Data Validation Saves Your Bacon

NEMC 2020

August 18, 2020

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Black Box Laboratory

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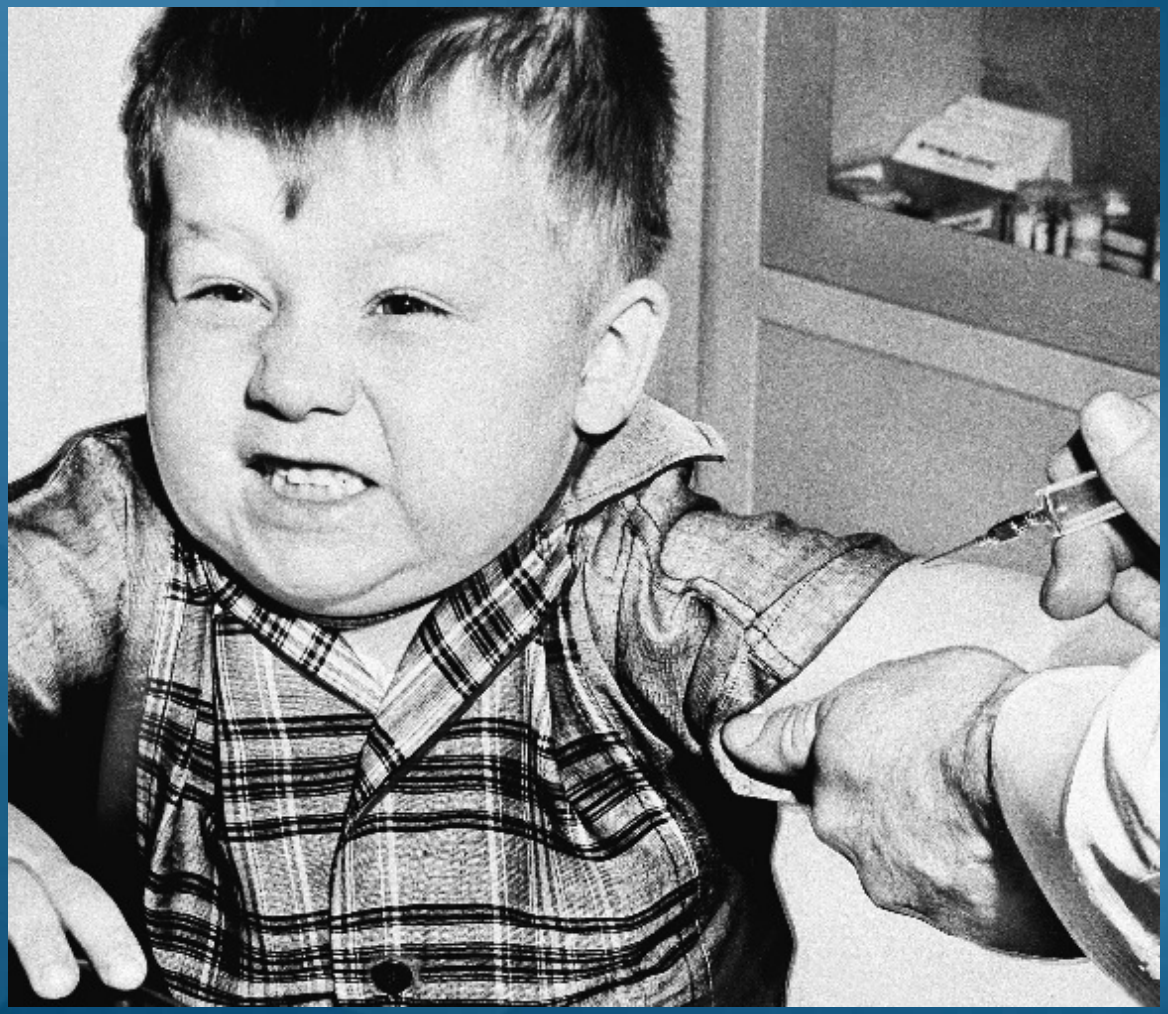
Why do Data Validation?

– It's like immunizations:



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But:
Having data validated just might save your bacon!

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“It takes too long”

- Validation adds too much time between the lab’s release of data and the availability of data that has been assessed for usability

“It adds to my costs.”

- Time =
- Money

- Data packages

“Qualifiers make my data look bad!”

MW-103	n-Butylbenzene	UJ	RPD high LCS/LCSD	
MW-103	Vinyl chloride	UJ	MS/MSD RPD biased high	
MW-103	Bromomethane	UJ	MS/MSD biased low	
MW-103	Dichlorodifluoromethane	UJ	MS biased low, MS/MSD RPD high	
MW-103	Chloromethane	UJ	MS biased low	
MW-103	1,1-Dichloroethene	UJ	Low reponse in CC	
MW-252	Bromomethane	UJ	RPD high LCS/LCSD;MS/MSD biased low	
MW-252	Bromodichloromethane	UJ	RPD high LCS/LCSD	
MW-252	Chloroethane	UJ	RPD high LCS/LCSD	
MW-252	cis-1,3-Dichloropropene	UJ	RPD high LCS/LCSD	
MW-252	Vinyl chloride	UJ	MS/MSD RPD biased high	
MW-252	Methyl ethyl ketone	UJ	Low avg RRF in IC	
MW-252	Methyl isobutyl ketone	UJ	Low avg RRF in IC	
MW-107	Vinyl chloride	UJ	MS/MSD RPD biased high	
MW-107	Dichlorodifluoromethane	UJ	MS biased low, MS/MSD RPD high	
MW-107	Chloromethane	UJ	MS biased low	
MW-107	Bromomethane	UJ	LCS biased low; MS/MSD biased low	
MW-65	Vinyl chloride	UJ	MS/MSD RPD biased high	
MW-65	Dichlorodifluoromethane	UJ	MS biased low, MS/MSD RPD high	
MW-65	Chloromethane	UJ	MS biased low	
MW-65	Bromomethane	UJ	LCS biased low;MS/MSD biased low	
MW-65 DUP	n-Butylbenzene	UJ	RPD high LCS/LCSD	
MW-65 DUP	Vinyl chloride	UJ	MS/MSD RPD biased high	
MW-65 DUP	Bromomethane	UJ	MS/MSD biased low	
MW-65 DUP	Dichlorodifluoromethane	UJ	MS biased low, MS/MSD RPD high	
MW-65 DUP	Chloromethane	UJ	MS biased low	
MW-65 DUP	1,1-Dichloroethene	UJ	Low reponse in CC	
MW-202	n-Butylbenzene	UJ	RPD high LCS/LCSD	
MW-202	Bromomethane	UJ	MS/MSD biased low	
MW-202	Dichlorodifluoromethane	UJ	MS biased low, MS/MSD RPD high	
MW-202	Chloromethane	UJ	MS biased low	
MW-202	Vinyl chloride	J	MS/MSD RPD biased high	
MW-202	1,1-Dichloroethene	J	Low reponse in CC	
MW-101	Vinyl chloride	UJ	MS/MSD RPD biased high	
MW-101	Dichlorodifluoromethane	UJ	MS biased low, MS/MSD RPD high	
MW-101	Chloromethane	UJ	MS biased low	
MW-101	Bromomethane	UJ	LCS biased low;MS/MSD biased low	

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“Most of the data don’t end up qualified so why bother”

- Only about 20% of my results end up with qualifiers so why bother with all that time and expense
- That means they must be good, right?
- OR…

“I need those really low RLs (or MDLs) to support the project limits”

The validator qualified the NDs as UJs and documented that the low end of the calibration wasn’t supported

“We’ve been doing these samples forever”

- We know the site history and we don’t expect any surprises

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“We’ve been using this lab forever”

- We know the lab and we aren’t expecting any surprises

And the all-time favorite is:

- My lab is certified, so everything is good, we can trust the results
  - What is accreditation and what does it mean
  - NELAP, DoD, DoE, A2LA, States, VAP, ISO17025, etc.
    - Quality System/Management System
      - Ethics
      - Corrective Action Process
      - Regular controls / limits
      - Validation of methods – demonstrate capability of the lab
      - Demonstration for the analysts capability to perform the method within control limits
    - Traceability
    - PTs

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Certified Lab

- Quality system
  - Training
  - Documented procedures
    - SOPs
    - QA manual
    - Policy statements
  - Oversight
  - Review
  - Ethics program

When you need defensibility

- Remediation – responsible parties – allocating costs
- Legal - Property transactions
- Liability
- Reporting to agency – discharge permits
- Natural Attenuation
- System/treatment efficacy
- Other ??

- Will your data stand up to scrutiny?

Sample Integrity

- Sample integrity
  - Field
  - Proper techniques
  - Equipment
  - Containers
  - Preservation
  - Documentation
  - Representative

In the field – Representative?

Sampling – what is used and how's it done

Example: MWs for property transfer – simple – water samples from MWs

Owner – clean - good to go

Buyer - high metals content

Requested the sampling logs, interviewed the samplers, and then went and watched how the samplers were collecting the samples.

Samplers dropping the pump and stirring up the silt

What are you really trying to sample? (Representativeness)

(Like the soil sample in the desert.)

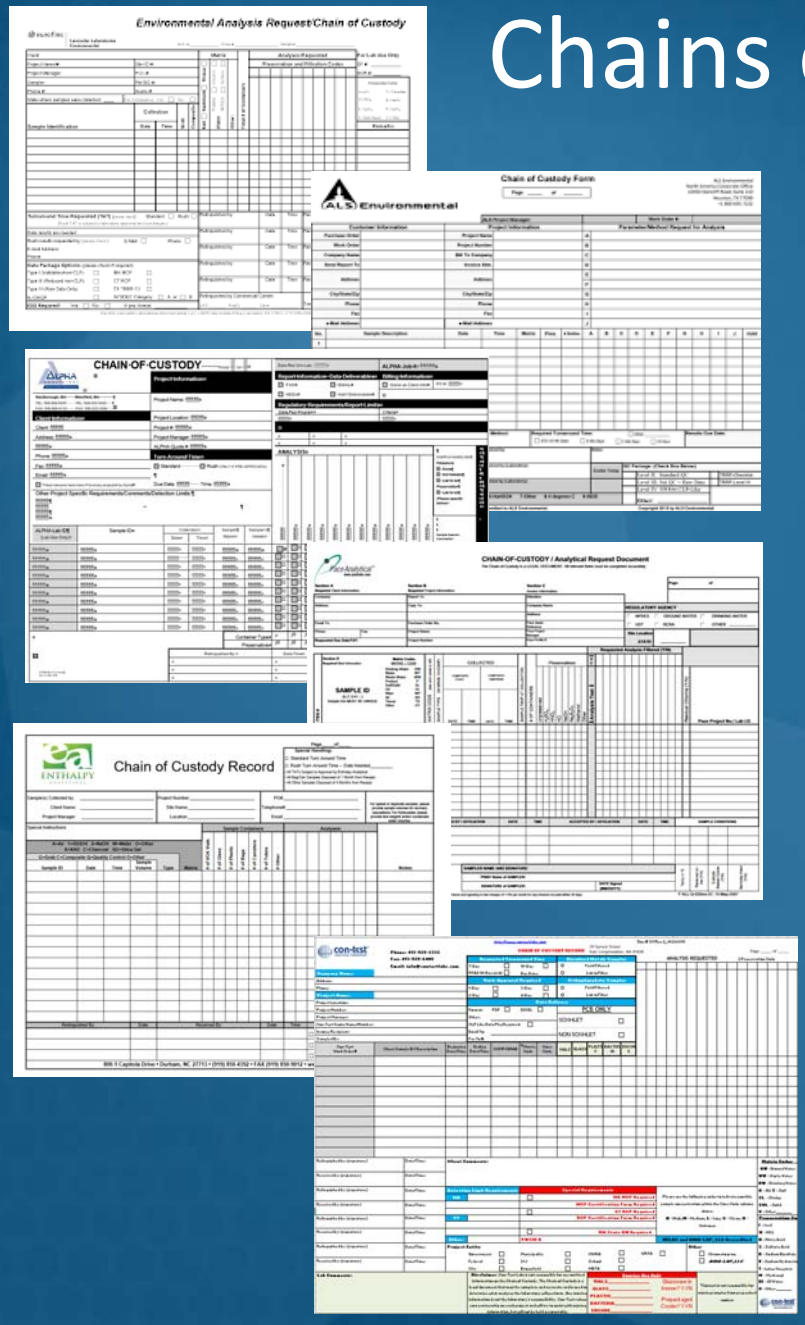
Sample Integrity/ Representativeness

- After lab receipt:
  - Headspace for VOCs
  - Solids/Soils - How is aliquot chosen?
  - Decant moisture?
  - Dry the sample?
  - Remove materials from the sample?
  - Representative of the entire sample?
    - ISM
    - Cone and quarter
    - Particle size reduction / sieving
  - Storage

Field Blanks – Why bother?

- BTEX in air samples from truck/generator exhaust
- Toluene from tape used to seal the VOC vials
- Solvents in the trunk with the sample bottles even in the same cooler
- THMS (used tapwater for decon and EBs)
- Gloves – LL Hg
- MeHg – dental work
- PFAS – EVERYTHING!!
- TB container wasn't with the sample containers until they were shipped

Chains of Custody



- On paper or online
- Essential info.
- Sample IDs
- Collection date/time
- Samplers
- Signatures, dates, times,affiliations
- Analysis requests
- Etc.

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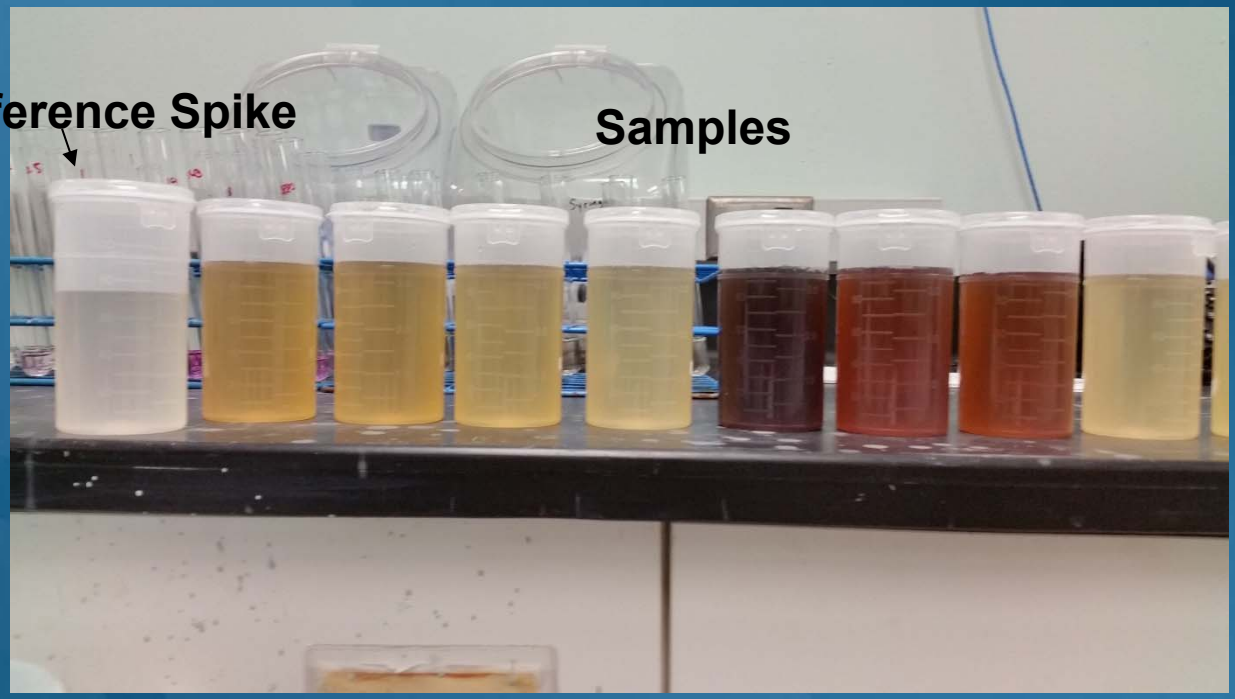
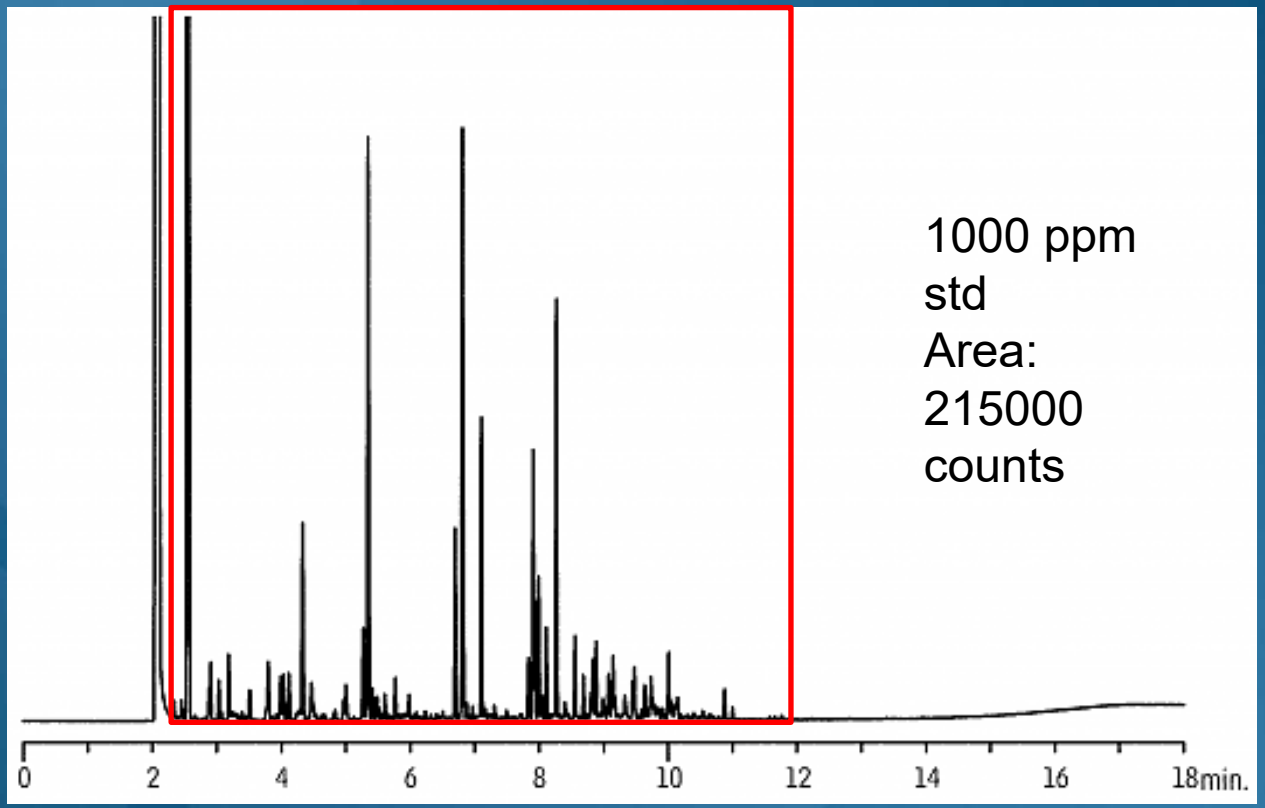
Methodology

You may get what you ask for.

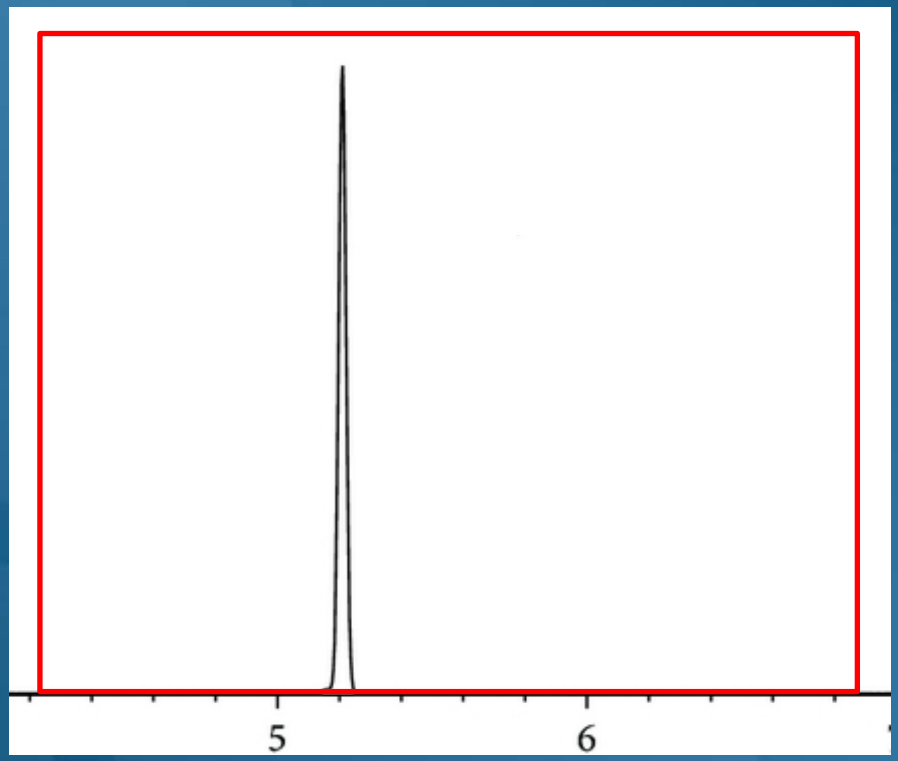
Hexavalent Chromium (Cr+6) Colorimetric



GRO – gasoline range organics



GRO – gasoline range organics



980 ppm
Response:
207000 counts

PCE

GRO/DRO

- Other things – Imposters

	GASOLINE (ppm)	DIESEL (ppm)
SPINACH	<10	60
CARROTS	<10	10
DEADORA TREE	1,200	600
MOSS	<10	<10
CEDAR TREE	1,400	2,200
PINE TREE	450	400
DANDELION	<10	140
DAISY	40	40
RHODODENDRON	20	80
ORANGE JUICE	300	

Lisa Bentley, Amy Gray, Jane Dorr - Friedman & Bruya, Inc.

TPH by EPA 8015: Measurement of Non-PHCs (2)

Measurement System – Verify Performance/Tuning/Resolution

- Chromatography
- Mass Spec
- Weight measurement
- Absorbance
- Detector specificity
- Etc.

Measurement System - Calibration

- RFs / CFs / RRFs (reflects a linear response)
- Linear regression
- Quadratic equation (reflects issues)
  - Some compounds that don't respond well to the methodology used and results are a WAG no matter what
  - Other uses for Quad:
    - Contamination in the system throws off the low range
    - Detector response is maxed out to meet the reporting limits so it flatlines
    - Poor practice in standards – dilutions from stocks with poor precision which has a higher effect at the lower concentrations

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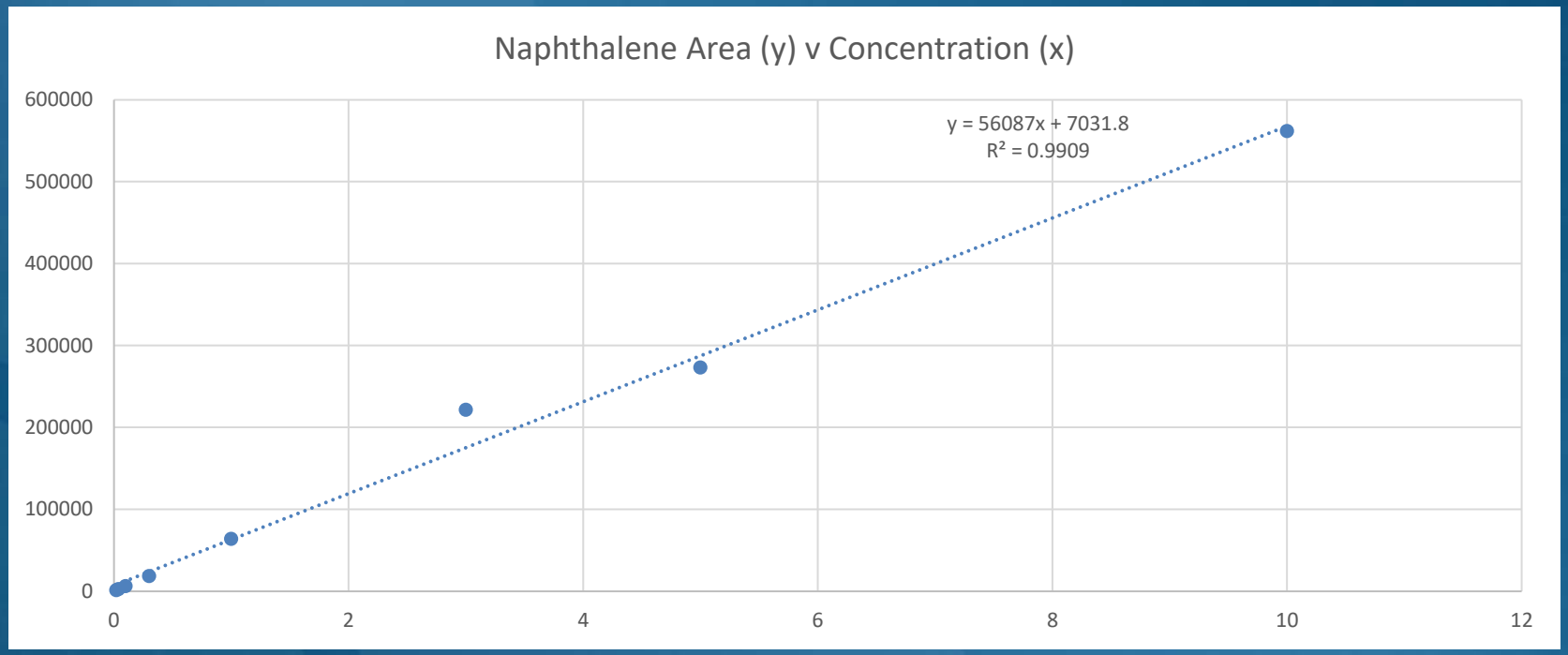
Ideal = Direct Correlation Response / Concentration



Problem Analytes – Poor Performers

- Methods
  - Ideally - method designed for each analyte and the sample matrix
  - There are hundreds of analytes of interest so they have to be run together
  - There are some that the method will cover well, some not so much – poor performers
    - Kepone by 8270
    - Ketones by 8260
    - MMA by 8151

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Alternate Calibrations – How about a Quadratic Equation

- There are compounds (poor performers) that are a problem – quadratic is the best you can do
- But a quadratic is not a good solution for a good performer on a measurement system that is performing poorly
- There are reasons they should be a last resort and used with great caution

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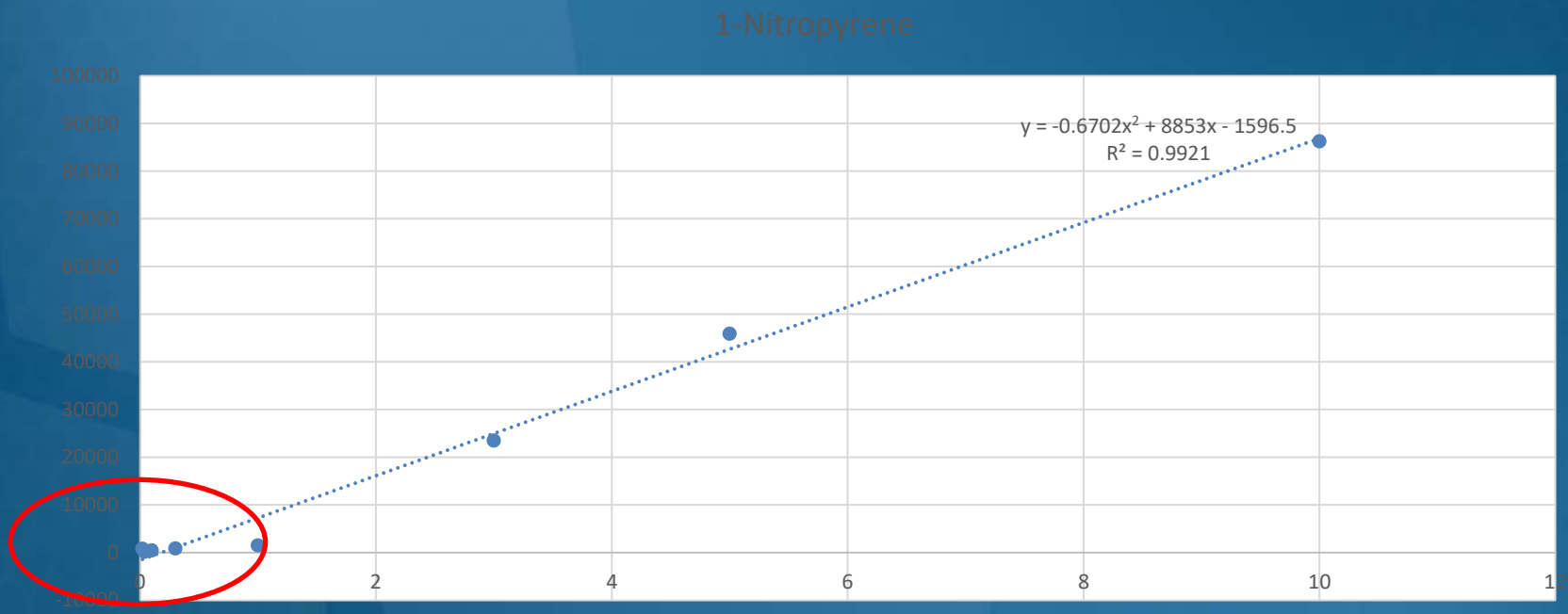
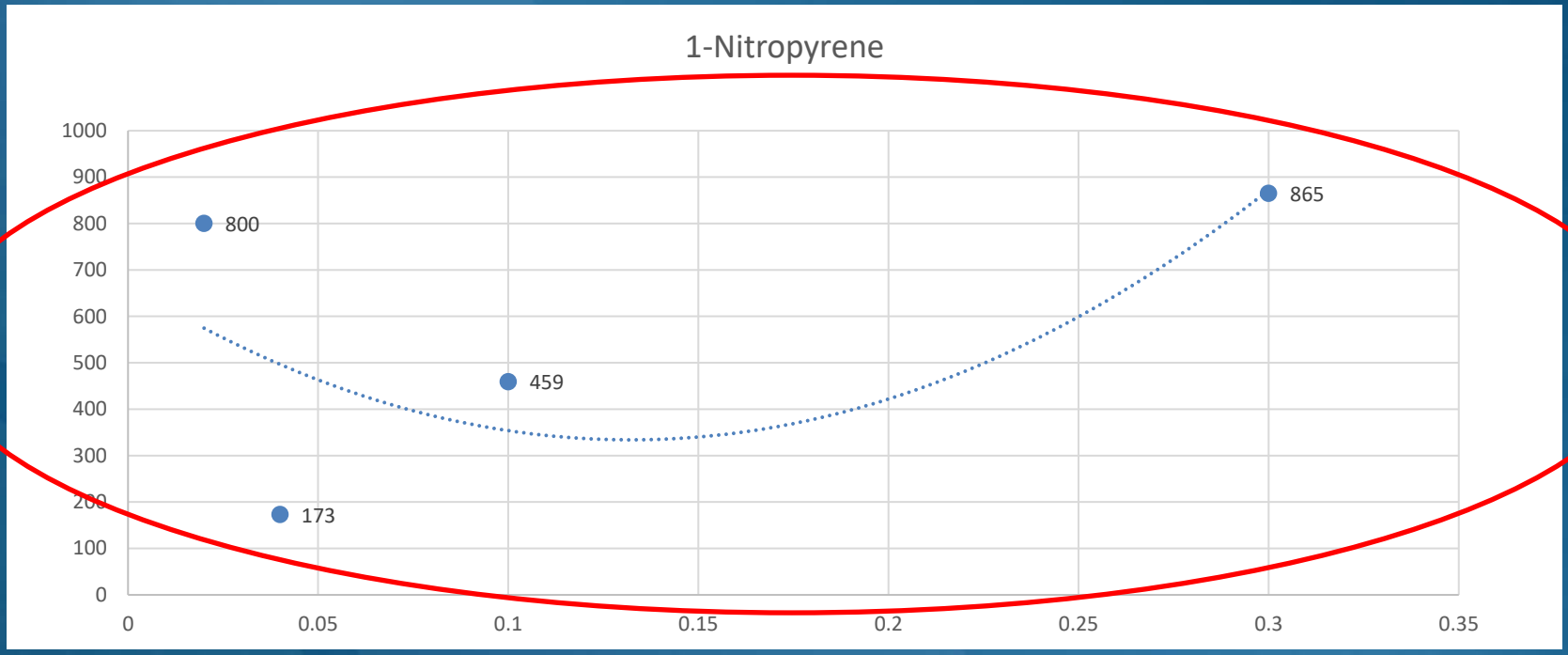
Looks pretty good right?



The low end


1-Nitropyrene
1000
900
800
700
600
500
400
300
200
100
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
800
459
173
865

Measurement System

- Other Calibration Issues that steal your bacon

- Lab using grand mean – not okay!
  - Can have some pretty big flyers and still pass
- Marginal exceedances – sort of okay
  - Again, can have some biggies and still get by (are the exceedances the site compounds of concern?)

- Keep in mind the difference between lab performance criteria and DV – usability of the results – limitations / liabilities

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Measurement System

ICV

- Verify with a second source
- Separate source where available
- At least a different lot
- Verify concentration of primary standards

CCV

- Verify ongoing accuracy of calibration model

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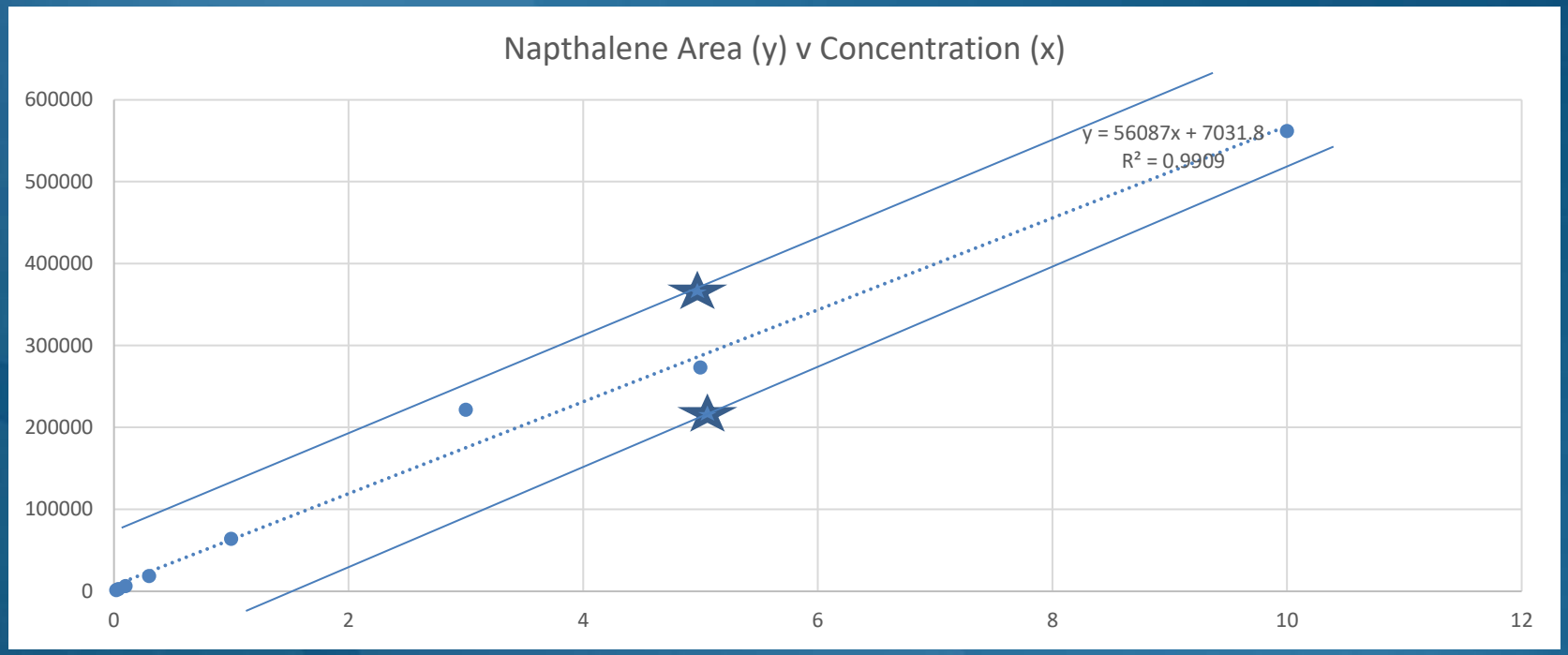
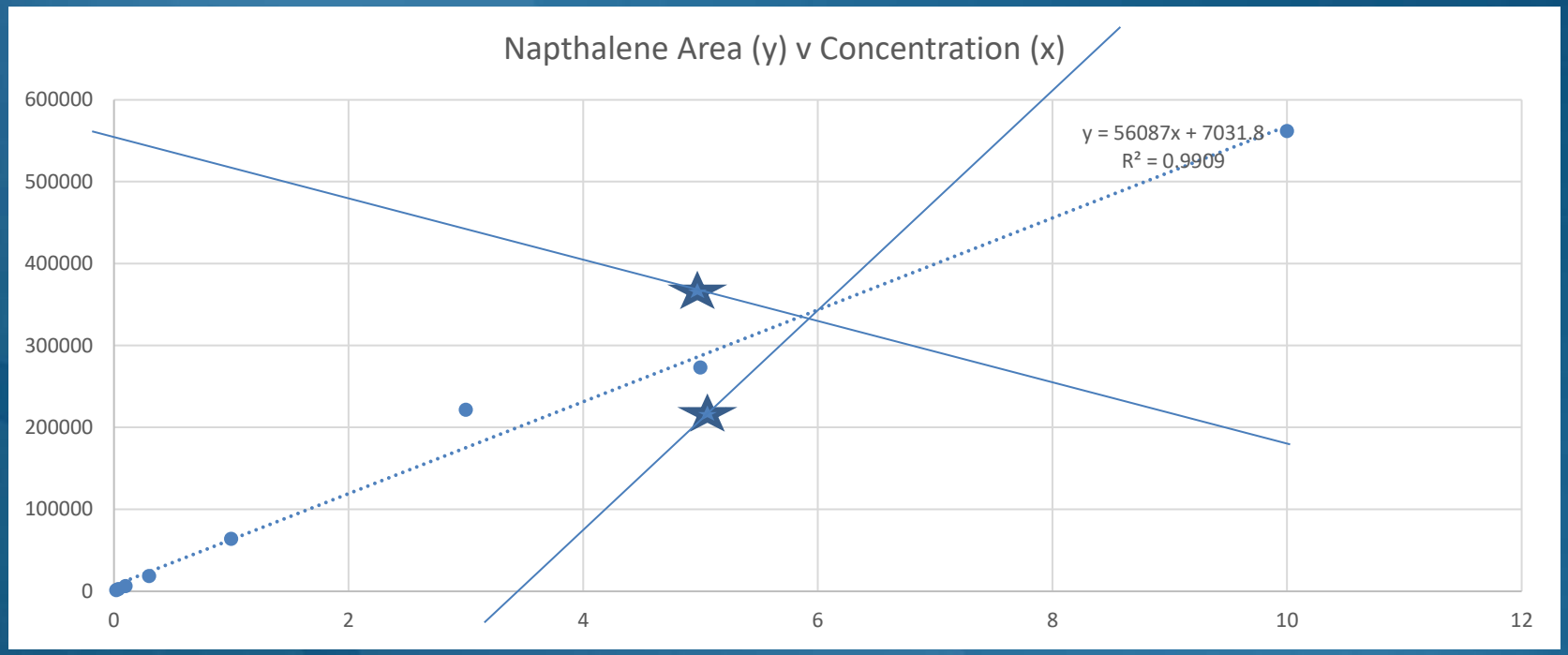
CC – measured at midpoint



CC – measured at midpoint



Who knows?

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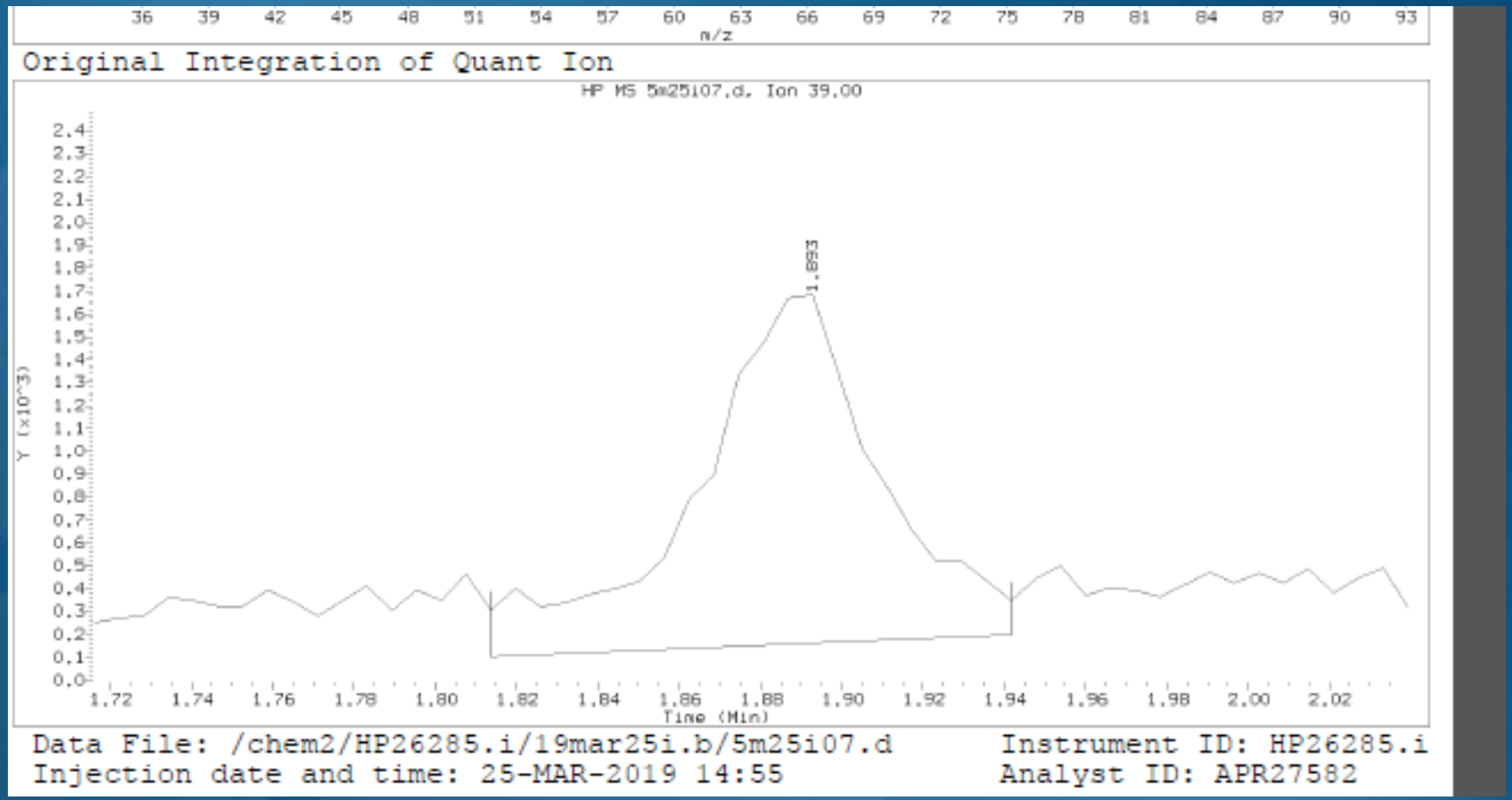
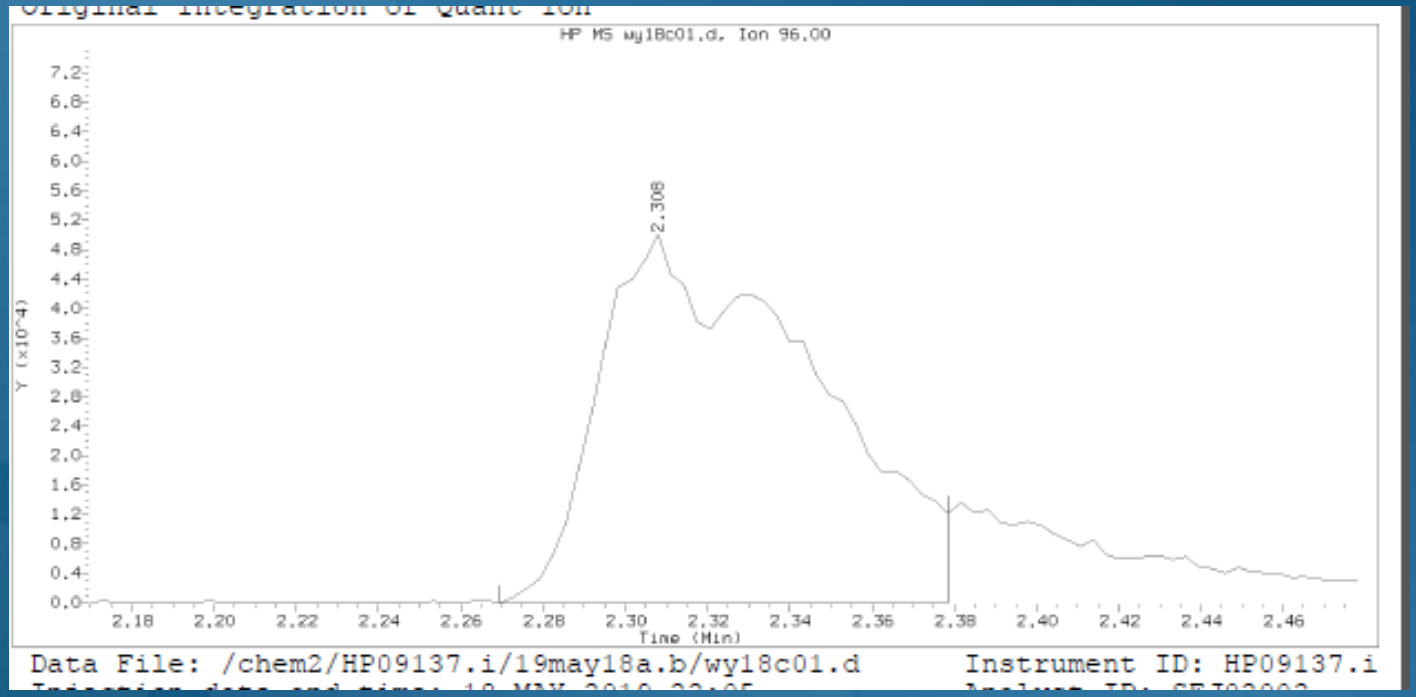
Quantitation – when it depends on integration

- Integration
  - Consistent
  - Normal gaussian peak – good integration
  - How do you integrate bad peaks? Tailing, split, co-elution - Consistency
  - Slice taken to baseline on a hump of UCM – high bias
  - Integration across noise
  - Integrating several discontinuous peaks

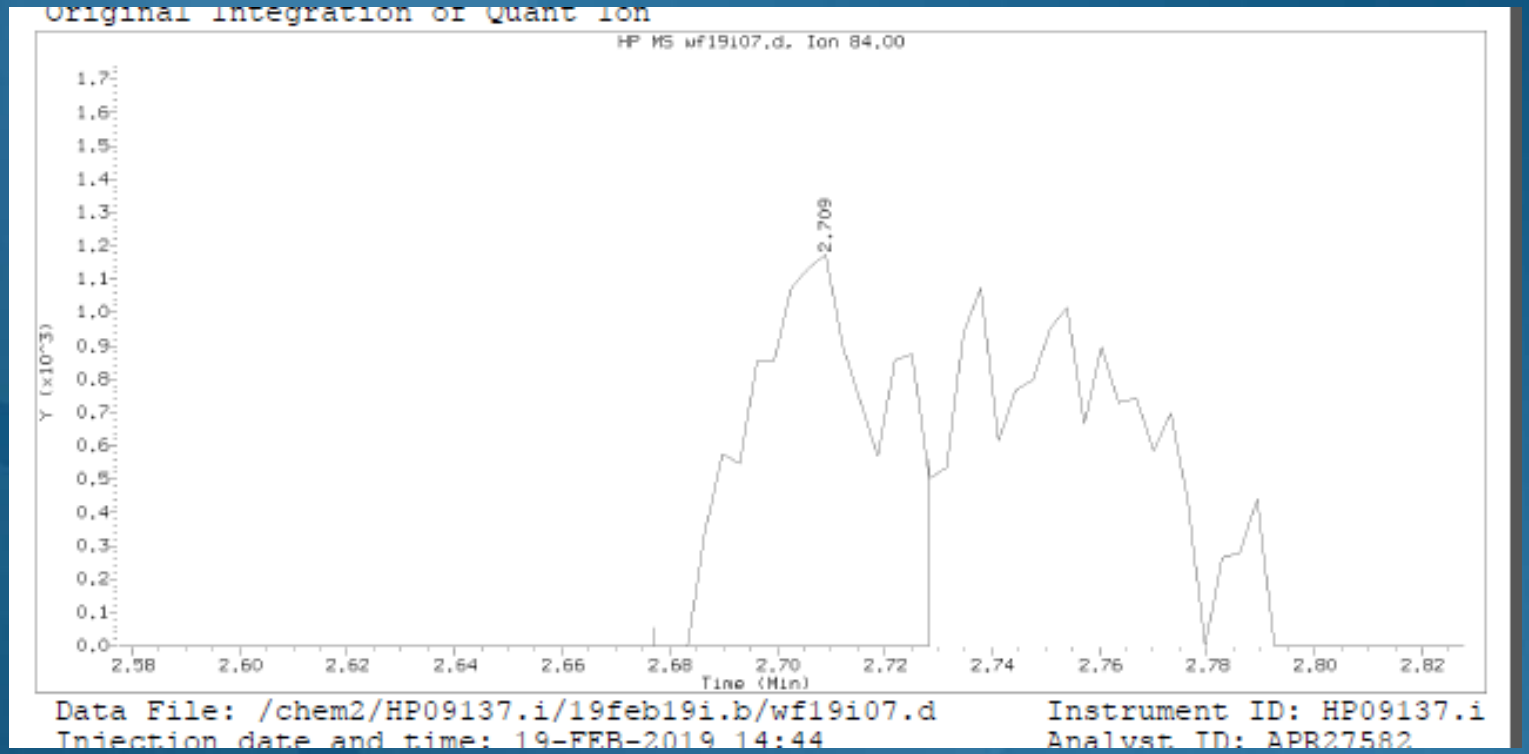
What about this?



How about this one?



Meanwhile at the reporting limit…..



Reporting limits ? Unsupported ?

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MDLs/RLs/PQLs/LODs/LOQs/LOL

- RL = PQL = LOQ
  - Authentic standard at known concentration
  - Part of the calibration
    - Can be lowest point
    - Cannot be below the lowest point
  - BUT WAIT:
    - The standards are prepared in clean solvent
    - Methods where the standards are extracted, digested, derivatized – they are blanks!
    - May be verified (MRL) or a LL CC, or may not
    - Some methods and programs require verifying with every sequence/batch
    - But if only run at the beginning - > What happens by the end of the run?

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How sturdy is that limb ?

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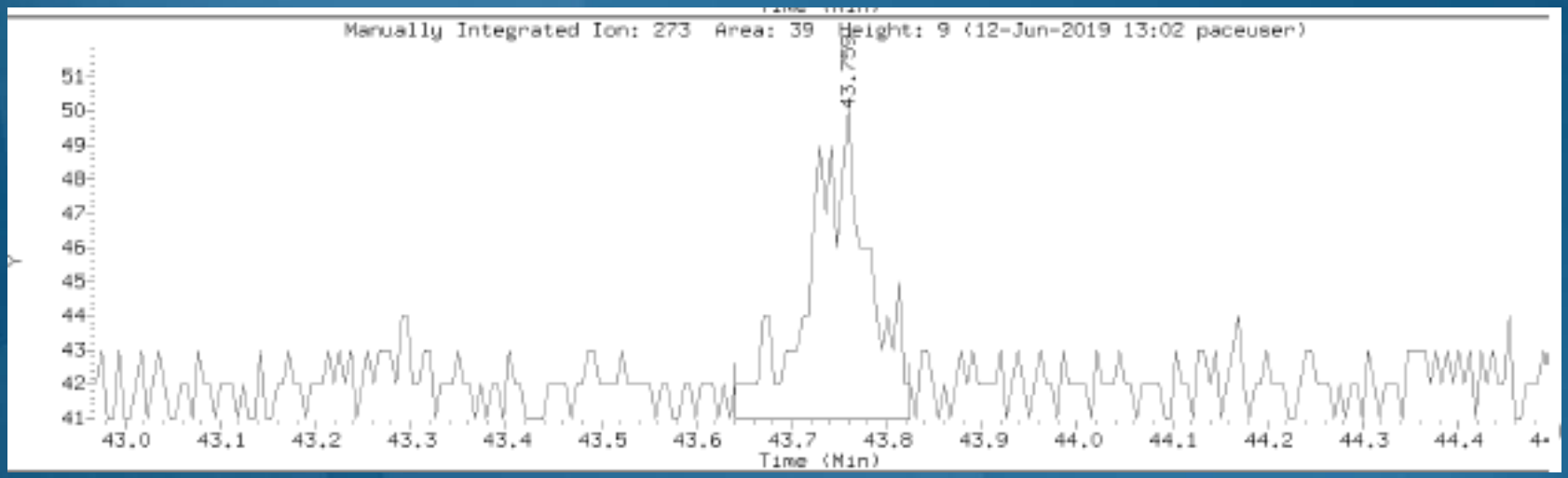
MDLs/RLs/PQLs/LODs/LOQs/LOL

- MDL = LOD = DL = IDL
  - Statistical determination of the concentration level at which the confidence that laboratory would detect the analyte is 99:1
  - Based on replicate analyses of clean blank spikes at low concentrations (2-4 times the expected MDL)
  - If it's verified – concentration is at least 2 times the MDL, maybe more
  - And again, it's a clean matrix, ideal conditions
  - Old Method
  - New Method

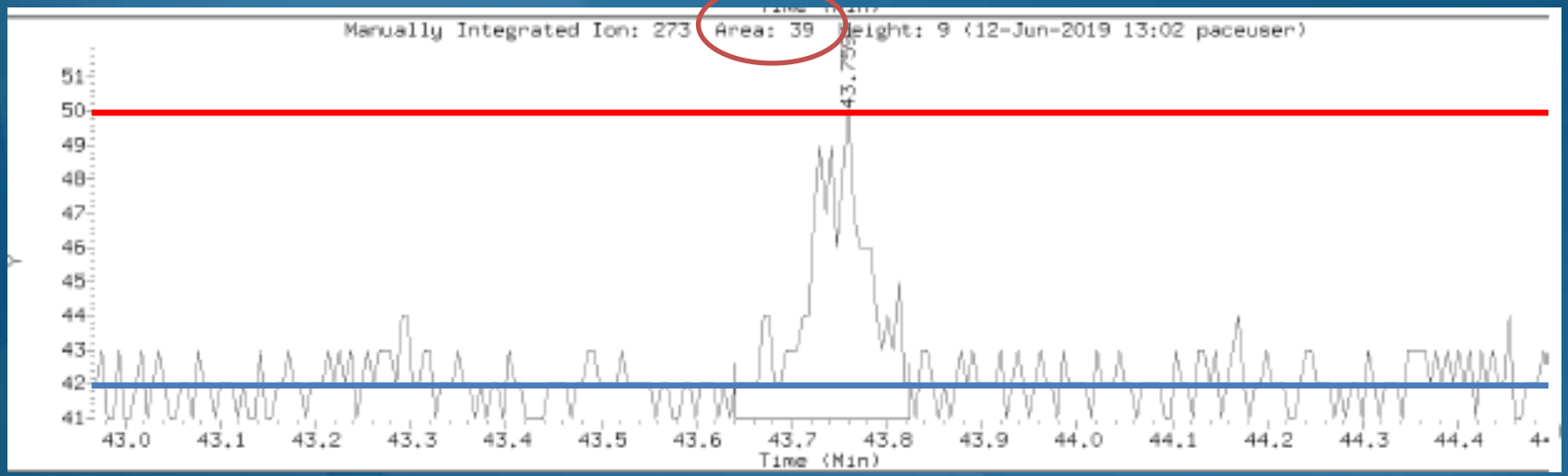
Spiked Analytes

- Blank spikes – Ideal conditions, clean matrix
- Matrix spikes – sample matrix, but only 1 per batch
  - May be from another project or client so not pertinent to your samples
  - What concentration is it spiked at?
    - High concentration
    - Mid-level concentration
    - Is there anything spiked at a low concentration to support NDs?

Understanding S/N:



Understanding S/N:



Identification

- The target compound list reported doesn't match the calibration standards
  - What if the compound(s) you are most interested in wasn't actually analyzed for
  - What if the calibration wasn't accurate
  - What if the lab never checked the accuracy of their calibration standard concentrations – second source

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BLANKS
Look very closely

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BLANKS

You may miss something important.

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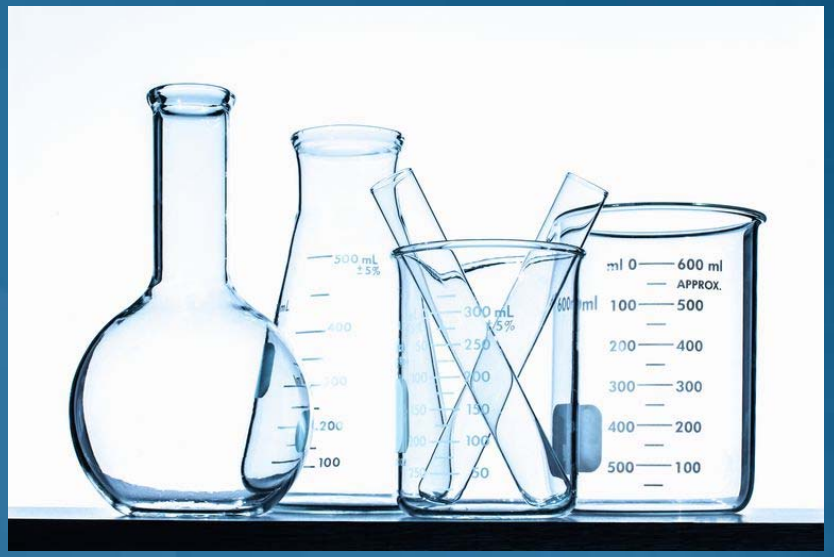
Laboratory Blanks

- Calibration
- Instrument
- Method
- Dilution
- Disaggregation
- Leachate
- Preparation
- Clean up



BLANKS

- Lab blanks sanitized
  - Software set to not report anything below the RL
  - QAPP requirements <RL so not reporting anything <RL
  - Hits removed from the quant report by

What's really out there?

- Dioxins and furans reported in all of the site samples and lots of those concentrations were above the RLs, many above the project action limits

- SPLP leachate blanks

Problems from lab contamination

- PFAS contamination – raised reporting limit
  - Same issues with PCBs and DDs/DFs
- Pure transformer oil – PCBs
- Pure PCP
- Cyanide
- Sulfide
- LL Hg from PTs sent by an industrial client's QA program

Error Term

- IC 15 – 30 % sometimes higher (concentration/accuracy)
- ICV - 30 % (concentration/accuracy)
- CC - 20-30 % sometimes higher (accuracy/sensitivity)
- IS – 50-200 % (sample specific) (injection quality/sensitivity)
- SS – lab limits!! 70-130 % for DV limits so another 30 % (sample specific) (recovery/accuracy)
- LCS/MS – 70-130 % (batch specific) (recovery/accuracy)
- Duplicate precision – 30 – 50% (batch specific) (precision)

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Surrogates / Spikes

- Lab limits will reflect what is “in control” for them
- Method may stipulate – lab may use NCMs, CAs, to handle excursions
- But what does it mean to the data user
- What about bad %R in a blank or blank spike – “matrix effect” (from the lab narrative)

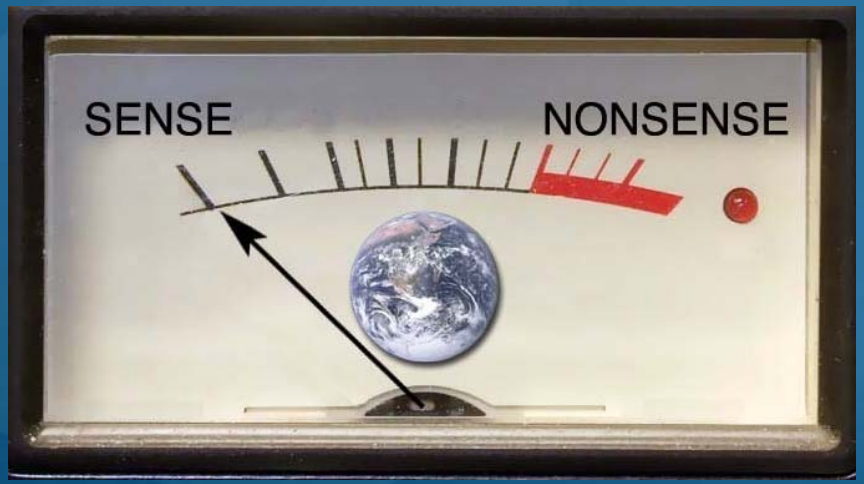
Observations

Report Narratives - If there was a problem the lab would tell me, right?

- Complete?
- Reviewed by lab?
- Specific – deviations
- Specific – associated samples

Things that don’t make sense

- Total smaller than the parts
- Dissolved greater than total
- Species greater than the total



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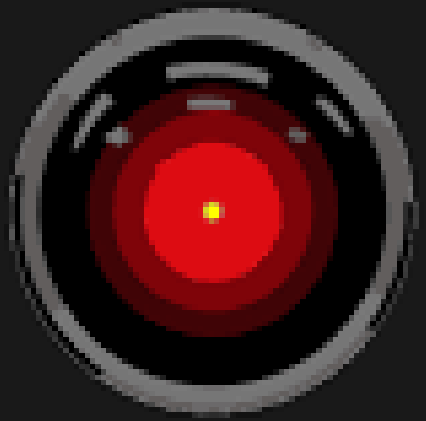
LIMS isn't always right

- Sample pH
- Solid samples reported with high (caustic) pH
- Must be treated as hazardous waste under RCRA
- No reason for high pH based on the nature of the samples
- Turns out the lab adjusted the pH value for percent solids (when you don't know what your LIMs is doing)



I AM COMPLETELY
OPERATIONAL AND
ALL MY CIRCUITS
ARE FUNCTIONING
PERFECTLY.

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Sometimes it's what you aren't looking for…..

- Not a target list compound for the site so not reported

- Sometimes TICs are important

Preservative in cutting oil – leach field

Questions?

ECS

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