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Ultra-Fast Determination of the Hydrocarbon Oil Index by Gas Chromatography using a Modular Accelerated Column Heater (MACH)

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ABSTRACT

Ultra-fast gas chromatographic methods for determination of the hydrocarbon oil index according to ISO 9377-2 were developed using a modular accelerated column heater (MACH). The column heater consists of a module that enables very fast and controlled heating of the capillary column. The speed of analysis for the hydrocarbon group eluting between C₁₀ and C₄₀ could in this way be increased by up to a factor 18 compared to the conventional method. Since the column can also be cooled very quickly, the total cycle time can be reduced to less than 2 minutes.

In addition to ultra-fast screening and a fully compliant method, an analytical method was developed that allows the separation of groups of hydrocarbons eluting between n-C₁₀ and n-C₂₀, n-C₂₀ and n-C₃₀, and n-C₃₀ and n-C₄₀, respectively. The cycle time for this analysis was 4.5 min. The quantitative performance of chromatographic analysis, with respect to linearity and sensitivity, is comparable to the conventional method.

INTRODUCTION

The mineral oil index or hydrocarbon oil index (HOI) according to ISO 9377-2 (formerly known as H-53) is defined as the sum of compounds being extractable from water using an apolar hydrocarbon solvent with a boiling point between 36 and 69°C, and not being retained during clean-up of the extract with Florisil. The resulting extract may include a complex mixture of mainly non-polar, long chain or branched aliphatic, alicyclic, aromatic or alkyl substituted aromatic hydrocarbons. Analysis of an aliquot of the extract is performed by capillary gas chromatography with flame ionization detection (CGC-FID) measuring the total peak area of the group of hydrocarbons eluting between n-decane (C₁₀H₂₄, boiling point 174°C) and n-tetracontane (C₄₀H₈₂, boiling point 525°C) on an apolar capillary GC column. An external standard consisting of two different types of mineral oil (e.g. diesel fuel and lubricant oil) within a specified range is used for quantitation.

This method provides increased qualitative and quantitative performance compared to the previously used FTIR analysis, but is substantially slower and dramatically affects the sample throughput for HOI analyses. Since environmental laboratories are constantly faced with the need to increase sample

throughput due to shrinking margins, every gain in speed of analysis that does not sacrifice data quality is of great value.

A modular accelerated column heater (MACH) system was recently introduced that enables heating of capillary columns at rates of up to 1800°C/min. The module is mounted on the door panel of a classical GC, with heated transfer lines going through the oven door and column ends connected to inlet and detector either directly or with deactivated fused silica capillaries using low dead volume connectors. The module can also be cooled very rapidly, making total analysis cycle times very short. Three fast GC methods were developed using a MACH system for the hydrocarbon oil index application.

EXPERIMENTAL

An Agilent 6890 GC was equipped with a PTV (CIS 4, GERSTEL) and Low Thermal Mass (LTM) column module. This module is commercially available from GERSTEL GmbH (Mülheim an der Ruhr, Germany) as the Modular Accelerated Column Heater (MACH™) and includes an adapted GC oven door that is equipped with one or several column modules. Figure 1 shows a GC with a column set mounted.



Figure 1. Single column MACH connected to 6890 GC system.

Each column is coiled separately with an insulated heating wire and a temperature sensor wire along the full length of the capillary column (Figures 2, 3) and mounted in a protective case. Temperatures between ambient + 5°C and 400°C can be programmed at a maximum temperature ramp of 1800°C/min. Fast cooling is performed by a set of ventilators mounted underneath each column module. The GC oven serves

as a heated interface for the transfer lines and is set to a constant temperature of 320°C. Injections are performed using an MPS 2 autosampler (GERSTEL). MPS 2, PTV and the column module are programmed and controlled using GERSTEL MAESTRO software that is fully integrated in the GC Chemstation software (Agilent Technologies). The data acquisition frequency of the FID is adjusted to 200 Hz.

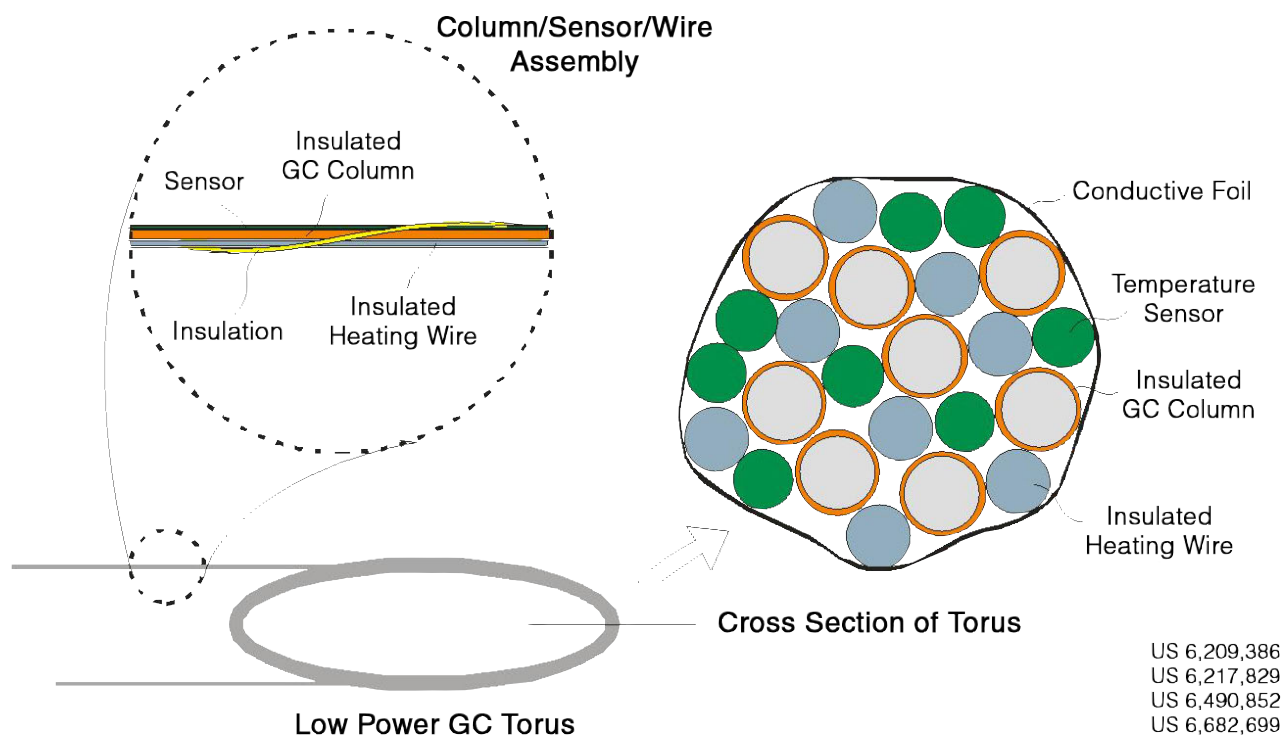


Figure 2. Low thermal mass column module diagram.

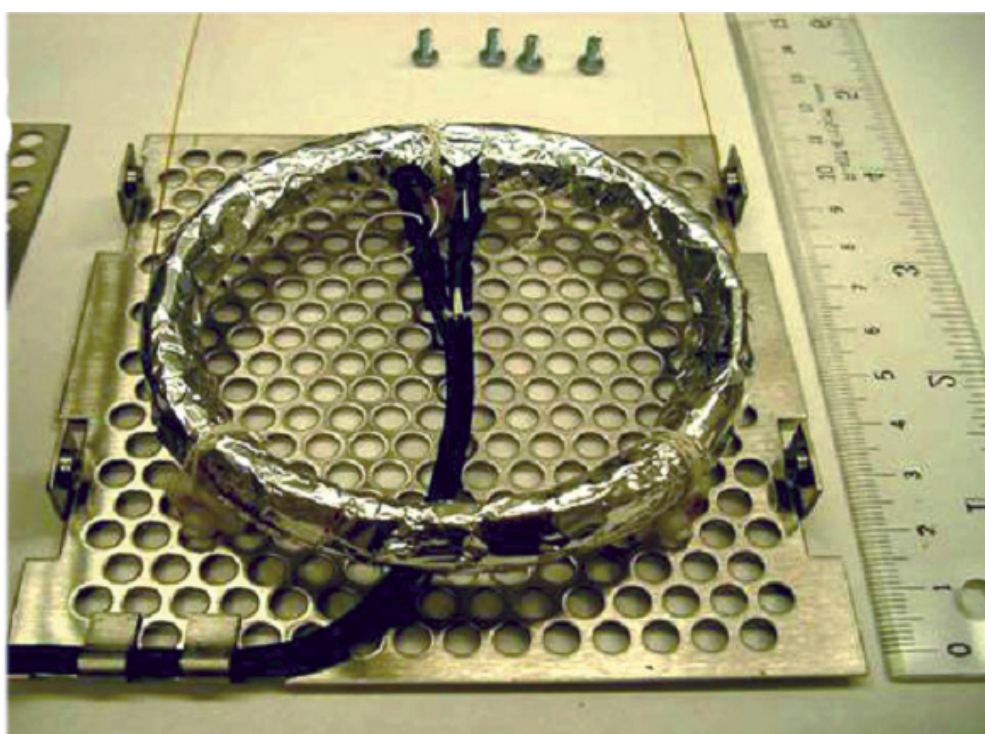


Figure 3. Low thermal mass column module.

Analysis conditions.

Injection: 1 μ L, MPS 2
PTV: splitless
60°C; 12°C/s; 320°C (3 min)
GC Oven: 320°C, held for duration
MACH Module: 5 m Rtx[®]-1 (Restek)
 $d_i = 0.32$ mm, $d_f = 0.25$ μ m
He, constant flow
40°C (0.75 min); 200°C/min;
350°C (3 min)
FID: 350°C, 200 Hz

Sample preparation. Calibration solutions were prepared by diluting a standard mix stock solution (#31630, Restek, Bellefonte, USA), containing Diesel Fuel #2 composite and mineral oil (5000 μ g/mL each) to the required levels using hexane and an extraction solvent stock solution. This extraction solvent stock solution (#31634, Restek, Bellefonte, USA), containing Decane and Tetracontane (20 ng/ μ L each), was added

to each level to give a concentration of 10 ng/ μ L in each of the solutions.

A standard mixture of n-alkanes (#31633, Restek, Bellefonte, USA), containing C₁₀ to C₄₀ n-alkanes at a level of 50 ng/ μ L each, was used for system performance testing.

RESULTS AND DISCUSSION

An important system performance test to check the analytical equipment for compliance with method ISO 9377-2 is the analysis of a standard mixture of n-alkanes, containing n-C₂₀, n-C₄₀, and at least 3 additional n-alkanes. The peaks of the n-alkanes have to be baseline separated, and the relative response of n-C₄₀ compared to n-C₂₀ should be at least 0.8, otherwise the injection system has to be regarded as too discriminating and can not be used for the analysis. Figure 4 shows the corresponding chromatogram of an appropriate standard mixture run under fast MACH conditions.

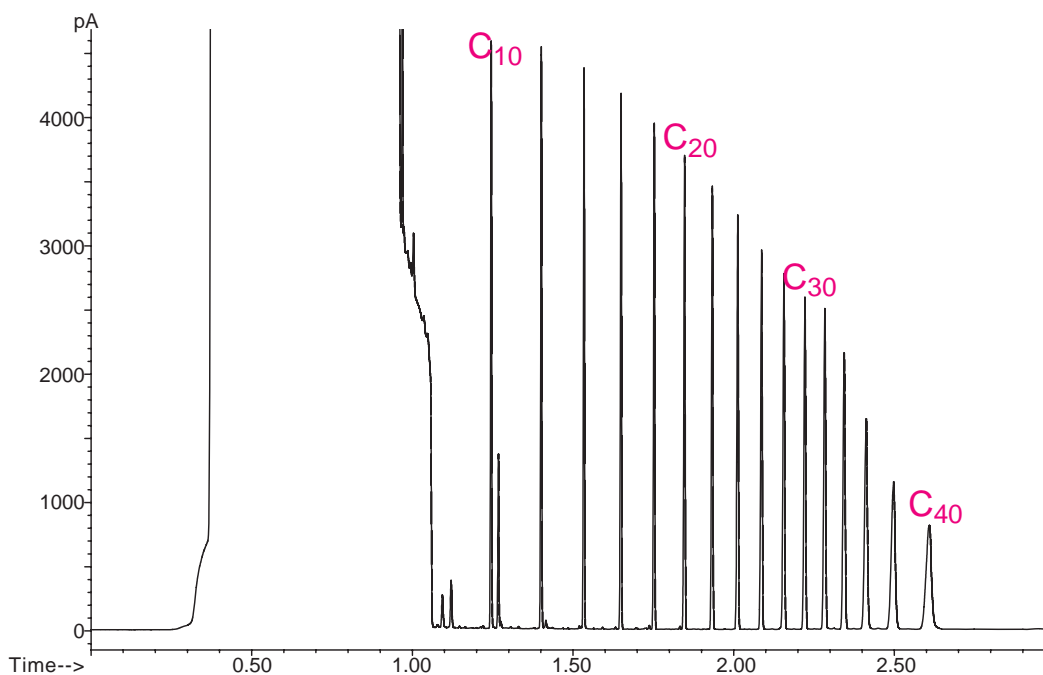


Figure 4. System performance test with n-alkane test mixture.

All n-alkanes were clearly baseline separated, and the ratio of n-C₄₀ vs. n-C₂₀ was found to be higher than 0.9. This demonstrates, that the MACH column and the PTV injection system easily meet the criteria of the ISO 9377-2 system performance test.

This test was followed by the injection of a standard mixture containing two types of mineral oil (type A and B), e.g. Diesel fuel (type A) and lubricant oil (type B). The resulting chromatogram should show discrete peaks for A, whereas B should have unresolved signals. To this mix n-C₁₀ and n-C₄₀ were added as marker compounds since all compounds between these markers are integrated as a group and represent the hydrocarbon oil index. Figure 5 shows a „conventional“ analysis of this standard representing a hydrocarbon oil index of 50 ng/ μ L. This analysis was performed on a 30 m x 320 μ m d_i , 0.25 μ m d_f HP-5 column. The GC oven was programmed from 40°C (1 min) to 320°C at a rate of 20°C/min. Helium was used at a constant flow of 2 mL/min. One μ L was injected in splitless mode with a splitless time of 1 min.

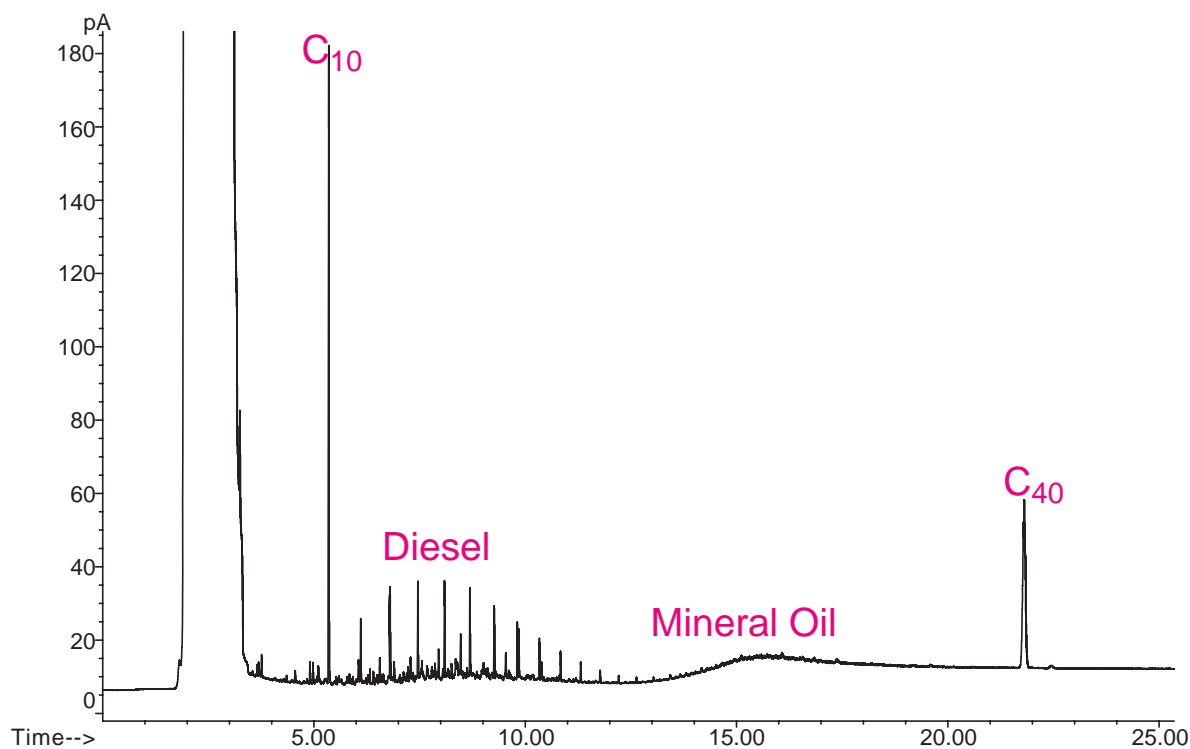


Figure 5. Conventional analysis of standard mixture at the 50 ng/μL level.

n-Decane (n-C₁₀) and n-tetracontane (n-C₄₀) eluted at 5.4 and 21.8 minutes. All compounds were eluting within 25 minutes and the column was additionally baked out for another 5 minutes to elute less-volatile material. Classical GC ovens can cool down relatively fast until the temperature approaches ambient temperature. In this case, the time required to cool the oven from 320°C to 40°C was about 9 minutes. This

gave a total GC cycle time of 39 minutes.

The same sample, run under MACH conditions, is shown in Figure 6. n-C₁₀ and n-C₄₀ eluted at 1.2 and 2.6 minutes. All compounds were eluted in less than 3 minutes, an additional column bakeout of 1 minute at 350°C was used. Cooldown time of the MACH from 350°C to 40°C was 1.5 minute resulting in a total GC cycle time of 5.5 minutes.

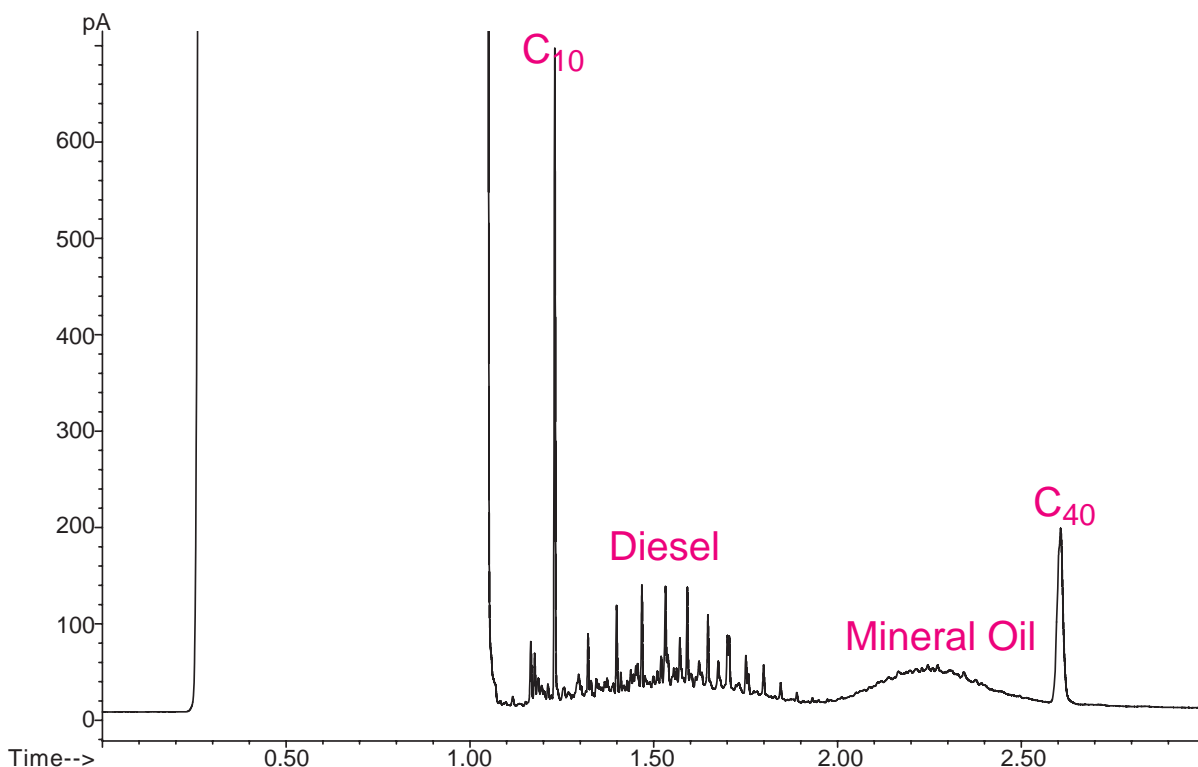


Figure 6. MACH analysis of standard mixture at the 50 ng/μL level.

Both chromatograms clearly show discrete peaks, originating from the diesel oil fraction in the standard, while the unresolved hump indicates the presence of the lubricant oil.

Linearity of the MACH method was checked by injecting the standard mixture at different

concentration levels, ranging from 50 to 1000 ng/ μ L. The calibration curve is displayed in figure 7, revealing an excellent correlation coefficient, well above 0.999. Figure 8 shows an overlay of the corresponding chromatograms.

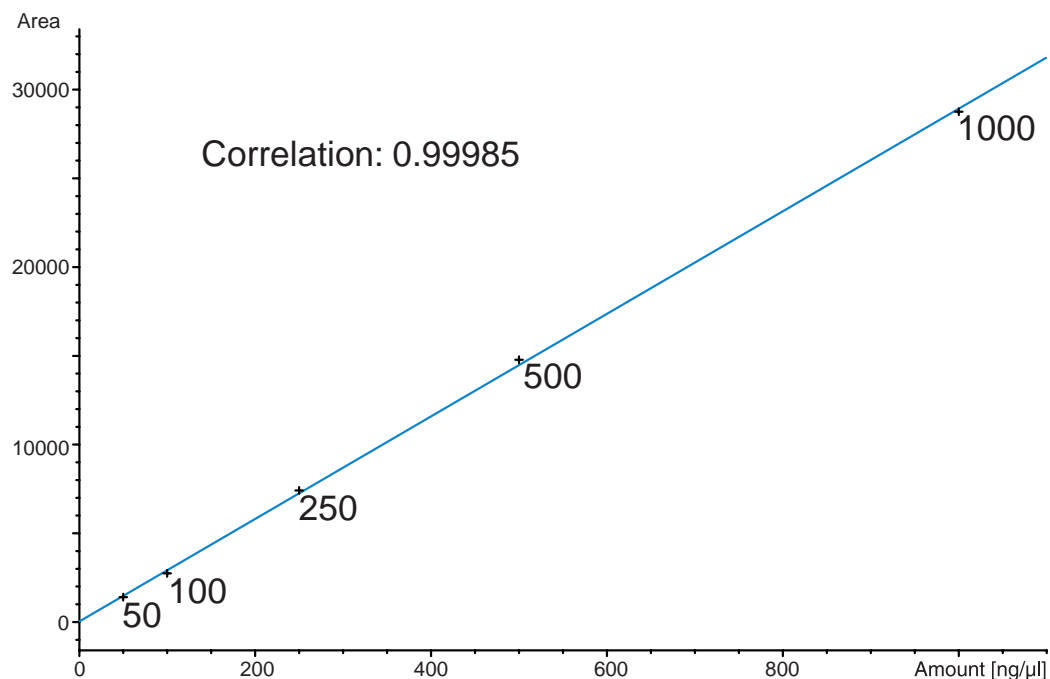


Figure 7. Calibration curve.

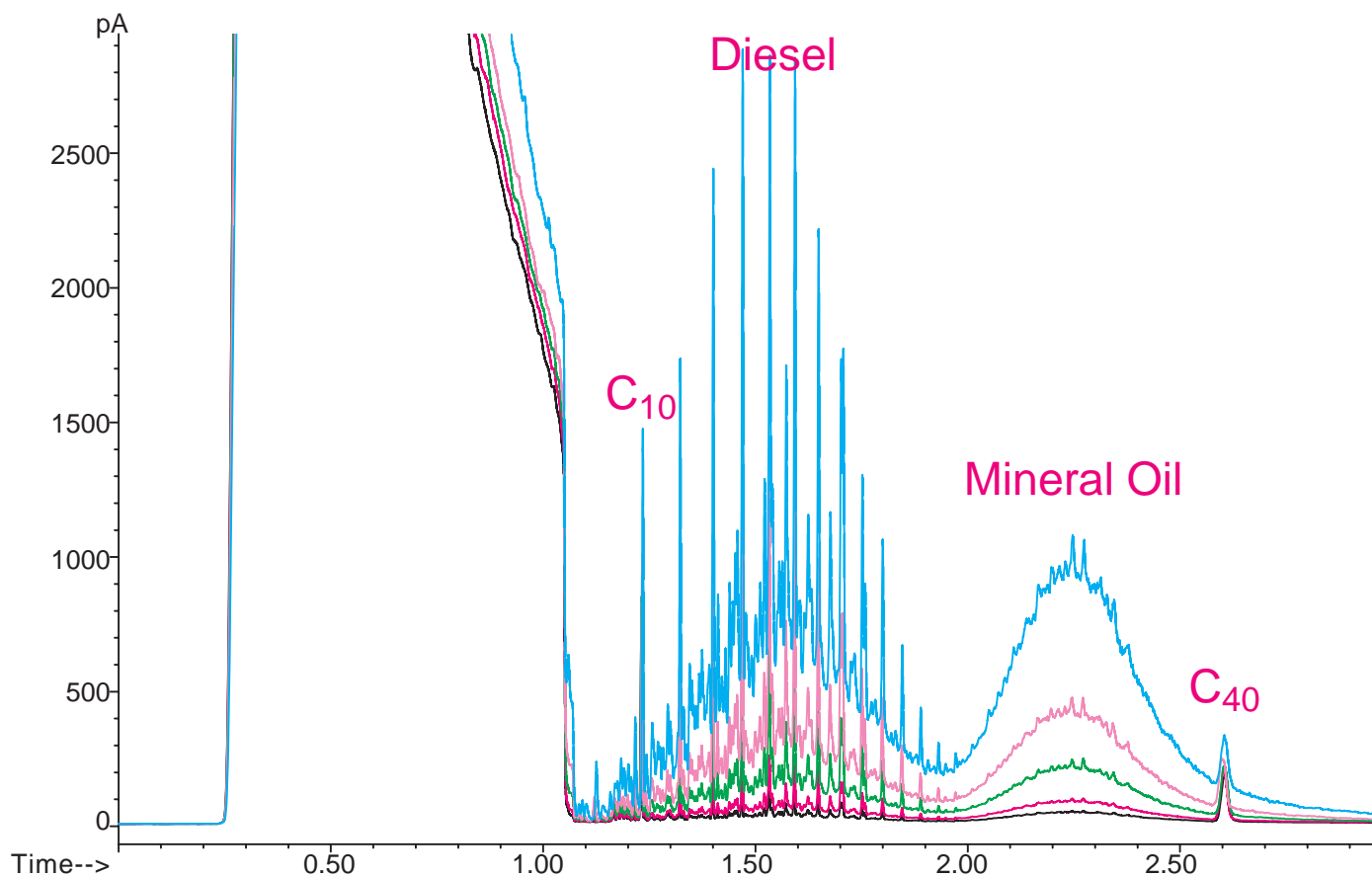


Figure 8. Overlay of chromatograms used for calibration.

To test system reproducibility and robustness the 50 ng/ μ L standard mix was injected 3 times, followed by 100 injections of a 1000 ng/ μ L mineral oil sample and a final injection of the standard mix. Comparing the peak areas of the 4 standard mix injections resulted in an RSD of less than 1%, proof of an excellent overall system robustness and stability.

An ultra-fast screening method was developed using a slightly different instrumental setup with a 5 m x 180 μ m d_i, 0.18 μ m d_f DB5-MS column. New conditions were calculated from the Method Translation software (Agilent Technologies, Little Falls, DE, USA). The MACH column module was programmed from 35°C (3 sec) to 60°C at a rate of 123°C/min and to 350°C (30 sec) at a rate of 369°C/min. The carrier gas (hydrogen) pressure was set at a constant value of 71.4 kPa, giving a column flow of 3.1 mL/min at 35°C. Figure 9 shows

a chromatogram based on split injection (split ratio 1:20, 0.2 μ L) of a hydrocarbon index standard solution (10 μ g/ μ L, Sigma-Aldrich, Bornem, Belgium). All hydrocarbons up to n-C₄₀ elute in less than 1.4 minutes. The total cycle time was less than 2 minutes (cooling included). This was a gain in speed of a factor 18, compared with the conventional analysis done before, but the chromatogram shows less resolution than the original profile, due to the lower sample capacity of the fast GC column. However, for fast screening, resolution is less important than speed since the hydrocarbon fraction between n-C₁₀ and n-C₄₀ is quantified as a group. The linearity of the method was verified using HOI standard solutions of 1, 2, 5 and 10 μ g/ μ L. A correlation coefficient higher than 0.999 was achieved.

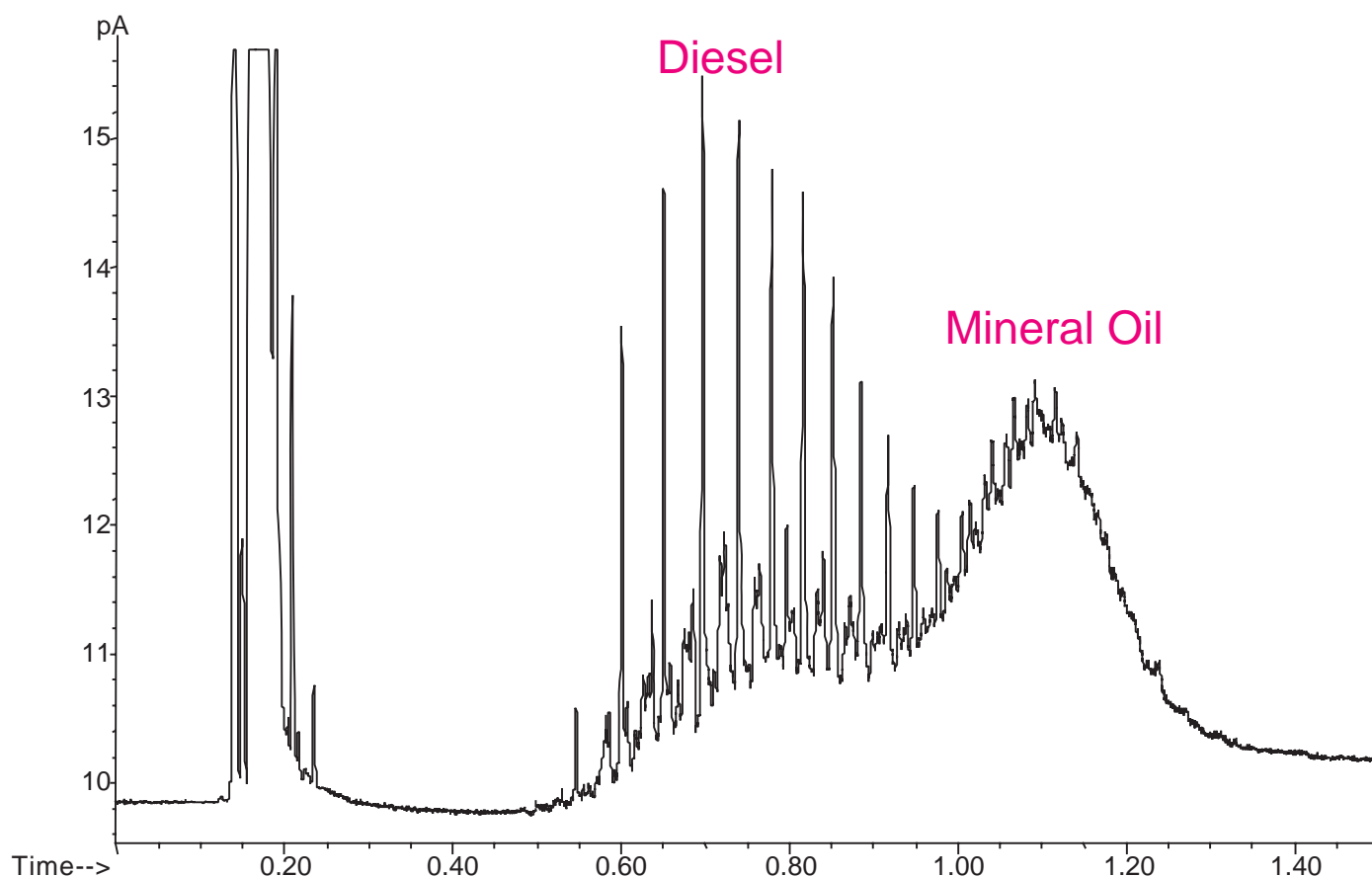


Figure 9. Ultra fast screening of HOI-Mix.

Recently, some laboratories have demanded additional qualitative information from the HOI analysis. By integration of the n-C₁₀₋₂₀, n-C₂₀₋₃₀ and n-C₃₀₋₄₀ fraction, additional information can be obtained on the origin of contamination (diesel oil, lubricant oil, heavy crude,...). This approach requires increased separation performance compared with the ultra-fast separation shown in Figure 9.

The resolution could be improved significantly by lowering the heating rate of the column. To achieve this, the column was programmed from 35°C (10 sec) to 350°C (30 sec) at a linear rate of 100°C/s. The carrier gas (hydrogen) was set to a constant pressure of 71.4 kPa. The total cycle time was still under 4.5 min. The resulting chromatogram is shown in Figure 10 and it is obvious that a higher resolution is obtained and more discrete peaks are detected in comparison with Figure 9.

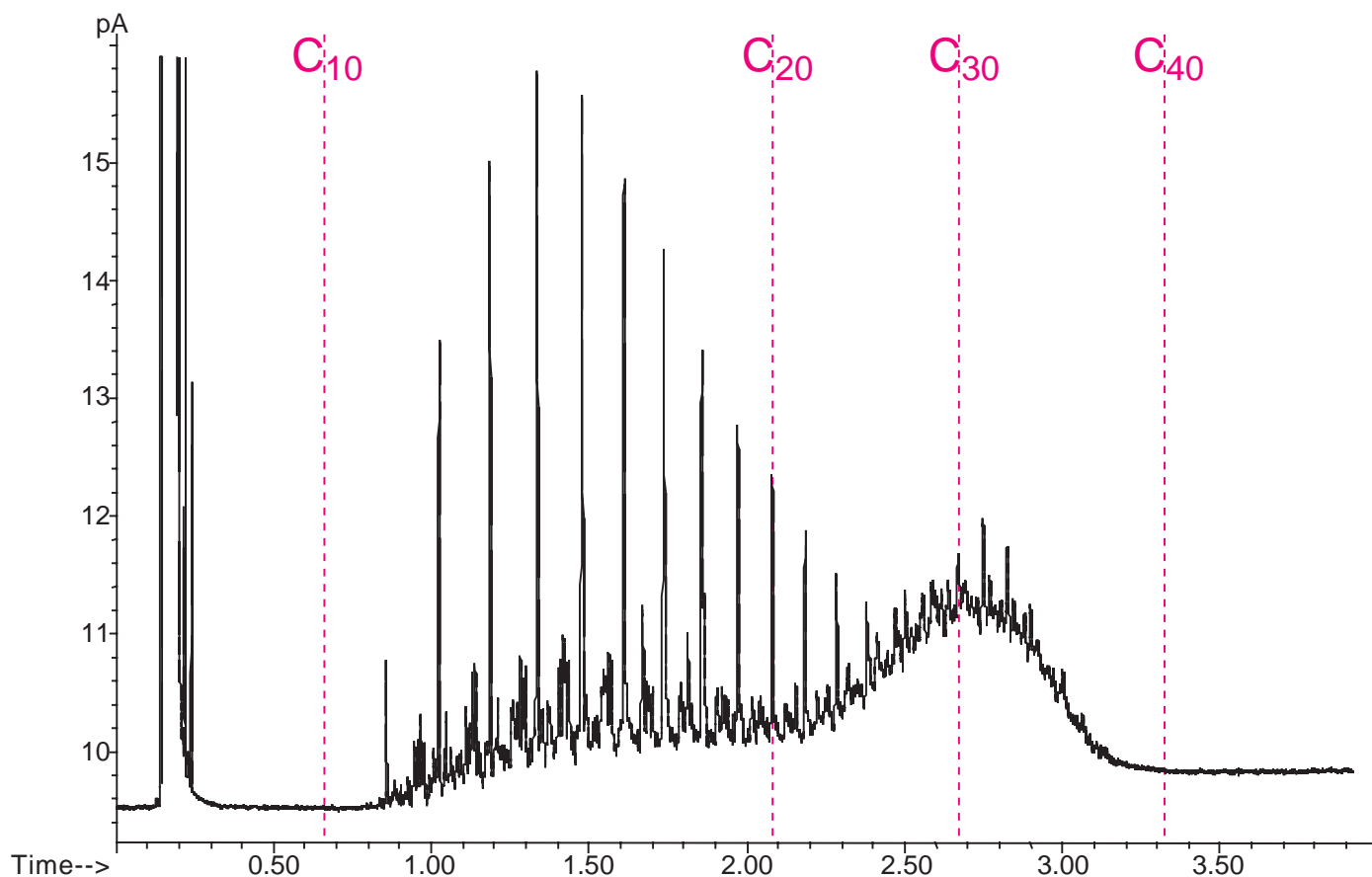


Figure 10. Chromatogram using parameters for higher resolution.

Using these conditions, the analysis could also be performed using splitless injection, with comparable sensitivity (or better due to “band compression”) to the conventional method, with maintained separation and the possibility to integrate the n-C₁₀₋₂₀, n-C₂₀₋₃₀ and n-C₃₀₋₄₀ fractions individually.

CONCLUSION

Three fast GC methods were developed for the determination of the hydrocarbon oil index (HOI) using a modular accelerated column heater (MACH).

A fully ISO 9377-2 compliant method allows cycle times of 5.5 mins. Alternative methods enable either a further reduction of the total analysis time (including column cooling) to less than 2 min for screening purposes, or a group separation of n-C₁₀₋₂₀, n-C₂₀₋₃₀ and n-C₃₀₋₄₀ hydrocarbons, using a somewhat slower temperature program. In the latter case the total cycle time was still under 4.5 min. Sensitivity and linearity were maintained in comparison with the conventional method.



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