Evaluation of New HPLC Technologies for the Separation of Preservatives in Cosmetics

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This study evaluates the performance of five different HPLC columns used in a fast, selective screen to determine several common preservatives in cosmetics. The work demonstrates the higher performance of three core-shell silica products (Kinetex® XB-C18, HALO® C18, and Poroshell® 120 SB-C18) compared to two traditional fully porous HPLC columns (Luna® C18(2) and XSelect™ CSH™ C18).

Introduction

In 1969, the FDA found that of 169 cosmetic products sampled, 20 % were contaminated with microorganisms, posing a definite health risk to the consumer. As a direct result, preservatives – ingredients that have anti-microbial activity – were added to cosmetics. Today, most of cosmetic products on the market contain preservatives approved by the German Cosmetic Decree (KVO). These preservatives prevent product deterioration and deter any possible health risks microorganisms may cause to the consumer. A disadvantage of using such agents is that they may cause adverse effects, such as allergic responses and irritation. Examples of preservatives that are less tolerated, especially at increased concentration, are the parabens and phenoxyethanol. There is a need today for a fast, efficient, and selective HPLC method to screen for such common and dangerous preservatives.

Materials and Methods

Analyses were performed using an HP 1100 LC system (Agilent Technologies, Palo Alto, CA, USA) with an upper pressure limit of 400 bar, equipped with a UV detector. The HPLC columns used for the analysis include:

1. Kinetex XB-C18, 2.6 µm (Phenomenex, Inc., Torrance, CA, USA)
2. HALO C18, 2.7 µm (Advanced Materials Technology, Inc., MA, USA)
3. Poroshell 120 SB-C18, 2.7 µm (Agilent Technologies, Palo Alto, CA, USA)
4. Luna C18(2), 3 µm (Phenomenex, Inc., Torrance, CA, USA)
5. XSelect CSH C18, 3.5 µm (Waters Corporation, Milford, MA, USA)

Conditions for all columns:

Dimensions: 100 x 4.6 mm
Mobile Phase: A: Water with 0.1 % TFA
B: Acetonitrile with 0.1 % TFA
Gradient: (85:15) A/B for 20 min, then to (15:85) A/B
Flow Rate: 1.5 mL/min
Column Temperature: 30º C
Detection: UV @ 214 mm (ambient)
Injection Concentration: 50 µg/mL
Sample:
1. Benzyl alcohol
2. Phenoxyethanol
3. Sorbic acid
4. Benzoic acid
5. Methyl paraben
6. p-Anisic acid
7. Dehydroacetic acid
8. Salicylic acid
9. Ethyl paraben
10. Isopropyl paraben
11. Propyl paraben
12. Isobutyl paraben
13. Butyl paraben
14. Triclosan
15. Triclocarban

Results and Discussion

Cosmetic products can only use a limited number of preservatives selected from a positive list, Annex VI of the Cosmetics Directive, which also defines preservative maximum permitted levels and areas of use. The esters of parahydroxybenzoic acid (paraben), methyl paraben, ethyl paraben, propyl paraben and butyl paraben are standard substances among the preservatives list.

There are situations where a fast and selective HPLC screen is required to determine the presence and relative levels of these common preservatives. This work examines the effectiveness of five different HPLC columns to rapidly and efficiently separate many of the more common preservatives in a single run using common chromatographic conditions.

Chromatograms of the results are shown in **Figures 1-5.**

APPLICATIONS

Figure 1.
Phenomenex® Kinetex® XB-C18, 2.6 µm

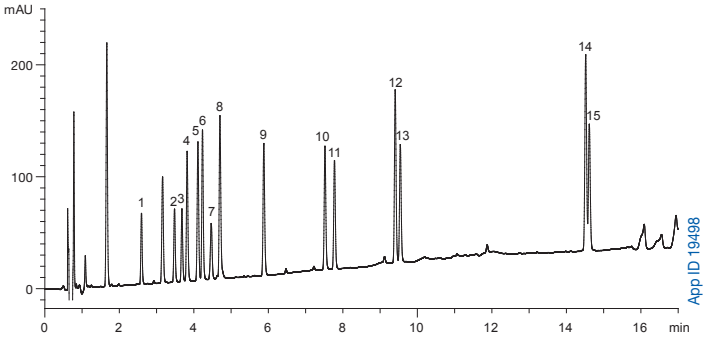

Figure 2.
Agilent® Poroshell® SB-C18, 2.7 µm

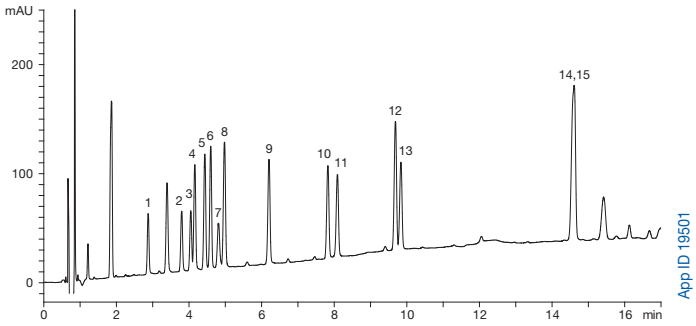

Figure 3.
Advanced Materials Technology HALO® C18, 2.7 µm

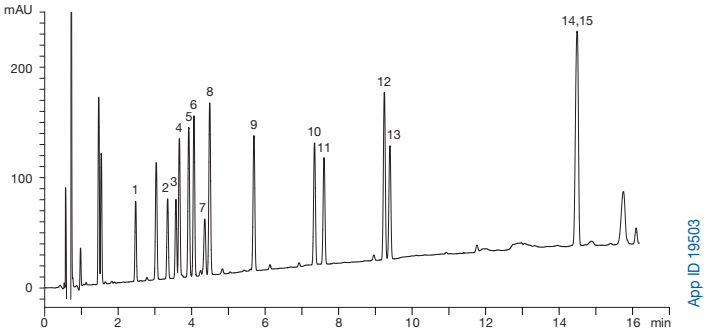

Figure 4.
Waters® XSelect™ CSH™ C18, 3.5 µm

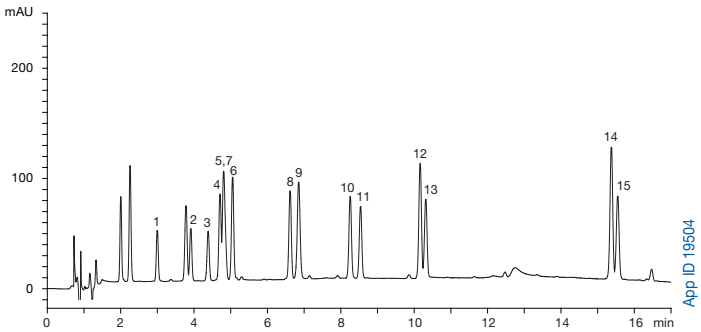

Figure 5.
Phenomenex® Luna® C18(2), 3 µm

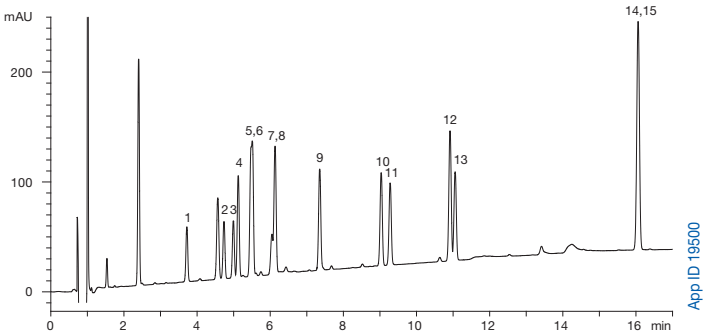

Figure 1 illustrates the ability of the Kinetex XB-C18, 2.6 µm core-shell column to rapidly screen and separate all 15 compounds. In this separation, the Kinetex XB-C18 column offered the highest peak capacity of all of the five columns used in the experiment. Peak capacity is the best measure of performance for a gradient separation and high peak capacity values indicate increased analyte resolution over a given analysis time.

The peak capacity can be determined by the formula: P = 1 + Tg/w, where Tg is the gradient time and w is average peak width at the baseline. Peak capacities achieved in this experiment for all five columns are listed in **Table 1** and graphically displayed in **Figure 6.**

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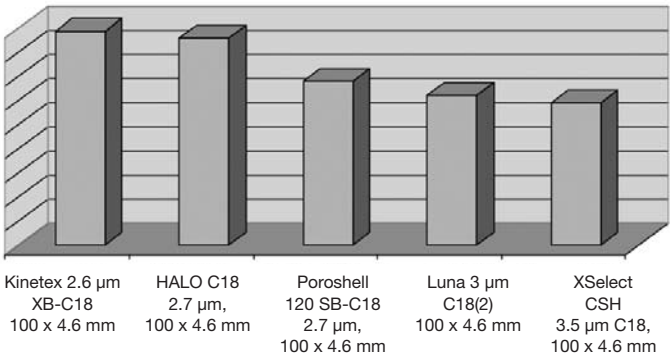
Table 1.

HPLC Column	Peak Capacity
Phenomenex® Kinetex® XB-C18, 2.6 µm, 100 x 4.6 mm	445
Advanced Materials Technology HALO® C18, 2.7 µm, 100 x 4.6 mm	431
Agilent® Poroshell® 120 SB-C18, 2.7 µm, 100 x 4.6 mm	340
Phenomenex® Luna® C18(2), 3 µm, 100 x 4.6 mm	312
Waters® XSelect™ CSH™ C18, 3.5 µm, 100 x 4.6 mm	297

Figure 6.
Peak Capacity: Core-Shell vs. Fully Porous Columns



Based on the peak capacity data generated and represented in **Figure 6**, it is apparent that the three core-shell silica HPLC technologies provide an advantage over the two fully porous silica products used in the experiment when it comes to resolving power. **Figures 1-5** also indicate that the core-shell columns provide higher signal response due to the very narrow peak widths achieved, which allow for lower levels of detection for analytes present in lower concentration.

The core-shell particle morphology allows for faster mass transfer of analytes into and out of the stationary phase as compared to fully-porous silica particles. In addition, the very narrow particle size distribution inherent in core-shell silica particles, as compared to fully-porous particles, results in less band broadening.

Of the three core-shell silica columns, only the Kinetex 2.6 µm XB-C18 was able to separate the chlorinated compounds triclosan and triclocarban. This is likely due to the unique XB-C18 selectivity. The Kinetex XB-C18 chemistry contains protective di-isobutyl side chains that shield the silica surface. In addition, the surface is endcapped with trimethylsilane.

The two traditional fully porous silica columns in **Figures 4** and **5** show the lowest signal intensity and peak capacity, most likely due to the relatively slower mass transfer of the analytes into the fully porous particle and the relatively larger particle size distribution. All columns were operated under 400 bar and may therefore be used on conventional HPLC systems without the need for specialized ultra-high pressure equipment.

Conclusion

An ultra-high performance liquid chromatography method has been developed for the simultaneous determination of 15 preservatives in cosmetics. The method was developed to achieve the best balance of analysis time and separation. Newly developed core-shell silica technology HPLC/UHPLC columns were found to generate higher peak capacity and higher sensitivity than traditional fully porous silica particle columns.

The Kinetex XB-C18, 2.6 µm column provided the highest peak capacity of all columns tested and the unique selectivity of the XB-C18 was well-suited for the application. The results achieved did not require the use of ultra-high pressure capable HPLC instrumentation.

APPLICATIONS

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Kinetex® Ordering Information

2.6 µm Analytical Columns (mm)

	30 x 4.6	50 x 4.6	75 x 4.6	100 x 4.6	150 x 4.6	SecurityGuard™ Ultra Cartridges‡ /3pk	KrudKatcher™ Ultra In-Line Filter* /3pk
XB-C18	—	00B-4496-E0	00C-4496-E0	00D-4496-E0	00F-4496-E0	AJ0-8768	AF0-8497
C18	00A-4462-E0	00B-4462-E0	00C-4462-E0	00D-4462-E0	00F-4462-E0	AJ0-8768	AF0-8497
C8	—	00B-4497-E0	00C-4497-E0	00D-4497-E0	00F-4497-E0	AJ0-8770	AF0-8497
PFP	00A-4477-E0	00B-4477-E0	00C-4477-E0	00D-4477-E0	00F-4477-E0	AJ0-8773	AF0-8497
HILIC	—	00B-4461-E0	00C-4461-E0	00D-4461-E0	00F-4461-E0	AJ0-8772	AF0-8497

for 4.6 mm ID

2.6 µm MidBore™ Columns (mm)

	30 x 3.0	50 x 3.0	75 x 3.0	100 x 3.0	150 x 3.0	SecurityGuard Ultra Cartridges‡ /3pk	KrudKatcher Ultra In-Line Filter* /3pk
XB-C18	—	00B-4496-Y0	—	00D-4496-Y0	—	AJ0-8775	AF0-8497
C18	00A-4462-Y0	00B-4462-Y0	00C-4462-Y0	00D-4462-Y0	00F-4462-Y0	AJ0-8775	AF0-8497
C8	—	00B-4497-Y0	—	00D-4497-Y0	—	AJ0-8777	AF0-8497
PFP	00A-4477-Y0	00B-4477-Y0	00C-4477-Y0	00D-4477-Y0	00F-4477-Y0	AJ0-8780	AF0-8497
HILIC	—	—	—	—	00F-4461-Y0	AJ0-8779	AF0-8497

for 3.0 mm ID

2.6 µm Minibore Columns (mm)

	30 x 2.1	50 x 2.1	100 x 2.1	150 x 2.1	SecurityGuard Ultra Cartridges‡ /3pk	KrudKatcher Ultra In-Line Filter* /3pk
XB-C18	00A-4496-AN	00B-4496-AN	00D-4496-AN	00F-4496-AN	AJ0-8782	AF0-8497
C18	00A-4462-AN	00B-4462-AN	00D-4462-AN	00F-4462-AN	AJ0-8782	AF0-8497
C8	00A-4497-AN	00B-4497-AN	00D-4497-AN	00F-4497-AN	AJ0-8784	AF0-8497
PFP	00A-4477-AN	00B-4477-AN	00D-4477-AN	00F-4477-AN	AJ0-8787	AF0-8497
HILIC	—	00B-4461-AN	00D-4461-AN	00F-4461-AN	AJ0-8786	AF0-8497

for 2.1 mm ID

1.7 µm Minibore Columns (mm)

	50 x 2.1	100 x 2.1	150 x 2.1	SecurityGuard Ultra Cartridges‡ /3pk	KrudKatcher Ultra In-Line Filter* /3pk
XB-C18	00B-4498-AN	00D-4498-AN	—	AJ0-8782	AF0-8497
C18	00B-4475-AN	00D-4475-AN	00F-4475-AN	AJ0-8782	AF0-8497
C8	00B-4499-AN	00D-4499-AN	—	AJ0-8784	AF0-8497
PFP	00B-4476-AN	00D-4476-AN	00F-4476-AN	AJ0-8787	AF0-8497
HILIC	00B-4474-AN	—	—	AJ0-8786	AF0-8497

for 2.1 mm ID

‡SecurityGuard Ultra cartridges require holder, Part No.: AJ0-9000. Check for availability in your country.
*KrudKatcher Ultra requires 5/16 in. wrench. Wrench not provided.

guarantee

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