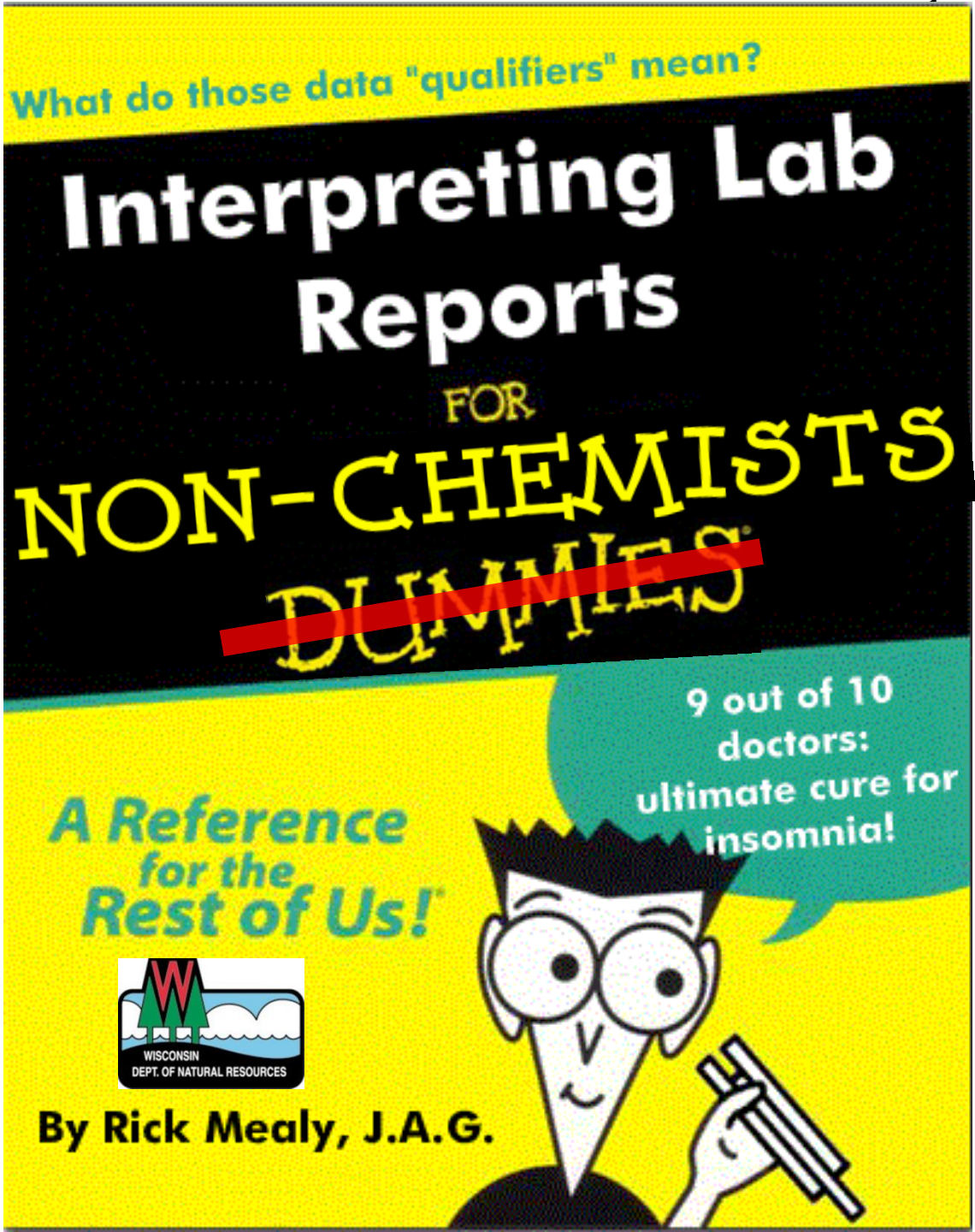
Wednesday 10/12/16
Session A
Presentation 2
11:25-12:00

WISCONSIN
DEPT. OF NATURAL RESOURCES

Rick Mealy

Lab Certification



Report Reading 101 – What to look for

6 Lg WI Testing Labs' Reports

Looking only at data column headers

Results	Units	LOQ	LOD	DF	Prepared	Analyzed	CAS#	Qual
Results	Units	LOD	LOQ	Dil.		Method	Analyzed	Codes
Result	Units	Dilution	LOD	LOQ	Analyzed	Method	Lab	
Result	Units	LOD	LOQ/RL	Dilution	Prepared	Analyzed	Method	Qualifier
Result	Flags	Units	Date	Dil. Factor	LOD	LOQ		
Result	Units	LOD	LOQ	Dilution	Method	Ext Date	Run Date	Analyst	Code

Result/s:	6/6	Qual/Codes/Qualifier/Flags/Code:	5/6
Units:	6/6	Analyzed (or Run Date"):	5/6
LOD:	6/6	Method:	4/6
DF/Dil./Dilution/ Dil. Factor:	6/6	Prepared (or Ext Date):	3/6
LOQ or "LOQ/RL"):	6/6		

NR 149 specifies what information is to appear on test reports, but has no authority over how the information is labelled or where it appears

6 Lg WI Testing Labs' Report

Looking only at data column headers

Results	Units	LOQ	LOD	DF	Prepared	Analyzed	CAS#	Qual	
Results	Units	LOD	LOQ	Dil.		Method	Analyzed	Codes	
Result	Units	Dilution	LOD	LOQ	Analyzed	Method	Lab		
Result	Units	LOD	LOQ/RL	Dilution	Prepared	Analyzed	Method	Qualifier	
Result	Flags	Units	Date	Dil. Factor	LOD	LOQ			
Result	Units	LOD	LOQ	Dilution	Method	Ext Date	Run Date	Analyst	Code

"Flags" next to result. Makes it easier to notice.

What is "date"? Sampled? Received? Analyzed?

Do we need "CAS #"? Can help identify some organics

"Lab" is nice. Clearly identifies which lab did the testing.

DATA QUALIFIERS

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- Qualifiers
- Flags
- Notes
- QC codes

They mean something.

It doesn't necessarily mean "bad data"…but it does mean that there's something about the data you should be aware of.

Common qualifiers

Code: "J" OR [*result*]

Estimated concentration ; Detected but < LOQ.
Estimated concentration ≥ LOD and < LOQ.
Estimated concentration < LOQ
Result is approximate value < RL but ≥ MDL.

Code: "ND" or "U"

Not Detected at or above LOD.
Compound was analyzed for, but not detected > adjusted LOD

Code: "B"

Compound was found in the blank and sample.

Code: "1"

All lab QC requirements were met for this sample, OR
Laboratory QC within limits.

Code: ***Many variations***

A whole host of variations exist for flags used to identify LCS/MS/MSD/precision failures.

Example J flag

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ANALYTICAL RESULTS

Project: WPDES

Sample: OUTFALL 004 **Lab ID:** Collected: 06/02/16 08:26 Received: 06/07/16 15:05 Matrix: Water

Parameters	Results	Units	LOQ	LOD	DF	Prepared	Analyzed	CAS No.	Qual
200.7 MET ICP	Analytical Method: EPA 200.7 Preparation Method: EPA 200.7								
Copper	**<3.4**	ug/L	10.0	3.4	1	06/14/16 15:14	06/15/16 18:33	7440-50-8	
Iron	**178**	ug/L	100	15.9	1	06/14/16 15:14	06/15/16 18:33	7439-89-6	
Zinc	**7.7J**	ug/L	40.0	5.8	1	06/14/16 15:14	06/15/16 18:33	7440-66-6	
200.8 MET ICPMS	Analytical Method: EPA 200.8 Preparation Method: EPA 200.8								
Arsenic	**1.9**	ug/L	1.0	0.099	1	06/09/16 08:47	06/09/16 23:02	7440-38-2	
365.4 Total Phosphorus	Analytical Method: EPA 365.4 Preparation Method: EPA 365.4								
Phosphorus	**0.044J**	mg/L	0.045	0.015	1	06/10/16 02:35	06/10/16 07:14	7723-14-0	

Zinc 7.7 J

TP 0.044 J

- Note that the “J” flag does not appear under the “Qual” column

Qualifiers: So, what do we DO with 'em?

- Most qualifiers are simply saying, "there's something bout this data you should know"
- "J" flags are easy. They are just saying *"I have a detectable amount, but I cannot quantitate it with certainty."*
- Blank qualifiers ("B") require you to check the level reported for the blank. Ask the question: *"How significant is the blank relative to my result"?*

If your BOD result is 3 and the blank is over 1 mg/L, then your NR 101 fees could be impacted.
BOD blanks are allowed to run as high as 0.24 mg/L

Qualifiers:

But what do we DO with 'em?

- LCS exceedances: These are matrix free, so meeting control limits should happen 99% of the time
- Matrix QC: is it your sample?
- Matrix Spikes: The rule of 1:5 (some use 1:4)
  - A. If spike amount >>5 X sample background OR
  - B. If spike amount << sample background, then
  - C. The spike level is inappropriate and ignore any qualifiers
- Miscellaneous flags

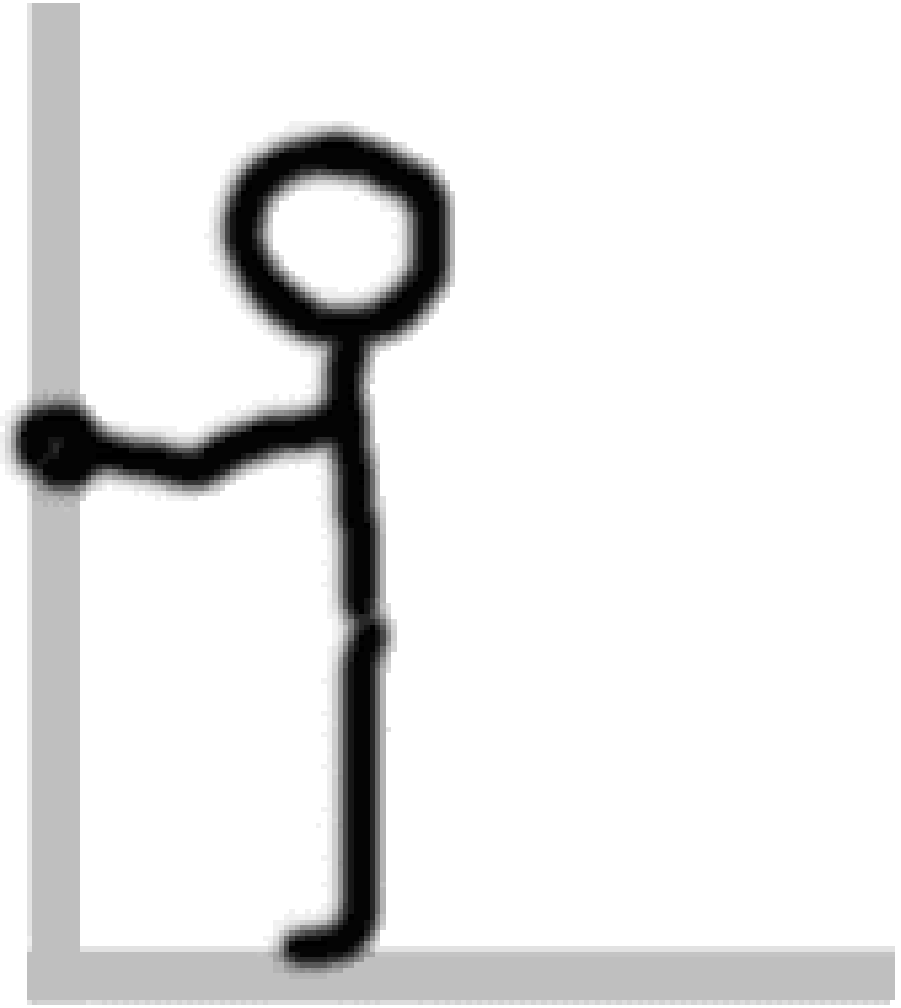
The devil is in the details

LabCert has authority to require WHAT data must be qualified.

But we do not have authority to specify either

- The detail of what the qualifiers say, or
- Where the qualifier appears on a report

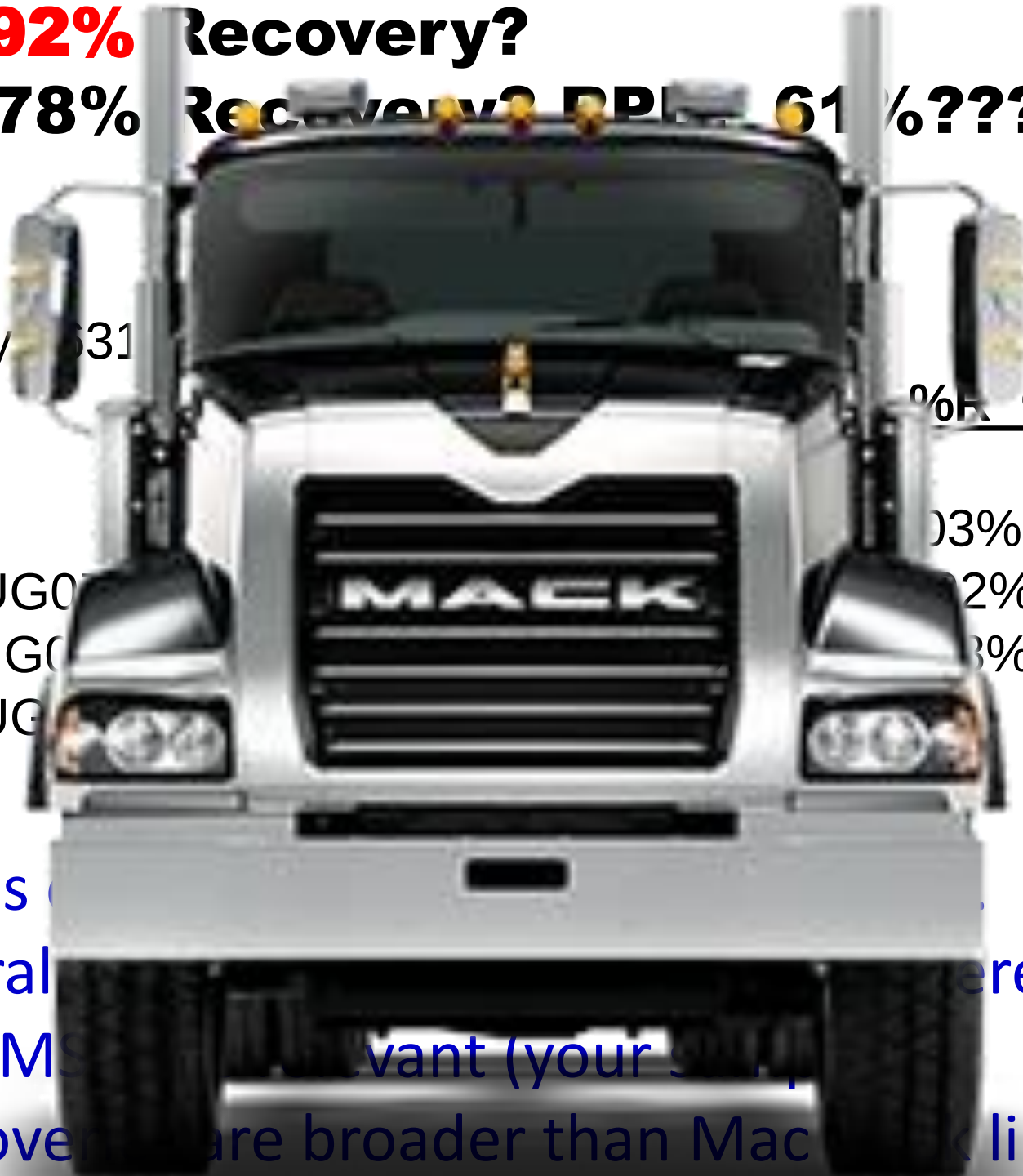
Are you there, yet?



Matrix QC issues

MS: - 492% Recovery?

MSD: 578% Recovery? RPD 61%????



Mercury by 631

	%R	%RPD	Qual
Blank			
LCS	03%		
MS (WUG0	2%		F
MSD (WUG0	3%	61%	4F
Lab ID WUG			B

1-2 pages

The overal erent flags.

The MS/M vant (your

And recove are broader than Mac limits

MS: - 492% Recovery?
MSD: 578% Recovery? RPD: 61%???

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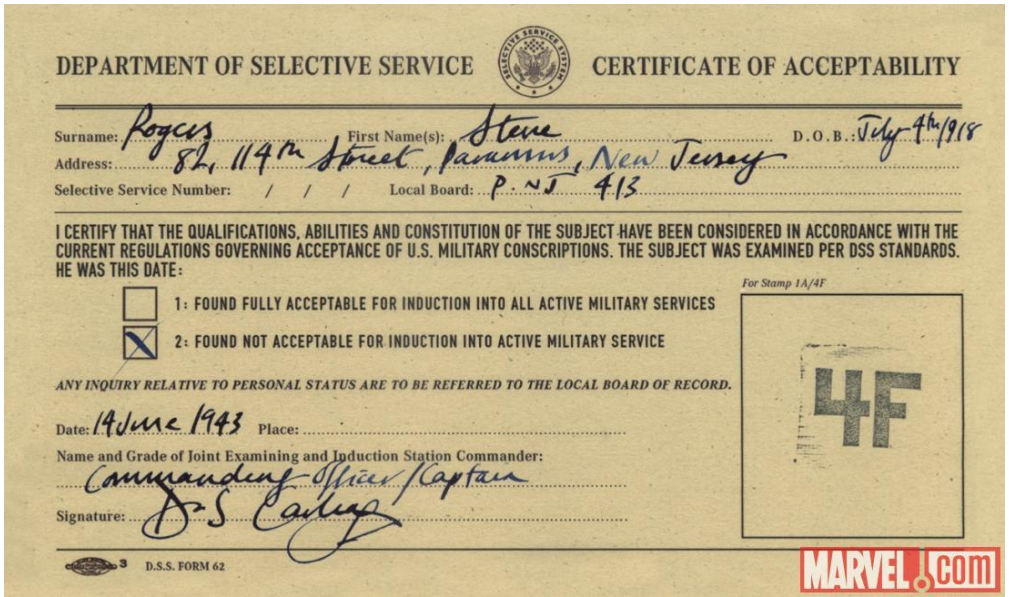
- Analyze the influent….reported 86 ng/L
- Add 5 ng for MS; Expect 91 ng/L….get 61.5
- Add 5 ng for MSD; Expect 91 ng/L….get 115
- So…the influent is somewhere b/w 60 - 115 ng/L?
- That's the best we can do? Qualify result as "4F"

…and if that wasn't bad enough…it was YOUR sample that was spiked!



DEPARTMENT OF SELECTIVE SERVICE — CERTIFICATE OF ACCEPTABILITY

Surname: Rogers — First Name(s): Steve — D.O.B.: July 4th 1918

Address: 82, 114th Street, Queens, New Jersey

Selective Service Number: / / / — Local Board: P.NJ 413

I CERTIFY THAT THE QUALIFICATIONS, ABILITIES AND CONSTITUTION OF THE SUBJECT HAVE BEEN CONSIDERED IN ACCORDANCE WITH THE CURRENT REGULATIONS GOVERNING ACCEPTANCE OF U.S. MILITARY CONSCRIPTIONS. THE SUBJECT WAS EXAMINED PER DSS STANDARDS. HE WAS THIS DATE:

☐ 1: FOUND FULLY ACCEPTABLE FOR INDUCTION INTO ALL ACTIVE MILITARY SERVICES

☒ 2: FOUND NOT ACCEPTABLE FOR INDUCTION INTO ACTIVE MILITARY SERVICE

ANY INQUIRY RELATIVE TO PERSONAL STATUS ARE TO BE REFERRED TO THE LOCAL BOARD OF RECORD.

For Stamp 1A/4F: 4F

Date: 14 June 1943 — Place:

Name and Grade of Joint Examining and Induction Station Commander: Commanding Officer / Captain

Signature: S. S. Carlisle

D.S.S. FORM 62

MARVEL.com

The 25% Principle: Trouble with Matrix Spikes

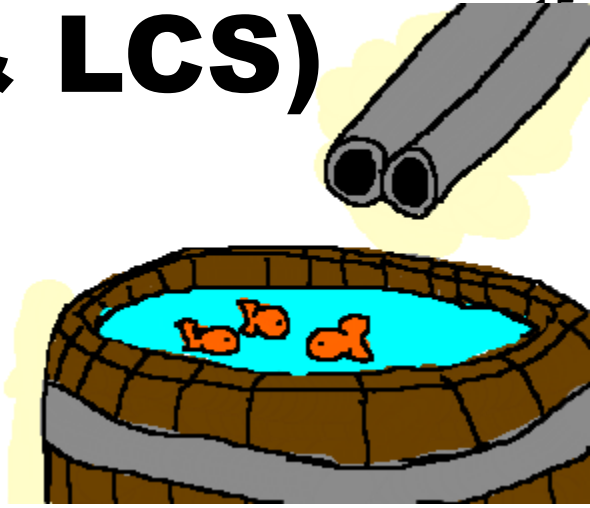
- **If recoveries/RPD are good and….**
  - Your sample was spiked……
  - Some other client's sample was spiked……

- **But if they aren't something to be proud of and…**
  - Your sample was spiked……
  - Some other client's sample was spiked……

Scenarios are 3:1 AGAINST you being able to be happy about MS/MSD or RPD data.

=25% chance MS/MSD have any value for you

Spiking too high (MS & LCS)



Arsenic by Method 200.8 (ICP/MS)

	Result	Units	Spike	%R	%RPD
Blank	< 0.099	ug/L			
LCS	469		500	94%	
MS (40133395004)	478		500	95%	
MSD (40133395004)	476		500	94%	0%
Lab ID 40133395004	< 0.099				

Spiking at 5000 X LOD is like shooting fish in a barrel!

Also consider that in a routine sample one would not expect to find arsenic present at more than 10 ug/L.

Thus…anyway you slice it, a 500 ppb spike is overkill.

Channeling your inner Mel?

Spiking too low

Mercury, Low Level by Method 1631E (CVAFS)

	Result	Units	Spike	%R	Limits	%RPD	Limit	Qual
Blank	0.354	ng/L						J
LCS	5.15		5.00	103%	77-125			
MS	61.5		5.00	- 492%	71-125			4
MSD	115		5.00	578%	71-125	61	24	4F
Sample	86							B

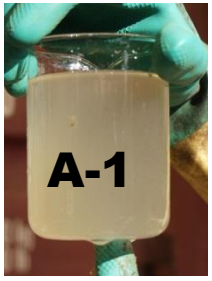
Spiking at ~ 5% of the amount in the sample is like trying to find a needle in a haystack.

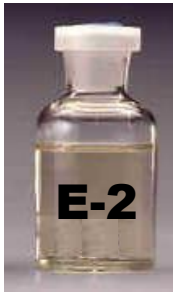
Also consider that the variability (range) between the MS and MSD (53.5ng/L) is > 10X the spike level.

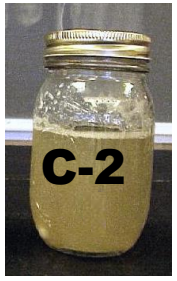
Which sample is spiked matters!

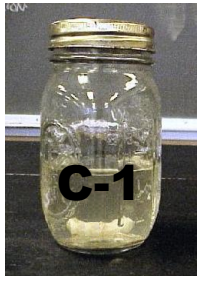
⇦If we spike sample E-1 and get 38% recovery…does that mean ALL of our sample results must be qualified? Even… ⇨ ⇨ ⇨ ⇨ ⇨ ⇨ ⇨ ⇨ ⇨ ⇨ ⇨ ⇨

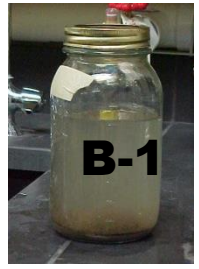
⇦ If we spike sample G-1 and get 100% recovery…does that mean there are no matrix effects in ANY of the other samples? Even ⇨ ⇨



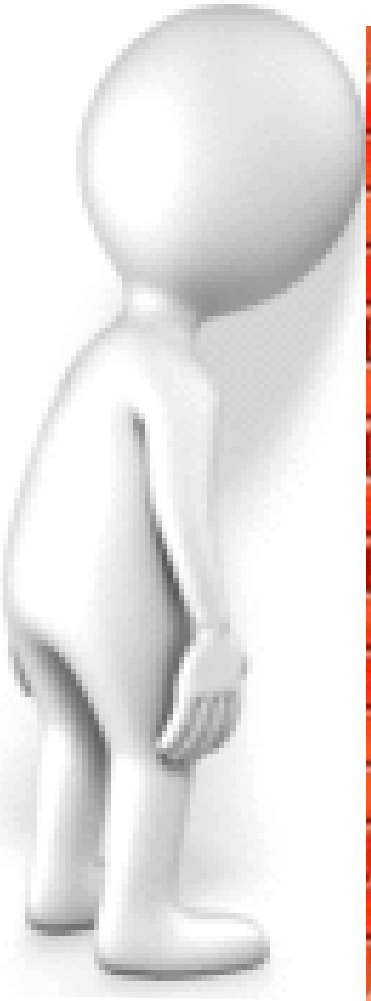


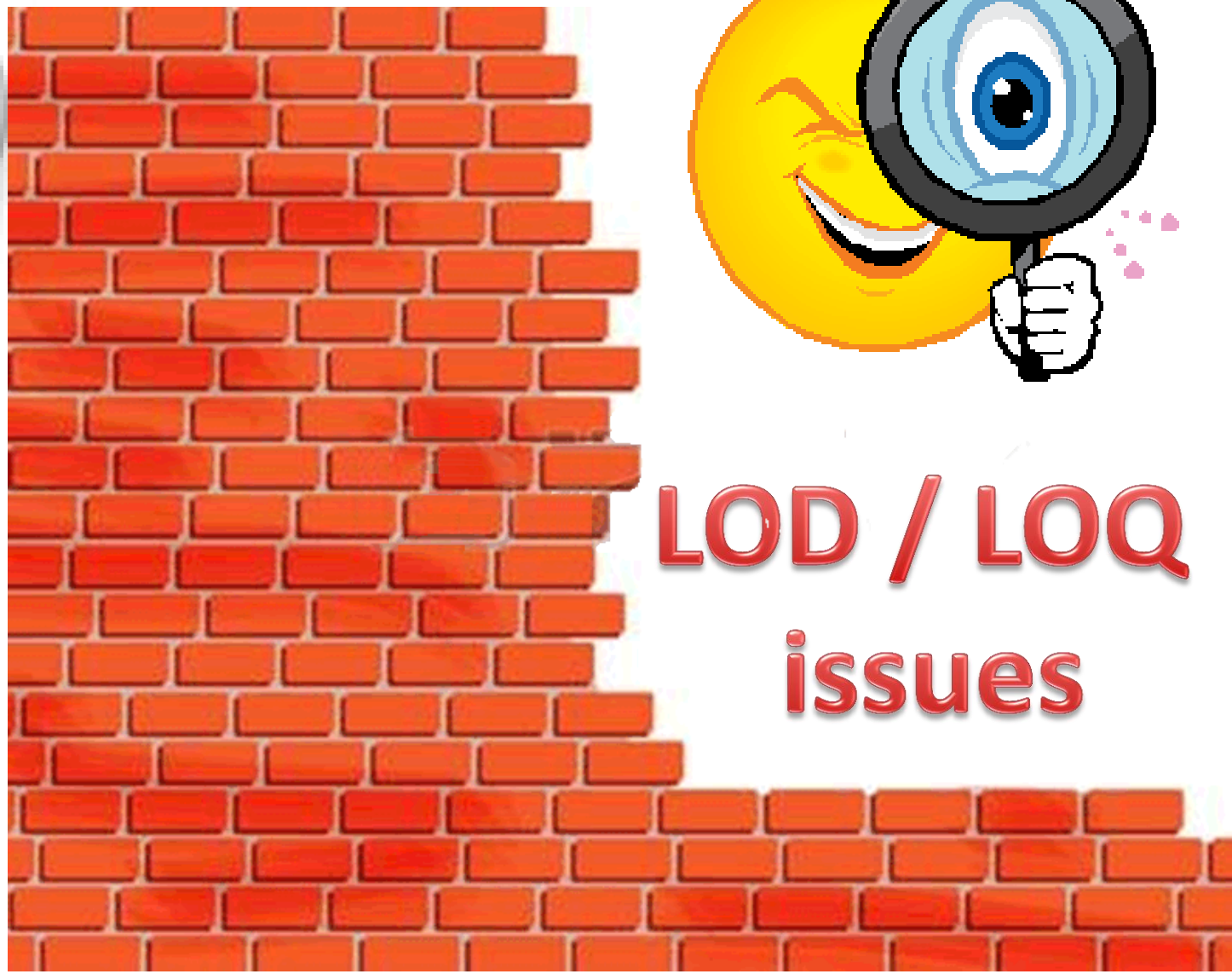






How about now?





LOD / LOQ issues

8 different ratios/13 metals

EPA 6010B - Diss.	Results	Units	LOD	LOQ	DF	Qual	LOQ/LOD
Dissolved Boron	56.4	ug/L	6.00	10.0	1		1.66X
Dissolved Sodium	16.9	mg/L	0.50	0.50	1		1X

1X to 10 X with no visible rationale…why?

EPA 6020 - Diss.							
Dissolved Arsenic	2.41	ug/L	0.60	2.00	1		3.33x
Dissolved Barium	81.1	ug/L	2.0	5.0	1		2.5X
Dissolved Cadmium	ND	ug/L	0.20	2.00	1		10X
Dissolved Chromium	ND	ug/L	1.60	5.00	1		3.125X
Dissolved Copper	ND	ug/L	0.60	2.00	1		3.33X
Dissolved Lead	ND	ug/L	0.30	2.00	1		6.66X
Dissolved Manganese	65.6	ug/L	1.0	3.3	1		3.33X
Dissolved Selenium	ND	ug/L	0.60	2.00	1		3.33X
Dissolved Silver	ND	ug/L	0.20	2.00	1		10X
Dissolved Zinc	6.06	ug/L	2.00	5.00	1		2.5X

EPA 7470A - Diss.							
Dissolved Mercury	ND	ug/L	0.070	0.230	1		3.29X

LOD>LOQ

This one might have needed more time in data review

Client: **Job #:** 40998

Project:

Date Received: 6-14-20 **Date Reported:** 11-1-20

Sample Results

Sample No. / ID / Description / Matrix	Result	Flags	Units	Date	Dil. Factor	LOD	LOQ
40998-001 / OW 64 / Water							
Trace Metals - Dissolved							
Barium (d)	0.13		mg/L	6-25-2012	1	0.002	0.001
Method: 6010B	Prep: 3010A						

LOD is GREATER THAN the LOQ!

…and it took nearly 5 months to report a Barium result?

LOD / LOQ: What to look for

- **The LOQ MUST be greater than the LOD!!!**
- LOQ SHOULD be about 3X LOD
- Labs should be consistent in LOD:LOQ ratios for different tests. (LOQ is a statistical concept!). They are related. As LOD increases, the LOQ should rise incrementally.
- Generally speaking, LODs for multi-analyte methods should not all be the same.

Method madness

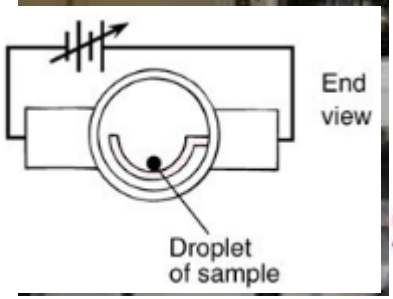
Method madness

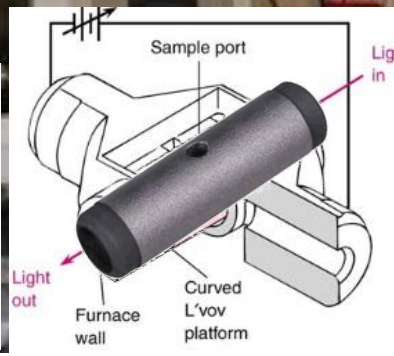
- BOD is easy…there is only ONE method!
- Phosphorus is pretty easy…only one technology.
- Ammonia can be tricky: ISE? Or Colorimetry?
- Most organic parameters can be analyzed by GC, GC/MS, or even LC or LC/MS technologies.
- But metals are the worst…
  - There's Flame AA (FLAA)
  - Graphite furnace AA (GFAA)
  - ICP
  - ICP/MS, and even
  - Colorimetry!

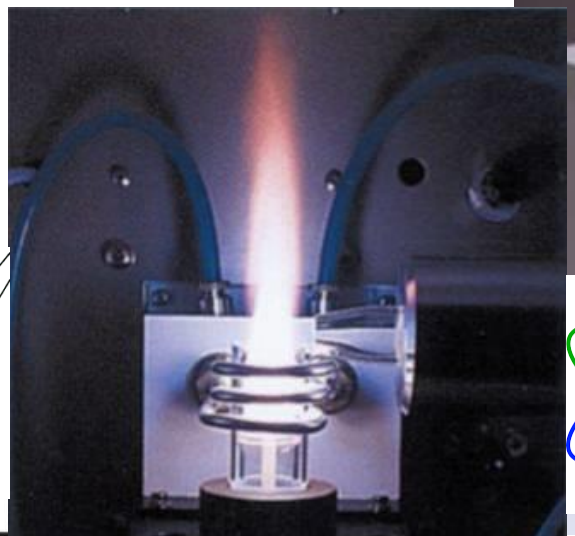
…and mercury?…

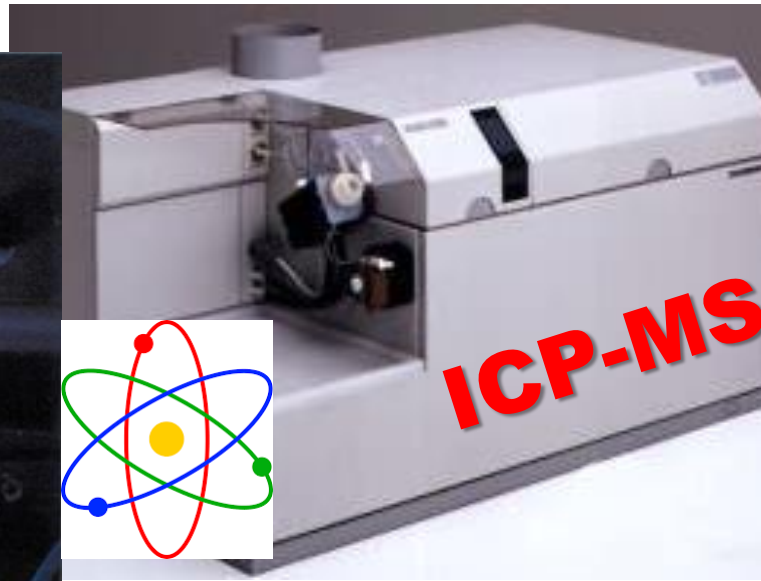
- Cold vapor AA (CVAA)
- Low level
- Cold vapor atomic fluorescence (CVAFS)
- Thermal Desorption

Metals – so many choices









Metals Detecting

- Typically WWTPs simply ask a lab to analyze for a suite of metals…
- …leaving the selection of technology to use up to the lab.

Metals Technologies

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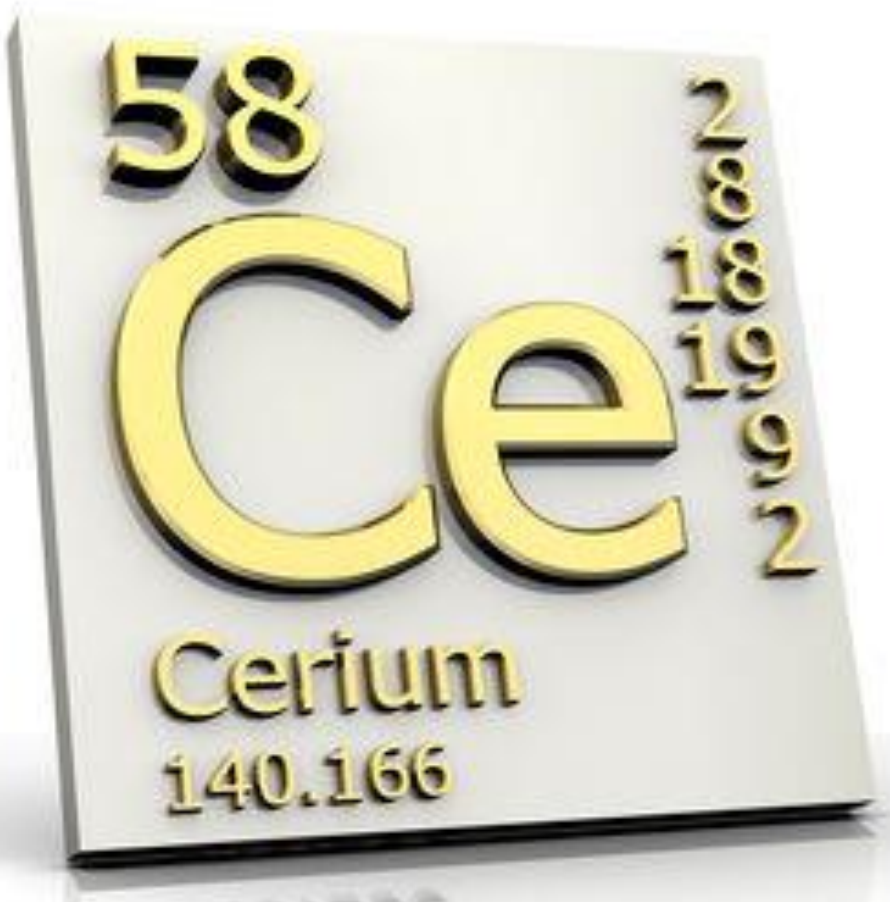

Subcontracting to other labs

Do you know if your contract lab is "subbing" to another lab?

Ultimately, what you report is YOUR responsibility!

Example: Subcontract lab identified

Sample Matrix Water
Sample Date 12/4/2014

	Result		Unit	LOD	LOQ	Dil	Method	Run Date	Analyst	Code
Inorganic										
Metals										
Arsenic, Total		< 32	ug/l	32	100	5	6010B	12/11/2014	ESC	1
Barium, Total	24		ug/l	5	25	5	6010B	12/11/2014	ESC	1
Cadmium, Total		< 3.5	ug/l	3.5	25	5	6010B	12/11/2014	ESC	1
Chromium, Total		< 9	ug/l	9	50	5	6010B	12/11/2014	ESC	1
Copper, Total	350		ug/l	35	100	5	200.7	12/11/2014	ESC	1
Lead, Total		< 10	ug/l	10	25	5	6010B	12/11/2014	ESC	1
Mercury, Total		< 0.049	ug/l	0.049	0.2	1	245.1	12/9/2014	ESC	1
Nickel, Total		< 29	ug/l	29	100	5	200.7	12/11/2014	ESC	1
Selenium, Total		< 38	ug/l	38	100	5	6010B	12/11/2014	ESC	1
Silver, Total		< 14	ug/l	14	50	5	6010B	12/11/2014	ESC	1
Zinc, Total		< 17	ug/l	17	150	5	200.7	12/11/2014	ESC	1

"J" Flag: Analyte detected between LOD and LOQ LOD Limit of Detection LOQ Limit of Quantitation

Code	*Comment*
1	Laboratory QC within limits.

ESC denotes sub contract lab - Certification #998093910

All solid sample results reported on a dry weight basis unless otherwise indicated. All LOD's and LOQ's are adjusted for dilutions but not dry weight. Subcontracted results are denoted by SUB in the analyst field.

Subcontract lab – Alternate means of ID

Project: Waste Testing

Carbon Media Waste
COC: 203421:1 Matrix: SL
Collected: 05/27/16 08:00 Received: 06/01/16

Parameter	Result	Units	Dilution	LOD	LOQ	Analyzed	Method	Lab
pH, lab (soil/sludge)	7.7	s.u. pHw	1		*	06/01/16	SW846 9045	721026460
Sulfur, tot. recoverable as S by ICP	4800	mg/Kg WWB	5	54	160	06/09/16	SW846 6010	721026460
	Sulfur is run as a non-compliance analyte.							
Sulfide, reactive	[37]	mg/Kg DWB	1	18	58	06/08/16	EPA 9034 & Chapter 7	632021390
Water, Free EPA 9095	ND	mL/100g	1	1.0*		06/02/16	SW846 9095	721026460
Metals digestion - tot. recov (solid) ICP	yes					06/08/16	SW846 3050M	721026460
TCLP Extraction	yes					06/07/16	SW846 1311	721026460
TCLP Zero Head Space Extraction	yes					06/07/16	SW846 1311	721026460
Flashpoint	>140.0	Deg. F	1		*	06/06/16	EPA 1010	157066030

Values in brackets represent results greater than or equal to the LOD but less than the LOQ and are within a region of "Less-Certain Quantitation". Results greater than or equal to the LOQ are considered to be in the region of "Certain Quantitation". LOD and/or LOQ tagged with an asterisk(*) are considered Reporting Limits. All LOD/LOQs adjusted to reflect dilution and/or solids content.
ND = Not Detected (< LOD) LOD = Limit of Detection LOQ = Limit of Quantitation NA = Not Applicable
DWB = Dry Weight Basis %DWB = (mg/kg DWB) / 10000 1000 ug/L = 1 mg/L
MCL = Maximum Contaminant Levels for Drinking Water Samples. Shaded results indicate >MCL.

Is your contract lab checking to be sure that any lab they in turn subcontract your samples to is properly certified?

Other things to watch out for

- Check units before transferring results!
  Particularly for metals, labs may switch units :

	Results	Units	LOD	LOQ	Dilution Factor
EPA 6010B - Diss.					
Dissolved Boron	56.4	ug/L	6.00	10.0	1
Dissolved Sodium	16.9	mg/L	0.50	0.50	1
EPA 6020 - Diss.					
Dissolved Arsenic	2.41	ug/L	0.60	2.00	1
Dissolved Barium	81.1	ug/L	2.0	5.0	1
Dissolved Cadmium	ND	ug/L	0.20	2.00	1
Dissolved Chromium	ND	ug/L	1.60	5.00	1
Dissolved Copper	ND	ug/L	0.60	2.00	1
Dissolved Lead	ND	ug/L	0.30	2.00	1
Dissolved Manganese	65.6	ug/L	1.0	3.3	1
Dissolved Selenium	ND	ug/L	0.60	2.00	1
Dissolved Silver	ND	ug/L	0.20	2.00	1
Dissolved Zinc	6.06	ug/L	2.00	5.00	1

LabCert can help

How Can LabCert help?

- First…we're chemists. We speak fluent lab-ese.
- We are expert report interpreters.
- We audit the labs; ask us to see a lab's audit report
- We can help you decide whether you need a pea-shooter or an elephant gun for your needs
- Flame AA? Furnace AA? ICP? ICP/MS? We can help

http://dnr.wi.gov/regulations/labcert/index.html#tabx5

Thanks for listening!

Any questions?