Application Brief

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LC/MS/MS Optimization of Organic Ultraviolet (UV) Filters

Using the Agilent 6470B triple quadrupole LC/MS with polarity switching

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Abstract

Ultraviolet filters (UVFs) are found in many commercial and personal products, serving to deflect or absorb ultraviolet (UV) rays across the UVA to UVB spectrum. This application brief presents a single mass analysis method using high-performance liquid chromatography-tandem mass spectrometry (HPLC/MS/MS) with polarity switching for the determination of eight common UVFs. Unlike traditional UV-DAD methods, this technique allows positive-mode and negative-mode UV filters to be analyzed in a single run and delivers lower detection limits in environmental matrices.

Introduction

Ultraviolet filters (UVFs) are a diverse group of chemicals found globally in numerous commercial and personal products. Their primary role is to deflect or absorb ultraviolet (UV) rays in the spectrum from UVA (longer λ) to UVB (shorter λ).[1,2] For ease of analysis, UVF compounds are ideally quantified using a single, unified method. Gas chromatography employed in earlier studies is not suitable for all UVFs, as some are hydrophilic and nonvolatile, necessitating derivatization.[1,3-5] Mass analysis by UV-DAD (diode array detector), although quick (and appropriate, considering these compounds absorb UV light), suffers the consequence of higher detection limits than tandem mass spectrometry. Thus, UV-DAD analysis is not particularly useful for biological (for example, µmol L^{-1}) and trace environmental (that is, ng L^{-1} to µg L^{-1}) concentrations.[4,6-8] Moreover, some UVFs simply do not ionize efficiently in either a single positive-mode or negative-mode method with electrospray ionization (ESI). Separate runs and calibration curves are then required, unless protocols for polarity switching can be established.

This study demonstrates a single mass analysis method using high-performance liquid chromatography-tandem mass spectrometry (HPLC/MS/MS) and polarity switching for the determination of eight of the most popular and frequently used UVFs.

Experimental

Chemicals and reagents

Avobenzone (CAS 70356-09-1), dioxybenzone (CAS 131-53-3), homosalate (CAS 118-56-9), octinoxate (CAS 5466-77-3), octisalate (CAS 118-60-5), octocrylene (CAS 6197-30-4), oxybenzone (CAS 131-57-7), and sulisobenzone (CAS 4056-45-6), as well as dioxybenzone-d_3, homosalate-d_4, octisalate-d_4, octocrylene-$^{13}C_3$, and oxybenzone-d_3, were purchased from Toronto Research Chemicals (Toronto, ON, Canada) as neat powders or oils.

Instrumentation

Separation of target analytes was performed on an Agilent 1260 Infinity II LC system equipped with an Agilent InfinityLab Poroshell 120 EC-C18 column, 2.1 mm × 50 mm, 1.9 µm (part number 699675-902). An Agilent InfinityLab Poroshell 120 EC-C18 guard column, 2.1 mm × 5 mm, 1.9 µm (part number 821725-940) was also used. The LC parameters are presented in Table 1.

Mass spectral analysis was performed using dynamic multiple reaction monitoring (dMRM) on an Agilent 6470B triple quadrupole LC/MS, operated in both negative (ESI–) and positive (ESI+) electrospray ionization modes with polarity switching. To maximize abundances for the suite of compounds, Agilent source optimization was performed. Triple quadrupole parameters are presented in Table 2. MRM parameters were determined with Agilent Optimizer software.

Table 1. Agilent 1260 Infinity II LC system parameters.

Parameter	Value
Agilent 1260 Infinity II Multicolumn Thermostat (MCT; G7116A)	
Column Heater	42 °C
Agilent 1260 Infinity II Multisampler (G7167A)	
Injection Volume	10 µL
Sample Loop	100 µL
Seal Wash	Standard
Agilent 1260 Infinity II Flexible Pump (G7104C)	
Flow Rate	0.4 mL/min
Mobile Phase A	0.05% formic acid in DI water
Mobile Phase B	0.05% formic acid in acetonitrile
Gradient Elution	Time (min) %B 0 5 2 100 5 100 6 5 12 5

Table 2. Agilent 6470B triple quadrupole LC/MS parameters.

Parameter	Value
Desolvation Gas Flow	10 L/min
Capillary Voltage	3,000 V
Sheath Gas Flow	12 L/min
Nozzle Voltage	2,000 V
Sheath Gas Temperature	250 °C
Drying Gas Temperature	260 °C
Nebulizer Pressure	25 psi
Collision Gas Flow	16.8 L/min
MS1 Heater	100 °C
MS2 Heater	100 °C

Results and discussion

Figure 1 shows separation of target analytes on the InfinityLab Poroshell 120 EC-C18 column, and Table 3 shows the results of the compound optimizer. The most abundant product ion, whether $[M + H]^+$ or $[M - H]^-$, depending on the mode, served as the quantifier ion. The second most abundant product ion acted as the qualifier.

Upon optimizing the source, it was found that octisalate and homosalate exhibited signal abundances that were approximately one to two orders of magnitude lower than those of the other six unlabeled analytes. This discrepancy is significant because isotopically labeled standards used for quantitation should ideally be equi-responsive, meaning they should produce similar peak heights and areas. To address this, dioxybenzone-d_3, homosalate-d_4, octisalate-d_4, octocrylene-$^{13}C_3$, and oxybenzone-d_3 were selected to quantify their respective unlabeled counterparts. Additionally, oxybenzone-d_3 was chosen to quantify avobenzone and sulisobenzone, as it was the closest internal standard in terms of signal area.

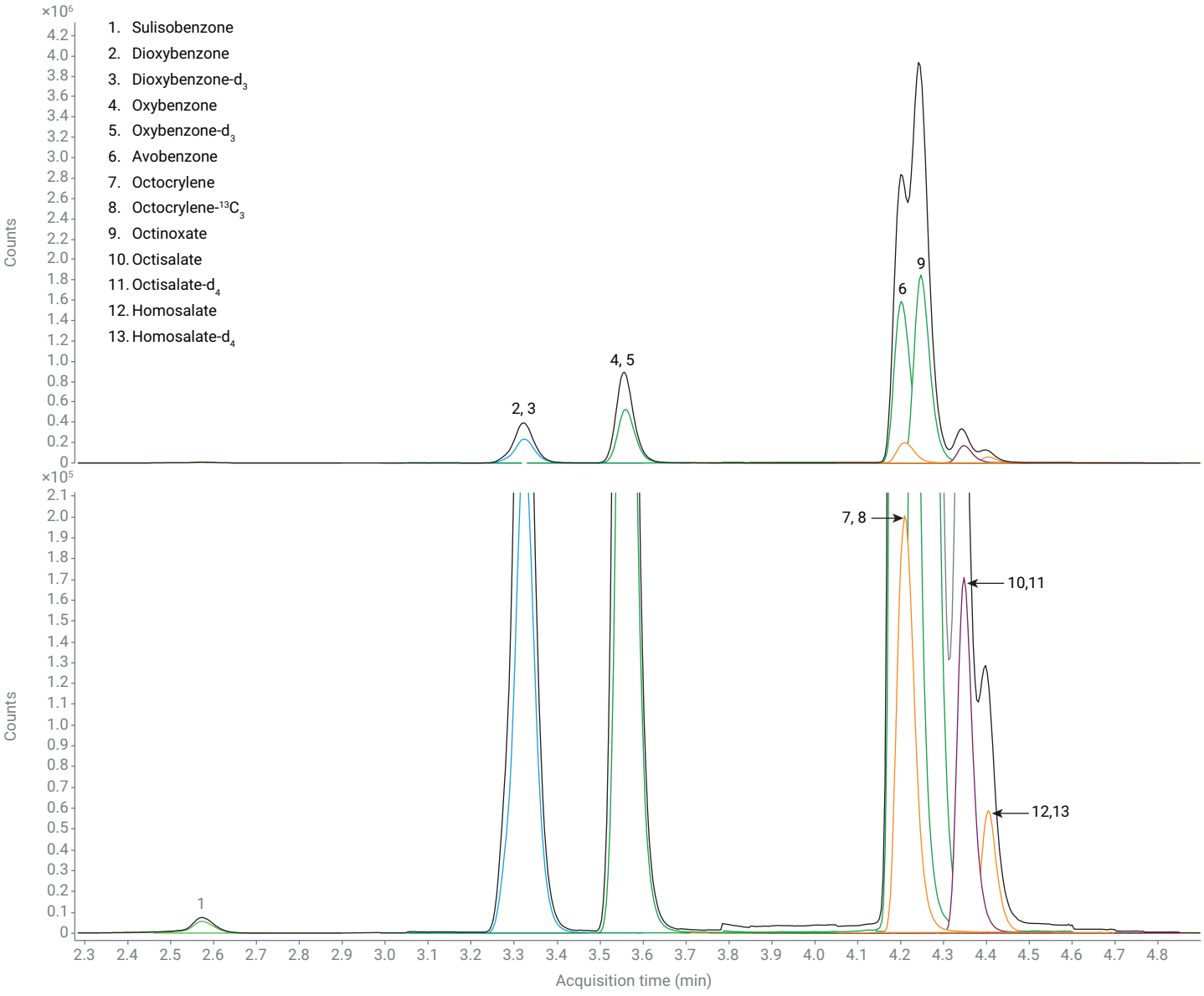

Figure 1. Chromatographic separation of target analytes.

Table 3. Optimized MRM transitions for target analytes.

Compound	Retention Time	ESI Mode	Precursor Ion (*m/z*)	Product Ion (*m/z*)	Frag (V)	CE (eV)
Sulisobenzone	2.56	Neg	307.3	211, 80	160	40, 52
Dioxybenzone	3.32	Pos	245.1	151, 121	107	20, 16
Dioxybenzone-d_3	3.32	Pos	248.1	154, 121	125	20, 16
Oxybenzone	3.56	Pos	229.1	151, 77.1	116	20, 44
Oxybenzone-d_3	3.56	Pos	232.1	154, 105	128	20, 20
Avobenzone	4.20	Pos	311.2	161.1, 135	113	24, 24
Octocrylene	4.21	Pos	362.2	250.1, 232	147	4, 20
Octocrylene-$^{13}C_3$	4.21	Pos	365.5	253.1, 235.1	147	8, 20
Octinoxate	4.25	Pos	291.2	179, 161.1	82	4, 20
Octisalate	4.35	Pos	251.2	139, 121.1	76	4, 24
Octisalate-d_4	4.35	Pos	255.2	143.1, 125.1	85	4, 32
Homosalate	4.40	Pos	263.2	139.1, 121.1	76	4, 28
Homosalate-d_4	4.40	Pos	267.2	143, 125.10	76	8, 32

CE = collision energy

Conclusion

This study presents an LC/MS/MS method that utilizes polarity switching to allow for the analysis of both positive-mode and negative-mode UV filters in the same method. Furthermore, the optimized MRM transitions from this analysis can augment current DAD protocols and allow for lower detection limits in environmental matrices.[8-9]

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