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Quantitative Analysis of Polymer Contamination in Solvents by Pyrolysis-GC-MS Method

Application Note

Environmental, Polymer

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Abstract

This application note demonstrates quantitative analysis of polymer contamination in solvents by pyrolyzing the sample into a GC-MS.

Introduction

A solvent is a substance in liquid phase that is capable of dissolving a solute. Various solvents are widely used in a broad range of industries. Typical applications include dissolving oil, grease, or paint; thinning pigments, glues, or resins; cleaning tools, electronics, or automotive parts[1]. Many of these applications require the solvent maintains relatively high purity since impurities in the solvent could interfere with the manufacturing process or product performance[2]. Modern analytical techniques, such as GC-MS and FT-IR, are commonly employed as the quality control tool in the solvent manufacturing process to identify the contaminants. However, it is also crucial to maintain Standard Operation Procedures of the analytical laboratory to prevent secondary contaminations that could be introduced during the testing process from containers, syringes, septa, and most importantly, solvents that are used to introduce the sample into the instrument. Therefore, research grade solvents with the highest attainable purity are required in the laboratory.

Even using a research grade solvent, a reliable analytical chemistry technique is desired to quantify contaminants, which could be volatile, semi-volatile, or even polymeric in nature. While volatile and semi-volatile contamination can be traced by GC-MS in the ppb range, polymer contamination proves to be more challenging to GC-MS due to its high boiling point and large molecular weight. One example of such polymer contamination is silicone, which is widely used in many products, from toys to cosmetics, and even laboratory supplies like seals and septa[3]. When analyzed by FT-IR, silicones have strong adsorption bands in the mid-infrared spectrum range. Absorption at 1258.52 cm^{-1} and 864.27 cm^{-1} can be attributed to bending vibration and rocking vibration of Si-CH$_3$. Adsorption at 1080 cm^{-1} and 1009.28 cm^{-1} would be from a stretching vibration of Si-O-Si on the backbone[4]. Therefore, FT-IR is very limited in confirming whether contamination is polymeric. As shown in this application note, the analytical pyrolysis coupled with GC-MS provides a perfect solution for detection of silicone contamination as it extends the range of a GC-MS to cover polymeric identification and quantification.

Experiment Setup

A bottle of Isopropyl alcohol sample, which was suspected of silicone contamination implied by a separate FT-IR analysis, was collected from a solvent manufacturer. By following the CDS Pyroprobe Application Decision Making Tree, an aliquot of sample was first added into a DISC (Drop-In-Sample Chamber) tube and allowed to dry at room temperature for 30 minutes, then analyzed by a CDS 6150 Pyroprobe with the Evolved Gas Analysis (EGA) method as the first screening step. Then the EGA data determined the setpoint of the Pyrolysis-GC-MS (Py-GC-MS) run for molecular structure identification. Quantification was followed after the structure match by making a calibration curve from corresponding standards, and data fitting to calculate the concentration of the contamination.

EGA

Pyroprobe

Initial:	100°C
Final:	800°C
Ramp Rate:	100°C per min
Interface:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

GC/MS

Column:	Fused silica (1m x 0.10mm)
Carrier:	Helium 1.25mL/min 80:1 split
Injector:	360°C
Oven:	300°C
Ion Source:	230°C
Mass Range:	35-600amu

Pyrolysis

Pyroprobe

Pyrolysis:	700°C
Interface:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

GC/MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium 1.00mL/min, 50:1 split
Injector:	360°C
Oven:	50°C for 2 minutes 20°C/min to 320°C (15min)
Ion Source:	230°C
Mass Range:	35-600amu

Results and Discussions

EGA run from 10 μL of dried solvent showed a low signal to noise ratio, indicating a low level of concentration. As shown in Figure 1, m/z 207 was evident between 400 °C and 700 °C. The relatively high temperature at which m/z 207 evolved indicated the contamination is likely from degradation of a polymeric material. When the mass spectra under this peak was integrated and matched by the CDS polymer library, the top two candidates were silicone caulk and polydimethyl siloxane polymer (silicone).

Using the information obtained from the EGA, 700 °C was chosen for a single step PY-GC-MS. This ensures rapid and complete pyrolysis. The resulting Py-GC/MS chromatogram in Figure 2 exhibited a series of peaks, identified as cyclic siloxanes by matching to the library as the top candidate. This pyrogram confirmed the findings of the EGA-MS and future determined the compound structure, which showed that polydimethyl siloxane based product such as silicone caulk could be the source of contamination.

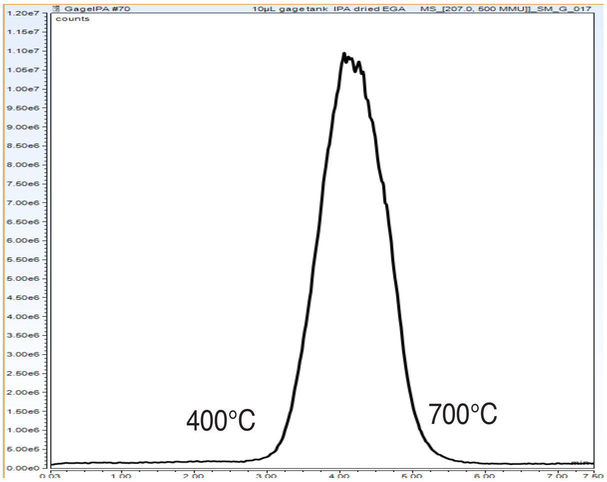

Figure 1: EGA m/z 207 of residual contamination in the isopropyl alcohol sample

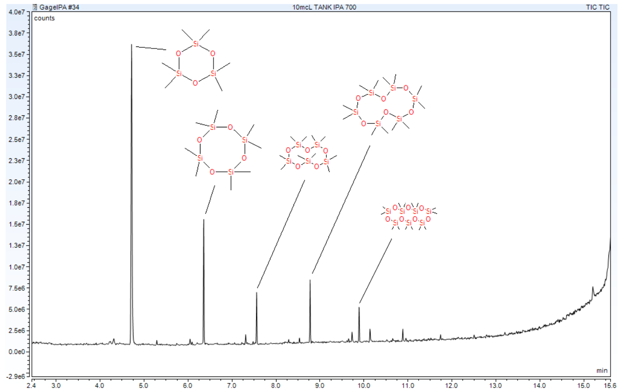

Figure 2. Pyrogram of the isopropyl alcohol sample at 700 °C.

After matching the compound structure, to determine the compound concentration, 1 μL of silicone standard was diluted into 1 mL of HPLC grade isopropyl alcohol to make the calibration stock solution. Four aliquots of the stock solution with the volume at 1 μL, 3 μL, 7 μL and 10 μL were pyrolyzed at 700 °C respectively. The series of the pyrograms from the calibration stock solution are shown in Figure 3. The area of the first peak, hexamethyl cyclotriloxane, was used to correlate to the absolute mass of silicone. Figure 4 showed the 4-point calibration curve with a linearity of 0.99. Using this calibration curve, a 5 μL volume sample was calculated to contain 2.26 μg of silicone, which is equivalent to a concentration level of 452 ppm in the isopropyl alcohol sample.

Conclusions:

An isopropyl alcohol sample with silicone contamination was analyzed quantitatively by Py-GC-MS method in CDS 6150 Pyroprobe, which was demonstrated as a useful tool in investigating the polymer contamination in solvent on 100 ppm level.

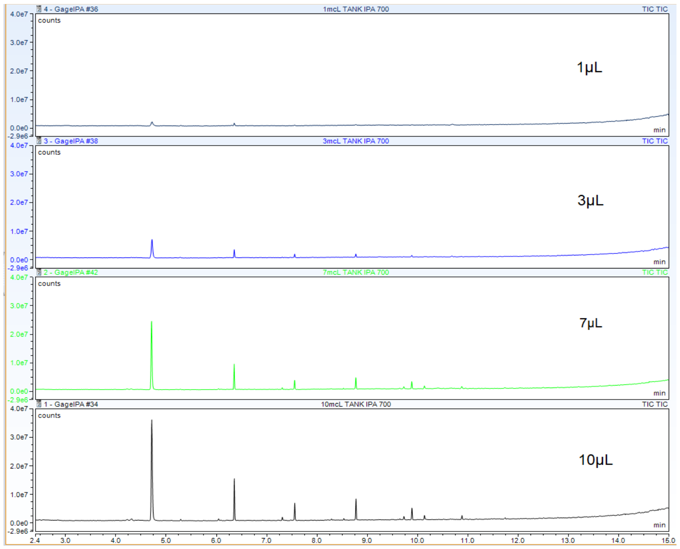

Figure 3: Pyrograms of the calibration standard with different volume at 700 °C.

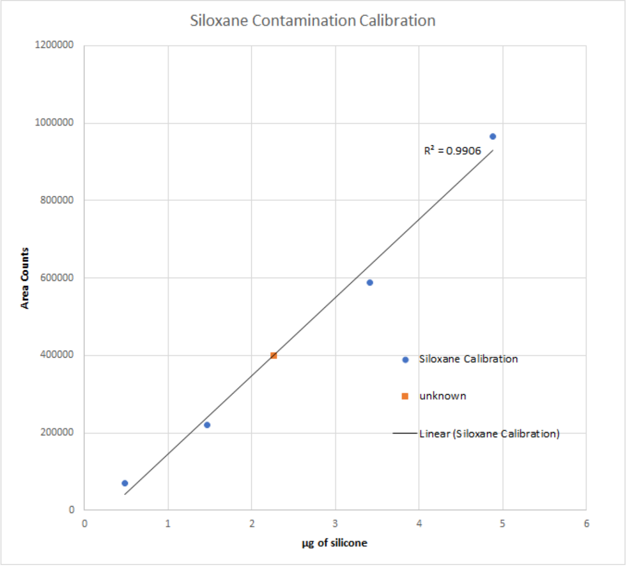

Figure 4: Siloxane calibration curve with first order polynomial fitting and unknown sample plugged in.

References

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