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Evaluation of Detection Performance of Turbidity Analysis for Alcohol–extracted Hydrocarbons by Comparison with Other Analytical Methods for Petroleum in Soil Samples

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To verify the validity of the simple detection method aimed at in this study and confirm the ability of the turbidity analysis as a screening method for alcohol–extracted organic compounds, the performance was compared with the methods commonly used in laboratories or gravimetry and gas chromatography–flame ionization detection technique (GC–FID). As a result, the turbidity analysis worked to simply detect petroleum at concentration levels of 500 to 10,000 mg kg^{-1} and was comparable to other methods over a variety of soil properties and petroleum hydrocarbon compounds. The turbidity analysis is helpful for screening soils polluted with organic compounds extractable with alcohol, without any special reagents or apparatus at a site.

INTRODUCTION

Petroleum hydrocarbons scattering over the surface and the subsurface environment give degradation of the quality of soil and water resources, resulting in substantial health risks to the human beings, plants and animals. To remove petroleum from the ground, it is supposed that the petroleum be extracted directly from the site or the ground be remediated by decomposing petroleum using oxidizing agents. However, a problem involved in the work is to know how large and deep it is in the ground when taking care of petroleum as a pollutant in the ground. It is important to effectively track petroleum leaked into the environment in a simple and quick manner. On–site screening methods have been desired, therefore, across the world for wide application to the inspection of hydrocarbon contaminants in soil.

We already reported an easy method based on a turbidity analytical technique to quickly and semi–quantitatively detect organic compounds through a simple procedure using ordinary chemicals and common equipment at a site (Sakai *et al*., 2011). Organic compounds can be detected at concentration levels of 2,000 to 15,000 mg kg^{-1}. The indication of the presence of petroleum suggests that the ground be polluted with the pollutant at the site. But the performance could be influenced by a variety of factors such as soil properties or texture, water contents and chemical characteristics of petroleum in soil samples. In this study, we compared the performance of the turbidity analysis with that of two other methods commonly used in laboratories or gravimetry and gas chromatography–flame ionization detection (GC–FID). We also evaluated the ability of a turbidity analysis–based screening method using a typically available test–kit in the market based on the turbidimetry analytical principle.

MATERIALS AND METHODS

Samples:

To compare the performance of the turbidity analysis for organic compounds extracted with alcohol, petroleum spiked in soil samples were detected individually in three analytical ways or the following detection procedures. The samples were prepared using two sorts of soil, or fine (sand) and granule (loam) particle soils, which were spiked with three species of petroleum or gasoline, kerosene and light oil at three levels of concentration of 500, 1,500 and 10,000 mg kg^{-1}. Each species of petroleum was added and well stirred with a glass rod to the 100 g of species kind of soil sample in a 1000 mL grass bottle. The grain size of the soil samples was checked prior to this trial as listed in Table 1. Water contents of soil samples were approximately 20% for every sample. Petroleum was purchased from commercial gas stations in Japan just before the sample preparation. The quality

Table 1. Grain size distribution of the soil samples used in this study

Grain size	Content ratio	
	Sand	Loam
Sand (0.075 – 2 mm)	100%	14%
Silt (0.005 – 0.075 mm)	0%	55%
Clay (<0.005 mm)	0%	31%

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of each petroleum is classified with JIS K 2202–2 for gasoline, JIS K 2203–1 for kerosene and JIS K 2204–2 for light oil, respectively. For each sample, the concentration of the target compounds in soil samples was measured twice.

Detection methods:

(1) Turbidity analysis

Organic compounds extracted with alcohol were salted–out. The turbidity caused was observed with a photometer. A soil sample weighed out at 1 g was mixed with 10 mL of 2–propanol as an alcohol solvent. The mixture was shaken for five min. and then filtrated with a 0.45 μm pored membrane filter after kept stood for five min. The filtrate was diluted with water up to 100 mL. A 30% sodium chloride solution, 1 mL in volume, was added to the diluted filtrate. The filtrate was shaken for 1 min. and was left for another 1 min. The absorbance of the solution was measured at the wavelength of 660 nm using a quartz cell with a 10–mm optical path. Figure 1 schematically illustrates the entire procedure.

(2) GC–FID

Organic compounds extracted with liquid carbon disulfide were analyzed by GC–FID according to the procedure described in U.S. EPA methods (U.S. Environmental Protection Agency Method, 2003). A sample, the weight 10 g, was mixed with liquid carbon disulfide. The mixture was shaken three times with a vortex mixer for 3 min., and then left to stand for 2 h after the first shaking operation and for 1 h each after the second and third operation. The resulted solution was finally filtered with a 0.45–μm pored filter for the detection work. A column modified with methyl silicon was used for the GC–FID analysis. The temperature was maintained at 375 °C for the detector. The total amount of hydrocarbons was calculated by summarizing the area of each peak C6 to C44 recorded in a chromatogram.

(3) Gravimetry

The entire organic compounds extracted with n–hexane at 80 °C were weighed. A soil sample, the weight 20 g, was mixed with a solvent containing 20 mL of n–hexane and 50 mL of water. The mixture was shaken for 10 min. The extraction was repeated twice for each soil sample with another solvent. The residue was weighed with a balance, which was prepared by heating the extract at 80 °C for 30 min. and keeping in a desiccator for 30 min. thereafter.

(4) Test–kit

PetroFLAG® (Dexsil Corporation, Hamden, CT. USA) is a test–kit commercially available for screening petroleum, which applies the turbidity analytical principle to the detection of petroleum (U.S. Environmental Protection Agency Method, 1996). It consists of a simple balance and a small–scale photometer and uses an alcohol as a solvent and a reagent containing salts for salting–out. Detection with the test–kit was carried out according to the manufacture's protocol. A soil sample weighed at 10 g was mixed with 10 mL of an alcohol based extraction solution ready for use. The mixture given after shaken for four min. and then filtered with a membrane filter was added with a developer solution containing salts after standing for 1 min. The developer solution containing the filtrate was shaken for 10 s and stood for 10 min. The absorbance of the resulted solution was measured with an analyzer furnished as a component of the kit or a small photometer pre–programmed with response factors corresponding to respective hydrocarbon types.

RESULTS AND DISCUSSION

Table 2 lists all the results of the comparison. Figures 2 and 3 schematically show the same data as that in the Table for easier comprehension. The concentration detected by the turbidity analysis with alcohol extraction showed good agreement with that of petroleum spiked in soil samples as a standard, especially in the cases of kerosene and light oil. Regarding analytical capacities, the performance of the method is comparable to that of GC–FID which is one of the precise analytical methods commonly used in laboratories. Observation of the concentration in each sample twice gave good reproducibility. With gasoline, the concentration value obtained through each method was less than that of gasoline spiked into soil or sometimes lower than the detection limit as the concentration of gasoline spiked was low. This is because that petroleum is easily vaporized, first of all. Furthermore, the turbidity analysis would have sensitively been affected since the amount of the soil sample applied to the extraction procedure is smaller than that for other methods. To use a larger amount of soil samples simply provides easier operation and better results for the detection of volatile hydrocarbons. Gravimetry of extracts with n–hexane gave the poorest results. In the cases of gasoline and kerosene, all of the concentration values measured by gravimetry were below the detection limit. This would also have been due to volatiliza-

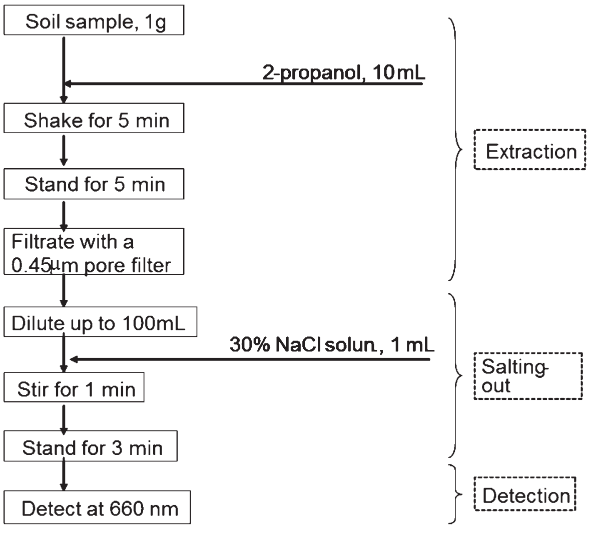

Fig. 1. Procedure for the turbidity analysis of petroleum using 2–propanol as a solvent.

tion occurring 30 min. after heating at 80 °C in the preparation procedure.

The results from the detection with a commercial test–kit or PetroFLAG® also showed good accordance with the concentration of petroleum samples spiked in the range of low concentrations. At a high concentration or 10,000 mg kg^{-1}, the photometer dedicated in the test–kit indicated a message “over range” for some soil samples giving high turbidity intensities over the service range, which is installed therein to cover up to 10,000 mg kg^{-1} for 10 g of soil samples. The manufacture’s guidance instructs that 1 g of soil samples is applied instead of 10 g designated as the original protocol in this case. The concentration values obtained following the instructions were below those of spiked petroleum samples. Because the PetroFLAG® is originally designed for soil samples with low water contents, higher water contents about 20% or higher may negatively work in the extraction and development processes. It should be recommended that a higher volume of extracting solvents or 25 mL be used, which is commercially available for soil samples with higher water contents, especially when high concentration of hydrocarbons is contained in soil samples.

With soil characterization, there is a little difference between sand and loam in the concentration values obtained. Although concentration values measured for loam samples are actually slightly lower than those for sandy samples, the detection performance will be good

Table 2. Detection of petroleum spiked in the soil samples

Sample		Concentration detected (mg kg^{-1})			
	Petroleum spiked in matrix (mg kg^{-1})	Alcohol extraction / Turbidity analysis (Sample, 1 g)	Carbon disulfide extraction / GC–FID (Sample, 10 g)	n–Hexane extraction / Gravimetry (Sample, 20 g)	Test–kit detection (PetroFLAG®) (Sample, 10 g)
Gasoline in sand	500	Not detectable	38	< 50	48
	500	Not detectable	39	< 50	60
	1500	Not detectable	260	< 50	240
	1500	Not detectable	300	< 50	270
	10000	8700	3600	< 50	Over range**
	10000	6900	3200	< 50	Over range**
Gasoline in loam	500	Not detectable	28	< 50	75
	500	Not detectable	28	< 50	72
	1500	Not detectable	250	< 50	210
	1500	Not detectable	240	< 50	240
	10000	5300	3900	< 50	1500
	10000	3900	3300	< 50	1400
Kerosene in sand	500	400	500	< 50	660
	500	300	500	< 50	680
	1500	1400	1700	< 50	1700
	1500	1300	1500	< 50	1600
	10000	10000	8900	< 50	Over range**
	10000	8300	9100	< 50	Over range**
Kerosene in loam	500	300	270	< 50	410
	500	400	310	< 50	510
	1500	750	1100	< 50	1700
	1500	640	1000	< 50	1600
	10000	11000	7300	< 50	Over range**
	10000	11000	7500	< 50	Over range**
Light oil in sand	500	400	690	79	810
	500	260	690	64	740
	1500	1100	1700	240	1400
	1500	1000	1800	190	1500
	10000	7800	8600	3600	Over range**
	10000	8700	9500	3700	Over range**
Light oil in loam	500	300	200	< 50	320
	500	300	220	66	360
	1500	560	1200	< 50	1100
	1500	690	1100	100	1000
	10000	8400	9800	970	Over range**
	10000	9400	9400	510	Over range**

** : The expression of “Over range” in the results on the PetroFLAG® detection means concentration values higher than 10,000 mg kg^{-1} due to high turbidity intensities observed over the service range installed in the PetroFLAG® photometer.

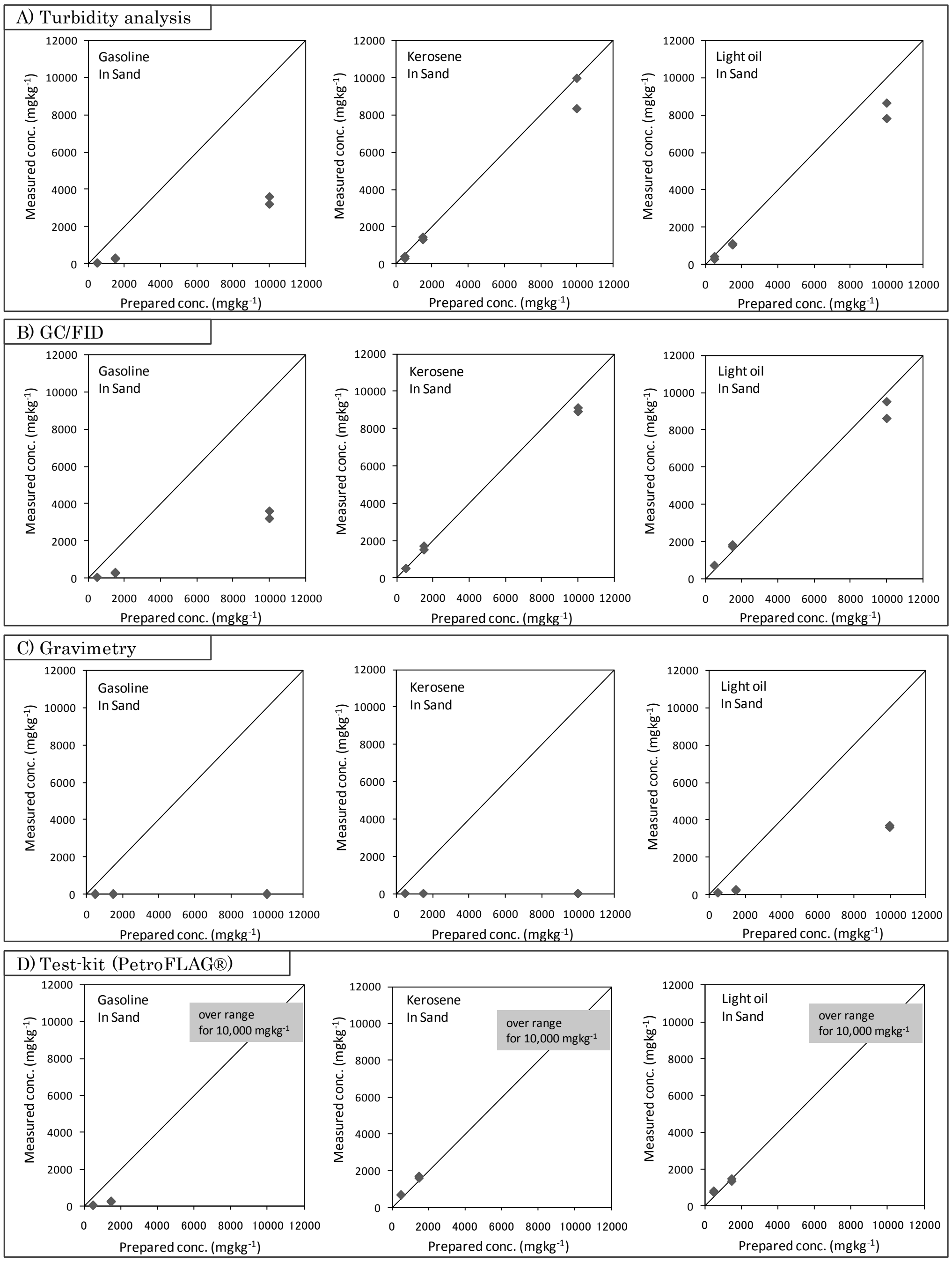

Fig. 2. Results of the test to detect petroleum in sandy samples spiked with gasoline, kerosene or light oil, which was tried by each analytical method; A) alcohol–extraction/turbidity analysis, we have developed, B) GC–FID, C) gravimetry and D) Test–kit detection based on turbidimetric detection.

enough to work as a turbidity analytical method as well as GC–FID.

In this study, the distribution of the carbon numbers of each species of petroleum was also analyzed by GC–FID. Hydrocarbons C6 to C44 were observed, while gasoline, kerosene and light oil corresponded to less than C6, C6 to C21 and C6 to C44, respectively. These results indicate that the turbidity analysis method can detect hydrocarbons approximately from C6 to C44. This suggests that a large variety of petroleum compounds and products containing these alkanes can be detected in this manner.

In conclusion, the turbidity analytical method can be used as a screening method for alcohol–extractable petroleum in soil in a simple manner directly at a site. The performance is comparable with or in some cases better than that of other methods commonly used in laboratories, with a large variety of soil properties and organic compounds. The turbidity analysis without requiring any special reagents and apparatus will be helpful in screening soils polluted with organic compounds at a site with good cost performance.

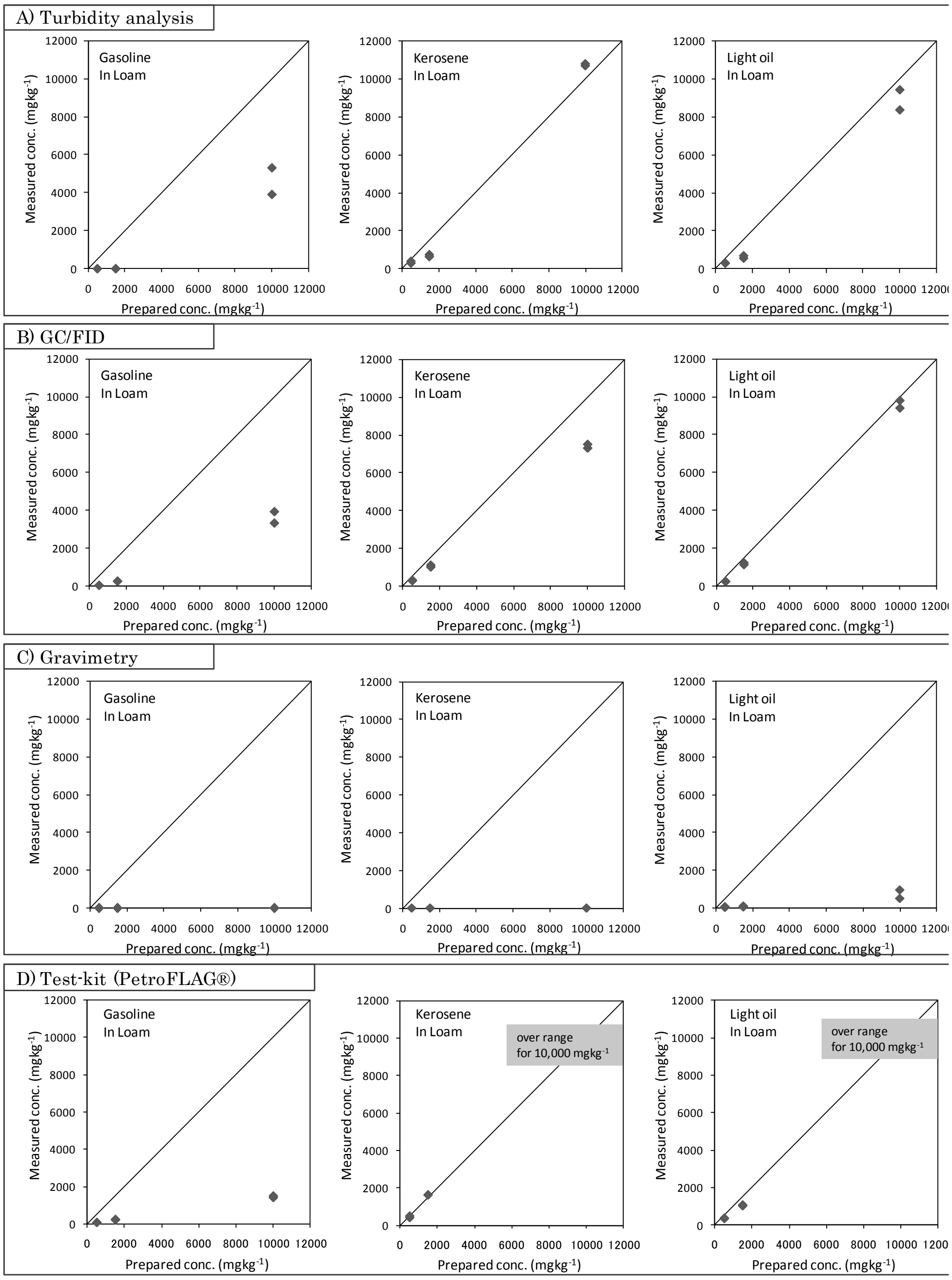

Fig. 3. Results of the test to detect petroleum in loam samples spiked with gasoline, kerosene or light oil, which was tried by each analytical method; A) alcohol–extraction/turbidity analysis, we have developed, B) GC–FID, C) gravimetry and D) Test–kit detection based on turbidimetric detection.

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