FTIR in microplastic research: Towards a harmonized and standardized analysis

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FTIR spectroscopy

Fourier transform infrared (FTIR)
Fourier transform infrared (FTIR) spectroscopy

IR radiation

Absorption
FTIR spectroscopy

Fourier transform infrared (FTIR)

- **Stretching vibration**
  - Symmetrical stretching
  - Asymmetrical stretching

- **In-plane bending**
  - Scissoring
  - Rocking

- **Out-of-plane bending**
  - Wagging
  - Twisting

**IR radiation**
FTIR spectroscopy

Fourier transform infrared (FTIR)
Analysis via Library Search
Analysis via Library Search

Spectrum

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Analysis via Library Search

Spectrum

© CC 3.0 / The Photographer
Analysis via Library Search

Spectrum

Spectral database

polyurethane
polyester
silicone
polyamide
polyethylene

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Why FTIR for MP analysis?

- Chemical imaging via a non-destructive method.

- Sample preparation compared to RAMAN microscopy is less demanding.

- Complete mapping of membrane filters is possible.
Particles > 500 µm

If the particles can be sorted by hand:

- Filtration onto filter meshes with 500 µm pore size
- Optical sorting of the particles
- Attenuated total reflection (ATR)-FTIR-measurement
Particles > 500 µm

If the particles can be sorted by hand:
Particles > 500 µm

If the particles can be sorted by hand:
Example – ATR-FTIR-spectroscopy

Bibliothekssuche

18.01.2018 14:56:16

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FTIR Imaging

Using the common Fourier-transform infrared (FTIR) spectroscopy

Allows the analysis of large filters (diameter usually 10 - 13 mm)

Applicable in transmission and reflection mode

Example: Sediment sample
Chemical Imaging

Manual analysis based on false color images

Polymer signatures

FT-IR spectrum

Visual image

Chemical Image (Polymer)

= polypropylene
Example – Treated Waste Water

Sampling of several waste water treatment plants
Sampled at the plant effluent

- Filtration on 10 µm stainless steel cartridges
- Sample volume ranged from 0.39 to 1 m³
- Purified by enzymatic digestion

Example – Drinking water

Manual Analysis via FTIR Imaging

High expenditure of time:

- Manual selection of possible particles
- Manual library search
- Size determination of the particles limited

Overall the process is prone to human bias!

Additionally a high demand of personnel requirements
Manual Analysis via FTIR Imaging

High expenditure of time:

- Manual selection of possible particles

Unsuitable for standardization of microplastic analysis

Additionally a high demand of personnel requirements
Requirements for standardization

- Low expenditure of time
- Impartial analysis
- A minimum of personnel requirements
- Fast and reliable measurements
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Automatization of microplastic analysis based on FTIR imaging
Automated Analysis

Combination of two library searches with different data handling

- Correlation of the original spectrum with vector normalization

- Correlation with the 1st derivative of the original spectrum with vector normalization

Successfully automated data generation with a 3% error value

Transformation into images possible

Image Analysis

Implementation of an analytical program based on Python and SimpleITK

Image Analysis

Implementation of an analytical program based on Python and SimpleITK

Allows determination of particle sizes

Resulting in high quality data within a short time

Sediment sample as example

And on larger scale
After Particle Analysis

Size distribution and polymer numbers accessible
After Particle Analysis

Or even combined:

size class distribution [μm]

- polyethylene
- polyethylene oxidized
- polyethylene-chlorinated
- polypropylene
- polystyrene
- polycarbonate
- polyamide
- polyvinylchloride
- nitrile rubber
- polyester
- acrylates/PUR/varnish
- polysulfone
- ethylene-vinyl-acetate
- polyoxyethylene
- coal
- rubber 3
After Particle Analysis

And as zoom in:

![Size class distribution chart](chart.png)

- polyethylene
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- polyethylene-chlorinated
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- polystyrene
- polycarbonate
- polyamide
- polyvinylchloride
- nitrile rubber
- polyester
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- polysulfone
- ethylene-vinyl-acetate
- polyoxymethylene
- coal
- rubber 3
Standardization

Automatization of microplastic analysis based on FTIR imaging

- Data analysis independent from human bias via automated analysis
- Identification and Quantification of MP already within this process
- Time saving due to parallelization
- High comparability of results!
Standardization!

Water samples (surface etc.)
- Lorenz et al., submitted
- Tekman et al., in preparation

Treated waste water
- Primpke et al., 2017, CHIUZ
- Primpke et al., 2019, Analytical Methods
- Mintenig et al., 2019 in preparation

Time series
- Song et al., in preparation

Automatization of microplastic analysis based on FTIR imaging

Sediments
- Bergmann et al., 2017, ES&T
- Haave et al., 2019, Marine Pollution Bulletin
- Lorenz et al., submitted
- Mani et al., submitted

Biota
- Currently in progress

(Arctic) Sea Ice
- Peeken et al., 2018, Nature Communications

Snow
- Bergmann et al., submitted
Standardization!

Automatization of microplastic analysis based on FTIR imaging

Primpke et al., 2017, CHIUZ
Primpke et al., 2019, Analytical Methods

Treated waste water
Treated Waste Water

Two sample sides, one with post filtration unit (Oldenburg)

Additional sampling prior to filtration unit

Sampling on two days

Collaboration with working group of Prof. Laforsch (Univ. Bayreuth) and OOWV (Water Board of Oldenburg and East Frisia)

Treated Waste Water

Particle sizes in general

Treated Waste Water

Efficiency tests for filtration unit in Oldenburg:

Lets go for fibers in waste water!

Particles

Fibers

Fibers

Fibers

- MP dominated most of the samples
- Cellulosic fibers dominated
- MP was removed by ~ 86% during filtration
- Synthetic MF was removed by ~ 89% during filtration
- Cellulosic MF was removed by ~ 78% during filtration

Towards Harmonization of Analysis

Manufacturer independent software including automated analysis and link to the available scripts (former MPhunter)

siMPle: Standardized Identification of MicroPLastics in the Environment

In collaboration with Jes Vollertsen of Aalborg University
Towards Harmonization of Analysis

Single particles via attenuated total reflection (ATR) – FTIR:
Reference database available via Open Access in Primpke, S. et. al., Analytical and Bioanalytical Chemistry 2018, 410, (21), 5131-5141

1. Primpke, S. et. al., Analytical and Bioanalytical Chemistry 2018, 410, (21), 5131-5141
Towards Harmonization of Analysis

FTIR microscopy and imaging: Automated analysis and reference database published via Open Access

1. Primpke, S. et. al., Analytical and Bioanalytical Chemistry 2018, 410, (21), 5131-5141
Summary

- Low expenditure of time:
  - Data analysis time currently reduced from 24 hours to 3 hours by MPhunter for the automated analysis.
  - Depending on FTIR system 1 hours or less of manual labor per sample

- Impartial analysis
  - Evaluation within a fixed confidential interval

- Minimum of personnel requirements
  - One person can perform and analyze several samples in parallel
  - Data analysis can be parallelized

- Fast and reliable measurements
  - Measurement time 4 hours to 16 hours for the same region depending on lenses used.
Standardization by automatization of microplastic analysis based on FTIR imaging

- Low expenditure of time
- Impartial analysis
- Minimum of personnel requirements
- Fast and reliable measurements
Conclusion

Standardization by automatization of microplastic analysis based on FTIR imaging

- Low expenditure of time
- Impartial analysis
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Questions ?
Towards Harmonization of Analysis

- **Agilent**
  - By import of the native Agilent .dmd file

- **Bruker**
  - Data export from OPUS into smaller fields in JCAMP-dx file format and import into MPHunter
  - Available as OPUS macro

- **ThermoFisher**
  - Export into JCAMP-dx

- **PerkinElmer**
  - Import via PerkinElmer files
FTIR Imaging

Samples are collected on 0.2 μm Anodisc filters

Imaging via focal plane array (FPA) detector with a resolution of 11 μm
FTIR Imaging

Example for a FPA field (16 x 16 pixels)
FTIR Imaging

Example for a FPA field (16 x 16 pixels)