SIMPLIFIED METHOD FOR THE DETERMINATION OF TOTAL KJELDAHL NITROGEN IN WATER AND WASTEWATER

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Director of Regulatory Affairs

GOALS OF THE PRESENTATION

- Review Traditional Total Kjeldahl Nitrogen
  - Advantages and Disadvantages
- Present New Simplified Total Kjeldahl Nitrogen System
  - Theory
  - Chemistry
  - Results
  - Advantages and Disadvantages

TOTAL KJELDAHL NITROGEN (TKN) HISTORY

- TKN Method first presented on 7-March-1883 by Johan Kjeldahl (1849-1900) as a novel method for analyzing protein

- Numerous Applications:
  - Wastewater Treatment for nitrogen testing and removal
  - Food and Beverage production for protein analysis
  - Agriculture

- One of the most challenging, dangerous and labor-intensive tests performed in wastewater treatment plant laboratories.

REGULATORY SIGNIFICANCE

- TKN is used as a indicator for wastewater treatment performance, pre-treatment loading fees, and is limited in discharge to receiving waters

- More than 3000 wastewater treatment plants in the United States have a NPDES discharged permit limiting TKN

TRADITIONAL TKN CHEMISTRY

TKN Method: Digestion, distillation, capture, and titration

Degradation: Org-N + H_2SO_4 + $Hg_{(catalyst)}$ + $Heat_{(189°C)}$ → $(NH_4)_2SO_4$ + $CO_{2\ (gas)}$ + $H_2O_{(gas)}$

Distillation: NH_4^+ + $(NH_4)_2SO_4$ + 2NaOH → Na_2SO_4 + $2H_2O$ + $2NH_{3\ (gas)}$

Capture: $B(OH)_3$ + H_2O + NH_3 → NH_4^+ + $B(OH)_4^-$

Back Titration*: $B(OH)_3$ + H_2O + Na_2CO_3 → $NaHCO_3$ + $NaB(OH)_4$ + $CO_{2\ (gas)}$ + H_2O

* Typically Methyl Orange Indicator: <pH 3.1:RED; >pH 4.4:YELLOW

COLORIMETRIC DETECTION

- Nessler
  - Nessler reagent (K_2HgI_4) reacts with ammonia under strong alkaline conditions to produce a yellow-colored species. The intensity of the color is directly proportional to the ammonia concentration.
    - 2KsHgI4 + NH3 + 3KOH $\rightarrow$ $Hg_2OINH_2 + 7KI + 2H_2O$
    - Chemistry downside - Contains mercury

COLORIMETRIC DETECTION

- Phenate
  - Ammonia combines with hypochlorite (OCl^-) to form monochloramine (NH_2Cl) which then reacts with phenate to form 5-aminophenate.
  - The 5-aminophenate is oxidized in the presence of a catalyst (nitroprusside), which results in the formation of indophenol (a blue-colored compound).

Chloramination: $NH_3 + OCl^- \rightarrow NH_2Cl + OH^-$

Phenate Reaction: NH2Cl + phenate → H_2N-phenol

Color Formation: H_2N-phenol + $Fe(CN)_5NO_2^-$ (nitroprusside) → Indophenol

Chemistry Downside: Phenol Odor

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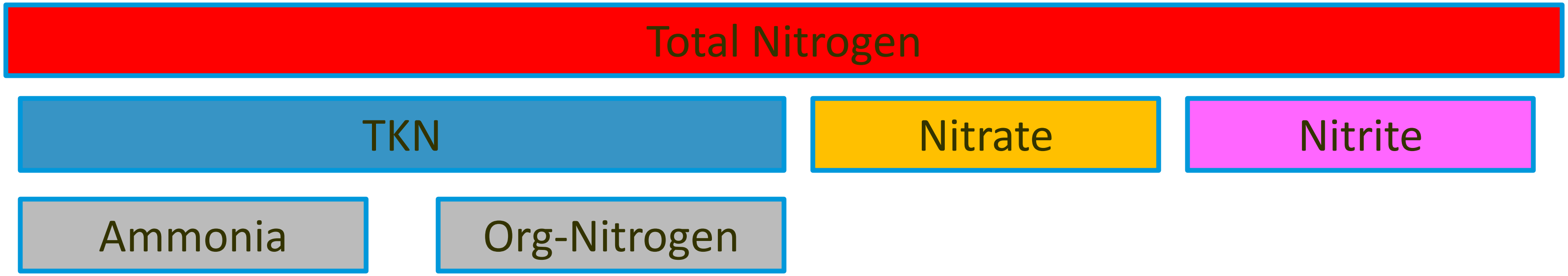
ELECTROCHEMICAL DETECTION

- Ion Selective Electrode (ISE)
  - Potentiometric sensor for ammonia measurement
  - Multi-point calibration curve must be generated and the ISE technology must be maintained.

TKN – WHAT IT IS / IS NOT?



$$\text{Total Nitrogen} = NH_3 + \text{Org-N} + NO_3^- + NO_2^-$$

By definition, TKN, which is a component of total nitrogen, is the sum of organic nitrogen and ammonia. Therefore, the above relationship may be re-written as:

$$\text{Total Nitrogen} = \text{TKN} + NO_3^- + NO_2^-$$

or

$$\text{TKN} = \text{Total Nitrogen} - (NO_3^- + NO_2^-)$$

SIMPLIFIED TOTAL KJELDAHL NITROGEN

- The simplified TKN (s-TKN™) method utilizes two simple measurements to calculate the TKN value as:
  - The difference between the concentration of TN and NO_3^- + NO_2^-.

S-TKN™ EQUATION

- TKN is a component of total nitrogen, and is the sum of organic nitrogen and ammonia. Therefore, the TKN equation may be re-written as:

$$\text{Total Nitrogen} = NH_3 + \text{Org-N} + NO_3^- + NO_2^-$$

- The s-TKN method is based on this nitrogen relationship. s-TKN is defined as the difference between the concentration of TN and Nitrate-Nitrite

$$\text{s-TKN} = \text{Total Nitrogen} - (NO_3^- + NO_2^-)$$

S-TKN CHEMISTRY

- TN is determined by digesting the sample for 1 hour at 100 º C with $K_2S_2O_8$ under alkaline conditions, oxidizing all forms of nitrogen to NO_3^-.

Digestion: $\mathbf{NH_3}$ **+ Org-N +** $\mathbf{NO_3^-}$ + $\mathbf{NO_2^-}$ **+** $\mathbf{K_2S_2O_8}$ **+ NaOH** → $\mathbf{NO_3^-}$

Analysis: **TN** digestate for $\mathbf{NO_3^-}$

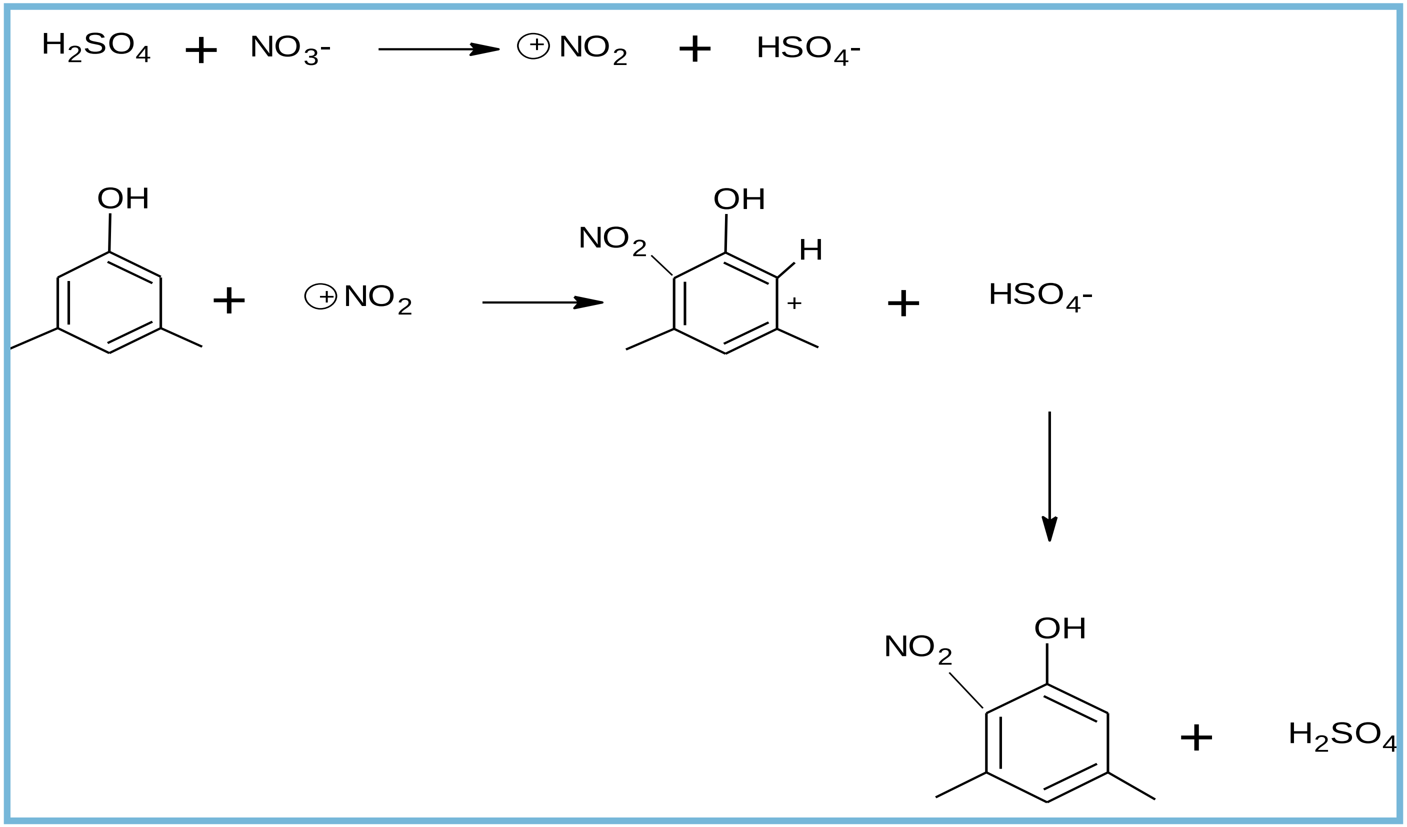
Undigested sample for ($\mathbf{NO_3^-}$ **-** $\mathbf{NO_2^-}$)

TN($\mathbf{NO_3^-}$) - ($\mathbf{NO_3^-}$ **-** $\mathbf{NO_2^-}$) **= TKN**

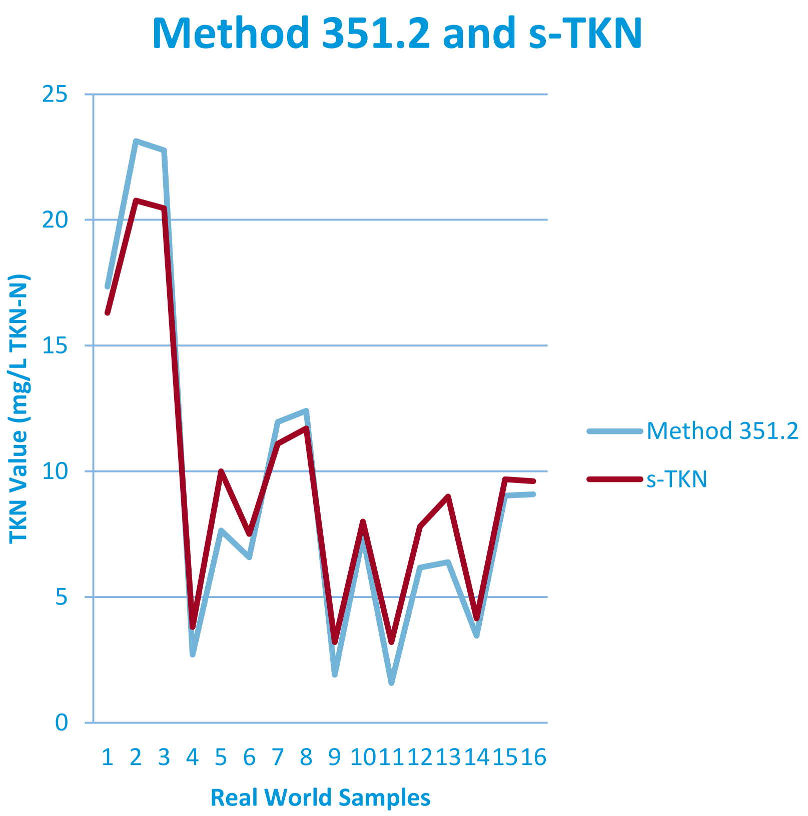
DIMETHYLPHENOL CHEMISTRY

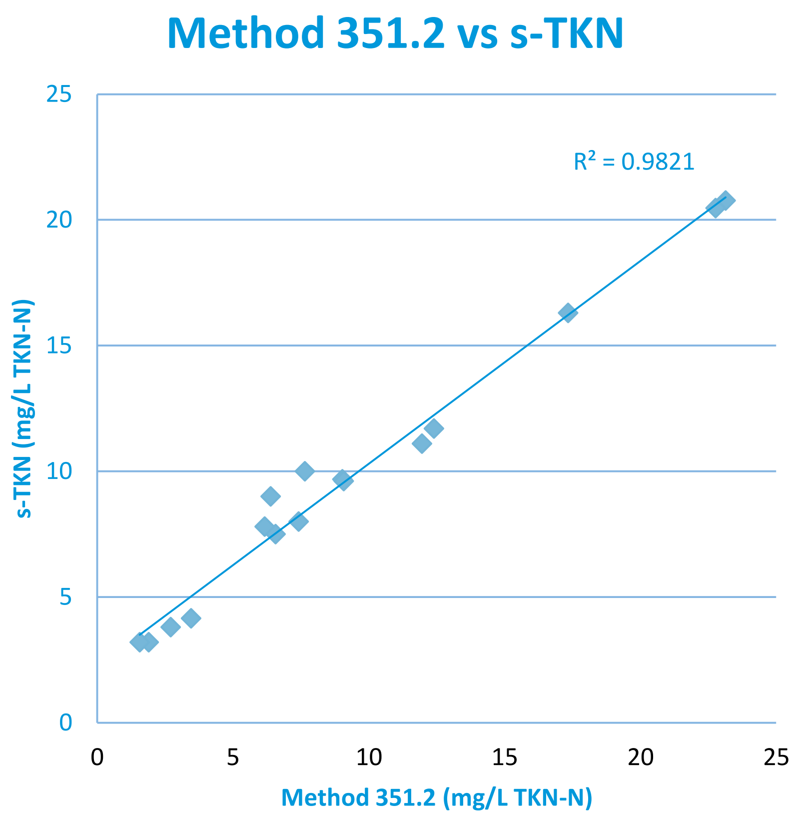
- NO_3^- reacts with 2,6-dimethylphenol, forming a colored complex.
  - NO_3^- in the presence of sulfuric acid yields a nitronium ion (NO_2^-) and HSO_4^-.
  - Nitronium ions are electrophiles that attack the aromatic ring of the dimethylphenol reagent to form intermediate nitro-carbonium ions.
  - The basic HSO_4^- ion extracts a hydrogen ion from the nitro-carbonium intermediate to yield a stable substitution product (o, or p-nitro-dimethylphenol).

DIMETHYLPHENOL + NITRATE REACTION



METHOD PERFORMANCE CORRELATION PLOTS S-TKN WITH TKN





These matrices included wastes from dairy processing, brewing, photo-processing, and geographically dispersed municipal waste facilities.

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AMMONIA NITROGEN MATRIX SPIKE RECOVERY OF S-TKN WITH TKN

Sample Matrix	% Recovery (s-TKN)	% Recovery (EPA 351.2)
Industrial Chemical Effluent 1	96.8%	102.8%
Municipal Waste Effluent 1	113.6%	99.2%
Municipal Waste Effluent 2	91.2%	105.3%
Municipal Waste Effluent 3	97.6%	107.5%
Industrial Food Effluent 1	102.4%	95.6%
Industrial Beverage Effluent 1	105.4%	107.0%
Average	**101.2%**	**102.9%**

These matrices included wastes from dairy processing, brewing, photo-processing, and geographically dispersed municipal waste facilities.

FOOTPRINT OF S-TKN DIGESTION BLOCK AND ANALYSIS EQUIPMENT

BENEFITS OF S-TKN METHOD

- Green Chemistry
- Eliminates the use of hazardous mercury
- One hour digestion, no need for fume hood
- Three results in one test (TKN, TN, (NO_2^- + NO_3^-))
- Performance equally effective to other EPA approved TKN methods
- Small lab space footprint (No Fume Hood Needed)
- Startup Cost - $4200 (digestion block and spectrophotometer)
- s-TKN Cost per test - $4 per test (Traditional TKN Cost - $25 - $50)

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EPA ATP VALIDATION STUDY

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

THE ADMINISTRATOR

Cary B. Jackson, Ph.D.
Director of Regulatory Sciences
Hach Company
5600 Lindburgh Drive
Loveland, CO 80539

SUBJECT: Review of Hach Company Method 10242, Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater (ATP Case No. N10-3010)

DATE: January 31, 2013

I have reviewed Hach Company Method 10242 (ATP Case No. N10-0010), "Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater", and the supporting validation data in ATP Case No. N10-0010. I determined that this method meets all requirements for measurement of total Kjeldahl nitrogen in wastewater. That is, the performance of this method is substantially similar to methods listed at 40 CFR Part 136 for measurement of total Kjeldahl nitrogen.

I will recommend that this method be included in future regulatory actions in which EPA periodically adds to the list of approved methods at 40 CFR Part 136. However, this ATP review does not replace this notice and comment rulemaking process. In the interim a user may, on a facility-by-facility basis, seek approval from their regional authority for use of this method in measuring total Kjeldahl nitrogen in Clean Water Act (CWA) programs.

If I can be of any additional assistance on this matter or others, please contact me at walker.lemuel@epa.gov .

Sincerely,

Lemuel Walker
CWA ATP Coordinator
Engineering and Analytical Support Branch
Engineering and Analysis Division
Office of Science and Technology

cc: Quality Assurance Managers (all Regions)
ATP Coordinators (all Regions)

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QUESTIONS

BACKUP SLIDES

ORGANIC NITROGEN RECOVERY

TN Organic compounds

2 mg/L Nicotinic Acid, Urea , separate and equally combined
30 mg/L Nicotinic Acid, Urea, separate and equally combined
80 mg/L Nicotinic Acid, Urea, separate and equally combined

mg/L N Spike	Urea (%)	Nicotinic Acid (%)	Combined Urea/Nicotinic Acid (%)	Average % Recovery
2.00	97.5	99.5	99.5	102
2.00	102	104	105	
30.0	97	96.7	97.3	96.7
30.0	101	98.0	96.0	
80.0	94.1	93.8	93.9	95.3
80.0	96.3	94.4	96.6	
Average % Recovery	**98.0**	**97.7**	**98.0**	

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