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Inter-laboratory Comparison Trials for Turbidity Analysis of Petroleum in Soil Samples to Confirm Its Performance for Universal Practical Application

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To confirm the performance of turbidity analysis (TA) of petroleum in soil samples, comparison tests were organized between two countries. For this purpose, two TA procedures were checked; one is in batch-wise operation and the other by a method using a commercially available test kit. To evaluate the performance, the petroleum spiked in the soil samples was determined also by GC-FID, which were provided for the TA detection in the two procedures. The results support that TA quickly detects the petroleum extracted with lower alcohols in easy operation and with good recoveries equal to those given by GC-FID.

Key words: Petroleum, Screening test, Soil pollution, Turbidimetry

INTRODUCTION

Turbidity analysis (TA) was a minor detection technique for petroleum with few papers reporting its application to analytical or environmental sciences. Only one kind of test kits is commercially available based on this analytical principle (U.S. Environmental Protection Agency, 1996). However, commercial products are basically users' convenience oriented without scientific information in detail, especially when they are arranged with test kits ready to use. TA is to detect clouds caused in a mixture of polar organic solvent and water. The petroleum solvated with such organic solvents or lower alcohols is salted out to make the mixture white as micelles or tiny oil pools generated in the mixture system when the ion strength is immediately increased with salt added. The intensity to scatter optical light introduced into the system depends on the concentration of the micelles or oil pools originating from the petroleum extracted with the alcohols. Thus, the turbidity degree would be proportional to the concentration of the petroleum as a sample. Under specific analytical conditions, the turbidity detection gives semi-quantitative information on sample concentrations as a concentration level.

Analytical applications have never been seen besides the test kit or PetroFlag in the TA detection work. However, no principle of the test kit is shown in detail.

This has limited its applications as users hesitate to refer to the results from the test kit in any technical reports due to the difficulty in describing the principle of the test kit, on which little information is given by the manufacture. To create a variety of applications of the TA detection system, simple turbidity analytical detection was developed using 2-propanol alone as a solvent and sodium chloride as a salt (Sakai *et al.*, 2011; Fujita *et al.*, 2011). The petroleum extractable with 2-propanol can be detected at the concentration levels 1,000 mg kg⁻¹ to 2,000 mg kg⁻¹ as a sample in soil. The whole process of this method has to manually be operated as it is not automatized or arranged like test kits for convenience. However, it is easy to try the batch-wise TA in normal analytical laboratories as the reagents and instruments needed are common, simple and low in cost. Furthermore, the experience in the process is helpful in realizing how it is going with TA detection of petroleum because the operation exactly follows the turbidity generating procedure fully disclosed with scientific data.

The basic performance of TA was confirmed by the developed 2-propanol method and the commercial test-kit method. This short paper reports the results of a comparison to support TA as a screening method to detect petroleum in soil matrices which is extractable with lower alcohols.

PRINCIPLE

As described above, TA is sort of a scattering or absorption analytical detection technique to observe white clouds appearing in a mixture containing the petroleum extracted with lower alcohols. For the details, refer to the papers (Sakai *et al.*, 2011; Fujita *et al.*, 2011). For the test kit commercially available based on the same analytical principle, check the technical report (U.S. Environmental Protection Agency, 2006). Gas-

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chromatographic separation–flame ionization detection (GC–FID) followed the standard (Korea Environmental Protection Agency, 2009) to provide the concentration of the petroleum existing in the prepared samples.

MATERIALS AND METHODS

To make sure of the performance of the TA, laboratories in Korea and Japan applied the two methods, or the 2–propanol TA and the test–kit method to the same samples. A sandy material like silica sands was used as a matrix of the samples. Light oil and a lubricant were added as a target compound or petroleum into the soil matrix. Their concentrations were $1,000 \text{ mg kg}^{-1}$ and $2,000 \text{ mg kg}^{-1}$, respectively. Eventually, four kinds of soil samples were prepared for the check in the two countries. The original soil material, 1.2 kg in weight, was autoclaved at 120°C for 1 h to deactivate microbes and divided into four portions to add the two kinds of petroleum at two concentrations. Each portion of the divided

soil material was carefully mixed with the petroleum dissolved into acetone at a calculated amount. The solvent was vaporized little by little over time in a hood at room temperature. However, the light fractions with short carbon chains in the petroleum would be gone while leaving the soil samples in the ambient environment. In Korea, 100 g of each sample was sent to a laboratory after they were prepared. The rest was kept in Japan for trials.

The analytical procedures were according to the papers (Sakai *et al.*, 2011; Fujita *et al.*, 2011) or the instructions designated by the manufacturer for the 2–propanol TA and the test–kit method, respectively. With the test–kit method, it is instructed that 10 g of soil sample is used for the method as a common way suggested by the manufacturer. However, 5 g of soil samples was taken this time since the concentration levels were a bit too high for the test kit detection.

To confirm the concentration of the petroleum in soil matrix after the matrix material was added with the petroleum, dried at room temperature and delivered to the laboratories for these comparison trials, GC–FID was performed for all the same soil samples following the standard (Korea Environmental Protection Agency, 2009). All the tests including the 2–propanol TA, the test–kit method and the GC–FID were completed for continuous three weeks after the sample preparation.

RESULTS AND DISCUSSION

Table 1 shows the concentrations suggested by the two turbidity analyses as screening methods and determined by GC–FID as a reference method. Most of the concentration values are below those of the petroleum used for spiking, including the case with GC–FID. The 2–propanol TA estimated the concentrations higher than those detected by other methods. The amounts of the soil samples applied were 1 g, 5 g and 10 g for the 2–pro-

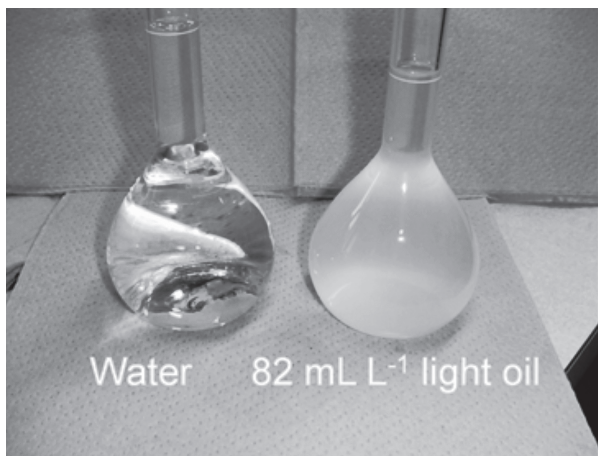


Fig. 1. Turbidity caused with 82 mg mL^{-1} of light oil in a 2–propanol solution.

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

Sample	Determined or detected concentration / mg kg^{-1} (n=3)				
	GC–FID (Sample, 10 g)	2–Propanol extraction method (Sample, 1 g)		Test kit (PetroFlag) (Sample, 5 g)	
	Korea	Korea	Japan	Korea	Japan
1,000 mg kg^{-1} light oil in sandy soil	360	750	910	500	460
	390	550	770	560	400
	370	610	910	480	420
2,000 mg kg^{-1} light oil in sandy soil	870	2,210	1,520	1,180	850
	990	2,420	1,710	1,470	930
	890	1,960	1,710	1,170	910
1,000 mg kg^{-1} lubricant in sandy soil	820	670	880	760	680
	860	690	770	810	680
	860	1,070	830	840	660
2,000 mg kg^{-1} lubricant in sandy soil	1,580	1,940	1,630	1,530	1,240
	1,470	1,380	1,800	1,620	1,300
	1,600	1,720	1,760	1,570	1,240

panol TA, the test-kit method and GC-FID, respectively. Thus, the 2-propanol TA shows concentration reproducibility lower than that given by other methods that need soil samples at an amount five or 10 times larger. Efforts are required and special equipment is needed to successfully deal with large volumes of soil samples from pre-treatment through analysis. Screening methods should be expected for outdoor use in the field or for a lot of samples to be checked at a time. Thus, small amounts of soil samples make the operation easier and contribute to time saving. It should be borne in mind that screening methods are not concerned with the concentration values but aim at the levels of target compounds. There is no interest or intention in obtaining exact concentration values. To say nothing of cost, the method should be helpful in reducing it, which requires common reagents and instruments available wherever. The 2-propanol TA, a simple detection method based on the TA principle, is suitable to the situation where screening methods are applied.

The test kit is completely organized to enable users, who are not necessarily experienced or trained, to effortlessly and casually try the turbidity analytical technology. However, everything technical including the chemical compositions of the reagents used for the test kit is protected to the public as black boxes for commercial reasons to keep intellectual property secret. Thus, this would avoid popularization of the good idea to perform

turbidity analysis in application fields because no technical report can refer to the principles that are not clearly disclosed by the manufacturer. In this comparison, the two TAs indicated the petroleum concentration in the same levels as those obtained through GC-FID. This suggests that the TA methods work as a quantitative detection method under the optimum specific analytical conditions even while the principle of the test kit is still in a black box due to manufacturer's non-disclosure of the secret. To confirm this, further comparison tests should be arranged with a variety of soil matrices, petroleum species and concentration levels.

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