Verifying the Reliability of EPA Method 314 to Measure Perchlorate at Sub ppb Levels vs New EPA Method Options

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Why Do We Care About Accuracy at the Sub-PPB Level?

- MA has promulgated a requirement for all water suppliers (including bottled water vendors) in the State submit compliance data using method 314 with an MRL of <1 ppb
- The UCMR2 (2006) will likely require monitoring of ClO_4 at sub-ppb levels
- The jury is still out on the health effects issues.

What are the Analytical Options for ClO_4 at This Concentration Range?

- MA - 314 with required modifications
- EPA UCMR2
  - 314.1 IC/On-Line Concentration/Conductivity
  - 314.0 - modified with different column/suppressor to handle higher solids
  - 330.0 IC/MS
  - 331.0 LC/MS/MS
  - Customized methods

Principles of Method 314

- Inject a relatively large volume sample (1-2 ml)
- Use a high capacity Anion Ion Exchange Column (e.g. Dionex AS-16)
- Measure retention time and conductivity
- Evaluate sensitivity to TDS through use of a maximum conductivity threshold (MCT) sample to determine signal suppression.

Principles of Method 314.1

- Use different functional group to trap ClO_4 to concentrate larger volumes
- Separate on high capacity Anion Ion Exchange Column
- Measure using retention time and conductivity
- Use different column type to confirm identity and concentration

Principles of Method 330.0

- Inject small sample (e.g. 100 ul)
- Separate on conventional Anion Ion Exchange column
- Eluent goes into Mass Spectrometer through an electrospray inlet
- Measure mass 101/99 ($^{37}Cl/ ^{35}Cl$)
- Quantify against calibration curve

Principles of Method 331.0

- Inject small sample (e.g. 100 ul)
- Separate on HPLC Column
- Eluent goes into Mass Spectrometer through an electrospray inlet
- Do secondary fragmentation and measure mass transitions
- Use mass ratio to confirm identity
- Quantify against calibration curve

Comparison of These Methods as Far as "Figures of Merit"

- Sensitivity
  - 331 (0.02)>>330=314.1>314 (0.5)
- Specificity
  - 331>330>314.1>314
- Cost
  - 331>>330>314.1>314
- Freedom from Interferences
  - 331>330>314.1>>314
- Current Availability
  - 314>331=330>314.1

There Are 3 Basic Issues When Measuring at This Level

- Is there adequate signal/noise?
  - e.g. Can you detect ClO_4?
- Are there interferences that would lead to false positives or false negatives?
  - e.g. TDS, Co-eluting substances
  - Retention Time stability
  - Re-analysis of samples with hits
- Is the calibration accurate?
  - Are the numbers precise and accurate?

Massachusetts has Tried to Address All of These Issues

- Initial QC Requirements
- Batch QC Requirements
- Confirmation Sampling and Analysis

SO IS THE APPROACH SUCCESFUL OR DO WE NEED TO LOOK AT OTHER TECHNIQUES?

Massachusetts "Demonstration of Capability" - Criteria for <1 ppb MRL

- IPC/IDC at 5 ppb (vs 25 ppb for 314)
- MDL determined using 1 ppb spike
- MDL <=0.33 ppb with 1 ppb spike
- MCT determination at <=5 ppb
- 1 ppb recovery of 70-130% at 90% of MCT level
- Pass 2 low level PT samples

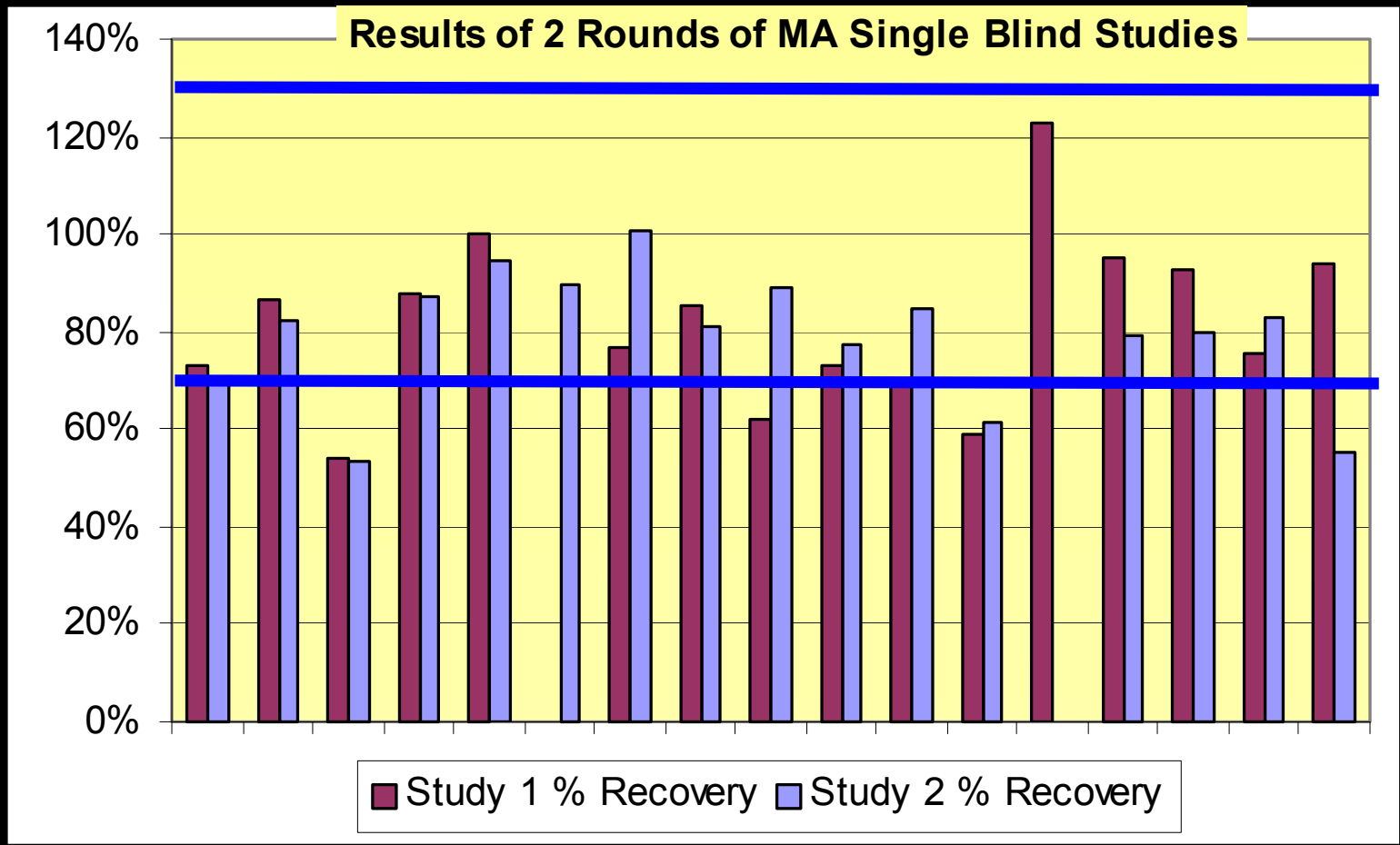
Massachusetts Batch QC Criteria for sub-ppb Analysis

- IPC at <5 ppb at 90% of MCT (80-120%)
- ICCS at 1 ppb (75-125%)
- LFB 1/batch of <=20 at 1 ppb (85-115%)
- Document EC for each sample
- LFM 1/batch of <=20 at 1 ppb (70-130%)
- Re-analyze any field samples with hits and spike at ~1 ppb
  - report original and re-analysis plus spike

Required Single Blind PT Studies for MA

- 17 labs participated in first 2 rounds
  - only 7 were actually MA approved
- 2 samples in each study
  - 1 blank, 1 spiked at 1.04 ppb in first
  - 1 blank, 1 spiked at 1.25 ppb in second
  - Matrix had anions with EC~500 uhmo
  - Labs KNEW these were PTs
- Acceptance based on mean +/-2SD
- Average recovery was 83% in each study

Clearly Performance is Generally Adequate in a Single Blind Test



Data provided by Wibby Environmental, the MA contractor for this study

Single Blind Performance Demonstrates That Some Labs Have Systematic Problems and Others are more Random

- A few of the labs were systematically biased very low in both studies
- Overall recovery was slightly low (~83%)
- Most labs met the requirements, suggesting that in this matrix it is possible to measure perchlorate accurately with IC at the 1 ppb level.

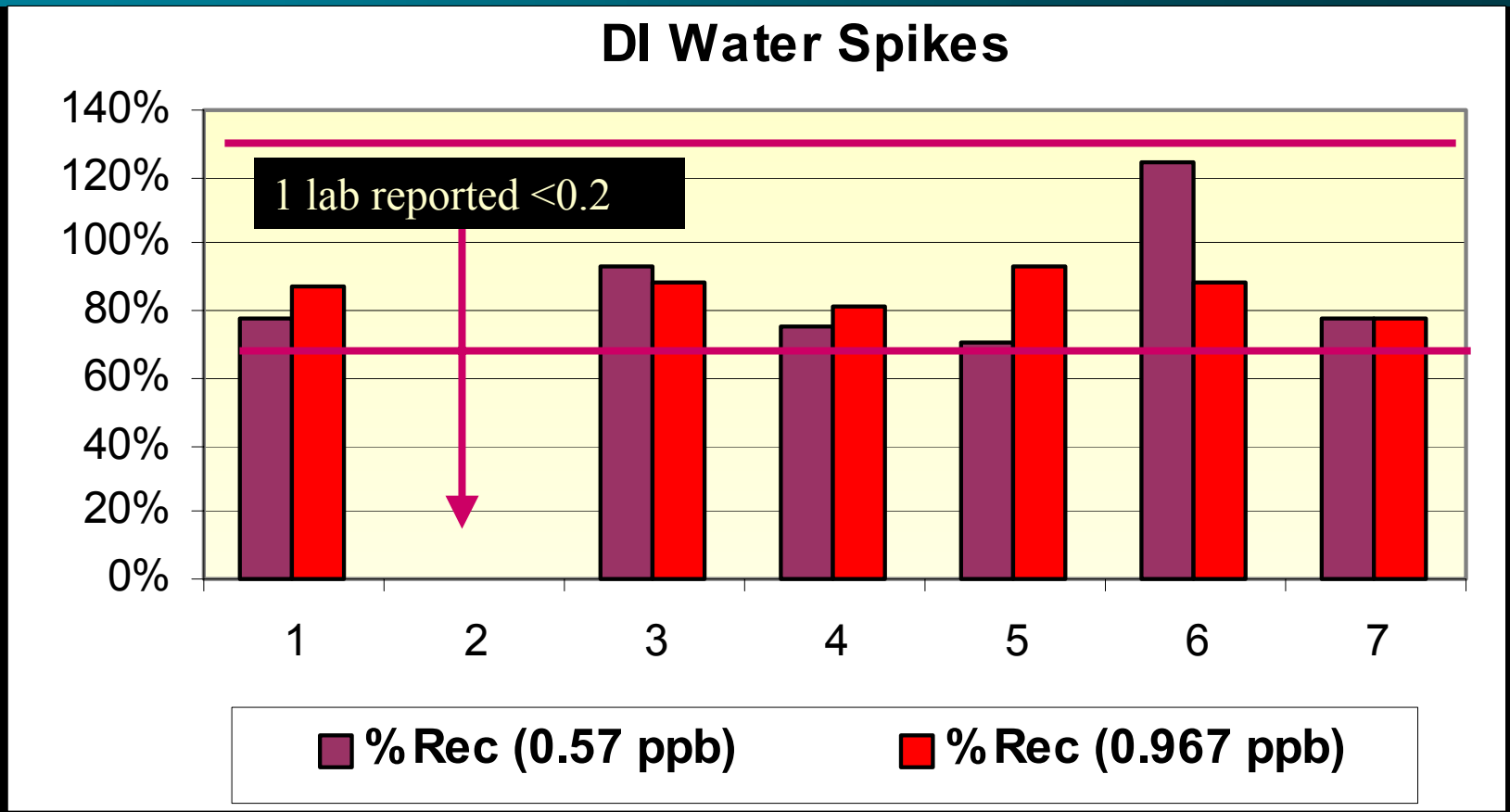
We Tried Something a Little Different to Assess Performance

- Designed a Double Blind Study for the 7 MA approved labs
  - Labs did not know they were being tested
    - (1 lab may have figured it out)
- Had samples in both DI and in a medium TDS matrix (EC~ 1200)
  - Twice as high as level used in MA official PT
- Used a series of samples (7) at varying levels from <0.4 to just over 1 ppb, with pairs approximately 20% apart

More on the Study Plan

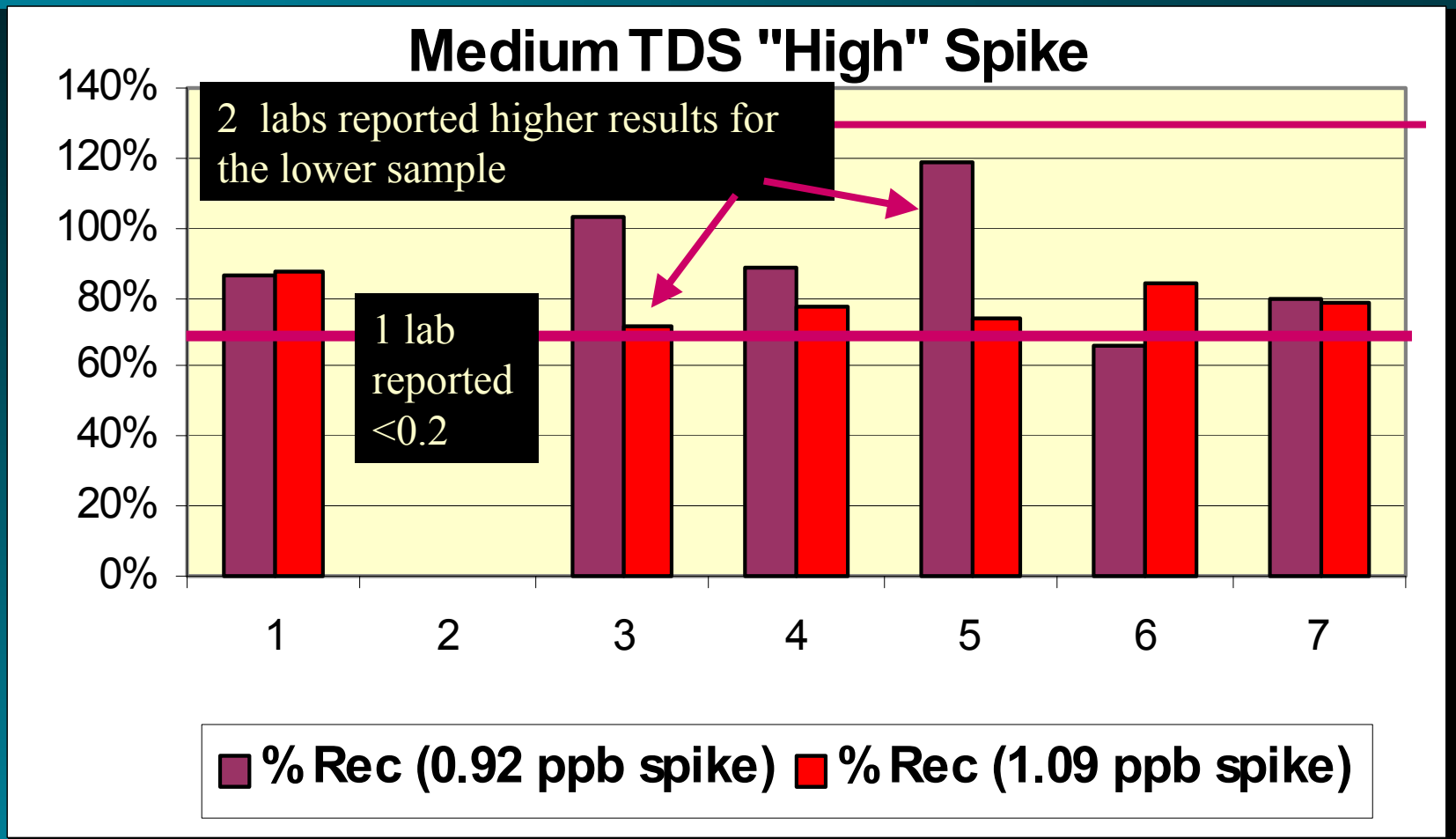
- Wanted to test:
  - Ability of labs to quantify below 1 ppb
  - Ability of labs to differentiate samples with minor differences in ClO_4
  - Ability of labs to measure accurately in DI and in a more typical nationally representative drinking water matrix
- Wanted to determine whether false negatives or false positives are more likely

Results of Double Blind in a DI Matrix Demonstrate Generally Good Performance Among 7 Approved Labs



Note that recoveries were generally biased low as in the official MA PT study

Not All Labs Could Measure With Good Precision in this Matrix

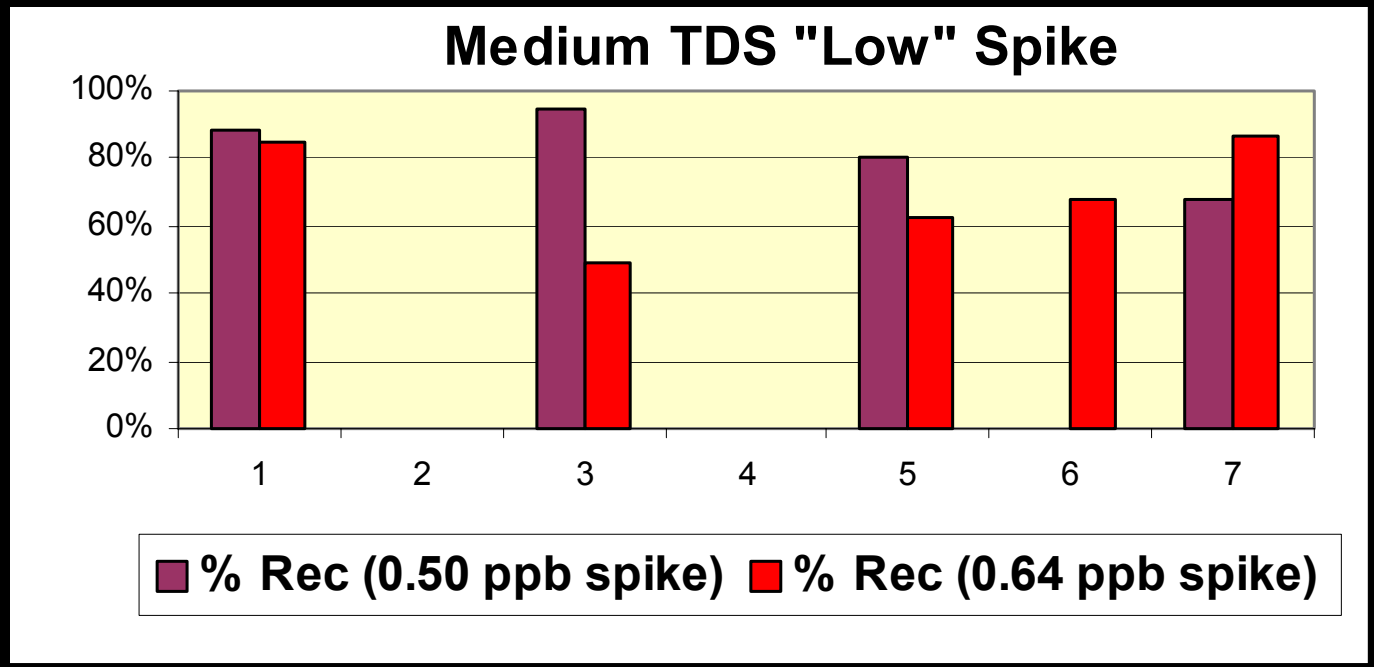


Note that recoveries were again generally biased low

Observations at 1 ppb Spike Level and ~700 ppm TDS

- 1 lab did not detect ClO_4 in either sample
- 2 other labs could not differentiate between the two samples (high bias on the lower sample and/or low bias on the higher sample, but all recoveries still within limits)
- Overall low bias (as in MA sponsored study)

At Higher TDS, Performance Slips a Lot at the 0.5-0.6 ppb Level



- 2 Labs did not detect ClO_4 in either sample
- All labs had low bias
- 2 labs could obviously not differentiate reliably between the two samples

How Does This Fit With the MA Requirements?

- MDLs for all labs were reported as 0.3 or less
  - 1 lab had an elevated in DL in the high salts that impacted their ability to detect the low spikes
- 1 lab only reported all data as <0.2 ppb, so it is clear that they can't detect in this range
- 6 of the 7 labs reported data that would still meet the MA requirements for P&A.

What Does This Say About the Ability to Measure Below 1 ppb Using 314?

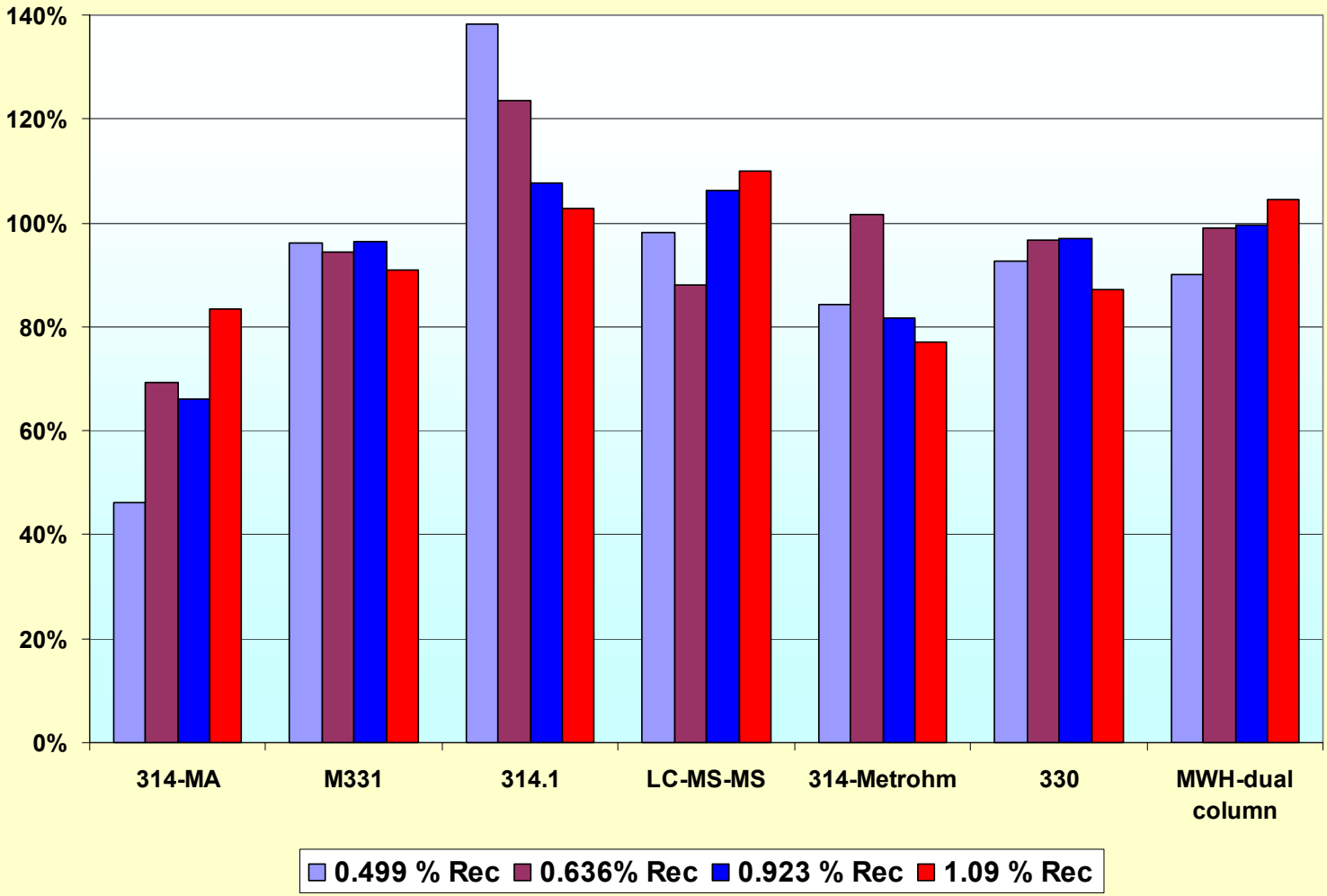
- Even in the hands of experienced labs, method 314 is pushing the limits at 0.5 ppb.
  - but SOME labs have clearly "tweaked" things more than others and generate consistent data.
  - Some labs don't have very good precision at <1
- TDS can lead to false negs-may be better to use 80% of MCT as a guideline for treating
- If we really want to measure at these concentrations, we need to look beyond 314 as currently ROUTINELY practiced.

Following the "Double Blind" Portion of the Study, We Solicited Participation From Labs Doing "New" Methods

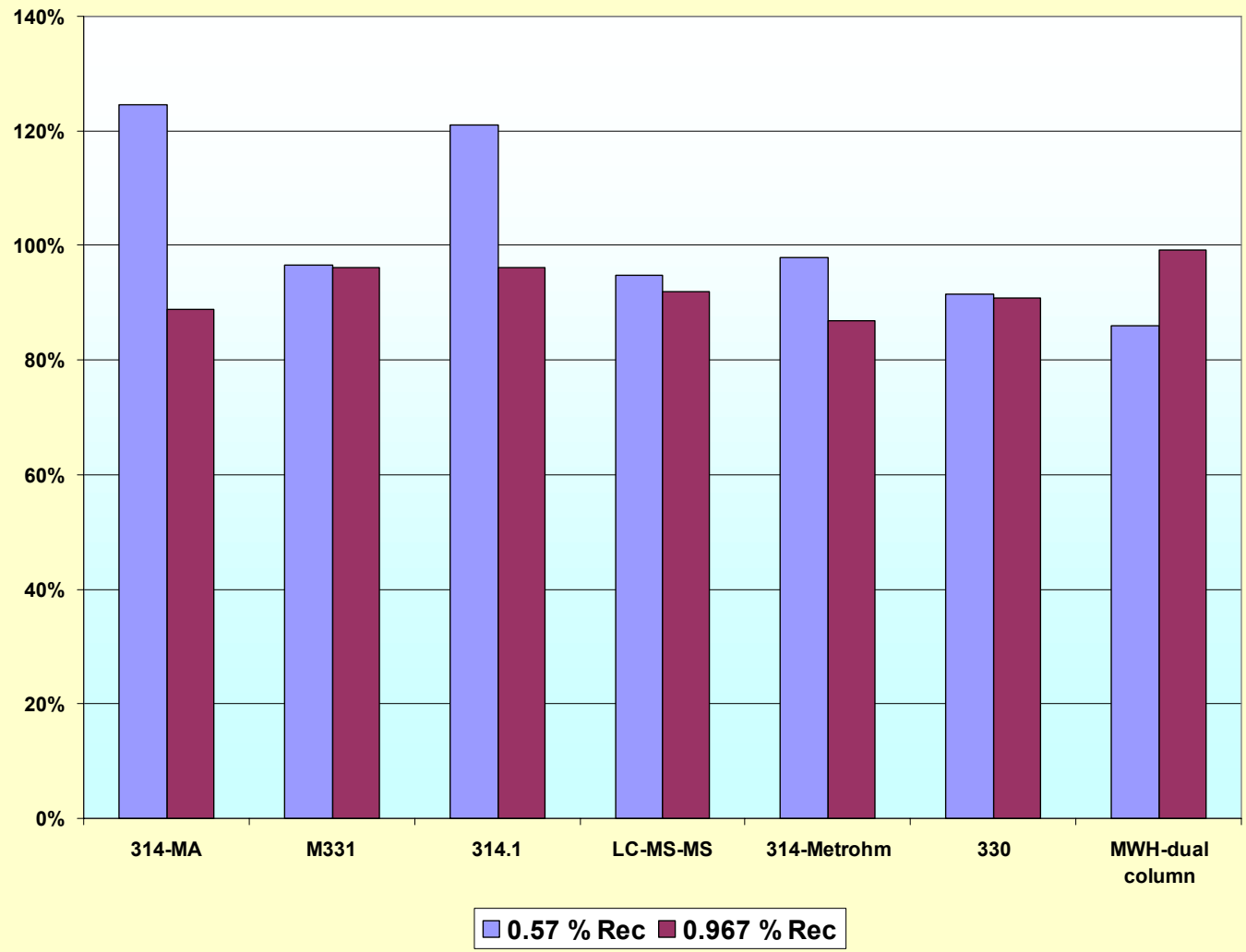
- EPA (331)
- SONVWA (customized LC-MS-MS)
- Dionex (314.1)
- Metrohm (314 and 330)
- MWH (Custom dual channel method)

- Note: In Subsequent slides we have also shown the 314-MA data from one lab from the double blind study for comparison

In 700 ppm TDS Almost All of the Methods Produce Valid Data

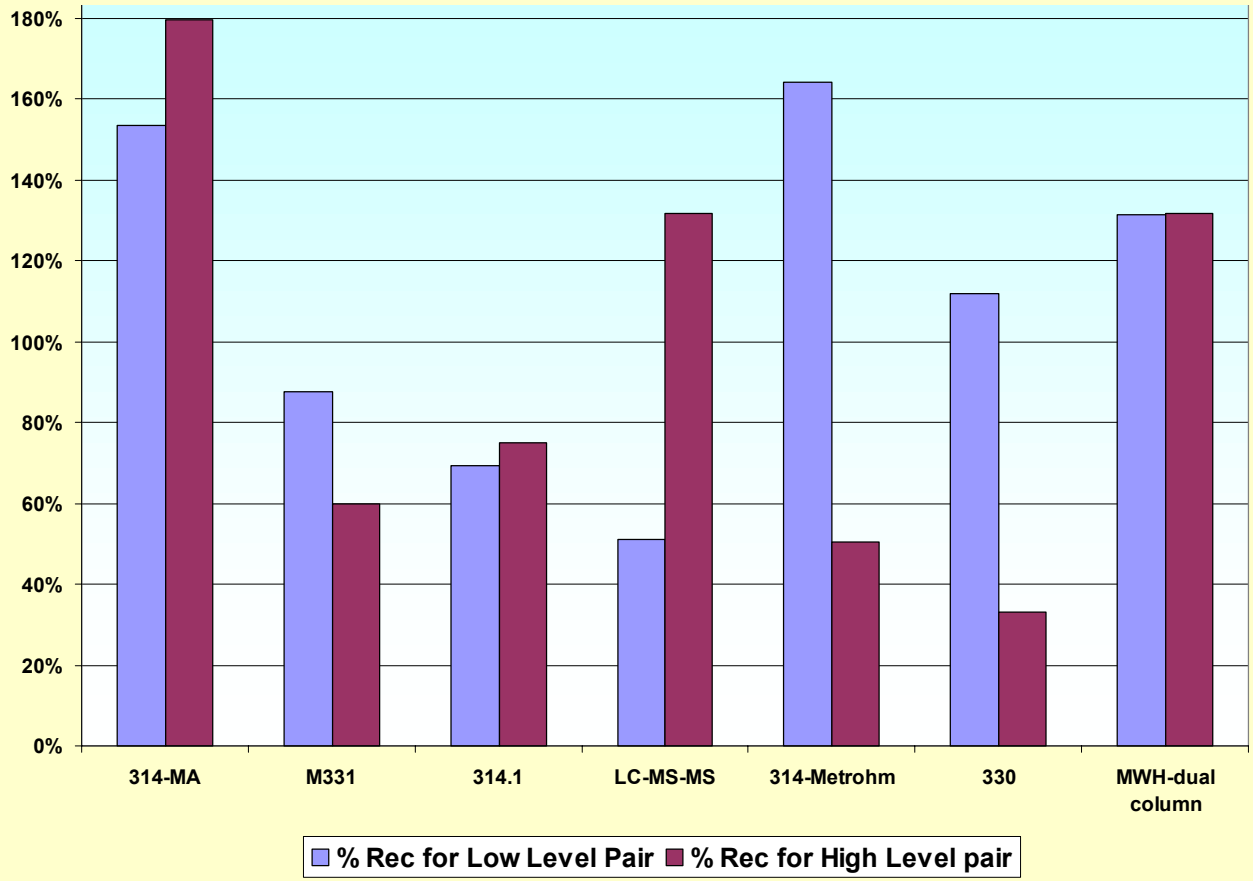


In DI Water, Each Method is Reliable, Even Down to 0.5 ppb



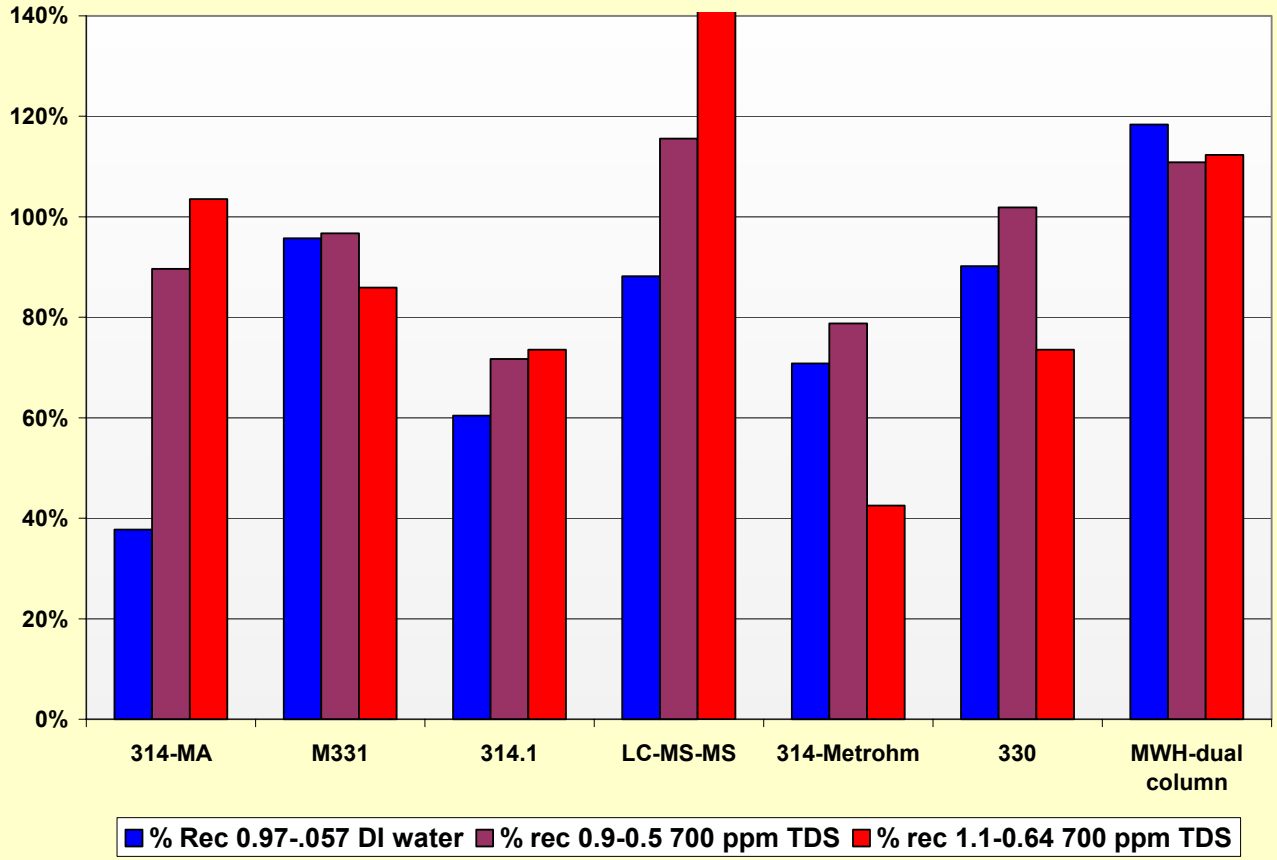
Although All Are Accurate, They Are Not Necessarily Able to Measure Small Differences (0.2 ppb) in 700 ppm TDS.

A method with an MRL of 0.2 ppb should be able to accurately differentiate values that are 0.2 ppb different



Precision is Better for 0.4 ppb Differences, But Not all Methods Are Sufficiently Precise, Even at Those Levels

A method with an MRL of 0.4 ppb should be able to accurately differentiate values that are 0.4 ppb different.



What Do These Data Say About Any of These Method at These Levels?

- Although "Detection" is reliable below 1 ppb, quantitative accuracy to establish trends is not necessarily robust
- Recovery for any of the NEW methods is good - averaging 80-120%
- Precision is not that good - each of the methods can differentiate 0.4 ppb, but not necessarily 0.2 ppb
- ergo - we need to be cautious in interpreting data at these levels

Conclusions

- There are Lots of available techniques to detect sub ppb CLO_4
- NONE of them are as precise as we would like
- ALL of them are adequate if one doesn't set P&A criteria too tight