Anhydrous Ammonia Measurements

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Orono Spectral Solutions, Inc.
A Full Spectrum Innovator.

Measurement Options

Technology applications in a wide range of products

- **Anhydrous Ammonia – oil & std water level**
- **Urea – oil**
- **DEF – oil**
- **UAN – oil**
- Water – oil
- Air - oil

Orono Spectral Solutions

Leading edge solid state surface technology driven organization

- Spinoff of University of Maine (US) Laboratory for Surface Science and Technology
- Awarded 14 government projects ($8.6 M)
- 2013 Tibbets Award & 2016 CF Safety Award

Measuring oil in Ammonia

Request from a leading ammonia manufacturer led to application

- CF Industries looking for solutions to
  - Safely test oil contamination in ammonia
  - Quickly identify process control issues
  - Reduce corporate risk

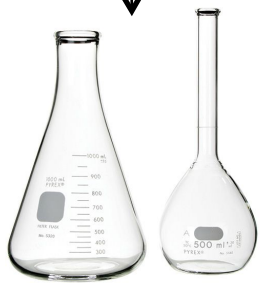
Materials Required to Measure

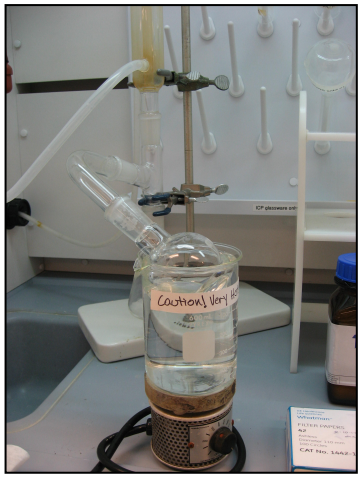
Glass ware, hot plate and dangerous chemicals

Oil Determination – Process

Current method is long, complex, dangerous and costly

Collect Large Sample → Evaporate Ammonia → Add Hexane





Evaporate Hexane

Mass corresponds to concentration of extractable material

Test Time: 8+ hours Tech Time: 3+ hours

Issues with the Current Process

Several factors with current method are driving development

- Large sample size
- Safety risk: carrying sample through the plant
- Solvent (n-Hexane) & acid use
- Complex process
- Time consuming
- One “shot”
- Costly

n-Hexane

Colorless, volatile liquid; sweet/gasoline odor. Irritating to eyes/skin/respiratory tract. Also causes: dizziness, fatigue, muscle weakness, hallucinations. Chronic: peripheral neuropathy (muscle weakness, motor loss, sensory disturbances). Flammable.

CAS No. 110-54-3

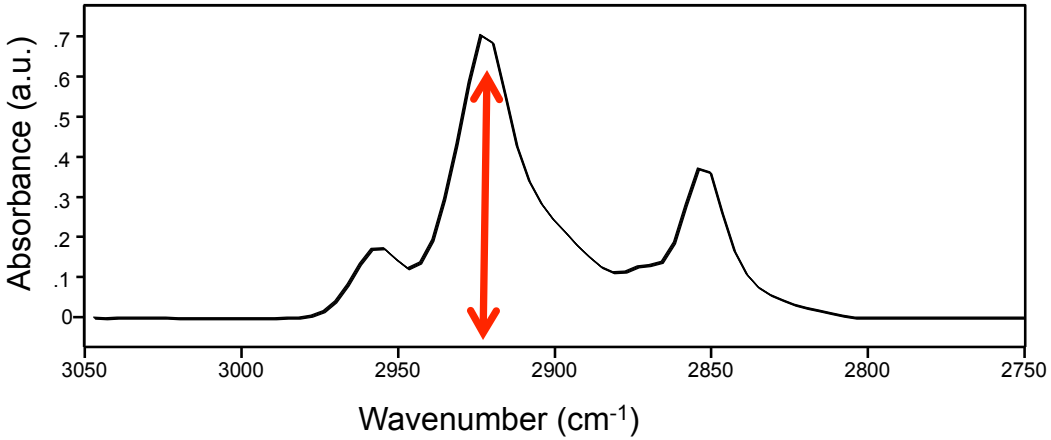
New Process Equipment

No glassware, no chemicals, simple process

New Process Summary

Simple, quick, accurate and less costly process addesses SHE

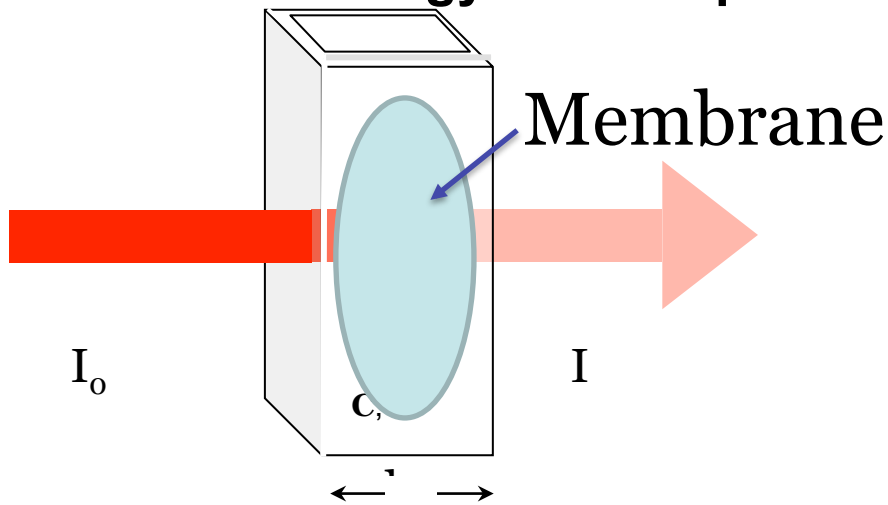
Collect Small Sample → Extract Sample → Place in FTIR



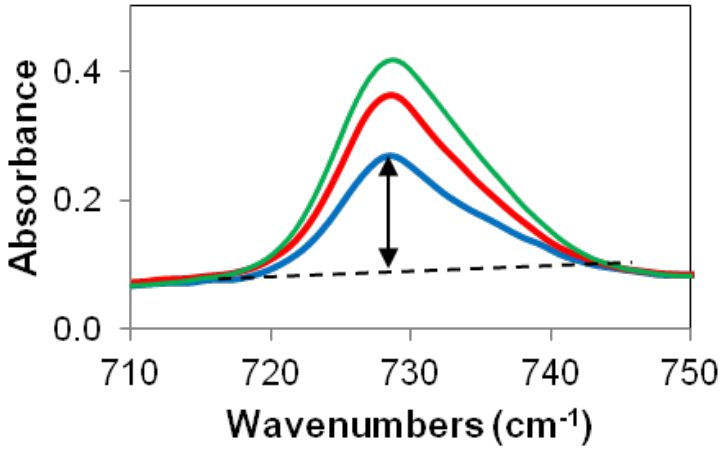
Time: < 20 minutes

FTIR Measurement

Infrared technology enables precise quantitative measurement



$$A = -\log_{10}\frac{I}{I_o} = \varepsilon\, l\, c$$



Where:

A = absorbance

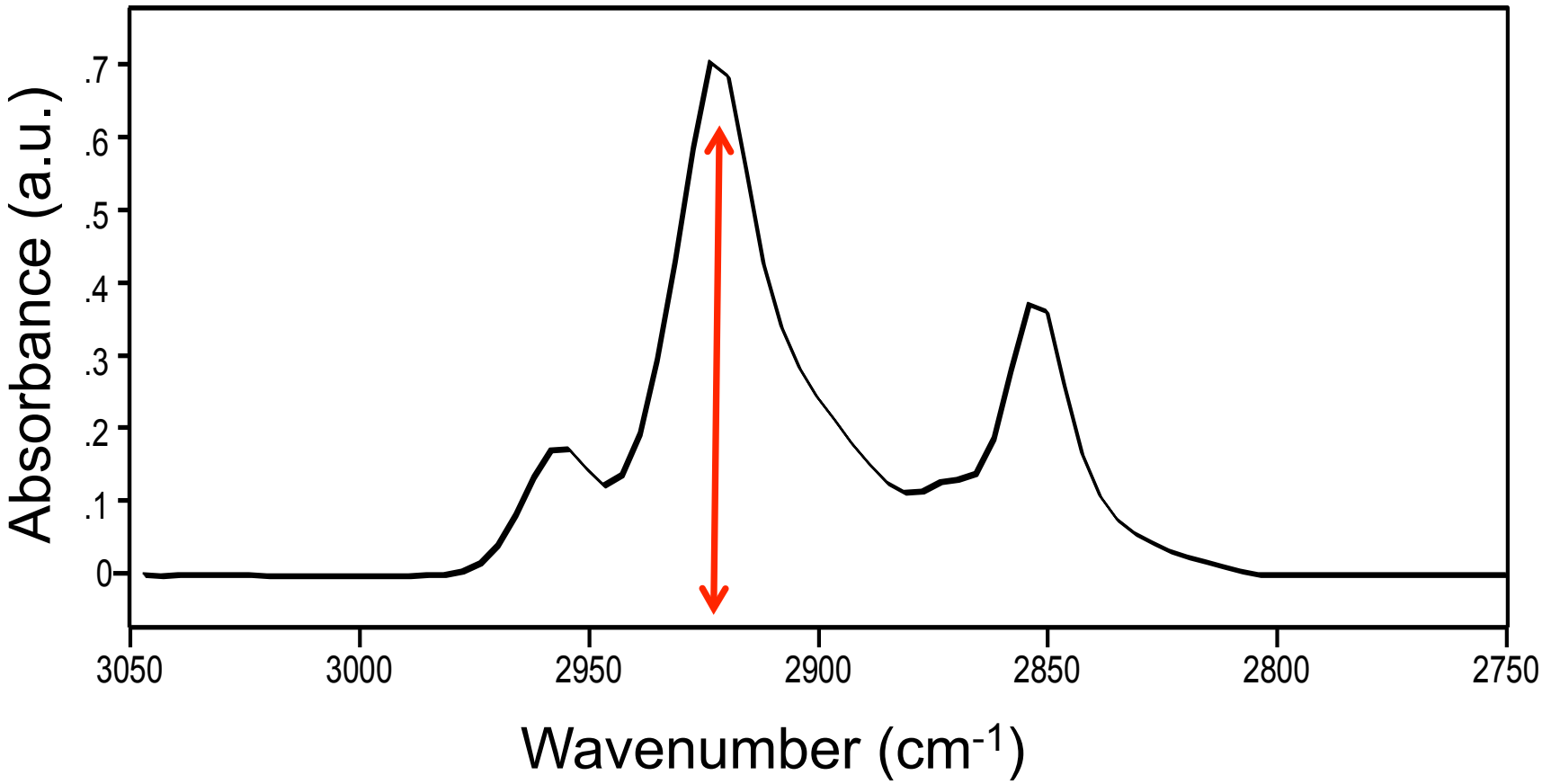
ε = absorptivity

l= pathlength

c = concentration

Oil in Ammonia Output

Oil absorbance at 2920 and height relates to concentration



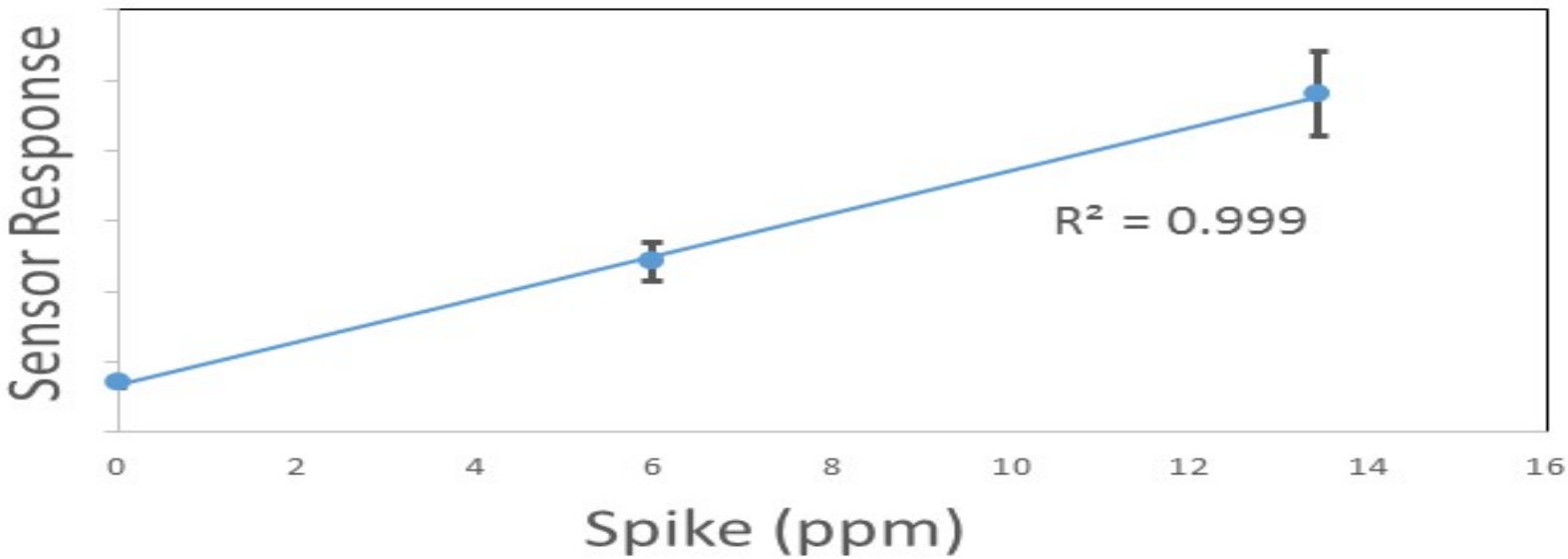
Summary of New Process

Simple, accurate, safe and creates a permanent record

- Sample 10 mls for each test - triplicate
- Place the extractor into the FTIR beam
- Program provides operator with a ppm oil level
- Permanent record of the results

Measurement of Known Amount

Spiking amount of mineral oil and measuring using technology



Method Performance Summary	Data
Method Detection Limit	0.2 mg/L (ppm)
Detection Range	0.2 – 20 mg/L (ppm)
Precision at 3.5 mg/L	12%

Benefits of the New Process

Proven overwhelming advantages of new technology

Old Method	New Method
Complicated	Simple
Fragile Glassware	No Glassware
500+ mL Ammonia (1 sample)	30 mL Ammonia (3 samples)
Boiling Water, Hot Plate	No Heat Source Required
Hexane, Hydrochloric Acid	No Additional Chemicals
1-Day Turnaround Time	20-Minute Turnaround Time
3 Hours for Lab Technician	20 Minutes for Lab Technician
Hazardous Waste	Recyclable, Reusable Filters
Chemistry	EPA Green Chemistry
Operating Cost	Operating Cost 25 – 30% less

Site Advantages

Financial impact of new technology is significant

- Reduce risk – safety, environmental
- Lower material on hold and rework potential
- Ability to ”dial in” water content
- Proven quality data and sample retention

Oil in DEF and Urea

Process is similar to oil in ammonia but with drying required

- Use similar syringe and same sample size
- 10 mls of sample into extractor (10 sec)
- 10 mls of deionized water into extractor (20 sec)
- Drying of extractor
  - Oven drying
  - Air drying (dry air)

Water in Ammonia

In US process is regulated by US Department of Transportation (DOT)

- For transportation by truck, rail or pipe
  - Minimum 0.2% water content (US Gov. requirement)
- Current process
  - Time consuming
  - Inaccurate
- Alternative process submitted to US DOT
  - Once approval granted, companies can follow process
- Commercial requirement 0.5% maximum

Water in Ammonia - Challenge

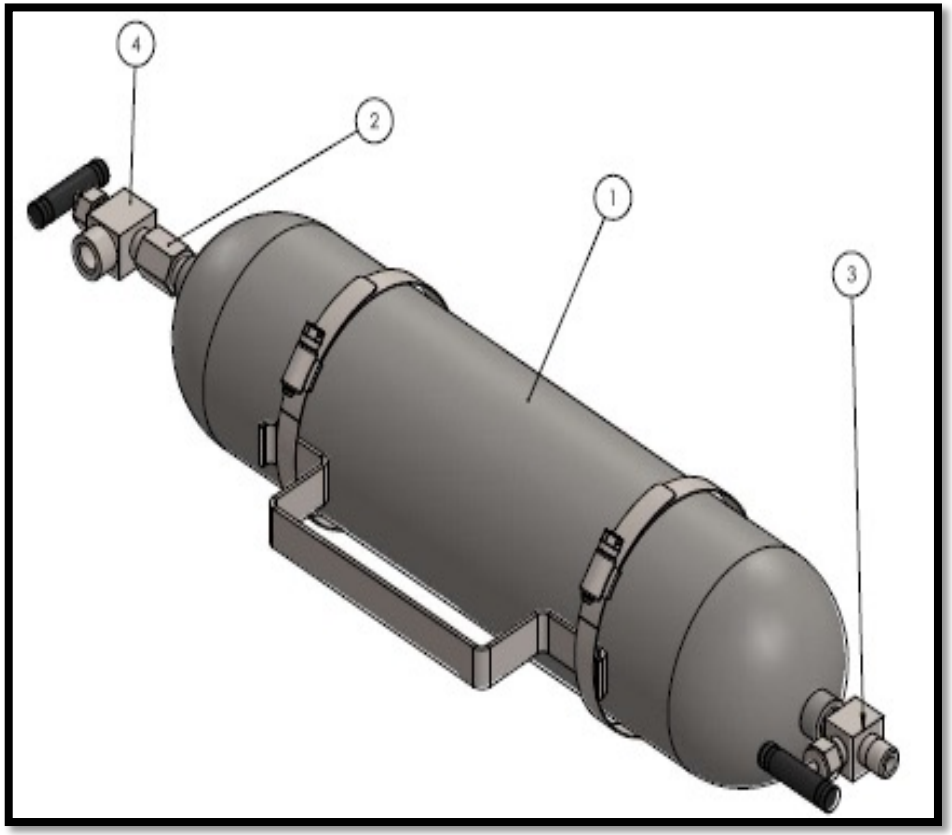
Protect sample from moisture in the air

- Small sample from manufacturing site
  - Representative sample
  - Protect sample from moisture
- Transfer to sampling container
  - Protect sample from moisture
- Present the sample to the FTIR unit
  - Protect sample from moisture

Sampling for water in Ammonia

In process sample bottle to protect ammonia from moisture

- Pristine sample
- Protect technician
- Protect sample



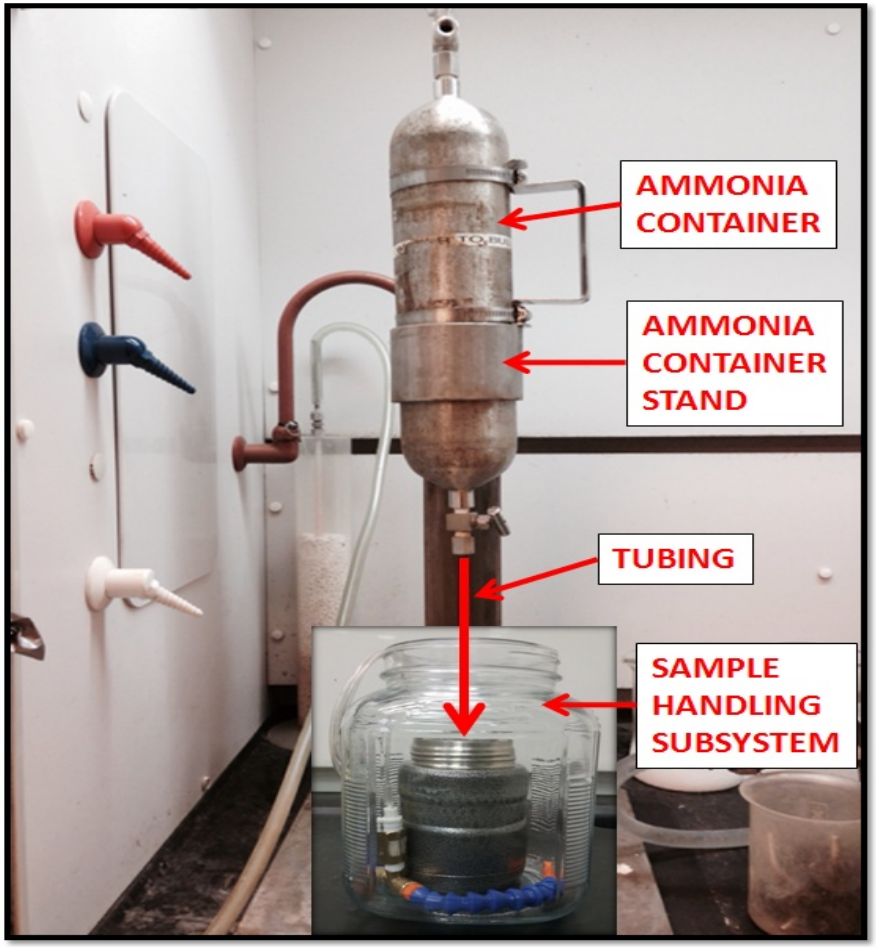
Sample Carrier and Stand

Sample bottle stand and holder inside air hood

View of Sample Prep System

Maximize operator safety and sample integrity

- In lab system
- Ensures safety
- Uniform sample

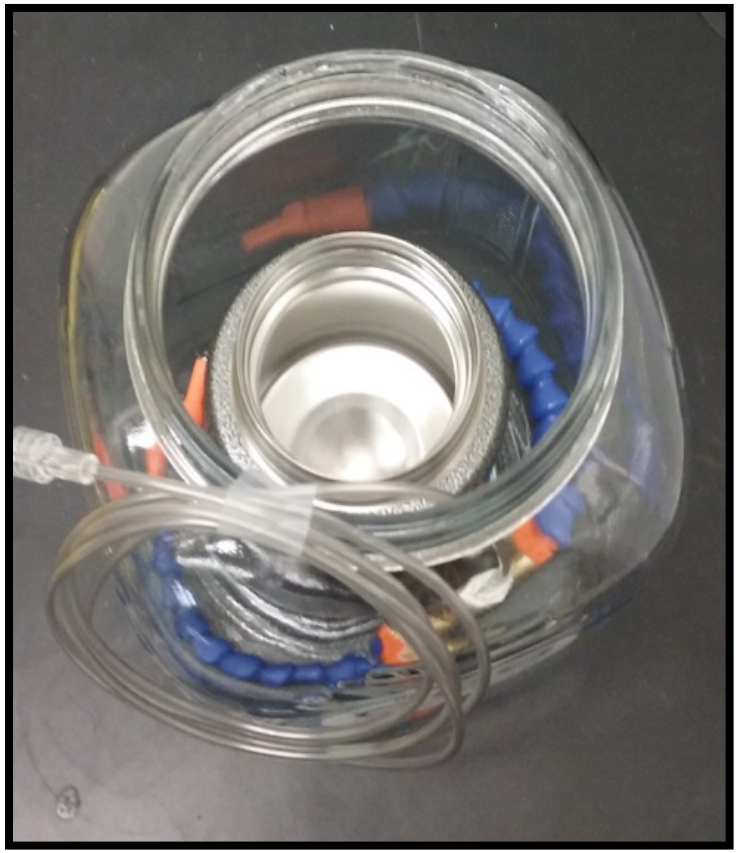


Dry Air System

Portable air curtain supply kit to ensure sample integrity

Sample container for extraction

Transfer jar under dry air curtain



Details of Dry Air System

Positive dry air flow maintains curtain around sample

- Ammonia container
- Dry Air Container
- Dry Air Delivery

Water in Ammonia extractor

Extractor, FTIR Card and Hoses to provide dry air

- Extractor
- FTIR Card
- Dry air lines

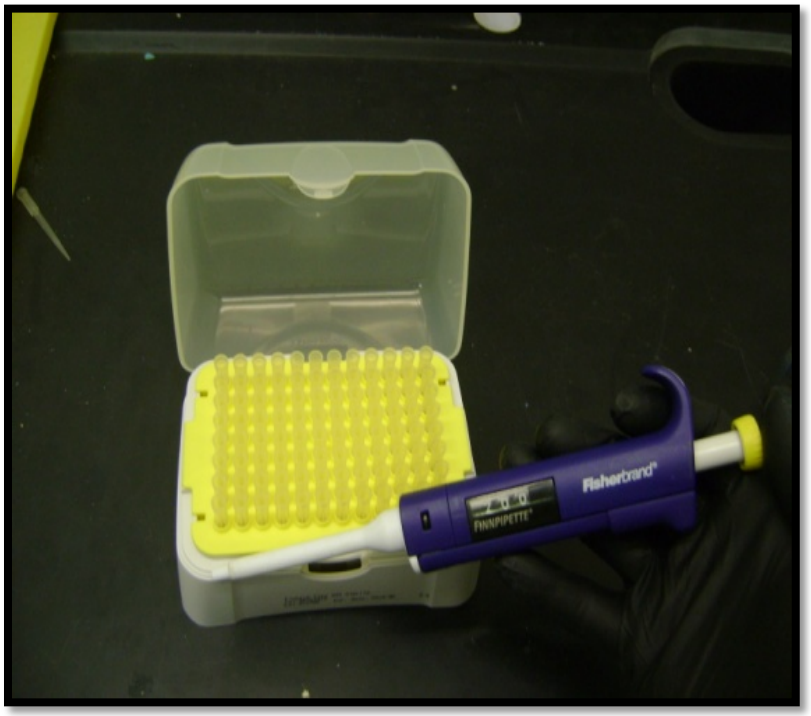
Water in Ammonia extractor

Extractor, FTIR Card and Hoses to provide dry air

Accurate delivery of Ammonia

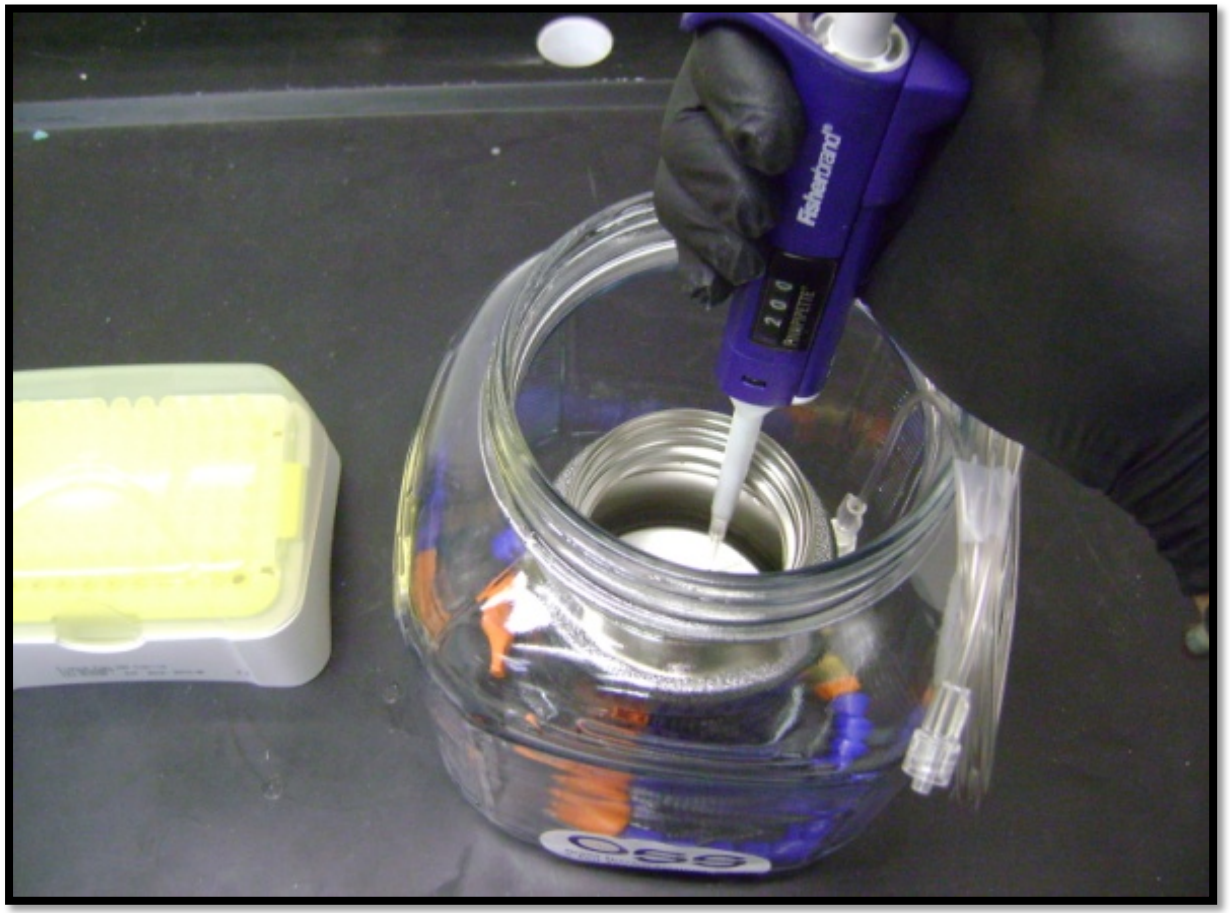
Small amount of sample required for test method

- Pipette
- Disposable tips



Sampling Ammonia

Using Pipette to sample exact amount for test

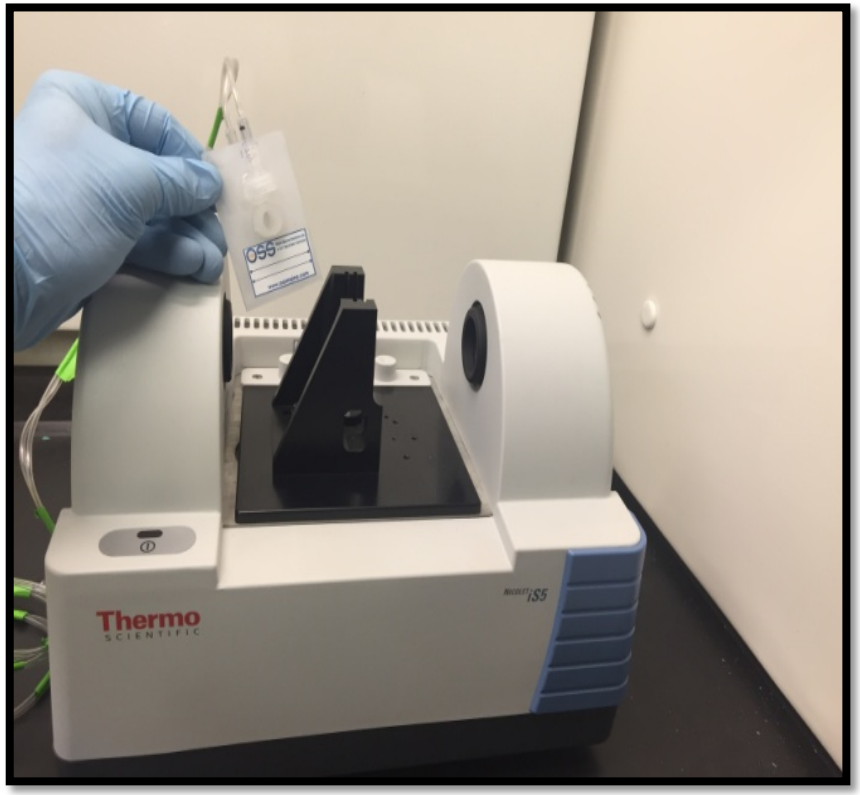


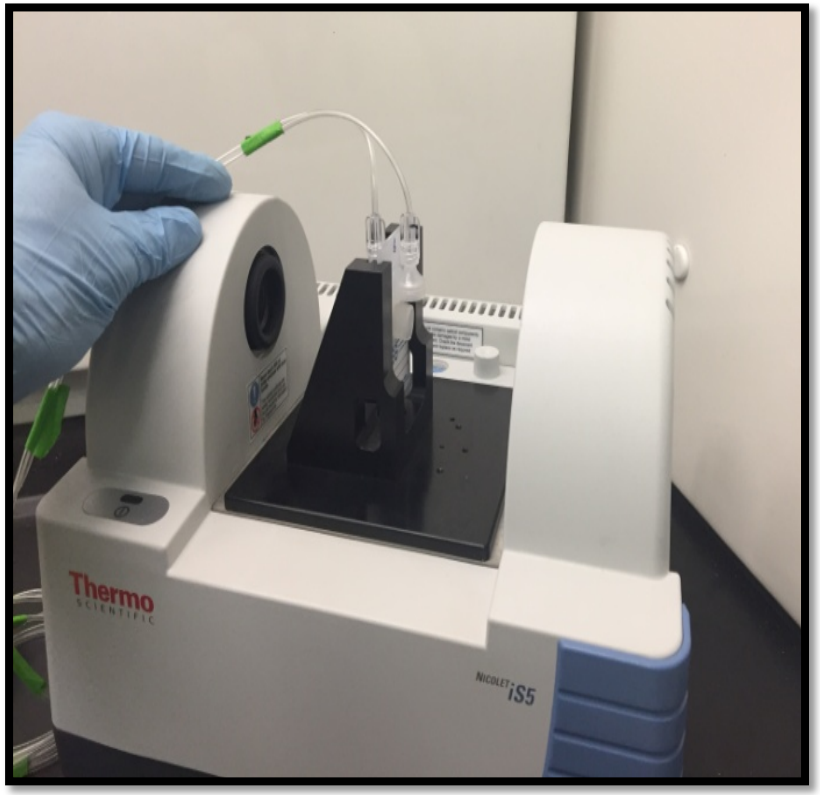
Ammonia sample on Extractor

Small sample will evaporate until extractor is dry

Inserting FTIR card into Unit

Place card into unit and run software





Test Method Detection Range

Measurement range is well within system capabilities

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

Customer Site Measurement

Accuracy of system demonstrated in test results

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

Accuracy of Method

Measurements at the low end of the test requirements

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	

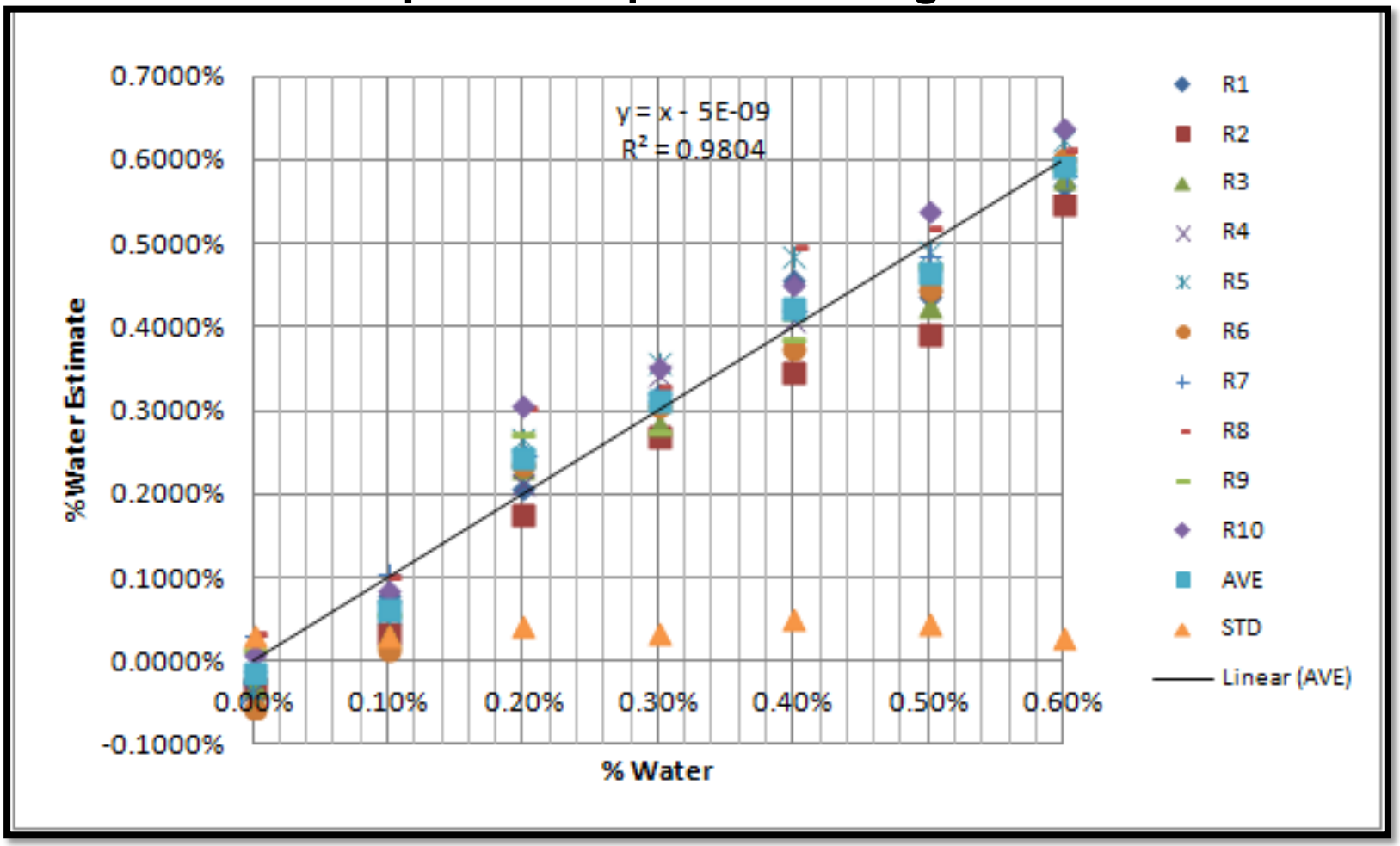
Accuracy of Method

Measurements at the high end of the test requirements

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	

Accuracy of Method

Water content of spiked samples over range 0 to 0.6%



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