Lab **Matters**

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Understanding Ammonia (NH_3)

Introduction – Ammonia (NH_3) is one of the many forms nitrogen takes as it makes its way through the environment. In high enough concentrations, it is toxic to fish and everyone is aware of the unpleasant odor it spreads. In nature ammonia occurs from the decomposition of organic compounds that contained nitrogen (almost all of them) or the hydrolysis of urea (the compound that gives urine its name). Generally speaking, natural sources of ammonia are dispersed far and wide enough that we would never notice it. However, if enough of those natural sources of ammonia are concentrated into one stream (a sewer) it can become a problem in the water source.

Approved Methods – For NPDES/CWA reporting there are several methods available for ammonia analysis. Most of the time a preliminary distillation is necessary – EPA 350.1, SM4500-NH_3 B, or AOAC 973.49 all contain this step. There are some requirements to document when you choose not to distill. Consult your local regulations to see if you qualify. The analysis of ammonia is accomplished through the following methods:

- Nesslerization – SM4500-NH_3 C 18th edition, ASTM 1246-98, and AOAC 973.49 (losing popularity and favor-due to is use of mercury);
- Titration – SM4500-NH_3 C 19th and later editions;
- Ion selective electrode – SM4500-NH_3 D and ASTM D1426-98;
- Phenate – EPA 350.1, SM4500-NH_3 G, and USGS I-4523-85.

Of all these options, preliminary distillation followed by ISE or phenate method tends to be the most commonly used method.

Method Summary – The distillation consists of heating an alkaline buffered solution and condensing the vapors into a mildly acidic trapping solution. The ISE analysis utilizes a standard ammonia ISE to detect ammonia in solution. The phenate method reacts alkaline phenol and hypochlorite with ammonia. This forms indophenol blue with an intensity proportional to the amount of ammonia present. The color intensity is measured photometrically to determine the final concentration.

What You Should Know – To distill or not to distill is always the biggest question with this method. The current (as of this writing) table in 40 CFR part 136.3 has the following note about distillation: *"Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however manual distillation will be required to resolve any controversies."* There are two things to note about this –

- Only effluent samples are mentioned as being potentially exempt and
- If there are any controversies you will have to distill anyway to resolve them

Additionally, if you are using ISE, you will have to prepare your standards in a matrix to match the level of dissolved ions in your samples. If you are using the phenate method you will need to correct for turbidity and/or color as well as pH match your standards to your samples.

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The best way to ensure consistency is to simply distill your samples. Your choice of analytical methods will determine your trapping solution. You would use boric acid if you are titrating and H_2SO_4 if you are using the phenate method or ISE. Distillation works because of the properties of ammonia. When samples are collected for ammonia analysis they are typically acidified to a pH of less than 2.0. The acid conditions and subsequent cooling not only minimizes microbial activity but also converts all NH_3 (a gas) in solution to NH_4^+ (an ion). Generally speaking, NH_4^+ will not leave the solution under ordinary conditions, giving us the 28 day holding time. Buffering the solution at alkaline conditions forces the NH_4^+ to convert back to NH_3. This is a volatile gas that can be removed from solution through simple heating. It is important to ensure an alkaline pH when distilling. Theoretically, anything basic will suffice. However, at the increased temperature of distillation, cyanates or organic compounds containing nitrogen can hydrolyze to form ammonia where none previously existed. A pH of 9.5 minimizes these rates of formation, thus the specific pH buffer requirement.

Traditional distillations have required distilling long enough to collect water along with the ammonia to bring your trapping solution up to volume. This also ensured sufficient time to maximize the recovery of ammonia. Recent advances in distillation technology use hydrophobic frits in the assembly. This not only eliminates potential boil-over but also reduces the volume of non-analyte that can distill over. The simple fix is to distill long enough for complete removal and then add the needed distilled water yourself to bring up to final volume. Additionally, the SimpleDist system from Environmental Express has the added benefit of eliminating the need for cooling water.

One of the nice things about distillation is that because it is a separation technique, spiking and reagent additions do not affect the concentration calculations. You are moving the actual analyte of interest from one place to another and leaving the rest of the original solution behind. Accurate measurement of the actual sample aliquot and an accurate final volume of distillate are all that are required to measure properly. This means that if you overshoot your pH in either direction a few times, the only thing it affects is your time spent and possibly gives you a larger volume in your distillation tube.

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Method Procedure

Note – This is not intended to be a standalone method and does not address all safety or quality control aspects that may be required. Please consult your local regulations to comply with all requirements.

1. Collect your sample in a HDPE 500 mL or 250 mL container and preserve with the appropriate volume of sulfuric acid.
2. Aliquot a 25 mL portion (or if the sample is known to contain ammonia in excess of the test range, an acceptable amount diluted to 25 mL) into a beaker and adjust the pH to 9.5 with H_2SO_4 or NaOH of the appropriate strength. Add borate buffer.
3. Set up the SimpleDist system with enough sample tubes. (A midi-distillation system, Microblock, is also available) Pour samples into the sample tubes and connect caps and vacuum tubes according to instructions.
4. Turn on the vacuum and adjust bubbling rates to the proper flow.
5. Distill according to instructions for the system of use. SimpleDist Instructions or Microblock Instructions.
6. Collect the distillate and store in a properly labeled sample collection container.
7. Analyze according to your preferred method:
    a. Ion Selective Electrode
    b. Phenate – Reagents (note: if your analyzer uses heat to speed up the reaction rate you may see a brown precipitate form after the hypochlorite is added. This can be eliminated by adjusting the pH of that reagent to 10.0-10.5 SU with 1:1 HCl)
        i. Automated through your favorite discrete analyzer, flow-injection, or segmented flow analyzer. Contact your Sales Rep for autosampler supplies.
        ii. Manual on a spectrophotometer.

Don't forget your calibration standard.

We all like things that make life easier. Was this document helpful? Or do you…disagree with something?

Have something to add? Contact me at DavidS@envexp.com to let me know what you think.