Low Level Detection of Ammonia

New Method Validated Following EPA Guidance

ATP Case #: N08-0004

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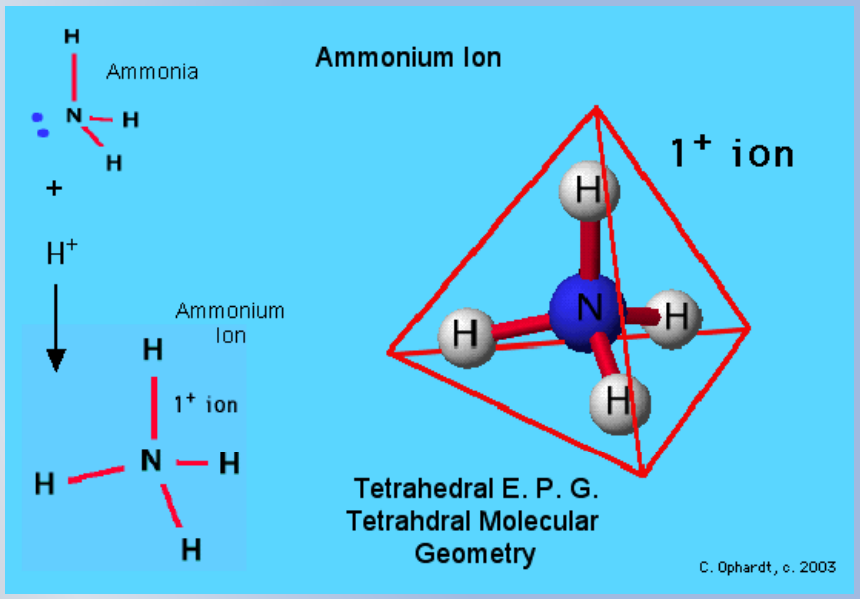
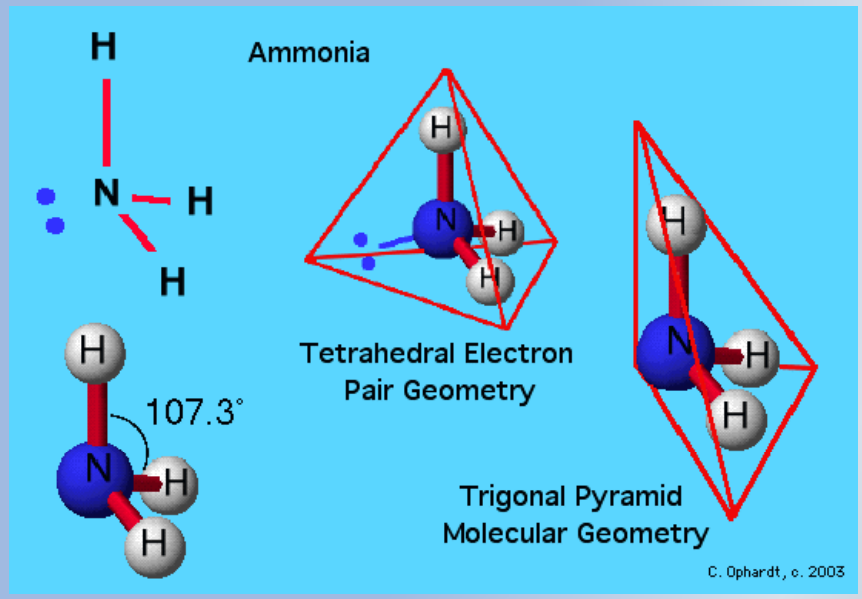
Askew Scientific Consulting

Ammonia???

Ionized



Un-ionized



Ammonia Detection

$$2\ NH_3 \xrightleftharpoons{H_2SO_4} (NH_4)_2SO_4$$

Green — Lavender

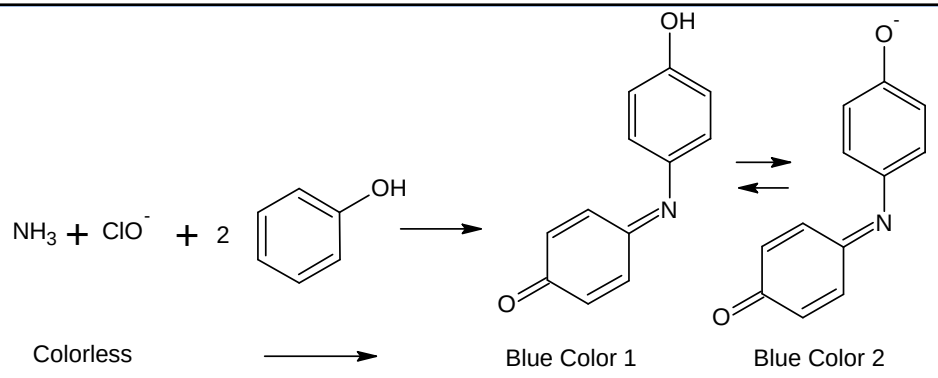
Titration

Inside ISE

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

pH

Reaction Inside the Ion Selective Electrode (ISE)



Berthelots (Phenate) Reaction

$$2\ K_2(HgI_4) + 2\ NH_3 \rightarrow NH_2Hg_2I_3 + 4KI + NH_4I$$

Colorless → Orange Brown

Nesslers Reaction

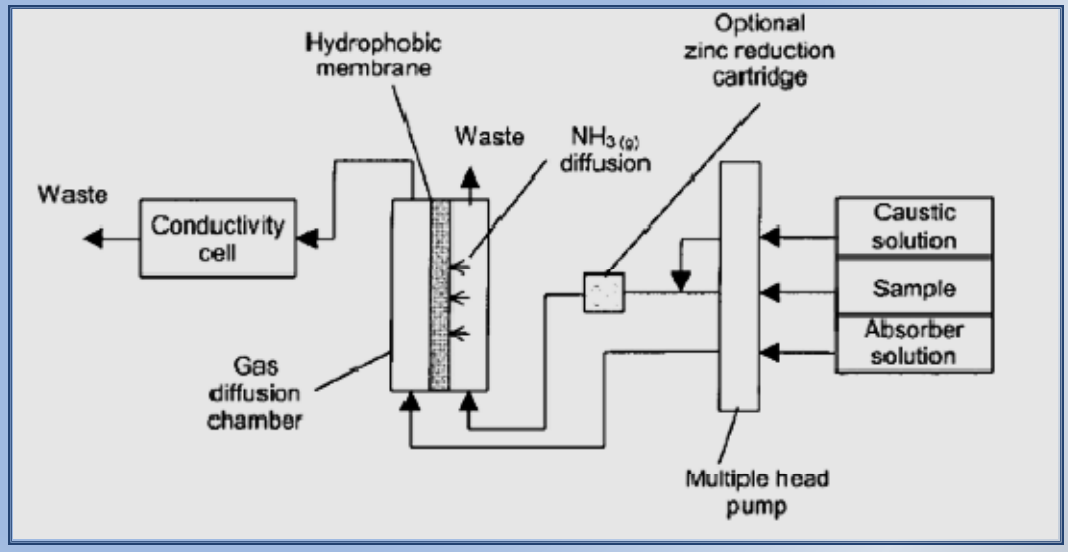
Inside Membrane

$$NH_3 + \text{Caustic} \rightleftharpoons NH_4^+ \text{ (Conductance)}$$

Boric Acid

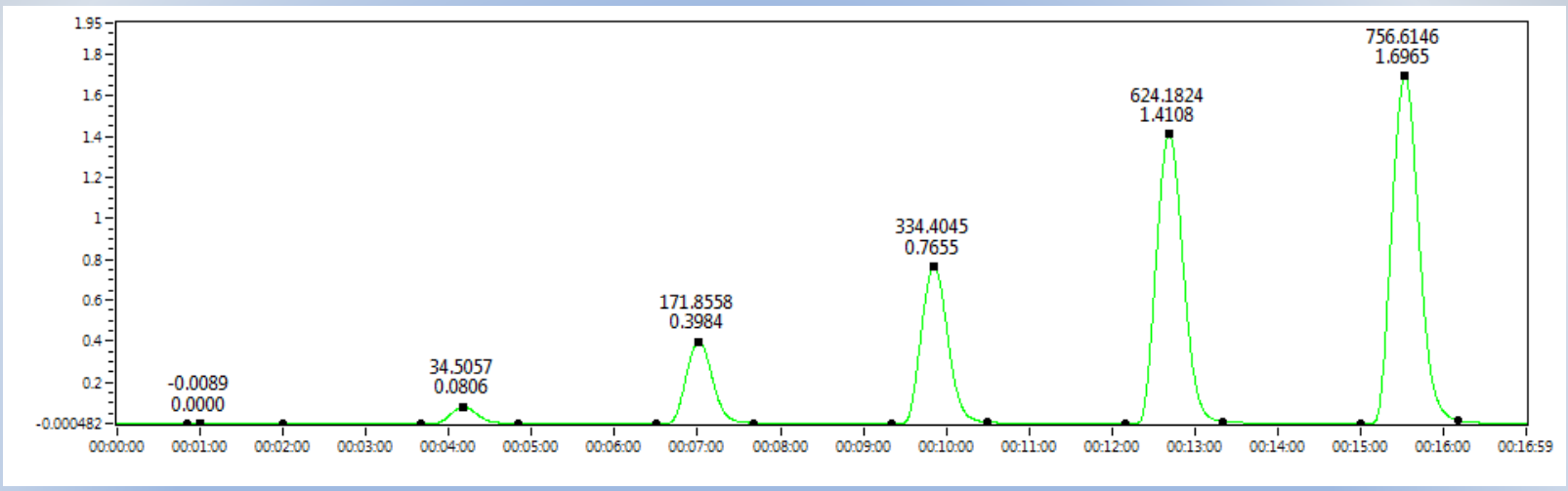
Reaction for Membrane Extraction/Conductance

Timberline TL series



New Method Validation References

- Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water, March 1999, EPA 821-B-98-003
- Standard Practices for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water, ASTM D2777-06
- Standard methods for the Examination of Water and Wastewater, Parts 1000 and 4000, Online


1.95
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
-0.000482
-0.0089
0.0000
34.5057
0.0806
171.8558
0.3984
334.4045
0.7655
624.1824
1.4108
756.6146
1.6965
00:00:00
00:01:00
00:02:00
00:03:00
00:04:00
00:05:00
00:06:00
00:07:00
00:08:00
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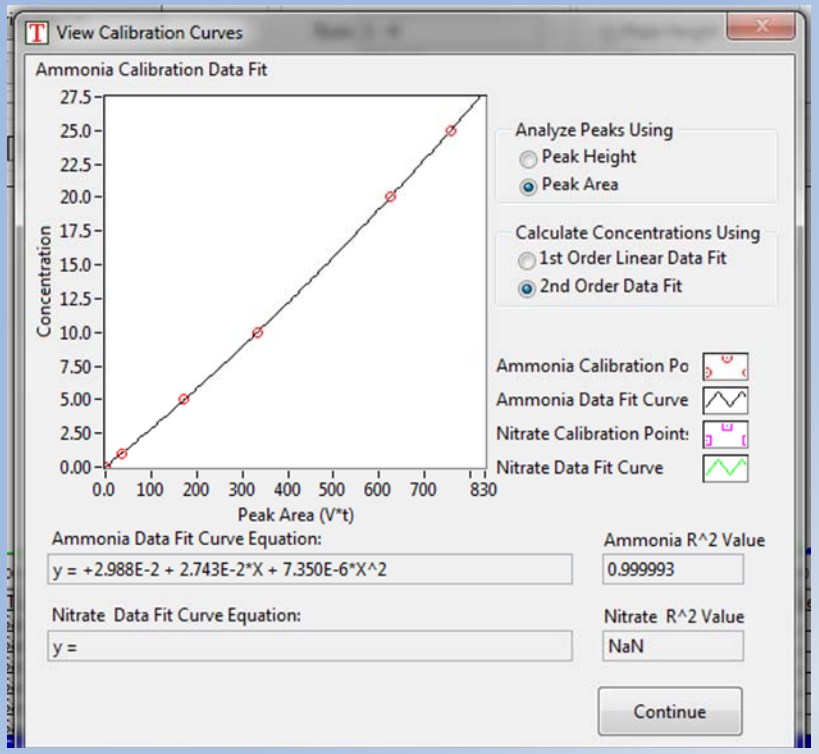
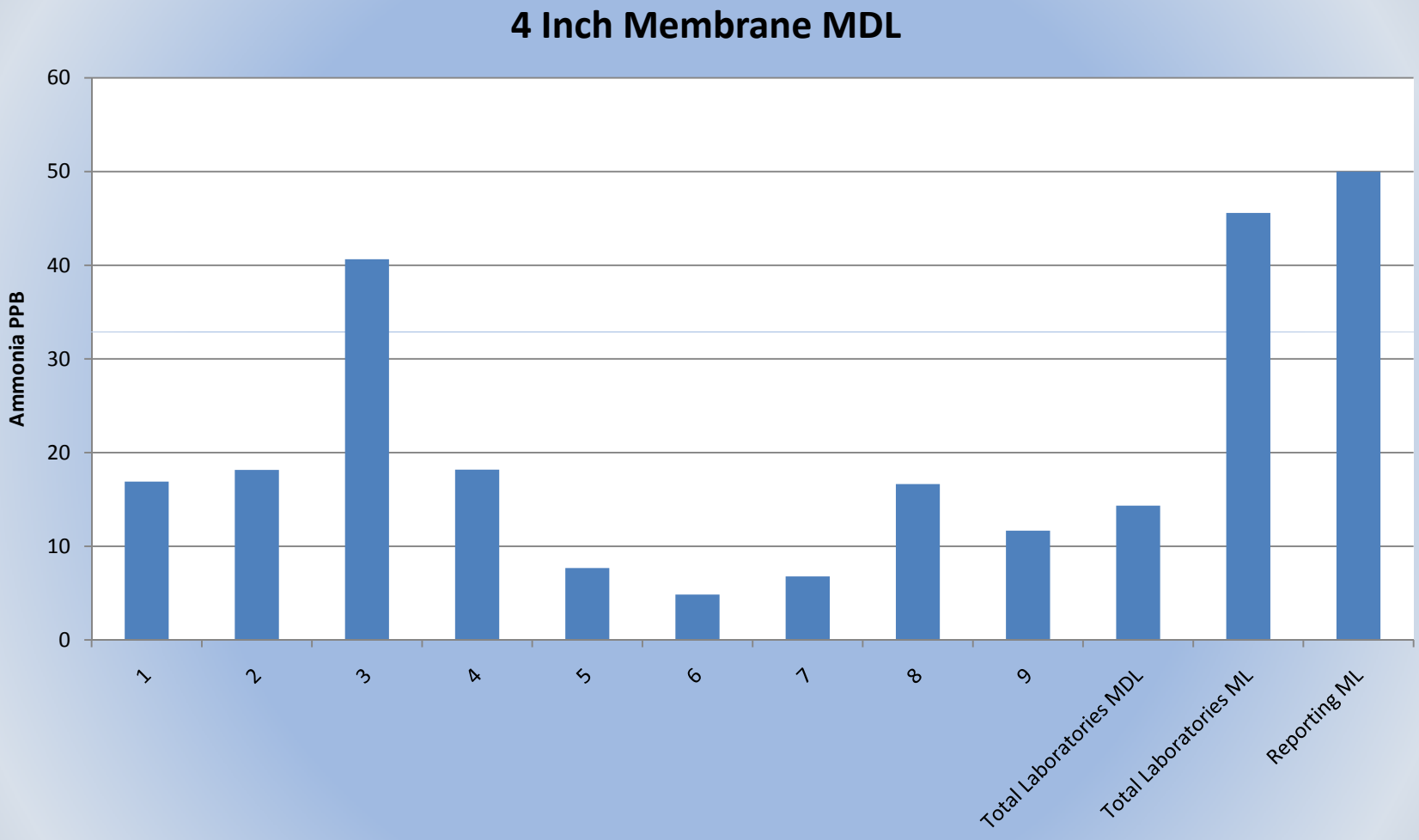
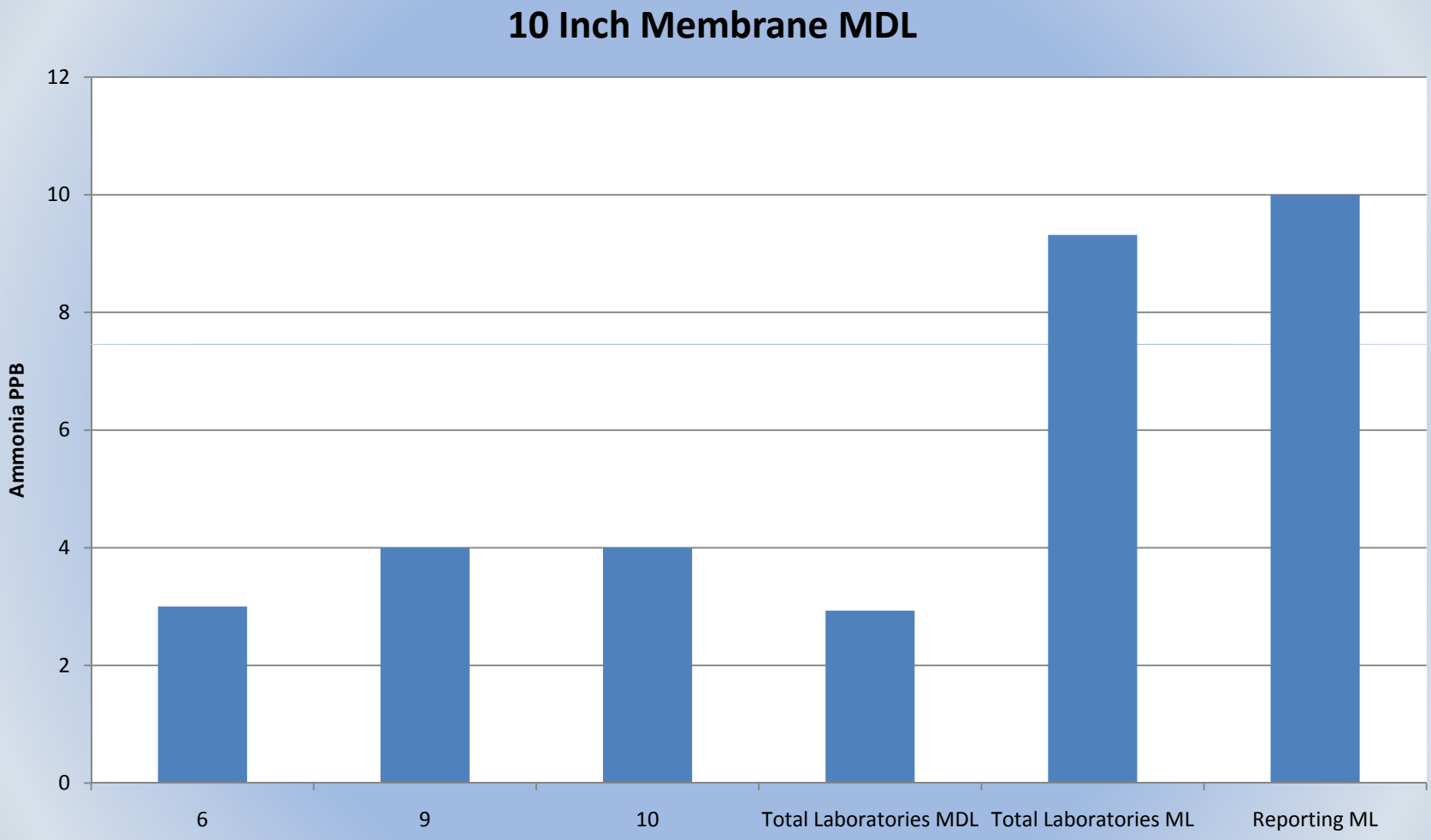
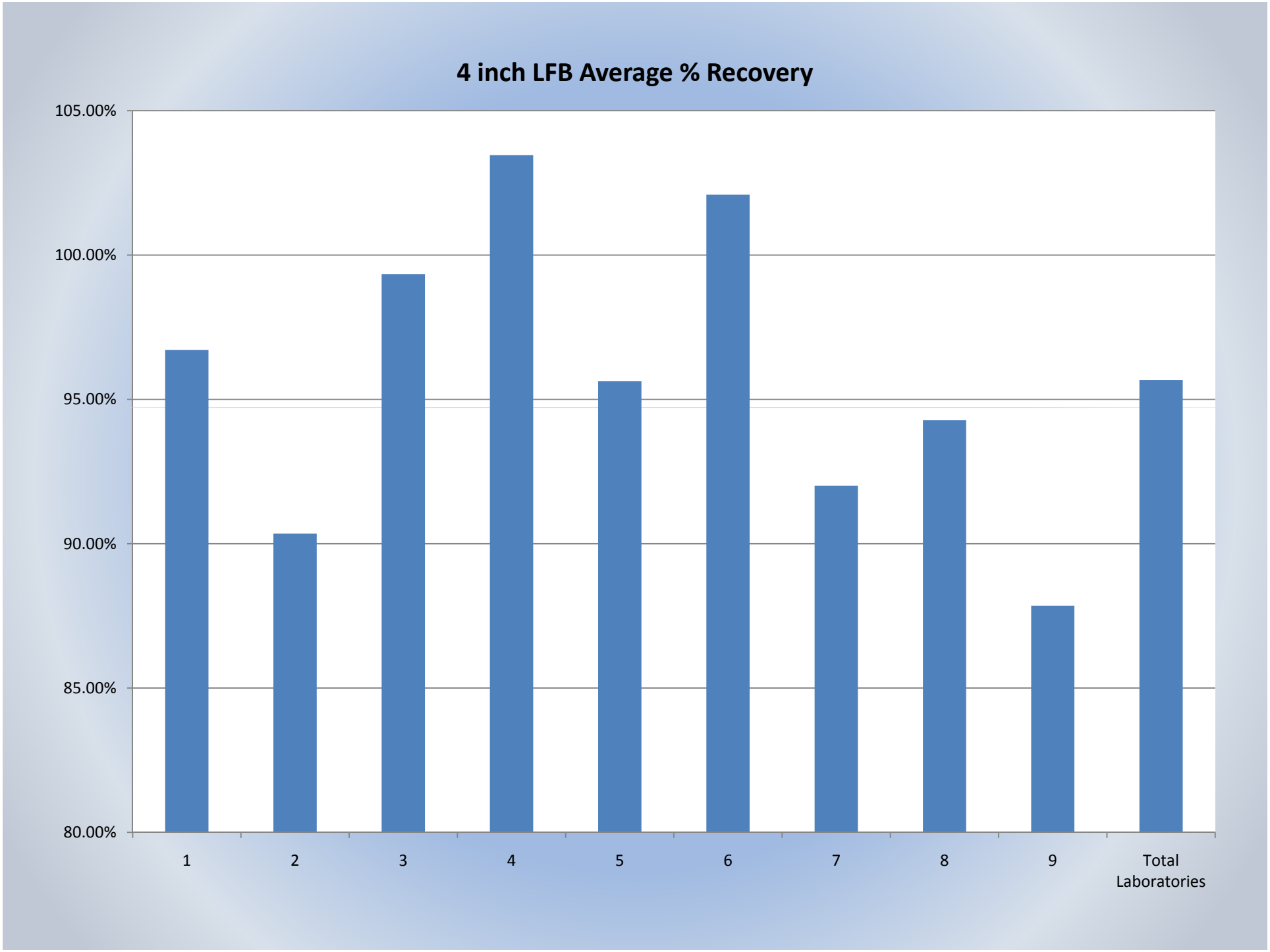
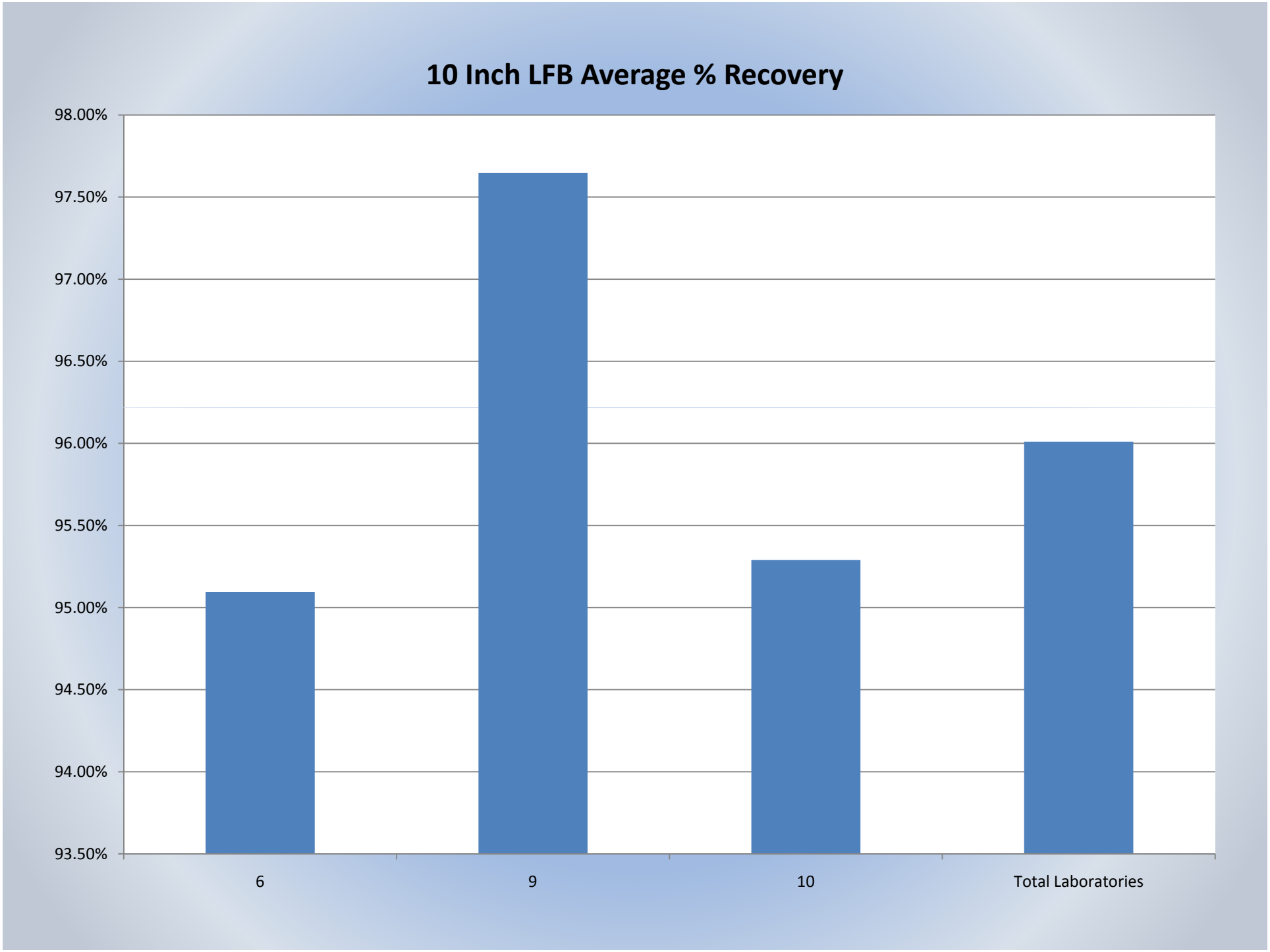
00:14:00
00:15:00
00:16:00
00:16:59


View Calibration Curves
Ammonia Calibration Data Fit
Concentration
27.5
25.0
22.5
20.0
17.5
15.0
12.5
10.0
7.50
5.00
2.50
0.00
0.0
100
200
300
400
500
600
700
830
Peak Area (V*t)
Analyze Peaks Using
Peak Height
Peak Area
Calculate Concentrations Using
1st Order Linear Data Fit
2nd Order Data Fit
Ammonia Calibration Po
Ammonia Data Fit Curve
Nitrate Calibration Points
Nitrate Data Fit Curve
Ammonia Data Fit Curve Equation:
y = +2.988E-2 + 2.743E-2*X + 7.350E-6*X^2
Ammonia R^2 Value
0.999993
Nitrate Data Fit Curve Equation:
y =
Nitrate R^2 Value
NaN
Continue


4 Inch Membrane MDL
Ammonia PPB
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
Total Laboratories MDL
Total Laboratories ML
Reporting ML


10 Inch Membrane MDL
Ammonia PPB
12
10
8
6
4
2
0
6
9
10
Total Laboratories MDL
Total Laboratories ML
Reporting ML

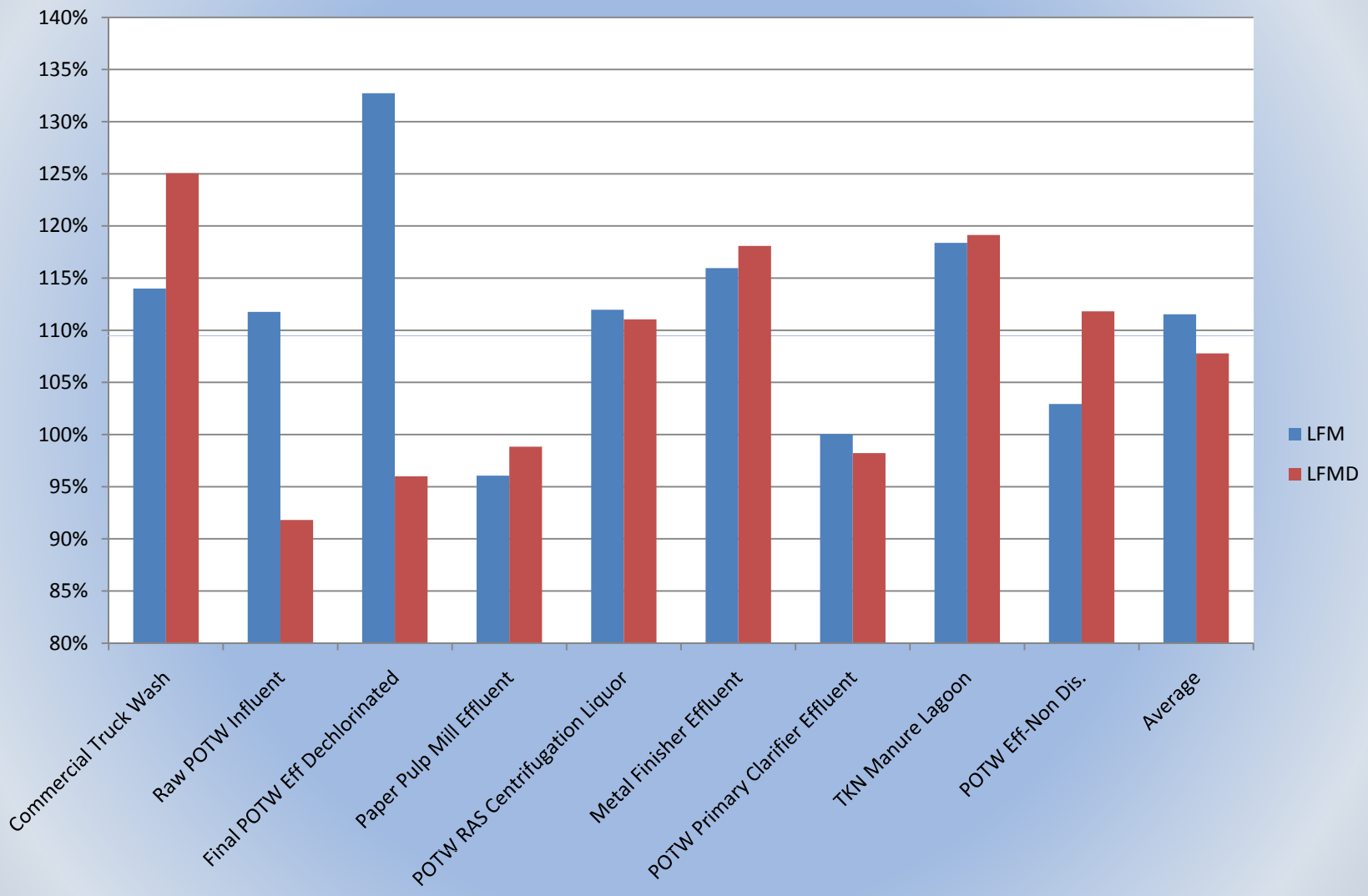

4 inch LFB Average % Recovery
105.00%
100.00%
95.00%
90.00%
85.00%
80.00%
1
2
3
4
5
6
7
8
9
Total Laboratories


10 Inch LFB Average % Recovery
98.00%
97.50%
97.00%
96.50%
96.00%
95.50%
95.00%
94.50%
94.00%
93.50%
6
9
10
Total Laboratories

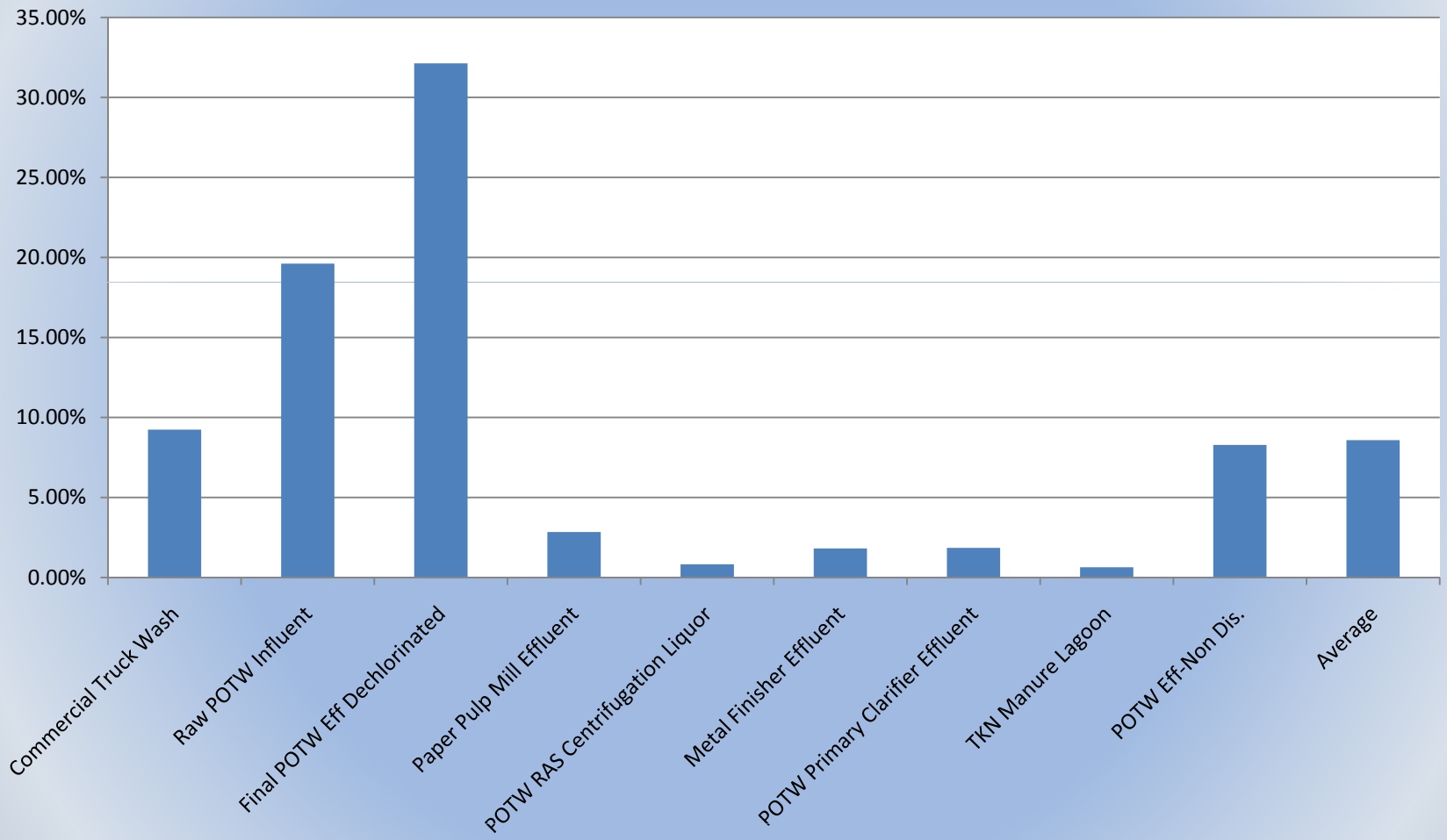
Matrixes

- **Raw POTW Influent:**
  - Raw domestic and industrial wastewater that is received at the headworks of a POTW
- **POTW Primary Clarifier Effluent:**
  - Wastewater that is discharged from the primary clarifier at the POTW. Contains dissolved and suspended solids.
- **POTW Return Waste Activated Sludge Centrifugation Liquor:**
  - High strength ammonia wastewater from the POTW activated sludge centrifuge.
- **Final POTW Effluent, Non Disinfected:**
  - Final effluent from the POTW that has not been disinfected.
- **Final POTW Effluent, Dechlorinated:**
  - Final effluent from the POTW that has been disinfected with chlorine and dechlorinated with a sulfur based compound.
- **POTW Receiving Watershed:**
  - Surface water that receives the POTW final dechlorinated effluent.
- **Categorical Industrial Effluent, 40 CFR 433 Metal Finisher:**
  - Raw industrial wastewater discharge to a point in the collection system.
- **Categorical Industrial Effluent, 40 CFR 442 Commercial Truck Wash:**
  - Raw industrial wastewater discharge to a point in the collection system.
- **Categorical Industrial Effluent, 40 CFR 430 Pulp and Paper Mill:**
  - Wastewater from a paper pulp mill treatment process.
- **Significant Industrial Effluent Kjeldahl Digestant:**
  - Wastewater lagoon (liquid manure) that has been digested by an approved Kjeldahl method.

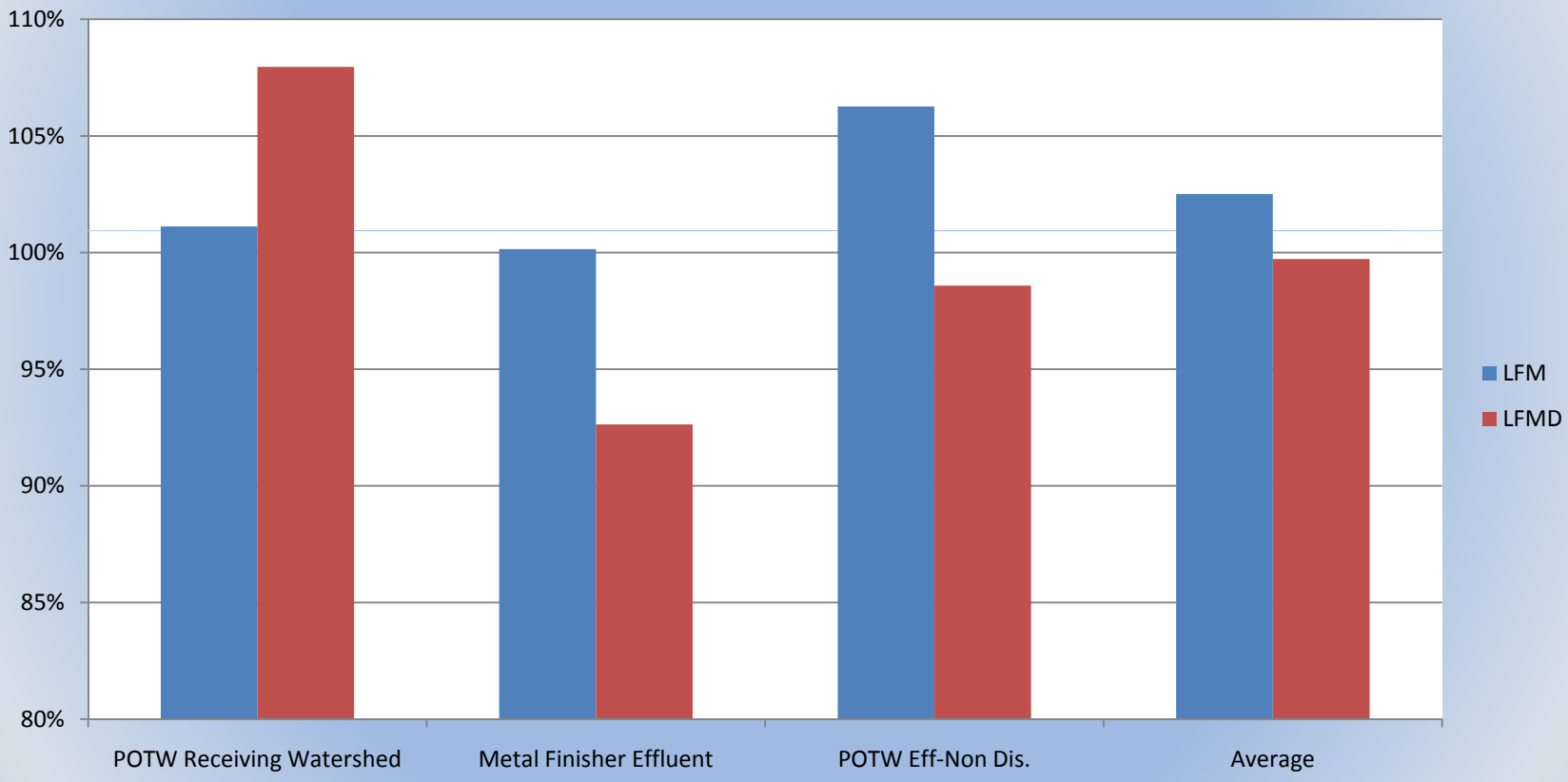
LFM/LFMD Recoveries
4 Inch Membrane



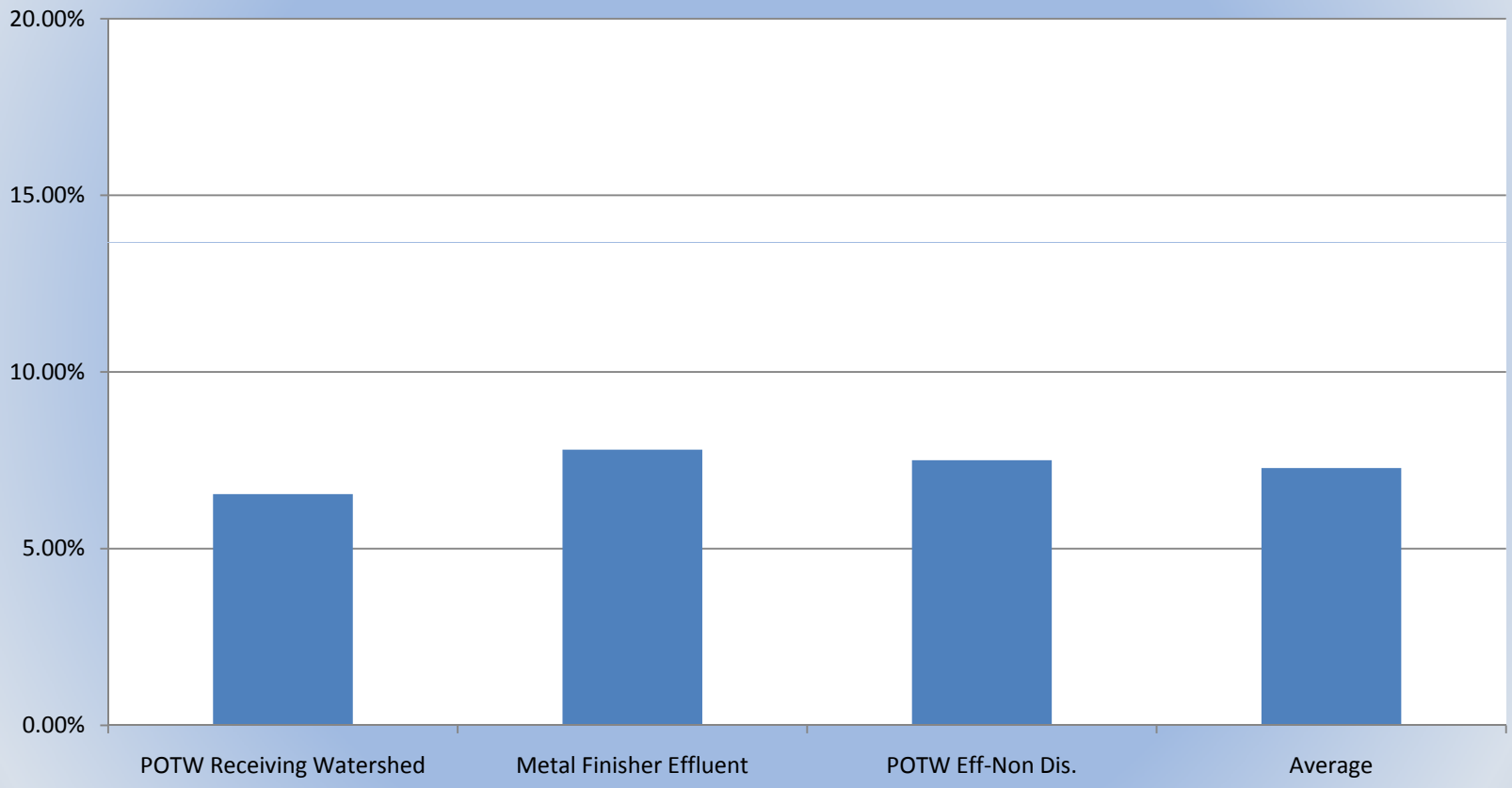
4 Inch Membrane
LFM/LFMD RPD

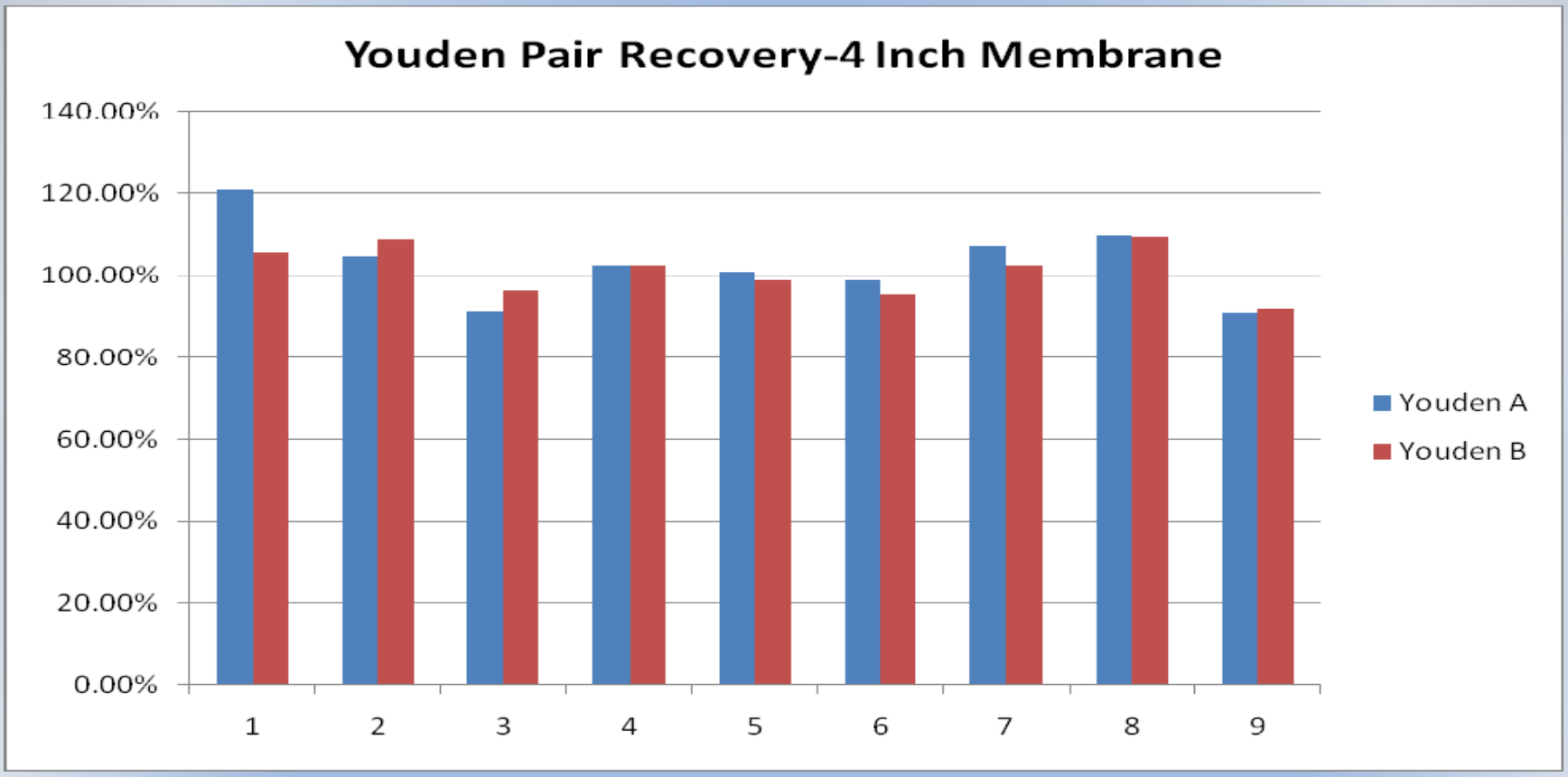


LFM/LFMD Recoveries
10 Inch Membrane

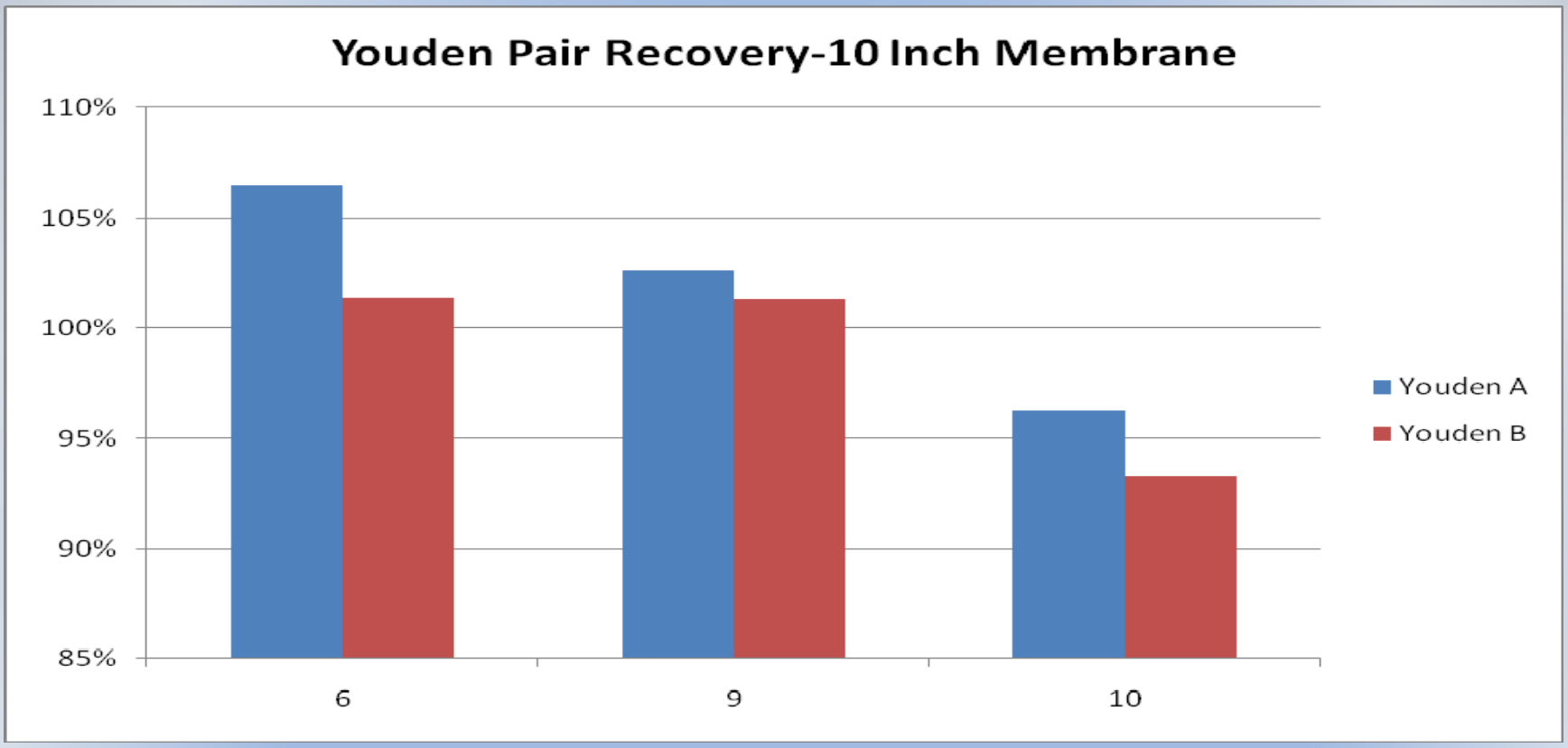


10 Inch Membrane
LFM/LFMD RPD





Summary Single Operator Standard Deviation and %RSD – 4 Inch Membrane			
Youden Pair	**Youden 1**	**Youden 2**	**Youden 3**
Single Operator So (Standard Deviation)	0.24	0.0049	0.049336281
Single Analyst %RSD	4.08%	0.22%	1.63%



Summary Single Operator Standard Deviation and %RSD – 10 Inch Membrane	
Youden Pair	**Youden Pair 1**
Single Operator So (Standard Deviation)	0.07
Single Analyst %RSD	0.06%

New Method Improvements

- 40 CFR Part 136.7
  - (1) Demonstration of Capability (DOC);
  - (2) Method Detection Limit (MDL);
  - (3) Laboratory reagent blank (LRB), also referred to as method blank;
  - (4) Laboratory fortified blank (LFB), also referred to as a spiked blank, or laboratory control sample (LCS);
  - (5) Matrix spike, matrix spike duplicate, or laboratory fortified blank duplicate (LFBD) for suspected difficult matrices;
  - (6) Internal standards, surrogate standards (for organic analysis) or tracers (for radiochemistry);
  - (7) Calibration (initial and continuing), initial and continuing performance (ICP) solution also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV);
  - (8) Control charts (or other trend analyses of quality control results);
  - (9) Corrective action (root cause analyses);
  - (10) QC acceptance criteria;
  - (11) Definitions of a batch (preparation and analytical); and
  - (12) Specify a minimum frequency for conducting these QC checks.

Initial Demonstration of Capability

- Initial Demonstration of Capability: A laboratory fortified blank whose concentration is between the 10% and 50% of the dynamic range is analyzed four times. The mean recovery and standard deviation are calculated and evaluated for acceptance.
  - Acceptance Criteria: IDC control limit for the laboratory is based on the limits determined in this method and shall not exceed 82%-110 % with a percent Relative Standard Deviation less than 8%.
  - Corrective Action: If the IDC recovery falls outside of these limits, the analyst or instrument is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the IDC repeated until passed.

Continuing Calibration Verification

- Continuing Calibration Verification: At least one CCV standard will be prepared so as to have a concentration in the dynamic range of the instrument. The CCV will be run at least once per each batch. The CCV percent recovery is calculated and evaluated for acceptance.
  - Acceptance Criteria: CCV control limit for the laboratory is based on the limits determined in this method and shall not exceed 90%-110 %.
  - Corrective Action: If the CCV recovery falls outside of these limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

Laboratory Reagent Blank

- Laboratory Reagent Blank: A LRB is analyzed as a sample at least once per batch. The LRB concentration result will be evaluate for acceptance.
  - Acceptance Criteria: The LRB concentration result will be below the lowest calibration standard in the dynamic range.
  - Corrective Action: If the LRB falls outside of the acceptance limit, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

Laboratory Fortified Blank

- Laboratory Fortified Blank: A LFB with a concentration of ammonia between 10% and 50% of the dynamic range is analyzed at least once per batch. The LFB concentration result will be evaluate for acceptance.
  - Acceptance Criteria: LFB percent recovery is based on the limits determined in this method and shall not exceed 87%-104 %.
  - Corrective Action: If the LFB recovery falls outside of these limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

Sample Matrix Spikes (LFM/LFMD)

- Laboratory Fortified Sample Matrix Spikes (LFM/LFMD): A duplicate set of ammonia or Kjeldahl samples are spiked with a known amount of ammonia with a concentration that is between 10% and 50% of the dynamic range
  - Acceptance Criteria: The LFM/LFMD percent recovery is based on the limits determined in this method and shall not exceed 84%-115 %. The relative percent difference (RPD) shall not exceed 20%.
  - Corrective Action: If the LFM and LFMD percent recovery or the RPD fall outside of these limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

Ongoing Demonstration of Capability (ODC)

- Ongoing Demonstration of Capability (ODC): A LFB with a concentration of ammonia between 10% and 50% of the dynamic range is analyzed at least once per batch. The LFB percent recovery will be charted by control charts and be evaluated for acceptance.
  - Acceptance Criteria: LFB percent recovery must stay within the control limits calculated for the control chats.
  - Corrective Action: If the LFB percent recovery falls outside of these control limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

Sample Analysis Sequence

- Sample Analysis Sequence: Typical sample analysis sequence
  - Instrument Start Up
  - Calibration zero
  - Calibration standards, 1-5
  - LRB
  - LFB
  - Sample used for LFM/LFMD
  - LFM
  - LFMD
  - Samples (First half of batch)
  - CCV
  - Samples (Second half of batch)
  - Repeat CCV (Optional)

Initial Calibration:

- Initial Calibration:
  - Initial calibration is performed at the beginning of each batch.
  - Calibrate instrument with calibration zero and five calibration standards of ammonia.
  - Apply linear or polynomial curve-fitting statistics, as appropriate, to analyze the concentration–instrument response relationship.
    - Acceptance Criteria: The linear or nonlinear correlation coefficient for standard concentration-to-instrument response shall be greater than or equal to 0.995.
    - Corrective Action: If the correlation coefficient falls outside of the limit, the initial calibration is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the initial calibration repeated.

Standard Back Calculation

- Back calculate the standard concentration of each calibration point using the calibration equation determined by the curve fitting statistics.
  - Acceptance Criteria: The back-calculated and true concentrations should agree within ± 10% and cannot exceed ± 15%.
  - Corrective Action: If the standard back calculations fall outside of the limits, the initial calibration is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the initial calibration repeated.

Continuing Calibration Verification:

- Continuing Calibration Verification:
  - A CCV is analyzed at the midpoint of the batch sample set. The CCV is prepared from a different source (chemical lot) than that used for the calibration standards.
    - Acceptance Criteria: CCV control limit for the laboratory is based on the limits determined in this method and shall not exceed 90%-110 %.
    - Corrective Action: If the CCV recovery falls outside of these limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

Ongoing Demonstration of Capability

- Ongoing Demonstration of Capability Analyst Proficiency: A LFB is analyzed using the same instrumental conditions and procedures used to analyze samples at least once per batch. The LFB percent recovery will be charted by control charts and be evaluated for acceptance.
  - o Acceptance Criteria: LFB percent recovery must stay within the control limits calculated for the control chats.
  - o Corrective Action: If the LFB percent recovery falls outside of these control limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

Corrective Action (Root Cause Analysis)

- Corrective Action (Root Cause Analysis): The laboratory analyst(s) and laboratory management will perform a root cause analysis for any QC failures. The analysis will have at a minimum the following areas described in detail:
  - Identify the problem: Identify the QC failure. Include instrument, reagent, sampling, personnel and any other problems.
  - Investigate to identify the root cause: Determine how each problem identified interacted with each other to create the QC problem.
  - Come up with the solution: Develop an encompassing solution to address all problems that created the QC failure.
  - Implement the solution: Develop an implementation plan that includes all components of the developed solution and have laboratory management implement it.
  - Document the solution: Document all corrective action steps taken under laboratory management implementation of the corrective action.
  - Communicate the solution: Develop training and management programs to communicate and evaluate all personnel included in the corrective action solution.
  - Evaluate the effectiveness of the solution: Document QC results in trend charts and laboratory staff performance to validate corrective action solution.

In Conclusion

- **Webinar:**
  - ***Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis, Wednesday, August 24, 2011, 2:00 PM - 3:00 PM EDT***
- Please contact Sara Bury at **awtimber@t-line.com** for further information on the webinar.
- Register at: https://www3.gotomeeting.com/register/662000630

Questions ???