Fraunhofer CSP

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Novel membrane filter cascade system for the selective analysis of nano and micro plastic particles from water and air

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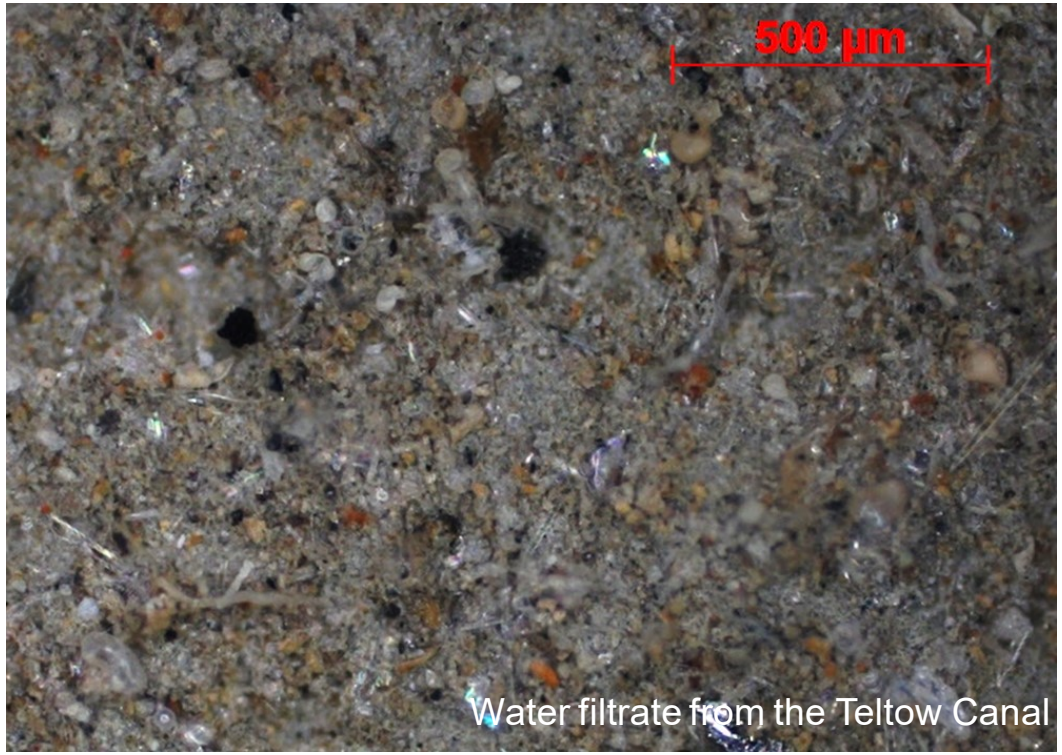
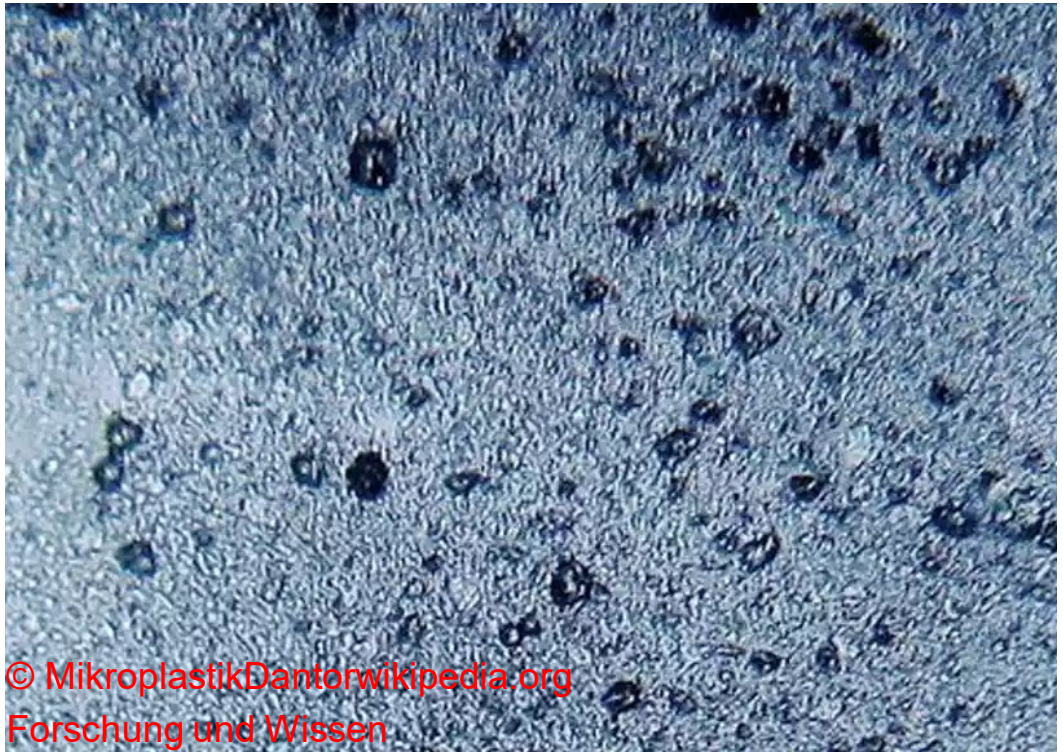
Motivation

What is the plastic pollution and how can it be measured?

Detection of micro- and nanoplastics and the assessment of water and air quality is an important issue in drinking water supply and wastewater treatment as well as the air quality in offices, transport units or playgrounds.



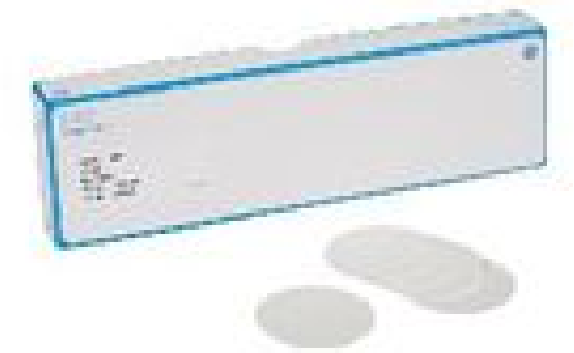
Water filtrate from the Teltow Canal



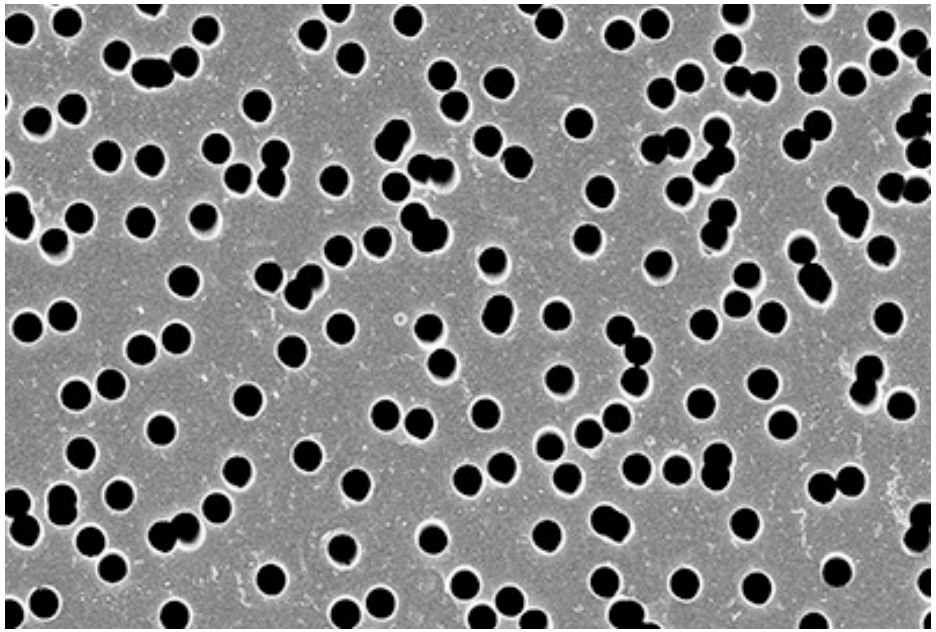
Motivation

Most used

For microparticles the most used filters are Quartz filters (mass studies) of Nucleopore (Analytics)

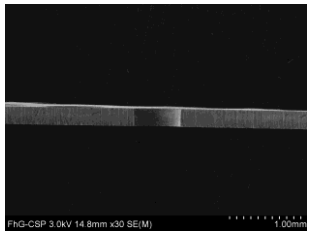


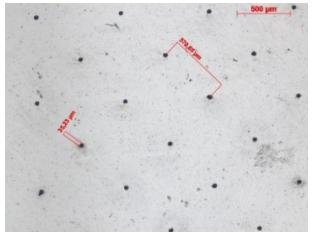
Quartz Microfiber Filter(https://www.analytics-shop.com/gb/wh1855-090-gb.html)

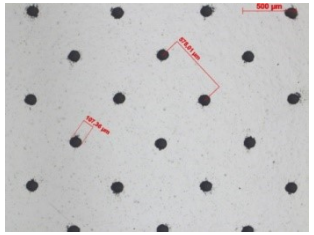


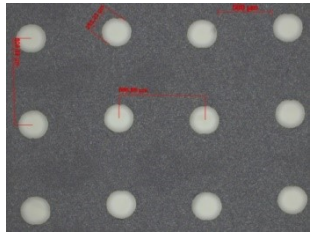
Nucleopore Gold Coated (https://www.i3membrane.de/en/lab-pharma/asbestos-analysis/i3-trackpor/)

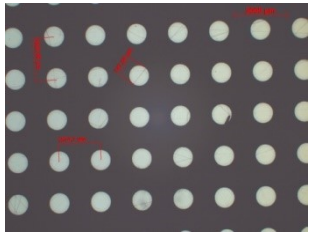
Filter material
Si-Filter production by ns/fs-Laser drilling

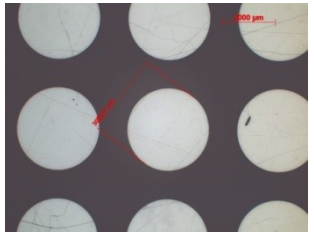

less then10µm


10 – 50µm


50 – 100µm


100 – 500µm

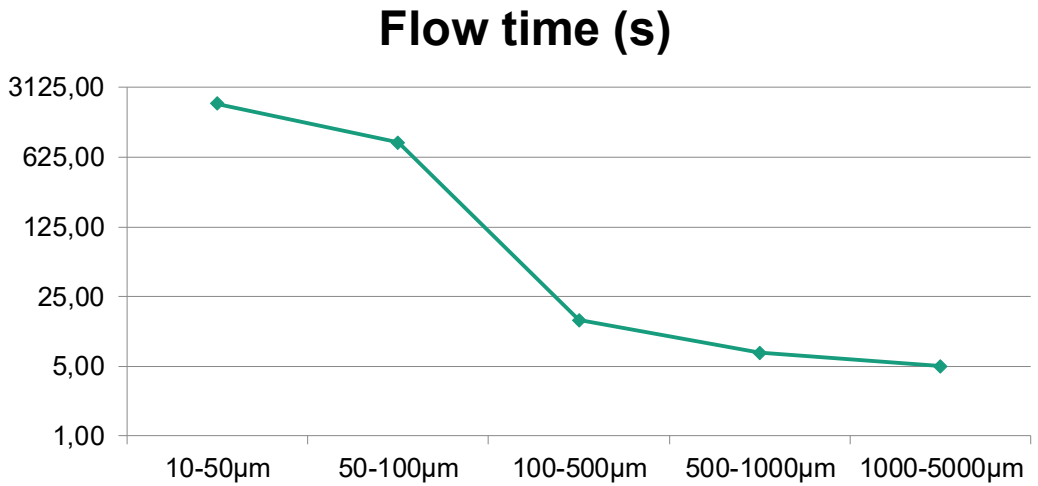

500 – 1000µm


1000 – 3000µm

Material:

- Silicon Wafer double side polished
- Dimensions: 5 - 300 mm
- Thickness: 180 - 500 µm

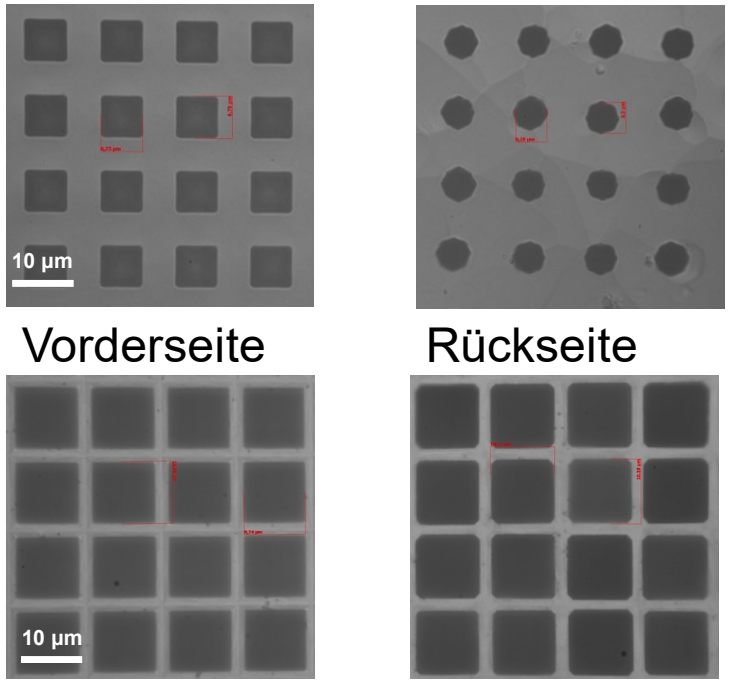
- Development of Laser processes for Si filter production
- Variable design
- Variable pore size, pitch and Filter geometry



→ **Filters with smaller pore sizes (<10 µm) produced by electrochemical etching from** smart MEMBRANES

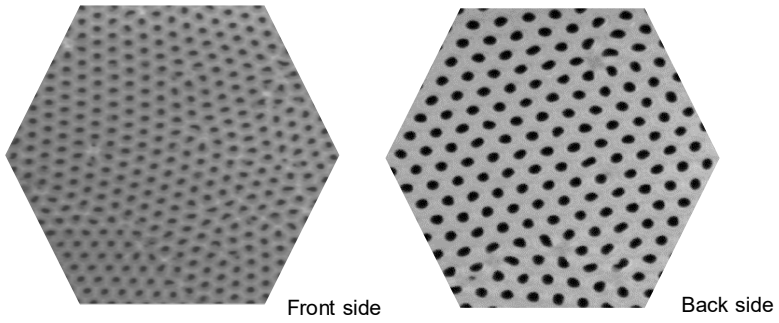
Comparison different Filters with small pore sizes

MakroPor Si



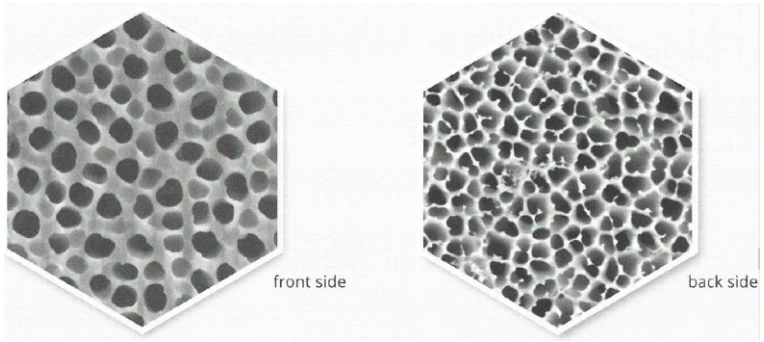
- Electrochem. etched Si-Filter
- Pore size von 10 to < 1 µm

SmartPor Al_2O_3



- Selfordered Periodical Structure
- Pore sizes: 20 nm, 90 nm up to 400 nm

Flexipor Al_2O_3



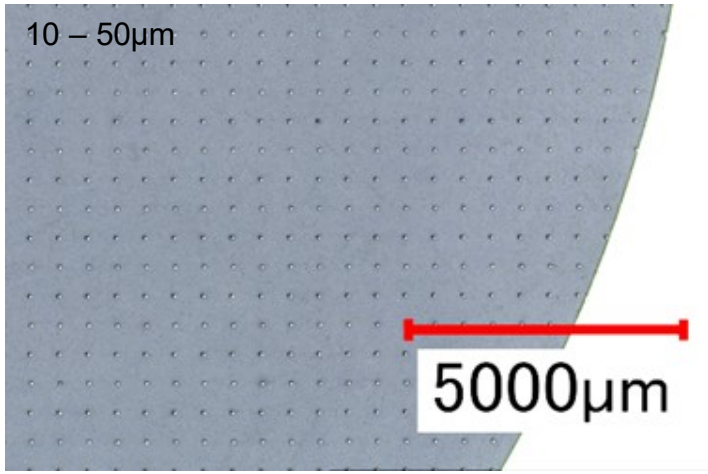
- Nanoporous Structure
- Pore sizes: 20 nm, 100 nm und 200 nm

Process development for Si-Filter production by laser drilling

ns-Laserdrilling of Si wafers (180 to 500 µm dick) for pore sizes until 25 µm (hole exit)

Process development now delivers small pores ~ 10 µm and thus closes an important gap to SMB materials

Used material: both sides polished Si-Wafer (thickness: 180 - 500 µm)



Optimized process for:

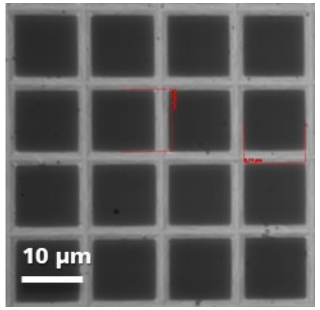
Small drilling radius (r = 10-15 µm)

Scan speed/Puls overlap

Focus shift during drilling process (number of passages)

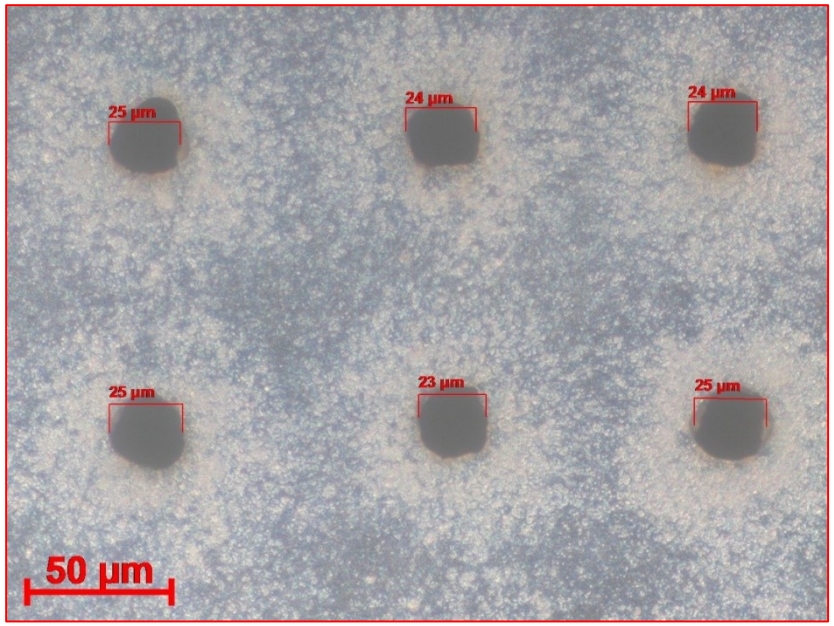
Proof of Concept and small samples successful demonstrated

Process development for laser drilled Si-Filter



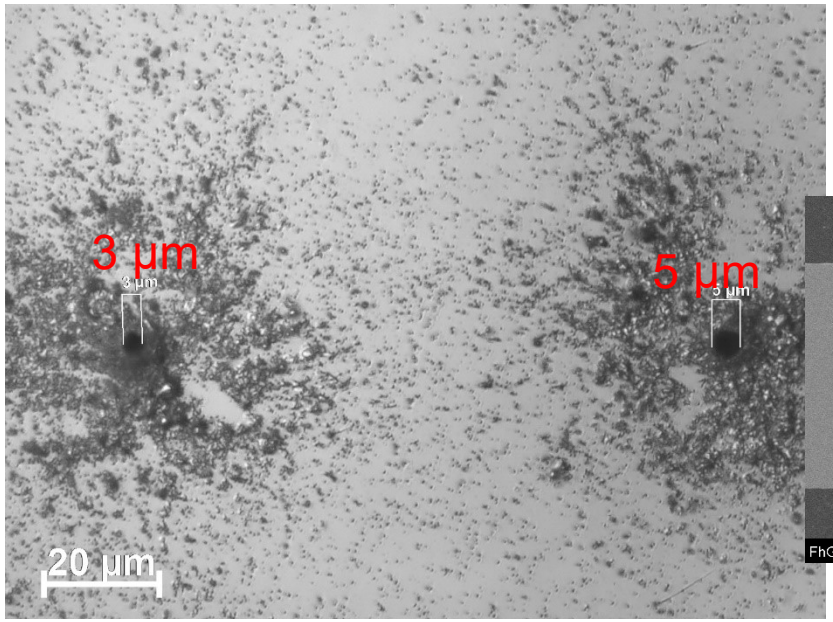
Electrochem. etched Si filter (10 bis <1 µm)

Optimization of ns-drilling process

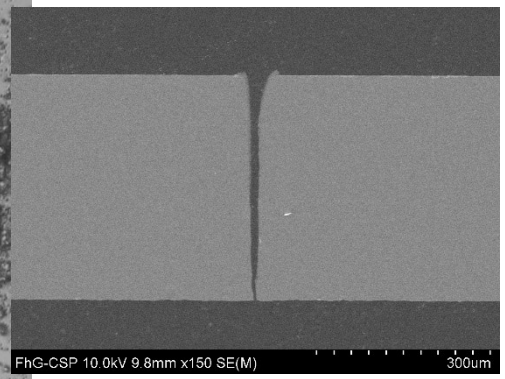


Optimization

Laser processed Si filter
(5 mm bis 100 µm → now until 10 µm*)



Side view

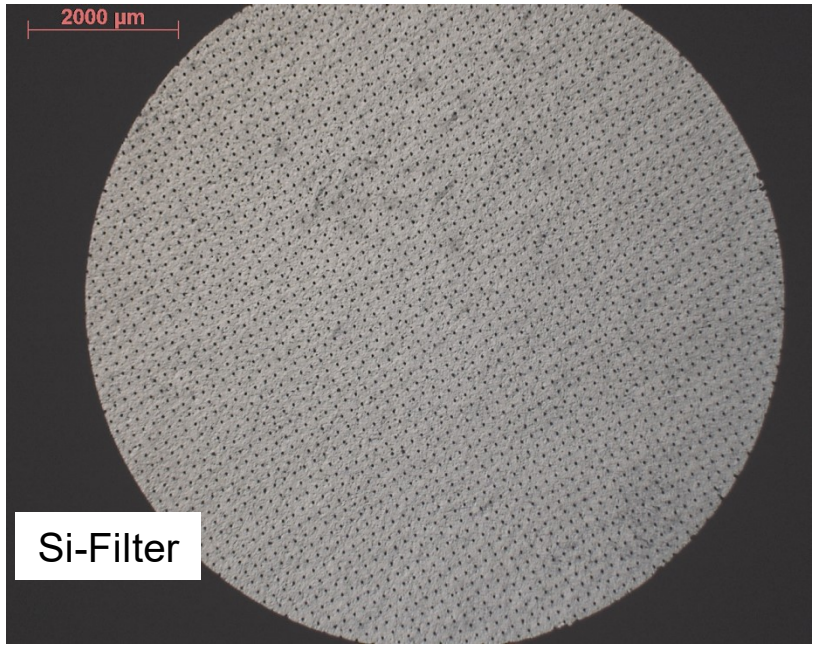


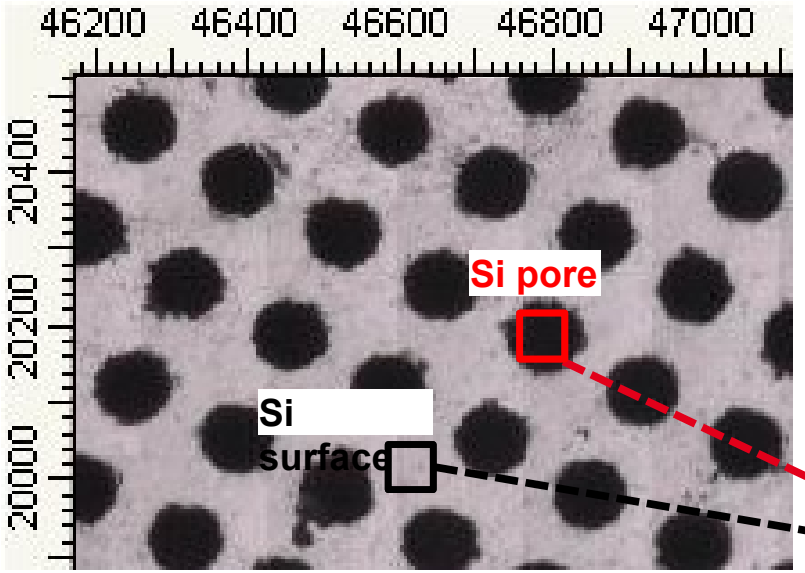
Proof of Concept (before/ and after cleaning not optimised)

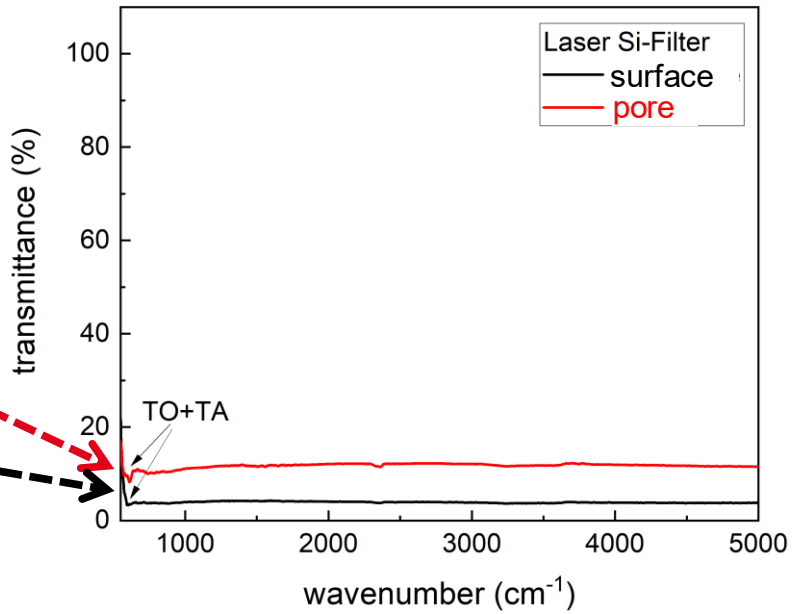
- Conical pore geometry
- Necessary used of the back side surface of the Filter for particle separation with sizes below 10 µm

Usage example: Optical microscopy and FTIR spectroscopy

Laser Si-Filter (CSP)



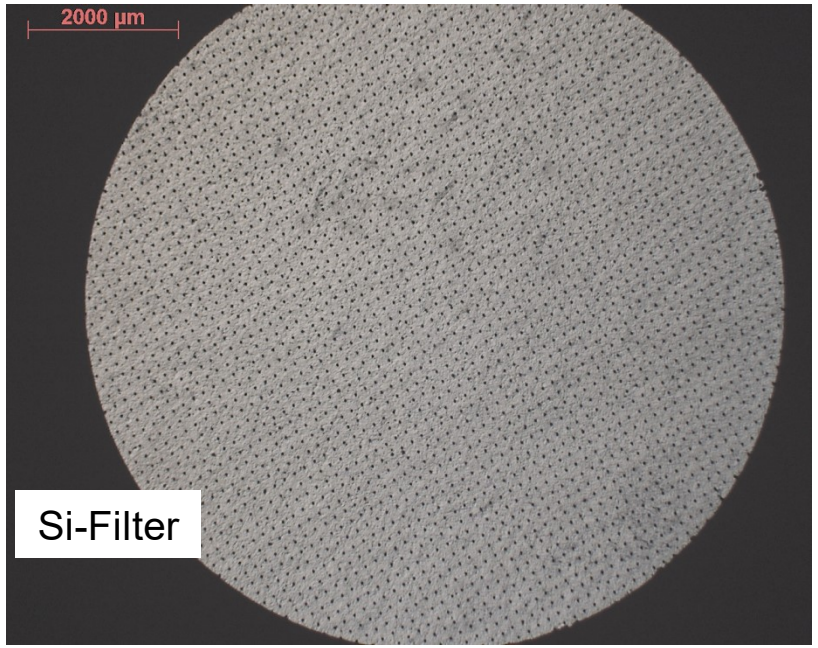


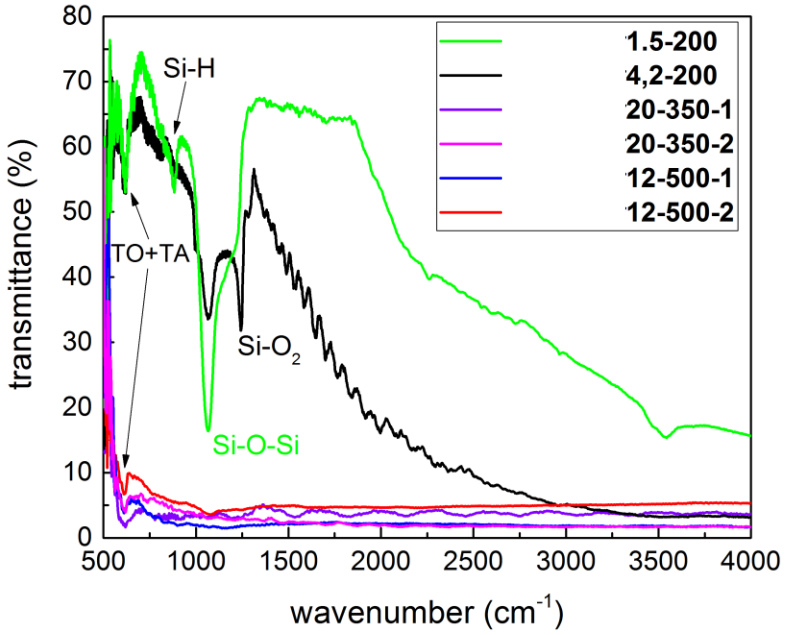


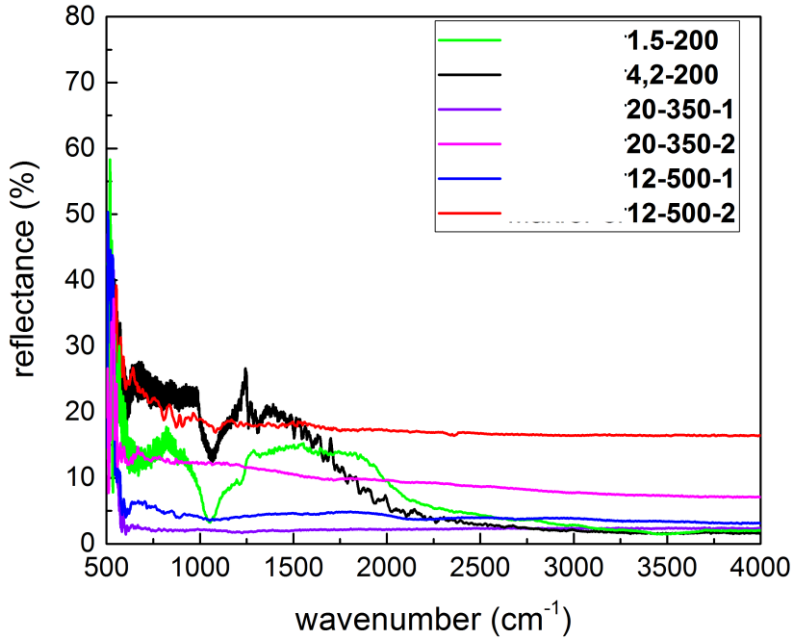
- Optical microscopy to initialize the ROI
- Determination of spatially resolved transmittance spectra
- Consideration of IR spectroscopic features

Usage example: FTIR spectroscopy

Laser Si-Filter (SMB)



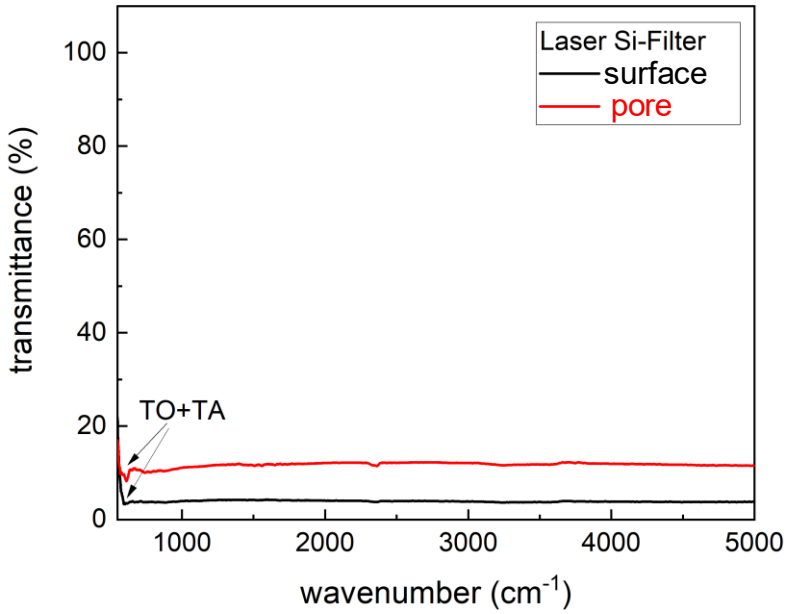




- Optical microscopy to initialize the ROI
- Transmission Spectra of different Si Filters
- IR Reflectance spectra of Si Filters

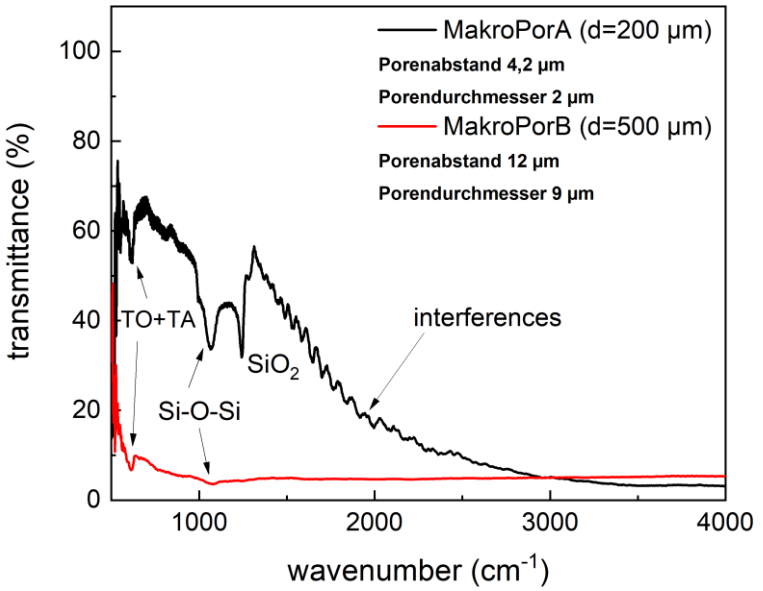
IR spectroscopic behavior of the filter types

Laser Si-Filter (CSP)



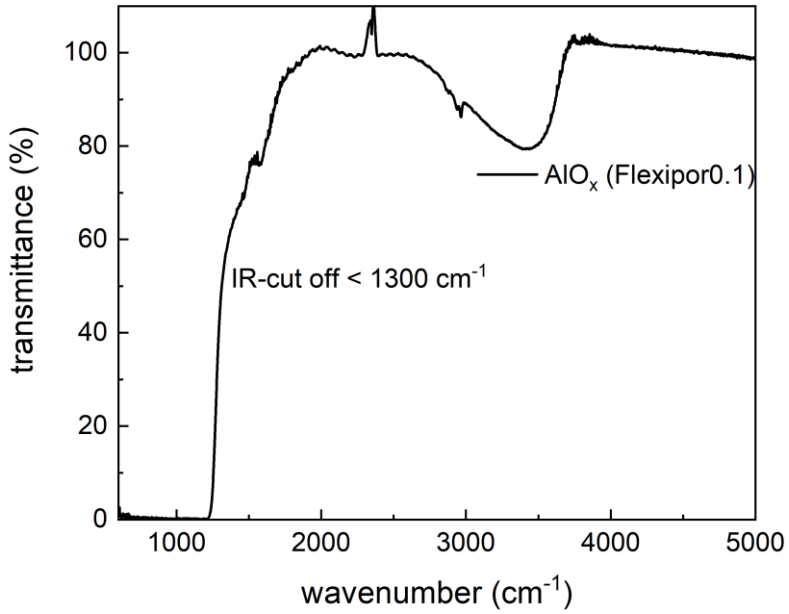
- Homogeneous IR transparency in the MIR (500-5000 cm-1)
- TO, TA are optical/acoustic modes of Si

Macropor Si (SMB)



- Homogeneous IR transparency for 500 µm thick sample B
- Additional IR scattering and absorption effects for 200 µm thick sample A

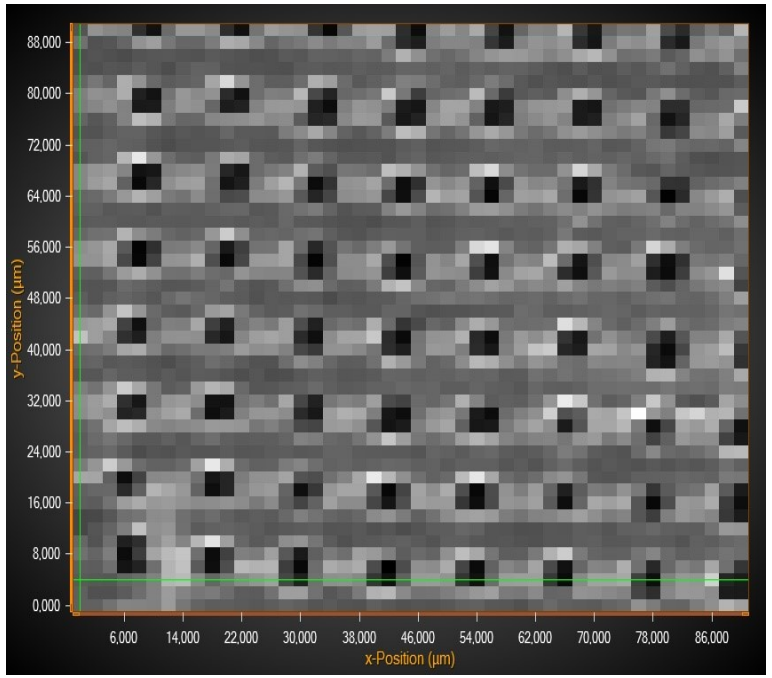
Flexipor AlOx (SMB)

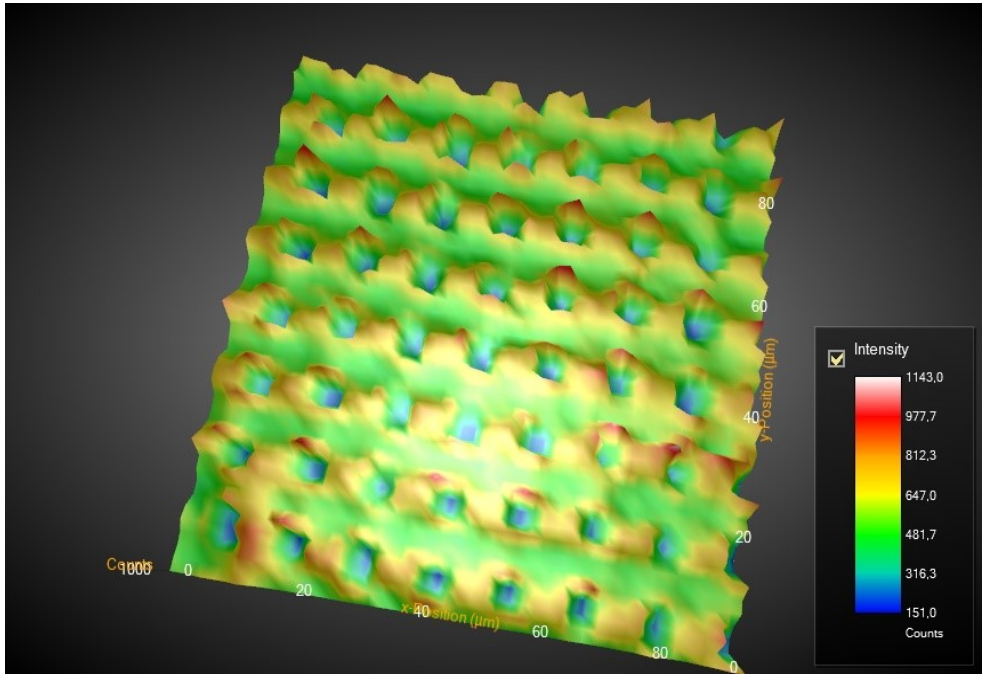


- Narrow-band, but high IR-transparent areas
- Self-absorption in the polymer fingerprint area (< 1800 cm^{-1})

Usage example: Raman spectroscopy

Laser Si-Filter (SMB)



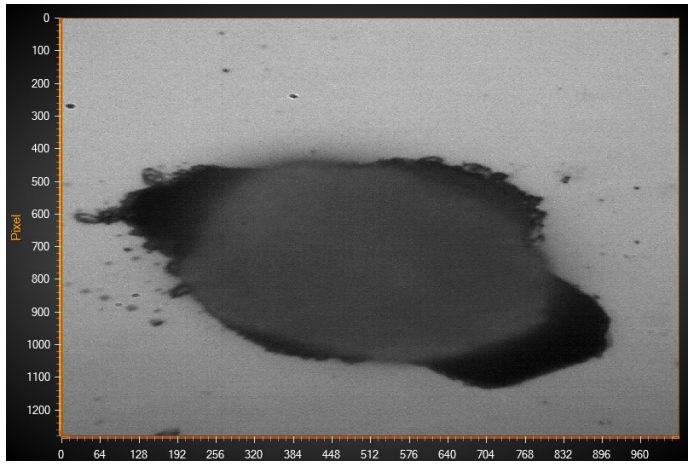


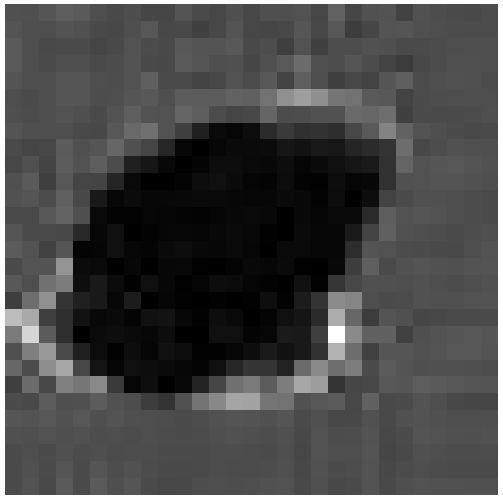
- Optical microscopy to initialize the ROI
- Raman Mapping on Si Line at 520 cm^{-1}

smart MEMBRANES

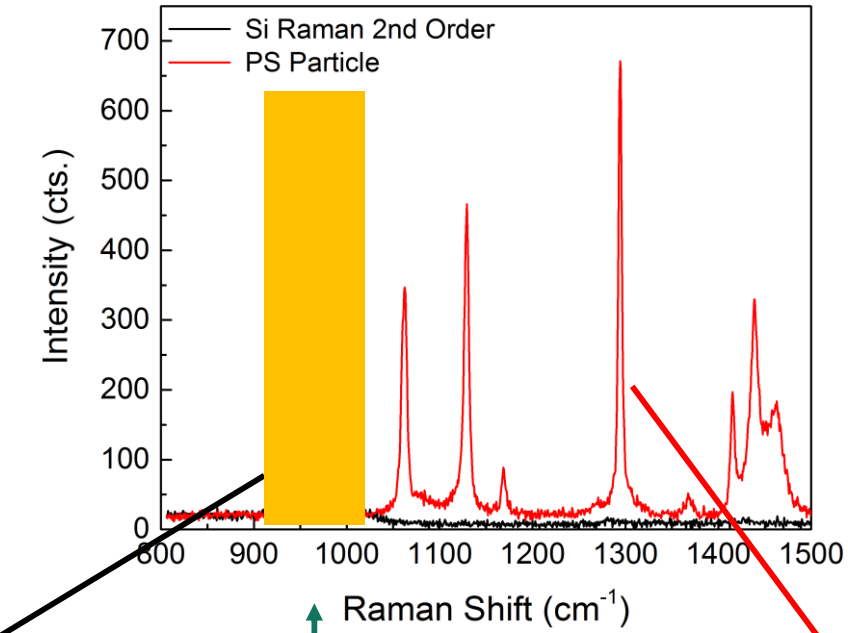
Usage example: Raman spectroscopy

Laser Si-Filter (CSP)



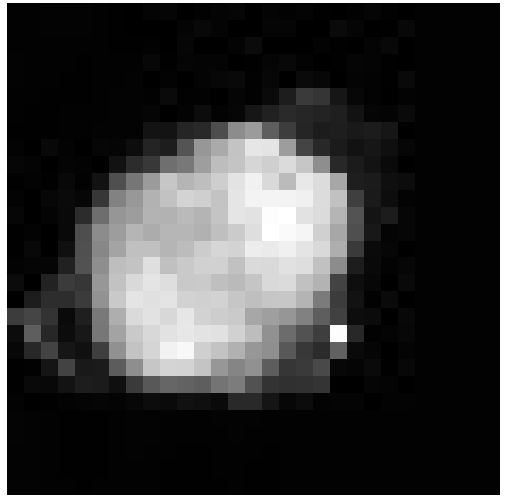


Raman Mapping Si



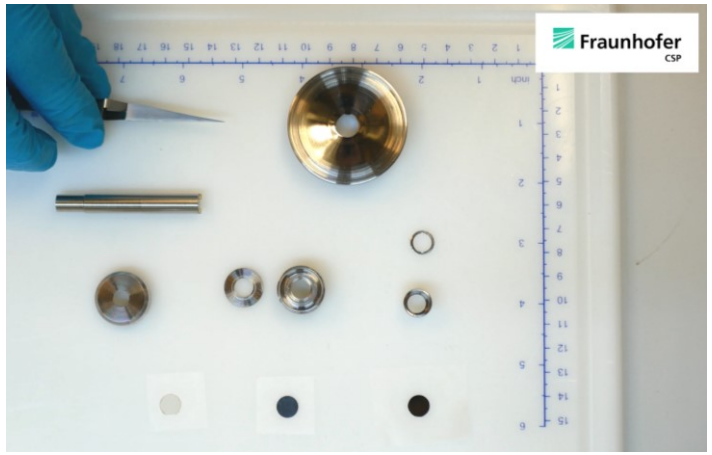
Forbidden spectral region by using Si Filters

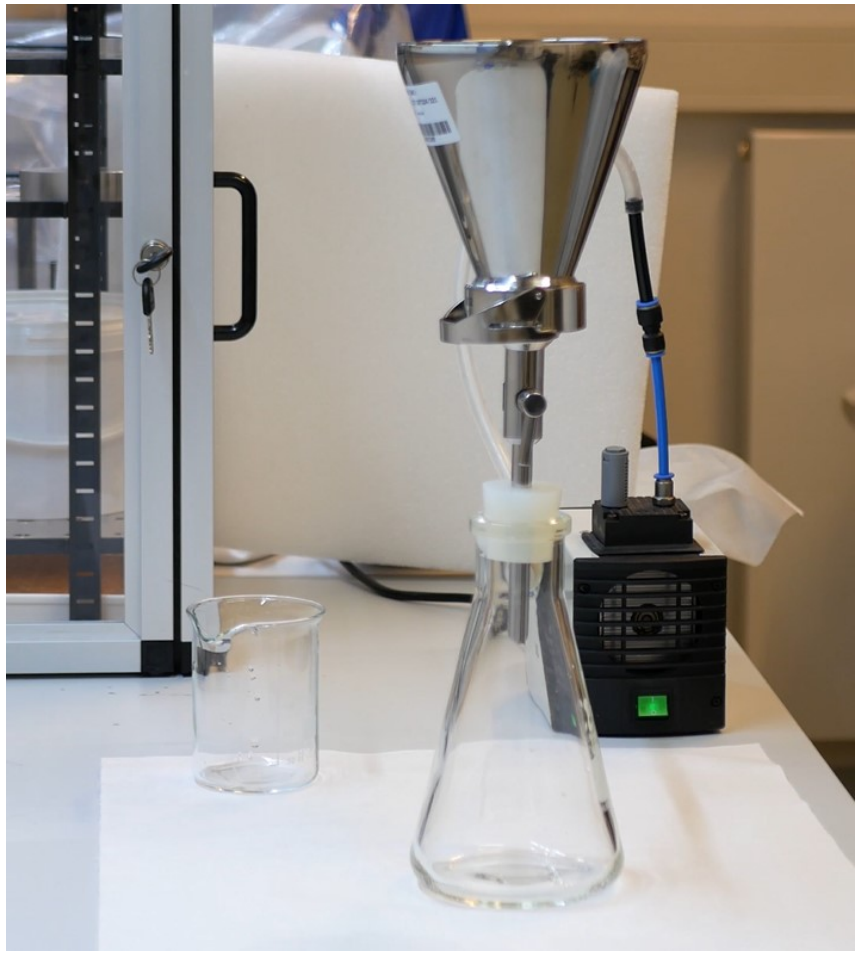
Raman Mapping PS Particle



Filtration equipment
Water/liquid Filtration

- Integration up to 3 filters in filter adapter (cascade)
- Filter adapter is inserted into funnel
- Filtration with the help of a vacuum pump



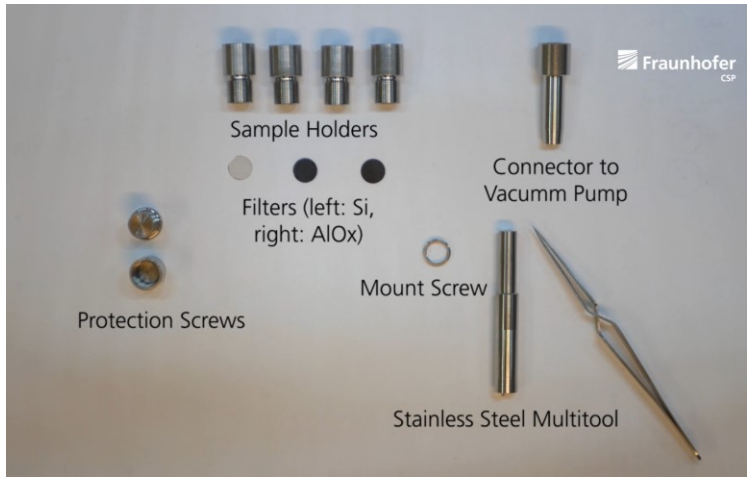


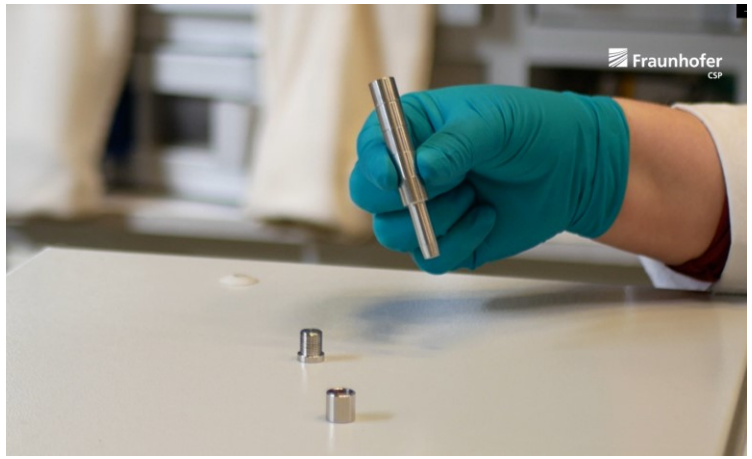
http://siliziumfilter.de/

Link Video

Filterequipment
Air filtration

- Integration up to 3 filters in filter adapter (cascade)
- Filter adapter is inserted into dispersion chamber
- Filtration with the help of a vacuum pump





http://siliziumfilter.de/

Link Video

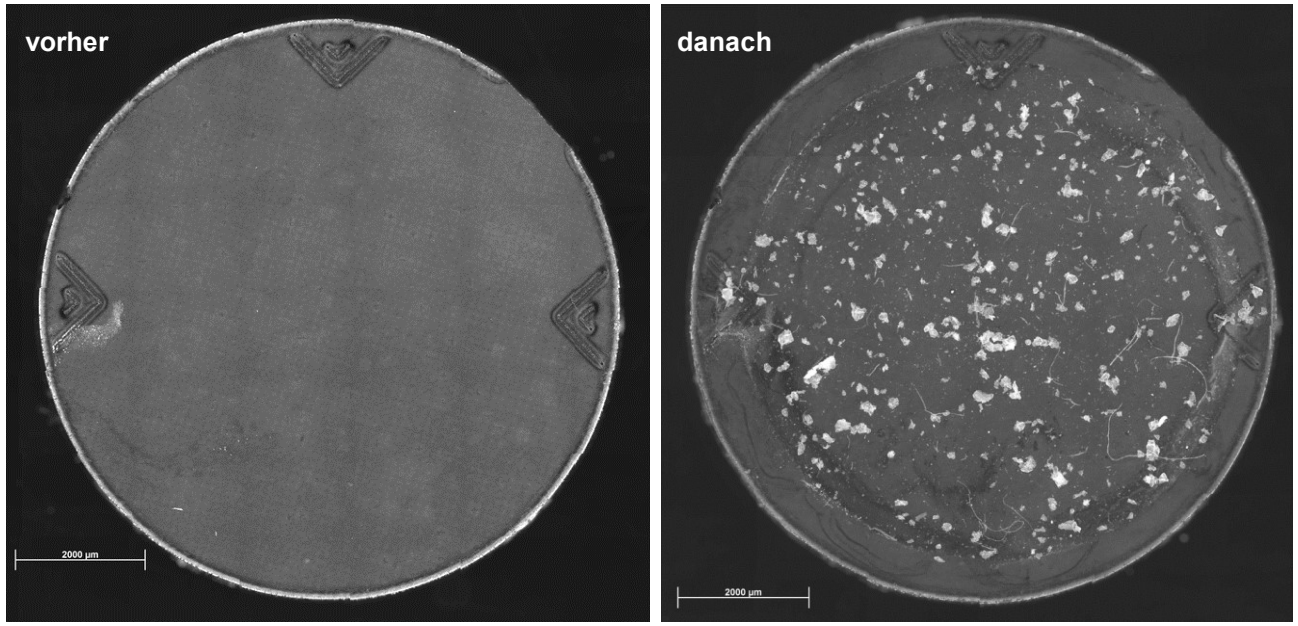
Workflow MP Filtration

Sampling
- Analysis Samples
- Blanks
- Reference

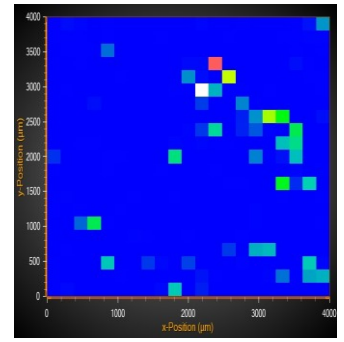
Filtration
- Setup Cleaning
- Sample Handling
- Filter Drying

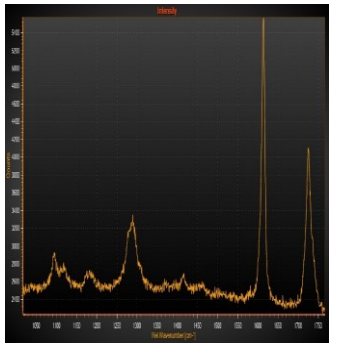
Detection/Evaluation
- Optical Microscopy
- µ-Raman Spectroscopy
- µ-FT-IR Spectroscopy
- Electron microscopy

Transport
- Preparation
- Furter Analysis

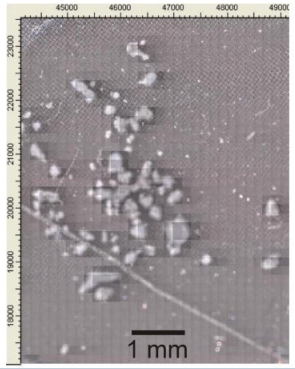


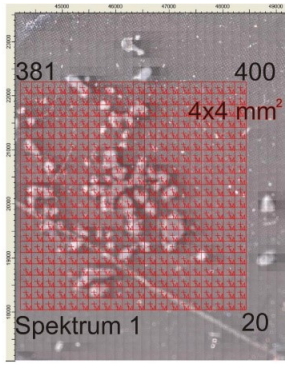
Raman



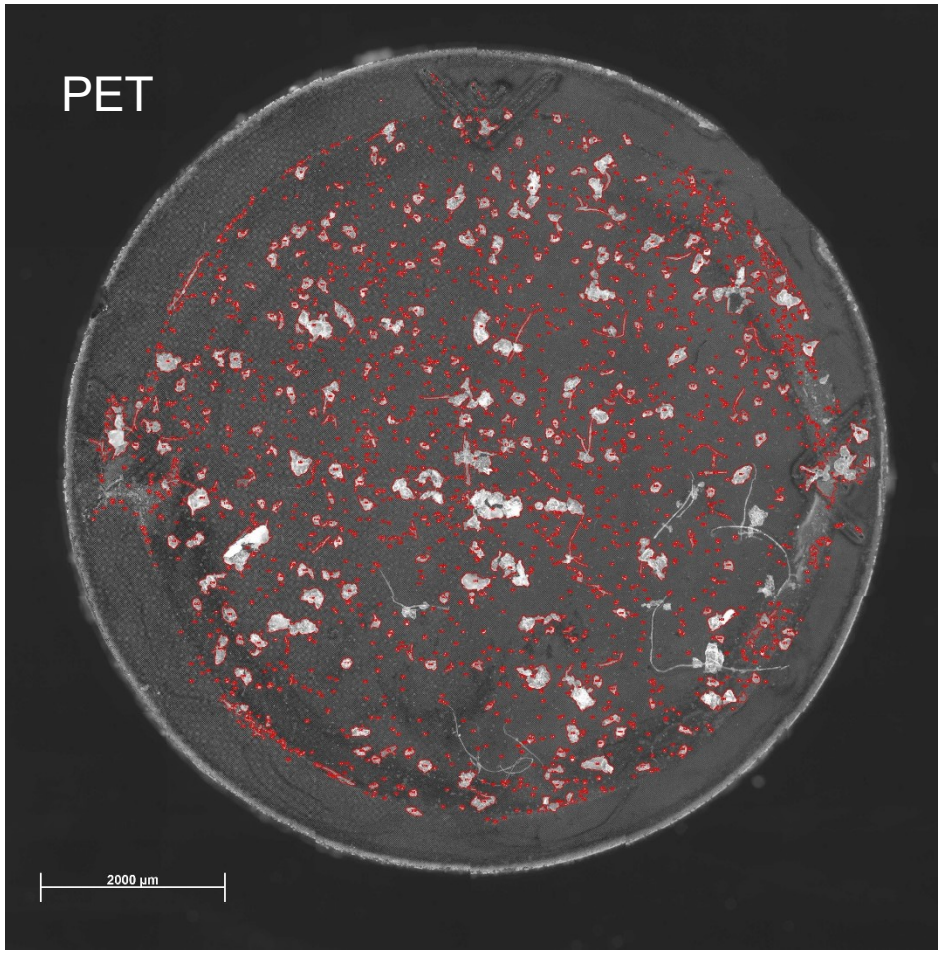


FT-IR

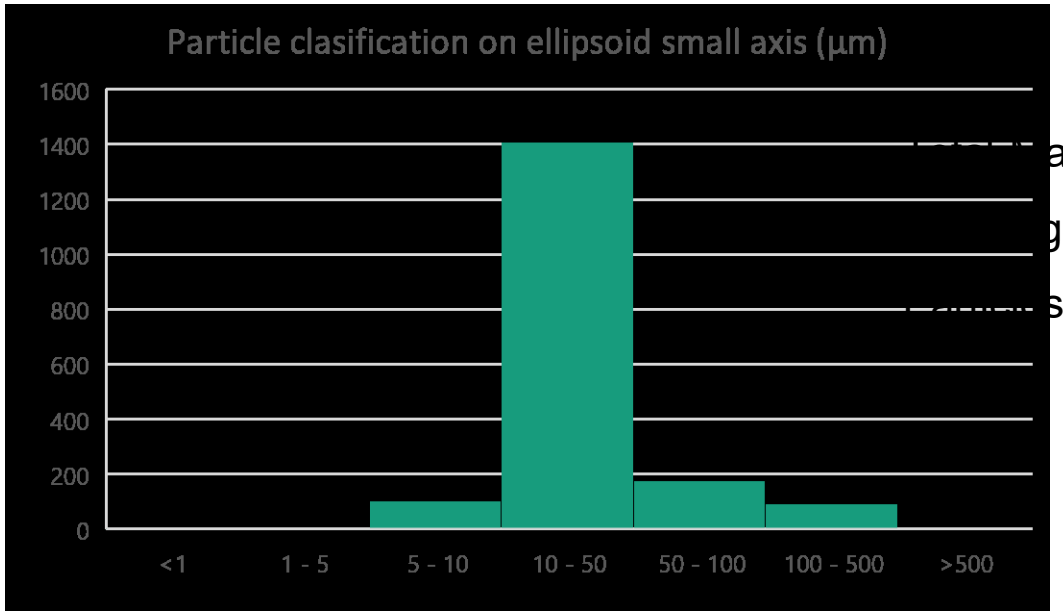




Particle Statistic



SmartMembranes Filter (10 µm)



ass: 0,584 mg

ge: 12 %

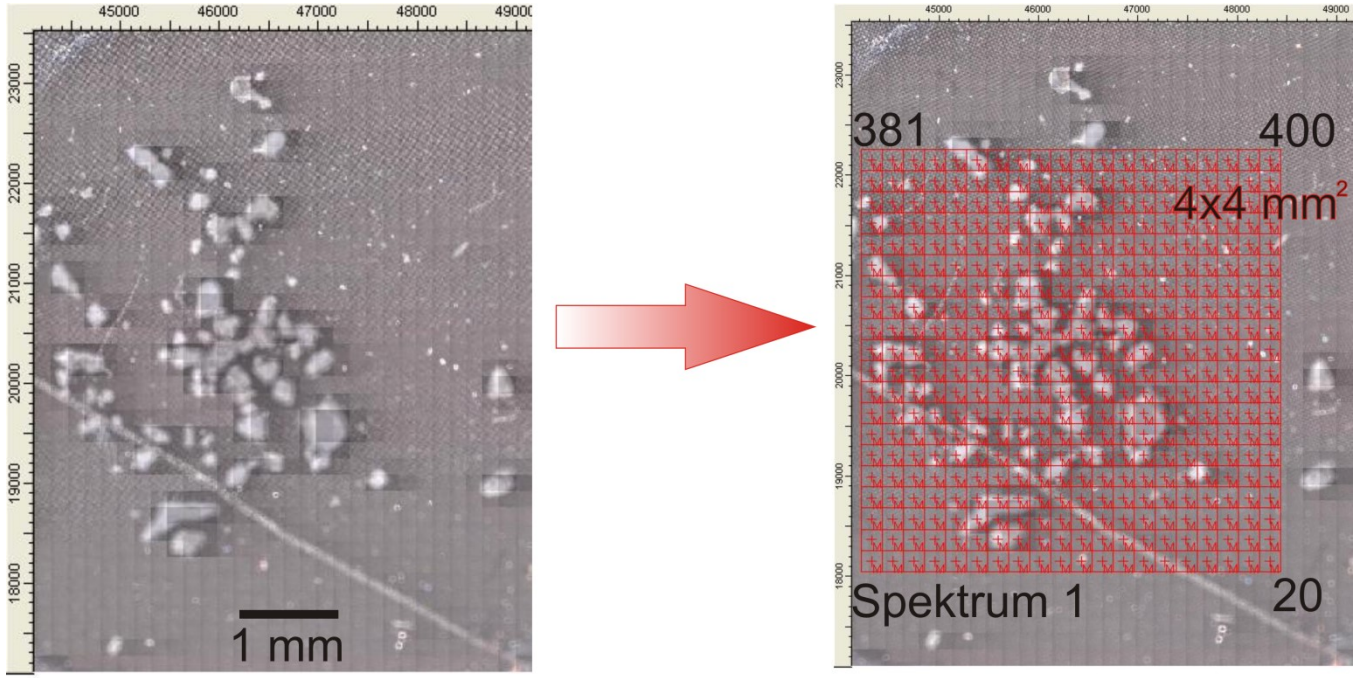
s/Area: 4172 /cm²

- Image recognition algorithm (Macro / ImageJ) evaluates the number of particles by size class
- Application in particular for round robin tests
- Averaging of several attempts for statistical evaluation
- Determination of blank values from blank filtrations

µ-FT-IR Measurement

Example: PET particles on Si Filter (BAM)

µ-FT-IR-Transmission microscopy
X15 Objective
Smallest aperture 20 x 20 µm^2

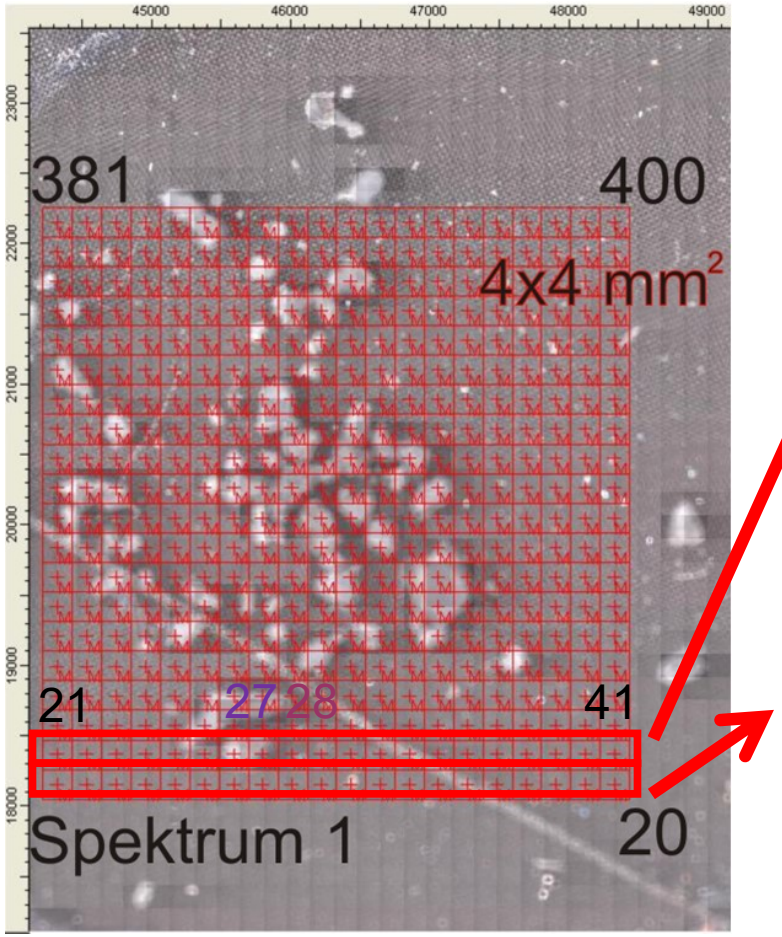


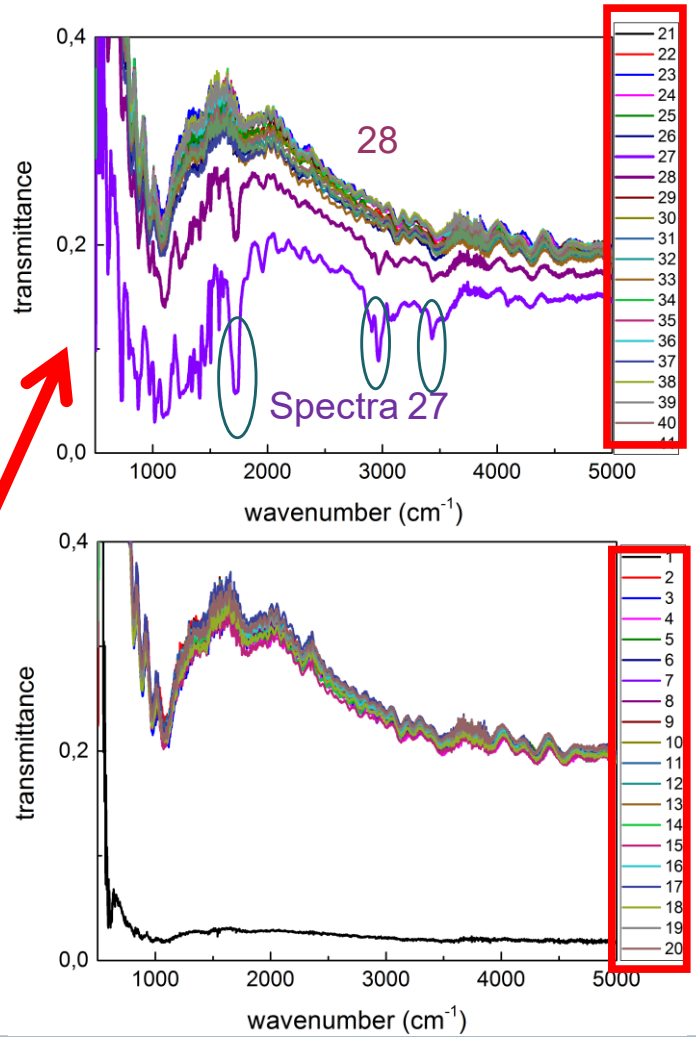
Method:

1. Create measurement overview, microscopic scanning of the measurement field
2. Define scan area (here e.g. 4 x 4 mm^2)
3. Assign µ-FT-IR spectra true to position → derive particle type and number

µ-FT-IR Analysis

Multiparticle analysis on ROI using µ-FTIR-mapping on PET Particles (BAM)





Spectra 27 and 28 with Fingerprints at ca. 1700 cm^{-1} 2900 cm^{-1}, 3400 cm^{-1}
→ comparison PET-, PE-reference

No Fingerprints
→ comparison with KBr filter reference

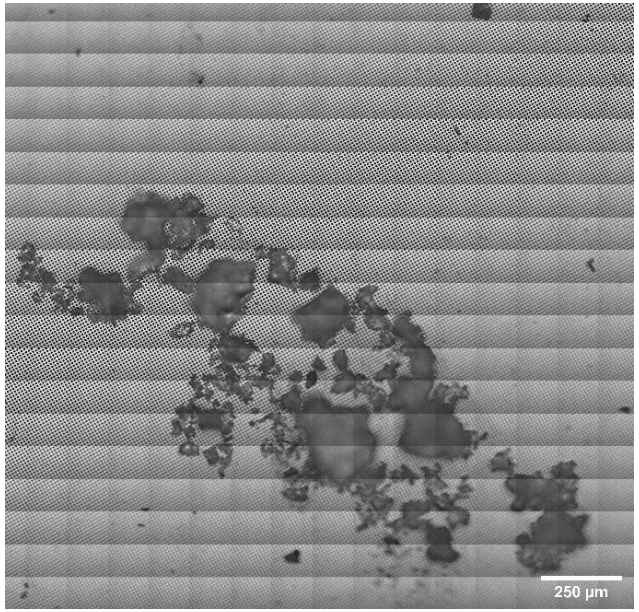
µ-FT-IR-Transmission microscopy
X15 Objective
Smallest aperture 20 x 20 µm²

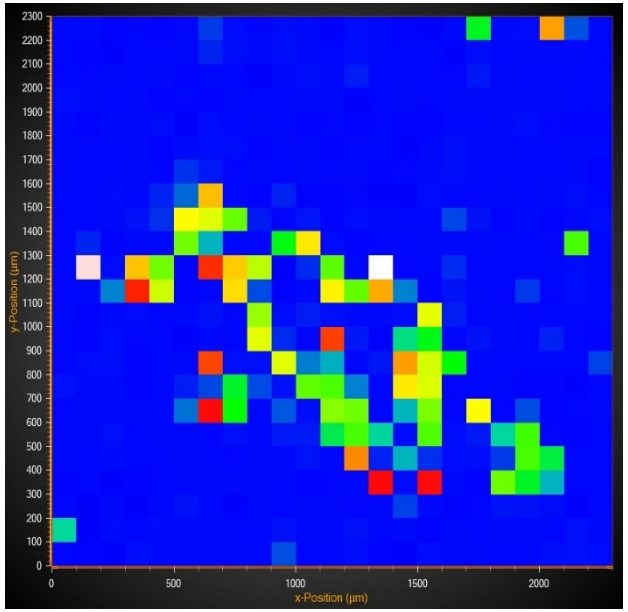
Method:

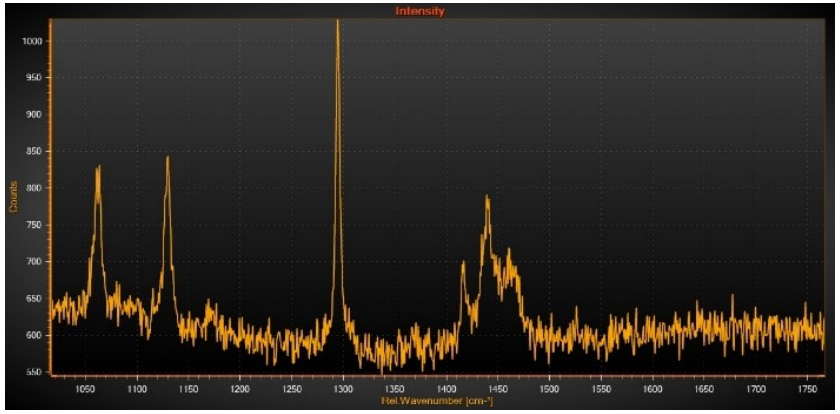
- Create measurement overview, microscopic scanning of the measurement field
- Define scan area (here e.g. 4 x 4 mm²)
- Assign µ-FT-IR spectra true to position → derive particle type and number

µ-Raman Measurement

Example: PE microparticles on Si Filter (BAM)







Excitation: 488 nm
Power: 100mW
Integration: 5 sec
Raman resolution 2 µm + screen ruling

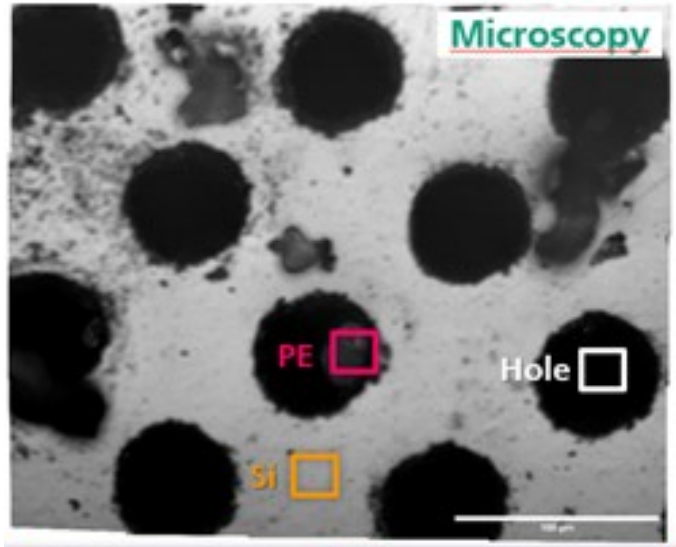
Microscopy image (left), Raman mapping (middle) and Raman fingerprint of PE microparticles (right) on Si filter

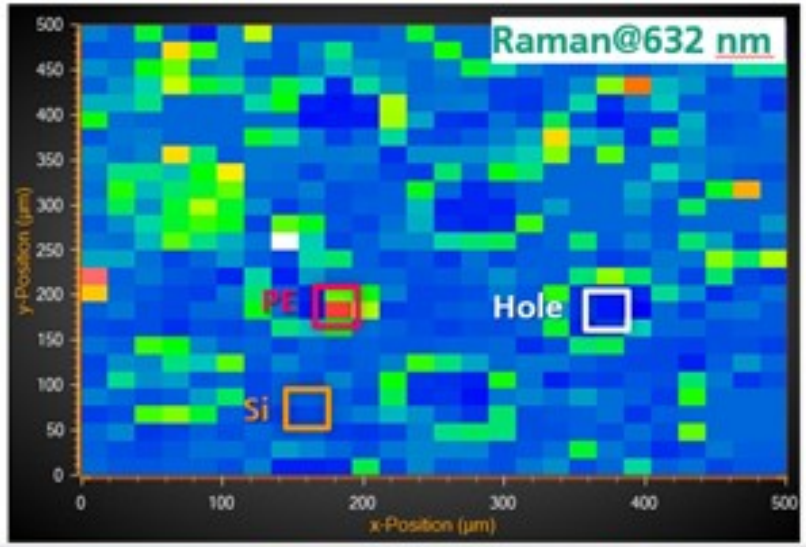
Method:

- Create measurement overview, microscopic scanning of the measurement field
- Define scan area (here e.g. 4 x 4 mm^2)
- Assign µ-Raman spectra true to position → derive particle type and number

µ-Raman Measurement

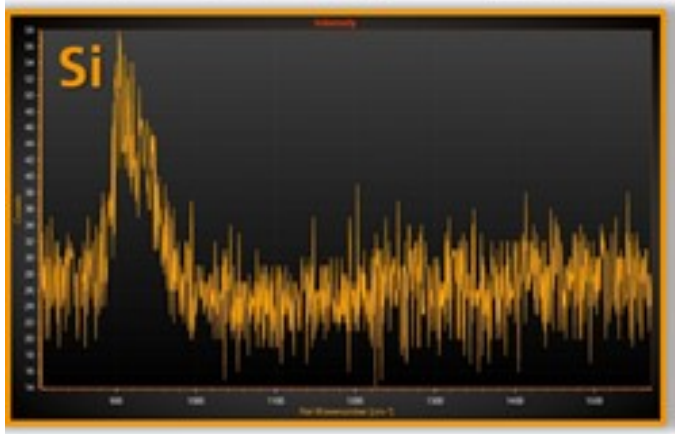
Example: PE microparticles on Si Filter (BAM)

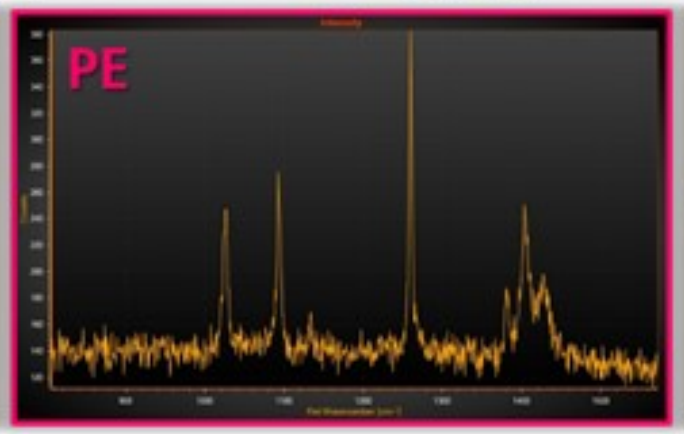




Top: Optical microscopy image and Raman Mapping

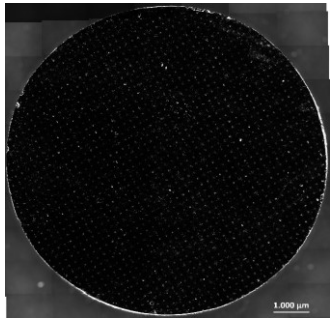
Bottom: Raman Spectra of Si, PE Particle and hold be 632 nm excitation



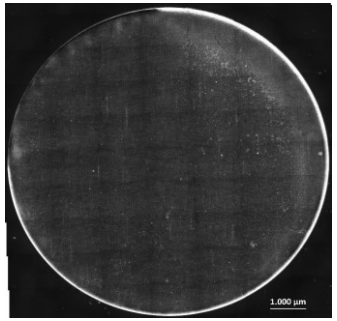


3 Filter System Model with PET (BAM- 57 µm), PMMA (1.3 µm) and PS (140 nm)

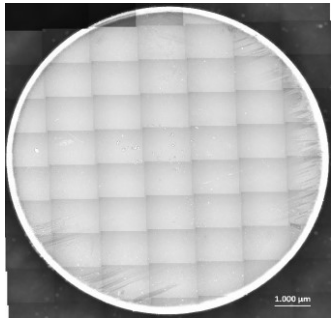
Water Filtration



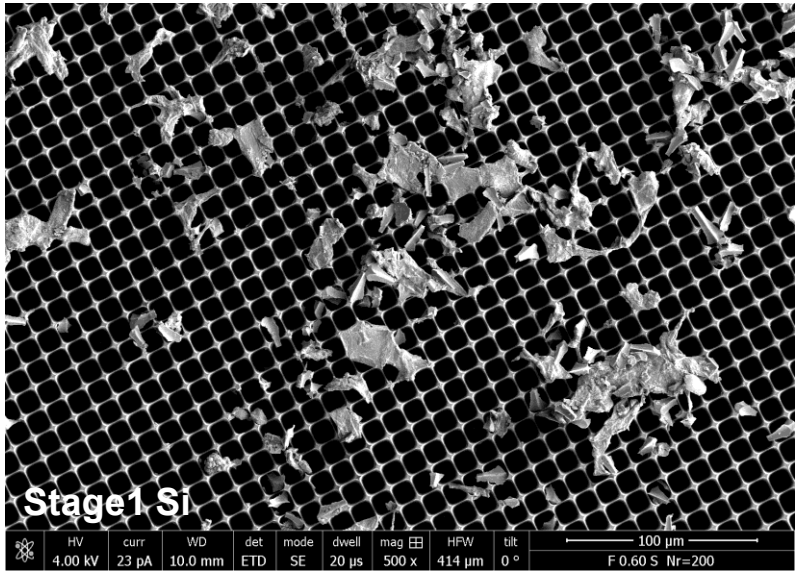
Si Filter :
25µm pore size

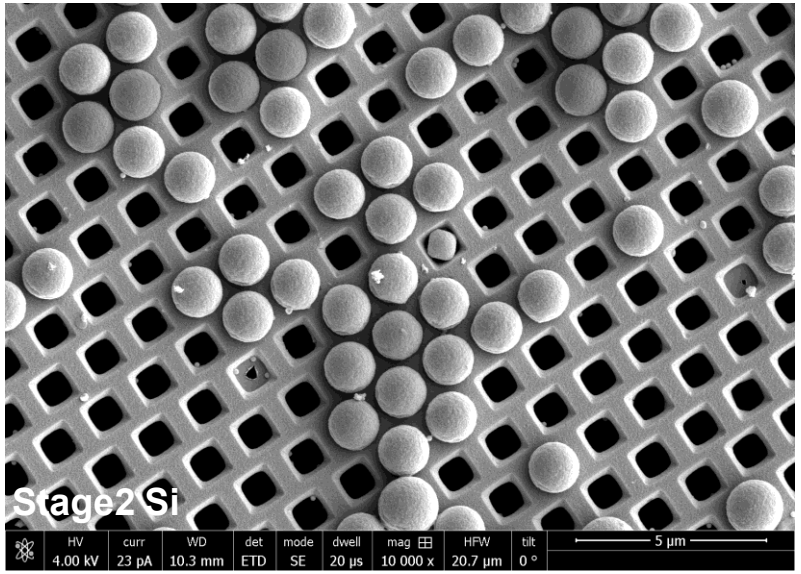


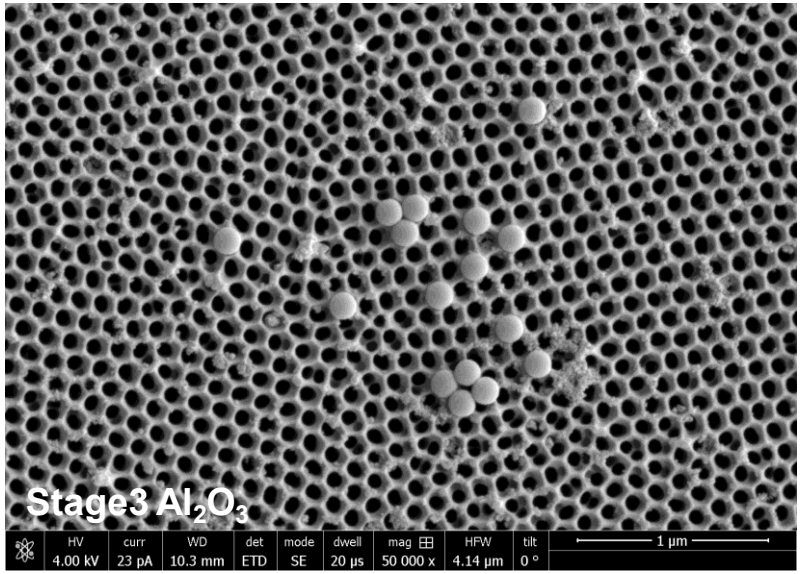
Si Filter:
1µm pore size



Aluminium Oxide Filter:
100nm pore size

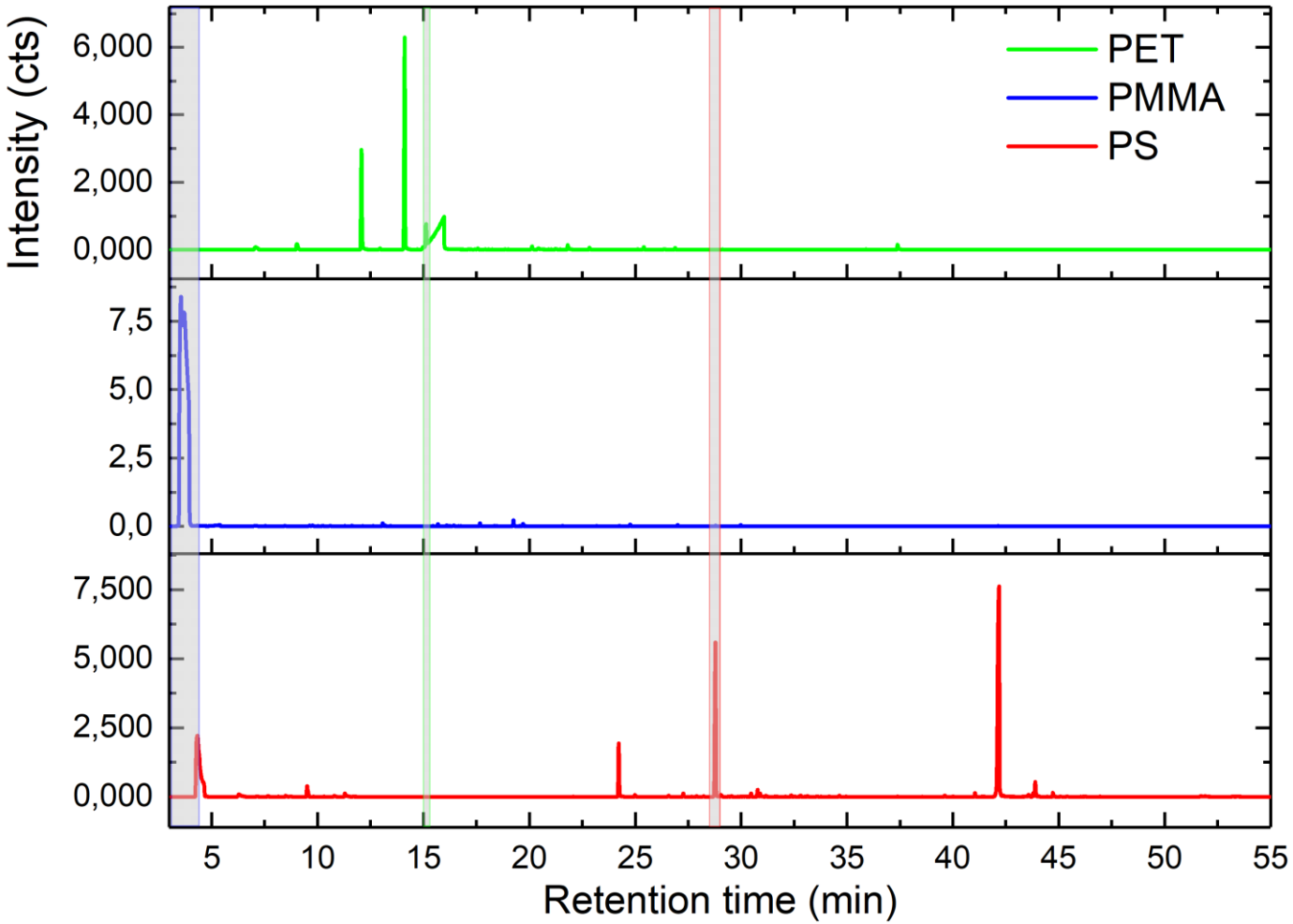


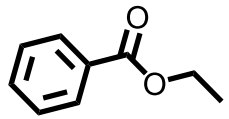




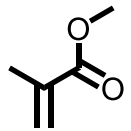
PET+ PMMA + PS Particles model System

TED-GC/MS Analysis at BAM
Fingerprints of components materials

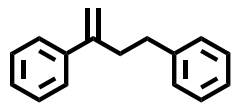




ethyl benzoates

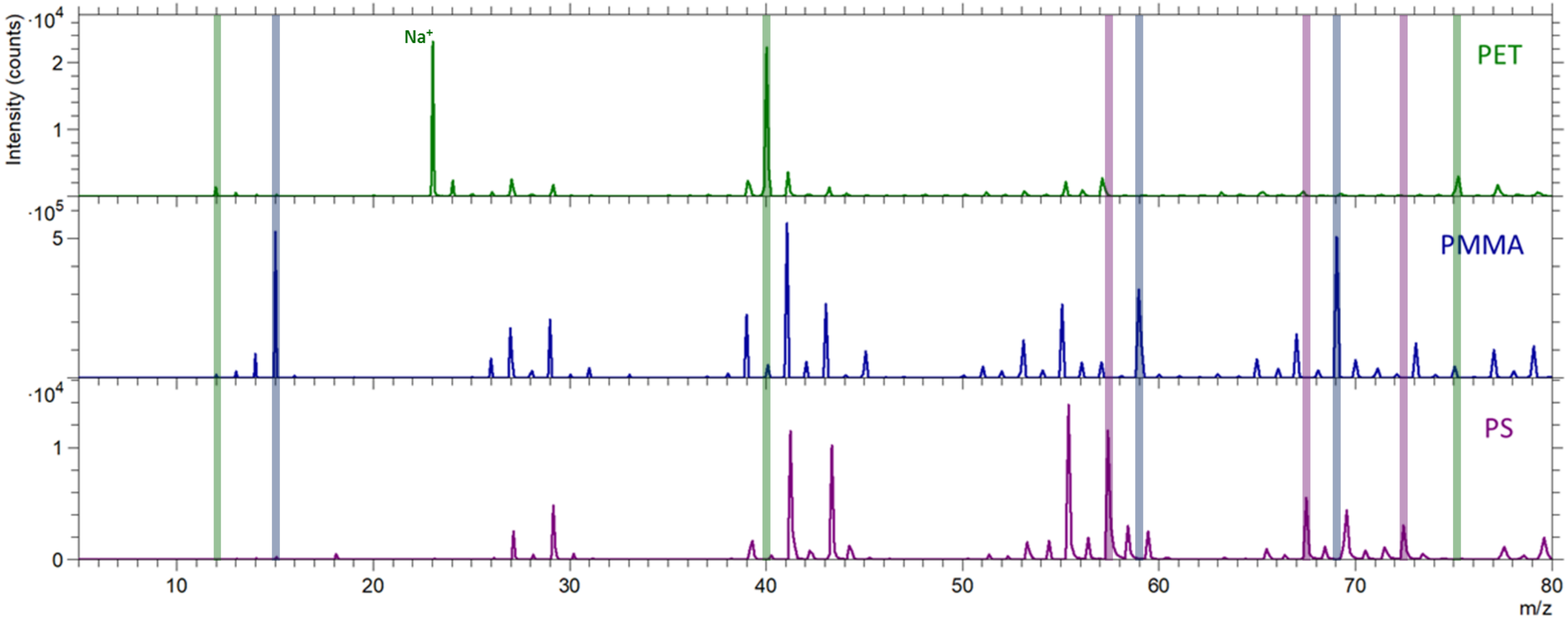


Acrylate



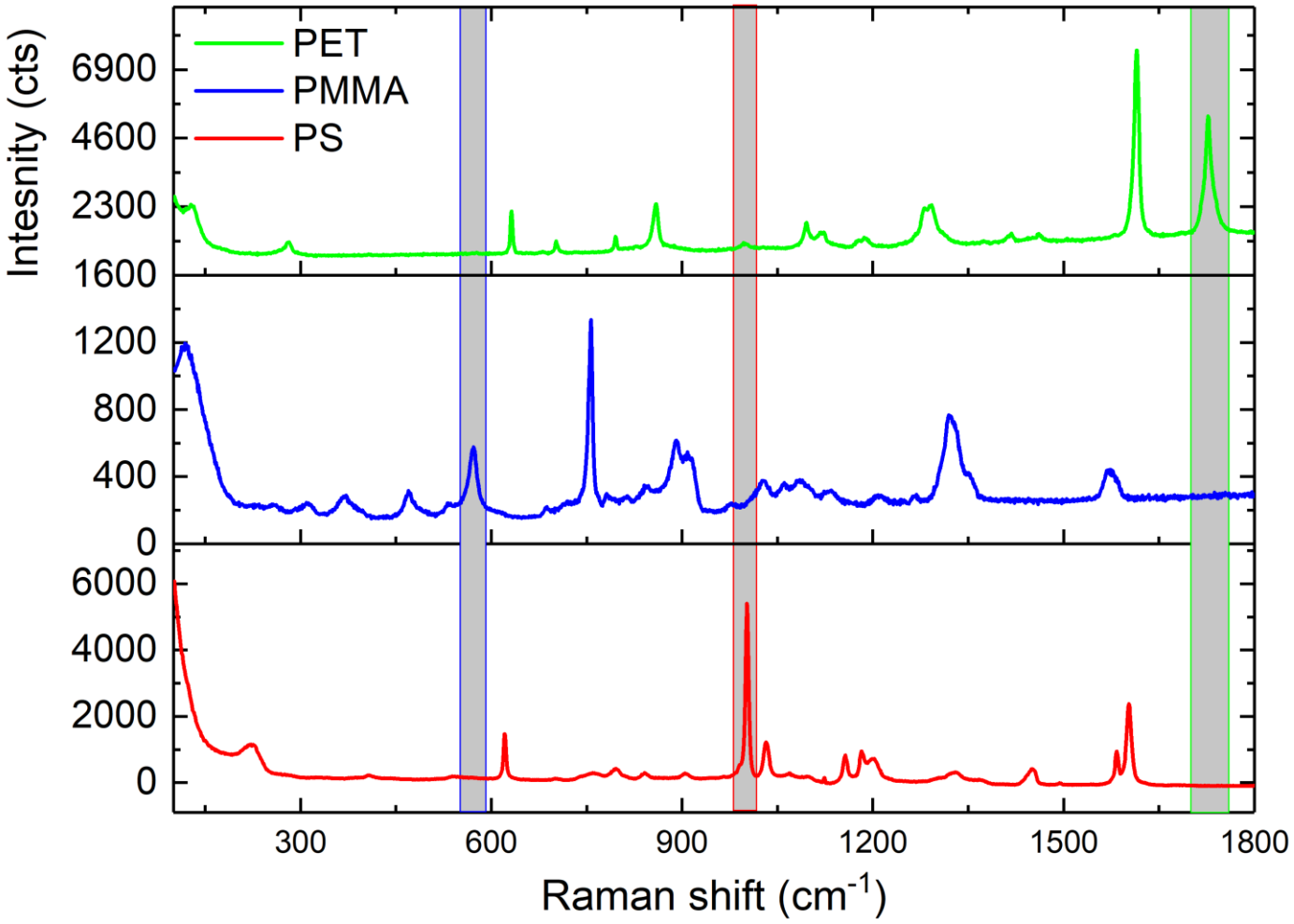
2,4-diphenyl-1-butenes

ToF-SIMS Analysis
Fingerprints of components materials



Raman Analysis

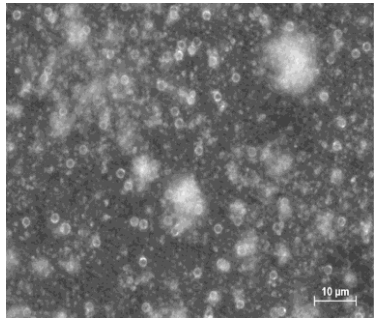
Fingerprints of components materials



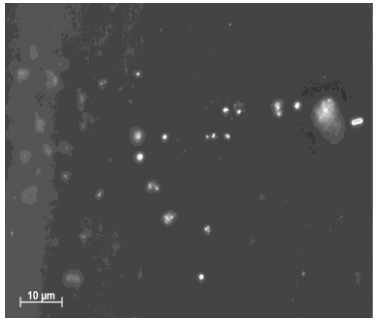
- Measurement with different Laser: 514, 785nm in order to reduce the fluorescence
- Integration time from msec to sec dependent on the filter/microplastic type
- For PMMA better use the line at 570 cm^{-1} that the one at 1000cm^{-1}. The first order Si Raman sharper than his second order

2 Filter System Model with PMMA (1.3 µm) and PS (140 nm)

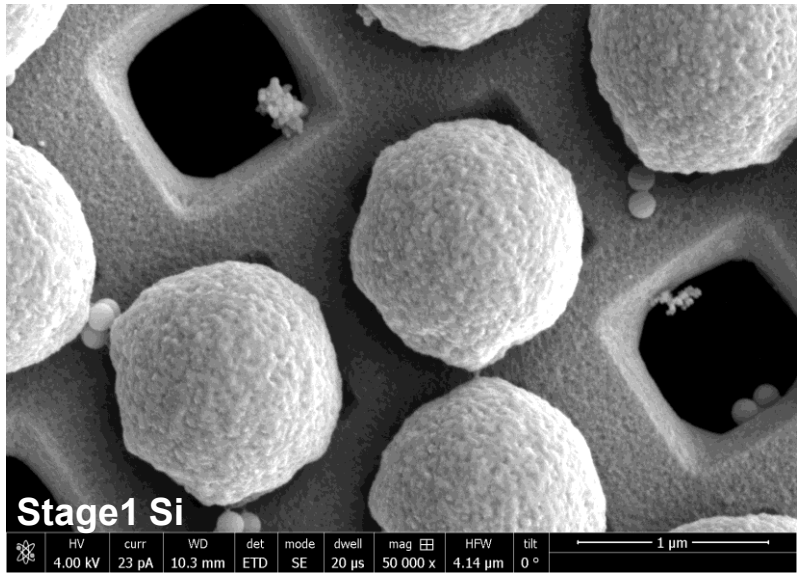
Air Filtration

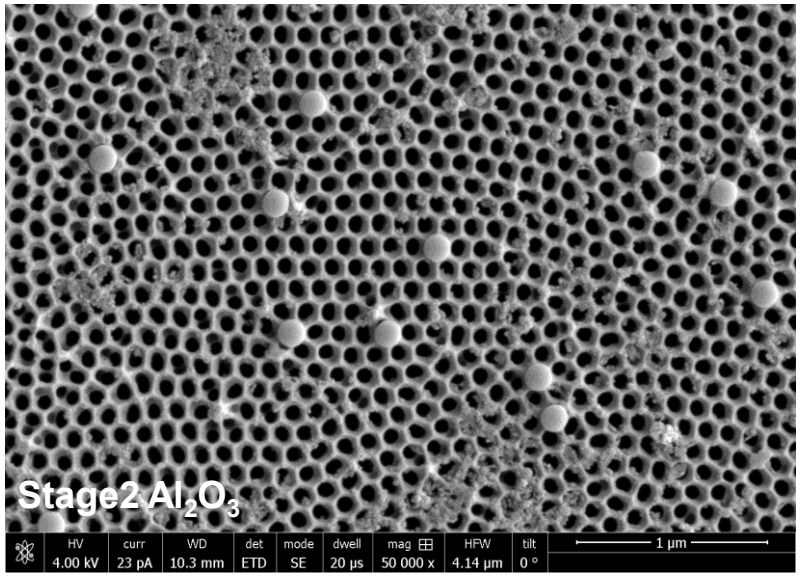


Si Filter:
1µm pore size



Aluminium Oxide Filter:
100nm pore size





PMMA + PS Particles model System

2 Filter System Model Transport

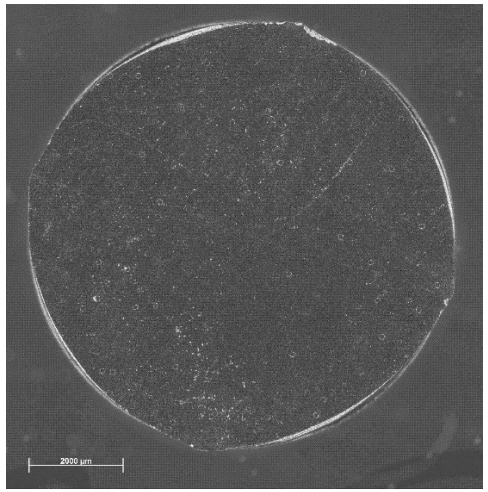
Water Filtration

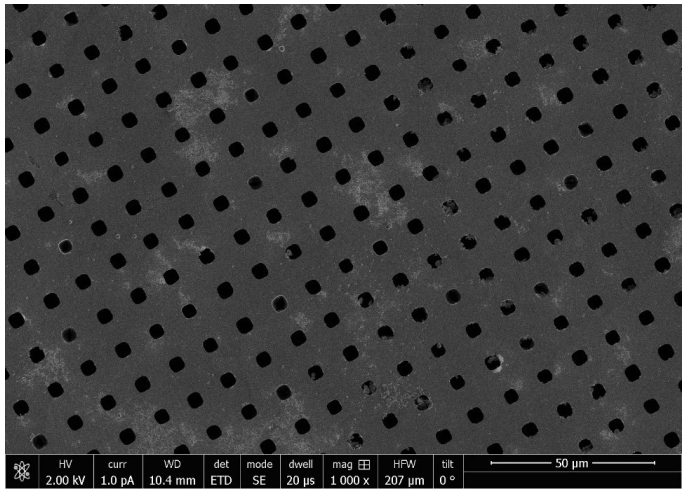
Overview

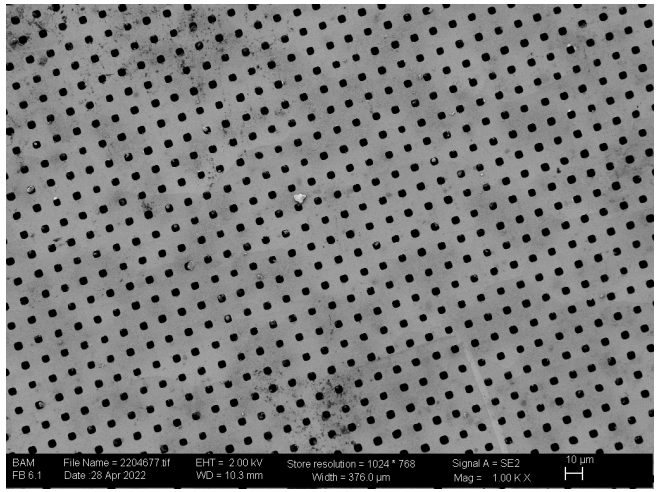
At Start

At Destination

Si Filter:
1µm pore size



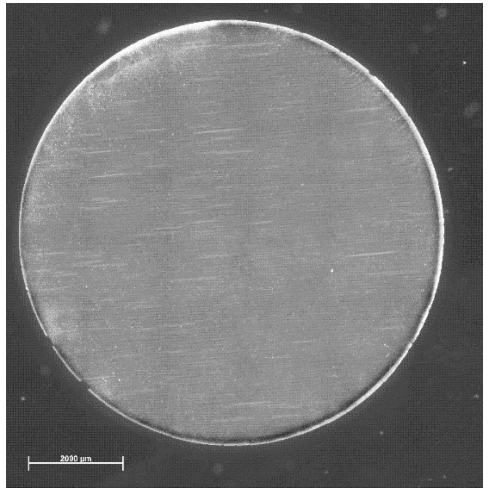


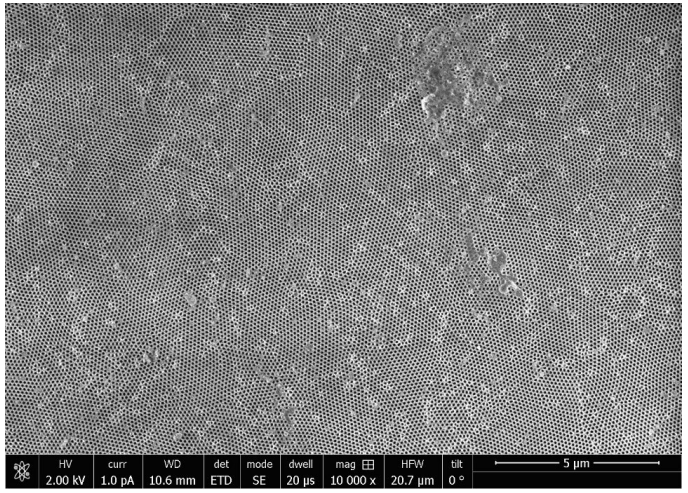


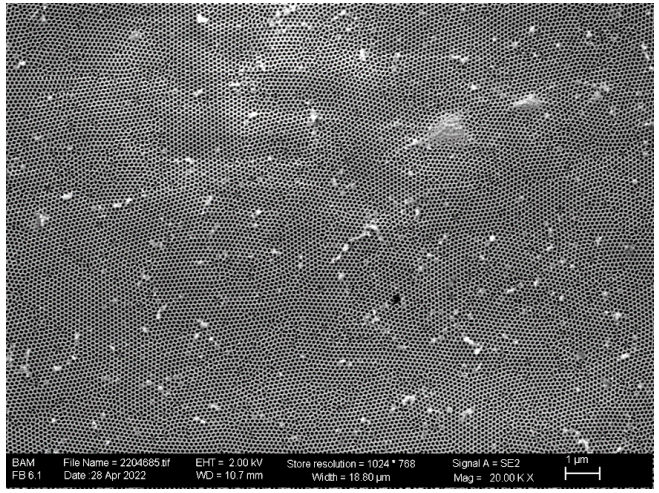
150

km

Aluminium Oxide Filter:
100nm pore size







smart MEMBRANES

BAM Bundesanstalt für Materialforschung und -prüfung

Conclusions and Outlook

- A novel filtration system using Si and Al_2O_3 is proposed
- The new system is carbon-free and can be used in mass spectrometry as well as in microanalytics.
- The Si filters can by used down to 1 µm and the Al_2O_3 down to 25 nm.
- Because of high porosity the filters can be used more effective
- Filter and filters systems resist at elevated temperatures (up to 700°C)
- System for air filtration can be directly used for transportation of the filters (also for long distances)
- No plastic free sample are needed for comparison

Thank you for your attention

FKZ: 964766

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