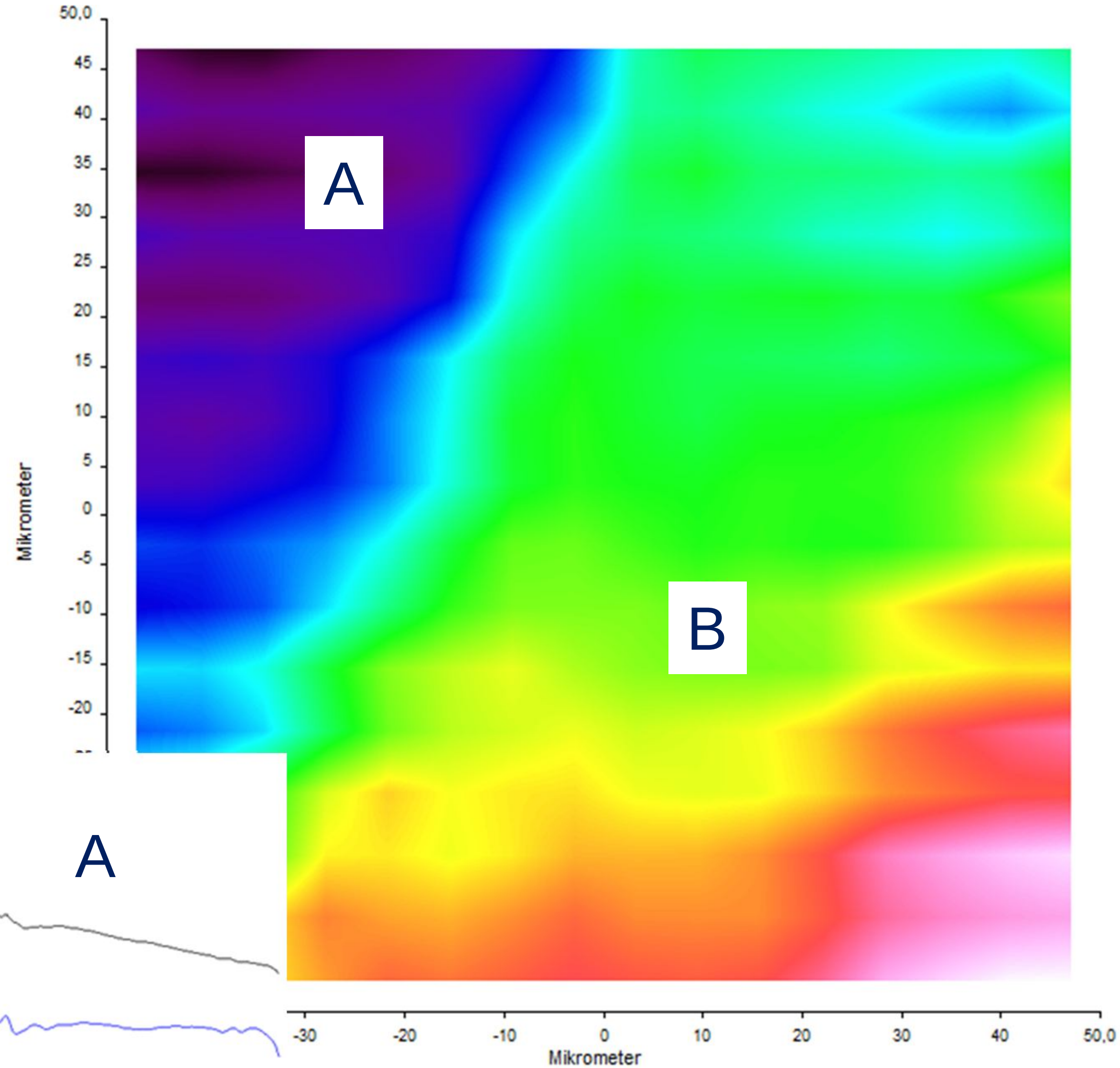


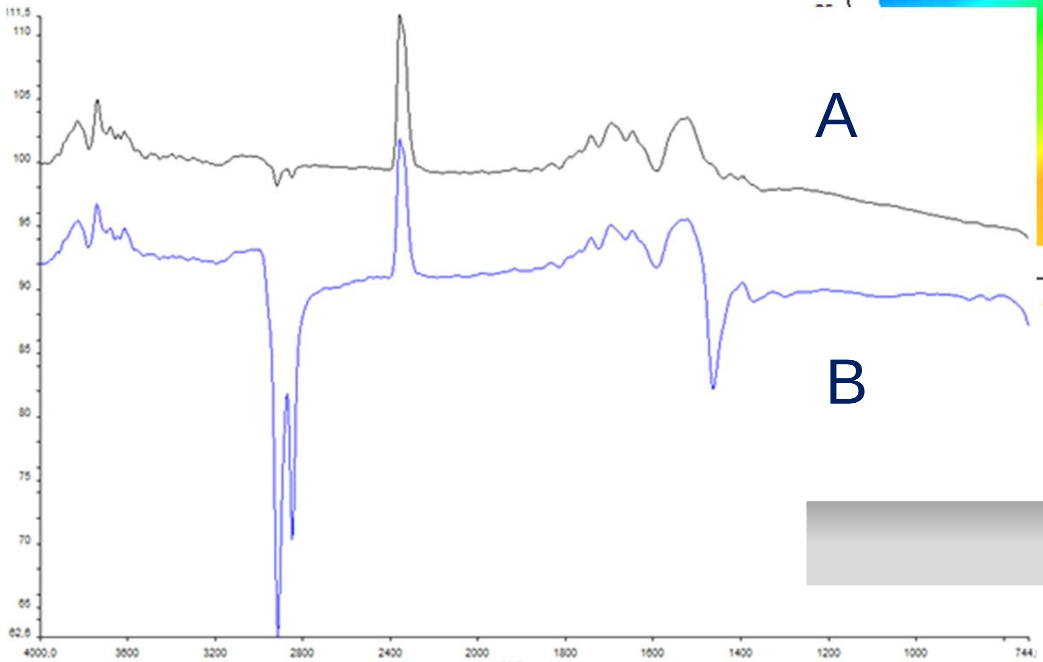




Artificial sand samples

PE in sand sample
(3.7%)





µFTIR as analytical alternative

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Motivation

Polymer analysis needs identification and **quantification**

The environment is not only affected by insoluble plastics but also by **water soluble polymers**

→ **Py-GC/MS**

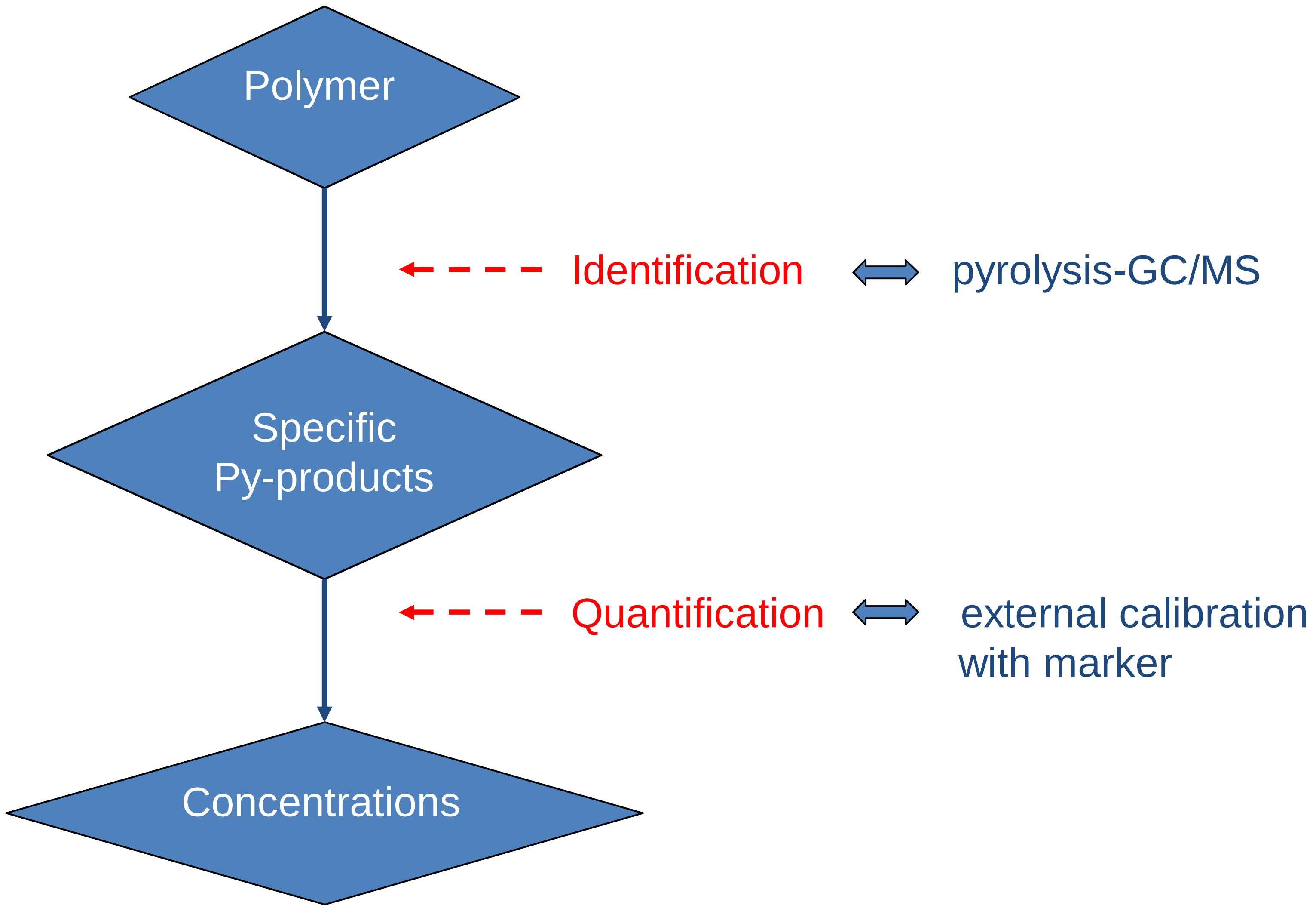
Pyrolysis GC/MS – specificty of pyolytic products → Pyrolysis GC/MS – quantification

Polyvinylpyrrolidone - PVP → Municipal sewage effluents → Surface water

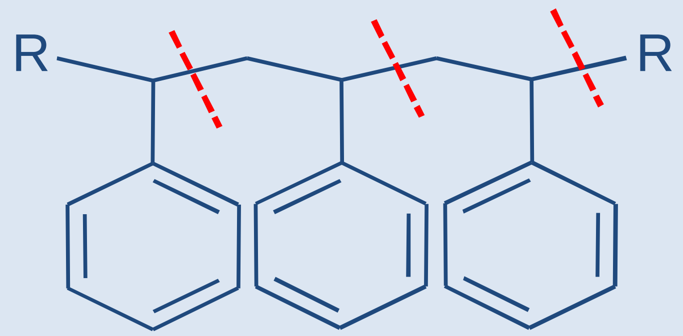
Chemically modified Polyacrylamide - PAbF → Flocculants in STP → Soils and aquatic sediments

Chemically modified cellulose - CEC, HEC → Drilling fluids → Marine water and sediments

Pyrolysis-GC/MS approach



Polystyrene in polluted sediments, Po river, Italy:



Comparison with reference material (styrene)

Signal linearity of styrene vs polystyrene content

Quantitative results: 1.0 to 3.9 mg/g

(Fabbri, Trombini, Vassura, J Chromat Sci 1998)

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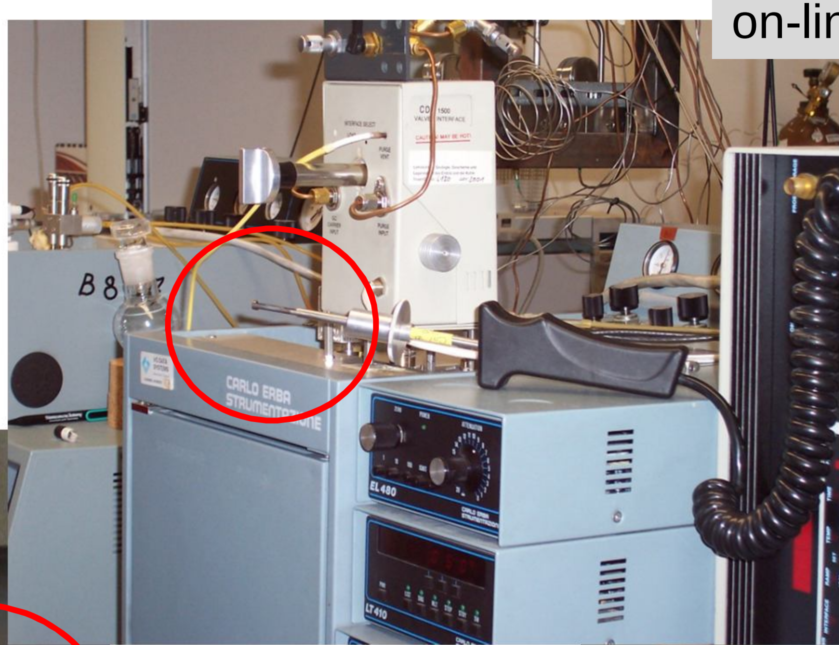
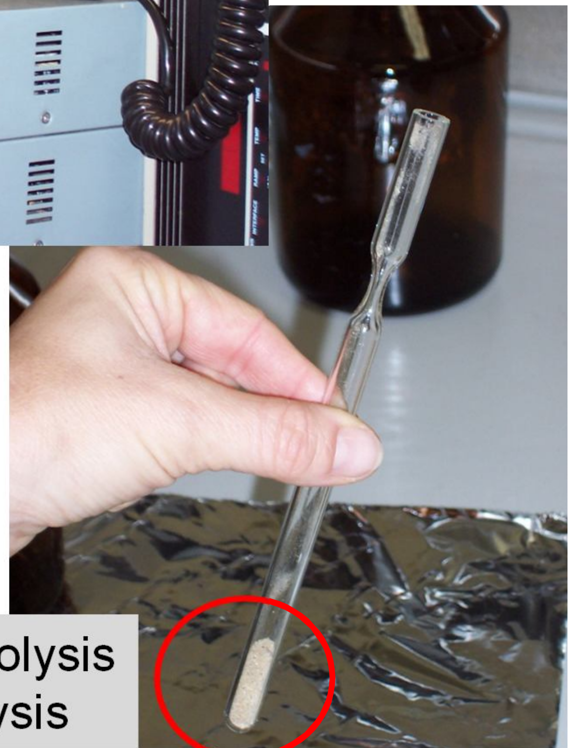
Pyrolysis-GC/MS approach

off-line continous flow pyrolysis

on-line Py-GC/MS





TMAH Thermochemolysis
Closed off-line pyrolysis

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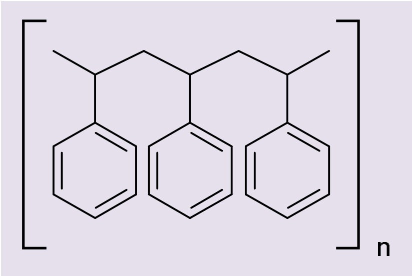
Identification of specific pyrolysis products



PS

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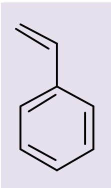

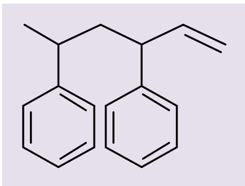

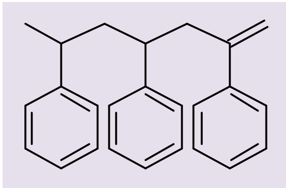

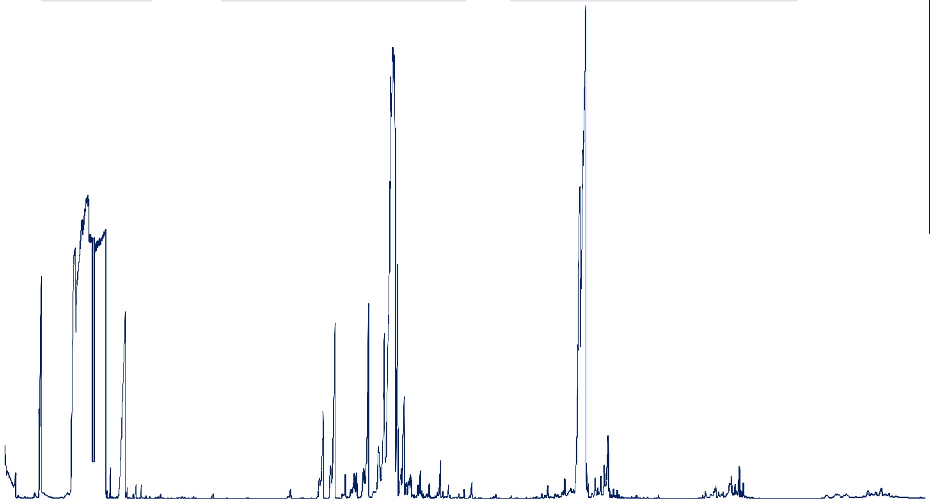

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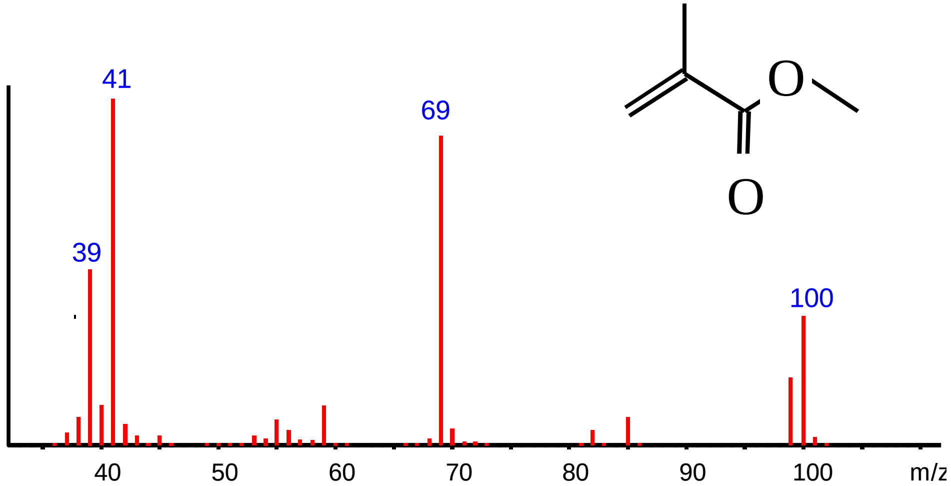
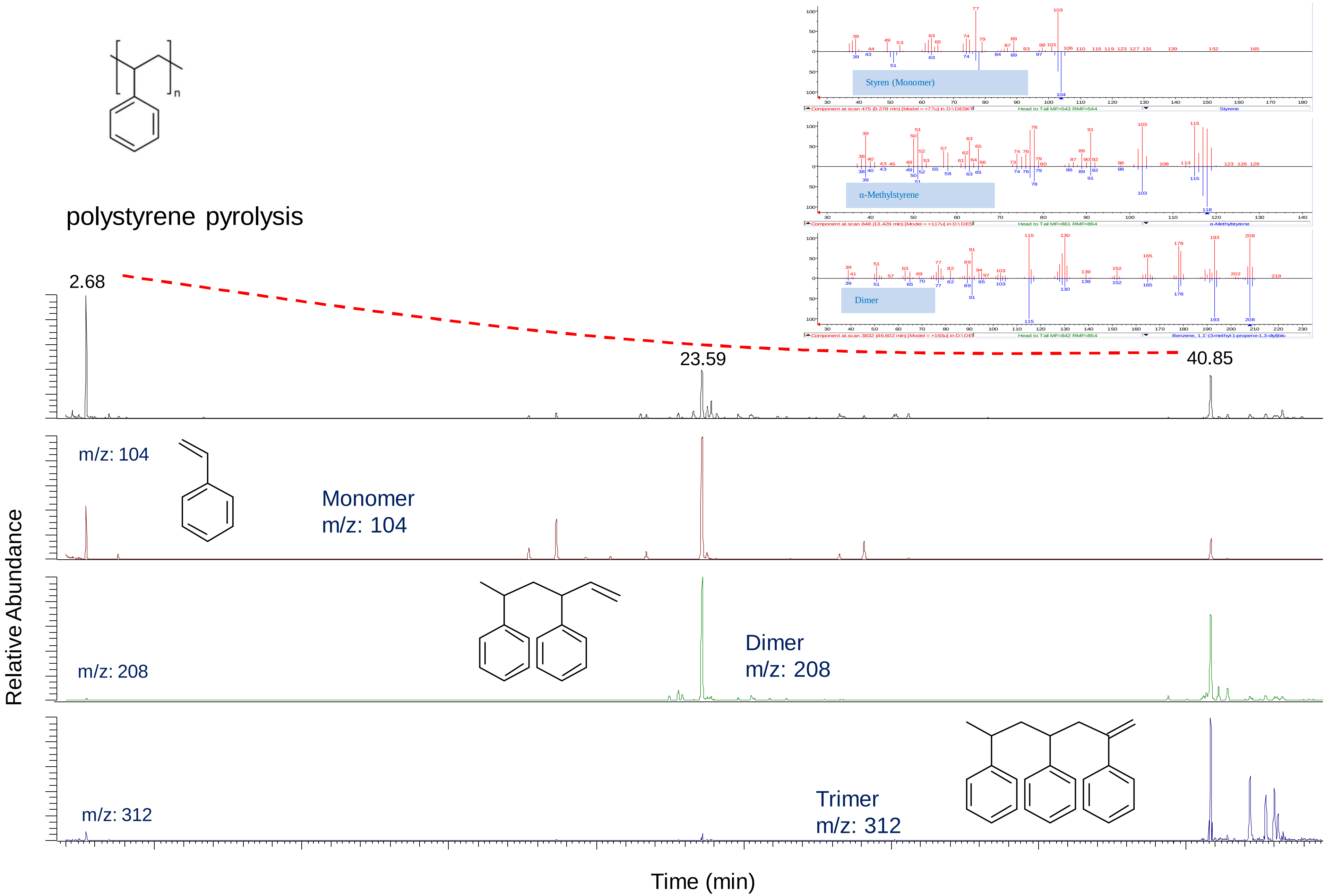
PMMA → MMA



Identification of specific pyrolysis products



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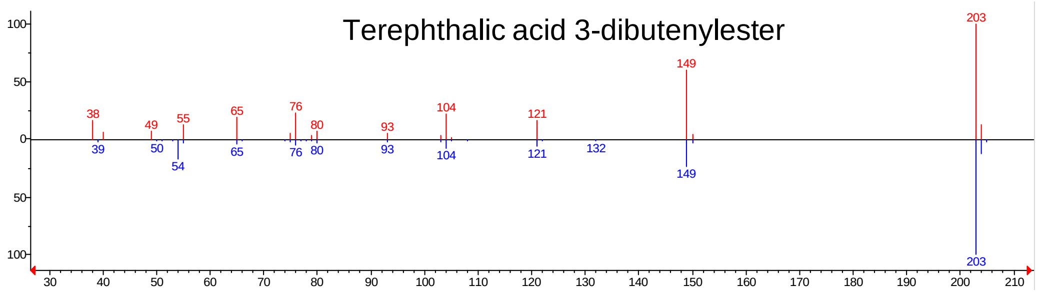
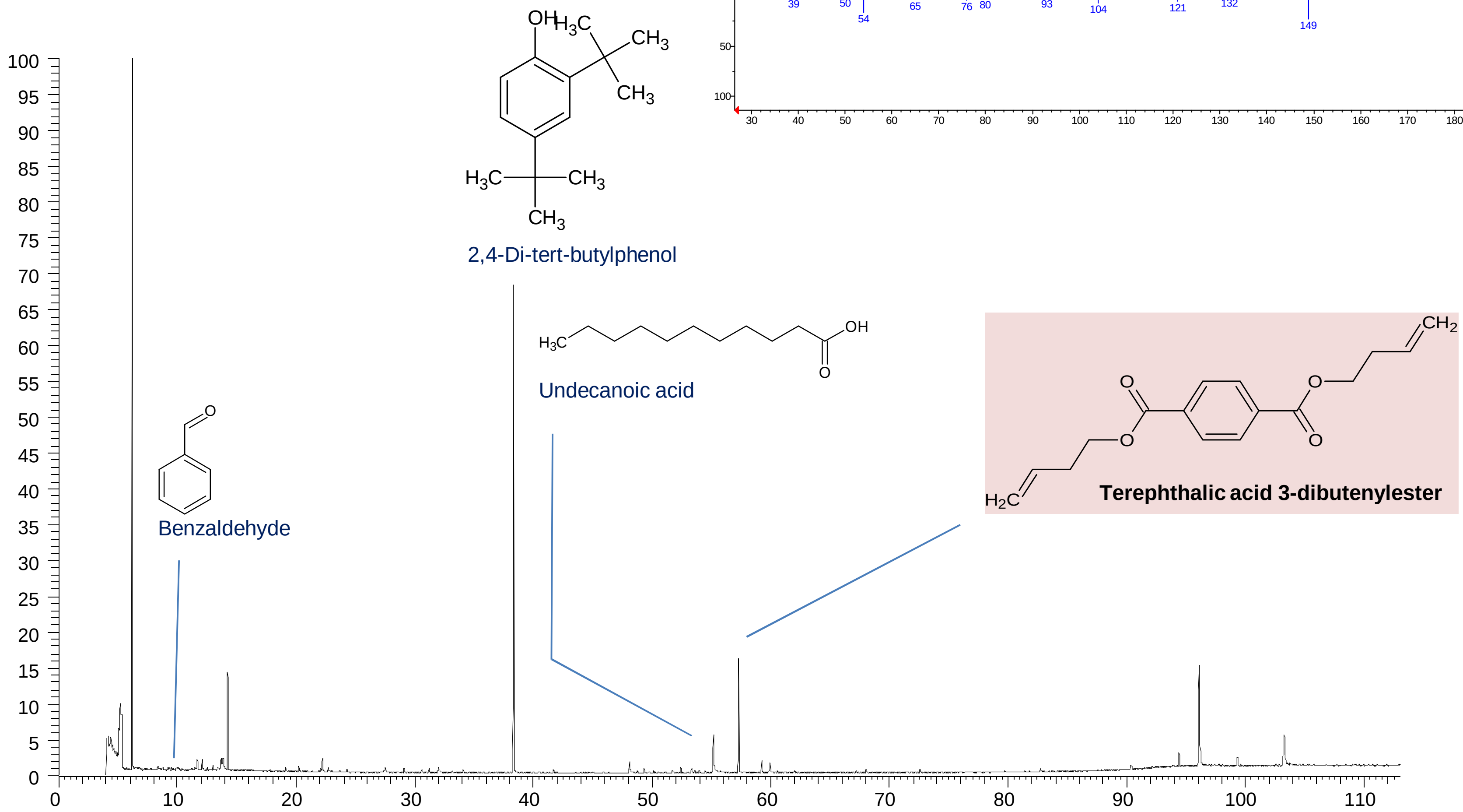
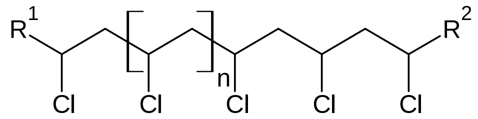
Identification of specific pyrolysis products

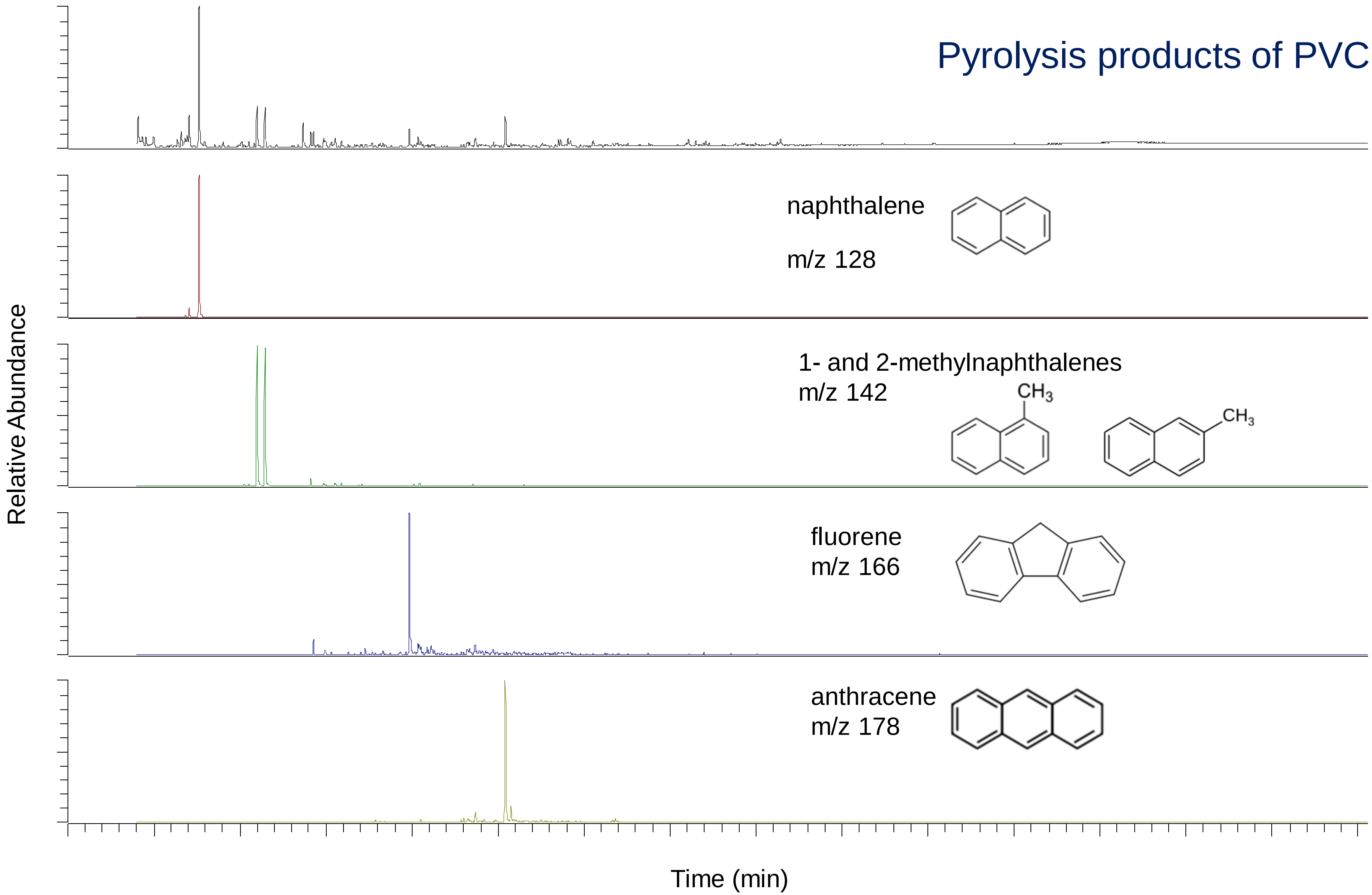
polyethyleneterephthalate pyrolysis



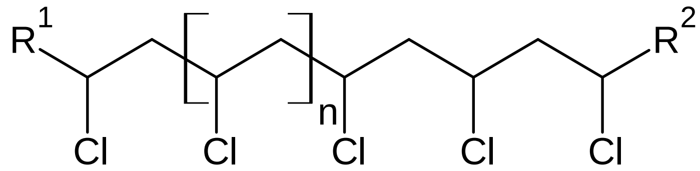


Identification of specific pyrolysis products

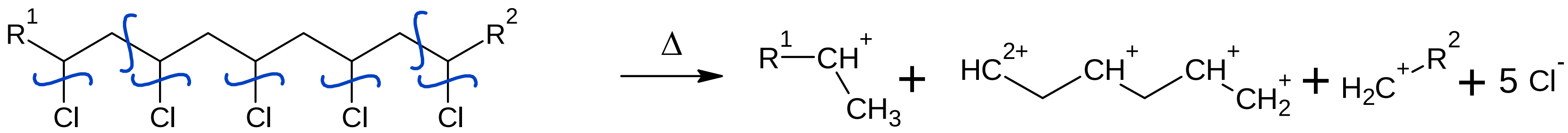




Formation of pyrolysis products of PVC

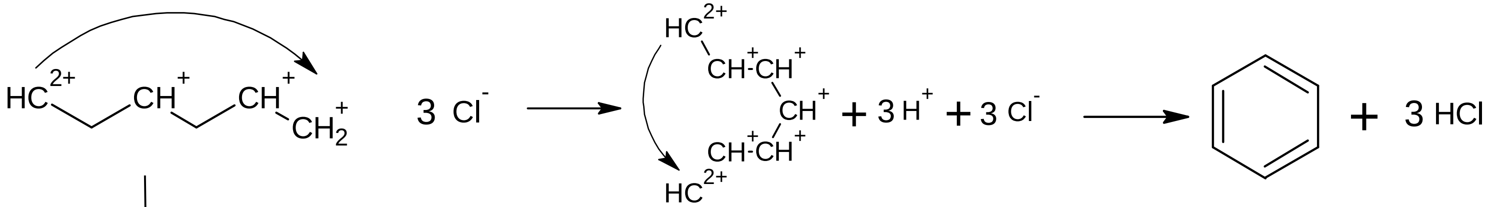


Molecular structure of PVC

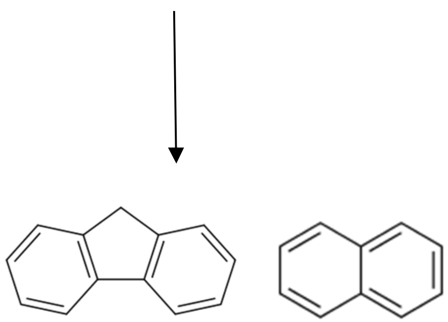


Potential cleavage

Reactive species

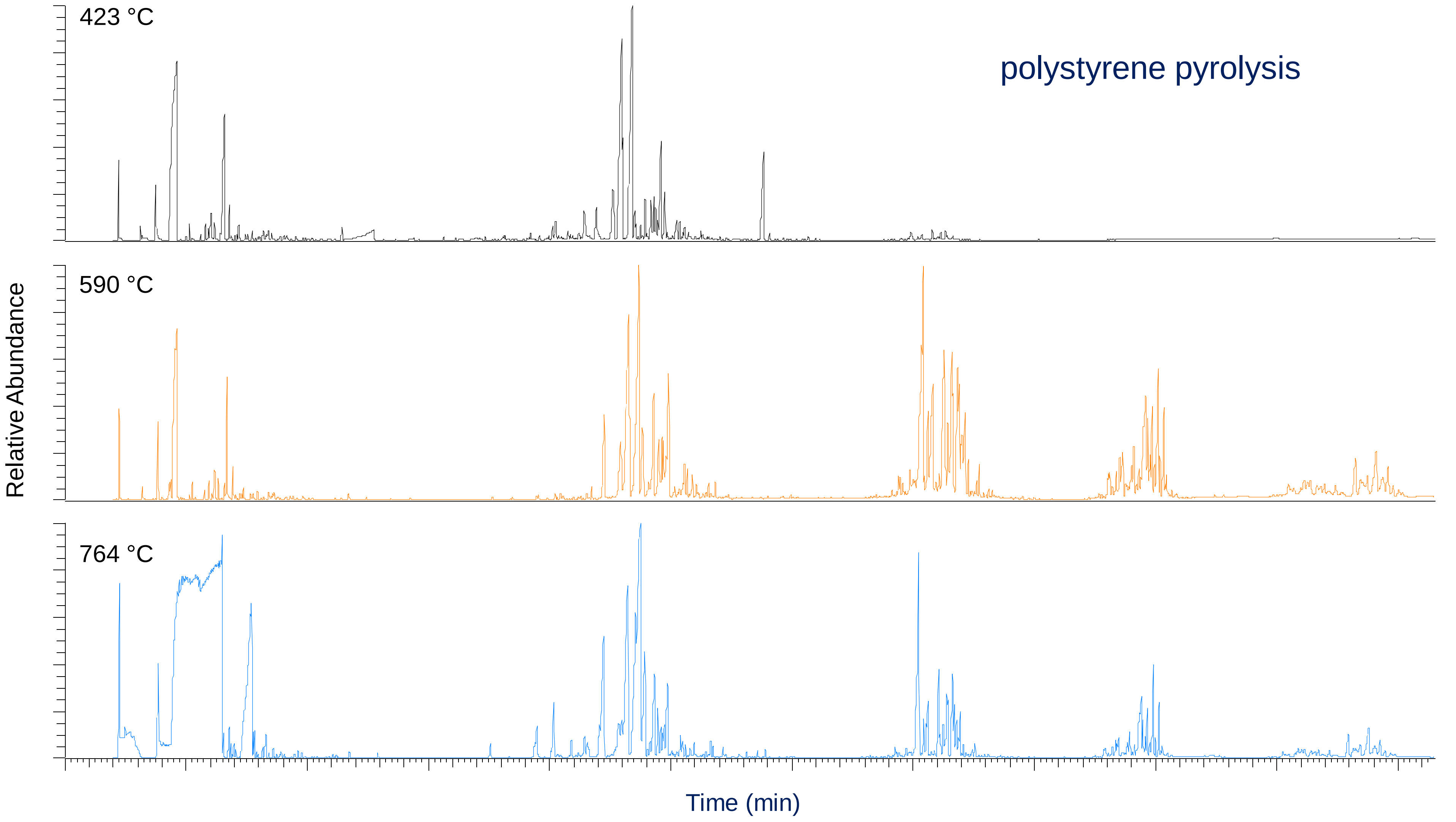


formation of monocyclic structures and hydrochloric acid - **stabilisation**

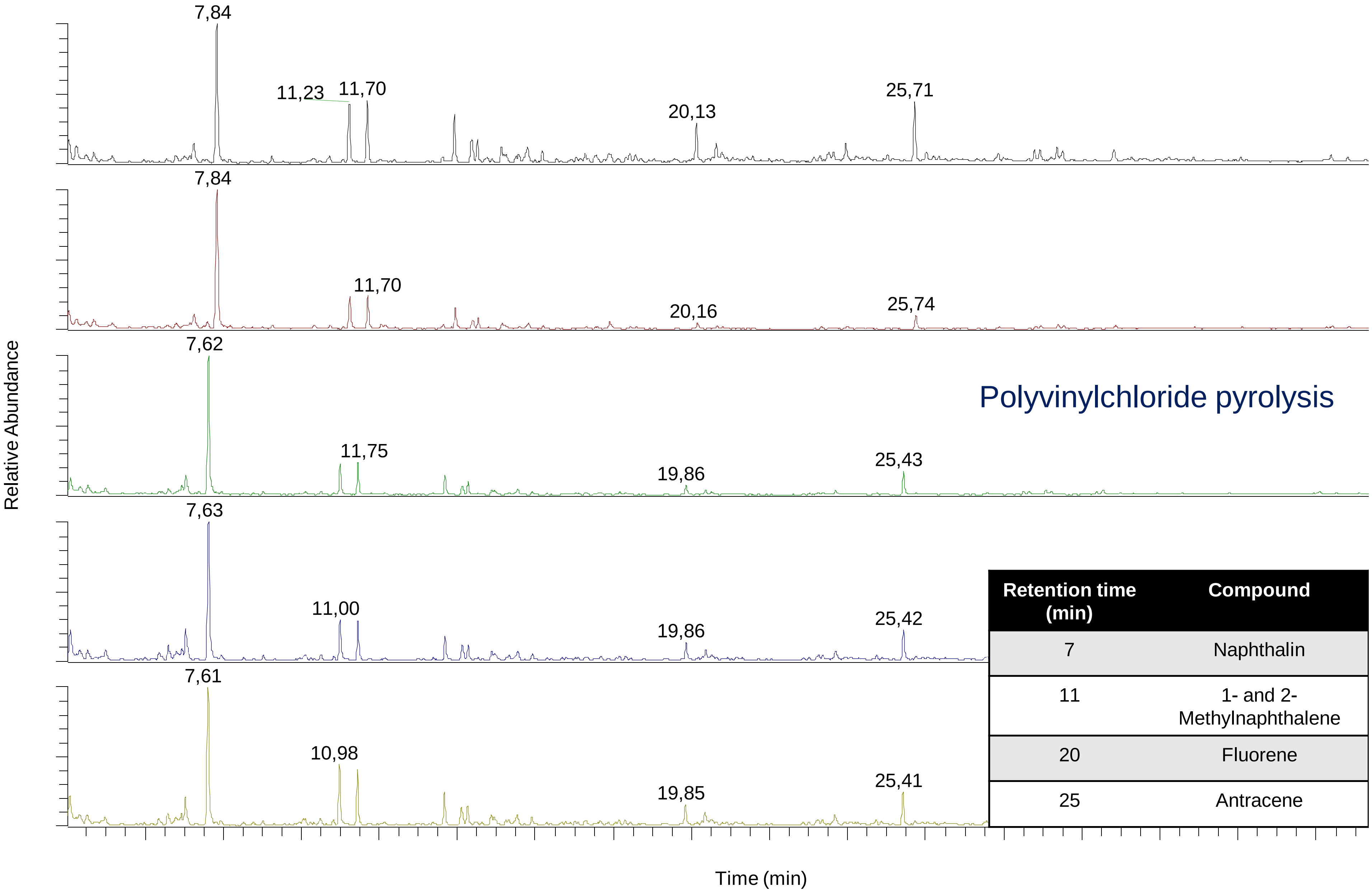


Formation of polycyclic aromatic compounds

Variation of pyrolysis temperatures



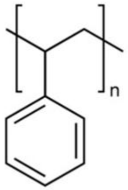
Reproducibility

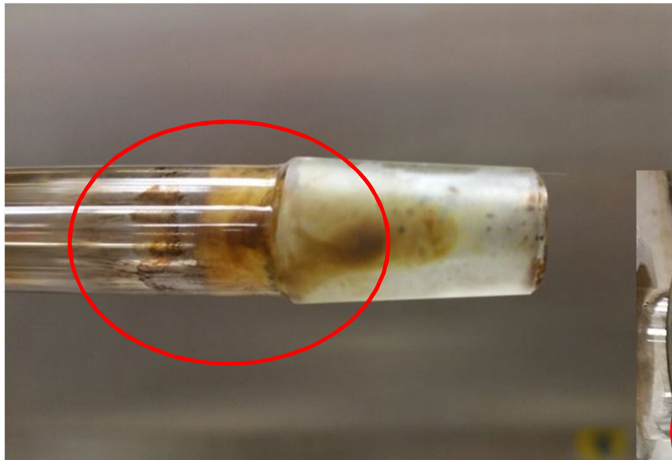


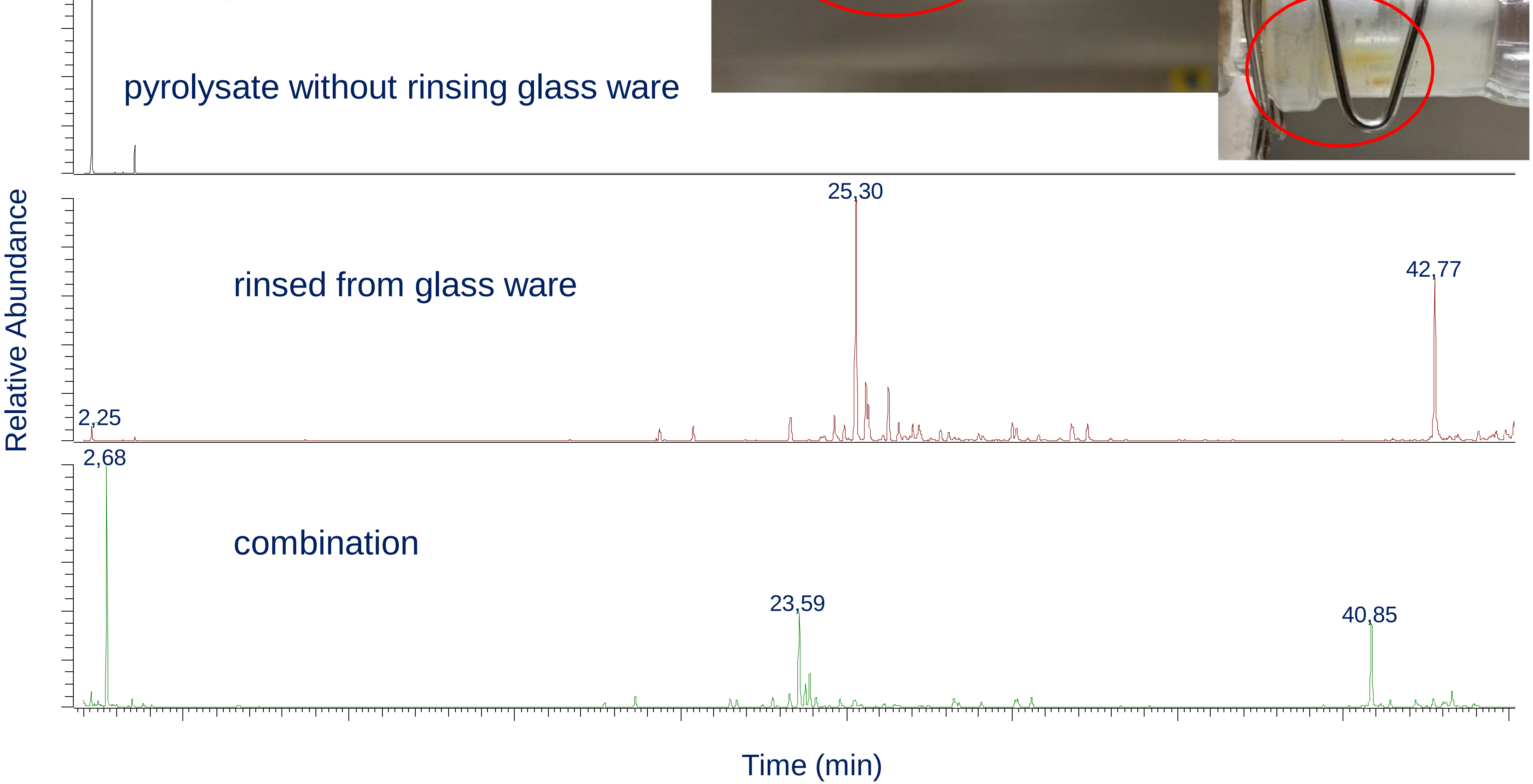
Retention time (min)	Compound
7	Naphthalin
11	1- and 2-Methylnaphthalene
20	Fluorene
25	Antracene

Pittfalls

polystyrene pyrolysis







- Hygroskopic (soluble in water and polar organic solvents)
- M_w of 2.500 to 2.500.00 Dalton
- High production rate
- Wide application

Example 1

PVP-Iodine disinfectant

Contact lense cleaner

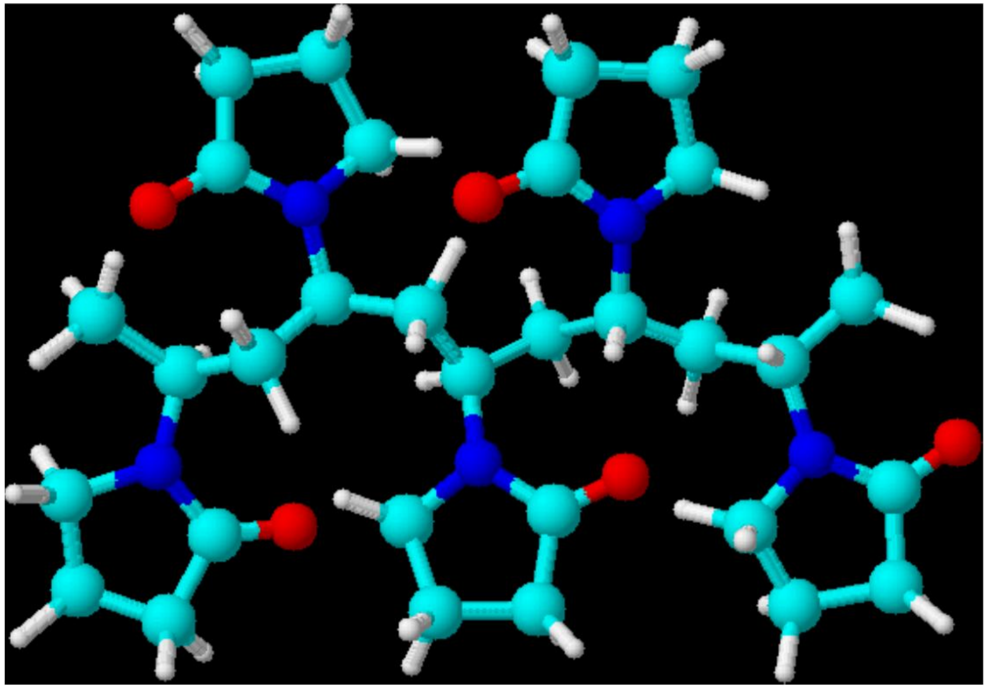
Shampoos

Hair spray

Ink transfer inhibitor in washing agents

Binder in tablets

Blood plasma expander



Membranes in drinking water filtration

Food additive E1201

- High environmental stability (Trimpin et al. 2001)
- No information avalaible about environmental behaviour

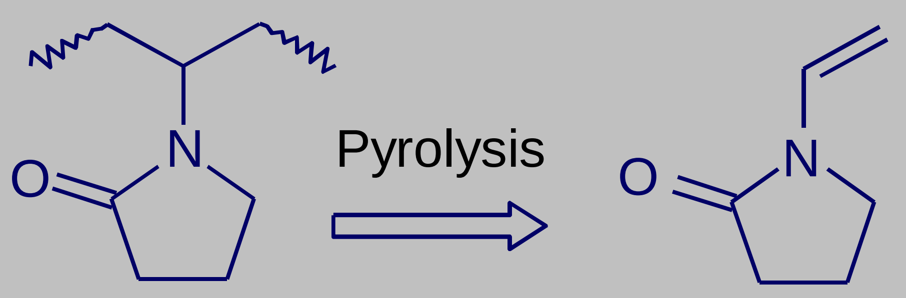
Analytical problems in detecting PVP in environmental samples:

- Isolation from water matrices
- Low concentration level

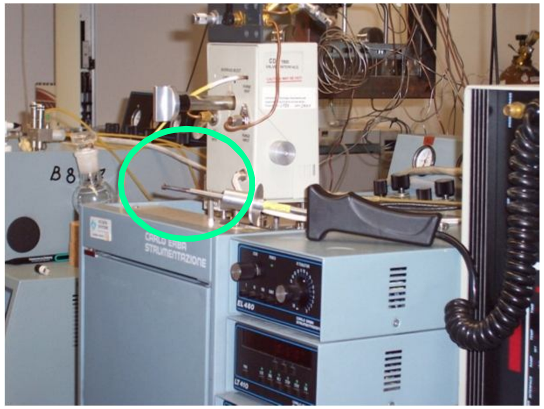
S Trimpin, P Eichhorn, H J Räder, K Müllen, T P Knepper
Recalcitrance of poly(vinylpyrrolidone): evidence through matrix-assisted laser desorption- ionisation time-of-flight mass spectrometry
Journal of Chromatography A 938, 67-77

Py-GC/FID (1990)
Membranes: ~ 1.0 µg/g

Py-GC/MS (1998)
Washing agents: LOD 0.05%



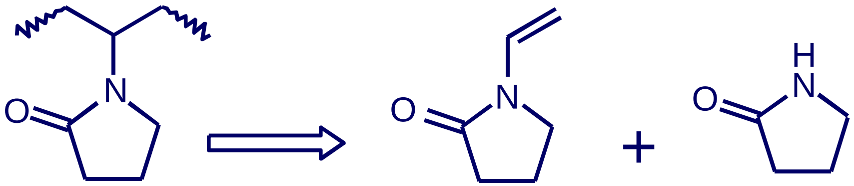
Polyvinylpyrrolidone PVP

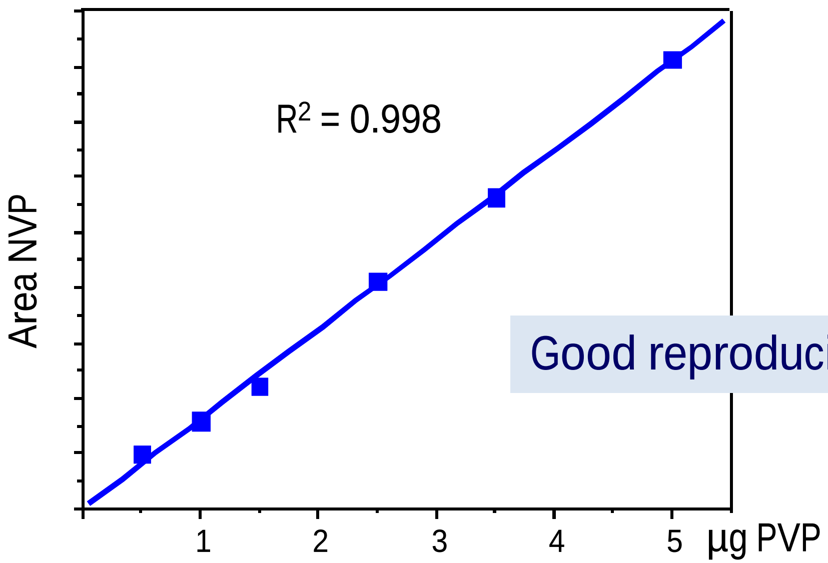


PVP K30 (Sigma-Aldrich) M_w 55.000 g/mol

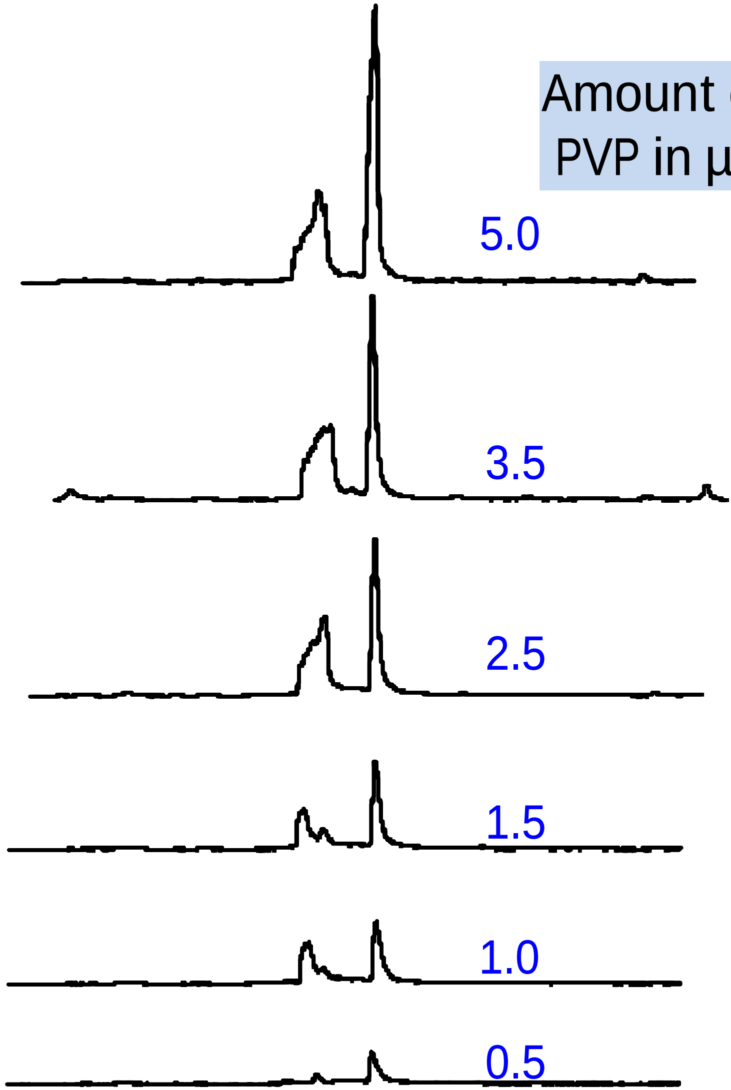
online-pyrolysis

T = 750°C; t = 5s





Good reproducibility



Polyvinylpyrrolidone PVP

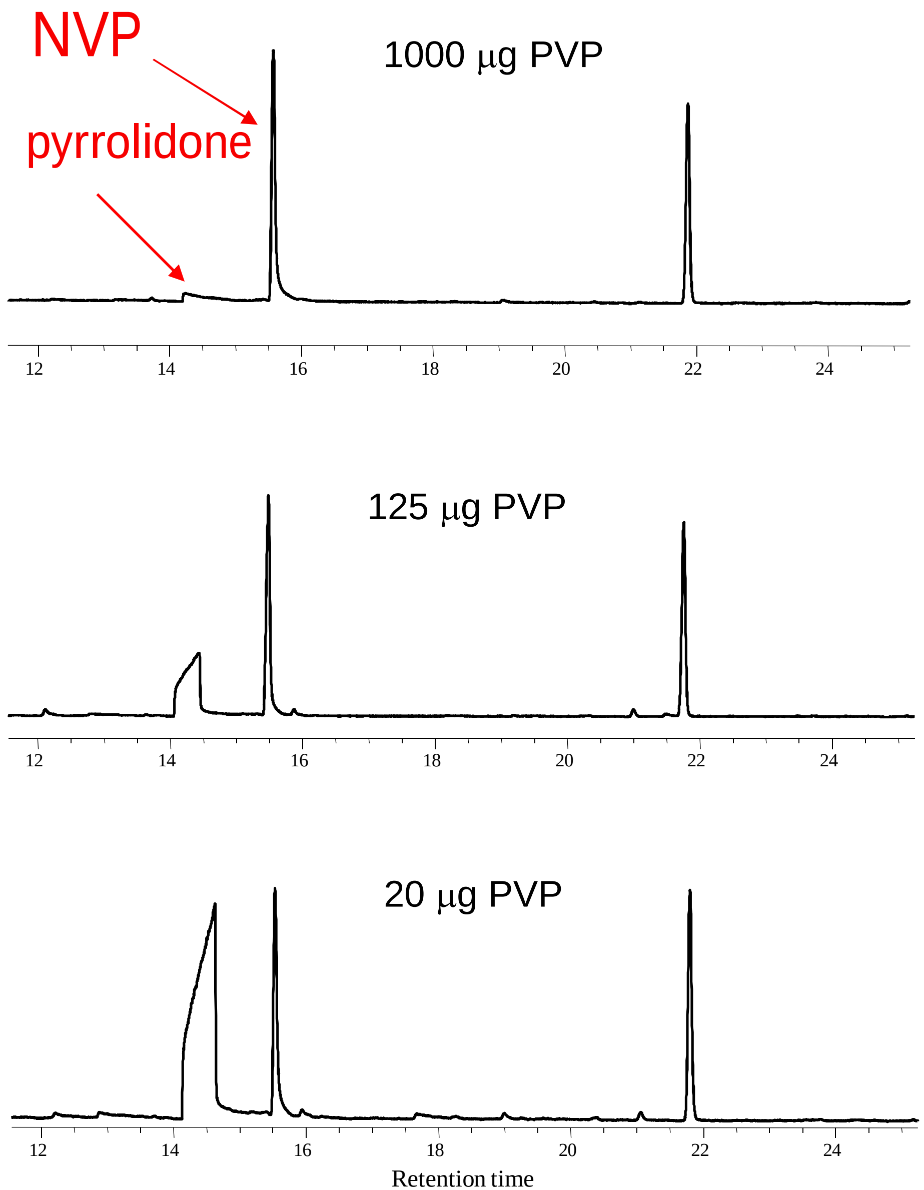
Continous-flow offline-pyrolysis

Relative increase of pyrrolidone vs NVP with decreasing amount of pyrolysis educt

⇓

Adsorption of PVP on ceramic surfaces shifts pyrolysis yields as observed

V M Bogatyrev, N V Borisenko, V A Pokrovskii (2001)
Thermal Degradation of Polyvinylpyrrolidone on the Surface of Pyrogenic Silica
Russian Journal of Applied Chemistry 74, 839-844.



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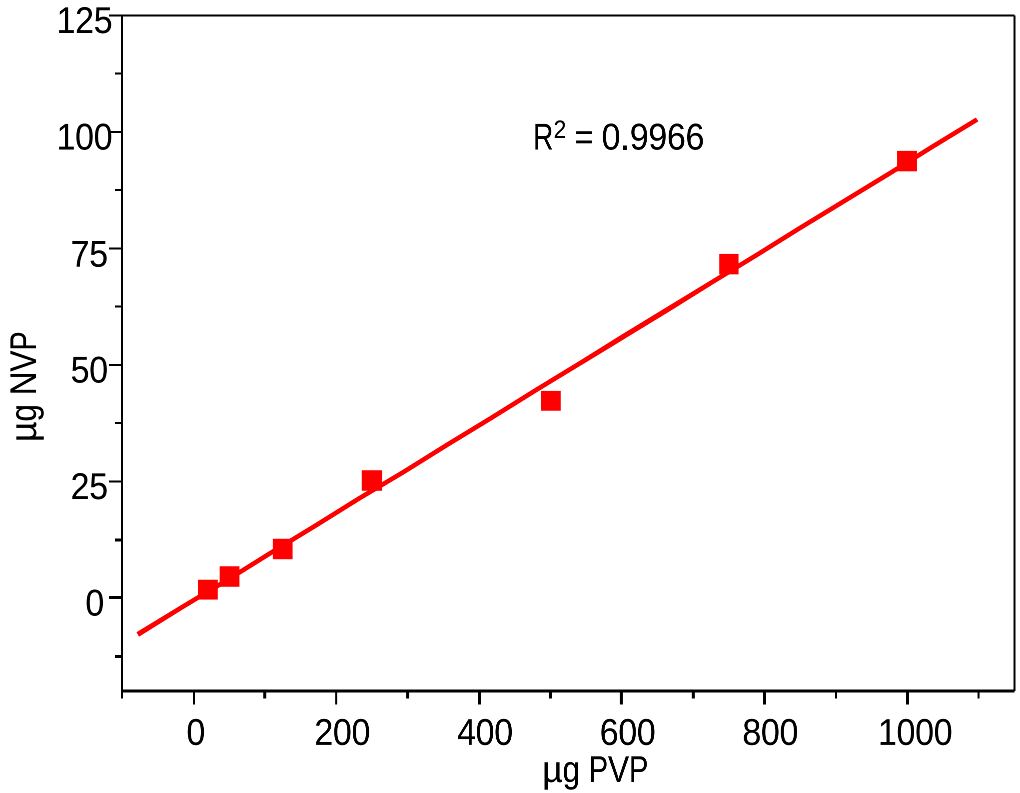
Polyvinylpyrrolidone PVP

Continous-flow offline-pyrolysis

Pyrolysis yield (n=3)

PVP [µg]	NVP
1000	9.4 % ± 0.2
750	9.6 % ± 0.1
500	8.5 % ± 0.8
250	10.1 % ± 0.7
125	8.4 % ± 0.3
50	9.2 % ± 0.1
20	9.2 % ± 0.1



Reproducibility

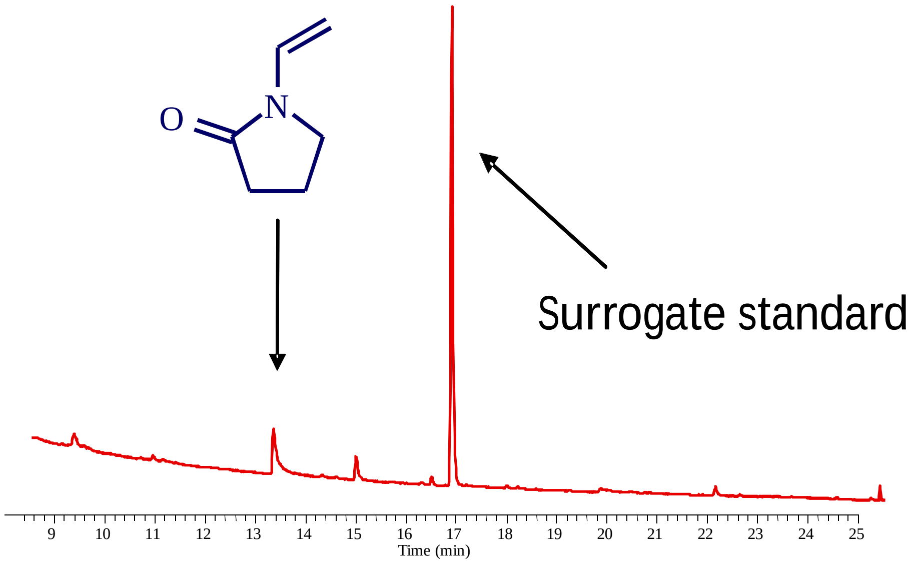
Recovery rates determined by spiked waste water samples (n=6, PVP ca. 100µg): 92.3 % - 96.5 %; average: 94.6 % ± 1.5 % (abs.)

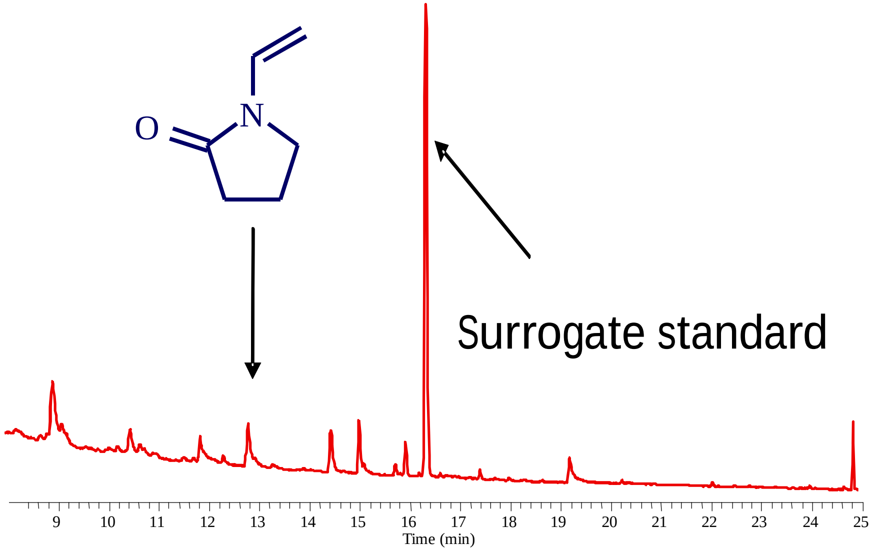
Polyvinylpyrrolidone PVP

Continous-flow offline-pyrolysis

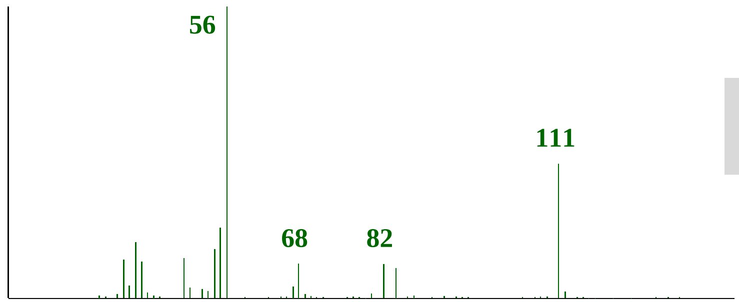
Municipal waste water Aachen

Waste water Pancevo





C_{PVP} = 7.1 mg/L



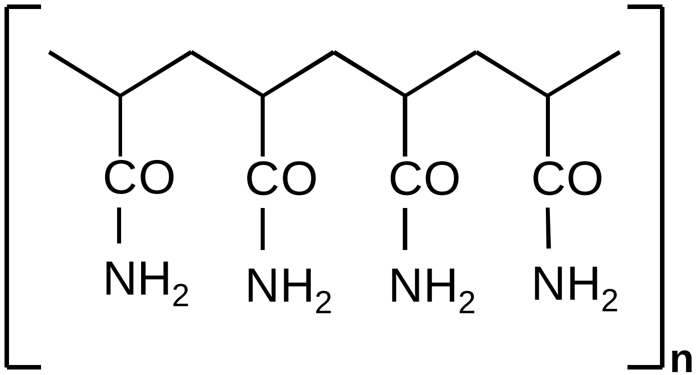
C_{PVP} = 2.9 mg/L

Polyacrylamide based flocculants PAbF

Example 2

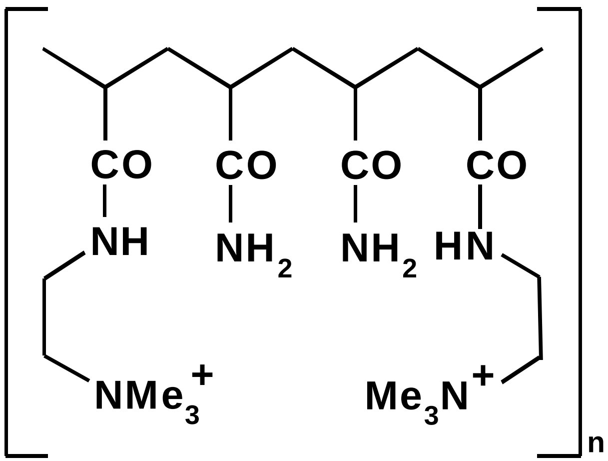
Polyacrylamide based flocculants [redacted]

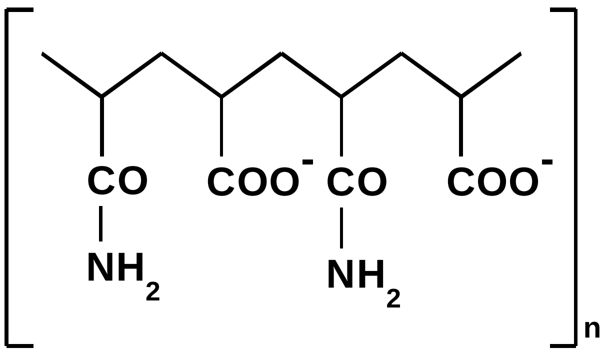
Chemical properties



- Molecular mass : 10^5 to 10^7 Da
- Stable below 210 ° C
- Soluble in water, formamide, morpholine, DMSO, ethylene glycol etc.

cationic-modified	anionic-modified





Economical aspects

World wide production of polyacrylamides :

approx. 100.000 to 200.000 t/a

Polyacrylamides used as flocculants: approx. 50%

Geographically distribution of polyacrylamides usage :

40% USA 30% Europe 30% Japan

Consumption in Germany :

approx. 10.000 to 20.000 t per year

Release of PAbF to the pedosphere

Sewage slugdes are used for fertilisation in agriculture
(Germany : approx. 35% , 15 Mio t/a)

Restrictions by law (Germany):

Within 3 years a maximum of 5 to 10 tons (dry matter) sewage slugde per 10.000 m^2 can be discharged on agricultural soils

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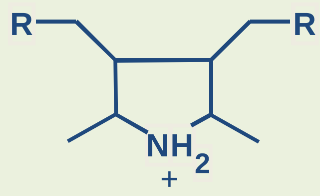
To a minor extend polyacrylamide based thikening agents mixed with pesticides are used to aid in reducing spray drift

Environmantal aspects of PAbF

Canadian diamond mine effluents :



Cationic DADMAC

48h median lethal concentrations (LC50) for *Ceriodaphnia dubia*

0.3 to 0.7 mg/L

Rosemund, Liber (2004) Environ Toxicol Chem

PAbF are known to show

- a high environmental stabilitity
- high geoaccumulation rates
- no bioaccumulation
- no significant biotic degradation
- ecotoxicological effects in the aquatic environment

Organismn	LD_{50} / EC_{50} (mg/L) cationic PAbF (dispers)
Bacteria	0.9 -7500
Algae	0.2 - 7500
Fishes	0.06 - 1000

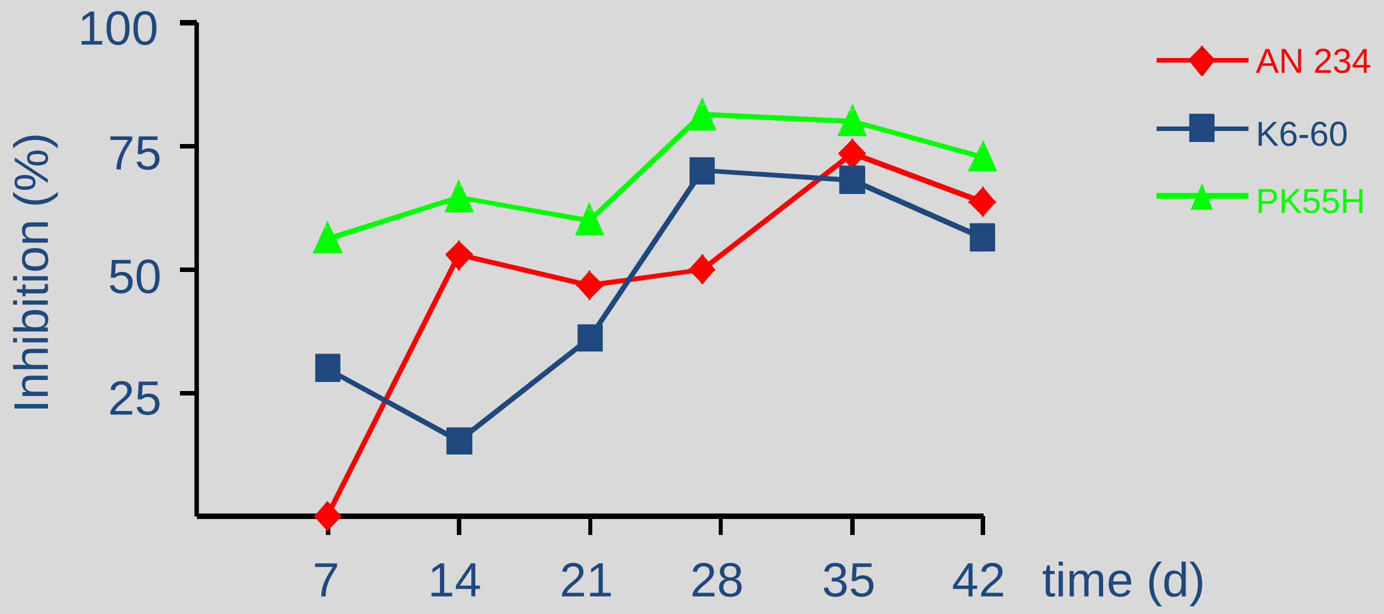
State-of-the-Art

• No data are reported concerning the ecotoxicological effects of PAbF in the pedosphere

• No analytical methods are known for identification and quantification of PAbF in environmental samples

→ Although high amounts of PAbF are released to the environment no information about the distribution, fate and ecotoxicological effects in soils are available or can be aquired.

Respiration activity in soil spiked with PAbF (250 to 500 mg / kg)



Estimated maximal concentrations in soils

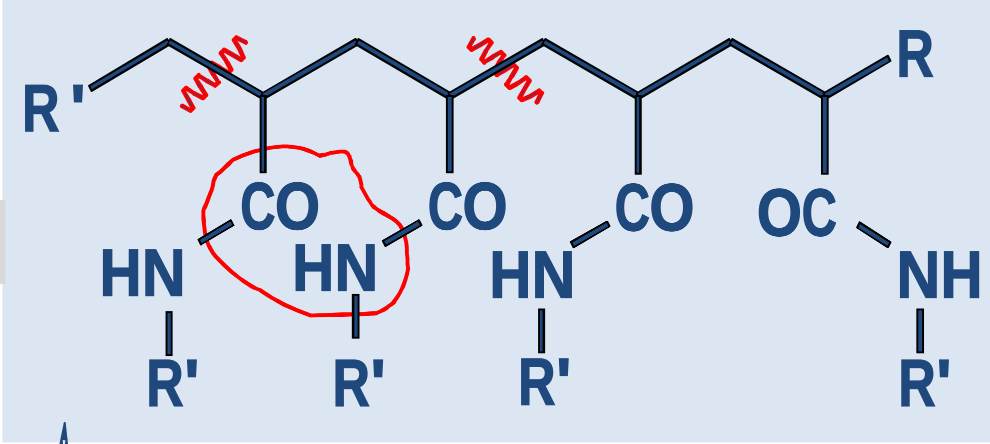
Assumptions:

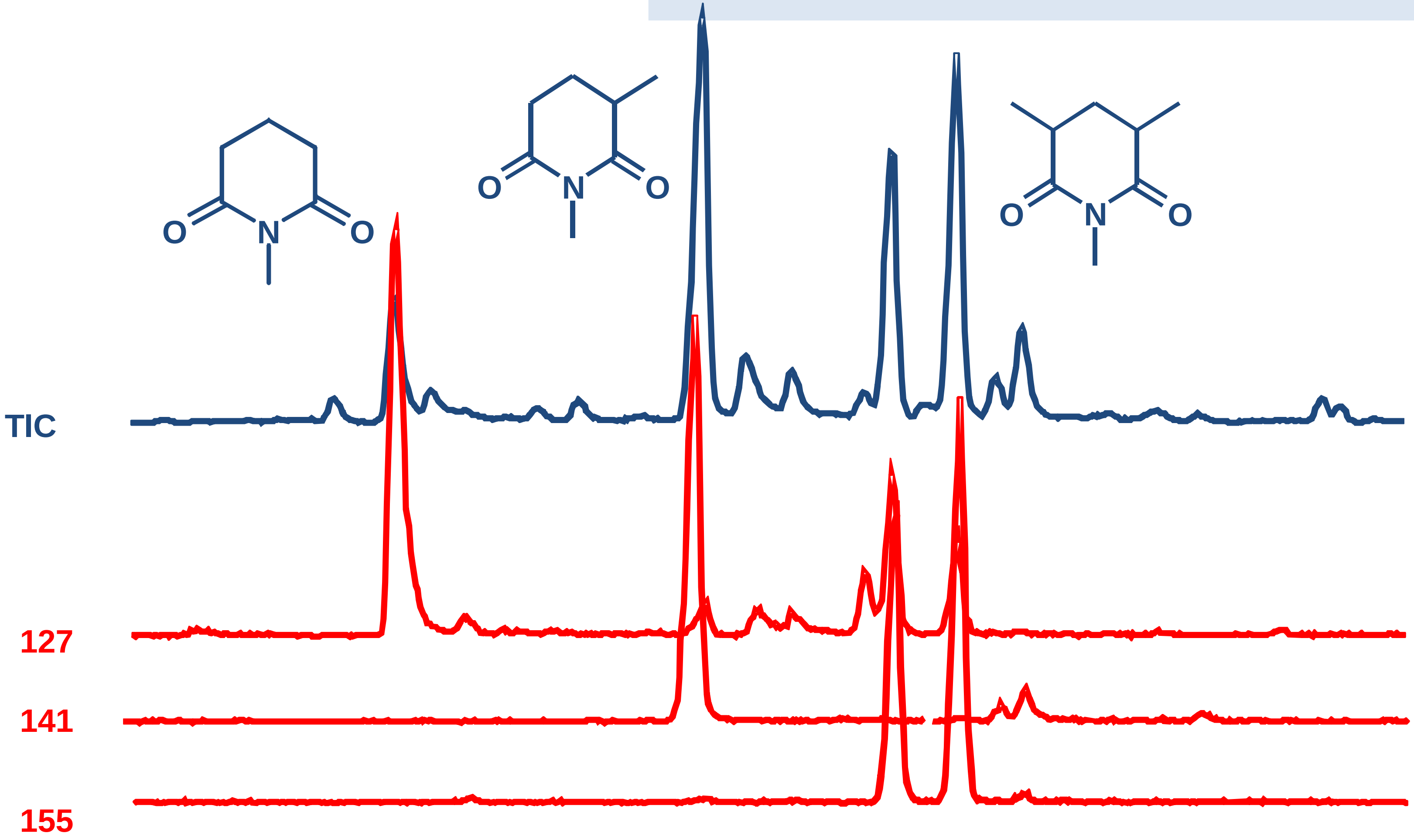
- 5 t sewage sludge (dry matter) applied on 10.000 m^2
- Content of PBaF in sewage sludges: 10 kg/t (dry matter)
- Soil density: 1.5 - 1.8 g/cm^3
- Depth of agricultural treatment: 0.3 - 0.5 m

→ 5 - 10 mg / kg soil

or 1 - 3 mg / kg per year

Products of TMAH thermochemolysis

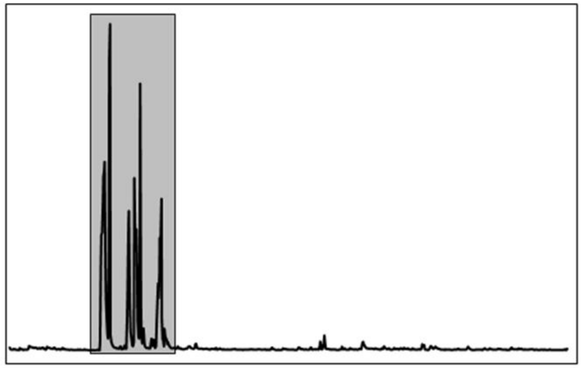


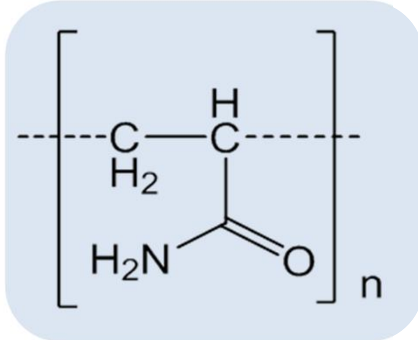


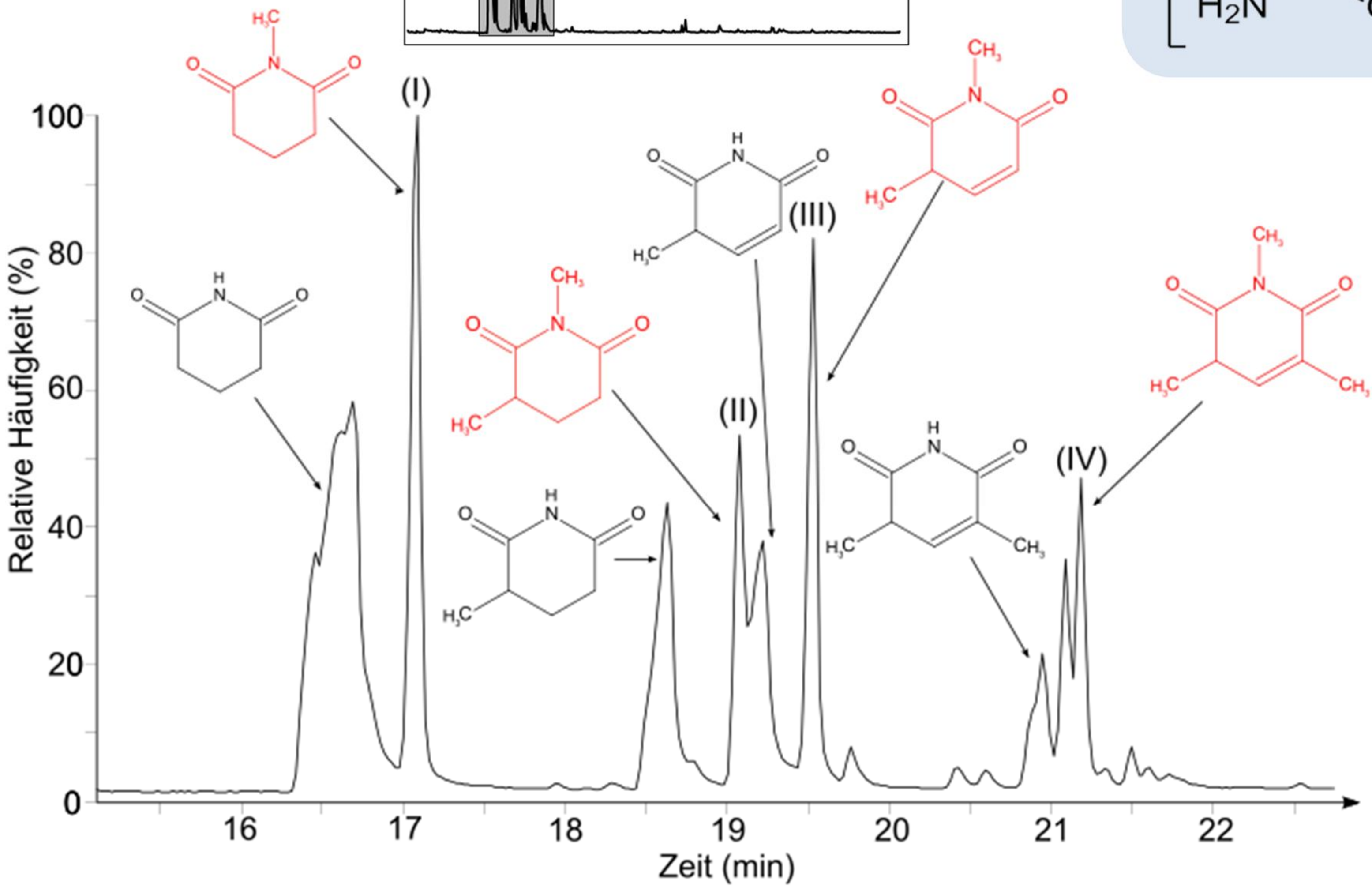
Polyacrylamide based flocculants PAbF

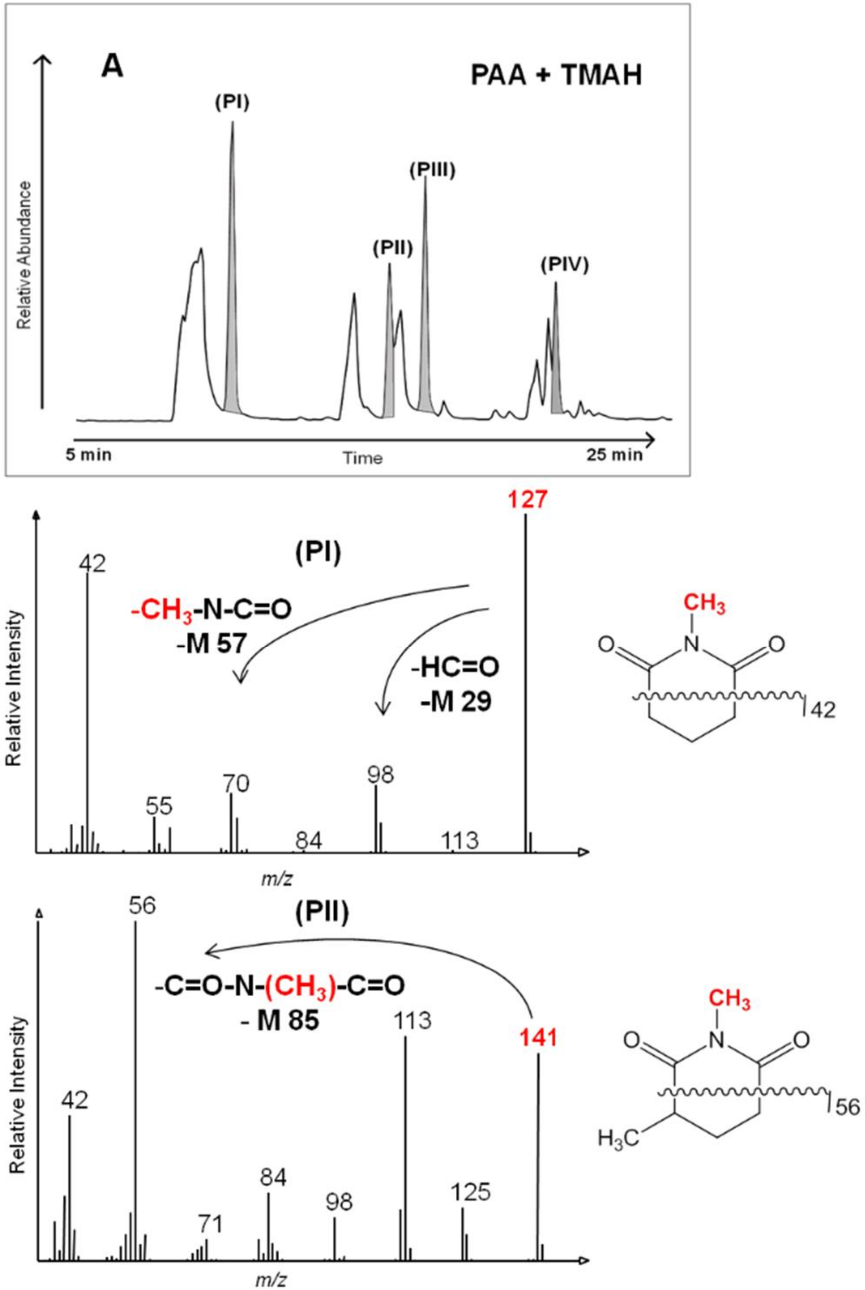
with TMAH

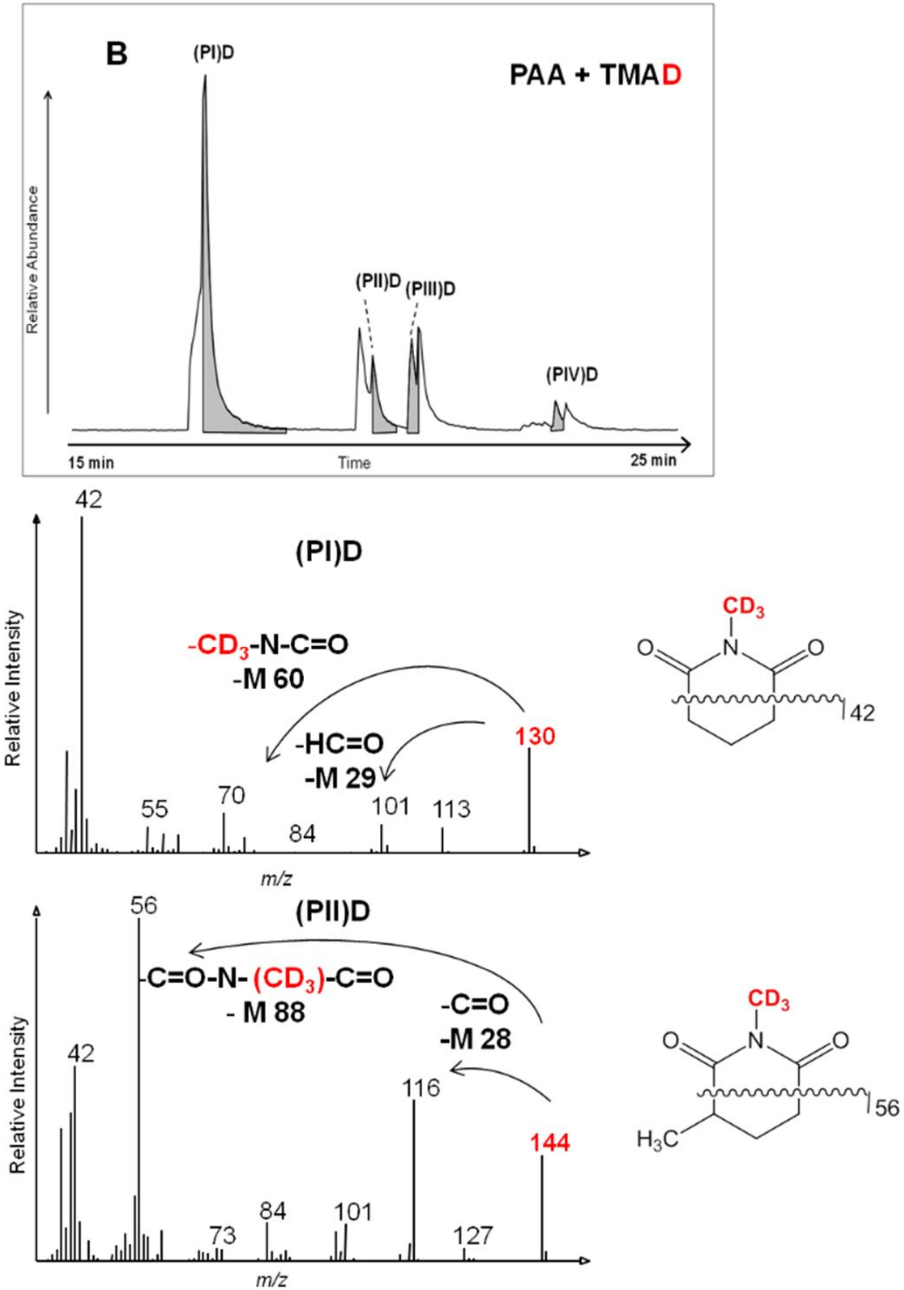
without TMAH



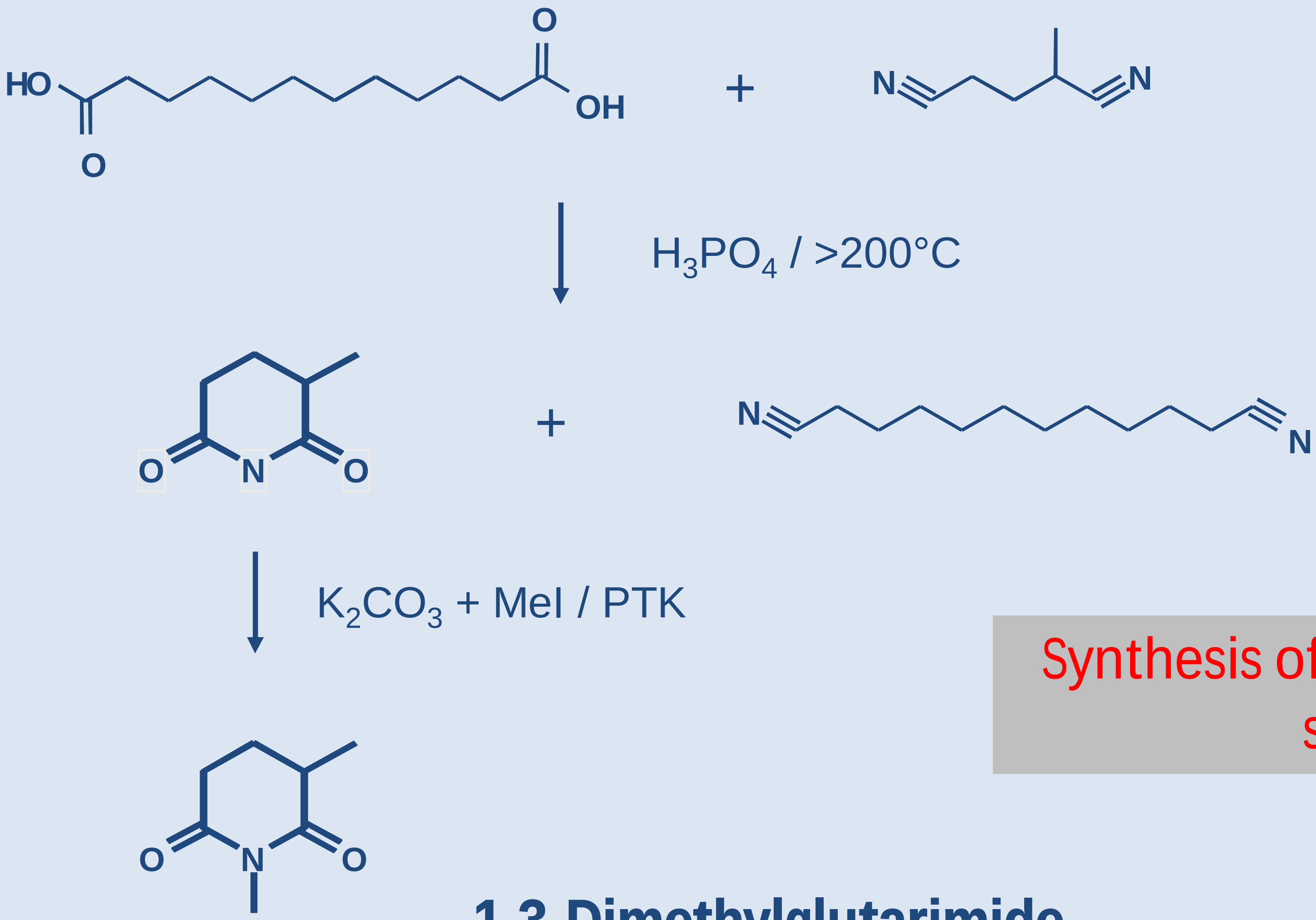





A
PAA + TMAH
(PI)
(PII)
(PIII)
(PIV)
Relative Abundance
5 min
Time
25 min
127
42
(PI)
-CH3-N-C=O
-M 57
-HC=O
-M 29
Relative Intensity
55
70
84
98
113
m/z
CH3
O
N
O
42
56
(PII)
-C=O-N-(CH3)-C=O
- M 85
113
141
42
71
84
98
125
m/z
CH3
O
N
O
56
H3C


B
(PI)D
PAA + TMAD
(PII)D
(PIII)D
(PIV)D
Relative Abundance
15 min
Time
25 min
42
(PI)D
-CD3-N-C=O
-M 60
-HC=O
-M 29
130
Relative Intensity
55
70
84
101
113
m/z
CD3
O
N
O
42
56
(PII)D
-C=O-N- (CD3)-C=O
- M 88
-C=O
-M 28
42
116
144
73
84
101
127
m/z
CD3
O
N
O
56
H3C

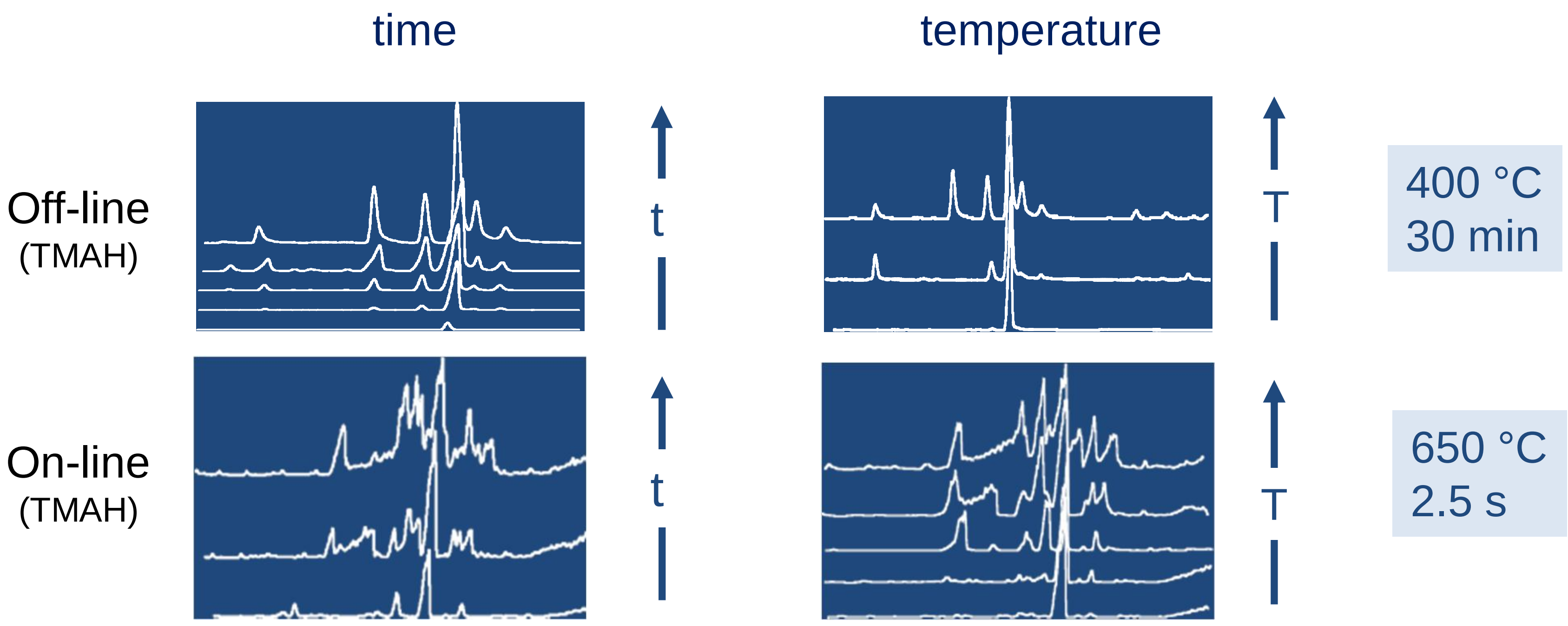
Polyacrylamide based flocculants PAbF

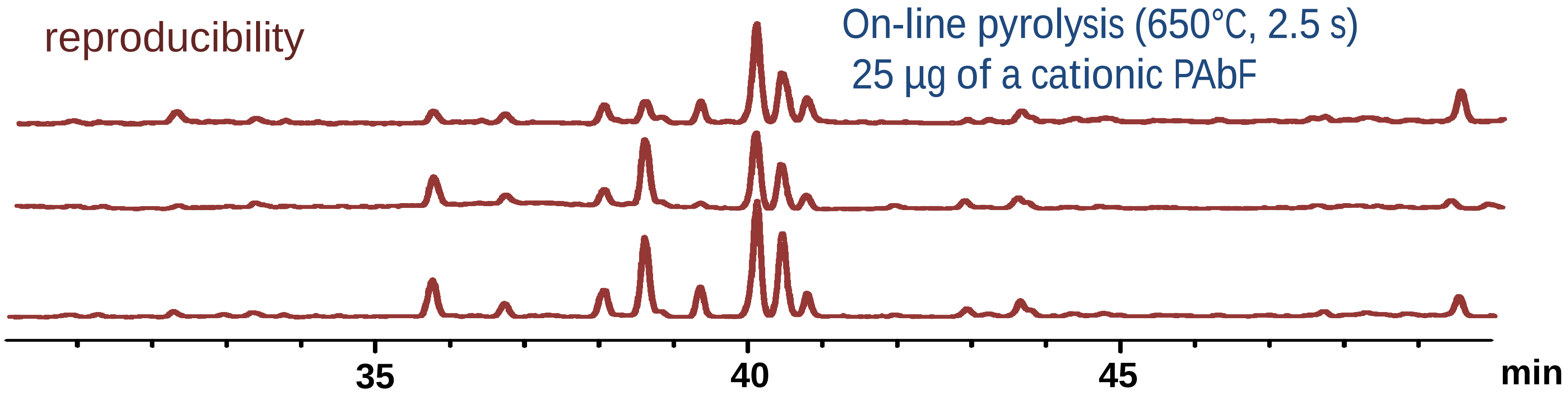


1,3-Dimethylglutarimide

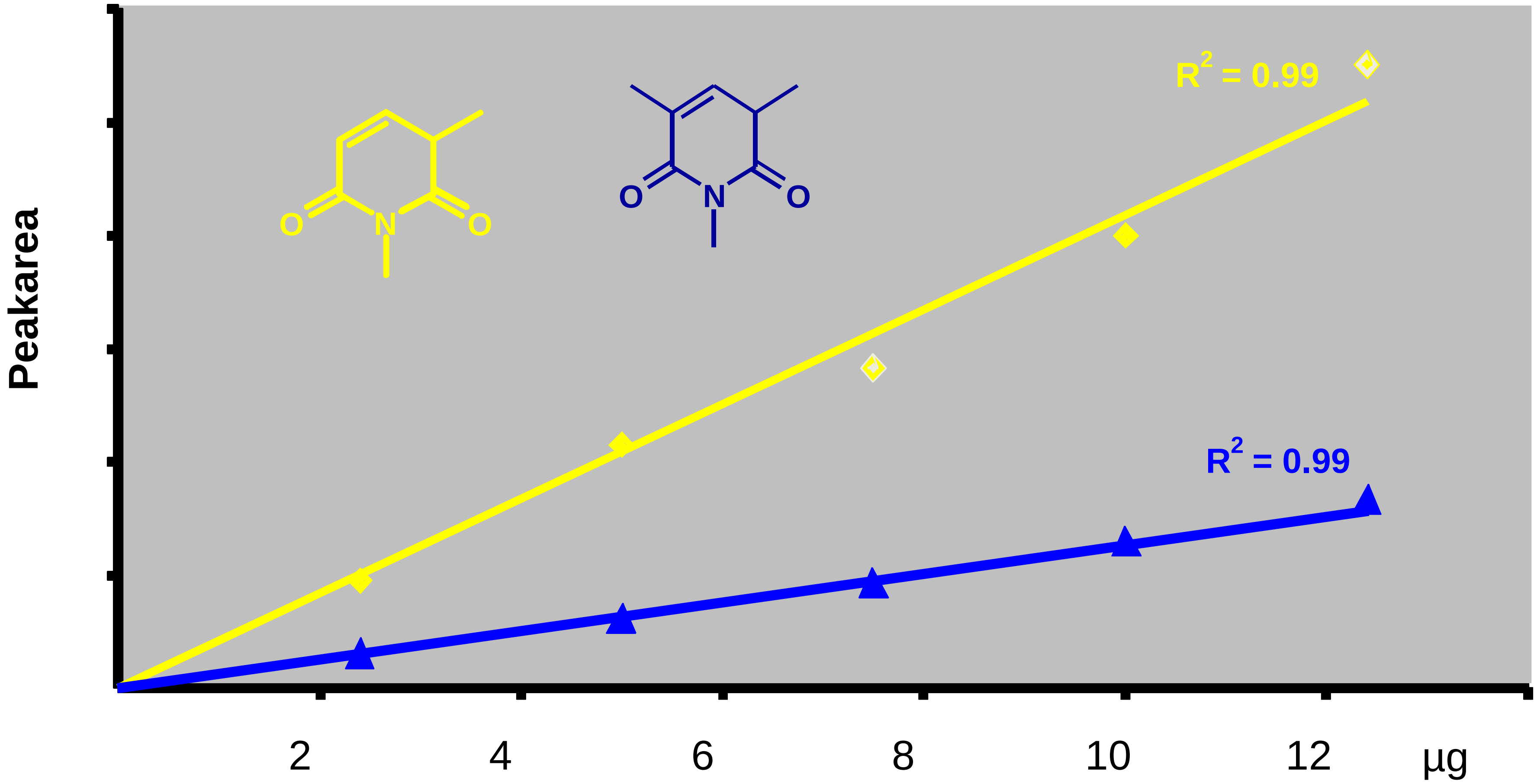
Synthesis of reference substances

Optimization of pyrolysis





Linearity / Sensitivity



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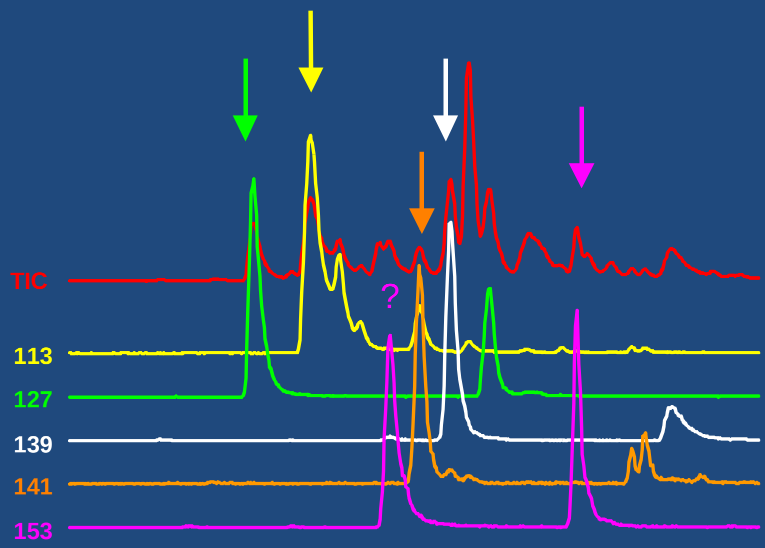
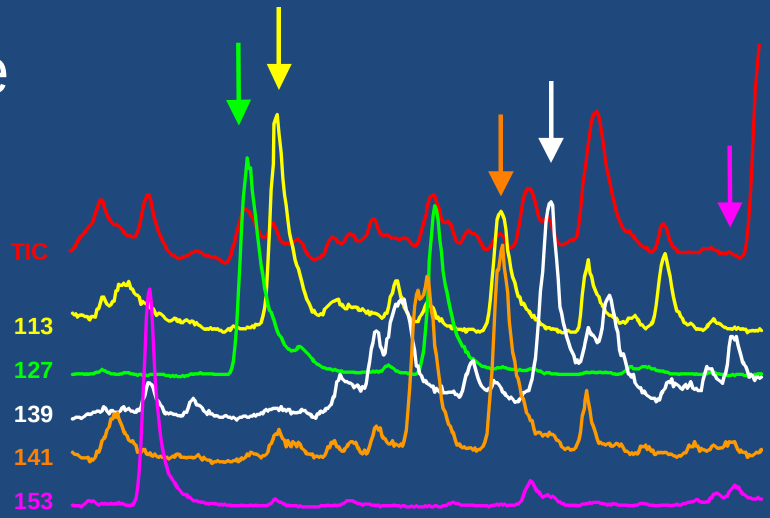
Detection of PAbF in a complex matrix

Sewage sludge sample

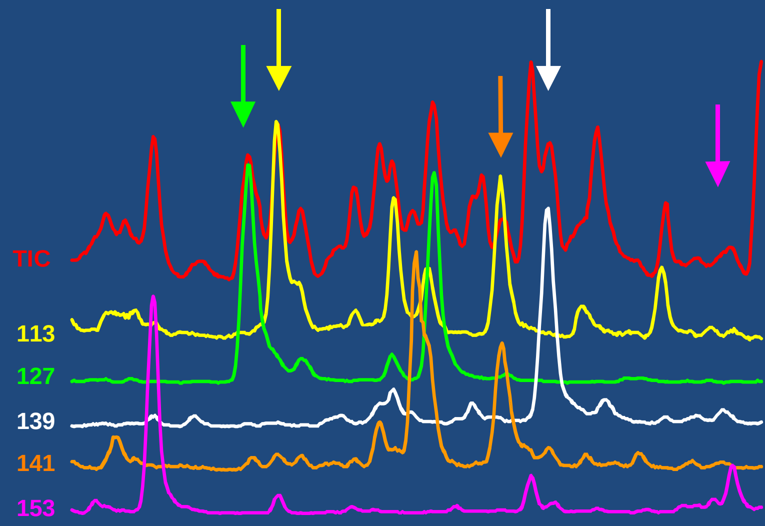
Cationic PAbF



Sewage slugde

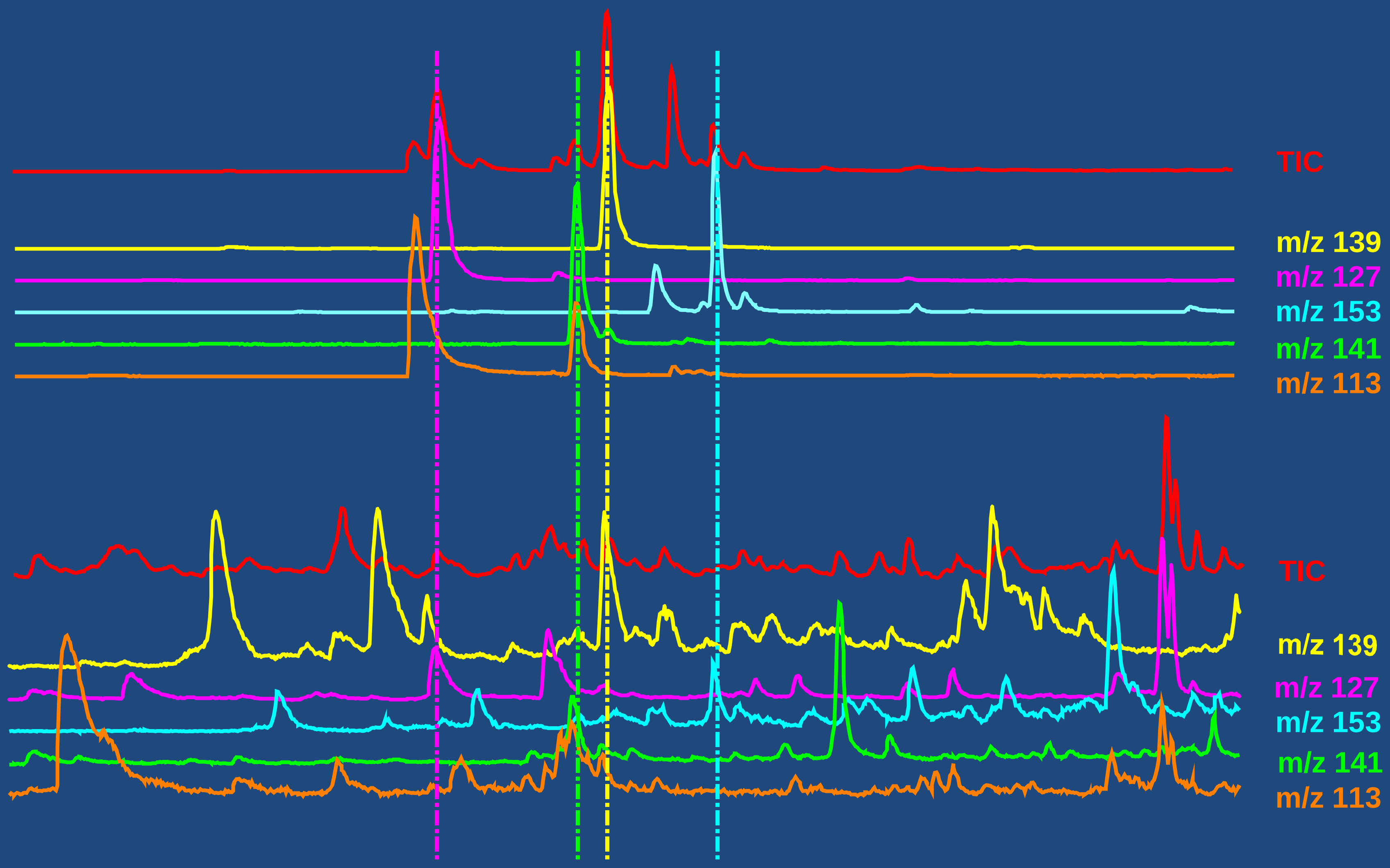


Sewage slugde
(preextracted with acidic MeOH)

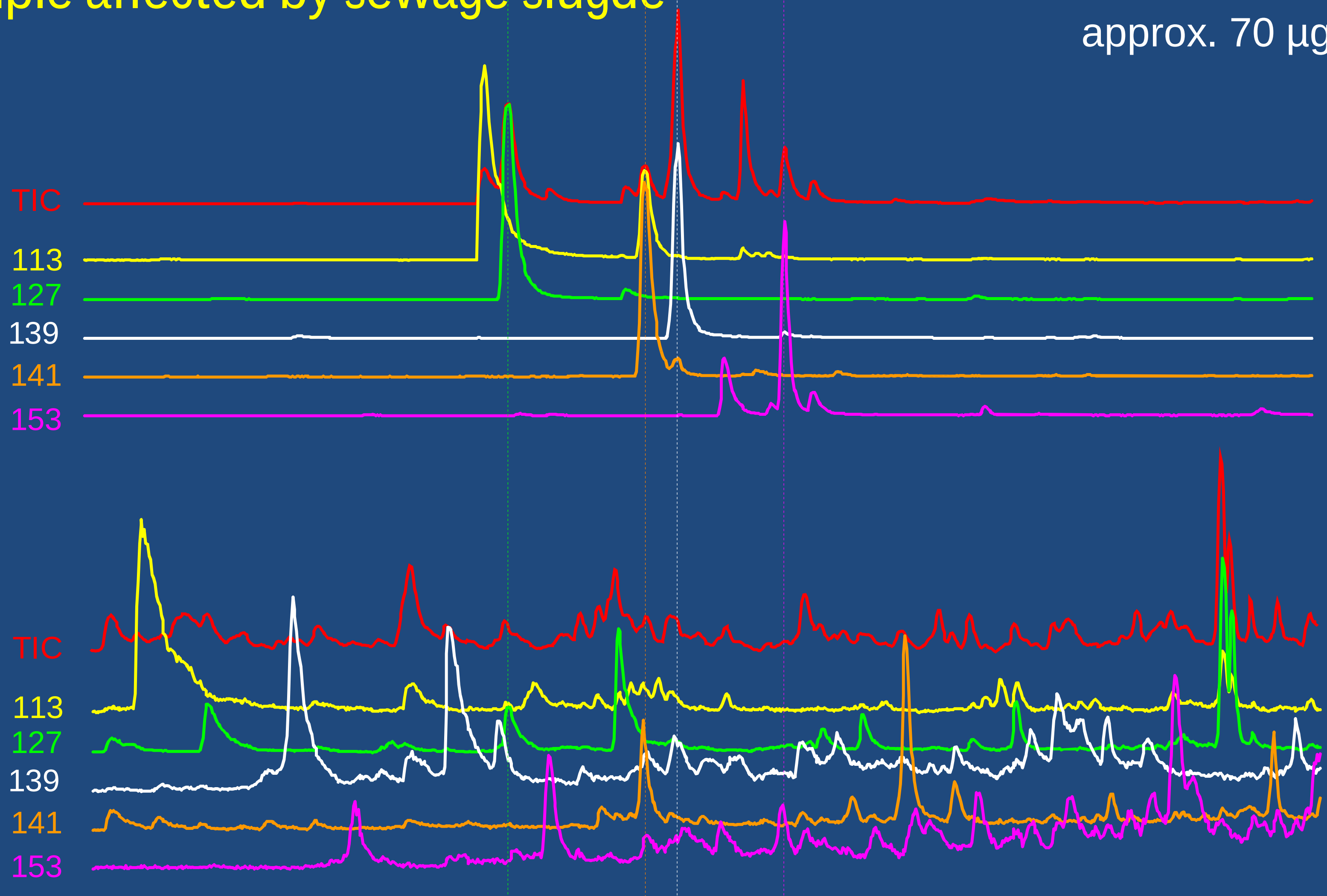


Polyacrylamide based flocculants PAbF

Soil sample spiked with PAbF

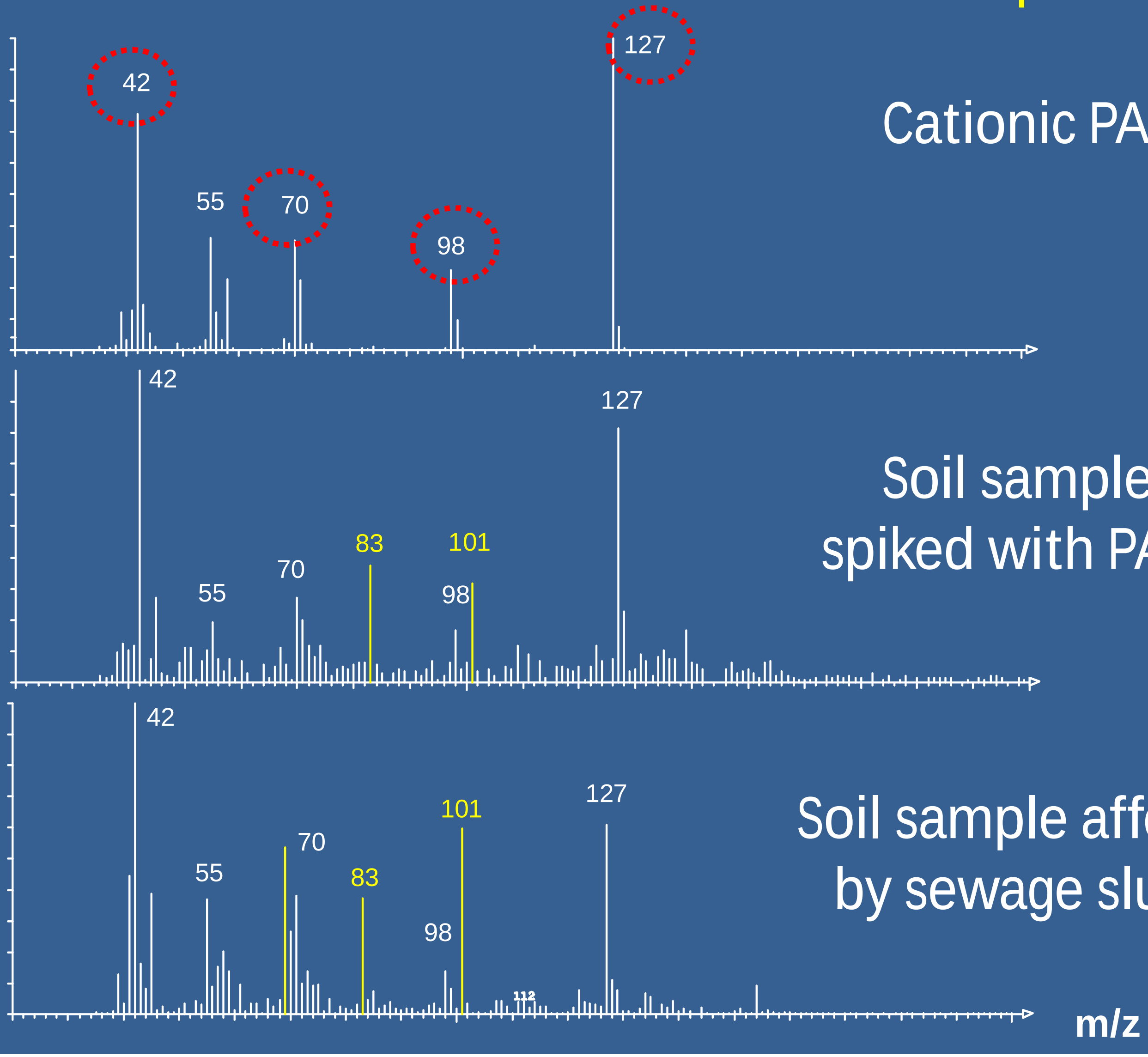


Soil sample affected by sewage slugde

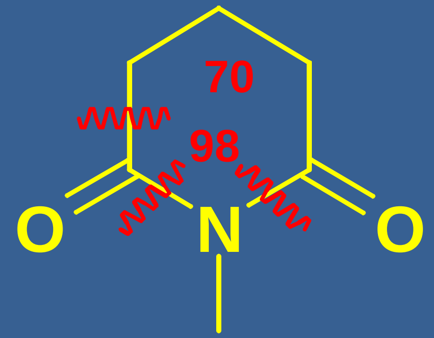


Polyacrylamide based flocculants PAbF

Mass spectrometic identification



Cationic PAbF



Soil sample spiked with PAbF

Soil sample affected by sewage slugde

Example 3

Drilling fluids are important additives for exploration and production drilling in terrestrial and marine environments. Up to 95% of all exploration and production wells used water-based muds. These are mixed with clays and polymers, in order to meet subsurface requirements like stabilization of the borehole and regulation of the flow and filtration properties

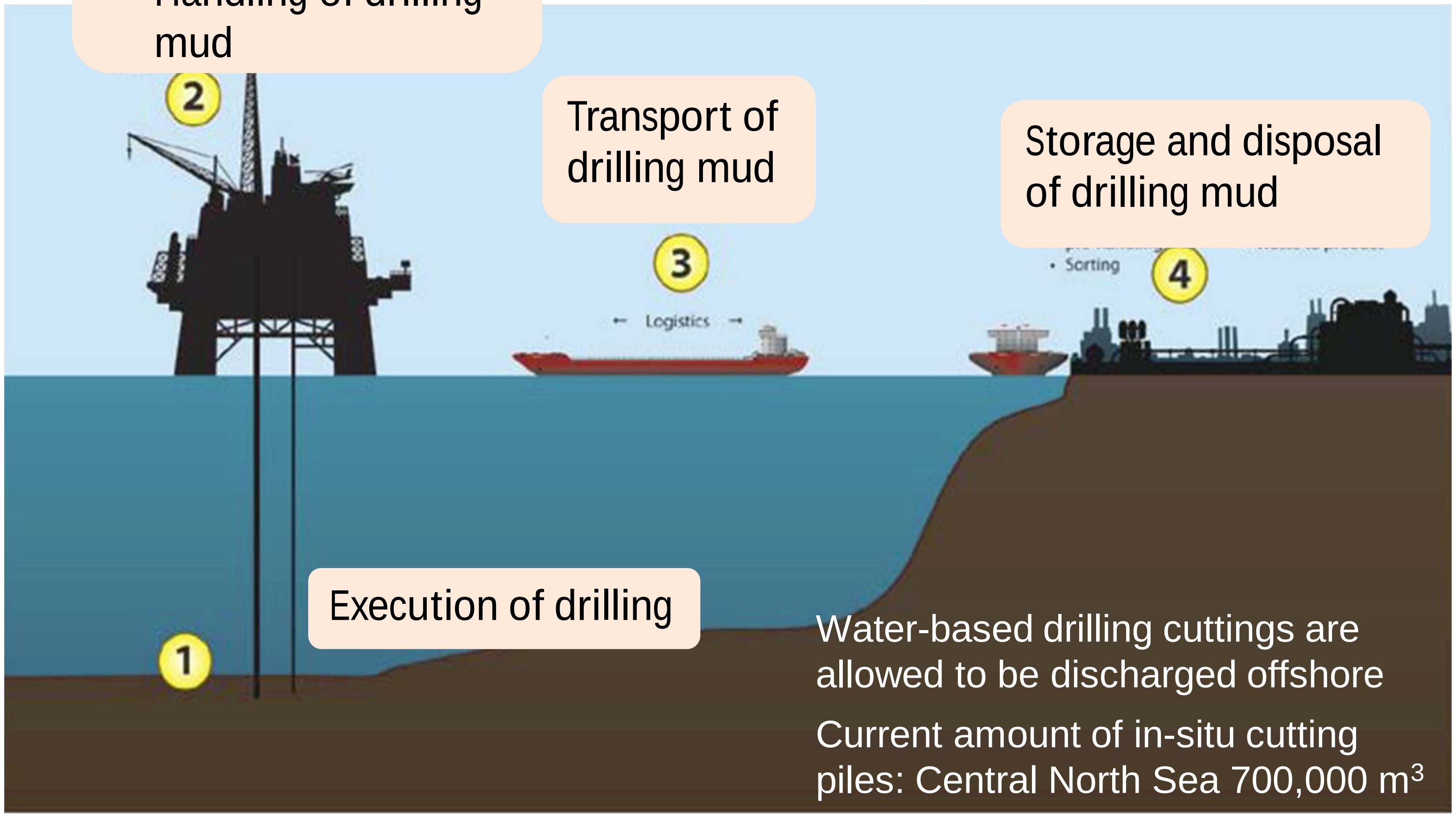
Harmful effects are described e.g. by Khodja et al. (2010), Dijkstra et al. (2013), Trannum et al. (2011), Bechmann et al. (2006)

Their usage is not a strictly closed system application, hence continuous emission of drilling fluids towards ecosystems are evident.
(Apaleke et al. 2012)

Detection and quantitation of drilling emissions are highly relevant

Polymers in drilling fluids

In average 25% of drilling cuttings are released during off-shore drilling



- Preparation and execution of drilling
- Handling of drilling mud

Transport of drilling mud

Storage and disposal of drilling mud

Execution of drilling

Water-based drilling cuttings are allowed to be discharged offshore

Current amount of in-situ cutting piles: Central North Sea 700,000 m^3

Polymers in drilling fluids

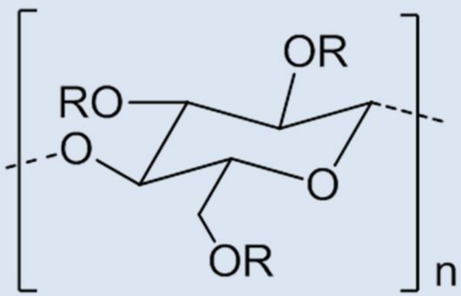
Drill cutting – 4300 times enlarged

Detection of drilling activities in marine environment

Identification of characteristic pyrolysis products of polymers used as main compounds in drilling fluids

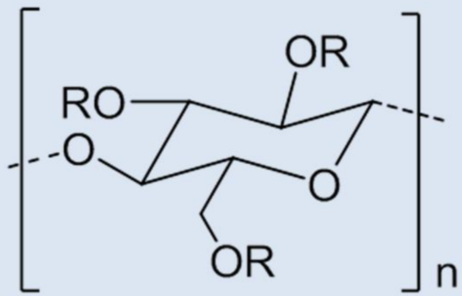
Proof of ability if these specific substances can act as drill cutting indicators

Chemical structures of common drilling additive polymers



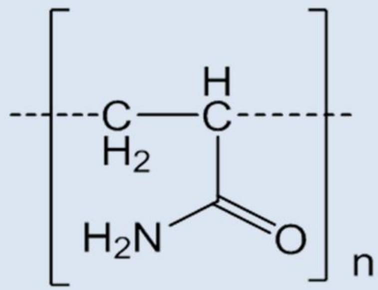
R = H or CH_2CO_2H

Carboxymethyl-cellulose
(CMC)



R = H or CH_2CH_2OH

Hydroxyethyl-cellulose
(HEC)

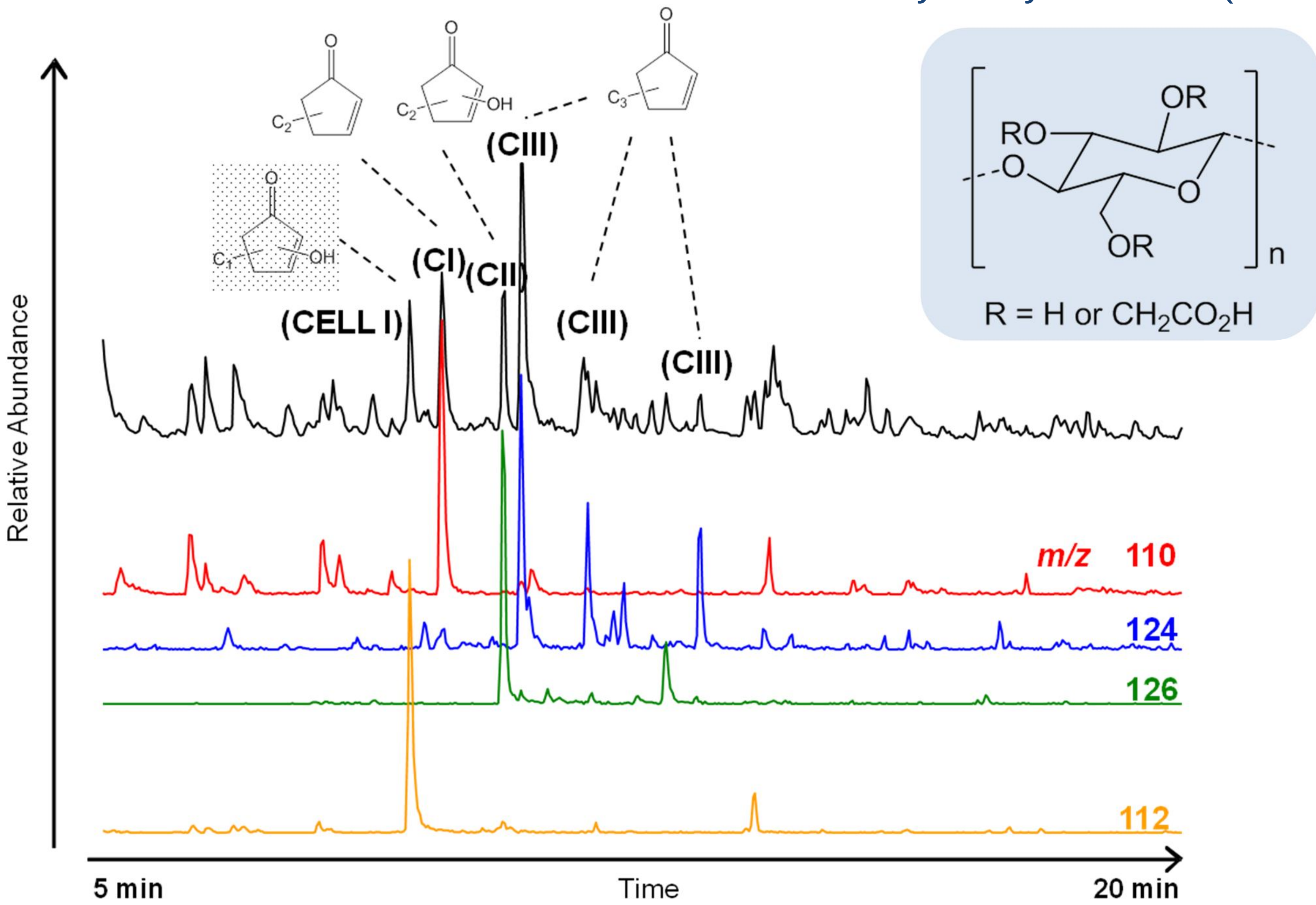


Polyacrylamide
(PAA)

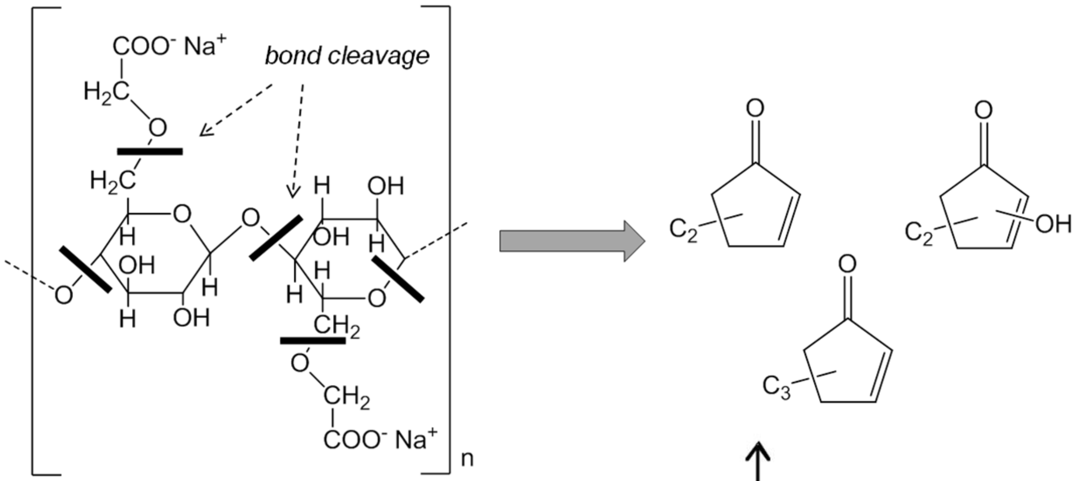
Further components: Xanthan, Bentonite, Barite, etc.

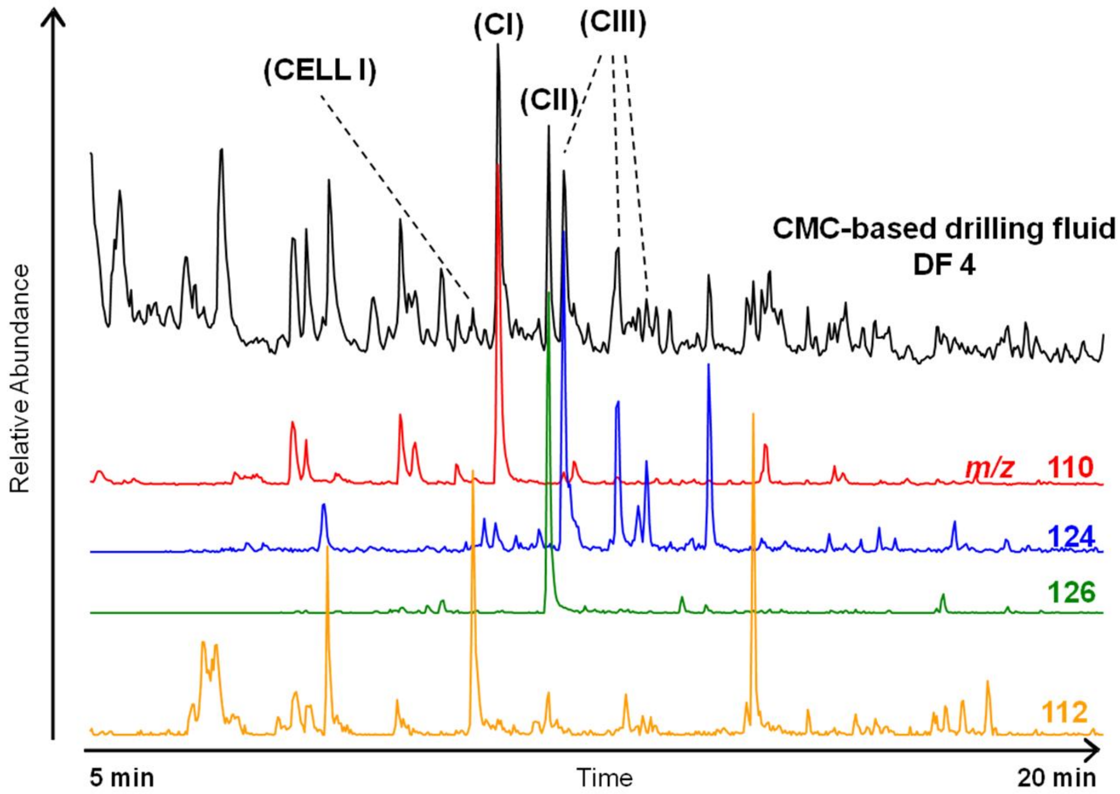
Polymers in drilling fluids

Carboxymethylcellulose (CMC)

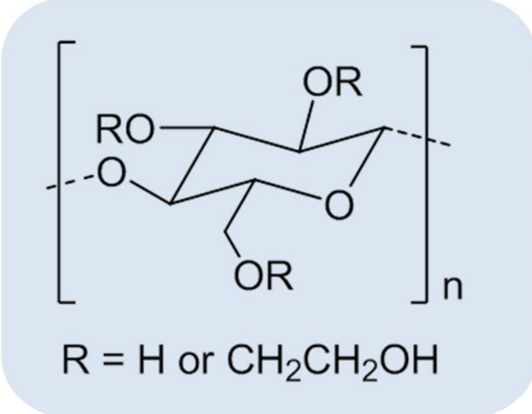


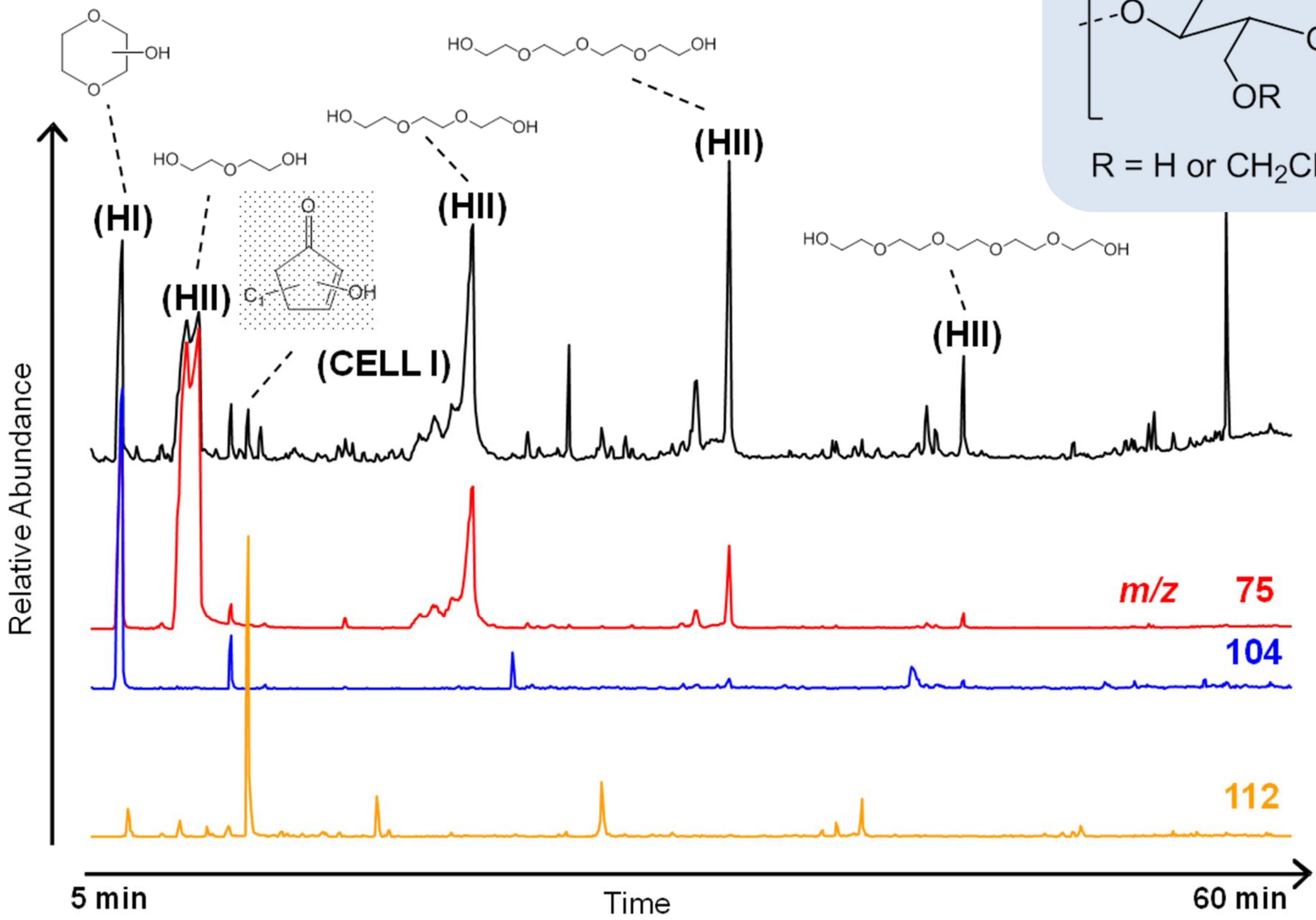
Polymers in drilling fluids

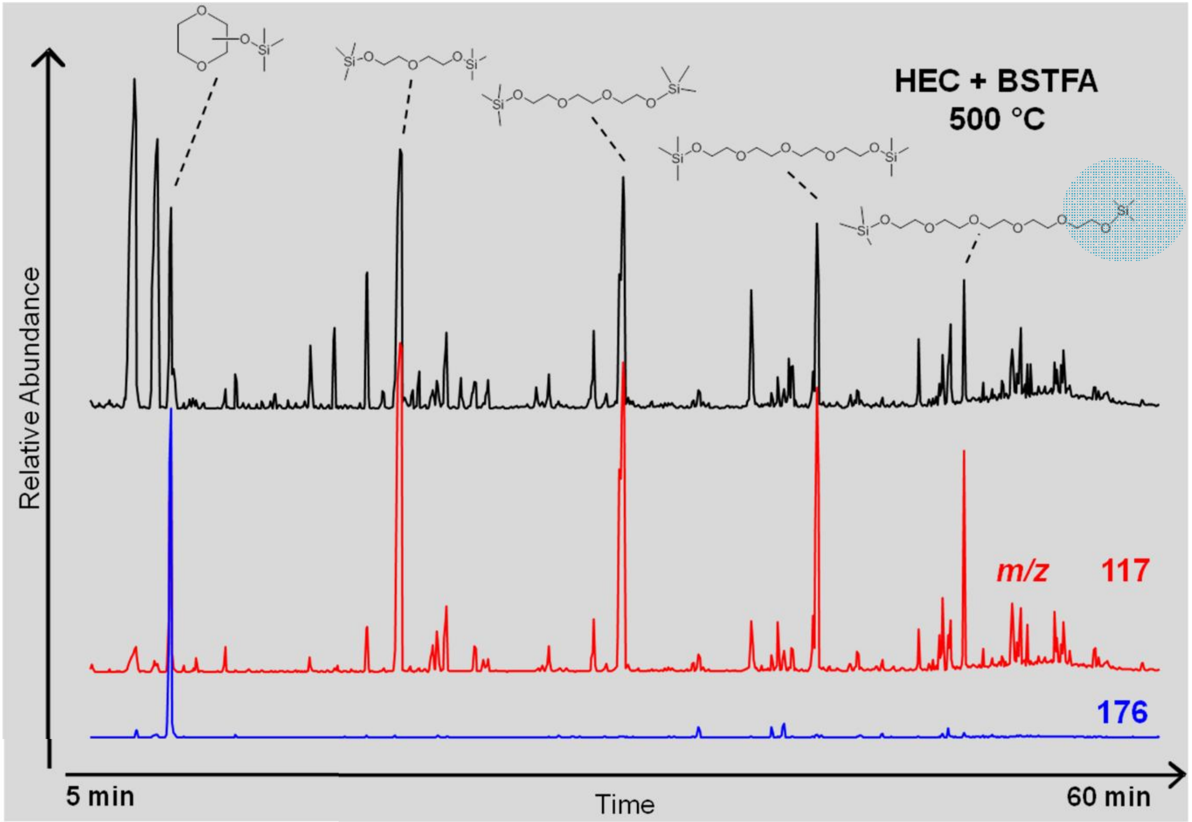


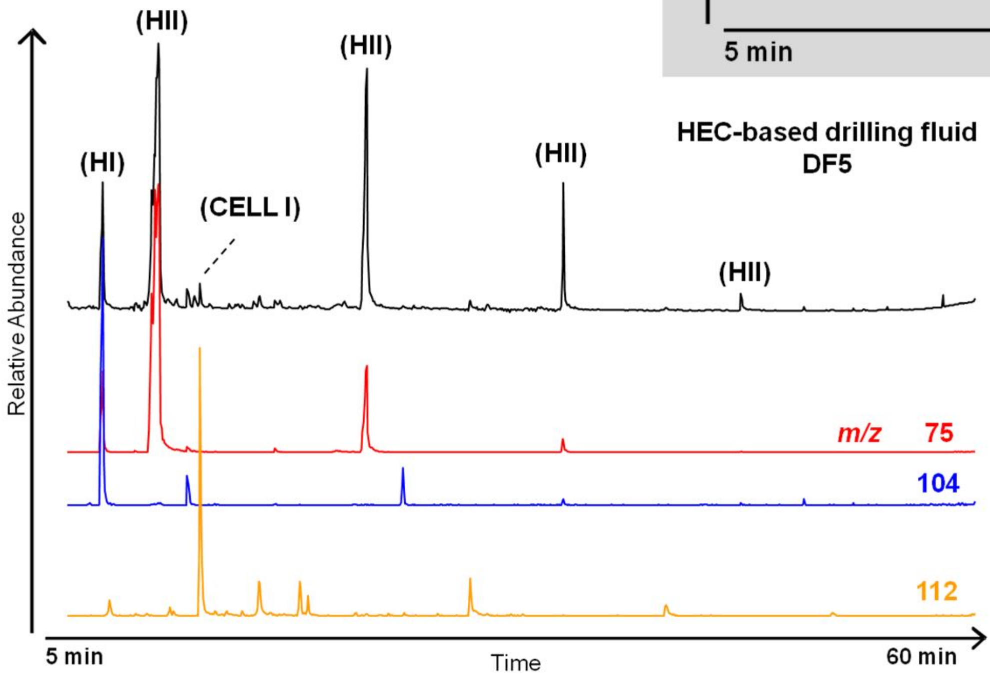


Hydroxyethylcellulose (HEC)

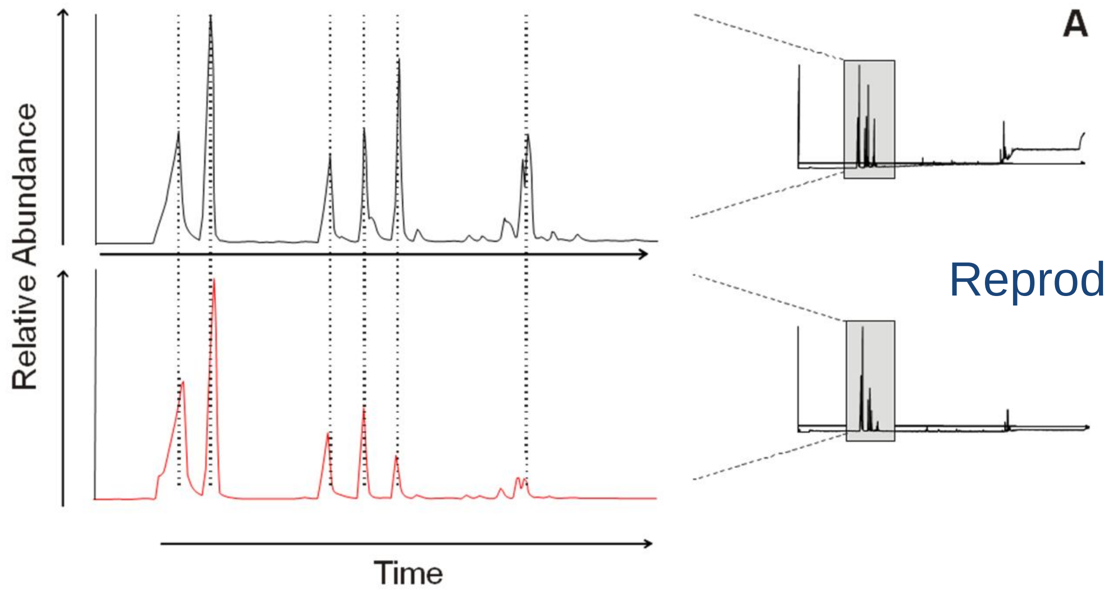




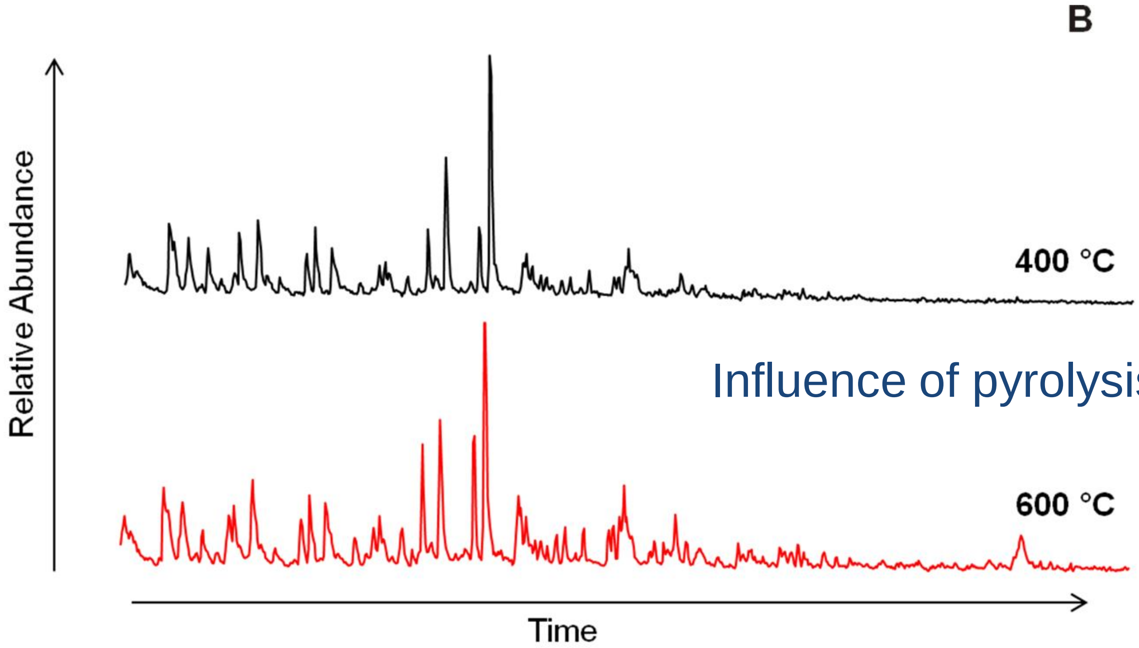

HEC + BSTFA
500 °C
Relative Abundance
m/z 117
176
5 min
Time
60 min


(HI)
(HII)
(HII)
(HII)
(HII)
(CELL I)
HEC-based drilling fluid
DF5
Relative Abundance
m/z 75
104
112
5 min
Time
60 min

Polymers in drilling fluids

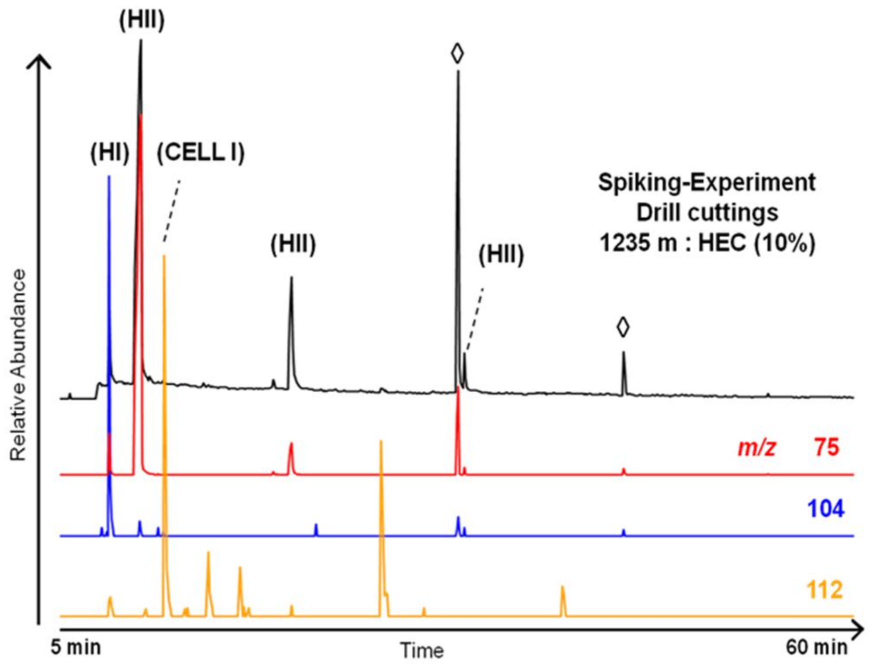


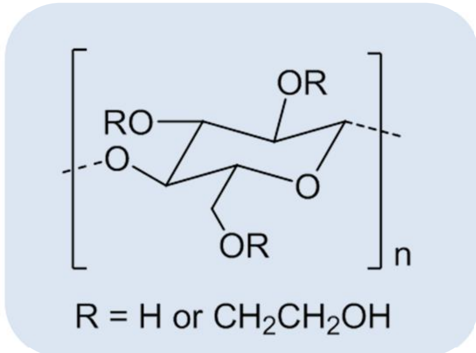
Reproducibility



Influence of pyrolysis temperature

Quantity/LOQ





< 1 mg DF/g

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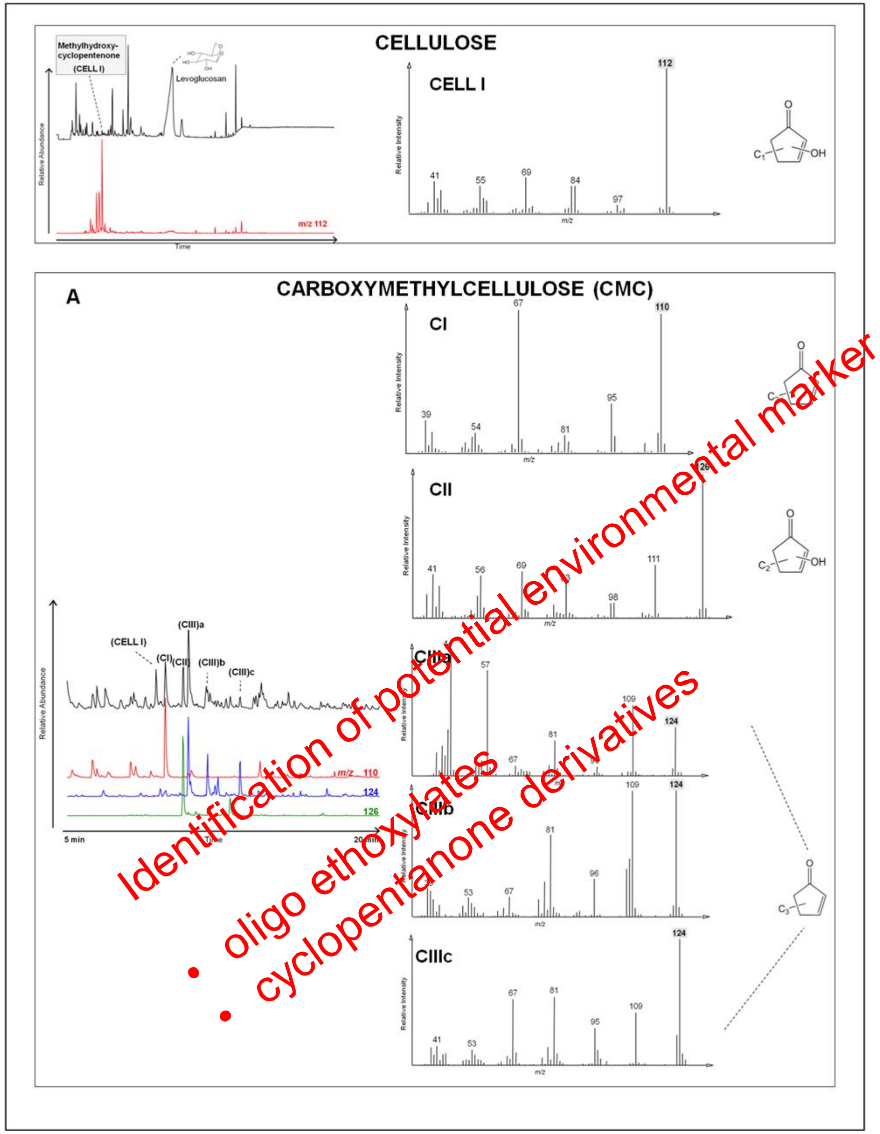
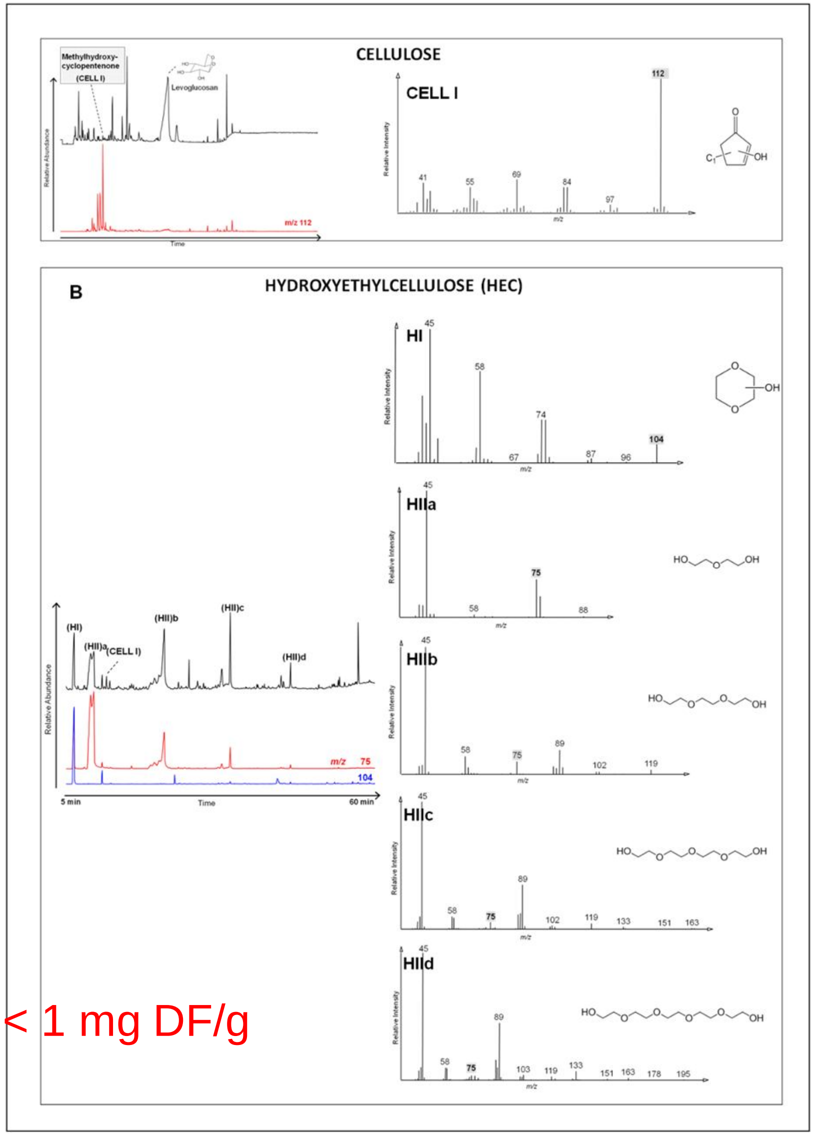
Cellulose based drilling fluids





Identification of potential environmental marker

- oligo ethoxylates
- cyclopentanone derivatives

< 1 mg DF/g


Conclusions
Py-GC/MS is a key method for polymer analyses
–
but not a simple one