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Surfactant Interference in Turbidity Analysis for Petroleum in Soil Samples

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To confirm the performance of turbidity analysis (TA) for petroleum in soil samples and assess false negative risks thereto, surfactant interference effects were investigated on TA. Anionic and nonionic surfactants were spiked into 2–propanol extracts of petroleum, which were brought in the analytical procedure. The relation between the concentration of surfactants and the turbidity degree or absorbance of the solution resulted when petroleum was salted–out was evaluated. The absorbance value decreased with the concentration of surfactant increased, resulting in occurrence of interference. However, the shapes of working curves remain the same even when surfactants were added. The results support that TA is still robust enough and works as a detection method when applied to samples in the environment where surfactants were controlled not to interfere with the detection.

Key words: petroleum, screening test, soil pollution, turbidimetry

INTRODUCTION

Turbidity analysis (TA) is to detect clouds caused in a mixture of water and a polar organic solvent. The petroleum solvated in 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 as salt is 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 sample petroleum. Under specific analytical conditions, the turbidity detection gives semi–quantitative information on sample concentrations that can be indicated as a concentration level.

Analytical applications have never been seen besides commercially available test kits or PetroFlag in TA detection work (U.S. Environmental Protection Agency Method, 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. This has limited its applications as users hesitate to refer to the results from such test kits in any technical reports due to the difficulty in describing the principle of test kits. To create a variety of applications of the TA detection system, simple turbidity analytical detection has been developed using 2–propanol alone as a solvent and sodium chloride as a salt (Sakai et al., 2011; Fujita et al., 2011; Sakai et al., 2012). It is easy to try in normal analytical laboratories as the reagents and instruments needed are common, simple and low in cost. The petroleum extractable with 2–propanol can be detected at concentration levels of 1,000 mg kg⁻¹ to 20,000 mg kg⁻¹ as a sample in soil.

Surface–active agents such as soap or common surfactants may adversely affect the detection and reduce the degree of turbidity. To avoid false negative results given by TA detection, surfactant behavior to interfere with the detection should be verified.

This short paper reports the results of an investigation on surfactant interference effects on the TA detection system. Common anionic and nonionic surfactants were tested to show the behavior of interference with the formation of turbidity.

MATERIALS AND METHODS

As described above, TA is a sort of scattering or absorption analytical detection technique to observe white clouds appearing in a mixture containing petroleum extracted with lower alcohols. In summary, 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 it was 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 one min and was left for another one min. The absorbance of the solution was measured at a wavelength of 585 nm using a quartz cell with a 10–mm optical path. Refer to the papers (Sakai et al., 2011; Fujita et al., 2011; Sakai et al., 2012) for the details.

To investigate interference effects by surfactants on the TA detection system, a surfactant was added to a 2–propanol extraction solvent of petroleum at several levels of concentration. The relation between the concentration of a surfactant and the turbidity degree or absorbance of the solution resulted when petroleum was salt-
ed-out was evaluated. Light oil and lubricant were used as a target compounds or petroleum. Sodium dodecyl sulfate and heptaethylene glycol monododecyl ether were used as a representative of common anionic and nonionic surfactants, respectively. The range of surfactant concentrations was from 0.1 mg L\(^{-1}\) to 1,000 mg L\(^{-1}\) in a 2-propanol extract, which corresponds to those from 1 mg kg\(^{-1}\) to 10 g kg\(^{-1}\) if in soil.

RESULTS AND DISCUSSION

Figure 1 illustrates the effect of surfactants on working curves of light oil and lubricant when an anionic or nonionic surfactant was spiked. The absorbance value decreased with the increase of the surfactant concentration. However, the shapes of working curves did not change with addition of surfactants. This means that interference occurs depending upon the concentration of surfactants. Its effects on working curves can be estimated over the range of surfactant concentration tested in the study. False negative false detection results can be avoided if users confirm the concentration level of surfactants in the sample. Shaking a soil sample with water to look for the formation of pronounced foam may be useful for indicating if significant amounts of surface-active agents are present in the soil sample.

Figure 2 shows the magnitude of interference by surfactants. The horizontal axis shows surfactant concentration in a 2-propanol extract while the vertical axis indicates relative absorbance normalized by the absorbance without surfactants. Results are given with surfactants, anionic or nonionic, each in two cases when combined with light oil and lubricant individually. The concentration of oils in a salting-out solvent was 88 mg L\(^{-1}\) and 86 mg L\(^{-1}\) for light oil and lubricant, respectively. The figure indicates that there was no significant interference at concentrations of surfactants up to 0.1 mg L\(^{-1}\) (1 mg kg\(^{-1}\) in soil) and around 30% suppression of the turbidity degrees at 1 mg L\(^{-1}\) (10 mg kg\(^{-1}\) in soil) for the anionic surfactant tested. For the nonionic surfactant, there was also no significant interference at concentrations up to 1 mg L\(^{-1}\) (10 mg kg\(^{-1}\) in soil) and about 30% suppression of the turbidity degrees at 60 mg L\(^{-1}\) (600 mg kg\(^{-1}\) in soil). Given that approximately 80% suppression was observed for both anion and non-ion surfactants at a concentration higher than 100 mg L\(^{-1}\) (1 g kg\(^{-1}\) in soil), petroleum at a concentration not less than 50 mg L\(^{-1}\) in a salting-out solvent was detected as a value of turbidity degree, which corresponds to 5,000 mg kg\(^{-1}\) in soil.

This showed different behavior of interference between anion and non-ion surfactants. Non-ion surfactants have specific concentration levels where they start interfering with the TA detection. In contrast, anionic surfactants work as interferences even while their
concentration is low. This might be associated with the difference in molecular structures between anionic and nonionic surfactants. This makes the behavior different as a surface-active agent in oil contained in 2-propanol in the salting-out system. A number of chemical and physical processes and mechanisms could coexist in emulsification through salting-out. This brings difficulties in fully understanding what take place with the interference behavior observed in the turbidity system. For successful application of the TA detection or such an easy and practical detection system for petroleum to unknown soil samples, however, it is to be born in mind that surfactants bother detection performance when they exist at significant concentrations in samples.

REFERENCES