Orono Spectral Solutions, Inc.

STANDARD OPERATING PROCEDURE

for ASTM Method D7575, Oil and Grease in Water

REVISION # 5 Effective date: April 5, 2014

APPROVED BY

Signature _____

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1 Scope and Application

1.1. This method is used to determine membrane recoverable oil and grease in wastewater and water.

1.2. The practical range of the determination is 5 mg/L to 200 mg/L. Results reported outside this range must be qualified on the final report.

1.3. Data generated by this method are used for self-monitoring and reporting for the permits for compliance with the Federal Clean Water Act.

1.4. This SOP is to be used by all personnel conducting this analysis.

2 Summary of Method

2.1. The sample is homogenized in an ultrasonic bath.

2.2. An aliquot of the sample is delivered through the OSS Extractor.

2.3. The extractor is dried.

2.4. The extractor is analyzed.

3 Deviations From Method

3.1. There are no deviations from the method in this version.

4 Definitions

4.1. *Oil and grease,* n; "membrane-recoverable oil and grease" is a method-defined analyte; that is, the definition of membrane-recoverable oil and grease is dependent on the procedure used.

4.2. *OSS Extractor,* n: a device that contains an infrared-amenable oil-and-grease solid-phase-extraction membrane and directs water flow through the membrane under applied pressure.

5 Interferences

5.1. Method interferences may be caused by contaminants in instrumentation, reagents, glassware, and other apparatus producing artifacts. Routine laboratory method blanks will demonstrate all these materials are free from interferences.

5.2. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences can vary considerably from sample to sample.

5.3. In cases of samples which contain a relatively large amount of particulate or biological material, processing the standard 10 mL sample aliquot may not be possible.

> NOTE: It is important to note that the capture of solid matter on the extractor does not preclude IR measurement; in the majority of cases there is sufficient IR throughput to perform the measurement as described.

6 Safety

6.1. All personnel working in the laboratory are required to follow the *Laboratory Chemical Hygiene Plan*.

6.2. Practice good personal hygiene, and be extra careful if you have cuts or open wounds.

6.3. A reference file of material safety data sheets (MSDS) is available to all personnel involved in these analyses.

7 Equipment and Supplies

7.1. Extractor – a onetime use device which contains an infrared-amenable oil and grease solid phase extraction membrane, includes a connection to a syringe, such as a Luer connection, and is designed for pressurized flow of water through the membrane and capable of meeting the performance specifications of ASTM D7575. Ex. OSS part: 1018 SPE.

7.2. Calibration Standard Devices Set – set of seven devices with a specified amount of oil and grease that covers the reporting range; used for calibration. Ex. OSS part: 1018 SPE-CSD.

7.3. Sample Bottles – a glass bottle with a Teflon lined cap capable of containing 1 L of sample. Ex. – Environmental Sampling Supply part: 1000-0150-UC.

7.4. Syringe – a onetime use plastic syringe with low-extractable components and connection to attach to the extractor, capable of flowing the 10 mL sample volume to be processed. Ex. – Norm Ject 10 mL (12 mL) Plastic Syringe with Luer Lok tip

7.5. Spectrometer – instrument capable of infrared absorption measurement. Ex. – ABB MB3000, Nicolet IS10

7.6. Ultrasonic Bath – a device that uses ultrasonic waves to agitate liquids; used for homogenizing samples. Ex. - Fisher Scientific Ultrasonic Cleaner, part: 15-335-105

7.7. Computer – with Microsoft Excel or comparable spreadsheet program.

7.8. Syringe Pump – a device capable of forcing the fluid through the extractor. Ex. New Era Pumps part: NE-1011

7.9. Drying System – a system capable of drying the extractor sufficiently for infrared analysis without compromising analyte retention (e.g. 60 psi, clean, dry air supply compatible with Extractor).

7.10. Volumetric Pipette – 10 mL and 1 mL

7.11. Volumetric Flask – 1 L

8 Reagents and Standards

8.1. Laboratory Reagent Water, Deionized Water from the house system.

8.2. Hydrochloric Acid – concentration of 12.1 M

8.3. Acetone – ACS, residue less than 1 mg/L

8.4. Hexadecane – 98% minimum purity

8.5. Stearic Acid – 98% minimum purity

8.6. (This section is only for the raw materials and reagents, making the spiking solution is part of the procedure. The procedure to make the spiking solution is found in the section below this from the reagents that are listed in this section)

9 Sample Collection and Preservation

9.1. Samples are to be collected in a cleaned glass container. Do not allow the sample to overflow during collection. If samples must be stored, they are refrigerated at ≤6 ^{o}C, but not frozen, until the time of analysis.

9.2. Add a sufficient quantity of hydrochloric acid to a pH of 2. If the amount of acid required is not known, make the pH measurement on a separate sample that is not to be analyzed.

9.3. The maximum holding time is 28 days.

10 Quality Control

10.1. Preparation of Spiking Solution

10.1.1. All Oil and Grease spiking will be done with a 1:1 Hexadecane and Stearic Acid spiking solution.

1.1.1.1. Place 200 mg +/- 2 mg Hexadecane and 200 mg +/- 2 mg Stearic Acid in a 100-mL volumetric flask.
1.1.1.2. Fill to the bottom of the neck with acetone.
1.1.1.3. Dissolve hexadecane and stearic acid by warming the solution or placing it in an ultrasonic bath.
1.1.1.4. Allow solution to cool to room temperature and add acetone to the mark.
1.1.1.5. Stopper the volumetric flask or transfer the solution to a 100-150 mL vial with fluoropolymer-lined cap. Mark the solution level on the vial and store in the dark at room temperature.

10.1.2. Immediately prior to the first use, verify the level on the vial and bring to volume with acetone, if required. Warm to redissolve all visible precipitate, if required.

NOTE: If there is doubt of the concentration, remove 10.0 ± 0.1 mL with a volumetric pipette, place in a tared weighing pan, and evaporate to dryness in a fume hood. The weight must be 40 ± 1 mg. If not, prepare a fresh solution.

10.1.3. The spiking solutions should be checked frequently for signs of degradation or evaporation.

10.1.4. If necessary, this solution can be made more or less concentrated to suit the concentration needed for the matrix spike. A fresh spiking solution should be prepared weekly or bi-weekly.

10.2. Each analytical batch must include a Method Blank, a Laboratory Control Sample (LCS), and a Matrix Spike

10.2.1. The Method Blank is prepared using 1 L of laboratory reagent water, which is acidified to a pH of 2 using HCL, and then analyzed.

10.2.2. The LCS is prepared on the day of analysis

1.2.2.1. Measure 1 L of laboratory reagent water with a 1-L volumetric flask and pour into a sample bottle.
1.2.2.2. Acidify sample to pH of 2.
1.2.2.3. Measure 10 mL (for a 40 mg/L spike) of spiking solution with a volumetric pipette.
1.2.2.4. Submerge the tip of the volumetric pipette at least 1 inch below the surface of the sample. The tip of the pipette should be in the center of the bottle.
1.2.2.5. Dispense the spiking solution into the sample.

10.2.3. The Matrix Spike is prepared in a duplicate field sample of known concentration.

1.2.3.1. Acquire a duplicate bottle of at least one sample per batch.
1.2.3.2. Measure 10 mL (for a 40 mg/L spike) of spiking solution with a volumetric pipette.
1.2.3.3. Submerge the tip of the volumetric pipette at least 1 inch below the surface of the sample. The tip of the pipette should be in the center of the bottle.
1.2.3.4. Dispense the spiking solution into the sample.

NOTE: The final concentration of a Matrix Spike must be 1.5 times the original concentration of the field sample. If the original concentration of the sample is greater than 80 mg/L, the spike volume must be increased. The final concentration of the Matrix Spike sample cannot exceed 200 mg/L.

10.3. Before discarding samples make sure all QA/QC analysis are within control limits.

11 Initial Precision and Recovery (IPR)

11.1. Each analyst must complete an IPR study prior to reporting any data using this method.

11.2. An IPR study will be performed on a sample containing 40 mg/L of oil and grease.

11.2.1. Measure 1 L of laboratory reagent water with a 1-L volumetric flask and pour into a sample bottle

11.2.2. Acidify sample to pH of 2 using HCL.

11.2.3. Measure 10 mL of spiking solution with a volumetric pipette.

11.2.4. Submerge the tip of the volumetric pipette at least 1 inch below the surface of the sample. The tip of the pipette should be in the center of the bottle.

11.2.5. Dispense the spiking solution into the sample.

11.2.6. Analyze at least four replicates of the spiked sample according to the procedure in section 14.

11.2.7. Input the measured values into an Excel spreadsheet.

11.2.8. Calculate the average of the measured concentration of the IPR replicates using the AVERAGE function.

11.2.9. Calculate the standard deviation of the measured concentration of the IPR replicates using the STDEV function.

1.2.9.1. Calculate %RSD = 100*STDEV/AVERAGE

NOTE: The math functions described in this operating procedure are for use in Microsoft Excel. An Excel worksheet may be provided with this operating procedure. If the user does not have access to a computer, the calculations must be performed manually. All necessary equations can be found in Section 15.

11.3. The average recovery of the four samples must be between 88% and 105% of the target and the %RSD must be $\leq$ 10.5%.

12 Method Detection Limit (MDL)

12.1. An MDL study must be performed prior to reporting any data from this method.

12.2. The MDL study is performed on a sample containing 4 mg/L of oil and grease.

12.2.1. Measure 1 L of laboratory reagent water with a 1-L volumetric flask and pour into a sample bottle

12.2.2. Acidify sample to pH of 2 using HCL.

12.2.3. Measure 1 mL of spiking solution with a volumetric pipette.

12.2.4. Submerge the tip of the volumetric pipette at least 1 inch below the surface of the sample. The tip of the pipette should be in the center of the bottle.

12.2.5. Dispense the spiking solution into the sample.

12.2.6. Analyze at least seven replicates of the spiked sample according to the procedure in section 14.

12.2.7. Input the measured values into an Excel spreadsheet.

12.2.8. Calculate the standard deviation of measured concentration of the replicates using the STDEV function.

12.2.9. Determine Detection Limit and Reporting Limit:

MDL = 3.143 x (Std. Dev)
RL = 10 x (Std. Dev.)

13 Calibration and Standardization

13.1. Quantification of Oil and Grease requires a correlation between infrared absorbance and Oil and Grease concentration. It is important to ensure that the instrument used in this analysis is operating properly according to manufacturer's specification before calibration.

13.2. Calibration is carried out using the set of Calibration Standard Devices (CSD) (OSS part # 1018 SPE-CSD). Each of the CSDs is certified with an Oil and Grease value.

NOTE: CSD sets are stored in a refrigerator. Before using, remove the set from the refrigerator, and allow it to come to room temperature. Do not remove the CSD set from the sealed bag until the set has come to room temperature, as to avoid condensation on the CSD membrane.

13.2.1. Record a reference through CSD B

13.2.2. Record an absorbance spectrum of each of the CSDs

13.2.3. Measure the absorbance of the hydrocarbon peak near 2920 cm^{-1} according to the procedure in section 14

13.2.4. Input the absorbance values into an Excel spreadsheet.

13.2.5. Plot an X-Y scatter plot of the certified value of each CSD versus the measured absorbance.

13.2.6. Plot a best fit line through the seven points to determine the linear relationship between absorbance and concentration.

13.2.7. Record the slope and intercept of the best fit line.

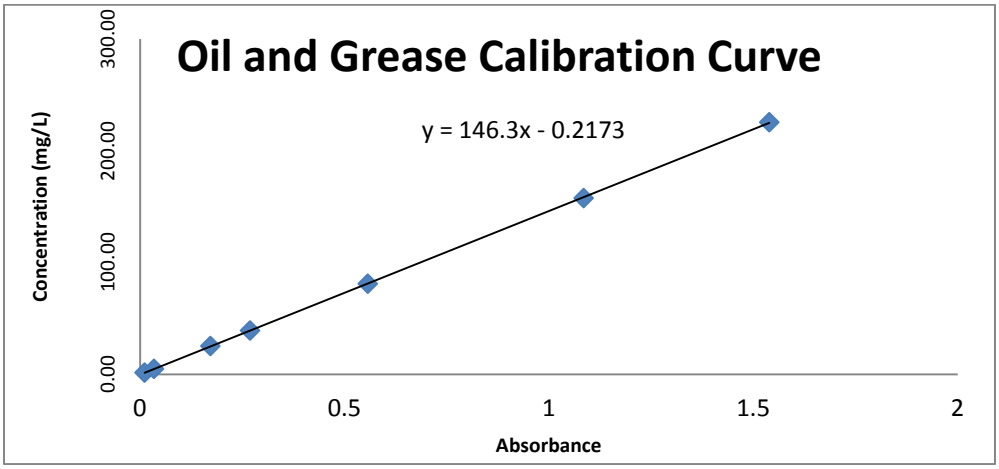

Figure 1: Example of a calibration curve.

13.3. A Calibration Verification must be conducted daily on CSD 4 (at or near 40 mg/L). The measured value must be within 5% of the certified value. If the measured value falls outside of this range, a new calibration must be determined.

14 Procedure

14.1. Sample Homogenization

Careful sample preparation is critical for accurate Oil and Grease Determination. Because a small aliquot of the sample is all that is required for measurement, it is imperative to ensure the sample is homogenous before processing.

14.1.1. Heat the ultrasonic bath to 40°C.

14.1.2. Ensure the caps to the sample bottles are sufficiently tightened. If there is a possibility of leaking, seal the cap with waterproof tape.

14.1.3. Shake the bottle vigorously by hand for 30 seconds.

14.1.4. Submerge the bottles in the bath. Ensure the bottles are fully covered by the water.

14.1.5. Turn on the ultrasonic vibration. If the ultrasonic cleaner you are using has variable power settings, ensure that the unit is operating on the highest power setting.

14.1.6. Homogenize samples for 20 minutes. Rotate samples in bath every 5 minutes or so.

14.2. Processing Sample Through Extractor

14.2.1. Remove the cap from the sample bottle.

14.2.2. Fill a 12 mL syringe with sample. Ensure that more than 10 mL is in the syringe before processing the sample. If multiple replicates are being taken from the same bottle, user should shake the sample vigorously for 10 seconds between draws.

Figure 2: Fill syringe with at least 12 mL of sample

14.2.3. Place the syringe into the syringe pump so that the syringe is vertical facing upwards.

14.2.4. Run the syringe pump for a short time (>1 mL) to push all air bubbles out of the syringe. Reset the syringe pump before proceeding.

Figure 3: Syringe pump loaded with two sample syringes

NOTE The syringe pump could be lying horizontally to facilitate syringes loading. However, the pump shall be brought back vertically for the next steps.

14.2.5. Attach an Extractor to the syringe.

Figure 4: Extractors attached to sample syringes.

14.2.6. Program the Syringe Pump to process 10 mL of sample at 5 mL/min.

NOTE: In instances of low particulate concentration in the sample, the user is encouraged to use a faster flow rate to ensure uniform flow through the extractor. For samples with little to no particulate content, a flow rate of 30 mL/min is acceptable.

14.2.7. Start the syringe pump.

NOTE: While the sample is being processed, watch carefully for leaking in the syringe. This is an indication that Extractor membrane has clogged and is no longer processing sample. If the syringe pump is unable to process the entire 10 mL volume through the extractor, record the total volume that has been processed, and proceed with drying. A correction will be made to the measured value to accommodate for this loss of volume.

14.2.8. Remove the syringe and extractor from the syringe pump, and discard the sample effluent that has collected in the reservoir of the extractor. The water that remains in the headspace of the Extractor is part of the measured sample, and must be retained. This will be processed through the membrane during the drying step.

14.3. Drying Extractor Using Drying Manifold.

14.3.1. Attach the Extractor onto the Luer-Lok fitting of the drying manifold, making sure the extractor remains upright.

Figure 5: OSS Drying Manifold

14.3.2. Open the air valve of the channel that the Extractor is attached to. While the sample that is left in the headspace is pushed through the membrane, ensure that the Extractor remains upright.

14.3.3. Allow air to flow through the Extractor. Check the extractor every 5 minutes for dryness

NOTE: Check the extractor for dryness visually based on two indicators: 1) Make sure any water droplets on the backside of the membrane support have dried. 2) As the membrane dries, the user will notice a color change from dark to light. Watch for dark spots on the membrane, indicating wetness. Ensure that the entire membrane appears dry before proceeding to the next step.

14.3.4. Dryness will be verified in the next step. If dryness verification in step 14.5 fails, reattach the Extractor to the Drying Manifold and continue drying.

NOTE: In some cases, iterative drying may be necessary. With experience, users quickly learn to recognize when extractors are dry. Samples can take as little as 5 minutes to dry. Samples with heavy particulate loading can take up to an hour to dry.

14.4. Infrared Measurement

14.4.1. Load a clean and unused Extractor into the sample card in the spectrometer beam.

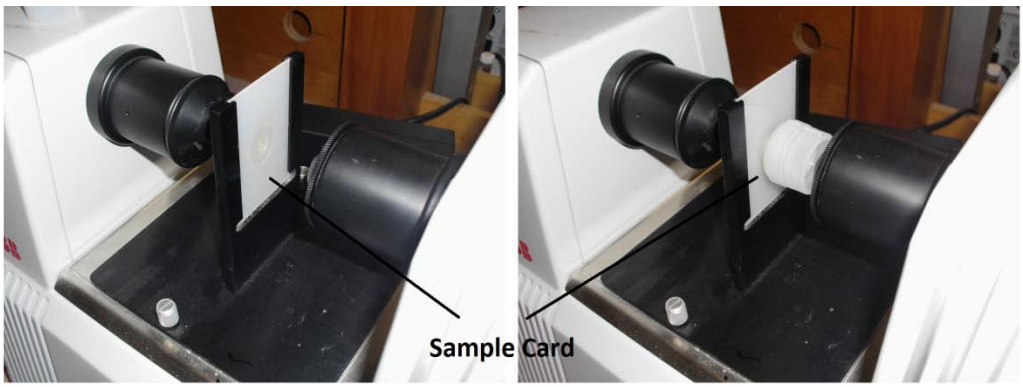

Figure 6: OSS Sample Card

14.4.2. Record a 200 scan reference

14.4.3. Load the processed Extractor into the sample card

14.4.4. Collect a 50 scan absorbance spectrum.

14.4.5. Using baseline endpoints of 2800 cm^{-1} and 2990 cm^{-1}, measure the height of the maximum at 2920 cm^{-1}, as shown below.

NOTE: Height measurement is a standard feature in spectroscopy software. The procedure for this measurement can vary based on spectrometer and software manufacturers. See Appendix A for examples. Users should consult the software manual for help with features specific to that software package / instrument.

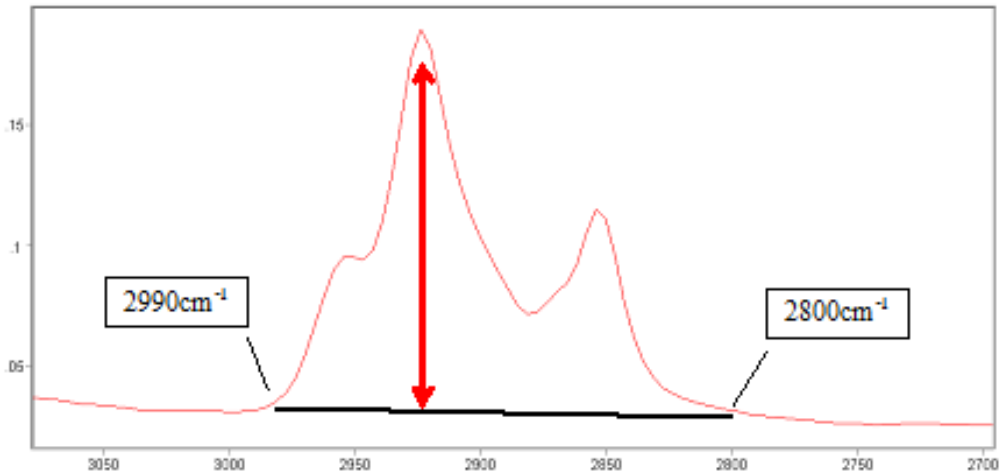

Figure 7: Peak height measurement of the hydrocarbon peak at 2920 cm^{-1}. A straight baseline is drawn between 2800 cm^{-1} and 2990 cm^{-1}.

14.5. Determining Dryness Spectroscopically

14.5.1. Water absorbs strongly in the infrared, with a peak centered approximately at 3400 cm^{-1}. When too much water is present on the membrane, the water peak may interfere with the hydrocarbon peaks, leading to inaccurate analysis. Moreover, the peak due to water can potentially influence the placement of the baseline points, also leading to inaccurate analysis.

14.5.2. Dryness can be determined from spectral analysis by monitoring the water peak. As the membrane dries, the water peak flattens, and no longer interferes with the hydrocarbon peak. This is shown below.

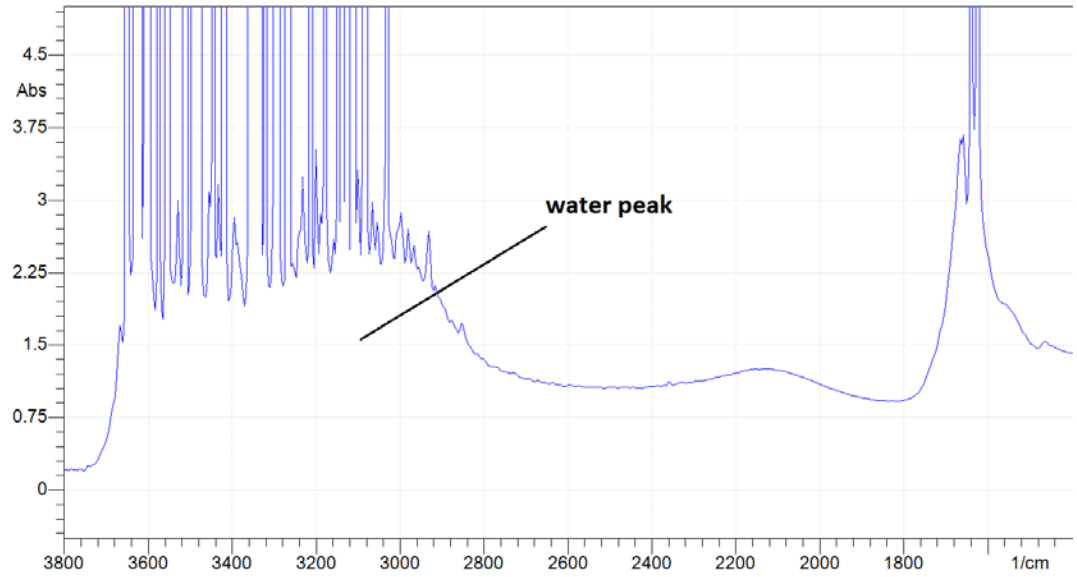

Figure 8: Spectrum 1 - An example of a very wet membrane. The hydrocarbon peak at 2920 cm^{-1} is totally obscured by the water peak. Quantification of Oil and Grease is not possible. This Extractor must be dried further.

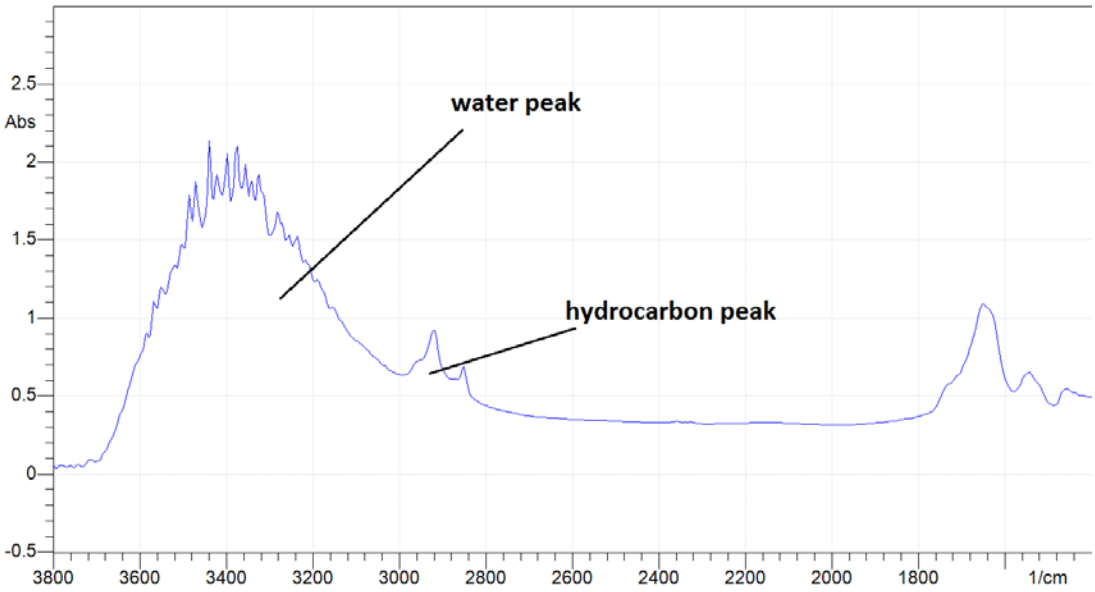

Figure 9: Spectrum 2 - The Extractor has been dried further. The water peak is still prominent, but doesn't totally obscure the hydrocarbon peak. The water peak, however, could still affect baseline point position, resulting in inaccurate height measurement. This Extractor should be dried further and rescanned.

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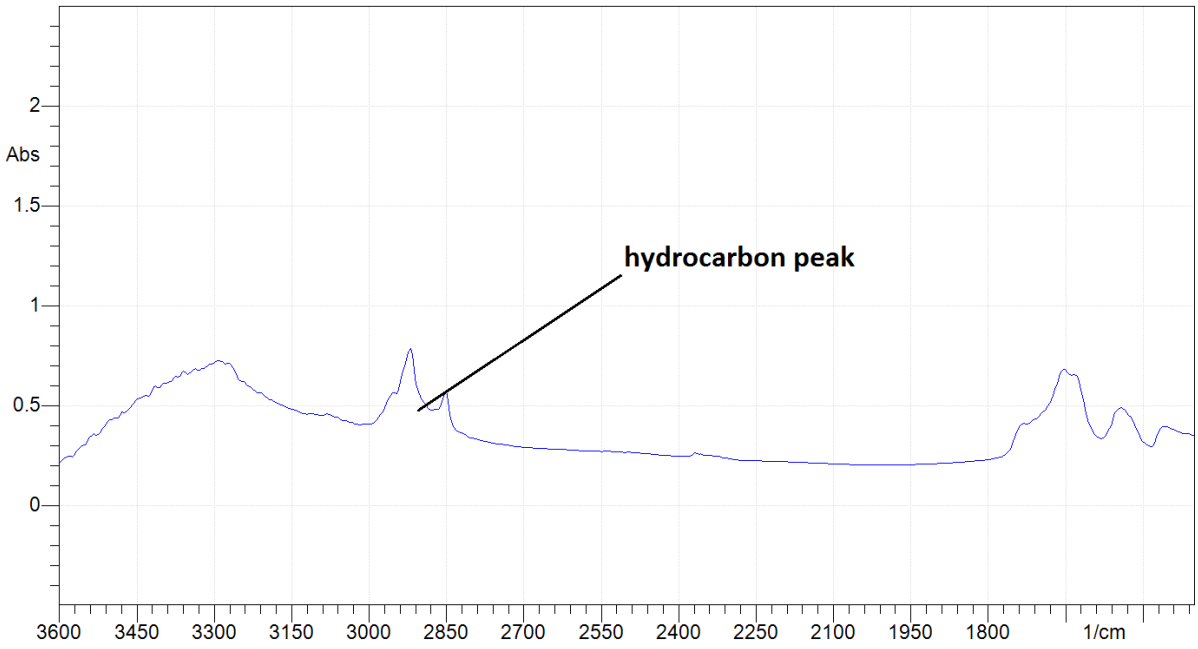

Figure 10: Spectrum 3 - The water peak no longer will affect measurement of the hydrocarbon peak. Iterative drying has shown that all the water has been removed.

14.5.3. It is the responsibility of the user to ensure that the Extractor is properly dried before final measurement and quantitation. In any case where the user is unsure if the Extractor is properly dried, it is recommended to dry further (>5 min). If further drying does not result in any further drying, the Extractor can be considered dry.

15 Calculations

15.1. Calculate the result using the following equation:

Total Oil and Grease , mg/L = (AB + C)(10/D)

Where: A = height of peak at 2920 cm^{-1}
B = slope of linear calibration
C = intercept of linear calibration
D = total volume processed

Report results to three significant figures.

15.2. Average

$$\text{Average} = \bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} = \frac{x_1 + x_2 + \ldots + x_n}{n}$$

15.3. Standard Deviation

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

16 Method Performance, Data Review and Acceptance Criteria

16.1. Method performance is monitored through the evaluation of the Method Blank results, Laboratory Control Sample recoveries and Matrix Spike precision.

16.2. Method Blank

16.2.1. Calculate the result of the Method Blank analysis.

16.2.2. The result should be ≤ 1.0 mg/L.

16.2.3. If the result exceeds this limit, investigate the source of the contamination. When the system is corrected, the samples must be re-analyzed or reported with qualification.

16.3. Laboratory Control Sample

16.3.1. Calculate the percent recovery of analyte in the LCS.

16.3.2. The LCS recovery must be between 79% and 113%.

16.3.3. If the recovery is not within acceptance limits, check the analytical system for error. Fix any errors discovered. If the recovery is still outside acceptance

limits, reanalyze all of the associated samples with a passing LCS or report the data with appropriate qualification.

16.3.4. If it is not possible to reanalyze the samples (*e.g.*, insufficient sample quantity, expired holding time), report the data with appropriate qualification

16.4. Matrix Spike

16.4.1. Calculate the matrix spike recovery.

$$MSR = 100\ [(A(Vs + V) - BVs] / (CV)$$

Where: A = concentration found in spiked sample
B = concentration found in unspiked sample
C = concentration of analyte in spiking solution
V_s = volume of sample that is spiked
V = volume of spiking solution added
MSR = percent recovery

16.4.2. Matrix Spike Recovery must be between 70% and 126%.

16.4.3. If the value is outside of the acceptance limits, either reanalyze the samples or report the data with appropriate qualification of the duplicate parent sample and any other samples of similar matrix.

17 Pollution Prevention and Waste Management

17.1. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

17.2. There is low to no potential pollution attributable to the method. Samples are poured in the sink after analysis is complete.

18 References

18.1. EPA-Methods for Chemical Analysis of Water and Wastes-600/4-79-020, Issued

1971, Editorial revision 1978 and 1982.

18.2. NELAC Standards, 2003 Edition

19 Tables

Not Applicable

20 Worksheets

Infrared Determined Oil and Grease (ASTM D7575)

DATE:				ANALYST:			
CSD concentration:			Measured abs:				
Calibration Slope:	146.4		Intercept	0.18		0.99	
LCS spike vol:			Matrix Spike vol:				40

Sample	pH < 2	Homogenous	File Name	Dry time (min)	scans	Prediction	Observations
test							