

Orono Spectral Solutions, Inc.

STANDARD OPERATING PROCEDURE

for ASTM Method DXXXX, Hydrocarbon Contamination in Anhydrous ammonia

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 anhydrous ammonia
- 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 collected.
- 2.2. An aliquot of the sample is delivered through the OSS Extractor.
- 2.3. The residual ammonia is allowed to evaporate.
- 2.4. The extractor is analyzed.

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 fluid 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 matrix spikes will demonstrate all these materials are free from interferences.

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 fluid through the membrane. Ex. OSS part: 1013 SPE-AA.
- 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. 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
- 7.4. Spectrometer – instrument capable of infrared absorption measurement. Ex. – Nicolet iS5.
- 7.5. Computer – with Microsoft Excel or comparable spreadsheet program.
- 7.6. Volumetric Pipette – 10 mL and 1 mL

8 Reagents and Standards

- 8.1. Acetone – ACS, residue less than 1 mg/L
- 8.2. Heavy Mineral Oil (CAS# 8042 47 5) ex. Fisher Scientific Part # O1221

- 8.3. (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.
- 9.2. Open the valve and purge the ammonia line for 30 seconds before collecting sample.
- 9.3. Rinse the LDPE container with 50 ml of anhydrous ammonia to cool the container before collecting sample.
- 9.4. Fill the container with enough anhydrous ammonia to ensure there is enough to cool the sample syringe and collect an adequate amount of sample.



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 anhydrous ammonia matrix. It is recommended to perform spiking with a 1 mg/ml 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.

10.3. To ensure quality in the test method, a routine Matrix Spike is recommended.

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

- 1.3.1.1. Acquire a 200 mL sample of known concentration.
- 1.3.1.2. Measure 1 mL (for a 5 mg/L spike) of spiking solution with a volumetric pipette.
- 1.3.1.3. Submerge the tip of the volumetric pipette at least 1 inch below the surface of the sample.
- 1.3.1.4. Dispense the spiking solution into the sample.
- 1.3.1.5. Swirl the sample to disperse the spike.

1.3.1.6. Test as directed below.

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.

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.

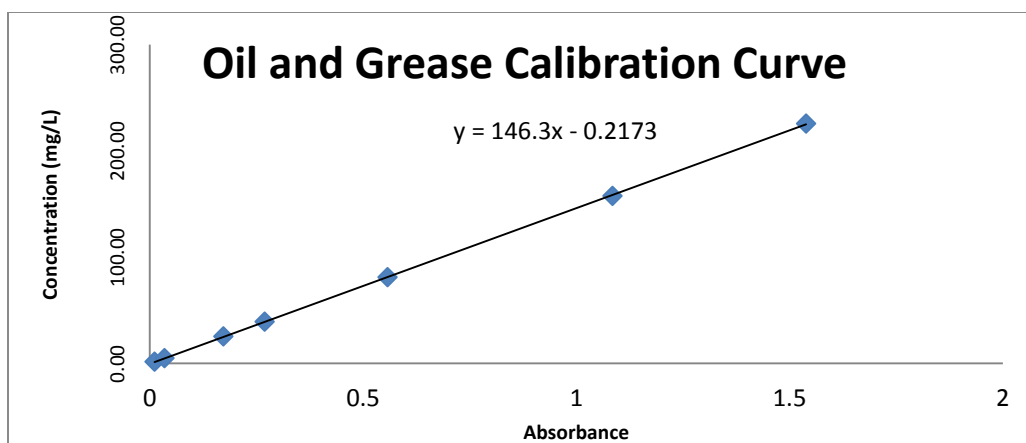


Figure 1: Example of a calibration curve. Your CSD set may have fewer data points.

- 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. Processing Sample Through Extractor

12.1.1. Attach a syringe to the end of the remote sampler.

12.1.2. Submerge the tip of the syringe in the anhydrous ammonia.

12.1.3. By pulling on the remote sampler plunger, fill and empty the syringe 3-4 times to cool the syringe.

12.1.4. Fill the syringe until the remote sampler plunger stops. Ensure that syringe is filled completely with liquid.

NOTE: If the syringe hasn't properly been cooled before pulling the actual sample, the sample will evaporate in the syringe, leaving a bubble of ammonia vapor and skewing results. Ensure the syringe is filled entirely with liquid ammonia before attaching the extractor.



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

12.1.5. Attach an Extractor to the syringe.

NOTE: Keep the remote sampler horizontal while attaching or ensure that the sampler plunger does not force sample out due to gravity.

12.1.6. Using the remote sampler plunger, slowly push the ammonia sample through the Extractor. Ensure the entire sample is passed into the extractor.

12.1.7. Remove the extractor from the syringe.

12.1.8. Pull back on the remote sampler plunger, filling the syringe with air.

12.1.9. Reattach the extractor to the syringe.

12.1.10. Push the air from the syringe through the extractor.

12.1.11. Remove the extractor from the syringe. Allow the remaining ammonia to evaporate. (1-2 minutes)

12.2. Infrared Measurement

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



Figure 6: OSS Sample Card

12.2.2. Record a 200 scan reference

12.2.3. Load the processed Extractor into the sample card

12.2.4. Collect a 50 scan absorbance spectrum.

12.2.5. 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.

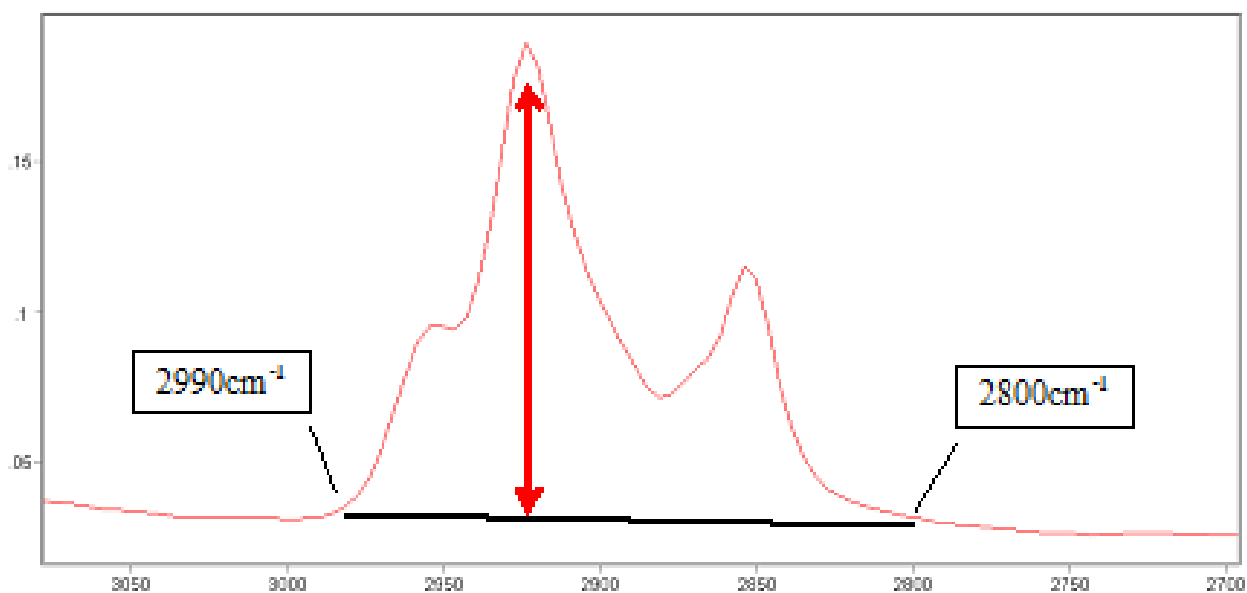


Figure 7: Peak height measurement of the hydrocarbon peak at 2920 cm^{-1} .
A straight baseline is drawn between 2800 cm^{-1} and 2990 cm^{-1} .

13 Calculations

13.1. Calculate the result using the following equation:

$$\text{Total Hydrocarbon, mg/L} = (AB + C)(10/D)$$

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

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

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