

ADVANCED Lab Exam Review

April 29, 2014

Why are we here?

A brief history of lab exam results

How to best prep for an exam?

Why should we care?

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WI DNR Lab Certification

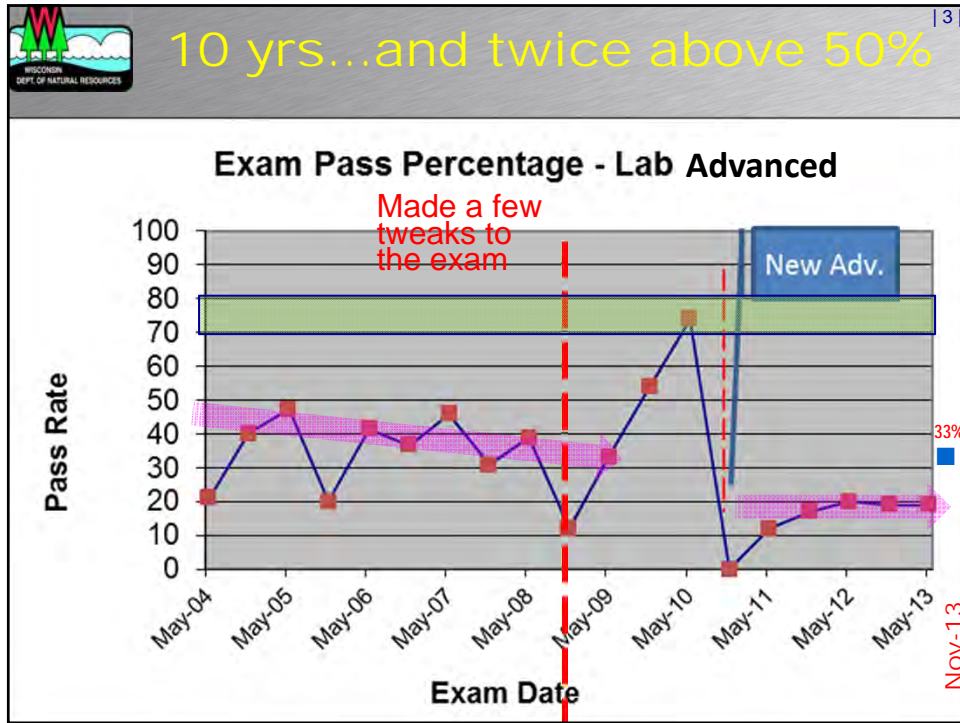


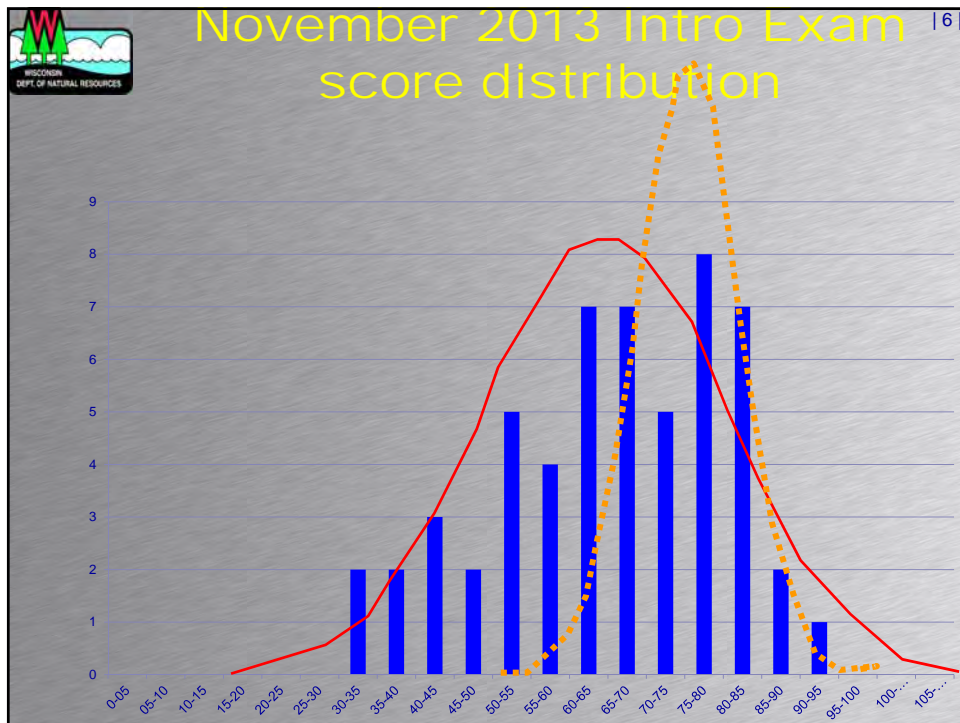
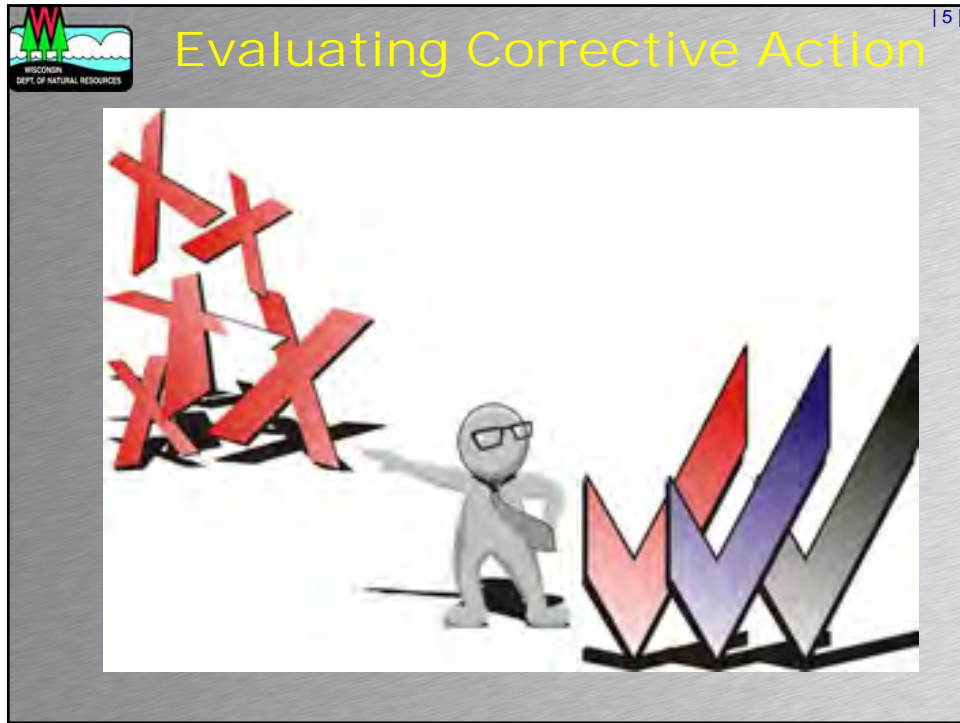
Score required to PASS


2

75%

- That's 30 of 40 questions
- You can miss no more than 10 questions








ADVANCED NOV 2013

55 took the exam, 18 passed = **33% pass rate**.
Average score = 64.2

Those who attended the 10/7/13 training
5 of 14 taking passed (**36%**),
average score= 69.8 (**5.6 pts better** than all
Those that took exam previously & attended 10/7:
2 people at least doubled previous test scores.
Overall, a **18 point improvement in scores** from
the previous attempt (**about 7 questions**).




WHY are people failing this exam? | 8 |

- What's hard about it?
- Did you look at the Study Guide first?
- Did you take a prep class?
- If you took a class...do you think it helped?
- No different than corrective action in the lab
- Gun analogy...is it you, the ammo, or the rifle?
- Can we rule out things one at a time?
- **But if you repeat the same process, you should expect the same results.**
- If it's not you or the rifle...maybe switch ammo

WISCONSIN DEPT. OF NATURAL RESOURCES

Mentality issue

- Some think that one needs to pass the test BEFORE one does any lab testing.
- Often lab supervisors wont let people do the testing until they pass the OpCert exam (as part of an “IDC”).



- You need to know the lab testing and methods FIRST.


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WISCONSIN DEPT. OF NATURAL RESOURCES


Exam Review: Good News 1st

ADV Knowledges with >75% Pass



- You know about MSDS and Chemical Hygiene plans.
- You know about Beer-Lambert's law.
- You know how to re-certify balance weights.
- You know about reducers.
- You know how to use the $C_1V_1=C_2V_2$ formula.
- You know how oil&grease affects TSS.





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 Now the Not-so-Good News.... | 11 |


ADV Knowledges with 50 - 75% Pass

- 63%: Understand how incubator temperature affects BOD results.
- 61%: Know when the fill-hole on a pH electrode must be open. 
- 60%: Understand deionization & reagent water
- 59%: Can explain what causes slow phosphorus color development.. 
- 59%: Know how to improve pipeting accuracy.
- 52%: Understand over-dechlorination & BOD.
- 51%: Understand what dictates whether a sample exceeds the calibration range.

 ...and the REALLY not-so-good news | 12 |

ADV Questions with < 50% Pass Rate 


- 56% still **don't how** an ISE works.
- 57% **don't how** what causes low GGA.
- 61% **don't how** how to determine the best volume for BOD.
- 61% **don't** understand sample pres. Temp.
- 65% **don't** understand linear regression.
- 69% **don't** know how TKN and NO₃+NO₂ re used in process control.
- 73% **don't how** required blanks for TP testing.
- 85% **don't how** causes of reduced color (TP).



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Post-Exam QA/QC

- We DO look at Exam results!
- A Quality Assurance review to ensure that the exam is properly measuring operator knowledge.
- Ask the questions:
 - Is the passing rate acceptable?
 - Particular question(s) too easy?
 - Particular question(s) too difficult?
 - Is there more than one perceived correct answer?
- Additionally, review operator comments/concerns about the exams




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Don't just slap a bandaid on it!






- **DO NOT** go study only **the concepts** just presented!
- Remember: Exams are generated randomly from a bank of questions.
 - There are over 120 questions in each exam bank. Less than 2/3 have appeared so far.
- There are questions that have yet to appear tied to **OTHER** knowledges that operators lack.
- **READ** the Study Guide.
- ...and did we mention...**READ the Study Guide!**




READ THE STUDY GUIDES!

- **Kaffee**: You gotta trust me, Sherby, you read the Study Guide and your chances of passing the exam increase by a factor of 10




How to effectively study/prepare for an exam:


Reading for Comprehension




| 16 |

 | 17 |

Reading for Comprehension



- **Highlight** important ideas.
- Circle or bracket **key terms**.
- Identify the **main point(s)** of the info.
- Can you eliminate certain parts that just seem to be a lot of extra words—like tangential observations — that don't really add anything of particular note other than length to the information as “**extraneous**” information?
- Look for “telling” words: “**always, must, require**”
- What **question(s)** would YOU create?

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Reading for Comprehension isolating critical info

5.1.04 Define super-saturation.

- Supersaturation **means** that the water contains more DO than it **SHOULD** contain according to physical tables.
- **According to tables,** the saturation point of oxygen in water at 20° and 760 mm pressure -which is standard temperature and pressure at sea level- is 9.06 mg/L. So, yes, at sea level and 20°C, anything over 9.06 mg/L represents supersaturation.
- The method kind of “defines” super-saturation as anything above 9.0 mg/L. **However,** in reality saturation will vary with temperature and pressure. Consult a DO saturation table.



Multiple Choice Test Taking Tips

- Read the question before you look at the answer.
- Come up with the answer in your head before looking at the possible answers, this way the choices given on the test won't throw you off or trick you.
- Eliminate answers you know aren't right.
- Read all the choices before choosing your answer.
- Don't keep on changing your answer, usually your first choice is the right one, unless you misread the question.



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Many multiple choice answers have a dichotomy, or branching, to them. It's almost like a fork in the road and at the end of each fork are two doors.



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Good precision can be defined as closeness of....

- A. Agreement between repeated measurements; some systematic/ random error
- B. Agreement between repeated measurements; no systematic/ random error
- C. Measurement to the true value; some systematic/ random error
- D. Measurement to the true value; no systematic/ random error

Agreement between repeated values

A

Some systematic and random error

B

No systematic or random error

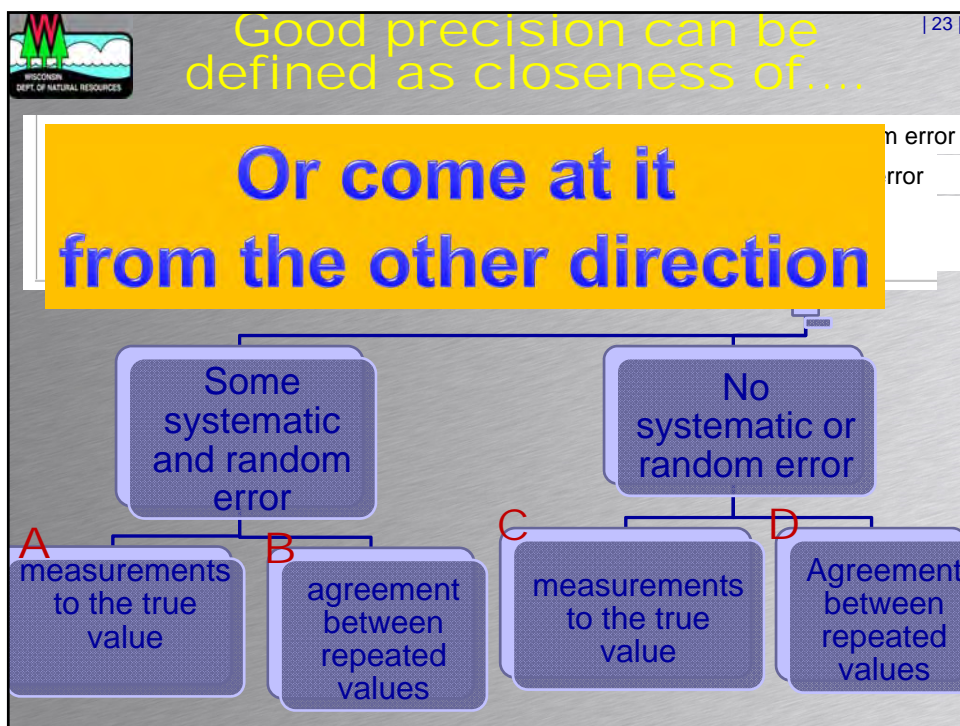
Measurements to the true value

C


Some systematic and random error

D

No systematic or random error



Let's look at some sample Lab related questions from other exam sources

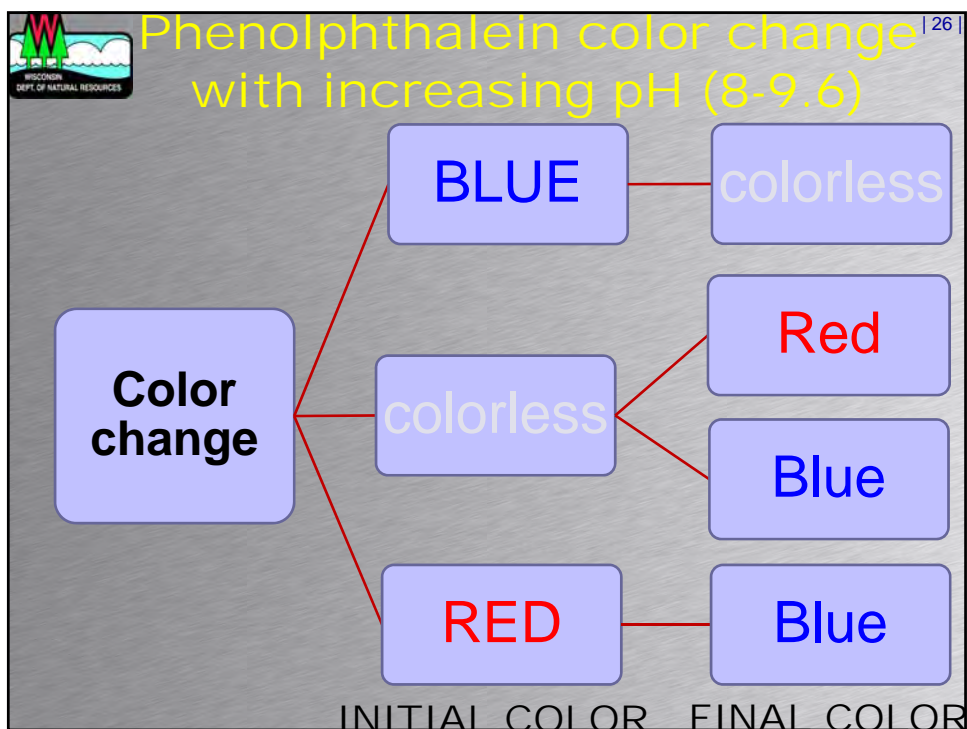



PHOSPHORUS

Between the pH range of 8.0 - 9.6 s.u., the indicator phenolphthalein undergoes what color change with increasing pH?

- A. Colorless to blue
- B. Colorless to red
- C. Red to blue
- D. Blue to colorless

- Break this question down to its basics.
- 3 of the 4 answers involve the color blue
- Does phenolphthalein ever give a blue color?
- If so, then at least you've eliminated 25% of the choices
- If not, then you've identified the correct answer





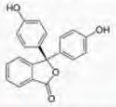
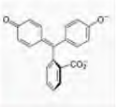
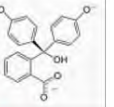
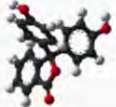
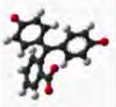
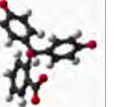

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Phenolphthalein

From Wikipedia, the free encyclopedia

"phph" redirects here. For Ph-Ph, see biphenyl.

Phenolphthalein /ˌfiːnɒlfˈθeɪliːn/^[d] is a **chemical compound** with the **formula** $C_{20}H_{14}O_4$ and is often written as "**HIn**" or "**phph**" in shorthand notation. Often used in **titrations**, it turns colorless in **acidic** solutions and pink in **basic** solutions. If the concentration of indicator is particularly strong, it can appear purple. In strongly basic solutions, phenolphthalein's pink color undergoes a rather slow fading reaction and becomes colorless again. The molecule has four forms:


Species	H_2In	In^{2-}	$In(OH)^{3-}$
Structure			
Model			
pH	0–8.2	8.2–12.0	>12.0
Conditions	acidic or near-neutral	basic	strongly basic
Color	colorless	pink to fuchsia	colorless
Image			

Thanks,
Wikipedia

<8.2 colorless

8.2-12 pink

>12 colorless



Calibration

When calibrating an instrument that uses a linear curve, what is the minimum number of concentrations that must be used?

A. One
 B. Two
 C. Three
 D. Five

- Read carefully! Do not leap to conclusion or decide on the answer without reading the question fully.
- It says calibrate...not CHECK the calibration.
- MINIMUM...not how many standards YOU use in your lab.

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How do you preserve a sample for ammonia if it cannot be analyzed when collected ?

1. Temperature
2. Acid? Or Base

Cool to $\leq 10^{\circ}\text{C}$

1 2

Add NaOH to pH > 11 **A**

Add H₂SO₄ to pH < 2 **B**

Cool to $\leq 6^{\circ}\text{C}$

1 2

Add NaOH to pH > 11 **C**

Add H₂SO₄ to pH < 2 **D**

BASIC ?s

Agitating a sample before measuring DO for BOD ...

a. Decreases the DO.
b. Increases the DO.
c. Decreases the SS.
d. Increases the SS.


Dissolved Oxygen

Increases it Decreases it

TSS

Increases it Decreases it

Example of a bad question...why?




BASIC - BOD

The BOD of wastewater determines the milligrams per liter of oxygen required...

- a. During stabilization of decomposable organic matter by aerobic bacterial action.
- b. To produce an equilibrium between the oxygen of the wastewater and atmospheric oxygen.
- c. To unite chemically with the inorganic matter present in the sample.
- d. For the oxidation of sulfites and thiosulfates to sulfates.

Minimal rewording of answers




BASIC - BOD

The BOD of wastewater determines the milligrams per liter of oxygen required...

- a. Bacterial action on organic matter
- b. Equalize wastewater Oxygen with air
- c. Bond with inorganic matter
- d. Oxidize sulfites and thiosulfates



Minimal rewording of answers

 **BASIC - BOD**

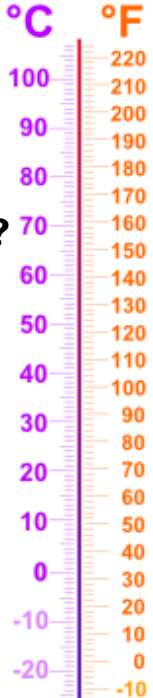
BOD incubation is at:


- 37° C.
- 98° F.
- 20° F.
- 20° C.

Incubate? or Hibernate?

- 37 °C equals about 98 °F...so since both can't be right, neither is!
- Where would you prefer to incubate? At 20 °F or 20 °C?




 **You're guessing!** | 34 |

The reporting limit for residual chlorine must not exceed:

- A. 0.380 mg/L [21% chose this]
- B. 0.100 mg/L [26% chose this]
- C. 0.200 mg/L [18% chose this]
- D. 1.00 mg/L [35% chose this]

Retired INTRO question




| 35 |

You're guessing!

The temperature preservation requirement for most wastewater tests is that they not be frozen and must be stored at:

- A. ≤ 4 °C [10% chose this]
- B. 4 ± 2 °C [45% chose this]
- C. ≤ 6 °C [43% chose this]
- D. 6 ± 2 °C [2% chose this]

Retired ADVANCED question




| 36 |

Creating Flashcards

- Summarize the CRITICAL information from the study guide and copy to index cards.
- Use THESE to study

Writing your own questions


- If you were quizzing someone on the topic, what questions would you ask?
- Writing the question and correct answer is the easy part.
- Coming up with 3 “wrong” answers without using all/none of the above and not being too tricky is a challenge!



What questions would YOU write for this? | 37 |


5.4.10 Explain why temperature is so critical when using the ion-selective electrode.

- Ammonia electrodes function according to the physical constraints of the Nernst equation, and in that equation temperature is the only variable. Each one degree (°C) change in temperature is associated with a 1-2% error due to changes in the electrode slope. Therefore, calibration standards and samples must be at the same temperature.



How about these.... | 38 |

- What is the principle that governs electrode operation: **the Nernst equation.**
- What is the only variable in the Nernst equation: **Temperature**
- 1 degree C temp change = **1-2% error.**
- Standards & samples must be: **same temp.**



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It's time to take a look at the Study Guides

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Advanced Study Guide...

where the knowledge detail expands considerably.
But stick to your tactical approach!

Identify “buzz” words:
shall, must, require, only always, every, **however**

Take note of any numbers/values (criteria)

Ignore extraneous words

Find the point(s) being made.

Try to separate informative but non-critical info

Frequently the 1st sentence contains critical info

Create flashcards

Write your own questions

ADV 1.1.4 Define oxidizing chemicals. | 41 |

Historical: 2Q 36.5%/40.7% pass

November 2013: 71% passed

An oxidizing chemical is one that oxidizes another chemical, the reducing chemical. In doing so, it becomes reduced. This type of reaction is called an oxidation-reduction, or redox, reaction. The oxidizing chemical GAINS an electron, while the reducing chemical LOSES an electron.

Common oxidizing agents that may be found in small labs include: Oxygen gas (O₂), ozone (O₃), halogens (fluorine, chlorine, bromine). Hypochlorites: such as household bleach, chlorination chemicals. Nitric acid (HNO₃), Nitrate salts such as sodium or potassium nitrate (NaNO₃, KNO₃).

Permanganates and persulfates: such as potassium permanganate (KMnO₄). Oxidizers you might encounter include:

- For **BOD**: bleach, hypochlorite
- For **Ammonia**: none
- For **Phosphorus**: ammonium persulfate
- For **Chlorine Residual**: hypochlorite, potassium dichromate

ADV 1.1.4 Define oxidizing chemicals. | 42 |

Historical: 2Q 36.5%/40.7% pass

November 2013: 71% passed

Generally speaking, chemicals whose names end in “-ate” or “ite” are those that contain a significant amount of bound oxygen, and thus are frequently oxidizers.

There are two main categories of oxidizing agents:

- (1) reagents that contain an oxygen-oxygen bond, and
- (2) reagents that contain metal-oxygen bonds.

Examples of oxidizing agents containing an O—O bond include oxygen gas (O₂), ozone (O₃), and hydrogen peroxide (H₂O₂).

The most common oxidizing agents with metal-oxygen bonds contain either hexavalent chromium (Cr⁺⁶) or heptavalent manganese (Mn⁺⁷). Common Cr⁺⁶ reagents include chromate (CrO₃) and sodium or potassium dichromate (Na₂Cr₂O₇ and K₂Cr₂O₇). The most common Mn⁺⁷ reagent is potassium permanganate (KMnO₄).

ADV 1.1.4 Define oxidizing chemicals. | 43 |

Historical: 2Q 36.5%/40.7% pass

November 2013: 71% passed

NFPA 704 is a standard maintained by the National Fire Protection Association (NFPA). It defines the commonly named, "fire diamond" used by emergency personnel to quickly and easily identify the risks posed by nearby hazardous materials. The four divisions of the "fire diamond" are typically color-coded, with blue indicating level of health hazard, red indicating flammability, yellow (chemical) reactivity, and white containing special codes for unique hazards. Each of health, flammability and reactivity is rated on a scale from 0 (no hazard; normal substance) to 4 (severe risk).

Oxidizers are designated in the white, "special" code area, using a code of "OX" or "OXY"

ADV 1.2.1 Explain the importance of storing oxidizers separately from reducers. | 44 |

Historical: 2Q 36.5%/40.7% pass

November 2013: 55% passed

Mixing oxidizers with reducers can produce violent reactions, even explosions. Generally these reactions are exothermic, which means a great deal of heat is generated. Based on these reactions oxidizers and reducers need to be stored separately.

Chemical incompatibilities to be aware of in the laboratory:

- *Acetone - incompatible with acids, oxidizers
- *Ammonia - incompatible with acids, bleach (hypochlorite), oxidizers
- *Chlorine - incompatible with alcohols, ammonia, combustible materials, flammable compounds, hydrocarbons, hydrogen peroxide, iodine, metals, nitrogen, oxygen, sodium hydroxide .
- *Hypochlorites - incompatible with acids, activated carbon
- *Nitrates - incompatible with acids, nitrites, metals,

| 45 |


Oxidizer
+
Reducer = 

| 46 |

EXOTHERMIC

EXO = External, or on the outside

As in, Iron Man is a multifunctional exoskeleton designed by Tony Stark



THERMIC = Heat producing

∴... an exothermic reaction produces external heat

ADV 1.2.1 Explain the importance of storing oxidizers separately from reducers. | 47 |

Historical: 2Q 36.5%/40.7% pass
November 2013: 55% passed

- *Nitric acid - incompatible with alcohols, (concentrated) ammonia, organic materials, plastics
- *Potassium permanganate - incompatible with sulfuric acid
- *Sulfuric acid - incompatible with potassium permanganate
- *Special cases (explosive compounds)

Some compounds have reducing groups and oxidizing groups in the same molecule. These tend to be heat and shock sensitive.

Ammonium nitrate

Examples:

Chlorites, chlorates, perchlorates, nitrates, e.g. NH_4NO_3 . The NO_3^- is the oxidizing agent; the NH_4^+ is the reducing agent. Organic nitrates and nitro compounds, (e.g., TNT, trinitrotoluene, $\text{CH}_3\text{C}_6\text{H}_2(\text{NO}_2)_3$). The nitro (NO_2) groups are oxidizing agents; the carbon atoms are reducing agents.

ADV 2.2.1 Explain the significance of the $\leq 6^\circ\text{C}$ preservation requirement for samples. | 48 |

Historical: 2Q 36.5%/40.7% pass
November 2013: 60% pass

Historically, federal rules regarding temperature preservation stated only that samples **must** be maintained at a temperature of " $< 4^\circ\text{C}$ ". This appeared to be a very firm temperature, with no variance associated with it.

For example, labs are familiar with the acceptable temperature range for drying of TSS samples as $103\text{-}105^\circ\text{C}$ (which really translates to $104 \pm 1^\circ\text{C}$), and of the requirement that BOD incubators be maintained at a temperature of $20 \pm 1^\circ\text{C}$. No such flexibility appeared to exist for sample temperature. Consequently a growing national trend established a new requirement that sample temperature be maintained at $4 \pm 2^\circ\text{C}$, or 2 to 6°C . This range clearly identifies that the target temperature for sample preservation is 4°C , but offers a flexible window of compliance.

ADV 2.2.1 Explain the significance of $< 6^{\circ}\text{C}$ preservation requirement for samples. | 49 |

2Q 36.5%/40.7% pass

What the $4 \pm 2^{\circ}\text{C}$ approach does not recognize, however is that preservation temperatures below 2°C are not unacceptable. In fact, the only limiting criterion for the lower acceptable range for sample temperature is that samples must not be frozen, as freezing samples can change the physical or chemical nature of certain analytes. Consequently, when ch. NR 219, Wisconsin Administrative Code (which governs analysis of wastewater samples) was revised, this code specifies a temperature of "less than or equal to 6°C " with a footnote that specifies that samples also are not to be frozen.

The most critical thing to remember is that just because the upper limit has been expanded to 6°C , the overall goal of sample preservation has not changed. Therefore, labs should still consider the target sample preservation temperature to be 4°C . If autosamplers or refrigerators appear to be creeping upwards of 4°C , then corrective action should be initiated to provide more cooling to samples. This may include adjusting (and noting in maintenance logs) that the thermostat was adjusted to reduce cooling temperature.

ADV 3.2.6 Explain how the accuracy of autopipettors is verified. | 50 |

Historical: 37.0% pass

November 2013: 58% passed

Calibration of autopipettors can be done either photometrically or gravimetrically. The photometric approach is rarer due to the need for expensive instrumentation and reagents.

The gravimetric approach is what most labs use. This approach assumes that purified water (i.e., lab reagent water) weighs approximately 1.0 gram per milliliter, mL. The exact density of water is based on temperature and can be obtained from a reference table. Pipets are tested by pipetting consecutive aliquots (specific milliliter volume) of reagent water and comparing the resulting mean and standard deviation of the weight of each aliquot to the nominal weight (based on $1\text{ mL} = 1\text{ gm}$). The accuracy of all pipets must be verified quarterly by analyzing the weights resulting from at least four replicate pipettings.

Replicate analyses must meet acceptance criteria or use of the pipet should be discontinued until the problem has been corrected.

Suggested acceptance criteria to use are:

% Inaccuracy: $[(\text{Corr. Mean} - \text{true value}) \div \text{true value} \times 100]$

(must be $< 2\%$ and no single replicate may be $> 2\%$ from the true value).

ADV 3.2.6

37.0% pass

Explain how the accuracy of autopipettors is verified.

| 51 |

%CV: [(Standard Deviation ÷ Corr. Mean × 100)] (must be < 1.00)

If you are checking an adjustable volume pipet, at least three different volumes should be tested; 10% of maximum volume, mid volume and maximum volume.

PROCEDURE

1. Place a clean, dry disposable beaker on the balance, close and tare the balance.
2. Apply a clean tip to the pipet.
3. Operate the pipet's action a few times prior to using. This will redistribute the lubricant and ensure a smooth positive action.
4. Wet the tip by drawing up an aliquot of reagent water and discard.
5. Open the balance. Pipet an aliquot of reagent water into the disposable beaker. Take care to touch off any remaining liquid on the tip.
6. Close the balance. Once the weight has stabilized, record the value on a benchsheet or spreadsheet.
7. Tare the balance and repeat for as many replicates are needed. If a mistake was made during one replicate, repeat using a new replicate.
8. Verify that results fall within the lab's acceptance criteria.

ADV 3.3.3

Historical: 13.0% pass

November 2013: 42% pass

Describe the operating principle of the Beer-Lambert Law.

| 52 |

Because of a special relationship between absorbance and concentration, known as the Beer-Lambert (often referred to as Beer's Law), the concentration of a substance can be determined using absorbance measurement. This relies on the same principles that a student would use to rank a series of concentrations according to the darkness of their color.

For example, if you use a solution of red food coloring in water and measure the amount of blue light absorbed when it passes through the solution, a measurable voltage fluctuation can be induced in a photocell on the opposite side. If now the solution of red dye is diluted in half by the addition of water, the color will be less intense and the voltage generated on the photocell will be approximately half as great.

$$\text{Abs} = \lambda \times b \times c$$

Where:

Abs = Absorbance

 λ = a molar extinction constant, specific to the analyte of interest

b = the path length (cm) of the cuvette or cell

c = concentration of the analyte

ADV 3.3.3 Describe the operating principle of the Beer-Lambert Law.⁵³

Historical: 13.0% pass

November 2013: 42% pass

The Lambert law states that absorption is proportional to the light path length, whereas Beer's law states that absorption is proportional to the concentration of absorbing species in the material. Combining the two laws to form the Beer-Lambert law, which describes how absorbance can be converted to concentration. See Figure 3.3.03A for the Beer-Lambert equation.

Thus, since the molar extinction constant and the cell path are both constant for a given analysis, the equation boils down to: $Abs = c$. Subsequently, the absorbance for a given analyte will increase as cell path length increases.

The Beer-Lambert law can be used to increase analytical sensitivity (lower detection limit) on occasion. Using phosphorus as an example, the absorbance of a 0.1 mg/L standard, using a typical cuvette with a 1.0 cm path length, is approximately 0.05 absorbance units. If the cell path length is increased to a 5 cm cuvette, the absorbance would be effectively increased five-fold to about 0.250 absorbance units.

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$$Abs = \lambda \times b \times c$$

Where:

Abs = Absorbance

λ = a molar extinction constant, specific to the analyte of interest

b = the path length (cm) of the cuvette or cell

c = concentration of the analyte

- **Absorbance = λ x path length x concentration**
- **Since λ is a constant it doesn't matter**
- **Thus, if either concentration or path length increases, absorbance will increase**
- **Conc =1, path length = 1 then Abs = λ**
- **Conc =1, path length = 5 then Abs = 5λ**
- **Conc =5, path length = 1 then Abs = 5λ**
- **Conc =5, path length = 5 then Abs = 25λ**

ADV 4.1.2 Discuss how conductivity relates to laboratory reagent water quality.⁵⁵

Historical: 44.4% pass

November 2013: 40% pass

In theory, lab reagent water should be “pure” and thus contain no dissolved solids or ions. Therefore one would expect the conductivity of lab reagent water to be zero.

Pure water is actually a poor conductor.

If water has even a tiny amount of such impurities, then it can conduct electricity much better, because impurities such as salts separate into free ions in aqueous solution by which an electric current can flow.

* Fact:

* The theoretical maximum electrical resistivity for water is approximately 18.2 megaohm-cm at 25 degrees Celsius.

* Electrolytic conductivity (EC) is the inverse of resistivity. Therefore $1/18.2 = 0.055$, the theoretical maximum conductivity ($\mu\text{S}/\text{cm}$) of pure water.

* A salt or acid contaminant level exceeding that of even 100 parts per trillion (ppt) [0.1 ppb] in ultrapure water will begin to noticeably lower its resistivity level (RAISING conductivity)

ADV 4.1.2 Discuss how conductivity relates to laboratory reagent water quality.⁵⁶

Historical: 44.4% pass

November 2013: 40% pass

* An alkalinity of 1 ppm as calcium carbonate (CaCO_3) will raise EC to 0.7 $\mu\text{S}/\text{cm}$

* 100 ppb each of sodium and chloride raises EC to 0.45 $\mu\text{S}/\text{cm}$

- Just 25 ppb of NaCl (about 2-3 grains of sand worth) dissolved in purified water will raise the EC to the maximum allowable level for ASTM Type I water.

Conductivity gives us a measure of water quality. The ASTM has defined Type I reagent water as water having a maximum conductivity of 0.056 $\mu\text{S}/\text{cm}$ at 25°C. ASTM “Type II” water has a maximum conductivity of 1.0 $\mu\text{S}/\text{cm}$ at 25°C. Conductivity means ions are present and the presence of ions clearly means that the water is not “pure”. Conductivity is useful as an indication that ion exchange resin is overloaded, that a reverse osmosis membrane has been breached, or simply that your reagent water may not be of sufficient quality for use in testing.

ADV 4.1.2 **Discuss how conductivity relates to laboratory reagent water quality.**⁵⁷

Historical: 44.4% pass

November 2013: 40% pass

The drawbacks to using conductivity alone as a means of verifying water quality are:

1. Conductivity **ONLY** measures substances that ionize...i.e. form ions. You can dissolve 1000 ppb of sugar in pure water and still not exceed ASTM Type I water criteria for conductivity.
2. It is **virtually impossible** to measure conductivity accurately to Type I or Type II levels without a closed system and VERY sensitive conductivity equipment. The nominal levels of CO₂ in the atmosphere will cause gaseous CO₂ to enter pure water causing a chemical reaction which increases conductivity.

The theoretical conductivity in pure water with addition of CO₂ is approximately 0.8 μSiemens. Therefore, just by exposure to air, lab reagent water will not be able to meet the requirements of ASTM Type I water. Lab reagent water criteria specified in Standard Methods and for the EPA's Safe Drinking Water program (2 μS at 25°C) are more realistic targets.

Conductivity & Reagent Water “takeaways”⁵⁸

- **Water is electrically neutral.**
- **Water that is not 100% pure may contain some measure of dissolved solids**
- **Dissolved solids are often salts, which “ionize” into ⊕ and ⊖ “fragments”.**
- **Conductivity essentially measures these dissolved substances and provides an indication of the water quality.**
- **Conductivity is not a perfect tool, because it cannot measure dissolved organic compounds which do not ionize.**

ADV 4.4.2 Identify the laboratory tests affected if the following problems occur with laboratory reagent water:

Historical: 79% pass
November 2013: 62% pass

HIGH COPPER (CU) OR CHROMIUM (CR) LEVELS

Copper and chromium are quite toxic to organisms. High levels of either could significantly affect any biological tests (BOD, fecal coliform) by inhibiting biological growth.

DISSOLVED BIODEGRADABLE SOLIDS

Any dissolved solids which are biodegradable will cause high blank depletions in the BOD tests, and may affect the fecal coliform test as well. It could affect the ammonia nitrogen test by shortening the life of ion exchange columns used to make ammonia-free water.

HIGH CONDUCTIVITY

Elevated conductivity is an indication of an increase in dissolved ions in the water. Some of these can be interfering substances, such as, copper, chromium, or ammonia. The more substances which are dissolved in the theoretically "pure" lab reagent water, the more likely it will be to have interferences in the tests. Elevated levels of trace metals could affect BOD results, while elevated ammonia levels will impact ammonia test results.

ADV 5.1.2 Define pH.

| 60 |

Historical: 41.7% pass November 2013: 62% pass

The pH is a range of numbers expressing the relative acidity or basicity of a solution. Mathematically, the pH value is the negative logarithm of the molar hydrogen-ion concentration in a solution.

- $\text{pH} = -\log [\text{H}^+]$
- Since the scale is logarithmic, the pH changes by one for every power of ten change in hydrogen-ion concentration. pH meters typically employ a probe with a glass electrode. The probe contains an acidic aqueous solution enclosed by a special glass membrane that allows migration of hydrogen ions. The electromotive force generated in the probe is linearly proportional to pH. A selection of buffers of a known pH are used to establish this linear relationship and sample pH is interpolated.
- Pure water dissociates to yield equivalent concentrations of hydrogen $[\text{H}^+]$ and hydroxide $[\text{OH}^-]$ ions: $\text{H}_2\text{O} \rightarrow [\text{H}^+] + [\text{OH}^-]$
The equilibrium for pure water is $[\text{H}^+] \times [\text{OH}^-] = K_w = 10^{-14} = 10^{-7} \times 10^{-7}$
Therefore, at equilibrium $[\text{H}^+] = [\text{OH}^-] = 10^{-7} = \text{pH of } 7$
The scale ranges from 0 to 14 $[\text{H}^+] = 10^0 \text{ to } 10^{-14}$

ADV 5.2.1 Discuss the testing differences between BOD and cBOD. | 61 |

Historical: 79% pass
November 2013: 62% pass

The **only** difference between samples analyzed for BOD and those analyzed for cBOD is the addition of a chemical inhibitor to all samples for which cBOD is determined.

In the absence of nitrogenous demand and nitrifying organisms, BOD and cBOD values should be equivalent. This is because the inhibitor theoretically suppresses only *Nitrosomonas* sp., the microorganism which is responsible for the first reaction in the nitrification bio-chemical reactions. In a sample in which no nitrification is expected to occur, adding the inhibiting agent should not change the results, thus explaining why, in these cases, BOD and cBOD would be expected to be equivalent.

In practice, however, a low bias has been reported for cBOD results relative to BOD results, when nitrification would not be expected. This may be due to a toxic affect that the inhibitor agent has on microbial species other than *Nitrosomonas*.

ADV 5.2.2 Discuss how to determine the proper sample volumes for the BOD test. | 62 |

4 Q's: 35.7% to 48.2% pass
November 2013: 1 Q, 69% pass

There are tables and charts that have been developed to assist analysts in making the best dilutions for any given sample. See Figure 5.2.02 for a chart developed by chemists at the State Laboratory of Hygiene, to help analyst choose proper volumes for BOD analysis. To use these charts, however, the analyst needs to have some idea of the sample BOD. All of these tables work off of a simple concept:

1. In typical conditions, at saturation in WI, initial DO should be ~8.5 mg/L.
2. The FINAL DO cannot be less than 1.0 mg/L.
3. Thus the working range of DOs for any dilution is about 7.5 mg/L.

To determine optimal dilution, divide the expected BOD of the sample by 7.5. For example, if you have a very clean effluent and BOD is typically 5 - 10 mg/L, then 5 divided by 7.5 = 0.7 and 10 divided by 7.5 = 1.3. Therefore your optimal dilution factor is between 0.7 and 1.3.

The middle of this range is a dilution factor of 1.0. Now divide the maximum volume of sample in a BOD bottle (300 mLs) by that dilution factor. 300 mLs divided by 1.0 = 300 mLs. Therefore, the **BEST** dilution for a sample with an expected BOD of 5-10 mg/L is 300 mLs.

• 75 - 300 mLs of sample (25 - 100% dilution)

ADV 5.2.2 Discuss how to determine the proper sample volumes for the BOD test.

4 Q's: 35.7% to 48.2% pass
November 2013: 1 Q, 69% pass

Typically you would then use one dilution using slightly more volume and one dilution of slightly less volume, to bracket the expected BOD range. Since this sample requires a full bottle, you can't use MORE sample volume. Therefore, a second dilution of about 250 mL is appropriate. 300 divided by 250 represents a dilution factor of 1.2.

Now consider an influent wastewater sample which typically ranges between 150 and 250 mg/L for BOD. $150 \text{ divided by } 7.5 = 20$ and $250 \text{ divided by } 7.5 = 33$ (round it to 30). The **best dilutions** for this sample would be using dilution factors of 20 to 30. A dilution factor of 20 means a sample volume of 15 mLs, and a dilution factor of 30 means a sample volume of 10 mLs. Therefore use sample volumes between 10 and 15 mLs.

In the absence of prior knowledge, use the following guidelines for dilutions:

- strong industrial wastes: < 3 mLs of sample (<1% dilution)
- raw and settled wastewater: 3 - 15 mLs of sample (1 - 5% dilution)
- biologically treated effluent: 15 - 75 mLs of sample (5 - 25% dilution)
- polluted river waters: 75 - 300 mLs of sample (25 - 100% dilution)

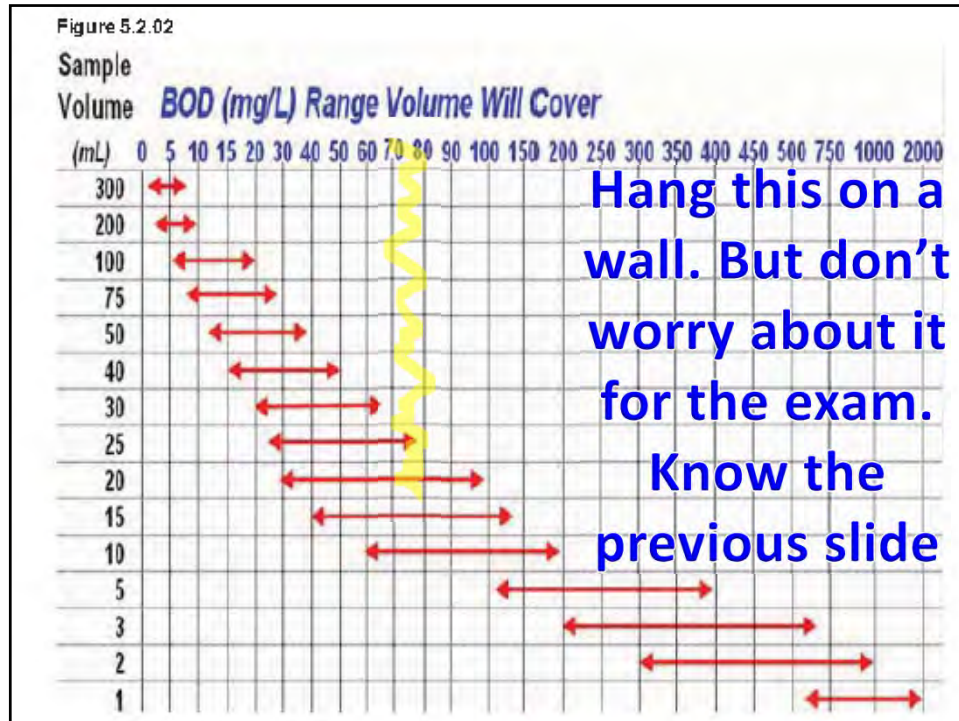
EXAMPLE

| 64 |

- Sample has a BOD expected to be about 75-80 ppm
- What is the best dilution to make?

$$\frac{75}{7.5} = 10 \quad \text{So a } 10 \times \text{ dilution}$$

$$\text{USE } \frac{300 \text{ mL}}{10} = 30 \text{ mL}$$



ADV 5.2.8

Historical: 70% pass
November 2013: 65% pass

(1) CALIBRATION

The **single greatest** cause for blank "failures" (DO depletion greater than 0.2 mg/L) stems from calibration problems.

Blank depletions due to calibration errors generally tend to be SMALL effects (depletion of 0.2 - 0.5 mg/L)

The effect can be either LOW or HIGH bias (blanks deplete > 0.2 mg/L or GAIN > 0.2 mg/L).

Since it violates laws of physics to gain oxygen, and if the final DO is greater than the initial DO, this is **nearly always** a sign of calibration errors.

The basic problem is that errors in calibration cause the initial DO reading to be biased high (or the final DO reading is biased low). The net result is that it appears to be a DO depletion.

(2) SUPERSATURATION

If the initial DO of the blank is above the saturation point, **all** of this DO will come out of the solution during incubation (sometimes seen as micro-bubbles just underneath the bottle stopper.) This appears to be depletion, but it is actually degassing.

Discuss factors that would result in excessive DO depletion in blanks.

ADV 5.2.8 **Discuss factors that would result in excessive DO depletion in blanks.**

Historical: 70% pass
November 2013: 65% pass

(3) CONTAMINATION (organic matter + micro-organisms)
Contamination, when it occurs, tends to be LARGE effect (i.e. DO depletions of > 0.5 mg/L).

Contamination problems will **ALWAYS** result in excessive depletions. Note that contamination from organic material or micro-organisms alone **will NOT cause** an exceedance in blanks.

There **must** be contamination from BOTH organic matter and microorganisms. Without the presence of microorganisms, there is nothing to break down the waste material and thus no oxygen will be utilized. Even if there is microbial contamination, without the presence of waste material, there is nothing for the microorganisms to break down and thus no - or minimal - oxygen will be utilized. Be aware that over-engineered water purification systems can result in insufficient water utilization creating a stagnancy within the water system. This can become a breeding ground for microbes, and thus the use of water from a purification system may be the cause of failures.

ADV 5.2.13 **Explain the potential reasons why GGA results could be unacceptably high.**

HIGH BIAS IN GGA

Historical: 66% pass November 2013: 58% pass

(1) Nitrification

Seed source selection is **critical** if the plant process includes recycling final effluent into primary clarifiers, you could be adding nitrifying organisms to the seed (if you use primary effluent as seed material). To determine if nitrification is occurring, try adding a nitrification inhibitor. Compare GGAs seeded with domestic wastewater vs. commercial (Polyseed, BOD seed). If nitrification is occurring, select another source (that does not receive final wastewater) or use a commercially obtained synthetic seed.

(2) Cold GGA

If you don't warm the GGA to room temperature (20 — 3°C) before use, results will be consistently high.

(3) Contamination – organic matter

The contamination is likely "dirty glassware", providing a food source. Your blanks may even meet depletion criteria because -despite availability of a food source (the "crud") - there is no source of bugs and therefore no oxygen can be used. GGAs will typically fail high due to the extra oxygen consumed by the bugs as they attack both the GGA and the "crud".

ADV 5.2.13 Explain the potential reasons why GGA results could be unacceptably high.

Historical: 66% pass
November 2013: 58% pass

HIGH BIAS IN GGA

Contamination can also result from insufficient rinsing of the DO probe after measuring highly concentrated samples.

(4) Contamination – bugs

The contamination source may be from “bugs” in the lab reagent water, possibly from a bad filter in a DI system. As long as your glassware is clean, blanks will meet depletion criteria. If there is no “food source” (e.g., “crud” on the glassware) to keep bugs going and expending oxygen, GGAs will generally fail high due to the extra oxygen consumed by the bugs as they attack the GGA.

Contamination, when it occurs, tends to be a LARGE effect (i.e. DO depletions of > 0.5 mg/L).

NOTE: Contamination from either “bugs” or BOD material alone will cause high bias in GGA but is not likely to cause an exceedance in blanks. There must be contamination from BOTH “bugs” AND waste material for contamination to result in blank exceedances. This explains a common statement from lab analysts that “my GGA is failing high, but my blanks are fine”.

ADV 5.2.14 Explain the potential reasons why GGA results could be unacceptably low.

Historical 42.9% pass

LOW BIAS IN GGA

(1) Not enough seed

The main cause of low GGAs is either not enough seed material (“bugs”) or a very weak seed material. Adjust the amount used until you consistently achieve GGA results in the acceptable range.

(2) Old or contaminated GGA

If GGA is too old, or has been broken down by contamination, low results will be observed. Discard expired or contaminated solutions.

(3) Seed material is too weak or variable

Try another GGA source. There are several different types/vendors that offer synthetic seeds. On occasion, there have been reports of poor quality lots

ADV 5.2.18 Discuss the problems associated with over-dechlorinating a sample.

Historical: 3Q...33.3% / 47.6% / 74.1% pass

November 2013: 60% pass

Sodium sulfite is used to dechlorinate for BOD, because sodium thiosulfate has a significant oxygen demand if any excess is present. Because it is important to add only as much sodium sulfite as you need for dechlorination and no more, the operator must first determine how much chlorine is present before dechlorination. The excess could deplete DO and interfere with the test.

The most common dechlorinating agent is sulfite. The following forms of the compound are commonly used and yield sulfite (SO₂) when dissolved in water. The greater the amount required to neutralize a standard concentration of chlorine, the greater the oxygen depletion affect.

ADV 5.2.18 Discuss the problems associated with over-dechlorinating a sample.

Historical: 3Q...33.3% / 47.6% / 74.1% pass

November 2013: 60% pass

Theoretical mg/L Required Dechlorination Chemical to Neutralize 1 mg/L Cl₂

Sodium thiosulfate (solution)	0.56 mg/L
Sulfur dioxide (gas)	0.90
Sodium meta bisulfite (solution)	1.34
Sodium bisulfite (solution)	1.46
Sodium sulfite (tablet)	1.78

Theoretical values may be used for initial approximations, to size feed equipment with the consideration that under good mixing conditions 10% excess dechlorinating chemical is required above theoretical values. Excess sulfur dioxide may consume oxygen at a maximum of 1.0 mg dissolved oxygen for every 4 mg SO₂.

NOTE: Standard Methods specifies that sodium sulfite be used for dechlorination of BOD samples.

ADV 5.3.1 **Discuss the importance of TSS in wastewater analyses.**

Historical: 4Q...mean 76% pass range 63-93%

November 2013: 64% pass

Total suspended solids (TSS) are those which are visible and in suspension in the water.

They are the solids which can be removed from wastewater by physical or mechanical means such as sedimentation, flocculation, or filtration. TSS will include the larger floating particles and consist of silt, grit, clay, fecal solids, paper, fibers, particles of food, garbage, and similar materials.

Suspended solids are approximately 70% organic and 30% inorganic. TSS determinations may be used to assess wastewater strength, process efficiency, and loadings.

By reducing the TSS in your effluent discharge, you are going to get better disinfection, which will reduce your fecal coliform and/or E. coli counts, allowing you to maintain compliance.

The organic fraction of suspended solids is comprised generally of animal or vegetable matter, but may also include synthetic organic compounds. Organic compounds are substances which contain carbon, hydrogen, and oxygen, some of which may be combined with nitrogen, sulfur, and phosphorus. The principle organic compounds found in wastewater are proteins, carbohydrates, and fats, together with their products of decomposition. In general, they are combustible.

ADV 5.3.1 **Discuss the importance of TSS in wastewater analyses.**

Historical: 4Q...mean 76% pass range 63-93%

November 2013: 64% pass

The inorganic fraction of suspended solids is inert and typically not subject to decay. Exceptions to this characteristic are certain mineral salts, such as sulfates, which, under certain conditions, can be broken down. Inorganic solids are frequently called mineral substances and include sand, gravel, and silt, as well as the mineral salts in the water supply which produce the hardness and mineral content of the water. In general, they are not combustible.

High TSS can block light from reaching aquatic vegetation. Photosynthesis is inhibited as the amount of light passing through the water is cut down. Without photosynthesis, aquatic plants produce less oxygen, which is a significant source of DO. If light is completely blocked from bottom dwelling plants, the plants will stop producing oxygen and will die. As the plants are decomposed, bacteria will consume what oxygen (DO) is present in the water. Low DO is a major contributor to fish kills.

High concentrations of TSS can also result in an increase in surface water temperature, because the suspended particles absorb heat from sunlight. Higher temperatures consequently result in a reduced ability of the water to hold DO.

Bottom line on TSS and wastewater | 75 |

- High TSS interferes with disinfection efficiency
- High TSS reduces light for aquatic plants
 - Without light, plants die
 - Plants provide oxygen, so less plants = less DO
 - Dying plants suck up available DO (demand)
 - Low oxygen results in fish kills
- High TSS raises surface water temp. (particles absorb sunlight)...which also lowers DO



TSS

Organic
70%

Inorganic
30%

ADV 5.4.3

Historical: 1Q...78% pass
November 2013: 11% pass

| 76 |

Explain why temperature is the only variable that affects electrode response and why each ten-fold change in concentration should result in a slope (net difference in millivolt response) of -54 to -60 millivolts.

Response of any electrode is governed by physics. The slope of electrode response between concentrations of standards that are exactly ten-fold different from one another is governed by the Nernst factor.

The Nernst factor ($2.3 RT/nF$), includes the Gas Law constant ($R = 8.31451$ Joules-Kelvin/mole), Faraday's constant ($F = 96.487$ coulombs), the temperature in $^{\circ}\text{K}$ (T) and the charge of the ion (n). For ammonia, $n = 1$ because the charge of the ion is "+1", or one hydrogen equivalent. Since "R" and "F" are constants, and "n" becomes a constant for any specific parameter, the factor and therefore electrode behavior is dependent only on temperature.

Nuts to Nernst!

| 77 |

$$\text{Nernst factor} = 2.3 \times \frac{RT}{nF}$$

$$= \frac{2.3 \times [\text{constant}] \times \text{temperature}}{[1] \times [\text{constant}]}$$

$$= \frac{[\text{constant}] \times [\text{constant}] \times \text{temperature}}{[\text{constant}] \times [\text{constant}]}$$

so... **temperature** is the only variable!

...and that's why temperature is critical for electrode determinations

ADV 5.4.3

Historical: 1Q...78% pass
November 2013: 11% pass

| 78 |

Explain why temperature is the only variable that affects electrode response and why each ten-fold change in concentration should result in a slope (net difference in millivolt response) of -54 to -60 millivolts.

Substituting 298 for "T" (25 °C expressed as Kelvin), the Nernst factor calculates to be 59.16. This represents the theoretical electrode slope (millivolts per ten-fold increase in concentration) at 25 degrees C, the base temperature for electrode analysis.

A Nernst factor (slope) of 54 millivolts is associated with a temperature of 0°C, and a slope of 60 mV translates to 30 degrees C. Therefore, one would only expect a slope of 60 or more if the temperature of the calibration solution was 30°C. At 20°C, the theoretical slope is 58.15 mV.

Many ion meters display the slope as a percentage of the theoretical value. For example, a 98.5% slope is equivalent to a slope of 58.27 mV (at 20 degrees C).

ADV 5.4.7 **Discuss the importance of pH and temperature in determining ammonia toxicity.** | 79

47.6% pass

November 2013: 40% pass

Other choices: 4%, 7%, 49%

Ammonia-nitrogen is a major end product of fish metabolism, it is toxic to aquatic life and toxicity is affected by system pH. Ammonia-nitrogen (NH₃-N) has a **more toxic** form at high pH [un-ionized ammonia or NH₃] and a **less toxic** form at low pH [ionized ammonia or NH₄⁺]. In addition, ammonia toxicity **increases** as temperature rises. The un-ionized form is considered more toxic since it can diffuse passively across the gill membrane.

At or below a pH of 8.5, less than 20% of ammonia exists in the highly toxic un-ionized (gaseous) form. Above a pH of 8.5, the percentage of ammonia that exists in the un-ionized form increases rapidly. The effect of temperature increases is **far less** significant than increases of pH. Consider a lagoon or pond system containing 10 mg/L ammonia (NH₃-N). As can be seen from the table in Figure 5.4.07, the temperature change during the day from 20°C to 30°C accounts for less than 20% of the increase in toxicity as compared to a rise in pH from 7.0 to 8.0.

ADV 5.4.7 **Discuss the importance of pH and temperature in determining ammonia toxicity.** | 80

47.6% pass

Essentially, the **higher the pH and temperature**, the greater the proportion of total ammonia in the system will be in the form of the **highly toxic** un-ionized ammonia (NH₃). A useful rule of thumb is that

at a pH of 8 ammonia is 10 times more toxic than at a pH of 7, and at 20°C it is two (2) times more toxic than at 10°C.

To calculate the amount of un-ionized ammonia present, the Total Ammonia Nitrogen (TAN) must be multiplied by the appropriate factor selected from the table in Figure 5.4.07 using the pH and temperature from your water sample.

To calculate the amount of un-ionized ammonia present, the Total Ammonia Nitrogen (TAN) must be multiplied by the appropriate factor selected from the table in Figure 5.4.07 using the pH and temperature from your water sample.

Figure 5.4.07

pH	Temperature													
	42.0 (°F)	46.4	50.0	53.6	57.2	60.8	64.4	68.0	71.6	75.2	78.8	82.4	86.0	89.6
	6 (°C)	8	10	12	14	16	18	20	22	24	26	28	30	32
7.0	.0013	.0016	.0018	.0022	.0025	.0029	.0034	.0039	.0046	.0052	.0060	.0069	.0080	.0093
7.2	.0021	.0025	.0029	.0034	.0040	.0046	.0054	.0062	.0072	.0083	.0096	.0110	.0126	.0150
7.4	.0034	.0040	.0046	.0054	.0063	.0073	.0085	.0098	.0114	.0131	.0150	.0173	.0198	.0236
7.6	.0053	.0063	.0073	.0086	.0100	.0116	.0134	.0155	.0179	.0206	.0238	.0271	.0310	.0369
7.8	.0084	.0099	.0116	.0135	.0157	.0182	.0211	.0244	.0281	.0322	.0370	.0423	.0482	.0572
8.0	.0133	.0156	.0182	.0212	.0247	.0286	.0330	.0381	.0438	.0502	.0574	.0654	.0743	.0877
8.2	.0210	.0245	.0286	.0332	.0385	.0445	.0514	.0590	.0676	.0772	.0880	.0998	.1129	.1322
8.4	.0328	.0383	.0445	.0517	.0597	.0688	.0790	.0904	.1031	.1171	.1326	.1495	.1678	.1948
8.6	.0510	.0593	.0688	.0795	.0914	.1048	.1197	.1361	.1541	.1737	.1950	.2178	.2422	.2768
8.8	.0785	.0909	.1048	.1204	.1376	.1566	.1773	.1998	.2241	.2500	.2774	.3062	.3362	.3776
9.0	.1190	.1368	.1565	.1782	.2018	.2273	.2546	.2836	.3140	.3456	.3783	.4116	.4453	.4902
9.2	.1763	.2008	.2273	.2558	.2861	.3180	.3512	.3855	.4204	.4557	.4909	.5258	.5599	.6038
9.4	.2533	.2847	.3180	.3526	.3884	.4249	.4618	.4985	.5348	.5702	.6045	.6373	.6685	.7072
9.6	.3496	.3868	.4249	.4633	.5016	.5394	.5762	.6117	.6456	.6777	.7078	.7358	.7617	.7929
9.8	.4600	.5000	.5394	.5778	.6147	.6499	.6831	.7140	.7428	.7692	.7933	.8153	.8351	.8585
10.0	.5745	.6131	.6498	.6844	.7166	.7463	.7735	.7983	.8207	.8408	.8588	.8749	.8892	.9058
10.2	.6815	.7152	.7463	.7746	.8003	.8234	.8441	.8625	.8788	.8933	.9060	.9173	.9271	.9389

ADV 5.5.1

27.1% pass

November 2013: 33% pass

0%, 16%, 51% other answers

Discuss the calibration blank required for phosphorus testing.

| 82 |

Translation:

Blanks tell us if there is bias or contamination.

Different types of blanks tell us the SOURCE of the contamination/bias

Calibration blank

A calibration standard containing no added analyte, but all the other reagents that are in other calibration standards, such as color reagent, and digestion reagent (if standards are digested). In many cases, the calibration blank may be virtually identical to a method blank.

<p>ADV 5.5.1 Historical: 27.1% pass November 2013: 33% pass 0%, 16%, 51% other answers</p>	<p>Discuss the calibration blank required for phosphorus testing.</p>	<p> 83 </p>
<p>Generally, Calibration blank</p> <ul style="list-style-type: none"> • Consist of the solvent used plus all of the same reagents used to prepare the calibration standards. <ul style="list-style-type: none"> • If the standards are digested - the same as the samples are, then the calibration blank consists of reagent water plus all other reagents including the combined color reagent. • If the standards are not digested, therefore handled differently than the samples, then the calibration blank consists of reagent water plus combined color reagent, but not the digestion reagents. • Indicate the absorbance response of a zero concentration standard (0.0 mg/L). • This blank is not used to zero the instrument. <p>The absorbance of this blank is measured and used in the calibration curve as (x = concentration = zero; y = response = measured absorbance). It is possible for the measured absorbance of this blank to be zero, but it is not expected to be zero.</p>		

<p>ADV 5.5.3 Historical: None November 2013: 51% pass 0%, 9%, 40% other answers</p>	<p>Discuss additional blanks which may be useful in troubleshooting phosphorus testing.</p>
<p>Additional blanks that can be useful in troubleshooting :</p> <p>Instrument blank</p> <p>An instrument blank is used to establish a baseline for how much light passes through the sample compartment without a sample being present. In addition to absorbance stemming from the solvent itself, any reduction in light transmission that is caused by a film or scratches on the cuvette surface are also taken into consideration. In wastewater lab testing, the solvent is lab reagent water.</p> <p>Therefore, the instrument blank:</p> <ul style="list-style-type: none"> • Consists of only the solvent used - which is reagent water for total phosphorus. • Allows instrument to be zeroed on background attributed to just the solvent used and therefore what the "Zero" should be when using the solvent. 	

ADV 5.5.3 Discuss additional blanks which may be useful in troubleshooting phosphorus testing.

Historical: None

November 2013: 51% pass

0%, 9%, 40% other answers

Reagent blank

This kind of blank is **not routinely measured**; it is used more in unique situations or for troubleshooting purposes. One of the more difficult blanks to prepare, the reagent blank, is **designed to quantify the amount of background response (or contamination) that results from absorbance at the characteristic wavelength by the reagents themselves.** The difficulty is in adding only those reagents that are not directly involved in developing the characteristic color associated with the analyte in a colorimetric procedure.

For example, the phosphorus color reagent is composed of 4 different reagents, several of which can have "color" and therefore may absorb light at the characteristic wavelength. In order to absolutely quantify the contribution of each of the 4, separate blanks would have to be prepared by making 4 separate color blank solutions, each with one of the 4 reagents. Lab reagent water would be substituted at the same proportions for the other 3 reagents.

ADV 5.5.3 Discuss additional blanks which may be useful in troubleshooting phosphorus testing.

Historical: None

November 2013: 51% pass

0%, 9%, 40% other answers

Reagent blank

For total phosphorus analysis, a commonly used reagent blank for the color reagent solution can be prepared by **substituting lab reagent water for the potassium antimonyl tartrate and the ascorbic acid.**

Refer to the term **Sample color blank** for a close relative of the reagent blank. **With a sample color blank, we are trying to quantify the background response associated with the sample itself.** Typically, in total phosphorus analysis, the digestion process destroys any natural sample "color". If a lab were to test for orthophosphate however, a sample color blank - for each sample - is **frequently required**.

ADV 5.5.6 Explain what might be the cause of slow color development in samples or standards. 71
 Historical: 59% pass
 November 2013: 65% pass

When potassium antimonyl tartrate is absent, old, or weak, the color reaction proceeds slowly.

**SLOW color development?
Think P-A-T**

ADV 5.6.1 Explain how the chlorine electrode works. 88

Historical: 47% pass
 November 2013: no data

- The electrode is based on iodometric measurement of chlorine.
- Iodide (I-) and hydrochloric acid (H+) are added to a sample.
- Iodide reacts with chlorine to form iodine.
- The iodine concentration is equal to the chlorine concentration.

1. Add **iodide** (reagent)
2. **Iodide** reacts with **chlorine** to produce **iodine**
3. **Iodine** level = **chlorine** level

- Iodine concentration = total residual chlorine concentration.

ADV 5.6.2

Historical: 48% pass
November 2013: 56%

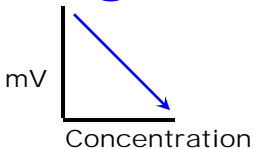
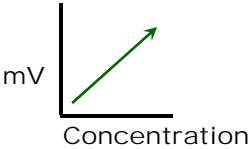
Discuss the major differences between the ion selective electrode analyses of ammonia and chlorine residual.

The total residual chlorine ISE analysis differs from the ISE analysis of ammonia in that:

- The ammonia electrode measures the potential caused by ammonia GAS crossing a gas permeable membrane whereas chlorine electrodes measure potential caused by IONS crossing the membrane.
- The electrode slope for chlorine is positive (millivolts increase with increasing concentration). Ammonia has a negative slope (millivolts increase with decreasing concentration).
- The slope change in mV per decade of concentration is 29.0 for chlorine electrodes vs. 58.3 for ammonia at 20 °C.

Chlorine v. Ammonia electrode

| 90 |

	<u>Ammonia</u>	<u>Chlorine</u>
Measures	Gas	Ions
Slope	Negative	Positive
		
mV/10x	~ 58	~ 29

ADV 5.7.10 Explain why the fill-hole on a reference electrode should be open when testing for pH, and closed when the probe is not in use.

Historical: 61% pass
November 2013: 58% pass

The reference solution should seep out of the reference junction during measurements. If the fill-hole is closed while using a probe, the reference solution **will not** seep out as needed, because vacuum will prevent it from doing so.

The fill-hole should be closed when a pH probe is not in use to prevent the probe solution from seeping out of the reference junction and crystallizing on the probe and storage container.

OPEN when in use

Why? To allow seepage of reference solution

ADV 5.7.11 Explain how total Kjeldahl Nitrogen (TKN) and Nitrate Plus Nitrite Nitrogen are measured and how they are used in process control:

Historical: 31% pass (24-37%)
November 2013: 38%

Reagent blank

TOTAL KJELDAHL NITROGEN (TKN)

TKN is the sum of the organically held nitrogen plus the ammonia nitrogen present in a sample. It does not include the oxidized nitrate plus nitrite nitrogen. It is measured by digesting the sample to break down all the organically held nitrogen and converting it into ammonia. The ammonia generated is then distilled from the sample into an acid solution.

The ammonia concentration can be determined by several

Total Nitrogen (TN) is the sum of all nitrogen forms = $TKN + NO_2 + NO_3$

TKN = Total Kjeldahl Nitrogen and represents the sum of NH_3 + Organic Nitrogen

ADV 5.7.11

Historical: 31% pass (24-37%)
November 2013: 38%

Explain how total Kjeldahl Nitrogen (TKN) and Nitrate Plus Nitrite Nitrogen are measured and how they are used in process control:

Ammonia Nitrogen

Organic Nitrogen comes from amino acids & proteins (e.g. urea, uric acid). Ammonia (NH₃) values represent approximately 60% of the TKN of a waste, and the organic nitrogen is generally removed in the settled sludge. Also, TKN generally equals 15 - 20 % of the BOD of raw sewage.

Nitrate + Nitrite

___NO₂ = Nitrite NO₃ = Nitrate

Nitrate and nitrite nitrogen are most often tested by the cadmium reduction method. The electrode is not acceptable for wastewater effluent permit required testing. In addition, the electrode is specific only for nitrate, not nitrite. Results should be reported in mg/L as nitrogen (N).

The levels of nitrate and nitrite become important due to their involvement in de-nitrification and disinfection.

Nitrite levels should be very low throughout the entire treatment process. High levels of nitrite (NO₂) in the system indicate there may be a problem with the nitrification cycle.

ADV 5.7.11

Historical: 31% pass (24-37%)
November 2013: 38%

Explain how total Kjeldahl Nitrogen (TKN) and Nitrate Plus Nitrite Nitrogen are measured and how they are used in process control:

Nitrosomonas bacteria are harder to kill than Nitrobacter bacteria. If the Nitrobacter bacteria are killed off, the Nitrosomonas bacteria will continue working on the ammonia (NH₃) and you will have a jammed cycle with high levels of nitrite (NO₂). An effluent with high nitrite (NO₂) concentrations will be difficult to disinfect because of the tremendous chlorine demand it poses.

Denitrification is an anaerobic process (meaning without oxygen) in which the oxygen bound in nitrate (NO₃⁻) becomes the primary oxygen source for microorganisms. When bacteria break apart nitrate (NO₃⁻) to gain the oxygen (O₂), the nitrate is reduced to nitrous oxide (N₂O), and nitrogen gas (N₂). Since nitrogen gas has low water solubility, it tends to escape as gas bubbles. These gas bubbles can become bound in the settled sludge in clarifiers and cause the sludge to rise to the surface.

An advantage of denitrification is the production of alkalinity (which will help buffer against pH changes) and an increase of pH. Approximately 3.0 to 3.6 mg of alkalinity (as CaCO₃) is produced per milligram of nitrate reduced to nitrogen gas. Optimum pH values for denitrification are between 7.0 to 8.5.

ADV 6.1.3

Define Linear Regression. | 95

Historical: 35% pass (35%,36%)
November 2013: 2Q; 55% each

Linear regression is a statistical tool for determining the relationship that exists between a dependent variable (instrument response, such as absorbance) and an independent variable (concentration), for a given set of data (calibration standards). As with other statistical tests, the more data provided, the more accurate the relationship will be defined. For instance, a linear regression based on seven (7) calibration standards spanning a concentration range of 0.1 to 1 ppm will be far more accurate than one based on only three (3) standards over the same concentration range.

As the name suggests, linear regression results in an equation for the straight line which describes the relationship. The important parameters that result from a regression are the slope and intercept of the resultant line. The correlation coefficient can also be calculated to provide an estimate of the strength or validity of the relationship between concentration and response.

ADV 6.1.3

Define Linear Regression. | 96

Historical: 35% pass (35%,36%)
November 2013: 2Q; 55% each

The math behind the commonly used linear regression function is to adjust the values of slope and intercept to find the line that best predicts response (Y) from concentration (X). More precisely, the goal of regression is to minimize the sum of the SQUARES of the VERTICAL distances of the actual data points from the regression line; this is why it is commonly known as the "least squares" technique.

Understanding the rationale for minimizing the "sum of squares" is critical to understanding how linear regression works. If random data variability follows a normal distribution, it is far more likely to have 2 data points each with moderate deviations (say 5 units each) than to have one data point with a small deviation (1 unit) and one with a large deviation (9 units) from the regression line. A procedure that minimizes the sum of the absolute value of the distances would have no preference over a line that was 5 units away from two points and one that was 1 unit away from one point and 9 units from another. The sum of the distances (more precisely, the sum of the absolute value of the distances) is 10 units in each case.

ADV 6.1.3

Define Linear Regression. | 97 |

Historical: 35% pass (35%,36%)
November 2013: 2Q; 55% each

However, a procedure that minimizes the sum of the squares of the distances prefers to be 5 units away from EACH of two points (sum-of-squares = $5^2 + 5^2 = 25 + 25 = 50$) rather than 1 unit away from one point and 9 units away from another (sum-of-squares $1^2 + 9^2 = 1 + 81 = 82$). Assuming that random variability follows a normal distribution, the line determined by minimizing the sum-of-squares is most likely to be correct.

ADV 6.2.7

Discuss how to identify if results exceed the calibration range of an instrument and action to be taken. | 98 |

Historical: 51% pass (48%,54%)
November 2013: 2Q; 62%, 56%

Samples having RESPONSES (not concentration) greater than that of the most concentrated standard of an initial calibration, established using at least 3 different standard concentrations, must be diluted and reanalyzed.

When samples cannot be diluted and reanalyzed (i.e., beyond holding time, or insufficient sample remains), sample results shall be reported with appropriate qualifiers or narrative warnings.

It is critical to note that a calibration is established based upon absolute response as a function of concentration. Subsequently, the determination of whether or not a sample exceeds the calibration range is based on its absolute response rather than concentration.

ADV 6.2.7

Discuss how to identify if results exceed the calibration range of an instrument and action to be taken. | 99

Historical: 51% pass (48%,54%)
November 2013: 2Q; 62%, 56%

What is the proper way of determining whether a sample requires dilution?

Given that:

SR = Sample Response (absorbance, etc.)

SC = Sample Concentration

UCSR= Upper Calibration Standard Response (absorbance)

UCSC= Upper Calibration Standard Concentration

The following sample would require dilution and reanalysis

SR= 0.915 | SC= 0.98 mg/L | UCSR=0.900 | UCSC= 1.00 mg/L

Because...even though the concentration is within the calibration range, the RESPONSE is not (0.915 > 0.900)

ADV 6.2.7

Discuss how to identify if results exceed the calibration range of an instrument and action to be taken. | 100

Historical: 51% pass (48%,54%)
November 2013: 2Q; 62%, 56%

Even though the concentration determined by linear regression is less than that of the highest calibration standard, the sample **must** be diluted because we are really calibrating response. Response is the KNOWN (independent variable). Sample concentration is the UNKNOWN.

The following sample would **NOT require** dilution and reanalysis:

SR= 0.875 | SC= 1.10 mg/L | UCSR=0.900 | UCSC= 1.00 mg/L

...because even though the sample concentration exceeds the calibration range (the concentration of the uppermost calibration standard), the sample response is well below that of the uppermost calibration standard.

Focus on response not concentration

ADV 6.2.10 **Discuss the types of QC samples that are used to assess accuracy and those used to assess precision.** | 101

Historical:
14.8% pass

QC samples used to assess accuracy:

Accuracy is a measure of the proximity of an unknown to the "true value" or the expected result.

PT (an external **unknown** standard; goal: determine true value)

QCS (an external **known** standard; goal: determine true value)

ICV (an internal **known** standard; goal: determine true value, validate calibration)

LCS (an internal **known** standard; goal: determine true value)

Matrix Spikes (an internal **known** addition; goal: recover true value)

Split samples [sent to a contract lab] (goal: determine which lab is correct) [range or RPD] (goal: reproducibility)

ADV 6.2.10 **Discuss the types of QC samples that are used to assess accuracy and those used to assess precision.** | 102

Historical:
14.8% pass

QC samples used to assess precision:

Precision is a measure of the reproducibility of an analysis or the ability to obtain the same result on consecutive measurements of the same sample. In order to determine precision, then, multiple sample analyses are required.

Replicates [duplicates] (goal: reproducibility)

Matrix spike duplicates [range or RPD] (goal: reproducibility)

ac·cu·ra·cy (ăk'yəf-ə-sē)

n.

1. Conformity to fact.
2. Precision; exactness.
3. The ability of a measurement to match the actual value of the quantity being measured.

pre·ci·sion (prī-sīzh'ən)

n.

1. The state or quality of being precise; exactness.
2.
 - a. The ability of a measurement to be consistently reproduced.
 - b. The number of significant digits to which a value has been reliably measured.



Accuracy v. Precision

| 103 |

- Accuracy: Can I get the right answer
- Precision: Can I get that answer again

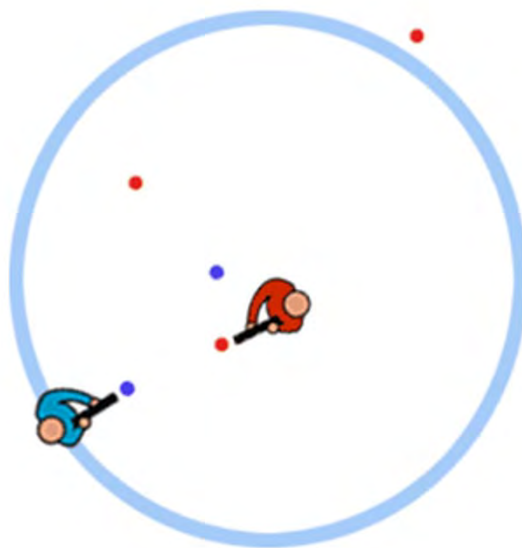


**Precision
in practice**

- Measuring precision requires multiple attempts....more than one check. That forces it to relate to duplicates or replicates

Is either accurate? Precise?

| 104 |



Accuracy & Precision recap

| 105 |

- We've tried the target and hunting analogy.
- Let's try something else.

Remember: True value for GGA is 198

Accuracy? Precision?

GGA = 200



GGA =

160,231,172,225,158



GGA =

224,226,221,228,222



GGA =

196,202,199,203,200

