

High Throughput Mineral Oil Analysis (Hydrocarbon Oil Index) by GC-FID using the Agilent Low Thermal Mass (LTM II) System

Application Note

Environmental Analysis

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Abstract

Cycle time for GC-FID analysis of mineral oil in environmental samples was dramatically reduced and sensitivity increased by fast oven temperature programming using an LTM II oven module. Regulated method requirements for environmental analyses of soil and water extracts are met using splitless injection with an analysis time for the C10-C40 hydrocarbon fraction of less than 3 min. Cool-down time is less than 2 min, resulting in an injection-injection cycle time of 5 min. Method performance criteria, including repeatability, linearity and solute discrimination are presented.



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Introduction

Environmental contamination by hydrocarbon fractions, such as diesel or motor oil, is currently measured using GC-FID. This method, also called hydrocarbon oil index (HOI), mineral oil or total petroleum hydrocarbon (TPH) determination is one of the most important applications in environmental analysis, representing the highest sample loads in many laboratories. For analysis, samples (water, soil, sediment) are extracted by an apolar (hydrocarbon) solvent with a boiling point between 36 °C and 69 °C (for example, hexane). The extract is cleaned by passing over Florisil (to retain more polar solutes such as lipids), concentrated by N₂ blowdown (or Kuderna-Danish) and analyzed by GC-FID [1]. The fraction eluting on an apolar (HP-1, HP-5) column between decane (C₁₀) and tetracosane (C₄₀) is defined as mineral oil or HOI, over which the area is summed for quantitation.

The ISO 9377 method specifies the use of a column with a high phase ratio (thin film) to facilitate elution of C₄₀. GC oven program conditions should, however, also allow the separation of the extraction solvent from the first peak (decane) and therefore low initial temperatures (35 °C–40 °C) are often necessary. An important method requirement is that the injection method should minimize solute discrimination. The method specifies that the relative mass response for tetracosane (C₄₀) and eicosane (C₂₀) should be higher than 0.80. Typically, the analysis is performed using a 10–30 m column using splitless, PTV, or cool on-column injection and oven programming from 40 °C to 340 °C at 10–20 °C/min, resulting in analyses times in the order of 20–30 min [2]. Oven cool-down time to the low initial temperature typically requires an additional 5 min or more, resulting in a total cycle time of 30 min or longer.

Currently, environmental laboratories are seeking ways to improve throughput and decrease cost per sample. By adding an LTM II module to an Agilent 7890A GC system with SSI inlet, Agilent ALS, and FID significantly improved cycle times can be achieved. In this application note, optimized method conditions and performance metrics are presented. Cycle times of 5 min are demonstrated, while still meeting all method requirements.

Experimental Conditions

Solutes and Sample

An alkane standard containing even numbered n-alkanes from C₁₀ to C₄₀ was purchased from Restek (cat no 31678, Restek, Bellefonte, USA). The sample was diluted to 5 ng/μL in hexane. Mineral oil calibration was done using a 1:1 mixture of diesel and motor oil (cat no 31630, Restek). Calibration samples were prepared at concentrations between 40 and 1,000 mg/L in hexane. In addition, a reference sample from RIVM (NMI, the Netherlands) containing diesel and motor oil was used. This sample, was diluted at 1,000 mg/L in hexane.

GC-FID Conditions

Analyses were performed on an Agilent 7890A GC system equipped with a S/SSI inlet, FID and a five inch format LTM II column module containing a 10 m × 0.32 mm id × 0.1 μm DB-5HT (p/n 123-5701LTM). Non-coated but deactivated pieces of fused silica (each 0.5 m × 0.32 mm id) were used to connect the column to SSI inlet and FID.

The fast GC conditions are listed in Table 1. As seen, the LTM column is operated in constant flow mode. The EPC takes into account the fact that two 50 cm pieces of tubing are connected to the column and that these pieces of tubing are at 340 °C isothermal (while the main part of the column is heated by the LTM module). These column and connecting fused silica dimensions are input into column configuration. The overall result is accurate, constant flow mode.

Table 1. GC-FID Setpoints for Fast Mineral Oil Analysis Using a Low Thermal Mass Oven

Injection	1 μL, splitless (0.4 min purge delay), 350 °C
Inlet liner	Split/splitless p/n 5183-4647 (bottom taper, glass wool near top, 4 mm id)
Carrier gas	9 mL/min He constant flow
Standard oven program	40 °C (0.5 min), → 340 °C (0.5 min) @ 15 °C/min [total run time = 21 min]
GC oven temp when using LTM II	340 °C isothermal (3 min)
LTM II oven program	40 °C (0.5 min), 200 °C/min → 240 °C, 100 °C/min → 340 °C (0.5 min) [total time = 3 min]
FID	340 °C, H ₂ = 40 mL/min, Air = 400 mL/min
LTM II System	G6680A, 5 inch, with two power supplies
7890A Firmware	A.01.12.1 or greater
GC ChemStation	B.04.03 DSP 1, includes LTM II control software

Results and Discussion

System suitability was checked using a C₁₀–C₄₀ alkane test mixture. The obtained chromatogram is shown in Figure 1. Decane elutes at 0.8 min and is well separated from the solvent. Tetracosane elutes at 2.5 min. Retention time repeatability and peak area repeatability were determined for six runs and the results are summarized in Table 2.

The repeatability of retention times was excellent, with a standard deviation < 0.001 min (< 0.03% RSD). This effectively demonstrates that the LTM oven module reproducibly heats the capillary column and that the constant flow mode works properly. Peak area repeatability was also excellent (≤ 1% RSD).

This is due to the combination of fast autoinjection (Agilent 7683 or 7693 ALS) and liner selection.

Discrimination was checked against requirements by measuring the peak area ratio of C₄₀–C₂₀. In addition, discrimination for C₁₀–C₂₀ and C₄₀–C₁₀ were also determined and are presented in Table 2. The C₄₀–C₂₀ ratio was 0.92 (± 0.03), well above the method criterion (> 0.80). This provides a nice margin for maintaining compliance and demonstrates that the standard SSI inlet can meet method requirements. Splitless injection is also the most robust injection method and applicable to extracts from both clean samples (surface water) and contaminated samples (soil, sediment,...).

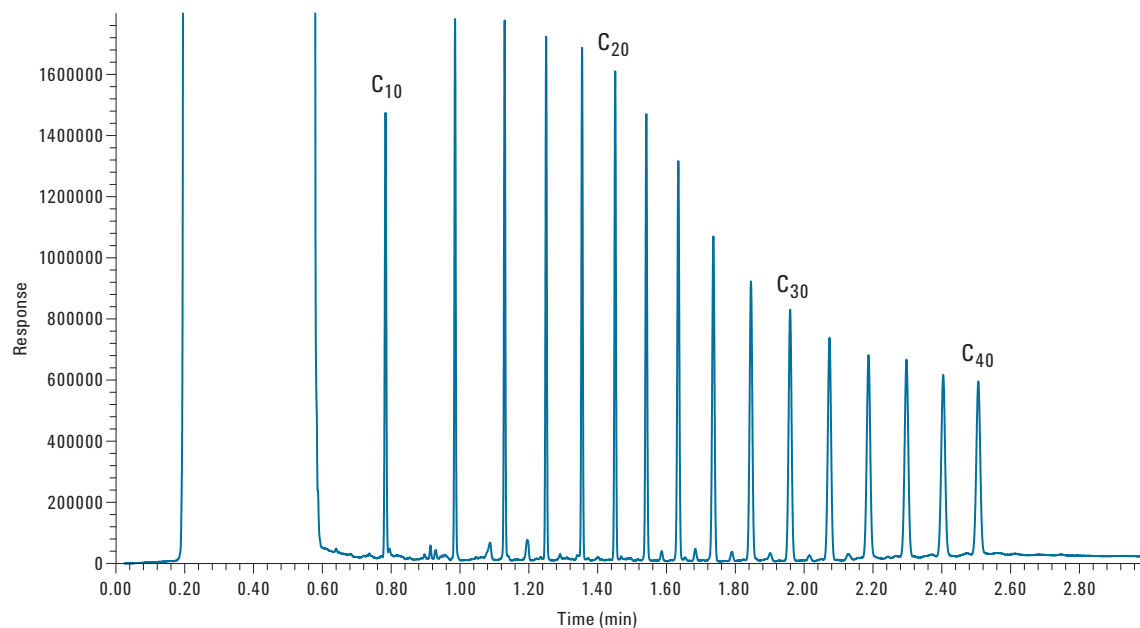


Figure 1. n-Alkane test mixture with fast oven program on LTM II oven module.

Table 2. Figures of Merit

Solutes/sample	t_R (min) mean (n=6)	t_R s (min) (RSD%)	Peak area mean (n=6)	Peak area RSD (%)
C ₁₀	0.783	0.00015 (0.022%)	61.640	0.70
C ₂₀	1.450	< 0.0001 (< 0.01%)	65.114	0.67
C ₄₀	2.507	0.00073 (0.027%)	60.024	0.77
Ratio C ₄₀ -C ₂₀ (*)			0.922	0.30
Ratio C ₁₀ -C ₂₀			0.947	0.19
Ratio C ₄₀ -C ₁₀			0.974	0.47
Mineral oil (**)	1.293	< 0.0002 (0.011%)	10421.564	0.57
RIVM C ₁₀ -C ₂₀			4549.987	1.6
RIVM C ₂₀ -C ₄₀			5871.667	1.0
RIVM ratio (***)			1.29	2.4

(*) ratio of C₄₀/C₂₀ should be > 0.80

(**) Restek cat. no. 31630, at 400 mg/L

(***) ratio of area sums C₂₀-C₄₀/C₁₀-C₄₀ should be between 1.25 and 1.40

Next, a calibration mixture of diesel and motor oil was analyzed. The chromatogram for a 400 mg/L calibration sample is shown in Figure 2. The two humps corresponding to diesel and motor oil fractions can easily be detected. Calibration is normally done with a synthetic mineral oil made from a composite of diesel and motor oil in the concentration range from 100 and 1,000 mg/L. The linearity of the fast GC-FID LTM method was tested from 40 mg/L to 1,000 mg/L. The obtained calibration curve of the peak area (sum of peak area from end of decane peak to start of tetracosane peak) in function of concentration is shown in Figure 3. The linearity was excellent ($R^2 > 0.999$). The repeatability of the peak area (sum C₁₀-C₄₀) of the calibration mixture at 400 mg/L was better than 1% RSD and the limit of detection was below 25 mg/L. As an additional benefit of fast oven programming, the hydrocarbon fraction is compressed into a narrower and higher hump. As a result, method sensitivity is higher than standard methods that use slower temperature programming.

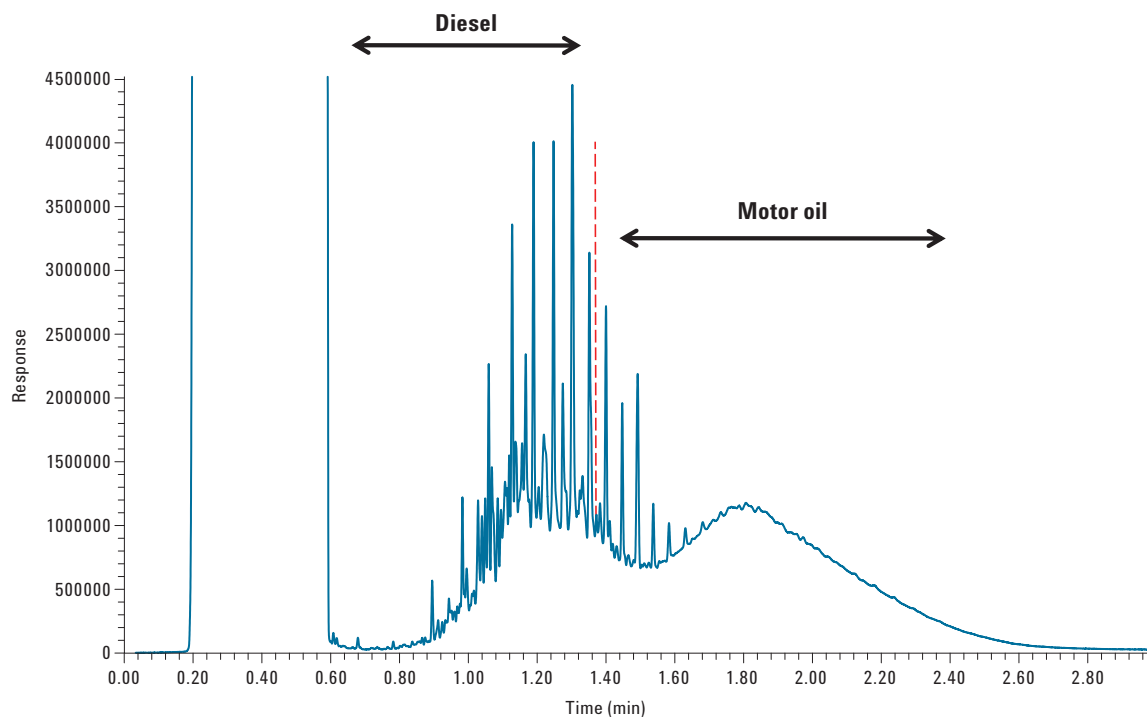


Figure 2. 400 mg/L calibration sample of diesel plus motor oil.

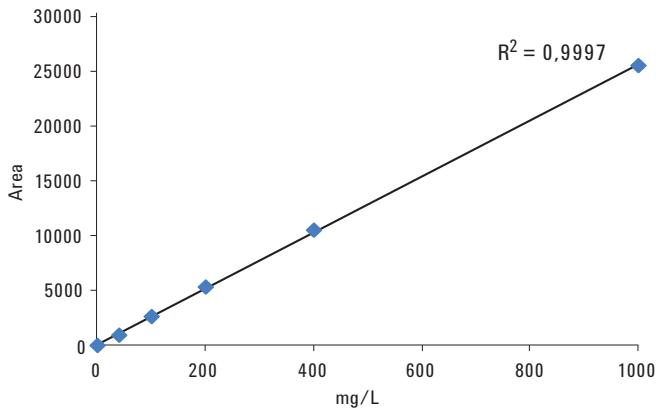


Figure 3. Mineral Oil Calibration: calibration from 40–1000 mg/L; Linearity: $R^2 > 0.999$; Repeatability at 400 mg/L: RSD on peak area = 0.57 %; LOD < 0.25 mg/L.

A comparison of a standard oven program with the fast LTM program (3 min run time) is shown in Figure 4 for a 400 mg/L calibration sample. The compression and higher signal gained from the 7X faster LTM run is obvious.

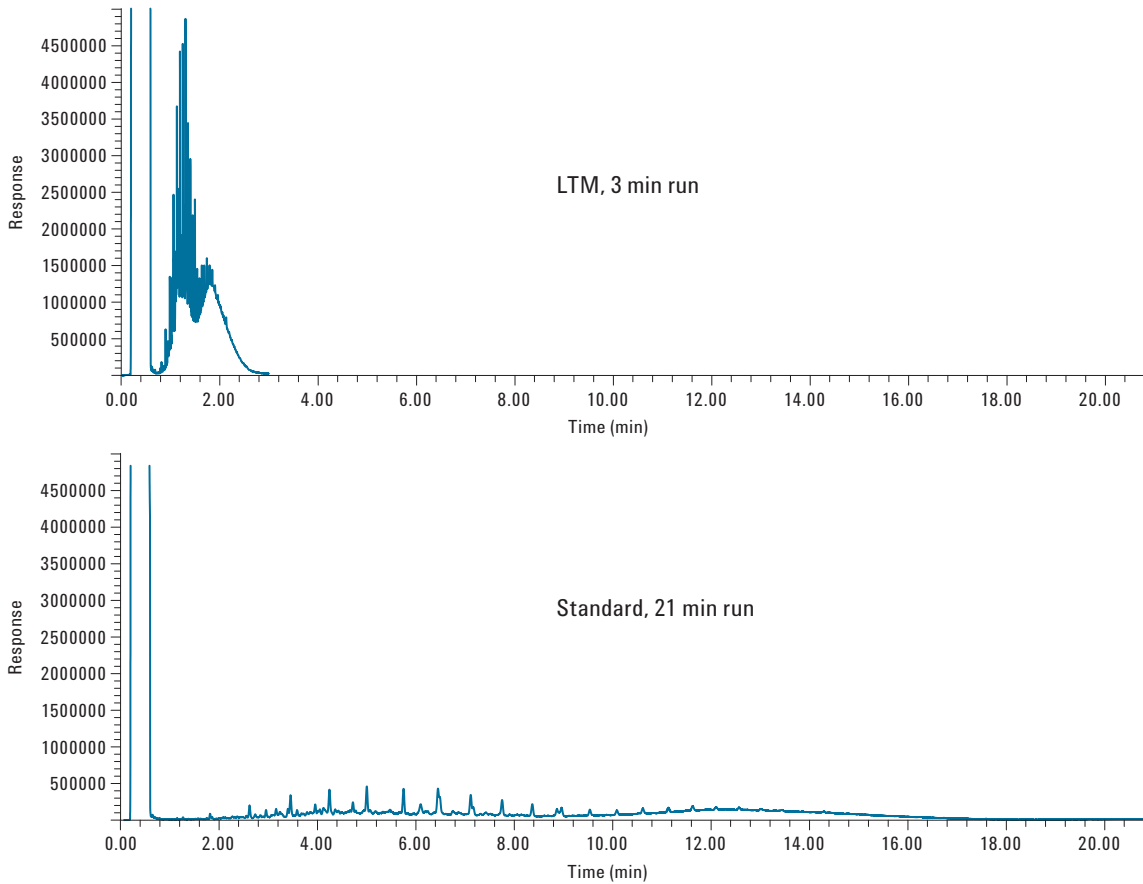


Figure 4. Comparison of Sensitivity gain from standard oven program to fast LTM program. Diesel plus motor oil standard at 400 mg/L.

Additional discrimination testing was done using a popular reference sample (RIVM sample). Peak areas were measured for the C_{10} – C_{20} and C_{20} – C_{40} fractions. The mean peak areas ($n = 6$) and corresponding RSDs are included in Table 2. The repeatability of peak area was again excellent with a relative standard deviation < 2%. The ratio of the peak areas of the C_{20} – C_{40} fraction (motor oil) versus the C_{10} – C_{20} fraction (“diesel”) was 1.29 (2.4% RSD); within the specifications (methods require a value be between 1.25 and 1.40). This test also clearly shows that solute discrimination was minimal using a split/splitless inlet and fast autoinjection, and that the fast temperature program easily meets method performance criteria.

As can be deduced from the repeatability data, automated integration of areas (using fixed integration event times) will remain valid and accurate for the whole C_{10} – C_{40} range, as well as for specific regions (smaller fractions, for example, C_{10} – C_{20} , C_{20} – C_{30} , etc.), reducing or eliminating the need for manual integration.

Conclusion

By adding an LTM II module to a 7890A GC, great improvements can be achieved in the GC-FID analysis of mineral oil in environmental samples. Analysis time for the separation of C₁₀ to C₄₀ alkanes is below 3 min. Cool-down time to 40 °C was also very short (2 min), resulting in a total injection-injection cycle time of 5 min. Excellent repeatability (retention times and peak areas), linearity and low LOD were achieved. The fast autoinjection allowed method criteria to be met using a standard hot SSI inlet.

References

1. International standard ISO 9377-2, Water Quality, Determination of hydrocarbon oil index, part 2: Method using solvent extraction and gas chromatography, 2000.
2. B. Wuest, Agilent Technologies publication 5988-0621EN, 2000.

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