

Analysis of TPH in Soil (Part 1)

Soil contamination with oil is being addressed as a social issue due to the disruption of the environment caused by infiltration of oil into underground water, oil slicks, oil odor and other deleterious effects. The Ministry of the Environment announced in June 2006 the "Oil Pollution Measures Guideline" and the "Policy for Action on Oil Odor and Oil Slick Problems due to Contamination of Soil with Mineral Oils by Landowners, etc.". Prescribed in Volume 2 of this Guideline, under the Technical Material Part 2 Specialty Section, Chapter 1 Situation Ascertainment Investigation¹⁾ is the "TPH Test Method using GC-FID" (hereafter, "Guideline").

Three types of analytical conditions are prescribed in the Guideline, two of which specify the on-column

injection method using a 0.53 mm I.D. (wide-bore) column (column temperature programs start at -30 °C and 35 °C, respectively), and one set of analytical conditions specifying the splitless method, using a 0.32 mm I.D. (capillary) column (column temperature program starts at 35 °C). The applicable range and compounds of interest are the same in both methods, but the instrument configurations, temperature conditions and columns differ.

This Application News introduces the analysis of TPH in soil by the on-column injection method using a 0.53 mm inner diameter wide-bore column and the temperature program in which column temperature starts at 35 °C.

■ Determining Quantitation Range of TPH

The method described in the Guideline specifies that the TPH quantitation range be determined using standard solutions containing n-C₆H₁₄ and n-C₄₄H₉₀. Specifically, the quantitation range is to begin from 0.1 minute prior to the beginning of the n-C₆H₁₄ peak (starting retention time RT-C₆) up until 0.1 minute following the end of elution of n-C₄₄H₉₀ (ending retention time RT-C₄₄).

Fig.1 and 2 show the chromatograms obtained from analysis of paraffin mixture samples for determination of the quantitation range.

■ Calibration Curve for TPH Quantitation

The Guideline prescribes that the calibration curve for quantitation of TPH be generated using a standard sample consisting of ASTM-specified standard light oil. The ASTM standard light oil sample was prepared using carbon disulfide (CS₂) for dilution. The volume injected into the GC was 1 μL for both the standard solution and soil extract solution. The chromatograms are blank-subtracted using a CS₂-only (blank) chromatogram. The calibration curves were generated with a high concentration range of 250 to 10000 mg/L and low concentration range of 50 to 1000 mg/L, respectively.

Fig.3 shows the chromatogram obtained from analysis of 1000 mg/L standard light oil. The calibration curve of the 250 to 10000 mg/L standard light oil solution is shown in Fig.4.

Quantitation of TPH in the soil extract solution was conducted using the above-mentioned standard light oil calibration curve, as described in the Guideline. The procedure used for extraction of TPH from the soil is shown in Fig.5. Fig.6 shows the chromatogram obtained from analysis of Extract Solution A prepared from a simulated TPH-contaminated soil sample (soil spiked with light oil).

It is prescribed to write clearly that the quantitation results were obtained in the carbon range of n-C₆H₁₄ to n-C₄₄H₉₀.

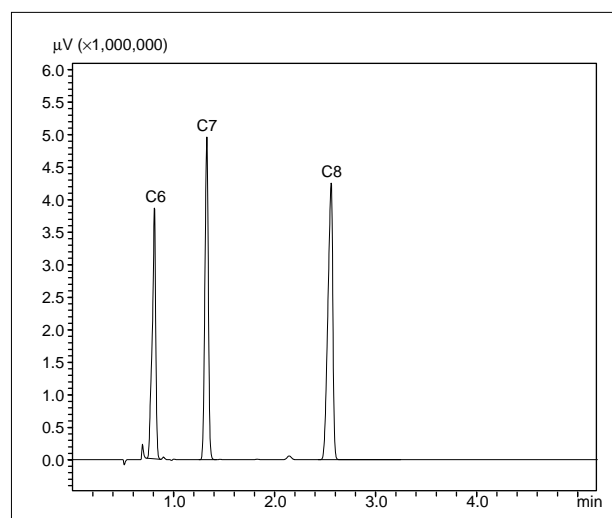


Fig.1 Chromatogram of Standard Solution (n-C₆H₁₄-n-C₈H₁₈)

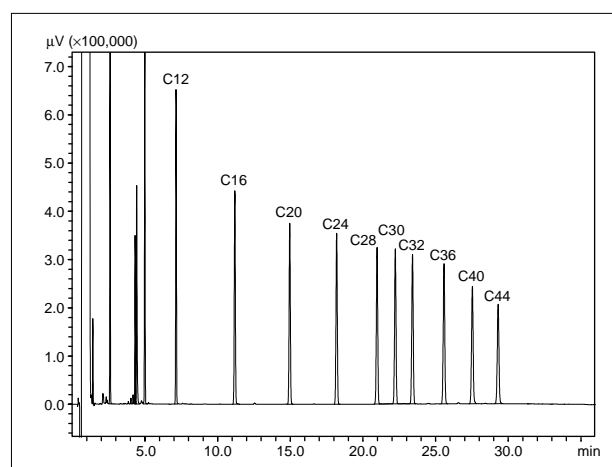


Fig.2 Chromatogram of Standard Solution (n-C₁₂H₂₆-n-C₄₄H₉₀)

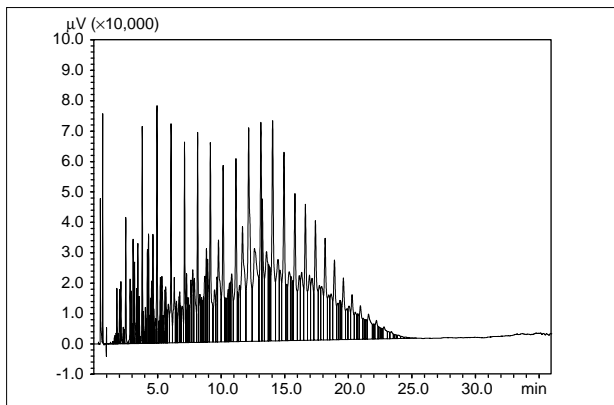


Fig.3 Chromatogram of ASTM Standard Light Oil Solution (1000 µg/mL)

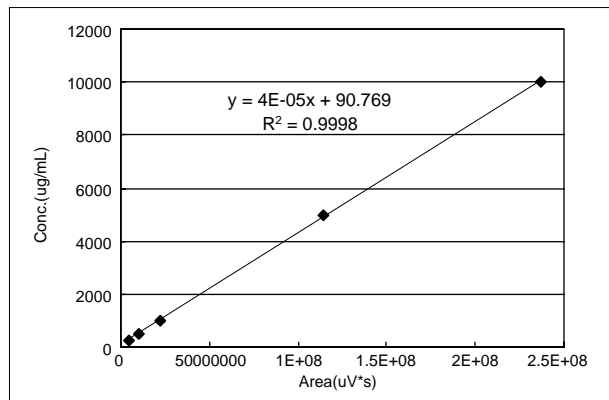


Fig.4 Calibration Curve of ASTM Standard Light Oil Solution (250 to 10000 µg/mL)

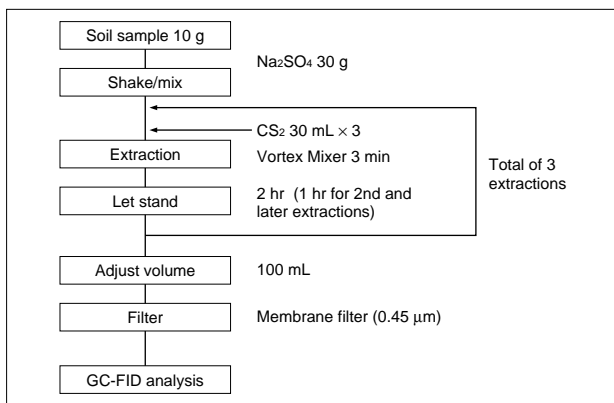


Fig.5 Procedure for Extraction of TPH from Soil

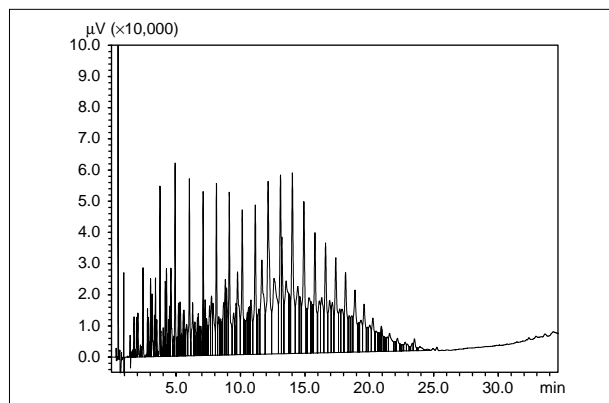


Fig.6 Chromatogram of Extract of TPH-Spiked Soil Sample (Soil spiked with 5000 µg/g light oil)

The Guideline provides explanations of the concentration calculation methods employed for the "Gasoline Carbon Range", "Light Oil Carbon Range" and "Residue Oil Carbon Range" in the annotation for quantitation of TPH. It describes that the area is calculated by dividing the chromatogram area values based on the standard paraffin elution times. The elution ranges for the gasoline carbon range, light oil carbon range and residue oil carbon range, respectively, are:

- (1) Gasoline carbon range (C₆ to C₁₂) : from 0.1 minute prior to the start of the n-C₆H₁₄ peak start to the retention time of C₁₂H₂₆
- (2) Light oil carbon range (C₁₂ to C₂₈) : from the retention time of n-C₁₂H₂₆ to the retention time of C₂₈H₅₈
- (3) Residue oil carbon range (C₂₈ to C₄₄) : from the retention time of n-C₂₈H₅₈ to 0.1 minute after the end of elution of the n-C₄₄H₉₀ peak, and calculation of the total peak area is performed for each carbon range.

The Guideline describes the determination of the total of the area values within the respective carbon ranges described above, but thereafter, there is no mention of the calculation method.

Shown below is one example of carbon ranges and the TPH quantitation method.

1. Generate a calibration curve based on the total area value of the RT-C₆ to RT-C₄₄ fraction using ASTM standard light oil, and calculate the sensitivity correction coefficient

(F : standard light oil concentration with respect to 1 area).

2. Multiply this F value by the area value for the gasoline fraction (C₆ to C₁₂), the light oil fraction (C₁₂ to C₂₈) and the residue oil fraction (C₂₈ to C₄₄) of the extraction sample to calculate the concentration for the respective ranges.

3. Sum the concentration of each fraction and calculate the amount of TPH.

For details of the operations and conditions, refer to the Ministry of the Environment internet home page¹⁾.

Table1 Analytical Conditions

Model	: GC-2010AF/AOC (FID), GC-solution
Column	: UA-TPH 8 m × 0.53 mm I.D. df=0.9 µm (Frontier Lab) or BPX-1 8 m × 0.53 mm I.D. df=0.9 µm (SGE, 10 m column cut to 8 m)
Detector	: FID
Column Temp.	: 35 °C (2 min) -10 °C/min -375 °C
Carrier Gas	: 5 mL (2 min) -2 mL/min -19 mL
Inj.Temp.	: 100 °C -10 °C/min -375 °C
Det.Temp.	: 375 °C
Injection Method	: Cool on-column, Injection Volume:1 µL

References:

- 1) Ministry of the Environment internet home page: <http://www.env.go.jp/water/dojo/oil/02-3.pdf>

NOTES:

- *This Application News has been produced and edited using information that was available when the data was acquired for each article. This Application News is subject to revision without prior notice.



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