Utilization of Comprehensive Two-Dimensional Gas Chromatography (GCxGC) for Comparison of Automobile Lubricants for Crime Scene Investigations

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Introduction

Experiments using GC-MS to compare automobile lubricants for the purpose of matching spots left at a crime scene to those contained in a suspect vehicle have been attempted in the past with little or no success. The lack of success can be attributed to the complexity of such matrices, which do not lend themselves well to single-dimension chromatography. There is a wealth of information that can be obtained from these samples if the appropriate analytical tools are utilized. Motor oils, brake fluids, and hydraulic steering fluids can vary greatly depending on their type and manufacturer. The work contained in this poster will focus primarily on the differentiation of motor oils. Many types of motor oils exist, including conventional, fully synthetic, and synthetic blends. These oils also contain additives packages, including corrosion inhibitors, viscosity modifiers, and other compounds that can be used to differentiate one oil from another. All of these things lead to a great number of chemical features that can be used to create a fingerprint to differentiate oils from different vehicles.

This study will focus on the development of a method utilizing comprehensive two-dimensional gas chromatography (GCxGC) with time-of-flight mass spectrometry to effectively differentiate motor oils from various vehicles. The increased chromatographic resolution, detectability enhancement, and structured chromatograms inherent to GCxGC separations make it well suited for successfully fingerprinting motor oils for the purpose of crime scene investigations.

Experimental Methodology

The data presented here were produced using the LECO Pegasus® 4D TOFMS, a GCxGC-TOFMS instrument, in conjunction with the ChromaTOF® software package.

The motor oil samples were taken directly from each car's dipstick. The oil was directly placed inside autosampler vials and diluted with hexane to a concentration of approximately 0.17 g/mL.

The GCxGC-TOFMS analysis conditions are shown below in Table 1.

Carrier Gas	Helium, corrected constant flow control
Injection Volume (µL)	1
Split Ratio	100:1
Flow Rate (mL/min)	1.0
Primary Column	60 m x 0.25 mm x 0.25 µm Rxi-1ms
Secondary Column	1.1 m x 0.15 mm x 0.15 µm Rxi-17Sil MS
Primary Oven Ramp	40°C for 0.5 min then 2°C/min to 300°C with 20 min hold
Secondary Oven Ramp	+10°C offset from primary oven
Modulator Offset	25°C
Modulation Period	5 s period (1.6 s hot)
Transfer Line Temperature	300°C
Ion Source Temperature	200°C
Mass Spec Acquisition Delay (s)	1200
Mass Range (m/z)	40-400
Acquisition Rate (spectra/s)	100
Electron Energy for EI (V)	-70
Collection/Processing Software	ChromaTOF 4.44

Table 1. Experimental conditions for the GCxGC-TOFMS analysis of motor oil.

Table 2 lists the motor oil samples analyzed with details of the oil's source vehicle's make, model, and year, approximate mileage, and whether or not the oil comes from a recent oil change. Only a representative selection of the samples are displayed on this poster.

Motor Oil Samples					
Sample #	*Make*	*Model*	*Year*	*Approx. Mileage*	*Pre/Post Oil Change*
1	Toyota	Camry	1999	142,000	Pre
2	Toyota	Camry	1999	142,000	Post
3	Toyota	Camry	2005	49,000	Pre
4	Ford	Club Wagon	1995	66,500	Pre
5	Toyota	Venza	2009	20,800	Pre
6	Toyota	Venza	2009	20,800	Post
7	Honda	Fit	2011	8,500	Pre
8	Honda	Fit	2011	8,500	Post
9	Lexus	RS350	2007	85,000	Pre
10	Lexus	RS350	2007	85,000	Post
11	Nissan	Quest	2004	164,000	Pre
12	Chrysler	Town & Country	2006	78,000	Pre
13	Chevy	Tahoe	2009	55,400	Pre

Table 2. Description of the source vehicles for the motor oil samples analyzed.

Results

Figure 1 shows an overlaid 1D chromatogram for two of the motor oil samples. The extremely complex samples are only discernible from the overall peak apex of the unresolved hydrocarbon compounds and not from individual components.

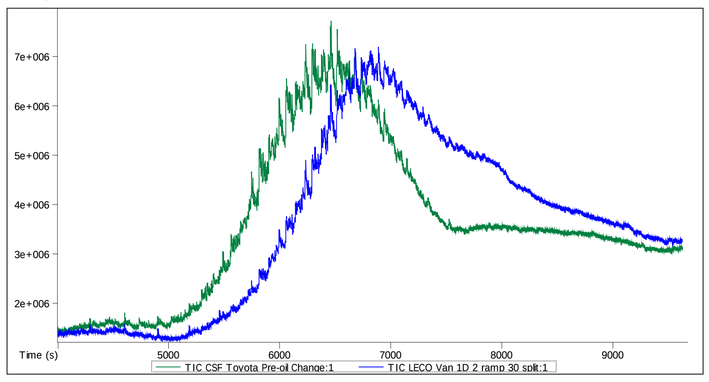

Figure 1. GC-MS motor oil samples from the 1999 Toyota Camry and the 1995 Ford Club Wagon.

The four figures displayed below are GCxGC contour plots of motor oils from four different vehicles, all before any recent oil changes. The contour profile of the hydrocarbon mass is different for each, and many components separated from the main mass can be used for fingerprint matching methods.

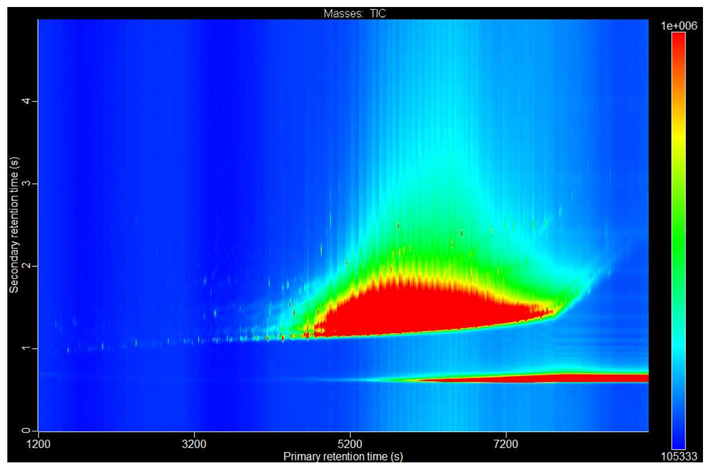

Figure 2. GCxGC-TOFMS TIC contour plot of the oil from the 2005 Toyota Camry pre-oil change.

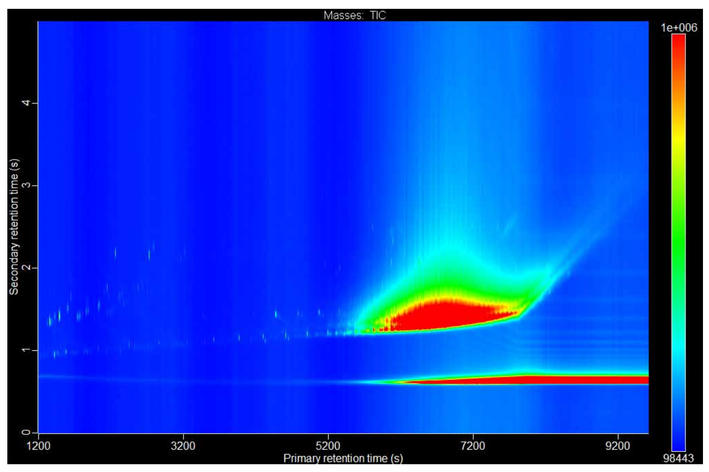

Figure 3. GCxGC-TOFMS TIC contour plot of the oil from the 1995 Ford Club Wagon pre-oil change.

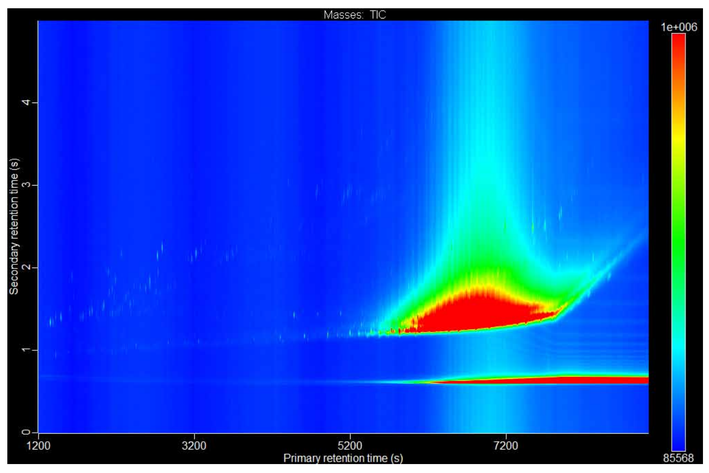

Figure 4. GCxGC-TOFMS TIC contour plot of the oil from the 2004 Nissan Quest pre-oil change.

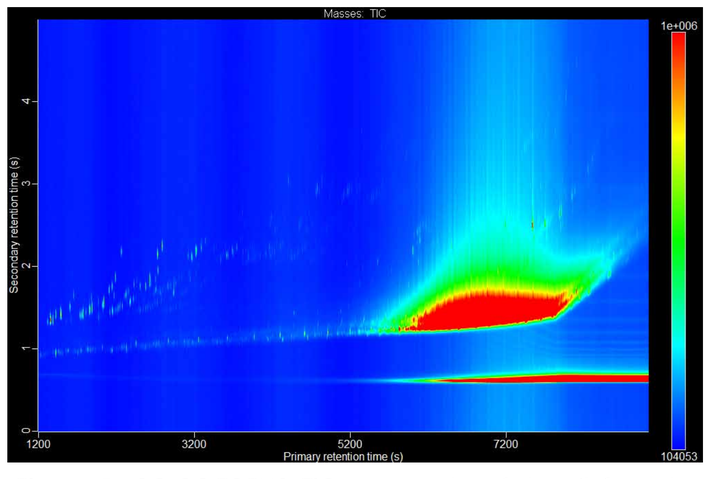

Figure 5. GCxGC-TOFMS TIC contour plot of the oil from the Toyota Venza 2009 pre-oil change.

The figure pairs shown below demonstrate pre- and post-oil change GCxGC contour plot comparisons. Areas demonstrating peaks lost after the oil change are highlighted with red circles.

For the 1999 Toyota Camry, little change was exhibited aside from a few late-eluting compounds.

For the 2011 Honda Fit, there were many more compounds in the matrix isolated from the hydrocarbon mass, many of which decreased in concentration after the oil change. A number of peaks were removed after the oil change, while one of the highlighted peaks appeared after the oil change, standing out in the hydrocarbon mass due to high intensity.

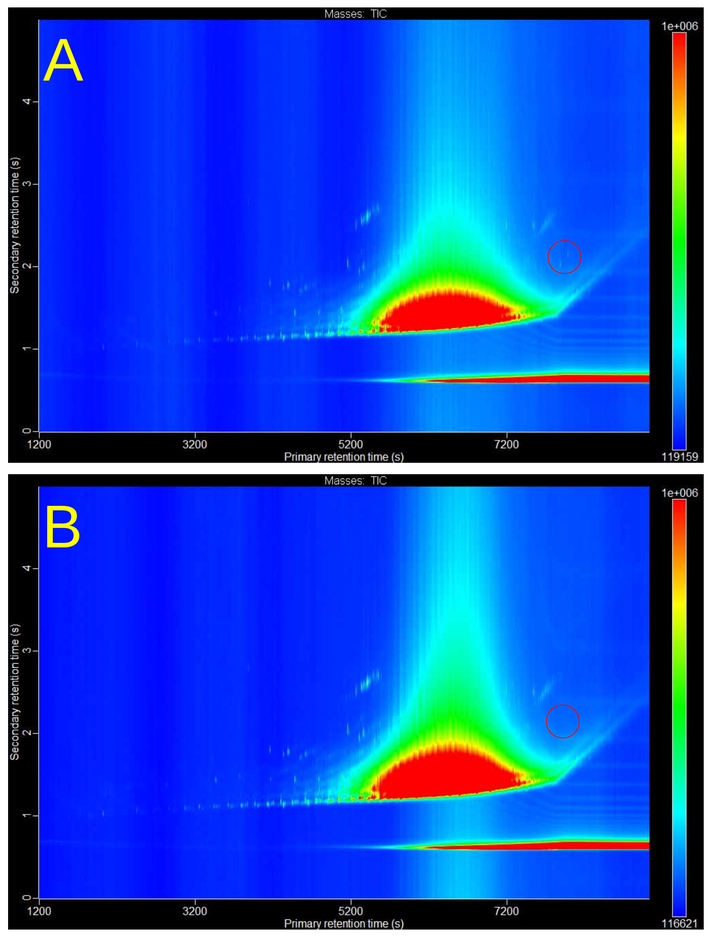

Figure 6. GCxGC-TOFMS TIC contour plots of the motor oil from the 1999 Toyota Camry (A) pre-oil change and (B) post-oil change.

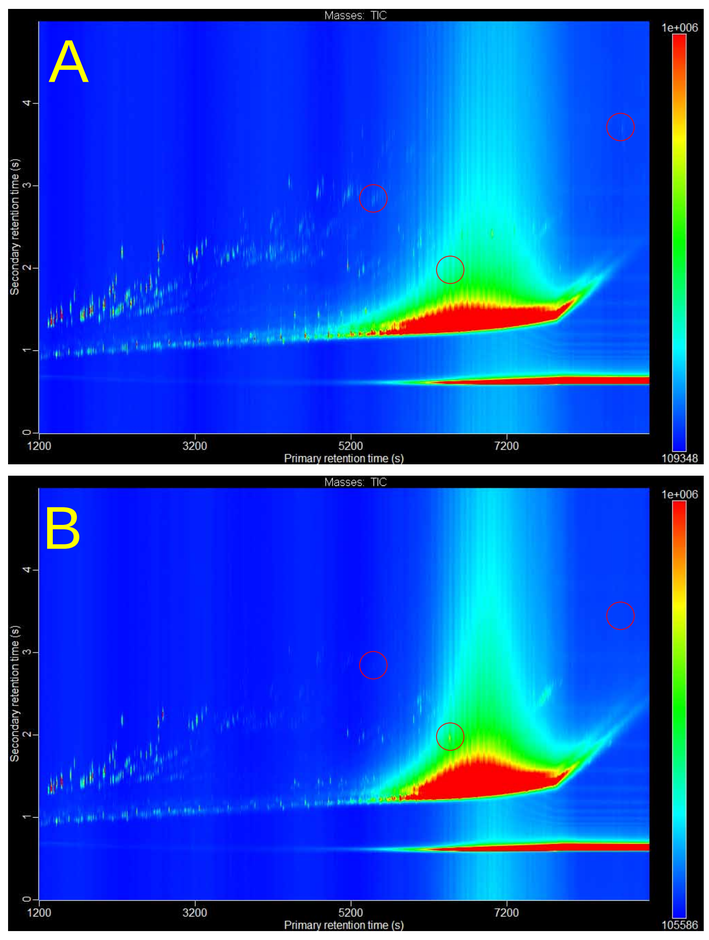

Figure 7. GCxGC-TOFMS TIC contour plots of the motor oil from the 2011 Honda Fit (A) pre-oil change and (B) post-oil change.

Conclusions

The LECO Pegasus 4D GCxGC-TOFMS system was successfully used to analyze motor oil for fingerprinting. The preliminary results show that these samples can be differentiated from one another by the overall hydrocarbon mass profile and by individual components separated from the main mass. Oil changes ended up affecting the oil profile less drastically than expected.

Additional work to be performed includes further optimization of run conditions, confirmation of marker compounds with standards, and testing of oils exposed to the environment.