



World Leader in Sample Preparation, Segmented Flow and Discrete Analyzer Technology





# Total Kjeldahl Nitrogen Colorimetric Testing for Discrete and Segmented Flow Analyzers

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## Topics for Discussion

- Method Principle
- Digestion Protocol
  - Temperature
  - Digestion Block
  - Acid and Salt Content
  - Catalysts
  - Interferences



## **Topics for Discussion**

- Colorimetric Detection
  - Distillation Requirements
  - Reagents
  - Interferences
  - pH and Matrix Matching
  - Synthetic Diluent





#### Method Principle

- TKN and Ammonia Colorimetric Reaction
- Hypochlorite
  - Ammonia + Hypochlorite  $\rightarrow$  Monochloramine
  - pH < 12
- Salicylate
  - Monochloramine + Salicylate  $\rightarrow$  Indosalicylate

#### Nitroferricyanide

Catalyst





#### **TKN Digestion Protocol**

#### SEAL Analytical

#### **TKN Digestion Protocol**

- TKN is Measured as Ammonia by Colorimetric Analysis
- TKN Converts Organic Nitrogen to Ammonia
  - Sulfuric Acid
  - Potassium Sulfate
  - Heat to 380°C
  - Catalyst
- Troubleshooting Digestion Protocol
  - Incomplete Digestions
  - Sample Acidity Level





#### Temperature

- Potassium Sulfate Increases the Boiling Point to 380°C
  - Insures all Compounds Decomposed
  - Decreases Time Required for Digestion
- Evaporation Step in Protocol
  - Reduces Sample Volume Prior to Temperature Increase
  - Decreases Potential for Splatter
  - Final Volume
  - Example:

Step to 160°C and Hold for 30 min Step to 190°C and Hold for 30 min Approximately 5 mL Final Volume





# **TKN Digestion Block** Draft Shield **Digestion Block** Controller



#### **TKN Digestion Block**

#### • Temperature

- Stability Across the Block
- Flat Plate Heating and Graphite Rod Heating
- Final Sample Volume and Acidity Level



#### Acid to Salt Content

- Samples with High Salt Content
  - Brines and Inorganic Salts
  - Loss of Nitrogen Above 400°C
  - Approximately 1 mL Sulfuric Acid per 1 g Salt Recommended
- Salt Crystallization
  - Adjust Flow Rate of Exhaust System
  - Adjust Acid Concentration





#### Reconstitution

- Cooling
  - Acid Volume Remaining in Digestion Tube
  - DI Water Addition
  - Cool Digestion Tubes
  - Reconstitute
- Dispense Accurately
  - Bottle Top Dispenser or Auto-Pipette
  - Samples and Standards Same Final Volume
  - Volumetric Digestion Tubes
- Vortex Mixer





#### Catalysts

- Mercury
  - Documentation
  - Reproducibility
  - Colorless Digest
  - Preparing Digestion Reagent
  - Toxic
  - Waste Disposal Considerations
- Copper
  - Substitute for Mercury Catalyst
  - Blue/Green Final Digest
  - Less Toxic Alternative







#### Interferences

- High Salt Content
  - Acid to Salt Ratio
  - Boiling Point
  - Nitrogen Loss
- High Nitrate and Nitrite
  - Excess of 10 mg/L
- Organic Matter
  - Consumption of Acid
  - Digestion Tube Considerations





#### **TKN Colorimetric Reaction**

#### Distillation Requirements

- Distillation
  - EPA Requirements
  - 40 CFR 136.3
  - Sample pH
- Automated Colorimetric Detection
  - Strong Buffer
  - Sample pH
  - Conversion from Ammonium to Ammonia
  - Buffer Aids in Colorimetric Reaction





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#### Reagents

- Stability
- Storage
- Preparation
- Additional Considerations





# Sodium Hypochlorite

- Purchased Reagents
  - Expiration Dates
- Bleach Stable 1 Month if Opened
  - Store in Refrigerator
  - Sodium Hypochlorite Volatizes in Heat
- Solution is Unstable
  - Chlorine Evaporates if Exposed to Air
  - Reduced Free Chlorine Concentration
  - DCI Stable 1 Day in Solution



### **TKN Buffer Solution**

- EDTA or Sodium Potassium Tartrate
- Store at Room Temperature
- Extended Shelf Life
- pH Adjustments



#### Sodium Potassium Tartrate

- Ammonia Contamination
- Alkaline Boil for 1 Hour
- Adjust pH between 7 and 8
- Purchase from Vendor
- Stable 6 Months in Solution





#### Salicylate

- Refrigerate and Store in Amber Bottle
- Stable 1 Month
- Filtration
- Precipitates in Acidic Conditions





#### Nitroferricyanide

- Stable for 1 Month
- Discard if Blue in Color
- Included in Salicylate Reagent





#### Interferences

- Calcium and Magnesium
  - Precipitation
  - Addition of EDTA or Sodium Potassium Tartrate
- Turbidity or Color
  - Gas Diffusion Membrane
  - Filtration





#### pH and Matrix Matching

- Testing Reaction pH
  - Salicylate Reagent
  - pH 12.6 to 13.1
  - Segmented Flow Testing
  - Discrete Analyzer Testing
- Adjusting pH
  - Hypochlorite Solution
  - Addition of NaOH





#### pH and Matrix Matching

#### • Preserved Samples

- Adjustments in the Buffer Solution
- Some Methods Include Modification
- Matrix Matching
  - Sample Preservation
  - Digestion Catalyst
  - Synthetic Diluent





#### Synthetic Diluent

- Prepare Solution with Matching Acidity Level as Digest
- Test for Organic Nitrogen Contamination in Digestion
- Addition of Copper Sulfate
- Troubleshoot
  - pH
  - Linearity
  - Contamination







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