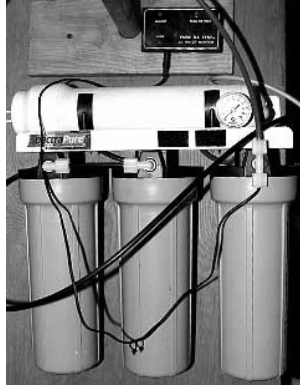


Lab Reagent Water Concerns



*...in search of
ultrapure water*

Rick Mealy
Wisconsin Dept. of Natural Resources
George Bowman
Wisconsin State Lab of Hygiene

Disclaimer

*Any reference to product or company
names does not constitute endorsement by
the Wisconsin State Laboratory of Hygiene,
the University of Wisconsin, or
the Department of Natural Resources.*



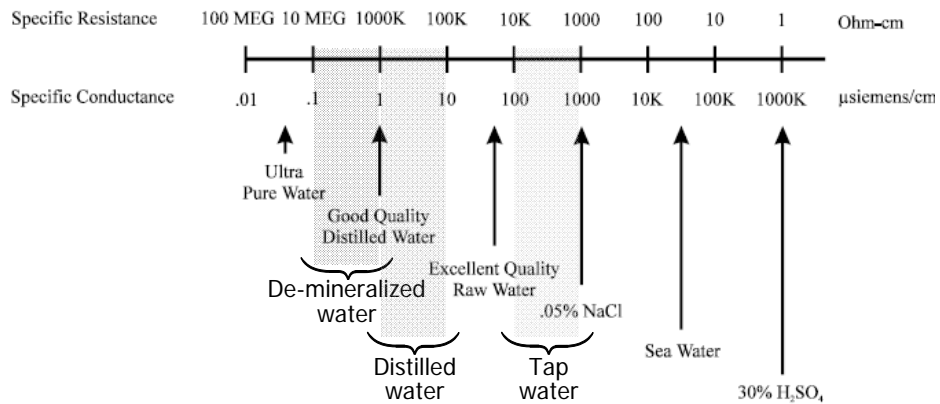
Objectives

- What is “ultrapure” water?
- Review ASTM standard D-1193
- Review currently understood reagent water monitoring requirements
- Focus heavily on Conductivity...which historically has been emphasized
- Identify critical reagent water monitoring tools and benchmarks

What is “ultra pure water”

- *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 salt 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 megohm-cm at 25 degrees Celsius.
- Electrolytic conductivity (EC) is the inverse of resistivity. Therefore $1/18.2 = 0.055$, the theoretical maximum conductivity (uS/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)
- An alkalinity of 1ppm as CaCO₃ will raise EC to 0.7 uS/cm
- 100 ppb each of sodium and chloride raises EC to 0.45 uS/cm
- Just 25 ppb of NaCl dissolved in purified water will raise the EC to the maximum allowable level for ASTM Type I water

Generally Recognized Conductivity Ranges of Various Solutions

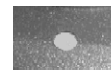


Remember...this is SOLELY based on conductivity

State of the Industry?

“As long as the little light on top is green, the water meets ASTM Type I standards”

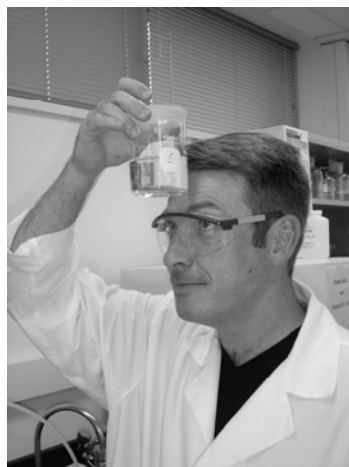
- frequently heard by auditors



Unacceptable techniques for determining reagent water quality



"...smells fine to me"



"...I'm sensing that this water quality meets our needs"

ASTM Standard D1193

Limit	Type I	Type II	Type III	Type IV
Electrical conductivity , max, uS/cm at 25°C	0.056 [18.2]	1.0 [10]	0.25 [4]	5.0 [0.2]
pH at 298 K (25°C)	A	A	A	5.0 to 8.0
Total organic carbon (TOC), max, ug/L	50	50	200	n/a
Sodium , max, ug/L	1	5	10	50
Chlorides max, ug/L	1	5	10	50
Total silica , max, ug/L	3	3	500	n/a

^A The measurement of pH in Type I, II, and III reagent waters has been eliminated from this specification because these grades of water do not contain constituents in sufficient quantity to significantly alter the pH.

When bacterial levels need to be controlled, reagent grade types should be further classified as follows:

	<u>Type A</u>	<u>Type B</u>	<u>Type C</u>
Max. heterotrophic bacteria count	10 per 1000 ml	10 per 100 ml	100 per 10 ml
Endotoxin , EU/mL ^B	< 0.03	0.25	n/a

^B EU = Endotoxin Units

The process defines the Type

- 1.2 The method of preparation of the various grades of reagent water determines the limits of impurities
- 1.2.1 Type I grade of reagent water shall be prepared by distillation or other equal process
 - followed by polishing with a mixed bed of ion exchange materials
 - and a 0.2-um membrane filter.
- *[Note that there are many different types of distillation. Also, what would be considered "equal"]*

The process defines the Type

- 1.2.2 Type II grade of reagent water shall be prepared by distillation using a still designed to produce a distillate having a conductivity of less than 1.0 uS/cm at 298 K (25°C).
- Ion exchange, distillation, or reverse osmosis and organic adsorption may be required prior to distillation if the purity cannot be attained by single distillation
 - Note - Because distillation is a process commonly relied upon the levels specified for Type II reagent water were selected to represent the minimum quality of water that a distillation process should produce.

The process defines the Type

- 1.2.3 Type III grade of reagent water shall be prepared by distillation, ion exchange, continuous electrodeionization reverse osmosis, or a combination thereof, followed by polishing with a 0.45-um membrane filter.
- 1.2.4 Type IV grade of reagent water may be prepared by distillation, ion exchange, continuous electrodeionization reverse osmosis, electro dialysis, or a combination thereof.

ASTM D1193 – What's missing?

- Any mention of "the table"...in fact it is not named/numbered and is never directly referenced.
- A lot of detail
- For those that read it, it generates more questions than answers

To further understand the problem this standard presents, we need to look back to "the table" and review the rationale for each measure identified

Why Conductivity?

Type I/II:
0.056/1 uS/cm

Pros

- Conductivity means ions are present
- Ions mean the water is not pure
- Useful as an indication that ion exchange resin is overloaded or reverse osmosis membrane has been breached.

Cons

- 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
- Virtually impossible to measure conductivity accurately to Type I, II levels without a closed system and VERY sensitive conductivity equipment
- CO₂ in atmosphere

Reagent Water Conductivity and CO₂



- Henry's Law: Solubility of a gas and equilibrium vapor pressure is directly proportional to the pressure above the solution.

$$P_{\text{CO}_2} = k_{\text{CO}_2} \times C_{\text{CO}_2}$$

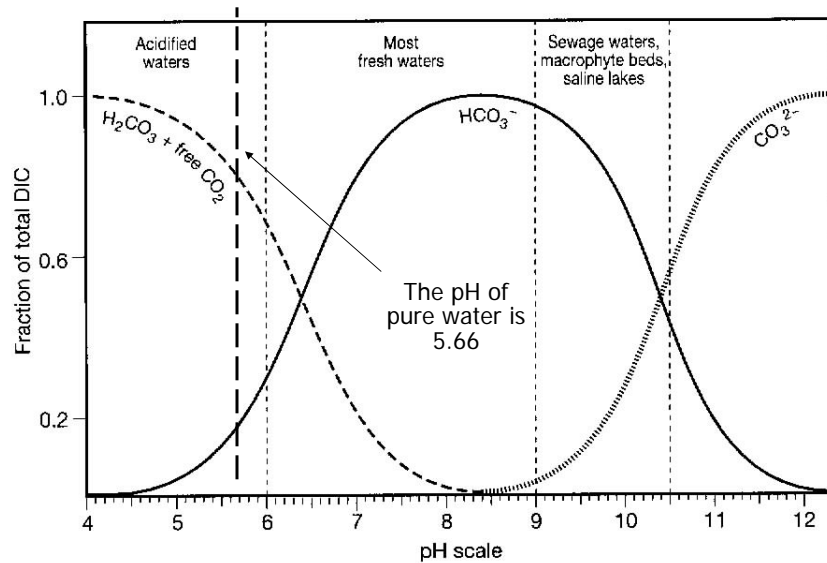
P = currently about 376 ppm
or 0.000376 atm

k = 32 L•atm / mol at 25 °C

P = partial pressure of gas directly above solution
k = Henry's law constant, in L•atm / mol, at 25 °C
C = concentration of gas in solution

- Solving for Concentration of CO₂, the concentration of CO₂ in pure water in equilibrium with air = 1.1881E-05 moles.
- At 44000mg per mole, the concentration of CO₂ in pure water will be 0.53 mg/L

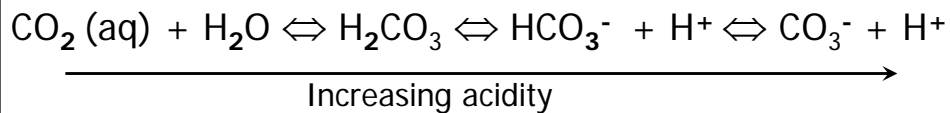
...but it doesn't remain as CO₂...



Which form of carbon will dominate? ...depends on the pH

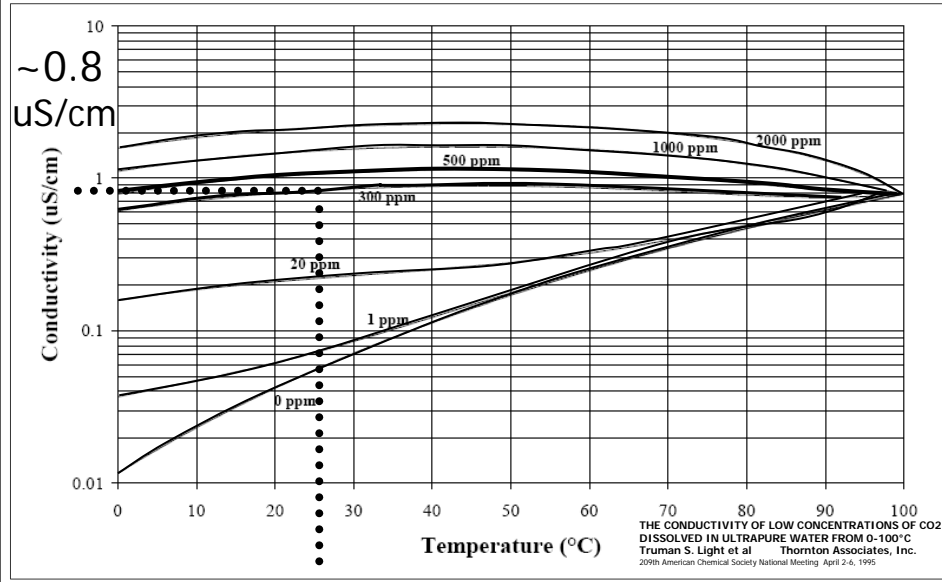
Reagent Water Conductivity and CO₂

- CO₂ reacts with water to form carbonic acid which ionizes to bicarbonate ion which further ionizes to carbonate ion
- This reaction is based on pH.



- 1 mole of CO₂ reacts with water to form 1 mole of bicarbonate ion (HCO₃⁻)
- Therefore 0.52 mg/L of CO₂ results in formation of 0.72 mg/L of (HCO₃⁻)

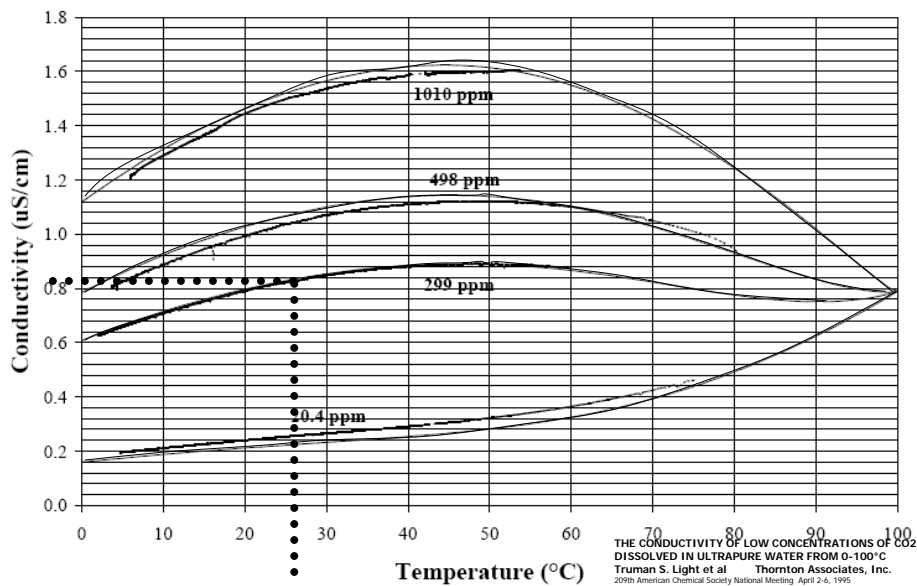
Theoretical conductivity in pure water with addition of CO₂



Predicted vs. Actual Conductivity

CO₂ dissolved in pure water

— = theoretical — = actual



..and If you're STILL not convinced...



Low-level conductivity measurement concerns



Need flow-thru probe
Need cell constant = 0.1

Cell constant	Optimum Conductivity Range (μS/cm)
0.1	0.5 to 400
1.0	10 to 2000
10.0	1000 to 200,000



- Certified low-level standards are expensive
- Certified 25.0 uS/cm = \$360
- ± 1.25 uS/cm ...is this of value when trying to measure below 1 uS/cm

Cell Constant & Conductivity Range

Guide to Cell Constant Usable Ranges

<i>CELL CONSTANT</i> <i>cm⁻²</i>	<i>DESIGN RANGE</i> <i>μS/cm</i>	<i>LOWEST RANGE</i> <i>μS/cm</i>	<i>HIGH RANGE</i> <i>μS/cm</i>	<i>OVER-RANGE *</i> <i>μS/cm</i>
0.01	0 to 10	0 to 1	0 to 100	0 to 1 000*
0.02	0 to 20	0 to 2	0 to 200	0 to 2 000*
0.1	0 to 100	0 to 10	0 to 1 000	0 to 10 000*
0.2	0 to 200	0 to 20	0 to 2 000	0 to 20 000*
0.5	0 to 500	0 to 50	0 to 5 000	0 to 50 000*
1.0	0 to 1 000	0 to 100	0 to 10 000	0 to 100 000*
2.0	0 to 2 000	0 to 200	0 to 20 000	0 to 200 000*
5.0	0 to 5 000	0 to 500	0 to 50 000	0 to 500 000*
10.0	0 to 10 000	0 to 1 000	0 to 100 000	0 to 1 000 000*
20.0	0 to 20 000	0 to 2 000	0 to 200 000	0 to 1 000 000*
50.0	0 to 50 000	0 to 5 000	0 to 500 000	0 to 1 000 000*

From: IC Controls, <http://www.iccontrols.com/files/4-1.pdf>

So...now are you ready to tell your auditor that the ASTM “requirements” for conductivity of reagent water are illogical?

Why Sodium or Chloride?

Type I/II:
1/5 ppb

Origin: 1 ppb of NaCl dissolved in pure water will increase the conductivity from 0.055 to 0.057 uS/cm at 25 °C

Pros

- Sodium will be first ion seen if ion exchange resin is overloaded
- Useful as an indication that ion exchange resin is overloaded or reverse osmosis membrane has been breached.

Cons

- Redundant, since already measuring conductivity
- Technologies capable of measuring these species down to 1 ppb are either too expensive or non-existent
- Typical detection limits are 10-20 ppb for each (ASTM procedures 40 and 24 ppb)
- The conductivity of water with just 10 ppb of each is 43 uS/cm

Why Silica?

Type I/II: 3 ppb

Origin: No one seems to know why this analyte was ever required.

Pros

- Silica is among 1st constituents seen when mixed bed ion-exchange columns fail.
- Good indicator if dealing with diatoms.

Cons

- Appears to be no evidence that traces of silica cause non-specific interference for the great majority of reagent water applications.
- ASTM D 4517 hasn't been tested below 35 ppb
- The non-ASTM reference has an SD of 6% at 25 and the limit of detection is 2.5.
- Measuring resistivity and using serial ion-exchange cartridges better deals with breakthrough

Why TOC?

Type I/II: 50 ppb

Origin: Replaced the former KMnO_4 60 min. color retention time in 1991 update to D1193.

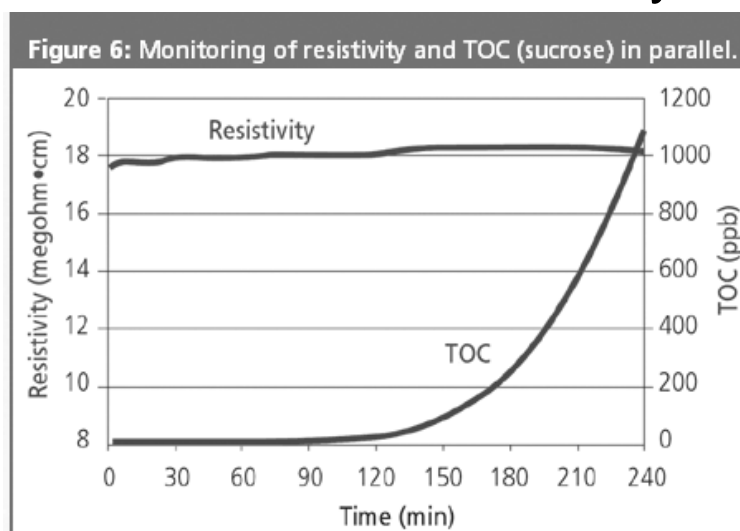
Pros

- Necessary because conductivity measurement cannot identify presence of organics.
- TOC provides a measure of confidence that organic contamination is below a specific level
- Organics can cross ion-exchange systems, and even past exhausted carbon filters

Cons

- Cost can be high if lab doesn't already have the instrumentation
- TOC doesn't provide an indication of WHAT the contaminants are

TOC and Resistivity



From (July 2005):

LC/GC Europe: The Misunderstood Laboratory Solvent: Reagent Water for HPLC
<http://www.lcgceurope.com/lcgceurope/article/articleDetail.jsp?id=167310&pageID=3#>

Sources of Organic Matter in High Purity Reagent Water

- Ion exchange are manufactured from organic material (styrene and divinylbenzene) and contain significant amounts of impurities (residual monomers)
- New resins can release ppm levels of organic leachables
- New resins require vigorous cleaning to remove leachables.
- Dominant leachables in cation resins are sulfonated aromatic compounds
- Older resins will leach more organics; resins break down or become loaded with organics
- Organics are never completely removed from resin with typical regeneration

Minimizing Organic Leachables from Ion Exchange Resin

- Most manufacturers offer special grades of "virgin" or "ultra-pure" resins with extremely low levels of leachable organics.
- Ultra-pure resins are typically regenerated in a way to remove organics and not damage the resin
- Resins can develop high levels of leachables during storage-do not store very long before use.

Special Considerations for BOD

☞ Simple deionizer systems can work well but can quickly be overgrown with bacteria and mold particularly if they are seldom used.

Can leach organics if not maintained regularly.

☞ Chlorinated water feeding ion exchange systems: resin can break down / leach O₂ demanding material.

Solution: pass water thru activated charcoal cartridge prior to resin.

Special Considerations for BOD

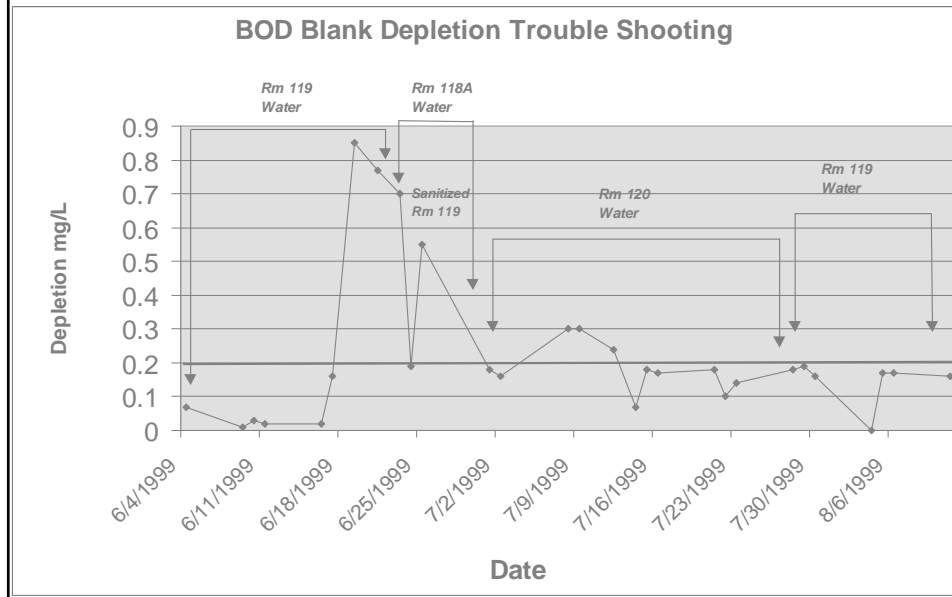
☞ If using simple deionizer system, use ultra-pure grade or virgin resin.

*i.e., Lower grade, "re-used" and old resins **WILL** leach organic matter and cause problems.*

☞ Distillation using an all glass still and storage in a glass container may be the simplest solution if little volume is needed.

A still must be properly maintained for optimal performance and to insure good water

SLH's dilution water experiences



Why Bacteria?

Type A/ B/ C:
10/100/10,000
CFU per 1000 ml

Pros

- For a microbiological lab, water must be organism-free
- For BOD, water should be bacteria free as well

Cons

- Heterotrophs are too generic
- Micro-organisms tend to grow biofilms and even flourish within cartridge systems—these won't be detected
- Plate counts only detect those organisms capable of growth on the nutrient selected and under the physical conditions chosen for incubation.
- Most of the microbiological contamination in purified water will be cellular debris, not viable cells

Why Endotoxins?

Type A/ B/ C:
 <0.03/0.25/---
 EU/mL

Pros

- Relatively quick, simple test
- Identify gram-negative organisms or their byproducts that are in the water

Cons

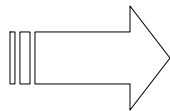
- Won't detect gram-positive bacteria
- Of little use for strict chemistry labs
- Gel clot methods only sensitive to about 0.03 EU/mL. Photometric tests required below that level.

So...what does it all mean?

We need to refocus on what's really critical to reagent water quality monitoring

Then

Conductivity
 TOC
 Chloride
 Sodium
 Silica
 Bacteria
 Endotoxins



Now

- 1. TOC
- 2. Conductivity
- 3. Endotoxins
- 4.
- 5.
- 6.
- 7.



Recommendations (tools)

- Monitor conductivity
- Use in-line monitor provided by mfr/water polisher
 - If polisher has green "idiot" light, swap it out for a direct readout monitor
 - Record conductance daily
 - Use conductance to monitor changes over time as a maintenance tool
- Std Methods/ SDWA criteria are more realistic
- If having BOD problems, consider monitoring TOC and endotoxin levels
- Use info from QC "tools": blanks and controls

Drinking Water Certification Manual 5th ed. (Microbiology)

<u>Parameter</u>	<u>Limits</u>	<u>Frequency</u>
Conductivity	>0.5 Mohms resistance or <2 umhos/cm (uS/cm) at 25 ° C	Monthly ⁴
Pb, Cd, Cr, Cu, Ni, Zn	Not greater than 0.05 mg/L per contaminant. Collectively, no greater than 0.1 mg/L	Annually
Total Chlorine Residual ¹	<0.1 mg/L	Monthly
Heterotrophic Plate Count ²	< 500 CFU/mL ⁵	Monthly
Bacteriological Quality of Reagent Water ³	Ratio of growth rate 0.8 to 3.0	Annually

¹ DPD Method should be used. Not required if source water is not chlorinated.

² Pour Plate Method. See *Standard Methods* 9215B.

³ See *Standard Methods* (18th or 19th eds.), Section 9020B, under *Laboratory Supplies*. This bacteriological quality test is not needed for Type II water or better, as defined in *Standard Methods* (18th and 19th eds), Section 1080C, or Medium quality water or better, as defined in *Standard Methods* (20th ed.), Section 1080C. If Type II or Medium quality water or better is not available, and a glass still is used for reagent water, a silicon test that meets the specifications of *Standard Methods*, Section 1080C (20th ed.) should also be accomplished.

⁴ Monthly, if meter is in-line or has a resistivity indicator light; otherwise, with each new batch of reagent water

⁵ CFU means colony-forming units (same as colonies, but is a more precise term)

What can I expect during an audit?

- Auditors will want to see that you have a system in place to evaluate the suitability of your reagent water for intended use
- That will mean different things for different labs
- DNR – an internal decision to not cite labs for failing to verify the quality of laboratory reagent water (with an external method), or to calibrate in-line conductivity meters

Summary

- Most lab people have not read the detail in ASTM D1193
- The standard is not well written and does not provide clear guidance
- Clearly, many of the “requirements” for Type I and II water are simply unachievable
 - Conductivity
 - Sodium
 - Chloride
- Conductivity (*reasonable*), TOC, and Endotoxin monitoring (*for microbiology*) provide the best measures of reagent water quality

Some Great References for further detail on this issue

A Critique of ASTM Standard D1193
Standard Specification for Reagent Water
American Society for Testing and Materials International
2001 Annual Book of Standards – Volume 11.01
Edition 2.6

Senior Editor Erich L. Gibbs, PhD
11/01/03

http://www.high-q.com/pdf/astm_d1193_critique.pdf

AH/LabWater™ - 1.10
Standard For Laboratory Reagent-Grade Water
April 8, 2005

<http://www.high-q.com/standards.html>

Thanks for having us!

For More Information

George Bowman
Chemist Supervisor

WI State Lab of Hygiene
Environmental Health Division
2601 Agriculture Drive
Madison, WI 53718

(608) 224-6279

GTB@mail.slh.wisc.edu

Rick Mealy
Program Chemist

WI DNR
Lab Certification – SS/7
PO Box 7921
Madison, WI 53707

(608) 264-6006

richard.mealy@wisconsin.gov



