

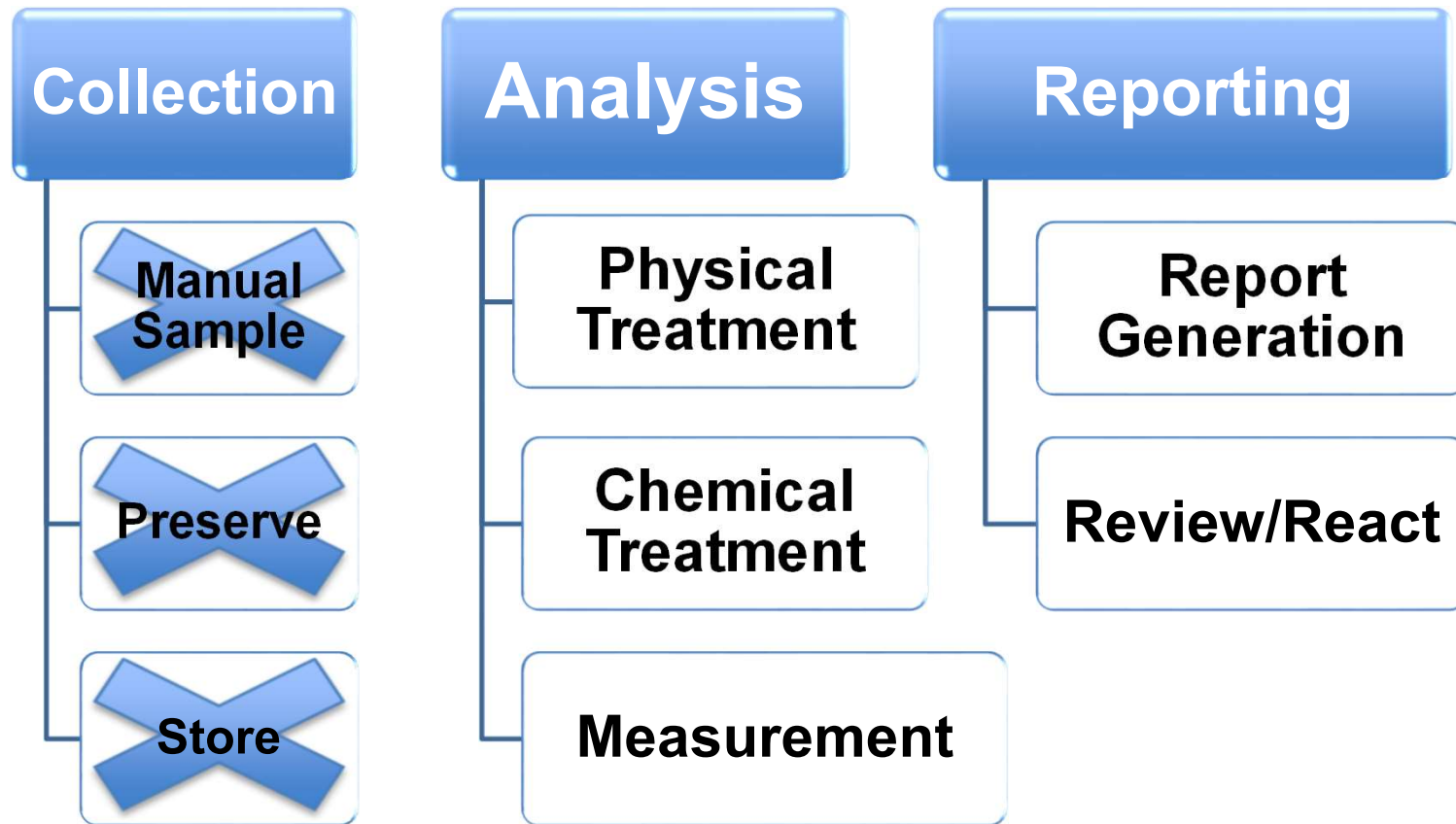
# **How to Make Online Methods Ready for Compliance Monitoring**

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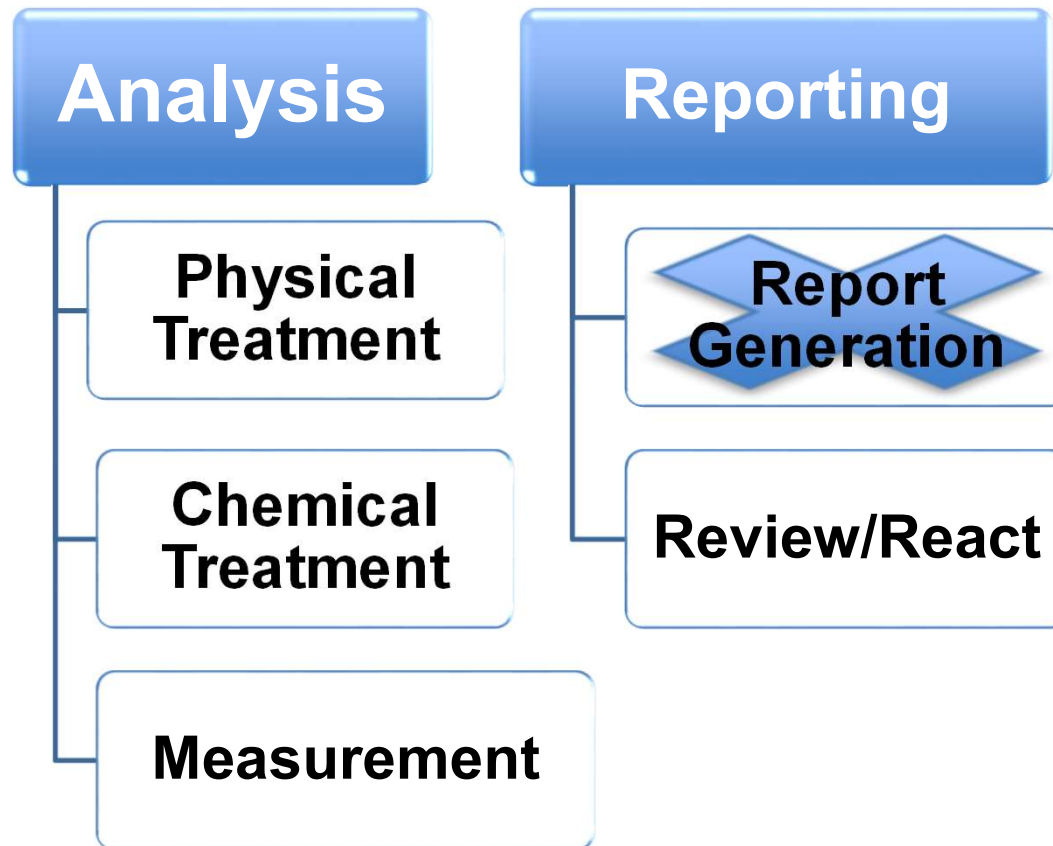
# **There are no or few USEPA approved methods for on-line analysis of water!**

- **EPA approves methods**
- **Methods include:**
  - **Sampling**
  - **Preservation**
  - **Calibration Verification**
  - **Duplicates**
  - **Spikes**
  - **LCS**

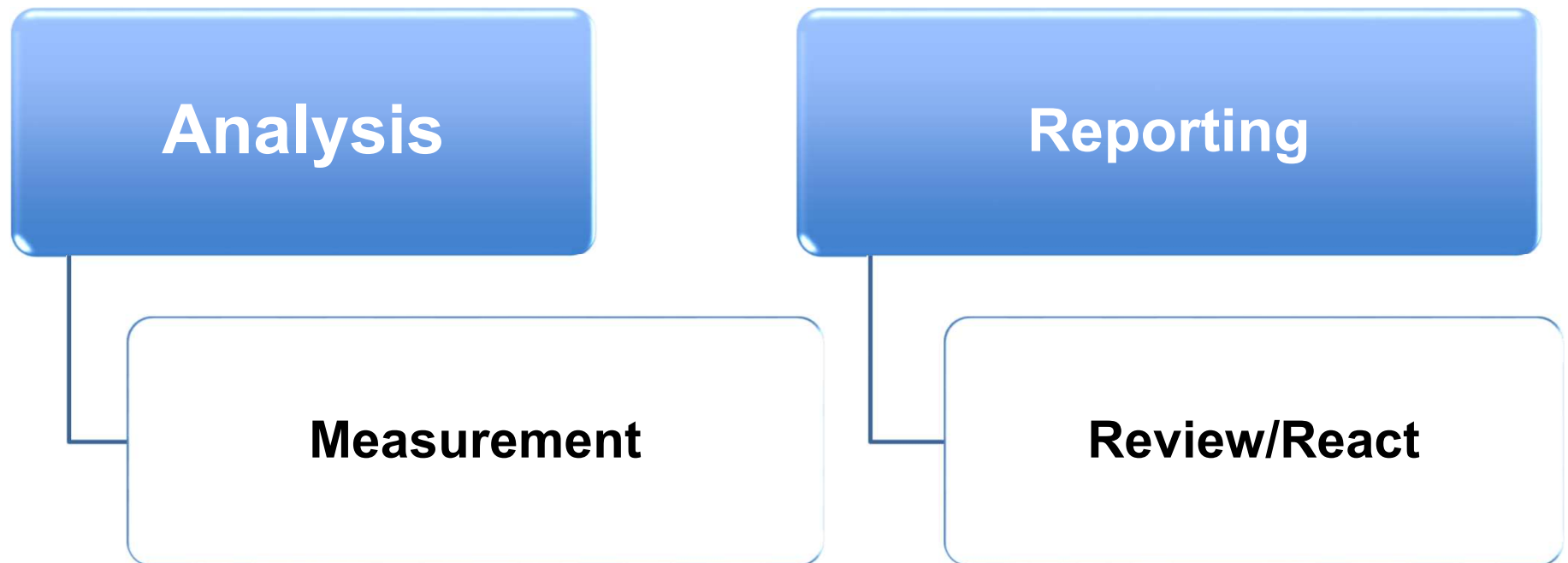
**Can get around sampling and preservation  
since analysis is immediate**



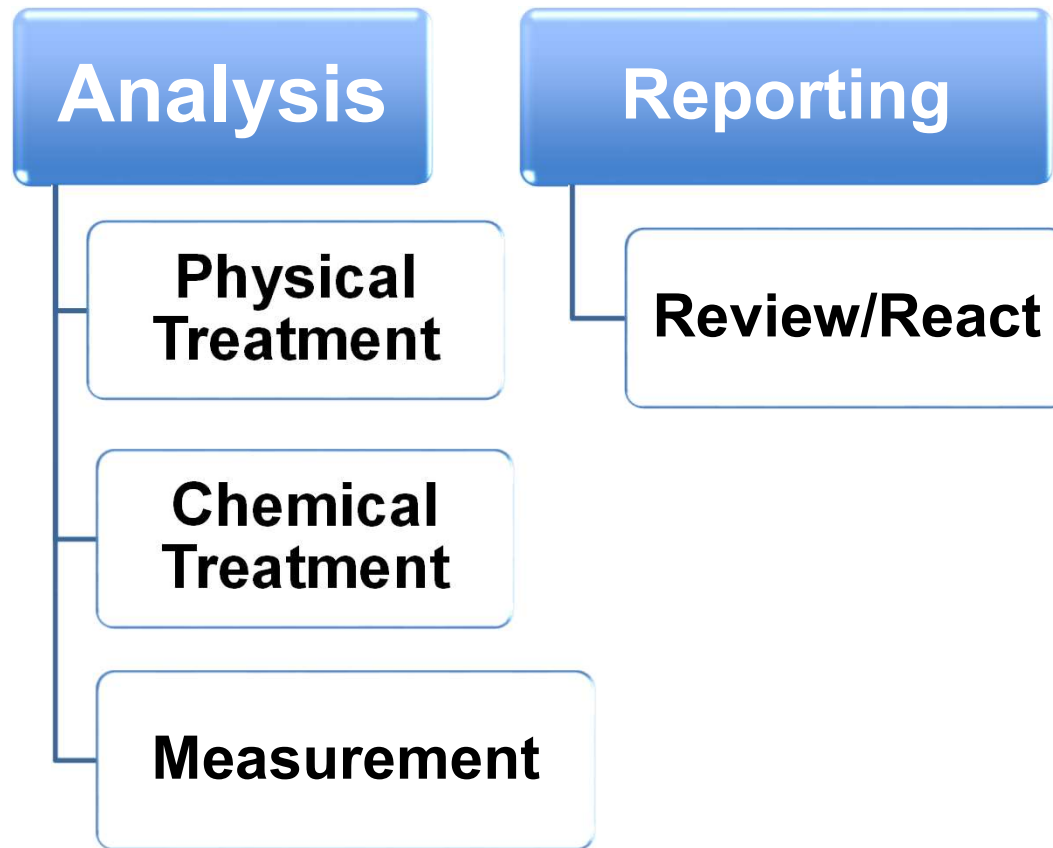
# There is no generation of a laboratory report



**A significant portion of a typical method is eliminated (sensors)**



# On-line analyzers include a few more steps than sensors



**Existing methods includes “batch” QC steps that “must” be done according to 40 CFR Part 136.7**

- **Calibration and Calibration Verification**
- **Blanks**
- **Duplicates**
- **Matrix Spikes**
- **Analysis of Control Samples**

# Definitions to consider

- **Sensor**
- **Analyzer**
- **In-Situ**
- **Ex-Situ**
- **Continuous**
- **Discrete**



**A sensor is a self contained device that produces a signal in response to analyte**

- **Examples of sensors are:**
  - pH probes
  - Conductivity probes
  - Dissolved Oxygen probes
  - Temperature probes
  - Turbidity probes
  - UV absorbance probes



YSI Turbidity probe

**An analyzer is a device that processes a sample then measures an analyte**

- **Examples of analyzers are:**
  - **TOC instruments**
  - **Gas chromatographs**
  - **Atomic absorption spectrophotometers**



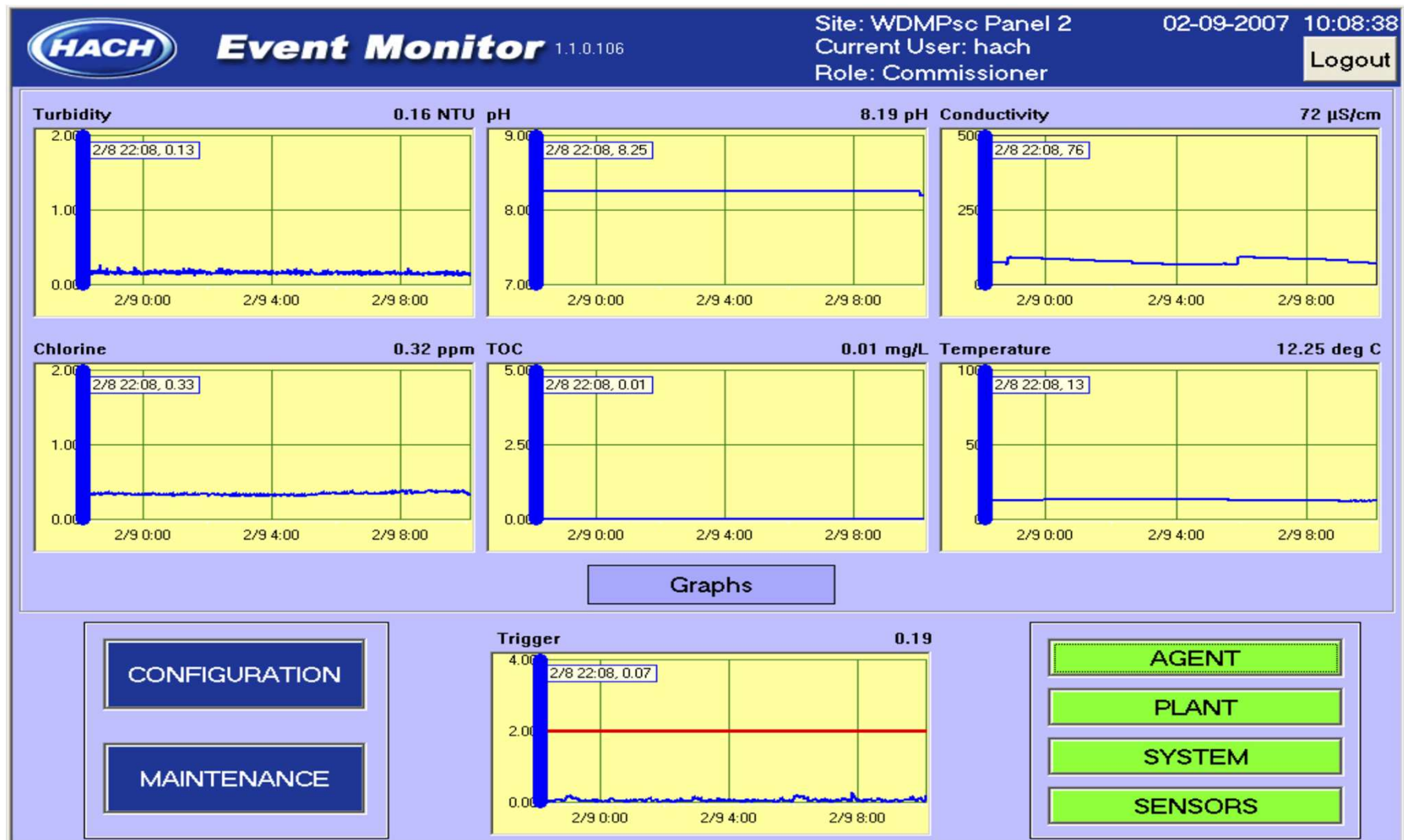
ICP-MS is an analyzer

**In-Situ means that the measurement takes place in the sample**

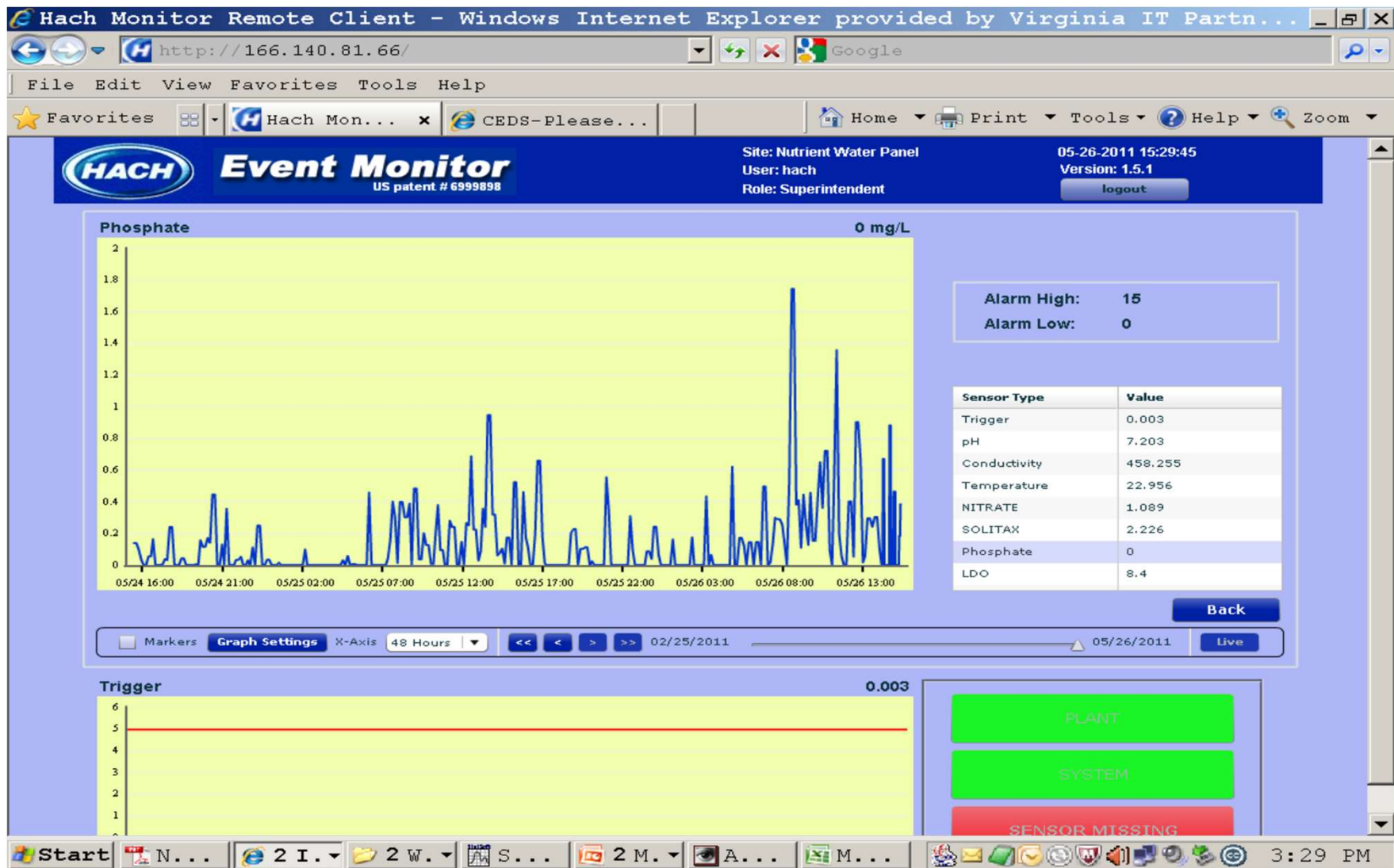


Endress + Hauser probe

# Continuous measurements do not distinguish individual sample readings



# Discrete measurements are distinguished as individual sample readings



**Existing methods include “batch” QC steps that “must” be done according to 40 CFR Part 136.7**

- **Calibration and Calibration Verification**
- **Blanks**
- **Duplicates**
- **Matrix Spikes**
- **Analysis of Control Samples**

**On-line analyzers can be automatically calibrated, sensors cannot.**

- **Methods should ensure that analyzers automatically recalibrate with multiple points.**
- **Methods must ensure sensors are re-calibrated at known intervals.**

# **Online analyzer methods can automatically check the calibration**

- **Methods should ensure that analyzers automatically verify the calibration in a fixed interval**
- **Failed CCV should repeat calibration or flag**
- **Methods should ensure on-line sensor calibration is verified**



# Method should require “blanks” if target analyte varies

- **Process control**



**blanks**

- **Ambient water**



**blanks**

**The concept of “duplicates” does not apply,  
however precision should be evaluated**

- **The on-line method should require a way to collect repeatability data**
- **Stick the sampling straw or probe in a beaker at commissioning**

**The concept of “spikes” does not apply,  
however recovery should be evaluated**

- **The on-line method should require a way to determine recovery in the matrix**
- **Recovery determined on commissioning**

**The concept of “LCS” does not apply, however precision and recovery should be evaluated**

- **The on-line analyzer method should periodically evaluate an LCS**
- **Sensors methods should compare data to approved lab method**

# **Any new “method” for continuous on-line monitoring should:**

- **Obtain equivalent results to approved laboratory methods**
- **Be “rugged”**
- **Use few reagents**
- **Have a sufficient range**
- **Sample/”handle” a complex matrix**
- **Calibrate with multiple points**
- **Require periodic check samples compared to lab**

## **Online method approval may be easier if test is approved technique:**

- **Nitrate → ISE but needs reagent**
- **Ammonia → ISE but needs reagent**
- **Phosphate → sample prep?**
- **TP → sample prep?**
- **TN → no method as yet, sample prep**

- **Nitrate and Ammonium “probes” need to be validated**
- **Or analyzers used that add reagent before ISE measurement**

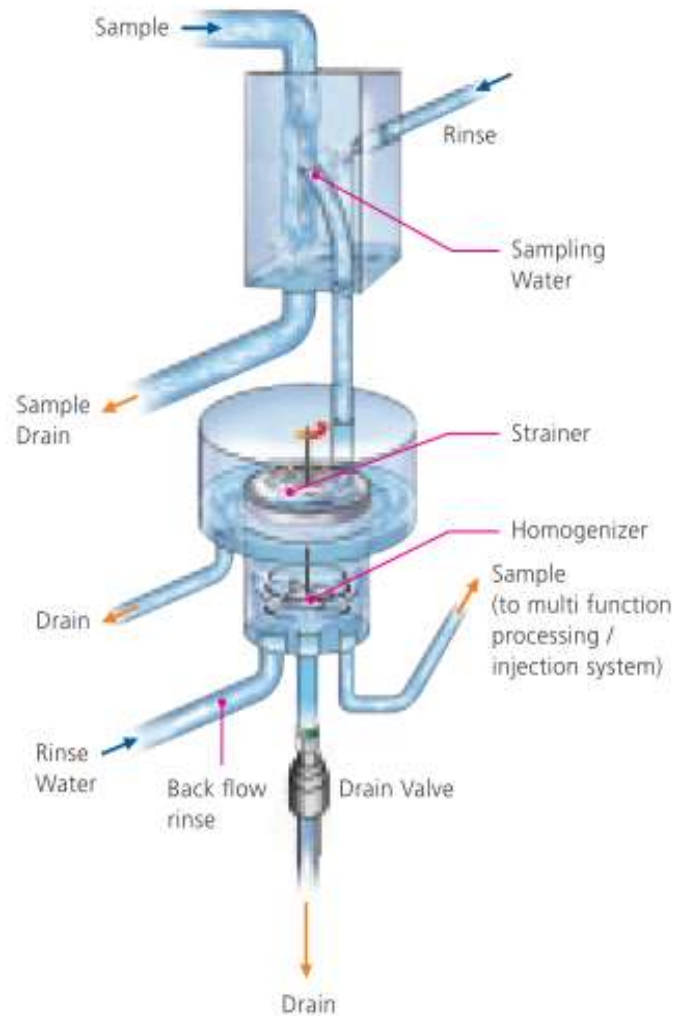
**The on-line methods need QC acceptance criteria determined by multi-analyzer or multi-lab tests**

**A bunch of probes in a big bucket**

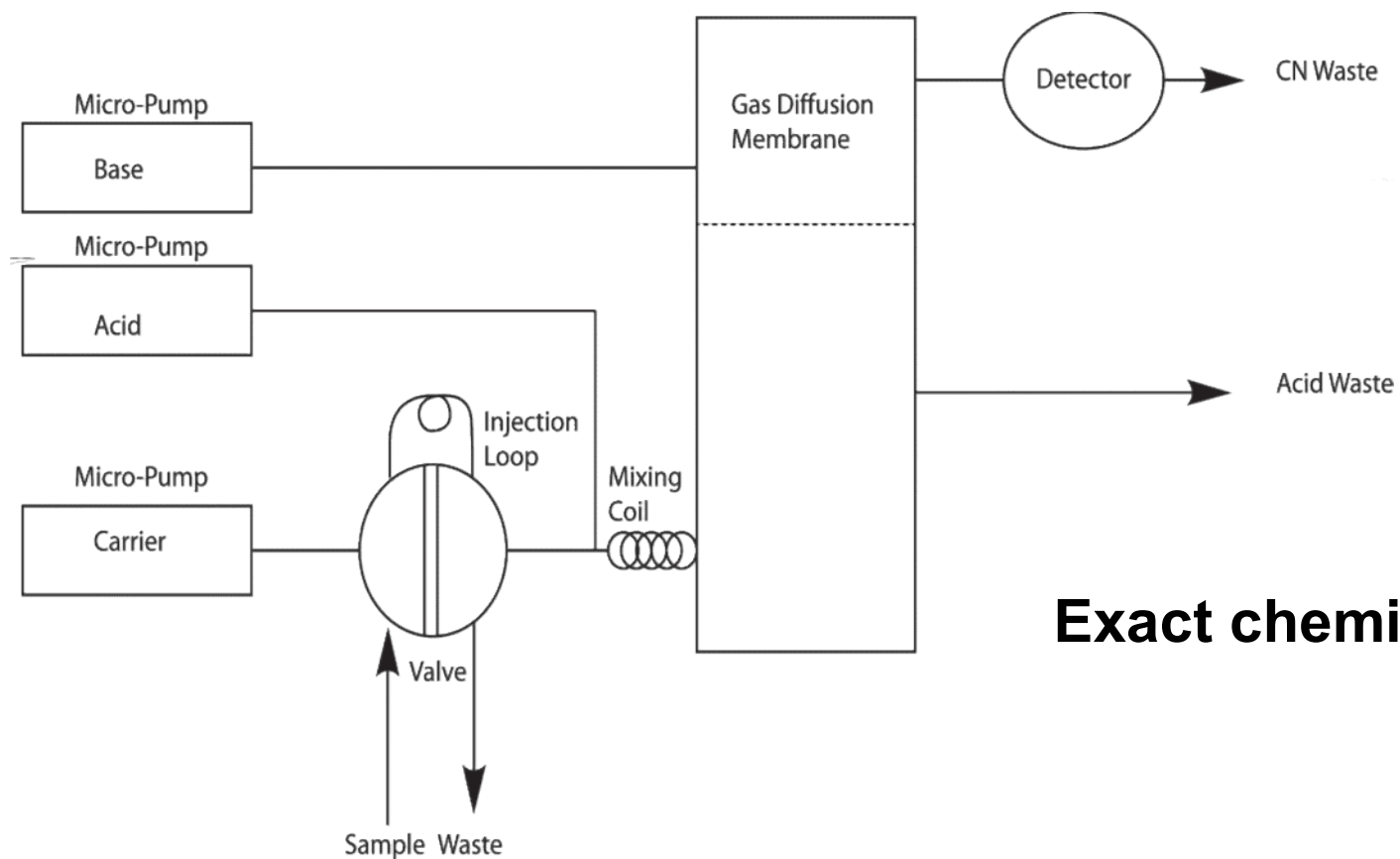
**A bunch of analyzers around a bucket**



**The on-line analyzer should be capable of handling high TSS if necessary**



# Example of an on-line cyanide analyzer method



**Exact chemistry as OIA-1677**

# Analyzer could not multi-point calibrate, but calibration was verified

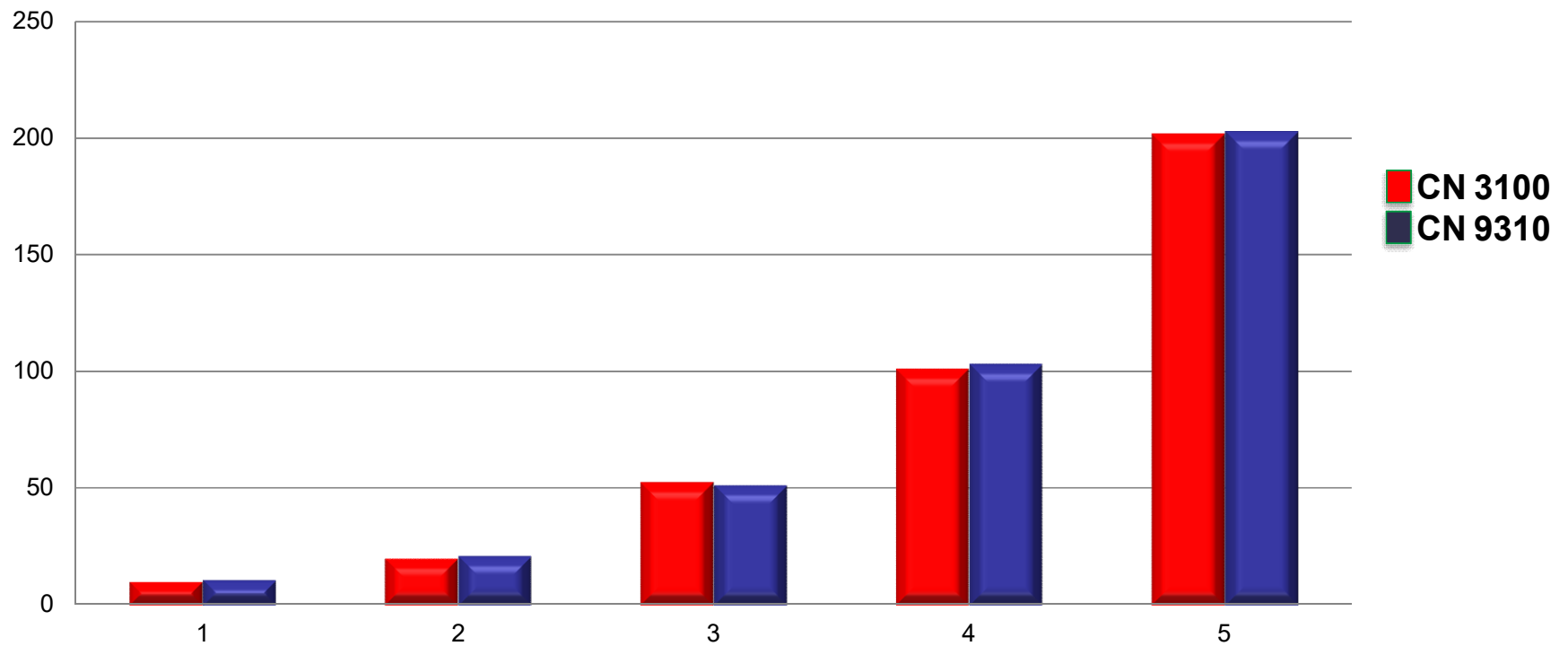
Standard	Instrument 1	Instrument 2	Instrument 3	Instrument 4	Instrument 5
2 ppm	2.17	1.95	2.12	1.95	2.14
5 ppm	5.25	5.04	5.03	4.93	5.40
10 ppm	10.2	10.3	9.50	10.1	10.7
20 ppm	21.5	20.3	19.4	20.5	20.7
50 ppm	50.7	49.5	48.5	49.5	50.5
100 ppm	101	99.6	96	101	104
200 ppm	199	193	198	205	201

# Repeatability on the calibration standards verified

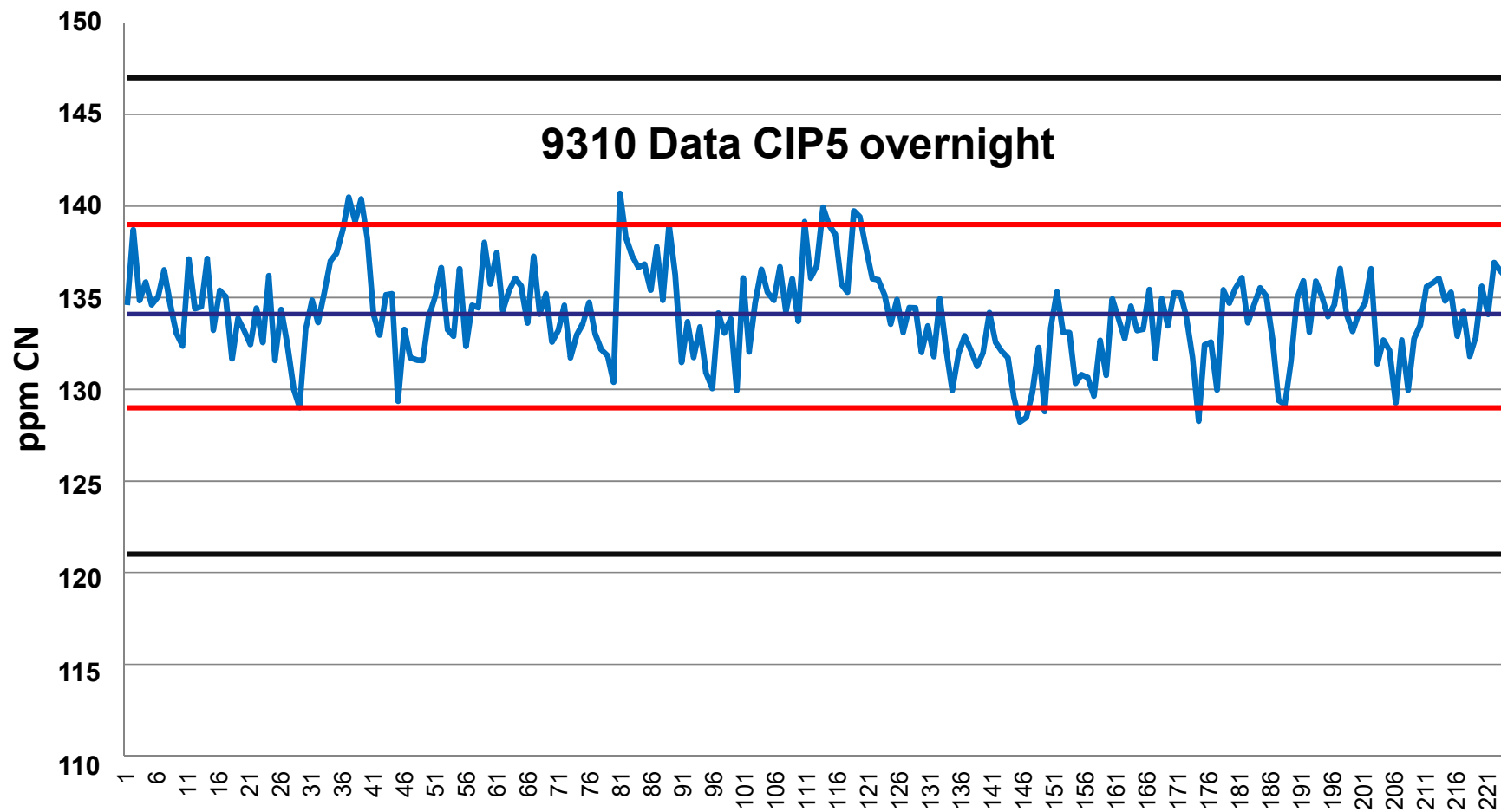
Standard	Instrument 1	Instrument 2	Instrument 3	Instrument 4	Instrument 5
2 ppm	3.5	1.1	2.6	3.8	1.7
5 ppm	1.3	0.73	0.8	5.4	0.9
10 ppm	0.7	3.19	0.9	5.4	1.9
20 ppm	1.1	1.38	3.4	3.4	1.8
50 ppm	1.7	1.02	1.4	2.7	1.3
100 ppm	0.6	0.43	0.3	3.6	1.7
200 ppm	0.4	3.61	0.4	2.8	1.4

# On-line data compared to laboratory data

**Lab Data versus 9310 Data  
Spiked Samples**



# Overnight data collected at commissioning



Data from Carbon-In-Pulp (CIP) Leach Tank 5

# **On-line analyzer methods are needed if data is to be reported for compliance**

- **Some QC in existing methods does not apply**
- **New methods can be written that still provide sufficient QC**
- **On-line results should be based on approved techniques or compared to lab results**
- **New methods needs multi-manufacturer validation**

# Thank You!

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For more information contact

