Analytical Challenges in Quantifying Organic UV Filter

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Outline

Organic UV filter structures and quantification challenges

Stability in solution (saponification, trans-esterification)

Tautomeric behavior and its effect on quantification

Solubility

Optimized chromatography and remaining challenges to quantify most UV filters in a single method

Isolation techniques (Solid-phase extraction, liquid-liquid extraction)

Adsorption challenges and contamination risks

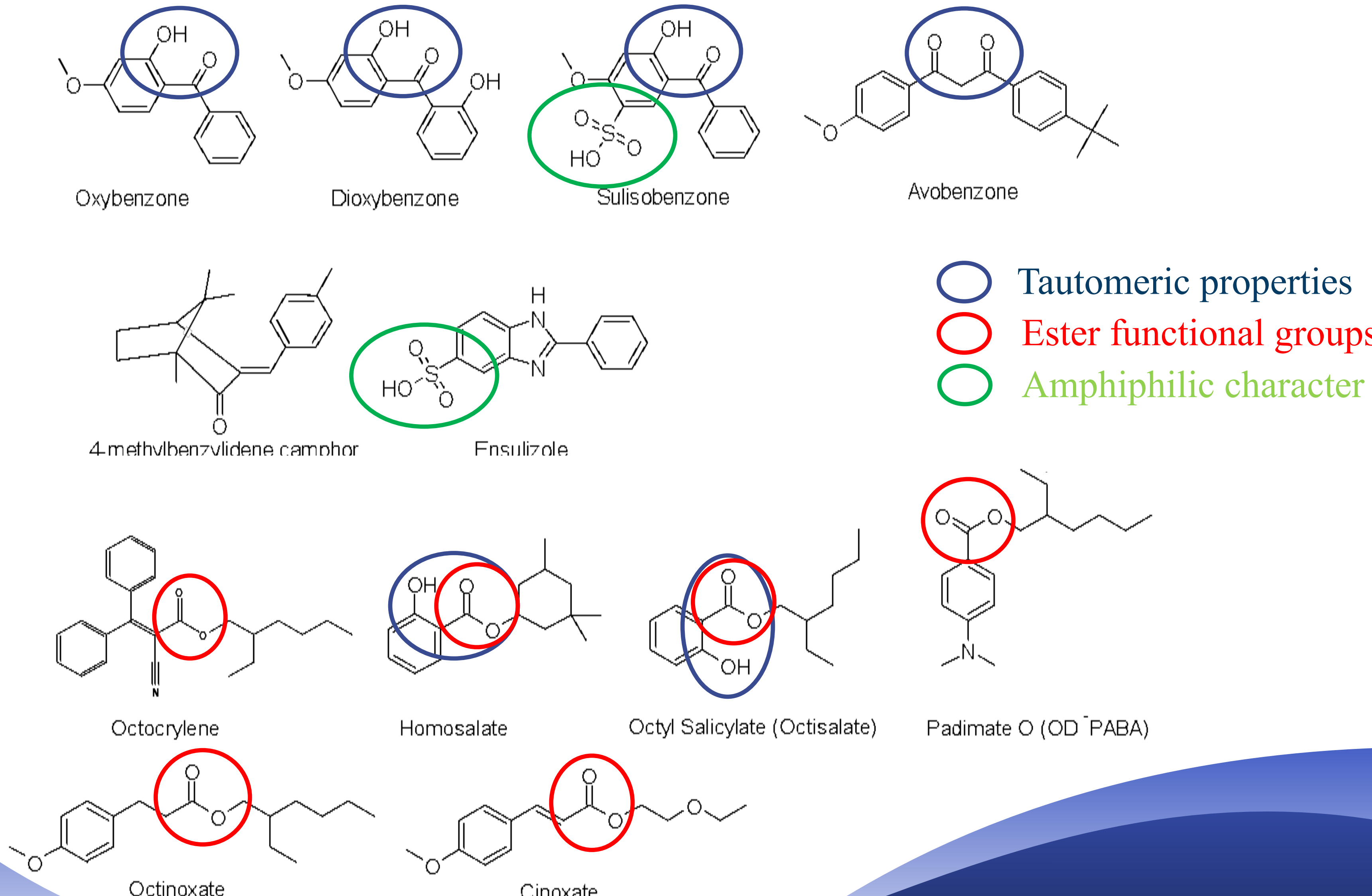
Organic UV filter structures and quantification challenges

Stability

Tautomer equilibrium

Solubility

Major Organic UV filters and their Structures

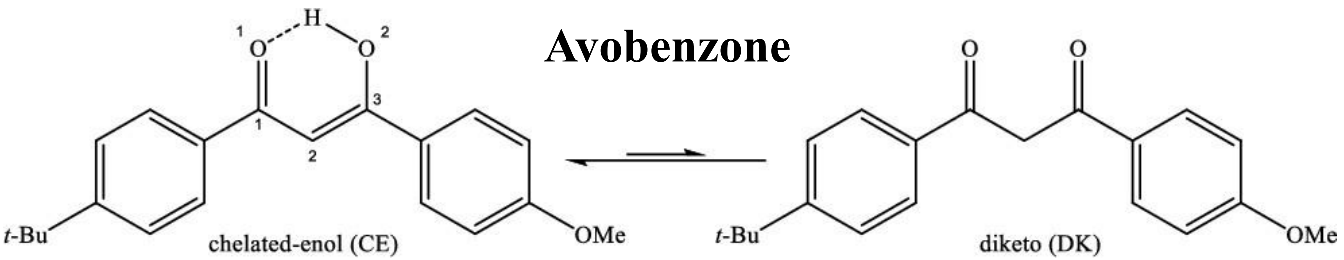


Stability

- Calibration solutions may not stable over long period of time (potentially solvent dependent)
  - Issues: possible transesterification, hydrolysis, photodegradation
  - Recommendation: Research is needed to determine reasonable storage times in different solvents

- pH interferences in standard solutions and acidic internal standards should be avoided
  - Issue: possible acid-catalyzed hydrolysis

Tautomers of specific UV filters

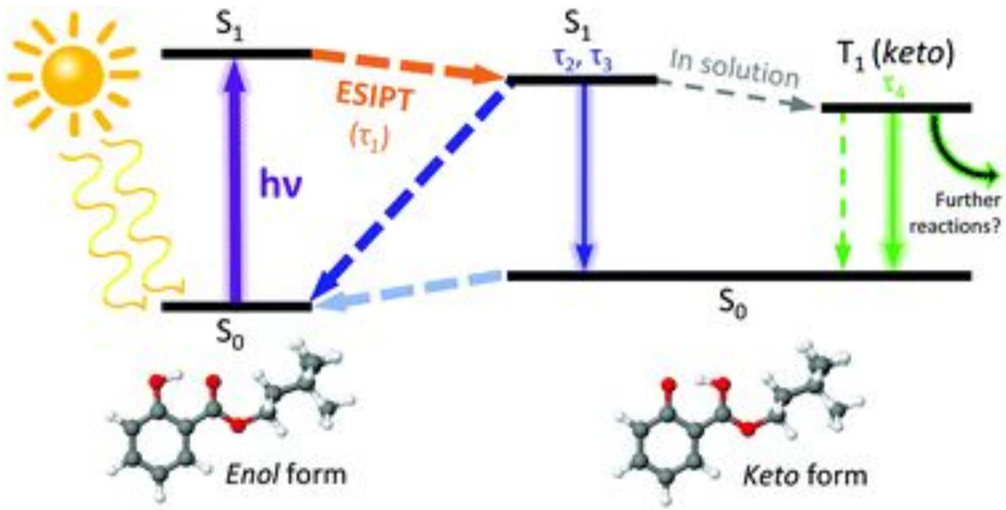


Dark: ~97% ~3%

Sunlight:

Tautomers of specific UV filters

Homosalate (Octisalate)



Holt, E. L., K. M. Krokidi, M. A. P. Turner, P. Mishra, T. S. Zwier, N. d. N. Rodrigues and V. G. Stavros (2020). "Insights into the photoprotection mechanism of the UV filter homosalate." Physical Chemistry Chemical Physics **22**(27): 15509-15519.

Solubility and Photostability

- Solubility in water is very low for some organic UV filters (e.g., octocrylene, avobenzone), and no reliable data exists about solubility in seawater.

- Partitioning between dissolved and particulate forms is critical in understanding environmental fate and is obviously dependent of solubility.

- Photochemical degradation is fundamentally different in protic and aprotic solvents, meaning between the sea surface microlayer and the truly dissolved forms.

- Photochemistry will solubilize organic UV filters due to photo transformation and the likely production of much more hydrophilic photo-products.

- All the factors above have consequences for toxicity

Optimized chromatography and remaining challenges to quantify most UV filters in a single method

Extraction and Adsorption to surfaces

Extraction and adsorption challenges

- **Most used methods are solid-phase extractions (SPE) and liquid-liquid extractions**
- **Contamination, adsorption to surfaces and carry over is extreme for octocrylene and to a lesser extent for homosalate, octisalate and avobenzone.**
  - **Issue 1: efficiency loss due to adsorption on glass, filtration equipment, etc.**
  - **Issue 2: Carry over for most hydrophobic compounds can occur**
  - **Issue 3: Lab contamination through plasticware, insufficient cleaning and carryover**
  - **Issue 4: Drying of extracts leads to drastic loss of several organic UV filters**
  - **Issue 5: Efficient elution from solid-phase extraction cartridges is needed**

Optimized method for 12 common UV filters

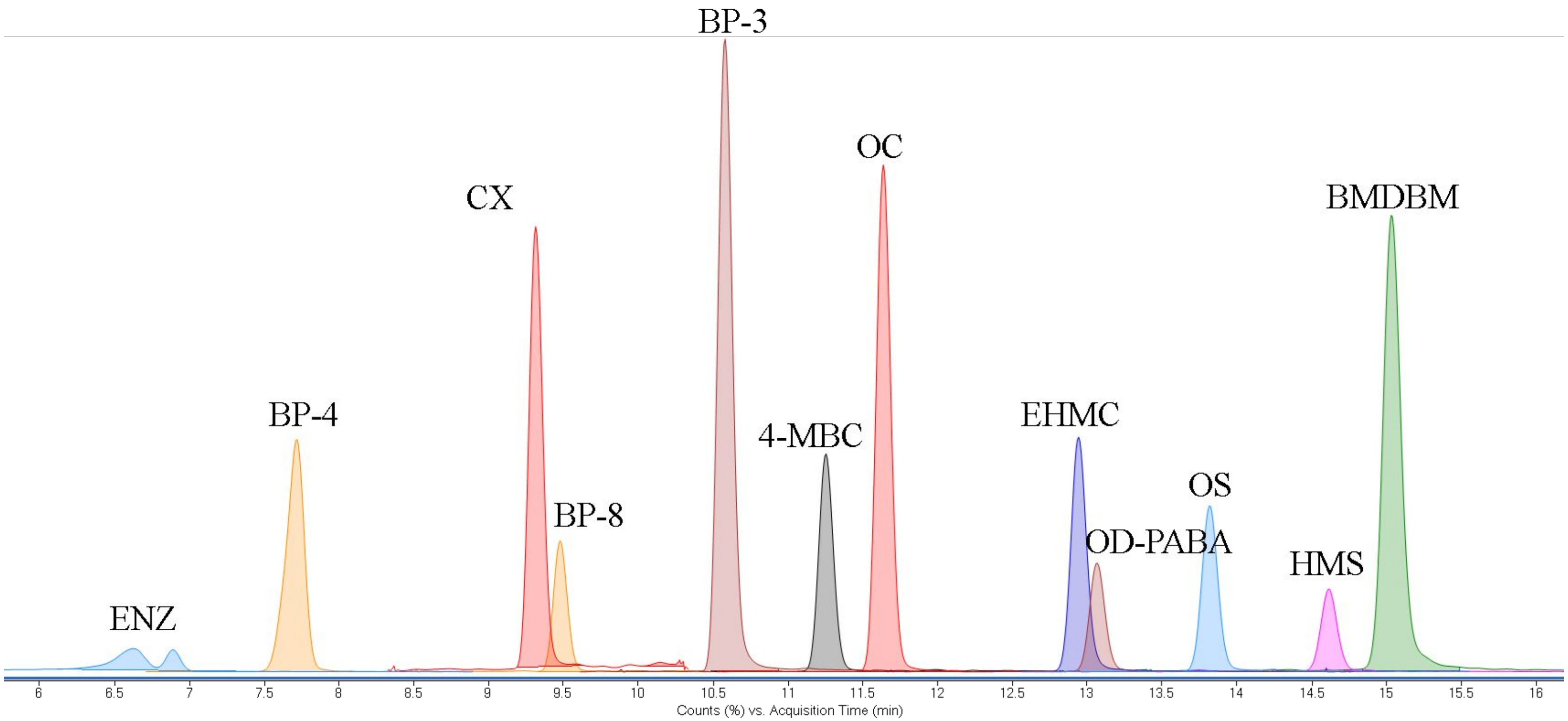
- **A single method based on solid phase extraction can be optimized for most organic UV filters with reasonable extraction efficiencies and protocols to minimize adsorption and contamination.**

- **Excellent chromatography is critical to mitigate false positives and to be able to quantify different tautomers.**

- **Optimized electrospray ionization (ESI) conditions are critical to be able to quantify most organic UV filters at nanomolar detection limits using LC-qqq MS.**

- **Optimal and indicative fragmentation for all organic UV filter are known, including isotope standards.**

Optimized method for 12 common UV filters



Method includes gradient mobile phase, isotope internal standards, qualifier transitions and is based on LC-qqq-MS.

Questions?
More Information?

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