Thermal Desorption Screening Analysis of Asphalt Binder Samples Contaminated with Automotive Fluids

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Application Note
Environmental

Abstract
This application note demonstrates a method for using thermal desorption as a way to screen asphalt binder samples for the presence automotive fluids. Automotive fluids such as gasoline, power steering fluid, brake fluid, and motor oil are added to asphalt samples to qualitatively identify the presence of VOC's.

Introduction
In recent years, roadway asphalt has begun to draw attention due to the VOC's that are emitted from the roadway material. When paved fresh, hot roadway asphalt emits numerous VOC's that directly represents potential health concerns for the construction workers performing roadway maintenance and development.[1,2] Moreover, even after asphalt has been laid and dried, asphalt still possesses the ability to emit VOC's as it heats up under the direct sunlight. The VOC's emitted from both fresh and dried asphalts have the potential to undergo chemical reactions in the atmosphere to form aerosols that can impact both human health and climate.[3]

Although asphalt binder materials combined with automotive fluids is a complex mixture of VOC's, thermal desorption has presented itself as an effective solution for initial sampling and screening. Here the CDS 7550S automated Thermal Desorber is combined with GC-MS analysis to directly analyze asphalt samples. For complex and dirty samples, such as asphalt binder, the sample split of the 7550S can be utilized to reduce the mass loading of VOC's entering the flow path of the 7550S to reach the injection port of the GC. The sample splitting feature and inert flow paths of the 7550S are key components in preventing carryover when performing thermal desorption analysis on dirty samples.

Experiment Setup
Asphalt samples were collected from a nearby roadway to the CDS Analytical headquarters in Oxford, PA that had been paved within the last year. Regular, unleaded gasoline was obtained from a nearby gas station. The other fluids were Advanced Auto brand power steering fluid, DOT 3 brake fluid, and SAE 5W-20 vehicle motor oil.

Asphalt samples were then ground down using mortar and pestle, allowing asphalt binder to be separated from stone. Asphalt binder samples were analyzed directly in the 7550S by placing samples into empty, fritted ¼" × 3.5" quartz thermal desorption tubes manufactured by CAMSCO. Each quartz tube is large enough to hold in excess of 0.4 g of asphalt binder sample. Doing so, however, resulted asphalt binder melting inside the tube causing permanent damage the thermal desorption tube. To reduce the signal intensity and avoid destruction of the thermal desorption quartz tubes, asphalt binder samples were placed in fire-polished, constricted quartz tubes commonly used for pyrolysis-GC-MS applications. The constricted quartz tube is 1.5" long with a sample cup located at the top of the tube that is ¼" deep. The OD of the tube 0.1". Approximately 4 mg of asphalt binder was placed into the constricted quartz tube for analysis. Once the asphalt sample was loaded into the constricted quartz tube, this tube was then placed inside the empty, fritted quartz thermal desorption tube (Figure 1). The asphalt binder inside was analyzed with and without spiking regular unleaded

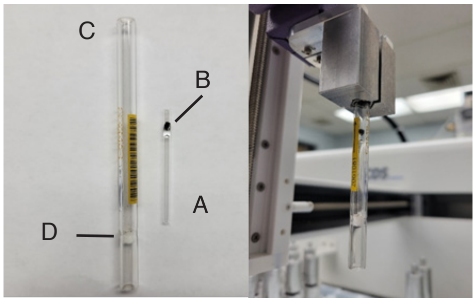

Figure 1. Left: Shown are the constricted quartz tube (A), asphalt sample in tube (B), fritted quartz thermal desorption tube (C), and frit (D). Right: Constricted quartz tube inside the thermal desorption tube being transported by the 7550S.

Table 1:

7550S Thermal Desorber:

Valve oven:	250 °C
GC transfer line:	250 °C
Tube purge flow:	60 mL/min
Pre-heat time:	15 s
Tube Rest temp.:	40 °C
Tube Dry purge temp.:	40 °C
Tube Dry purge time:	0.1 min
Tube Desorb temp.:	300 °C
Tube Desorb time:	8 min
Primary sample tube:	Camsco P/N G60F
Trap Rest temp.:	-20 °C with Peltier
Trap Desorb temp.:	300 °C
Trap Desorb time:	2 min
Trap Type:	CAMSCO P/N CTC30401
Peltier transfer line:	250 °C

GCMS QP-2010

GC conditions:

Column:	Restek Rxi 5Sil MS
Oven temp.:	35.0 °C
Injection temp.:	240 °C
Injection mode:	Split
Column Flow:	1.01 ml/min
Split Ratio:	40.0 : 1
Temp. program:	35.0 °C hold 4 min
	10.0 °C/min to 150.0 °C
	50.0 °C/min to 320.0 °C
	Hold 8.10 min

MS conditions:

Ion Source:	200.00 °C
Interface Temp.:	220.00 °C
Start m/z:	35.00
End m/z:	260.00

gasoline, brake fluid, power steering fluid, and motor oil. Gasoline and brake fluid were diluted to 1% v/v in methanol. Motor oil and power steering fluid were applied directly to the asphalt binder samples. A CDS 7550S automated thermal desorber was employed with the sample split and Peltier options. The VOCs desorbed from the thermal desorption sample tube are first split

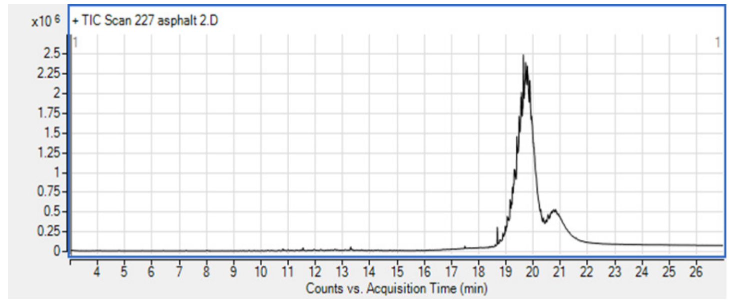

Figure 2. TIC of 4 mg of asphalt binder desorbed at a temperature of 300 °C.

in the 7550S before the Peltier trap at a user-selected split ratio, which was fulfilled by a mechanism electronically controlled by a Mass Flow Controller (MFC).GC-MS was performed using a Shimadzu QP 2010. TD-GC-MS analysis was performed according to the parameters in Table 1. The empty, fritted quartz sample tubes were manufactured by Camsco (P/N G60F). Operating conditions for the 7550S can be found below in Table 1.

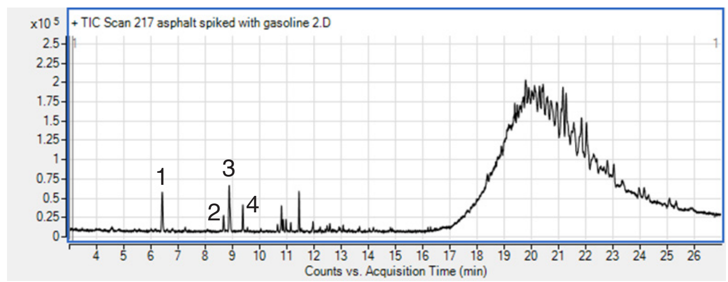

Figure 3. TIC of 4 mg of asphalt binder spiked with gasoline solution with 50% split on the 7550S.

Results and Discussions

Asphalt binder was initially sampled without splitting to see the TIC resulting from VOC's contained within the binder. The chromatogram resulting from thermal desorption of 4 mg of asphalt binder at 300 °C can be seen in Figure 2. The dominant feature of the chromatogram is the large distribution of hydrocarbons that are unable to resolved simply by GC-MS. The TIC is too intense to identify any individual hydrocarbons appearing in the chromatogram. Individual VOC's can start to be identified when different automotive fluids are added into the asphalt binder. This was first done by spiking the asphalt sample with regular, unleaded gasoline. The resulting chromatogram can be seen in Figure 3. The gasoline sample was analyzed using a 75% sample split on the 7550S to attenuate the amount sample reaching the focusing trap and the GC inlet. On the 7550S, a 75% split would mean that 75% of the VOC's desorbed from the sample would go the vent and the other 25% go the analytical focusing trap. Individual VOC's, such as toluene, ethylbenzene, m- and p-xylene, and o- xylene, shown as peaks 1, 2, 3, and 4 respectively, can be identified. Aromatic components are vital components to chemical make up of automotive gasoline. Interestingly, the hydrocarbons from the asphalt look different and are also lower in intensity in Figure 3 compared to

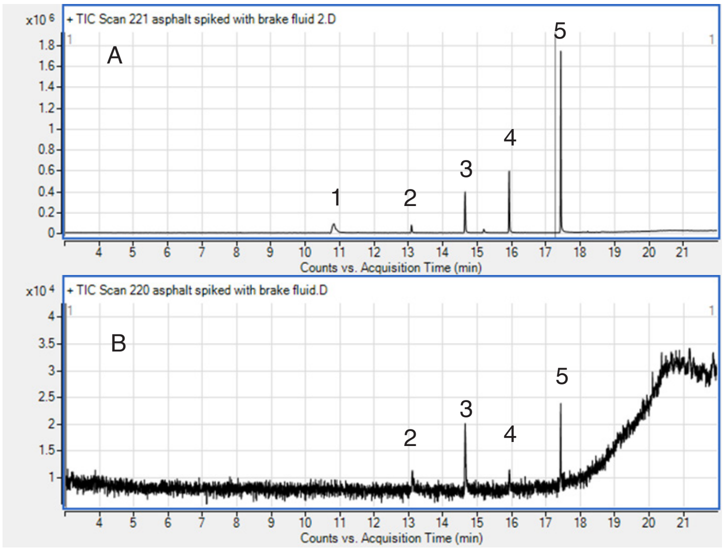

Figure 4. TIC of 4 mg of asphalt binder spiked with brake fluid solution with 50% split (top) and 99% split (bottom) on the 7550S.

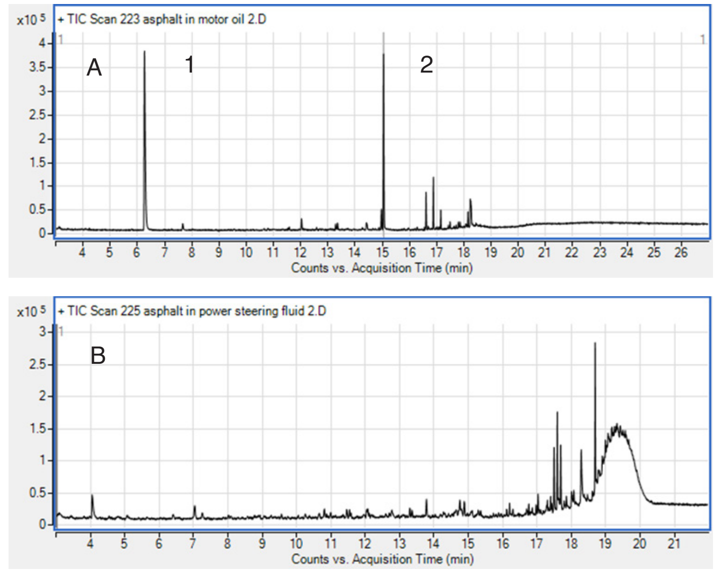

Figure 5. TIC of 4 mg of asphalt binder spiked with motor oil with 50% split (top) and power steering fluid analyzed without split (bottom) on the 7550S.

Figure 2. The decreased signal intensity is in part due to the decreased sample reaching the column because of the 7550S sample split but also likely from matrix effects of the gasoline. This consistent with other observations where the asphalt signal also decreased in the presence of the other automotive fluids as well.

Figure 4 shows asphalt binder samples after being spiked DOT 3 brake fluid utilizing a 50% and 99% split. Observed in the chromatogram in Figure 4a are VOC's such as glycol containing species at a 7550S split of 50%. Diethylene glycol, diethylene glycol monobutyl ether, triethylene glycol monoethyl ether, and triethylene glycol monobutyl ether are peaks 1, 3, 4, and 5 respectively. Many other larger glycol components can be found brake fluid as well, however, are not expected to be seen under typical thermal desorption conditions. Peak 2 was identified as 1-isopropoxy-2-propanol, which can often be found in brake fluid as an additive.

Figure 4b shows a chromatogram when the 7550S split is 99%. In this chromatogram, only the most intense glycols from Figure 4a are present. In the 7550S, sample splitting occurs before the analytical focusing trap. Any contamination of the flow path or trap of the 7550S would be expected to be seen in this chromatogram, however, this chromatogram indicates that the 7550S is resistant to sample carryover. Additionally, the sample split of the 7550S extends the splitting capabilities when combined with the split of the GC injector port. This helps to reduce the mass of sample reaching the GC column and can extend the dynamic range of the GC-MS.

Other automotive fluids, such as pure motor oil and power steering fluid were added asphalt binder samples and were allowed to soak overnight to closely mimic roadway asphalt becoming contaminated with automotive fluids. The chromatograms for motor oil and power steering fluid can be seen in Figures 5a and b respectively. Motor oil was qualitatively analyzed using 50% split on the 7550S. Power steering fluid did not produce high intensity VOC's, therefore, no additional splitting was done using the 7550S. In 5a, VOC's resulting from thermal desorption of motor are observed. Two major peaks, labeled as 1 and 2, were identified as methyl isobutyl carbinol and 1-decene. Both components are known to be used in the production of or as an additive to lubricants such as automotive motor oil. For the power steering fluid on the other hand, while peaks unique to the sample were observed, none could be conclusively identified over the hydrocarbons observed from the asphalt binder. Power steering fluid is primarily composed of heavy paraffinic petroluem distillates, so it is not surprising that power steering fluid presents a greater analytical challenge for identifying VOC's by TD.

Conclusions

This application note has showcased a method for performing a qualitative analysis of VOC's resulting mixture of roadway asphalt binder and various automotive fluids. Asphalt binder presents a unique analytical challenge in that it continues to release a vast array of VOC's. When contaminated by automotive fluids, however, thermal desorption can be utilized to detect key identifying VOC's for fluids such as gasoline, brake fluid, motor oil, and power steering fluid. The 7550S thermal desorber is well-suited for applications such as this where desorption directly from asphalt binder is needed. The sample split option on the 7550S can be utilized for dirty samples such as the asphalt binder to reduce the amount sample reaching the GC injection port and remains resistant to carryover from run to run.

References

1. Cui, P.; et. al.; VOC emissions from asphalt pavement and health risks to construction workers, Journal of Cleaner Production, 2019.
2. Espinoza, J.; et. al.; Evaluation of Reductions in Fume Emissions (VOCs and SVOCs) from Warm Mix Asphalt Incorporating Natural Zeolite and Reclaimed Asphalt Pavement for Sustainable Pavements, Sustainability, 2020.
3. Khare, P.; et. al.; Asphalt-related emissions are a major missing nontraditional source of secondary organic aerosol precursors, Atmospheric Science, 2020.