

## Analysis of TPH in Soil (Part 2)

Previously, we introduced the "Analysis of TPH in Soil (Part 1)" in Application News G247, which discussed 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." as announced by Japan's Ministry of the Environment in June 2006. Moreover, we described the "TPH Test Method using GC-FID" (hereafter, "Guideline") which is contained in Volume 2 of this Guideline, under the Technical Material Part 2

Specialty Section, Chapter 1 Situation Ascertainment Investigation<sup>1)</sup>, and specifically introduced the on-column injection method for analysis of TPH in soil using the 0.53 mm I.D. wide-bore column.

This Application News introduces the other analysis method for TPH in soil prescribed in the same Guideline, using the splitless method with a 0.32 mm I.D. capillary column (where column temperature program starts at 35 °C).

### ■ Determining Quantitation Range of TPH

In the Guideline, the quantitation range of TPH is determined using a standard solution containing n-C<sub>6</sub>H<sub>14</sub> and n-C<sub>44</sub>H<sub>90</sub>.

The quantitation range is from 0.1 minute prior to the start of the n-C<sub>6</sub>H<sub>14</sub> peak (starting retention time, RT-C<sub>6</sub>) to 0.1 minute after completion of elution of the n-C<sub>44</sub>H<sub>90</sub> peak (ending retention time, RT-C<sub>44</sub>).

Figures 1 and 2 show chromatograms of paraffin mixtures used 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 (CS<sub>2</sub>) 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 CS<sub>2</sub>-only (solvent blank) chromatogram, and the calibration curve is generated with a high-concentration range of 250 to 10000 mg/L or a low-concentration range of 50 to 1000 mg/L, according to the sample concentration.

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-C<sub>6</sub>H<sub>14</sub> to n-C<sub>44</sub>H<sub>90</sub>.

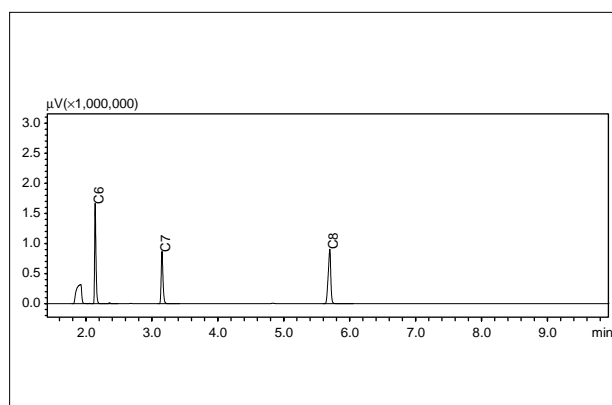


Fig.1 Chromatogram of Standard Solution (n-C<sub>6</sub>H<sub>14</sub> ~ n-C<sub>8</sub>H<sub>18</sub>)

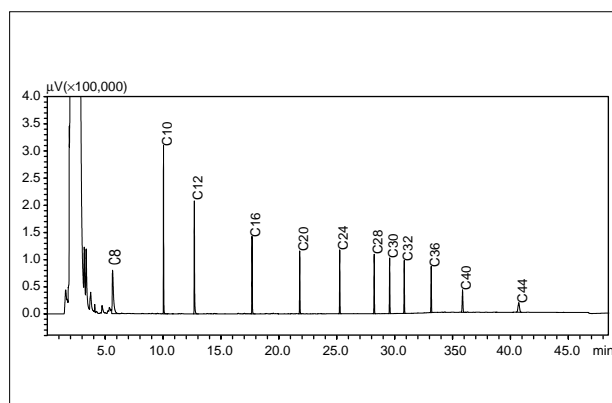


Fig.2 Chromatogram of Standard Solution (n-C<sub>8</sub>H<sub>18</sub> ~ n-C<sub>44</sub>H<sub>90</sub>)

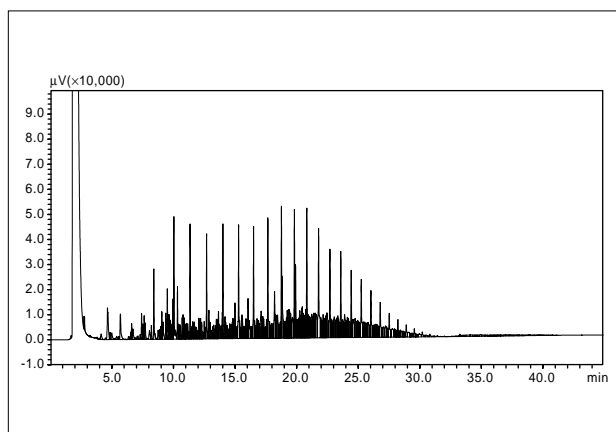


Fig.3 Chromatogram of ASTM Standard Light Oil Solution (1000 µg/mL)

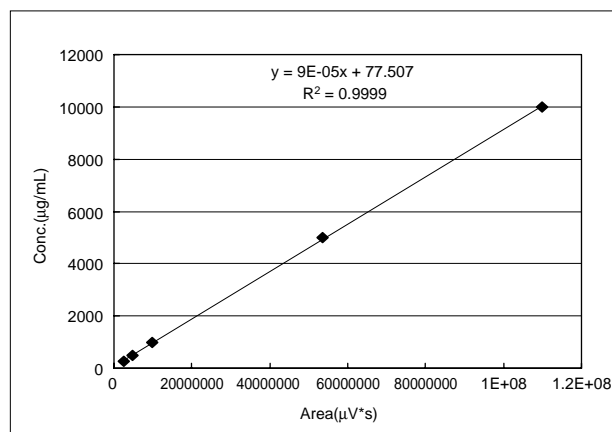


Fig.4 Calibration Curve of ASTM Standard Light Oil Solution (250 to 10000 µg/mL)

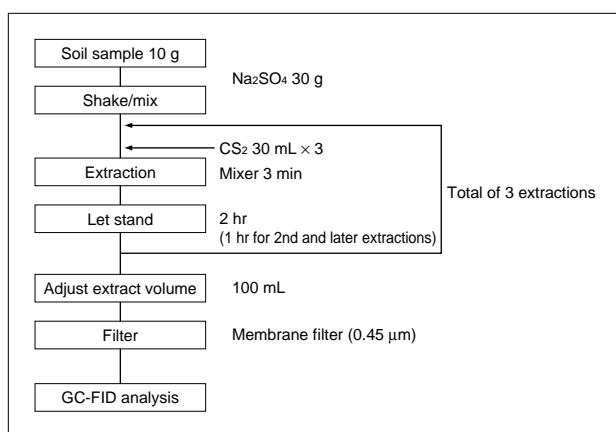


Fig.5 Procedure for Extraction of TPH from Soil

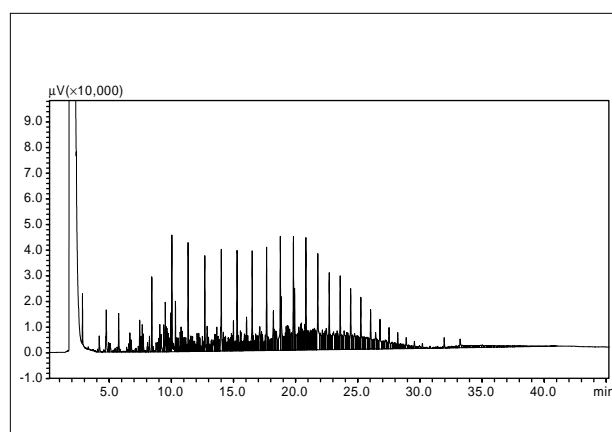


Fig.6 Chromatogram of Extract of TPH-Spiked Soil Sample

The Guideline provides explanations of the concentration calculation methods employed for the "Gasoline Carbon Range", "Light Oil Carbon Range" and "Residual 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 residual oil carbon range are:

(1) Gasoline carbon range (C<sub>6</sub> to C<sub>12</sub>) : from 0.1 minute prior to the start of the n-C<sub>6</sub>H<sub>14</sub> peak to the retention time of C<sub>12</sub>H<sub>26</sub>

(2) Light oil carbon range (C<sub>12</sub> to C<sub>28</sub>) : from the retention time of n-C<sub>12</sub>H<sub>26</sub> to the retention time of C<sub>28</sub>H<sub>58</sub>

(3) Residual oil carbon range (C<sub>28</sub> to C<sub>44</sub>) : from the retention time of n-C<sub>28</sub>H<sub>58</sub> to 0.1 minute after the end of elution of the n-C<sub>44</sub>H<sub>90</sub> 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-C<sub>6</sub> to RT-C<sub>44</sub> 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 (C<sub>6</sub> to C<sub>12</sub>), the light oil fraction (C<sub>12</sub> to C<sub>28</sub>) and the residue oil fraction (C<sub>28</sub> to C<sub>44</sub>) of the extraction sample to calculate the concentration for each range.

3. Sum up the concentrations of all the ranges to obtain the TPH content.

For details of the operations and conditions, refer to the Ministry of the Environment internet home page<sup>1)</sup>.

Table 1 Analytical Conditions

Model	: GC-2010AF/AOC (FID), GC-solution
Column	: Rtx-5 MS 30 m × 0.32 mm I.D. df=0.25 µm (Restek)
Detector	: FID
Column Temp.	: 35 °C (5min) -10 °C/min - 320 °C (10 min)
Carrier Gas	: He 62.2 kPa (5 min) - 2.72 kPa/min - 75.8 kPa - 30.3 kPa/min - 136.4 kPa - 4.29 kPa/min - 228.7 kPa (10 min) (Corresponds to 2 mL (10 min) - 1 mL/min - 4mL)
Inj.Temp.	: 320 °C
Det.Temp.	: 320 °C
Inj. Method	: Splitless, Injection Volume : 1 µL

#### References:

1) Japan's 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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