

ThermoFisher
S C I E N T I F I C

The world leader in serving science

How Green Is Your Lab?

Environmentally-Friendly Developments
in pH and Ion Analysis

How Green Is Your Lab?

- About Thermo Fisher Scientific

- Thermo Fisher Scientific is the world leader in serving science, enabling our customers to make the world healthier, cleaner and safer. We help solve analytical challenges from routine testing to complex research and discovery. We offer the most convenient purchasing options to customers and continuously advance our technologies to accelerate the pace of scientific discovery, enhance value for customers and fuel growth for shareholders and employees alike.

How Green Is Your Lab?

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Water Analysis Instruments Group
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How Green Is Your Lab?

- Increased attention to environmental impacts has led to a closer scrutiny of even the most routine laboratory equipment and techniques.
- Instrument and equipment suppliers are responding by incorporating environmental issues in their R&D, not just for compliance with today's regulations, but with an eye on future requirements like the European Union ROHs standards.
- This seminar will highlight recent product introductions, changes in manufacturing procedures, and alternative lab techniques to help laboratory technicians, lab managers, and other users involved in wet chemistry and electrochemical measurements, to make greener choices.

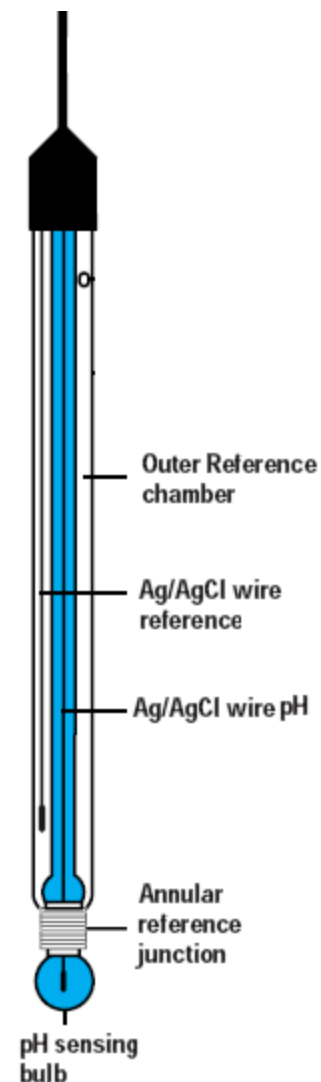
Electrochemistry fundamentals — a complete system

- Meter
 - Bench, Portable, or Pocket
 - Choose features as needed
- Electrode
 - Match to application
- Solutions
 - For calibration, storage, cleaning



Electrochemistry fundamentals — electrodes

- Measurement of voltage potential
- Sensing electrodes are available for a variety of ions
 - pH is most common parameter measured
 - ISEs are available for direct measurement of over 20 ions
 - Titrimetric methods expand ISE capabilities to over 500 applications
- Accurate measurement requires a stable reference
- Combination electrodes combine reference and sensing electrodes



Electrochemistry fundamentals — solutions

- Calibration
 - pH buffers
 - Ion concentration standards
 - ORP solutions
- Storage
 - Maintain electrode hydration where necessary
- Cleaning
 - Key to consistent results and electrode life when testing difficult samples



Electrochemistry's role in environmental monitoring

- EPA mandates measurement and recording of many water quality parameters by electrochemical methods. For example,
 - pH
 - Ammonia
 - Dissolved Oxygen / BOD (Biological Oxygen Demand)
 - Acidity and Alkalinity
 - Chlorine
 - Copper
 - Fluoride
 - Nitrate
 - Specific Conductance
 - Sulfide
 - Cyanide
 - Chloride



Common methods

- Electrochemical methods are well established and in common use.
- Electrode test methods are included in the approved methods for many organizations, including:
 - U.S. Environmental Protection Agency (EPA)
 - Standard Methods for the Examination of Water and Wastewater
 - United States Geological Society (USGS)
 - ASTM International
 - AOAC International
 - USP
 - Industrial standards such as paper institutes and petroleum institutes



New developments

- In 2007, EPA approved four more ISE methods for monitoring wastewater quality per NPDES compliance monitoring under the Clean Water Act.
 - Chloride
 - Cyanide
 - Nitrite
 - Sulfide



Federal Register

Monday,
March 12, 2007

Part III

Environmental Protection Agency

40 CFR Part 122, 136, et al.
Guidelines Establishing Test Procedures
for the Analysis of Pollutants Under the
Clean Water Act; National Primary
Drinking Water Regulations; and National
Secondary Drinking Water Regulations;
Analysis and Sampling Procedures; Final
Rule

Changing technology to address environmental concerns

- Electrode issues
 - Lead
 - Mercury
- Solution issues
 - Standard formulations
 - Reagent concerns



Lead in the environment

- Lead is ubiquitous in our environment
 - Previously used in paint and as a gasoline additive
 - Still in use in many applications
 - Lead may cause a range of health effects, from behavioral problems and learning disabilities, to seizures and death.
 - Children six years old and under are most at risk.
- <http://www.epa.gov/lead/>



*Barbie® Dream Puppy House™
recalled due to lead paint on dog
<http://www.cpsc.gov>*

Lead in electrochemistry

- pH glass
 - The pH measuring bulb is made of glass
 - Different glass formulations result in different measuring characteristics
 - Sodium error
 - Temperature range
 - Speed of response and stability
- Solder
 - Due to the high impedance of a pH signal, reliable connections are critical

Lead regulation

- Restriction of Hazardous Substances Directive
 - Restricts the use of 6 substances including lead and mercury
 - Adopted in February 2003 by the European Union
 - Took effect on 1 July 2006
- Electrodes are *currently* exempt from these regulations
 - Thermo Fisher Scientific is taking the initiative to be greener even though products not regulated yet



Green electrodes — construction

- Meets all *Restriction of Hazardous Substances Directive (RoHS)* requirement without any exemptions
- Lead free glass
 - Typical pH glass contains 20-30% lead
 - Green glass uses nickel-iron alloy
 - Lead free glass elutes fewer ions into IFS, causing less drift and faster response
- Lead free solder
- Recyclable packaging



Green electrodes — models

■ Four models

All are waterproof

- Single-Junction refillable
 - General purpose; quick response
- Double-Junction refillable
 - Compatible with Tris, sulfides, and proteins
- Single-Junction gel-filled
 - Low maintenance
- Double-Junction gel-filled
 - Low maintenance
 - Compatible with Tris, sulfides, and proteins



Mercury in the environment

- Mercury exposure at high levels can harm the brain, heart, kidneys, lungs, and immune system of people of all ages.
- Mercury is an element in the earth's crust. Humans cannot create or destroy mercury. Pure mercury is a liquid metal, sometimes referred to as quicksilver that volatilizes readily. It has traditionally been used to make products like thermometers, switches, and some light bulbs.

<http://www.epa.gov/mercury/about.htm>



Mercury in Electrochemistry

- The search for a stable reference electrode
 - Silver / silver chloride
 - Stable but reactive with TRIS, other common sample matrices
 - Calomel (Hg / HgCl)
 - Traditional choice in bio and life science labs
 - Many states now restrict shipment and disposal of calomel electrodes
 - REDOX pair (Iodide-triiodide)
 - Relatively new technology; developed in early 70s

Mercury-free electrodes

- Alternatives are now available that avoid mercury, while still providing resistance to TRIS, heavy-metals, sulfides, and organics
 - Double junction electrodes
 - Isolates silver behind second internal junction
 - REDOX pair electrodes
 - Contains NO metals
 - Added benefit; temperature independent



ORP standards — traditional options

- Oxidation Reduction measurement is useful in a number of applications from monitoring chemical reactions to testing strength of sanitizing solutions
 - As with any electrochemical measurement, calibration is critical to accurate measurement
 - Historically there have been limited choices for calibration
 - Zobell's solution
 - Light's solution
 - Quinhydrone solution
 - All have drawbacks
 - Recently developed Iodide/Tri-iodide solutions resolve many of these drawbacks



ORP Standards — non-hazardous alternative

- The Thermo Scientific Orion ORP Standard is
 - Non-hazardous
 - Stable
 - Pre-mixed and ready to use
 - Correlated to Eh (NHE, SHE) at temperatures ranging from 0 – 50 degrees C



ORP standards

- Traditional ORP standards typically are formulated using hazardous chemicals
 - Increased risk of harm to lab associates
 - Disposal issues

Standard	Redox Couple	Hazardous
Zobell's	ferricyanide/ ferrocyanide (iron(III)hexa-cyanoferrate and iron(II)hexa-cyanoferrate)	yes (ferrocyanide)
Light's	ferric/ferrous	yes (sulfuric acid); pH less than 2.0
Quinhydrone	quinone-quinhydrone	yes (quinhydrone)
Iodide/triiodide	I^3^-/I^-	no

ORP standards — storage issues

- While pH standards are easily buffered and for the most part stable, traditional ORP standards present difficulties
 - Relatively short life increases disposal issues

Standard	Stability	Storage
Zobell's	90 days at 4 deg C; 9 months at 2-8 deg C	Must refrigerate and exclude light (unstable when exposed to light)
Light's	12 months	Room Temperature OK, stable to light exposure, exposure to oxygen may degrade
Quinhydrone	8 hours	can't be stored
Iodide/triiodide	2 year shelf life at room temperature	No temperature, light, or oxygen issues

ORP solutions — added advantages of “green” solution

- In addition to advantages noted above, the iodide/tri-iodide solution offers greater accuracy

Standard	Accuracy	References
Zobell's	+/- 10 mV	USGS; Standard Methods
Light's	+/- 10 mV	Standard Methods; ASTM
Quinhydrone	+/- 30 mV (3)	ASTM
Iodide/triiodide	+/- 3 mV	ASTM; (USGS pending)

Changing methodologies to address environmental concerns

- Ammonia determination
- Oxygen determination



Ammonia methods — requirement for NH₃ monitoring

- Ammonia can have many negative effects on the environment and it is becoming an increasingly more important aspect of wastewater management.
- The overall efficiency of a wastewater plant is based upon the reduction of ammonia to nitrogen by converting the ammonia via oxidation to relatively harmless nitrate and nitrite.
- High levels of ammonia result in visible contamination in wastewater ponds and reservoirs.
 - The potential ecological impacts include excessive algae growth, and excessive sludge generation causing poor water quality for the support of aquatic life and can harbor organisms that contribute to disease.

Ammonia methods — traditional Nesslerization

- Nessler reagents
 - Traditional colorimetric measurement
 - Contains mercury
 - Health hazard and disposal issues
 - Has additional drawbacks
 - Colored and turbid samples present problems
 - Calcium and magnesium interfere
 - Not accurate in dirty samples
 - Distillation required to overcome these interferences and achieve maximum accuracy

Ammonia methods — ion selective electrode

- The ammonia nitrogen in wastewater is determined by direct measurement with a gas-sensing electrode
- No mercury!
- The method requires no titration and has no turbidity or color interferences.

Note: Pre-distillation of the sample may be required for EPA reporting purposes.



Ammonia methods — ISE advantages

- Accurate results down to 0.01 ppm
- Linear electrode response down to low detection limits
- Response time of 1 minute in sample concentrations of 1 ppm and higher
- Concentration Range
 - 5×10^{-7} M to 1 M as NH_3
 - 0.01 to 17,000 ppm as NH_3
 - 0.01 to 14,000 ppm as N



Dissolved oxygen methods — Winkler titration

- Winkler titration is a method for determining DO and requires many reagents, some of which are hazardous and/or corrosive.
 - Concentrated H_2SO_4 (10N) - corrosive
 - Alkali-iodine-azide
 - Sodium azide is very toxic (comparable to cyanide) as it releases a toxic gas when combined with acid, water or solid metal which causes adverse health effects when breathed in as it prevents cells from using oxygen.
 - It can also get into the body through the skin.
 - Sodium hydroxide used in this reagent is very strong (12.5M in solution)
- The Winkler titration is not easily portable to the field
- The Winkler titrant must be standardized against a properly prepared standard solution.

Probe method

- DO probe requires no reagents
 - Greener — no reagents
 - Faster — less sample prep time & direct measurement (vs. titration for Winkler)
 - Simple and quick calibration
- DO probe is fully portable to the field
- DO probe provides proven alternative
- Precision is comparable in wastewater using the probe or titration
 - 0.05 mg/L with probe
 - 0.06 mg/L with titration
- Full line of probes for lab and field (w/ stirrers, epoxy bodies, metal housing, etc)



Future challenges

- Green concerns will continue to drive green methods and green products
- Our technical team welcomes your questions, feedback, and requests for green method needs

Call us at 800-225-1480



Thank you

- Questions?

