Everything you wanted to know about a DNR Lab Audit…

…but were afraid to ask!!

Sponsored by:
the Wisconsin Rural Water Association, the Wisconsin Wastewater Operator's Association

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Session Goal

We will go through the actual audit process

- what kinds of questions you'll be asked
- what information you will be asked to show

Unfortunately, we just do not have the time to get into the technical details of or troubleshooting techniques for the methods

This session is designed to follow the analytical checklists (*available on the website*) which have been developed by the program.

This text style for audit questions.

This text style for reminders on what you need to do/have available.

This text style relates to background information about the subject at hand.

Parts of an Audit

1. How about those Packers!
2. General Housekeeping (the big list)
3. Sampling concerns
4. Detailed review of methods:
5. Data: Records and Reporting
6. QA/QC

Checklists

- Sample Storage and Pretreatment
- Equipment
- Calibration/Sample Measurement (NH_3 & TP)
- General Procedural Observations
  - BOD
    - Sample Seeding
    - Glucose-Glutamic Acid (GGA) Standard
    - BOD-Specific Quality Control
  - Total Phosphorus
    - Standard Persulfate Digestion
- Quality Control
- Other Observations

Obtain checklists:
www.dnr.state.wi.us/org/es/science/lc/OUTREACH/Checklists.htm

-- BASIC HOUSEKEEPING --

Certification or Registration?

Do you test for any other facility?
If "yes", is the lab certified?

The intent of the Code was to require certification for any facility doing other than their own testing

Ensure that your certificate indicates "Certification" if you perform compliance sample testing for other municipalities or industries.
If it does not, then submit a revised application to make the change.

Balance Maintenance

How is balance calibration verified?
Is the balance verified at least monthly?

Should do it every time you use it.
Don't just note this event with a ☑ mark.

Is at least one weight in the gram range, and one in the milligram range used?

Choose values that reflect ranges you typically encounter.

Ex. Filter weighs ~150-180 mg: use a 100 mg weight
Aluminum weigh dish ~1-2 g: use a 1g weigh

What acceptance criteria are used?

± 5% is not OK. Guidance from manufacturer/SLH

Certified Weights

Do you have class "S" (Type 1) weights?

- MUST be this type.
- These are silver, rather than brass.

Are the weights stored appropriately?

- These are precision calibration tools.
- Putting two or more of them in a plastic vials and letting them roll around against each other is NOT appropriate.

Have they been re-certified?

If your weights are old, tired, scratched, or stored as above, have your balance service re-certify them.

Desiccator Concerns

Bowl-type desiccators: Is there a seal?

If operating properly, one should almost be able to lift the entire desiccator by its lid
Apply a silicone based grease (refer to manufacturer's recommendations).

Using Indicating Drierite?
Drierite more blue than pink?

- Re-generate regularly
- If not using indicating drierite, need to demonstrate moisture removal ability.

Thermometer Calibration

Calibrated annually?

Reference should be an NIST certified thermometer or one traceable to NIST.
Check against typical standard concentrations: ice point; 4°C; boiling point; 20°C.

Check LabNotes Archive for more information

Correction factors placed on each?

Helps ensure the factors are actually used.
Include date of calibration.

Documentation available?

Lab Temperature

Can you maintain a temp. of 20 ± 3°C?

Required for BOD testing!
(IGNORE the 20+ 1°C in [18th ed.]…it's an error

Cut down on heat sources.
Vent TSS oven to the outside (or a hood).
Health & Safety issue beyond LabCert concerns!

Is lab temperature highly variable?

Effects on Ammonia testing:
1-2% error per degree C change.
Samples & standards must be at the same temperature

Equipment Temperatures

TSS oven temperature records?

Document oven temperature (103-105 °C) when TSS samples are drying.

Place thermometer bulb in a jar of clean sand or vermiculite (Traceable thermometers like this are available commercially).

BOD incubator temperature records?

Document incubator temperature (20 ± 1° C) when BOD samples are inside.

If no samples are in the oven/incubator for a given day, write in “no samples” in the comment box.

Barometers

Calibrated correctly?

Make sure you are doing this correctly!!!

Calibration checked at least monthly?

Increase frequency if you find your barometer drifts from a reference (airport).

Know what normal pressure swings are.
At sea level, normal range is 29.6 to 30.4 inches.
At 1000 feet elevation, normal pressure drops about 1 inch of Hg, and “normal” would be 28.6 -29.4”.
Storm systems can drop pressures 0.5 or more!

This needs to be done on internal barometers, too!

Reagents

Generally, we recommend purchasing!

Chemicals dried before use??

Dry glucose and glutamic acid each at 103°C 1 hr

Critical reagents used within expiration?

Reagent contents clearly labeled?

Prepare ascorbic acid fresh weekly, store 4°C.

TP Combined color reagent stable only 4 hours.

Reagent logbook clearly documents *when*, *how*, and *who* prepared each?

What is it? Concentration? Who made it? When?

Standard Pedigree

Are critical reagents made correctly?

Document the preparation of reagents

Who?, What?, When?

Discard of expired reagents properly!

Are critical reagents expired?

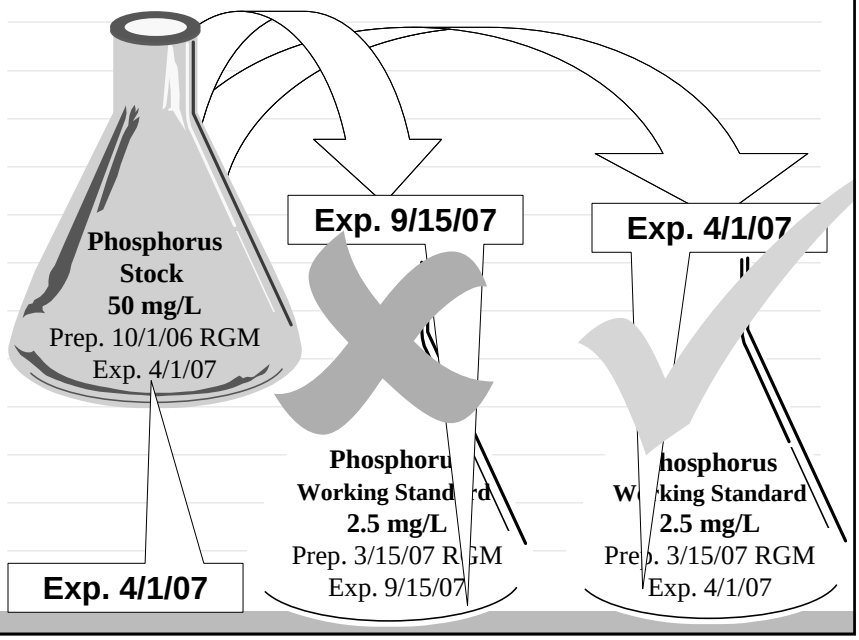
Place an expiration date on all reagents

Refer to method or manufacturer.

"Parents" expired but "children" in use?

When a stock solution expires, every solution prepared from it also expires.

Parents & Children



Sampling Records

Take me to your: Autosampler & Refrigerator records

Document autosampler & refrigerator temperatures.

Use a thermometer which allows measurement estimates to within 0.1°C. Do NOT just write "6".

If you notice the temperature creeping above 6°C, turn the thermostat to increase cooling power, note on that day as "↓" . If the dial can't be turned any colder, consider calling in for repairs or replacing the unit.

Document the accuracy of thermometers annually

Sampling Records

Autosamplers set for flow compositing?

This a is a permit requirement.

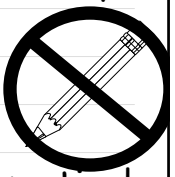
Autosampler maintenance records available?

Maintain records related to maintenance of the autosamplers including cleaning or replacing tubing and adjustment of the refrigerated compartment.

Sampling

Sampler tubing cleaned regularly?

You could be cited for this if the tubing is heavily coated and your replicates tend to fail due to "solids" problems



Are autosampler temperatures faithfully recorded? In ink?

Do not get lazy and "falsify" this information! Temperature records must be "unalterable".

Are temperatures 6°C and not frozen?

EPA does not define anything other than "4°C ".
NR 219 has adopted 6 °C.

*** BOD ***

BOD - Equipment Maintenance

Electrode dirty?

Membrane fouled?

Air bubbles?

DO membrane changed regularly?

Manufacturers: change every 2-3 months
With any type of oily samples, every 2-3 weeks is best

Any service/maintenance performed?

Keep a maintenance logbook. Document:

Membrane changes Probe replacement
Meter servicing

Probe –calibration in air-saturated WATER

- Place the probe in a BOD bottle filled with air-saturated (well-shaken) water
  - Leave probe in the water w/ stirrer operating long enough for the probe temperature to equalize with the water temperature
  - Determine barometric pressure and adjust meter's internal barometer as necessary
  - Check temp. of source water to be sure the probe thermistor is working correctly
- Use a detailed DO saturation table to determine the theoretical DO concentration
- Adjust meter to read the DO concentration determined from the saturation table.

Probe –calibration in water-saturated AIR

- Place the probe in a BOD bottle with about 3 cm of water
  - Shake BOD bottle prior to inserting probe to assure saturation. We recommend leaving the stirrer on (*although manufacturer says it's not necessary*) ---it speeds up equilibration.
  - The probe may need to sit in the bottle for 30-35 minutes in order to match the temperature of the air.
  - Determine barometric pressure and adjust meter's internal barometer as necessary
  - Check temp. of the air to be sure the probe thermistor is working correctly
- Use the meter's auto-calibration function to calibrate the probe and meter

Calibration Options-Bottom Line

- Winkler calibration takes longer than the other techniques… with no net gain in quality.
- Calibration with air saturated water takes less time because the probe's temperature equilibrates quicker in water than air. **Water is a more effective heat sink**
- Obvious advantage: You don't have to worry about droplets on the probe tip when calibrating in air saturated water (DUH!).
- All three methods work. The results of the seed control and GGA were the same even though the IDO's and DO_5's were different. Consistency is the key to good results regardless of calibration technique.

BOD - Supersaturation

Are samples super-saturated?

- Compare the initial DO (DO_i) of the sample to the theoretical saturation point for that temperature and pressure.
- Dead giveaway: the higher the dilution the lower the DO_i
- Nearly always related to samples that are not at room temperature or unshaken

If you shake samples once they are at room temperature, this should NOT be an issue

BOD Sample Pre-treatment

Sample tested for residual chlorine?

Document test results

Document that no test is required

Is there any disinfection performed?

Is it downstream of BOD autosampler?

Does the sample need pH adjustment?

If undiluted sample pH <6 or >8.5, must adjust pH to between 6.5 and 7.5 and then seed.

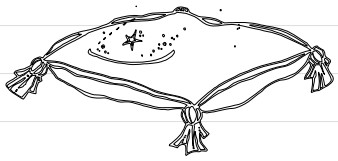
Document sample pH

Document any adjustment made required

Any sample which requires de-chlorination or pH adjustment should be seeded

Dilution Water Preparation

One word of advice: "pillows"



Using single-use nutrient buffer pillows will avoid many of the pitfalls….

Save yourself some headaches

Measuring out samples

ROTATE BOD bottles!!!!!

"Fast attack" vs. slow; accurate volume?

Tubing used does not leach BOD?

Should be latex rubber (surgical latex) or C-flex

BOD bottles filled slowly?

Insert stopper without leaving air bubbles.

Using enough sample volume?

Effluents < 7 mg/L: Must use a 300 mL dilution

Measuring out samples

At least 2 unique dilutions per sample?

More dilutions is better

Document initial dilution prep. detail

- Sample volume
- Final volume
- Volume of dilution used

Initial dilution if sample volumes ≤ 3 mL?

Using wide-bore pipettes (3 - 100 mLs)?

Grad. Cylinders OK for volumes ≥ 100 mL

Extra nutrients added as needed?

Sample volume 201-249 mL; + 0.2 mL (each) required….or one pillow
Sample volume ≥ 250 mL; + 0.3 mL (each) required….or one pillow

Measure initial DO

Time from dilution to DO_I minimized?

Standard Methods suggests no longer than 30 mins.
Concern is for samples with "instantaneous" BOD

Measuring DO_I of <u>each</u> sample dilution?

Do not just take the DO_I of one of the dilutions!

Incubation

Incubation time is 5 days ?

Brake and Raynovic book: ± 2 hours
The 21st ed. of SM says ± 6 hours
Best: stay within 5 days ± 4-6 hours

Document date & time samples go in
Document date & time samples come out
(Use military time or note "am" or "pm")

Incubation temperature is 20 ± 1°C ?

Have documentation of incubator temperature for each day samples are in the incubator.

BOD - Depletion Criteria

Dilutions must deplete ≥ 2 mg/L.

Deplete = use up = uptake.
Often referred to as "delta DO" or ΔDO

Good idea to include a "ΔDO" column on your benchsheet

Oxygen residual must be ≥ 1 mg/L.

Residual = leftover = remaining = DO_{final}.

Average any dilutions that meet both these criteria.

Toxicity

Reporting results correctly?

Sample mLs	Depletion (mg/L)	BOD mg/L
25	6.5	78
50	5.1	31
100	2.6	7.8
		42

Report?
42 ?
78 ?
____ ?

DO NOT report the "average" of dilutions (42)
DO NOT report the highest value (78)
Best answer: report ">" plus the highest BOD (> 78)
MUST qualify these results as exhibiting "toxicity"
Should repeat w/ additional dilutions (**e.g., 5, 10 mLs**)

Using enough dilutions to detect toxicity?

Carbonaceous BOD

Does your permit specify CBOD?

Cannot switch to CBOD because of nitrification. Work with DNR Basin Engineer.

Are you certified/registered for CBOD?

If not on your certificate and you are required to report CBOD, you MUST submit a completed application

Inhibitor added?

How would I know inhibitor is added?
Document the addition! (a checkbox?)

BOD – Seeding (BUGS!!!!)

What is the seed source?

Document the source (commercial? Plant?)

What samples/QC were seeded?

Document which samples receive seed

How much seed was added?

Document how much seed was added

Do what you oughta…
Only add seed to dilution woughta (water)

Prepare commercial seed in DILUTION water (containing nutrients)! Deionized or distilled water will kill seed.

BOD - Seed Controls

At least two dilutions?

Treat just like a sample…

Adequate depletion from seed control?

Same depletion criteria as samples

Reasonable mg/L O_2 depletion?

SHOULD be 0.6 to 1.0 mg/L O2 depletion.
If higher, GGA can run high and vice versa

Is the depletion/mL of seed consistent?

Variability here translates to GGA; can cause failures.

Seed Correction Factor (SCF)

SCF calculated correctly?

SCF represents the amount of oxygen depletion (mg/L) per mL of seed added.
Frequently, labs merely write down the total oxygen depletion attributed to seed.

Seed Control 1 (10 mLs) depletes 4.5 mg/L
Seed Control 2 (15 mLs) depletes 7.2 mg/L
SCF1 = 0.45 (4.5/10)
SCF2 = 0.48 (7.2/15)

Avg SCF = 0.465mg/L/mL

Seed Control Inconsistency

Sample	# mLs	DO_i	DO_f	ΔDO	SCF/mL	
Seed Control	10	8.33	3.83	4.50	0.45	
Seed Control	5	8.31	3.00	5.31	1.06	**Avg=0.76**

Sample	# mLs	seed	Do_i	DO_f	-SCF	ΔDO	BOD	Report
GGA	6	1	8.30	3.00	- 0.76	4.54	227	
GGA	6	1	8.32	3.15	- 0.76	4.41	220.5	

If SCF = 0.45/mL, then *GGA* = 242.5, 236
If SCF = 1.06/mL, then *GGA* = 212, 205.5

BOD - *GGA*

Correct solution being used?

The only approved solution is one consisting of 150 mg/L each of glucose and glutamic acid.

Do you make it?...or purchase it pre-made?

- [Commercial] Record lot # and expiration.
- [Prepared in lab] document the following:
  - ↗ Expiration date of glucose & glutamic acid stocks
  - ↗ Glucose & glutamic acid dried at 103°C for 1 hour

Is the GGA being used still "good"?

- Document lot # and expiration.

BOD - *GGA*

Is the GGA stored in refrigerator?

It's a food source for bugs so in case it does get contaminated, keep it cold.

GGA warmed to room temp. before use?

Cold solutions have greater density (mass per unit volume). Therefore if pipetted while cold, results will be biased high. Warm only what you need!

Pipet out of the stock bottle?

Avoid contamination of the stock!
Always pour off into a clean disposable beaker.

BOD - *GGA*

Do you use exactly 6 mLs?
Do you seed GGAs? Use inhibitor?
Is GGA analyzed at least once/week?

Document the following:

- ↗ using exactly 6 mLs of GGA
- ↗ if seeded, exactly how many mLs were added
- ↗ whether inhibitor was used

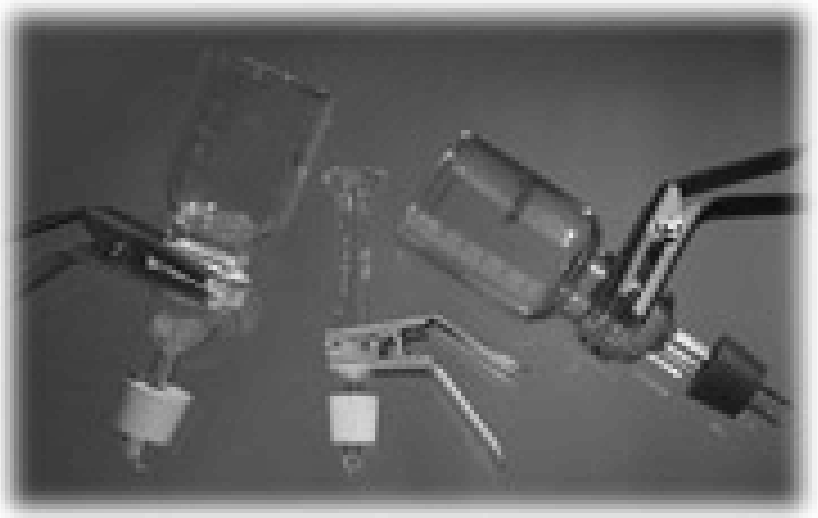
GGA control limits at <u>least</u> 167.5-228.5 mg/L?

Method <u>does</u> allow use of statistical limits but only if they are <u>tighter</u> than 167.5 - 228.5 mg/L

Comparing <u>each</u> individual GGA to limits?

Cannot average to meet limits.
Each GGA standard must pass.

*** TSS ***



TSS - Filtration apparatus

Using correct filter paper?

SM 2540 D: Whatman 934AH or equivalent

Filter papers pre-rinsed and tared?

Appropriate Filtration device?

Gooch crucibles tend to
(a) present weighing challenges, and
(b) limit the maximum volume that can be filtered.

Filter support screens well-maintained?

Ensure filter support screens are not excessively clogged with particulates, resulting in uneven drying.

TSS - Sample Volume

Using enough sample volume?

Effluents measuring < 10 mg/L: up to 500 mL must be filtered, providing effective LOD of 2 mg/L. Need to capture at least 1 mg or use 500 mLs.

Using too much sample volume?

Residue amounts greater than 200 mg on a filter can lead to "flash" surface drying and the formation of a salt crust layer that traps moisture beneath it. This can cause sample results to be biased high. Generally expected to be a problem related to process control samples with heavier solids loading.

Re-analyze (if possible) with lower volume.

TSS - Ensuring Constant weight

Dry every filter & sample to constant weight?
Dry overnight (8 hours); verify constant weight quarterly?

EPA and Standard Methods procedures REQUIRE all measurements be made to constant weight.

- Be able to demonstrate verification that routine samples are dried to constant weight quarterly.
- Plan how you will record this information.
- Ensure the data is traceable back to actual raw results.

TSS Benchsheet Reminders

Column information makes sense?

Crucible/Filter AFTER drying (g)	1st weighin	8110
Crucible/Filter tare weight (g)	1st weight	8000
Weight of dry solids (mg)		110

We frequently see data such as this.

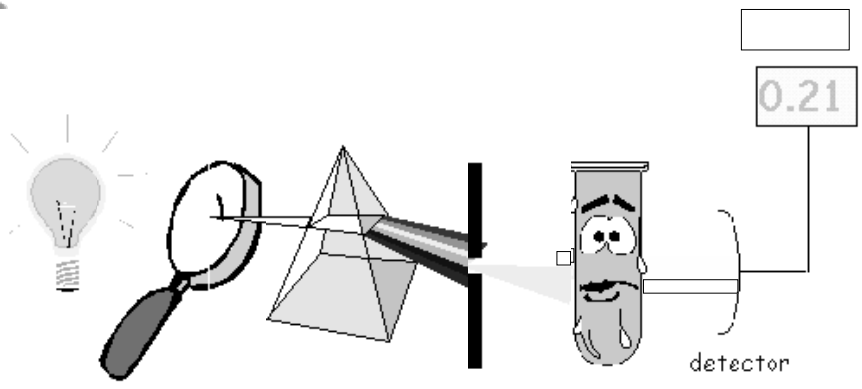
In this case the lab records only those digits to the right of the decimal point.

The values are neither g nor mg.

Crucible/Filter AFTER drying (g)	1st weighin	1.8110
Crucible/Filter tare weight (g)	1st weight	1.8000
Weight of dry solids (mg)		11

Ensure that values recorded accurately reflect the units indicated in that specific column/row

- PHOSPHORUS -



TP - Digestion - Hotplate

Samples allowed to boil dry?

If samples boil dry, they must be re-prepared.

Documentation of digestion?

Retain records related to the digestion:

- What samples/standards/QC were digested?
- What digestion procedure was followed?

What is the final volume?

Samples diluted to 50 mL + color reagent
Samples + color reagent diluted to 50 mL (*NCL*).

TP - Digestion - Autoclave

Autoclave for 30 mins @ 15-20 psi?

Document time and conditions.

Documentation of digestion?

Retain records related to the digestion:

- What samples/standards/QC were digested?
- What digestion procedure was followed?

What is the final volume?

No volume change; add color reagent to samples

Digestion - Test N' Tube (TNT)

COD Reactor set for 150°C?

Digestion for 30 minutes?

+2 mLs 1.54 N NaOH after digestion?

Total volume = 9 mL?

(5 mL sample, 2 mL 1.00 N H_2SO_4, 2 mL 1.54N NaOH

** Read samples between 2 and 8 mins. after PhosVer 3 addition*

TP Analytical Technique

Using an approved method?

NR 219 Table B Phosphorus - Total,:
Persulfate digestion -Manual ascorbic acid, or
Followed by: -Automated ascorbic acid

Three (3) techniques approved by the EPA:
- Single reagent, ascorbic acid *[650 or 880nm, BLUE]*
- Two reagent, ascorbic acid *[650 or 880nm, BLUE]*
- Automated, ascorbic acid *[650 or 880nm, BLUE]*

Other methods available (**but not approved under NR 219**)
- Vanadomolybdophosphoric acid *(400-490 nm, YELLOW color)*
- Stannous chloride *(690 nm, BLUE color)*

Bottom line: change procedures if….
(1) you measure absorbance at less than 650 nm,
(2) the color of the solution you are measuring is yellow, or
(3) if you are using stannous chloride in the color-producing step.

Zeroing the Spectrophotometer
Program Guidance

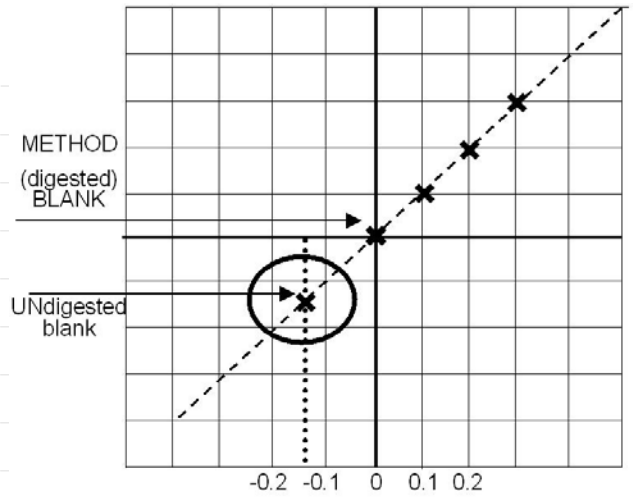
If the method blank is used as a zero standard, you will not have a true method blank and will not have a measure of background contamination.

	No Curve	With a Curve
Instrument Blank (θ)	**RW + DR** **No CR**	**RW + DR** **No CR**
Calibration Blank	----------	**RW + DR + CR** Only digest if curve is digested
Method Blank	**RW + DR + CR**	**RW + DR + CR**

RW= Reagent Water DR= Digestion Reagents CR= Color Reagent

Zeroing vs. Method Blank

- If you zero on your method blank or set method blank as your zero standard, your blank will always “pass” and you will NOT identify contamination issues
- Basic spectrometry principle is to zero on the solvent of interest (i.e. , water)
- A calibration blank gets assigned a concentration of “zero” by definition—even if its has measurable absorbance
- If you “zero” on something that contains measurable absorbance, the solvent (reagent water) will have less than zero absorbance (relative to the “zero”



Absolute value of -0.15 mg/L = 0.15 mg/L
Lowest calibration standard = LOQ LOD=0.03 (30% of LOQ),
Contamination (0.15 mg/L) is 5 times the LOD

Background color

Do samples have background color? Is background color subtracted?

Prepare a "color blank" reagent.
Split sample into (2) 50 mL aliquots: (A) and (B).
To (A), add color reagent, to (B): color blank reagent.

(A) Absorbance of sample + color reagent
— (B) Absorbance of sample + color blank reagent
= Absorbance due to phosphorus in sample

Combined Color Reagent (100 mLs)	Color Blank Reagent (100 mLs)
50 ml 5N sulfuric acid,	35 ml reagent water
5 ml potassium antimonyl tartrate,	50 ml 5N sulfuric acid, and
15 ml ammonium molybdate, and	15 ml ammonium molybdate
30 ml ascorbic acid	

------- AMMONIA -------

NH3 Distilling? Or Not

If ISE and municipal effluent, does the lab have a copy of the SLH variance?

The lab must have a copy of this on file.

Is there documentation of distillation?

Document that the distillation was performed, who did it, what reagents were used, when it was done, what was distilled.

NR 149.06 (1)(g) Records to be retained include ….Log books, bench sheets, journals or notes necessary to demonstrate that method or legal requirements have been met.

NH3 Analytical Technique

Using an approved method?

NR 219 Table B

Ammonia (as N), mg/L: Manual

Distillation[8] (at pH 9.5):

Followed by:

Nesslerization, Titration, Electrode **Automated phenate, or Automated electrode**

[8] Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies.

NH3 Analytical Technique

Using an <u>appropriate</u> method?

Nessler **Levels 0.05 to 1.0 ppm.**

Nessler reagent contains 100 g mercuric iodide per liter
Each 2 mL of Nessler reagent contains 88 mg of pure mercury, added to 50 mLs of sample
88 mg in 52 mLs = 1.69 mg/L as mercury
Drinking water limit for mercury is 0.0002 mg/L [~ 1/10,000]
Contents of ONE tube would have to be diluted with ~ 130 gallons of water

Titration **For levels above 1 ppm**

Phenate, automated **For levels 0.01 to 0.5 ppm**

Electrode **For levels 0.03 to 1400 mg/L**

NH3 Is that probe any good?

Is the probe stored appropriately?

Essentially, probe must be stored in an ammonium chloride solution more concentrated than the highest calibration standard.

Probe will be ruined if stored in distilled water for any length of time.

How old is that probe?

Average life expectancy is 2 years or less.

Is the probe conditioned properly?

Requires ~ 24 hrs to stabilize after membrane change.

How often is the membrane changed?

Document membrane changes in maintenance log.

Is that probe any good?

Is millivolt (mV) response acceptable?

- Document the mV response for each calibration standard.
- Monitor for changes over time.
- Replace probe if mV response for standard < 20 ppm drops below zero

If, after changing the membrane and replacing the internal filling solution, a probe still yields erratic results, perform an “inner body” check. Generally, manufacturers will not even consider replacing a probe until this test is performed.

NH3 Sample Analysis

NaOH buffer added after probe?

Ammonia is in gas phase at this pH and will be lost .

Constant (slow) stirring for samples/stds?

Keep electrode at an angle to minimize air bubbles

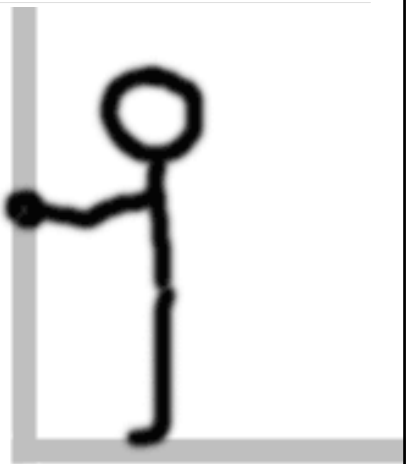
Is lab subject to temperature changes?

1-2% error per °C temperature change.
Samples & standards must be at the same temperature

Do results exceed the calibration range?

Dilution required for any result > top standard

QA/QC



2nd source standards

Second source standards available?

It is recommended that standard reagents be purchased from two different suppliers, each of which is then used to prepare a 1000 mg/L stock standard.

Stock A= calibration standards

Stock B= solution to prepare spikes or 2nd calibration check.

If the same solution that is used to prepare calibration standards is also used to prepare spiked samples, errors made in the preparation of the stock standard cannot be easily identified.

NOT required; a recommendation only.
But this is a good thing!

LOD

Has the lab determined its LOD?

The LOD should be re-determined annually.

Maintain records to substantiate this task.

For phosphorus, spike at 0.1 and OR 0.2 ppm.
Generally, do NOT spike lower than 0.1 ppm.

For ammonia, spike between 0.2 and 0.5 ppm.
Do NOT spike lower than 0.2 ppm.

Is the LOD acceptable?

The calculated LOD cannot exceed the spike level

The LOD must not be lower than 10% of spike level

Basically, the LOD must be 10-99% of the spike level

Is the LOD considered when reporting?

Be sure to USE the LOD once you've determined it.

Method Blanks

At least one blank prepared each day ?

Include the blank on your benchsheet

Is blank concentration < LOD? (NH3, TP)

Method blank fails if higher than the highest of: (1) The LOD, (2) 5% of permit limit, (3) 5% of the sample.

Is depletion < 0.2 mg/L? (BOD)

Individual blanks MUST pass criteria!

Document the initial and final DOs.

Should have a column to record depletion

NH3: stabilization time is critical!

The lower the concentration, the longer stabilization time required. Not allowing enough time can lead to "apparent" blank failures.

Calibration – General concerns

Calibration levels appropriate?

Calibrating at 0.05, 0.5, 1, 1.5, 2.0 and 2.5 ppm will not provide good data if all samples analyzed are <0.5 ppm.

Standards evenly spaced?

0.1, 0.2, and 1.0 are NOT good levels for a calibration.

Recommended TP calibration = 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mg/L

Recommended NH3 calibration = 0.2, 2.0, and 20 mg/L
NOTE: Calibration ranges for ammonia may change with the season

Calibration range too high or too low?

- Phosphorus: generally non-linear above 1.0 ppm.
- Ammonia: Below about 0.2 ppm, electrode response is so slow it is difficult to obtain a stable reading, resulting in a poor calibration.

Calibration –more concerns

TP: When was last calibration performed?

Approved methods: calibration when reagents replaced.
Required when known standard recovery exceeds ± 10%
Recommend new calibration at least quarterly.

NH3: New calibration performed daily?

Ammonia methods require full calibration daily.

Using at least 3 calibration levels?

Approved methods require at least 3 standards

NH3 Calibration Evaluation

Slope within 54-60 mV?

A slope within these parameters= a valid calibration.

Slope is based on the Nernst equation.
The only variable is temperature; slope decreases with temperature
Theoretical slope is 59.1 mV @ 25°C **58.1 mV @ 20°C**

Older Orion pH meters display the slope as a %-age of the theoretical.
For example, a 98.5% slope = slope of 58.27 (98.5% of 25 °C target)

Each segment slope within 54-60 mV?
Total mv difference within 108-120?

Many ion meters will only display a slope of 58.6 for this calibration
(which represents only the slope from the last segment calibrated)

Does analysis proceed if slope fails?

Analysis should not proceed until slope meets criteria.
If analysis proceeds, data MUST be qualified.

TP Calibration Evaluation

Correlation coefficient, "r" ≥ 0.995?

A correlation within this parameter = a valid calibration.
Document the correlation on your benchsheets.

Does analysis proceed if "r" fails?

Analysis should not proceed until "r" meets criteria.
If analysis proceeds, data MUST be qualified.

Any other evaluation "tools" used?

Looking at residuals & documenting recoveries is best.
At least initially (and regularly) review response factors.

Known Standards

Was a full calibration analyzed?

If no "full" calibration, a known standard is required
Acceptance criteria must be ± 10% of true value
if exceed criteria, a new calibration is required

Analyzing more than 20 samples/day?

Known standard required after 20 analyses in a day.

What are the acceptance criteria?

NR 149 requires ± 10% of true value.

Obtaining acceptable results on a known standard following a matrix spike exceedance is a means of substantiating that the exceedance is due to matrix effect vs. laboratory-related problem.

Replicates (General)

- ☑ **Replicates for EACH matrix type?**
- ☑ **Frequency at least 1/20 samples/matrix?**
- ☑ **Is there a concentration dependency?**

If there is ….then separate control limits are required to address the dependency

- ☑ **Prepared at same dilutions as sample?**

Treat replicates exactly like a separate sample.

- ☑ **Are replicates reviewed against limits?**

Clearly document what limits are in effect and whether you pass or fail.

Suggest:
Range for effluent;
RPD for influent

Replicates (General)

Using enough significant figures?

Always record at least one extra decimal place for QC samples

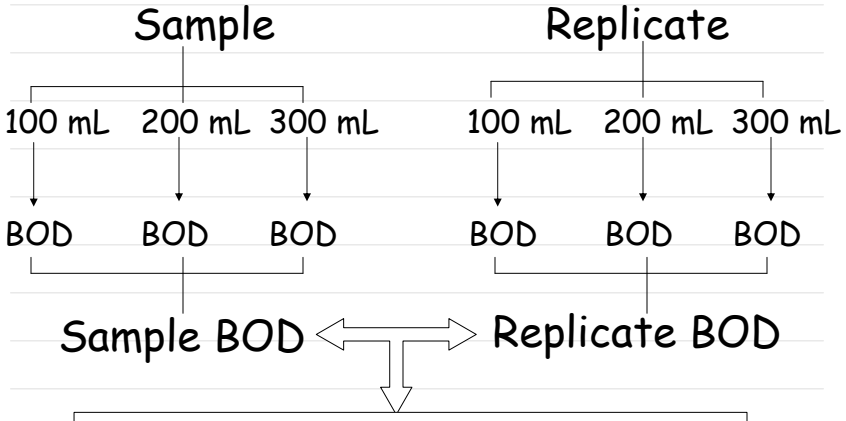
Plan for corrective action?

It's a good idea to keep a portion of each days sample refrigerated and/or preserved in order that repeats can be done in the event of a QC failure.

Replicates (BOD)

Precision calculated/evaluated correctly?

Duplicating a single dilution is not acceptable.



Spikes

Spikes for each matrix (influent v. effluent)?

Influent and effluent are two different matrices.
Anything required to be reported on DMRs counts.

Frequency at least 1/20 samples/matrix?

If you wait till you hit 20 samples, and the spike fails, you will have to qualify a LOT of data.
Many labs do spikes weekly, alternating influent/effluent each week.

Prepared at same dilutions as sample?

You must have the same amount of matrix in the spiked sample as in the sample itself.

Spikes

Spike prepared at the appropriate level?

Spike concentration should be 1-5 X sample concentration.

Is spike volume < 10% of sample volume?

Limit spike addition to ≤ 10% of sample volume.
If spike addition is < 1%, no volume correction is required.

Are spike preparation details documented?

Traceability issue. Clearly document the volume of sample and spike solution, concentration of spike solution, and total volume of sample + spike.

Calculating Spike Recovery

Are recoveries calculated correctly?

This continues to be a deficiency.
Remember to account for any volume differences
Spiking "on top" vs. "dilute to volume" differences

If errors have been made over time, control limits may have to be re-calculated/adjusted.

Are recoveries <u>evaluated</u> immediately?

Write in control limits on benchsheets.
Indicate whether results pass or fail.
How would an auditor know this is reviewed?

Calculating Spike Recovery

$$\frac{\text{Spiked sample (concentration or mass)} - \text{The amount of sample in the spiked sample (concentration or mass)}}{\text{The amount spiked (concentration or mass)}} \times 100$$

Remember to consider the effects of digestion technique.
Calculation is the same (for hot plate) whether you use:
50 mLs + 1 mL of a 50 ppm, or
50 mLs + 50 mLs of a 1 ppm

Control Limits (General)

Control limits available for past 3 years?
Keep clear records of past control limits

Are control limits "reasonable"?

Control limit should generally be no more than 20% of the average sample concentration. (~20% RPD)

Control Limits updated regularly?

Any time a significant change is made, updating control limits may be necessary.

What are Control Limit effective dates?
Control limit package should include :
- ⇨ Data used to generate limits (and dates)
- ⇨ When the control limits take effect

Control Limits (General)

Statistically based?

Statistical limits required unless the lab generates less than 20 QC points/year.

Are outliers excluded?

Demonstrate that a statistical procedure is used to identify and exclude outliers.

If using charts…plotted correctly?

Control limits are used to evaluate FUTURE data. Many control charts merely plot the data used to generate new limits against those same limits.

Blind Standards

Results available for past 3 years?

Keep results, raw data and acceptance criteria together

Performed at requisite frequency?

At least 3 times annually:

- at least 3 months after the previous blind standard
- no longer than 5 months after previous blind standard.

Remedial sample ordered upon failure?

Do not wait for next scheduled shipment

MUST order immediately

QA Manual

Written QA Plan available?

Document what your lab does; be specific.

> The "QA Document for a Small Wastewater Lab" is NOT your QA Manual. It's purpose is to provide guidance to help you write your own.

Does the QA Manual reflect lab policy?

The auditor will compare the QA Manual to benchsheets and what was said.

Are SOPs available for procedures ?

> Though not specifically required at this time, they may be in the future.

Corrective Action Records

Is corrective action taken in response to QC failures?

Each QC failure must be investigated.

Is the corrective action documented?

Documentation is required.:

- what action was taken…and by whom
- what was the result.
- include on the DMR

Did corrective action resolve the problem?

Do not just "put a bandaid" on the problem.

Document that the problem is resolved.

Record-keeping Reminders

Are records generated in a manner that ensures they are unalterable?

No pencil, correction fluid, or eraseable ink.
Electronic records: move towards audit trail software or other security measures.

Are records traceable?

Can someone unfamiliar with the facility re-generate your results?

- **If you didn't document it, you didn't do it**
- **You did the work.....take credit for it!**

Defensible Reagent Documentation - Simple Approach

Pre-print labels for new chemicals and reagents

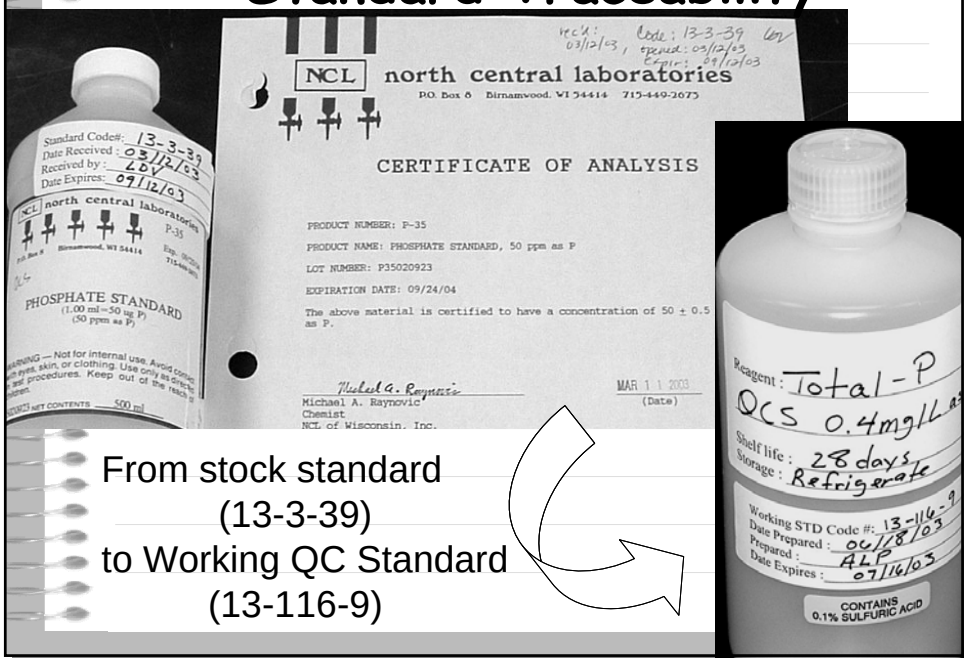
New Chemical or Reagent Label

Date received: *4/2/07* **Expires:** *6/07*
Received by: *Hannah Banana* **Opened:** *5/12/06*
Required Storage: *Room temperature, away from light*
Chemical or Reagent: **Ascorbic Acid (for Phosphorus)**

New Working Standard Label

Standard: *Phosphorus, 5 µg/mL* **Std. Code:** *100-3*
Date Prepared: *3/5/07* **Preparer:** *H. Montana*
Date Expires: *9/5/07* **Storage:** *4°C*
Stock Std Code: *50-25*

Standard Traceability



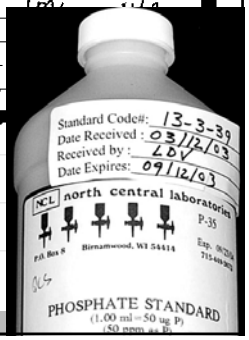
From stock standard (13-3-39) to Working QC Standard (13-116-9)

Standard Traceability - Stock Standard Log

Stock STD Code	Parameter / Compound	Manufacturer	Lot#	Date Recd	Date Exp.	mg/L Stock Conc	Initials	Preservative Code
13-3-33	Chlorophyll a/Anacystis	Sigma	052K1547	12-26-02	12-26-03	1mg	GDK	Store @ <0°C
13-3-34	Chlorophyll a/Anacystis	Sigma	102K1137	12-26-02	12-26-03	1mg	GDK	Store @ <0°C
13-3-35	Chlorophyll b/Spinach	Sigma	091K7018	12-26-02	12-26-03	1mg	GDK	Store @ <0°C
13-3-36	COD ICV	BC011124	BC011124 →1	1-6-03	7-6-03	6566	GDK	NONE
13-3-37	NITRATE as N	ERA	11572	01/29/03	07/29/03	1000 mg/L	KA	NONE
13-3-38	FLUORIDE	MERCK	22223	02/03/03	08/03/03	1000 mg/L	GDK	NONE
13-3-39	Phosphorus	NC Lab	P35020923	03/12/03	09/12/03	50	LDV	—
13-3-40	phosphorus	MCR	3027	03/12/03		50		
13-3-41	Sulfate	ERA	30013	04-15-03		1000		
13-3-42	Nitrite	ERA	05023	04-15-03		1000		
13-3-43	Ammonia as N	HACH CHEM	3041-25	08-07-03	11-08-03	1000ppm		
13-3-44	Nitrate	ERA	02053	6-4-03	May 2005	1000 ppm		

13-③-39

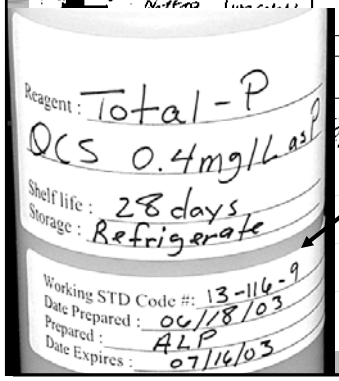
Logbook # Page # Entry/Line #

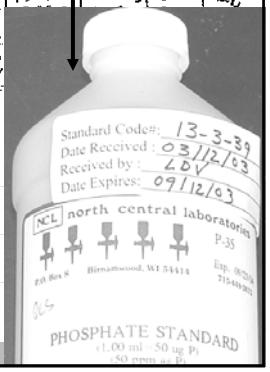


Standard Traceability - Working Std Log

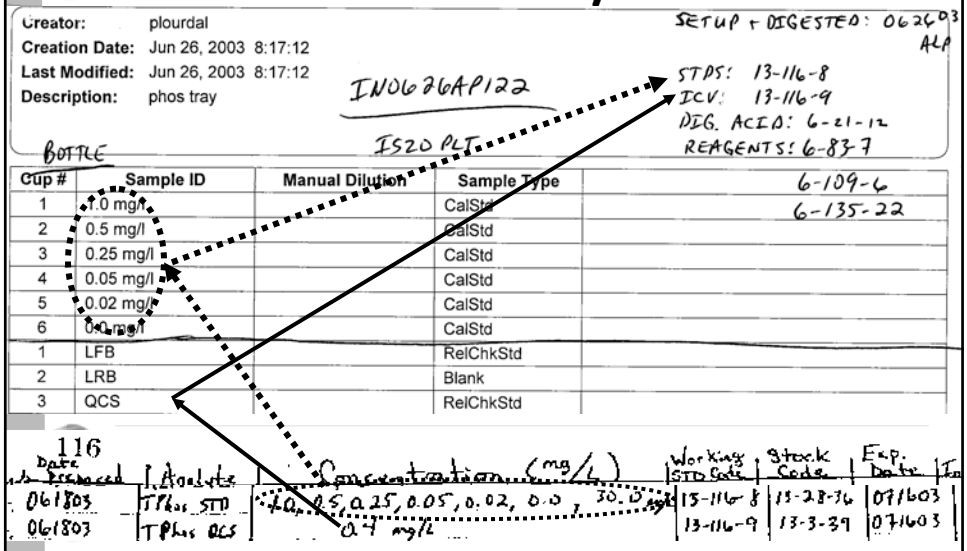
116

Date Prepared	Analyte	Concentration (mg/L)	Working STD Code	Stock Code	Exp. Date	Initials
061303	NO2 coeff	10.0 mg/L	13-116-1	13-28-26	06/1/03	ALP
6-16-03	SLP Std	0.20, 0.15, 0.10, 0.05, 0.025, 0.005, 0.0 / 5.0	13-116-2	13-28-36	6-[illegible]-03	RER
6-16-03	SolP QCS	0.135	13-116-3	13-3-39	6-22-03	RER
06-17-03	Granular Std	50 µg/L	13-116-4	13-28-18	06-15-03	LDV
06-17-03	Solids QCS	35, 100, 135, 55, 705, 75 mg/l	13-116-5	13-28-28	06-24-03	ALP
6-17-03	NO2 coeff	10.0 mg/L	13-116-6	13-28-26	6-18-03	JM
6-18-03	ALK STD	201, 50, 25	13-116-7	13-28-18	6-19-03	CEK
061803	TPlus STD	1.0, 0.5, 0.25, 0.05, 0.02, 0.0, 30.0 mg/L	13-116-8	13-28-36	07/1/03	ALP
061803	TPlus QCS	0.4 mg/L	13-116-9	13-3-39	07/16/03	ALP
		3.0	13-116-10	13-28-2[illegible]	06/19-03	LDV
		10.0 mg/L	13-116-11			
		0.5, 0.3, 0.2, 0.1, 0.0, [illegible] 20	13-116-12			
		0.25	13-116-13			
		100 mg/L	13-116-14			
		2.8	13-116-15			
		2.3 mg/L	13-116-16			
		[illegible], 7.5, 5.0, 2.5, 1.0, 0.4, 0.0 Sp 25.0				





Standard Traceability - Benchsheet



Creator: plourdal
Creation Date: Jun 26, 2003 8:17:12
Last Modified: Jun 26, 2003 8:17:12
Description: phos tray

SETUP + DIGESTED: 062603 ALP
IN0626AP122
IS20 PLT
STDS: 13-116-8
ICV: 13-116-9
DIG. ACID: 6-21-12
REAGENTS: 6-837
BOTTLE
6-109-6
6-135-22

Cup #	Sample ID	Manual Dilution	Sample Type
1	1.0 mg/l		CalStd
2	0.5 mg/l		CalStd
3	0.25 mg/l		CalStd
4	0.05 mg/l		CalStd
5	0.02 mg/l		CalStd
6	0.0 mg/l		CalStd
1	LFB		RelChkStd
2	LRB		Blank
3	QCS		RelChkStd

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Date Prepared	Analyte	Concentration (mg/L)	Working STD Code	Stock Code	Exp. Date
061803	TPhos STD	1.0, 0.5, 0.25, 0.05, 0.02, 0.0, 30.0	13-116-8	13-28-36	071603
061803	TPhos QCS	0.4 mg/L	13-116-9	13-3-39	071603

NOTE: Different stock standards used for calibration standards and QCS

****You must also link the date of the last calibration to the data if you do not calibrate each day****

Dilutions

Is there documentation of dilutions?

Dilutions made quantitatively?

Clearly document any dilutions made.
In addition to including a dilution factor, laboratories should clearly indicate the specific volume of sample and diluent.

If a 10 X dilution is made, it is important to know whether 1 mL of sample was diluted to 10 mL vs. 50 mL diluted to 500 mL.

The greater the volume of sample used to create a dilution, the more representative is the resulting dilution.

All dilutions should be made on a quantitative basis.
To make a quantitative 10 X dilution:

- Dilute 50 mLs of sample with DI in a class A volumetric flask
- **rather than** adding 50 mLs (grad cylinder) of sample to 450 mLs (grad. Cylinder) of DI water

Filling in benchsheets

Was there a digestion (or distillation)?
- Who performed it?
- What was digested (*samples? Standards? QC?*)

Who performed the analysis?

When was the analysis performed?

When was the last full calibration?

How was it evaluated?

Document everything related to digestion.
Record absorbance (mV) of standards & samples.
Record calibration correlation, slope, intercept.
Document any dilutions.

BOD - Benchsheet Reminders

Who did the initial set-up?

Who did the measurements after 5 days

Document analyst ID (both DO_I and DO_F)

How do you show samples incubated 5 days?

Document date & time samples go in incubator

Document date & time samples come out

Use military format or designate “am” v. “pm”

*** Odds & Ends ***

Reporting Results on DMR

Correct LabCert ID for each parameter?

Only record your LabCert ID for the tests you perform.

Are LOD & LOQ recorded on DMR?

DMR reporting specifically requires the LOD and LOQ to be reported for ammonia.

Reporting correct LOD?

LOD = 2 **only** if include a 300 mL dilution

Check "QC Exceedance" box as needed?

ANY type QC exceedance means the box for that test (e.g. BOD) must be checked.

Methods

Does the laboratory have a copy of the procedure(s) it references?

NR 149.11 (7) Laboratories shall make copies of the analytical methods, department regulation and department guidance pertaining to environmental sampling and analysis available to the analysts.

Are analysts provided access to the referenced methods?

Data Audit

Records available for past three years?

The auditor will generally want to see some records going back as far as three years.

Tests the facility's compliance with record-keeping requirements. A filing system that allows for ready retrieval of all supporting information should be maintained.

All supporting information available?

The auditor will be looking for autosampler records, temperature records, corrective action, etc…..basically all information necessary to reconstruct prior data.

Audit Survey

- This is your opportunity for input
- Help guide program direction
- Describe your audit experience
- Surveys go directly to David Webb, section chief
- Only “trends” are shared with auditors

Remember:
Audit goal is to obtain compliance

Having to make changes is all a part of improving

Audit ≠ bad experience

Resources

Your Regional Auditor
State Lab of Hygiene
Talk to other facilities
Wisconsin Rural Water (Chris Groh)
Kay Curtin (SEH)

Audit reports
QA Document for a Small Wastewater Lab
Past Training materials (website)
LabNotes Newsletter
LabCert website (e.g. the BOD Resource):
www.dnr.state.wi.us/org/es/science/lc/

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