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Application News

Fourier Transform Infrared Spectrometer IRXross™

Analysis of Total Oil and Grease (TOG) and Total Petroleum Hydrocarbons (TPH) in Water Using FTIR Spectroscopy Based on ASTM D7678-17

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User Benefits

- Quantitative analysis of TOG and TPH in water based on ASTM D7678-17 is possible with quantitation mode in LabSolutions™ IR.
- Low concentrations of hydrocarbon in water can be measured using IRXross with high sensitivity.

■ Introduction

Hydrocarbon contamination in various water bodies has become increasingly common around the world. It typically results from spills, leaks, or runoff from industrial activities. Once present in water, hydrocarbons can disperse throughout the environment, causing detrimental effects on environmental and human health as they infiltrate the food chain and pollute drinking water. Thus, it is essential to monitor and assess hydrocarbon contamination in these water bodies.

There are various regulated methods available for determining hydrocarbon content in water samples, such as ISO 9377-2:2000 [1], which is based on gas chromatography, and ASTM D7678-17 [2], which uses Fourier Transform Infrared (FTIR) spectroscopy. In ASTM D7678-17, the total oil and grease (TOG) and total petroleum hydrocarbons (TPH) can be determined from water samples. Cyclohexane is used for solvent extraction, which is relatively safer and more environmentally friendly than the halogenated solvents employed in previous methods, such as ASTM D3921.

This application news demonstrates the analysis of hydrocarbon in water with cyclohexane as the extraction solvent using IRXross (Figure 1), Shimadzu FTIR spectrometer.

Fig. 1 IRXross™

■ Experimental

Standard Preparation and Calibration

A stock standard solution (18,000 mg/L) was prepared by weight with tetradecane (Sigma Aldrich, USA) in cyclohexane. This stock solution was then used to prepare a series of calibration standards with a concentration range from 18 to 1,800 mg/L.

To calibrate based on the equivalent concentration of oil in water, the standard concentrations were adjusted using an enrichment factor. This factor is calculated by dividing the sample volume (450 mL) by the extraction solvent volume (25 mL) as shown in the equation below.

$$\text{Enrichment factor} = \frac{\text{Sample Volume (450 mL)}}{\text{Solvent Volume (25 mL)}} = 18$$

Table 1 shows the concentrations of oil in cyclohexane and the equivalent concentrations of oil in water after adjustment using the enrichment factor.

Table 1 Calibration Standards

Oil in cyclohexane concentration (mg/L)	Oil in water concentration (mg/L)
18	1
90	5
180	10
360	20
900	50
1,800	100

Sample Preparation

Based on the extraction process in ASTM D7678-17, 450 mL of environmental water sample was acidified with hydrochloric acid and extracted with 25 mL of cyclohexane (Kanto Chemical, Japan). The extract was measured directly using the IRXross to determine the TOG concentration. The extract was then filtered through sodium sulfate and Fluorisil to remove traces of water and polar substances. The filtrate was measured with the IRXross to determine the TPH concentration.

Analytical Conditions

All standard and sample solutions were measured using the IRXross. Transmission measurements were carried out using Specac Omni-Cell™ liquid cell with calcium fluoride windows and a 1 mm path length Mylar spacer. Each standard and sample solution was measured in duplicates, and blank measurements were performed using cyclohexane. The instrument conditions are shown in Table 2. The calibration curve was generated in quantitation mode of LabSolutions IR using peak height derived from the baseline to the peak at 1377 cm^{-1}, with the baseline drawn from 1365 to 1392 cm^{-1}.

Table 2 Analytical Conditions

Instrument	: IRXross Specac Omni-Cell (1 mm path length, CaF_2 windows)
Resolution	: 8 cm^{-1}
Accumulation	: 45
Apodization function	: SqrTriangle
Detector	: DLATGS

■ Results and Discussion

The IR spectra and calibration curve of tetradecane in cyclohexane standards are displayed in Figure 2 and Figure 3 respectively. A good correlation coefficient (r^2) of more than 0.999 was obtained, indicating a high level of linearity.

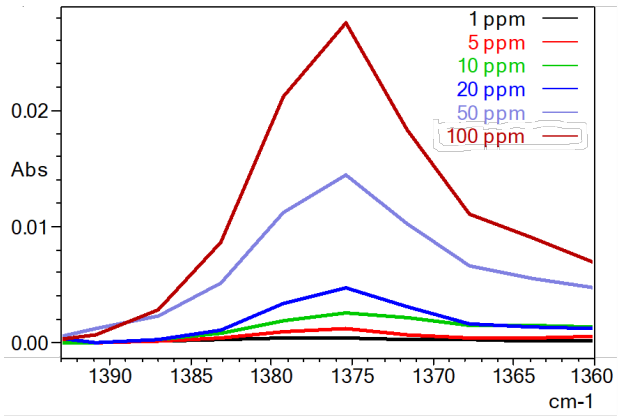

Fig. 2 Overlayed IR Spectra of Tetradecane in Cyclohexane Standards

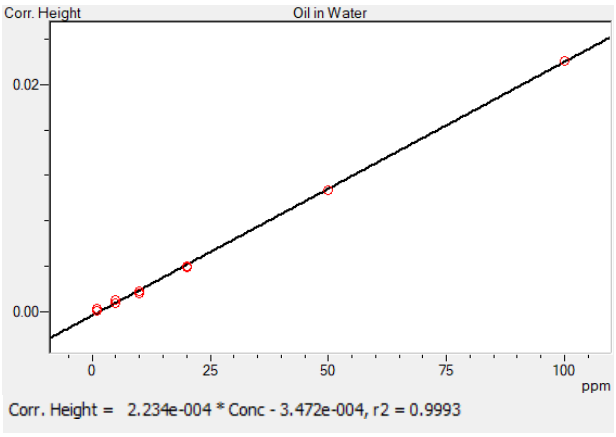

Fig. 3 Calibration Curve of Tetradecane in Cyclohexane

Method Validation

To check the accuracy and precision for this method on IRXross, a validation standard was prepared by spiking tetradecane (10 mg/L) into deionized water and extracted based on the procedure in "Sample Preparation" section. The extract was measured 4 times and the TPH results are displayed in Table 3. A good recovery of the validation standard (100.2%) indicates an accurate extraction and calibration process, and a low relative standard deviation of around 3% suggests a good level of precision.

Table 3 Validation Standard Measurement Results

Prepared oil in water concentration (mg/L)		10.0
Measured oil in water concentration (mg/L)	1	10.4
	2	9.84
	3	10.1
	4	9.70
	Mean	10.02
Recovery (%)		100.2
Relative Standard Deviation (RSD, %)		3.08

Sample Measurement

A seawater sample was collected and prepared based on the procedure outlined in the "Sample Preparation" section. Based on the TPH and TOG results as shown in Table 4, this sample has similar TPH and TOG concentrations.

Table 4 Sample Measurement Results

Total Petroleum Hydrocarbon (TPH, mg/L)*1	Total Oil and Grease (TOG, mg/L) *1
4.92	4.65

*1 Mean value of duplicate measurements

■ Conclusion

This application news demonstrates that IRXross is suitable for the determination of hydrocarbon in water based on ASTM D7678-17 with relatively good sensitivity. Good linearity obtained from the calibration indicates high level of data correlation. Additionally, the results from validation standards shows the method's high accuracy and good level of precision.

<References>

1) ISO 9377-2:2000: *Water quality. Determination of hydrocarbon oil index Method using solvent extraction and gas chromatography*.
2) ASTM D7678-17: *Standard Test Method for Total Oil and Grease (TOG) and Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy*.

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