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NEMC

Examples of In-Depth Data Integrity Review

-out of the box approaches

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Purpose

- Discuss ideas of how to check data integrity beyond the typical quality control and data review procedures.

- Focusing more in the details and thinking out of the box can reveal biases and unexpected consequences.

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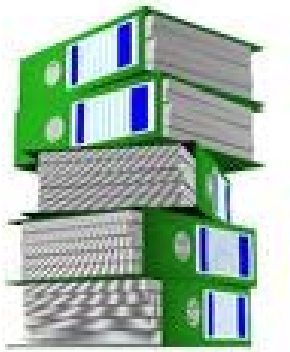
The Basics

- Quality Management System
  - Quality Manual, Policies
  - Audits, Management Reviews, etc.
  - Standard Operating Procedures
  - Training
  - Quality Control Checks
  - Data review
  - Control Charts
- Regulation, methods



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The Basics Revisited

- Understanding vs. assuming the reasons behind the basics

- Thinking that some bureaucrat came up with all that QA/QC….
- Assuming that costs will be higher with all the QC requirements….
- Training does not include a good understanding behind the reasons of basic QC requirements!!!

- Not so true right now…new generation at EPA, consensus at TNI, consensus at Standard Methods, consensus at NEFAP, etc.
- Most of us know better! When QC is incorporated up front, it becomes part of the system, helps make better decisions, including saving money in the long run. Data of known quality.
- True!

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.....supporting the Basics

- The PARCCS parameters
  - Precision
  - Accuracy
  - Representativeness
  - Comparability
  - Completeness
  - Sensitivity

BIAS

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Field - Basics

- Is there a QA Manual?
- Standard Operating Procedures?
- Training Records?
- Proper Documentation?
- Internal Audits?
  - Mislabeled sample?
    - Dry lab
- Data Review?
  - What does it include?

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Field considerations

- Unusual Results
- Positive results when historically samples were non-detects

- Wrong Preservation
  - pH still <2 but…. wrong acid in the container
  - Acid preservation needed, non in the container, no resampling done

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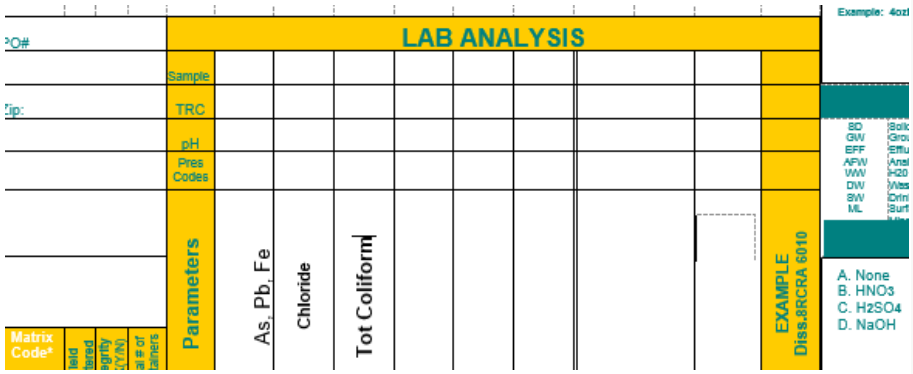
Chain of Custody

- Chain broken, incomplete, or not kept
  - Missing signatures
  - Missing seals
  - Missing dates or times
  - Type of analysis requested not listed



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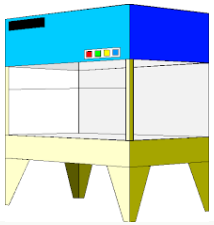
Sample Handling

- Samples sitting in sample receipt bench area for long periods of time
- Samples not returned in proper storage
- Dusty prep areas, hoods, balance, bench areas (behind or in between equipment.)
  - Dust carries contaminants
- Glassware (i.e. Volumetric flasks, pipettes have not been adequately cleaned.)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Interviews with analysts

- If you do not already know, ask how they got the responsibility to run a particular method.
- Who taught and trained them? Was the training a "Crash Course"?
- Do they feel comfortable running the analysis?
- Is there anything they want to talk about?
- What do they like most about what they are doing?
- What do they like the least?

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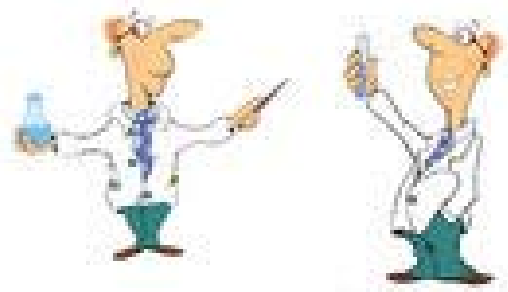
Interviews with analysts

- "How long do you digest samples?"
  - water samples? solid samples?
  - Compare answers vs. the bench sheets, vs. the SOP, vs. the method
  - Compare answers from different analysts that perform the same procedure
    - Compare QC Recoveries, sample results (historical data)
  - Consider who you perceive as a good worker.
    - Is one person in prep faster than others?



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Maintenance Logs

- Is the logbook there just to meet a requirement?
- Is it being used only when something major happens?
- Is there another place where routine maintenance is documented?

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Maintenance Logs

- How often do you look in the maintenance log book?
  - What can it tell you beyond the obvious?
    - Is something happening routinely?
    - Are there any identifiable trends?

Connect the dots…….

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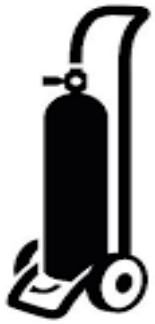
Maintenance Logs

- **Gas Chromatography (GC/GCMS)**
  - Decreased detector sensitivity by increasing detector background noise
  - Baseline drift or wander
  - Contaminant peaks
  - Noisy or high offsets of baselines



New gas tank

www.agilent.com/chem

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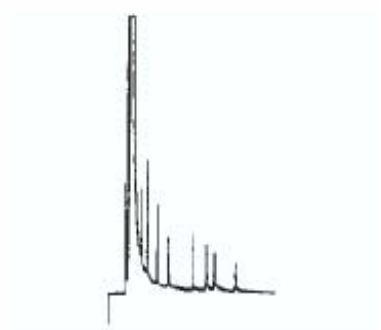
Maintenance Logs

- **Gas Chromatography (GC/GCMS)**

Normal Peaks

Tailing Solvent Peaks



Wrong Peak Ratios

Replaced a damaged ferrule

www.agilent.com/chem

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Maintenance Logs

- Ion Chromatography:
  - High background conductivity, low noise
  - Linearity issues

New Eluent

-contaminated with an anion of strong acid

-eluent too weak or too strong

ION manual, SeQuant

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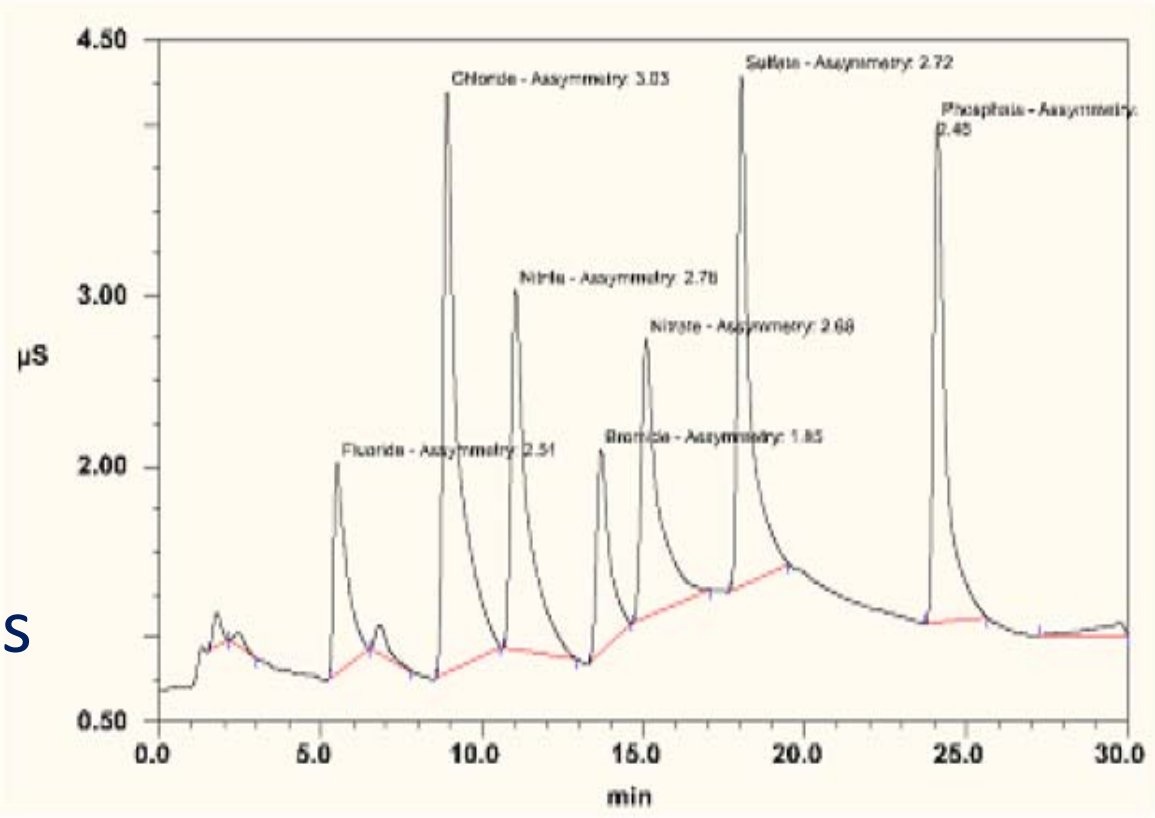
Maintenance Logs

- Ion Chromatography:

  Tailing Peaks



Incorrectly Installed Capillary Tubing Fittings

https://www.thermofisher.com/search/results?query=Dionex&persona=DocSupport&navId=4294959596

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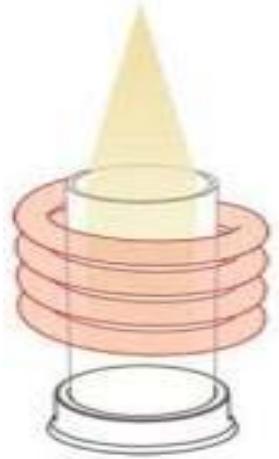
Maintenance Logs

Metals ICP: Lost sensitivity

Replaced or removed the ICP torch for cleaning



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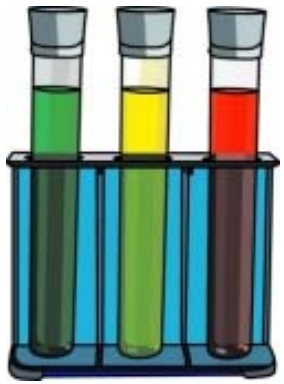
PT Samples

- PT has failed but all my QC is passing
- I always pass my PTs
  - Low biased, high biased passing PT results.



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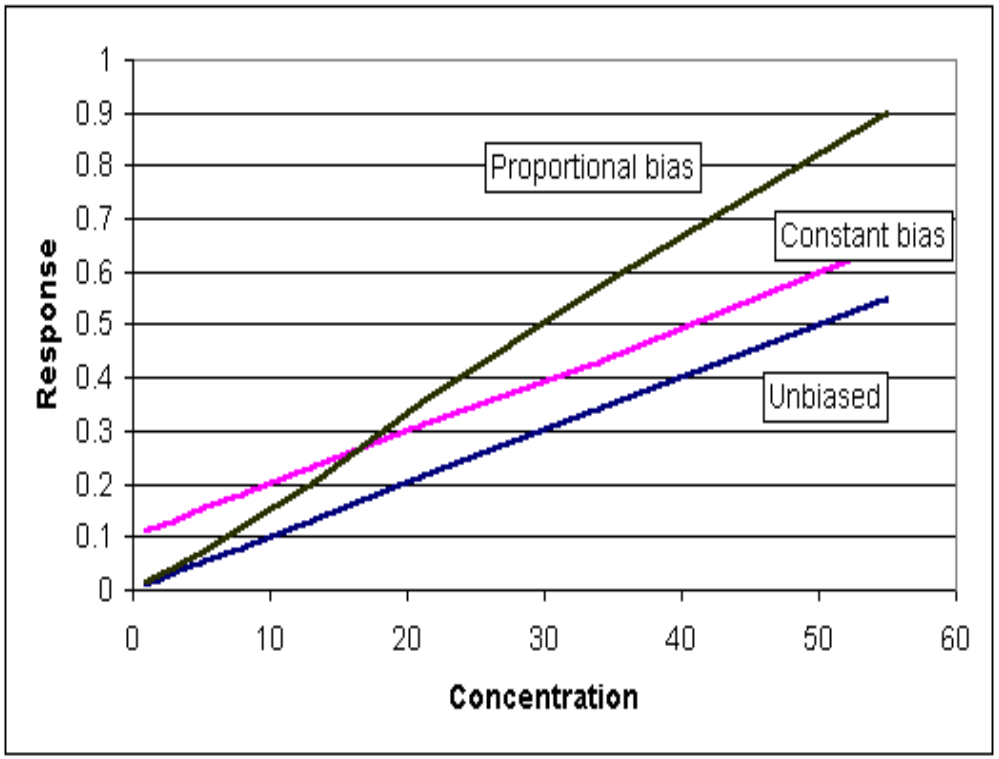
Calibration Considerations

- Calibration Errors Leading to Bias
  - Unbiased results (blue),
  - Constant bias (possibly due to a contaminated matrix)
  - Proportional bias (perhaps associated with a standard that was higher than stated, and then serial dilution was made).



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Calibration Considerations

- Significant figures
  - in your calibration
  - absorbance
  - calibration point recoveries
  - responses
- What volume is the instrument injecting and what resolution does its absorbance meter report?
- What is the true value of the standard in the COA vs. what the instrument is reading?

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Recalculating the results

- ICP SW 846 6010B

$$\text{Concentration} = \frac{(Cx)(Vt)(Df)}{(Vo)(\%M)}$$

Where:

Cx = Raw data concentration

Vt = Final Extract Volume

DF = Dilution factor

Vo = Volume or weight of sample extracted

%M = Percent moisture, applicable to soils and solids matrices only. (For water, %S = 1)

#	Sample I.D.	Compound	Raw Data Conc.	Final Volume (mL)	Dilution Factor	Sample wt/vol (g)	% moi	Reported Concentration (mg/Kg)	Calculated Concentration (mg/Kg)	% Diff	Acc (Y/N)
1	[redacted]	Al	709.7	50	1	2	1	18,000	17,922	-0.4	Y
		Ba	4.216	50	1	2	1	110	106	-3.2	Y
		Be	0.0231	50	1	2	1	0.58	0.58	0.6	Y
		B	0.0975	50	1	2	1	2.4	2.5	2.6	Y
		Ca	46.64	50	1	2	1	1,200	1,178	-1.9	Y
		Cr	2.858	50	1	2	1	71	72	1.7	Y

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GC/MS Compound Quantitation

- Evaluate criteria for quantitation such as formulas and calculations used for calibration response factors, linearity assessment, and final analyte concentration

- Must use all contributing data and attain the data from raw data printouts

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Example calculations

[redacted]

VALIDATION FINDINGS WORKSHEET
Sample Calculation Verification

Page: 1 of 1
Reviewer: QR
2nd reviewer: _____

METHOD: Inorganics, Method SeeCover-353.2

Please see qualifications below for all questions answered "N". Not applicable questions are identified as "N/A".

Y N N/A Have results been reported and calculated correctly?
Y N N/A Are results within the calibrated range of the instruments?
Y N N/A Are all detection limits below the CRQL?

Compound (analyte) results for NO_3/NO_2-N reported with a positive detect were recalculated and verified using the following equation:

Concentration = $y = 0.112x - 0.00413$

Recalculation: $(3.72(0.112) - 0.00413)10 = 4.125 mg/L$

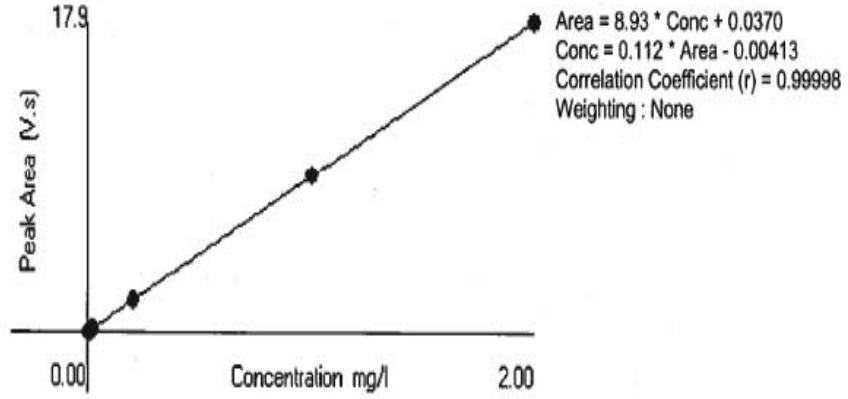
area = 3.72

#	Sample ID	Analyte	Reported Concentration (mg/kg) mg/L	Calculated Concentration (mg/kg) mg/L	Acceptable (Y/N)
	1	NO_3/NO_2-N	4.1	4.1	Y

Table : 1 (Nitrate/ Nitrite)

	Known Conc. (mg/l)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Residual	Det. Conc (mg/l)	Detection Date	Detection Time
1	2.00	1	17.9	1.76	0.0	0.2	2.00	7/27/2018	8:48:23 AM
2	1.00	1	9.05	0.888	0.0	-0.9	1.01	7/27/2018	8:48:57 AM
3	0.200	1	1.82	0.179	0.0	0.0	0.200	7/27/2018	8:49:32 AM
4	0.0200	1	0.211	0.0214	0.0	2.3	0.0195	7/27/2018	8:50:05 AM
5	0.0100	1	0.118	0.0113	0.0	6.7	0.00907	7/27/2018	8:50:40 AM
6	0.00	1	0.0120	0.00155			-0.00278	7/27/2018	8:51:14 AM

Figure : 1 (Nitrate/ Nitrite)



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Supporting info

- Is supporting information in your raw data correct?
  - The right analyst's initials typed in chromats, instrument printouts, logbooks?
  - Dilution factors?
  - File names?

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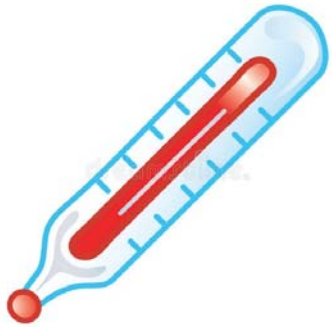
Lab Temperature

Is lab temperature highly variable?

- Effects on Ammonia testing:
  - 1-2% error per degree C change.
    - Samples & standards must be at the same temperature
- Effects on ICP testing:
  - Difficulty maintaining calibration
  - Variation of temperature is the enemy
- Other
  - BOD/CBOD
  - Ambient stored Standards
  - Balance



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Lab Temperature

- Take the ambient temperature into account
  - Your pipet will have been calibrated at room temperature. If you are working at a different temperature (e.g. in a colder room) your pipet will not be dispensing the displayed volumes.
- Take the sample temperature into account
  - When repeatedly pipetting cold samples, the first dispensed volume is always larger than expected, but subsequent pipetting with the same tip gives the correct volume.
  - The same would be true for hot samples, except that the first dispensed volume was smaller than expected.

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Lab DI water

- High Copper or Chromium Levels
  - Copper and chromium are toxic to organisms. High levels affect any 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.

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Lab DI 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.
  - Elevated levels of trace metals could affect BOD results, while elevated ammonia levels will impact ammonia test results.

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Lab DI water

- Organic contaminants
  - Deionized water may contain detectable amounts of ammonia, volatile, or semi-volatile organic compounds.
  - Deionized water can be a problem because the resin cartridges themselves will release organic compounds into the water.
    - These compounds are undetectable by conductivity measurements, and conductivity measurements are one of the main ways that purity of deionized water is determined.

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Balance

- Weighing table
  - Vibrations (counter…. consider other instruments, vehicles, trains)
- Humidity/moisture
  - AC settings change after 5pm? (but you still have a second shift?)
  - Don’t put your hand in weighing chamber, both temperature and humidity can change (use tongs/tweezers)
- Air flow
  - Balance placed near doorways? Under AC vent?
- Electrostatic Influences
  - i.e. No nylon (including garments)
  - Electrostatic charged material can appear to be too light or too heavy

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Warning Signs- Organics

- Multiple manual integrations performed on QC samples or calibrations
- Manual Integration in lieu of instrument maintenance
  - Poor peak shapes
  - Short run times
  - Calibration Outliers
  - GC/MS tune issues
- Inappropriate manual integrations: peak shaving and enhancement
- Unnecessary baseline adjustment

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Warning Signs - Inorganic

- Time gaps in calibration sequences
- Interference Check Sample outliers
- Poor precision caused by dirty systems
- Running rinse blanks before QC samples
- Expired standards or gaps in traceability
- Instrument replicates significantly differ

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Unusual activities

- QC Recoveries not changing
- Reanalysis of QC until it passes
- Sample containers empty when only half the amount is needed for analysis
- Missing electronic or paper files
- Avoiding the QA Officer
- Always too busy to answer questions
- Excessive Surrogate failures

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Unusual activities

- Analyst secretive about their routine
- Instrument Sequences not in sequence
- Multiple curves (switching curves until QC passes)
- Sample containers full but data reported

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Sensitivity

- Time intervals between readings of same sample
  - Does the sample have enough time to reach the analysis destination before the instrument records the first reading?
  - How many seconds/minutes does it stay in column, etc. ?

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Electronic Data Review

- Examine your procedures, look for spots where QC or data can be changed without documented traceability.

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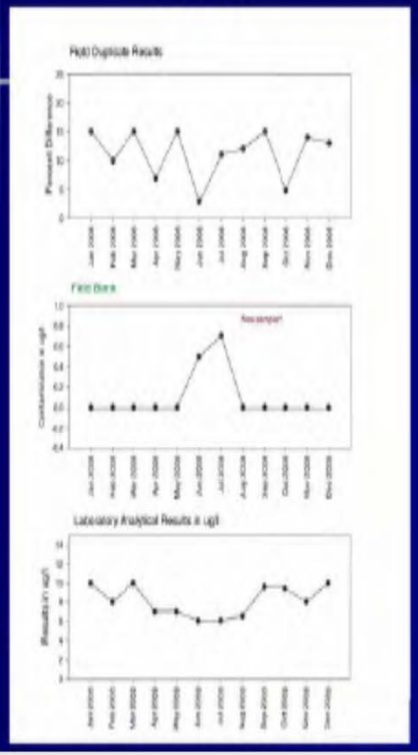
Use of control charts

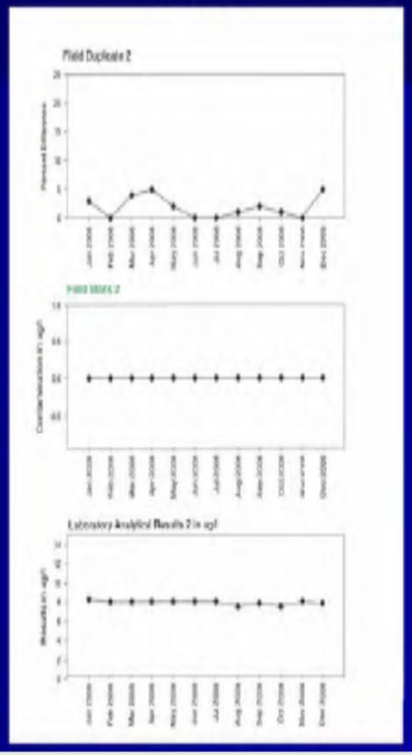
Field QC Samples

Duplicate, Blank, and Sample Results from Two Samplers

Novice

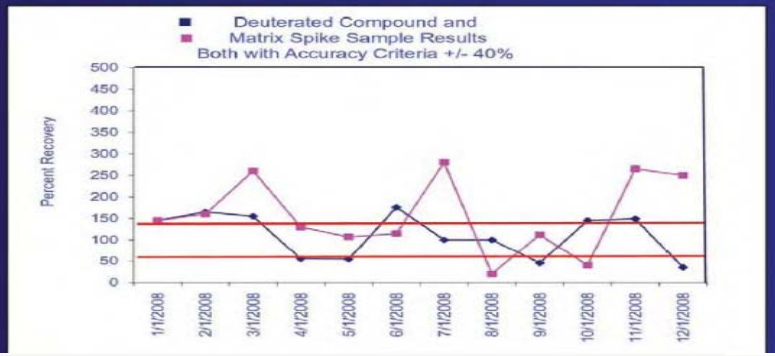


Trainer



Field and Lab Audit Findings

Placing two graphs on one, where limit scale similar



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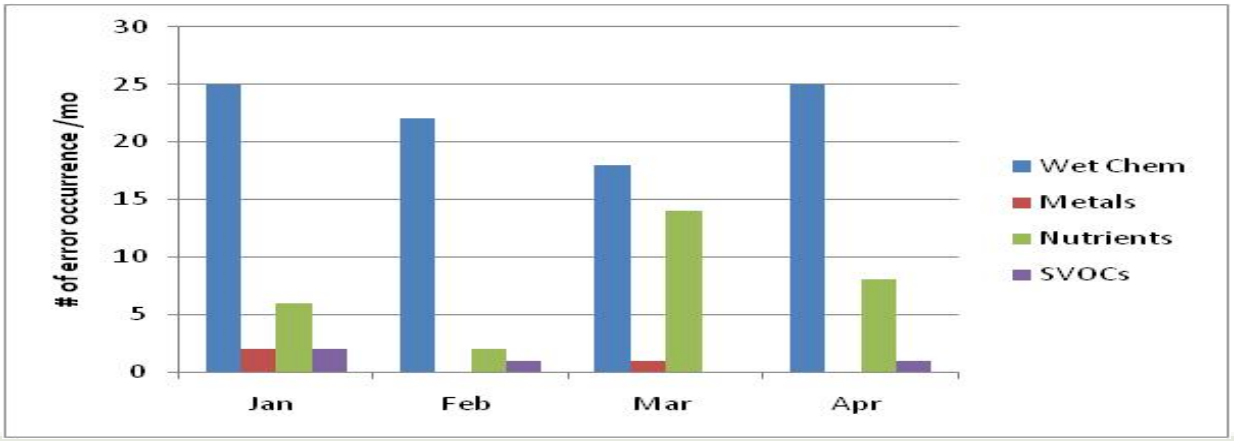
Tracking Other Performance Indicators

Ex. Monthly Data Entry Errors

	Jan	Feb	Mar	Apr
Wet Chem	25	22	18	25
Metals	2	0	1	0
Nutrients	6	2	14	8
SVOCs	2	1	0	1



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Tracking Other Performance Indicators

- Non Conformances
- Corrective actions
- Follow up
- Second Follow up
- Repeated customer complaint

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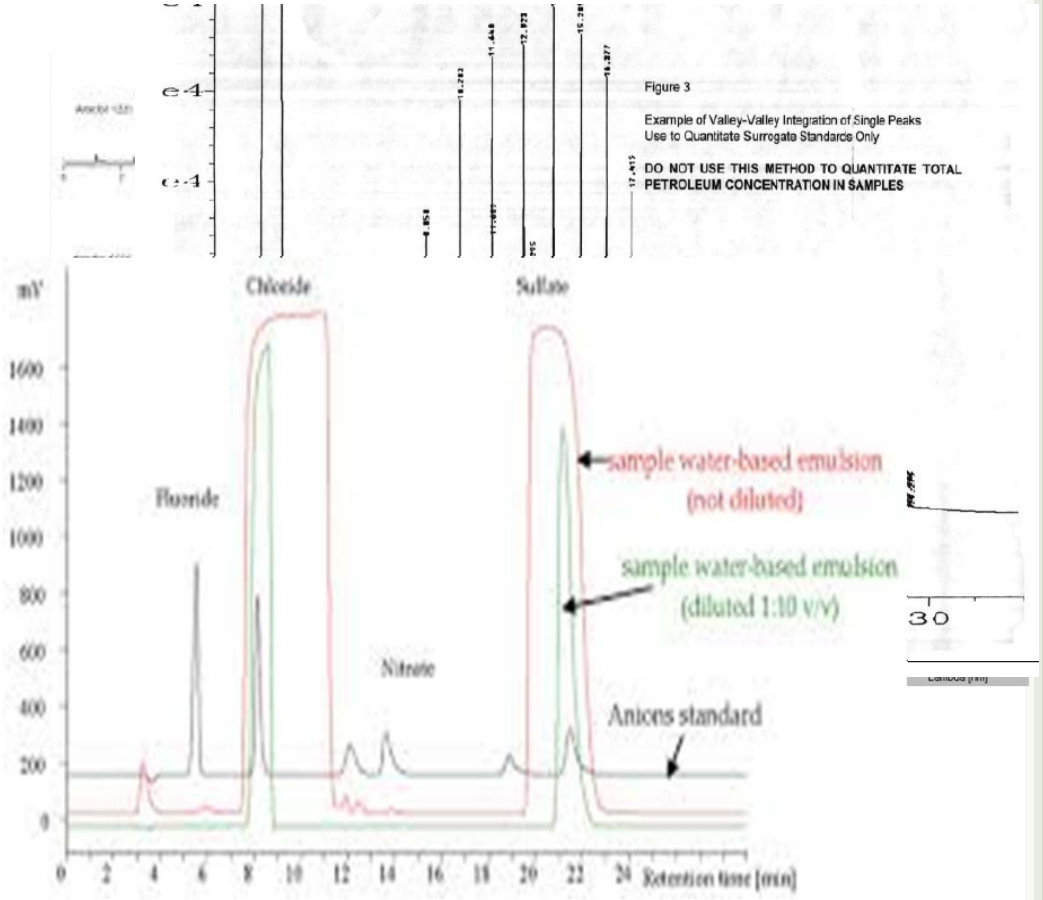
Method Specific Training

Training beyond IDOC/DOC

- Complex matrices examples
  - ICP interferences
  - PCB patterns recognition
  - FLPRO quantification
  - IC interferences
  - Cyanide
  - Ammonia



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The one repeating issue…

- The most basic of basics, the most simple fix and yet the one that can make your data questionable
- Can you guess?
  - Obliterating errors in data records instead of line through and the records do not include a reason for the change or date or the identity of the person responsible for making the changes.

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Thoughtful Review

- Method Flexibility vs. Deviations
  - Data review must distinguish between program allowed flexibility and improper deviations in method implementation.

RI State Health Laboratories, Henry Leibovitz, Ph.D.

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USEPA Data Usability Policy

"Data Quality Assessment is built on a fundamental premise: data quality is meaningful only when it relates to the intended use of the data."

USEPA, 2006a. Data Quality Assessment 1

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Final Thoughts

"If you are going to achieve excellence in big things, you develop the habit in little matters. Excellence is not an exception, it is a prevailing attitude."

-Colin Powell

"Someone who is trustworthy in a small matter is also trustworthy in large ones, and someone who is dishonest in a small matter is also dishonest in large ones."

Luke 16:10

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References

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- https://www.thermofisher.com/search/results?query=Dionex&persona=DocSupport&navId=4294959596
- *https://www.nestgrp.com/pdf/Zp1/Sp1/ION_Manual.pdf*
- , Laboratory Quality Assurance And Quality Control Data Quality Assessment And Data Usability Evaluation, Guidance Document
- QC Audit revealed WI DNR, Lab Certification Program
- Internal and Electronic Audits, Advanced Systems, Inc.
- Agilent Technologies, ICP-OES Maintenance & Trouble Shooting, www.agilent.com/chem GC-Agilent-Troubleshooting-1.pdf
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