

# Solvent-free quantification and composition/source analysis of total oil and grease in cooling water

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## Abstract

Total oil and grease (TOG) in water is measured in industrial process waters to determine the concentration of petroleum products present. A common application for TOG measurement is to detect a hydrocarbon leak in circulated cooling water systems. A hydrocarbon leak from a heat exchanger has a negative effect on the stable operation of upgrading and refinery units. Detecting and quantifying a hydrocarbon leak is straightforward; however, identifying the source of the leak can be very time consuming and require a lot of trial and error. In this study, a solvent-free TOG method using *ClearShot extractors* and Fourier transform infrared spectroscopy (FTIR) was developed and optimized for the quantification of bitumen derived hydrocarbon analytes in water. This was further expanded upon to develop a rapid method for hydrocarbon identification in the cooling water by combining chemical fingerprinting with a discriminant analysis classification model. Following the optimized solvent-free TOG method, chemical fingerprints for six different hydrocarbon classes in water were analyzed by FTIR. The classification model for these hydrocarbon classes was constructed using a discriminant analysis algorithm with a 100% classification rate at a TOG mass loading greater than 150  $\mu\text{g}$ . The optimized solvent-free TOG method decreases exposure risk and ergonomic strain for technologists, improving overall safety and environmental performance. The hydrocarbon fingerprinting enables rapid prediction of a leak source which reduces the time and analysis required to isolate a leak as well as reducing the cost and environmental impact associated with blowdown and purge (disposal and treatment) of contaminated water.

## KEYWORDS

fingerprinting, Fourier transform infrared spectroscopy (FTIR), gas oils, solid-phase extraction, solvent-free, total oil and grease (TOG), water quality

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## 1 | INTRODUCTION

Water quality testing in the oil and gas industry is important for both environmental performance as well as for maintaining reliable operations. Total oil and grease (TOG) is a vital water quality parameter serving as a general indicator of the amount of hydrocarbon in water and is recognized as one of the five conventional pollutants designated in the EPA 1974 Clean Water Act.<sup>[1]</sup> In the oil sands industry, measuring water quality, and specifically TOG, is crucial to many aspects of operations, including cooling the upgrading process units through a cooling water system. The methods used to measure TOG have varied greatly over the past decades. Previously accepted methods, such as EPA 413 and ASTM D3921, involved liquid–liquid extractions using Freon (CFC-113) as an extraction solvent. In these methods, TOG content was measured via Fourier transform infrared (FTIR) spectroscopy by measuring the absorbance of the CH<sub>2</sub> stretch at  $\sim 2920\text{ cm}^{-1}$ .<sup>[1,2]</sup> The Montreal Protocol was enacted in 1989 with the goal of eliminating the production and consumption of substances responsible for ozone depletion, such as Freon and other chlorofluorocarbons (CFCs).<sup>[3]</sup> This resulted in the abandonment of the EPA 413 method. As a replacement, the EPA 1664A method was developed. This method still involves a liquid–liquid extraction but uses n-hexane as an extraction solvent in place of Freon. The hexanes are then evaporated and the remaining TOG content is measured gravimetrically.<sup>[2,4]</sup> Due to poor extraction of heavy bitumen-derived hydrocarbons by n-hexane, Syncrude historically has used a method based on ASTM D3921-96. This method involves a liquid–liquid extraction using tetrachloroethylene (TCE) as the extraction solvent and analyzing the extract via FTIR. In more recent years, ASTM D7575 was developed as a solvent-free alternative to these historic solvent extraction methods with equivalency to EPA 1664A. This involves the use of a solid-state Teflon-based extraction membrane called a *ClearShot extractor*, which was developed by Orono Spectral Solutions Inc. (OSS). In this method, a homogenized 10 mL subsample is obtained using a syringe, the subsample is processed through the *ClearShot Extractor* (which attaches directly to the syringe with a luer lock connection), the extractor is dried, then the extractor is analyzed directly using FTIR, and the oil concentration is measured using the maximum peak height of the C–H stretch of the CH<sub>2</sub> functional group at  $\sim 2920\text{ cm}^{-1}$ . ASTM D7575 offers many advantages over EPA 1664A including reduced contact time, reduced ergonomic strain, reduced cost, eliminated solvent use, ability to characterize and identify the oil (because the extractor membrane is transparent to infrared radiation throughout most of the mid-infrared

region), and the flexibility to perform testing in the field or in a laboratory.<sup>[1]</sup>

A common application for TOG measurement in the petroleum industry is detecting hydrocarbon leaks in cooling water systems. Cooling water systems are responsible for heat exchange and the removal of waste heat of oil products in upgrading/refinery units.<sup>[5,6]</sup> Hydrocarbon contamination in a recirculated cooling water system can cause many problems including biofouling, scaling, and microbiologically-induced corrosion. These fouling and corrosion mechanisms can result in operational inefficiencies, equipment failure, and environmental hazards.<sup>[7]</sup> There are also major costs associated with the continuous addition and treatment of clean water and disposal of contaminated water while an exchanger is leaking. If the leak was severe enough that a cooling tower had to be taken offline, this would result in major production, financial, and greenhouse gas (GHG) performance losses. Fast detection of a leak and remediation of contaminated water is essential as the restoration of clean water is required for plants to run smoothly and to ensure future leaks can be detected. Currently, the detection of a leak is done easily by monitoring the concentration of TOG in the cooling water; however, identifying the specific leaking exchanger can be a major challenge. The process involves a lot of trial and error where individual exchangers must be sampled and analyzed. This process can take weeks or months as there are often many potential sources of a leak (for example, there are over 150 heat exchangers in the cooling water system at Syncrude's Mildred Lake plant).

A wide range of analytical techniques are available to evaluate the origin of spilled hydrocarbons. Gas chromatography (GC) techniques are the most widely used for this purpose. However, these techniques have several drawbacks including being expensive and time-consuming, requiring hazardous solvents, and being ill-fit for field measurements.<sup>[8–13]</sup> Spectroscopic methods, such as FTIR, have also been used to analyze the dominant properties of various oils and refined oil products. This type of analysis allows for high throughput, fast response, and can distinguish compounds with similar structures.<sup>[9,10,14–16]</sup> There are dissimilarities in the characteristics of crude oil feedstocks and differences in refinery processes. Due to these differences, most crude oil and petroleum products, to an extent, have chemical compositions that are distinct from each other.<sup>[8]</sup> The variability in chemical compositions results in unique chemical 'fingerprints', providing a basis for identifying sources of oil spills and leaks.

Pairing FTIR with chemometric methods, such as principal component analysis (PCA) and discriminant analysis (DA), can assist in the classification and

identification of hydrocarbon classes.<sup>[9,14–16]</sup> PCA transforms original sample data into new, smaller variables called principal components. These principal components are linear combinations of the original measurement data sets. When plotting principal component scores in scatter plots, samples with similar chemical compositions will be clustered together and notably separated from samples containing different chemical compositions.<sup>[8,14,17]</sup> DA is similar to PCA, the primary difference being that PCA summarizes the overall variability among the spectra as the program has no previous knowledge of the groups, whereas DA exclusively summarizes the differentiation between different groups as the groups are classified prior to analysis.<sup>[18,19]</sup> The use of FTIR analysis combined with PCA and DA has been shown to be useful for the determination of whether an unknown sample matched a known oil sample. This method has been recognized as a simple, economical, and easy access method for oil fingerprinting.<sup>[9,14–16]</sup>

In this study, a method is established for the simultaneous quantification and classification of leaking hydrocarbon in a cooling water system. The solvent-free ASTM D7575 method using the *OSS ClearShot Extractors* was optimized for Syncrude specific analytes (which include heavy gas oils and crudes such as bitumen). Spectral differences from hydrocarbon streams from six different classes (treated light gas oil [LGO], untreated LGO, virgin LGO, treated heavy gas oil [HGO], untreated HGO, and lube oil) were used to develop a discriminant analysis model for hydrocarbon fingerprinting using spectra obtained following the optimized solvent-free TOG method.

## 2 | MATERIALS AND METHODS

### 2.1 | Chemicals and materials

Acetone (spectrophotometric grade), mineral oil, and concentrated hydrochloric acid were purchased from Thermo Fisher (USA). 13 mm *ClearShot Extractors*, *ClearShot* holding cards, polypropylene calibration standard devices and *ClearShot* drying apparatus were purchased from Orono Spectral Solutions Inc. (Maine, USA). Ultrapure 18 M $\Omega$  water produced in-house was used in the experiments. A Branson Bransonic CPXH Digital Bath 8800 (Emerson, USA) was used for sample dispersion. An Alpha FTIR spectrometer manufactured by Bruker was used for all analyses (Ittlingen, Germany). DA models were created using TQ Analyst 9 software from Thermo Fisher (USA). Hydrocarbon samples were obtained from various sample points in Syncrude's Mildred Lake plant site (Mildred Lake, Alberta, Canada).

The number of hydrocarbon samples collected for each of the six general classes as follows: 4 treated LGO, 6 untreated LGO, 3 virgin LGO, 6 treated HGO, 5 untreated LGO, and 6 lube oil. 1 L samples of cooling water for method testing were also collected from the cooling towers on Syncrude's Mildred Lake plant site. Hydrocarbon and water samples were stored at 4°C.

### 2.2 | Method development and optimization

Optimization of ASTM D7575 for oilsands-related analytes focused on (1) sonication and dispersion, (2) drying time, (3) quality control (QC), and (4) calibration. In the first three optimization experiments, a series of samples were prepared in a 32 oz. (946 mL) glass jar with a PTFE-lined lid containing a specific hydrocarbon in 750 mL ultrapure water. A two-inch PTFE stir bar and 75  $\mu$ L concentrated hydrochloric acid were added to the samples. Samples were placed in a sonicating bath preheated to 40°C and sonicated. All samples were shaken by hand for 5 s two to three times during sonication. Once sonicated, a 10 mL subsample was extracted by submerging a 10 mL Hamilton gas tight syringe 2 inches below the solution's surface. The subsample was processed vertically through a 13 mm *ClearShot Extractor* and then the extractor was dried with instrument air at 60 psi for a known amount of time. The processed and dried extractors were loaded in the Bruker Alpha FTIR spectrometer and the maximum peak height of the CH<sub>2</sub> absorbance at  $\sim$ 2920 cm<sup>-1</sup> was recorded using a baseline from 2990 to 2800 cm<sup>-1</sup>. All samples were background corrected to their respective unused extractor.

#### 2.2.1 | Sonication and dispersion

For the sonication and dispersion experiment, a series of 25 mg/L untreated HGO samples were prepared. Sonication times in the 40°C bath were varied from 3 to 5, 8, 12, and 20 min. All these samples were dried with instrument air at 60 psi for 4 min and measured using 200 scans. The effect of adding a 2" PTFE stir bar on the standard deviation of subsampling was also evaluated.

#### 2.2.2 | Drying time

For the drying time experiment, a series of 22 mg/L treated LGO samples were prepared. Samples were sonicated for 20 min (as per the ASTM D7575 method). The processed extractors were dried for 30 s intervals with

instrument air at 60 psi up to 240 s of total dry time and measured using 32 scans after each drying interval.

### 2.2.3 | Quality control

The QC approach used involved an in-jar spike recovery. The QC involved spiking a 100 mL sample of ultrapure water with 1 mL of a 2000 mg/L mineral oil in acetone solution to produce a 20 mg/L mineral oil in water solution. The QC samples were acidified, sonicated for 12 min, subsampled, and processed following the optimized version of the ASTM D7575 method described herein. The processed extractors were dried for 4 min and measured using 200 scans.

### 2.2.4 | Calibration

A set of 13 mm control standard devices (CSDs 0–7) consisting of *ClearShot extractors* with polypropylene vapour deposited on the membrane surface at concentrations of 0.2–40 mg/L were used for calibration. These CSDs are certified by OSS to be equivalent to the EPA 1664A calibration standards. A blank *ClearShot extractor* was scanned as the background in the Bruker Alpha FTIR spectrometer. The CSDs 0–7 were then measured with 200 scans. The maximum peak height of the CH<sub>2</sub> absorbance at  $\sim 2920\text{ cm}^{-1}$  was recorded. Additionally, to understand the effect of calibration standards, 1:1 mixtures of stearic acid:hexadecane and hexadecane:isooctane were prepared in TCE and their CH<sub>2</sub> response was measured using a 1 cm fixed pathlength cell.

## 2.3 | Hydrocarbon classification model development

### 2.3.1 | Standard acetone spike preparation

Hydrocarbon spike solutions were prepared with a target concentration of 1000 mg/L. About 100 mg of hydrocarbon was weighed in a tared clean dry aluminium pan using a disposable pipette. The hydrocarbon was quantitatively transferred to a clean dry 100 mL volumetric flask using spectrophotometric grade acetone. The volumetric flask was filled with spectrophotometric grade acetone, shaken, and sonicated in a room temperature (20°C) sonication bath until the solution was visually homogenous (no suspended oil droplets). The spike solutions were transferred to clean 4 oz. (119 mL) glass jars with PTFE-lined lids.

### 2.3.2 | Standard spike processing

The plunger was removed from a 10 mL Hamilton gas tight glass syringe and a clean luer cap was attached to the syringe barrel. The capped syringe was placed vertically in a holder and filled to the 10 mL mark with ultrapure water. Using a calibrated pipette, the desired amount of acetone spike solution was spiked into the water in the syringe to obtain samples with concentrations of 40, 25, 20, 15, 10, and 5 mg/L. The plunger was replaced in the syringe barrel and the syringe was shaken for 10 s. Once the solution was homogenous, the luer cap was removed, the headspace was cleared, the 13 mm *ClearShot extractor* was attached to the syringe, and the standard was processed vertically through the extractor. The extractors were dried for 30 s, 4 min, and 20 min using instrument air at 60 psi. The FTIR spectra were recorded for each extractor after each drying period with a resolution of  $2\text{ cm}^{-1}$  and measured with 100 scans. All standards were background corrected to their respective unused extractors.

### 2.3.3 | Discriminant analysis method development

The discriminant analysis model was developed using Thermo Fisher TQ Analyst software. The method used discriminant analysis with the pathlength type defined as multiplicative signal correction (MSC). Six classes were defined: treated LGO, untreated LGO, virgin LGO, treated HGO, untreated HGO, and lube oil. All spectra to be used in the model were opened as standards and manually sorted into their classes. The model contains spectra from standards at concentrations of 40, 25, 20, and 15 mg/L after their extractors had been dried for 30 s (or until water was removed). There were 108 total standard spectra in the model, with 1/3 of them set as validation standards. The search region was set to  $3100\text{--}1275\text{ cm}^{-1}$  and one distribution was used for all classes to account for within-class variance.

### 2.3.4 | Discriminant analysis method validation

The discriminant analysis model was externally validated using mock samples. The analytes used for this test included subsets of the six general hydrocarbons. Clean 32 oz. (946 mL) glass jars with PTFE-lined lids were filled with 750 mL of ultrapure water. About 11 mg of hydrocarbon was added directly to the water to create 15 mg/L mock samples. The samples were treated like real



samples and processed following the R&D TOG method. FTIR spectra were collected for the dried extractors with a resolution of  $2\text{ cm}^{-1}$  and measured with 100 scans. All mock samples were background corrected to their respective unused extractors. The collected FTIR spectra were analyzed in the discriminant analysis model.

### 2.3.5 | Hydrocarbon fingerprinting method development

The final fingerprinting method development was tested on mock samples with concentrations of 15, 5, and 2 mg/L. The 15 mg/L mock samples used for external validation were reused for this study. 5 mg/L samples were prepared by adding about 4 mg of hydrocarbon directly to 750 mL ultrapure water. 2 mg/L samples were prepared by adding 1.5 mL of a 1000 mg/L acetone spike solution to 750 mL ultrapure water. The mock samples were treated like real samples and processed following the R&D TOG method with an adaptation to the subsample volume processed and the dry time method. A 10 mL subsample was processed for the 15 mg/L sample, a 30 mL subsample was processed for the 5 mg/L sample, and a 60 mL subsample was processed for the 2 mg/L sample. The extractors were dried for 30 s (or until water was removed) and then for 20 min with instrument air at 60 psi. FTIR spectra were collected after each drying period with a resolution of  $2\text{ cm}^{-1}$  and measured with 100 scans. The maximum peak height of the  $\text{CH}_2$  absorbance was measured. The spectra collected after minimal dry time were quantified in the discriminant analysis model.

The loading ability for samples containing solids was tested using cooling water samples. The maximum volume of sample possible was processed through a *ClearShot* extractor when the sample was left as-is and when it was centrifuged. For centrifugation, the sample was first homogenized following the optimized solvent-free TOG method and then was subsampled into glass 8 oz. (237 mL) jars with PTFE-lined lids. The subsamples were centrifuged at 2000 RPM for 30 min. After centrifugation, the water was decanted into glass 4 oz. (119 mL) jars and processed following the optimized solvent-free TOG method starting from the homogenization step.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Method development and optimization

The ASTM D7575 method was tested and optimized for Syncrude specific (oil sand related) hydrocarbon analytes.

The main steps in the method that were optimized include sonication and dispersion, drying time, calibration approach, and method QC.

#### 3.1.1 | Sonication and dispersion

The ASTM D7575 method states that a minimum sonication time of 20 min in a  $40^\circ\text{C}$  sonication bath is required for homogenizing samples. Sonication time optimization was performed to reduce sample analysis time while still ensuring complete dispersion of oil in water. The reported recovery of the untreated HGO samples tested are plotted against an increasing sonication time in Figure 1. The results show that at  $40^\circ\text{C}$ , an increasing sonication time will increase reported recovery and decrease sample deviation, up to a plateau (represented by the green line). Notably, sonication of 20 min has a greater deviation between duplicates than 12 min; however, it does not have a significantly different reported recovery.

At 3 and 5 min, the samples are not visually homogenized as oil is adhered to the walls of the glass jar. At 8 min, there is no oil adhered to the glass, the solution appears uniformly cloudy, and there are no visible oil droplets. At 12 min, the solution remains visually homogenized and appears slightly darker. There is no visual change in the solutions past 12 min of sonication.

A magnetic stir bar was added to the solutions to help keep the hydrocarbon homogeneously dispersed after the sample is removed from the sonication bath. The relative standard deviation between two subsamples decreased significantly with the addition of a stir bar from 15% to 4%. This confirms that constant agitation provided by the stir bar vortex helps to better maintain the homogenous dispersion.

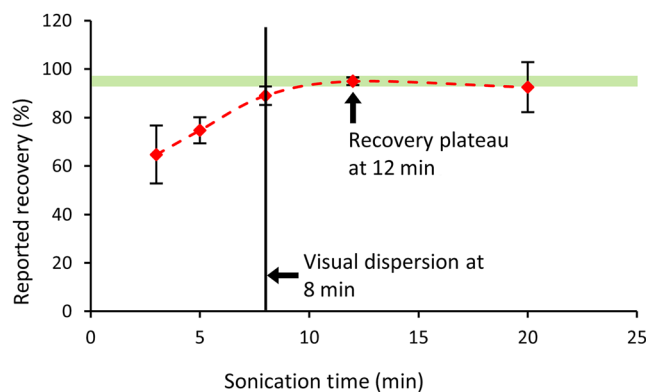


FIGURE 1 Recoveries of untreated heavy gas oil (HGO) mock samples versus sonication time at  $40^\circ\text{C}$  (error bars represent one standard deviation  $n = 2$ ).

### 3.1.2 | Drying time

The ASTM D7575 method states that *ClearShot extractors* must be dried with instrument air at 60 psi for 15 min to remove all residual water and volatiles to remain equivalent to EPA 1664A. This results in considerable loss of light ends, which is not ideal for certain applications including maximizing spectral signal for fingerprinting. The dry time procedure was optimized to reduce analysis time and limit light end loss as much as possible while still removing adequate amounts of residual water to allow for measurement of the  $\text{CH}_2$  stretching region. If residual water is not removed, the water will absorb in this region and impair measurement. The average reported recovery of treated LGO samples tested are plotted against dry time in Figure 2. Treated LGO samples were used for this study as they contain a significant amount of light ends. The results show that there is a continual decline in the average reported recovery with increasing dry time, which is due to the gradual loss of light ends. A minimum dry time of 30 s was chosen as it consistently removed adequate amounts of residual water to allow for measurement. When solids are present, the time required to adequately remove water can increase. Removal of water can easily be verified spectrally by the absence of the broad water O—H stretch. From the results, the greatest reported recovery was recorded after 30 s of dry time with a reported recovery of  $78.4\% \pm 2.5\%$ . Based on this, it was concluded that routine samples should be dried for 30 s with instrument air at 60 psi to lessen light end loss and measure the total TOG content in aqueous samples. If desired, the extractors can be dried for an additional extended period of time to exclusively measure non-volatile TOG content without having to complete a repeat extraction.

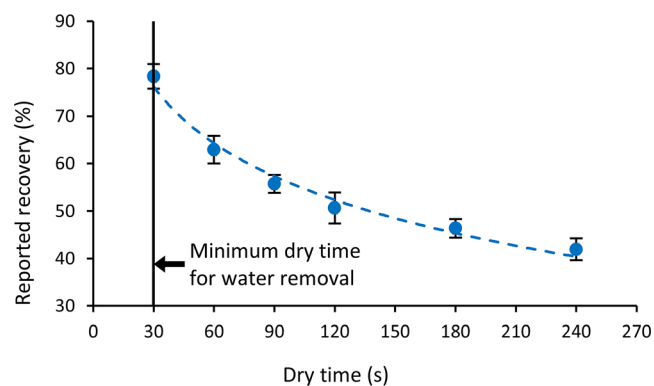


FIGURE 2 Average recoveries of treated light gas oil (LGO) samples versus dry time with instrument air at 60 psi (error bars represent 1 standard deviation  $n = 2$ ).

### 3.1.3 | Quality control

QC is an important part of all analytical methods as QC samples ensure the method and instrumentation are performing as expected. A robust approach to QC analysis accounts for as many procedural steps as is reasonably possible while still allowing for the QC samples to be prepared accurately and efficiently. Mineral oil was selected for our QC samples as it is commercially available, and it is the same analyte used to prepare the QC samples in the ASTM D7575 method. Mineral oil is a good QC material as it will not experience any loss to evaporation, it is easily handled, and it has a near identical  $\text{CH}_2$  peak height response per unit mass as stearic acid and hexadecane, which are the calibration standards used in the EPA 1664A method. In this QC method, a jar of ultrapure water was spiked with a solution of mineral oil in acetone as the jar could be processed like a real sample and experience all the methods' procedural steps. This method was adopted as there is no significant difference in the sample recovery using a mineral oil acetone spike compared to adding mineral oil directly to ultrapure water. This procedure allows samples to be prepared rapidly with high precision as this approach does not require very accurate weighing of very small masses. Individual QC samples can be quickly and accurately prepared from a single QC stock solution. Overall, this QC method was chosen as it allows for QC samples to be prepared rapidly and it accounts for all the procedural steps real samples experience, including sonication and subsampling. Once the QC method was finalized, the initial working QC limits were calculated by preparing and extracting 4 oz. (119 mL) jar spikes at a target of 20 mg/L. Upper and lower control limits ( $+/-3\sigma$ ) were found to be 116.6% and 91.10% with an average recovery of 103.8% ( $n = 5$ ).

### 3.1.4 | Calibration

The ASTM D7575 method was published with equivalency to EPA 1664A using CSDs prepared by vapour-depositing polypropylene directly onto a *ClearShot extractor* membrane. The measured polypropylene  $\text{CH}_2$  response is matched with the  $\text{CH}_2$  response of a 1:1 mixture of stearic acid and hexadecane (which are the calibration materials in EPA 1664A) to maintain method calibration equivalency. The CSDs, which can be purchased fully prepared, are a much easier calibration approach than preparing stearic acid and hexadecane extractions directly. Additionally, the CSDs are certified for 1 year, maintain stability in a lab fridge, and can be re-measured to ensure no instrument drift.

A correction factor can be applied to the CSDs stearic acid and hexadecane matched response to achieve calibration equivalency with the current Syncrude TCE extraction method based on ASTM D3921-96. The correction factor was determined by comparing the  $\text{CH}_2$  response per unit mass of stearic acid and hexadecane to the  $\text{CH}_2$  response per unit mass of hexadecane and iso-octane (which are the calibration materials in ASTM D3921-96). The  $\text{CH}_2$  peak height response in units of absorbance are plotted against concentration in Figure 3. The results show that the  $\text{CH}_2$  peak height response per unit mass of materials is higher for the EPA 1664A calibration materials than that of the ASTM D3921-96 calibration materials. This is because the ASTM D3921-96 calibration material is a mixture of branched and unbranched hydrocarbons. A correction factor of 1.86x can be applied to the CSDs to match the response of the ASTM D3921-96 material. This correction factor was calculated from the differences in respective calibration slopes.

The limit of detection ( $\text{LOD} = 3\sigma$ ) and limit of quantitation ( $\text{LOQ} = 10\sigma$ ) were determined by measuring the standard deviation ( $\sigma$ ) of the blank CSD ( $n = 7$ ). For the 13 mm extractors, the LOD was 0.09 mg/L and the LOQ was 0.30 mg/L.

### 3.1.5 | Summary of optimized method

After testing and optimizing every step of ASTM D7575 for Syncrude specific analytes, the optimized solvent-free TOG method is summarized in the steps listed below.

1. The unfiltered sample is acidified to pH 2 using concentrated HCl.
2. The acidified sample is sonicated in a sonication bath preheated to 40°C for 12 min, shaking the sample by

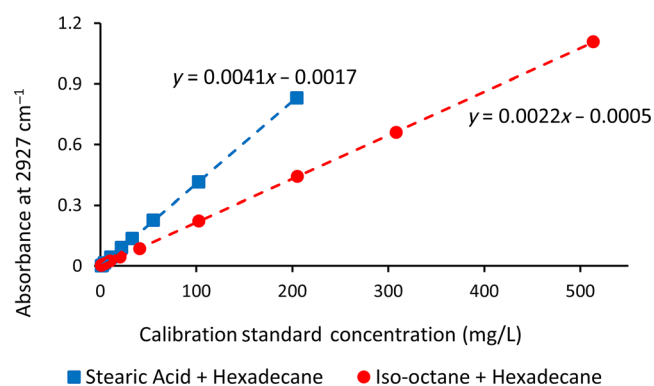


FIGURE 3  $\text{CH}_2$  peak height response of calibration standard solutions prepared in tetrachloroethylene (TCE) versus concentration.

hand for 5 s every 4 min, or until visual dispersion is reached.

3. The sample is mixed with a magnetic stir bar and a 10 mL subsample is taken using a 10 mL gas tight glass syringe.
4. A *ClearShot* extractor is attached to the syringe and the subsample is processed through holding the syringe vertically with the extractor on top.
5. The extractor is dried on a drying manifold with instrument air at 60 psi for 30 s (or minimal time until water is removed).
6. The dried extractor is analyzed directly on the FTIR spectrometer and the maximum peak height of the  $\text{CH}_2$  absorbance at  $\sim 2920 \text{ cm}^{-1}$  is measured and compared against a calibration curve to determine TOG concentration.

## 3.2 | Hydrocarbon classification model development

### 3.2.1 | *ClearShot* extractor drying curves

In the FTIR spectra for all acetone spike standards processed through *ClearShot* extractors, the absorbance intensity at  $\sim 2920 \text{ cm}^{-1}$  was measured after they had been dried for 30 s, 4 min, and 20 min. The average reported recovery of LGO and HGO samples is plotted against dry time in Figure 4. It was observed that the intensity of absorbance at  $\sim 2920 \text{ cm}^{-1}$  decreased for LGO samples and remained relatively unchanged for HGO samples as dry time increased. These results indicate that there is a greater loss of volatiles in LGO samples at longer dry times, which is anticipated as LGO samples contain more light ends. Based on this, the change in absorbance intensity of the  $\text{CH}_2$  stretching peak at  $\sim 2920 \text{ cm}^{-1}$  as dry time increases. The % recoveries at 20 min of dry time are

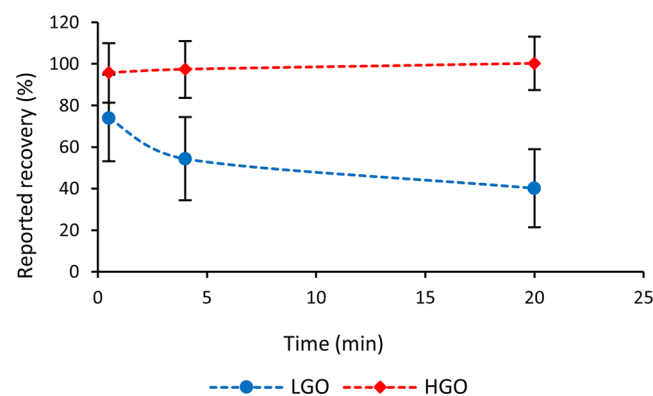


FIGURE 4 Average recovery of all light gas oil (LGO) ( $n = 13$ ) and heavy gas oil (HGO) ( $n = 11$ ) samples versus dry times (error bars represent one standard deviation).

statistically different and can be used to determine whether a sample is a LGO or HGO after it has been processed through a *ClearShot extractor*.

### 3.2.2 | Discriminant analysis model development

An initial visual assessment of the FTIR spectra for the six hydrocarbon classes showed that there were spectral differences between the spectra in each hydrocarbon class with the largest differences being observed in the C–H stretching region, examples of the differences in the C–H region for LGO samples are shown in Figure 5 and full spectra for the six classes are available in Data S1. Depending on the plant that the gas oils originate from and the extent of hydrotreating or hydrocracking they have experienced, they vary in their CH<sub>3</sub>, CH<sub>2</sub>, and CH ratios, which alters the appearance of their spectra. For example, untreated gas oils will have a higher degree of unsaturation and aromaticity, and then saturation of hydrocarbons during hydrotreating directly impacts the CH<sub>2</sub> and CH<sub>3</sub> ratios. The spectral region selected for the discriminant analysis model was 3100–1275 cm<sup>-1</sup> in order to include the C–H stretching region as well as the additional spectral information on structural components such as aromatics, olefins, and carbonyl groups, while avoiding any interference from solids (i.e., Si–O and clay hydroxy groups) and the C–F stretching from the Teflon based extractor membrane itself.

The discriminant analysis model contains a total of 108 standard spectra from the hydrocarbon samples sorted into six hydrocarbon classes (listed in Section 2) at concentrations of 40, 25, 20, and 15 mg/L. All standards had 10 mL of volume processed through the extractor at

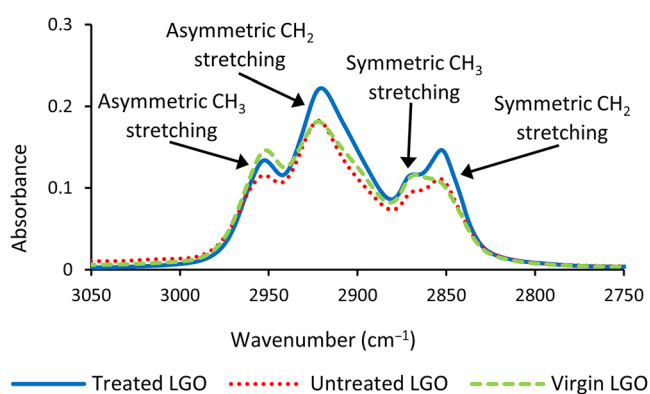


FIGURE 5 C–H stretching region of attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra for light gas oil (LGO) samples.

these concentrations. The concentration range of 40–15 mg/L was chosen as there was an apparent breakdown in signal-to-noise at concentrations below 15 mg/L when 10 mL was processed through the extractor. With 1/3 of the standards set to validation, using 15 principal components the model had no misclassifications and described 99.45% of the variability between the spectra. Figure 6 shows one example of a 2D principal component plot from the discriminant analysis model showing lube oil being clustered and separated from the other classes.

The discriminant analysis model was tested using hydrocarbon mock samples at concentrations of 15, 5, and 2 mg/L. The volume of subsample processed for analysis varied depending on the concentration of the sample itself. The purpose of this was to determine the mass loading required for successful fingerprinting. The greater the volume of sample processed through the *ClearShot extractor*, the greater the mass of TOG content loaded on the membrane for measurement. Based on the volumes processed, the 15 and 5 mg/L samples loaded 150 µg of TOG onto the membrane, and the 2 mg/L samples loaded 120 µg of TOG onto the membrane. When the spectra that experienced minimal dry time were quantified in the discriminant analysis model, two of the 2 mg/L samples and one of the 15 mg/L samples were misclassified. When a larger volume of the misclassified 15 mg/L sample was processed, the model correctly classified it. The model had a 100% classification rate at TOG mass loadings >150 µg, indicating that this is the minimum mass loading required to ensure correct classification.

In some samples, the presence of solids could present an issue as the solids would block the membrane and inhibit the ability to process large enough sample volumes to achieve the minimum mass loading (>150 µg for fingerprinting). To test the ability to remove solids, a

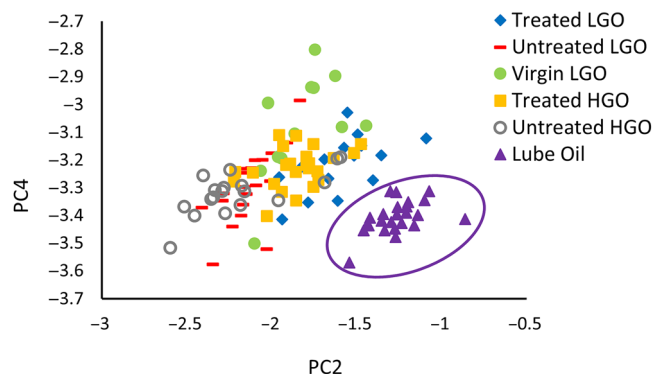
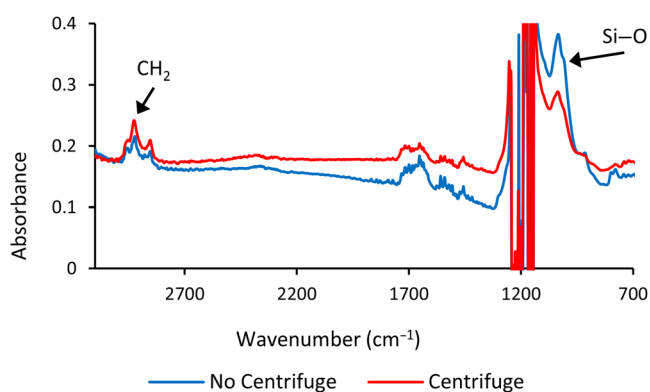


FIGURE 6 Example of a 2D principal component plot from the discriminant analysis (DA) hydrocarbon fingerprinting model showing lube oil being clustered and separated from the other hydrocarbon classes. HGO, heavy gas oil; LGO, light gas oil.



cooling water sample was processed when it was left as-is and when it was centrifuged (following sonication). The objective of this test was to see what the maximum volume of sample that could be processed in both scenarios was. When left as-is, 24 mL of sample was able to be processed. When centrifuged, 36 mL of sample was able to be processed. Based on the overlaid spectra collected for both scenarios in Figure 7, there is a decrease in the absorbance of the quartz Si—O stretching peak at  $1080\text{ cm}^{-1}$ <sup>[20]</sup> after centrifugation. This indicates that centrifugation successfully removes a portion of the solids from the sample, which enabled a greater volume of sample to be processed. With an increased volume of sample processed, there was a 30% increase in the  $\text{CH}_2$  absorbance at  $\sim 2920\text{ cm}^{-1}$ . This supports the previous statement that processing a larger volume of sample loads more TOG content onto the membrane to be analyzed and proves centrifugation can successfully remove solids from the sample matrix to achieve this.

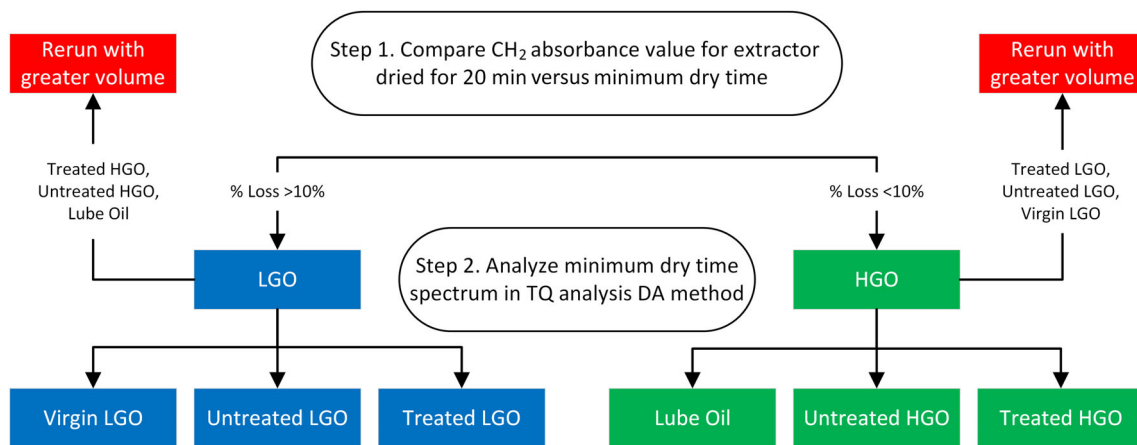


**FIGURE 7** Fourier transform infrared (FTIR) spectra of cooling water sample extractors showing the effect of an added centrifugation step for solids removal.

### 3.2.3 | Hydrocarbon fingerprinting classification method

Based on the *ClearShot extractor* drying curves, it was concluded that samples that experience  $>10\%$  loss of volatiles are LGO samples, and samples that experience  $<10\%$  loss of volatiles are HGO samples. The mock sample mass loading results had a 100% classification rate at TOG mass loading  $>150\text{ }\mu\text{g}$ , making this the minimum mass loading for the method. The volatile loss test has been put in place in the method to cross validate the discriminant analysis results. If the results do not agree, the sample should be reanalyzed by processing a larger volume through a new extractor. The hydrocarbon fingerprinting method is summarized in the steps listed below as well as shown graphically in Figure 8.

1. Following the solvent-free TOG method, the sample is prepared and processed through a 13 mm *ClearShot extractor* such that  $>150\text{ }\mu\text{g}$  of TOG content is loaded on the membrane.
2. The extractor is attached to the OSS drying apparatus and dried with instrument air at 60 psi for 30 s (or minimum dry time until water is removed).
3. The dried extractor is analyzed directly on the FTIR spectrometer and the  $\text{CH}_2$  absorbance peak height at  $\sim 2920\text{ cm}^{-1}$  is measured.
4. The same extractor is reattached to the OSS drying apparatus and dried with instrument air at 60 psi for a total of 20 min.
5. The extractor is analyzed again directly on the FTIR spectrometer and the  $\text{CH}_2$  absorbance peak is measured.
6. The volatile loss between the FTIR spectra collected at both dry times is calculated to determine whether the hydrocarbon is a LGO or HGO.



**FIGURE 8** Flow chart outlining the hydrocarbon leak source identification procedure for the cooling water system. DA, discriminant analysis; HGO, heavy gas oil; LGO, light gas oil.

7. The spectrum collected after minimal dry time is quantified in the discriminant analysis model to determine the specific hydrocarbon class.
8. If the volatile loss results do not agree with the discriminant analysis results, the sample should be reanalyzed with a greater volume processed.

## 4 | CONCLUSION

A solvent-free TOG method was developed and optimized for Syncrude specific analytes (bitumen derived process streams) using ASTM D7575 as a starting point. This new method has a reporting limit of 0.3 mg/L and contains a robust approach to QC that was previously lacking. Compared to historic solvent-based methods, this new method is cheaper, has decreased exposure risk, lowers ergonomic stress on technologists, has improved safety and environmental performance due to the elimination of solvents, and it can handle emulsion prone sample types (process water). On top of this, the *ClearShot extractors* allow for field testing as well as characterization and source identification of TOG material.

The ability to perform hydrocarbon fingerprinting using the *ClearShot extractors* displays great potential in hydrocarbon leak identification for heavier hydrocarbon analytes (gas oils and lube oil) in cooling water. The discriminant analysis model presented had a 100% correct classification rate for validation samples with TOG mass loadings >150 µg for six different hydrocarbon classes using 15 principal components. The fingerprinting method is adaptable to low concentration samples as the required mass loading can be achieved by processing larger volumes. This ability to identify hydrocarbon class in a cooling water sample instantly limits the number of plants that may be the source of the hydrocarbon leak. Rather than collecting and analyzing samples from all the plants/exchangers connected to the contaminated cooling water tower, samples will only need to be collected from the plants that contain that hydrocarbon class, reducing the number of samples that need to be analyzed by 90%. This eliminates the time that is spent collecting and analyzing samples from unnecessary plants, effectively minimizing the total amount of time required to pinpoint the leaking plant/exchanger. The ability to identify and isolate a hydrocarbon leak more efficiently also minimizes the amount of time that water blowdown, water treatment, and contaminated water purge procedures need to be employed, which has major cost and environmental benefits.

## AUTHOR CONTRIBUTIONS

**Kimberly Wong:** Investigation; formal analysis; writing – original draft; writing – review and editing. **Matthew Ripmeester:** Conceptualization; formal analysis; supervision; writing – original draft; writing – review and editing. **Daniel Thacker:** Investigation; formal analysis; writing – review and editing. **David A. Duford:** Formal analysis; writing – review and editing.

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The authors have no relevant financial or non-financial interests to disclose.

## PEER REVIEW

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## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supplementary material of this article.

## ETHICS STATEMENT

The submitted work should be original and should not have been published elsewhere in any form.

## CONSENT FOR PUBLICATION

All authors have consented to publish the article.

## REFERENCES

- [1] M. Garry, R. Rubinovitz, L. Doucette, D. Smith, T. Schwartz, *Measuring Oil and Grease in Water-Solvent Free (ASTM D7575)*, Application Note-Thermo Fisher Scientific Inc **2019**. <https://assets.thermofisher.com/TFS-Assets/MSD/Application-Notes/AN52663-measuring-oil-grease-water-solvent-free-astm-d7575.pdf> (accessed: April 2023).
- [2] I. Cirne, J. Boaventura, Y. Guedes, E. Lucas, *ChChT* **2016**, 10, 437.
- [3] T. Egorova, J. Sedlacek, T. Sukhodolov, A. Karagodin-Doyennel, F. Zilker, E. Rozanov, *Atmos. Chem. Phys.* **2023**, 23, 5135.
- [4] A. O. Adeniji, O. O. Okoh, A. I. Okoh, *J. Chem.* **2017**, 2017, 1.
- [5] B. Liu, Y. Wang, X. Feng, *Chin. J. Chem. Eng.* **2021**, 40, 167.
- [6] K. Ma, M. Liu, J. Zhang, *Energy* **2021**, 231, 120896.

- [7] Caring for Cooling Water Systems, Chemical Engineering | Page 1. <https://www.chemengonline.com/environmental-manager-caring-for-cooling-water-systems/> (accessed: November 2023).
- [8] Z. Wang, M. Fingas, D. S. Page, *J. Chromatogr. A* **1999**, 843, 369.
- [9] P. Fresco-Rivera, R. Fernández-Varela, M. P. Gómez-Carracedo, F. Ramírez-Villalobos, D. Prada, S. Muniategui, J. M. Andrade, *Talanta* **2007**, 74, 163.
- [10] J. M. Bayona, C. Domínguez, J. Albaigés, *Trends Environ. Anal. Chem.* **2015**, 5, 26.
- [11] F. S. Hashemi-Nasab, H. Parastar, *Microchem. J.* **2020**, 153, 104326.
- [12] G. Ma, H. Xiao, X. Wei, A. Xiao, X. Sun, X. Gao, *Environ. Sci. Pollut. Res. Int.* **2023**, 30, 24470.
- [13] X. Gao, S. Di, X. Tan, W. Zhang, J. Wang, L. Luo, X. Qu, J. Liu, S. Li, N. Jiang, S. He, S. Zhu, *Org. Geochem.* **2023**, 182, 104642.
- [14] R. Ren, K. Han, P. Zhao, J. Shi, L. Zhao, D. Gao, Z. Zhang, Z. Yang, *Constr. Build. Mater.* **2019**, 198, 662.
- [15] A. Loh, Z. Y. Soon, S. Y. Ha, U. H. Yim, *Sci. Total Environ.* **2021**, 760, 143354.
- [16] L. Zhang, X. Huang, X. Fan, W. He, C. Yang, C. Wang, *Environ. Technol.* **2021**, 42, 270.
- [17] R. Bro, A. K. Smilde, *Anal. Methods* **2014**, 6, 2812.
- [18] *Handbook of Applied Multivariate Statistics and Mathematical Modeling*, H. E. A. Tinsley, S. D. Brown, Elsevier **2000**.
- [19] T. Jombart, S. Devillard, F. Balloux, *BMC Genet.* **2010**, 11, 94.
- [20] A. Hahn, H. Vogel, S. Andó, E. Garzanti, G. Kuhn, H. Lantzsch, J. Schüürman, C. Vogt, M. Zabel, *Sediment. Geol.* **2018**, 375, 27.

## SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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