Application News

GC   Nexis™ GC-2030

High-Speed Analysis of Total Petroleum Hydrocarbons (TPH)

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User Benefits

◆ Analysis times can be significantly shortened by using the Nexis GC-2030 (230 V), an oven insert, and hydrogen as the carrier gas.
◆ Using dual injectors, throughput can be greatly improved, enabling the analysis of more than 380 samples per day.

■ Introduction

Total petroleum hydrocarbons (TPH) refer to mixtures of various types of hydrocarbons. In the production of petroleum hydrocarbon products, contamination of the environment including water or soil is a concern. There are also health risks, so it is very important to control the concentration of TPH.

This article introduces an example of the high-speed analysis of TPH using the Nexis GC-2030 (230 V) with an oven insert for rapid heating, and using hydrogen as the carrier gas. A system performance test was conducted using n-alkane, a calibration curve was prepared using mineral oil, and the linearity was checked, based on an international standard, the ISO 9377-2-2000, determination of hydrocarbon oil index for water quality.

Fig. 1 View of the Instruments (Left: Nexis™ GC-2030, Right: Dual Injectors)

■ Analysis of TPH

Typical oil content analysis methods include n-hexane extraction/quantitation and carbon tetrachloride extraction/infrared spectroscopy. However, these ways are incapable of separate analysis by carbon number, so in this case, the gas chromatography was used.

In ISO 9377-2-2000 "Methods using Solvent Extraction and Gas Chromatography," hydrocarbons in water or soil are extracted using a hydrocarbon solvent with a boiling point between 36 °C and 69 °C (such as hexane or heptane). Standard mixture of n-alkanes is analyzed for system performance tests, and n-tetracontane (C40) must have an area ratio of at least 0.8 with respect to n-eicosane (C20). In terms of quantitation, the total of the peak areas for all components between decane (C10) and tetracontane (C40) is calculated.

In an analysis, solvent extraction and C10 separation must be performed while satisfying the C40/C20 area ratio standard. Accordingly, the initial temperature must be lowered and the column film thickness must be increased, leading to issues with long analysis times.

In this article, hydrogen was used as the carrier gas, which enabled the introduction of a thick film column and a high column flowrate without lowering the initial temperature. Using the Nexis GC-2030 (230 V) with an oven insert enables rapid heating, thereby significantly shortening the analysis time.

■ Sample Preparation

The samples (1) to (3) were prepared as follows.

(1) Solvent Extraction/Background Correction Sample
Heptane was prepared.
(2) System Performance test Sample
A 50 µg/mL standard mixture of n-alkane (Sigma-Aldrich, P/N: 94234-2ML) was prepared.
(3) Calibration Curve Samples (Mineral Oil)
A diluting solvent was prepared by dissolving 2.0 mg of n-tetracontane and 2.0 µL n-decane in 100 mL of heptane. Using the prepared diluting solvent, a 5,000 µg/mL QC standard solution (Sigma-Aldrich, P/N: 51706-1ML) was diluted to prepare 50, 100, 250, 500, and 1000 µg/mL calibration curve samples.

■ Instrument Configuration and Analytical Conditions

The Nexis GC-2030 (230 V) was used, with two analysis lines and dual AOC™-30i mounted. The analysis was performed using a GC-2030 standard insert at the injection port, and an oven insert (P/N: 221-85807-41) to accelerate the rise in oven temperature.

Table 1 shows the analytical conditions.

Table 1 Analytical Conditions

Model	: Nexis GC-2030 (230 V)/ AOC-30i × 2
Injection Mode	: Sampler Navigator – Standard mode
Injection Volume	: 1 µL
Injection Temp.	: 280 °C
Injection Mode	: Split
Split Ratio	: 1:5
Carrier Gas	: H_2
Carrier Gas Control	: Column flowrate (7.00 mL/min)
Column	: Rxi-1ms (Restek Corporation, P/N: 13397) (12 m × 0.2 mm I.D. × 0.33 µm)
Column Temp.	: 100 °C (0.3 min)– 90 °C/min - 175 °C -70 °C/min - 250 °C - 55 °C/min - 340 °C (0.5 min)[*1]
Detector	: Hydrogen flame ionization detector (FID)
Detector Temp.	: 350 °C
Detector Gas	: H_2 32 mL/min, Air 200 mL/min
Makeup Gas	: N_2 24 mL/min

[*1] The analysis was performed within the range specified for column oven heating when the Nexis GC-2030 (230 V) and an oven insert are used.

■ System Performance Test Confirmation

A system performance test was conducted using the 50 µg/mL standard mixture of n-alkanes.

The chromatogram for the standard mixture of n-alkanes is shown in Fig. 2, and the area repeatability and average area ratio for C20 and C40 are shown in Table 2.

The area ratio of C40 with respect to C20 (C40/C20) was over 0.94, satisfying the standard value of at least 0.8.
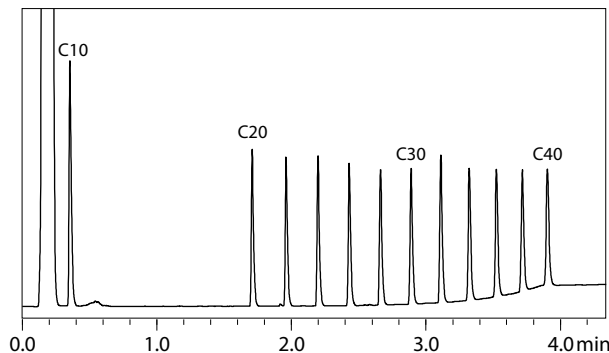
C10 was extracted in 0.4 min, with favorable separation by solvent extraction.

Table 2 C20 and C40 Area Repeatability and Average Area Ratio (n = 3)

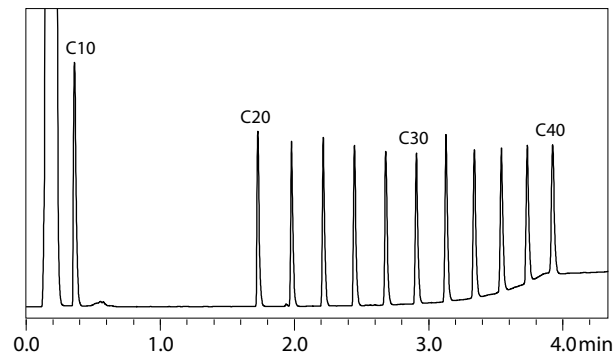| Line	C20 Area Repeatability (%RSD)	C40 Area Repeatability (%RSD)	C40/C20 Average Area Ratio
1	0.64	0.59	0.94
2	0.41	0.23	0.96

Fig. 2 Chromatograms for the Standard Mixture of n-Alkanes (Left: Line 1, Right: Line 2)

■ Mineral Oil Calibration Curve

Fig. 3 shows the superimposed chromatograms for the QC standard solutions. The area for mineral oil was calculated by totaling the peak areas for all the components detected between C10 and C40.

The average area and area repeatability for mineral oil are shown in Table 3, and the calibration curves are shown in Fig. 4. The calibration curve linearity R^2 was over 0.9996, indicating that favorable results were obtained.
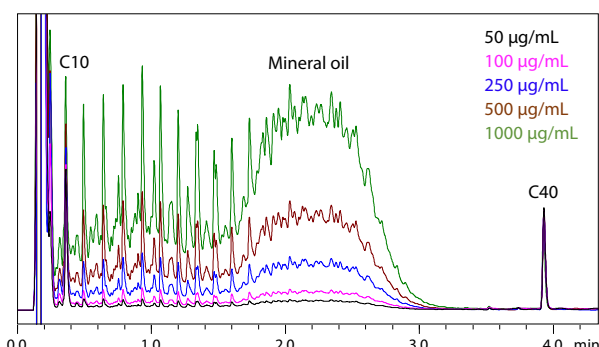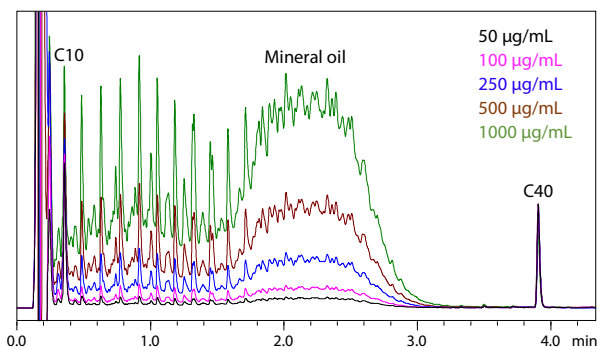
Fig. 3 Superimposed Chromatograms for QC Standard Solutions (Left: Line 1, Right: Line 2)

Table 3 Mean Area and Area Repeatability for Mineral Oil (n = 3, Left: Line 1, Right: Line 2)

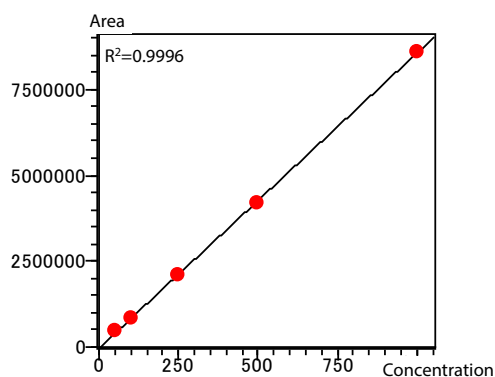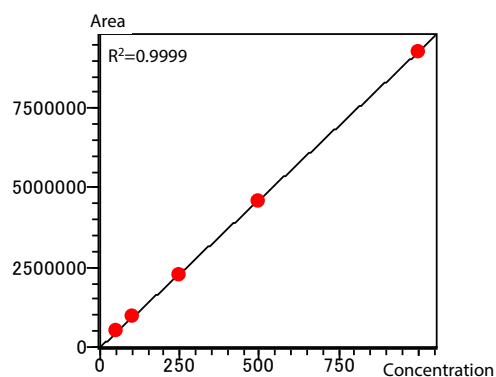| No.	Concentration (µg/mL)	Average Area for Mineral Oil	Area Repeatability (RSD%)	No.	Concentration (µg/mL)	Average Area for Mineral Oil	Area Repeatability (RSD%)
1	50	488,308	0.38	1	50	454,933	0.77
2	100	932,402	0.83	2	100	847,366	1.37
3	250	2,256,903	0.85	3	250	2,075,364	0.66
4	500	4,593,506	0.34	4	500	4,171,988	0.43
5	1000	9,285,038	0.37	5	1000	8,607,988	0.42

Fig. 4 Mineral Oil Calibration Curve (Left: Line 1, Right: Line 2)

■ Example of Peak Integration Using LabSolutions™

An example of the peak integration used in this analysis is shown below.

1. A compound table was prepared.
   On the [Compound] tab, "Solvent" and "Mineral oil" were entered as the compound names, and their respective retention times*2 were set.
2. A background correction was performed using the data from the solvent extraction/background correction samples (Fig. 5).
3. The following peak integration programs were set: (See Fig. 6).
   3-1. [NEG Peak Reject On]*3 before the solvent peak
   3-2. [HORIZ Baseline On] before the solvent peak
   3-3. [Peak Detect] immediately before the C10 peak
   3-4. [Peak Top] midway between the C10 peak and C40 peak
   3-5. [Peak End] immediately before the C40 peak
4. The following parameters were set:
   4-1. On the [Compound] tab, the band width*4 for solvent and mineral oil were set.
   4-2. On the [Identification] tab, [Window/Band] was set to [Band], and [Peak Selection] was set to [All Peaks].

4-3. On the [Peak Integration] tab, the peak integration parameters were set. E.g.: Width = 4, Slope = 1000, Drift = 0, T.DBL = 1000

*2 For the solvent, the peak top was set, and for the mineral oil, the retention time midway between those for C10 and C40 was set.

*3 This is set if a negative peak appears as shown in Fig. 5 when a background correction is performed because of a deviation in solvent peak position between the background correction sample and the calibration curve sample.

*4 [Default Bandwidth] was displayed by right-clicking on the compound tab to display the table styles menu. [C10 - solvent retention time] was set for the solvent, and [Peak end - Peak Detect /2 retention time] was set for the mineral oil.
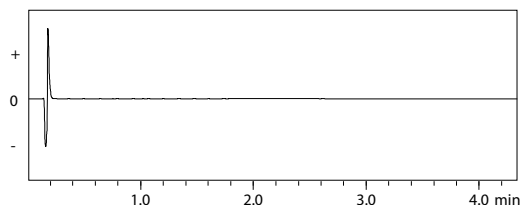

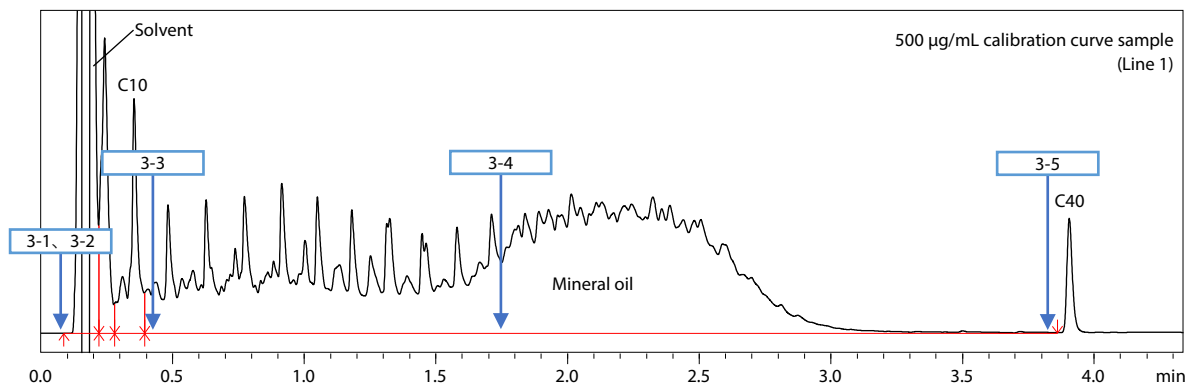Fig. 5 Example of a Negative Peak after Background Correction

Fig. 6 Peak Integration Program Setting

■ Analysis Cycle Time

The analysis time was approximately 4.3 min, the oven cooling time was approximately 1.5 min, the equilibration time was approximately 1.0 min, and the sample injection time*5 was approximately 0.5 min. Accordingly, the analysis cycle time was approximately 7.3 min.

In a single analysis, more than 190 samples can be tested per day (24 hours), and in a dual analysis, more than 380 samples can be tested per day.

*5 Assuming overlap is used.

■ Comparison of the Nexis GC-2030 (100 V, 230 V)

The standard mixture of n-alkanes was analyzed in the Nexis GC- 2030 (100 V), the Nexis GC-2030 (230 V), and the Nexis GC-2030 (230 V) + oven insert with the maximum specified temperature program within the specified column oven heating range. Fig. 7 shows a comparison of the chromatograms.

Using the Nexis GC-2030 (230 V) and oven insert shortened the analysis time by approximately 5 min. in comparison to the Nexis GC-2030 (100 V).
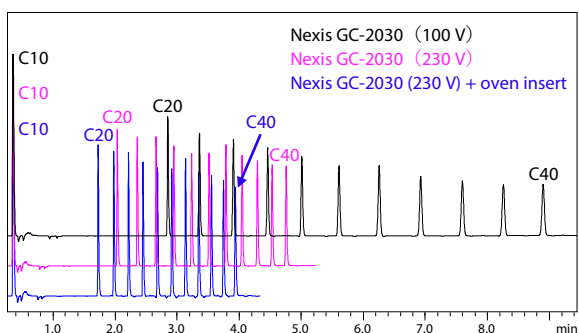

Fig. 7 Comparison of the Standard Mixture of n-Alkanes Chromatograms (1)

■ High-Speed Heating Using the Oven Insert

Fig. 8 shows the oven insert, and Table 4 shows a comparison of the specified column oven heating ranges when the Nexis GC-2030 (230 V) and Nexis GC-2030 (230 V) + oven insert are used.

Using the oven insert enables high-speed heating.

Table 4 Comparison of Specified Column Oven Heating Ranges*6

Fig. 8 View of the Oven Insert*6

Column Oven Temperature Range	Specified Heating (ºC/min)	
	No Oven Insert	Oven Insert
Up to 70 ºC	Up to 120	Up to 120
70 ºC to 115 ºC	Up to 95	Up to 110
115 ºC to 175 ºC	Up to 65	Up to 90
175 ºC to 250 ºC	Up to 55	Up to 70
250 ºC to 350 ºC	Up to 45	Up to 55
350 ºC to 450 ºC	Up to 35	Up to 40

*6 This differs depending on the sample vaporization chamber and detector mounting position.

■ Comparison with out of the Column Oven Temperature Control Range*7

Fig. 9 shows a comparison of the chromatograms for the standard mixture of n-alkanes obtained with the instrument configured as in these analyses when column oven heating was within the specification range (column temperature: Table 1) and out of the specified range (column temperature: 200 ℃/min).

When the column oven heating was out of the specified range, the analysis time could be shortened by approximately 1 minute in comparison to within the specified range.
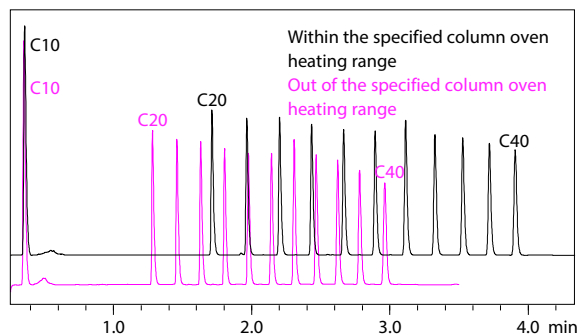

Fig. 9 Comparison of the Standard Mixture of n-Alkanes Chromatograms (2)

*7 If a value out of the specified oven heating range is used, the analysis results in this article might not be obtained depending on the room temperature and other aspects of the laboratory environment, so the analysis performance cannot be guaranteed.

■ AOC-30i Overlap Setting

Fig. 10 shows how to set the AOC-30i overlap in LabSolutions. With this function, cleaning of the syringe prior to injection overlaps with the previous analysis, so the analysis cycle time can be shortened.
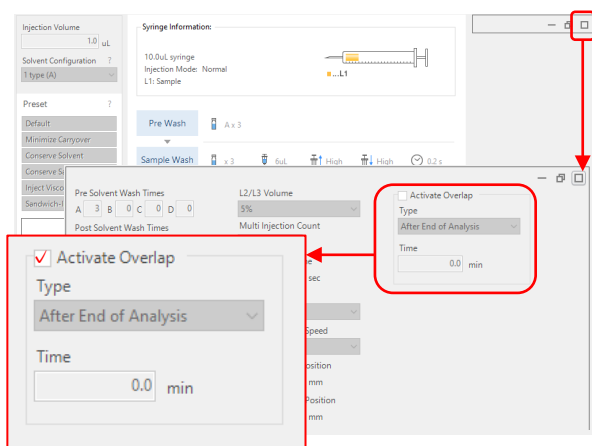

Fig. 10 Setting AOC-30i Overlap

■ Conclusion

In this article, high-speed analysis of TPH was achieved using the Nexis GC-2030 (230V) with an oven insert to enable high-speed heating and hydrogen as the carrier gas.

In the system performance test, the area ratio of C40 with respect to C20 was over 0.94, satisfying the standard value of 0.8. Favorable results were achieved for the linearity of the calibration curve produced using the QC standard solution.

The analysis time was approximately 4.3 min., and the analysis cycle time was approximately 7.3 min., so it was possible to greatly reduce the analysis time and the analysis cycle time.

Using dual injectors, the throughput can be greatly improved, enabling the analysis of more than 380 samples per day.

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