

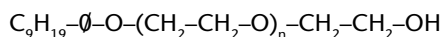
High-Resolution Separations of Nonionic Surfactant Oligomers, Using Normal Phase HPLC

Relative to the limited peak capacity of size exclusion chromatography, normal phase HPLC on a bonded diol phase SUPELCOSIL LC-Diol column significantly increases resolution of complex mixtures of nonionic surfactant oligomers. Relative to an unmodified silica column, the diol column is less affected by small amounts of water in the mobile phase, ensuring better reproducibility. The diol column also can be used in a reversed phase mode, to analyze anionic, cationic, and amphoteric surfactants.

Key Words:

- surfactants • detergents
- endocrine disrupting chemicals • EDCs

Complex mixtures of polyethoxylated alkylphenols are used as nonionic surfactants in cosmetics, industrial materials, and many other products. Differences in ethoxy chain length affect the viscosity, solubility, polarity, and other characteristics of the mixture, and make it important to monitor composition.



Nonionic Surfactant

Furthermore, because breakdown products of these materials are suspected of disrupting hormone balance in humans and animals, including hormones governing growth and reproduction, these compounds have been labeled "endocrine disrupting chemicals" (EDCs). EDCs have received a great deal of media attention, and the US Environmental Protection Agency is seeking more information on the health and environmental risks posed by these compounds, in order to decide whether to take regulatory action (1,2).

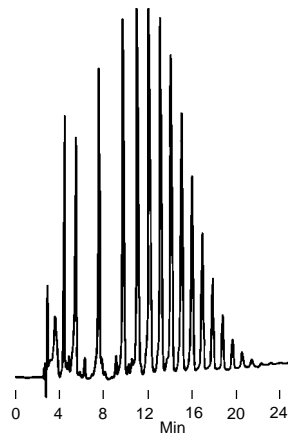
In addition to being time-consuming, most analyses of nonionic surfactants – size exclusion liquid chromatography, gas chromatography, spectrometry, wet chemistry – do not adequately separate complex mixtures of oligomers. In contrast, a normal phase HPLC analysis on a polar SUPELCOSIL™ LC-Diol column rapidly and efficiently separates surfactant components, by chain length, for product quality evaluation or other purposes.

In the example analyses shown here, commercial nonionic surfactants, produced by condensing ethylene oxide with octylphenol-based or nonylphenol-based materials, were used as samples. Mixtures averaging 2, 5, 10, 12, 18, 20, 30, 40, and 100 ethoxy units were analyzed by normal phase HPLC, using a SUPELCOSIL LC-Diol column and gradient conditions. Mixtures averaging up to 20 ethoxy units were resolved nearly to baseline (Figures A and B).

Figure A. Nonionic Surfactant Oligomers by Normal Phase HPLC

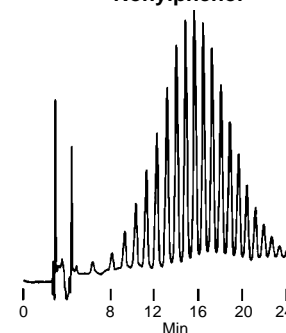
Column: SUPELCOSIL LC-Diol, 25cm x 4.6mm ID (5µm particles)
 Cat. No.: 58201
 Mobile Phase: A = hexane:methylene chloride, 95:5
 B = hexane:methylene chloride:methanol, 50:40:10
 gradient program shown on figure
 Flow Rate: 1mL/min
 Temp.: 35°C
 Det.: UV, 280nm
 Inj.: 10µL methylene chloride containing 20µg surfactant

9-10 Ethoxy Groups, Octylphenol (Triton® X-100)

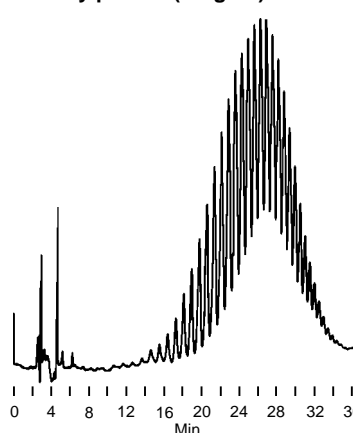


Gradient Program	
Time (min)	% B
0	30
8	50
15	60
25	80
35	100

20 Ethoxy Groups, Nonylphenol



30 Ethoxy Groups, Nonylphenol (Tergitol)



713-0782, 713-1068, 794-0876

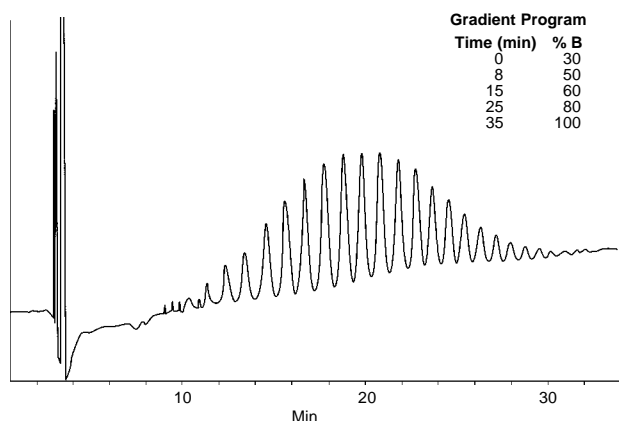
Other polar bonded phase columns, such as SUPELCOSIL LC-NH₂ columns (propylamine groups attached to 3µm or 5µm spherical silica), also have been used successfully to analyze nonionic surfactants (3,4). In our experience, however, the higher efficiency of the diol columns ensures better overall resolution of complex samples.

Size exclusion chromatography (SEC) on resin-based columns often is used in analyses of nonionic surfactants. Relative to the limited peak capacity of SEC, normal phase HPLC on a SUPELCOSIL LC-Diol column offers much greater ability to resolve complex surfactants, such as the 30-group surfactant in Figure A. Normal phase HPLC also is far less expensive. For mixtures averaging 9-10 ethoxy units, resolution comparable to that in Figure A can be obtained only by using several expensive SEC columns in series. The more complex samples in Figure A *cannot* be resolved by SEC.

Figure B. Nonionic Surfactant Oligomers by Normal Phase HPLC

Column: SUPELCOSIL LC-Diol, 25cm x 4.6mm ID (5µm particles)
 Cat. No.: 58201
 Mobile Phase: A = hexane:methylene chloride (95:5)
 B = hexane:methylene chloride:methanol (50:40:10)
 gradient program shown on figure
 Flow Rate: 1mL/min (40 bar)
 Det.: photodiode, 280nm
 Inj.: 50µL 550ng/µL surfactant in methylene chloride

18 Ethoxy Groups, Nonylphenol



Chromatogram provided by K. Simmons, Agricultural Experiment Station, Mass Spectrometry Facility, Chenoweth Laboratory, University of Massachusetts, Amherst, MA USA 01003.

796-0715

Analysis on a polar bonded phase column, such as SUPELCOSIL LC-Diol column or a SUPELCOSIL LC-NH₂ column, also offers an advantage over normal phase analysis on an unmodified silica column. Traces of water in the mobile phase can affect retention on a silica column, causing poor reproducibility over the long term. Bonded phase SUPELCOSIL LC-Diol columns are less affected by small amounts of water.

You can prolong the life of a diol column by protecting it with a Supelguard™ LC-Diol guard column filled with the same 5µm packing as the analytical column. A Supelguard column kit contains a 2cm disposable guard column, a column holder, and hardware to connect the holder to 1/16" tubing.

SUPELCOSIL LC-Diol columns provide excellent resolution of nonionic surfactant oligomers, as shown by the examples used here. The 5µm spherical packing particles ensure high column efficiency (16,500 plates or more per 25cm column). SUPELCOSIL LC-Diol columns also can be used in a reversed phase mode – the polar nature of the bonded stationary phase affords unique interactions with polar solutes. Thus anionic, cationic, and amphoteric surfactants can be analyzed on the same column.

Ordering Information:

SUPELCOSIL LC-Diol Column 25cm x 4.6mm ID, 5µm particles	58201
Supelguard LC-Diol Kit	59059
Supelguard LC-Diol Columns, pk. of 2	59069

References

1. *Environmental Policy Alert*, Apr. 10, 1996, pp. 35-36.
2. *Chemical Week*, May 8, 1996, pp. 29-36
3. *Application Note 106*, Supelco, Inc., Bellefonte, PA USA.
4. Boyd-Boylund, A.A. and J.B. Pawliszyn, *Anal. Chem.*, **68**: 1521-1529 (1996).

References 1, 2, and 4 not available from Supelco.

Trademarks

SUPELCOSIL, Supelguard – Sigma-Aldrich Co.
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For a rapid solid phase microextraction/HPLC screening analysis for surfactants in environmental samples, request Application Note 106.

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