SHIMADZU
Excellence in Science

Application News

No. G301

Gas Chromatography

Rapid Analysis of Low Molecular Weight Cyclic Siloxanes Using a Backflush GC System

Silicone features many useful characteristics such as excellent heat resistance, chemical resistance and low toxicity, and is widely used in electrical and electronic devices. The silicone used in such products often contains cyclic siloxanes with low molecular weight, which may become a cause of conduction faults. Cyclic siloxanes are compounds comprising three or more linked siloxane units and indicated as Dn with the "n" indicating the number of linked units. In many cases, the term low molecular weight cyclic siloxane refers to compounds with 3 (D3) to 10 (D10) linked siloxane units, and the total weight of such siloxanes from D3 to D10 is used as an index for quality standards.

Gas chromatography (GC) is frequently used to analyze low molecular weight cyclic siloxanes. However, the method has its drawbacks. Extracts from silicone products contain many components with high boiling points and the removal of such components from the column requires heating at a high temperature over a long period of time, which in turn elongates the analysis time. Furthermore, if the removal of components with high boiling points is insufficient, residues may be detected in the subsequent analysis.

This article introduces a backflush GC system which enables rapid analysis of low molecular weight cyclic siloxanes.

A. Miyamoto, S. Uchiyama

Backflush GC System

The backflush GC system reverses the flow of the carrier gas so that after the target component is detected, components with high boiling points are discharged from the split vent (Fig. 1).

By connecting a backflush element and a resistance tube to the detector side of the column, the pressure on the detector side of the column is controlled using an advanced pressure controller (APC).

When using the backflush function, analysis is done normally until the target component is detected. Once it is detected, the pressure gradient is reversed by raising the pressure on the backflush element while lowering the pressure at the sample injection port. Components with high boiling points are removed from the column by the backflushing and this prevents contamination of the column and detector, making possible greatly shortened analysis times.

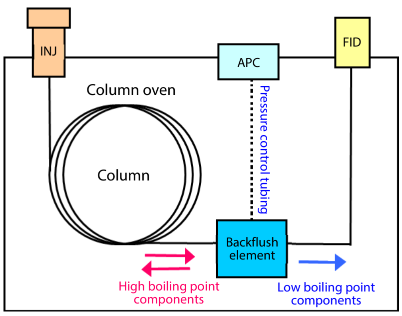

Fig. 1 Backflush GC System

Pretreatment and Analysis Method

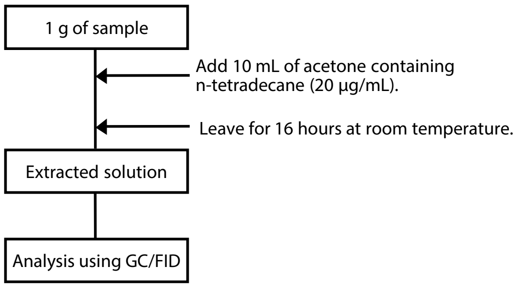

Fig. 2 Pretreatment Method for Silicone Products

A silicone sample of 1 g was prepared by adding 10 mL of acetone containing n-tetradecane (20 µg/mL) as an internal standard and leaving the solution for 16 hours at room temperature. The extracted solution was injected into a GC system.

The silicone extracted solution was analyzed using the SH-Rxi™ - 5 Sil MS column (30 m, 0.25 mm I.D., 0.25 µm) on a GC with a flame-ionization detector (GC/FID). Table 1 lists the normal measurement conditions and Table 2 lists the measurement conditions with a backflush GC system.

Table 1 Conditions for Normal Measurement (Without backflushing)

Model	: Nexis™ GC-2030 AF/AOC-20i
Column	: SH-Rxi™ - 5 Sil MS (30 m × 0.25 mm I.D. df = 0.25 µm)
Column Temp.	: 60 °C (0 min) - 25 °C/min - 250 °C (0 min) - 15 °C/min - 300 °C (60 min) Total : 70.93 min
Injection Temp.	: 300 °C
Carrier Gas	: He, 40 cm/sec
Injection Method	: Split 1 : 15
Carrier Gas Controller	: constant linear velocity mode (He)
Injection Volume	: 1.0 µL
Detector	: FID
Detector Temp.	: 320 °C

Table 2 Conditions for Measurement with Backflushing

Model	: Nexis™ GC-2030 AF/AOC-20i
Column	: SH-Rxi™ - 5 Sil MS (30 m × 0.25 mm I.D. df = 0.25 µm)
Column Temp.	: 60 °C (0 min) - 25 °C/min - 250 °C (0 min) - 15 °C/min – 300 °C (1 min) Total: 11.93 min
Injection Temp.	: 300 °C
Carrier Gas	: He, 40 cm/sec
Injection Method	: Split 1 : 15
Carrier Gas Controller	: constant linear velocity mode (He)
Injection Pressure	: 233.3 kPa (8 min) – 20 kPa
APC Pressure	: 100 kPa (8 min) – 225 kPa
Injection Volume	: 1.0 µL
Detector	: FID
Detector Temp.	: 320 °C

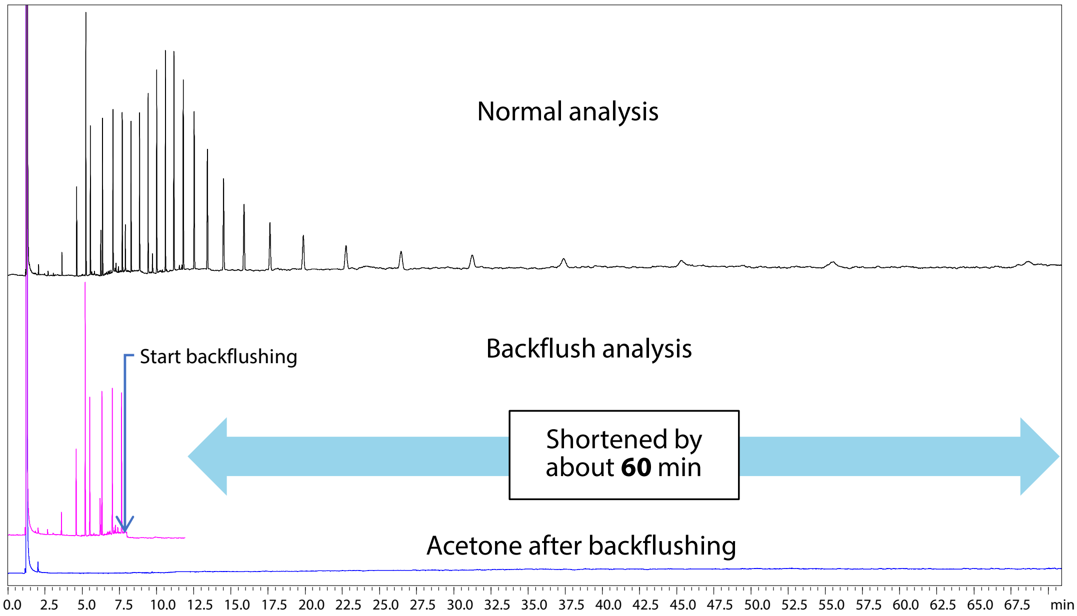

Fig. 3 Comparison of Chromatograms Obtained by GC/FID

Analysis Results of Cyclic Siloxanes

The extracted solution of a silicone product was analyzed by normal measurement and also by measurement with backflushing after the elution of D10 to compare the analysis results.

The two obtained chromatograms are shown superimposed on each other in Fig. 3. By normal measurement, the final temperature of the column may need to be maintained at 300 °C for 60 minutes in order to expel the siloxanes with high boiling points. For this particular sample, the total analysis time was abowut 71 minutes.

By measurement with backflushing, however, the total analysis time was shortened greatly by about 60 minutes to about only 12 minutes by backflushing the column to remove the components with high boiling points for about 4 minutes after the 8-minute point at which the D10 eluted.

A subsequent analysis of an acetone solvent after backflushing resulted in the detection of only the peak for acetone, indicating that the backflushing effectively removed the components with high boiling points from the column.

Reproducibility for Low Molecular Weight Cyclic Siloxanes

The chromatogram obtained from the measurement with backflushing is shown enlarged in Fig. 4. Table 3 indicates the %RSD (n = 5) of the peak area values for the cyclic siloxanes with low molecular weight and tetradecane.

The %RSD of each peak area value is less than 1 % indicating favorable reproducibility.

Based on these results, we can see that the use of a backflush GC system can greatly shorten the time necessary for analyzing cyclic siloxanes with low molecular weight and thereby improve productivity sixfold.

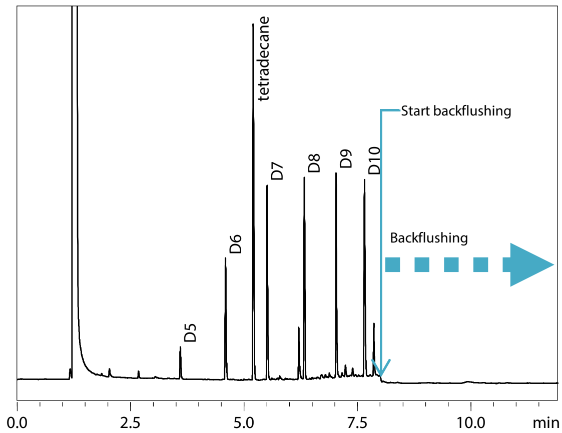

Fig. 4 Enlarged Chromatogram of Measurement with Backflushing

Table 3 Peak Area Reproducibility (%RSD, n = 5)

Compounds	Peak Area %RSD with Backflushing	Peak Area %RSD without Backflushing
D5	0.47	0.99
D6	0.48	0.87
tetradecane	0.33	0.63
D7	0.49	0.57
D8	0.48	0.59
D9	0.39	0.53
D10	0.48	0.62

Rxi is a registered trademark of Restek Corporation.

First Edition: May 2018

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/