

# Analysis of Silicone Oils by High Performance Liquid Chromatography and Corona Charged Aerosol Detection

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## Overview

**Purpose:** To develop HPLC methods for both the detailed, characterization of silicone oils and for rapid quantitation of silicone oils in samples using an HPLC system with a charged aerosol detector.

**Methods:** Two methods, one qualitative for characterization and one quantitative using a solid core C18 column, are outlined.

**Results:** Different silicone oils were characterized using the qualitative method; silicone oils in commercial products were measured, with a quantitation limit of approximately 100 ng on column.

## Introduction

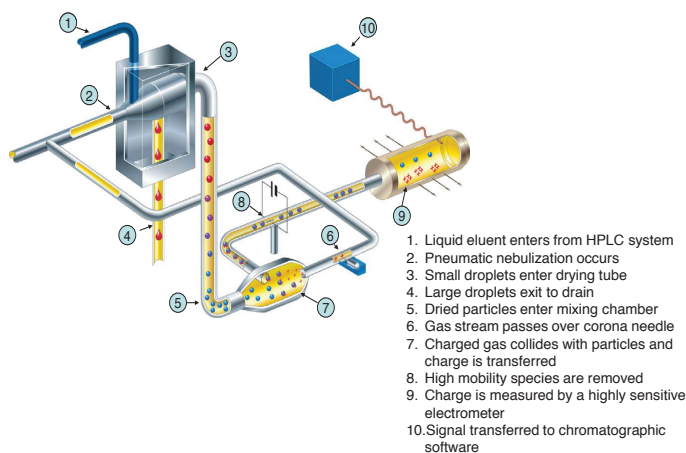
Silicone oils are unique materials with multitudes of significant uses in our modern world. Silicone-based materials are thermally stable, relatively inert, and are generally non-toxic, making them useful as oils and greases, lubricants, anti-foaming agents, and coatings. Silicone oils are often used in electronics, hydraulic systems, and many consumer products. The measurement of silicone oils is complicated by their solubility properties, their variations in basic structure including a wide variety of chemical moieties that may be part of this structure, as well as their general lack of chromophores making detection by ultraviolet absorption impractical.

The charged aerosol detector is a sensitive, mass-based detector, especially well-suited for the determination of any nonvolatile analyte independent of chemical characteristics. As shown in Figure 1, the detector uses nebulization to create aerosol droplets. The mobile phase evaporates in the drying tube, leaving analyte particles, which become charged in the mixing chamber. The charge is then measured by a highly sensitive electrometer, providing reproducible, nanogram-level sensitivity. This technology has greater sensitivity and precision than ELSD and refractive index (RI), is gradient compatible and is simpler to operate than a mass spectrometer (MS). Compounds do not have to possess a chromophore (unlike UV detection) or be ionized (as with MS).

Two charged aerosol detection methods were developed: one to characterize the individual components of silicone oils, and the other to provide quantitation of a near single peak of silicone oil to 100ng (o.c.). The characterization method used the Thermo Scientific™ Dionex™ UltiMate™ 3000 RS system, and the quantitation method used an UltiMate 3000 SD system in normal phase. Both methods used a solid core C18 column and the Thermo Scientific™ Dionex™ Corona™ ultra RS™ charged aerosol detector.

The combination of these chromatographic methods with the capabilities of the charged aerosol detection provides unique opportunities for detailed characterization of a silicone oil sample, as well as quantitation of silicone oil-containing samples.

**FIGURE 1. Schematic and Functioning of Charged Aerosol Detection**



## Methods

### Sample Preparation - Characterization

Samples of silicone oil were dissolved in chloroform, at a concentration of approximately 40 mg/mL.

### Liquid Chromatography – Characterization

HPLC System: Thermo Scientific™ Dionex™ UltiMate™ 3000  
DGP-3600RS pump, WPS-3000RS autosampler,  
and TCC-3000RS column oven  
HPLC Column: Thermo Scientific™ Accucore™ 2.6 µm C18,  
3.0 × 150 mm  
Column Temp.: 40 °C  
Mobile Phase A: Methanol  
Mobile Phase B: n-Propanol  
Flow Rate: 0.5 mL/min  
Injection Volume: 2–10 µL  
Sample: 38 mg/mL silicone oil in chloroform  
Detector: Corona ultra RS  
Nebulizer Temp.: 10 °C  
Filter: 5  
Data Rate: 10 Hz  
Power Function: 1.00  
Flow Gradient for Characterization:

Time (min)	%A	%B	Curve
-10	100	10	5
0	100	10	5
80	15	85	3
85	0	100	5
95	0	100	5
95	100	0	5
100	100	0	5

### Sample and Standard Preparations - Quantitation

Samples containing silicone oil were dissolved in tetrahydrofuran, at a product concentration of 10–20 mg/mL and centrifuged at 10,000 g for 3 minutes. HPLC sample vials were filled with the supernatant.

Standards (Silicone oil 1000 cP) were prepared by dissolving 10 mg/mL of silicone oil in tetrahydrofuran, diluted to 1 mg/mL and then sequentially diluted to lower concentrations.

### Liquid Chromatography –Quantitation

HPLC System: Thermo Scientific™ Dionex™ UltiMate™ 3000  
LPG-3400SD pump, WPS-3000RS autosampler, and  
TCC-3000RS column oven  
HPLC Column: Accucore 2.6 µm C18, 3.0 × 150 mm  
Column Temp.: 40 °C  
Mobile Phase A: 0.5% Formic acid/acetonitrile/tetrahydrofuran\*  
(35:35:30), helium sparge  
Mobile Phase B: Tetrahydrofuran\*, helium sparge  
Flow Rate: 0.3–1.0 mL/min  
Injection Volume: 2–10 µL  
Detector: Corona ultra RS  
Nebulizer Temp.: 10 °C  
Filter: 6  
Data Rate: 10 Hz  
Power Function: 2  
Flow Gradient for Quantitation:

Time (min)	Flow Rate (mL/min)	%A	%B
-5.0	0.6	100	0
-0.2	0.6	100	0
-0.1	0.3	100	0
0.0	0.3	100	0
0.5	0.6	100	0

Time (min)	Flow Rate (mL/min)	%A	%B
4.0	0.6	100	0
6.0	0.6	0	100
8.0	0.6	0	100
10.0	1.0	0	100
12.0	1.0	50	50
14.0	0.6	100	100

\*No BHT added.

### Data Analysis

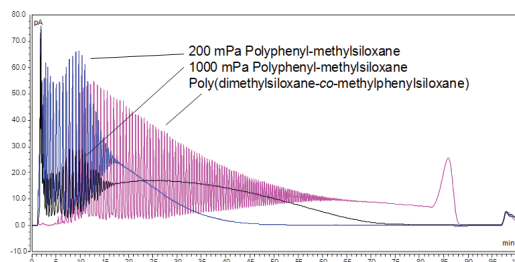
All HPLC chromatograms were obtained and compiled using Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data Station software, 7.1 SR 1.

## Results

### Sample Analysis

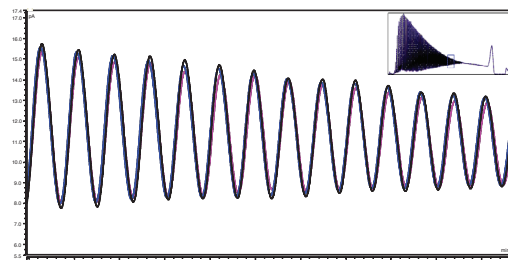
To investigate relative responses of different oils, three different silicone oil samples were characterized consisting of two similar oils with different viscosities (200 cP and 1000 cP) and a third oil that is used as a heating bath oil. From the overlay of chromatograms shown in Figure 2, the 1000 cP oil sample is comprised of a greater amount of larger molecular weight polysiloxanes (later elution) than the 200 cP oil sample, as characterized by the bulk of peak area at higher retention times. The heating bath oil is comprised of more isolable polysiloxane chain groups, as identified by over 170 different peaks that were at least partially resolved for this oil.

**FIGURE 2. Characterization of three different silicone oils, 200 cP (blue) and 1000 cP (black) viscosities, and a heating bath silicone oil (pink)**



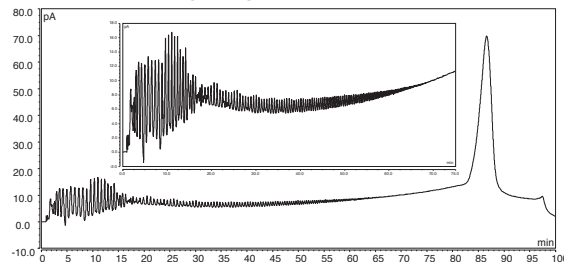
Retention time precision was demonstrated by repetitive analysis of the heating bath silicone oil sample (Figure 3). The UltiMate 3000 LC systems, controlled by the Chromeleon software, enables sample injections to be synchronized with the pump delivery, allowing for exact and matching system conditions for each injection. The percent relative standard deviation for retention time at 50 minutes was 0.02%.

**FIGURE 3. Overlays of three separate analyses of the heating bath silicone oil sample. Only the 50 to 55 minute segment of the total run (inset) is shown for clarity.**



A silicone-based topical product used for comfort with hearing aids was characterized using this method, as shown by the chromatogram in Figure 4. The material appears to contain a moderate amount of smaller molecular weight polysiloxanes mixed with an amount of higher molecular weight polysiloxanes that elute at the end of the gradient.

**FIGURE 4. HPLC chromatogram of a silicone-based topical product. Product appears to be made of high-molecular weight polysiloxane (85 minutes) mixed with moderate and low-molecular weight polysiloxanes. The inset shows the low to moderate molecular weight regions.**



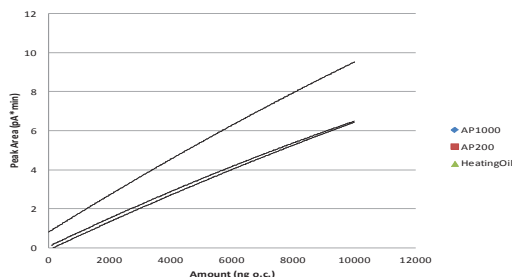
The method provides a high-resolution HPLC chromatogram for the detailed characterization of polysiloxane materials. The use of the solid core column in this method achieves the high number of theoretical plates and therefore, the high level of resolution shown in these figures. The charged aerosol detector provides both sensitive and consistent response for these analytes.

This quantitative method was evaluated using different silicone oils; using the 1000 cP silicone oil standards, a calibration curve was generated from 78 to 10,000 ng o.c., as shown in Figure 5. System precision (n=3) was acceptable, with peak area percent relative standard deviations 0.92 (10,000 ng o.c.) to 7.28 (156 ng o.c.). The quantitation limit is estimated at approximately 100 ng o.c, based on a signal to noise ratio of 3.0.

Samples that were tested included a 200 cP silicone oil, the heating bath oil, and three consumer products, including a shampoo, a hair conditioner, and a gas relief product containing different forms of silicones. The 200 cP oil and the heating bath oil were also used to generate single-injection calibration curves to investigate their response factors, relative to the 1000 cP oil standard. These results are in Table 1.

The 200 cP oil showed essentially equal response to that of the 1000 cP oil, but the heating bath oil differed in response at the two amounts used in this comparison. This may be associated with the differences of the groups or numbers of associated groups contained on the silicone. Thus, it is recommended that the silicone oil calibration standard is the same (or at least similar) to the silicone that is to be quantified. As seen in Figure 2, there is a clear difference between the 200 and 1000 cP silicones and the heating bath oil silicone.

**FIGURE 5. Silicone oil calibration curves, from 78 to 10,000 ng (1000 cP) in triplicate, 2000 to 10,000 ng o.c. (200 cP and Heating Bath Oil)**

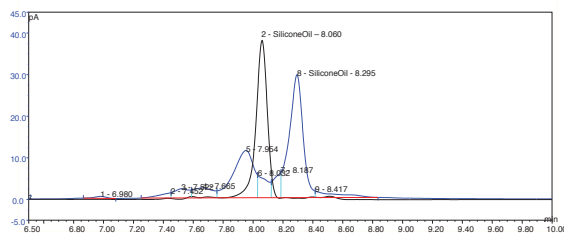


**TABLE 1. Response factors of different polysiloxanes at 5000 and 2000 ng o.c. relative to 1000 cP silicone oil**

Sample	Amount on Column (ng)	Amount Found (ng)	Relative Response
AP200	5000	5031	1.006
	2000	1994	0.997
Heating Bath Oil	5000	8681	1.736
	2000	4199	2.100

Two of the three oils (the two most closely related) showed a similar calibration curve, indicating that calibration curves derived from oils of a similar composition can be used for product concentration determinations. Differences in chain length and other structures may affect retention time. The heating bath oil, which characterized as a different oil, showed a greater response than the viscosity-rated oils.

**FIGURE 6. HPLC chromatogram overlay of over-the-counter gas relief product (blue), dissolved at a concentration of 500 µg/mL simethicone in tetrahydrofuran, and 500 µg/mL of 1000 cP silicone oil standard (black)**



**TABLE 2. Quantities of silicone oils found in products.**

Sample	Silicone Oil Type	Determined Silicone Oil (ng o.c.)	Product Silicone Amount	Recovery (%)
Shampoo	Dimethicone	3890	1.95 w/w-%	--
Conditioner	Phenyltrimethicone	2702	2.70 w/w-%	--
Gas Relief Product	Simethicone*	4559	4725 ng o.c.	96.5

\*simethicone is a mixture of silica (5.5%) and dimethicone (94.5%)<sup>1</sup>

The measurement of silicone oils in different commercial products showed the potential for quantitative determinations without extraction of the silicone from the sample or having the exact silicone oil as a calibrant. Samples were dissolved, centrifuged, diluted to a targeted amount, and analyzed. A gas relieve product chromatogram is shown in Figure 6 with an overlay of 1000 cP silicone oil. The recovery for the gas relief product (prepared at 500  $\mu\text{g/mL}$  of simethicone) was 96.5%, as shown in Table 2, demonstrating the potential for this method to measure silicone oils with unknown composition in different samples.

## Conclusions

Two methods were developed for the characterization and quantitation of silicone oils as standards and as part of products. The long characterization method can readily be modified to address specific regions of the chromatogram or to fully characterize a specific oil in less time. The quantification method is sensitive to 100 ng o.c. and it was shown that similar oils provide similar response factors. The method also had sufficient specificity to allow for analysis of different products and silicone oils.

The use of the solid core C18 column, combined with the detection capabilities of the charged aerosol detector, enables convenient and accurate characterization and quantification of silicone oils and silicone oil-containing products.

## References

1. DailyMedPlus website  
<http://www.dailymedplus.com/monograph/view/setid/da8eba22-33e1-4f46-b43c-9ca3d8789740> (last accessed 30 Jan 13).

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