

Field Analysis Quality Control

Presentation to:

DOW

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**Department for Environmental Protection
Energy & Environment Cabinet**



To Protect and Enhance Kentucky's Environment

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Topics Covered

- Field-only Methods List
- Legal Defensibility
- Wastewater Reference Methods
- QA/QC Objectives
- QA/QC Criteria & Documentation
- Required QC for Field-only Methods
- Additional Information - Reference
- Method Theory & Key Points – Reference

Scope of Field Methods

- pH
- Conductivity
- Dissolved Oxygen (DO)
- Turbidity
- Total Residual Chlorine (TRC)
- Temperature

Legal Defensibility

- Legal Defensibility: Compliance monitoring data shall be made legally defensible by keeping thorough and accurate records.
- The Laboratory Quality Assurance Plan and/or SOPs shall describe the policies and procedures used by the facility for record integrity, retention, and storage.
- Chain of custody procedures shall be utilized.

Reference Methods

- 40 CFR 136.3 – list of EPA approved methods
- 40 CFR 136.4 & 136.5 – ATP Procedures
- 40 CFR 136.6 – Method Modification
- EPA Method Update Rule (Eff. 6/18/2012)
- SM Reference Nomenclature 4500-H⁺ B-2000
- Use QC from SM 20th, 21st or 22nd Ed. only
- SM 22nd Ed. has useful QC (e.g. 2020B)

Field QA/QC Objectives

QA/QC systems and procedures are employed to ensure that environmental results are of a known quality and meet their intended use (compared to data quality objectives; DQOs).

40 CFR 136.7

1. Demonstration of Capability (DOC).
2. Method Detection Limit (MDL).
3. Laboratory Reagent (method) Blank (LRB).
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.

40 CFR 136.7 (cont)

6. Internal standards, surrogate standards (for organic analysis) or tracers (for RADS).
7. Calibration (initial and continuing), initial and continuing performance (ICP) solutions also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV).
8. Control Charts (or other trend analyses of quality control results).

40 CFR 136.7 (cont)

9. Corrective Actions (root cause analyses).
10. QC acceptance criteria.
11. Definitions of a batch (preparation and analytical).
12. Specify a minimum frequency for conducting the QC checks.

**All QC elements must be addressed
in the QAP/SOP**

Quality Assurance

An integrated system of management activities involving planning, implementation, documentation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the client (intended use).

Quality Assurance Criteria

- QAP/SOP
- Calibration procedures
- Calibration verification – 2nd source standard
- Quality control samples (QCS)
- Equipment Logs / Field Notebooks
- Field personnel training
- Annual Performance Test Study
- Demonstration of Capability (DOC)
- Chain-of-Custody (C-O-C)

EPA Quality Standard - DRAFT

- EPA Quality Standard for Environmental Data Collection, Production, and Use by non-EPA (External) Organizations (CIO Standard 2106-S-02) – DRAFT
 - Replaces QA/R-2 – QMPs
 - Replaces QA/R-5 – QAPPs
- CIO Guidance 2106-G-05 QMP (Draft)
- Handbook for Developing QAPPs (Draft)

Equipment Log / Field Notebook

- Equipment
 - Manufacturer, model and serial number
 - Significant modifications
 - Repair and maintenance history
 - Calibration history (where relevant)
 - Performance history
- Calibration
 - Daily calibration / verification information
- Field activities

Proficiency Test Study

- Perform an annual PT Study for:
 - pH
 - Conductivity
 - Turbidity
 - Total Residual Chlorine
- DOW must receive a copy of the PT Study sent directly from the provider
- Two consecutive failures – submit a corrective action plan to DOW

Demonstration of Capability

- Perform DOC annually using the field method as written in the QAP/SOP
- Document DOC results
- DOC template for DOC results are provided on the DOW wastewater website
- Four (4) replicates ($\pm 20\%$ of their mean)
- Percent relative standard deviation $\leq 15\%$

Chain of Custody

- Type of sample (e.g. grab, composite, split sample, etc)
- Sample matrix
- Type of container (e.g. glass, plastic)
- Required sample volume
- Sample holding times
- Preservative required
- Field quality control

Quality Control

The overall system of technical activities that measure the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality.

Quality Control Criteria

- Blanks (reagent, field, equipment, etc)
- Accuracy (Bias)
- Precision

- Establish frequency of QC sample analysis
- Utilize acceptance criteria
- Document corrective action

pH Measurements

- Calibrate the instrument with 4.0, 7.0, and 10.0 S.U. buffer
- Record slope (0.95-1.05)
- Verify calibration with a 7.0 S.U. (mid-level) 2nd source buffer (± 0.1 S.U.)
- RECORD CALIBRATION INFORMATION
- Sample duplicate (one/twenty samples)
 - % Difference $\sim \pm 20\%$

Conductivity Measurements

- Calibrate instrument using known conductivity standards as per manufacturer
- Verify calibration using a 2nd source standard
- RECORD CALIBRATION INFORMATION
- Reagent blank (one/batch)
 - Result \geq reporting limit = corrective action
- Sample duplicate (one/twenty samples)
 - % Difference $\sim \pm 20\%$

Dissolved Oxygen Measurements

- Calibrate instrument as per manufacturer
- RECORD CALIBRATION INFORMATION
- Measure environmental samples
- Sample duplicate (one/twenty samples)
 - % Difference ~ $\pm 20\%$
- At new location where altitude may have changed the DO meter must be re-calibrated

Turbidity Measurements

- Calibrate instrument as per manufacturer
- 3 points minimum
- Verify calibration using a 2nd source standard
- RECORD CALIBRATION INFORMATION
- Reagent blank (one/batch)
 - Result \geq reporting limit = corrective action
- Sample duplicate (one/twenty samples)
 - % Difference $\sim \pm 20\%$

Total Residual Chlorine (TRC)

- Calibrate/verify instrument as per manufacturer
- Verify calibration using a 2nd source standard
- RECORD CALIBRATION INFORMATION
- Reagent blank (one/batch)
 - Result \geq reporting limit = corrective action
- Sample duplicate (one/twenty samples)
 - % Difference $\sim \pm 20\%$

Temperature Measurements

- Calibrate instrument as per manufacturer
- Apply NIST Correction Factor
- RECORD CALIBRATION INFORMATION
- Measure environmental samples

- Sample duplicate (one/twenty samples)
 - % Difference ~ $\pm 20\%$

Questions

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Additional Information

- Requirements for Field Analysis
- Documentation
- Reconstruction of Reported Results
- Field Activities – Sampling Techniques

Requirements for Field Analysis

- Permitted facility staff, laboratory field personnel, environmental consultants, etc
- Documentation of standard operating procedures, calibration procedures, quality assurance plans, and sampler training; and
- PT results for pH, residual chlorine, conductivity, and turbidity.
- Payment of fees

Required Documentation

- Standard Operating Procedures,
- Calibration procedures,
- Quality Assurance Plans, and
- Sampler training;
- All analysis results including any information need to recreate the results (such as dilutions & standards utilized).

Reconstruction of Reported Results

In order to reproduce data, laboratories shall include the following on laboratory reports of compliance samples, at a minimum:

- Sample collection location (code, if applicable)
- Sample collection date and time
- Sample analysis date and time (including any preparation, if applicable)
- Sample type (grab/composite)
- Analyst name (or initials)
- Specific sample analyte and method
- Sample result (including applicable units)
- Statement and initials/signature of peer review
- MDL or MRL utilized.

Field Activities – Sampling Techniques

All individuals that are involved in field activities shall be familiar with sampling techniques used to collect environmental samples, such as:

- Type of sample (e.g. grab, composite, split sample, etc);
- Sample matrix;
- Type of container (e.g. glass, plastic);
- Required sample volume;
- Sample holding times;
- Preservative required;
- Field quality control.

Additional Information & Documents

<http://water.ky.gov/permitting/Pages/labcert.aspx>

- Field SOP & QAP Templates
- Summary of EPA Draft QAPP Requirements
- KY Approved PT Provider List
- Demonstration of Capability Worksheets
- DOC Procedure
- Various Presentations

OVERVIEW - Field Sampling Methods

Method Theory
Method Key Points

pH Method Theory

- Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment is pH dependent.
- At a given temperature, pH measures the intensity of the acidic or basic character of a solution by measuring hydrogen ion activity.
 - p – potential
 - H – hydrogen
- pH utilizes a logarithmic scale (Not Linear)
 - At 25° C pH 7 is neutral & the activity of the hydrogen and hydroxyl ions are equal and has a corresponding activity of 10^{-7} moles/L.
 - pH 7 should then have a theoretical mV of 0
 - Rule of thumb $<_{\pm} 15$ mV calibrate as normal
 - $>_{\pm} 15$ mV clean electrode then calibrate
 - $>_{\pm} 35$ mV replace electrode

pH Method Key Points

- Follow manufactures instructions for calibration.
- Use fresh buffers
- Stir buffers & samples moderately
- Rinse & blot dry electrode between buffers & samples
- Must be accurate and reproducible to within 0.1 S.U.
- Buffers must bracket expected range
- Temperature adjusted or Temperature Compensated results.

Conductivity Method Theory

- Conductivity is a measure of the ability of an aqueous solution to carry and electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature.
- Conductivity is measured utilizing an electrode and reciprocal resistance across the cell. The cell constant of the electrode is adjusted by utilizing a standard with a known conductivity.
- Simply put conductivity is used to measure the concentration of dissolved solids which have been ionized in a polar (charged) solution.
- Conductivity is measured in $\mu\text{S}/\text{cm}$

Conductivity Method Key Points

- Follow manufactures instructions for calibration.
- Use fresh standards
- Rinse electrode with one or more portion of sample before analyses
- Allow the meter to stabilize prior to taking a reading
- Must be accurate and reproducible
- Calibrations must bracket expected range
- Temperature adjusted or Temperature Compensated results.

Turbidity Method Theory

- This method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of the light scattered by a standard formazin polymer under the same conditions.
- The method historically is based on the Jackson candle turbidimeter and was originally reported in Jackson Turbidity Units (JTU)
- The Nephelometer is now the standard instrument for turbidity measure. They have a scattered light detector at 90° to the beam. The units of turbidity are nephelometric turbidity units (NTU)

Turbidity Method Key Points

- Poor measurement technique can have a greater effect on measurement error than differences in instrument design.
- Keep sample cells scrupulously clean inside & out. Discard cells that are scratched or etched. Never handle them where the instrument's light beam strikes them
 - Cells may be coated on the outside with a thin layer of silicone oil to mask minor imperfection.
- Use same sample cell or matched sample cells for all calibrations and analysis.
- Follow manufacturer's instructions for calibration.
- Use fresh primary standards
- Mix sample well
- Test immediately
- Remove air bubble or degas samples
- No condensation on outside of sample cell (analyze at room temperature)

Residual Chloride Method Theory

- Chlorine's powerful disinfectant qualities come from its ability to bond with and destroy the outer surface of bacteria and viruses & is one of the most widely used disinfectants utilized in water & wastewater treatment.
- Chlorine once it has been applied to water undergoes hydrolysis to form a free or available chlorine. These free chlorines can react readily with ammonia and certain nitrogenous compound to form a combined chlorine. Both free and combined chlorines may exist simultaneously in a chlorinated system.
- The amperometric titration method is the standard of comparison for the determination of free or combined chlorine
 - Not subject to as many interferences & achieve low level determinations.
 - Specifically certain metals such as silver and copper.
- The DPD methods are operationally simpler
 - Subject to interferences by oxidized forms of manganese and blanks are needed.
 - Subject to interferences by color that may or may not be corrected by a blank.

Residual Chlorine Method Theory

Iodometric Method

- Method principles are based on the fact that chlorine will liberate free iodine from potassium iodide (KI) solutions at pH of ≤ 8 .
 - Iodometric method then titrates the liberated iodine with a standardized sodium thiosulfate with a starch indicator to a pH of 3. Chlorine is based on amount $\text{Na}_2\text{S}_2\text{O}_3$ used.
 - RL ~ 1 mg/L

Residual Chloride Method Theory

Amperometric Titration

- Method based on a special adaptation of the polarographic principle.
- Chlorine is titrated at a specific pH in the presence of KI.
- Phenylarsine oxide solution reacts one mole per every two equivalents of halogen.
- A nonpolarizable reference electrode is immersed in a salt solution & a readily polarizable noble metal electrode in contact with the salt and sample make up the amperometric sample cell.
- The higher the concentration, the higher the microammeter reading.
- The final result is the change in readings from beginning of titration to the end.
- Low level results are obtainable utilizing this method.

Residual Chlorine Method Theory

DPD Method

- N,N-diethyl-p-phenylenediamine (DPD) is an indicator with ferrous ammonium sulfate (FAS) titrant.
- Chlorine reacts instantly with DPD to produce a red color without the presence of iodide.
 - Titration method – The solution is titrated with FAS until color is gone
 - Colorimetric method – utilizes a spectrophotometer to determine intensity of red color based on a linear calibration.
 - Electrode method – considered a modification of the colorimetric method.
 - RL dependent on instrument and sample volume limitations.

Residual Chlorine Method Key Points

- All methods must be verified with a NIST traceable standard.
- All titrants must be verified
- Titrants must be stored in a cool dark place
- Colormetric methods must allow adequate reaction time
- Colormetric must use sample cells that are clean & scratch free & without fingerprints or DPD stains.
- Secondary standards (gel standards) cannot be utilized for calibration. But may be used for calibration verification.
- Colormetric methods with an internal calibration must be verified daily across the range of use (blank, low standard, & high standard) at a minimum
- Gel standards must be verified initially and annually against an NIST traceable standard & must be protected from direct sunlight & heat
- DPD reagent should be protected from extreme heat
- Though all these methods are approved they may not all be appropriate to meet your KPDES requirements or reporting limits.

Dissolved Oxygen Method Theory

- Dissolved oxygen (DO) has two basic methods for analysis. The Winkler or iodometric method and the electrometric method utilizing membrane electrodes.
- The iodometric method is a titration procedure based on the oxidizing property of DO.
- The membrane electrode procedure is based on the rate of diffusion of molecular oxygen across a membrane.
- The iodometric method is the most precise method. It is based on the addition of divalent manganese solution followed by strong alkali in a glass stoppered bottle. The end result of the reaction is liberation of iodine that is then titrated with a standardized solution of thiosulfate. The endpoint can be detected visually, with a starch indicator, electrometrically or colormetricly.
- The membrane method utilizes oxygen sensitive membrane covering two separate electrodes in an electrolyte. The “diffusion current” across the membrane is converted to mg/L utilizing the molecular weight of oxygen.

Dissolved Oxygen Method Key Points

- The titration method
 - Method is the standard of comparison for all other methods.
- Membrane method
 - Membranes must be checked & changed regularly
 - No air bubbles in membranes.
 - DO permeability in probes are temperature dependant. As temperature increases sensitivity decreases.
 - Must adjust calibration for altitude or barometric pressure
 - Calibrated in saturated air to 100% relative humidity on location or adjustments made based on altitude & pressure
 - If sample is not analyzed in stream care must be taken to not aerate the sample while transferring to a sample contain for immediate analysis.

Temperature Method Theory

- Accurate temperature readings are critical considering how many analysis are temperature dependant.
- Temperature is one of the fundamental principles of thermodynamics and is a measure of the thermal energy per particle of matter and is calibrated against a set temperature scale. (Celsius, Fahrenheit, Kelvin)
- The 1st thermometer was invented in 1592 by Galileo
- By 18th century nearly 35 different temperature scales had been devised.
- 1714 Daniel Gabriel Fahrenheit invented both the mercury and the alcohol thermometer.
- Anders Celsius simply took Fahrenheit's thermometer & created a more uniform scale.
- In the 1800's William Thomas Kelvin created a new scale utilizing Fahrenheit's thermometer based on a theoretical absolute 0
- In the 20th century there were additional refinements made to the temperature scales. The standard are in accordance with the International Temperature Scale of 1990 (ITS-90)

Temperature Method Key Points

- Thermometer must NIST traceable.
- No separation in thermometer liquid.
- Thermometer should not be touching bottom or sides, only immersed in the liquid.
- Final results must be adjusted to reflect NIST adjustment

Flow Method Theory

- **Flow measurement** is the quantification of bulk fluid movement. Flow can be measured in a variety of ways. Positive-displacement flow meters accumulate a fixed volume of fluid and then count the number of times the volume is filled to measure flow. Other flow measurement methods rely on forces produced by the flowing stream as it overcomes a known constriction, to indirectly calculate flow. Flow may be measured by measuring the velocity of fluid over a known area.

Flow Method Key Points

- If the facility does not have a flow meter, then a scientifically defensible method must be used to measure flow. These methods, though less accurate than a flow meter, can include the use of a bucket and timer or geometric calculations. If you are not sure if the flow measurement method you would like to use is scientifically defensible, you should consult your regional office inspector.