Application of HS-SPME/GC-MS for hydraulic fluid compound detection in jet fuels

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INTRODUCTION

Headspace solid phase microextraction/gas chromatography (HS-SPME/GC) is a modification of traditional GC that extracts volatile components from the headspace of a sealed vial containing the evidence. The main advantage of HS-SPME/GC is that it exclusively transports volatile components of the sample through the column, which is ideal for GC analysis[1]. When this technique is paired with mass spectrometry (MS), as most forensic GC methods are, the analyst has access to a plethora of chemical information. In this work, we used HS-SPME/GC-MS to analyze jet fuel samples contaminated with hydraulic fluids. Hydraulic fluids are hydrocarbon fluids used in engine-powered vehicles to transfer energy and provide lubrication among other functions. These materials can be made using petroleum-based or synthetic-based manufacturing processes. While petroleum-based hydrocarbon fluids are refined directly from crude oil distillates, synthetic-based hydrocarbon fluids are manufactured by organic synthesis. Inter-product variations exist between and within classes due to industrial additives[2], which makes it challenging to develop a comprehensive detection method. Nevertheless, this research work demonstrates that HS-SPME/GC-MS can detect a variety of hydraulic fluid contaminants in jet fuels.

MATERIALS & METHODS

Six different aviation hydraulic fluids, four synthetic-based and two petroleum-based, were used in this study. They were each separately spiked into jet fuel samples at a 1% concentration level. **Table 1** below contains information regarding each hydraulic fluid.

Hydraulic Fluid	Classification	Additional
MIL-PRF-87257C	Synthetic	Polyol ester-based
MIL-PRF-87252C	Synthetic	Polyalphaolefin-based
MIL-PRF-83282D	Synthetic	Polyalphaolefin-based
HyJet IV-A	Synthetic	Phosphate ester-based
MIL-PRF-5606H	Petroleum	Mineral oil-based
MIL-PRF-5606J	Petroleum	Mineral oil-based

Table 1. Classifications and additional information for the six hydraulic fluids used in this work.

RESULTS & DISCUSSION

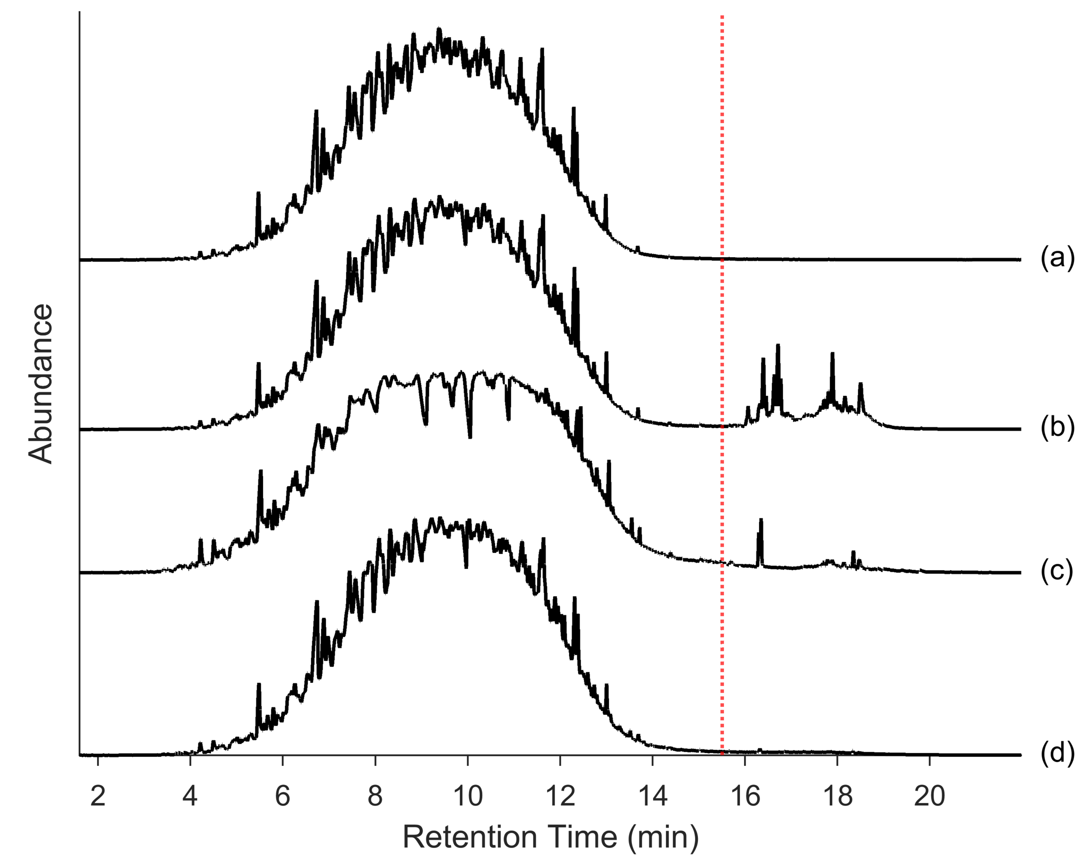

Figure 1. Total ion chromatograms of (a) neat jet fuel, and jet fuel samples spiked with a 1% concentration of a contaminant: (b) synthetic-based hydraulic fluid 83282D; (c) petroleum-based hydraulic fluid 5606J; (d) petroleum-based hydraulic fluid 5606H.

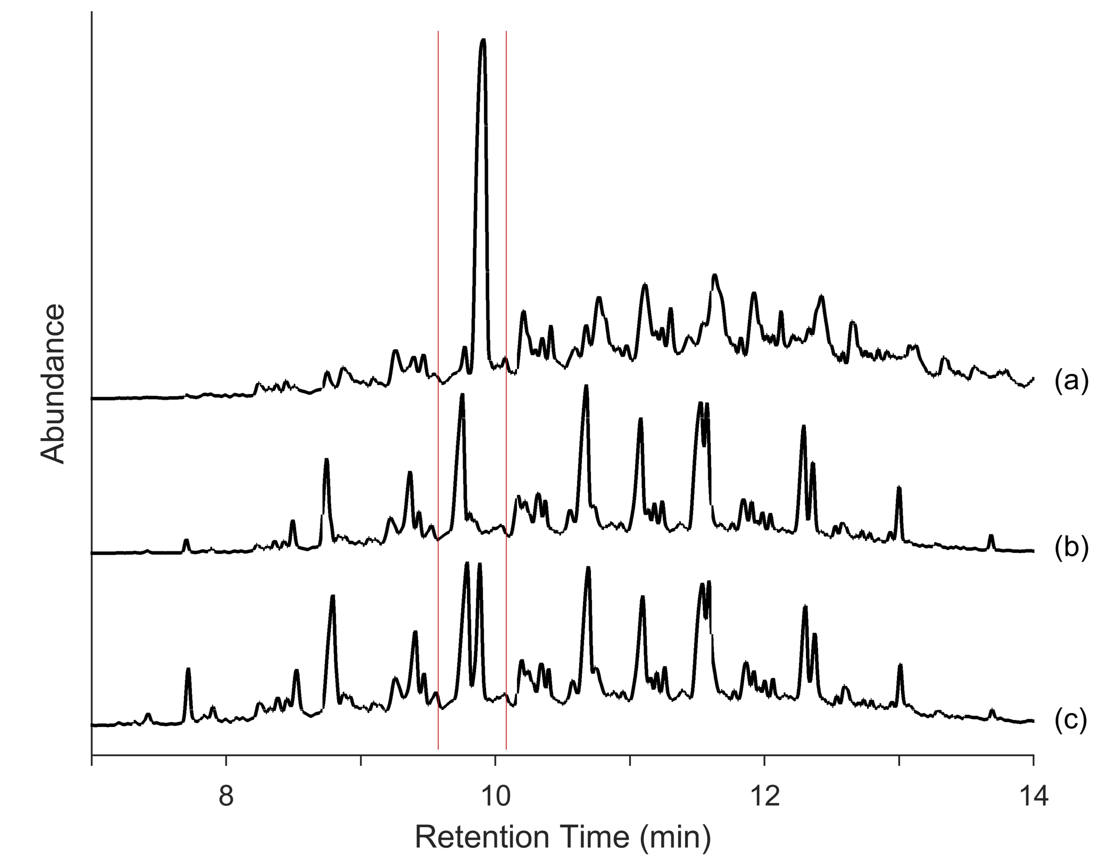

Figure 2. SIM chromatograms targeting 57, 205, and 220 m/z ions: (a) Petroleum-based hydraulic fluid 5606H; (b) Neat jet fuel; (c) Jet fuel contaminated with 5% 5606H.

Figure 1 above displays chromatograms for neat and contaminated jet fuel samples. For demonstrative purposes, only one synthetic-based hydraulic fluid contaminant is shown. However, all synthetic-based contaminants were readily detected in the total ion chromatograms (TICs) due to late-eluting ester-based compounds. Petroleum-based hydraulic fluid 5606J also had late-eluting compounds. Petroleum-based fluid 5606H, however, did not have characterizing compounds visible in the TIC when spiked in jet fuel. Selected ion monitoring (SIM), an MS acquisition method that targets ions of interest, was used to detect butylated hydroxytoluene (BHT), a compound in 5606H. **Figure 2** compares SIM chromatograms for jet fuel and 5606H samples.

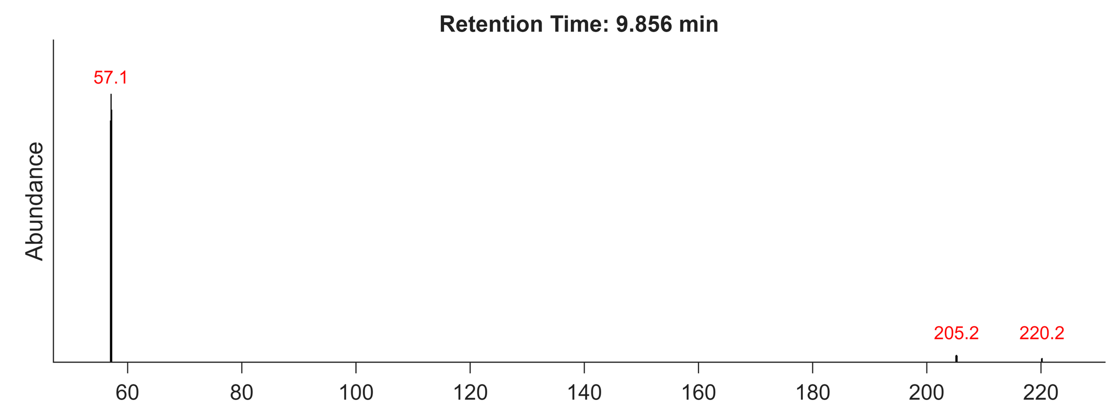

Figure 3. A SIM mass spectrum of neat jet fuel. The targeted ions are *m/z* 57, 205, and 220, which are characteristic of BHT.

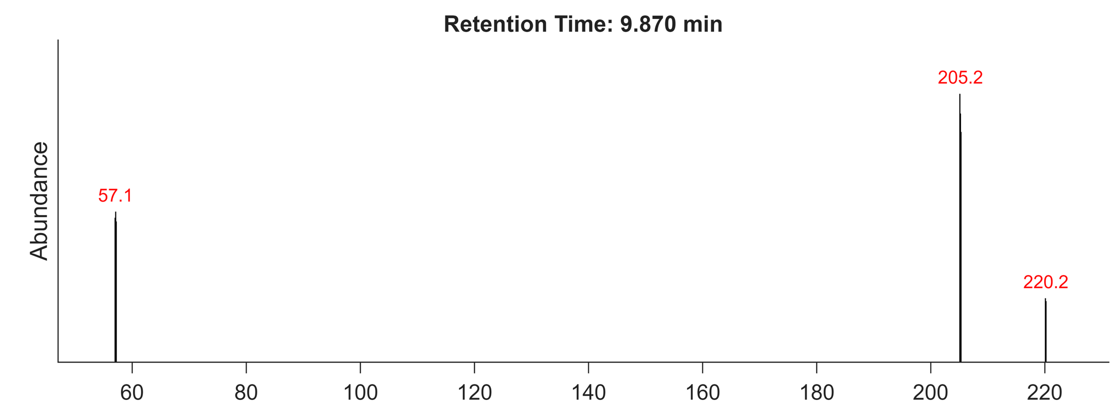

Figure 4. A SIM mass spectrum of jet fuel contaminated with 5% 5606H. The targeted ions are *m/z* 57, 205, and 220, which are characteristic of BHT.

Figures 3 & 4 display the SIM mass spectra for neat jet fuel and fuel spiked with 5606H, respectively. The ion ratios in **Figure 4** are characteristic of BHT and thus reveal the presence of contaminant 5606H. The traditional scan mode and SIM mode can be used simultaneously, meaning there is not an information trade-off when activating SIM.

ACKNOWLEDGEMENTS

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1. Robards, K.; Ryan, D. Principles and Practice of Modern Chromatographic Methods. Elsevier. 2022; 145-245. https://doi.org/10.1016/C2019-0-03803-4.
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MATERIALS & METHODS

GC-MS analysis was performed using an Agilent system comprised of a 7890A gas chromatograph, 5975C mass spectrometer, and GC Sampler 80 (Agilent, Santa Clara, CA). Chromatographic separation was achieved with a HP-5ms column (30 m x 0.25 mm x 0.1 µm, Agilent) with helium as the carrier gas at a flow rate of 1 mL/min. The oven program is shown in **Table 2**. The fiber used for headspace sampling was a polydimethylsiloxane SPME fiber (23 gauge, 100 µm) from Sigma-Aldrich (St. Louis, MO). MassHunter Workstation software (Agilent, Version B.06.00) was used for data acquisition. The mass detector was programmed in scan and SIM mode with selected ions characteristic of butylated hydroxytoluene (BHT) (57.1, 205.2, and 220.2 *m/z*; all ±0.1). The 2008 NIST/EPA/NIH Mass Spectral Library in MassHunter was used for data analysis. MATLAB R2025a (version 25.1.0.2943329, MathWorks, Natick, Massachusetts, USA) was used to generate **Figures 1-4**.

Oven Program Step	Condition
Initial temperature	60 °C
Hold time	2 min
Rate #1	13.333 °C/min
Temperature #1	260 °C
Hold time #1	0 min
Rate #2	5 C/min
Temperature #2	285 °C
Hold time #2	0.25 min

Table 2. The oven program used for chromatographic separation.

CONCLUSIONS

With SIM, this HS-SPME/GC-MS method can detect and identify different hydraulic fluid contaminants in jet fuel regardless of retention overlap. In future work, we will expand this analysis to capture more diverse contaminants, including other hydrocarbon fluids, fuel additives, and hydrophilic chemical species.

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