# The Analysis of Siloxanes by Supercritical Fluid Chromatography

## Introduction

*The physical properties of supercritical fluids give supercritical fluid chromatography (SFC) several advantages over other chromatographic techniques including gas chromatography (GC) and high performance liquid chromatography (HPLC) for the analysis of silicones . SFC uses a mobile phase which possesses densities similar to those of a liquid and viscosities and diffusivities closer to those of gases; therefore, is capable of providing rapid, efficient, and low temperature analyses of high molecular weight samples. Another advantage of SFC is the wide range of detector compatibility. This technique can be interfaced to virtually all HPLC and GC detectors. The "universal" flame ionization detector (FID) is among the most popular and is particularly beneficial for polymers due to their lack of chromophores. SFC is the method of choice over GC due to the high molecular weight of many of the polysiloxanes.*

*Polysiloxanes, also known as organosiloxanes or silicones, are polymers based on a structure consisting of alternating oxygen and silicon atoms with organic groups attached to the silicon. They have many unique properties which make them suited to a variety of uses. Silicones are excellent insulators, are stable over a wide range of temperatures, exhibit extreme water repellency, and make excellent lubricants. Silicones are resistent to oxidation and weathering and yet are permeable to gases. These properties among others make the polysiloxanes an important class of compounds for which accurate analysis and quality control are essential. In this note we will show the SFC analysis of a polydimethylsiloxane, a low molecular weight polydimethylsiloxane with trifunctional groups and a high molecular weight vinyl end blocked polysiloxane.*

## Experimental Conditions

*The analysis conditions for polydimethylsiloxane are shown in Table 1. Table 2 shows the conditions for the low molecular weight siloxane and Table 3 shows the conditions for the high molecular weight siloxane. All of the chromatographic analyses were performed with a Selerity Technologies Series 3000 SFC equipped with split/splitless injector and a flame ionization detector.*

Table 1 : SFC Conditions for Polydimethylsiloxane

| | |
|---|---|
| Oven Program | 100°C hold 15 minutes, ramp to 125°C @ 2°C/min |
| Pump Pressure | 100 atm hold, 10 minutes, ramp to 400 atm @ 7atm/min |
| Column | SB-Biphenyl-30, 5-m, 50µm ID x 195µm OD |
| Detector Temperature | FID at 400°C |
| Restrictor | Frit |
| Injection | Split/splitless, split opens 1.00 min after injection |

Table 2: SFC Conditions for low molecular weight siloxane with trifunctional groups

| | |
|---|---|
| Oven Program | 100°C hold 15 minutes, ramp to 150°C @ 2°C/min |
| Pump Pressure | 100 atm hold, 10 minutes, ramp to 400 atm @ 7atm/min |
| Column | SB-Biphenyl-30, 5-m, 50µm ID x 195µm OD |
| Detector Temperature | FID at 400°C |
| Restrictor | Frit |
| Injection | Split/splitless, split opens 1.00 min after injection |

Table 3: SFC Conditions for High molecular weight vinyl end blocked polysiloxane

| | |
|---|---|
| Oven Program | 100°C hold 25 minutes, ramp to 150°C @ 2°C/min |
| Pump Pressure | 90 atm hold, 10 minutes, ramp to 165 atm @ 5atm/minthen to 400 atm @ 7atm/min |
| Column | SB-Biphenyl-30, 5-m, 50µm ID x 195µm OD |
| Detector Temperature | FID at 400°C |
| Restrictor | Frit |
| Injection | Split/splitless, split opens 1.00 min after injection |

## Results and Discussion

*As can be seen in Figures 1- 3 SFC utilizes the advantages of high densities and is able to elute each of the siloxanes. The polydimethylsiloxane in Figure 1 is a linear chain and is easily separated with high resolution on a SB-Biphenyl-30 capillary column. Figure 2 shows the chromatographic results of a low molecular weight, yet very complex siloxane. This separation is very useful for quality control when calculating the trifunctional groups that are contained in this sample. Finally Figure 3 demonstrates the ability of SFC to resolve high molecular weight siloxanes and from this chromatogram you can see that the sample contains a mixture of oligomeric distributions.*

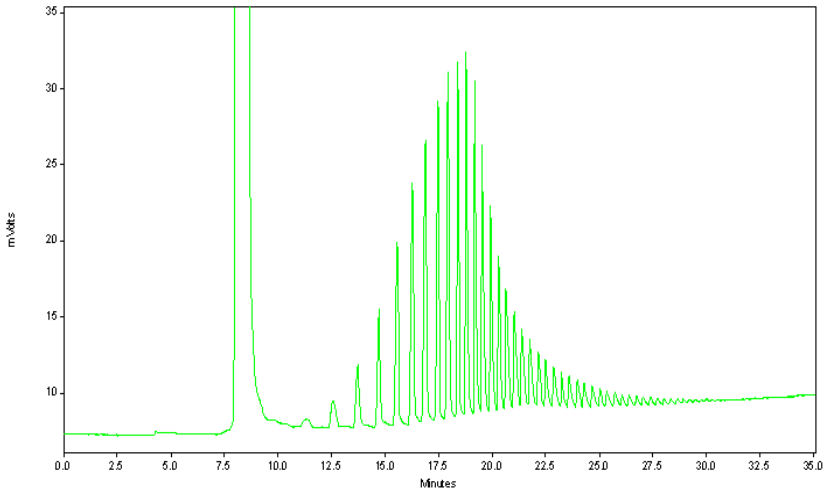


Figure 1: SFC analysis of Polydimethylsiloxane, MW 900

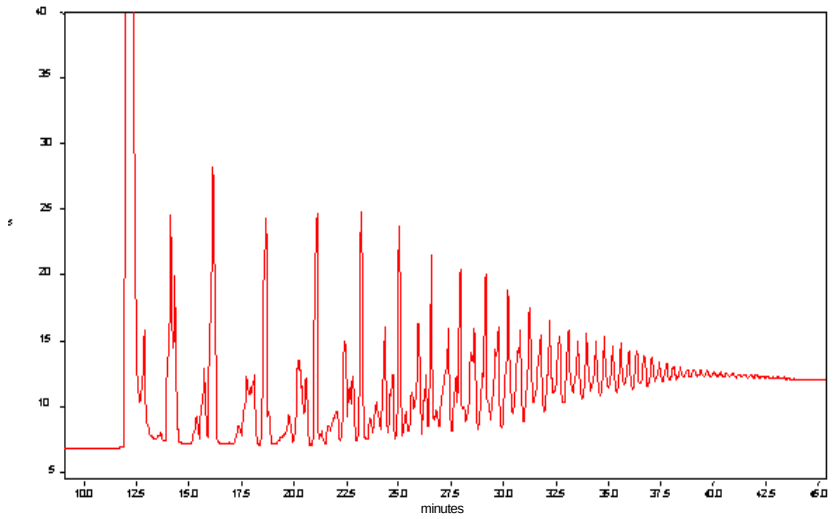


Figure 2: SFC analysis of a Low MW polydimethylsiloxane with trifunctional groups

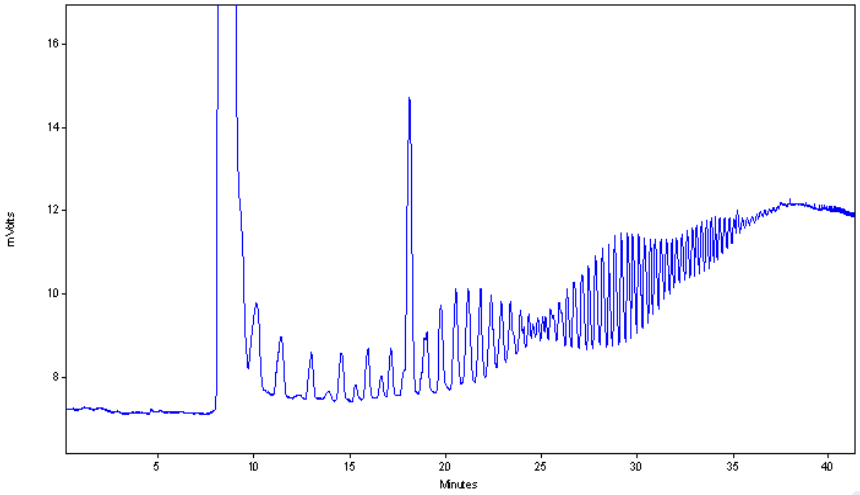


Figure 3: SFC analysis of a High MW polysiloxane