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Photography encouraged

Raman microspectroscopy as a tool for microplastic particle analysis

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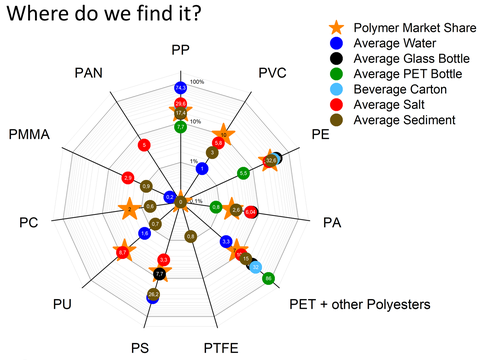
Microplastic

What is microplastic?

→ Anthropogenic polymer fragments 1 µm – 5 mm incl. particles and fibers

Where do we find it?



→ Relative proportions of microplastic species found are highly matrix dependent

Why Raman microspectroscopy ?

- Chemical information through inelastic light scattering resulting in a *"fingerprint"* spectrum.
- Single particle analysis in the µm range
- Morphological characterization of particles

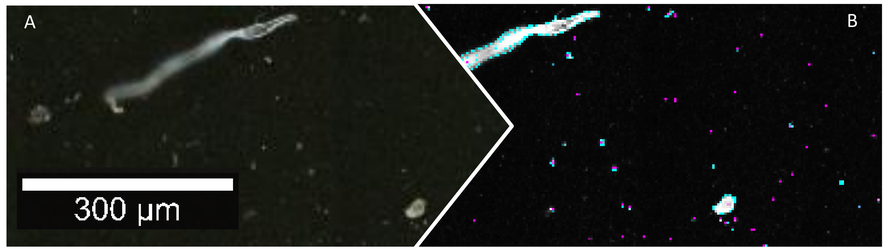
→ Particle size distribution and compound abundance

Sample workup → Filtration

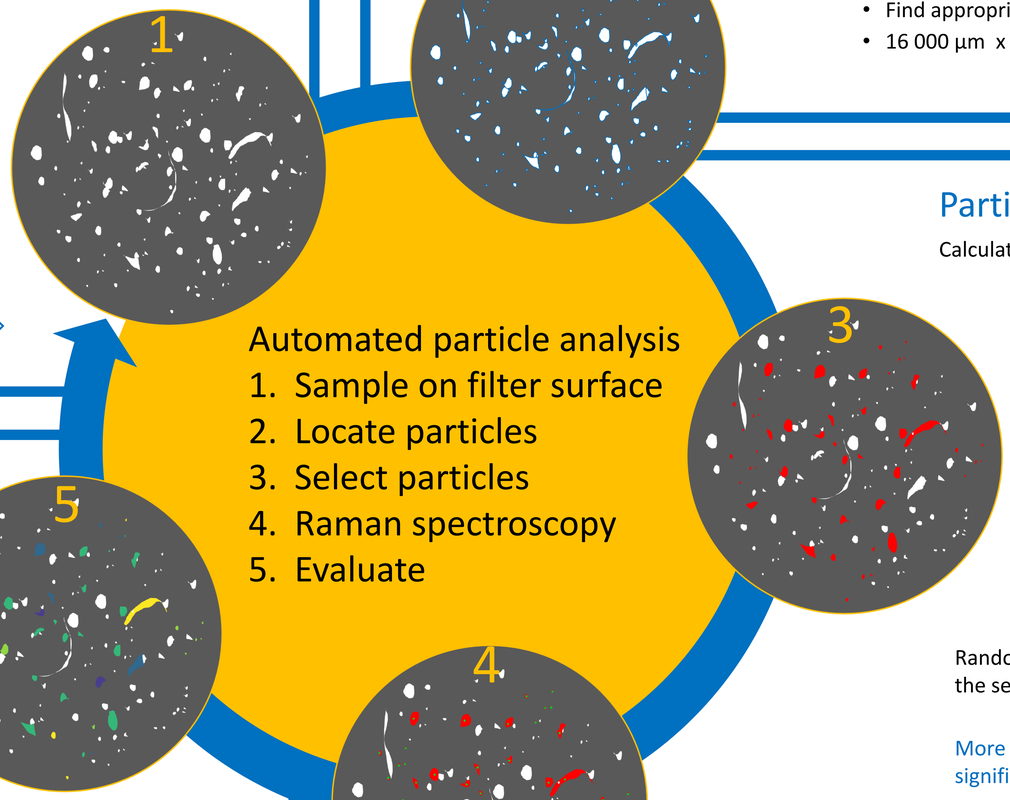
Particle detection and morphological characterization

Challenges:

- Different sizes 1 µm – 5 mm require different objectives and focusing
- Particles and fibers require different recognition algorithms



- Find appropriate settings for image capture
- 16 000 µm x 16 000 µm image = entire filter
- Localize all objects (particles and fibers)
- Determine total number of fragments *N* and measurement coordinates



Automated particle analysis

1. Sample on filter surface
2. Locate particles
3. Select particles
4. Raman spectroscopy
5. Evaluate

Particle selection for Raman measurement

Calculate the minimum required objects *n* for a representative sub set based on *N*

$$n \geq \frac{P(1-P)}{\frac{e^2}{\sigma^2} + \frac{P(1-P)}{N}}$$

Variable	Symbol	Required information
Confidence interval	σ = 1.65	for 90%
Total number of particles	*N*	Particle count from detection
Estimated MP content	*P*	From prior experiments/ literature
Margin of error	*e*	Inherent to research question
Sample size	*n*	

e.g. $N = 10^6$	P = 5% MP	P = 0.5% MP	P = 0.05% MP
e =	0.01	0.0015	0.00015
n ≥	1 292	5 984	57 022

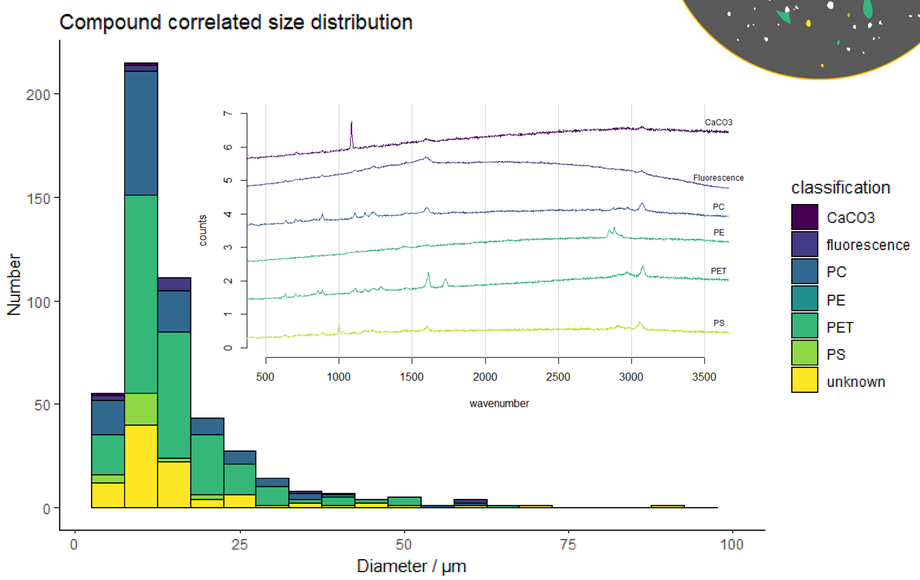
Random sampling over the whole filter corresponds to a virtual mixing and lowers the segregation error.

More is not always better, there is a limit where more measurements do not significantly improve the measurement error

Goal: Representative MP analysis

Evaluating results:

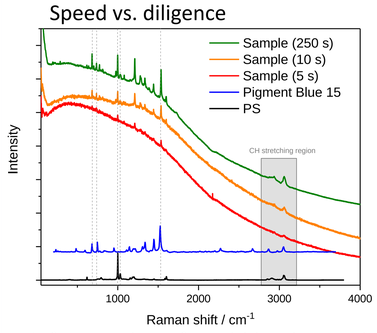
- Morphological and chemical composition for each particle
- Combine information on particle composition and size distribution
- Extrapolate to entire population *N*
- Replace estimated error with actual error



Size distribution for particles from a PET reference sample correlated with the identified compound for each size class. Spectra illustrate the unambiguous identification by Raman microspectroscopy

Longer measurement = better spectra = more information? balancing individual and overall measurement time

Speed vs. diligence



Speed vs. number of particles

Study	Measurement time per particle	Number of particles for each measurement session			
		5 h	15 h	24 h	48 h
Imhof et al. 2016	500 s	36	108	173	346
Käppler et al. 2017	10 s	1 800	5 400	8 640	17 280
Schymanski et al. 2018 Imhof et al. 2016	5 s	3 600	10 800	17 280	34 560
Ossmann et al. 2018	2 s	9 000	27 000	43 200	86 400
Sujathan et al. 2017	0.5 s	36 000	108 000	172 800	245 600

Left comparison of acquisition time vs. signal quality (633 nm laser, 4 mW mit 50× magnification (NA = 0.5)). Right comparison of current measurement protocols to estimated sample sizes n for 5%, 0.5 and 0.05% microplastic content

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Acknowledgements:
The authors thank the Bavarian Research Foundation (Bayrische Forschungsstiftung, BFS) for funding of the MiPAq project.

References:
P. M. Anger[1] & E. von der Esch[1], T. Baumann, M. Elsner, R. Niessner & N. P. Ivleva, *Trends in Analytical Chemistry* **2018**, 109 214-226, [1] shared first authorship

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