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Short Communication

Analysis of silanised polyglycerols by supercritical fluid chromatography

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Abstract

A supercritical fluid chromatography method for the analysis of polyglycerols is described. The oligoglycerols are baseline separated up to a degree of polymerization of $n = 5$ and peak maxima can be seen up to $n = 10$ on a SE-54 column. The higher oligoglycerols (presumably $n > 20$) are eluted too; an evaluation similar to that used in size-exclusion chromatography can be used.

1. Introduction

Polyglycerols are used as intermediates for polyglycerol fatty esters which find wide application as emulsifiers in food and personal care industries [1]. Polyglycerol is typically prepared by base-catalyzed polymerization of glycerol. A distribution of polymers is formed with the degree of polymerization (n) ranging from 1 up to 20 or higher, dependent on the reaction conditions (Fig. 1). Several structural isomers of each value of n are formed [1]. Glycerol and oligomers up to hexaglycerol were separated by paper chromatography [1]. An HPLC method with refractive index detection on a carbohydrate column was described for polyglycerols up to $n = 11$, higher polyglycerols are likely not eluted [2]. There has been no analysis method for higher polyglycerols. For the analysis of polyglycerol fatty esters, supercritical fluid chromatography (SFC) was used [3]. SFC is known for successful analyses of various oligo- and polymers [4,5]. It is therefore reasonable to investigate the applicability of SFC to the analysis of polyglycerols.

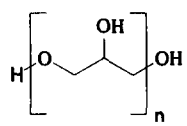

Fig. 1. Structural formula of polyglycerols.

2. Experimental

2.1. Materials

Two polyglycerol samples were obtained from

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Lonza, USA: sample A with an average polymerisation degree of $n = 10$ and sample B with an average polymerisation degree of $n = 6$ (determined by hydroxyl number analysis). N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) was purchased from Fluka. All other chemicals used were reagent grade (Fluka). Supercritical fluid was carbon dioxide, SFC-grade UN1013, Scott Specialty Gases (< 5 ppm O_2, < 3 ppm H_2O).

2.2. Apparatus and chromatographic conditions

The system used was a Carlo Erba SFC 3000 chromatograph comprising a SFC 300 syringe pump and SFC 3000 GC oven equipped with an flame ionization detector (320°C). Columns used were (1) Macherey-Nagel SE-54, 10 m × 50 μm, $d_f = 0.25$ μm, integrated restrictor 2.1 ml/min CO_2(g) at 10 MPa and 25°C or (2) the same but 20 m long and with an integrated restrictor 2.6 ml/min CO_2(g) at 10 MPa and 25°C. The analyses were run isothermally at 80°C. The following pressure gradient was used: 0 min, 6 MPa; 3 min, 6 MPa; 53 min, 31 MPa; 60 min, 31 MPa.

Samples were derivatized with MSTFA (100 mg sample + 1.0 ml MSTFA) at 100°C for 10 min under stirring and directly injected. Injection was done in a time-split mode (*ca.* 130 ms effectively from an 0.1-μl loop), injection temperature was 30°C. Integration parameters were: acquisition speed, low; peak width (PW) = 10 s; peak threshold (PT) = 500 μV; minimum area (MA) = 20 000 μV/s.

3. Results and discussion

Preliminary experiments showed that high-temperature GC analysis of the polyglycerols after silylation or acetylation is difficult with $n \approx 6$–10 or greater. Also, size-exclusion chromatography partially separated oligoglycerols up to $n \approx 6$ whereas the higher polyglycerols were noticeably excluded from the column.

Chromatograms obtained after silylation with MSTFA are shown in Fig. 2. The assignment of the peaks to the corresponding number n of the structural unit is based on the analogy with previous high-temperature GC–MS analyses of acetylated and of silylated sample A which were similar to the SFC chromatograms up to $n = 6$ (higher oligomers could not be eluted from the non-polar GC column).

Chromatograms in Fig. 3 show the separation

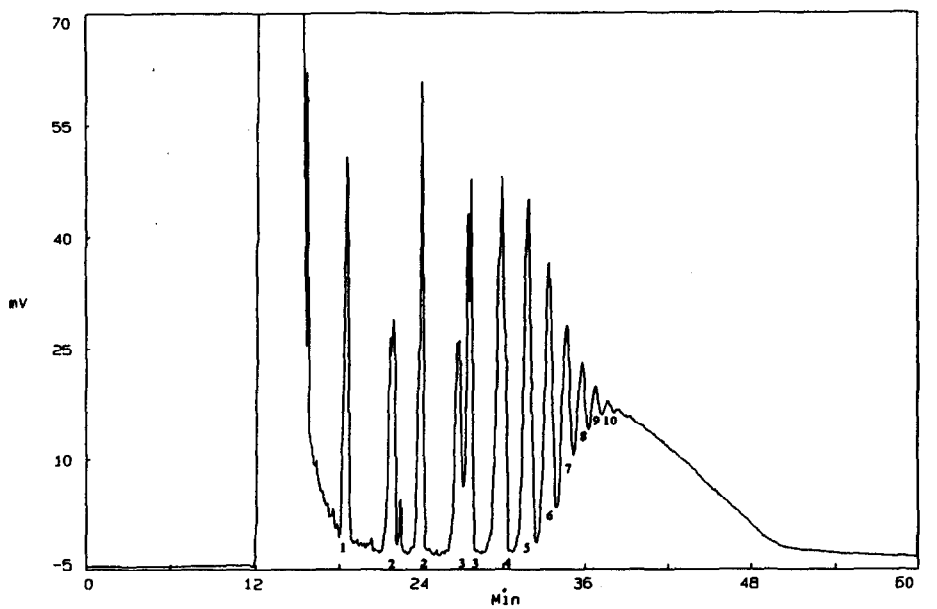

Fig. 2. SFC chromatogram of a MSTFA derivative of the polyglycerol sample A (column length 10 m).

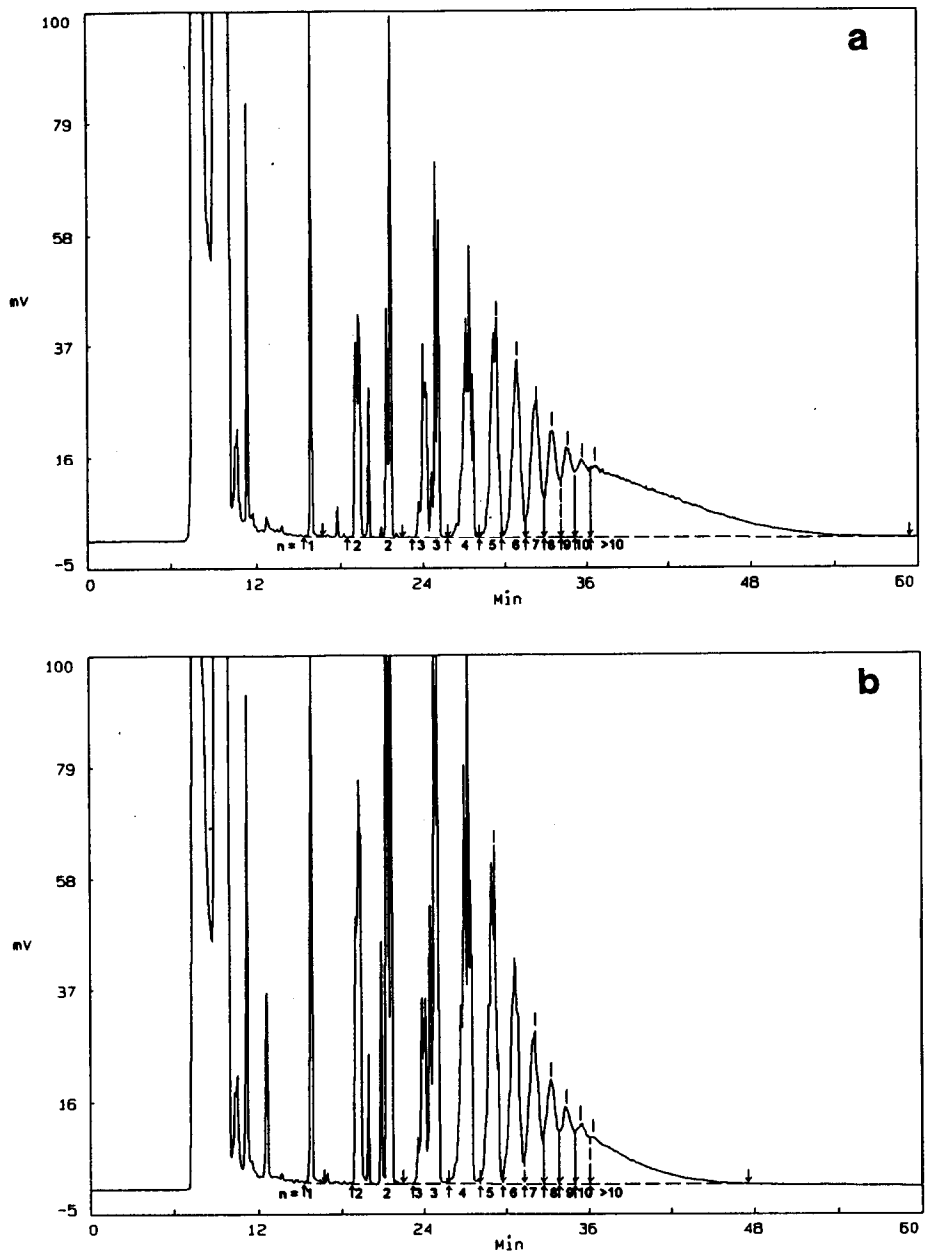

Fig. 3. SFC chromatograms of MSTFA derivatives of (a) polyglycerol sample A (column length 20 m) and (b) polyglycerol sample B (column length 20 m).

of the two samples A and B on a 20-m SE-54 column at 80°C. On this longer column, a better separation of the low ($n = 2$–4) oligomers can be observed whereas the higher polymers are not much affected (compare sample A in Fig. 2). A comparison of the chromatograms of the samples A and B clearly shows a different oligomer distribution.

The integrated areas of the chromatograms in Fig. 3 are shown in Table 1. Although the polyglycerol peaks of $n > 10$ are not separated at all, the differences in the areas under the curve

Table 1
Comparison of the relative peak areas of the two samples

n	Relative peak areas (%)	
	Sample A	Sample B
1	5.0	5.4
2	10.6	22.0
3	9.8	16.8
4	8.5	12.9
5	7.6	9.8
6	7.0	7.6
7	6.3	6.1
8	5.5	4.4
9	4.7	3.6
10	4.7	3.0
>10	30.2	8.4
Total	100	100

at $n > 10$ between the samples A and B are significant (30.2 and 8.4% relative, respectively).

4. Conclusions

Using SFC, silylated polyglycerols up to $n = 20$ (and presumably higher) can be eluted from the column which is a distinctive advantage compared to GC methods and also to the LC method on the carbohydrate column. Size-exclusion chromatography, another method that allows high polyglycerols to be eluted, does not separate the low oligomers as good as SFC. This method is therefore very useful for the comparison of samples of different origin. For oligomers of $n > 10$ which are not separated by the SFC method an "envelope" curve corresponding to the oligomer distribution is obtained. In this case, an evaluation similar to that used with size-exclusion chromatography can be applied.

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