Ionic Liquid Capillary Columns for the Analysis of FAME Isomers

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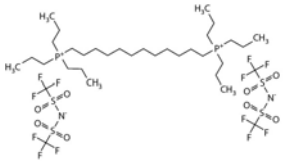
Abstract

Analyses of fatty acid methyl esters (FAMEs) are continuing to gain importance as more research is focusing on their biomedical impacts. This includes the analysis of saturated and polyunsaturated FAMEs along with the positional geometric FAME isomers. Traditionally, FAME analyses have been performed using polysiloxane or polyethylene glycol phases that yield typical elution patterns. Analysts performing the task of analyzing the fatty acid composition of food have a wide variety of capillary column selectivity's available for resolving the fatty acids as FAMEs depending upon the information they require from their analyses. Nonpolar columns provide a boiling point separation of the isomers with limited resolution of polyunsaturated isomers. Polyethylene glycol columns resolve the isomers by degree of unsaturation with minimal overlap of the carbon chain lengths. The highly polar cyano columns will resolve cis and trans isomers along with possibly providing positional geometric isomer separations depending upon the column type.
New classes of stationary phases based on Ionic Liquid technology have been developed and have demonstrated to provide unique elution patterns for FAME isomers. The two new phases are SLB-IL60 with a PEG like selectivity and the SLB-IL111 with highly polar selectivity. We will compare and contrast the selectivity of the ionic liquid phases with polymeric based phases for various FAME samples.

Introduction

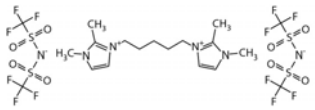
SLB-IL60i
Phase Structure

1,12-Di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide



SLB-IL111i
Phase Structure

1,5-Di(2,3-dimethylimidazolium)pentane bis(trifluoromethylsulfonyl)imide

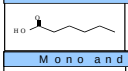
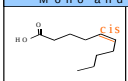
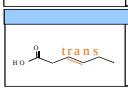


The SLB-60i and SLB-IL111i phases are both dicationic ionic liquid phases. The SLB-IL60i is based on a phosphonium cation while the SLB-IL111i is utilizes a imidazolium cation. Both phases have bis (trifluoromethylsulfonyl) imide (NTf2) as the anion.

Experimental

Types of Fatty Acids

Types of Fatty Acids

Structure	Common Sources	Health Effects
Saturated Fatty Acids (no double bonds)		
	Palm kernel, Palm oil, Coconut (tropical oils), Butter, Hydrogenated Oils and Shortenings	Raise LDL cholesterol, and increase risk of cardiovascular disease
Mono and Polyunsaturated Fatty Acids (≥ 1 *cis* double bond)		
	Fluid/Liquid oils such as Soybean, Canola, Olive, Sunflower and Corn oils.	Lower LDL cholesterol, associated with reduced risk of cardiovascular disease.
Trans Fatty Acids (≥ 1 *trans* double bond)		
	Partially Hydrogenated Oils, Shortenings, Margarines, and Chips	Raise LDL cholesterol like saturated fat, may also lower HDL. Associated with increased risk of cardiovascular disease and possibly type II diabetes.

Omega 3 and 6 Fames
These types of fatty acids are cis-cis methylene interrupted polyenoic fatty acids with the first double bond at the third carbon from the methyl end of the compound (**Omega 3**) or the sixth carbon from the methyl end of the fatty acid (**Omega 6**). Linolenic acid (C18:3n3) is and example of an Omega 3 fatty acid. Linoleic acid (C18:2n6) is an example of an Omega 6 fatty acid.

Column Choices for FAME Analysis

The column choice for FAME analysis will depend upon the information required from the analysis. Nonpolar capillary columns are routinely used to provide results on the amount of saturated versus unsaturated fatty acids. Polyethylene glycol based columns are used to provide carbon chain length & degree of unsaturation resolution. Prime examples of this analysis are marine fish oils or animal blood samples.

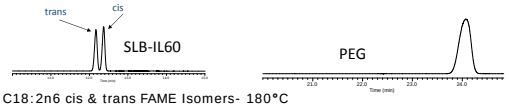
The analysis of cis and trans FAMES, along with resolving their positional isomers, requires the use of highly polar cyanosilicone capillary columns. Hydrogenated and nonhydrogenated vegetable oils are typical samples.

IONIC LIQUID PHASES

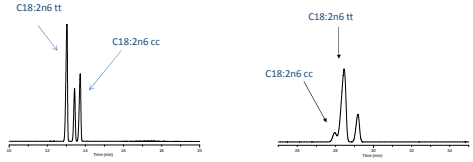
Ionic Liquid GC stationary phases have a number of properties that make them excellent choices for a GC stationary phase. One property is that they remain liquid over a wide temperature range and typically offer a higher thermal stability compared to the similar siloxane or polyethylene glycol (PEG) based phases. SLB-IL60i has a maximum temperature of 300°C compared to the 280°C maximum temperature for Supelcowax 10. Another property of the ionic liquid phases is that they are highly polar. All of the commercially available ionic liquid phases have a polarity similar to or greater than a PEG phase. The SLB-IL111i is the most polar phase available being more polar than a TCEP. TCEP also has a much lower maximum temperature of 140°C compared to the 270°C maximum temperature of the SLB-IL111i. The third interesting property of the ionic liquid phases which makes them unique compared to traditional phases is that they have the widest solvation interactions of any known solvent. This allows them to offer unique selectivity.
SLB-IL60i is a phosphonium ionic liquid that provides a selectivity that is similar to a PEG but there are some differences in selectivity compared to a traditional PEG phase. This is shown in the following figures.

Cis/ trans FAMES on SLB-IL60i vs. PEG Type Phase

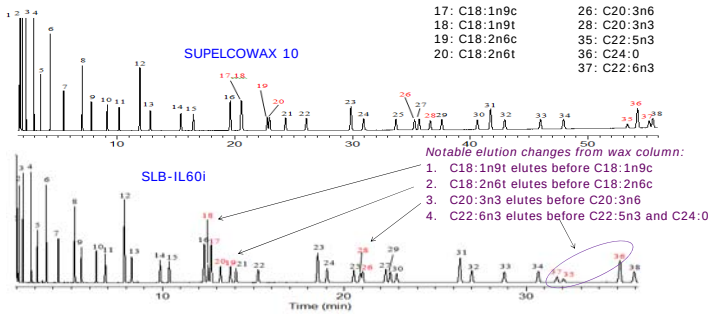
C18:1n9 cis / trans FAMEs @ 180°C



C18:2n6 cis & trans FAME Isomers- 180°C

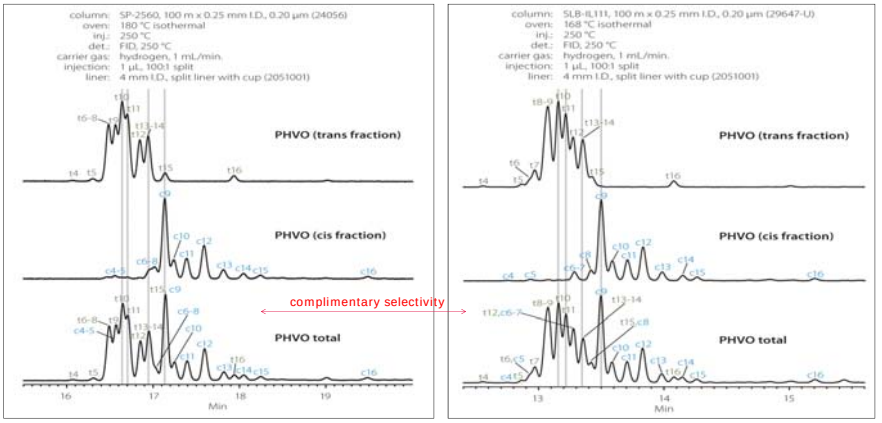


The SLB-IL60i column has additional interaction mechanisms compared to a PEG phase which provides it a selectivity similar to a highly polar cyanosilicone phase which elutes the trans FAMEs earlier than the cis FAMEs. The unique selectivity is also demonstrated in the following figures.



C18:1 cis/trans FAME Isomers in Partially Hydrogenated Vegetable Oil (PHVO)

The SLB-IL111i phase is the highest polarity phase available. The high polarity is similar to the polarity of a highly polar biscyanopropyl polysiloxane phase like SP-2560. A highly polar phase coupled with a long length (100 meters+) is typically required for the separation of highly complex samples like a partially hydrogenated vegetable oil (PHVO). Partially hydrogenated vegetable is a complex sample requiring the separation of positional, geometric (cis and trans) FAME isomers. The unique selectivity of the SLB-IL111i phase makes it a complimentary phase to the widely used SP-2560 for this analysis. The figure shows the separation of the trans and cis FAME fractions of the PHVO individually along with the composite sample. The trans and cis fractions were prepared by using silver ion SPE to separate them. There are differences in the resolution of the positional geometric FAME fractions on the SLB-IL111i column which will allow for identification and quantitation of additional FAME peaks.



Summary

The SLB-IL60i and SLB-IL111i are a polar and highly polar ionic liquid stationary phase similar in polarity to a polyethylene glycol (SLB-IL60i) and a cyanosilicone phase (SLB-IL111i). Both phases offer higher temperature stability than the corresponding traditional phases. The both provide a unique selectivity for the analysis of FAME containing samples.

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