

Are we ready for On-line Sensor and Analyzer methods for Environmental Compliance Monitoring?

William Lipps
NEMC
August 2021

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

**EPA approves methods,
not analyzers**

Methods include:

- **Sampling**
- **Preservation**
- **Calibration Verification**
- **Duplicates**
- **Spikes**
- **LCS**

No need for sampling and preservation information since analysis is immediate



Collection

Manual Sample

Preserve

Store

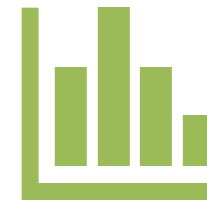


Analysis

Physical Treatment

Chemical Treatment

Measurement



Reporting

Report Generation

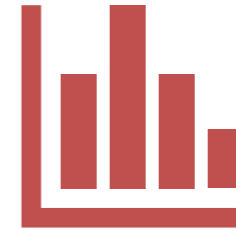
Review/React

There is no generation of a laboratory report, but a continuous feed of data to somewhere



Analysis

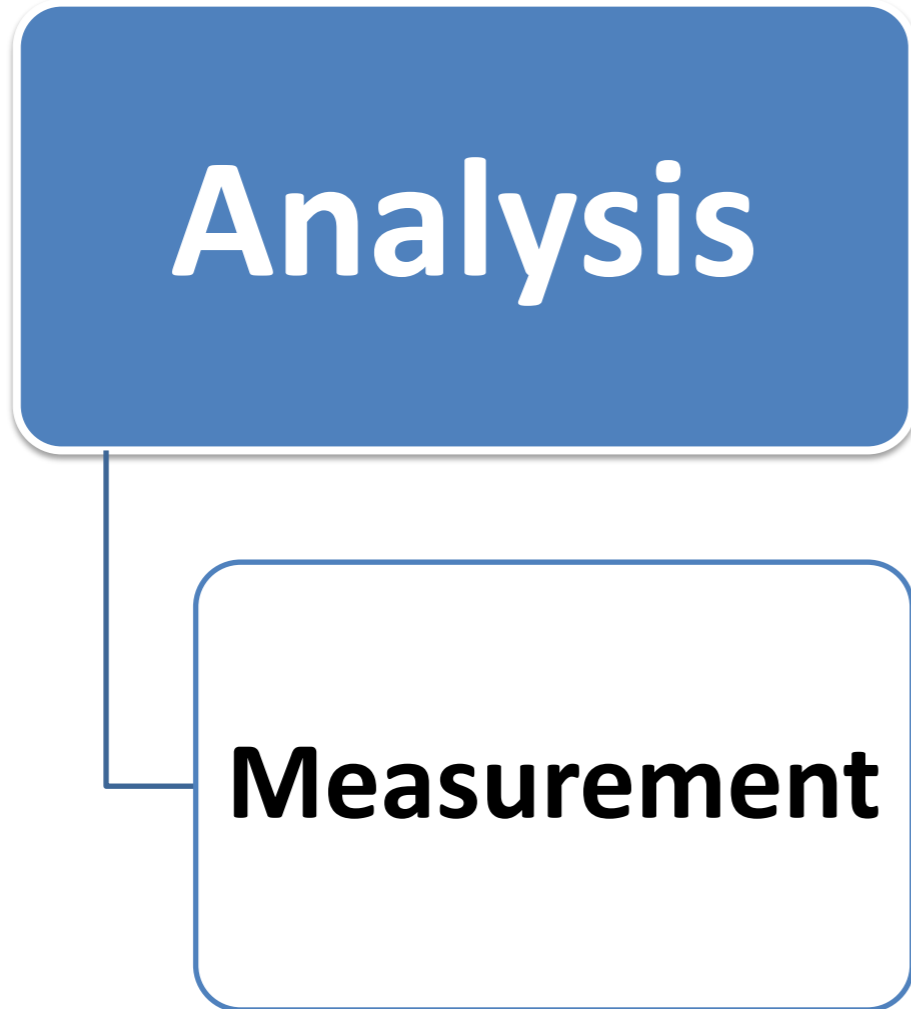
Physical Treatment
Chemical Treatment
Measurement



Reporting



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

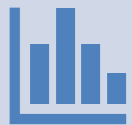


On-line analyzers include a few more steps than sensors



Analysis

Physical Treatment
Chemical Treatment
Measurement



Reporting

Review/React

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



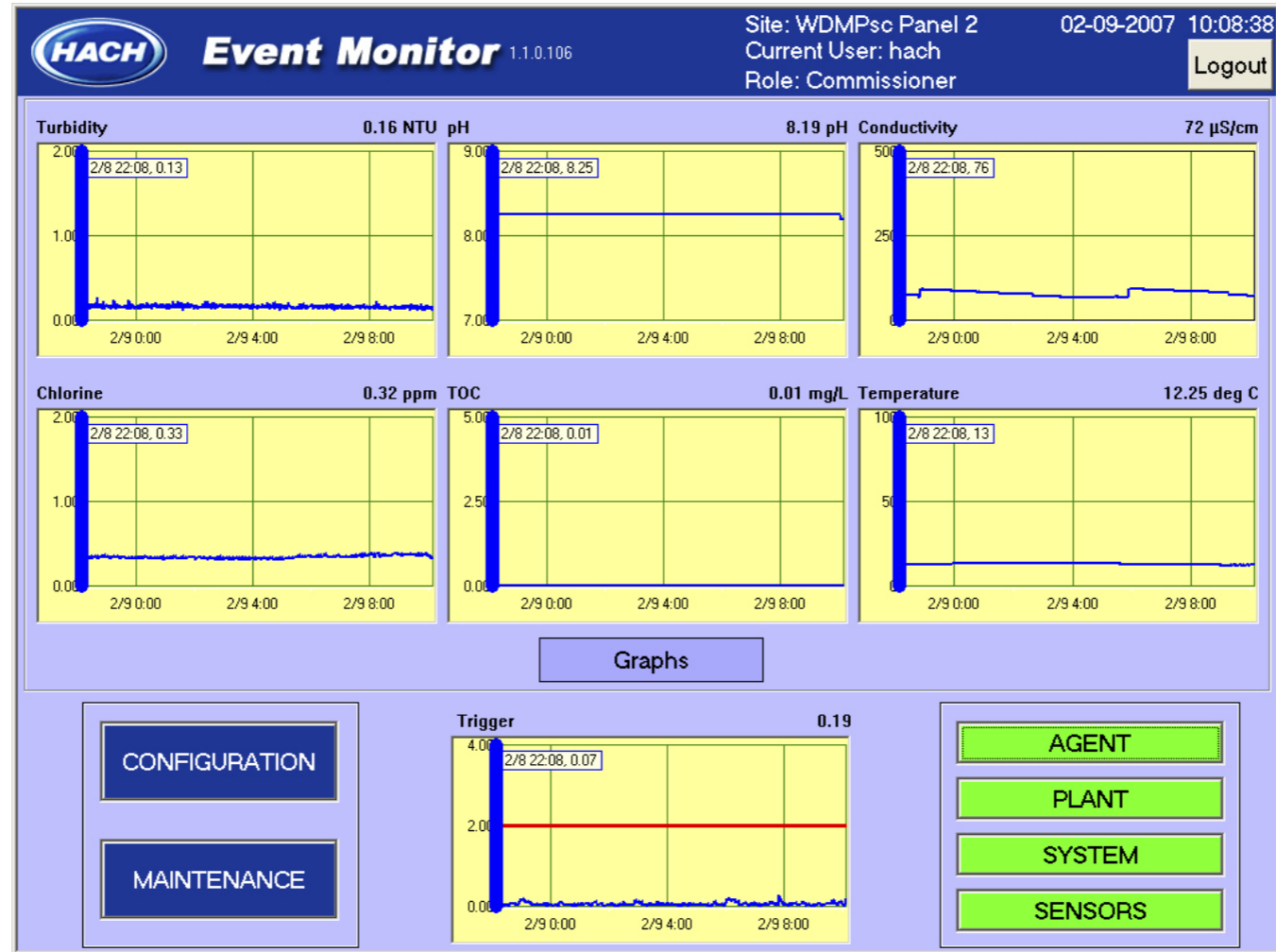
ICP-MS is an analyzer

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

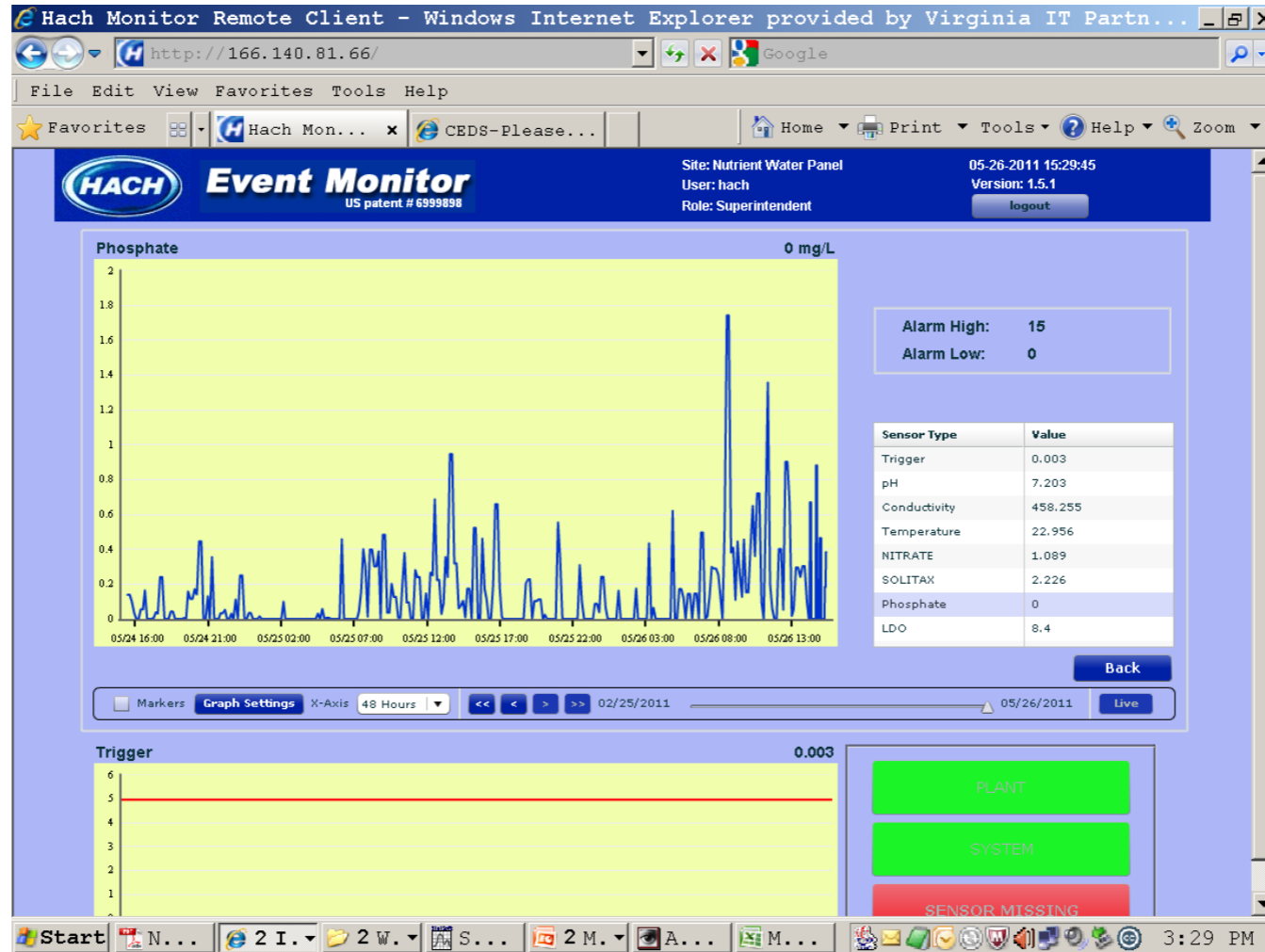
Endress + Hauser probe



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

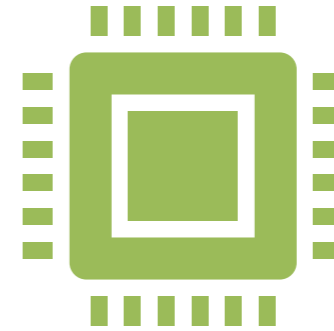
Matrix Spikes

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.

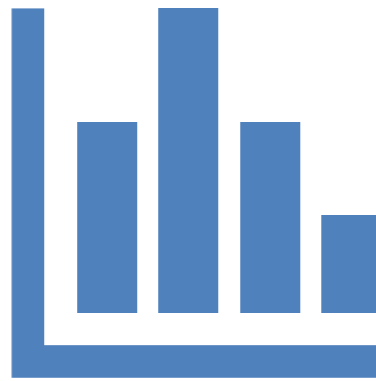
Online analyzer methods can automatically check the calibration

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



Ambient water or
NPDES



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

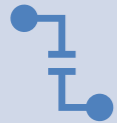


The on-line method should require a way to collect repeatability data



Stick the sampling straw or probe in a beaker at commissioning

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

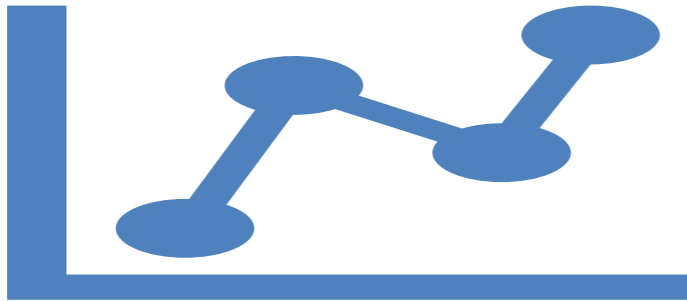


The on-line method should require a way to determine recovery in the matrix



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



Sensor 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

- **Standard methods for the Examination of Water and Wastewater**
 - Developing new on-line analyzer methods

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



Nitrate
Ammonia
COD
BOD
TOC



Phosphate
Nitrite
Total phosphorus
Total Nitrogen
TOC

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

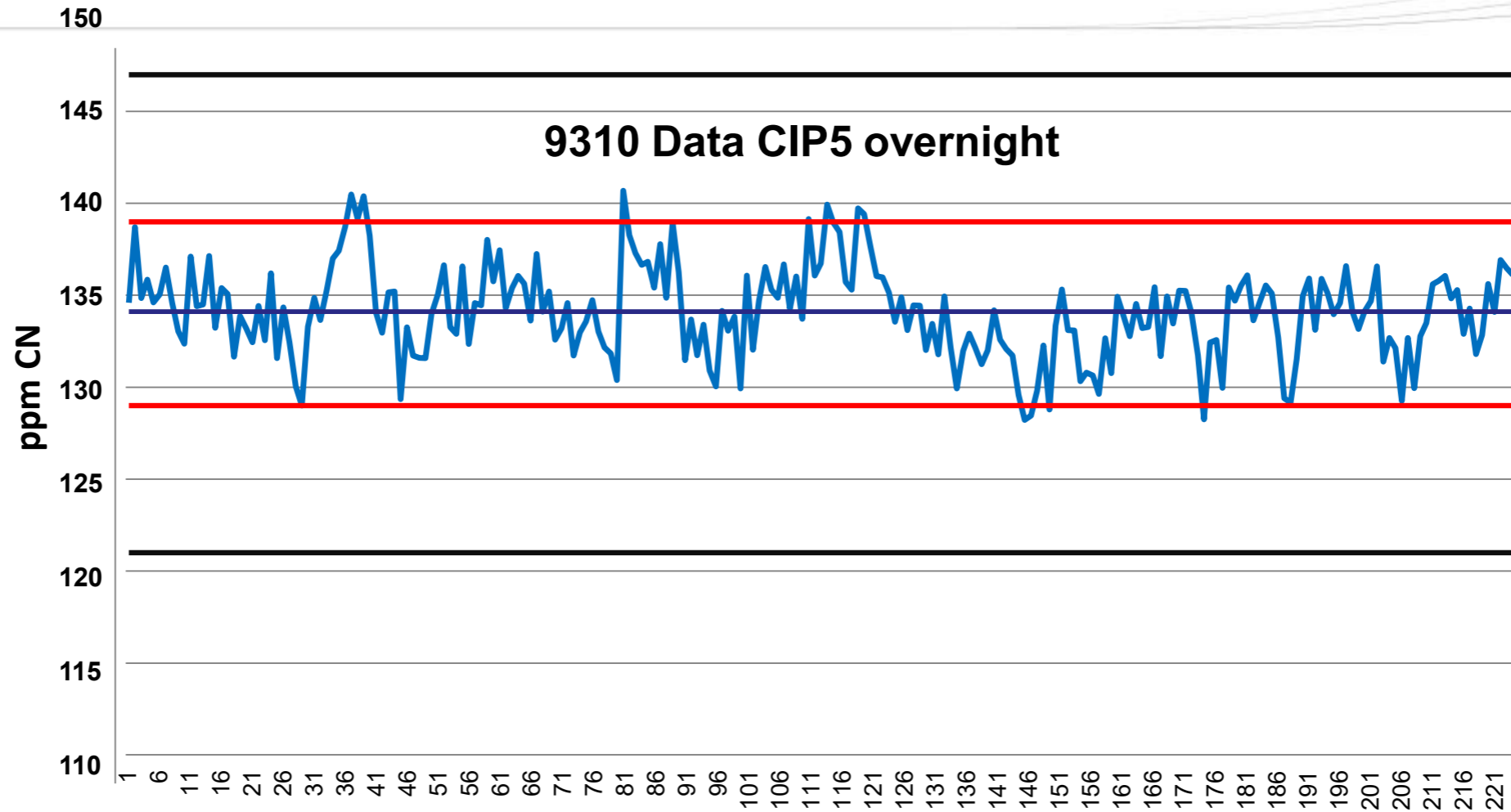
Verify the calibration of multiple analyzers in same sample

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

Verify the repeatability of multiple analyzers in the same sample

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

Collect 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!

Wclipps@shimadzu.com

For more information contact

