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Identification of VOCs in In-Vehicle Interior Using TD-GC/MS-Olfactory Port

Introduction

Customer complaints of odors within a new car are rising with the increasing number of new car buyers. Although odors can be subjective, it is now well known that the new car smell is the result of chemicals emitted from the in-vehicle interior components such as the dashboard, interior panels, seat coverings, flooring materials, and so on. Most of the in-vehicle interior components are comprised of plastics, rubber, leather, textiles, glues, sealants and other materials that contain various amounts of volatile organic compounds (VOCs) and other chemicals. Exposure to these chemicals can have a significant impact on human health and many are regarded as the cause of cancer and neurological effects.

While many countries have established regulations and methods for assessing VOCs levels in automobile interiors, it does not provide a direct relationship between the compounds and their odors. The GC SNFR™ Olfactory Port enables the analyst to achieve a powerful insight into both the chemical composition and the sensory characterization of each sample from a single run. Such information provides a fuller profile of each sample to enable improvements to be made by automotive manufacturers.

This application note describes a method for the automotive industry that provides a qualitative analysis and the olfactory character of each component using the TD-GC/MS-Olfactory Port.

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Experimental Details

A PerkinElmer TurboMatrix™ 650 ATD is connected to a PerkinElmer Clarus® SQ 8 GC/MS with a GC SNFR™ Olfactory Port to perform these experiments. A schematic diagram of the system is presented in Figure 1. The Thermal Desorption transfer line is directly connected to a 60 m × 0.25 mm × 1 µm 5MS column. The column eluent is split between a PerkinElmer SNFR™ GC olfactory port and the MS detector by an S-SwaferTM in a standard active splitting configuration. The split ratio and flows to the MS detector and the Olfactory Port are defined by the carrier gas pressure and transfer line geometries which are conveniently calculated using the Swafer Utility Software. Figure 2 shows the operating conditions for the S-Swafer used for this study with the analytical conditions presented in Tables 1 to 5.

Test samples of sponge in seats, PU leather, real leather, PU foam, non-woven fabric, plastic and rubber vehicle interior parts are prepared by the ISO/FDIS 12219-2, bag method.[1] Each raw material test specimen with a size of 10 cm × 20 cm is placed into a 10 L bag. For the larger auto parts such as a seat, door panel, luggage compartment upholstery, seal assembly door and spare cover, the test specimen is placed into a 1000 L bag. The sampling bag will be evacuated and then filled with pure, dry air. Then the bag will be heated at 60 °C for two hours in a thermostatic oven. A Tenax tube is connected to the sampling bag to collect 5 L of gas after heating. The resulting chromatograms were analyzed with the unknown peaks identified from their spectra using the NIST spectral library while the sensory experience was recorded by the analyst via the olfactory port.
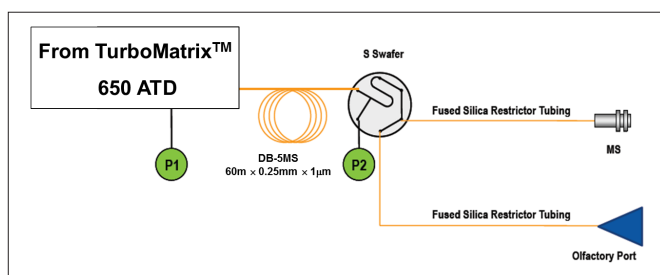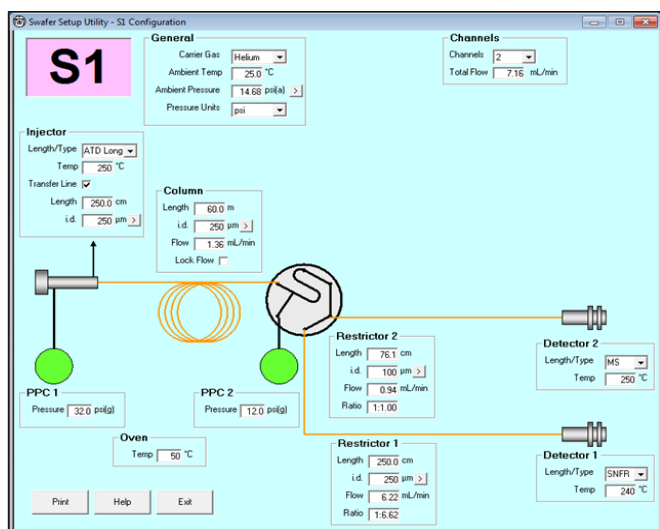

Figure 1. Schematic diagram of the GC system.

Figure 2. The Swafer utility software showing the settings used for this study.

Table 1. Thermal Desorber conditions.

Tube Desorb Temp	280 °C
Tube Desorb Time	10 min
Tube Desorb Flow	40 mL/min
Concentrator Trap Low	-30 °C
Concentrator Trap High	280 °C
Concentrator Trap Hold	6 min
Concentrator Trap Heating Rate	40 °C/min
Valve Temp	180 °C
Transfer Line Temp	200 °C
Column Pressure	32 psi (Helium)
Inlet Split	100 mL/min
Outlet Split	100 mL/min
Transfer Line Temp	200 °C
Column Pressure	32 psi (Helium)
Inlet Split	100 mL/min
Outlet Split	100 mL/min

Table 2. GC conditions.

Gas Chromatograph/ Mass Spectrometer	Clarus SQ 8
Column	60 m × 0.25 mm × 1 µm 5MS column
Oven	50 °C for 3 min, then 5 °C/min to 280 °C for 5 min
P2 Swafer Pressure	12 psig (Helium)

Table 3. MS conditions.

Mass Range (amu)	35 to 350
GC Inlet Line Temp	280 °C
Ion Source Temp	280 °C
Scan Time	0.25 s
Interscan Delay	0.05 s

Table 4. Olfactory port conditions.

Olfactory Port	PerkinElmer GC SNFR
Transfer Line	225 cm x 0.250 mm at 240 °C
Humidified Air	500 mL/min with jar set to 37 °C

Table 5. Swafer conditions.

Swafer	PerkinElmer S-Swafer in the S1 configuration
Settings	Established by the Swafer utility software – see Figure 2

Results and Discussion

Figure 3 shows the total ion chromatograms (TIC) of four different in-vehicle interiors. Chromatogram A in Figure 3 is from the door interior seal assembly. The door seal assembly is a rubber strip between the window glass and the door frame in the window groove. As the window glass is raised and lowered, water droplets, mist and dust on the glass surface can be removed. Many volatile organic compounds are found in the chromatogram such as aromatics, ketones, esters, alcohols etc. which are used as vulcanization accelerators, stabilizers and solvents. These sorts of compounds provide strong odors (burned, ethereal, sweet and fruity) which may make people feel faint or have a sore throat. Chromatogram B in Figure 3 is from a rubber sealing strip. A large peak in the chromatogram is identified as carbon disulfide which is used as a solvent for sulfur chloride and as a vulcanization accelerator in the rubber industry. Carbon disulfide has a strange bad odor which is similar to rotten eggs. Other compounds in the chromatogram are the amines, morpholine and benzothiazole commonly used as vulcanization accelerators and other short-chain hydrocarbons that are used as solvents such as cyclohexanone. These compounds provide an ammonia like smell as well as a burnt or other unpleasant odor. Chromatogram C in Figure 3 is from the luggage compartment upholstery including felts, polyethylene (PE) and polyethylene terephthalate (PET) plastic. The main compounds are alkanes, alkenes and acetic acid, etc. with odors that range from floral to aromatic to burnt and acidic. Chromatogram D in Figure 3 is from a door panel including polyurethane (PU) foam and plastic. Large amounts of ethyl acetate, methylcyclohexane and a number of aromatics are discovered which provide intense odors (fruity, aromatic and burned). The amount of the compounds identified can be quantified by calibrating the GC/MS with standard mixtures of this compound. Figure 4 shows an example of the sample TIC with the overlaid audio narration and intensity recordings. There are two signals under the TIC, an audio stream (blue) and an intensity stream (purple). The audio narration is stored in a standard WAV file format which can be played back from this screen or from most other media applications. The recorded aroma intensity and the audio data transcribed into text are stored as a comma-separated value (CSV) file which can import into Microsoft® Excel® or other application software.

To further clarify the odor source, vehicle interior samples were classified according to their materials and analyzed respectively. For example, Figure 5 shows the
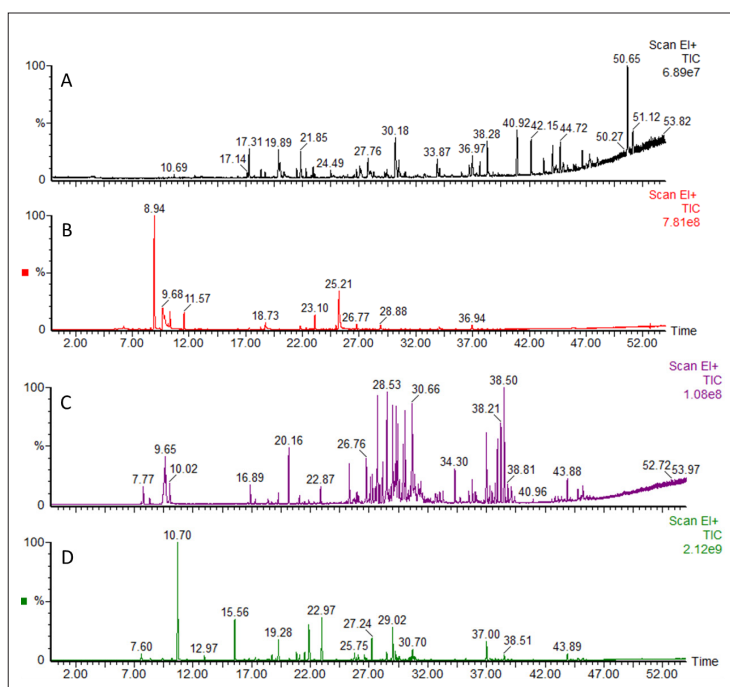

Figure 3. Total ion chromatograms of four samples; (A) Door interior seal assembly, (B) Sealing strip, (C) Luggage compartment assembly, (D) Door panel.
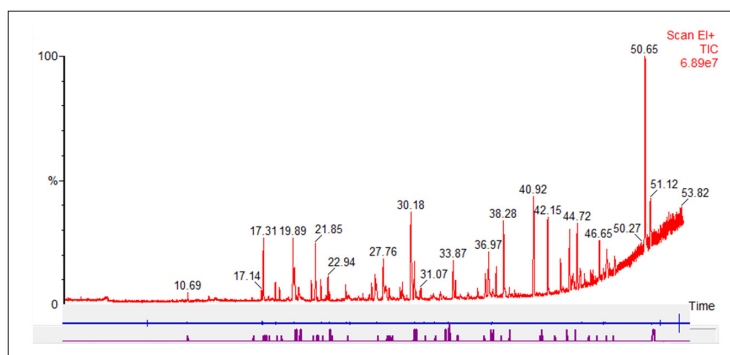

Figure 4. Example of a total ion chromatogram with the overlaid audio narration and intensity recording.

TICs of three materials used in car seats: sponges in seats, PU leathers used around seats and plastic parts. The peak eluting at 28.51 minutes from the sponge sample has an ammonia like smell and was investigated further to identify the compound. The mass spectrum and the search result of the NIST spectral library are given in Figure 6 and 7 which identified the peak as triethylenediamine, an important catalyst for sponge production. The second obvious peak is bis(2-(Dimethylamino) ethyl) ether eluting at 30. 67 minutes which is a foam catalyst used to form porous structure in sponges. The peaks eluting at 39.24, 43.91 and 48.18 minutes are polysiloxanes which are common foam stabilizers in sponge production and together with the foam catalyst these four chemicals have an unpleasant aroma. Table 6 summarized the results for the compound source, odor description and strength in three materials that are used in car seat manufacture. Using this information enables the odor source to be identified which helps suppliers to develop new materials with lower emissions.

Table 6. TD-GC/MS- Olfactory Port results.

RT/Min	Compound Name	Compound Use	Odor Description	Odor Strength/1-6	Source
31.70	1-Ethyl-2-Pyrrolidinone	Mold Release Agent	Pungent	5	Plastic Part
10.20	2-Butanone	Solvent	Acetone	1	PU Leather
17.32	Toluene	Solvent	Burned	2	
17.51	Formamide, N,N-dimethyl-	Solvent	Ammonia	2	
18.71	Isobutyl Acetate	Solvent	Fruity	1	
25.13	Cyclotetrasiloxane, Octamethyl-	Foam Stabilizer	Burnt	2	
31.05	p-Trimethylsilyloxyphenyl-bis(trimethylsilyloxy)ethane		No Smell		
36.96	1-Triethylsilyloxyheptadecane		No Smell		
28.51	Triethylenediamine	Catalyst	Ammonia	2	Sponge
30.67	Bis(2-(Dimethylamino)ethyl) ether	Foam Catalyst	Aromatic	1	
39.24	Hexasiloxane, Tetradecamethyl-	Foam Stabilizer	Aromatic	1	
43.91	Heptasiloxane, Hexadecamethyl-		Aromatic	3	
48.18	Heptasiloxane, Hexadecamethyl-		Aromatic	1	

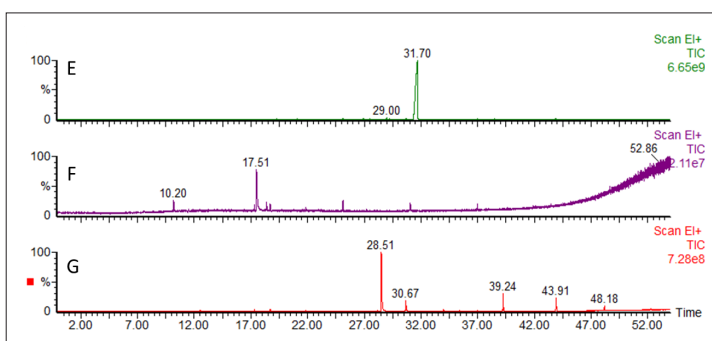*Figure 5.* Total ion chromatograms of three materials used in car seats; (E) Plastic part, (F) Polyurethane leather, (G) Sponge.
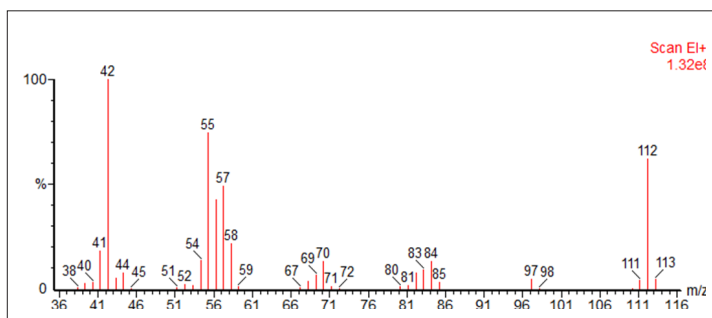

Figure 7. Results from library search on mass spectrum shown in Figure 6.

Figure 6. Mass spectrum from the peak eluting at 28.51 minutes in Figure 5.

Summary

In this study, an olfactory port is added to a TD-GC/MS system which makes it possible to combine the chromatographic, mass spectral and olfactory data from one sample analysis. Users can correlate organoleptic perception to the results obtained with the GC/MS to easily identify which compounds are the main contributors to off-odors in the vehicle.

Reference

1. ISO/FDIS 12219-2, 2012, Interior air of road vehicles - Part 2: Screening method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials - Bag method.

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