Water Analysis

TN using persulfate digestion and DMP

Standard under development

Dr. Christian Prokisch I CProkisch@mn-net.com I 01.08.2024

Agenda

Introduction

Persulfate digestion followed by detection using DMP

Data

Standard Methods 4500-N F

Summary

Introduction

Introduction

Significance of detecting Nitrogen in Water

- Essential for environmental and human health
- Indicator of water quality and ecosystem balance
- Critical for regulatory compliance and pollution control
- Impacts drinking water safety and aquatic life

Introduction

Current regulatory background

- EPA sets standards for nitrogen in drinking water
- Clean Water Act regulates nitrogen discharge
- Nutrient Criteria Program guides state-level standards
- Ongoing efforts to adopt numeric nutrient criteria

Introduction

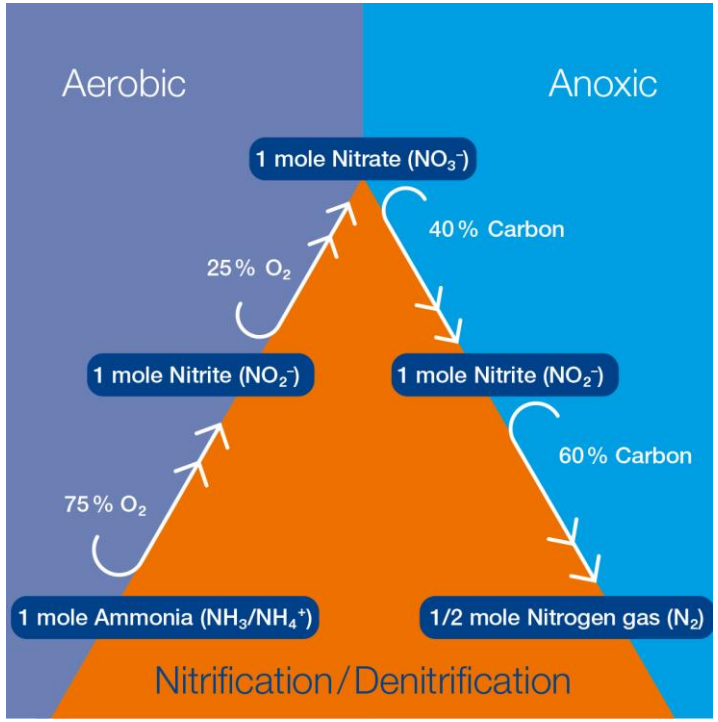
Goal of this presentation

- Revisit an established method for total nitrogen detection in water
- Propose standardization for potential nationwide regulation
- Present data supporting method's reliability and applicability
- Discuss implications for future water quality regulations

Introduction

Sources and forms of Nitrogen

- Sources: Agriculture, wastewater, atmospheric deposition, urban runoff
- Forms: Organic nitrogen, ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-)
- Natural vs. anthropogenic sources
- Nitrogen cycle in aquatic environments



Introduction

Effects and Global Trends

- Effects of excess Nitrogen
  - Eutrophication and algal blooms
  - Hypoxia and fish kills
- Global trends in Nitrogen pollution
  - Drinking water contamination (e.g., blue baby syndrome)
  - Global increase in nitrogen pollution over past century
  - Regional variations and hotspots

Introduction

Existing methods

- ISO 23697-1:2023 and ISO 23697-2:2023: Small-scale sealed tube methods
- ISO 29441:2010: UV digestion method
- Standard Methods including but not limited to
  - Flow injection analysis
  - Persulfate digestion followed by any Nitrate determination
  - Conductimetric determination of inorganic nitrogen
  - High temperature combustion

Introduction

Limitations of the current methods

- Lack of validation data acceptable for EPA regulation
- Insufficient statistical robustness for US regulatory purposes
- Absence of comprehensive interlaboratory studies for some methods

Gap between existing methods and EPA regulatory requirements

Persulfate digestion followed by detection using DMP

Persulfate digestion followed by detection using DMP

Brief overview

- Established method for total nitrogen detection
- Persulfate digestion converts all nitrogen to nitrate
- Detection using 2,6-Dimethylphenol colorimetry
- Small-scale sealed tube method Potential applications

Persulfate digestion followed by detection using DMP

Digestion step using Persulfate

- Alkaline oxidation at 120 °C
- Converts organic and inorganic nitrogen to nitrate
- Uses potassium persulfate and NaOH
- Requires heating block and digestion tubes

Persulfate digestion followed by detection using DMP

Detection step using Dimethylphenol

- Nitrate detection via colorimetric reaction
- 2,6-Dimethylphenol as the color reagent
- Photometric evaluation at specific wavelengths
- Requires acid mixture and photometer

Persulfate digestion followed by detection using DMP

Preparation

- Collection of water samples (groundwater, surface water, wastewater)
- Filtration if necessary to remove particulates
- Preparation of calibration standards using nitrate solution
- Creation of digestion check standard using glutamic acid solution
- Preparation of reagent blanks

Persulfate digestion followed by detection using DMP

Equipment and reagents

- Equipment: Heating block, digestion tubes, detection tubes, photometer
- Key reagents: Potassium persulfate, NaOH, 2,6-Dimethylphenol
- Acid mixture: Phosphoric acid and sulfuric acid (1:1)
- Ammonia-free and nitrate-free water
- Stock and intermediate solutions for standardsCollection of water samples (groundwater, surface water, wastewater)

Persulfate digestion followed by detection using DMP

Analytical Procedure

- Sample preparation and standard creation
- Digestion: Sample + persulfate reagent, heated at 120°C for 30 min
- Cooling of digested sample
- Detection: Addition of acid mixture and 2,6-Dimethylphenol
- Photometric measurement at 340–365 nm
- Quality control measures throughout

Persulfate digestion followed by detection using DMP

Advantages

- High accuracy and precision in nitrogen measurement
- Consistent results across different water types
- Simplified procedure with commercially available test kits
- Reduced need for complex sample preparation

Persulfate digestion followed by detection using DMP

Advantages

- Lower operational costs compared to traditional methods
- Reduced reagent consumption and waste generation
- Environmentally friendly with fewer hazardous chemicals
- Supports sustainable water quality monitoring practices

Low operational costs

Data

Data

ISO interlab trial – design

Sample ID	Matrix	NO_3-N	NH_4-N	TNb
A	Ground water	1	0,1	n.a.
B	Swimming pool water	7 – 8	0,5	n.a.
C	Waste water 1	40	3	n.a.
D	Waste water 2	8	40	n.a.
E	Waste water 3	n.a.	n.a.	10
F	Waste water 4	n.a.	n.a.	60
G	Waste water 5	n.a.	n.a.	80
H	Surface water	10 – 12	0.8	n.a.
I	QC standard	1	8	13

ISO interlab trial – Symbols used

Symbols used	
I	number of laboratories after outlier rejection
n	number of individual test results after outlier rejection
o	percentage of outliers
X	assigned value
$\bar{\bar{x}}$	overall mean of results (without outliers)
η	recovery rate
s_R	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

Data

ISO interlab trial – results

Sample	Matrix	l	n	o	X	$\bar{\bar{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
				%	µg/L	µg/L	%	µg/L	%	µg/L	%
E	Waste water 3	41	164	10,9	-	16,30	-	0,864	5,3	0,281	1,7
F	Waste water 4	45	180	4,3	-	61,63	-	3,526	5,7	1,530	2,5
G	Waste water 5	45	179	4,8	-	70,42	-	9,996	14,2	2,341	3,3
I	QC standard	44	174	8,4	13,033	13,15	100,9	0,698	5,3	0,260	2,0

Standard Methods 4500-N F

Standard Methods 4500-N F

Current status

- Received charge in January 2024
- First draft created in March 2024
- Comments received in April 2024
- Second draft sent out in July 2024
- Comment period open until July 19, 2024
- Review and incorporation of comments pending

Standard Methods 4500-N F

Method validation plans

- Aiming for Tier 3-like validation (nationwide use)
- Nine-laboratory interlaboratory study planned
- Minimum of nine different matrix types to be tested
- Method detection limit (MDL) determination by each lab
- Recovery studies and real sample analysis across application range

Standard Methods 4500-N F – Current status and next steps

Facilitating Participation in the Interlaboratory Trial

- Custom-made vials compatible with market-leading instruments
- Fits HACH photometers and heating blocks
- Eliminates need for reagent preparation by participants
- Reduces potential sources of error
- Lowers barrier to participation for laboratories Aiming for Tier 3-like validation (nationwide use)

Standard Methods 4500-N F – Current status and next steps

Call to Action – Join Our Interlaboratory Trial

- Seeking laboratories for method validation
- Opportunity to shape future water quality standards
- Easy participation with provided custom vials
- Gain early experience with potential future regulatory method
- Contact information for expressing interest:
  - cprokisch@mn-net.com

Summary

Summary

- Established method for total nitrogen detection revisited
- Persulfate digestion with 2,6-Dimethylphenol colorimetry
- Advantages: accuracy, ease of use, cost-effectiveness
- Potential basis for nationwide regulation
- Ongoing standardization and validation process
- Call for participation in interlaboratory trial

Water Analysis

Volunteers needed for total nitrogen method validation!

Dr. Christian Prokisch I cprokisch@mn-net.com I 01.08.2024

Image credits

© Jürgen Nickel (1, 31), Kekyalyaynen (4), psdesign1 (6), Alexey Stiop (8), Orlando Florin Rosu (10), Paulista (15), Alexander Raths (17), Uwe Bumann, (18,19), fotomek (25), rdnzl (26), Alex White (27), kerkezz (28), Swapan(30) – Adobe Stock

EPA Logo (5)

https://de.wikipedia.org/wiki/Datei:Environmental_Protection_Agency_logo.png

ISO Logo (9)

https://commons.wikimedia.org/wiki/File:ISO_Logo_%28Red_square%29.svg