

# A Method for Analyzing Fuel in Oil Samples for Improved Reproducibility and Recovery

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## Key Words

- Fuel in Engine Oil
- PTV Injector
- Residual Gasoline
- Hydrocarbons

## Introduction

Residual gasoline or diesel fuel in engine oil has been a difficult type of sample for Gas Chromatographic analysis. This analysis is used to monitor the wear condition of an engine. When the fuel level in engine oil rises, this may indicate ring wear or some other wear problem. With large industrial engines, this monitoring is especially important because of the expense of maintenance on these engines. Gas Chromatography is a good technique for this monitoring because of its ability to separate and quantitate small amounts of similar hydrocarbons.

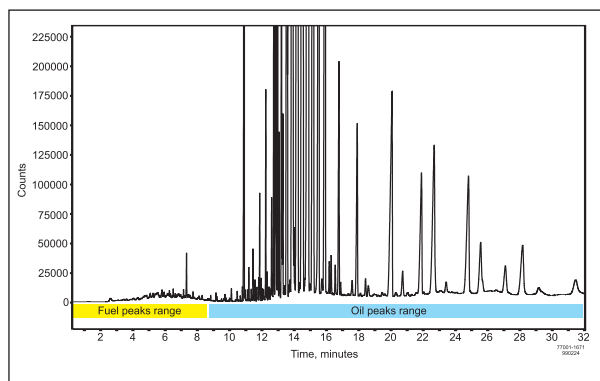


Figure 1.

Used engine oil contains a small amount of light hydrocarbons in a matrix of heavy hydrocarbons, and may be viscous and contaminated with solid residues. In addition, the small amount of light hydrocarbons is made up of a large number of components, making quantitation very difficult.

## Description

The ideal Gas Chromatographic technique for these samples would allow reproducible injection of samples with no preparation or dilution steps. Diluting an oil to reduce sample handling and volume reproducibility problems is not practical in this analysis for two reasons. First, dilution requires accurate measurement of the diluting solvent, which adds another step with its possible error. Second, the solvent used to dilute the samples will interfere with the measurement of the lighter hydrocarbons. Injection of the undiluted sample into the Capillary column of the GC can be accomplished with several techniques. Split injection onto a small-bore column, Cold On-Column injection into a wide-bore column, Direct injection onto a wide-bore column, and injections into a Programmed Temperature Vaporizing (PTV) inlet are all possible techniques. These four inlet types are shown graphically in Figure 2. We will look at each of these techniques and compare advantages and disadvantages of each.

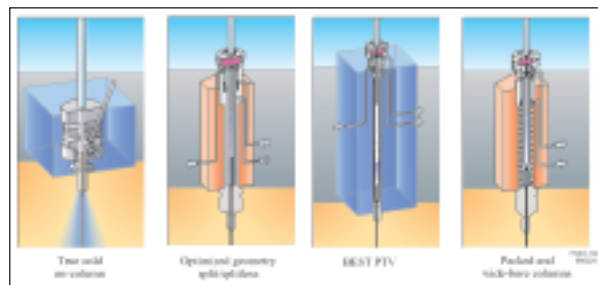


Figure 2: Injectors

The most common injection technique for liquid hydrocarbon samples in Gas Chromatography is vaporizing the sample into a Split/Splitless inlet. For this type of sample, however, the wide hydrocarbon range can cause heavy component discrimination, leading to poor reproducibility. Because of the very high boiling range of the engine oil samples, the inlet must be operated at temperatures exceeding 300°C. The lighter components in the sample vaporize so quickly at this temperature that discrimination may occur. If an inlet is not designed to minimize this discrimination, the performance with this type of sample is poor.

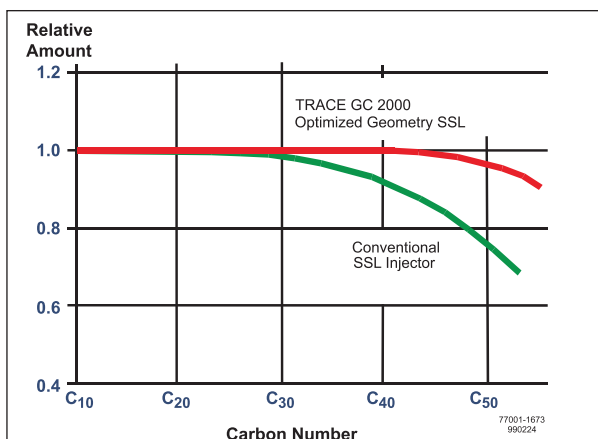


Figure 3: Optimized Geometry Split/ Splitless injector gives discrimination free sample transfer over a wide range of carbon numbers.

Cold On-Column injection would seem to be ideal for this type of sample. The Cold On-Column technique eliminates the high molecular weight compound discrimination that occurs with some vaporizing inlet techniques. Samples must be clean for this injection technique, however, since the sample is deposited as a liquid on the first few centimeters of the column. There must be no residue left from the samples or the column rapidly becomes contaminated. The presence of wear metal particulates or other solid residues in most used oils makes this type of sample unsuitable for On-Column injections.

Direct injection onto a Megabore column is possibly the simplest injection technique, but places some requirements on the sample. In this injection technique, a very small sample is injected into a hot inlet and the vaporized sample is all transferred to the column. Reproducible injection of the small sample size required for direct injection is difficult in part due to the viscosity of the oil matrix. Syringe repeatability is highest with low viscosity liquids and volumes between 10 and 90% of the syringe capacity. For the standard 10  $\mu\text{L}$  syringe, injections of greater than 1  $\mu\text{L}$  of this sample would exceed the capacity of the column and cause poor separation. Use of a smaller capacity syringe such as the 0.5  $\mu\text{L}$  "plunger in needle" syringe helps to overcome the difficulty volume repeatability. The use of Megabore columns has one other disadvantage with these samples in that the resolution of the components of interest is less. This places a greater burden on the data system for accurate placement of the baseline of the peaks. The better-resolved peaks from the smaller capillary columns are much easier to quantitate. Small capillary columns are not amenable to this direct injection technique.

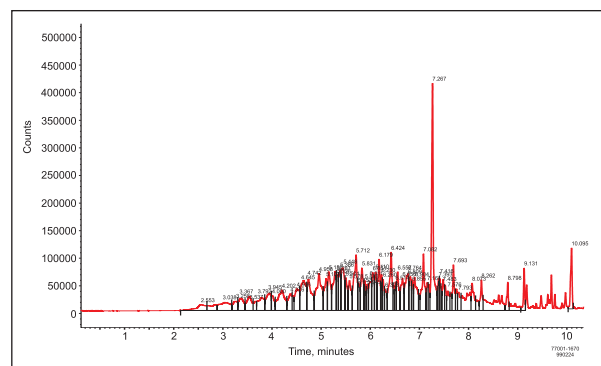


Figure 4: Expanded view of fuel peaks showing baseline

Injection into a Programmed Temperature Vaporizing inlet may be the best technique for these samples since it is designed to minimize the above problems. It is one of the less common inlet types in use, but has many advantages. In this injection technique, the sample is placed into the cold inlet liner as a liquid, then the inlet is rapidly heated to vaporize the components and transfer them to the column. This inlet can operate in Split mode, and even in a Large Volume mode with backflush of the inlet to vent heavier components to waste. This is the technique that is best suited to these samples. This technique allows the injection of relatively large samples, minimizing the syringe reproducibility error. The technique also allows the incremental vaporization of the sample. This means that a sample size that is too large for the column may be used if only part of the sample is vaporized. This also gives a better detection limit since there is a concentration effect using this technique. The method analysis time is improved since the heavier components are not sent through the column, but rather are vented with the inlet backflush. Any non-volatile residues remain in the inlet liner that can easily be changed to maintain optimum performance. Some of the features of the PTV inlet are shown in Figure 5.

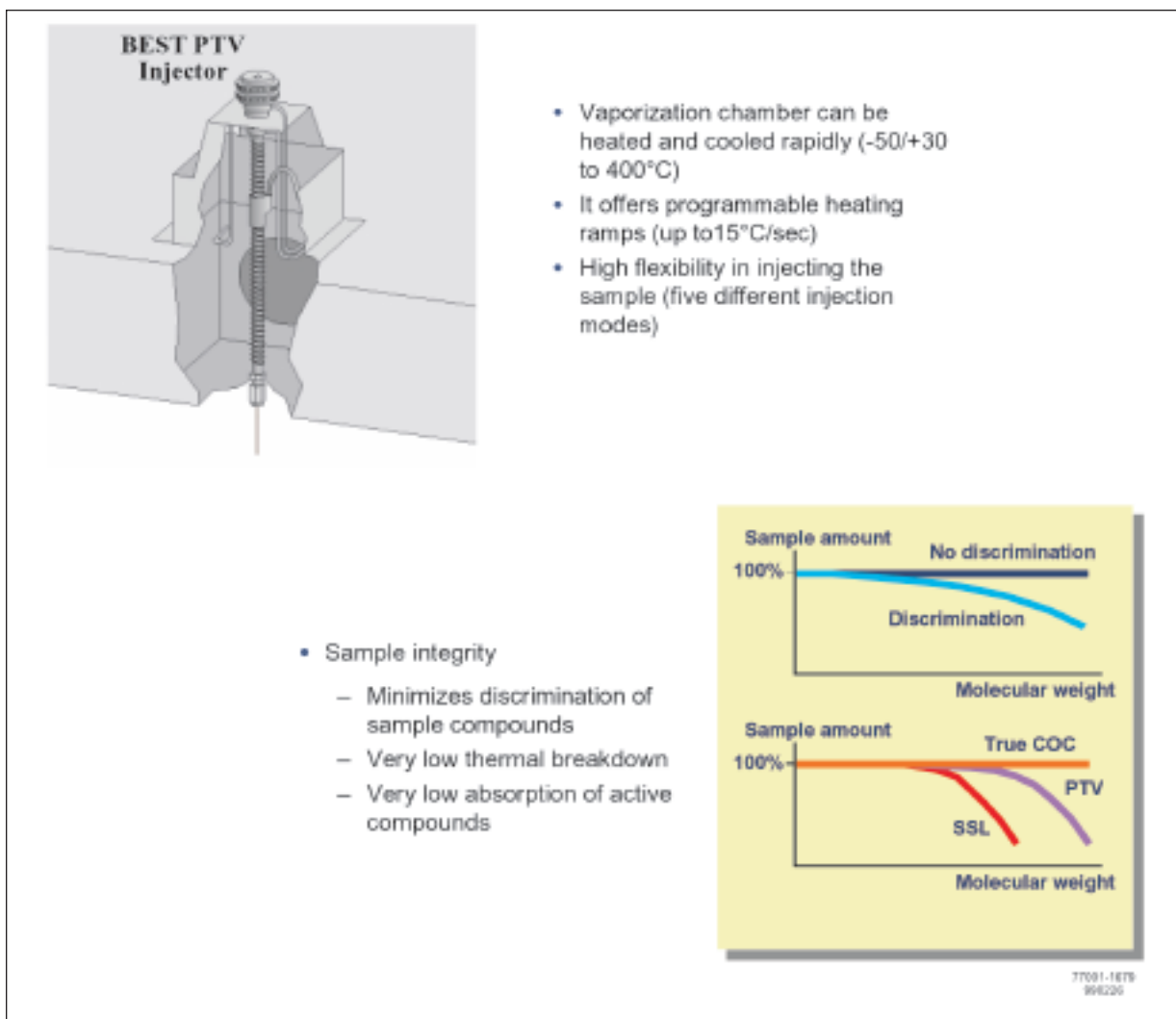


Figure 5. PTV Features

## Conclusion

This presentation describes improvements in all these problem areas. Repeatable injection is accomplished with an autosampler of uniquely flexible pro-grammability. Sample draw rate, injection rate, and delay times for all operations are optimized for viscous samples. A Split/Splitless inlet optimized for even temperature distribution at high inlet temperatures is essential for operation with this sample type. The reproducibility of the TRACE™ GC 2000 Split/Splitless injector is shown in Table 1. The reproducibility of injections for the PTV inlet is shown in Table 2.

FUEL-IN-OIL ANALYSIS - SPLIT INJECTION 50:1

	SUM - FUEL	SUM - OIL 1	SUM - OIL 2
Run # 1	15747680	53339397	136151390
Run # 2	15443682	53456751	136455214
Run # 3	15201037	53157557	135744503
Run # 4	15212513	53169409	135761857
Run # 5	15210171	53342670	136204774
Run # 6	15217951	53355338	136250730
Run # 7	15025132	53459981	136481902
Run # 8	15086992	53251761	135986049
Run # 9	15199701	53799424	137451955
Run # 10	15072359	53688923	137120653
Minimum	15025132	53157557	135744503
Maximum	15747680	53799424	137451955
Mean	15241722	53402121	136360903
Std Dev	211385	208877.7	522859.3
%RSD	1.387	0.391	0.405

Table 1.

## Reproducibility of PTV Injector

### SPLIT INJECTION MODE 1 µL

COMPOUNDS	AVERAGE PEAK AREA (COUNTS)	% RSD
C <sub>11</sub>	260710	1.1
C <sub>12</sub>	268478	1.0
C <sub>14</sub>	261899	1.0
C <sub>20</sub>	257738	0.6
C <sub>24</sub>	268059	0.8
C <sub>26</sub>	256264	1.0
C <sub>30</sub>	264393	0.8
C <sub>34</sub>	282190	1.2
C <sub>36</sub>	267484	1.5
C <sub>38</sub>	261301	1.6
C <sub>40</sub>	255546	1.6

Table 2.

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