

# Determination of Total Nitrogen in Wastewater by Steam Distillation





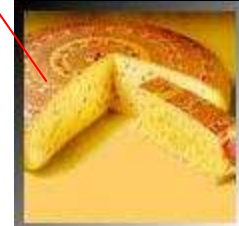
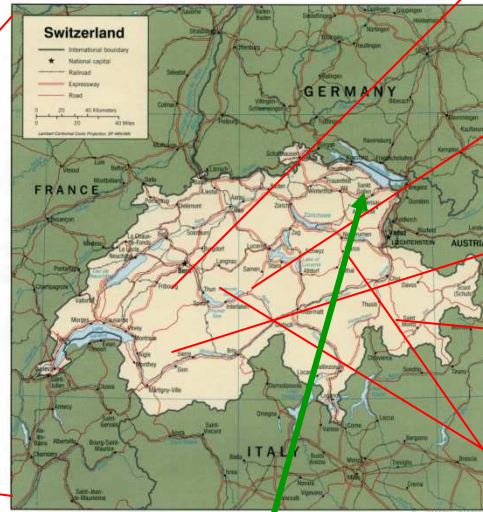
**Bill Ickes**  
**Product Manager Kjeldahl and Extraction**  
**Buchi Corporation**

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**Regional Sales Manager**  
**Buchi Corporation**

# Who is Buchi Corporation?



1996 MAOELLAN Geographical Systems, Bakers, CA 805 685-3100



# Buchi Headquarters



**Flawil  
Switzerland**



# Buchi Corporation



- Rotavapor®
- Parallel Evaporation
- Industrial Evaporation
- Kjeldahl Solutions
- Extraction Solutions (Soxhlet, Hot, Pressurized)
- Spray Drying
- Melting Point Determination
- Flash and Preparative Chromatography
- Near Infrared Spectroscopy
- Vacuum Pumps
- Chillers

# Buchi Corporation USA



- Direct Affiliate
- New Castle, DE
- 37 Employees Representing Sales, Marketing, Technical Support, Service, and Warehouse Activities

# Content

**BUCHI**

- Introduction to Total Nitrogen Analysis
- Introduction to the Kjeldahl Method
- Step I: Digestion
- Step II: Distillation
- Step III: Titration
- Calculation of Total Nitrogen
- Other Steam Distillation Analysis
- Summary

# Introduction to Analysis of Total Nitrogen



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# What is Total Nitrogen?

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- Ammonia (Volatile Gas)
- Ammonium Salts (Ex. Ammonium Sulfate)
- Organic Nitrogen (Derived from Protein, Urea, Nucleic Acids, etc.)
- Nitrates
- Nitrites

# Why Analyze for Total Nitrogen?

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- Good Indicator of Water Quality
- Clues to Nitrogen Source
- Comparison Between Influent and Effluent Waste Water
- Determines Waste Water Treatment Efficiency

## Differences in Analysis

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- **Ammonia** – Direct steam distillation of sample with no addition of NaOH
- **Ammonium Salts** – Direct steam distillation of sample with addition of NaOH
- **Organic Nitrogen** – Digestion, Distillation, and Titration by Kjeldahl Method
- **Nitrates/Nitrites** – Digestion, Distillation, and Titration by Kjeldahl Method with the addition of Devarda's Alloy prior to distillation

# Introduction to the Kjeldahl Method

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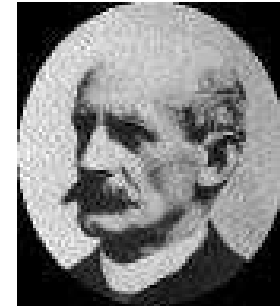


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# Who was Kjeldahl?

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Johan Kjeldahl 1849 – 1900



1849 born in Denmark

1867 graduation from university

1876 Scientist at Carlsberg Breweries

- ✓ Fermentation studies
- ✓ Development of a method for exact determination of nitrogen in animal and vegetable material
- ✓ Research on carbohydrates in barley and malt

1883 Publication of the Kjeldahl method

# Principle Kjeldahl Method

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1.  
Digestion

Conversion of  
Protein-  
Nitrogen to  
 $\text{NH}_4^+$

2.  
Distillation

Separation of  
 $\text{NH}_3$

3.  
Titration

Measure of  
the Amount of  
Acid that was  
neutralised by  
 $\text{NH}_3$

## Step 1: Digestion

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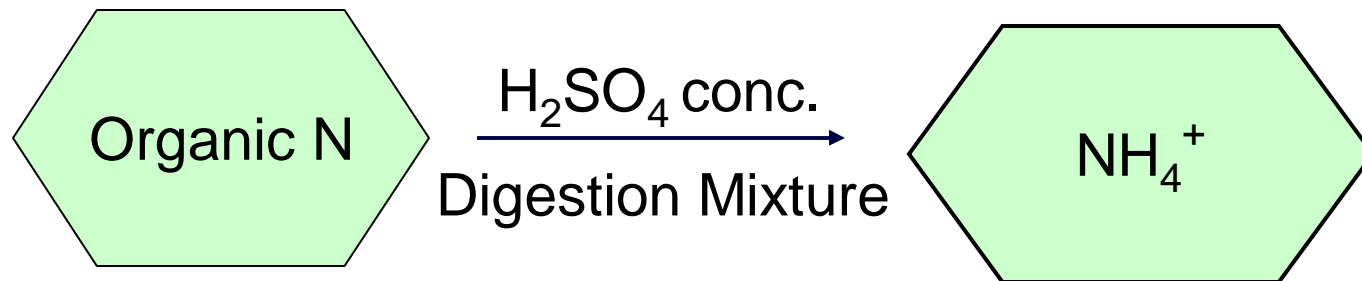
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# Digestion

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Target of digestion:

- Breakage of organic bonds
- Conversion of Nitrogen to Ammonium



# Digestion Mixture

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- Digestion mixture is a mixture of
  - a salt (i.g. potassium or sodium sulphate)
  - and a catalyst (Hg, Se, Cu or Ti)
- Reason for addition of digestion mixture  
Increasing of the digestion temperature  
→ faster and more efficient digestion

Important for reproducible results:  
Ratio of sulphuric acid and digestion mixture

Ideal proportion: 20ml/10g

# Ratio

## Sulphuric Acid – Digestion Mixture



The ratio sulphuric acid – digestion mixture defines the boiling point of the sulphuric acid

Ideal digestion temperature: 370°C

Quantity H <sub>2</sub> SO <sub>4</sub>	Quantity K <sub>2</sub> SO <sub>4</sub>	Boiling point	Remarks
20 ml	--	330 °C	pure H <sub>2</sub> SO <sub>4</sub>
20 ml	5 g	350 °C	
20 ml	10 g	370 °C	optimal digestion temp.
20 ml	15 g	390 °C	already first nitrogen loss

# Summary Digestion (I)

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## Sample Homogenisation, Weighing and Addition of Reagents

Sample

2 tabs of Catalyst

Sulphuric acid

1.072

Blank

**Weigh sample**

- 1 g of dry organic material (homogeneous)

**Add reagents**

- 10 g or 2 tabs of Kjeldahl catalyst mixture
- 20 ml of  $H_2SO_4$

**Sample Blank**

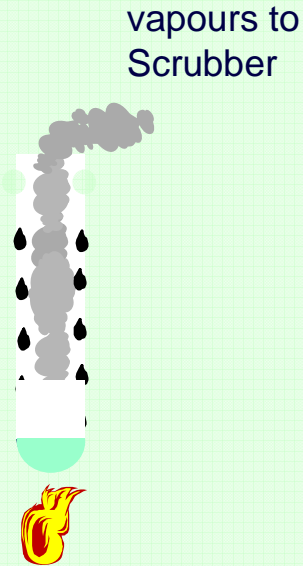
- add everything except sample

Digestion

# Summary Digestion (II)



## Digestion



## Digestion

- digest at 370 °C for 90 min or until the mixture is clear (green / blue color) + 30 min

Digestion

## Step 2: Distillation

## Step 3: Titration

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# Pre-Distillation Steps



- 1) Cooling  
Digested sample is cooled down to RT
- 2) Dilution  
Digested sample is diluted with deionised water
- 3) Preparation of receiving vessel  
Receiving solution necessary to capture volatile ammonia

# Preparation of Receiving Vessel (I)



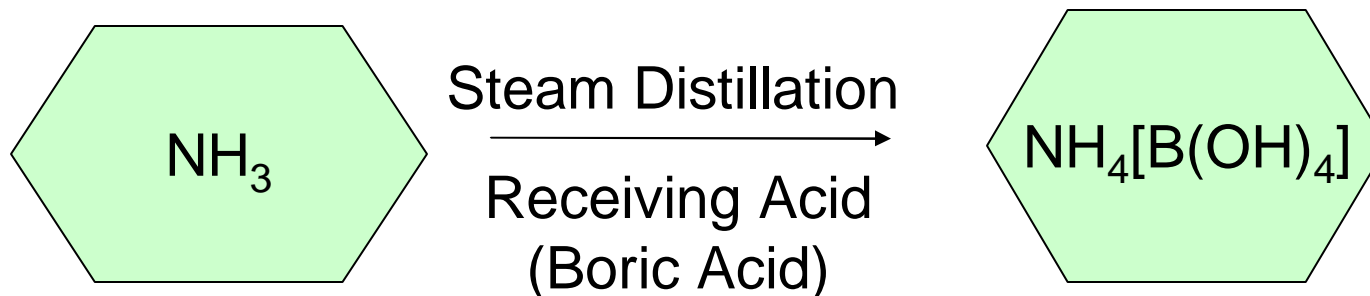
- Reason for receiving vessel:  
Ammonia is volatile -> has to be captured in receiving solution
- Possibilities for receiving solutions:  
Boric acid solution (2% or 4%)  
Mineral acid standard solution (HCl or H<sub>2</sub>SO<sub>4</sub>)

## Preparation of Receiving Vessel (II)

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Recommendation for Kjeldahl determination:  
Boric Acid 4%

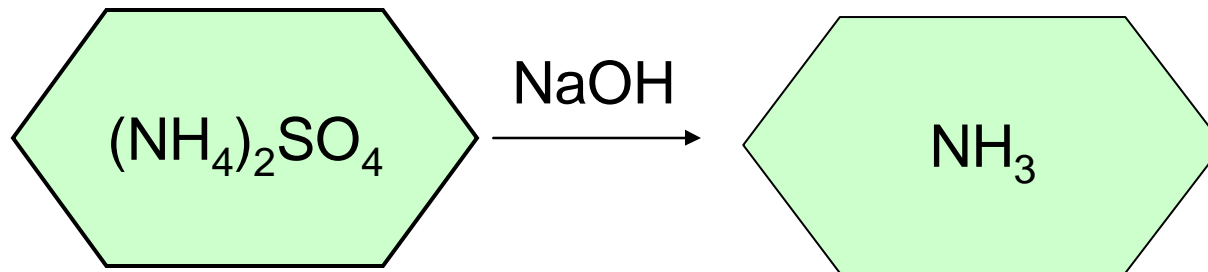
- Easier handling
- No risk of too low capacity to capture all  $\text{NH}_3$
- Method of most official methods



## Distillation: Addition of NaOH

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Target of addition of NaOH:  
Release of ammonia in the form of  $\text{NH}_3$



# Titration

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- Possibilities of titration methods
  - potentiometric titration (pH)
  - visual titration (colour)
  - colorimetric titration (absorbance)

## Recommendation for Kjeldahl determination: Potentiometric titration

- Advantages potentiometric titration:
  - more precise than visual and colorimetric titration
  - more robust than colorimetric titration  
(colorimetric titration is very susceptible)

# Potentiometric Titration

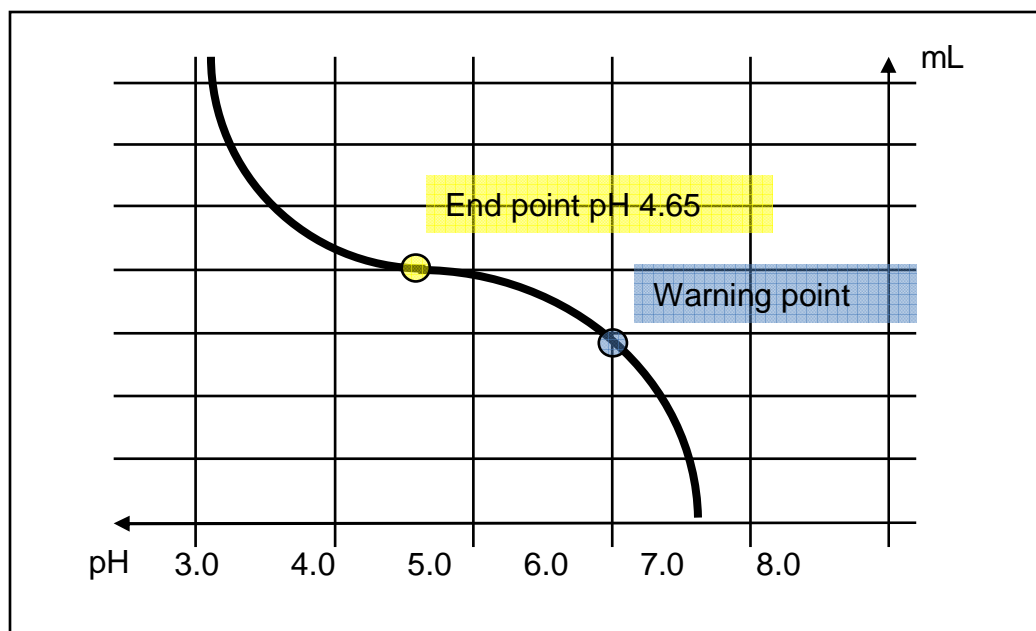


Points to consider:

- Initial pH of the boric acid should be 4.65
- Endpoint of the titration should be pH 4.65

Reason:

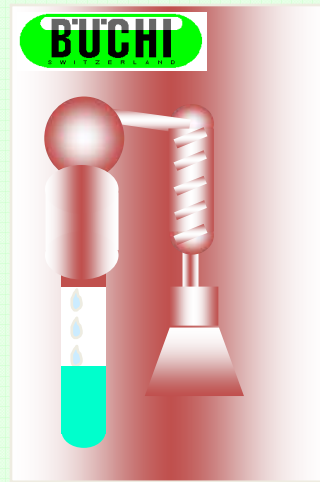
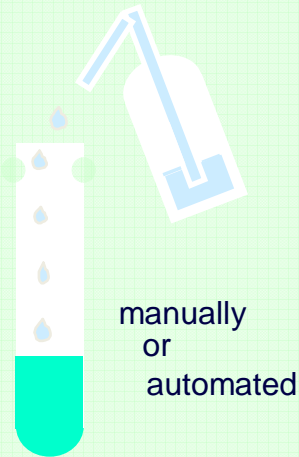
- pH 4.65 is turning point of the titration curve



# Summary Distillation / Titration (I)



## Dilution



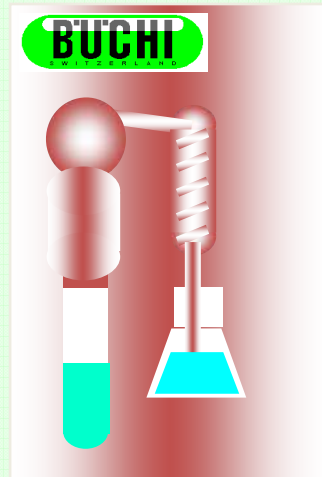
## Dilution

- dilute the cooled digestion solution with 50 ml deionised water

# Summary Distillation / Titration (II)



## Preparation of Receiver



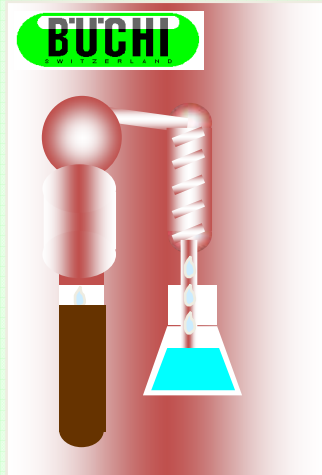
### Boric acid titration

- add 60 ml of Boric acid 4%
- add 2 to 3 drops of indicator according to Sher

# Summary Distillation / Titration (III)

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## Neutralisation and Distillation



### **Sodium hydroxide**

- add 90 ml of NaOH 32% to the diluted digestion solution

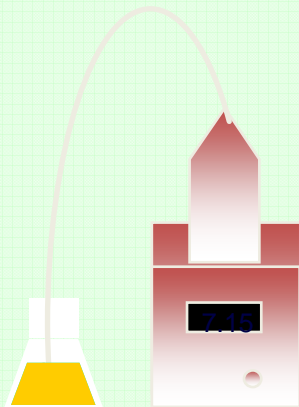
### **Distillation**

- distill for 4 min.

# Summary Distillation / Titration (IV)



## Titration



### **Boric acid titration**

- titrate the condensate with sulphuric acid standard solution (0.5 N or equivalent) to the end point of pH 4.65

# Calculation



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# Calculation



$$\% \text{ N} = \frac{(\text{Consumption-Blank}) \times 1.4007 \times n \times 100}{\text{Sample Size}}$$

$$\% \text{ P} = \frac{(\text{Consumption-Blank}) \times 1.4007 \times n \times \text{PF} \times 100}{\text{Sample Size}}$$

1.4007: 1 ml 0.1 N Volumetric Solution = 1.4007 mg N

n: Normality Acid

PF: Protein factor N → Protein  
(e.g. 6.25; Milk Sample 6.38; Nuts 5.4)

## Other Methods of Analysis w/ Steam Distillation

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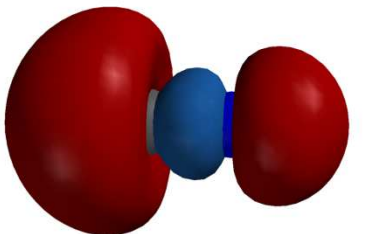
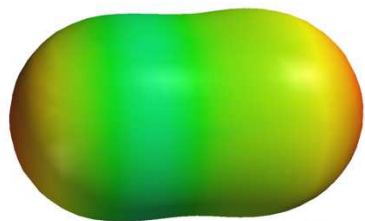
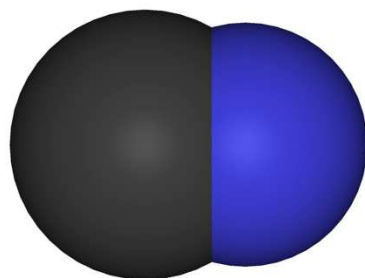
# Analysis Using Steam Distillation



- Cyanides
- Phenols
- Volatile Acids

# Cyanide Determination

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## **Method Reference: EPA Method 9010 C/335.2**

Determination of Free Cyanide and Weak Acid  
Dissociable Cyanide In Waste Water

# Why Analyze For Cyanide?



- One of Nature's Toxic Substances

# Sources of Cyanide?



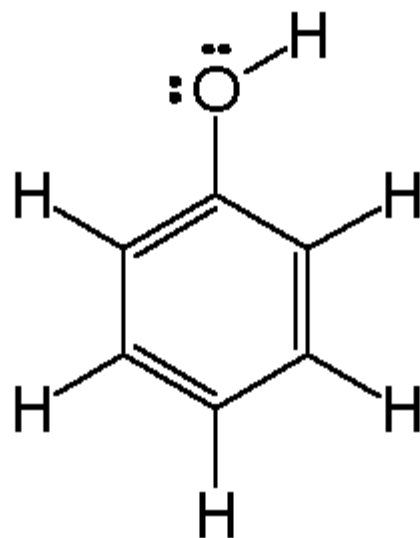
- Metal Finishing
- Photographic Bleaching
- Galvanic Industry Waste Water

## How is Cyanide Analyzed?

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- Steam distillation with strong acid
- Collected in a receiving solution of NaOH
- Cyanide concentration determined colorimetrically at 578nm

# Phenol Determination





## **Method Reference: EPA Method 9065**

Determination of Phenolic Material by  
Spectrophotometric 4-aminoantipyrine Method

# Why Analyze for Phenols?

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- Phenolic compounds are commonly found in sludge
- Phenolic compounds can be traced to different contamination sources

# Sources of Phenols?



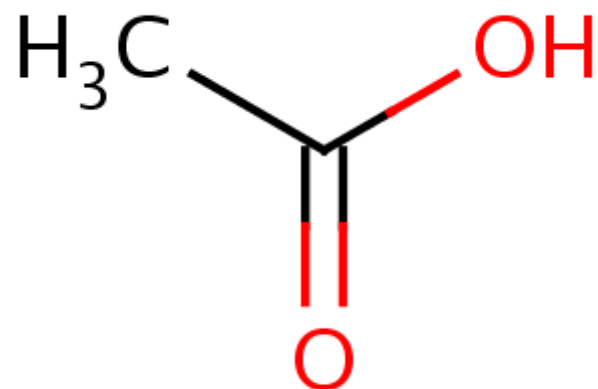
- Plant Material
- Chemical Industry Processes
- Wood Processing
- Plastic Processing

## How are Phenols Analyzed?

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- Steam distillation in the presence of acid
- Collected in water in the receiving solution
- Photometric measurement of the receiving solution

# Volatile Acids Determination





# **Method Reference: Buchi Application Note K-355.004 Version A**

Determination of Volatile Acids in Sludge

# Why Analyze for Volatile Acids?

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- Ratio of volatile acids -> total alkalinity content in sludge submitted to anaerobic conditions is a good index of process performance inhibition

# Source of Volatile Acids?



- Acetic Acid

# How are Volatile Acids Analyzed?



- Steam Distillation
- Titration

# Questions?

