MP analysis by FTIR spectroscopy. From macro scale analysis to micro scale imaging-FTIR. State of the art and future perspectives.

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The size range and the analytical techniques for MP analysis

<table>
<thead>
<tr>
<th>Size Range</th>
<th>Optical microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 µm</td>
<td>Increasing uncertainty</td>
</tr>
<tr>
<td>10 µm</td>
<td>μ-ATR-FTIR (single point analysis of particles on a filter)</td>
</tr>
<tr>
<td>100 µm</td>
<td>ATR-FTIR (particles hand-picked, analyzed on bench)</td>
</tr>
<tr>
<td>1000 µm</td>
<td>Increasing uncertainty</td>
</tr>
<tr>
<td>5000 µm</td>
<td>Microscopic analysis</td>
</tr>
</tbody>
</table>

**IR Molecular Spectroscopy**

- Imaging μFT-IR using filters, windows, or slides
- Imaging μRaman – possible method, not well proven
- Macro Raman (particles hand-picked, analyzed on bench)
- NIR (pre-sorting, bench analysis)
- Hy-Spec. Imaging NIR (not well proven)
- TDU-Pyr-GC/MS; TED-GC-MS

Increasing uncertainty
Spectroscopic techniques for MP analyses

Infrared (IR) molecular spectroscopy is the most used instrumental technique to identify polymers particles in environmental samples (28 studies – Hidalgo Ruz et al., 2012)
FT-IR spectroscopy

Vibrational spectroscopy which relies on the interaction (mostly absorption) of IR light with matter (sample).

IR vibrations are characteristic for each chemical bond, they "occupy" precise regions of the IR spectrum (specific wavenumbers ranges)

Identification of a wide range of substances (organic and inorganic)
### Quick overview of the IR vibration normal modes

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Radial</th>
<th>Latitudinal</th>
<th>Longitudinal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric</td>
<td>Symmetrical stretching</td>
<td>Scissoring</td>
<td>Wagging</td>
</tr>
<tr>
<td>Antisymmetric</td>
<td>Antisymmetrical stretching</td>
<td>Rocking</td>
<td>Twisting</td>
</tr>
</tbody>
</table>

**Direction → Symmetry ↓**

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FT-IR spectrometer

<table>
<thead>
<tr>
<th>Michelson Interferometer</th>
<th>Sample chamber</th>
<th>Detector</th>
<th>Data collection and management</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobile mirror</td>
<td>Sample</td>
<td>Interface</td>
<td>Computer</td>
</tr>
<tr>
<td>Fixed mirror</td>
<td>Sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Source</td>
<td>Source</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Interferogram

Mirror position (mm) vs. light measured by detector

Fourier Transform

Single beam

FTIR spectrum

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FT-IR for MP analysis

Sample preparation - Dependent by the signal acquisition mode. A clean-up step is suggested to remove organic matter; sample must be dried (H₂O absorbs in FT-IR)

MP identification according to their characteristic IR spectra (highly specific IR absorption, distinct band patterns in FT-IR spectra)

- Sample preparation
- FT-IR analysis

ATR (Macro/μ) - IR beam → Sample → ATR-cystal → I₀ → I → to detector

Diffuse Reflection - IR beam → Sample → Diffuse component → to detector

Trans-Reflection - IR beam → Sample → Specular component → to detector

Transmission - IR beam → Sample → Transmission window → to detector

LMPPs 5-1mm; SMPPs 1mm-300μm; SMPPs 300μm-5μm
Analysis of Large MP by ATR-FTIR spectroscopy

FTIR analysis of pre-sorted Large MP (5000 – 500/300 µm particles)

Advantages
- Good FT-IR spectra from massive and rough samples
- Diamond ATR, no issues with silicates or hard materials

Drawbacks
- Manual analysis (time consuming)
- Particle size limitation (500/300 µm)
Analysis of Small MP by FTIR spectroscopy: µFT-IR

µFT-IR Analysis of MP directly on filter/IR slide/IR windows

Single point µFT-IR Analysis
- Microscopic inspection of the sample (filter, petri dish, etc.)
- Analysis of selected single particles by FTIR choosing the right beam “size” (µATR; Reflection; Transmission)
- µFTIR spectrum from a single MCT detector

µFT-IR-Imaging analysis
- Analysis of the spatial distribution of the component materials in a sample
- FTIR imaging systems contain multi-element detectors, producing IR images (each pixel contains an IR spectrum)
Mirrors

Cassegrain Condenser

Cassegrain Objective

Sample

Detector

Interferometer

Source globar

Reflection

Transmission

IR Objective scheme

Single MCT detector

Linear array detector

FPA detector

µFT-IR

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µFT-IR-Imaging spectroscopy for Small MP analysis

µFT-IR-Imaging

Powerful and versatile analytical technique for spectrochemical imaging

- Analysis of the spatial distribution of the component materials in a sample
- FTIR imaging systems contain multi-element detectors, producing IR images (each pixel contains an IR spectrum) at relative hi-speed.
- The array detector allows to collect up to 16,000 pixels/spectra simultaneously and has therefore enabled the FT-IR microscopy to become also an imaging technique.
µFT-IR-Imaging spectroscopy for MP analysis (Linear array vs Focal Plane array detectors)

- 2 linear arrays of 16 MCT detectors
- Slower than FPA
- High spatial resolution (~10 µm)
- Spectral range ~ 4000 – 800 cm⁻¹

- FPA detector (32x32 up to 128x128 MCT detectors)
- Faster than Linear Array
- Best spatial resolution (~5 µm or more)
- Spectral range ~ 4000 – 900 cm⁻¹
FPA-μFT-IR-Imaging spectroscopy for Small MP analysis

Visible Image

IR Map

Spectral range Image filter

FTIR spectrum (PBT)
FPA-µFT-IR-Imaging spectroscopy for Small MP analysis

Powerful and versatile analytical technique for spectrochemical imaging

Sample (10 mm diameter) scan velocity up to 4.5h (128x128 FPA)

2-3 scans per day       Huge amount of data (Many GB!) to process

Multiple issues in data handling and managing

Most of FT-IR imaging softwares are not reliable for the MP analysis

A lot of clicking...     Inaccurate analysis!
FPA-μFT-IR-Imaging spectroscopy for MP analysis: First example of automatic pipeline (AWI)

Data acquisition from FPA-μFT-IR-Imaging → FTIR Data processing by Opus Macro → Image analysis (Python Script) → MP identification, quantification and image analysis (particle size distribution)

Based on a commercial FTIR software 😁

Primpke et al., 2017

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A dedicated MP analysis software

First steps in developing a dedicated software for FPA-Imaging data analysis

**MPHunter**

- Software written by Jes Vollertsen using RAD Studio (Embarcadero Delphi IDE)
- RAD Studio: an object oriented programming environment allowing easy construction of user friendly interfaces preserving fast computational speed
- .DMD (Agilent) and .DX (Bruker) file conversion to MPHunter software file format (.spe)
- Managing of FPA data from different FPA detectors (e.g. 64x64 and 128x128)
- Friendly User Interface (FT-IR software like 😊)
- Extremely "light" application...around 5 MB!
How does it work?

- Load a pre-converted mosaic
- Load reference spectra from a library (file .txt)
- Select one or more ref. spectra (we hope to use it with many ref. spectra 😊)
- Load the filters (to use afterwards)
- Select the spectral range (up to 4 ranges at the same time - here just 3750 – 860 cm⁻¹)
How does it work?

- Pearson’s Correlation Coefficient analysis
- Removing noise using filters
- Mark particles as MP
- Measure dimensions
- Save MP
- Display the found MP
To summarize...

- FTIR is the most promising analytical technique for MP analysis (ID, quantification)
- Macro ATR-FTIR is suitable for Large MP analysis, giving reliable results, but it is manual and time consuming
- Other IR techniques (like Hy-Spec NIR and Macro-Raman) has to be tested to automatize Large MP analysis
- Imaging-μFT-IR is the most suitable technique for Small MP analysis, avoiding manual pre-sorting
- A full automatization (or semi-automatization) of the data analysis is important to increase the accuracy and precision of the analysis
- ”AWI automatic pipeline” is the first example of fully automatized MP data analysis (very important step)
- ”AAU MPHunter” is another example of semi-automated software for MP analysis, user friendly and customizable
- A better automatization is required to make MPHunter more reliable and eventually get rid of the ”clicking nightmare”
- **Interface MPHunter with AWI Automatic Pipeline for MP analysis, creating a freeware program for MP data analysis**
Thank you

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