

**Determining the  
Procedures That Online  
and Remote Instruments  
Must Meet to Confirm  
Compliance with 40 CFR  
Part 136 Quality Control**

# Presented By

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# Definitions

- ▶ Regulatory Chemistry: What Is It?
- ▶ It is proscriptive rules on how your laboratory or plant must meet regulatory standards/limits.
- ▶ Failure to meet the requirements of a proscriptive rule can lead to:
  - Notices of Violations
  - Administrative Orders
  - Fines
  - JAIL

# What Is Required In 40 CFR §137.7


1. Demonstration of Capability (DOC),
2. Method Detection Limit (MDL),
3. Reagent blank (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 (MS), matrix spike duplicate (MSD), or laboratory fortified blank duplicate (LFBD) for suspected difficult matrices,
6. Internal standard/s, surrogate standard/s (for organic analysis) or tracer (for radiochemistry),
7. Calibration (initial and continuing),
8. Control charts (or other trend analyses of quality control results), and
9. Corrective action (root cause analyses),
10. Specific frequency of QC checks,
11. QC acceptance criteria, and
12. Definitions of a batch (preparation and analytical)




# What Is Required in Standard Methods For The Examination of water and Wastewater (23<sup>rd</sup> edition)

## 4500-H<sup>+</sup>

# 4500-H<sup>+</sup> QC Requirements


- ▶ Duplicates of the Sample will be run.
  - ▶ Additional QC Check with pH sample whose value is bracketed by calibration standards.
  - ▶ Verify Slope according to manufacturers instructions.
  - ▶ Refer to 4020B for other QC requirements.
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# Case Study


- ▶ An industry is discharging a wastewater to a city sewer.
  - ▶ The pH is exceeding the upper pretreatment regulatory limit of 9.5 SU consistently.
  - ▶ So, the city places a YSI EXO1 sonde with a single pH probe in the sewer to monitor the industrial discharge violations.
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# Initial QC Implemented

- ▶ The pH probe is initially calibrated with a 4, 7, 10 pH standards.
  - ▶ The slope is checked with instrument manufacturers requirements.
  - ▶ A 6 or 9 pH standard is then tested and must agree within  $\pm 0.1$  SU.
  - ▶ The pH probe is then placed in the sewer.
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# Ongoing QC Implemented


- ▶ The pH probe is removed from the sewer weekly.
  - ▶ It is cleaned and checked for damage.
  - ▶ The pH probe is calibrated with a 4, 7, 10 pH standards.
  - ▶ The slope is checked with instrument manufacturers requirements.
  - ▶ A 6 or 9 pH standard is then tested and must agree within  $\pm 0.1$  SU.
  - ▶ The pH probe is then placed in the sewer.
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# WHAT WAS MISSED?

## How Can We Fix It??

Duplicates of the  
Sample will be  
run!

# Here's the fix.

- ▶ YSI EXO1 will allow two (2) pH electrodes to be installed and the instrument can then take two pH readings continuously.
  - ▶ These two pH readings can then be compared and a difference between the two readings can be calculated.
  - ▶ The difference of the readings (precision) can then be determined.
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**But, What Value Is  
Acceptable for Precision**

# SM Lacks A lot On This

- ▶ By careful use of a laboratory pH meter with good electrodes, a precision of  $\pm 0.02$  pH unit and an accuracy of  $\pm 0.05$  pH unit can be achieved.
- ▶ However,  $\pm 0.1$  pH unit represents the limit of accuracy under normal conditions, especially for measurement of water and poorly buffered solutions

# In Conclusion

- ▶ EPA and the Consensus Bodies **MUST** actively update or create a new section or part that addresses the **ONLINE INSTRUMENT** currently being utilized in the water industry.

Questions ??