



**Standard Test Method for Water in Anhydrous Ammonia (0.2 to 0.5% level)
by Infrared Determination
Version 2017 - 03.2**

Scope

1.1 This test method covers the determination of water in anhydrous ammonia over the concentration range outlined in Table 1 that can be extracted with an infrared-amenable support and measured by infrared (IR) transmission through the membrane.

1.2 This method defines water in anhydrous ammonia as that which is retained in the test method and measured by IR absorption.

1.3 The test method detection limit (MDL) and recommended reporting range are listed in Table 1.

1.4 This method covers the range of 0.2 to 0.5% water with a 200 microliter sample size.

1.5 This method performs 3 or more tests per sample to increase confidence in the result accuracy.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 Compressed Gas Association Standards:

CGA G-2.2-1985 (Reaffirmed 1997): Guideline Method for Determining Minimum of 0.2% Water in Anhydrous Ammonia – Second Edition

CGA G-2, Anhydrous Ammonia, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151.



2.2 *ASTM Standards*¹:

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 3856 Guide for Good Laboratory Practices in Labs Engaged in Sampling and Analysis of Water

D 2777 Practice for the Determination of Precision and Bias of Applicable Methods of Committee D19 on Water

D 4840 Guide for Sample Chain-of-Custody Procedure

D 5810 Guide for Spiking into Aqueous Samples

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

D 7575 Standard Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination

E 168 Practices for General Techniques of Infrared Quantitative Analysis

E 178 Practice for Dealing With Outlying Observations

2.3 *ANSI*:

K61.1 (CGA G-2.1), American National Standard Safety Requirements for the Storage and Handling of Anhydrous Ammonia, American National Standards Institute, Inc., 1430 Broadway, New York, NY 10018 or Compressed Gas Association, Inc. 4221 Walney Rd., Chantilly, VA 20151.

2.4 *Code of Federal Regulations*: 49 CFR 173.315(1)(5)

3. Terminology

¹ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.



3.1 *Definitions:* For definitions of terms used in this test method, refer to ASTM Terminology D 1129 and Practices E 168.

3.2 *Definitions of Terms Specific to This Method*

3.2.1 *Extractor, n*—A device which contains an infrared-amenable substrate for the purposes of this test method.

3.2.2 *Water, n* – water inherent to the anhydrous ammonia sample under test.

4. Summary of Test Method

4.1 This is a performance-based method and modifications are allowed to improve performance.

4.2 Field-collected samples of ammonia are processed in replicates using Extractors that retain the water portion of the sample and optimally position and distribute it for analysis by infrared spectroscopy.

4.3 Infrared spectral data from each Extractor is examined by an infrared absorbance analyzer to determine water content.

4.4 Calibrations and data are processed using an infrared spectral processing algorithm to provide the user with water concentration values.

MDL and Reporting Range		
Analyte	MDL (%)	Reporting Range (%)
Water	0.09%	0.2 – 0.5

Table 1: MDL and Reporting Range.

5. Significance and Use

5.1 DOT Regulations – Anhydrous ammonia shipped in DOT Specification MC-330 or MC-331 cargo tanks constructed of quenched and tempered steel (QT) *must* have a minimum water content of 0.2 percent by weight. Shippers or carriers, except as provided



for in the regulations, are required to perform periodic analyses for the prescribed water content in the ammonia. See CFR 173.315(a) Note 14 and 173.315(1). [1]¹

5.2 Purpose – this method is intended to provide shippers and carriers with an alternative method of analysis to determine the presence in anhydrous ammonia at the minimum water content of 0.2 percent by weight as required by the DOT regulations. Lack of the appropriate percentage of water in single loads of ammonia has resulted in extensive stress and corrosion damage to QT cargo tanks. As well, a maximum of 0.5% water is typically required for commercial reasons. For example, when anhydrous ammonia is used as a refrigerant, water contamination will degrade refrigeration performance and result in premature equipment wear along with increased running costs. This method is intended for laboratory use and thus the equipment and procedure selected may vary slightly from that used under field conditions. Other proven methods of determining water content are acceptable.

5.3 Other methods for determining water content in anhydrous ammonia are available. A standard method (CGA G-2.2) per 49 CFR 173.351 has been established for monitoring of water in ammonia for commercial transport. This process is time consuming, takes several hours to perform, requires a significant amount of sample, usually more than 2,000 mls., does not easily allow for replicate samples, and is a safety concern in terms of the time and amount of ammonia exposure for laboratory technicians. The proposed method requires a volume that is 10,000 times smaller than the current method.

6. Interferences

6.1 Method interferences that produce artifacts may be due to contamination in the materials, equipment, or other apparatus. Routine quality performance checks and laboratory blanks are built into the method for determination of the presence of interferences.

6.2 It is important to conserve the integrity of the sample and to not allow external water to influence the measurement. System designs specifically built into this method are meant to minimize or eliminate the possibility of this interference. It is critical that the dry air



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curtain be maintained to ensure that no moisture is added into the extractor cavity, the sample container, or the subsample collection vessel.

7. Apparatus

7.1 *Extractor* – Device which contains an infrared-amenable water extraction substrate, and is designed for capturing and distributing the water analyte from the anhydrous ammonia sample for infrared transmission analysis. OSS apparatus is covered under US Patents 8,613,214 and 8,393,198.



Figure 1: OSS Extractor in an FTIR card holder and environmental control system

7.2 *Calibration Standard Devices Set* – Calibration standards have a similar outward appearance as the Extractor, however, these devices are unique solid-state standards (Figure 2). The standards set are designed to cover the 0.2% to 0.5% range and are used to validate the performance of the instrument and processing algorithms.





Figure 2: OSS Calibration Standard Devices

7.3 Pipette – this method uses a 200 ul sample of anhydrous ammonia transferred from the sample container to the Extractor using a clean and calibrated pipette using a disposable tip (Figure 3). The accuracy should be one percent or better at 200 ul ($< 1\%$). The pipette tips are for single sample use only. (e.g. Fisherbrand® Finnipipette II® pipette and Finntip Flex 200 tips).

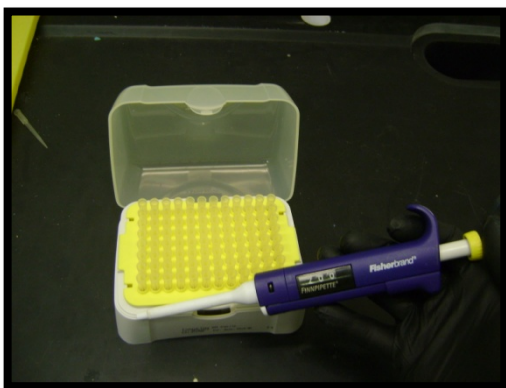


Figure 3: Typical Pipette and Disposable Pipette Tips

Infrared Instrument – Infrared absorption measurement instrument (Figure 4); the instrument may be spectroscopic or radiometric based. The method was validated and the detection limit was determined with an FTIR spectrometer according to **Section 16**; the detection limit may vary with the instrument chosen to perform the analysis; the user should perform a detection limit study as described in **Section 16** to determine the lower limit of detection when using the chosen instrument.



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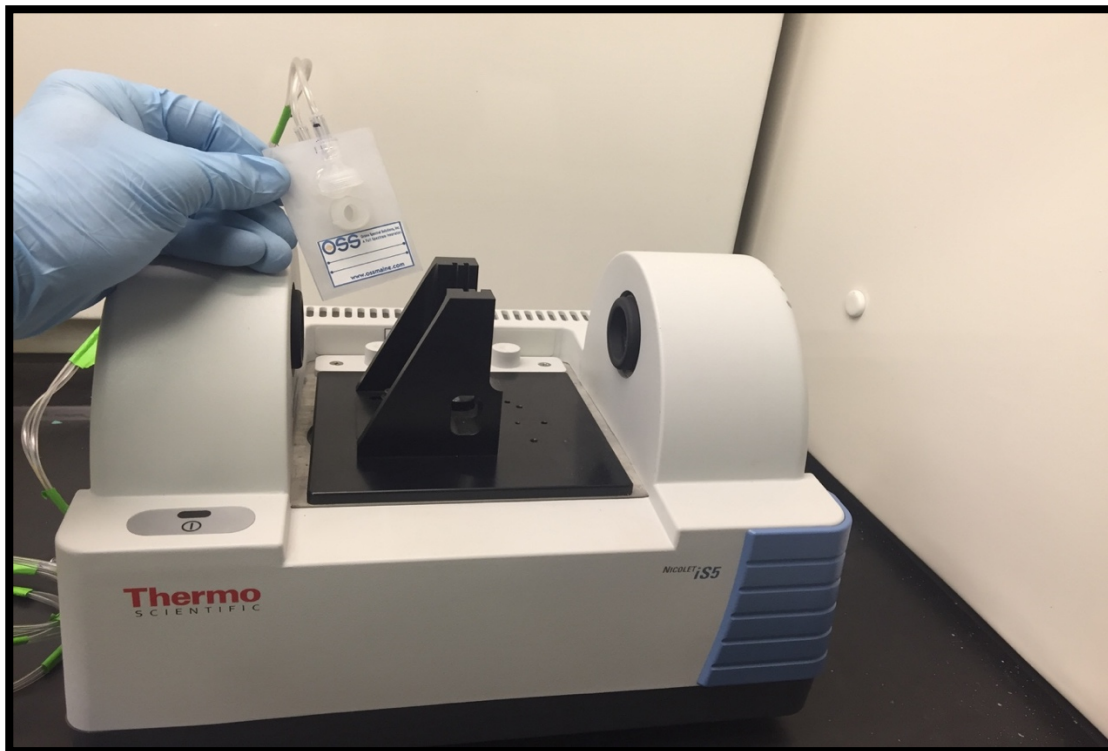


Figure 4: FTIR Unit and OSS Extractor

7.4 *Ammonia container* – an approved container that ensures safe collection and transport of anhydrous ammonia through a manufacturing facility to the test area without absorbing moisture into the sample. Ideally this is a closed design that eliminates the possibility of water / environmental contamination. Figure 5 shows an example container successfully utilized during the development and validation of the method. This equipment can be procured through Swagelok (Part Number KAW-FAI-730-025-0).



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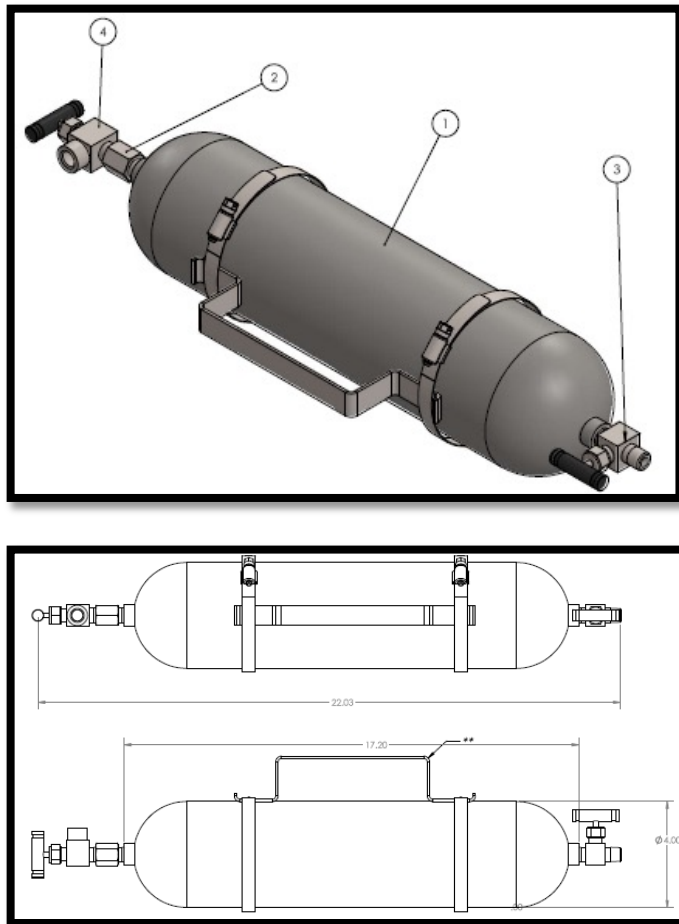


Figure 5: Sample Transfer Container

7.5 Extractor Environmental Control System – (Figure 6) this system has been designed to ensure the integrity of the sample so that no potential adsorption of ambient water on the device will negatively influence the test. Specifically, the system provides a constant curtain of dry air around the sample and Extractor during the performance of the measurement. This equipment is supplied by OSS and was specifically designed for this application.



Figure 6: Extractor Environmental Control System

7.6 In Laboratory Hood Ammonia Sample Environmental Control System – this system contains two sub-components a) an Ammonia Container Stand and b) a Sample Handling Subsystem both described below. This overall system has been designed to ensure the integrity of the ammonia sample taken from the ammonia container and presented to the Extractor. This system is designed to operate in a laboratory hood. It includes a stand for supporting the ammonia sampling cylinder along with a sample handling subsystem.

7.6.1 Ammonia Container Stand – (Figure 7A) this stand is designed to fit into a laboratory hood and support the ammonia sample container and to allow safe delivery of a liquid ammonia sample to the Sample Handling Subsystem that is positioned directly underneath (as shown in Figure 9). Once the ammonia sample container is set into the stand, a small piece of tubing is attached to allow transfer of the ammonia into the Sample Handling Subsystem.



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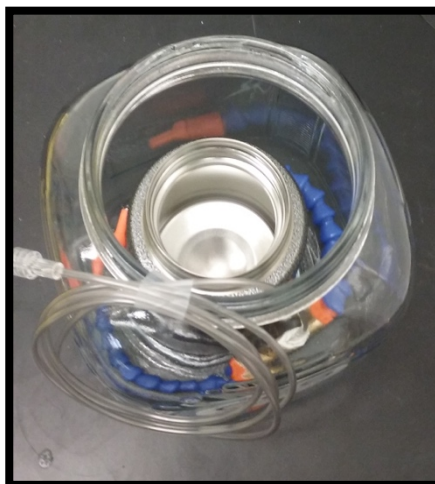


Figure 7A: Ammonia Container Stand



Figure 7B: Stand with Container in Place

7.6.2 Sample Handling Subsystem – This subsystem works with and is aligned directly underneath the Ammonia Container Stand. Its function is to allow uncompromised subsampling of the field-sampled ammonia from the Ammonia Container. It consists of a vacuum insulated subsample collection vessel encased in an environmentally controlled positive pressure dry air vessel that allows safe, easy and visible access to the subsample such that a pipette sample of ammonia can be presented to the Extractor. An example of this subsystem is shown in Figure 8.





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Figure 8: Sample collection subsystem

Figure 9 is a representation of the Complete In Laboratory Hood Ammonia Sample Environmental Control System:

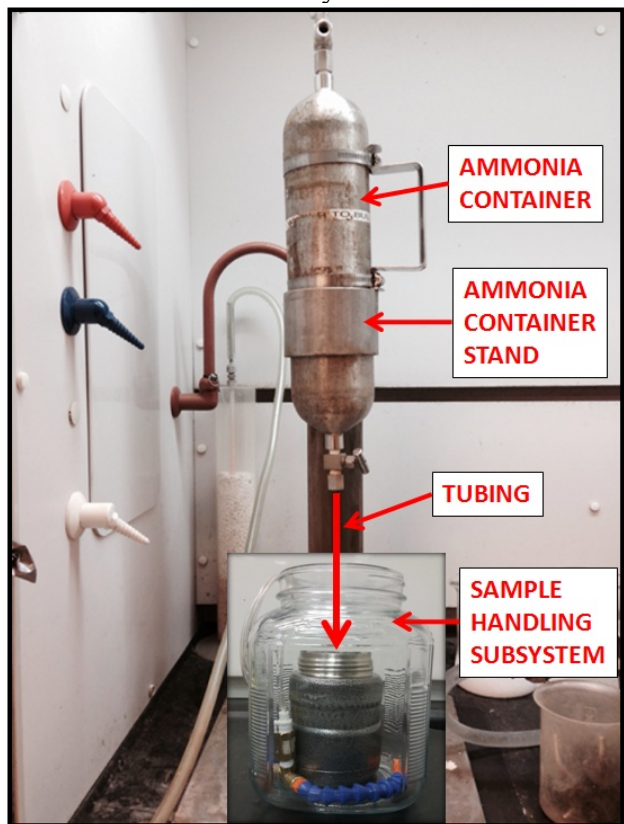


Figure 9: Complete system

8. Reagents and Materials



8.1 *Purity of Reagents* – Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.² Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water* – Unless otherwise indicated, references to water shall be understood to mean reagent water that meets the purity specifications of Type I or Type II water, presented in ASTM Specification D 1193.

8.3 *Laboratory Air* – since this test is to measure water in anhydrous ammonia samples, it is imperative that the outside environment not influence the test. To that end, environmental control subsystems have been developed to significantly control or eliminate any external environmental effects on the test by using house air. To perform optimally, it is helpful that the laboratory air that is the supply to the environmental control subsystem be as dry and clean as possible. It has been found that house air systems with < 40 um particle size, dew point of < -20 °F, > 20 psi, and > 10 LPM work well. It is up to the operator to determine if deviations from the conditions described here produce sufficient results.

9. Hazards

9.1 Ammonia Properties

At room temperatures and atmospheric pressure, anhydrous ammonia is a pungent, colorless gas. Ammonia vapor at a pressure of 1 atmosphere (101.325kPa) and a temperature of 32°F (0° C) is lighter than air, having a relative density of 0.5970. The sharp, pungent odor of ammonia serves as a warning signal such that very small concentrations of ammonia are present.

9.2 Physiological Effects

² *Reagent Chemicals*, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.



Ammonia is not a cumulative metabolic poison. However, depending upon the concentration in the immediate atmosphere, it can have an irritating or corrosive effect on human tissues and can cause laryngeal and bronchial spasm, edema, and asphyxia. Liquid ammonia may cause severe injury upon contact with the skin, resulting from frostbite and caustic burns.

9.3 Personal Protective Equipment

Personal protective equipment (PPE) and its use is the responsibility of the operator and facility where this method is being used. Consult the material safety data sheet (MSDS) for ammonia regarding appropriate PPE. It is suggested that anyone handling anhydrous ammonia shall wear the following protective equipment as a minimum.

9.3.1 Protective gloves impervious to ammonia

9.3.2 Chemical splash goggles

9.3.3 Full face shield over the chemical splash goggles as an option, but not a substitute.

9.3.4 Long sleeve shirt / lab coat.

9.3.5 Long pants.

9.3.6 Appropriate footwear.

9.4 Personal Safety

Individuals working with anhydrous ammonia must be trained in safe handling and operating practices, and be knowledgeable of appropriate actions to take, including applicable first aid procedures. In the event of an ammonia release emergency, information regarding these matters is given in CGA G-2, *Anhydrous Ammonia*, and ANSI K61.1/CGA G-2.1, *American National Standard Safety Requirements for the Storage and Handling of Anhydrous Ammonia*.

10. Sampling

10.1 It is the responsibility of the user to ensure a representative sample for analysis.

10.2 Sampling should only be performed by trained personnel.

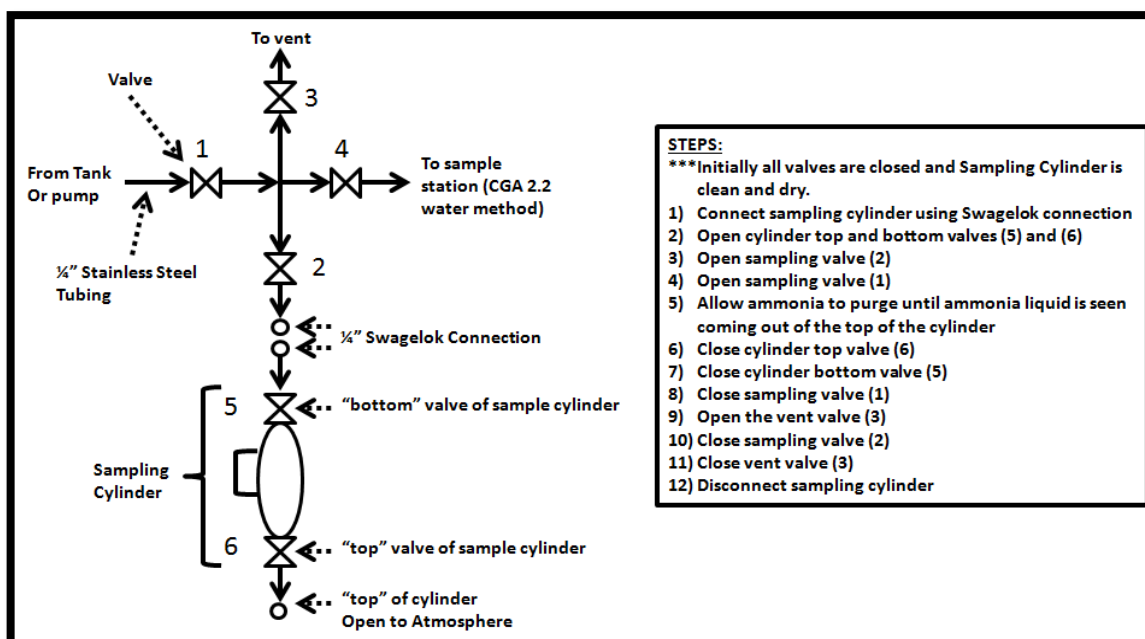


10.3 Physical hazards include extreme (cold) temperatures, thermal burns, chemical burns, stored energy, and inhalation / asphyxiation.

10.4 Personnel must wear appropriate protective equipment.

10.5 Sampling Procedure

10.5.1 Refer to the following diagram for details on the in-field sampling process:



10.5.2 Verify that the sample cylinder(s) are empty. If not, place the cylinder in the cylinder stand in the lab hood. Slowly open the drain valve location on the bottom of the cylinder and let the cylinder drain into a beaker or flask until there are no visible vapors coming out.

10.5.3 Inspect the sample cylinder for any defects, particularly around the screwed fittings on the ends of the cylinders.

10.5.4 Verify that the top and bottom valve of the sample cylinder is closed.

10.5.5 Proceed to the sampling point in the manufacturing location.



10.5.6 Connect the union on the sample tubing to the bottom valve of the cylinder. Ensure the fitting on the union is tight.

10.5.7 Open the bleed valve.

10.5.8 Open the sample valve to flush clean ammonia through the sample line and to clear the line of any potential debris.

10.5.9 Wait approximately 30 seconds (or the amount of time determined as necessary by the site).

10.5.10 Open the top valve on the cylinder to vent the cylinder. *****CAUTION***** The opening of the bleed valve must be pointing away from the Operator and downwind to ensure the Operator does not come in contact with vapor and liquid ammonia as the cylinder is filled.

10.5.11 Open the bottom valve of the cylinder. *****NOTE***** When ammonia is observed coming from the cylinder vent, the cylinder contains adequate sample volume. A dip tube within the cylinder prevents over pressuring, provided the cylinder is closed at this point.

10.5.12 Close the bleed valve.

10.5.13 Allow the cylinder to fill until liquid ammonia is observed coming out of the top vent.

10.5.14 When liquid ammonia is observed coming out of the top vent, close the top vent valve.

10.5.15 Close the cylinder bottom valve.

10.5.16 Close the sample valve.

10.5.17 Open the bleed valve on the sample line to bleed off the connection between the sample line to the cylinder.

10.5.18 When ammonia has stopped bleeding, loosen the connection of the sample line to the cylinder.

10.5.19 Remove the union from the bottom valve of the sample cylinder.



10.5.20 Remove ammonia personal protective equipment if appropriate to do so.

10.5.21 Deliver the filled sample cylinder to the Laboratory for analysis.

11. Calibration and Standardization

11.1 To ensure analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the instrument manufacturer's instructions and the following procedures must be followed when performing the test method.

NOTE X – Instruments other than FTIR spectrometers may have different procedures that should be followed according to the manufacturer's instructions.

11.2 Calibration is carried out using the set of Calibration Standard Devices (CSDs).

11.3 Follow the method provider's instructions to calibrate the instrument. Automated software makes this easy for the operator. In general, the steps of the software module includes:

11.3.1 Take a background reference file through the CSD labeled 'background'.

11.3.2 Scan each of the other CSDs to measure and record the spectral information related to water bands. Use the method manufacturer's validated algorithms to produce % water output data points for developing the calibration curve.

11.3.3 Use software (e.g. Microsoft Excel, or software provided by the method manufacturer) to plot the calibration curve points and to find an appropriate calibration fit.

11.3.3.1 Linear calibration may be used if the coefficient of determination, r^2 , is > 0.95 for the analyte. If one of the calibration standards other than the high or low point causes the r^2 to be < 0.95 this point must be reanalyzed. If the point still causes the r^2 to be < 0.95 , it may be excluded. The high or low point of the calibration may be excluded but the reporting range must be modified to reflect this change. If two points must be excluded to attain an $r^2 > 0.95$, calibration must be repeated, and if this still is not achieved, calibration must be repeated with a new set of calibration standard devices.

11.3.3.2 Quadratic calibration may be used if the coefficient of determination, r^2 , is > 0.97 for the analyte. If one of the calibration standards other than the high or low point



causes the r^2 to be < 0.97 this point must be reanalyzed. If the point still causes the r^2 to be < 0.97 , it may be excluded. The high or low point of the calibration may be excluded but the reporting range must be modified to reflect this change. If two points must be excluded to attain an $r^2 > 0.97$, calibration must be repeated, and if this still is not achieved, calibration must be repeated with a new set of calibration standard devices.

11.4 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example a new analyst or instrument, perform a method detection limit and precision and bias study to demonstrate laboratory capability.

11.5 *Method Detection Limit (MDL)*

11.5.1 The MDL procedure that follows is a paraphrased version of the MDL procedure in the 40 CFR Part 136, Appendix B.

11.5.2 Analyze at least seven replicates of a sample at a concentration near three times the expected method detection limit (e.g. 0.09 %). A laboratory spike sample, matrix sample, or a sample similar to the desired matrix to be examined may be tested. The complete method must be followed.

11.5.3 The method detection limit (MDL) is determined as the Standard T value for 98% confidence for the number of samples tested, e.g. 3.143 for seven samples test times the standard deviation of measured concentration of the seven replicates. The recommended reporting limit is 10 times the standard deviation of the seven replicates. The mean (average) measured concentration must be 1–5 times the calculated method detection limit; if this criterion is not met repeat the detection limit study.

11.5.4 This study should be repeated until the desired method detection limit is achieved.

12. Preparation of Infrared Instrument

12.1 Preparation of the infrared instrument will vary by type of analysis instrument chosen. Follow the instructions of the instrument manufacturer.

13. Preparation of the Extractor Environmental Control System



13.1 Check the cleanliness, dryness, and integrity of the Extractor Environmental Control system. The desiccant / particulate filter module of the system should show that the desiccant is in proper condition (e.g. there is still some blue desiccant in the column). If not, replace the module.

13.2 Place the system in a location close to the laboratory hood where the ammonia sampling will take place and close to the infrared instrument for easy access for performing the analysis.

13.3 Close the valve of the Extractor Environmental Control System. Connect the extractor environmental control system input hose to the house air source (note the expectation is that the house air source is of suitable grade for laboratory use – e.g. dry and particulate free and less than 100 psi). Ensure a proper connection. Using the pressure regulator on the system, set the pressure to be around 20 psi. Plug in the power connection of the system to a properly regulated power supply (e.g. 120 volts) and turn on the system power strip. Set the flow rates of the system mass flow controllers (MFCs) to 1.5 liters per minute (LPM). Observe that the MFCs are operating properly before proceeding to the next step.

13.4 Connect a new water in ammonia Extractor to the two output lines of the system. One line attaches to the top front of the Extractor and one to the top back of the Extractor. Ensure a proper connection and confirm flow to both the front and back of the Extractor, creating a ‘curtain’ of dry air across the device.

13.5 During the procedure section below, always allow the Extractor to acclimate with the flow across it for at least one minute before analyzing.

14. Procedure

14.1 *Calibration Verification* – Verify the calibration each day the test is to be performed by re-analyzing the CSD at or near the 0.2% water concentration level. If the verification value varies from the CSD value by more than +/- 10%, recalibrate the instrument as described in Section 11.2.

14.2 Laboratory analysis



14.2.1 Take the ammonia sample container from the field sampling and place it into the Ammonia Container Stand of the Lab within the Laboratory Ammonia Sample Environmental Control System. Place the Sample Handling Subsystem **under** the output of the Ammonia Container. Make sure that the components of this subsystem are clean and dry. Turn on the dry air flow and verify the proper air flow rate (e.g. > 20 liters per minute (LPM) for the system shown) and direction (e.g. swirling vortex within the enclosure) to ensure positive pressure within the subsystem and a dry air ‘shield’ around the insulated subsample collection vessel.

14.2.2 Attach the small hose to allow transfer of the liquid ammonia sample from the Ammonia Container to the vacuum insulated subsample collection vessel in the Sample Handling Subsystem. Ensure a secure connection.

14.2.3 Open the output valve of the Ammonia Container to transfer a subsample to the vacuum insulated subsample collection vessel. A liquid level of around 3 inches (3”) from the bottom of the vessel allows easy pipetting of the sample and is sufficient for multiple replicate testing of this method and allows easy pipetting of the sample.

* You are now ready to process samples with Extractors.

14.2.4 Prepare the Extractor for processing:

14.2.4.1 Start the software program on the calibration validated FTIR from (Section 14.1). The first step in the program is to collect a background for the Extractor to be processed.

14.2.4.2 Take a new, clean, dry Extractor from its packaging and attach it to the Extractor Environmental Control System tubing described in (Section 13.4) and verify flow. The Extractor will remain attached to the control system tubing for the remainder of processing using this device. Allow at least one minute to for the Extractor to acclimate in the Environmental Control System.

14.2.4.3 Now place the Extractor into the FTIR sample card holder.

14.2.4.4 Follow the software instructions to collect the background.

14.2.4.5 Once the background is set, take the Extractor (still attached to the Extractor Environmental Control System) to the hood. The Extractor and FTIR are now ready for sample processing.

14.2.5 Using a calibrated pipette, the user will extract a 200 microliter (ul) sample of the ammonia under test in the following manner:

- a) Note: it is assumed that the operator is familiar with the proper use, calibration, and sample collection of the pipette.
- b) Secure a new, dry, clean pipette tip to the pipette that has been set to collect 200 ul of sample.

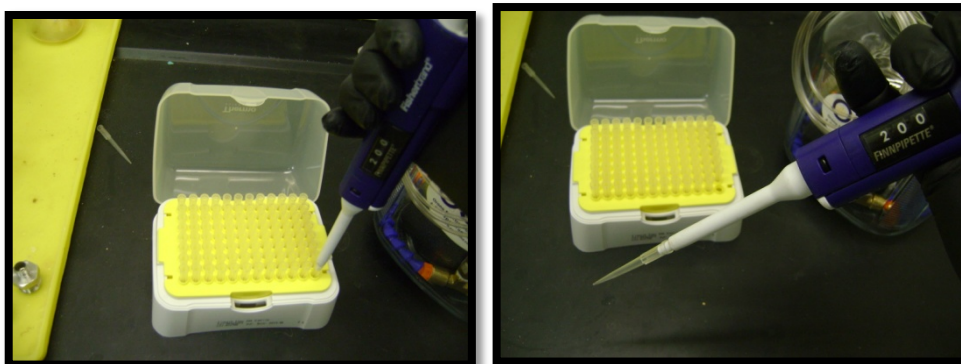


Figure 10: Pipette

- c) Hold the pipette plunger down and submerge the pipette tip into the ammonia sample to a level of the pipette tip that will be past the 200ul sample volume. In the left picture below (Figure 11) the vessel is taken out of the chamber to show better detail. The right picture represents how this process is actually done in the subsystem.



Figure 11: Pipette sampling example.

- d) Steadily hold the pipette tip at this depth level in the sample. This will avoid any potential for tip water condensation on the pipette tip.
- e) While continuing to hold the plunger down, and the tip at a consistent level in the sample, count to ~ 10 seconds to allow the pipette tip to cool to the temperature of the ammonia sample.
- f) Release the plunger to draw the 200 ul sample into the pipette and transfer the sample to the center area of the input side well of the horizontally-oriented Extractor. Maintain a horizontal orientation of the extractor while evaporation takes place.
- g) Allow the ammonia in the sample to evaporate until there is only a small amount (e.g. no liquid layer above the substrate but the membrane is still clear meaning that it is still saturated with sample) of sample covering the extractor substrate remains and the device can be oriented vertically without spilling any sample out of the device.



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Figure 12: Extractor orientation during the sample presentation process.

- h) Now place the Extractor into the FTIR instrument that was just prepared (via Section 14.1 calibration verification and 14.2 device background and macro software running) to process this sample and measure the water content by recording the absorption spectra and then processing the band heights and areas in the water regions per the validated algorithm. The FTIR instrument will continually observe the spectral features and process the water content to provide the user with an automatic answer in percent water concentration (e.g. 0.32% water).

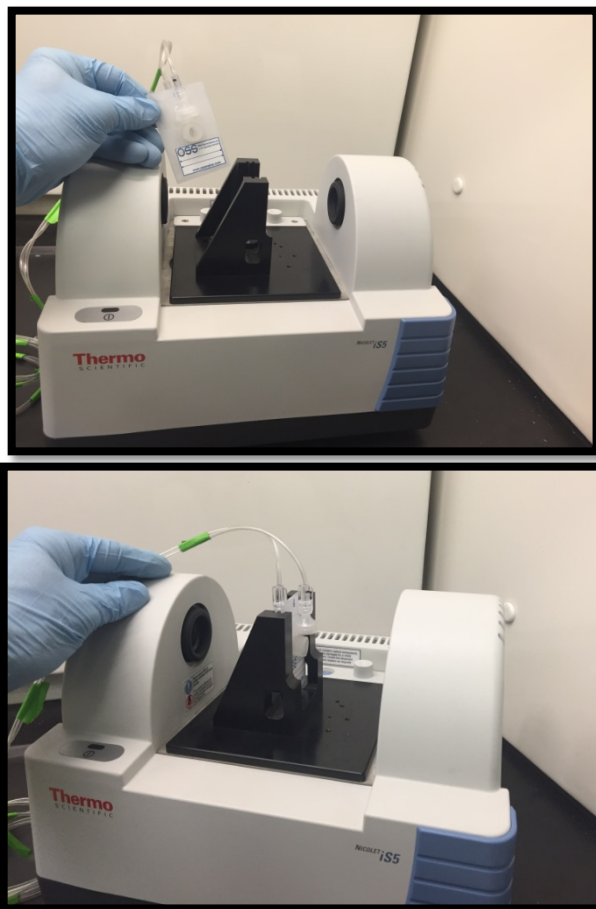


Figure 13: Extractor processing in the FTIR instrument.

- i) Repeat Section 14.2.4 to Section 14.2.5-h to process replicate Extractor samples. It is recommended that three or more replicates are taken and the results averaged to give a final result for the percent water concentration in the anhydrous ammonia sample.

15. Report

15.1 Determine the results in unit of percent water in ammonia. All data that does not meet the specifications in the test method must be appropriately qualified.

16. Precision and Bias

16.1 Initially, a single-laboratory study was performed to determine preliminary method values of performance. Data is shown in Tables 2 - 5.



16.2 Plans are actively being put into place to perform multi-lab studies at ammonia manufacturers that are industrial leaders with extensive background and data on performing water in anhydrous ammonia using the CGA G-2.2 method. As more data is collected and this method improves, the method will be refined to include components and procedural adjustments that improve performance.

16.3 It is the user's responsibility to ensure the validity of precision and bias outside of the validation study ranges.

Initial Precision and Recovery Validation Summary:

An overview of the validation testing is provided below. Validation of this method occurred in the OSS facility in Bangor, ME as well as various large Nitrogen/Fertilizer manufacturing facilities in the United States and Canada. It should be noted that the calibration, detection range, and repeatability limits of this method are subject to change as processes and systems improve and more data is collected. Reproducibility and bias will be defined as laboratory comparability data is collected from additional end-user facilities. The procedures used to determine the precision data and method limits is detailed below.

Method Data Summary	
METHOD DETECTION LIMIT (98% Confidence) MDL	Detection Range
0.09%	0.2% - 0.5%

Table 2: Summary of the limits determined in method development

Detection Limit:

Method Detection Limit (MDL) – Before the start of this study, a sample of AA was drawn from the truly ‘anhydrous’ part of the manufacturing process at the AA manufacturing facility to confirm that this sampling point and sample product has indiscernible water content ($\ll 0.2\%$). This sample was processed using the current CGA G-2.2 method and it was confirmed that the water content was below the detection limit of the method (e.g. $\sim 0.0\%$ water) as it should be. Thus, a pristine sample was available to fortify with a known



amount of water to achieve the desired water content to test. A sample was taken from the same sample point and product batch and spiked to the desired 0.3% water content concentration using a calibrated pipette. Ten replicate analyses were performed. The MDL was calculated by multiplying the standard deviation of the 10 replicate analyses by the Student's t value for (n – 1) degrees of freedom, where n equals the number of replicates. The Student's t value for 10 replicates is 2.821 for the 98% confidence level. See Table 3.

Method: Water in Anhydrous Ammonia									
Fortification Level of CGA G-2.2 Verified Dry Anhydrous Ammonia: 0.3% Water									
Measured Result: % Water									
REP 1	REP 2	REP 3	REP 4	REP 5	REP 6	REP 7	REP 8	REP 9	REP 10
0.32	0.27	0.28	0.34	0.36	0.30	0.31	0.33	0.28	0.35
Average of 10 Replicates:						0.3154 % Water			
Standard Deviation of 10 Replicates:						0.032 % Water			
MDL (Student's t 2.821 x Standard Deviation) (98%Confidence): 0.09 % water									

Table 3 Method Detection Limit Study Data (98% Confidence Level)

Repeatability:

Tests were run at the ends of the water concentration range of interest (0.2% and 0.5%) to understand the repeatability performance.

The first repeatability study was conducted at a water concentration in AA of 0.2%. The sample was made by fortifying a CGA G-2.2 verified dry anhydrous ammonia sample with water. The water content was analyzed 7 times. The results can be found below in Table 4.

Method: Water in Anhydrous Ammonia		
Fortification Level of CGA G-2.2 Verified Dry Anhydrous Ammonia: 0.2% Water		
Rep.	Recovery (% water in AA)	Recovery as a % of known fortification amount (0.2%)
1	0.2084	104.2%
2	0.1753	87.6%
3	0.2324	116.2%



4	0.2125	106.2%
5	0.2697	134.8%
6	0.2365	118.2%
7	0.2464	123.2%
Average	0.2259	112.9%
St. Dev.	0.0304	

Table 42 Raw data from the repeatability study (water fortification level 0.2%).

A second repeatability study was conducted at a water concentration of 0.5% - the upper end of the range of interest. The sample was made by fortifying a CGA G-2.2 verified dry anhydrous ammonia sample with water. The water content was analyzed 7 times. The results can be found below in Table 5.

Method: Water in Anhydrous Ammonia		
Fortification Level of CGA G-2.2 Verified Dry Anhydrous Ammonia: 0.5% Water		
Rep.	Recovery (% water in AA)	Recovery as a % of known fortification amount (0.5%)
1	0.4574	91.5%
2	0.4923	98.4%
3	0.4475	89.5%
4	0.4843	96.8%
5	0.5191	103.8%
6	0.4744	94.9%
7	0.5401	108.0%
Average	0.4879	97.6%
St. Dev.	0.0329	

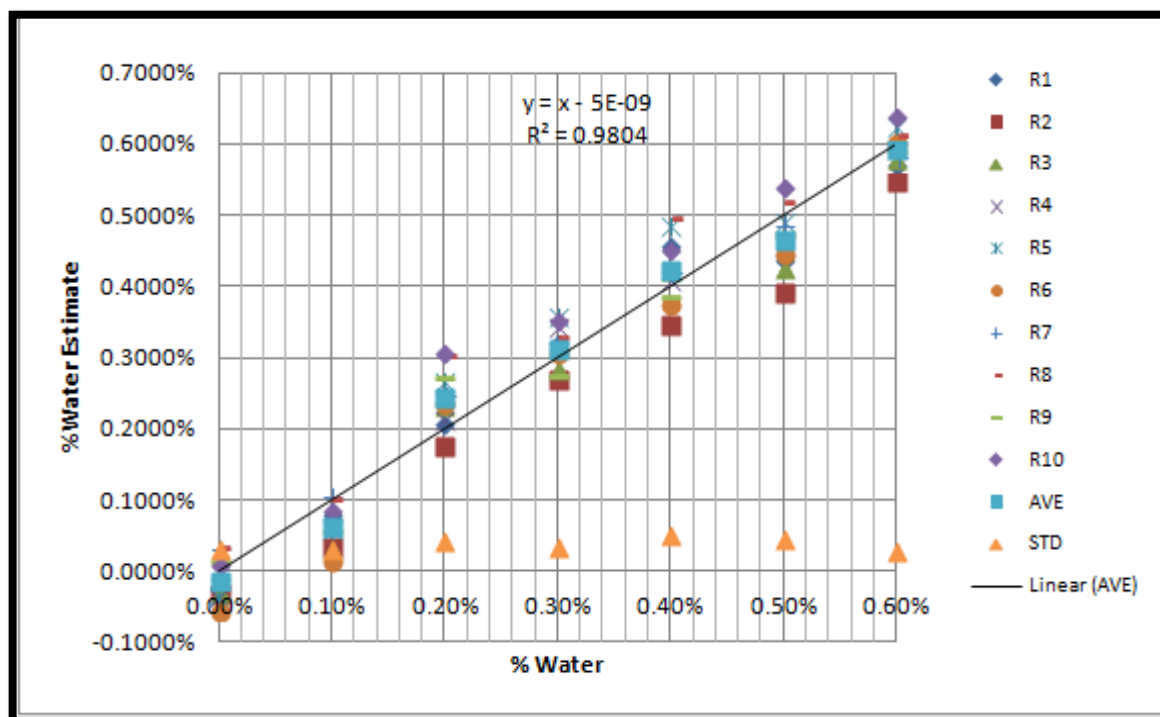
Table 5 Raw data from the repeatability study (water fortification level 0.5%).

Reproducibility and bias of this method will be determined as additional data is collected through interlaboratory studies.



Calibration Data:

Figure 14 shows the calibration data from testing water fortified CGA G-2.2 dry validated samples. It is a representation of all spike data performed to this date via the OSS Oil in Anhydrous Ammonia method. The data is linear with an R^2 value of 0.9804. As more data becomes available and more experience is gained from end-users, method improvement will be implemented as appropriate.



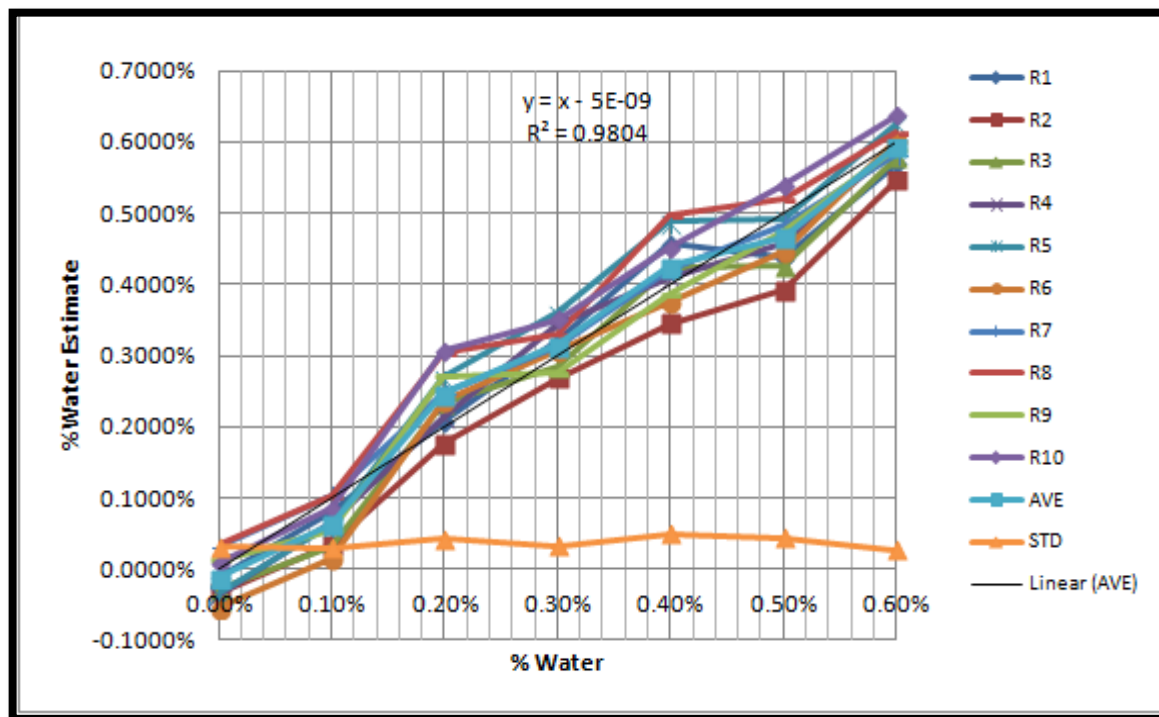


Figure 14 Method Calibration Data

17. Keywords

17.1 anhydrous ammonia, water, FTIR analysis, spectroscopy

Companies and locations that could use this new method are anhydrous ammonia producing locations across the US and Canada and also transfer terminals where ammonia is trans-loaded into different containers.