

Headspace Assay of Polymers used in the Automotive Industry with Teledyne Tekmar HT3™ Dynamic Headspace Instrument

Introduction

Synthetic and natural materials are used extensively by the motor vehicle industry to provide customers appealing and safe vehicle interiors. The materials used in all aspects of vehicles interior, range from cloth and leather seats to the plastics used in the dashboards. The manufacturing process used for these materials typically include volatile (VOC) and semi volatile organic compound (SVOC) which are released into the interior of vehicles.

These compounds give the vehicles that new smell but can also lead to fog on the interior glass surfaces of the car and health issues with the occupants. Vehicle manufactures and government regulatory agencies are investigating limits relating to the VOC and SVOC and their allowable concentrations in the interior of vehicles. The Japanese Automotive Manufactures Association (JAMA) and the voluntary program for the European Automotive Industry, VDA, whose limits are defined by TÜVRheinland are two of these agencies. Their limits are listed in Table 1.

The typical method of collecting VOC and SVOC from the vehicle cabin is to flow air through the cabin and collect these compounds on thermal desorption tubes. The tubes are then tested with a thermal desorption instrument.

Thermal desorption is well suited for the final testing of the vehicle interiors. However, it has limitations for use by the manufactures of products that go into the vehicles interior prior to final assembly.

One method from the VDA for testing these materials, Method VDA-278, uses thermal desorption. It instructs the parts suppliers of the vehicle interior materials how to test their products to meet the vehicle manufactures requirements for VOC and SVOC.

Thermal desorption has some known disadvantages listed in VDA 278. Section 4.4.1, Trimming and Weighing of Samples for Thermal Desorption Tubes indicates that the sample must be reduced to fit into the thermal desorption tube, which has an internal diameter of 4mm. Section 6, Possible Errors, Known Problems, also indicates that heating of the sample that may be generated during the mechanical reduction can drive off VOC's creating false negative results and should be avoided.

A headspace method was investigated to provide an alternate method for thermal desorption.

Instrument Parameters

Teledyne Tekmar's HT3™ Static Headspace instrument was connected to a Thermo Focus GC and DSQII mass Spectrometer. The headspace instrument conditions for the HT3™ are presented in Table 2. The GC and MS conditions for VDA 278 for both the VOC portion of the method are listed in Table 3. This work only used the VOC GC/MS conditions so the difference between the VOC and the FOG headspace parameters could be compared.

Sample Preparation

Four automotive polymers were used for this report. Polymer A was a white polymer pellet ranging in size from 4 to 6mm in length and approximately 4mm in diameter. Polymer B was a black polymer rod approximately 3mm in diameter and approximately 10mm

| JAMA Standard | | TÜV Rheinland Standard | |
|--|---|---------------------------------|---|
| Substance Name | Indoor Concentration Guideline Value, ug/m3 | Substance / Class | Limit Value, without air exchange ug/m3 |
| Formaldehyde | 100 | Formaldehyde | 60 |
| Acetaldehyde | 48 | BTEX (except benzene) | 200 |
| Toluene | 260 | Benzene | 5 |
| Xylene | 870 | Stryene | 30 |
| p-Dichlorobenzene | 240 | Halogenated hydrocarbons | 10 |
| Ethylbenzene | 3800 | Esters and Ketones | 200 |
| Stryene | 220 | Aldehydes (except Formaldehyde) | 50 |
| Chlorpyrifos | 1 / 0.1 (Child) | Alcohols | 50 |
| Di-n-butyl Phthalate | 220 | Glycol – este1rs-ethers | 100 |
| Tetradecane | 330 | Nitrosamines | 1 |
| Di-2-ethylhexyl Phthalate | 120 | Amines | 50 |
| Diazinon | 0.29 | Phenols | 20 |
| Fenoxycarb | 33 | Phthalates | 30 |
| TVOC (Total Volatile Organic Compound) | 400 (Provisional Guideline Value) | TVOC (C6-C16) | 3000 |

Tables 1: VOC and SVOC allowable concentration limits

| Variable | Value | Variable (Cont'd) | Value |
|---------------------|------------------------------|-------------------|-----------|
| Valve Oven Temp | 150°C | Dry Purge Time | 0.50 min |
| Transfer Line Temp | 150°C | Dry Purge Flow | 50mL/min |
| Platen/Sample Temp | VOC – 90°C FOG – 120°C | Dry Purge Temp | 25°C |
| Sample Preheat Time | 5 min | Desorb Preheat | 275°C |
| Sweep Flow Rate | 75mL/min | Desorb Temp | 280°C |
| Sweep Flow Time | VOC – 30 min FOG – 60 min | Desorb Time | 2.00 min |
| Trap Material | No 1 (Tenax TA) | Trap Bake Temp | 300°C |
| | | Trap Bake Time | 5 min |
| | | Trap Bake Flow | 450mL/min |

Table 2. Dynamic HT3 Parameters (Trap)

| | |
|---------------|--|
| Column | HP-5, 30m x 0.32µm D, 0.25µm film, column flow of 10mL/minutes |
| Inlet | 1.3mL/min Constant Flow, Split ratio 30:1, inlet temperature of 280°C |
| Transfer Line | 280°C |
| Oven | VOC – 40°C for 2 min, then 3°C/min to 92, 0 min hold, then 5°C /min to 160°C, 0 min hold, then 10°C /min to 280 C, 10 min final hold |
| MS | Source 200°C, Stat Scan 1 min, 29.0 to 280.0m/Z, Scan Rate 806.3 |

Table 3: Thermo Focus GC with DSQII MS Conditions

long. Polymer C was a black sheet of polymer 60mm square and 2mm thick. Polymer D was a white sheet of polymer 80mm square and approximately 1mm thick.

Approximately 100mg of each sample in duplicate were weighed into separate 22mL headspace vials. Six pellets of A were used without cutting the sample. Two rods of B were used without cutting the sample. Square pieces (approximately 7mm) of C were cut from the sheet. The first sample of C was a single sample cut from the sheet. The second sample was two pieces cut from the sheet, which increased the sample surface area due to the second cut. Single pieces (approximately 10mm by 7mm) of D were cut from the sheet.

The 2 vials for each polymer were analyzed first with the VOC headspace method and the VOC GC/MS method. Following VDA 278, only the second vial was then analyzed with the FOG headspace method but with the VOC GC/MS method. The VOC GC/MS method was used for this FOG headspace analysis to allow a comparison of the data from both headspace methods with the peaks of interest at the same retention time instead of separate retention times.

Data

All four polymer samples produced numerous peaks. The Total Ion Current (TIC) chromatograms of the two vials for each polymer analyzed by the VOC headspace method were compared to determine if the headspace method was reproducible. Figures 1, 2, 3 and 4 are the comparison of the same sample in 2 separate vials.

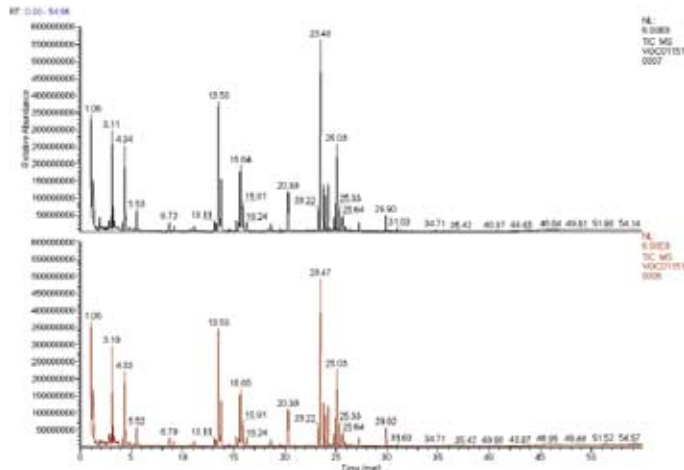


Figure 1: Comparison of the TIC chromatogram for 2 samples of polymer A.*

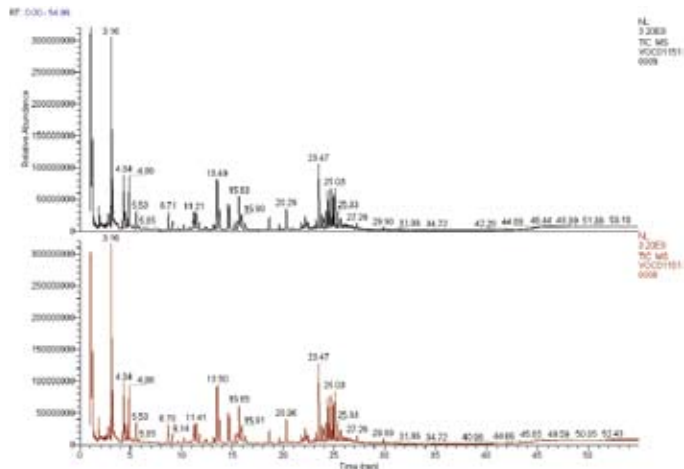


Figure 2: Comparison of the TIC chromatograms for 2 samples of Polymer B.*

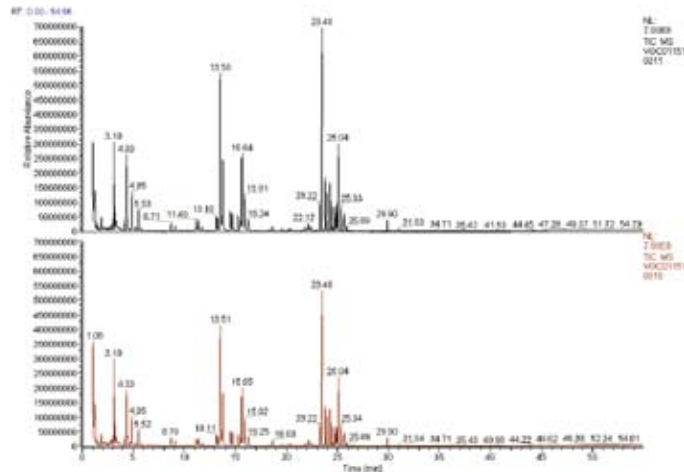


Figure 3: Comparison of the TIC chromatograms for the 2 samples of Polymer C. The upper TIC is of the sample with 2 pieces in the vial instead of a single piece exhibiting the influence of surface area of this method.*

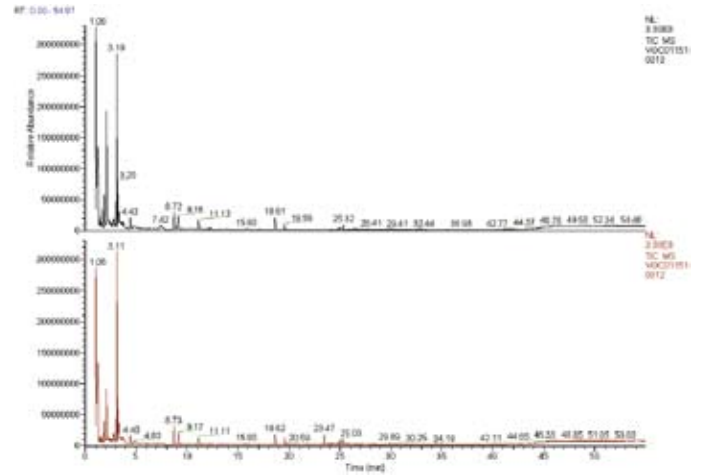


Figure 4: Comparison of the TIC chromatograms for 2 samples of Polymer D.*

The TIC chromatogram from the second vial used for the VOC headspace analysis was compared to the TIC chromatogram of the FOG headspace analysis of the second vial. Figures 5, 6, 7, and 8 are the comparison of the second vials VOC TIC chromatogram and the FOG TIC chromatogram. Figure 9 is the same polymer from Figure 8, but expanded.

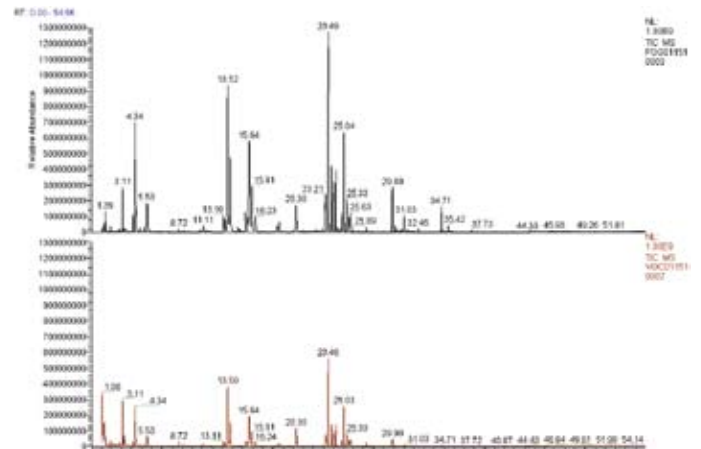


Figure 5: Comparison of the second vial's VOC (lower) and FOG (upper) TIC Chromatogram for Polymer A. The FOG headspace analysis has additional peaks not observed in the VOC headspace analysis.*

*The scale is the same for both chromatograms showing the reproducibility of the method.

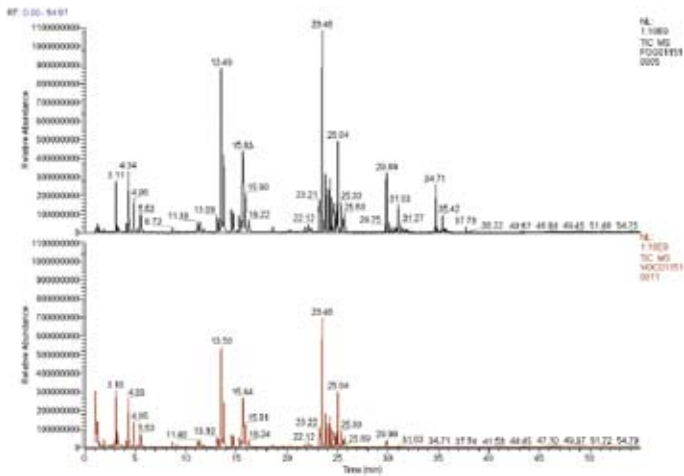


Figure 6: Comparison of the second vial's VOC (lower) and FOG (upper) TIC Chromatogram for Polymer B. The FOG headspace analysis has additional peaks not observed in the VOC headspace analysis.*

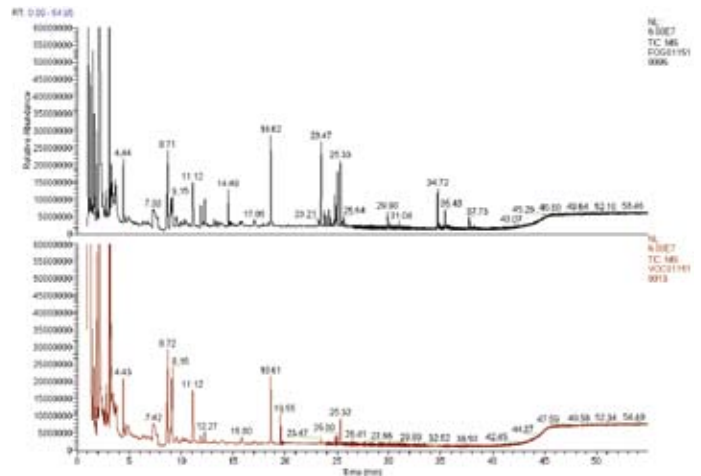


Figure 9: Enlarged scale of the TIC chromatograms from Figure 8 indicating the additional peaks in the FOG headspace analysis.

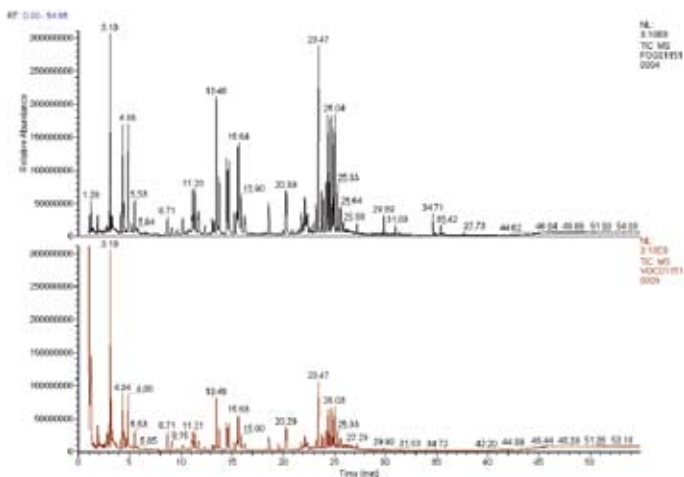


Figure 7: Comparison of the second vial's VOC (lower) and FOG (upper) TIC Chromatogram for Polymer C. The FOG headspace analysis has additional peaks not observed in the VOC headspace analysis.*

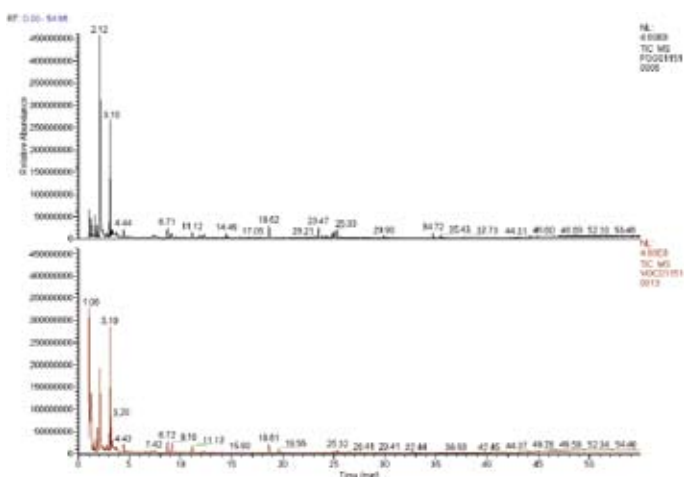


Figure 8: Comparison of the second vial's VOC (lower) and FOG (upper) TIC Chromatogram for Polymer D. The FOG headspace analysis has additional peaks not observed in the VOC headspace analysis.*

Conclusion

VDA 278 is currently used by the vehicle manufacturers and their suppliers to test manufactured materials for VOC and SVOC emissions. The method uses thermal desorption to analyze the sample. This requires reduction of the sample size to fit into thermal desorption tubes internal diameter of 4mm. The method indicates that care must be taken to avoid heating the sample during sample size reduction to avoid driving off the VOC and SVOC's.

The headspace method using Tekmar's HT3™ with the dynamic option and the same trap material used in VDA278 provides a consistent method for the analysis of these polymers. Two of the samples were raw polymer pellets and were placed directly into the headspace vial without the need for sample size reduction. Two polymers samples were sheets of the material, and required that a square piece cut from the sheet.

Polymer A, B, and D indicated consistent results between the sample vials when similar pieces of polymer was present. Polymer C samples consisted of a single piece of polymer for one vial and two pieces of polymer for the second vial to maintain the same sample weight. The same peaks were observed for the two samples. However the sample with a greater surface area had higher concentrations of these peaks.

The headspace method was also used to determine if difference in the polymers could be detected when the same vial was used for both the VOC analysis at 90°C and then reused for the FOG analysis at 120°C. All four polymer samples showed a difference between the VOC and the FOG headspace method.

The Tekmar HT3™ can provide an alternative method for VDA 278, while provide VOC and FOG data from a single sample. The HT3™ also reduces the amount of sample handling reducing the potential of a false negative for these samples.

*The scale is the same for both chromatograms showing the reproducibility of the method.