The Analysis of Sunscreen UV Filters Agents and Preservatives

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INTRODUCTION

UV filter agents and preservatives are widely used in a broad range of applications including cosmetics and personal care products, household products, plastics, paints, inks, and adhesives.[1-5] Worldwide government regulations and guidelines impact labelling, composition and registration of personal care, cosmetics and packaging products. It is important to use the best science and instrumentation to evaluate not only the final products but the ingredients as well. In the United States, 9 UV-B filter agents and 7 UV-A filter agents have FDA approval for use in sunscreen formulations.[6] Whereas, 28 UV filter agents are permitted for sunscreens in Europe.[6]

Formulators of sunscreen products in the U.S. must be in compliance with FDA regulations. It benefits both the chemical manufacturers of UV filter agents and the formulators to verify the identity and purity of these organic UV filters.

Preservatives, the biocides used in cosmetics and personal care products to prevent bacteria, mold, and other contaminants. To protect the environment and human health, many countries regulate biocide use. In the European Union, this is done through the Directive 98/8/EC (The Biocidal Products Directive) and Regulation (EU) No 528/2012 (The Biocidal Products Regulation). In the United States, regulatory control of biocides falls under the EPA and the biocides applications in cosmetics, food, and personal health care are regulated by the U.S. FDA. In the United States, more than 50% of preservatives used in personal care products are parabens, isothiazolinones, and formaldehyde donors such as imidazolidinyl urea. With common preservatives such as parabens coming under greater scrutiny due to regulatory and consumer perception issues,[7,8] manufacturers find themselves defending the use of these additives or searching for substitutes.

Traditionally, HPLC is used to analyze biocides and UV filter agents with a typical run time of 20 to 50 minutes.[1-5]

This poster describes a rapid seven minute separation and identification of nine structurally similar sunscreens and preservatives using the Waters® ACQUITY UPLC/PDA System with Empower 3 Software and library matching.

Rapid, reliable separation and confirmation can facilitate workflow for both raw material suppliers and personal care product formulators in quality control, regulatory compliance, new product development, and product troubleshooting.

METHODS

Data Acquisition and Processing:
All data were acquired and processed using Empower® 3 Chromatography Data Software (Waters Corporation).

Standards:
Analytes 1–9 (Figure 1) were dissolved in CH3CN to make 100 µg/mL stock solutions:

1. 2-Phenoxyethanol [122-99-6]
2. Benzoic acid [65-85-0]
3. Methylparaben [99-76-3]
4. Propylparaben [94-13-3]
5. Oxybenzone [131-57-7]
6. Avobenzone [70356-09-1]
7. Octinoxate [5466-77-3]
8. Octisalate [118-60-5]
9. Homosalate [118-56-9]

The working solution (50 µg/mL) was prepared by mixing 500 µL of the stock solution with 500 µL D.I. H_2O.

UPLC conditions:

UPLC system:	**ACQUITY UPLC**
Column temp.:	50 °C
Flow rate:	0.8 mL/min
Injection:	3 µL
Detection:	PDA 215 to 500 nm
Sampling rate:	20 pts/s
Filter response:	0.1 s
Linear gradient:	5% B to 100% B in 7 min
C18 column:	ACQUITY UPLC BEH C_{18}, 2.1 x 100 mm
Mobile phase A:	0.05 v% of TFA in H_2O
Mobile phase B:	0.05 v% of TFA in CH_3CN

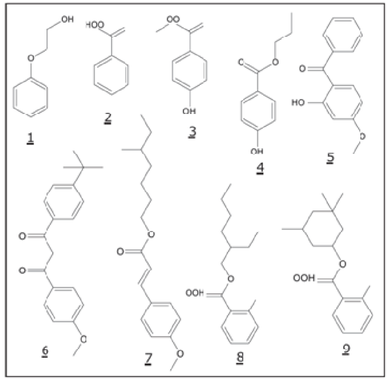
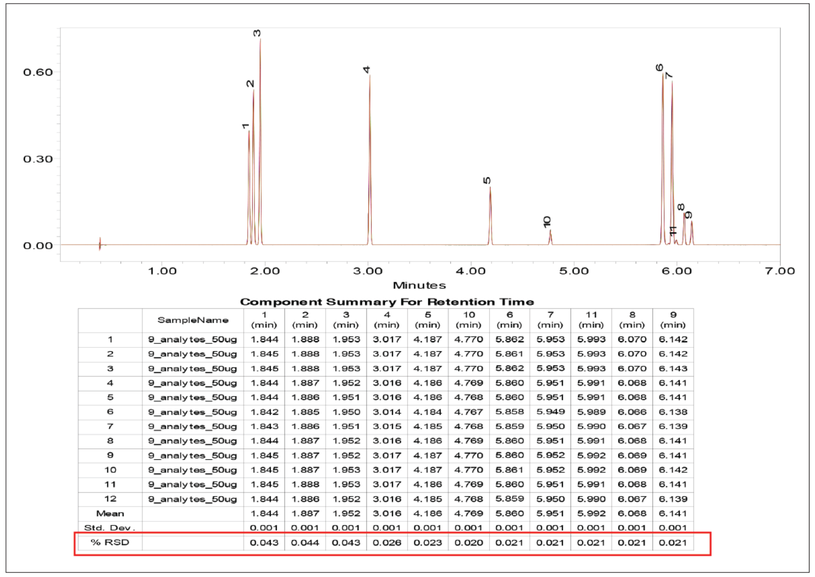


Figure 1. Chemical structures of UV filter agents and preservatives.



Component Summary For Retention Time

	SampleName	1 (min)	2 (min)	3 (min)	4 (min)	5 (min)	10 (min)	6 (min)	7 (min)	11 (min)	8 (min)	9 (min)
1	9_analytes_50ug	1.844	1.888	1.953	3.017	4.187	4.770	5.862	5.953	5.993	6.070	6.142
2	9_analytes_50ug	1.845	1.888	1.953	3.017	4.187	4.770	5.861	5.953	5.993	6.070	6.142
3	9_analytes_50ug	1.845	1.888	1.953	3.017	4.187	4.770	5.862	5.953	5.993	6.070	6.143
4	9_analytes_50ug	1.844	1.887	1.952	3.016	4.186	4.769	5.860	5.951	5.991	6.068	6.141
5	9_analytes_50ug	1.844	1.886	1.951	3.016	4.186	4.768	5.860	5.951	5.991	6.068	6.141
6	9_analytes_50ug	1.842	1.885	1.950	3.014	4.184	4.767	5.858	5.949	5.989	6.066	6.138
7	9_analytes_50ug	1.843	1.886	1.951	3.015	4.185	4.768	5.859	5.950	5.990	6.067	6.139
8	9_analytes_50ug	1.844	1.887	1.952	3.016	4.186	4.769	5.860	5.951	5.991	6.068	6.141
9	9_analytes_50ug	1.845	1.887	1.952	3.017	4.187	4.770	5.860	5.952	5.992	6.069	6.141
10	9_analytes_50ug	1.845	1.887	1.953	3.017	4.187	4.770	5.861	5.952	5.992	6.069	6.142
11	9_analytes_50ug	1.845	1.888	1.953	3.017	4.186	4.769	5.860	5.951	5.991	6.068	6.141
12	9_analytes_50ug	1.844	1.886	1.952	3.016	4.185	4.768	5.859	5.950	5.990	6.067	6.139
Mean		1.844	1.887	1.952	3.016	4.186	4.769	5.860	5.951	5.992	6.068	6.141
Std. Dev.		0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
% RSD		0.043	0.044	0.043	0.026	0.023	0.020	0.021	0.021	0.021	0.021	0.021

Figure 2. Overlay PDA timed wavelength chromatograms and retention time table of 12 replicate injections of 1–9 : (0.00 min, 220 nm), (1.92 min, 250 nm),(5.0 min, 360nm), (5.9 min, 300 nm).

RESULTS AND DISCUSSION

Figure 1 shows the chemical structures of four preservatives (1–4) and five UV filter agents (5–9) discussed in this poster. These compounds are among the most commonly used biocides and organic sunscreens in personal care and cosmetic products.[6-8] A mixture of 1–9 was separated using a Waters ACQUITY UPLC System with a 2.1 x 100 mm BEH C18 Column using a seven minute linear gradient method (5% B to 100% B).

The solvents employed for the separation are common, easy to prepare and suitable for use with mass spectrometry detectors, if needed: 0.05 v% TFA in H_2O (mobile phase A) and 0.05 v% TFA in CH_3CN (mobile phase B).

UV photodiode array (PDA) detection combined with Empower 3 Software enables a powerful range of detection and identity confirmation possibilities for chromatographic separations.

PDA timed wavelength chromatograms were plotted using the λmax of each analyte. This can increase the detection limit when the analytes have very different λmax and aid quantification. Figure 2 shows an overlay of 12 replicate injections of PDA timed wavelength chromatograms. Visual examination shows the overall reproducibility is excellent. Despite the similar groups of chemical structures, the components are well resolved by the 7-minute linear gradient method. Two impurities in the mixture that previously co-eluted are now separated. Peak 10 is an unknown impurity in the avobenzone (6) standard whereas peak 11 is an isomer of homosalate (9).

The Empower 3 report table in Figure 2 shows that the % RSD ranges from 0.02% to 0.04%. Retention time reproducibility is a good indicator of the robustness and suitability of UPLC with BEH column chemistry for preservatives and sunscreens.

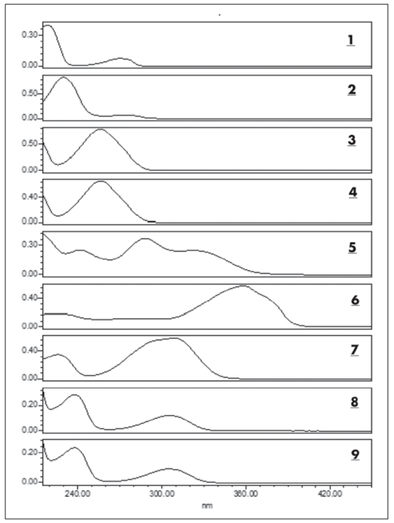


Figure 3. UV spectra of 1–9 extracted from PDA data.

To confirm peak identities and provide assurance regarding spectral peak purity or "non-coelution" a user can build a PDA library and perform library matching and peak purity analysis through Empower 3 Software.[9,10]

Figure 3 shows UV spectra extracted from PDA chromatograms of standards (1-9) that were used to create a library with names, concentrations, and retention times.

Empower 3 uses Spectral Contrast theory to quantitatively compare the shapes of UV spectra during library matching and peak purity analysis. The match angle or purity angle indicates how closely the spectra overlap. A spectral contrast angle of 0° means that the spectra overlay perfectly and the compounds these spectra represent are identical; a 90° angle means that the two spectra do not overlap and that the compounds are different.

The Threshold Angles are an indication of "uncertainty" or non-idealities. If the Match or Purity (Spectral Contrast) Angle is less than the Match or Purity Threshold Angle, this indicates that the differences between the spectra are from non-idealities and the match is "good" or the peak is spectrally pure.

	Name	RT	Match1 Spect. Name	Match1 Angle	Match1 Threshold	Purity1 Angle	Purity1 Threshold
1	1	1.845	Phenoxyethanol	0.290	1.497	0.359	0.407
2	2	1.888	Benzoic acid	0.103	1.112	0.069	0.302
3	3	1.953	Methyl paraben	0.060	1.036	0.046	0.289
4	4	3.017	Propyl paraben	0.058	1.043	0.056	0.290
5	5	4.187	Oxybenzone	0.056	1.064	0.067	0.291
6	6	5.862	Avobenzone	0.095	1.061	0.132	0.315
7	7	5.953	Octinoxate	0.082	1.045	0.088	0.287
8	8	6.070	Octisalate	0.167	1.171	0.142	0.336
9	9	6.142	Homosalate	0.156	1.218	0.156	0.366

Table 1. PDA library matching results for peak identification.

If the Spectral Contrast Angle is greater than the Threshold Angle, then the differences are due to true differences between the spectra.

After a library is available, the library matching and peak purity process can be automated in Empower for identification and peak purity confirmation.

Table 1 provides an example of a default Empower table with PDA library matching and peak purity results. The values Match Angle and Purity Angle indicate that the UV-filter agents and biocides were well matched with PDA library of sunscreen agents and preservatives.

CONCLUSION

- **The Waters ACQUITY UPLC System with PDA Detection and Empower 3 Software provide sensitive, baseline resolved, rapid separations with automated library matching.**
- **This has been demonstrated with a rapid, reproducible separation of a mixture of nine of the most commonly used organic UV sunscreens and biocides in cosmetics and personal care products.**
- **The easy-to-use experimental conditions are suitable for raw material suppliers, cosmetics, and personal care product formulators.**
- **Applications include quality control, new product development, and troubleshooting.**

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