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Three New Optical Dissolved Oxygen Methods for RDO® Probe: EPA ATP Approval for DO, BOD, & CBOD Methods

Thermo Scientific

Orion Laboratory Products

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Purpose

At the end of this presentation, you will understand:

- Which technologies and methods are EPA approved for NPDES reporting of DO, BOD, and CBOD test results
- The benefits of optical DO technologies
- The ATP testing process
- How these ATP approvals are different
- Results of ATP approval testing of optical RDO (stirred and non-stirred) as compared to membrane DO
- How to implement RDO optical DO test methods in your laboratory
- What Thermo Scientific Orion products you can use
- Where to get help

Approved DO Methods for Compliance Reporting

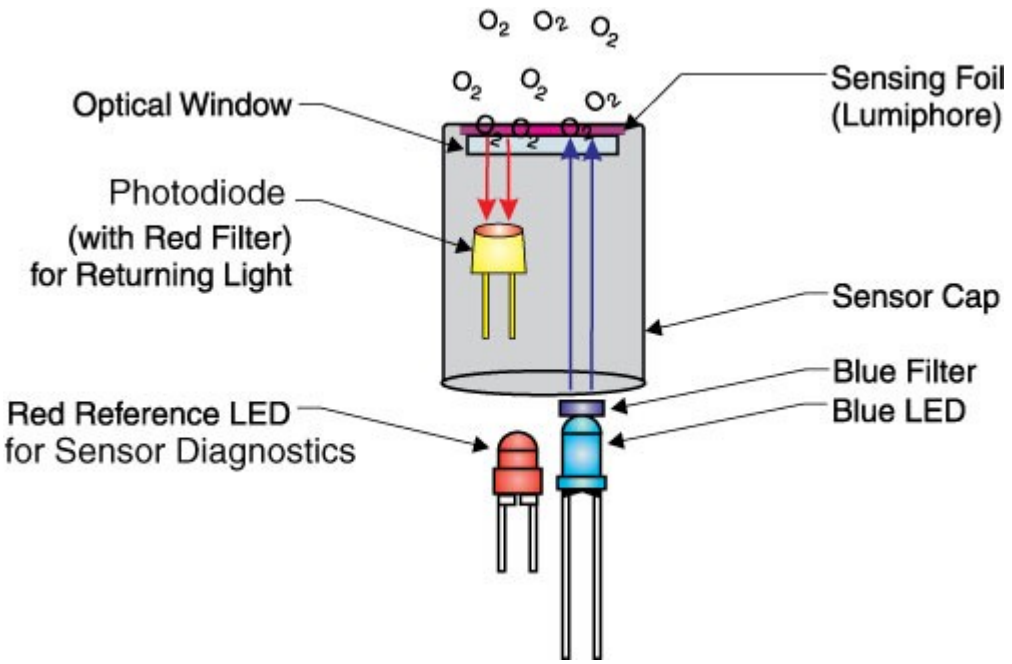
Approved test procedures for Dissolved Oxygen :

- Winkler
- Electrode - electrochemical

As published in the Method Update Rule (MUR), 40 CFR Part 136.3 on March 12, 2007

New Technology for DO measurement

- A new optical luminescence-based sensor technology has been developed and tested against the approved methods – Winkler and membrane electrode



- Interim approvals for use of optical DO technology have been granted through the ATP program by USEPA for use in NPDES compliance monitoring and reporting.

What is the Alternate Test Procedure (ATP) Process?

- EPA definition – Guideline establishing analytical methods for wastewater and drinking water that can be used in place of an approved method.
- Applies to samples analyzed under the Clean Water Act and Safe Drinking Water Act
- Approved ATP methods are recommended for inclusion in 40 CFR Part 136.3 on the next publication of the MUR.
- Between the time of ATP approval and the next MUR publication, NPDES permit holders can begin using the ATP method after seeking approval from regional authorities.

EPA Recommends Approval of In-Situ® RDO® Methods

- Approval letters released by EPA on Nov. 3, 2009.
- EPA approves ATP for 3 RDO® methods:
  - **DO Measurement** by Optical Probe (Method 1002-8-2009)
  - **BOD Measurement** by Optical Probe (Method 1003-2-2009)
  - **CBOD Measurement** by Optical Probe (Method 1004-2-2009)
- EPA will recommend inclusion of methods at 40 CFR Part 136.3.

What is Unique about these ATP Approvals?

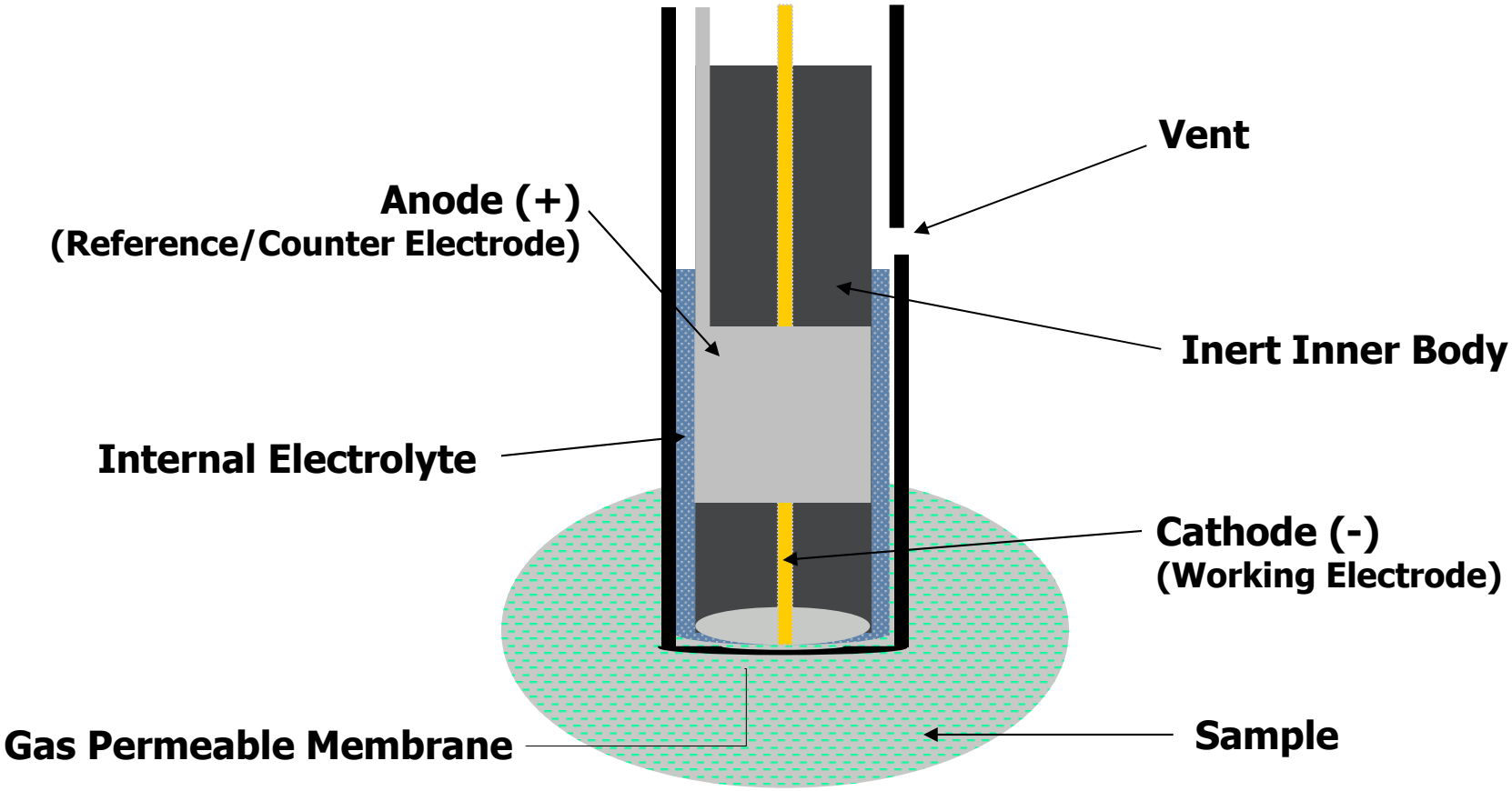
- First and only ATP applying luminescence-based sensor DO measurement for Carbonaceous Biochemical Oxygen Demand (CBOD).
- First and only ATP applying luminescence-based sensor DO measurement for a minimum of 9 unique matrices from water and wastewater.
- First and only ATP applying luminescence-based sensor DO measurement to samples analyzed both as stirred and non-stirred

Dissolved Oxygen Electrode Technologies

Dissolved Oxygen Electrode Technologies include:

- Electrochemical sensors
  - Also known as membrane electrodes or Clark cells
  - Includes polarographic and galvanic type electrodes
- Optical luminescence-based sensors
  - Known as optical, luminescence, or fluorescence probes

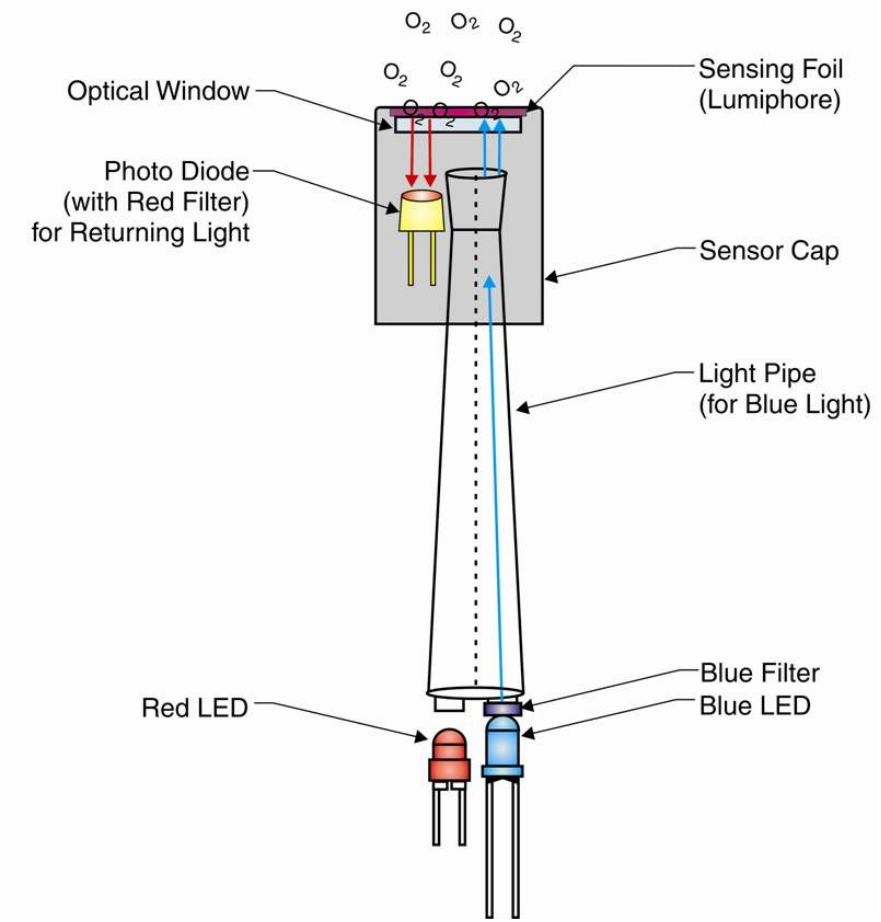
Electrochemical or Membrane “Clark” Method DO Probe



Oxygen crosses the gas permeable membrane at a rate directly proportional to the dissolved oxygen concentration. The higher the dissolved oxygen concentration, the higher the current.

RDO® Optical Method for DO Determination

Optical / Luminescence Method



A blue LED in the RDO® emits a light that causes the lumiphore molecules embedded in the gas-permeable sensing foil to react, emitting red photons.

The sensor then measures the "phase", or delay, of the returned signal compared to the excitation signal.

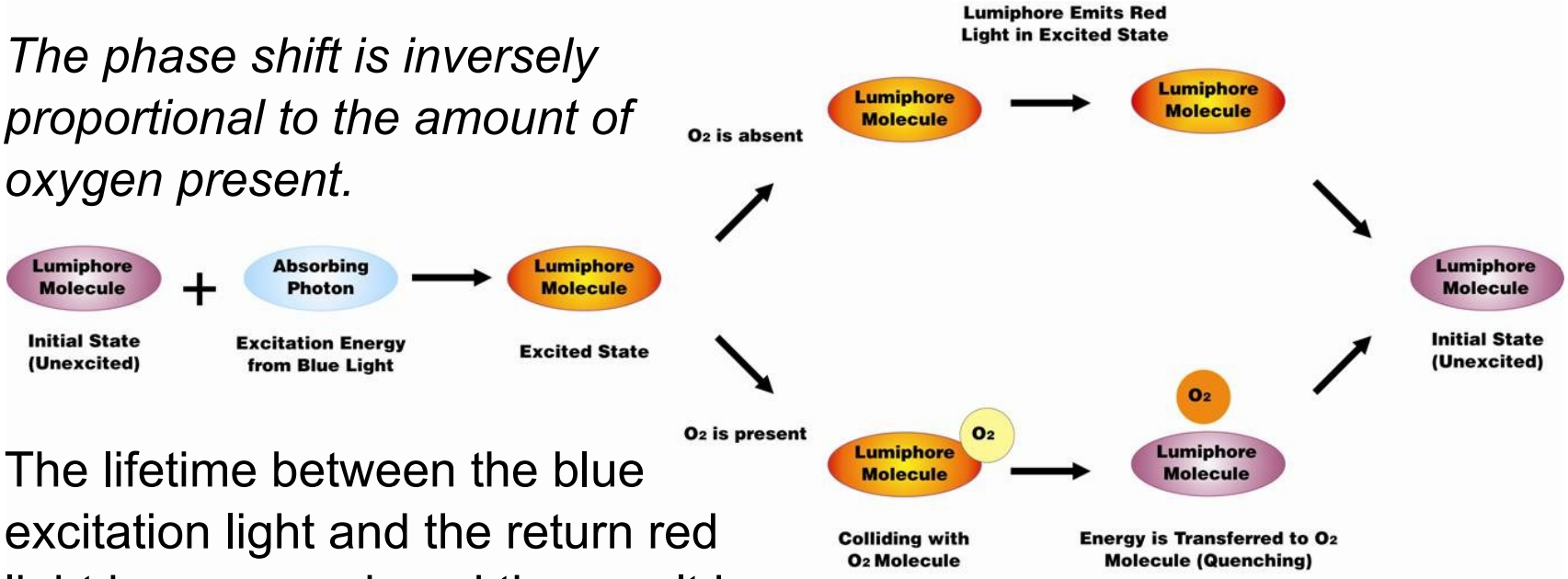
This dissolved oxygen measurement is based on luminescence "lifetime", which delivers the highest accuracy and widest operation range.

RDO®: New Method for DO Determination

Optical / Luminescence Method

The presence of oxygen in the foil quenches luminescence (blue light photons) and causes a phase shift in the return signal, detected by the photodiode.

The phase shift is inversely proportional to the amount of oxygen present.



The lifetime between the blue excitation light and the return red light is measured, and the result is used to quantify the dissolved oxygen present.

Features and Benefits of RDO® Optical DO Technology

- Provides an alternate technology that is as sensitive to low DO concentrations as a Winkler titration.
- Does not consume oxygen, thus it does not require stirring.
- Offers the same or better accuracy and reproducibility as a membrane electrode.
- Uses many of the same sampling requirements as a membrane electrode, thus requires minimal analyst training.
- No membranes to change and no filling solutions. Annual cap replacement is simple.
- Stable response with minimal drift and fewer calibrations.
- Ready to take readings right away – no polarization or warm-up time required.
- Readings are not affected by sample color or turbidity

ATP Testing Details

- Comprehensive ATP process validated 3 methods in 9 matrices.
- 10 municipal, state, and commercial wastewater labs performed tests:
  - 9 water and wastewater sample matrices
  - 1,300 samples tested
  - No significant matrix interferences were observed in any of the 1,300 samples

ATP Approvals: Participating Test Facilities

Laboratory Type and Qualifications							
Laboratory #	**POTW Laboratory**	**Commercial Laboratory**	**State Laboratory**	**Submits MORs for NPDES Compliance**	**Participates in DMRQA**	**State Certified**	**NELAC Certified**
1	X			X	X	X	
2	X			X	X		
3	X			X	X	X	X
4			X		X		
5	X			X	X	X	
6		X			X	X	X
7		X			X	X	X
8	X			X	X	X	
9	X			X	X		
10		X			X		

Samples Types Tested for BOD

Table 2A: BOD Data Sets Submitted												
Lab #	Lab Name		BOD									
		Total Samples	POTW Plant Influent	POTW Plant Effluent	Glucose/Glutamic Acid	DO Blank	Seed Correction	Surface Water	Tap Water	Industrial Sample 1	Industrial Sample 2	Industrial Sample, Other
1	Municipal POTW Laboratory	**240**	36	40	15	14	20	30	15	16	24	30
2	Municipal POTW Laboratory	**20**	3	4	3	1	3	†	2	2	1	1
3	Municipal POTW Laboratory	**14**	1	†	5	†	†	†	†	2	1	5
4	State Laboratory	**119**	19	20	8	12	12	13	9	16	10	†
5	Municipal POTW Laboratory	**60**	18	14	4	4	†	†	†	20	†	†
6	Commercial Laboratory	**30**	†	†	12	†	†	†	12	2	2	2
7	Commercial Laboratory	**59**	4	9	6	3	9	3	9	2	3	11
8	Municipal POTW Laboratory	†	†	†	†	†	†	†	†	†	†	†
9	Municipal POTW Laboratory	**83**	14	8	10	3	†	12	12	5	10	9
10	Commercial Laboratory	**75**	23	12	6	1	15	†	†	4	4	10
	Total Samples	**700**	**118**	**107**	**69**	**38**	**59**	**58**	**59**	**69**	**55**	**68**

Matrices Investigated

nfluent: This matrix will consist of the untreated wastewater at the headworks of a wastewater treatment plant. Each sample will be unique as the composition and consistency of influent changes daily and at each wastewater treatment plant.

ffluent: This matrix is the final product of wastewater treatment process discharged to a receiving water body. Each sample will be unique as the composition and consistency of effluent changes daily and at each wastewater treatment plant.

lank: This matrix is the BOD or CBOD water used to produce the GGA check sample and for dilution of any BOD or CBOD sample aliquot. As per SM 5210 B, the overall depletion of this blank should be less than 0.2 mg/l over a 5-day period. This matrix should be fairly uniform across the ten laboratories participating.

Matrices Investigated, continued

- **Glucose/Glutamic Acid (GGA)**: The GGA matrix consists of a known amount of a bacterial food source in dilution water. It is a measurement of the quality of seed used for seeded BOD and CBOD samples. The depletion of 198 ± 30.5 mg/L is listed in SM 5210 B as the expected depletion for a 5-day BOD or CBOD. This matrix should be fairly uniform across the ten laboratories participating.
- **Seed:** This matrix consists of a known amount of active bacteria in dilution water. The values from the seed matrix are used to correct for seed oxygen uptake in the BOD and CBOD calculation. Each sample will be unique as the composition and consistency of the active bacteria changes.
- **Surface Water**: This matrix will consist of the surface water utilized for receiving effluent from a wastewater treatment plant and/or for drinking water source water. Each sample will be unique as the composition and consistency of surface water changes with site location.
- **Tap Water**: This matrix will consist of finished drinking water. Each sample will be unique as the composition and consistency of tap water changes with site location.

Matrices Investigated, continued

- **Industrials**: A minimum of two different industrial matrices were to be analyzed. Each matrix was to be either a Significant Industrial User (SIU) or a Categorical Industrial User (CIU).
- A Significant Industrial User (SIU) is:
  - Any discharger subject to categorical pretreatment standards;
  - Any other industrial user that discharges an average of twenty-five thousand gallons per day or more of process wastewater (excluding sanitary, noncontact cooling and boiler blowdown wastewaters) to the POTW
  - That contributes a process wastestream which makes up five percent or more of the average dry weather hydraulic or organic capacity of the POTW treatment plant; or
  - That is designated as such by the control authority on the basis that the industrial user has a reasonable probability for adversely affecting the POTW's operation or violating any pretreatment standard or requirement.
- A Categorical Industrial User (CIU) is:
  - An SIU includes "All industrial users subject to Categorical Pretreatment Standards under 40 CFR Part 403.6 and 40 CFR Chapter I, Subchapter N" (40 CFR Part 403.3(t)(1)). For this purpose, an IU is deemed to be a categorical industrial user (CIU) when it meets the applicability requirements for a specific category and is subject to pretreatment standards for existing sources (PSES) or pretreatment standards for new sources (PSNS)

Significant Industrial User Sample Matrices

Significant Industrial User Matrices	
Significant Industry User Type	**Production Description**
1. Animal Blood Products	Dehydration, Extraction and Processing of Animal Blood
2. Animal Slaughter Facility	Slaughter and Processing of Beef, Pork and Poultry
3. Brewery	Production of Beer
4. Candy Manufacturer	Production of Candy
5. Dairy	Production of Milk, Cheese, and Other Dairy Products
6. Ethanol Plant	Production of Ethanol from Corn
7. Food Processors	Production of Bread, Rolls, Pasta, and Other Food Items
8. Gelatin Processor	Production of Gelatin from Beef Hides
9. Meat Byproduct Processor	Rendering Plant for Slaughter Houses
10. Meat Processor	Production of Meat Products from Beef, Pork and Poultry
11. Soda Pop Manufacturer	Production of Carbonated Beverages
12. Wet Corn Mill	Production of Starch, Corn Fructose, and Dextrose from Wet Milled Corn
13. Wood Products Processing	Production of Secondary Wood Products from Mill Waste

Categorical Industrial User Sample Matrices

Categorical Industry User Type	40 CFR Chapter I, Subchapter N Category
1. Iron and Steel Manufacturing	40 CFR 420
2. Metal Finishing	40 CFR 433
3. Centralized Waste Treatment	40 CFR 437
4. Transportation Equipment Cleaning	40 CFR 442

Samples Types Tested for CBOD

Table 2B: CBOD Data Sets Submitted											
Lab #	Lab Name	CBOD									
		Total Samples	POTW Plant Influent	POTW Plant Effluent	Glucose/Glutamic Acid	DO Blank	Seed Correction	Surface Water	Tap Water	Industrial Sample 1	Industrial Sample 2	Industrial Sample, Other
1	Municipal POTW Laboratory	**233**	30	40	15	13	20	30	15	16	24	30
2	Municipal POTW Laboratory	**14**	2	6	2	‡	2	‡	‡	1	1	‡
3	Municipal POTW Laboratory	**23**	‡	8	4	‡	‡	‡	‡	2	2	7
4	State Laboratory	**156**	34	18	8	22	12	13	9	16	24	‡
5	Municipal POTW Laboratory	**11**	6	5	‡	‡	‡	‡	‡	‡	‡	‡
6	Commercial Laboratory	**54**	15	12	12	‡	‡	8	‡	2	2	3
7	Commercial Laboratory	**60**	5	9	6	‡	9	6	9	2	3	11
8	Municipal POTW Laboratory	**55**	21	26	3	3	2	‡	‡	‡	‡	‡
9	Municipal POTW Laboratory	**82**	7	12	15	3	‡	12	12	4	8	9
10	Commercial Laboratory	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
	Total Samples	**688**	**120**	**136**	**65**	**41**	**45**	**69**	**45**	**43**	**64**	**60**

RDO® ATP Test Method for DO, BOD, and CBOD

Based upon Standard Methods 4500-O and 5210-B, with these changes:

- Stirring during measurement is optional.
  - Allow the probe & meter to come to equilibrium prior to accepting the DO value.
- Note: BOD sample preparation is the same as SM 5210-B: stir samples while taking aliquots for BOD dilutions.
- On Day Zero, if the DO measurement will be taken with a non-stirred RDO® probe, cap the BOD bottle and invert sample multiple times to mix well. Then measure DO.
- On Day 5, sample in BOD bottle may be stirred or not.

Comparison of RDO® and Membrane Results

- Each sample was tested three ways:
  - First step – take reading with non-stirred RDO®
  - Second step –stir* the sample and take reading w/ same RDO® probe
  - Third step – continue stirring the sample and take reading w/ the membrane electrode.

* - using magnetic stir plate and stir bars

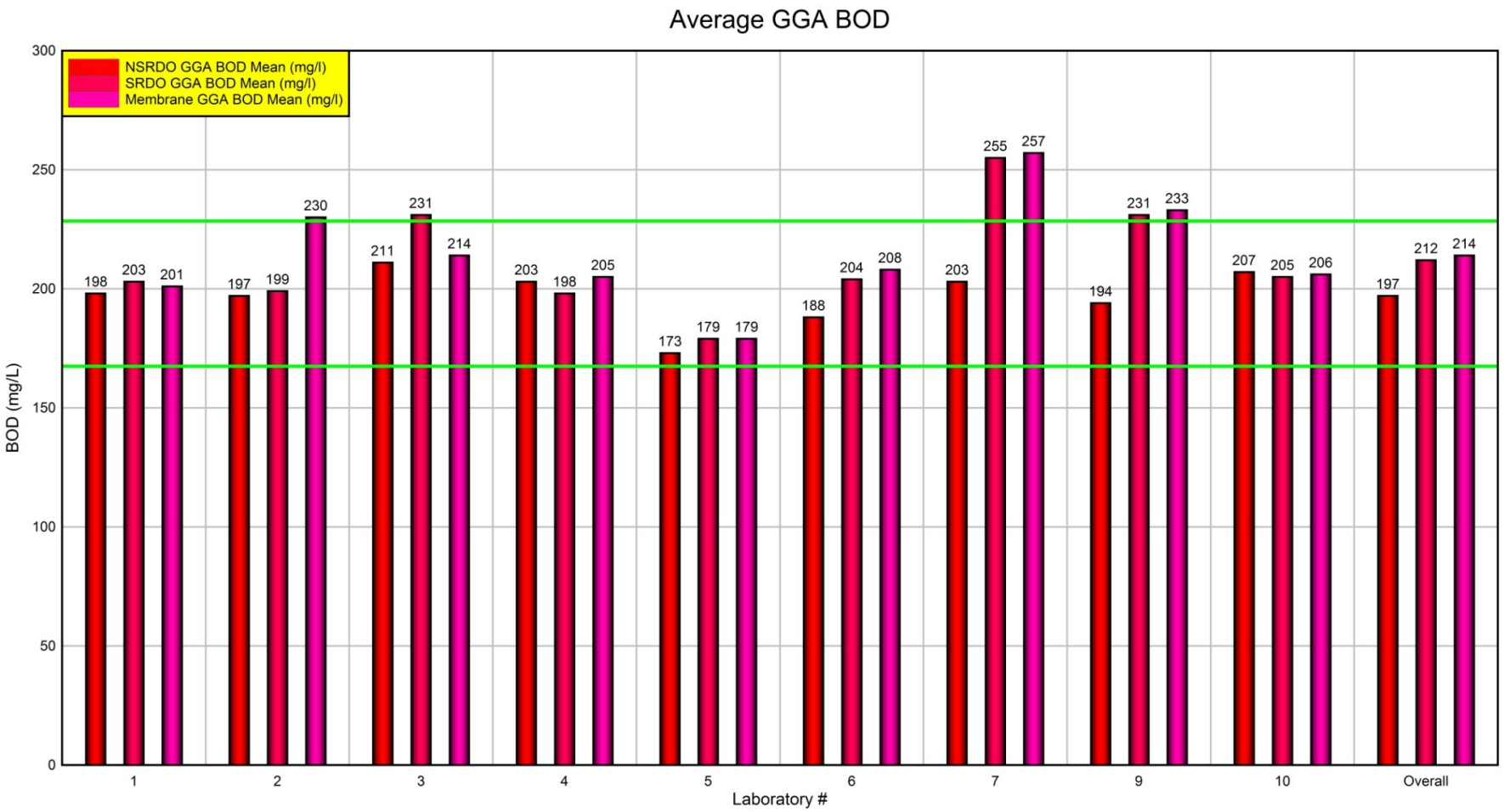
Review of Comparison Data

he following tables have the calculated BOD or CBOD for the non-stirring RDO (NSRDO), stirred RDO (SRDO), and Membrane. SM 5210 B lists 198 ±30.5 mg/L as the recognized standard deviation for the GGA analysis.

lthough each analytical probe, RDO and membrane, experience individual samples that exceeded theses limits, the overall standard deviation did not.

hese outliers were not removed from the statistical analyses so as to allow the F-Test to rigorously compare method comparability between the referenced method and the RDO method.

Average GGA BOD Results



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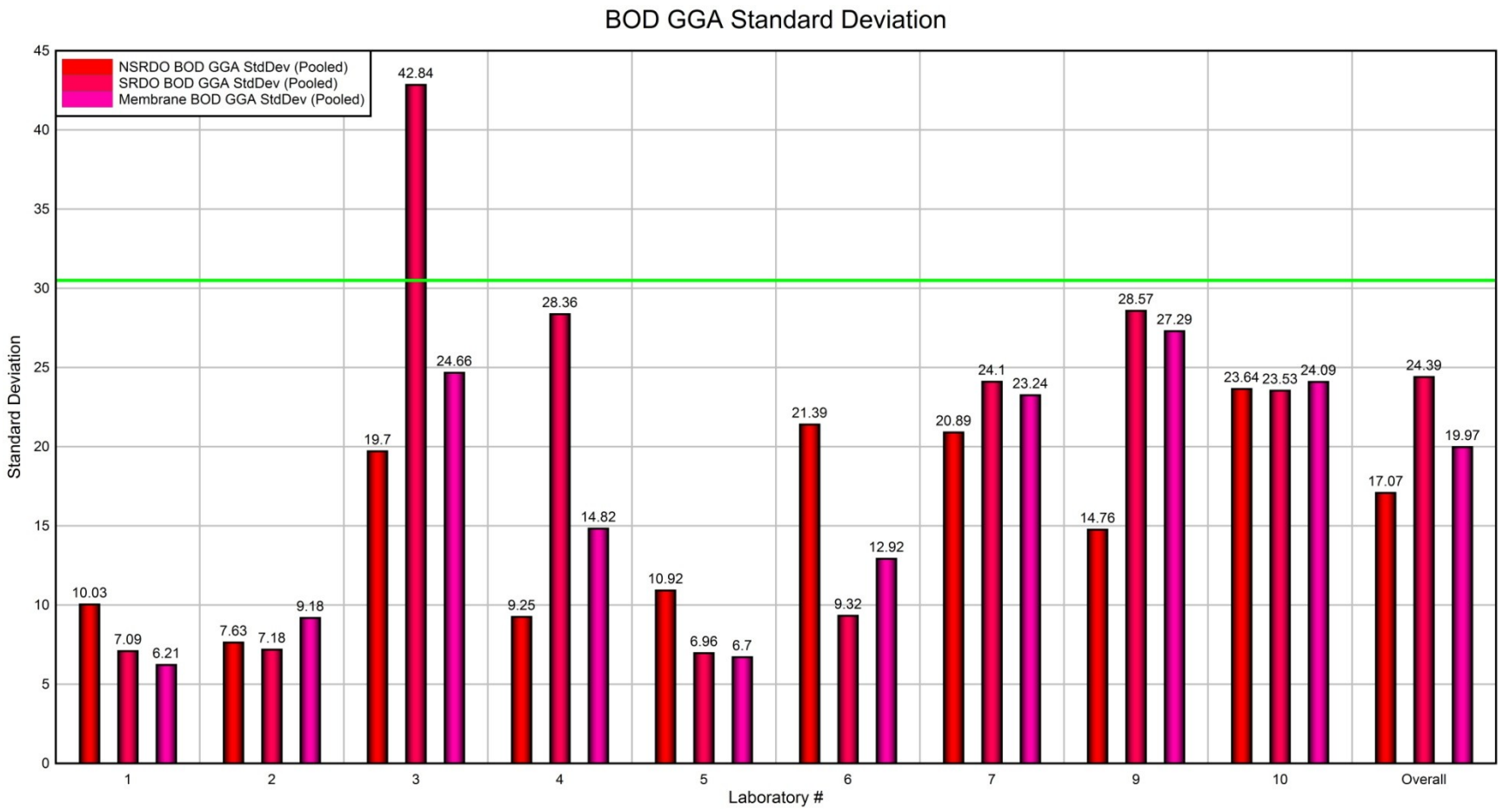
Precision of GGA BOD Results



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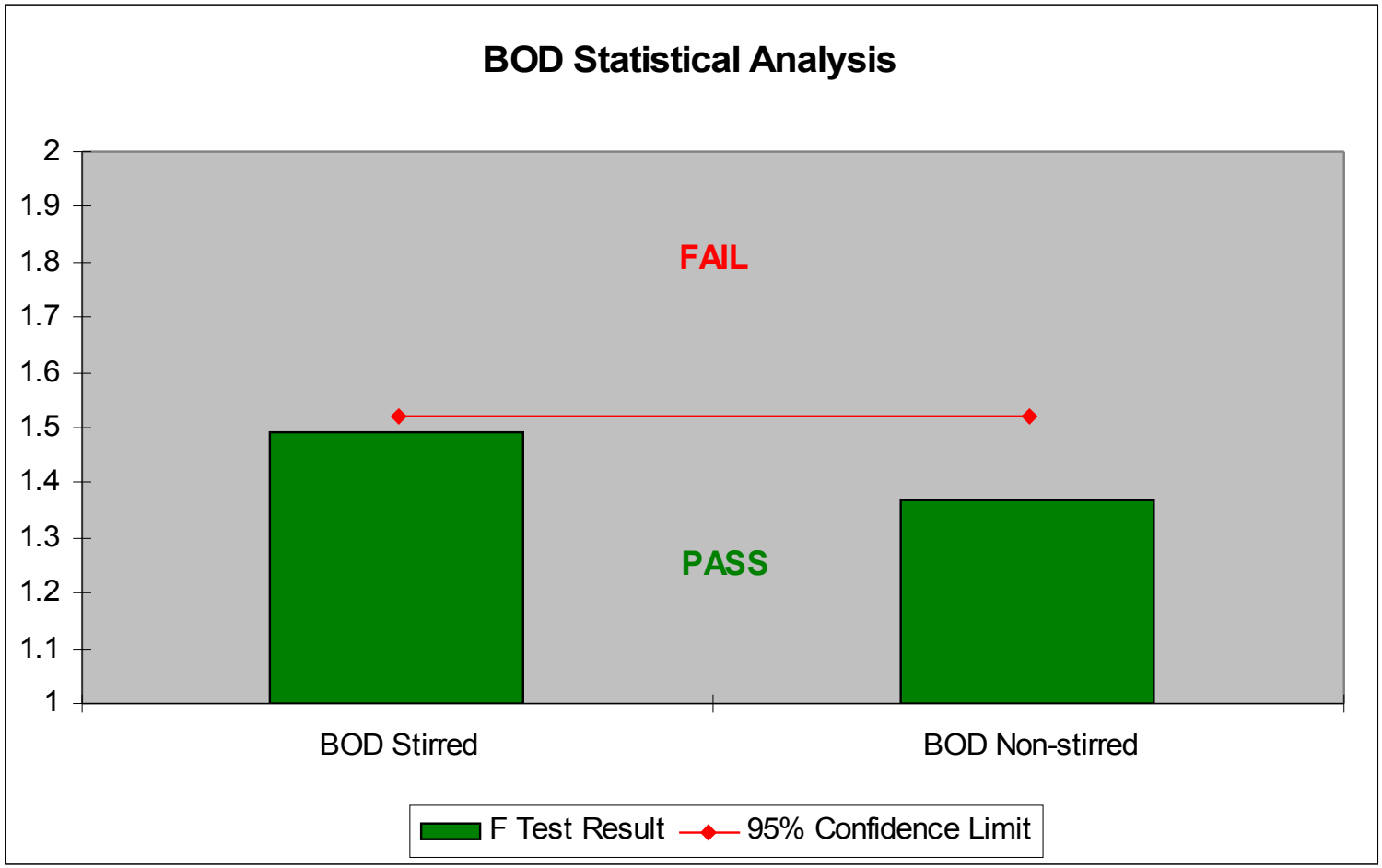
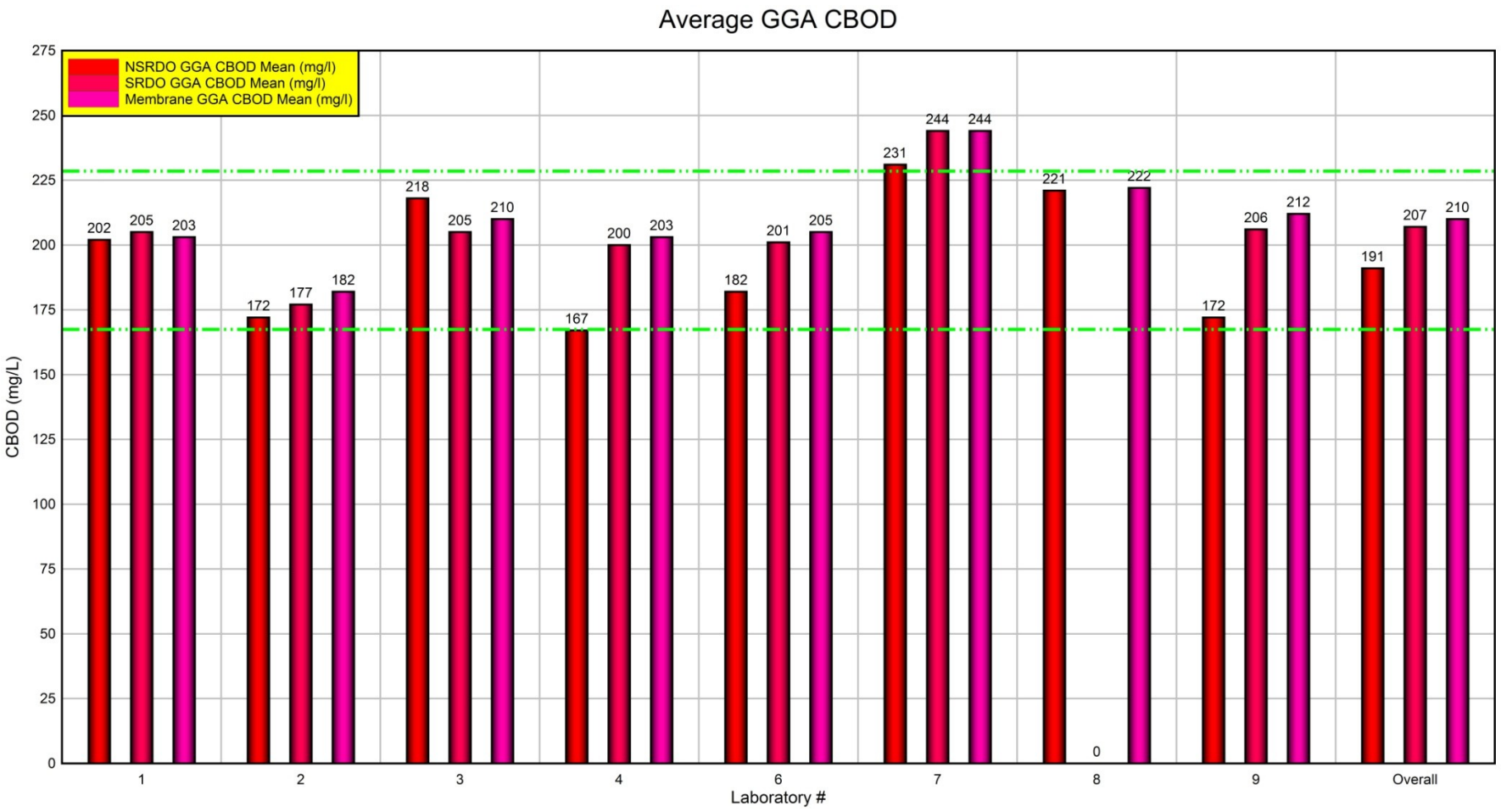
F-Test of GGA BOD results



F-Test compares RDO (stirred and non-stirred) precision to membrane electrode precision for BOD testing and finds that they are not significantly different.

Average GGA CBOD Results



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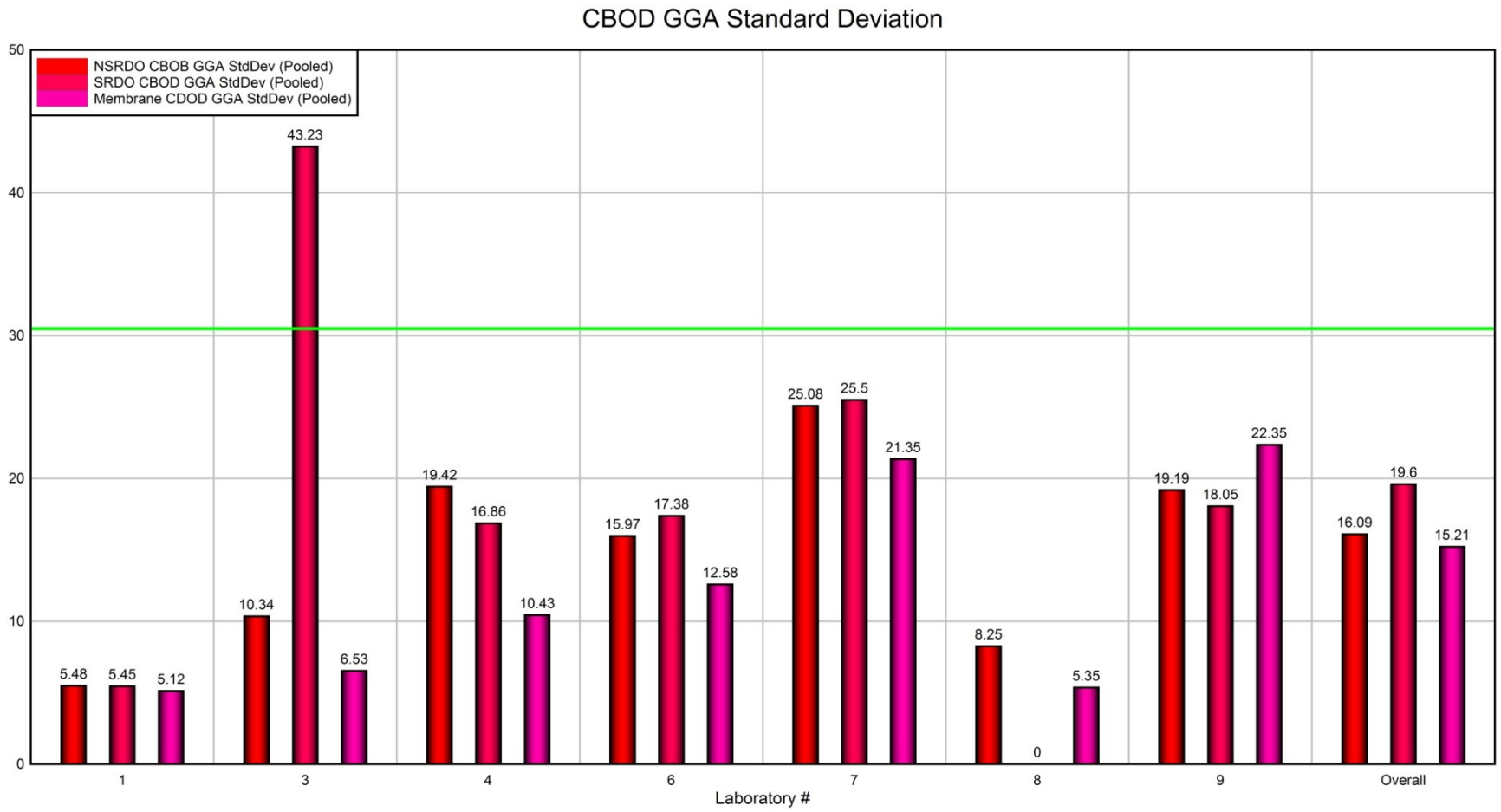
Precision of GGA CBOD Results



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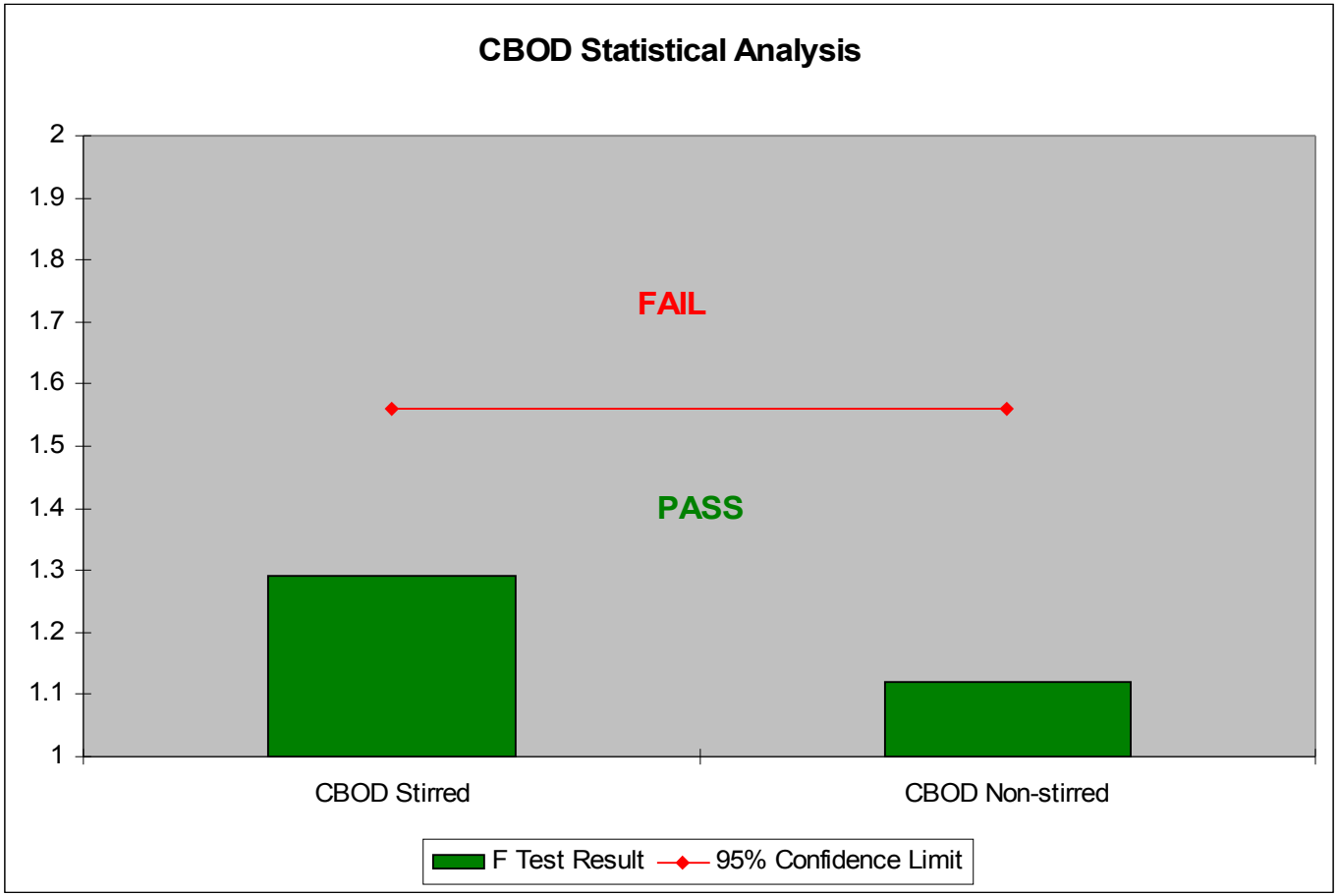
F-Test of GGA CBOD results



F-Test compares RDO (stirred and non-stirred) precision to membrane electrode precision for CBOD testing and finds that they are not significantly different.

Blanks: Agreement of RDO to Membrane Results

BOD Blanks – Comparison to Membrane				
	RPD NSRDO Initial	RPD SRDO Initial	RPD NSRDO Final	RPD SRDO Final
Average % Difference	1.25	1.00	1.43	0.99
Standard Deviation	1.51	1.58	1.71	1.74

CBOD Blanks – Comparison to Membrane				
	RPD NSRDO Initial	RPD SRDO Initial	RPD NSRDO Final	RPD SRDO Final
Average % Difference	1.34	0.73	1.54	0.73
Standard Deviation	1.18	0.62	1.57	0.93

Method Reporting Limits for RDO DO Measurements

Lower Limit of Determination			
Zero Solution Reading			
Laboratory #	Mean (mg/L)	Pooled Standard Deviation (mg/L)	Calculated Confidence Interval (mg/L)
1	0.053	0.025	0.03
2	0.072	0.053	0.07
3	0.043	0.006	0.01
4	0.022	0.007	0.01
5	0.047	0.021	0.04
7	0.162	0.008	0.01
9	0.067	0.047	0.10
Overall	**0.071**	**0.037**	0.04

Other Data Evaluated for ATP Approval

In addition to GGA, Blanks, and Zero Solution readings, comparison data submitted to EPA ATP program also included these samples:

- Influent for BOD and CBOD
- Effluent for BOD and CBOD
- Seed for BOD and CBOD
- Surface Water for BOD and CBOD
- Tap Water for BOD and CBOD
- Industrial samples for BOD and CBOD

Details of these results are found in the performance tables included at the back of each approved method.

Summary of ATP Results

In all cases, RDO® data compared favorably with the accepted method data, generated by the membrane electrode.

Each of the three RDO methods is approved for water, wastewater, effluent, and polluted water.

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When Can I Start Using RDO® Methods?

The EPA Office of Science and Technology will recommend the RDO® Optical Probe methods for inclusion at 40 CFR Part 136.3.

In the interim, NPDES permit holders can begin monitoring with the RDO® methods after seeking approval from their regional USEPA authority.

How to Implement RDO in your Laboratory?

Users who are testing for process monitoring and other non-permit requirements can begin using the RDO methods immediately, with or without stirring.

How to Implement RDO in your Laboratory?

Users who are testing for permit compliance can follow the interim approval process, which may include some or all of the following:

- Obtain a copy of the RDO test method(s) to be used.
- Obtain a copy of the EPA ATP approval letters for RDO.
- Generate QC data conforming to the method(s).
- Contact your USEPA Region to obtain an approval letter. Requirements may vary.
- Submit USEPA Regional approval letter to the state contact and request state approval letter. Requirements may vary.

Thermo Scientific RDO®: Resources on Web

Find useful information at

www.thermoscientific.com/waterapps

1. Choose “Conductivity & DO” link in the “Search for an application” box in the lower right corner.
2. Choose “RDO Regulations” link in the upper right corner.
    - Regional USEPA and State Approval Requirements
    - USEPA Letters recommending Interim Approval
    - Application Notes including Optical DO in groundwater, wastewater
      effluent, wastewater aeration basin, and seawater
    - FAQs

Thermo Scientific RDO®: Resources

- Contact us for any technical questions
  - *Technical Support: (800) 225-1480*
  - *Technical Support e-mail: info.water@thermo.com*
  - *Web site: www.thermoscientific.com/water*
  - *Chris Scott, Technical Sales Manager*
    - *e-mail: chris.scott@thermofisher.com*

Questions