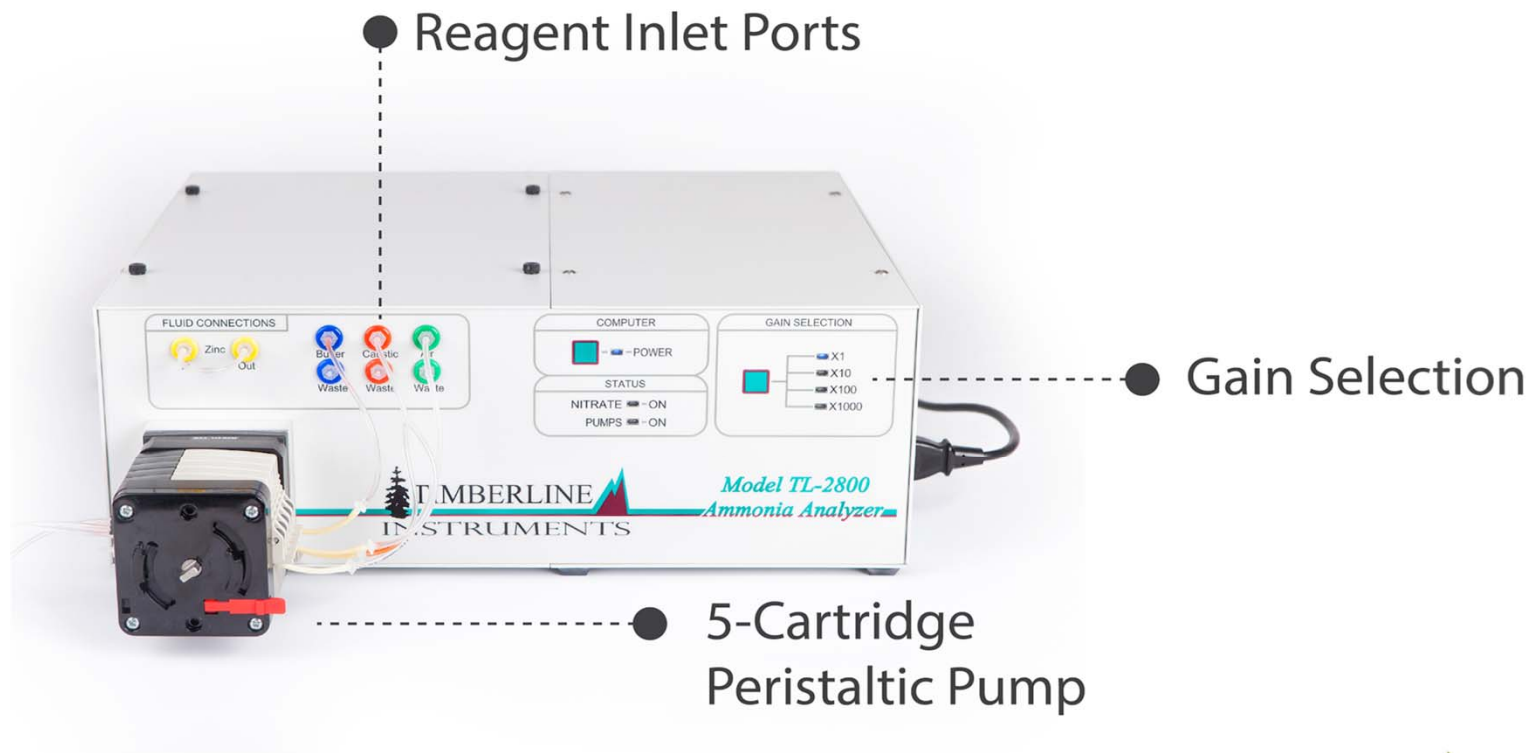# Automated Analysis of
Ammonia Using Membrane Diffusion Conductivity Detection:

How the Membrane Facilitates Automation

John Stillian, *Director of Applications & Product Development* at **Timberline Instruments**

TIMBERLINE INSTRUMENTS

Timberline Ammonia/Nitrate Analyzer

Automated Separation and Conductimetric Determination of Ammonia and Dissolved Carbon Dioxide

Robert M. Carlson

Department of Pomology, University of California, Davis, California 95616

A continuous flow instrument for automated determination of ammonia aor dissolved carbon dioxide has been developed. The sample solution stream is mixed with sodium hydrocxide for ammonia determination of perchloric acid for carbon dioxide determination. The ammonia or carbon dioxide diffuses from the sample stream through sillicone rubber hollow fibers into a stream of deionized water. As the water stream emerges from the hollow fibers, it passes through an electrical conductivity cell. The conductivity response is related to ammonium or carbon dioxide in the sample. The average relative standard deviation for total nitrogen in 39 leaf samples digested by the Kjeldahl procedure was 0.66%. Agreement between the new method and distillation-titration of Kjeldahl digests was very good. Recover of nitrogen for the Bureau of Standards orchard leaf reference sample was within one standard deviation of the certified value.

Various procedures for the determination of ammonia by electrical conductivity measurements have been reported. Hendricks et al. (1) described a vacuum distillation procedure in which the ammonia was collected in boric
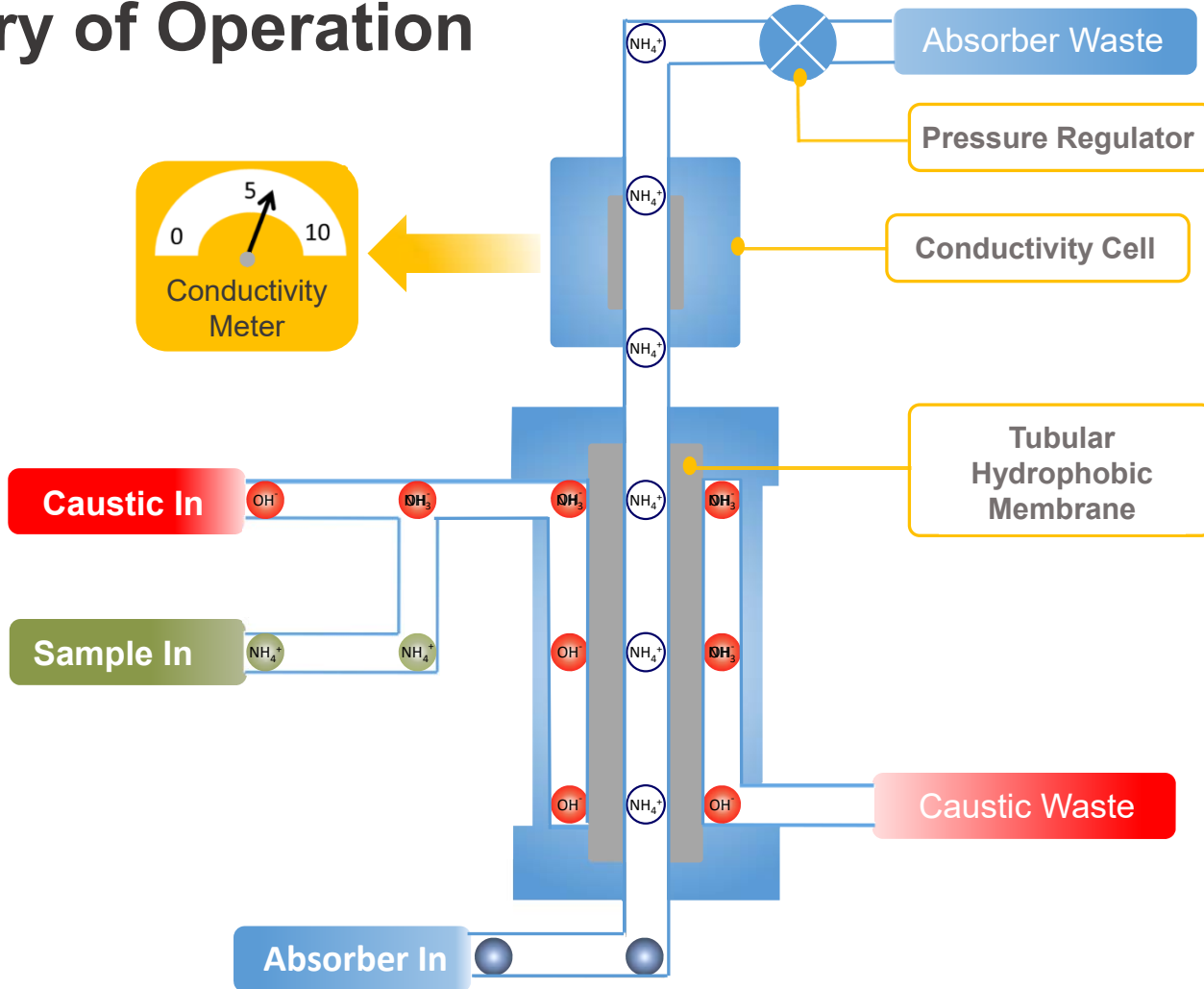
with short sections of silicone rubber tubing k(1/16-in. i.d.,3/16-in.o.d.). Twelve strands of Dow Corning silicone rubber hollow fibers (obtained from Bio-Rad Laboratories, Richmond, Calif.) were placed in the tube and potted into one branch of the Y connector on each end with Dow Corning silicone rubber sealer.

The electrical conductivity cell is shown schematically in Figure 2. The welll formed with the various sizes of vinyl tubing was filled with styrene casting resin to hold electrodes of the cell rigidly in place. This construction permits placement of the conductivity cell very close to the outlet of the hollow fiber bundle.
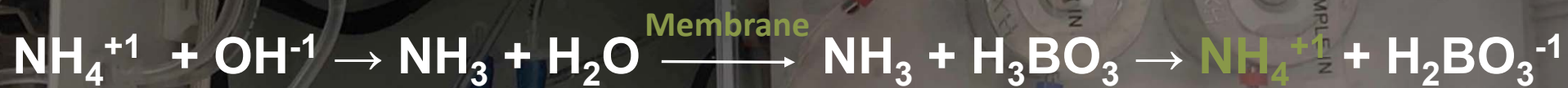
Figure 3 is a block diagram of the complete apparatus. Comonents used to assemble the apparatus are as follows: Arthur H. Thomas Co., Little Dipper Automatic Sampler, equipped with a timer adjustable from 0.2 to 5 min; Gilson Model HP-4, 4- channel peristaltic pump; Thermonix Model 4405 Conductivity Analyzer; and Linear Instruments Corp. Model 254 Strip Chart Recorder.

The sample and NaOH (or $HClO_4$) streams are mixed in a micromixing device constructed as described by Gugger and Mozersky(10). Air is injected into the mixed sample stream jest as it exits the micromixer. The stream then enters the thermostated water bath and passes

Theory of Operation

Chemistry across the Membrane

$$NH_4^{+1} + OH^{-1} \rightarrow NH_3 + H_2O \xrightarrow{\text{Membrane}} NH_3 + H_3BO_3 \rightarrow NH_4^{+1} + H_2BO_3^{-1}$$

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Simple Chemistry

Minimal Reagents = Minimal Impact

Simple to Make + Cost Effective + Easy to Dispose

Deionized Water + Buffer Solution: 250 ppm Boric Acid + Caustic Solution: 5%-15% w/w NaOH

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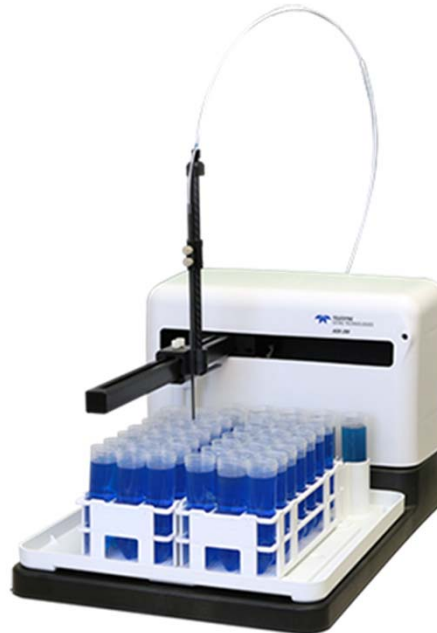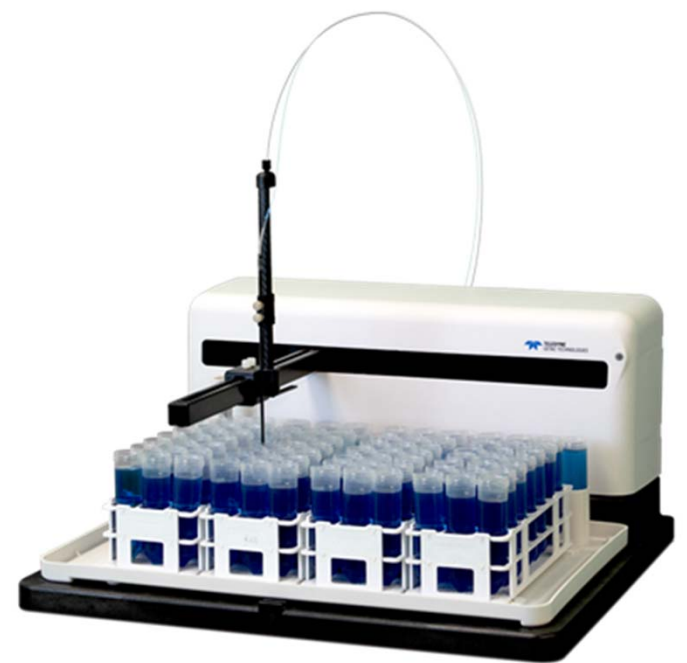# Timberline Diffusion Membrane Assembly

Autosamplers

Timberline 50 Position
Autosampler

Cetac 120 Position
Autosampler

Cetac 240 Position
Autosampler

Continous Flow Reduction of Nitrate to Ammonia with Granular Zinc

Robert M. Carlson

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Nitrate determination is one of the more frequently employed procedures in laboratories that process agricultural samples. An extensive discussion of various colorimetric, ion-selective electrodes, and reduction-distillation methods has recently been published. *(1)*. The colorimetric and ion-selective electrode methods are troubled by interferences. Reduction-distillation procedures are time-consuming and suffer from interference from hydrolysis of labile organic nitrogen. More recent methods employing ion chromatography require pretreatment to remove humic substances *(2)*. Mertens et al. *(3)* described an automated method in which nitrate is reduced to ammonia by a column of Devarda alloy in a continuous-flow apparatus. Ammonia is then quantified with a flow-through arrangement on a gas-sensing ammonia probe. The Devarda alloy is embedded in a polymer matrix, ground, and sieved to produce particle sizes that do not unduly restrict flow in the reduction column. Reduction of nitrate to ammonia is quantitative with a fresh column, but decreases slowly with column use. The maximum sampling rate is 30/h. The ammonium electode is the rate-limiting component.

I attempted to adapt the Devarda alloy-continuous flow reduction scheme for use with the continuous-flow ammonia analyzer described earlier *(4, 5)*. To simplify the reduction column preparation, alloy particles retained on a 100-mesh screen were used in place of the polymer embedding technique. A reduction column prepared from approximately 1 mL of alloy quantitatively reduced nitrate to ammonia for a period in excess of 3 h. However, after 1h the alloy developed a capacity to absorb ammonia so that increasing sampling times were required to maintain accuracy. In the course of try to rectify the problems with Devarda alloy, it was discovered that a bed of granular zinc, pretreated with copper in a manner similar to the conner treatment of cadmium for reducing

viously *(4, 5)*. In this instrument sample mixed with an alkaline reagent is passed over a gas-permeable membrane through which ammonia diffuses. The ammonia is collected in a stream of water and quantified by measuring changes in electrical conductivity. The bundle of gas-permeable silicone-polycarbonate hollow fibers in the original instrument was replaced with a microporous Teflon tube. This modification reduced response time and improved the detection limit.

A freshly prepared reduction column required 1-3 min conditioning with the DTPA/KOH reagent to reach quantitative reduction of nitrate. After completion of a set of samples, water was pumped through the reagent and sammples tubes for 5 min prior to shutdown.

Reduction column performance was evaluated by comparing instrument response to nitrate with the response to solutions containing equivalent concentrations of ammonium. Effects of ions commonly found in aqueous samples were evaluated by comparing responses to single salt solutions spiked with nitrate or ammonium.

RESULTS AND DISCUSSION

The precipitation of Ca^{2+} and Mg^{2+} when a smaple is mixed with alkaline reagent clogs the zinc column in the continuous-flow apparatus. The combination of NaOH and ethylenediaminetetraacetic acid (EDTA) used for ammonium determinations *(4, 5)* does not completely prevent precipitation of $Mg(OH)_2$. A mixture of KOH and DTPA is superiour for this purpose, because the MgDTPA chelate is more stable than MgEDTA and K has less tendency than Na to compete for the ligand. The concentrations used are designed to chelate up to 50 mM (Ca^{2+} + Mg^{2+}) and to neutralize up to 0.1 M acid with sufficient excess KOH and DTPA to maintain conditions necessary for nitrate reduction when the samples and reagent flow rates indicated in Figure 1 are used. Reagent composition

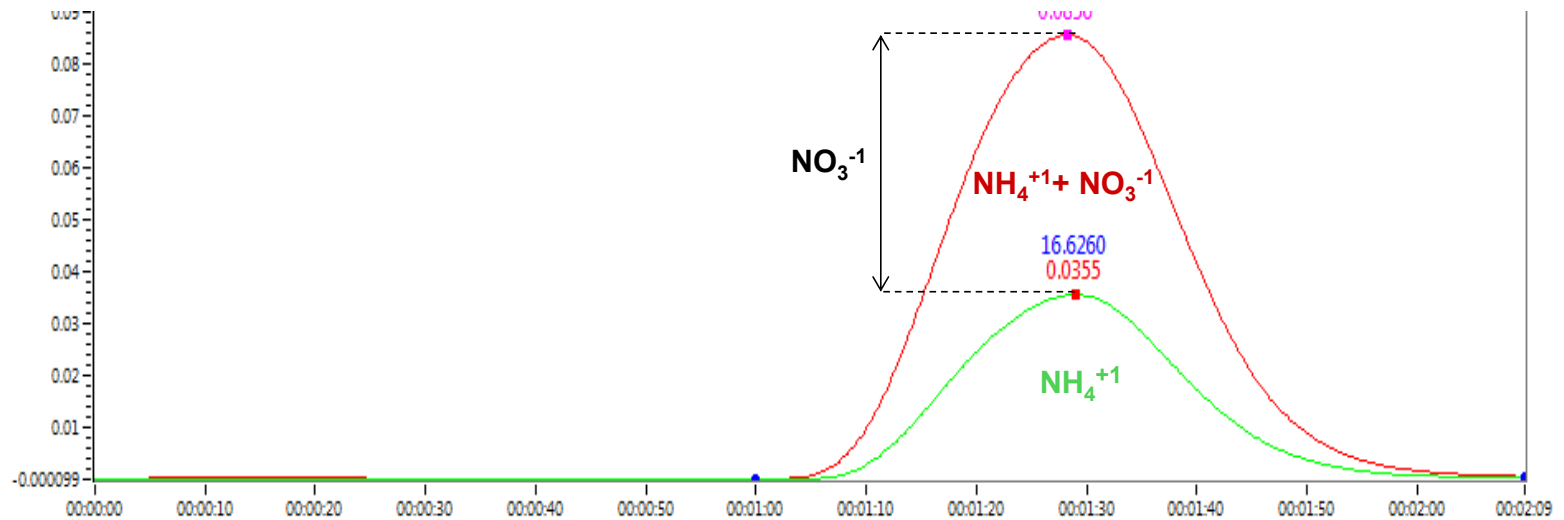# Timberline Activated Zinc Cartridge

Zinc/Nitrate Reduction Chemistry

$$NO_3^{-1}(aq) + 4Zn(s) + 7OH^{-1}(aq) \rightarrow 4ZnO_2^{-2}(aq) + NH_3(aq) + 2H_2O$$

- Not hazardous to use
- No hazardous material waste stream required for disposal
- No air bubble interference
- Long lifetime
- Easy to replace

Nitrate Analysis

- Direct measurement of ammonium ion
- Samples pass through an activated zinc reduction cartridge to produce a combined ammonia + nitrate measurement
- Nitrate concentration found through subtraction

For Regulatory Compliance

EPA Approved Method: Timberline Ammonia – 001

"Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis"

Approved for Analysis of Ammonia in Waste Water and for Ammonia in Kjeldahl Nitrogen Digests without Distillation.

Standard Methods: 4500 – N D

"Conductimetric Determination of Inorganic Nitrogen" Includes Ammonia and Nitrate Analysis

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For the determination of
Ammonia and Nitrate + Ammonia in:

Water & Wastewater

Kjeldahl Digestates
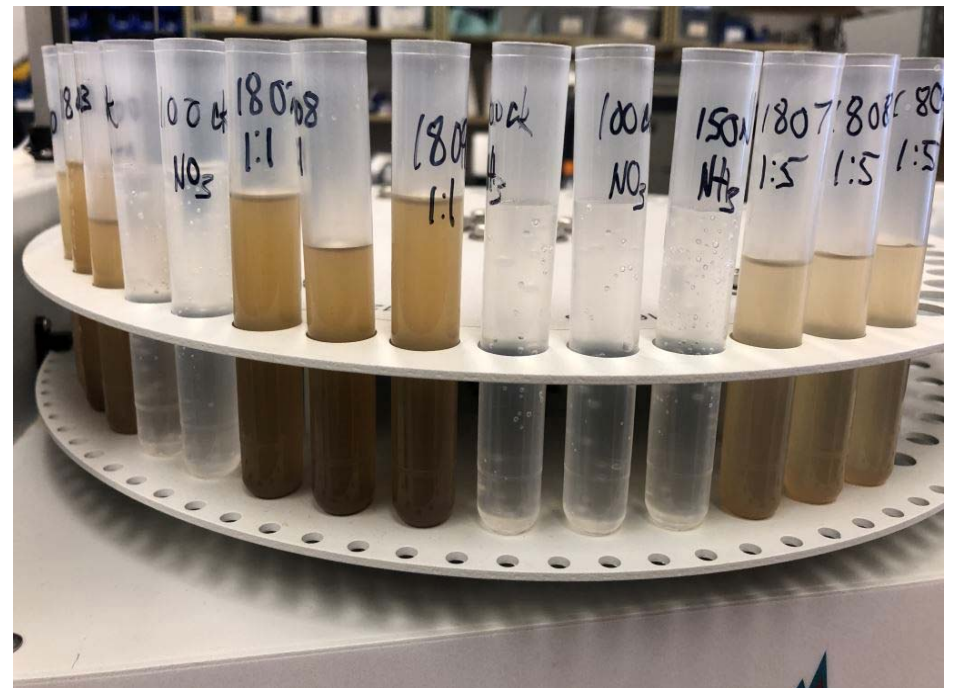(no distillation step required)

Soil Extracts

Compost/Manure

Plant Tissue Extracts

Feed & Forage

TIMBERLINE INSTRUMENTS

No Need to Filter Samples in Most Cases

Key Advantages

Low Interference

Results unaffected by sample turbidity or color.

Low Cost

Low yearly maintenance, consumables, & overall cost of ownership.
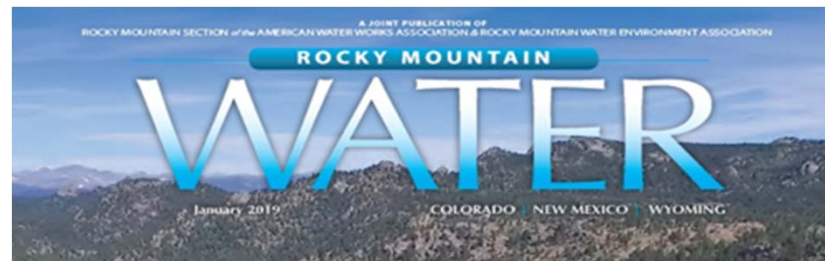
Wide Dynamic Range

Accurate results over a range from 10ppb to 500ppm.

Persulfate Digest for Total Nitrogen Determination

A JOINT PUBLICATION OF ROCKY MOUNTAIN SECTION of the AMERICAN WATER WORKS ASSOCIATION & ROCKY MOUNTAIN WATER ENVIRONMENT ASSOCIATION

ROCKY MOUNTAIN
WATER

January 2019 — COLORADO | NEW MEXICO | WYOMING

SCIENCE, RESEARCH & TECHNOLOGY

Novel Total Nitrogen Analysis in Wastewaters

By John Stillian, Lindle Aragon, and Evelyn Rhodes

NITROGEN IS AN ESSENTIAL NUTRIENT FOR MANY natural processes, however, too much nitrogen in a water body can have negative impacts, such as increased eutrophication. Nitrogen comes in many forms with both organic and inorganic components. The total sum of all forms of nitrogen (ammonia, nitrate, nitrite, and organic nitrogen) is known as total nitrogen (TN). All forms of nitrogen are interconvertible, and all can be found in natural waters and wastewater effluents. Ammonia has been primarily a concern for wastewater dischargers, because high levels of ammonia are toxic to aquatic life. Because of this, ammonia has long been regulated under the US Environmental Protection Agency (USEPA) National Pollutant Discharge Elimination System (NPDES) permitting program (USEPA, 1972). In recent years, due to increased concerns of harmful algae (cyanobacteria), regulators are studying the contributions of other forms of nitrogen as well, specifically nitrate/nitrite, TN, and likely dissolved and organic contributions in the near future.

The USEPA does not have approved methods for TN, therefore municipal water systems typically use the Total Kjeldahl Nitrogen (TKN) digestion method and then analyze with any one of a variety of analytical methods. TKN digestion is one of the oldest analytical methods still in use (Jones, 1991). It requires sample digestion in hot concentrated sulfuric acid with the addition of potassium permanganate and either a mercury or copper/titanium based catalyst. The digestion converts the

ASX-260). The instrument is based on membrane diffusion of ammonia from the sample stream into a buffer stream and conductivity detection of ammonium ion. Since the analyzer measures ammonia, the nitrate is first quantitatively reduced to ammonia by treating the sample, online, with an activated zinc cartridge. The peroxydisulfate digestion method is faster (30-minute digestion), requires less sample, and has significantly less hazardous operating conditions compared with TKN digestion. The sample is ready to analyze for the resulting nitrate when the digestion is complete without the need for distillation or any other sample preparation except in some cases a simple dilution.

Digestion method

The persulfate digestion method for TN was first reported as an alternative to TKN digestion in 1976 (Grasshoff). D'Elia et al also published a comparison of TKN to persulfate digestion of TN in 1977. Patton and Kryskalla, with the USGS, published an extensive report in 2003 on "The Evaluation of Alkaline Persulfate Digestion as an Alternative to Kjeldahl Digestion for Determination of Total and Dissolved Nitrogen and Phosphorus in Water." The digestion method we are reporting on is tailored after the method outlined in the Patton and Kryskalla paper and the APHA 4500-N-C Persulfate Method for Total Nitrogen in Standard Methods (2017), for the determination of nitrogen from organic nitrogen compounds. Method 4500-N-C is also approved for use under Colorado Regulation 85 by the Colorado Department of Public Health and Environment (CDPHE, 2016).

TIMBERLINE INSTRUMENTS

Persulfate Digest Matrix

- Standard Methods: "Method APHA 4500-N-C Persulfate Method for Total Nitrogen"

- Digestion Solution: 10.05g low nitrogen potassium peroxydisulfate and 1.5 g sodium hydroxide dissolved in 200mLs DI water.

- 5 mL aliquot of digestion solution added to 10 mL of sample.

- 30 minutes at 121ºC in autoclave.

- Analyzed directly on TL-2800 Analyzer for nitrate concentration.

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Persulfate Digested Samples

Picture courtesy of Lindie Aragon, Westminster Water Quality Lab, Westminster, CO

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Correlation of Method Data Between Labs

$y = 0.9758x + 0.2259$
$R^2 = 0.9892$
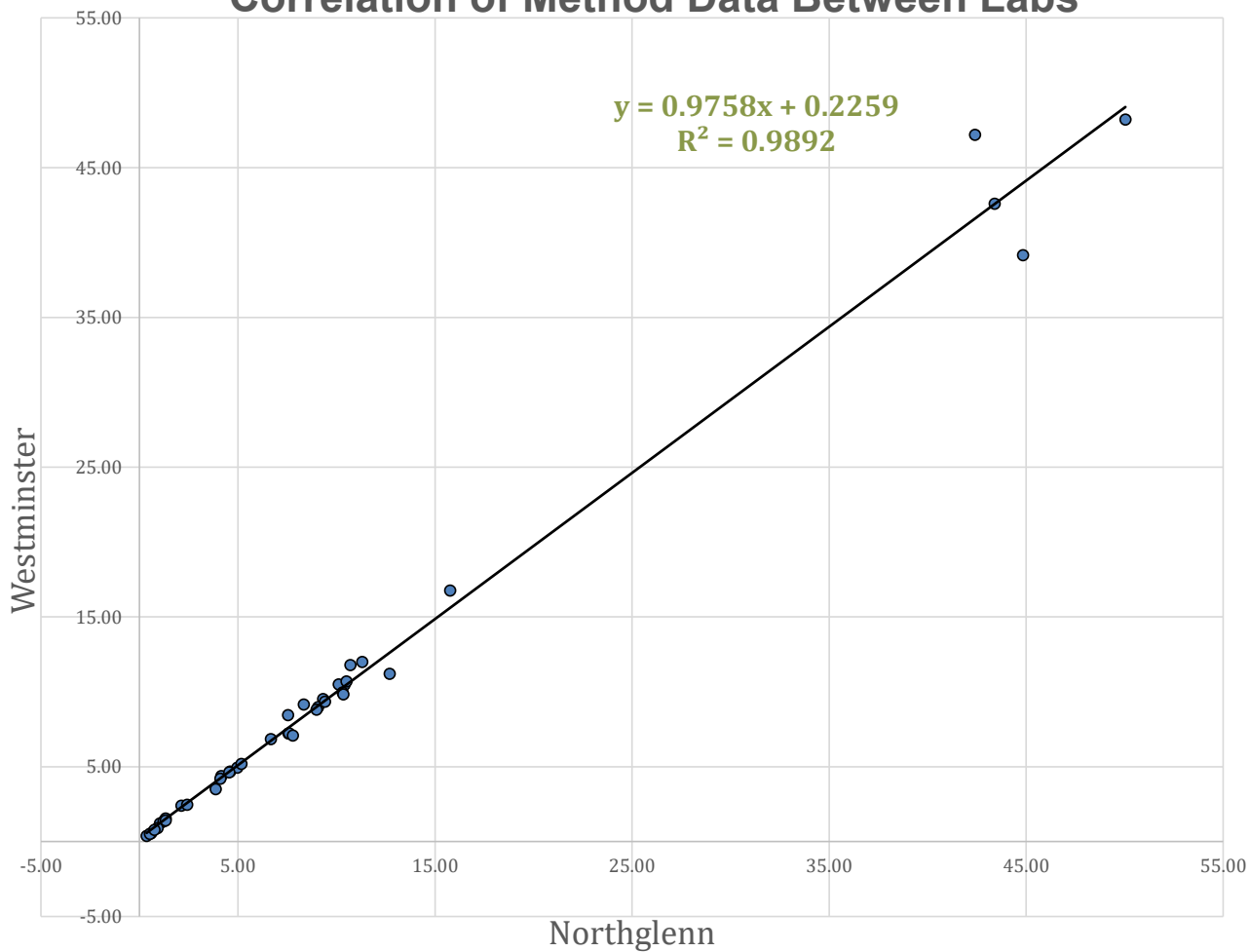
Measuring Ammonia in Kjeldahl Digestates from Municipal Wastewater Influent and Effluent Samples Using the Timberline Ammonia Analyzer

John Stillian
Timberline Instruments, Boulder CO

INTRODUCTION

Kjeldahl Digestion, also called Total Kjeldahl Nitrogen or TKN, is considered by many to be the one of the oldest analytical procedures still in use. The basic principle of the digestion has remained essentially the same since its introduction. The purpose of the digestion procedure is for determining the organic nitrogen (N) content by oxidation to ammonium ion (NH4+1). Kjeldahl digestion, named for its inventor, Johan Kjeldahl, was first described in 1883 at a meeting of the Danish Chemical Society and subsequently published in Zeitschrifte fur Analytische Chemie the same year.

Johan Kjeldahl's original technique was to heat the sample in a solution of concentrated fuming sulfuric acid and potassium permanganate (KMnO4) to near its boiling point of 330 ^{0}C (1). He also added phosphoric anhydride to speed up the digestion, probably because the phosphoric anhydride allowed a higher boiling point. Since then a variety of metal catalysts, including mercury, copper, iron and titanium dioxide, have been employed to reduce the digestion time and improve the degree of digestion. In the current Standard Methods procedure, method 4500-Norg B, the digest solution uses concentrated sulfuric acid, copper sulfate as a catalyst, and potassium sulfate to provide a higher boiling point. Typical digestion times are 30 minutes to 120 minutes depending on the sample being digested. It is important to note that nitrate and nitrite are not converted to ammonia in a TKN digest; in fact higher concentrations of nitrate and nitrite can interfere with complete digestion of organic nitrogen.

Since the result of digestion is ammonium ion and many samples contain ammonium ion prior to digestion, it is often necessary to measure ammonium before and after digestion. A number of different analytical methods have been used to quantitate ammonia before and after digestion. One of the first required neutralizing the digestion solution with base, converting ammonium to ammonia, followed by distillation of the ammonia into a weakly acidic solution and acid/base titration to determine the ammonia concentration present. Other methods include KI/KIO3 reaction and titration of the liberated iodine, colorimetric methods (for example phenol-hypochlorite, sodium salicylate-chlorine with nitroprusside or Nessler's reagent), and membrane diffusion/conductivity. Some methods require ammonium distillation after digestion; some only require dilution of the digestate.

Kjeldahl Digest Matrix

- Standard Methods: "Method 4500 – N_{org} D" (Block Digestion and Flow Injection Analysis)

- Digestion Solution:
  - 134g K_2SO_4 and 7.3g $CuSO_4$ dissolved in 800 mL DI water.
  - Add 134 mL concentrated H_2SO_4, bring to 1 Liter with DI water.

- 10 mL aliquot of digestion solution added to 25 mL of sample.

- Digest for 1 Hour at 200 C, then 1 hour at 380 C.

- Dilute digest with 25 mL DI water. The resulting concentration of sulfuric acid is approximately 2N.

- Analyze directly on TL-2800 Analyzer for ammonia concentration.

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Kjeldahl Digest Samples

Correlation Between Boulder Water Lab Data and Timberline Lab Data
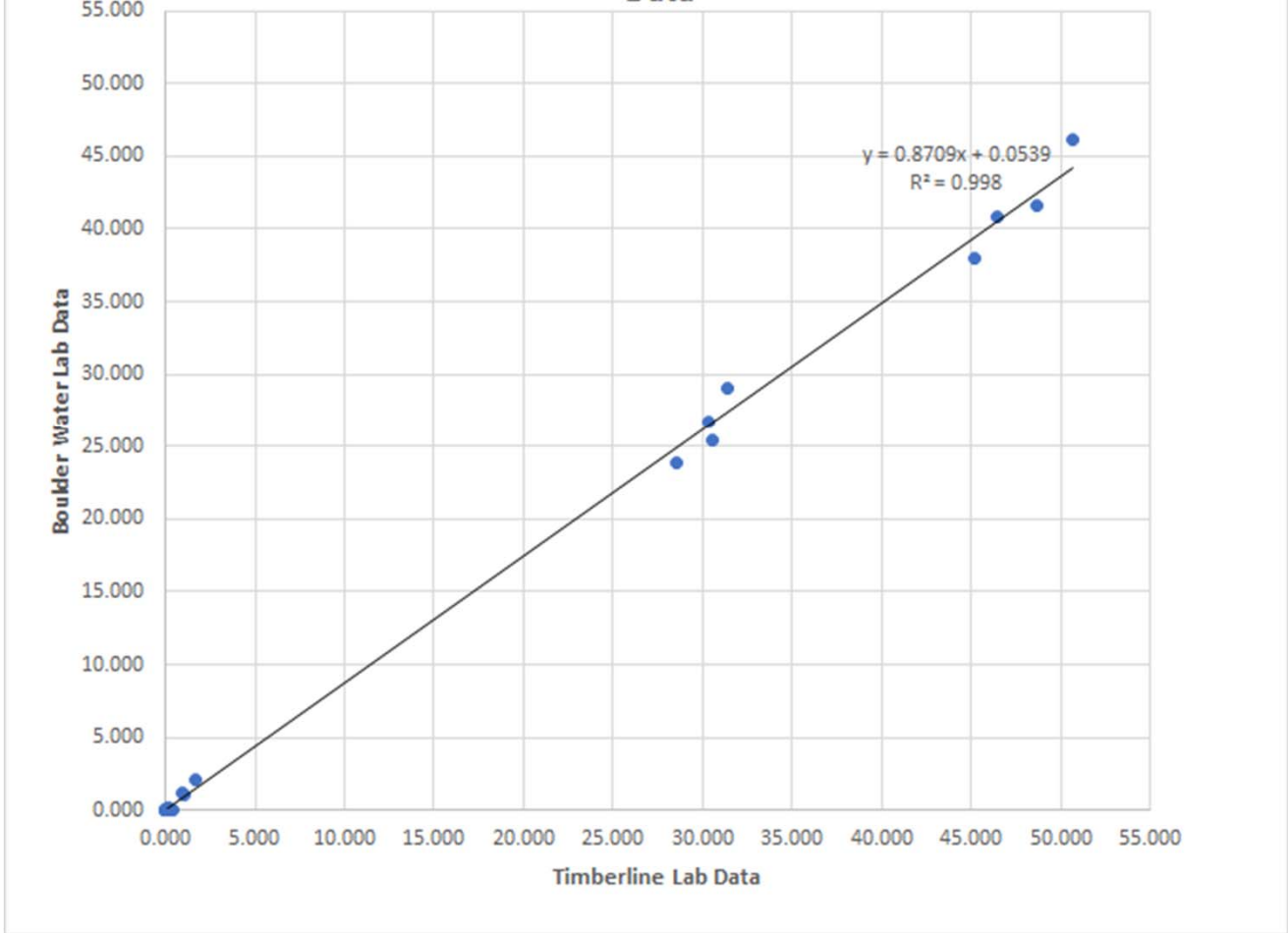
A Comparison of Ion Chromatography to Membrane Diffusion/Conductivity Detection for the Analysis of Nitrate in Agricultural Tile Samples

Tile drainage is a type of drainage system that removes excess water from the soil below the surface. The practice dates back to 200 B.C. but intensive use of tile drainage began in the 1800s in Europe with the development of ceramic tile (Figure 1). In the 19th century a C-channel tile atop a flat tile were often used. (Figure 2). Today "tile lines" are typically PVC, although some are still cast concrete or ceramic. It is important to remove excess water from the soil since healthy root growth requires oxygen as well as water. If water saturates the soil in the area where roots grow, the roots become starved for oxygen. The tile drainage system moves water away from the soil root level to prevent this. Tile lines are typically placed at least 3 feet below the soil level and drained to a common drainage ditch adjacent to the planting field (figure 3).

Since the water in tile lines has carried fertilizer through the soil, tile lines also provide a fortuitous place to sample irrigation water for nutrients to ensure crops aren't over or under fertilized. Figure 4 shows irrigation water sampling from a typical tile line. Nitrate is one of the most important nutrients to monitor.

Figure 1 - Modern day ceramic tile


Figure 2 - Cast cement tile

Figure 3 - Plastic tile lines and tile drainage ditch

TIMBERLINE
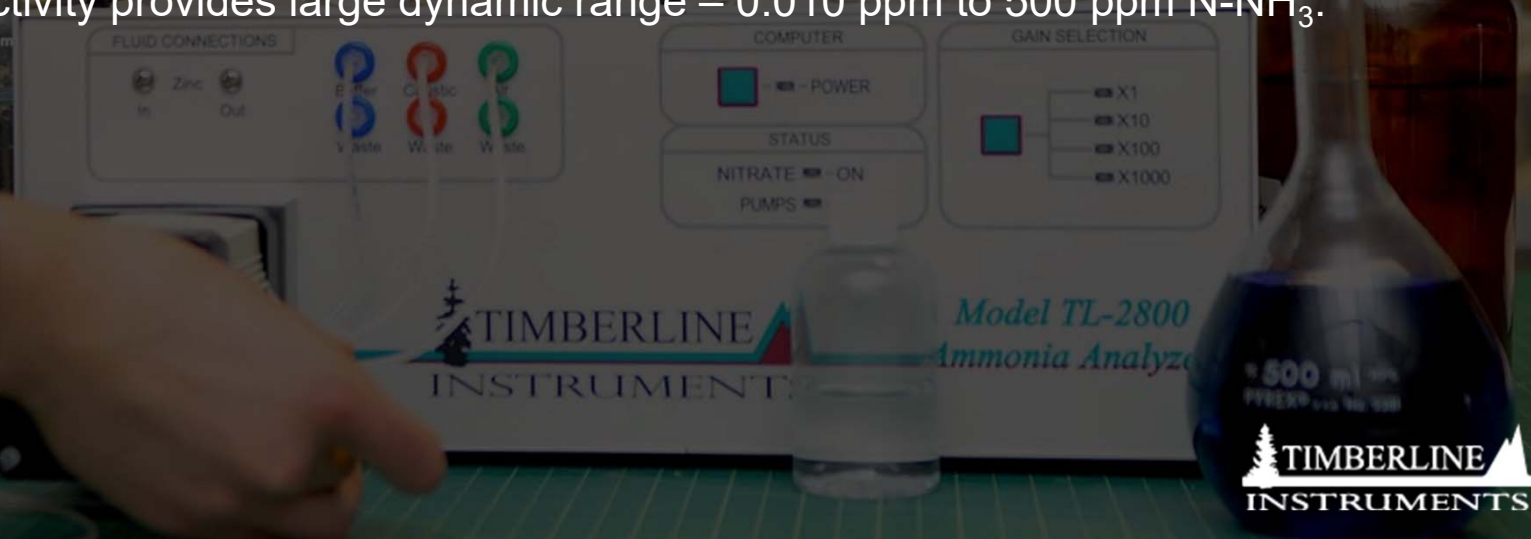INSTRUMENTS

Soybean Tile Water NO$_3^{-1}$

Sample	Nitrate Concentration (ppm)			% of IC Concentration	
	IC	TL Analyzer 1	TL Analyzer 2	TL Analyzer 1	TL Analyzer 2
Tile Water 1	5.1	5.1	5.2	100%	103%
Tile Water 2	18	17.9	17.6	100%	98%
Tile Water 3	2.17	2.2	2.2	102%	101%
Tile Water 4	21	20.4	20.5	97%	98%
Tile Water 5	1.5	1.4	1.4	95%	93%
Tile Water 6	28.4	28.7	28.2	101%	99%
Tile Water 7	2.6	2.7	2.7	105%	106%
Tile Water 8	17.9	18.1	18.1	101%	101%
Tile Water 9	9.6	9.9	10.0	103%	104%
Tile Water 10	23.6	23.6	22.8	99%	96%

TIMBERLINE
INSTRUMENTS

Nitrate in Soybean Tile Water:
Timberline Diffusion/Conductivity vs Ion Chromatography
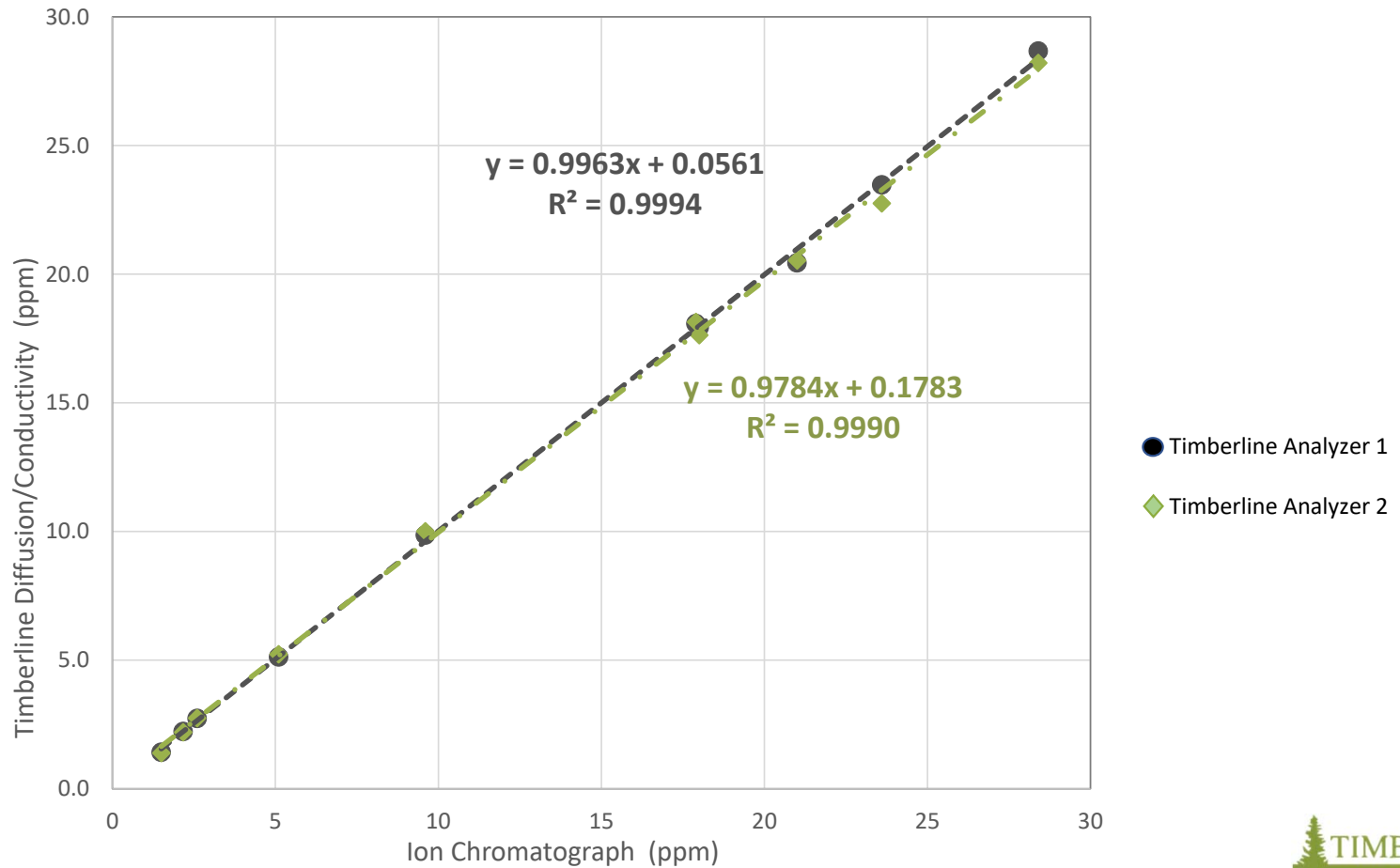
Summary

- Automated timed injection from autosampler (no injection valve) and 1mm id tubing
  - Minimal maintenance requirements, typically 90+% up time.
  - Soil KCl extract samples including extreme pH, turbidity, and color.
  - Waste water samples - dilution and settling only, typically no filtering.
  - Conductivity provides large dynamic range – 0.010 ppm to 500 ppm N-NH$_3$.

FLUID CONNECTIONS
Zinc In / Out
Buffer / Caustic
Waste / Waste / Waste

COMPUTER
POWER

STATUS
NITRATE — ON
PUMPS

GAIN SELECTION
X1
X10
X100
X1000

TIMBERLINE INSTRUMENTS

Model TL-2800
Ammonia Analyzer

TIMBERLINE INSTRUMENTS

Thank You!

👤

John Stillian

✉️

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🖥️

www.timberlineinstruments.com

📞

800.777.5996

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Summary

- **Membrane Diffusion Coupled with Conductivity Detection for Measuring Ammonia**
  - Membrane acts as an automated in-line sample preparation device.
  - Not sensitive to sample matrices including extreme pH, turbidity, and color.
  - Conductivity detection provides excellent sensitivity to single digit ppb N-NH$_3$ MDL.
  - Conductivity provides large dynamic range – 0.010 ppm to 500 ppm N-NH$_3$.

- **Simple Automated Flow Injection Technique**
  - Automated timed injection from autosampler (no injection valve) and 1mm id tubing
  - Minimal maintenance requirements, typically 90+% up time.

- **Minimum Sample Preparation Required – Typically Only Sample Dilution.**
  - Kjeldahl Digestates without distillation or filtering, dilution only.
  - Soil KCl extracts - no filtering.
  - Manure samples - dilution and settling only, typically no filtering.
  - Waste water samples - dilution and settling only, typically no filtering.

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