Environmental analysis of poly- and perfluoroalkyl compounds using a Q-Exactive Orbitrap: optimization for a laser diode thermal desorption method

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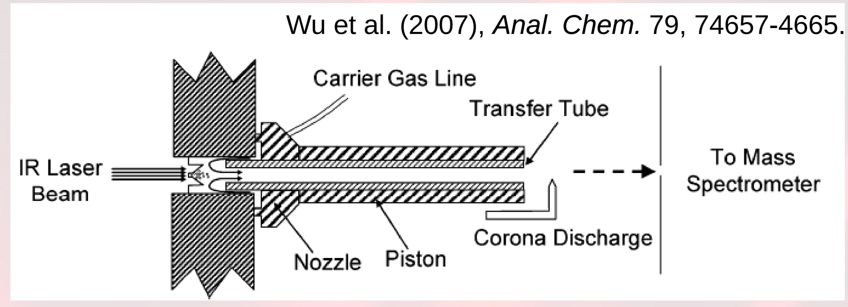
Overview

- 19 PFASs were analyzed in less than 20 seconds by LDTD/APCI-Q-Exactive.
- Optimization was conducted with the use of experimental designs.
- LODs were in the range 0.3–4 ng L^{-1} in wastewater and 0.03–2 ng g^{-1} dw in sediments.
- The method was successfully applied to a selection of environmental samples.
- Results were compared to liquid chromatography (LC/ESI-Orbitrap).

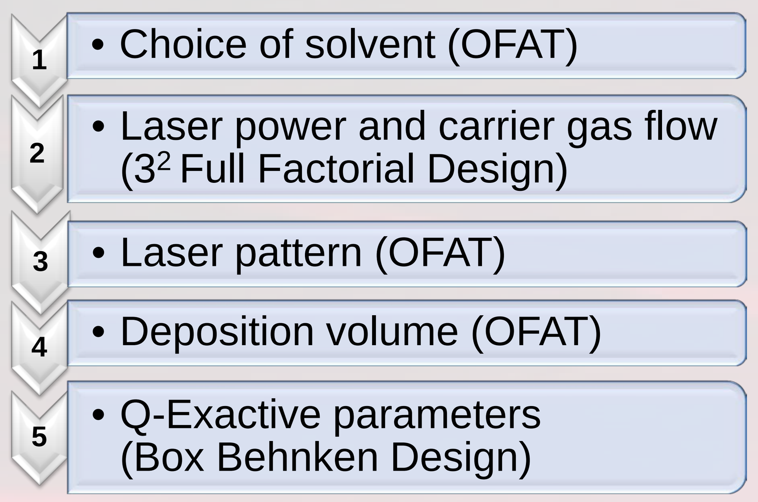
Introduction



Schematic of the LDTD source

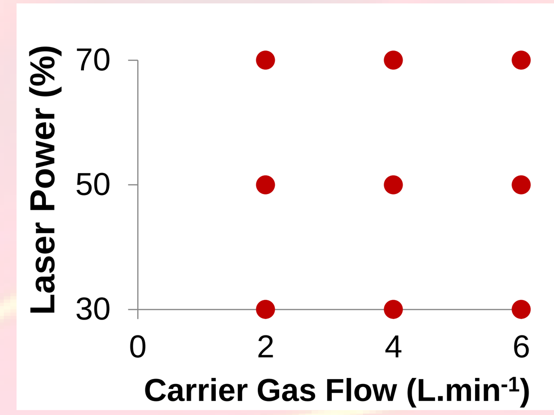
- An original analysis technique for the quantification of selected poly- and perfluoroalkyl substances (PFASs) in water and sediment is reported.
- Target molecules were analyzed in a 15-s single run with the use of Laser Diode Thermal Desorption Atmospheric Pressure Chemical Ionization (LDTD/APCI) technology coupled with a Q-Exactive Orbitrap high resolution mass spectrometer.
- Since no chromatographic separation is needed, analytical runs are reduced by about twenty to fifty-fold compared with the conventional LC-MS/MS method. Sample desorption is achieved with a focalized IR laser indirectly vaporizing analytes by thermal transfer. Desorbed analytes are then carried to the corona discharge region to be ionized, before transmission into the MS inlet.

Method optimization

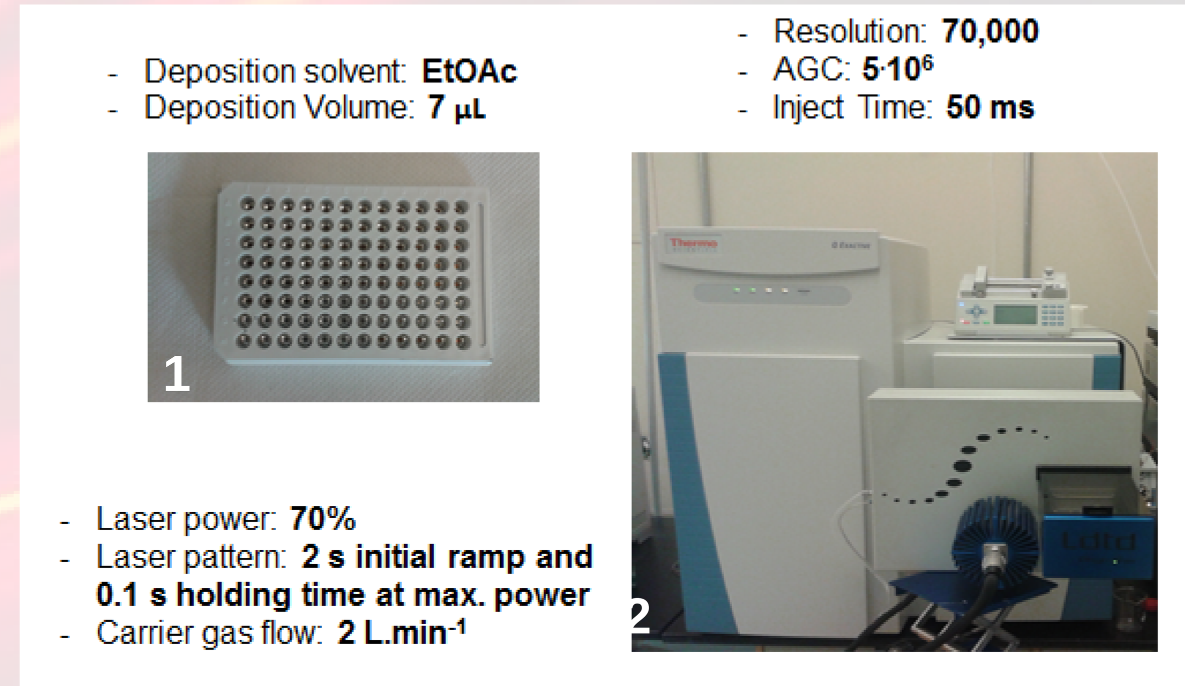


General Optimization Scheme

The optimization scheme combined both one-factor-at-a-time (OFAT) methods and experimental designs. OFAT consists in varying one variable at a time, with all other variables are held constant. In contrast, optimization studies conducted with the assistance of experimental designs can explore a greater range of parameter combinations, or identify main interactions between variables.
For instance, choice of deposition solvent was conducted in OFAT mode (EtOAc demonstrating better suitability over water, MeOH and ACN), while LDTD two main parameters (laser power and carrier gas flow) were optimized simultaneously via a 3^2 full factorial design. To reduce the number of analyses to a manageable number, a Box Behnken design was carried out for the 3 main Q-Exactive parameters which were optimized simultaneously at three levels for a total of 15 methods, instead of the 27 methods needed with a full factorial design. Response surfaces were then fitted to results using the rsm R-package.



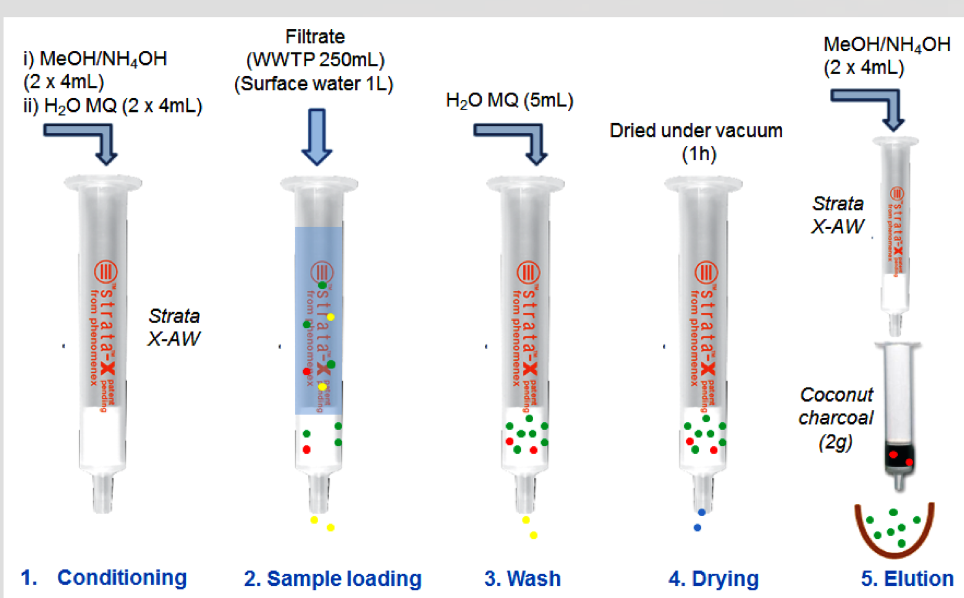
3² full factorial design
Each condition was run 10 times



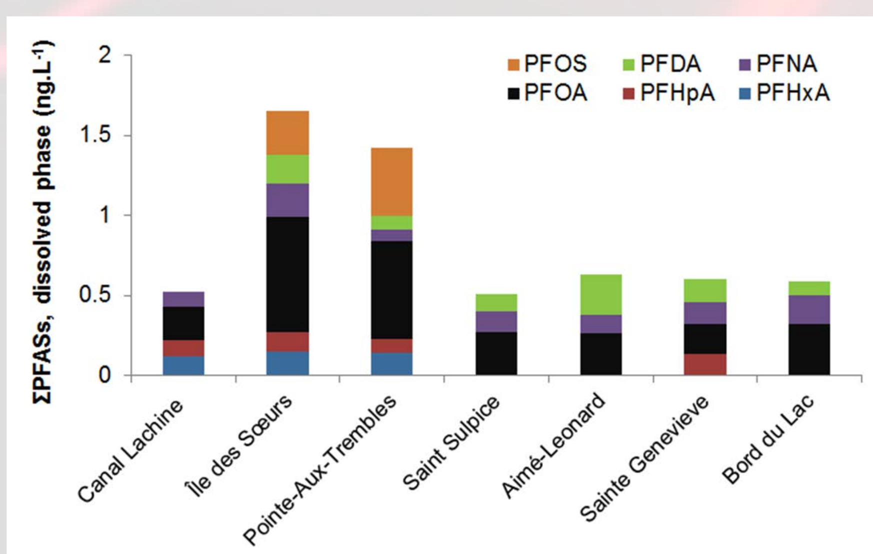
Optimized settings
(1) 96-well plate for sample loading. (2) LDTD/APCI-Q-Exactive interface.

Response surface modeling showing the influence of laser power and carrier gas flow on relative peak area (light red: max.; dark green: min.)

Application to environmental analysis

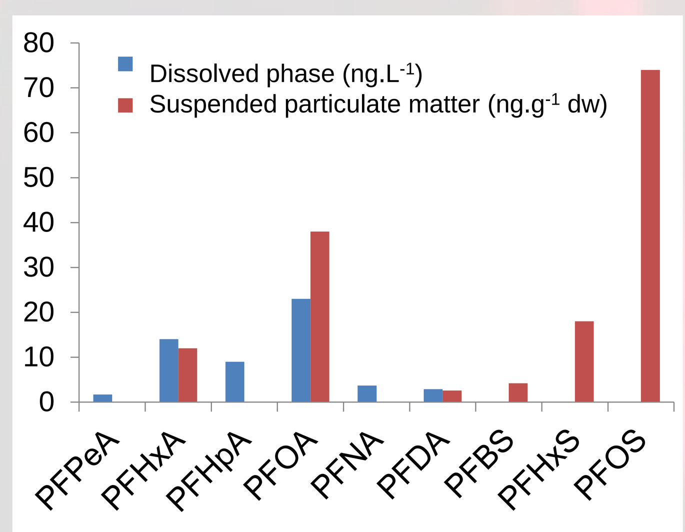


Water extraction procedure

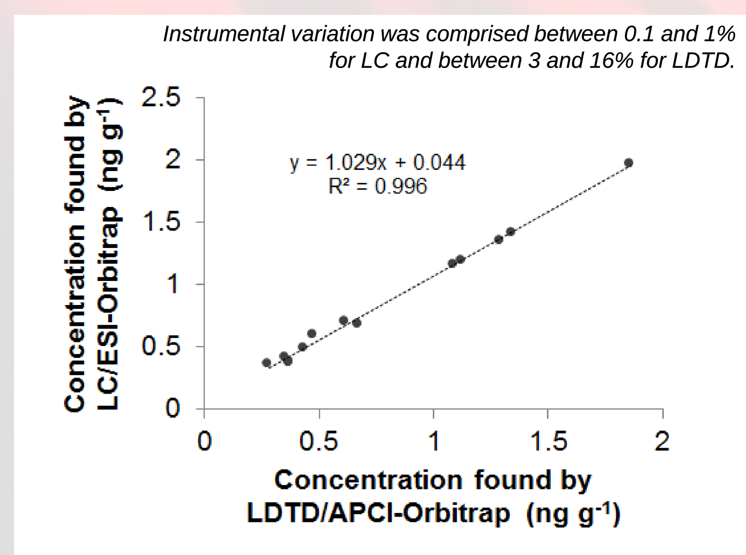


Molecular patterns in surface waters from the Montreal area (Canada)

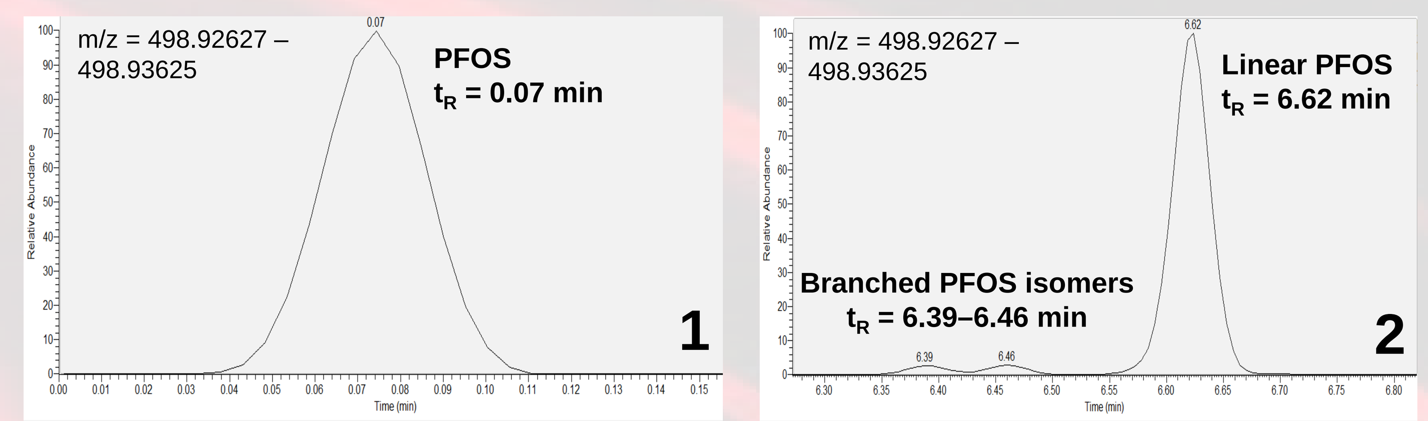
Target compounds were unequivocally detected in several wastewater influents (<LOD–23 ng.L^{-1} in the water filtrate and <LOD–74 ng.g^{-1} dw in the suspended particulate matter), as well as in surface waters from the Montreal area, albeit at lower concentrations (<LOD – 0.8 ng.L^{-1}). PFOS was the main congener in sediment samples from Quebec, and was quantified in 93% of samples by LDTD (<LOD–1.86 ng.g^{-1} dw) and in all samples by LC (0.36 – 1.97 ng.g^{-1} dw).



PFAS levels in a wastewater Influent from Ontario (Canada)



Correlation between PFOS levels found in sediment samples by LDTD and LC



PFOS signal by LDTD/APCI-Orbitrap (1) and by LC/ESI-Orbitrap (2) in a sediment sample from the Quebec city area (Canada)

Conclusions

The LDTD/APCI-Q-Exactive method proved reliable, with values close to those obtained with LC/ESI-Q-Exactive. Eliminating the chromatographic step prior to MS analysis reduced solvent consumption and potential contamination risk from tubings and mobile phases, as well as analysis times, making it an economic alternative for high-throughput sample screening.

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