Separation of Homologous Series of Technical Detergents with the Agilent 1290 Infinity 2D-LC Solution Coupled to an Evaporative Light Scattering Detector

Application Note

Food Testing & Agriculture – Consumer Products

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Abstract

This Application Note shows the separation of a series of homologous non-ionic surfactants in a technical product with the Agilent 1290 Infinity 2D-LC Solution by combination of a HILIC column in the first dimension and a reversed phase column in the second dimension. Surfactants typically do not show activity in UV detection, hence, the Agilent 1260 Infinity ELSD was used. The visualization of the compounds detected by the ELSD is demonstrated with dedicated 2D-LC software.

Verified for Agilent
1290 Infinity II LC

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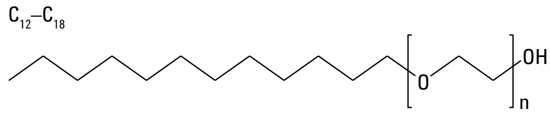
Introduction

Fatty alcohol ethoxylates belong to the class of non-ionic surfactants and are used for a large variety of consumer products like cosmetics, cleaners, colors, plant protection, textiles and other industrial applications. The production process starts with a homologous series of fatty alcohol compounds typically from lauryl alcohol (C_{12}) to stearyl alcohol (C_{18}). These compounds are reacted with ethylene oxide, which gives a second homologous series of ethoxylates at the other side of the molecule (Figure 1).

To monitor the quality and composition of the technical product, it is important to have a separation method in hand which is able to separate both homologous series, the fatty alcohol component and the successive series of ethoxylate units. The only separation technology which can fulfill this requirement is comprehensive 2-dimensional liquid chromatography by combination of the selectivity of a HILIC and an RP separation. The other challenge is to find the right detection method because UV detection is not possible due to the lack of UV activities of these compounds. Typically an Evaporative Light Scattering Detector (ELSD) is used for such a class of non-UV active and nonvolatile compounds. In addition, this is a cost-effective detection method useful for technical quality control.



n = degree of ethoxylation (EO)

Figure 1. Structure formula of fatty alcohol ethoxylat compounds.

Experimental

Method

1st Dimension pump	
Solvent A	Water, 50 mM ammonium acetate
Solvent B	Acetonitrile
Flow rate	0.025 mL/min
Gradient	0 min - 97 % B, 10 min - 97 % B, 60 min - 85 % B, 100 min - 85 % B, 120 min - 70 % B, 140 min - 70 % B, 160 min - 97 % B
Stop time	160 minutes
Post time	20 minutes
2nd dimension pump	
Solvent A	Water, 10 mM ammonium acetate
Solvent B	Methanol
Flow rate	3 mL/min
Initial gradient	0 min - 50 % B, 0.1 min - 70 % B, 0.65 min - 95 % B, 0.75 min - 95 % B, 0.80 min – 50 % B, 1.00 min – 50 % B
Stop time	1.00 minute
Modulation time	1.00 minute
TCC	
1st dimension column on the left side at 25 °C	
2nd dimension column on the right side at 50 °C	
Two 40-µL loops are connected to the 2-Position/4-Port Duo valve and are located on the left side.	
Autosampler	
Injection volume	5 µL
Sample temperature	8 °C
Needle wash	6 seconds in methanol
ELSD	
Evaporator temperature	80 °C
Nebulizer temperature	70 °C
Data rate	40 Hz
Gas flow	1.3 SLM

Equipment

The Agilent 1290 Infinity 2D-LC Solution consists of:

- Agilent 1290 Infinity Binary Pump (G4220A)
- Agilent 1260 Infinity Quaternary Pump (G-1311B)
- Agilent 1290 Infinity Autosampler (G4226A) with Thermostat (G1330A)
- Agilent 1290 Infinity Thermostatted Column Compartment (TCC) (G1316C) with 2-Position/4-Port Duo valve (G4236A) for 2D-LC
- Agilent 1260 Infinity ELSD

Software

Open Lab CDS ChemStation Rev. C01.03 with 2D-LC add-on software. LCxLC Software for 2D-LC data analysis from GC Image LLC., Lincoln, NE, USA.

Column 1st dimension

SeQuant, Sweden, ZIC-HILIC, 250 × 2.1 mm, 5 µm

Column 2nd dimension

Dr. Maisch GmbH, Germany, Reprospher C8-Aqua, 30 × 4.6 mm, 5 µm

Chemicals

All solvents used were LC grade. Acetonitrile and methanol were purchased from Merck, Germany. Fresh ultrapure water was obtained from a Milli-Q Integral system equipped with a 0.22-µm membrane point-of-use cartridge (Millipak). All chemicals used as standard were purchased from Sigma-Aldrich, Germany.

Sample

A synthetic, technical, fatty alcohol ethoxlyate with an alkyl chain from C_{12} to C_{18} was dissolved in acetonitrile/water 80/20 (v/v) and diluted to the final concentration of 3 mg/mL.

Results and Discussion

The comprehensive 2-dimensional separation of the technical mixture of fatty alcohol ethoxylates was done on a HILIC phase in the first dimension under typical HILIC conditions. The second dimension separation was done on a reversed phase column under typical RP conditions. The HILIC phase in the first dimension separates the compounds by their increasing degree of ethoxylation for compounds with 3 to 20 ethoxy units. The reversed phase column in the second dimension separates the fraction of ethoxylate with a defined degree of ethoxylation by their fatty alcohol chain length by increasing number of carbon atoms (Figure 2).

The 2-dimensional separation space is nearly perfectly orthogonal. It starts with the lowest carbon chain length and lowest degree of ethoxylation at the lowest retention time in first and second dimension time. The second dimension retention time increases by chain length and the first dimension retention time increases by ethoxylation yielding the highest 2-dimension retention time for long chain compounds with highest degree of ethoxylation (Figure 2).

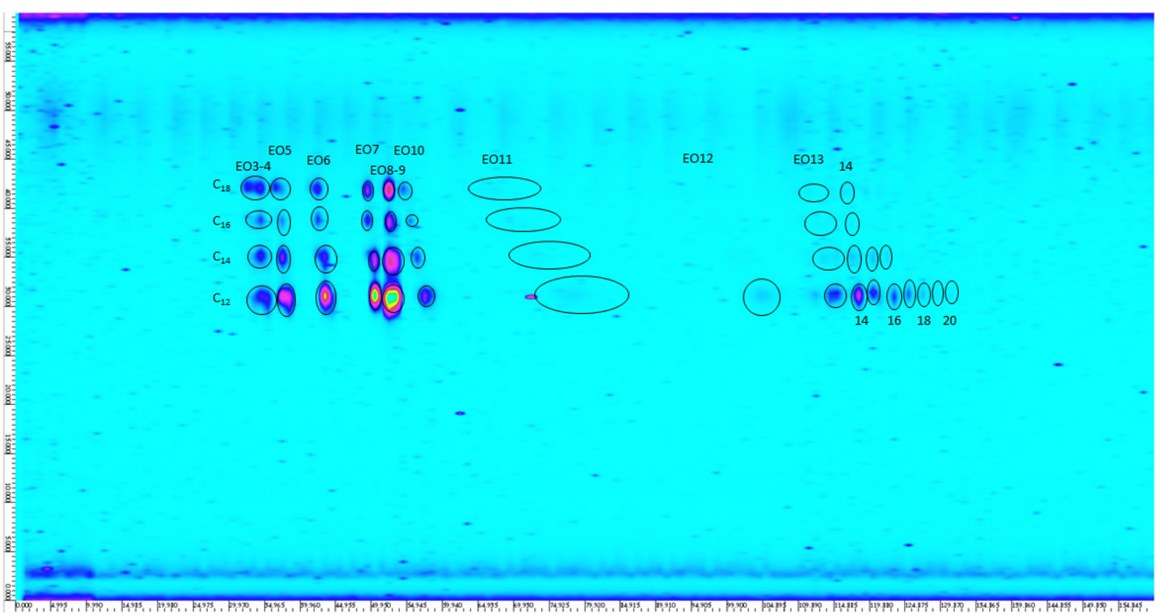


Figure 2. 2-dimensional separation of a technical mixture of fatty alcohol ethoxylates of fatty alcohols C_{12} to C_{18} and a degree of ethoxylation 3 to 20 (see formula in Figure 1).

The analysis under given conditions shows perfect separation for each compound in the mixture and allows its characterization. The ELSD is able to acquire data at a data rate sufficient to follow the fast chromatographic separation in the second dimension. For a product mixture which was well characterized in advance, the main compounds can be confirmed easily for a production batch. Lower level compounds can be seen on a lower signal intensity level. For a more reliable confirmation, a more sensitive detection such as mass spectrometry is required (data not shown here).

Conclusion

This Application Note demonstrates the capability to run the Agilent 1290 Infinity 2D-LC Solution with an ELSD as a detector for non-UV active compounds. This can be used for the separation and detection of complex oil and fatty alcohols or acids and their derivatives. These compounds are important technical basic chemicals typically occurring in complex mixtures from the production process and, hence, 2D-LC separation could be used for quality control of production batches.

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