Ultraviolet photodissociation for non-target screening based identification of organic micro-pollutants in water samples

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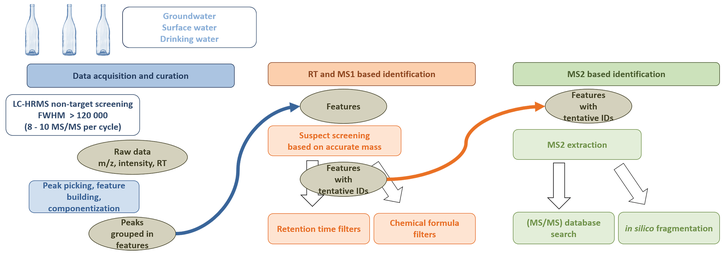
Monitoring of drinking water quality

- Reliable identification of micro-pollutants in water is essential to risk assessment and prediction of the behavior of a substance in the environment and in drinking water treatment.
- Non-target screening (NTS) based on the combination of liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS/MS) has become the key method to identify organic micro-pollutants in drinking water and its sources.



Schematics of NTS workflow

Current approaches rely on matching of the accurate mass and fragmentation spectra of an unknown peak with chemical and spectral database entries.

Analysis of organic micro-pollutants with the Orbitrap Fusion Lumos equipped with UVPD

Reference standards relevant for the water sector, including compounds known to not fragment well with Higher Collision induced Dissociation (HCD) were analysed using RP LC-MS/MS with an Orbitrap Fusion Lumos equipped with Ultra Violet Photo Dissociation (UVPD). Fragmentation spectra were acquired using the fixed collision energies 20, 35 and 60 in HCD experiments, and UVPD reaction times ranging from 25 to 800 ms. Fragment assignment was performed with the web based MetFrag version (https://msbi.ipb-halle.de/MetFragBeta/) as MetFrag does not apply rules, but breaks every bond in the molecule. No NTS data analysis software to date can analyse UVPD data. For high-throughput fragment assignment an R based data analysis workflow was therefore developed.

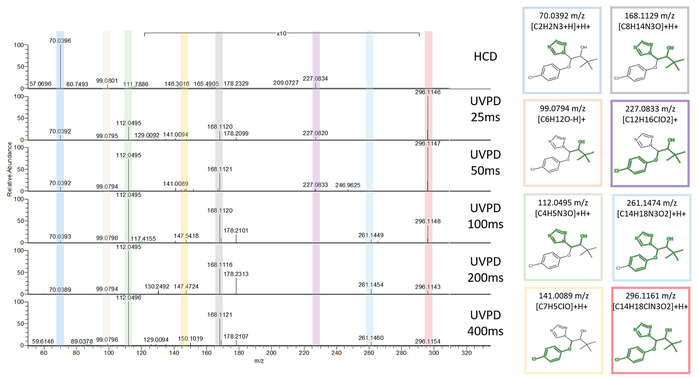
Increasing spectral quality

- A high number of compounds remains unidentified due to poor fragmentation spectra.
- Poor fragmentation spectra can result from suboptimal fragmentation methods.

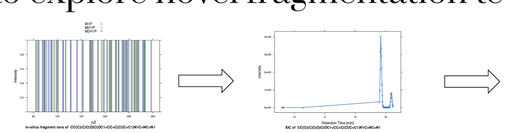
Here, the potential of the fragmentation technique UVPD to improve structural identification of organic micro-pollutants in water samples through unique fragments was evaluated.

Can UVPD fragment organic micro-pollutants that fragment poorly with HCD?

UVPD provides unique fragmentation information for structure information of triadimenol, a widely used fungizide that can be found in drinking water sources. Compounds that ionize in negative mode do not benefit of UVPD.



An R-based LC-HRMS data analysis workflow to explore novel fragmentation techniques

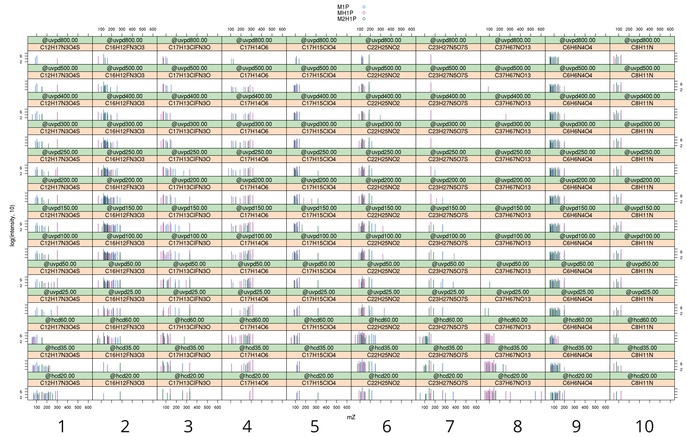


1) In-silico fragmentation of given set of SMILES with MetFrag in R
2) Thermo Fisher Scientific .raw file

1) APEX(MS1) determination for given SMILES; returns RT (Trachsel et al. 2018)
2) MS2 extraction at given RT and precursor window

1) Computation of matches between in-silico and MS2 fragment specs (Panse and Grossmann 2019)
2) Spectral assignment and annotation

High-throughput application of fragment assignment reveals HCD and UVPD fragmentation patterns



- Richer fragmentation with HCD (1,6,8)
- Richer fragmentation with HCD at high CE (7)
- Richer fragmentation with UVPD (2,3,5)
- Similar fragmentation with both (4,9,10)

UVPD fragmentation provides unique fragments in many of the compounds analyzed. These unique fragments provide additional information for structural identification complementary to HCD spectra. For its implementation in NTS workflows, databases need to be extended with UVPD spectra.

Conclusions

- Information rich MS2 fragmentation spectra achieved for compounds ionized in positive mode that fragment poorly with HCD
- An R-based LC-HRMS data analysis workflow was developed to investigate UVPD fragmentation of organic micro-pollutants
- UVPD and HCD generate both unique as well as overlapping fragments, demonstrating that some fragmentation pathways are specific to the respective fragmentation methods whilst others seem to be more generic.