Quantification of Compounds in the E7 Liquid Crystal Mixture by Supercritical Fluid Chromatography with UV Detection

Suitable for Agilent
1260 Infinity III LC

Application Note

Specialty Chemicals

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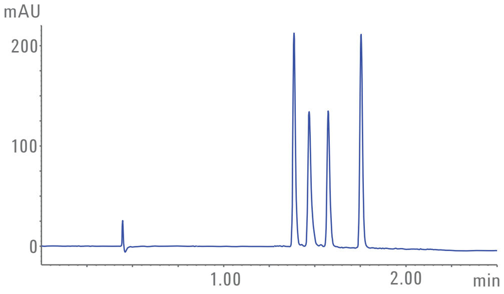
Abstract

This Application Note demonstrates the capability of the Agilent 1260 Infinity Analytical SFC System to perform quantitative analysis of liquid crystal compounds. It demonstrates that fast separation of commercial liquid crystal mixtures is possible within a few minutes. Detection was done by UV, and a relative quantification of the composition of the E7 mixture is described. The results are supported by a statistical evaluation.



Introduction

Liquid crystal is a type of matter that has physical properties between the solid state and the liquid state[1,2]. The liquid crystalline state of some chemical and biological compounds was discovered in 1888 by the physiologist Friedrich Reinitzer on derivatives of cholesterol[3]. He observed that such compounds have two melting points. At the first one, the compounds melt into a cloudy liquid, and at the second one into a clear liquid. This work was continued by the physicist Otto Lehmann, who examined the behavior of liquid crystals under polarized light[4]. A large number of synthetic liquid crystals were produced by the chemist Daniel Vorländer at the beginning of the 20th century[5].

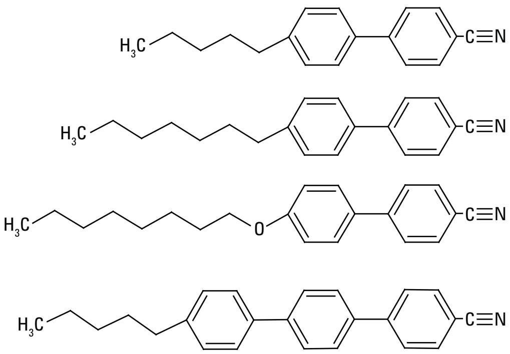
Liquid crystals can be obtained in thermotropic, lyotropic, and metallotripic phases. The thermotropic liquid crystals are, for example, rod-shaped organic molecules. They exhibit a phase transition to the liquid crystal phase with change of temperature. Typically, below a certain temperature range, thermotropic liquid crystals behave like a solid, and above like a liquid. Within the range of liquid crystallinity, they may show some nematic and smectic phases. In the nematic phases, rod-shaped molecules typically order along their axis and align to magnetic and electric fields. In smectic phases, the molecules are ordered in layers.

Typically, the nematic range is far above room temperature. But some molecules or mixtures exhibit a nematic temperature range within the temperature range required for the use of liquid crystal displays (LCD). An LCD consists of a layer of liquid crystals between two glass layers with electrodes and two polarization filters. Depending on the electrical field and the orientation of the liquid crystal, the LCD can be switched to a highly transparent ON state or to a light-scattering OFF state[6].

The compounds class of cyanobiphenyls and cyanoterphenols comprises liquid crystals that exhibit a nematic phase in the required temperature range. Their properties can be designed by synthesizing compounds that differ only in the length of the aliphatic moiety, or by mixing different liquid crystal compounds. The commonly used liquid crystal 4-cyano-4′-pentylbiphenyl (5CB) is about 20 Å long, and exhibits a phase transition at 18 °C to the nematic phase and to an isotropic state at 35 °C[7]. The widely used E7 liquid crystal mixture (Merck KGaA, Darmstadt, Germany) is such an example (Figure 1). It possess a high birefringence and positive dielectric anisotropy, which enables its broad use in polymer LCD[8]. The composition of the E7 mixture is critical to provide the physical properties and characteristics of the liquid crystal. Even small changes in the composition compromise, for example, the nematic to isotropic temperature (T_{NI}).

The liquid crystal compounds and mixtures are typically analyzed by reversed-phase, high-performance liquid chromatography (HPLC) with UV or mass spectrometric (MS) detection. A typical reversed-phase HPLC separation of a mixture of liquid crystals takes about a one hour run time[9,10].

This Application Note demonstrates the separation of a mixture of liquid crystal compounds in a short run time by means of the Agilent 1260 Analytical SFC System. The quantification of all compounds is demonstrated by creation of the respective calibration curves after UV detection. The relative quantification of the content of a commercially available liquid crystal mixture is shown.



4-cyano-4'-*n*-pentyl-biphenly (5CB)
CAS number: 40817-08-1

4-cyano-4'-*n*-heptyl-biphenyl (7CB)
CAS number: 41122-71-8

4-cyano-4'-*n*-oxyoctyl-biphenyl (8OCB)
CAS number: 52364-73-5

4-cyano-4''-*n*-pentyl-terphenyl (5CT)
CAS number: 54211-46-0

Figure 1. Chemical structures of cyanobiphenyls and cyanoterphenols used in this study and incorporated in the commercially available E7 liquid crystal mixture.

Experimental

Instrumentation

The Agilent 1260 Infinity Analytical SFC System (G4309A) comprised the following modules:

- Agilent 1260 Infinity SFC Control Module
- Agilent 1260 Infinity SFC Binary Pump
- Agilent 1260 Infinity High-Performance Degasser
- Agilent 1260 Infinity SFC Standard Autosampler
- Agilent 1260 Infinity DAD with high-pressure standard SFC flow cell
- Agilent 1260 Infinity Thermostatted Column Compartment

Column

Agilent ZORBAX SB-C8, 4.6 × 100 mm, 1.8 µm (p/n 828975-906)

Software

Agilent OpenLAB CDS ChemStation Edition for LC and LC/MS Systems, Rev. C.01.07.

Sample

All liquid crystal compounds (10 mg, each), as shown in Figure 1, were dissolved in 10 mL heptane/ethanol 90/10. The final mixed stock solution was at a concentration of 200 µg/mL each. The calibration curve was created using heptane as diluent with a 1:2 dilution pattern.

Chemicals

All solvents were purchased from Merck, Germany. Chemicals were purchased from Sigma-Aldrich (Germany).

SFC method

Parmeter	Value
Solvent A	CO_2
Modifier B	Acetonitrile
SFC flow	2.5 mL/min
Gradient	1 %B at 0 minutes, 13 %B at 1.5 minutes
Stop time	2.25 minutes
Post time	1 minute
BPR temperature	60 °C
BPR pressure	100 bar
Column temperature	60 °C
Injection volume	1 µL, nine-times loop over fill
Needle wash in vial and loop flush with heptane/ethanol 90/10	
Detection	280 nm/band width 4 nm; Ref. 360 nm/band width 100 nm; data rate: 20Hz

Results and Discussion

From the individual stock solutions of the liquid crystal compounds 5CB, 7CB, 8OCB, and 5CT, a mixed stock solution was generated. This solution was used for the development of the SFC separation method. The single wavelength at 280 nm for the detection of all compounds was determined from individual spectra, where the response of all compounds was sufficient. The developed method separated the four similar compounds between 1.38 minutes and 1.73 minutes (Figure 2). 5CB and 7CB, which differ only by the length of the alkyl chain by a $-CH_2CH_2-$ moiety, are baseline separated at 1.38 minutes and 1.46 minutes. The complete run time was 2.25 minutes, with a fast gradient of 1 to 13 % modifier in 1.50 minutes. In this separation on a SB-C8 column, acetonitrile was used as a modifier of medium polarity.

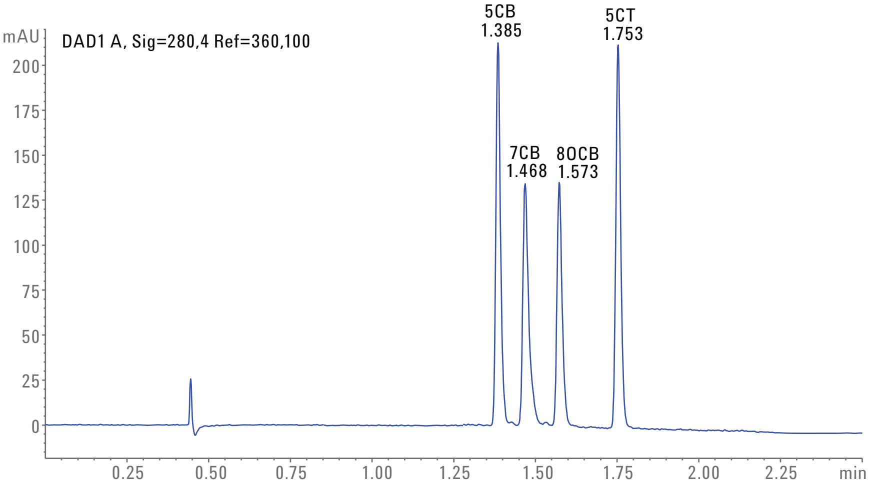


Figure 2. Separation of a mixture of liquid crystal compounds 5CB, 7CB, 8OCB, and 5CT using a fast gradient and within a short run time (50 µg/mL, each).

The mixed stock solution was also used to generate calibration curves for the individual compounds by a dilution in a 1:2 pattern down to a concentration of 6.25 µg/mL for each compound. All individual calibration curves showed a linearity better than 0.99990 (Figure 2). The calibration dilution of 50 µg/mL was injected 10 times for a statistical evaluation of the most important results (Table 1). The retention time RSDs were typically below 0.24 %, and confirm the high retention time precision even for these short retention times. The precision of the measured amount was between 1.75 and 1.97 %, and the calculated accuracies were approximately 98 %. The compounds eluted as sharp peaks with typical peak widths of about 0.015 minutes (0.9 seconds) at half height, and the resolution of all peaks was always above three.

Table 1. Results from a statistical evaluation of the liquid crystal mixture at 50 µg/mL, showing retention time RSDs, concentration precision, peak width, and peak resolution.

	5CB				7CB			
	RT (min)	Amount (mg/mL)	Peak width	Resolution	RT (min)	Amount (mg/mL)	Peak width	Resolution
Average	1.384	48.72	0.015		1.466	49.06	0.018	3.01
RSD (%)	0.25	1.97	1.09		0.24	1.95	1.69	1.29
	8OCB				5CT			
	RT (min)	Amount (mg/mL)	Peak width	Resolution	RT (min)	Amount (mg/mL)	Peak width	Resolution
Average	1.571	49.04	0.016	3.56	1.751	48.61	0.016	6.61
RSD (%)	0.24	1.75	1.09	1.31	0.21	1.76	1.01	1.01

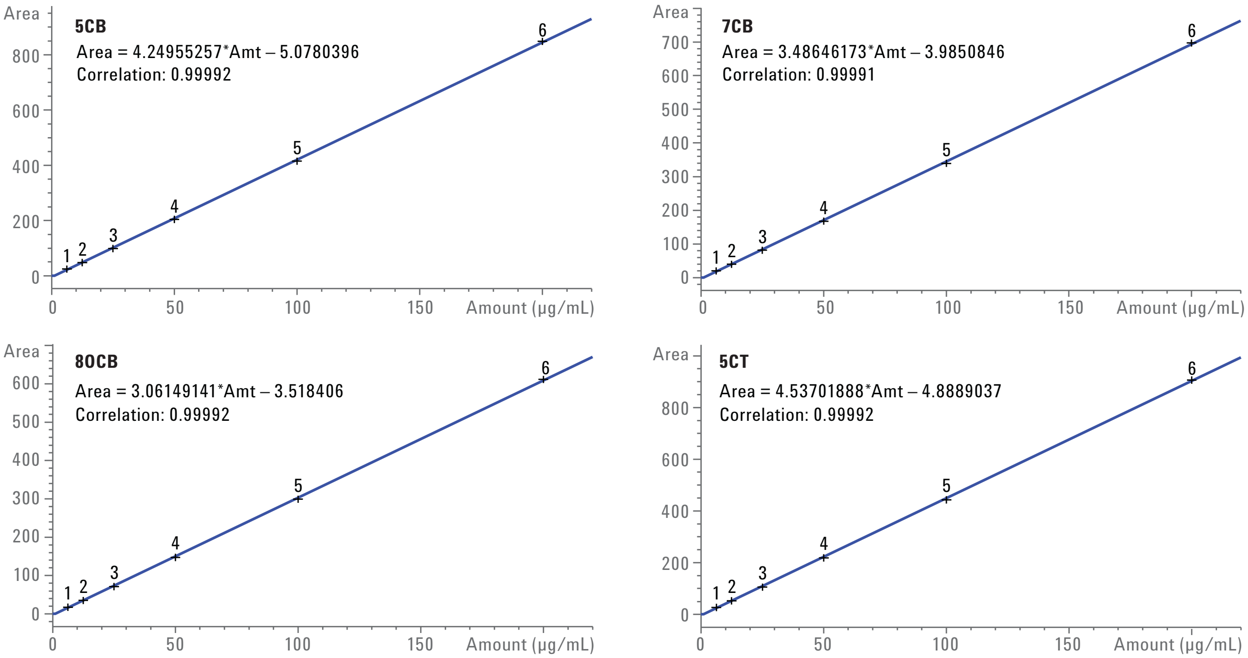
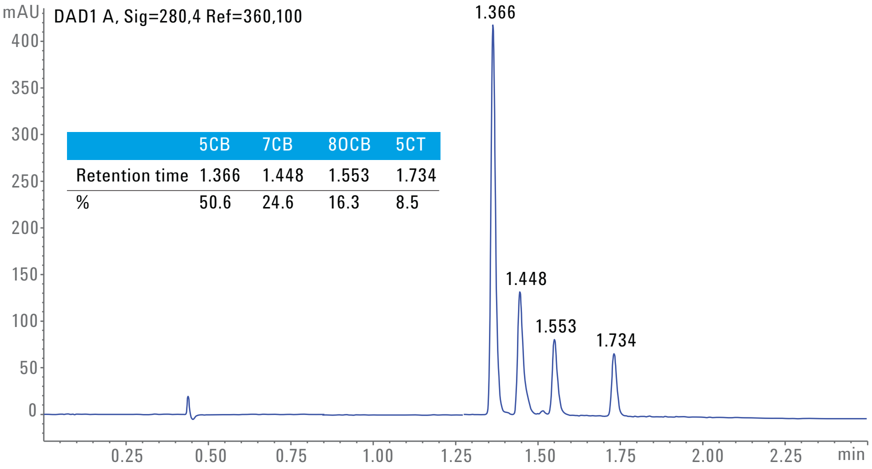


Figure 3. Calibration curves for liquid crystal compounds 5CB, 7CB, 8OCB, and 5CT in a mixture from 200 µg/mL down to 6.25 µg/mL with linearity better than 0.99990.

The compounds used are commercially available as the E7 liquid crystal mixture. This mixture has a composition of 51 weight percent (wt.%) 5CB, 25 wt.% 7CB, 16 wt.% 8OCB, and 8 wt.% CT. This is critical to ensure its required physical properties[8]. The developed method is able to be used in the quality control of the production of the E7 liquid crystal mixture, for example. For a fast decision whether the composition is within the tolerances, a report showing area percentages could be generated in ChemStation or customized by means of the Intelligent Reporter based on the above described calibration. Figure 4 shows a chromatogram of a typical E7 mixture.



	5CB	7CB	8OCB	5CT
Retention time	1.366	1.448	1.553	1.734
%	50.6	24.6	16.3	8.5

Figure 4. Chromatogram of an E7 liquid crystal mixture. The required composition is 51 wt.% 5CB, 25 wt.% 7CB, 16 wt.% 8OCB, and 8 wt.% CT.

Conclusion

This Application Note demonstrates the separation of a mixture of liquid crystal compounds using the Agilent 1260 Infinity Analytical SFC System. The baseline separation of a mixture of four liquid crystal compounds of technical importance is demonstrated in a fast, 2.25-minute run time. This fast run time is about a factor of 20-times faster than the typically used conventional RP-HPLC separations. The retention time RSDs are below 0.25 %, and the calibration curve linearity is better than 0.99990. The quantitative determination of the composition of a commercial E7 liquid crystal mixture is demonstrated.

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