


## Alternative Laboratory Methods for Analysis in WWTPs

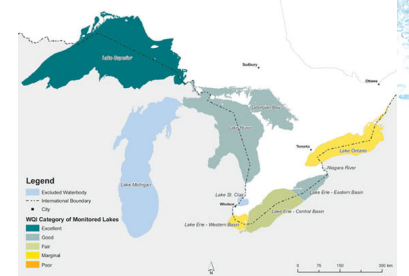
April 26, 2012

Derek Walker, Applications Development Manager  
Sara Simon, Regional Sales Manager




[Hach 2 O] Your formula for water analysis. Be Right™

### Water Quality in the Great Lakes




**Nutrients contributing to deteriorating water quality in highly populated and industrial areas**



[Hach 2 O] Your formula for water analysis. Be Right™

### Today's Agenda

1. Changing Regulations and Compliance Limits
2. Methods for laboratory measurement and reporting of N, NH<sub>3</sub>, NO<sub>2</sub>/NO<sub>3</sub>, P, and BOD
3. New methods for reporting and process control
4. Time for Q&A



[Hach 2 O] Your formula for water analysis. Be Right™

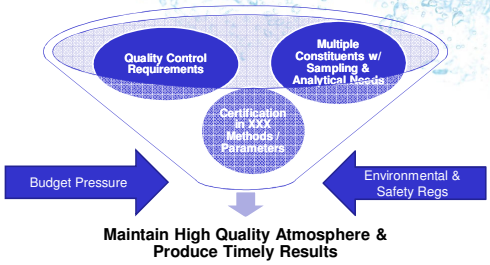

### Nutrients: What and Where?

- Nitrogen & Phosphorus
- Both are essential for plant & aquatic algae growth
- Both are present in wastewater plant effluents




[Hach 2 O] Your formula for water analysis. Be Right™

### Challenges in Compliance Labs






[Hach 2 O] Your formula for water analysis. Be Right™

### Nutrients: Why important?

- N & P discharged into Surface Waters
- Algae consume N & P and reproduce rapidly
- Bacteria eat algae and deplete oxygen levels
- Low DO kills fish, shellfish, invertebrates
- May increase toxicity of water due to ammonia

**Are there any changes to your permit?**





[Hach 2 O] Your formula for water analysis. Be Right™

## Michigan's Standards


- Phosphorous
  - Total Phosphorus (TP):
    - 1 mg/l and lower and are often based on loads (pounds of TP available in receiving waters).
- Nitrogen
  - Ammonia (NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup> as N)
    - Values often less than 1 mg/l and varies according to winter and summer based on water temperatures
  - Nitrate (NO<sub>3</sub> as N) – 10 mg/l or less
  - Total Nitrogen (TN)
    - TN loads (plants get TN limits based on design flow and effluent concentration of TN)

**What are some of the limits on your permit?**




## Most Commonly Measured Parameters in Wastewater

Parameter	Purpose of Test
Total Suspended Solids*	Most commonly measured and regulated parameter on NPDES permits. Used to measure mixed liquor suspended solids concentration, return activated sludge/waste activated sludge concentration, influent suspended solids concentration, effluent suspended solids concentration, and % removal.
pH*	Maintain proper (narrow) pH range for optimal biological processes—especially nitrification. Can indicate plant upsets by industrial discharges or development of anaerobic conditions within the plant. Important condition for methane formation and avoiding ammonia toxicity in sludge digesters.
Flow*	Measure standard in-pipe flow rate for NPDES permit requirements and to establish concentrations/total presence of key analytes.
Dissolved Oxygen (DO)*	Measure to control aeration and save money. Also measures the amount of available oxygen for aquatic life in the effluent. DO is also a commonly measured reportable parameter on NPDES permits.
BOD <sub>5</sub> & COD	Provides a relative measure of "food" available, the degree of stabilization of the wastewater and to estimate the effect of the effluent on the receiving water body. Used for plant loading/design, discharge rate for industrial facilities, and EPA NPDES reporting. 5 day test is too long for process control—many plants use COD or TOC as early estimate. Used to calculate % removal.
Chlorine, Total* & LR	Chlorine is used to disinfect WW plant effluents, prior to discharge to a receiving body. It is normally present as "combined" chlorine (chloramines). Chlorination is generally followed by de-chlorination with sulfur compounds, prior to release of effluent, ULR—This photometric method is EPA approved for ppb level chlorine determination in WW effluent chlorination/disinfection processes.
Coliforms, Fecal E. Coli	Monitor and quantify microbial concentrations in the effluent. NPDES reporting requirement for some facilities.
Nitrogen Total, (as N)*	Total of ammonia, nitrate, nitrite and organic nitrogen forms.



## Why Lab Methods are Important


- Lab analysis and trending critical for plant optimization & NPDES reporting
- Daily or weekly sampling and testing bridges the gap if online monitoring is not feasible
  - Ammonia
  - COD or BOD
  - Nitrate/Nitrite/TKN
  - Phosphorous, etc.
- Is there a plant upgrade being planned?
  - Frequent samples being run for engineering studies






## Most Commonly Measured Parameters in Wastewater (con)

Parameter	Purpose of Test
Phosphorus, Total* (As P)	Regulatory measurement for plants which remove phosphorus from the wastewater, either biologically or chemically.
COD	Used as a correlative/early indicator of BOD levels. Some NPDES permits include COD as a surrogate for BOD; however, BOD is the standard reportable parameter for oxygen demand in municipal wastewater. COD provides a measure of organic "food" available to biological treatment steps and to estimate the effect of the effluent on the receiving water. (Note: Can be correlated to BOD on a plant-by-plant basis, if influent characteristics are constant.)
Turbidity*	Surrogate measurement for solids concentration. Often used to indicate solids carry-over from secondary clarifiers.
Nitrite LR & HR	Indicative of the stage of conversion of ammonia and organic nitrogen forms to nitrate by the aerobic biological treatment steps (nitrification). Nitrite is the intermediate nitrogen form between ammonia and nitrate. Nitrite is highly toxic, and small amounts can upset the delicate biology of a wastewater plant.
Metals	Nickel, Molybdenum, Lead, Mercury, Zinc, Chromium, Copper, Arsenic—Measure heavy metal concentrations in effluent waters and ensure compliance with NPDES permit. Of concern in effluents and land-applied biosolids due to potential toxicity.
Chlorine, Total Amperometric Titration*	Chlorine is used to disinfect WW plant effluents, prior to discharge to a receiving body. It is normally present as "combined" chlorine (chloramines). Chlorination is generally followed by de-chlorination with sulfur compounds, prior to release of effluent. Amperometric titration is considered the "reference" method for comparisons.
Nitrate HR* & LR	Indicative of the stage of conversion of ammonia and organic nitrogen forms to nitrate by the aerobic biological treatment steps (nitrification).



## Asking the Right Questions


- Regulations or Permits
  - Am I in compliance?
- Process control
  - Is my plant operating correctly?
  - Is it time for preventative maintenance?
- Problems and Troubleshooting
  - What is wrong with my system?
  - How can I fix it?





## Analytical Techniques

- Photometric (Light)**
  - Visual
  - Spectrophotometry (Colorimetry)
  - Nephelometry (Turbidity)
  - Luminescent (LDO)
- Titrametric**
  - Drop Count
  - Digital Titrator
  - Traditional Buret
- Microbiological**
  - Qualitative
  - Quantitative
- Electrochemical (Probe)**
  - Potentiometric (pH)
  - Polarographic (DO)
  - Conductometric
  - ORP
- Gravimetric**
  - Total Dissolved Solids
  - Total Suspended Solids



## The Method and Procedure

Make sure that the procedure is correct for:

- Analyte
  - Nitrate vs. Nitrite
  - Ortho vs. Total Phosphorous
- Type of sample
  - WW vs. DW
- Concentration range
  - ULR, LR, MR, HR, UHR
  - ppb vs. ppm
- Is this for compliance reporting?



[Hach 2 O] Your formula for water analysis.



## Nitrogen: Why monitor?

- Why monitored in municipal wastewater?
  - Regulatory purposes
  - Plant efficiency
- Why monitor in industrial wastewater?
  - Regulatory purposes
  - Process efficiency
  - Must "fertilize" the microorganisms

[Hach 2 O] Your formula for water analysis.



## Photometry

Colorimetric and Spectrophotometric analysis

- Colorimeters (Visible Light)
- Spectrophotometers (UV, Visible, Near Infrared)
- Measuring the color of a reacted sample to determine concentration

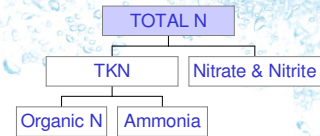


[Hach 2 O] Your formula for water analysis.



## Forms of Nitrogen

- Inorganic Nitrogen
  - Ammonia,  $\text{NH}_3$
  - Ammonium,  $\text{NH}_4^+$
  - Nitrate,  $\text{NO}_3^-$
  - Nitrite,  $\text{NO}_2^-$
  - Nitrogen gas,  $\text{N}_2$



- Organic Nitrogen
  - Organic nitrogen is found in living organisms:
    - Proteins
    - Peptides
    - Nucleic acids (DNA, RNA)
    - Urea
  - Also found in decaying dead organisms.

[Hach 2 O] Your formula for water analysis.



## Electrochemistry

- Ion Selective Electrodes (ISE)
  - Nitrate
  - Ammonium
- Gas Sensing Electrode
  - Ammonia
- pH
- Conductivity
- ORP
- DO
  - Galvanic
  - Polarographic



[Hach 2 O] Your formula for water analysis.



## Nitrogen Measurement

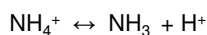
- Inorganic nitrogen changes forms by the processes of nitrification and denitrification.
- Nitrification:
  - Ammonia → Nitrite → Nitrate
- Denitrification:
  - Nitrate → Nitrite → Nitrogen Gas

[Hach 2 O] Your formula for water analysis.



## Ammonia (NH<sub>3</sub>) / Ammonium (NH<sub>4</sub><sup>+</sup>)

- Why Test?
  - **WW Process Control:** An excellent indication of the performance of aeration basin's ability to oxidize ammonia to nitrite/nitrate (typically looking at the removal of ammonia) – many nitrogen compounds take longer to oxidize than many organics and some facilities control their aeration basins based on ammonia oxidation
  - **Required on WW Permits:** Ammonia is a common regulated parameter on NPDES permits
  - Ammonia (NH<sub>3</sub>) can be toxic to aquatic life.
- Occurs naturally due to breakdown of organic nitrogen compounds in water.
- Which species is predominate in WW?
  - Depends on pH and temp of water



[Hach 2 O] Your formula for water analysis.



## Why use ISEs vs. other measurement techniques?

1. Cost of initial setup and per sample is low
  - Initial equipment cost lower than many competing techniques
  - Per test can be as little as \$0.10
2. Sample and standard preparation is simple
  - Only one reagent required
  - No shaking
  - No waiting steps
  - No filtration
3. ISE methodology is free from most interferences
  - No interference from sample color, turbidity, or particulates
4. Wide calibration range
  - Typical 3-point calibration will cover a range of 100x
  - Fewer calibration points required
  - Fewer dilutions required to bring sample results within range
5. Minimal equipment setup and maintenance required
6. Widespread regulatory approval for ISE methodology

[Hach 2 O] Your formula for water analysis.



## Lab Methods for Analysis

### Ammonia Nitrogen (NH<sub>3</sub>-N)

- Nessler Method\* (with distillation)
- Salicylate
- Salicylate TNTplus\*
- NH<sub>4</sub><sup>+</sup> Ion Selective Electrode
- NH<sub>3</sub> – Gas Sensing Electrode\*
  - \*EPA Approved or Accepted

### Traditional Methodology

- Distillation
  - Specialty glassware: preparation, clean-up
  - Time consuming: At least 20 minute distillation
- Ammonia determination by titration, ISE, or Colorimetry
  - May contain mercury (Nessler Method)
  - ISE upkeep is very labor intensive



[Hach 2 O] Your formula for water analysis.



## TNT+ Chemistry



- Barcoded vials
  - Automatically detects correct method
- Pre-measured reagent
  - Just add sample
- 10 Measurements
  - Eliminates outliers and improves results

### Ammonia Method

- Reduced volumes may eliminate need for distillation
- Only 0.5 mL sample required
- ~ 15 minute total analysis time, minimal "hands-on" time
- Does not contain mercury
  - Represents savings of over \$800/year based on running one test & blank 5 days a week (68% cost savings)

[Hach 2 O] Your formula for water analysis.



## Ammonia Ion Selective Electrode

**Range:** 0.10 mg/L to saturation

### Advantages:

- EPA approved method
- Broad range and cost effective for lots of samples
- Few interferences – solids and color do not interfere

### Disadvantages:

- Electrode requires maintenance for optimal performance
- Temperature sensitivity
- Calibration of probe required before measurement



[Hach 2 O] Your formula for water analysis.



## Selecting the Right Ammonia Method for Your Lab

Both Colorimetric and ISE methods are approved for use in Michigan

- How many samples are you running?
- How much time do you spend testing for ammonia?
  - Creating standards, Calibration of probe, Changing membranes
- What resources do you have available – lab techs and operators?
- Process control or compliance monitoring?


Individual facility needs are important to consider when selecting the right measurement method!

[Hach 2 O] Your formula for water analysis.



### Nitrate (NO<sub>3</sub>-)



- Present naturally in surface and ground waters
- Essential nutrient for plants
- End step of the nitrification process  
 $NH_3 \rightleftharpoons NO_2^- \rightleftharpoons NO_3^-$



[Hach 2 O] Your formula for water analysis. Be Right™

### Methods for TKN Analysis

- Total Kjeldahl Nitrogen
  - Ammonia plus organic nitrogen
  - Typically all nitrogen in influent
  - Digestion converts “all” organic to ammonia
  - Nessler method to measure ammonia





[Hach 2 O] Your formula for water analysis. Be Right™

### Methods for Nitrate Analysis

- Nitrate Nitrogen (NO<sub>3</sub>-N)
  - Ion Selective Electrode\*
  - Chromotropic Acid
  - Cadmium Reduction
  - UV absorbance
  - Dimethylphenol TNTplus





\*EPA Approved or Accepted





[Hach 2 O] Your formula for water analysis. Be Right™

### Methods for TKN Analysis

#### Simplified Total Kjeldahl Nitrogen



- TNTplus chemistries:
  - Total Nitrogen
  - Nitrate & Nitrite
- sTKN = TN - NO<sub>x</sub>


[Hach 2 O] Your formula for water analysis. Be Right™

### Methods for Nitrite Analysis

- Intermediate step of the nitrification process  
 $NH_3 \rightleftharpoons NO_2^- \rightleftharpoons NO_3^-$
- Nitrite is not highly stable
  - Tends to be either oxidized to nitrate or reduced to ammonia
- Nitrite Nitrogen
  - Diazotization\*
  - Ferrous Sulfate

\*EPA Approved or Accepted





[Hach 2 O] Your formula for water analysis. Be Right™

### Lab Methods for Analysis

#### Total Nitrogen


- All nitrogen present
  - Ammonia + Nitrate + Nitrite + Organic Nitrogen
- Digestion with an alkaline persulfate soln
  - Oxidizes everything to nitrate
  - Measured with chromotropic acid method

[Hach 2 O] Your formula for water analysis. Be Right™

### Why is Phosphorus Important?

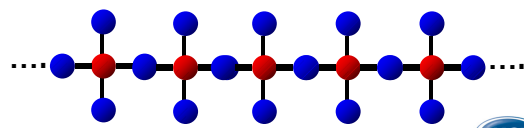
- Essential to the growth of organisms
- Limiting factor for photosynthesis
- Excess quantities can cause eutrophication



[Hach<sub>2</sub>O] Your formula for water analysis. **HACH** Be Right™

### How does Phosphorus Occur?

- Condensed phosphate
  - Metaphosphate
  - polyphosphate
  - pyrophosphate



[Hach<sub>2</sub>O] Your formula for water analysis. **HACH** Be Right™


### Phosphorus Measurement

- Phosphorus is a nutrient, essential to growth.
- Phosphorus occurs in natural waters and wastewaters primarily in the form of phosphate.
  - Orthophosphate
  - Condensed phosphate
  - Organic phosphate
  - Only orthophosphate (reactive) can be measured directly

[Hach<sub>2</sub>O] Your formula for water analysis. **HACH** Be Right™

### Lab Methods for Analysis

- Orthophosphate
  - Ascorbic Acid (PhosVer3)\*
    - 0 – 2.50 mg/L PO<sub>4</sub><sup>3-</sup>
    - “Blue method”
  - Molybdovanadate
    - 0 – 45.0 mg/L PO<sub>4</sub><sup>3-</sup>
    - “Yellow method”

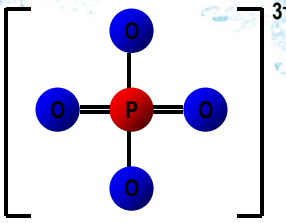


\*EPA Approved or Accepted  
[Hach<sub>2</sub>O] Your formula for water analysis. **HACH** Be Right™

### How does Phosphorus Occur?

The chemical formula for the phosphate ion is PO<sub>4</sub><sup>3-</sup>


- Orthophosphate
- Reactive phosphate



[Hach<sub>2</sub>O] Your formula for water analysis. **HACH** Be Right™

### Lab Methods for Phosphorus


- Total Phosphorus
  - Sum of Ortho, Condensed & Organic
  - Acid persulfate lab method\*
    - Digests everything to orthophosphate



\* EPA Approved or Accepted  
[Hach<sub>2</sub>O] Your formula for water analysis. **HACH** Be Right™

### Phosphate Test 'N Tube+ System


- Requires only 5 mLs of sample
- Total phosphorus and acid hydrolyzable phosphate both use the COD Reactor system to digest up to 25 vials at 105° C for 30 minutes, unattended
  - Entire test completed in one vial
  - Instrument is zeroed on the same vial
- Eliminate glassware clean-up and cross-contamination
- Test efficiency makes it highly suited for process control and reporting purposes
  - Orthophosphate and Total Phosphate are EPA accepted (ascorbic acid method)

 Hach 2 O Your formula for water analysis. Be Right™

### NEW! - ULR Phosphorus Test


Range: 10 to 500 µg/L PO<sub>4</sub>- P

- Application note with procedures available - Lit # 2097
- User entered calibration is required
  - Hach supplies you with all information for this calibration curve.
- Approved for Reporting?
  - Although same Ascorbic Acid chemistry...different sample cell path length
  - Must check with your state regulator


 Hach 2 O Your formula for water analysis. Be Right™

### Analysis of Total Phosphorus

1. Requires Acid or Persulfate Digestion
  - Boil the sample with acid for 30 minutes to break the condensed phosphate chains into orthophosphate
  - Hot plate or Test N Tubes
2. Neutralize with hydroxide and perform the most suitable orthophosphate test
3. Perform an orthophosphate test on an undigested portion of sample
4. **Final Results:** Subtract the orthophosphate results (undigested) from those of the digested sample.




**Digested – Undigested =  
mg/L Condensed Phosphate**

 Hach 2 O Your formula for water analysis. Be Right™

### EPA Method Approvals EPA Reference Method: 365.2


Hach Method 8048 **Reactive Phosphorus (Orthophosphate)**  
PhosVer 3 (Ascorbic Acid) Method (Also TNT+ Method 10209)  
USEPA Accepted Method for reporting wastewater analyses – (Standard Methods 4500 P-E)  
• EPA Letter dated March 1, 1999


Hach Method 8190 **Total Phosphorus**  
PhosVer 3 (Ascorbic Acid Method) with Acid Persulfate Digestion Method (Also TNT+ Method 10210)  
USEPA Approved for Reporting Wastewater Analyses (Standard Methods 4500 P-E)  
• EPA Letter dated March 1, 1999

 Hach 2 O Your formula for water analysis. Be Right™

### NEW! - ULR Phosphorus Procedure

- The detection limit for the LR TNT+ method is 50 µg/L, which may be too high for some state's nutrient standards plans to limit surface water eutrophication.
- Ultra Low Range Total & Reactive Phosphorus
  - Concentration range is 10 to 500 µg/L PO<sub>4</sub>-P.
- Instrumentation:
  - DR2700, DR2800, DR3800, DR3900, or DR5000
  - TNT 843: TNT+ phosphorus reagents
  - DRB200 Digital Reactor Block for TNT+
  - 5-cm semi micro cuvette, PN LZP341




 Hach 2 O Your formula for water analysis. Be Right™


### BOD: What is it?

- Biochemical Oxygen Demand is a measure of organic pollution
- A measurement of the oxygen demand impact of effluent into a receiving body; measures all oxygen demand including nitrogen-based oxygen demand

In other words...

- BOD measurements help in monitoring the effect of effluent on the dissolved oxygen concentration of the receiving water body



 Hach 2 O Your formula for water analysis. Be Right™

### BOD: How is it measured?

- BOD is measured by oxidizing organics using microorganisms (under specific conditions) and directly measuring the amount of oxygen consumed in the process.

- Changes in dissolved oxygen concentration are used as an indirect measure of organic content (food)
- BOD is the amount of oxygen, expressed in mg/L bacteria take from the water when they oxidize organic matter.

**HACH**  
Be Right™

### Issues and Root Causes

Failure Mode	Key Root Cause(s)
Blank depletion	1) Organic contamination in dilution water or bottles 2) Drift in DO sensor
Effluent fails to achieve 2 ppm depletion	- Insufficient nutrient or seed - Toxicity
Failed G/GA reference	- Inaccurate G/GA - Toxicity - Insufficient seed

Help out there:  
[www.boddoctor.com](http://www.boddoctor.com)

**HACH**  
Be Right™

### BOD: Why do we do it??

**Top 5 reasons:**

1. We have to!
2. It's on our permit
3. Week-by-week barometer of how the overall plant is performing
4. Historical data on the plant to know how seasonality plays into plant performance
5. We have to!!

**HACH**  
Be Right™

### Is there a better way?

- Failure of standards can often be traced to issues with membrane electrodes and calibrations
  - Oxygen consumptive reduction from an electrolyte and two metallic electrodes
  - Oxygen must diffuse through a membrane to be reduced at a cathode
- Limitations
  - Requires high flow across membrane
  - Narrow linearity range
  - Electrolyte and electrode degradation
  - Membrane fouling - must be changed frequently

**HACH**  
Be Right™

### BOD & cBOD: Any concerns?

Average number of hours/week a typical WW facility spends on BOD?	15 hours
Average number of bottles set per week for BOD?	20 - 40
Average number of times per week BOD is run?	2 sets
<b>Percent of BOD tests that FAIL to meet Standard Methods Guidelines?</b>	<b>5-10%</b>

**HACH**  
Be Right™

### Luminescence Based Oxygen Sensors


- Measures the light emission characteristics of a reversible luminescent reaction
- In the presence of oxygen the luminescence is quantitatively reduced or quenched
- Dissolved oxygen concentration is inversely proportional to the luminescence lifetime of the light emitted by the photo-luminescence process

**HACH**  
Be Right™



### How does LDO help reduce errors?

- Fast response and no sensor drift
  - No warm-up time
- Quick calibration in water saturated air
- No membrane to replace
  - No electrolyte to foul or poison
  - No more punctured membrane
- No H<sub>2</sub>S poisoning of the electrolyte



**Multiple sources of error eliminated from the BOD method!**

**HACH**  
Be Right™

[Hach 2 O] Your formula for water analysis.

### New Luminescent Technology Brings Faster, More Accurate CBOD Analysis

by Bob Dabkowski, Hach Company

*Measuring DO in the CBOD procedure was once troublesome and inefficient for lab personnel and operators alike at the Southside Wastewater Treatment Plant in Tyler, Texas. But all that changed when they adopted new luminescent technology that has eliminated problems with instrument drift, slow measurements, and frequent maintenance.*

The City of Tyler, Texas, has two wastewater treatment facilities that together serve upwards of 150,000 people. The smaller of the two plants, the Southside WWTP, is an activated sludge plant that uses mechanical aeration to achieve advanced secondary treatment. The 9 MGD facility, with an average daily flow of more than 5 MGD, serves approximately 40 percent of the city's service area.

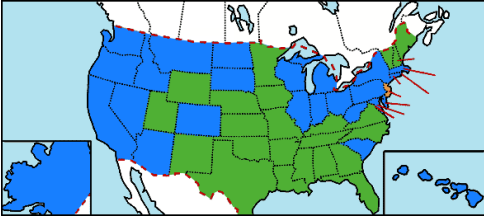
Carbonaceous biochemical oxygen demand (CBOD) testing at the Southside facility is one of the plant's most critical measurements and must be performed daily to satisfy NPDES permit requirements. The test had long been a troublesome and time-consuming procedure due to inefficiencies inherent with the dissolved oxygen (DO) probes the facility had used over the years.

**Reference Material**

**HACH**  
Be Right™

[Hach 2 O] Your formula for water analysis.

### What about EPA Approval?



Green: **Approved** - No data needed  
 Blue: **Approved with Performance Data\*** - Est. total time 2-8 Lab hrs/ 30-90 days  
 Orange: **Tier 1 Submission**  
<http://www.hach.com/hqguide-do>

**HACH**  
Be Right™

[Hach 2 O] Your formula for water analysis.

### Take Home Messages

- As regulations or certification requirements increase, alternative methods can be useful
- New methods may alleviate budget constraints
- Variability and inconsistency may also be reduced!
- Consult other plants and authorities for best practices!

**HACH**  
Be Right™

[Hach 2 O] Your formula for water analysis.

### Products for Reducing BOD Errors



**HACH**  
Be Right™

[Hach 2 O] Your formula for water analysis.

### Alternative Laboratory Methods for Analysis in WWTPs

**Thank you very much!**

Derek Walker, Applications Development Manager  
[dwalker@hach.com](mailto:dwalker@hach.com)

Sara Simon, Regional Sales Manager  
[ssimon@hach.com](mailto:ssimon@hach.com)

**HACH**  
Be Right™

[Hach 2 O] Your formula for water analysis.

## Backup Slides

### Regulatory Definitions Biological Nutrient Removal

[Hach 2 O] Your formula for water analysis.



## Definitions: USEPA Equivalent

### Hach Equivalent Methods:

All USEPA-Approved methods have specification criteria built into their procedural steps. When an approved or accepted EPA method has been packaged by Hach from the EPA reference method as a test method that meets or exceeds these specification criteria, these methods are deemed to be equivalent for use in EPA compliance monitoring. EPA does not normally review "Equivalent Methods" or issue equivalence letters of packaged reference methods. Hach maintains the formulation, procedure, and analytical data demonstrating equivalency and is available to end users and regulatory authorities upon request.

[Hach 2 O] Your formula for water analysis.



## Definitions – USEPA Approved

### USEPA Approved Methods:

The USEPA has evaluated and approved new technological methods developed by Hach Company. The methods have undergone a nationwide inter-laboratory validation study that was submitted to the EPA for approval. All USEPA-Approved methods are cited in the Federal Register and compiled in the Code of Federal Regulations at 40 CFR 136 and CFR 141.

[Hach 2 O] Your formula for water analysis.



## Method Modifications: Statute and Authority

- 40 CFR 136.6 Method Modification and Analytical Requirements
  - As described in the Consolidated Federal Register (FR/Vol. 72, No. 47/ Monday, March 12, 2007/Rules and Regulations)
  - Only for use of Clean Water Act Methods
- Allowable changes
  - Modify an approved test procedure (analytical method) provided that the chemistry of the method or the determinative technique is not changed

[Hach 2 O] Your formula for water analysis.



## Definitions – USEPA Accepted

### USEPA-Accepted Methods:

The USEPA has reviewed Hach methods and accepted them for use in compliance monitoring. These methods are defined by USEPA as **Acceptable** versions of previously approved methods. These methods are generally not published in the *Federal Register* or in the *Code of Federal Regulations*. The USEPA documents Acceptance in a formal letter to Hach Company. A facsimile of the USEPA-Acceptance letter is available upon request.

[Hach 2 O] Your formula for water analysis.



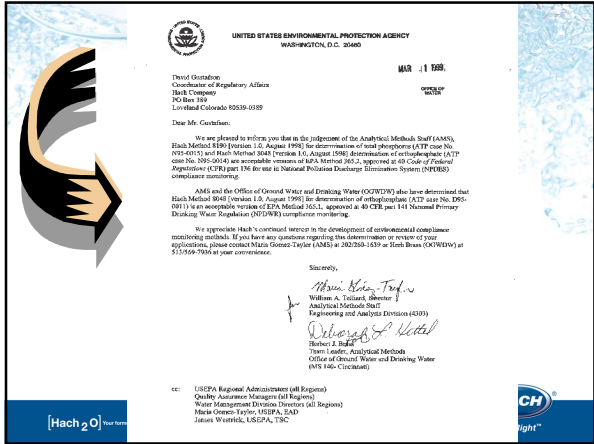
## Modified Methods: In a Nutshell

### Modified methods can be used with the following:

- Documented protocol and EPA method format on file in lab
- Validation studies showing equal or "better-than" performance
- On-going QC samples
- Documentation and QC data archived on site
- 40 CFR 136.6 provides guidance on modified method usage
- **Consult your local regulatory authority if there are questions about a particular method!**

[Hach 2 O] Your formula for water analysis.





## Units: P or PO<sub>4</sub><sup>3-</sup> ?

1mg/L PO<sub>4</sub><sup>3-</sup> = ? mg/L P

- 1mg/L PO<sub>4</sub><sup>3-</sup> x (wt P/wt PO<sub>4</sub>) = ? mg/L P
- 1mg/L PO<sub>4</sub><sup>3-</sup> x (31/95) = ? mg/L P
- 1mg/L PO<sub>4</sub><sup>3-</sup> x (0.33) = ? mg/L P
- **1mg/L PO<sub>4</sub><sup>3-</sup> x (0.33) = 0.33 mg/L P**

### Notice of Equivalency of TNT Plus® 843 and 844 Test Vials for Regulatory Compliance Reporting

To Users of the TNT Plus 843 and 844 Phosphorus Test Vials for Regulatory Reporting:

This document and its attachments are being provided as verification of equivalency when using Hach TNT Plus 843 and 844 Phosphorus Test Vials for regulatory reporting purposes. Hach TNT Plus 843 and 844 phosphorus test vials are formulated to the standards of the EPA accepted Hach TNT® 8048 and 8190 phosphorus test vials and meet all of the performance criteria of EPA Method 365.2 and Standard Method 4500-P E for wastewater.

The U.S. Environmental Protection Agency requires that supporting data of an equivalent method (minor modification or re-packaging of a EPA approved method) used for compliance reporting purposes be available for inspection. The attached side-by-side comparative study provides verification of equivalency to the EPA approved method for phosphorus, and may be used for discussions with your regulatory compliance officer.

Questions regarding this document and its accompanying side-by-side study should be directed to [Contact Information]

## Don't forget the Units P or PO<sub>4</sub><sup>3-</sup> ?

- The units used to express phosphate concentration are P and PO<sub>4</sub><sup>3-</sup>
- P (phosphorus)
  - Atomic weight = 31
- PO<sub>4</sub><sup>3-</sup> (phosphate)
  - Atomic weight = 31 + (16 x 4) = 95