Orono Spectral Solutions, Inc.

STANDARD OPERATING PROCEDURE

for ASTM Method DXXXX, Hydrocarbon Contamination in Urea Liquor

REVISION # 1 Effective date: April 5, 2012

APPROVED BY

Signature _____

Signature _____

1 Scope and Application

1.1. This method is used to determine hydrocarbon contamination in Urea Liquor

1.2. The practical range of the determination is 1 mg/L to 20 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.

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

2 Summary of Method

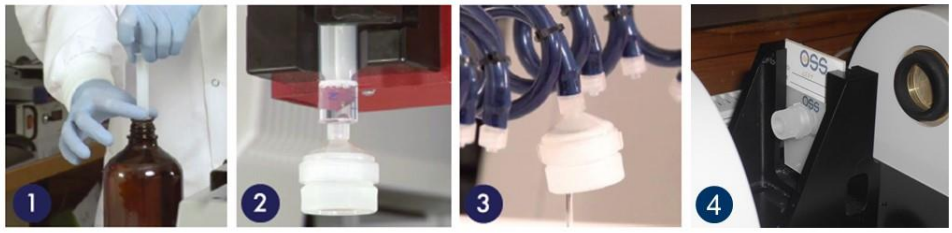
2.1. The sample is homogenized.

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

2.3. The extractor is rinsed

2.4. The extractor is dried.

2.5. The extractor is analyzed.



1. Draw sample into syringe	5 seconds
2. Process sample through extractor	2 minutes
3. Dry using compressed air	1 minute
4. Analyze OSS Extractor using FTIR	1 minute

3 Deviations From Method

3.1. There are no deviations from the method in this version of the Standard Operating Procedure

4 Definitions

4.1. *Hydrocarbon contamination*, n; "membrane-recoverable hydrocarbon contamination" is a method-defined analyte; that is, the definition of hydrocarbon contamination 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 hydrocarbon contamination 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: 1013 SPE-UL.

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

7.3. Sample Bottles – polyethylene (LDPE) with a polypropylene cap capable of containing 0.5 L of sample. Ex. – Fisher Scientific part: 02-893-4D.

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. – Nicolet iS5.

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

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

7.8. 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).

7.9. Volumetric Pipette – 10 mL and 1 mL

7.10. Volumetric Flask – 1 L

8 Reagents and Standards

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

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

8.3. Heavy Mineral Oil (CAS# 8042 47 5) ex. Fisher Scientific Part # O1221

8.4. (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 LDPE container. Do not allow the sample to overflow during collection.

10 Quality Control

10.1. In some cases, it may be necessary to perform control studies using standard additions of known amounts of oil into the Urea Liquor matrix. It is recommended to perform spiking with a 1 ppm solution of Mineral Oil in acetone. The procedure for preparing the spiking solution follows.

10.2. Preparation of Spiking Solution

10.2.1. All hydrocarbon spiking will be done with a mineral oil spiking solution.

1.2.1.1. Place 100 mg +/- 1 mg Heavy Mineral Oil in a 100-mL volumetric flask.
1.2.1.2. Fill to the bottom of the neck with acetone.
1.2.1.3. Dissolve the mineral oil by warming the solution or placing it in an ultrasonic bath.
1.2.1.4. Allow solution to cool to room temperature and add acetone to the mark.
1.2.1.5. 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.

10.2.2. 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 10 ± 1 mg. If not, prepare a fresh solution.

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

10.2.4. 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.

11 Calibration and Standardization

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

11.2. Calibration is carried out using the set of Calibration Standard Devices (CSD) (OSS part # 1013 SPE-CSD). Each of the CSDs is certified with a hydrocarbon 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.

11.2.1. Record a reference through CSD B

11.2.2. Record an absorbance spectrum of each of the CSDs

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

11.2.4. Input the absorbance values into an Excel spreadsheet.

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

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

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

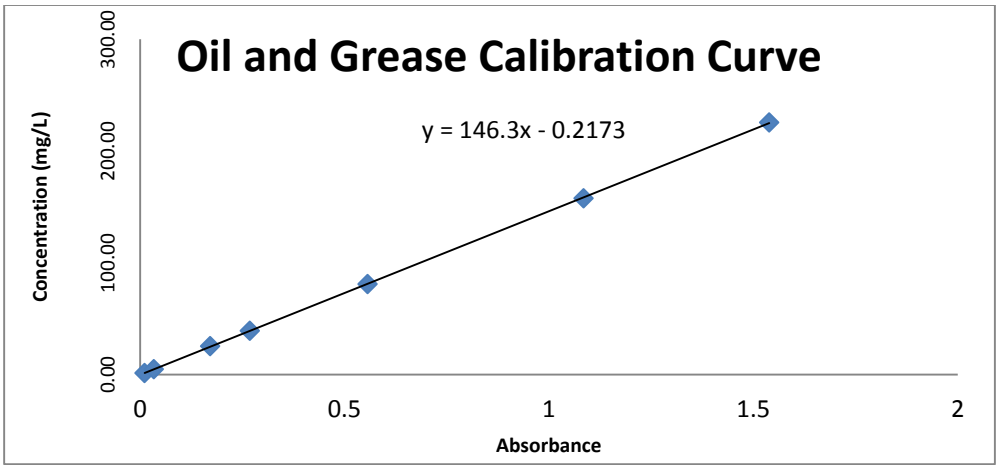


Figure 1: Example of a calibration curve.

11.3. A Calibration Verification must be conducted daily on CSD 3 (at or near 10 mg/L). The measured value should be within 5% of the certified value. If the measured value falls outside of this range, a new calibration must be determined.

12 Procedure

12.1. Sample Homogenization

Careful sample preparation is critical for accurate hydrocarbon 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.

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

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

12.2. Processing Sample Through Extractor

12.2.1. Remove the cap from the sample bottle.

12.2.2. 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

12.2.3. Place the syringe into the syringe pump so that the syringe is vertical facing downwards.

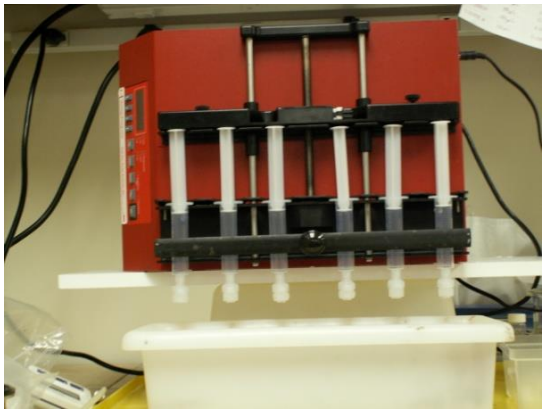


Figure 3: Syringe pump loaded with sample syringes

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

12.2.4. Attach an Extractor to the syringe.

12.2.5. Program the Syringe Pump to process 10 mL of sample at 2 mL/min.

12.2.6. 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.

12.2.7. Remove the syringe and extractor from the syringe pump. 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 rinsing step.

12.3. Rinsing the Extractor

12.3.1. It is necessary to rinse the residual urea salt from the extractor before infrared analysis can be conducted.

12.3.2. Fill a clean syringe with deionized water

12.3.3. Process the deionized water through the Extractor as detailed in section 12.2 of the operating procedure

12.3.4. Proceed to drying step.

12.4. Drying Extractor Using Drying Manifold.

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

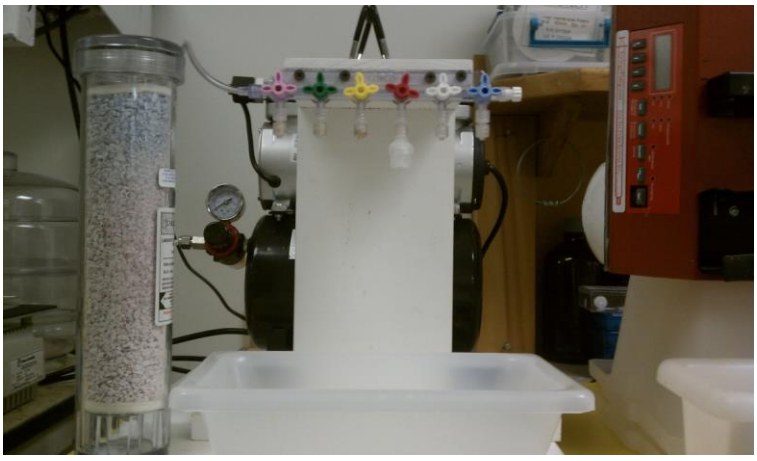


Figure 5: OSS Drying Manifold

12.4.2. 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.

12.4.3. Allow air to flow through the Extractor. Check the extractor every minute 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.

12.4.4. 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.

12.5. Infrared Measurement

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

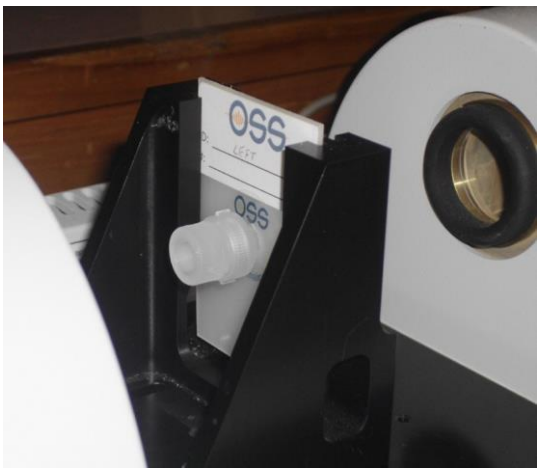


Figure 6: OSS Sample Card

12.5.2. Record a 200 scan reference

12.5.3. Load the processed Extractor into the sample card

12.5.4. Collect a 50 scan absorbance spectrum.

12.5.5. 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.

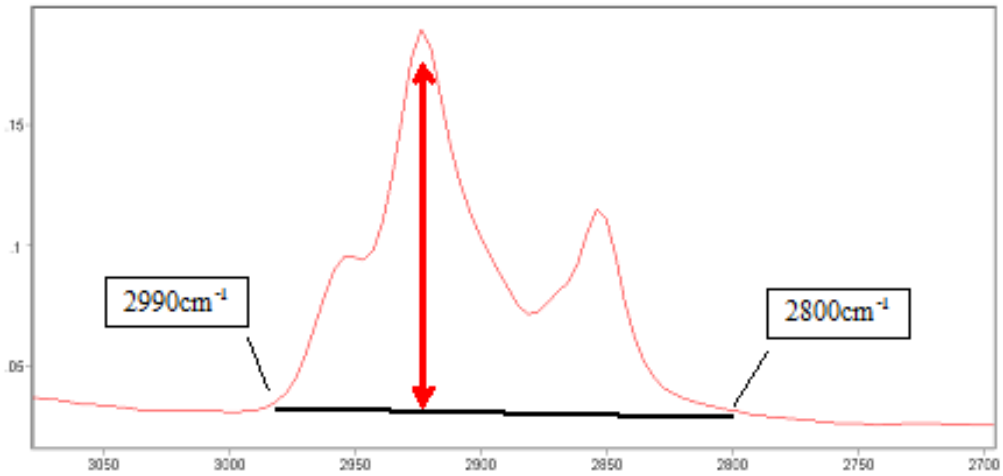


Figure 7: Peak height measurement of the hydrocarbon peak at 2920 cm^{-1}. A straight baseline is drawn between 2800 cm^{-1} and 2990 cm^{-1}.

12.6. Determining Dryness Spectroscopically

12.6.1. 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.

12.6.2. 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.

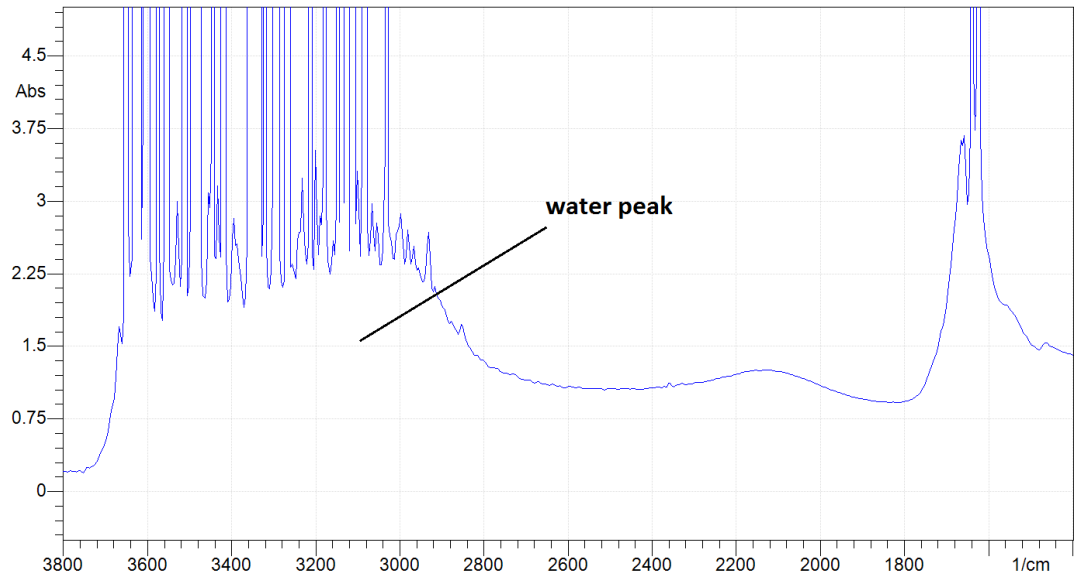


Figure 8: Spectrum 1 - An example of a very wet membrane. The hydrocarbon peak at 2920 cm^{-1} is totally obscured by the water peak. Quantification of Hydrocarbon is not possible. This Extractor must be dried further.

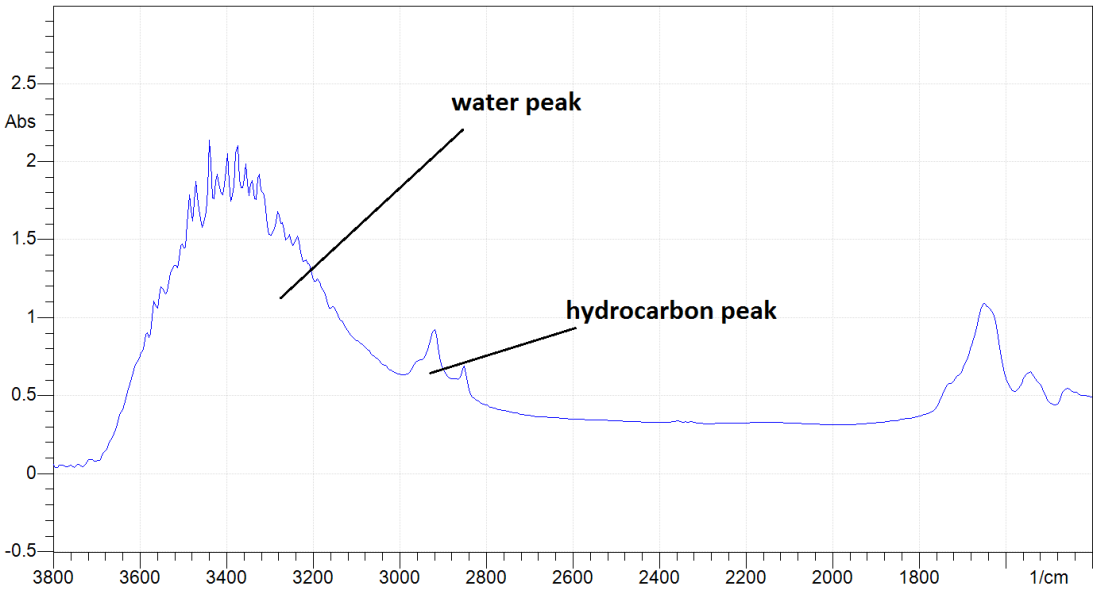


Figure 9: Spectrum 2 - The Extractor has been dried further. The water peak is still prominent, but doesn't totally obscure the hydrocarbon peak. The water peak, however, could still affect baseline point position, resulting in inaccurate height measurement. This Extractor should be dried further and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

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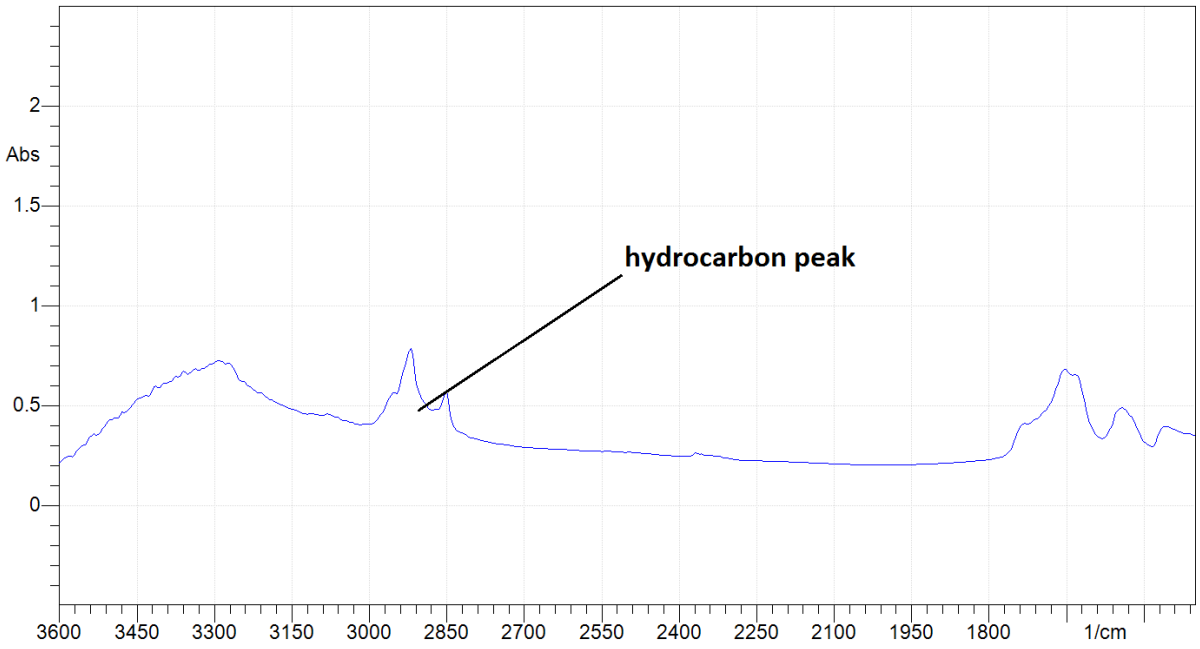

Figure 10: Spectrum 3 - The water peak no longer will affect measurement of the hydrocarbon peak. Iterative drying has shown that all the water has been removed.

12.6.3. 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.

12.6.4. If the extractor seems dry, or has been drying for more than 15 minutes without any further reduction in the water peak, repeat the rinsing step detailed in section 12.3 and dry again.

13 Calculations

13.1. Calculate the result using the following equation:

Total Hydrocarbon , 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.

13.2. Average

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

13.3. Standard Deviation

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

14 Pollution Prevention and Waste Management

14.1. 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.

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

15 References

15.1. NELAC Standards, 2003 Edition