EPA Colorimetric Testing for Nitrate plus Nitrite

National Environmental Monitoring Conference

Sarah Leibenguth

SEAL Analytical

Technical Support Chemist

Topics for Discussion

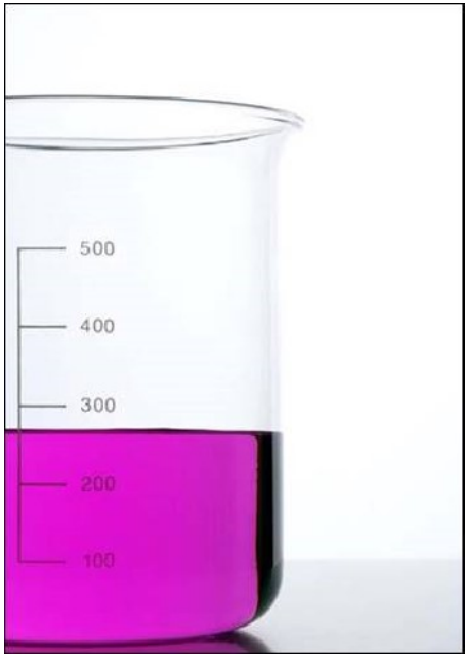
Nitrate to Nitrite Reduction Methods

- Cadmium
- Hydrazine
- Vanadium(III) Chloride
- Enzymatic

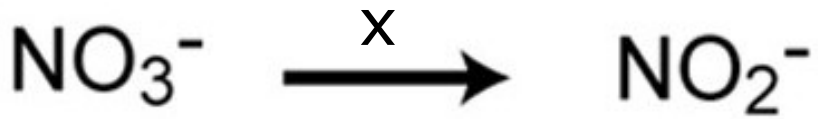
Things to Consider

- Approval
- Application
- Interferences
- Chemical Requirements
- Hardware Requirements

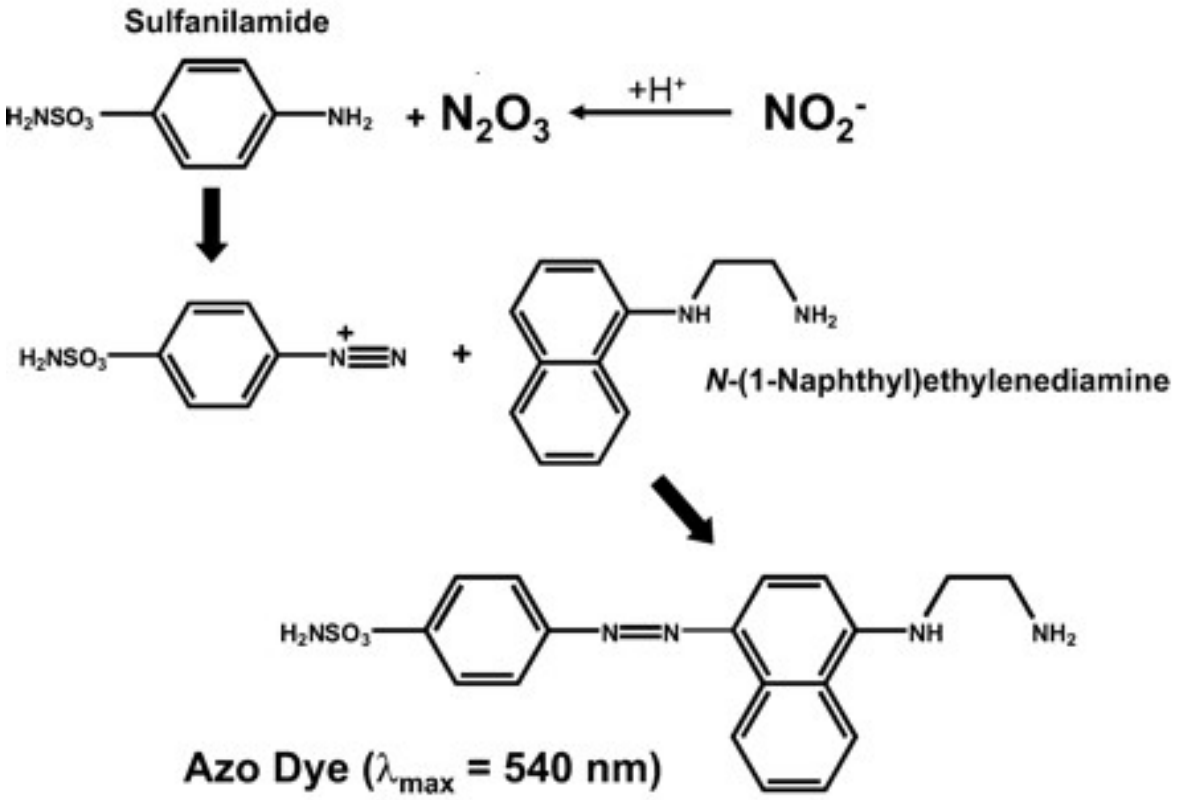
Griess Reaction



Nitrate to Nitrite Reduction



Griess Reaction



Cadmium Reduction

Cadmium Reduction

Approvals

- EPA (NPDES & NPDWR)
  - EPA 353.2 Rev. 2.0 (1993)
  - ASTM D3867-04 (A)
  - SM 4500-NO_3^- F-200
  - USGS I-2545-90

Applications

- Saline
- Surface
- Drinking
- Domestic
- Industrial

Cadmium Reduction

Hardware Requirements

- Cadmium Column
  - Prepare or Purchase
- Cadmium Coil
  - Purchase
- Switching Valve
  - Necessary for Online Reduction on Discrete Analyzer

User Requirements

- Column Preparation
- Column or Coil Conditioning
  - Activation with Copper Sulfate
  - Conditioned with High Standard

Cadmium Reduction

Interferences

- Oil and Grease
- Suspended Matter
  - Filtration Prior to Analysis
- Iron, Copper, and other Metals
  - EDTA in Approved Method
- Residual Chlorine
  - Sodium Thiosulfate

Cadmium Reduction

Things to Consider

- Hazard
- Cost
- Storage
- Stability

Cadmium Reduction

Chemicals

- Cadmium
  - Toxicity
  - Mesh Size of Cadmium Granules
  - Coated Cadmium Coil
  - Cost Effective
- HCl
  - Store at Room Temperature
  - Handle with Care
- Copper Sulfate
- Ammonium Chloride
- EDTA
  - Stable as Dry Chemical and Prepared Reagent

Cadmium Reduction

Summary

Pros

- Approval
- Wide Application
- Few Interferences
- Chemical Stability
- Documentation

Cons

- Cadmium Safety
- Cadmium Column Preparation
- Additional Hardware

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Hydrazine Reduction

Hydrazine Reduction

Approvals

- EPA (NPDES)
  - SM 4500-NO_3^- H-2000

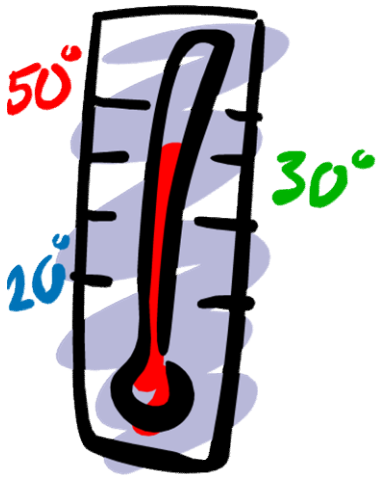
Applications

- Surface
- Domestic
- Industrial

Hydrazine Reduction

Hardware Requirements

- Heating



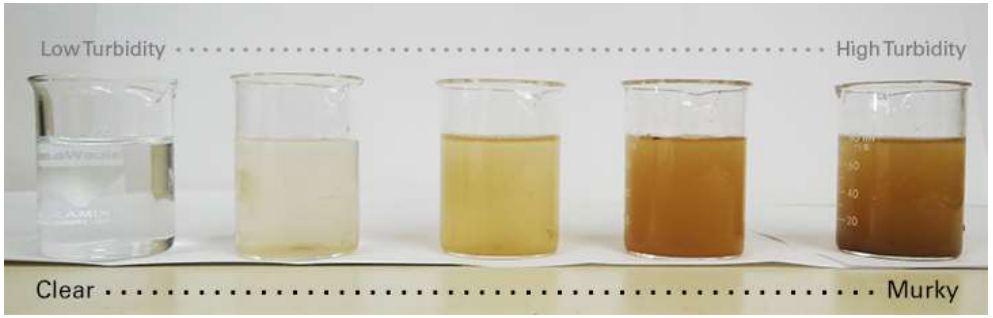
User Requirements

- Hydrazine Optimization

Hydrazine Reduction

Interferences

- Sulfide
  - 10% Nitrate and Nitrite Concentration Variations
- Turbidity
  - Filter Prior to Analysis
- Saline Samples



Hydrazine Reduction

Chemical Requirements

- Hydrazine Sulfate
  - Toxicity
  - Liquid Waste Product
  - Cost Effective
- Copper Sulfate
- Sodium Hydroxide
  - Handle with Care

Things to Consider

- Hazard
- Cost
- Storage
- Stability

Hydrazine Reduction

Summary

Pros

- Approval
- Minimum Hardware Requirements

Cons

- Not Applicable to Saline Waters
- Hydrazine Safety
- Hydrazine Concentration Optimization

Vanadium(III) Chloride Reduction

Vanadium(III) Reduction

Approvals

- EPA (NPDES & NPDWR)
  - Easy (1-Reagent) Nitrate Method, Revision November 12, 2011

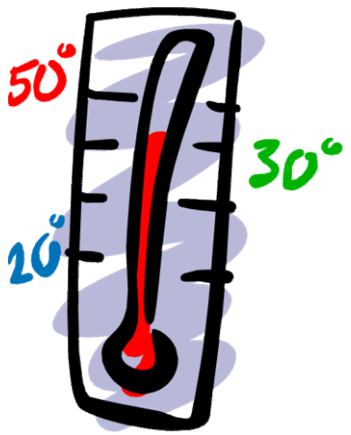
Applications

- Drinking
- Surface
- Domestic
- Industrial

Vanadium(III) Reduction

Hardware Requirements

- Heating
  - Capable of Heating to 80° C
  - Lower Temperature Heating Lengthens Reduction Period



Interferences

- Residual Chlorine
  - Sodium Thiosulfate
- Turbidity
  - Filter Prior to Analysis
- Sulfate, Phosphate
  - Concentrations Above 100 ppm May Reduce Reduction Efficiency

Vanadium(III) Reduction

Chemicals

- Vanadium(III) Chloride
  - Toxicity
  - Easily Oxidized
  - Liquid Waste Product
  - Moisture and Light Sensitive
- HCl

Things to Consider

- Hazard
- Cost
- Storage
- Stability

Vanadium(III) Reduction

Summary

Pros

- Approval
- Few Interferences

Cons

- Not Applicable to Saline Waters
- Vanadium(III) Chloride Safety
- Extended Reduction Time

Enzymatic Reduction

Enzymatic Reduction

Approvals

- ATP Accepted
  - USGS I-2547-11 and USGS I-2548-11
  - The Nitrate Elimination Company, Inc. Method N07-0003
- Method Update Rule – Proposed
  - Submitted for Approval

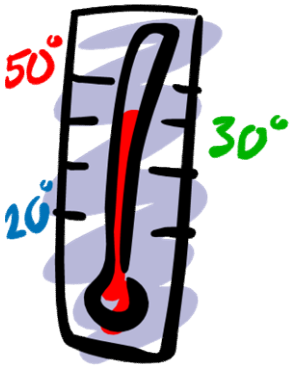
Applications

- Saline
- Drinking
- Surface
- Domestic
- Industrial

Enzymatic Reduction

Hardware Requirements

- Heating
- Reagent Cooler



User Requirements

- Manual Addition of Nitrate Reductase

Enzymatic Reduction

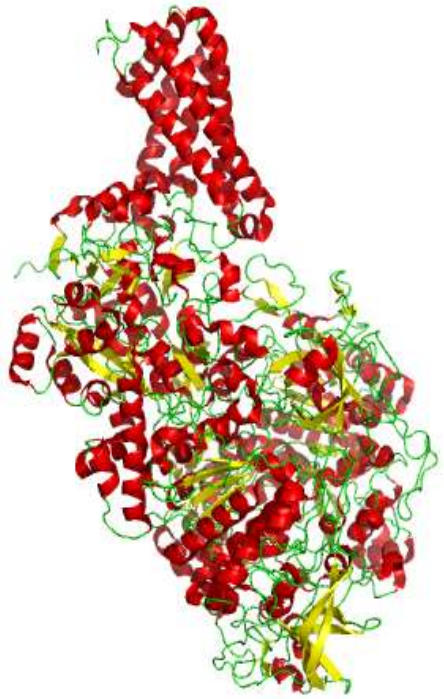
Interferences

- Turbidity
  - Filter Prior to Analysis
- Metal Ions
  - EDTA in Approved Method
- Sulfate, Chloride, Bromide
  - High Concentrations May Reduce Nitrate Recovery
- NADH
  - Interference in Griess Reaction

Enzymatic Reduction

Chemicals

- EDTA
  - Stable as Dry Chemical and Prepared Reagent
- Potassium Phosphate
  - Skin and Eye Irritant
- Potassium Hydroxide
  - Respiratory Irritant
- Nitrate Reductase and NADH
  - Non-Hazardous
  - Prepared Stable for 8 Hours
  - Prepared Reagent Volume of 20 mL



Enzymatic Reduction

Summary

Pros

- Chemical Safety
- Wide Application
- Minimal Hardware Requirements

Cons

- Approval
- Chemical Cost and Stability
- Extended Reduction Time

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	Cadmium	Hydrazine	Vanadium	Enzymatic
Approval	NPDES, NPDWR	NPDES	NPDES, NPDWR	ATP only
Applications	Waste, Drinking, Surface, Saline	Waste, Surface	Waste, Drinking Surface	Waste, Drinking, Surface, Saline
Hardware	Coil/Column Switching Valves	Heater	High Temperature Heater	Heater
Reagent Price	$	$	$$	$$$$
Reagent Stability	Very Stable	Very Stable	Stable	Unstable - made daily
Safety - Human	Carcinogen Mutagen Acute Toxicity	Carcinogen Irritant Acute Toxicity	Corrosive Eye Damage Acute Toxicity	Corrosive Irritant
Safety - Environmental	Toxic - but generally not in sample waste	Toxic	Non-Toxic	Safe