

APPLICATION NOTE

TNTplus[®] Ammonia Method 10205

Reducing Errors and Headaches with an EPA Equivalent Method

By Ruth Hecker, Nick Marusin, and Derek Walker

Traditional methods come with challenges

The laboratory staff at the Wastewater Treatment Plant in Loveland, Colorado is dealing with a few less headaches these days. A recent change in methods used to analyze and report ammonia influent and effluent levels has brought welcome relief to the small staff. The staff led by Ruth Hecker, Water Quality Lab Coordinator, made the decision to switch from the traditional Ion Selective Electrode method (SM4500-NH₃D) to Hach Method 10205 using TNTplus vial chemistry. Ion Selective Electrodes (ISE) have been the standard for ammonia measurement and compliance reporting in many wastewater and environmental laboratories. The ISE ammonia method is USEPA approved and has a wide measuring range that makes it attractive to many labs. However, ISE technology has some significant disadvantages including calibration, poor low-level performance, and frequent maintenance and membrane replacement requirements.

The 10 MGD Loveland wastewater treatment plant and its efficient process successfully removes influent ammonia of 25-30 mg/L to very low effluent levels, below 0.1 mg/L. At these low levels, the EPA approved SM4500-NH₃D ISE method can be a challenge to run in a timely manner. On a regular basis, the analysts were frustrated with the following issues:

- Daily preparation of calibration standards, including a low-level standard of 0.05 mg/L taking over 30 minutes of prep time per calibration
- Frequent unexplained issues with failed calibrations or electrode membranes, occurring “out of the blue” after several months of routine analysis
- Hours of wasted of time spent troubleshooting and subsequent concerns with sample holding times
- Frequent and costly electrode membrane replacements

Investigating and validating a new method

After learning about Hach Method 10205 which uses the TNTplus[®] chemistry for ammonia measurement, the lab was interested in investigating the procedure as an alternative to the ISE method. The TNTplus[®] ammonia method is classified as an EPA Equivalent method as it uses a slightly modified version of the previously approved indophenol/phenate chemistry. The method can be run in under 20 minutes of time, as all required reagents are included in the test vial. In the Hach method, ammonium ions react at pH 12.6 with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside as a catalyst to form indophenol. The amount of color formed by the reaction is directly proportional to ammonia concentration in the sample. Results are read at 690 nm. The TNTplus[®] vial with barcode communicates with compatible Hach DR2800, DR3900, DR5000, and DR6000 spectrophotometers and displays the concentration of ammonia in the sample at the



conclusion of the test.

Many states across the USA have approved the use of the method without further validation studies. In some states, a simple validation study may be required before using the modified method for compliance reporting purposes. This process is clearly outlined by the EPA and Federal Register in 40CFR Part 136.6, Method Modifications and Analytical Requirements. Because facilities in Colorado had not yet used the new method for compliance reporting, Nick Marusin, an analyst in Loveland’s water quality lab took on the task of the validation study for the Hach TNTplus® method. The study included standard QC samples and procedures typically followed in a laboratory Initial Demonstration of Capability. Method comparison studies ran included the Method Detection Limit, Initial Precision and Recovery, Matrix Spike, and Matrix Spike Duplicate.

According to Nick, “the study was easy to conduct and was a painless process. We ran about 10 effluent samples and the study report that we sent to the state authority only took about 4 hours to compile.” The results of the side by side method validation are below:

Determination of the Method Detection limit (MDL) and Quantitation Limit (QL)

The MDL was determined in this study for Method 10205 (TNT830) to find the Quantitation Limit of the method.

0.03 mg/L NH ₃ -N Spike (7 Replicates)			
Average	0.022 mg/L	MDL	0.002 mg/L
SD	0.001 mg/L	QL	0.01 mg/L

Determination of Initial Precision and Recovery

The Initial Precision and Recovery study consisted of the analysis of four replicates of a 1.0 mg/L NH₃-N solution with both the TNTplus® and the electrode methods.

TNTplus® Method 10205 (TNT830)			Ammonia Ion Selective Electrode (SM 4500-NH ₃ D)		
1.0 mg/L Spike	Result	% Recovery	1.0 mg/L Spike	Result	% Recovery
Replicate 1	0.984	98.4	Replicate 1	0.6217	62.17
Replicate 2	0.986	98.6	Replicate 2	0.6713	67.13
Replicate 3	0.982	98.2	Replicate 3	0.7035	70.35
Replicate 4	0.988	98.8	Replicate 4	0.7287	72.87
Avg. % Recovery		98.5%	Average % Recovery		68.1%
Precision (SD)		0.26 mg/L	Precision (SD)		4.62 mg/L

Sample Matrix Spikes and Matrix Spike Duplicate Analysis

Matrix spikes consist of the analysis of a wastewater matrix (WWTP effluent) and a duplicate analysis of the spiked matrix with both the TNTplus® and the electrode methods.

TNTplus® Method 10205 (TNT830)							
5.0 mg/L NH ₃ -N Spike							
Matrix	Result	Spike	Spike Dup	Spike % Rec	Spike Dup % Rec	Average % Rec	Precision (SD)
WWTP Effluent	0.028	4.84	4.94 mg/L	96	98	97	1.41 mg/L
Ammonia Ion Selective Electrode (SM 4500-NH ₃ D)							
5.0 mg/L NH ₃ -N Spike							
Matrix	Result	Spike	Spike Dup	Spike % Rec	Spike Dup % Rec	Average % Rec	Precision (SD)
WWTP Effluent	0.0405	3.368	3.76 mg/L	67	74	70	5.56 mg/L

Improved ammonia recoveries and consistency of results

As the side-by-side validation study shows, the TNTplus® method performed significantly better than the ISE method. Most notably, recoveries of standard additions or “spikes” in both reagent water and effluent matrix were significantly better with the Hach method. Additionally, method precision and consistency of results were also much improved over the ISE method. Accuracy and precision are improved due to several unique quality control features built-in to the TNTplus® vial chemistry and Hach spectrophotometers:

- Barcode recognition of the test vial ensuring the correct method settings are always used
- Automatic updating of built-in calibration factors
- Automatic 10-fold measurement which eliminates errors due to dirty or cracked glass vials
- Precise, consistent, and convenient delivery of reagents that are sealed in vial cap and tube

After reviewing the results of the validation study, the water quality laboratory staff made the decision to petition the state regulatory authority and gain approval to use Method 10205 for compliance reporting. After submitting the request and results of the validation study, approval was quickly granted. The facility now uses the new method for both daily process control and discharge monitoring reporting. In addition to the improved results and consistency of the method, analyst Nick Marusin states, “we have saved a significant amount of time in our daily samples and QC checks. We can now run a day’s worth of ammonia samples in about 30 minutes, where before it took over an hour and a half, even without electrode calibration problems. Overall, the new TNTplus® method is awesome and has solved a number of headaches for us.”

To learn more about Hach Method 10205 (TNTplus®) for ammonia measurement and the status of local regulatory acceptance, please contact your local Hach Sales Manager or visit www.hach.com.

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:

Tel: 800-227-4224 | E-Mail: techhelp@hach.com

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