Improve Lab Accuracy for Better Water Analysis

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Standard Methods Manager
American Water Works Association

Nathan oversees and manages the electronic and print production of Standard Methods for the Examination of Water and Wastewater and is in charge of a majority of the AWWA chemical standards committees. Nathan received his Bachelor of Science Degree in Chemistry from the University of Arizona.
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Panel of Experts

Jessica McVay  
Technical Support Specialist  
Metrohm USA

Lori Spafford  
Titration Product Manager  
Metrohm USA
I. What is Titration?  Jessica McVay

II. More on Endpoint Detection  Jessica McVay

III. What’s the Big Difference?—Buret Titration vs. Autotitration  Lori Spafford

IV. Application Tips & Tricks  Lori Spafford

V. So Many Samples, So Little Time  Lori Spafford

Ask the Experts

Jessica McVay  Metrohm USA

Lori Spafford  Metrohm USA

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Rationale & Objectives

• Firm up titration and electrode fundamentals

• Understand how autotitration can improve accuracy

• Overview of common water analysis tips and tricks

• Hear about technology improvements for colorimetric titration and high-throughput laboratory needs

• Identify potential areas of improvement in your lab operations

Today’s Topics

• Review fundamentals of titration

• Understand how electrodes work

• Getting better results from colorimetric titrations

• Common water analysis tips & tricks

• Improving throughput with a new concept in automation

• Live question and answer
What is Titration?
Fundamental review

What is titration?

Start

Endpoint

Finish

Titrant – reagent with known concentration

Analyte – unknown in sample
What was titration?

- Manual additions made by glass buret
- Manual control controlled by analyst
- Optical detection for visual confirmation the endpoint has been reached

Challenges of Manual Titration

- Need a neutral background
- Visibility of indicator in colored samples
- Consistent decision making between analysts
- Careful data recording and calculation

Even an experienced bench chemist can require 5 minutes per titration
What is titration now?

• Advanced dosing, titrating, and liquid handling

• Sophisticated measuring sensors

What is titration now?

• Thorough data evaluations and management

• Secured user administration
Endpoint Detection

• Different ways to detect
  • Color change
  • mV change
  • Temperature change

• Some of the challenges
  • Color change is subjective between analysts
  • Hanging burets are difficult to read
  • Manual calculations subject to human error

More on Endpoint Detection

How do electrodes work?
Measurements with Electrodes

Definition

• An electrode which produces a voltage dependent (logarithmically) on the concentration of a selected substance.

  • ISE e.g. H (pH electrodes)
  • ISE e.g. F, Cl, Cu, Pb, Surfactant
  • Redox Electrodes
  • Metal Electrodes e.g. Ag, Pt

Potentiometric Measurement

What is needed?
1. Measuring electrode
2. Reference electrode
3. pH/voltmeter meter
4. Sample

Measuring principle:
Measurement of potential differences
Combined Electrode Systems

How can I tell what type of electrode system I have?

Fill port & glass bulb

Closer Look at Combined Electrodes

electrode head
refilling opening
glass shaft
electrode tip
Ag/AgCl cartridge
diaphragm
glass membrane
Membrane Layers

- pH glass electrode responds to H⁺ ions in solution

![Diagram of Membrane Layers]

Same Function, Different Shapes

- Ball (12 mm) Titration
- Needle (4 mm) Measurement
- Half ball (12 mm) Titration
- Micro cylinder (3 mm) Measurement
- Cylinder Measurement/Titration
- Flat membrane Measurement/Titration
Reference Diaphragm

- Electrolyte solution must be in contact with sample solution
  - Outflow of electrolyte due to simple hydrostatic pressure
  - Fill port must be open for this to occur

- Outflow too low (A)
  - Contaminate reference

- Optimal outflow (B)
  - Must refill electrode regularly

Why is calibration needed?

- Electrode response is a mV signal
- The mV needs to be correlated to a pH value
- The factors that influence this relationship are slope and zero point (intercept)
Why is calibration needed?

• Aging of the glass membrane of the sensor or blockage of the diaphragm
• Change of electrode zero point and slope
• Meter is adapted by calibration to the actual characteristics

Calibration should be done frequently

Color Changing Titrations Need an Optical Sensor

• Think hardness titrations

• Optrode sensor detects color-changing endpoints

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>For Color Change To</th>
<th>Useable Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>470</td>
<td>Yellow</td>
<td>460 – 480</td>
</tr>
<tr>
<td>502</td>
<td>Orange/Red</td>
<td>485 – 520</td>
</tr>
<tr>
<td>520</td>
<td>Red</td>
<td>505 – 535</td>
</tr>
<tr>
<td>574</td>
<td>Violet/Purple</td>
<td>560 – 585</td>
</tr>
<tr>
<td>590</td>
<td>Blue</td>
<td>575 – 605</td>
</tr>
<tr>
<td>610</td>
<td>Blue/Green</td>
<td>595 – 625</td>
</tr>
<tr>
<td>640</td>
<td>Green</td>
<td>620 – 655</td>
</tr>
<tr>
<td>660</td>
<td>Black/Turbid</td>
<td>650 – 670</td>
</tr>
</tbody>
</table>
How the Optrode Works

• Choose correct wavelengths

• Connect directly to titrator

• Sample solution passes through optical window

• Signal converted to mV reading and is graphed like traditional potentiometric titration

What’s the big difference?
Manual buret titration vs. autotitration technology
What Matters the Most

• Achieve accurate results
• Perform repeatable analysis
• Reduce or remove human error

Achieving Accurate Results

<table>
<thead>
<tr>
<th>Manual Titrations</th>
<th>Autotitrator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buret increment limitations</td>
<td>Precise buret increments</td>
</tr>
</tbody>
</table>

Please consider the environment before printing.
Achieving Accurate Results

<table>
<thead>
<tr>
<th>Manual Titrations</th>
<th>Autotitrator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manual control of titration speeds</td>
<td>Controlled, dynamic titration speeds</td>
</tr>
</tbody>
</table>

Performing Repeatable Analysis

<table>
<thead>
<tr>
<th>Manual Titrations</th>
<th>Autotitrator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visual decision making</td>
<td>Absolute potential measurements</td>
</tr>
</tbody>
</table>
Performing Repeatable Analysis

<table>
<thead>
<tr>
<th>Manual Titrations</th>
<th>Autotitrator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endpoint volumes read by analyst</td>
<td>Precise endpoint volumes reported by instrument</td>
</tr>
</tbody>
</table>

- Example Scenario: Data trending between shift operators
Reducing Human Error

<table>
<thead>
<tr>
<th>Manual Titrations</th>
<th>Autotitrator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Over titration</td>
<td>Endpoint is never missed</td>
</tr>
</tbody>
</table>

Reduction of human error

<table>
<thead>
<tr>
<th>Manual Titrations</th>
<th>Autotitrator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manual data recording, calculations, &amp; data entry</td>
<td>Digital data collection, automatic calculations &amp; LIMS upload</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Conductivity mS</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>tap water</td>
<td>0.547</td>
<td>7.66</td>
</tr>
<tr>
<td>tap water</td>
<td>0.546</td>
<td>7.53</td>
</tr>
<tr>
<td>tap water</td>
<td>0.549</td>
<td>7.57</td>
</tr>
<tr>
<td>tap water</td>
<td>0.557</td>
<td>7.69</td>
</tr>
</tbody>
</table>
Application Tips & Tricks

Make Lab Analysis Easier!

Common Titration & Ion Analysis

- pH Measurement
- Conductivity
- Alkalinity
- Chlorine
- Total Hardness
  - Calcium, Magnesium Hardness
- Ammonia
- Chloride
- Fluoride
- Sulfide
- ...

Please consider the environment before printing.
pH Measurement & Alkalinity Titration

• Requires electrode calibration
  • Check slope, measure pH buffer

• Proper electrode storage ensures electrode responds quickly
  • Fill port closed
  • Electrode stored in storage solution – not water, buffer solution or electrolyte!

pH Measurement & Alkalinity Titration

• If required to perform hydroxide, carbonate and bicarbonate alkalinity calculations – automate as much as possible!

<table>
<thead>
<tr>
<th>Titration Result</th>
<th>Hydroxide Alkalinity</th>
<th>Carbonate Alkalinity</th>
<th>Bicarbonate Alkalinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>P = 0</td>
<td>0</td>
<td>0</td>
<td>T</td>
</tr>
<tr>
<td>P &lt; 1/2T</td>
<td>0</td>
<td>2P</td>
<td>T-2P</td>
</tr>
<tr>
<td>P = 1/2T</td>
<td>0</td>
<td>2P</td>
<td>0</td>
</tr>
<tr>
<td>P &gt; 1/2T</td>
<td>2P – T</td>
<td>2(T – P)</td>
<td>0</td>
</tr>
<tr>
<td>P = T</td>
<td>T</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Can all be programmed into titration software
Hardness Titration

• Hardness Titration
  • Applies to EPA 130.2 and SM 2340C
  • Complexometric titration using EDTA and color indicator

• Challenges come with identifying the endpoint
  • Color change is subjective
  • Makes reproducibility difficult
  • Colorblind?

Hardness Titration with the Optrode

• Using an optical sensor set to 610nm

• Typical titration curve below where endpoint is precisely identified

• Can automate titration, now!
Ammonia Using an Ion-Selective Electrode

- Measured potentiometrically using an ion-selective electrode
  - EPA 350.3

- Combined electrode
  - Measuring and reference electrode in one system
  - Gas-permeable, hydrophobic membrane that separates the sample and the measuring electrolyte (<1% NH₄Cl)

Review Ammonia Chemistry

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-
\]

- Excess strong base (NaOH) converts all NH₄ to NH₃
- Dissolved NH₃ gas diffuses through membrane causing a mV change until partial pressure is identical
- Potential change is proportional to NH₃ in sample
Ion-Selective Electrode Care for Ammonia

- Rinse electrode after every measurement

- Condition in DI water for up to ~10 minutes between samples
  - Low-level samples (<1 mg/L) may require up to 30 minutes

- Store properly
  - For 1-5 days: Store electrode in 0.1M NH₄Cl
  - For >5 days: Store dry

---

Ion-Selective Electrode Care for Ammonia

- Before first measurement or after longer storage in dry state
  - Soak inner glass electrode for 6-12 hours in pH 7 buffer

- After electrode has been fitted with new membrane
  - Shake gently to remove any air bubbles from membrane
  - Soak for 10 minutes in DI water
Tips for Better Ammonia Measurements

• Low-level samples will require more time to equilibrate

• High-level samples may require dilution because ammonia dissipates into the air

• Insert electrode into sample before adding hydroxide

• Drifting potential could mean:
  • Membrane is damaged
  • Wrong electrolyte
  • Concentration >1 mol/L
  • Temperature fluctuations

So Many Samples, So Little Time
New Innovations in Sample Throughput
Challenges for High-Throughput Labs

- Short hold times
- Fast turnaround
- Emergency/priority samples
- Large batch sizes
- Multiple analysts required over multiple shifts

Solutions for Increasing Sample Throughput

**Dedicated Analyzer**

- Routine analysis

- Automated QC
  - Blanks, duplicates, spikes
  - Standards

- Hands free, walk-away analysis

- Frees you up for other tasks!
Solutions for Increasing Sample Throughput

Multi-Parameter Analyzer

• Combine several analytes into one system
  • pH, Alkalinity, Conductivity, Hardness
  • Ammonia, Fluoride

• Space saving

• Simplified data handling

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>pH</th>
<th>Alkalinity</th>
<th>Total Hardness</th>
<th>Ca Hardness</th>
<th>Mg Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.66</td>
<td>126.9</td>
<td>257.96</td>
<td>199.76</td>
<td>57.00</td>
</tr>
<tr>
<td>2</td>
<td>7.59</td>
<td>136.5</td>
<td>257.46</td>
<td>199.28</td>
<td>58.12</td>
</tr>
<tr>
<td>3</td>
<td>7.57</td>
<td>136.2</td>
<td>257.08</td>
<td>199.12</td>
<td>57.96</td>
</tr>
<tr>
<td>4</td>
<td>7.59</td>
<td>132.7</td>
<td>256.96</td>
<td>195.47</td>
<td>58.42</td>
</tr>
<tr>
<td>5</td>
<td>5.03</td>
<td>60.0</td>
<td>66.87</td>
<td>46.00</td>
<td>13.27</td>
</tr>
<tr>
<td>6</td>
<td>5.02</td>
<td>60.0</td>
<td>66.85</td>
<td>46.58</td>
<td>13.47</td>
</tr>
</tbody>
</table>

Expandable Analyzers

• Completely expandable and designed to grow with the needs of your laboratory

• From 18 to 175 samples

• Automate up to 4 analysis (different or same!) simultaneously
Summary

• Titration can be improved by converting manual titrations to autotitrations

• Understanding how electrodes work improves troubleshooting practices

• Proper storage and calibration of electrodes is critical to ensuring accurate titration data

• Add a sample changer can improve repeatability, automate QC, reduce re-analysis and free up analysts to perform other tasks

Need Additional Information

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Presenter Biography Information

Lori Spafford is the Product Manager for Titration for Metrohm USA. She has a Bachelor’s Degree in Chemistry from St. Joseph’s College in Indiana and over 10 years of experience in the chemical, food and beverage, and environmental industries. During her prior three years as an Applications Chemist at Metrohm USA, she has focused on the development of thermometric titration and has successfully brought innovative solutions to difficult applications in a variety of industries.

Jessica graduated with a Bachelor of Science Degree in Forensic and Toxicological Chemistry from West Chester University of Pennsylvania. After graduating, her career started in the pharmaceutical industry as a QC chemist. She then moved to Florida to continue her career as an R&D chemist, developing new methods for generic drugs. At Metrohm USA, she is a technical support specialist. She uses her technical skills to help customers troubleshoot their instruments and/or software when they are in need of assistance.

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