Optimization of analytical methods for photodegradation products of PAH and phthalate esters adsorbed on microplastics

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Microplastics (MPs) are particles smaller than 5 mm in diameter and present a global environmental pollution problem. MPs serve as vectors for organic pollutants and therefore modify their photodegradation pathways [1]-[3].

The aim of this research was the optimization of analytical methods for photodegradation products adsorbed on MPs for two groups of important environmental pollutants: phthalate esters and polycyclic aromatic hydrocarbons.

HPLC method

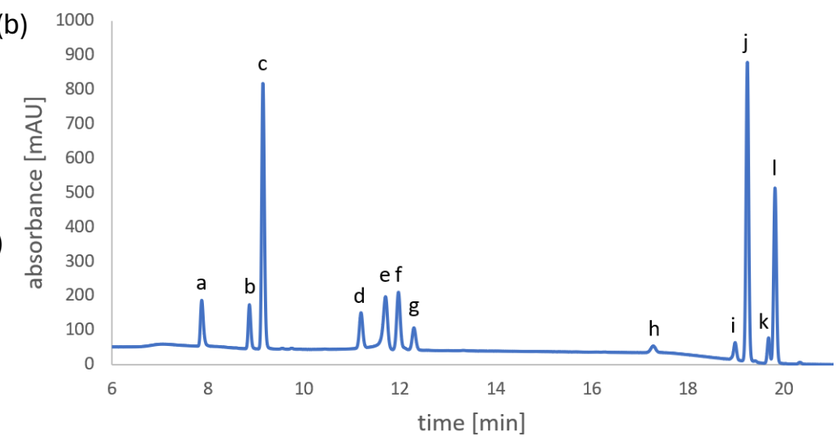
Standard solutions used

PHTHALATES

phthalic acid (a)
monomethyl phthalate (b)
dimethylphthalate (d)
monobutylphthalate (g)
dibutyl phthalate (k)

PAH

2,7-naphthalenediol (c)
acenaphtenequinone (e)
2-naphtol (f)
naphthalene (h)
acenaphtene (i)
phenanthrene (j)
fluoranthene (l)



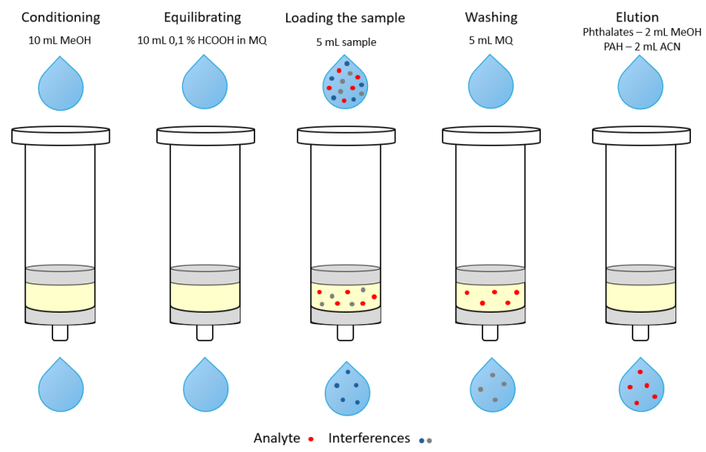
HPLC-DAD chromatogram of mix of analytes with concentration 10 mg/L in 10 % ACN in MQ at 270 nm

Solid Phase Exctraction

Optimised for both groups separately

Final procedure:

- Column:
  phthalates: HLB
  PAH: LC-8
- pH value of the sample:
  original
- Ion strength of the sample:
  38 ‰ NaCl (sea salinity) increases SPE yield*
- Washing step:
  5 mL MQ
- Elution solvent:
  phthalates: 2 mL MeOH
  PAH: 2 mL ACN

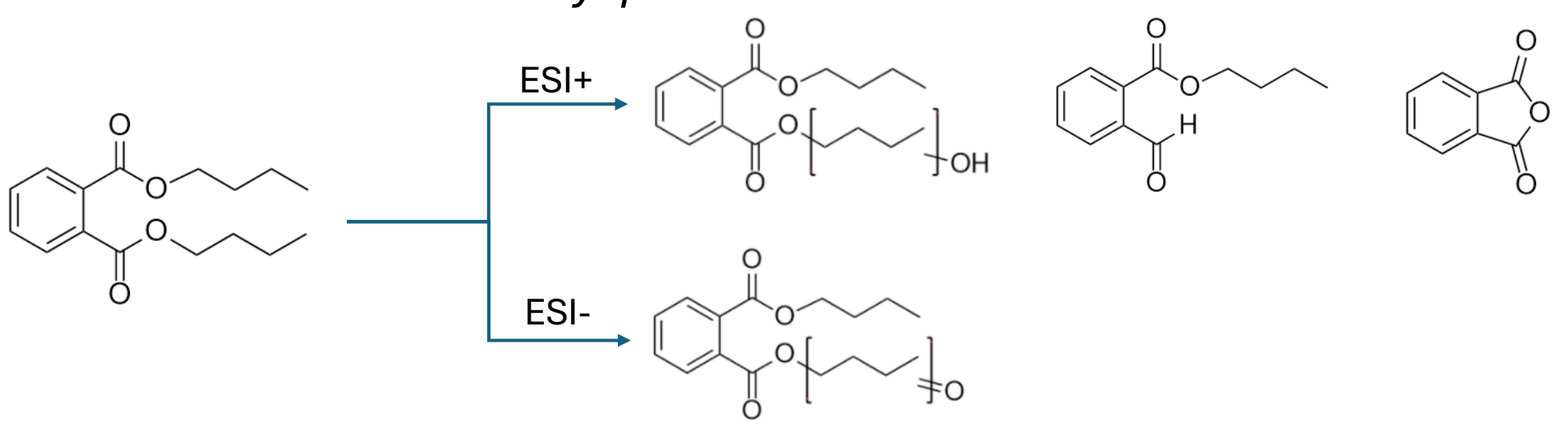


*did not use it on model samples to avoid formation of adducts

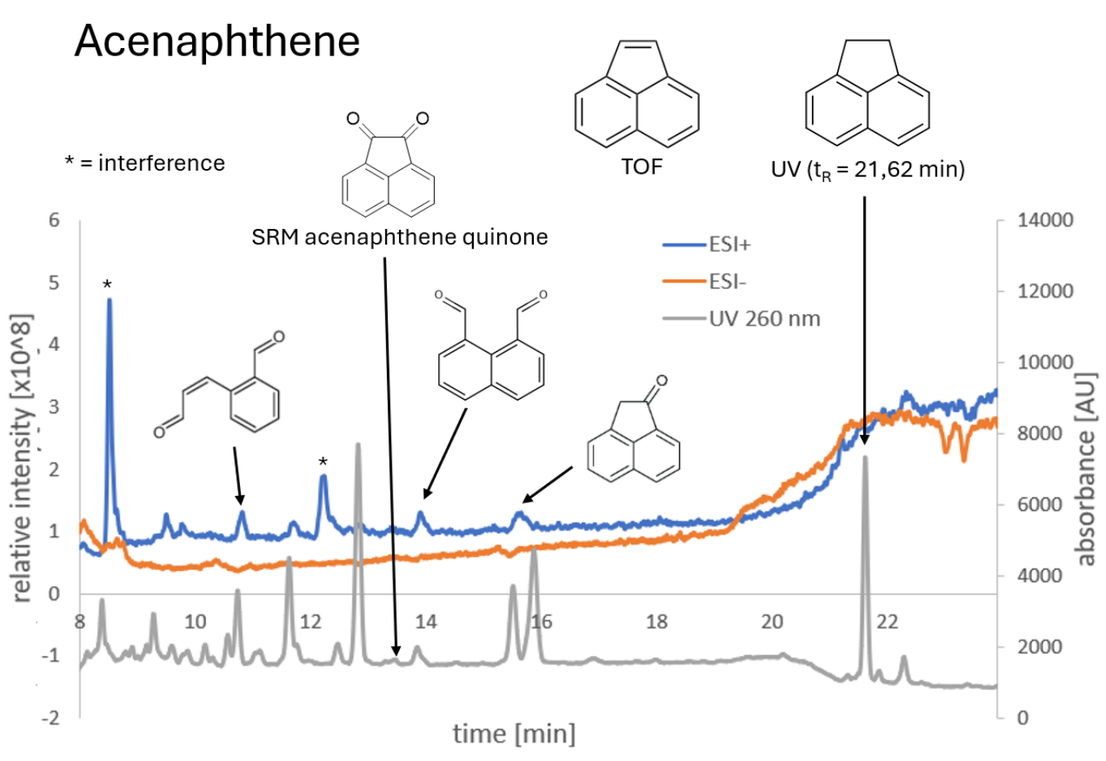
LC-MS/MS method and TOF MS analysis

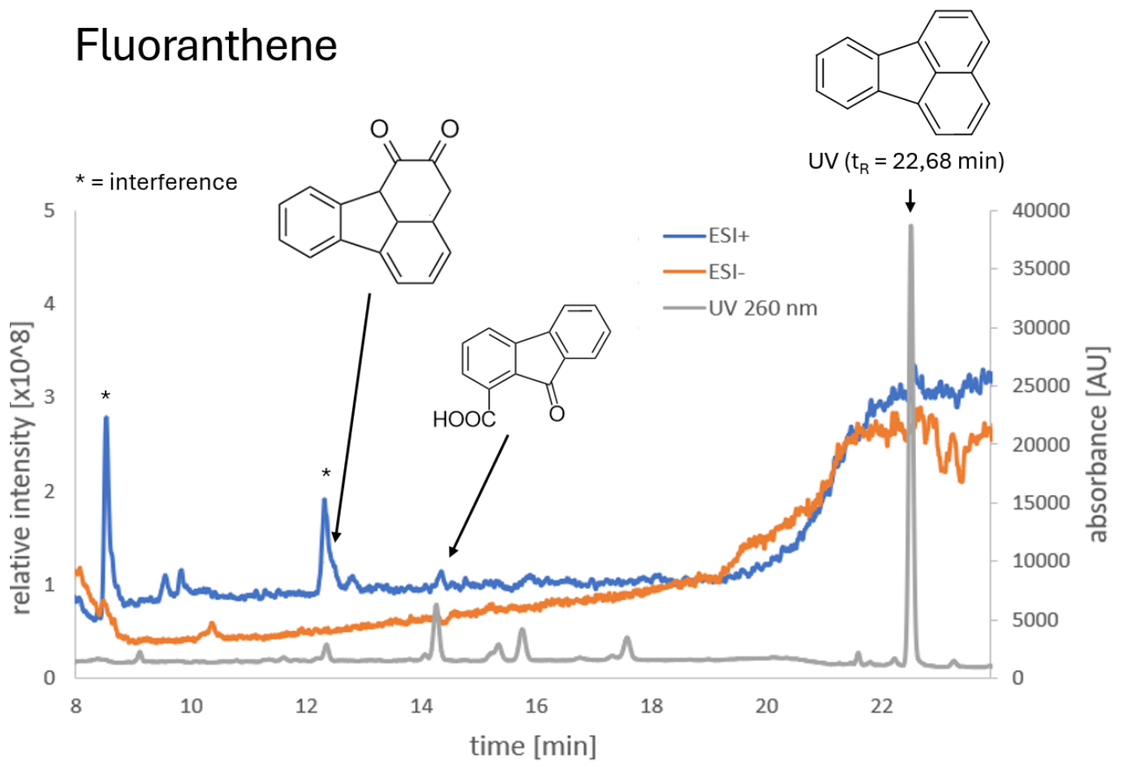
The complete optimised method was applied to model aqueous samples. Identities of peaks were proposed based on fragmentation patterns and confirmed with additional high-resolution MS analysis.

- *Electrooxidation of dibutyl phthalate*



- *Photodegradation of PAH adsorbed on MP's particles*





CONCLUSION

With the optimised method, some structures of degradation products of dibutyl phthalate and PAH were successfully determined.

Reference

[1] Y. Yu, W. Y. Mo, T. Luukkonen: Adsorption Behaviour and Interaction of Organic Micropollutants with Nano and Microplastics – A Review. *Sci. Total Environ*. **2021**, *797*, 149140.

[2] L. Fu, J. Li, G. Wang, Y. Luan, W. Dai: Adsorption Behavior of Organic Pollutants on Microplastics. *Ecotoxicol. Environ. Saf.* **2021**, *217*, 112207.

[3] J. Huang, P. Duan, L. Tong, W. Zhang: Influence of Polystyrene Microplastics on the Volatilization, Photodegradation and Photoinduced Toxicity of Anthracene and Pyrene in Freshwater and Artificial Seawater. *Sci. Total Environ*. **2022**, *819*, 152049.