



Analysis of TKN and Ammonia in NPDES Wastewater Samples by In-line Gas Diffusion

Introduction

Total Kjeldahl Nitrogen (TKN) is the U.S. EPA approved parameter used to measure organic nitrogen and ammonia. The TKN content of influent municipal wastewater is typically between 35 and 60 mg/L. Organic nitrogen compounds in wastewater undergo microbial conversion to NH_3 and ammonium ion NH_4^+ . Ammonium ion is the first inorganic nitrogen species produced during biological wastewater treatment.⁽¹⁾ Nitrification is a two-step biological process used to remove ammonium in wastewater. The bacterium *Nitrosomonas* converts ammonium to nitrite (NO_2^-). The bacterium *Nitrobacter* converts nitrite to nitrate (NO_3^-).

A denitrification process is used to reduce the nitrate generated in the preceding steps to nitrogen gas. The NPDES effluent limit for ammonium-nitrogen ($\text{NH}_4^+ - \text{N}$) can range from 0.1 to 1.0 mg/L and the limit for nitrate-nitrogen ($\text{NO}_3^- - \text{N}$) from 3-10 mg/L.

Regulatory Status of Gas Diffusion Methods for TKN and Ammonia Analysis

On April 17th, 2012, the U.S. EPA Administrator signed a Methods Update Rule (MUR) approving new analytical methods for testing of pollutants in wastewater under the Clean Water Act.⁽²⁾ The U.S. EPA published the final rule in the Federal Register of May 18, 2012.⁽³⁾

Part 136.3 Table 1b Parameter 4 Ammonia states; “Manual distillation or gas diffusion at pH >11 followed by” any of the approved methods for the analysis of ammonia. This means that gas diffusion is an approved alternative to manual distillation of ammonia samples.

Part 136.3 Table 1b Parameter 31 Kjeldahl Nitrogen - Total states; “Manual distillation and distillation or diffusion followed by” any of the approved methods for the analysis of TKN. This means that gas diffusion is an approved alternative to manual distillation of TKN samples.

Section 136.6 of the MUR covers Method Modifications and Analytical Requirements. Subsection 136.6(b) Method Modifications states; “If the underlying chemistry and determinative technique in a modified method are

essentially the same as an approved Part 136 Method, then the modified method is an equivalent and acceptable alternative to the approved method provided the requirements of this section are met. However, those who develop or use a modification to an approved (Part 136) method must document that the performance of the modified method, in the matrix to which the modified method will be applied, is equivalent to the performance of the approved method.”

Gas diffusion is specifically cited among allowed method modifications in Section 136.6 (xx) which states; “The use of gas diffusion (using pH change to convert the analyte to gaseous form and/or heat to separate an analyte contained in steam from the sample matrix) across a hydrophobic semi-permeable membrane to separate the analyte of interest from the sample matrix may be used in place of manual or automated distillation in methods for analysis such as ammonia, total cyanide, total Kjeldahl nitrogen, and total phenols. These procedures do not replace the digestion procedures specified in the approved methods and must be used in conjunction with those procedures.”

Principle of Operation

TKN Analysis

Wastewater samples are digested prior to analysis using sulfuric acid, potassium sulfate, and a copper catalyst at 380 °C. Free ammonia and organic nitrogen compounds convert to ammonium under these digestion conditions. Digested samples are transferred to the autosampler of an FS 3100 Automated Chemistry Analyzer. Samples are injected and mixed with a complexing reagent that raises the pH to >11, which generates ammonia gas. The ammonia passes through a gas diffusion membrane and is absorbed by an alkaline hypochlorite solution forming chloramine. The chloramine is mixed and reacted with salicylate to form an indophenol dye in an amount proportional to the ammonia concentration. The absorbance of the indophenol reaction product is measured at 660 nm. A flow diagram for in-line gas diffusion analysis of TKN and ammonia on the FS 3100 Automated Chemistry Analyzer is shown in Figure 1.

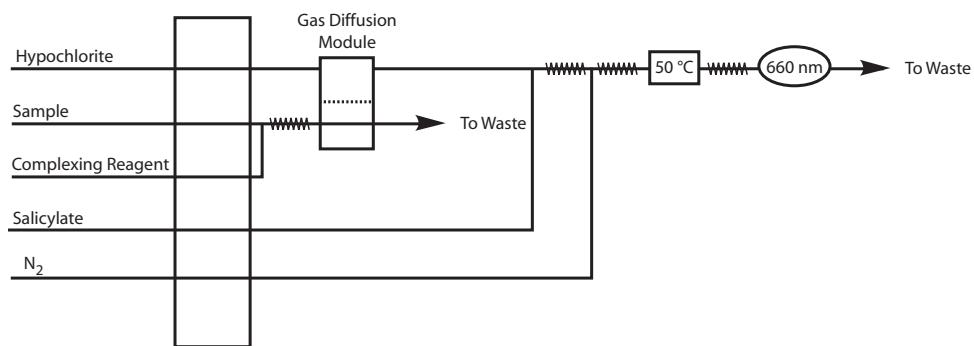


Figure 1. Flow Diagram for In-line Gas Diffusion Analysis of TKN and Ammonia

Summary of EPA 351.2 Method Modifications

A summary of USEPA-approved method modifications made to perform EPA 351.2⁽⁴⁾ TKN analysis by in-line gas diffusion is presented in Table 1. Notes in the “EPA 351.2” column refer to conditions in the original method. Notes in the “OI (327152)” column refer to the chemistry cartridge (PN 327152) and modifications made to the original method. OI Analytical’s methodology^(5,6) for in-line gas diffusion analysis of TKN and ammonia contains

the supporting documentation required for a method modification cited in Section 136.6 of the Method Update Rule.

Table 1: Summary of EPA 351.2 Method Modifications

TKN	EPA 351.2	OI (327152)	Comments
Scope	Transfer sample digests to flow analyzer for injection	Automated gas diffusion at pH>11	40 CFR Part 136.3 Table 1B 1 - Diffusion minimizes interferences from copper catalyst 2 - Eliminates need to matrix match carrier 3 - Is more selective 4 - Lowers detection limit
Method Summary	Chloramine reacts with salicylate to form an indophenol dye	Chloramine reacts with salicylate to form an indophenol dye	40 CFR Part 136.3 Table 1B
Calibration Range	0.01 - 2.0	0.01 - 20	40 CFR Part 136.6 Modification to calibration range
Interferences	Potassium Antimony Tartrate complexing reagent Hg catalyst	Sodium Citrate complexing reagent Copper catalyst	40 CFR Part 136.6 Interchange of buffers and complexing reagents 1 - Tartrate solutions commonly contaminated 2 - Lowers contamination 3 - Lowers detection limit 40 CFR Part 136.3 Table 1B 1 - Green chemistry

Ammonia Analysis

Wastewater samples for ammonia nitrogen analysis are placed in the autosampler of an FS 3100 Automated Chemistry Analyzer, injected and mixed with a complexing reagent that raises the pH to >11, which generates ammonia gas. The ammonia passes through a gas diffusion membrane and is absorbed by an alkaline hypochlorite solution forming chloramine. The chloramine is mixed and reacted with salicylate to form an indophenol dye in an amount proportional to the ammonia concentration. The absorbance of the indophenol reaction produced is measured at 660 nm.

Summary of EPA 350.1 Method Modifications

A summary of USEPA-approved method modifications made to perform EPA 350.1⁽⁷⁾ Ammonia analysis by in-line gas diffusion is presented in Table 2. Notes in the “EPA 350.1” column refer to conditions in the original

method. Notes in the “OI (327152)” column refer to the chemistry cartridge (PN 327152) and modifications made to the original method.

Table 2: Summary of EPA 350.1 Method Modifications

Ammonia	EPA 350.1	OI (327152)	Comments
Scope	Requires manual distillation	Automated gas diffusion pH>11	40 CFR Part 136.3 Table 1B
Method Summary	Chloramine reacts with phenolate to form an indophenol dye	Chloramine reacts with salicylate to form an indophenol dye	40 CFR Part 136.3 Table 1B
Interferences	EDTA complexing reagent	Sodium Citrate complexing reagent	40 CFR Part 136.6 Substitution of complexing reagents and buffers
Calibration Range	0.01 - 2.0	0.01 - 20	40 CFR Part 136.6 1 - Change in calibration 2 - Range to suit sample concentration

Advantages of Gas Diffusion TKN/Ammonia Methods for Lab Operation

Laboratories gain a number of operational benefits by employing in-line gas diffusion for TKN/Ammonia analysis beyond a reduction in matrix interferences and improved analytical performance.

Using an OI Analytical FS 3100 Automated Chemistry Analyzer equipped with chemistry cartridge (PN 327152) to perform in-line gas diffusion TKN/Ammonia analysis provides laboratories the following operational advantages.

- Higher sample throughput
- Lower labor costs
- Lower cost per analysis for reagents and consumables
- Eliminates analyst exposure to hazardous reagents (boiling concentrated base reagents (TKN) or boiling Borate buffer solutions (ammonia))
- Ability to analyze both ammonia and TKN using a single chemistry cartridge with the same reagents.*

* OI recommends using separate calibrations that match the sample matrix.

Labor Costs

Figure 2 illustrates the estimated annual labor costs required for manual distillation and analysis of 40 samples per month versus in-line gas diffusion and analysis. The labor involved in performing distillations includes estimated time spent on glassware setup, disassembly and washing. Labor also includes hands-on labor associated with pipetting samples and reagents.

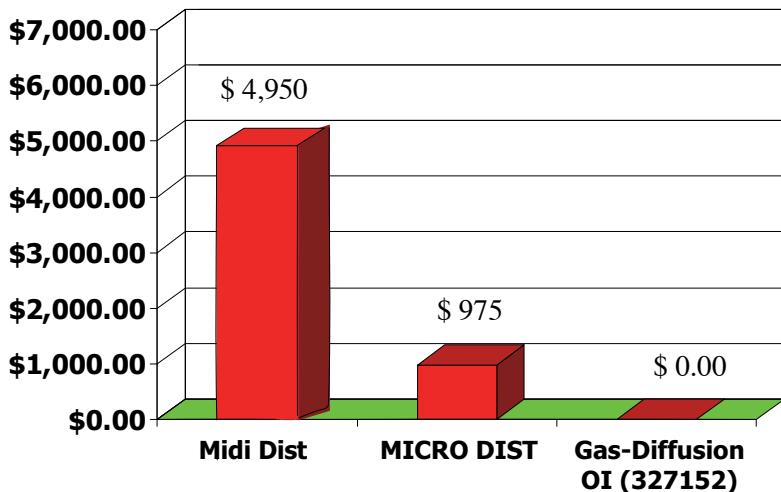


Figure 2. Estimated annual labor cost for distilling and analyzing 40 samples per month versus in-line gas diffusion

Summary and Conclusions

The Method Update Rule (MUR) signed and approved by the U.S. EPA Administrator on April 17, 2012 and published in the Federal Register on May 18, 2012 specified manual distillation or gas diffusion for all ammonia methods, and some TKN methods. Gas diffusion is now an approved alternative to, and eliminates the need for, distillation. This allows facilities with NPDES permits to use gas diffusion to test wastewater samples for TKN/Ammonia and Clean Water Act compliance reporting.

References

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5. OI Analytical Method Abstract, Publication # 3577, In-line Gas Diffusion TKN/Ammonia, USEPA by SFA/FIA, 2012.
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7. Nitrogen, Ammonia. *Methods for the Determination of Inorganic Substances in Environmental Samples*; EPA-600/R-93/100; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1993; Method 350.1.



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