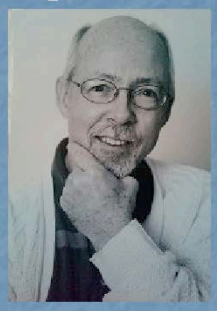
The Elements of Analytical Laboratory Data Quality



Charlie Appleby

Contract Laboratory Program
Office of Superfund Remediation and Technology Innovation

This presentation is intended for training purposes only.

Course Objectives

- Understanding the importance of planning
- Familiarity with the data elements
- Preserving Sample Integrity
- Familiarity with quality control metrics
- Knowledge of Data review and verification
- Recognizing signs of improper practices
- Understanding Data Usability

2

Agenda

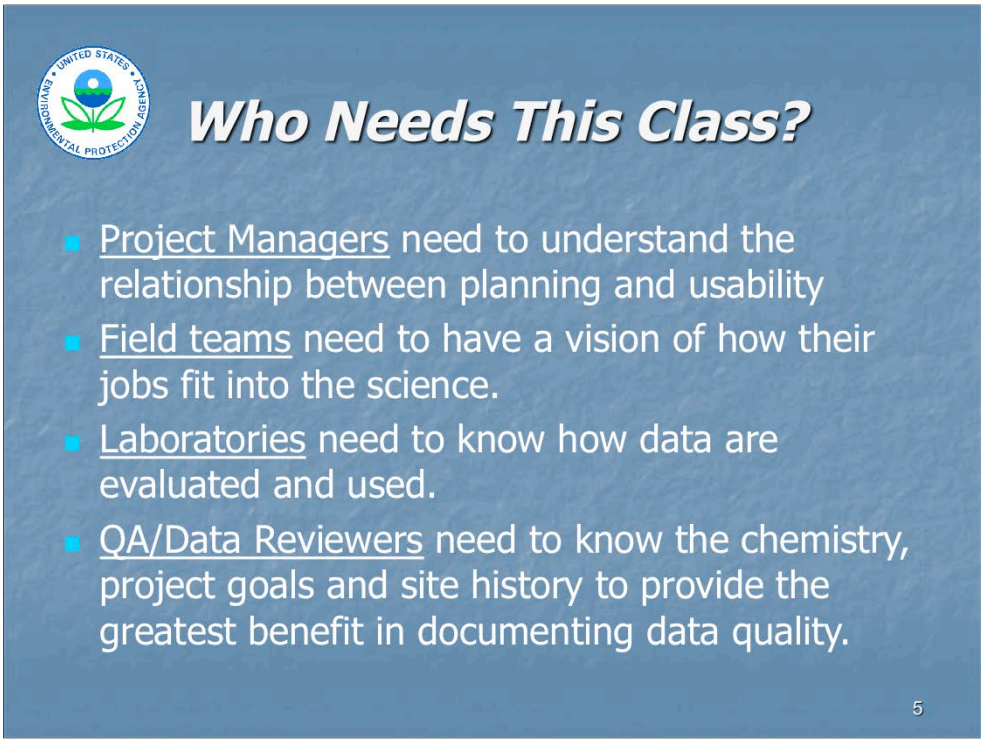
- Part 1: Introductory Topics
- Part 2: Project Planning
- Part 3: Overview of Analytical Chemistry
- Part 4: Sample Management
- Part 5: Data Review and Verification
- Part 6: Improper Laboratory Practices
- Part 7: Data Assessment

3

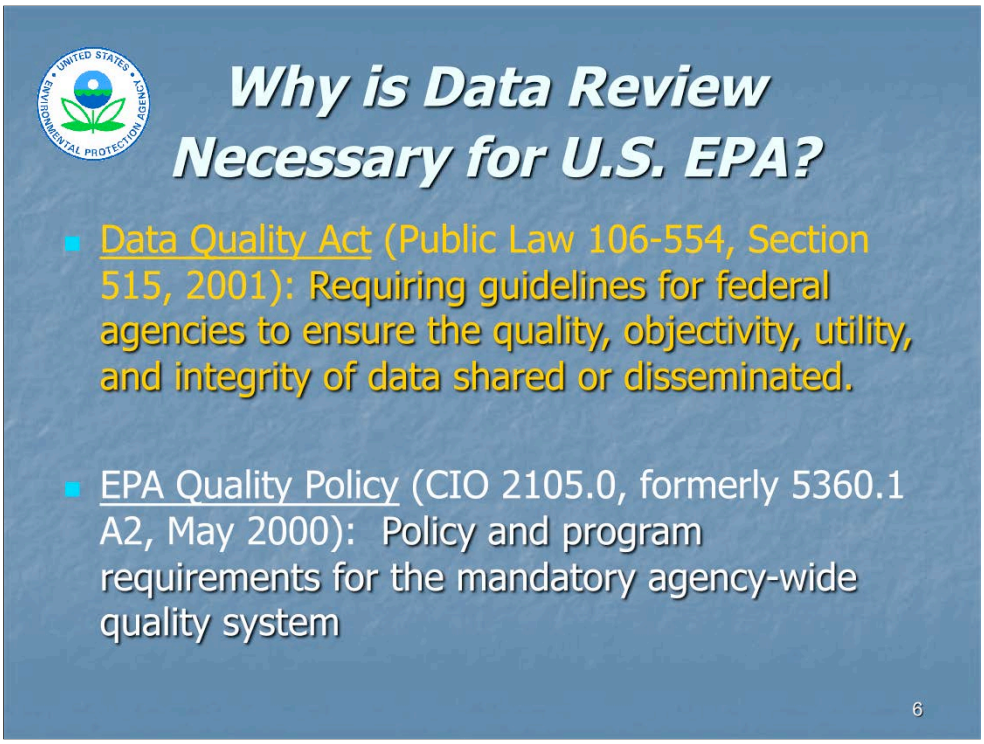
PART 1:
Introductory Topics

- Who needs this class?
- Why is Data Review Necessary?
- Terms You Should Know

4


Who Needs This Class?
Project Managers need to understand the relationship between planning and usability
Field teams need to have a vision of how their jobs fit into the science.
Laboratories need to know how data are evaluated and used.
QA/Data Reviewers need to know the chemistry, project goals and site history to provide the greatest benefit in documenting data quality.
5

.



Data Quality Act (Public Law 106-554, Section 515, 2001): Requiring guidelines for federal agencies to ensure the quality, objectivity, utility, and integrity of data shared or disseminated.

EPA Quality Policy (CIO 2105.0, formerly 5360.1 A2, May 2000): Policy and program requirements for the mandatory agency-wide quality system

Now, in truth, the CLP already had the National Functional Guidelines for Data Review available for the analytical chemistry community before 2001 when the data quality act became law, and was a leader in the drive for comparable quality systems across all Agency programs, offices, and in all grants and contracts before the first quality policy. But now it is the rule rather than the exception that quality is given early consideration in everything we do.

Terms You Should Know

- Field vs laboratory measurements
- Statement of Work
- Standard Operating Procedure
- Confidence
- Integrity
- Defensibility
- Usability
- Sample Custody
- Definitive Data
- Decision Unit

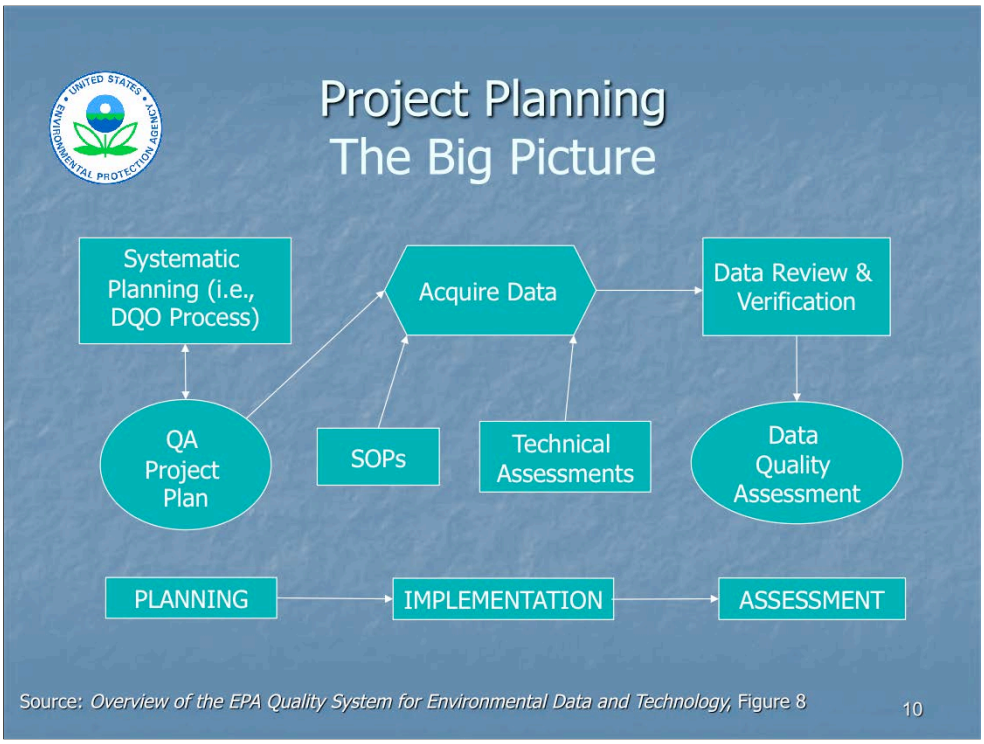
7


More
Terms You Should Know
Data Verification
Data Validation
Secondary Data
Data Qualification
Precision
Accuracy
Bias
Completeness
Representativeness
Comparability
Screening Data
8

PART 2:
Project Planning

- Communication
- Data Usability Needs
- Getting Useful Information
- Sample and Data Usability Characteristics

9


Project Planning
The Big Picture
Systematic Planning (i.e., DQO Process)
Acquire Data
Data Review & Verification
QA Project Plan
SOPs
Technical Assessments
Data Quality Assessment
PLANNING
IMPLEMENTATION
ASSESSMENT
Source: Overview of the EPA Quality System for Environmental Data and Technology, Figure 8
10

Environmental studies require input from a lot of different areas of expertise, including engineers, logistics specialists, technicians, chemists, biologists, lawyers, managers, and accountants, to name but a few. And there are issues like weather, site access, concerned citizens groups, and equipment problems. So it's easy to see that communication is vitally important. In fact, I recommend that formal lines of communication be set up, so as you plan, you can be confident that no one is left out.

It is a good idea to include the laboratory, because they will have valuable input on many questions during project planning, including areas such as using a fixed lab or a mobile or field lab, methods, detection limits that are attainable, appropriate sample containers and preservation, and holding time, as well as others. For an agency such as the EPA, the Regional laboratories are a great resource, even before the actual lab for the project has been chosen.

The QAPP should set out policies for dealing with QC performance issues. One of these is how to deal with **field QC** sample defects (i.e., does the reviewer qualify the data based on this or does the reviewer simply report the issues to project mgt).

A consideration for project data quality planning is whether PE samples performance will be used to qualify data for the entire set of samples or only for those samples with which it was analyzed, or not at all.

Another question you should ask during project planning is whether the choice of spiking analytes represents the analytes of interest to the project. For example, if your target analyte is toxaphene, its use as a matrix spiking compound should be specified, since the method specifies different pesticides for the MS solution.

These are just a few of the technical questions that should be asked, and a technical expert would be the one to think of questions

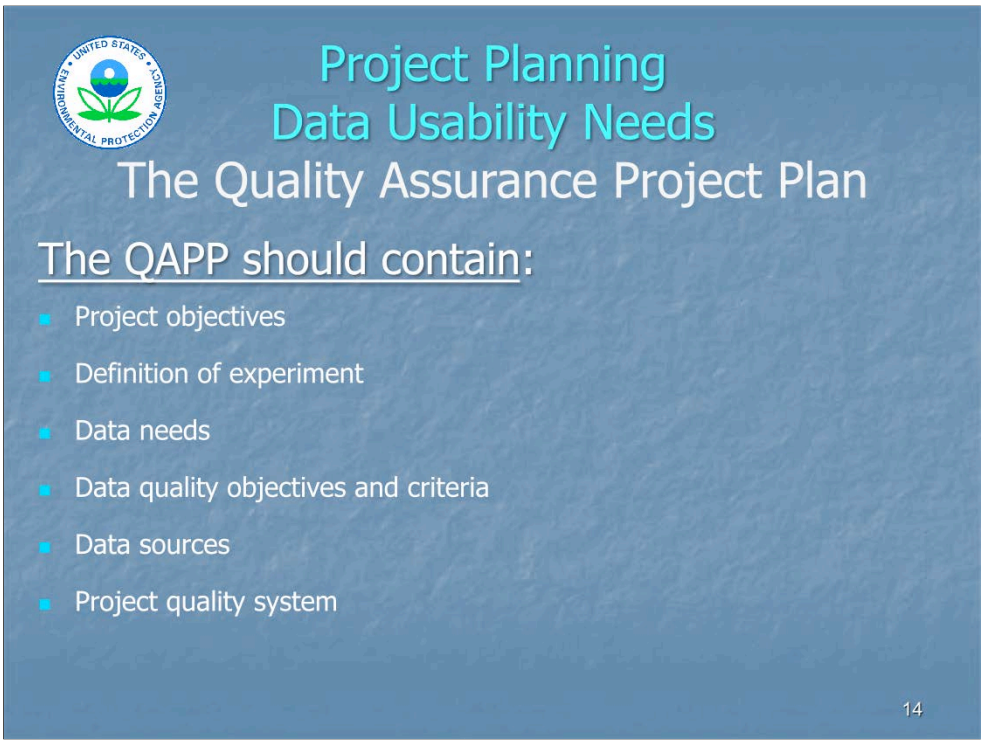
like these.

The planning process we are talking about should be Systematic Planning. It is a planning process based on the scientific method and concepts such as objectivity of approach and acceptability of results. It is a common sense, a graded approach to ensure that the level of detail in planning is commensurate with the importance and intended use of the data and the available resources.

You should also establish data quality objectives that will ensure the information you gather to support the decision, whatever it is, will be adequate and suitable for that task.

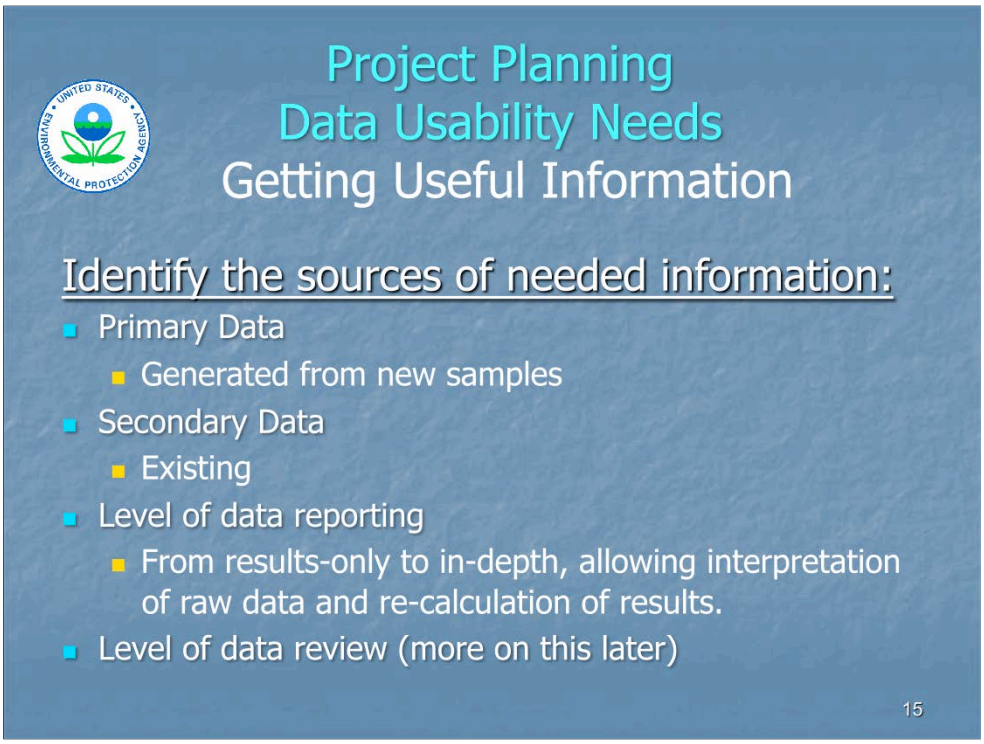
A QAPP is a formal document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

Besides the fact that generating a QAPP is required of all EPA projects or those funded by EPA grants, you will see as you go through the process in the G-5 series that it really helps you to organize your planning. In addition to these resources, the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) is a consensus document prepared by the Intergovernmental Data Quality Task Force (IDQTF) and initially published in 2005. This can be found at the It provides instructions for preparing Quality Assurance Project Plans (QAPPs) for any environmental data collection operation, and there are extensive training materials, including the original manual and workbook, Region-specific versions of the same, training videos, and templates to guide you through the planning process.

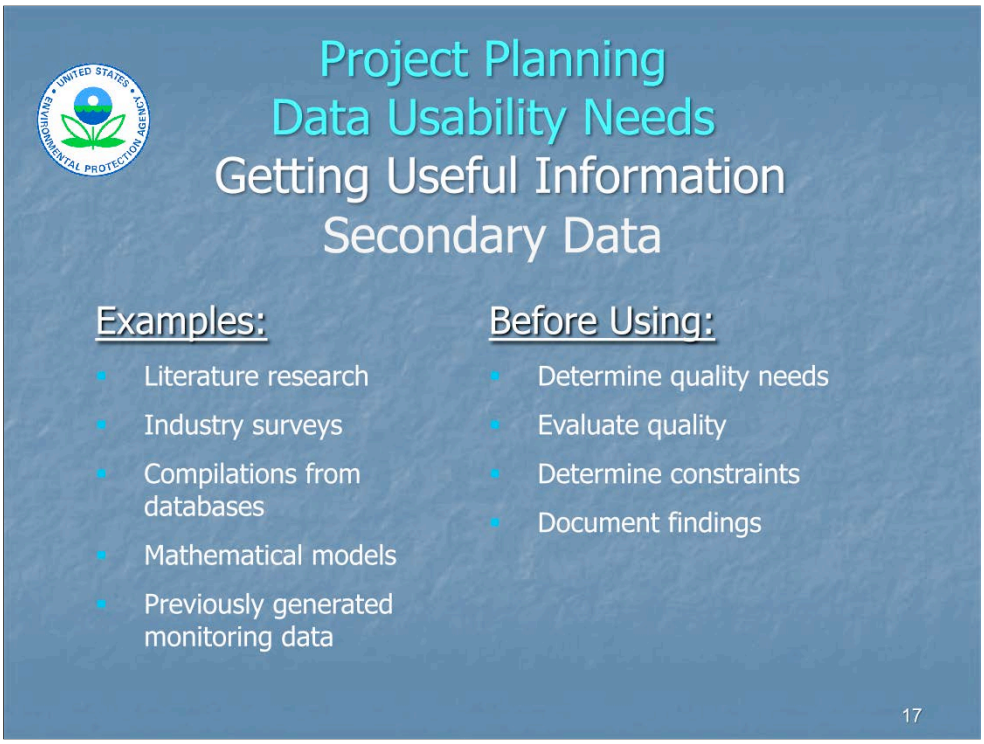


At a minimum, the QAPP should contain these items. I say “at a minimum”, because this list is at a very high level, and there is a popular saying that the devil is in the details. I leave that part up to you, but I recommend the resources presented on the previous slide to help you through the process. We are going to skip down this list to focus on planning for successful data collection part, beginning at Data Needs, or Getting Useful Information.

I hope you all understand at this point that up-front planning is critical for success in environmental studies.



We will identify data sources as being of two types: primary, or new data, and secondary, or existing data, and I have mentioned levels of data reporting and review, both of which we will discuss later, because along with decisions about the types of data needed is consideration of the level of detail required. For example, you may know of a source of existing data to help you make a decision about human health risks associated with a site. But the knowledge that this type of study would require a very high level of documentation about data quality, and a high level of confidence in the results should inform your decision about which data source will be acceptable. The high level of information required about data quality in this example would require that the data set be reviewed in depth by an experienced chemist.

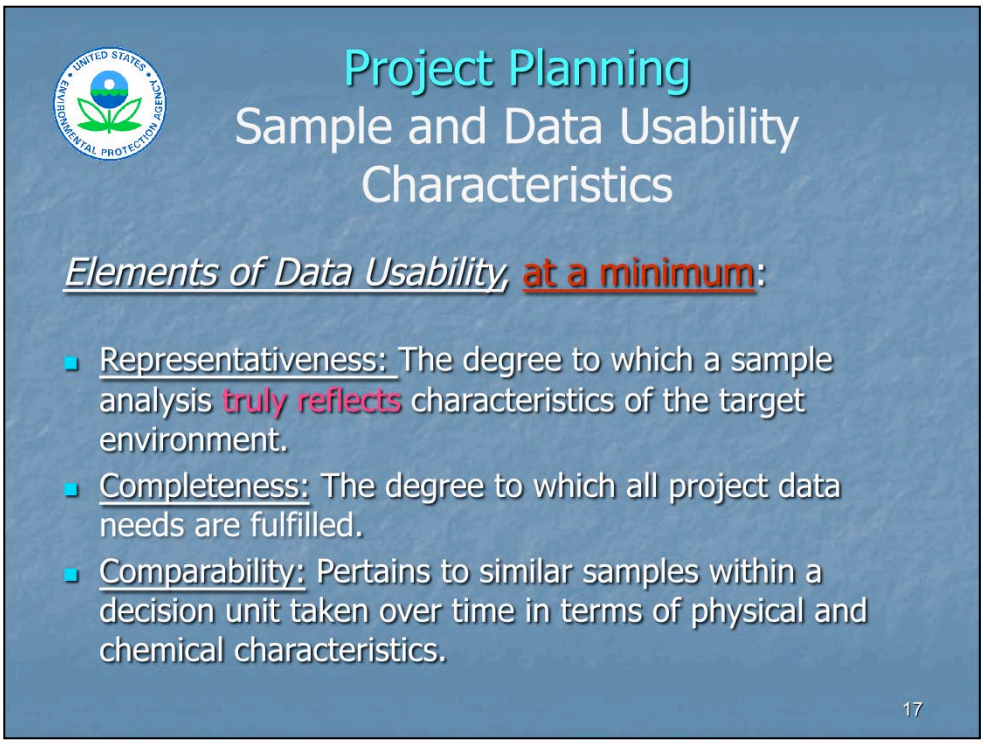


Here are some possible sources of secondary data, and the considerations necessary before using those data. Through your planning process, the types of 2ndary data to be used should be identified, along with the steps necessary to ensure adequate quality in those 2ndary data.

Using data and information that were not generated for the same quality objectives as the current investigation may cause errors in the decision. Therefore, it is essential to identify use limitations for secondary data. Accuracy, precision, representativeness, completeness, and comparability of these external data need to be addressed.

Here are some steps to take to approach the use of secondary data:

1. Identify the decision you are making or project objectives that these data will satisfy.
2. Identify the data and information from secondary sources proposed for the project/decision. Note that this may not be obvious. Include data bases, maps and literature, and don't forget anecdotal information. These all qualify as secondary data.
3. Determine where the acquired data will be used in the decision making process. That is, will it be used to scope the project, contribute to data collection in the project, verify the results of the decision, or substitute for all or some new data collection?



Here are three elements of data usability that would be defined among the Data Quality Objectives. That said, they are equally important when you consider where and how to collect your samples.

Representativeness: The degree to which a sample or a sample analysis truly reflects characteristics of the target environment.

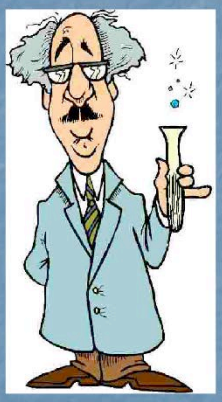
Completeness: The degree to which all project information needs are fulfilled. It also applies to a laboratory data package.

Comparability: Pertains to similar samples within a decision unit taken over time in terms of physical and chemical characteristics, or to decision units that are similar, or that have been repeatedly sampled over time.

This concludes our discussion of the importance of project planning. Let's go back to slide 10 and see where we are. Next, we will review the topic of analytical chemistry, so we will be ready to talk about data review.

PART 3: Overview of Analytical Chemistry

- Chemical Methods
- Chemical Properties
- Analytical System Performance
- Detection Limits
- Sample Analytical Sequence



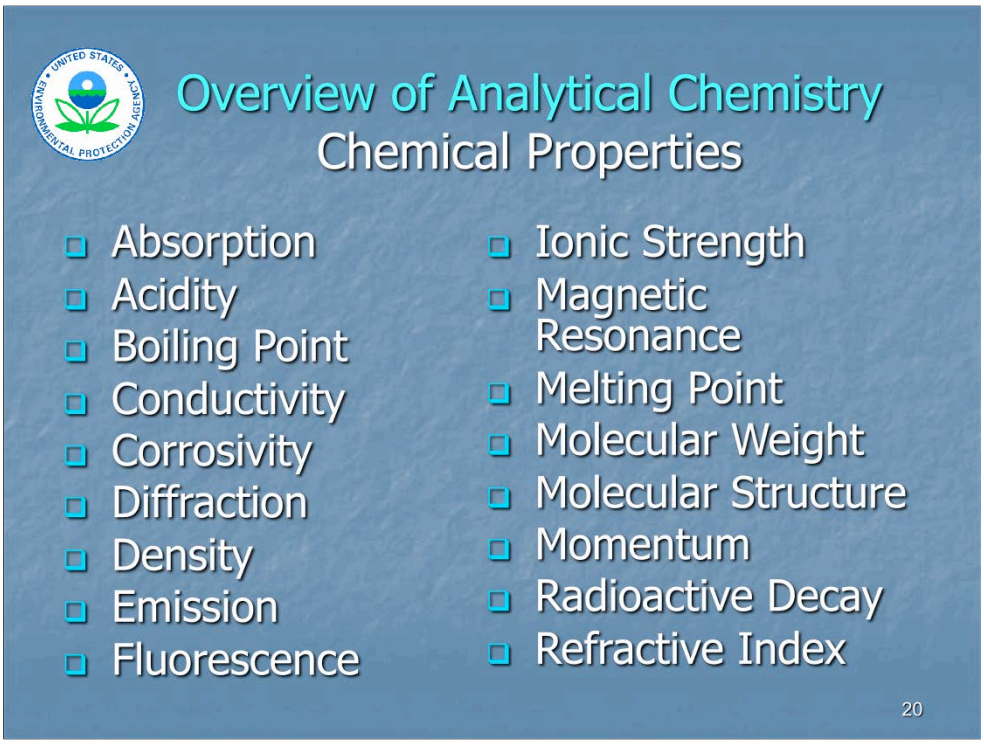
18

Overview of Analytical Chemistry
Chemical Methods

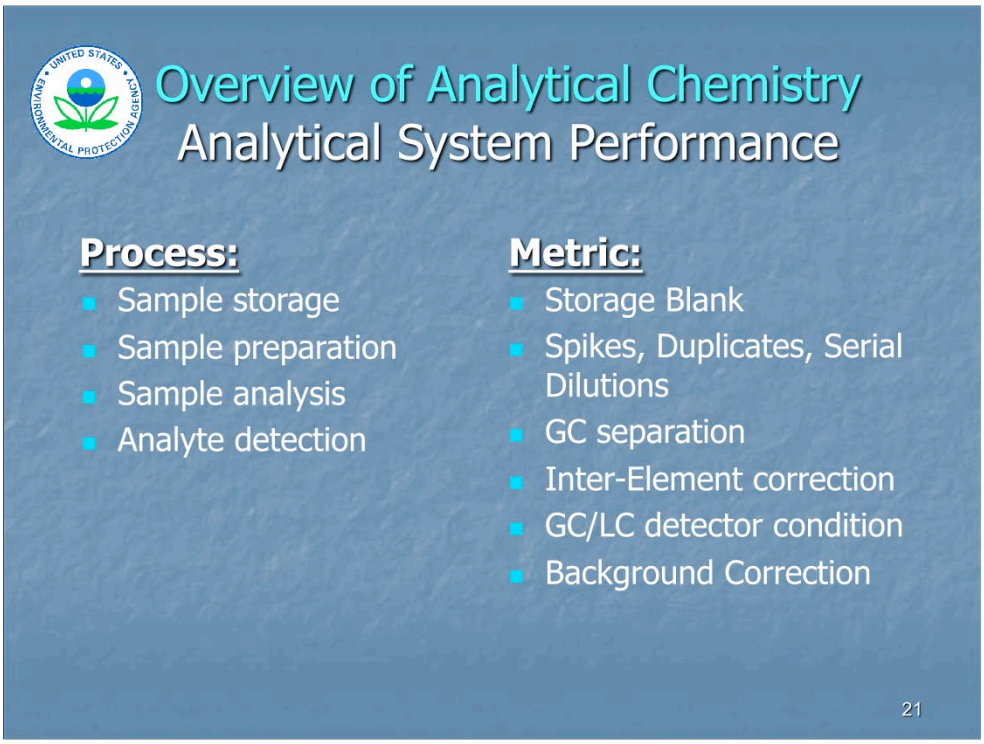
- Organic
- Inorganic
- Radiochemical
- Wet
- Physical
- Gravimetric
- Potentiometric
- Stoichiometric
- Microscopic
- Spectroscopic
- Chromatographic
- Titrimetric
- Direct Measurement

19

This is not an exhaustive list, but is meant to convey the wide range of analytical techniques available. The method types of “organic”, “inorganic”, “radiochemical, and “wet” are listed because they are familiar to most of us. However, these are really areas of application of the other method types.



Here is another incomplete list of the properties of materials that are utilized for analytical chemistry.

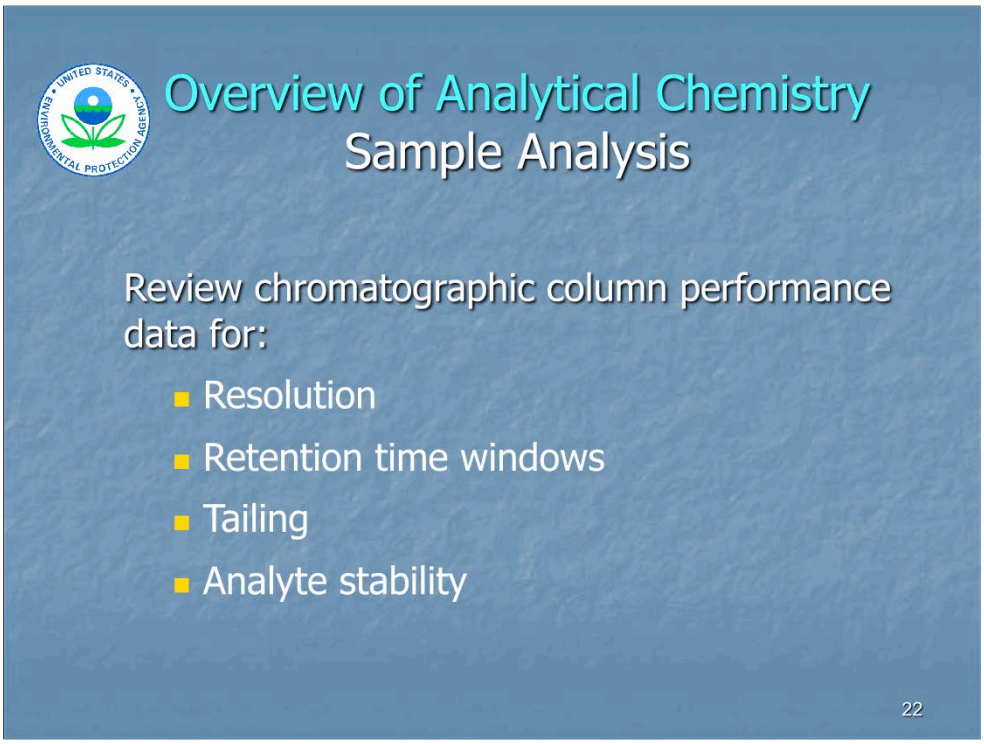


All of these laboratory processes have QC metrics built into the system, and hence there is a way to monitor how well they were controlled for your data set. Other types of metrics may also be out there. The columns of this slide aren't well lined up, so I will interpret for you:

Sample storage, which has been known as an avenue for cross-contamination of volatile analytes, relies on storage blanks for QC.

Sample preparation is monitored using spikes – and several types of spikes are used – and duplicates. Serial dilutions provide a check on both the prep area, the performance of dilutions, as well as an analytical consideration, the effects of interferences.

Analyte detection is monitored through GC separation or resolution checks, Inter-Element correction, GC/LC detector condition, and Background Correction



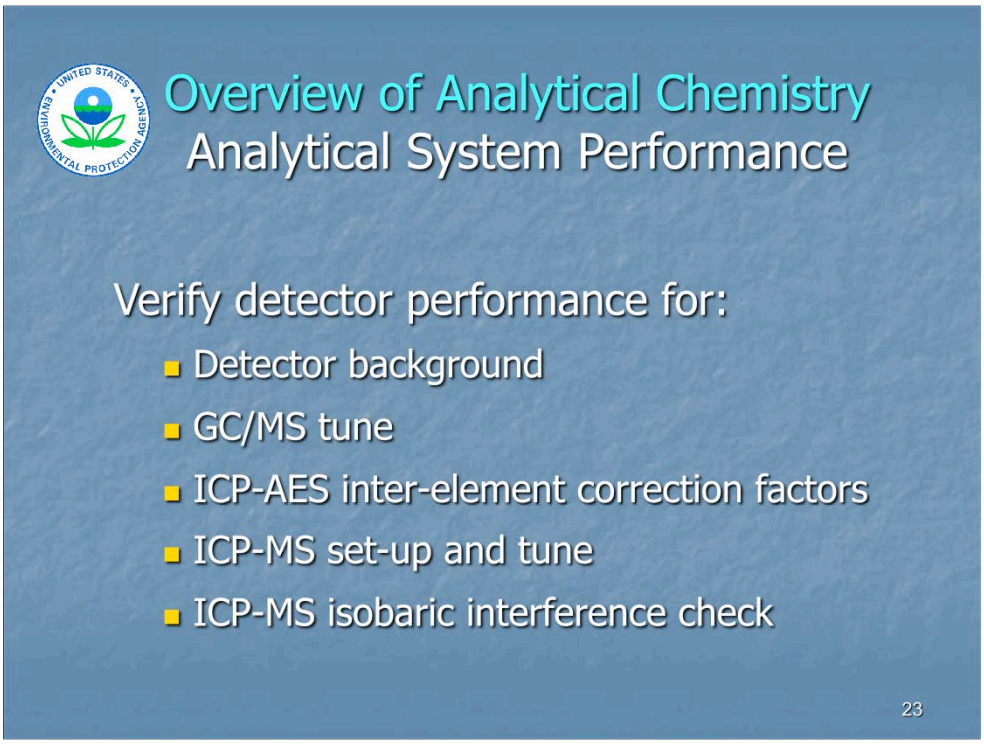
A few specific QC checks that we do to monitor chromatographic performance are:

Resolution: The degree of separation between two adjacent peaks

Retention time windows: Depends on column type

Tailing: Caused by interaction of the analyte with the column as it degrades

Analyte stability: Usually influenced by injection port condition and also the injector end of the column.



Detector background is evaluated in various ways: by examining the low standard to verify an adequate signal for each analyte above system background, checking the method blank for a noisy signal or low level positive hits, or by checking for what should not be present, as in evaluation of the Interference check sample for ICP-AES. In this case we look to see that, in the presence of an abundance of elements potentially causing positive interference, the IECs programmed into the instrument keep those interferences to a minimum.

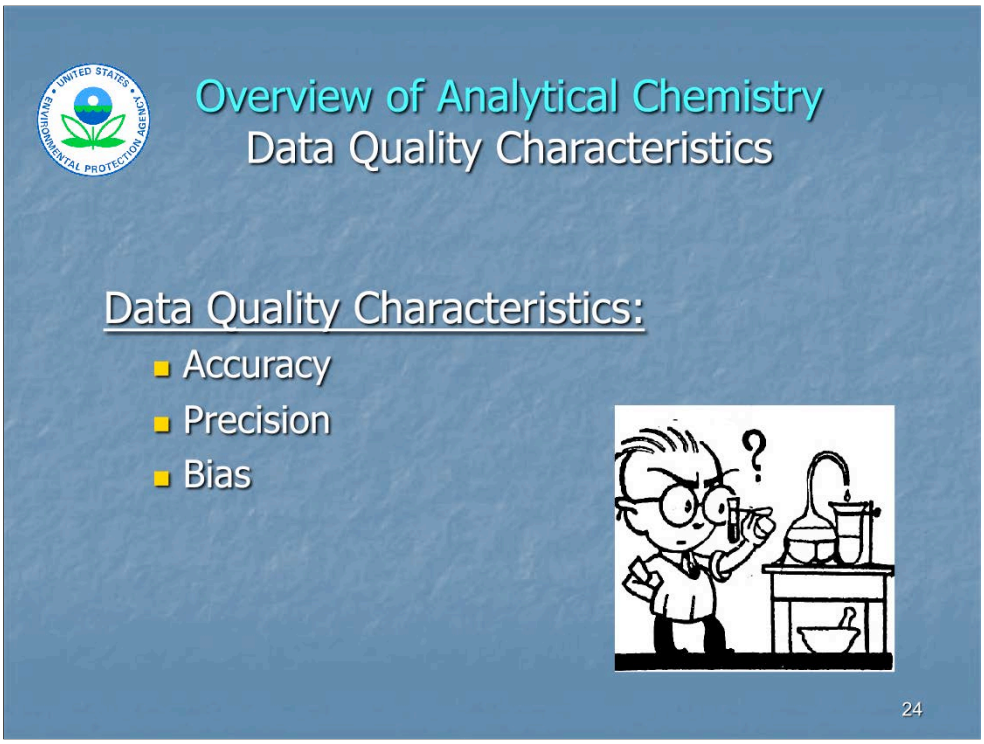
The ICS solutions for ICP-AES contain: Ag, As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Tl, V, and Zn at low levels. The interferents include Al, Ca, Fe, and Mg at moderately high levels. The ICS-A solution has just the elements subject to interference, while ICS-B has both.

The ICP-MS tuning solution contains beryllium, magnesium, cobalt, indium, and lead and is analyzed repeatedly to evaluate MS mass calibration and stability.

For ICP-MS, in addition to tuning the mass spectrometer, we want to verify that the system deals appropriately with isobaric interferences. The ICS for the method is evaluated for over, or under-compensation for possible interferences, which could cause false positives or false negatives.

Isobaric Elemental Interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio, and which cannot be resolved by the mass spectrometer. Ions of the various metals are chosen for analysis such that they do not have such interference, if possible. See Method 6020, Section 4.

MS interference check sample looks at the effects of common isobaric interferences such as the effect of 35Cl16O+ on the 51V+ ion, and the effect of 40Ar35Cl+ on the 75As+ion.



And now three parameters that apply to all analytical data. The first two need no introduction. However, the term, “Bias”, is often not well understood.

In the dictionary, it is said to mean an influence. However, in the EPA quality manual, it says the following:

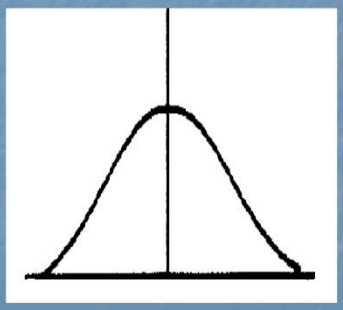
The systematic or persistent distortion of a measurement process which causes errors in one direction (i.e., the expected sample measurement is different from the sample's true value). This can result from improper data collection, poorly calibrated analytical or sampling equipment, or limitations or errors in analytical methods and techniques.

So we see that bias can originate in the lab or in the field. And, if I might take us back to precision and accuracy, and ask you to think about them in the context of taking non-representative samples, what effect would that have on the accuracy and/or precision of determining what truly was at the site? If, for example, there were results near an action limit, but due to a sampling error the sample gave inaccurate results that were different from a previous sampling, resulting in poor precision about the action limit, how could that affect the decision?

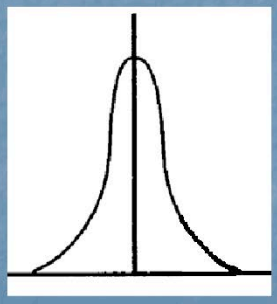
Overview of Analytical Chemistry
Data Quality Characteristics

Accuracy and Precision

Accurate but Poor Precision



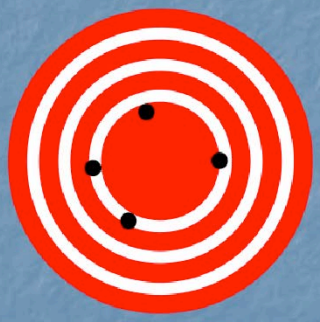
Accurate and Good Precision



25

Overview of Analytical Chemistry
Data Quality Characteristics

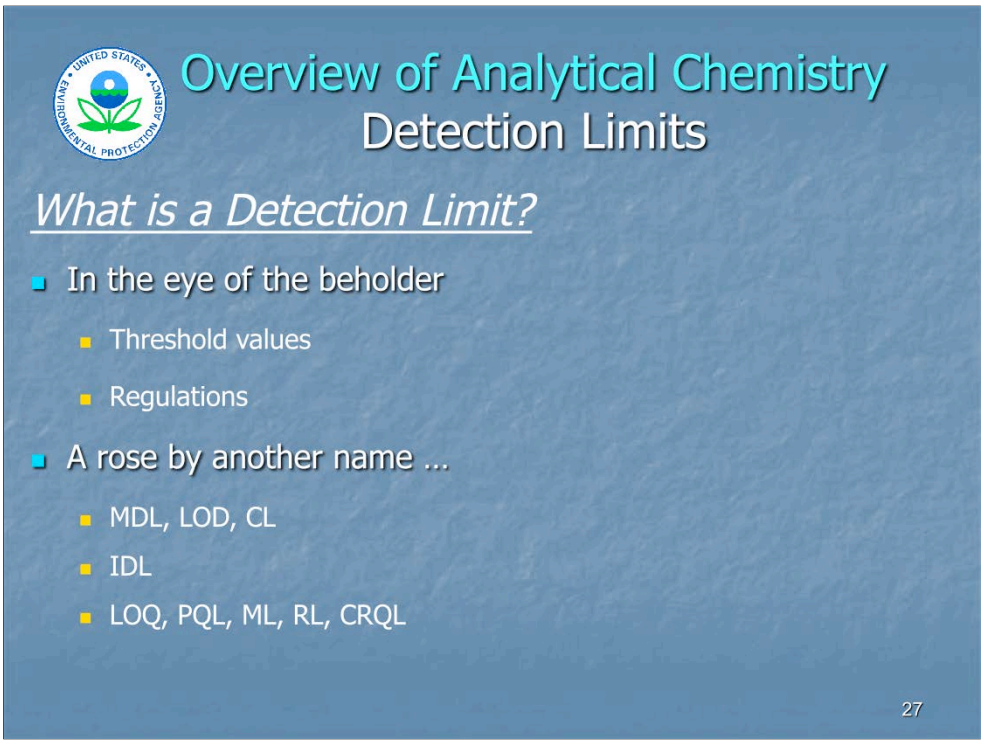
Accuracy, Precision, and Bias



Some Accuracy, Poor Precision, Low Bias

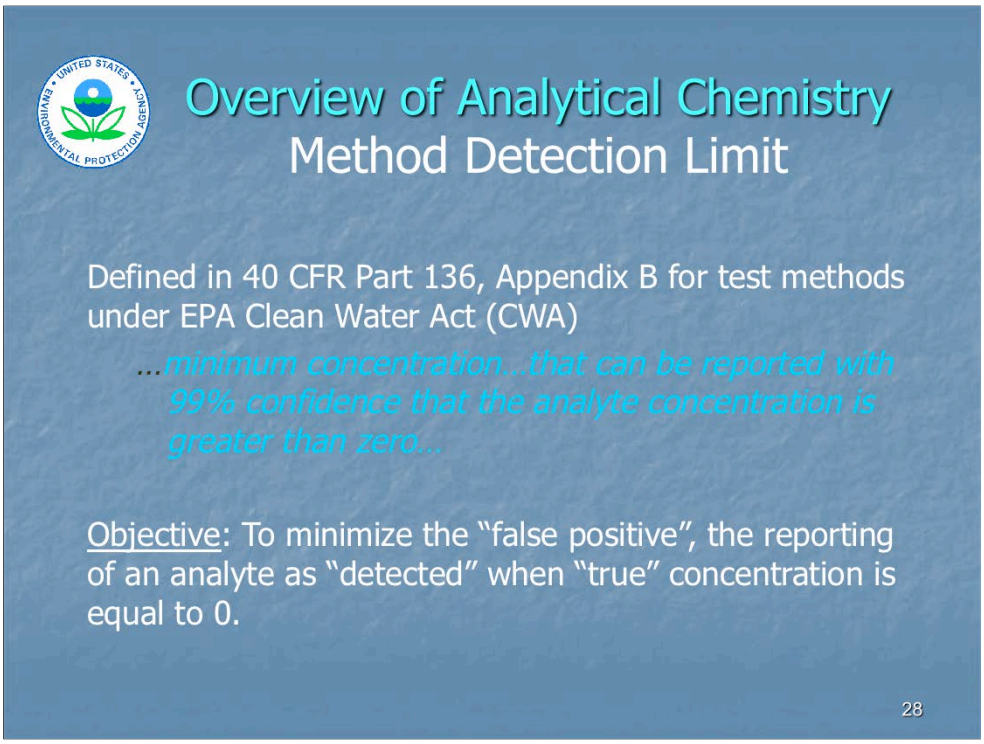
Low Accuracy, Good Precision, High Bias

26



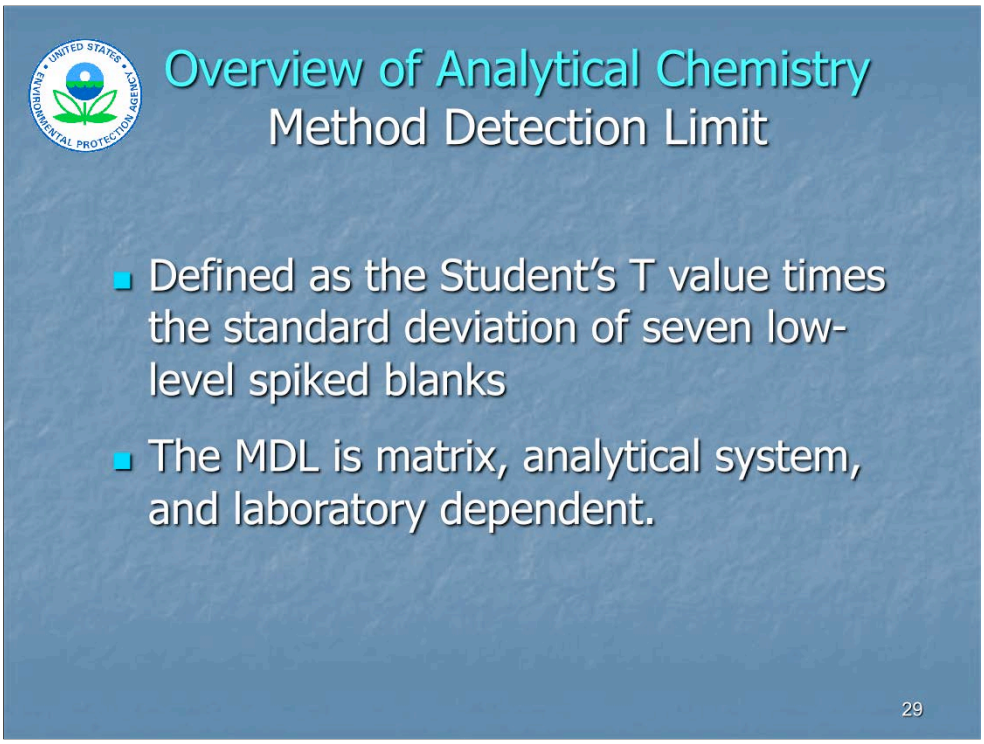
Now we'll switch to a purely analytical term: detection limit. Yet, you will see detection limit requirements stated in the QAPP because of risk assessment threshold values or on some cases, regulations (dioxin water quality criterion 0.014 pg/L). Current capability using approved methods is 2 pg/L.

As if this didn't introduce enough confusion, we've got analytical chemists calling detection limits by various names (not totally without reason, since method detection limit, limit of detection, and critical level are in fact slightly different, but to a lay person, it all seems unnecessary). The same phenomenon has occurred to the quantitation limit, also known as the practical quantitation limit, the limit of quantitation, the minimum level, the reporting limit, the contract-required quantitation limit, and I'm sure at least a half-dozen more.

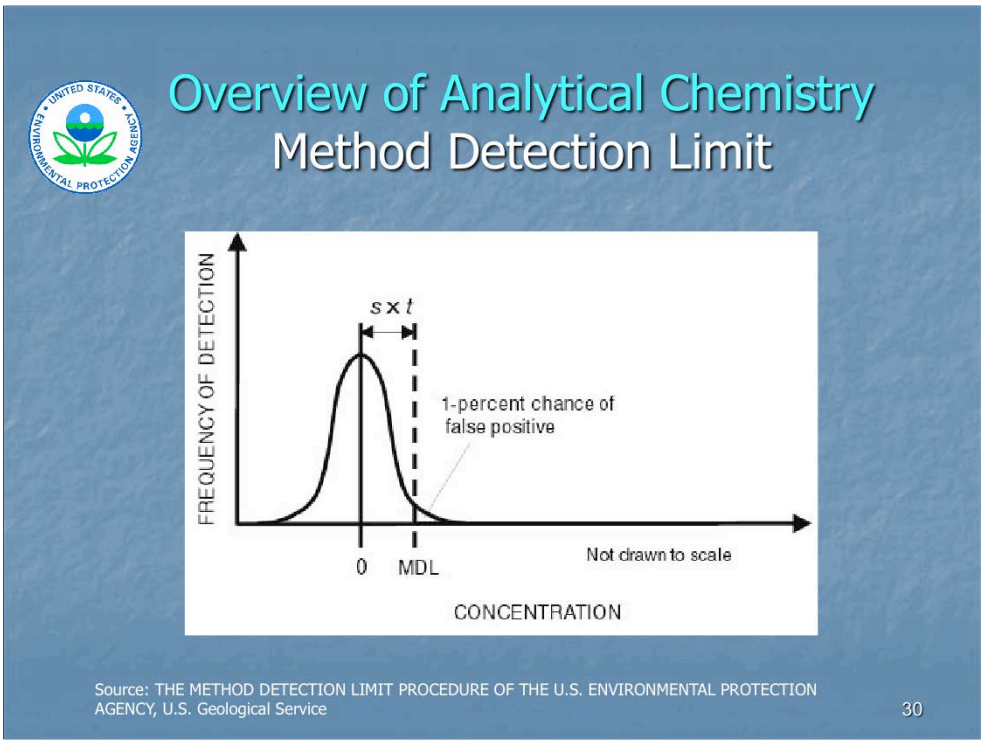


Why do we need MDLs?

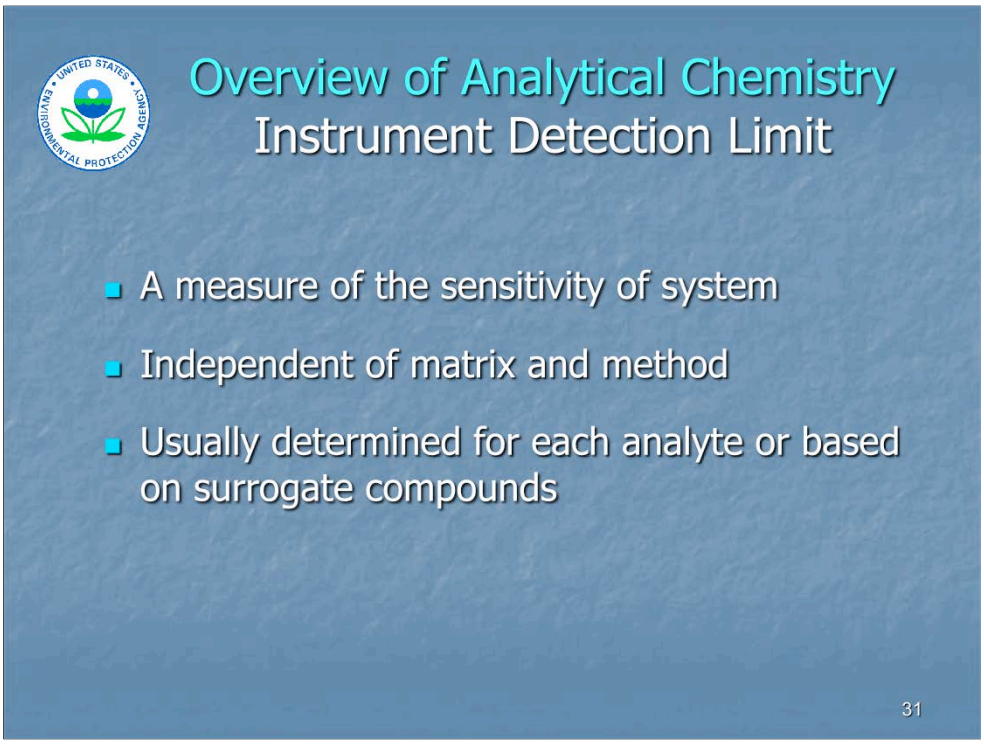
Method detection limits are a relative measure of the performance of a particular lab, method or analyst at the lower extreme of concentration. Reporting a method detection limit along with low level data alerts data users of the uncertainties and limitations associated with using the data. Data users in turn must understand these limitations in order to minimize the risk of making poor environmental decisions. Censoring data below unspecified or non-statistical reporting limits severely biases data sets and restricts their usefulness. This can lead to decision errors by data users when they calculate averages, mass balances or interpret statistics. A number reported as "<4" with no corresponding information is very difficult to interpret, and frankly isn't very useful. Just like we were taught in grade school to turn in our homework because "zeros don't average", in analytical chemistry, "less-thans" don't average either.



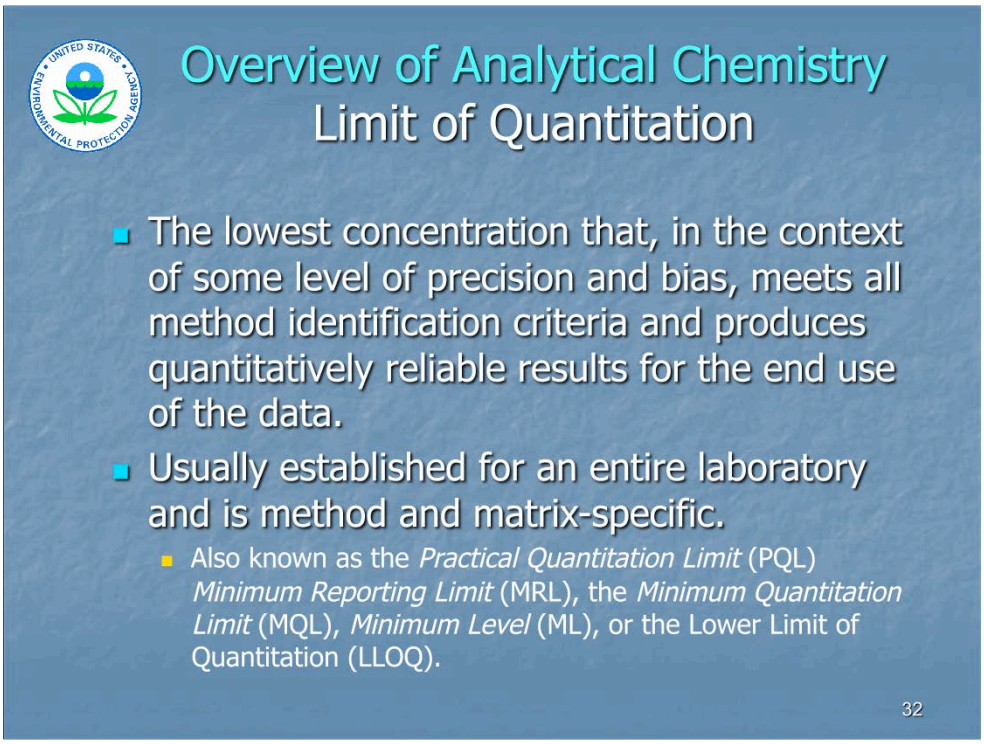
Here is a graphical representation of the MDL. You can see that, as in the definition, there is a 1% chance of a false-positive inherent in the MDL. If you would, visualize another peak over to the right, about 10-times the magnitude of the MDL. The range between is expected to have poorer precision that values greater that 10-times, and thus the target of the MDL study is values in this range that can then be used to derive the MDL. The calibration range of most instrumentation is then begun at two to ten times the MDL.



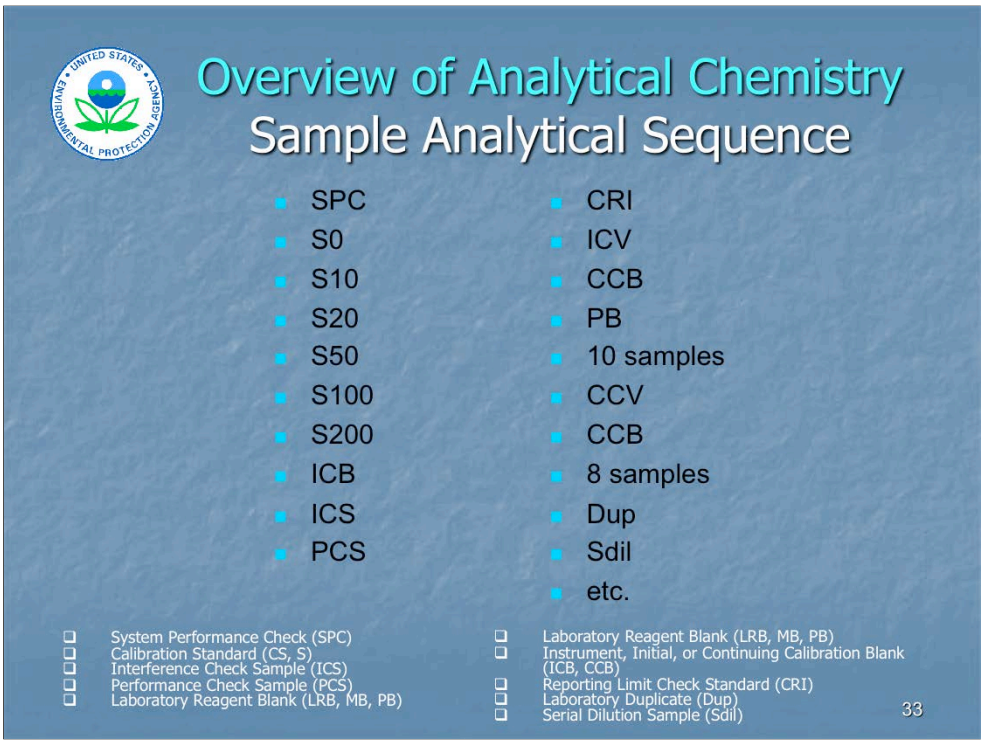
Here is a graphical representation of the MDL. You can see that, as in the definition, there is a 1% chance of a false-positive inherent in the MDL. If you would, visualize another peak over to the right, about 10-times the magnitude of the MDL. The range between is expected to have poorer precision that values greater that 10-times, and thus the target of the MDL study is values in this range that can then be used to derive the MDL. The calibration range of most instrumentation is then begun at two to ten times the MDL.



The instrument detection limit is a term used almost exclusively in the metals analysis realm, and is instrument-specific, independent of method.



The quantitation limit is the lowest concentration that, in the context of some level of precision and bias, meets all method identification criteria and produces quantitatively reliable results for the end use of the data. It is usually established for an entire laboratory and is method and matrix-specific.



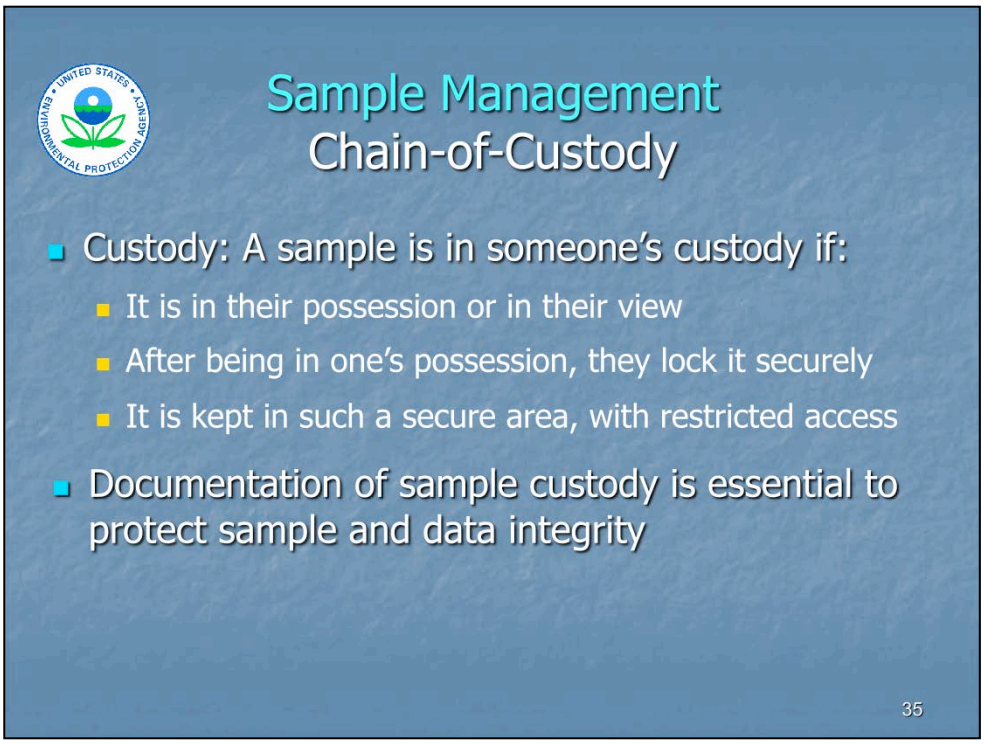
Here is a typical analytical sequence. Data Reviewers should be concerned with analytical sequences because they establish that the required Calibration and QC samples were analyzed in the most logical order (or not), and provide initial proof that all samples were analyzed and in what order. Of course the reviewer may want to verify the veracity of the analytical sequence provided (if it is required) In the interest of consistency, and for convenience in reviewing data, all of the CLP methods specify abbreviations for calibration, QC, and field samples that should be included in the typical analytical sequence, and they look something like this list. The definitions are shown below, although you may not be able to see them well enough.

Each analytical sequence should stand on its own, although on organics analysis, if a single calibration verification shows continued system stability, re-analysis of the multipoint initial calibration can be avoided.

PART 4:
Sample Management

- Chain of Custody
- Electronic Data Management Tools

34



Chain-of-custody is for the life of the sample, from collection to disposal.

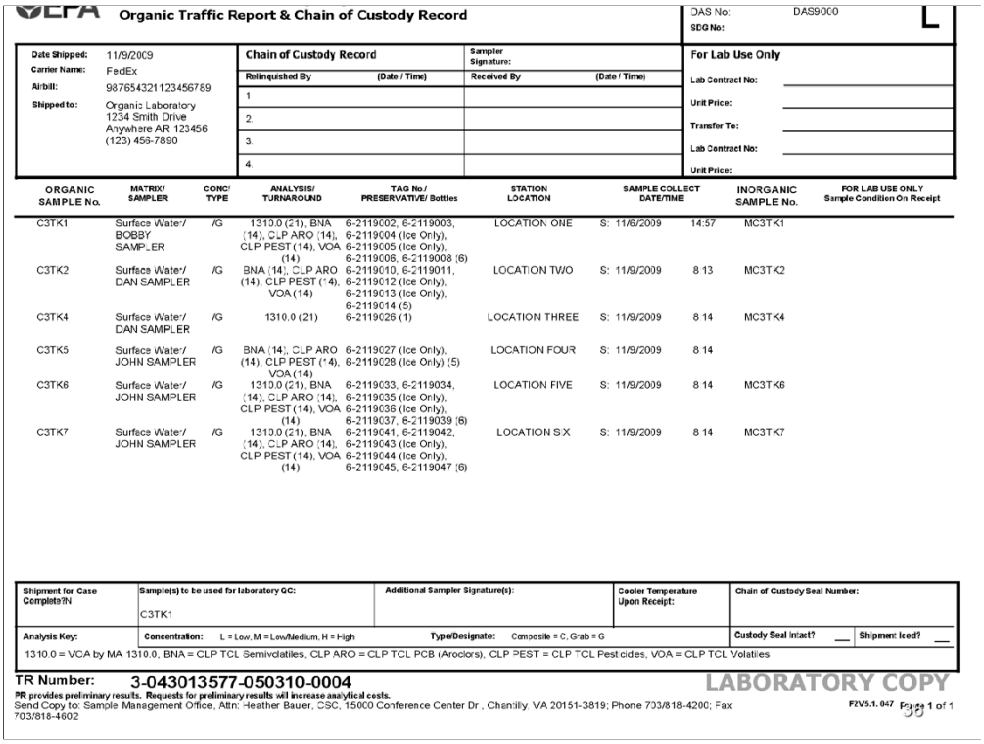
A sample is said to be in someone's custody if:

It is in their possession or in their view

After being in one's possession, they lock it securely

It is kept in such a secure area, with restricted access

Documentation of sample custody is essential to protect sample and data integrity



Organic Traffic Report & Chain of Custody Record

DAS No: DAS9000
SDG No:

Date Shipped:	11/9/2009
Carrier Name:	FedEx
Airbill:	987654321123456789
Shipped to:	Organic Laboratory 1234 Smith Drive Anywhere AR 123456 (123) 456-7890

Chain of Custody Record

Relinquished By	(Date / Time)	Received By	(Date / Time)
1.			
2.			
3.			
4.			

Sampler Signature:

For Lab Use Only

Lab Contract No:
Unit Price:
Transfer To:
Lab Contract No:
Unit Price:

ORGANIC SAMPLE No.	MATRIX/ SAMPLER	CONC/ TYPE	ANALYSIS/ TURNAROUND	TAG No / PRESERVATIVE/ Bottles	STATION LOCATION	SAMPLE COLLECT DATE/TIME		INORGANIC SAMPLE No.	FOR LAB USE ONLY Sample Condition On Receipt
C3TK1	Surface Water/ BOBBY SAMPLER	/G	1310.0 (21), BNA (14), CLP ARO (14), CLP PEST (14), VOA (14)	6-2119002, 6-2119003, 6-2119004 (Ice Only), 6-2119005 (Ice Only), 6-2119006, 6-2119008 (6)	LOCATION ONE	S: 11/9/2009	14:57	MC3TK1	
C3TK2	Surface Water/ DAN SAMPLER	/G	BNA (14), CLP ARO (14), CLP PEST (14), VOA (14)	6-2119010, 6-2119011, 6-2119012 (Ice Only), 6-2119013 (Ice Only), 6-2119014 (5)	LOCATION TWO	S: 11/9/2009	8 13	MC3TK2	
C3TK4	Surface Water/ DAN SAMPLER	/G	1310.0 (21)	6-2119026 (1)	LOCATION THREE	S: 11/9/2009	8 14	MC3TK4	
C3TK5	Surface Water/ JOHN SAMPLER	/G	BNA (14), CLP ARO (14), CLP PEST (14), VOA (14)	6-2119027 (Ice Only), 6-2119028 (Ice Only) (5)	LOCATION FOUR	S: 11/9/2009	8 14		
C3TK6	Surface Water/ JOHN SAMPLER	/G	1310.0 (21), BNA (14), CLP ARO (14), CLP PEST (14), VOA (14)	6-2119033, 6-2119034, 6-2119035 (Ice Only), 6-2119036 (Ice Only), 6-2119037, 6-2119039 (6)	LOCATION FIVE	S: 11/9/2009	8 14	MC3TK6	
C3TK7	Surface Water/ JOHN SAMPLER	/G	1310.0 (21), BNA (14), CLP ARO (14), CLP PEST (14), VOA (14)	6-2119041, 6-2119042, 6-2119043 (Ice Only), 6-2119044 (Ice Only), 6-2119045, 6-2119047 (6)	LOCATION SIX	S: 11/9/2009	8 14	MC3TK7	

Shipment for Case Complete?N	Sample(s) to be used for laboratory QC: C3TK1	Additional Sampler Signature(s):	Cooler Temperature Upon Receipt:	Chain of Custody Seal Number:	
Analysis Key:	Concentration: L = Low, M = Low/Medium, H = High	Type/Designate: Composite = C, Grab = G		Custody Seal Intact? ___	Shipment Iced? ___

1310.0 = VOA by MA 1310.0, BNA = CLP TCL Semivolatiles, CLP ARO = CLP TCL PCB (Aroclors), CLP PEST = CLP TCL Pesticides, VOA = CLP TCL Volatiles

TR Number: 3-043013577-050310-0004

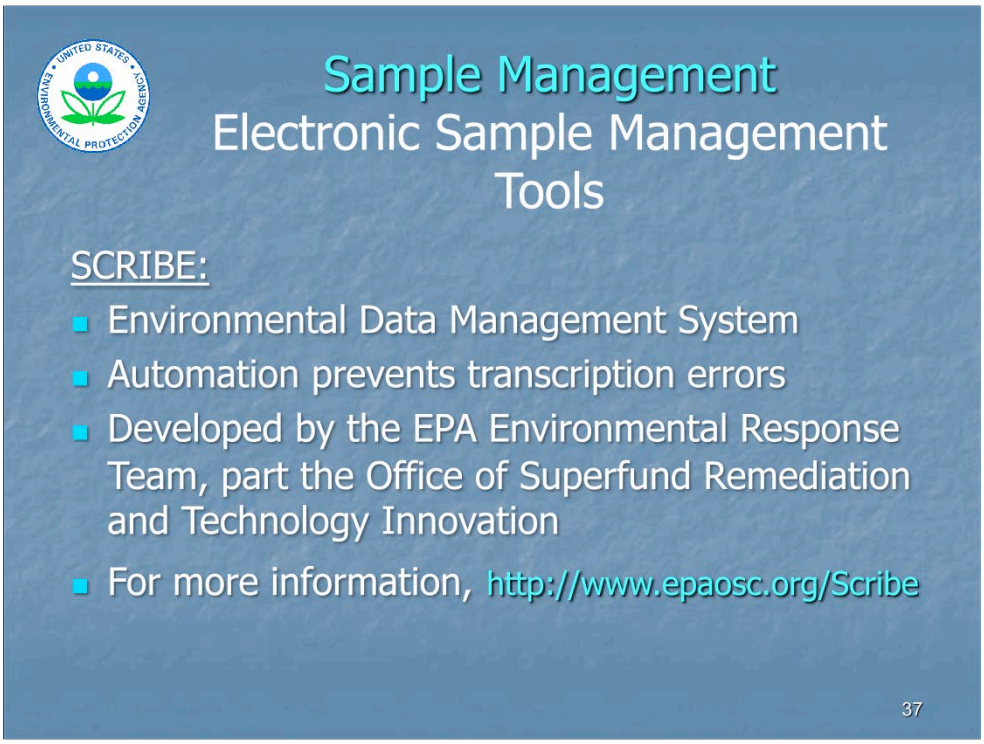
LABORATORY COPY

PR provides preliminary results. Requests for preliminary results will increase analytical costs.
Send Copy to: Sample Management Office, Attn: Heather Bauer, CSC, 15000 Conference Center Dr., Chantilly, VA 20151-3819; Phone 703/818-4200; Fax 703/818-4602

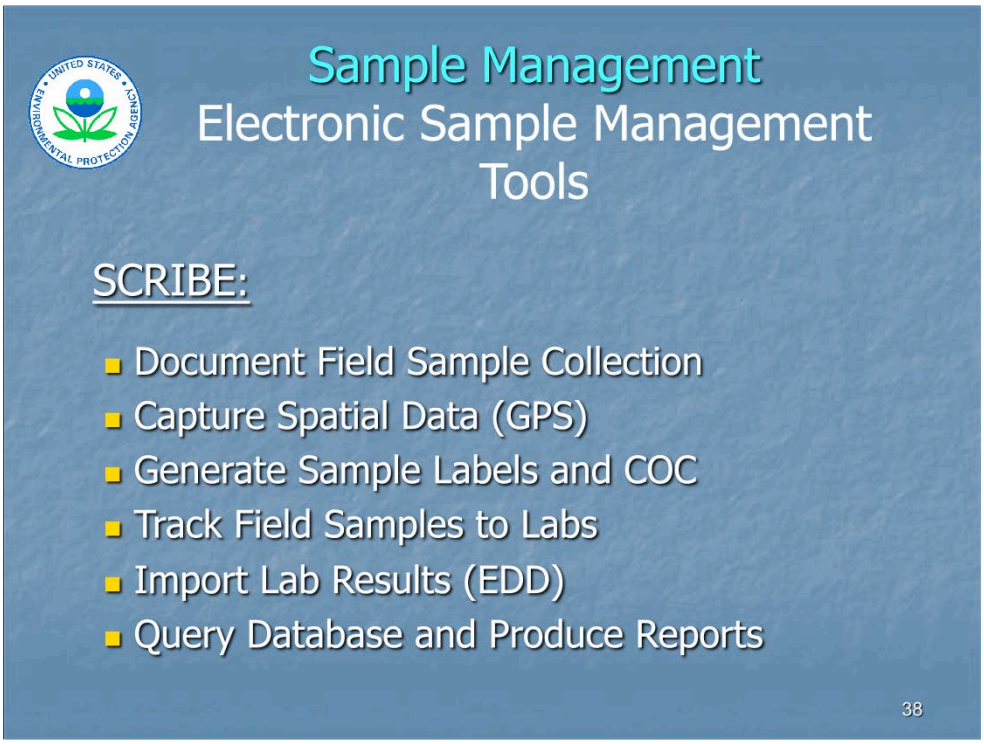
FZV5.1.047 Page 1 of 1

Here is an example of a chain-of-custody form, complete except for no signatures yet. There are a couple of things I would like to point out:

1. The chain-of-custody should contain sample identification, sampling dates and times, preservation, number of containers, and requested analyses for each sample in the shipment. Even though it is called a chain-of-custody, there is no chain of custody unless every person who received or relinquished the box or cooler containing the samples signed and dated the document. The laboratory should write on the chain-of-custody the temperature measured inside the container upon receipt.
2. The form has been filled out electronically, which helps to eliminate transcription errors. The form can be initiated at the beginning of the day in the order that the field team will visit the collection sites. The field team then processes the samples in order and completes the form with signatures before closing the cooler. If the day doesn't go as planned, the form can be re-printed.
3. The form includes a cross-reference to other associated samples for the benefit of project personnel and data reviewers.
4. The form is customizable for the particular type of samples, to include preservation, numbers of containers for each method, and individual sample IDs for ease of tracking and identification.



The form above was generated using a software tool called Scribe.

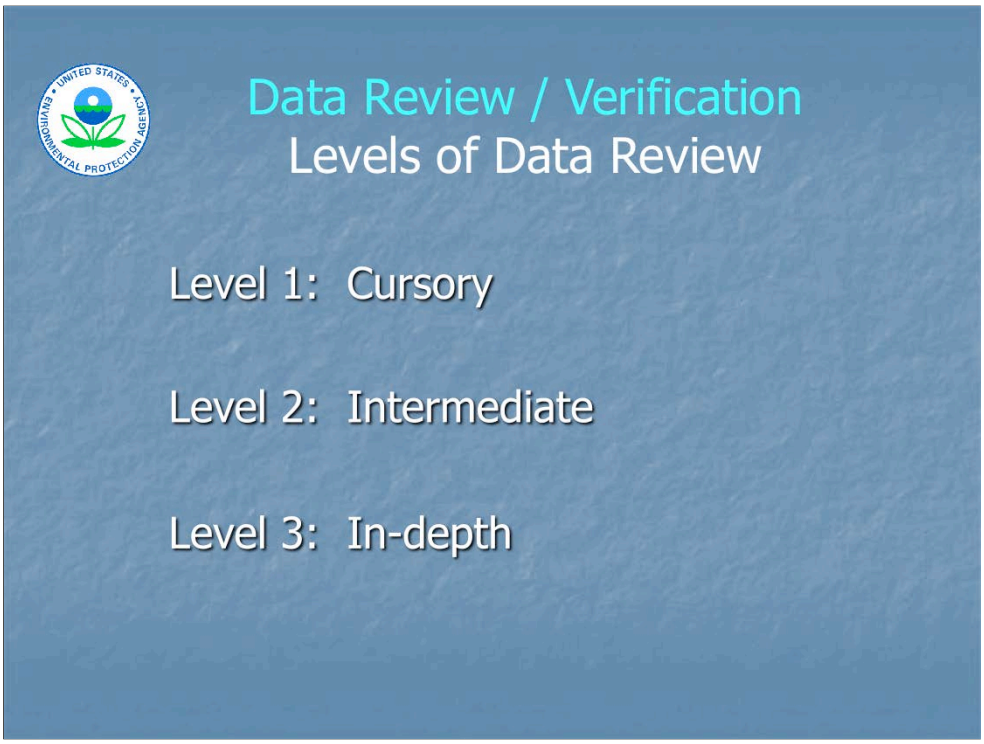


Not only does this tool document the collection of field samples, generate and print the labels, it also captures several other types of information including geospatial data, it facilitates sample tracking and allows upload of the final data for use in producing reports.

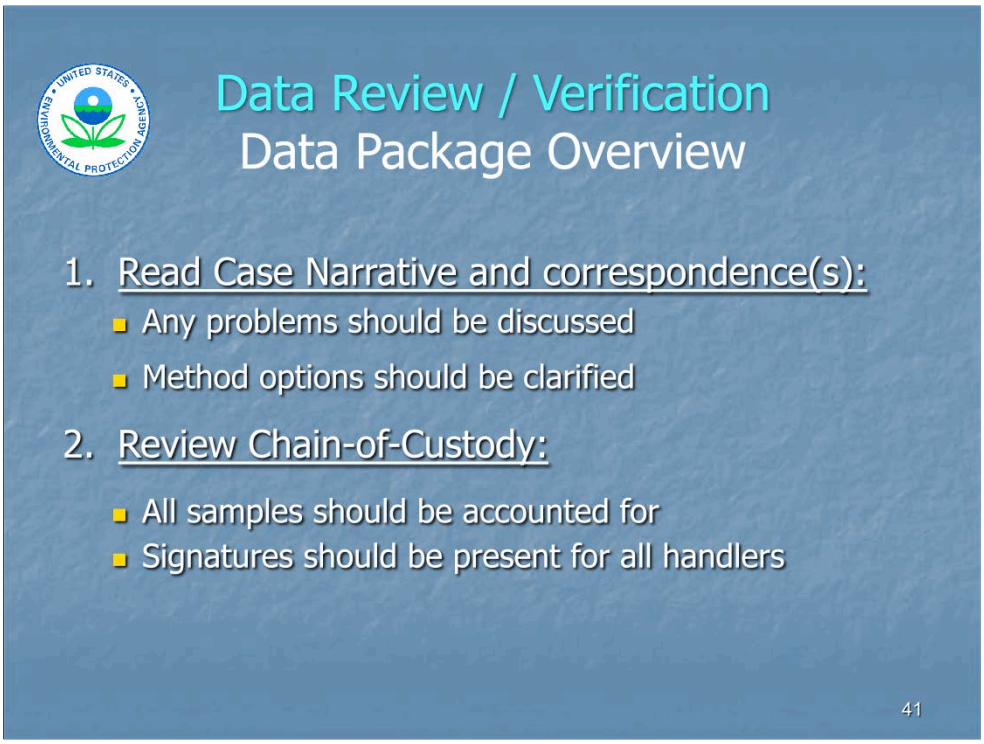
PART 5:
Data Review / Verification

- Levels of Data Review
- Data Package Overview
- Instrument Performance Checks
- Calibration Data
- QC Sample Data
- Sample Data
- Final Evaluation of Data
- Data Qualifiers used by the CLP
- Example Flag Hierarchy
- Data Reporting

39

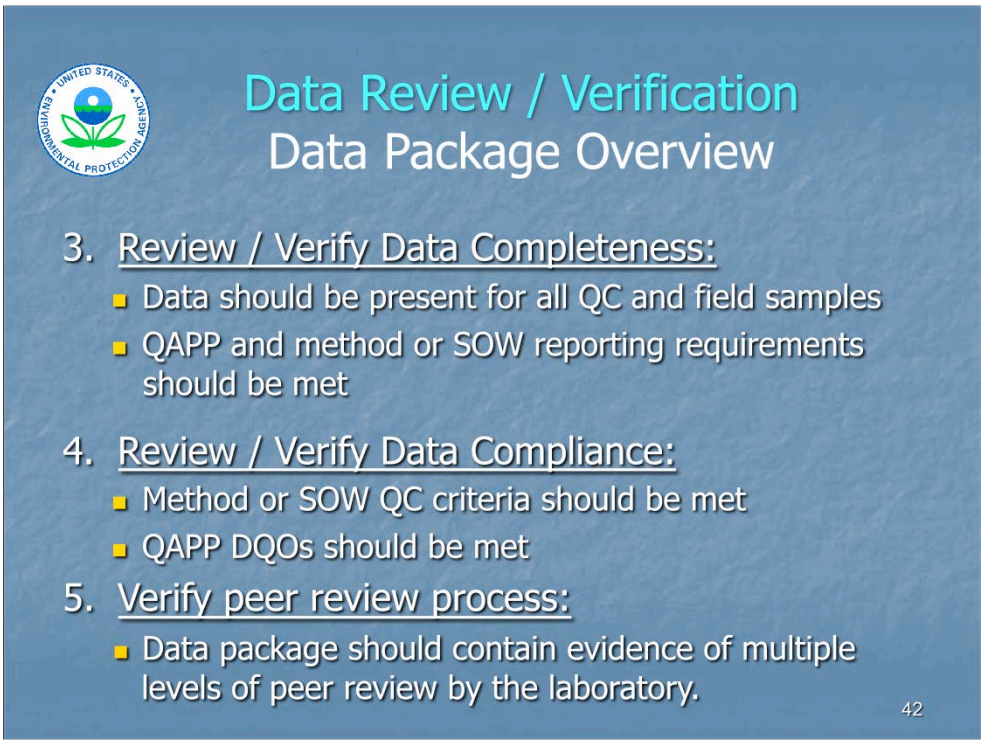


Earlier we mentioned that the level of data review to be performed was an item to consider during project planning. This is because the level of review should be commensurate with the information needs of the project. For example, if the decision only needs screening level data, why pay for an in-depth review? Hopefully the laboratory was asked to only produce screening level data in this case.



The **Case narrative** should contain a list of all samples analyzed for the sample group being reported (in the CLP, we call this a sample delivery group or SDG). A cross-reference between the sample ids on the chain-of-custody and the lab's sample ids is helpful, but you may have to ask for it. The narrative should describe any problems with analysis of the samples, and any QC deficiencies. The specific procedures followed by the laboratory when there are options presented in the method should also be discussed. A common example is the choice of GC columns. It is also very helpful for the reviewers if specific examples of all calculations performed in producing the results are provided in the narrative. Labs may not provide a narrative unless you ask for it.

Copies of Laboratory **correspondence** (typically at end of package) should further document any logistical problems or attempts to get information. As with the case narrative, labs may not provide copies of communication unless you ask for them.

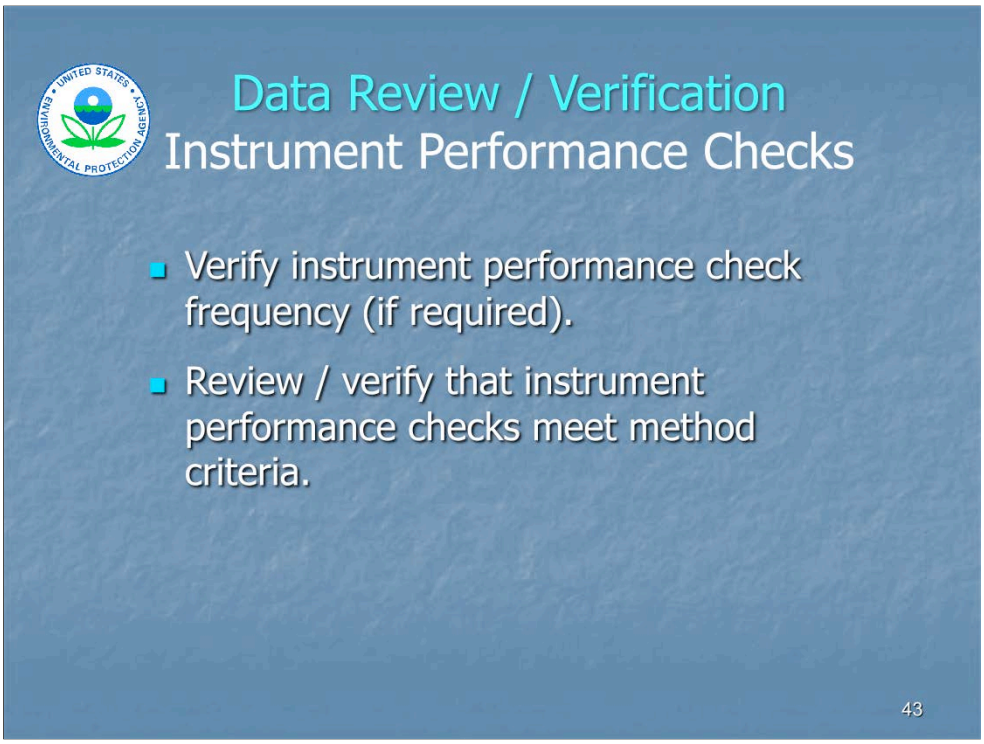


The reviewer's first pass through a package of data should be to make sure data are present for all requested samples, that they have all the requested information about each sample, all analytes are reported, are in the requested format, that QC sample results and calibration data are also present, and that each sample can be associated with the QC samples and calibration data provided. This last item can be verified by looking at copies of analysis run logs, or by checking analysis dates, times, instrument identifiers, and analysts' initials.

Along with analysts' initials either written or printed on the data, there should be evidence of peer review by at least one other individual at the lab, and preferably by two other people.

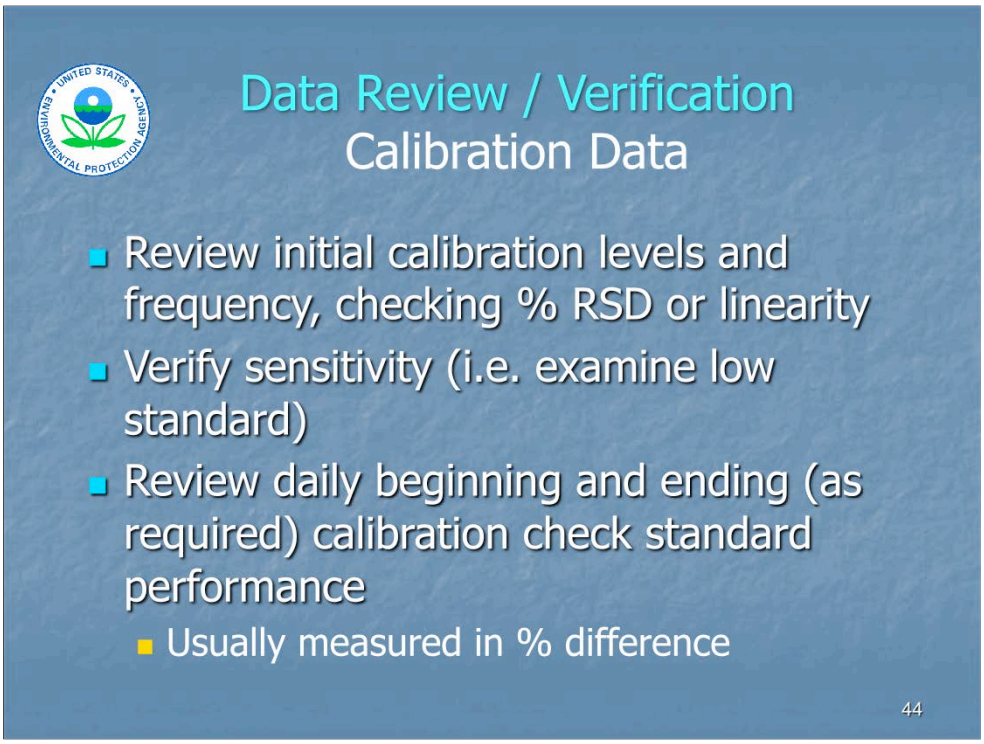
If there isn't enough information to make these determinations, it represents an information gap and may require follow-up with the lab.

Finally, review the data package for compliance with method and/or QAPP quality criteria.



1. Verify instrument performance check frequency (if required). Remember the types of performance checks we talked about: tune checks for MS, interference check samples for ICP for example.

2. Review / verify that instrument performance checks meet method and/or instrument manufacturer criteria.



Check the frequency of all calibrations.

Review initial calibration data for compliance with method criteria, including that the expected calibration model was used. For example, if the lab was supposed to use a first-order linear regression, that should be what is reported (you can check this with the concentrations and responses given). If this is not the case, then the data may not be comparable with other data for the site.

Verify system sensitivity. This is usually done by examining the low standard in the calibration series.

Calibration verifications also should be at the expected frequency and meet criteria. The CCV should be at the expected concentration, typically at the midpoint of the curve.

Note any calibration outliers for possible data qualification.

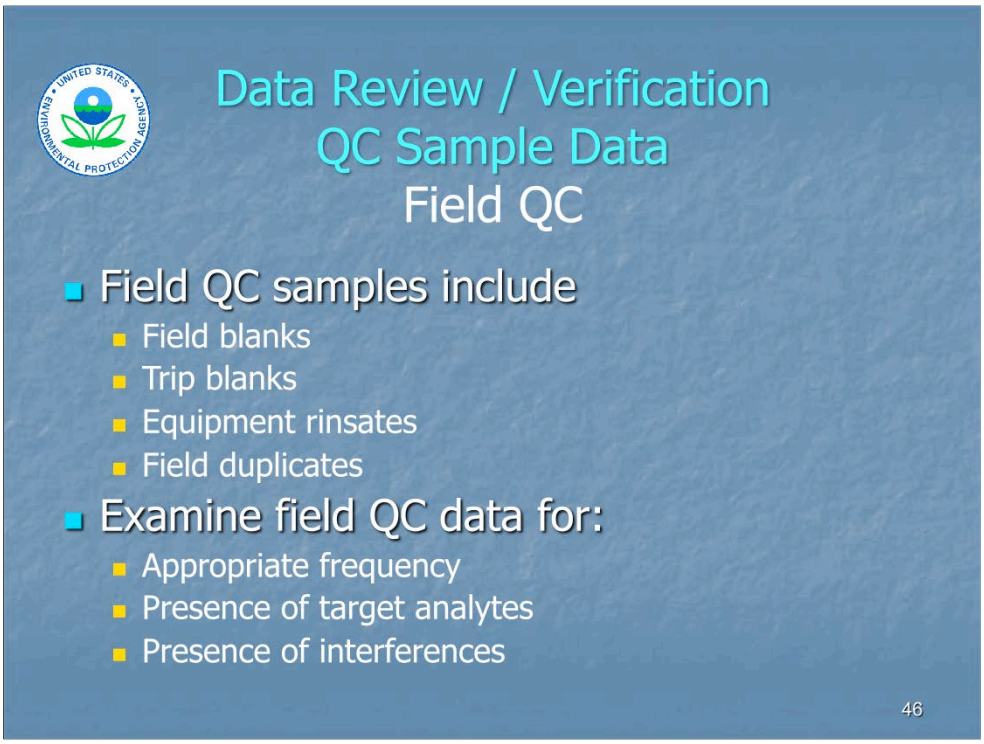
Data Review / Verification
QC Sample Data

Types of QC Samples:

- Laboratory Blanks
- Field QC
- Spikes
- Duplicates
- Serial Dilutions
- System Performance Check Samples
- Laboratory Performance Evaluation Samples

45

Next, check the QC samples for appropriate frequency and compliance with method and/or QAPP requirements. All laboratory-generated QC sample analyses should meet method requirements (if a lab can't successfully analyze a clean sample, or if there is a problem, doesn't fix the problem and start over, what does that say for the rest of the data?

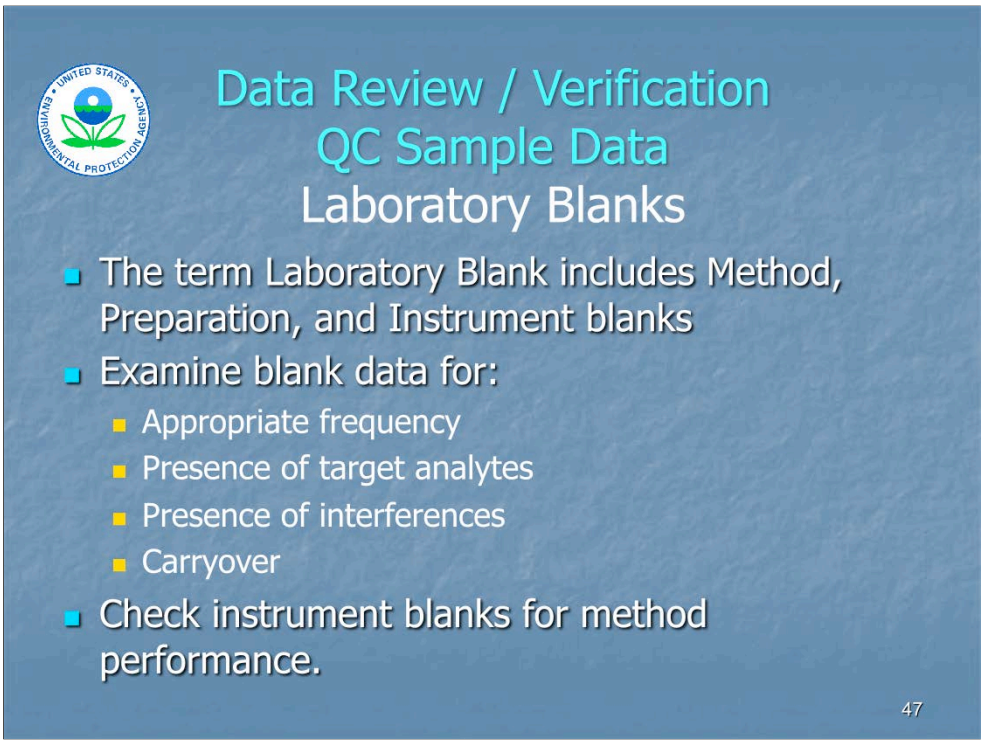


Field blanks are samples created with a certified clean matrix, that are taken to the field, opened in the field, and then transported to the lab in the same outer container as the field samples. They are preserved in the same manner and using the same chemicals (if chemical preservation is used) as field samples. The purpose of a field blank is to detect contamination introduced by sample handling techniques and the environment in the field.

Trip blanks are essentially the same as field blanks, except that they are not opened in the field. As with field blanks, they are preserved in the same manner as field samples. The purpose of trip blanks is to test the preservation chemicals, if any, and in the case of volatile analytes, to test for cross-contamination during shipment and handling of the samples.

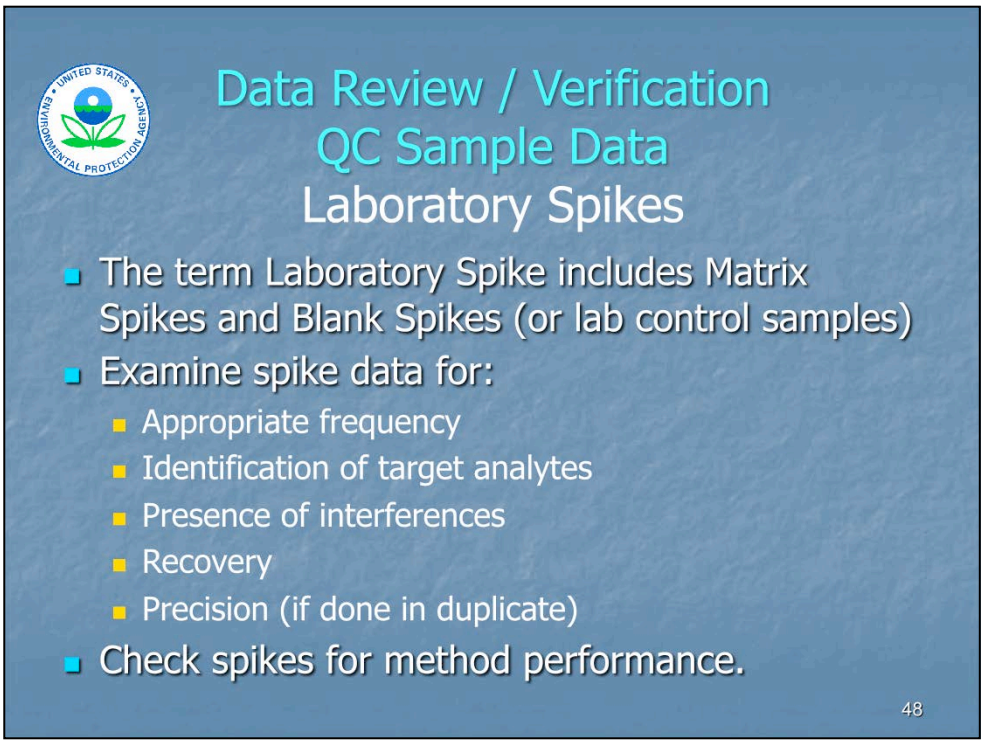
Equipment rinsates are generated with the same clean water used for aqueous field and trip blanks, by rinsing a piece of sampling equipment after washing (or decontamination) and just before re-use. They are preserved as with the other blanks and samples. The purpose of equipment rinsates is to test the decon procedure.

Field duplicates are self-explanatory. Their purpose is to test matrix homogeneity and sampling technique.



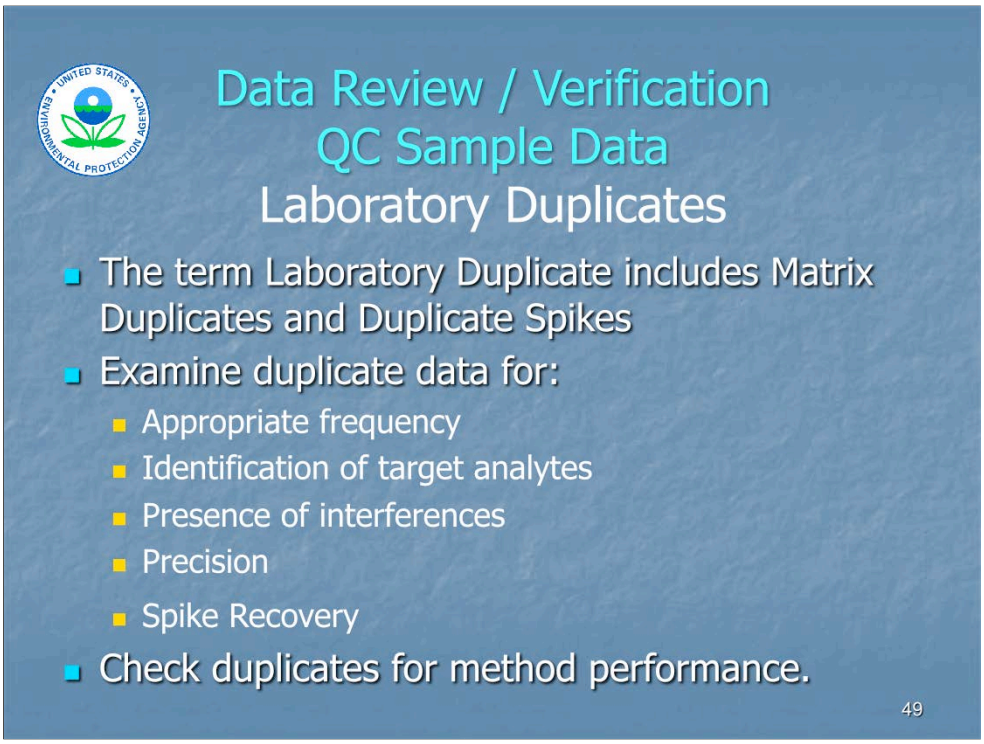
Method blanks and preparation blanks are the same, but in some methods you will see method blanks, while in others you will see prep blanks. As I described the blanks among field QC, method blanks and sample preparation blanks are created in the lab from a certified clean matrix. They should include any preservation chemicals, and are processed along with the field samples with the same reagents and equipment.

Instrument blanks are not processed with the samples until the analytical step, and consist of the same matrix or solvent as the final prepared sample. For example, an instrument for metals analysis will have acid in it. An instrument blank for pesticides will have the same solvent as the extracts. Their purpose is to test for carryover between sample analyses.

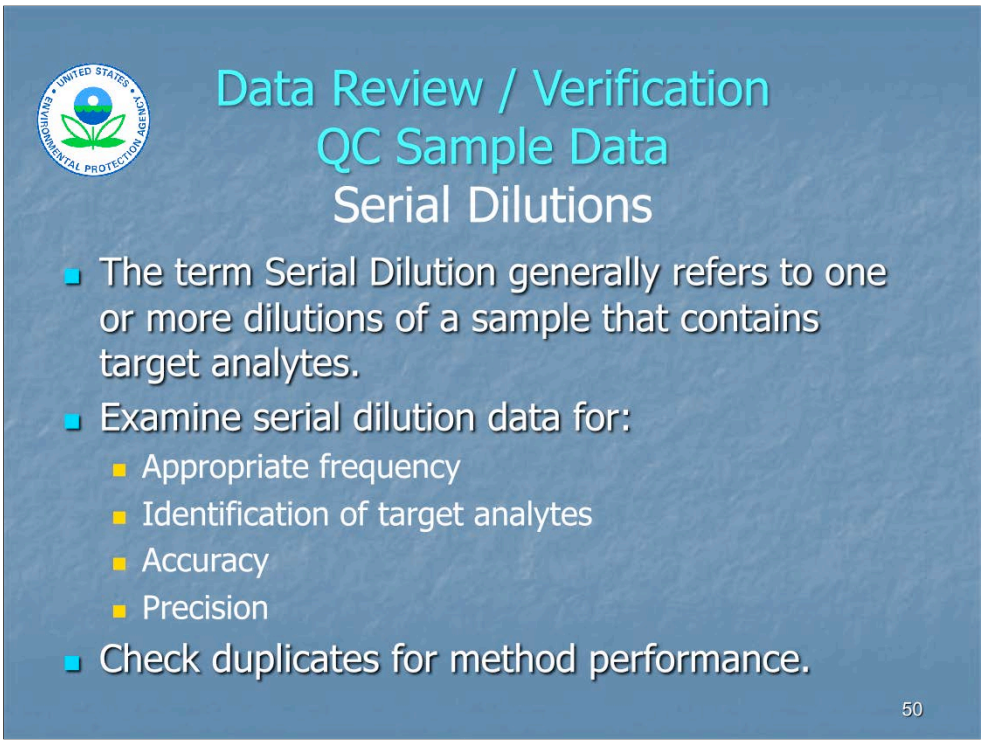


The term Laboratory Spike includes Matrix Spikes and Blank Spikes (or lab control samples)

Examine spike data for frequency, Identification of target analytes, Presence of interferences, Recovery, and Precision (if done in duplicate).

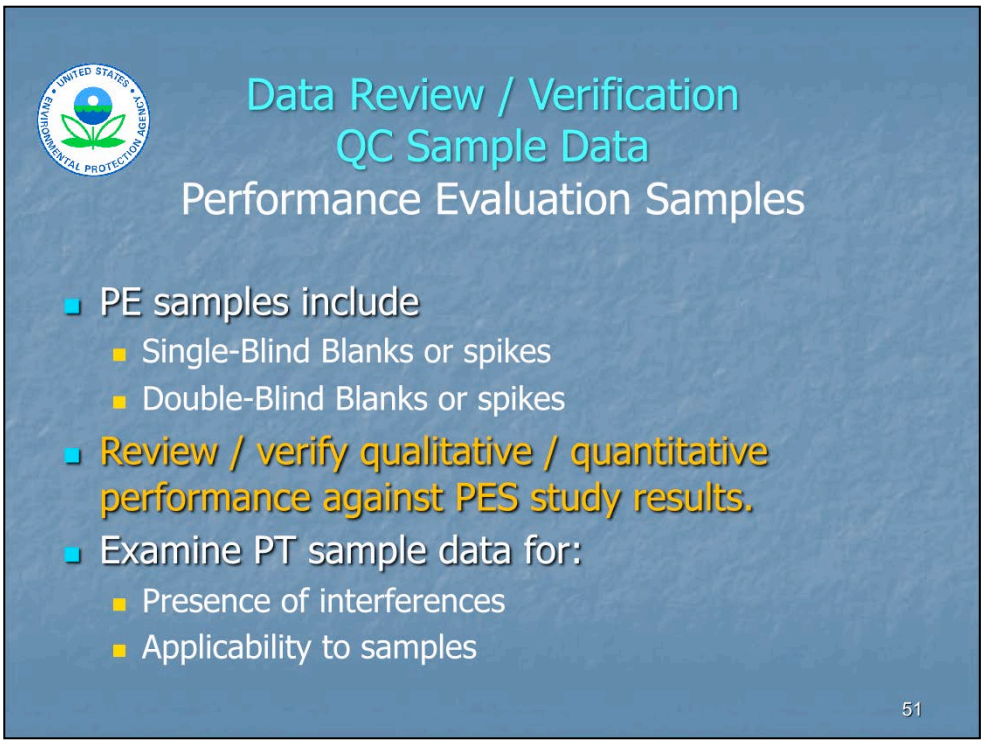


In the lab, the purpose of duplicates is to check precision and preparation technique. Lab duplicates are not required in all methods (especially organics), so if not, there should be a provision in the QAPP requiring either duplicate matrix spikes or blank spikes. I prefer blank spikes because they test whether a lab can do the method accurately and precisely with no matrix interferences.



The purposes for Serial Dilutions are to check technique and to check whether matrix interferences may have an impact on lower level response.

The reviewer should make sure the lab has chosen a sample for the dilution that has target analytes at an acceptable level.



PE samples include

Single-Blind Blanks or spikes

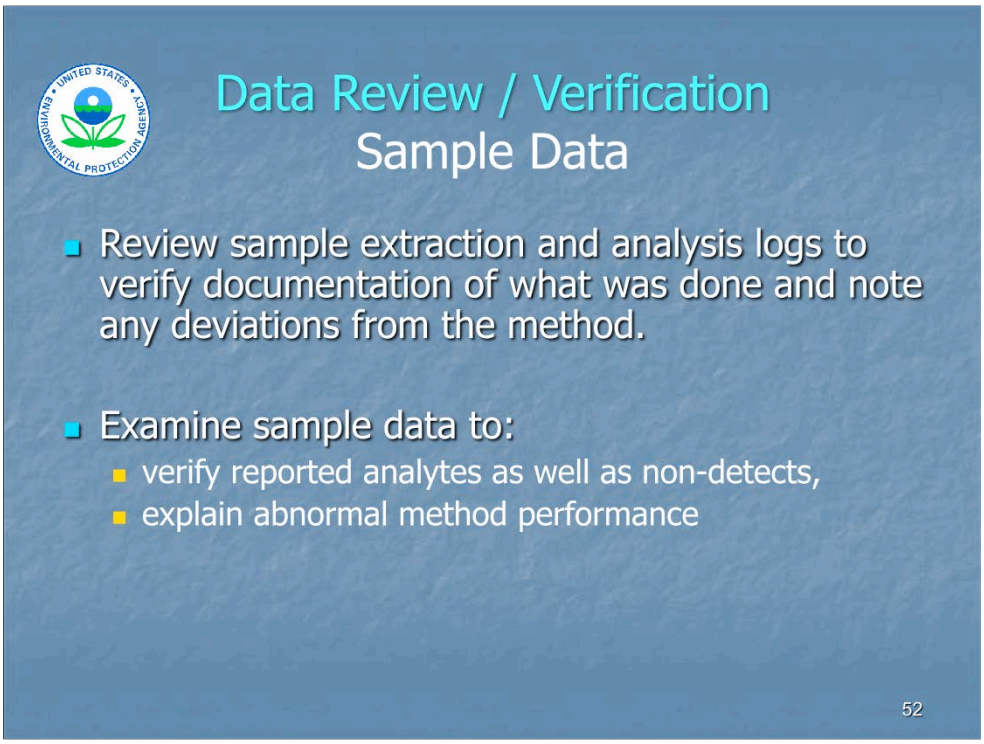
Double-Blind Blanks or spikes

Review / verify qualitative / quantitative performance against PES study results.

Examine PT sample data for:

Presence of interferences

Applicability to samples



Review sample extraction and analysis logs to verify documentation of what was done and note any deviations from the method.

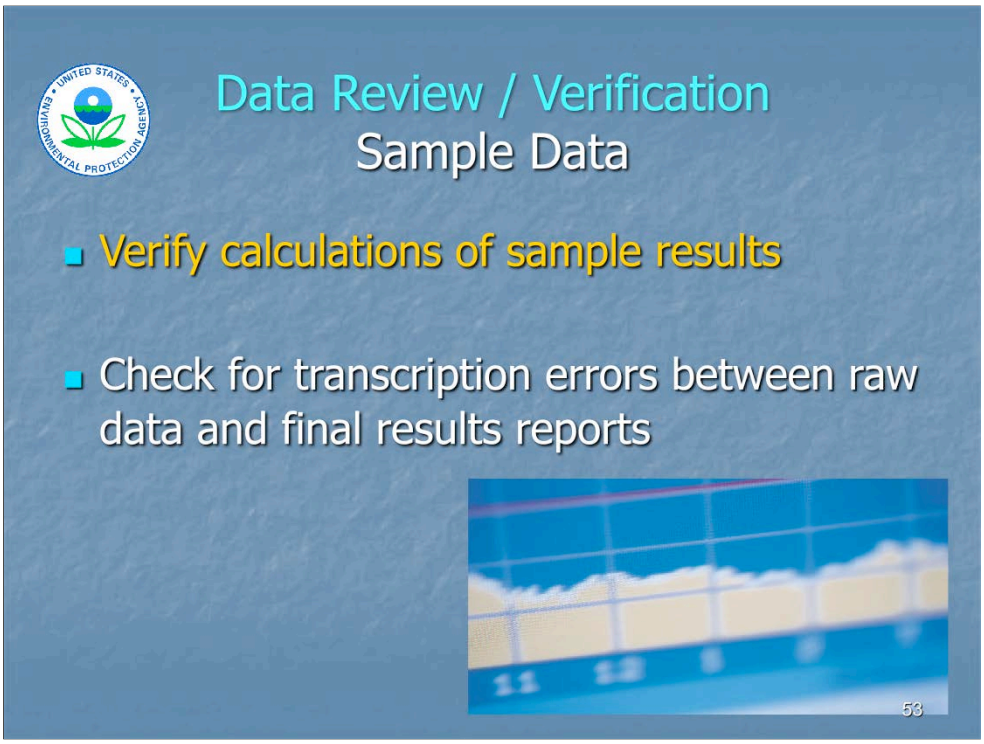
Examine sample data to:

verify reported analytes as well as non-detects,

explain abnormal method performance or problems with the sample. It may be that a different (or modified) method should be used for a particular sample.

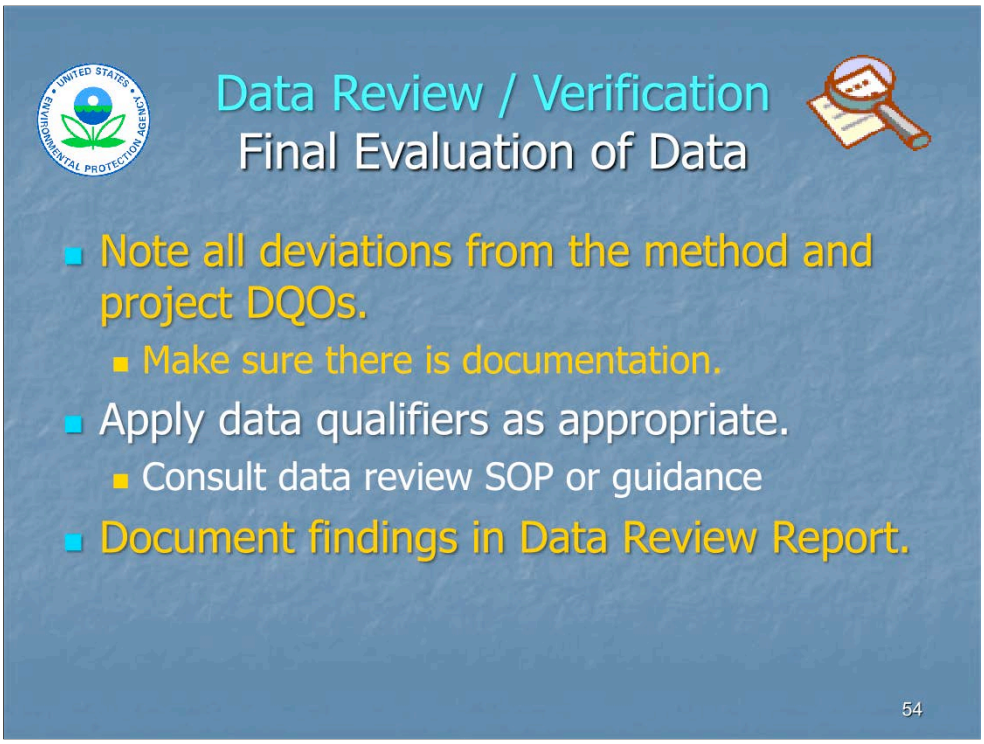
If the level of documentation will support re-calculation of results, at least one of each calculation leading to the production of the final result should be duplicated by hand. This step is automated for most data going through the CLP. Verify there is continuity of units, and that no rounding has been done prior to the last calculation.

Check for transcription errors between the processed data and the reporting form, and check for proper significant figures. The rule of thumb should be one significant figure for screening data and two, or perhaps three, for definitive data.

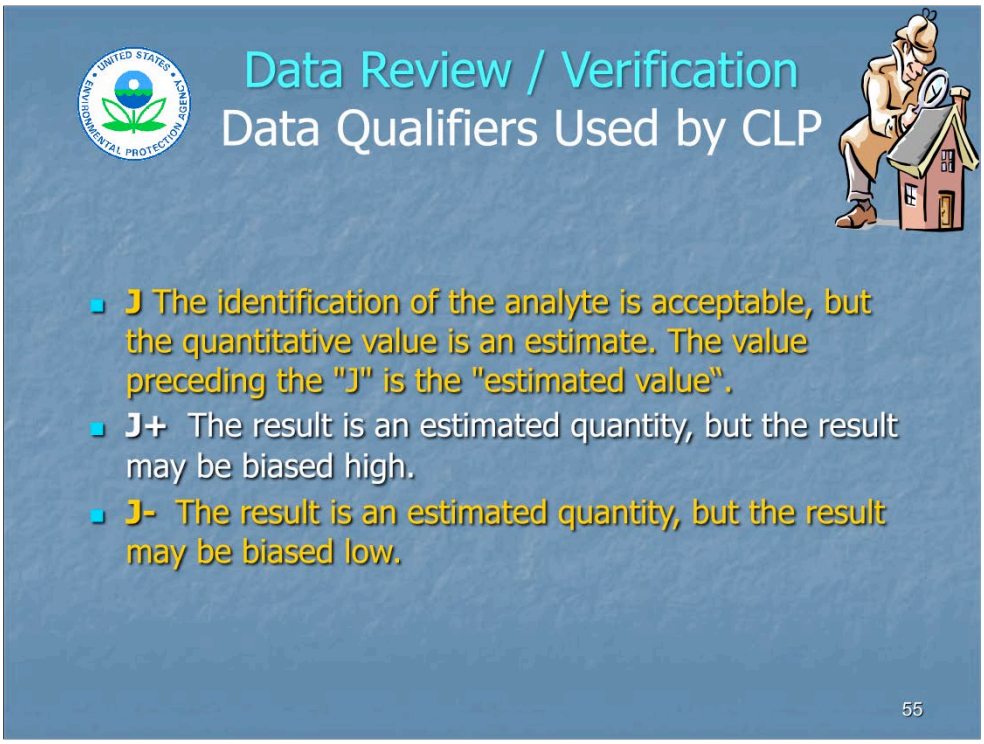


If the level of documentation will support re-calculation of results, at least one of each calculation leading to the production of the final result should be duplicated by hand. This step is automated for most data going through the CLP. Verify there is continuity of units, and that no rounding has been done prior to the last calculation.

Check for transcription errors between the processed data and the reporting form, and check for proper significant figures. The rule of thumb should be one significant figure for screening data and two, or perhaps three, for definitive data.



Based on your review of the data, decide whether any data need to be qualified to document and transmit information about data quality and usability to the end user. Summarize all your findings about the data package. Use tables, print-outs or copies of pages from the data package to illustrate particular findings in the review. Be sure to provide your honest recommendation as to the condition of the data, whether it is supported by the information supplied with it, and whether it should be considered usable as qualified (or not). Finally, have your data review report peer reviewed by a qualified individual.



While we are talking about data qualifiers, let me explain a little about data qualifiers used by the CLP. I am aware that there are many data qualification regimes out there, some simple, some incredibly complicated.

J, J+/J- A word of caution about using J+ or J-: use of these qualifiers could be misleading if you don't have information about all other sources of bias.

Data Review / Verification
Data Qualifiers Used by CLP

- **U** The analyte was analyzed for but not detected. The value preceding the "U" is the "minimum quantitation limit (MQL)".
- **N** There is presumptive evidence that the analyte is present, but it has not been confirmed. The analyte is "tentatively identified".
- **C** The presence of the analyte was confirmed, i.e., by GC/MS.

56

Data Review / Verification
Data Qualifiers Used by CLP

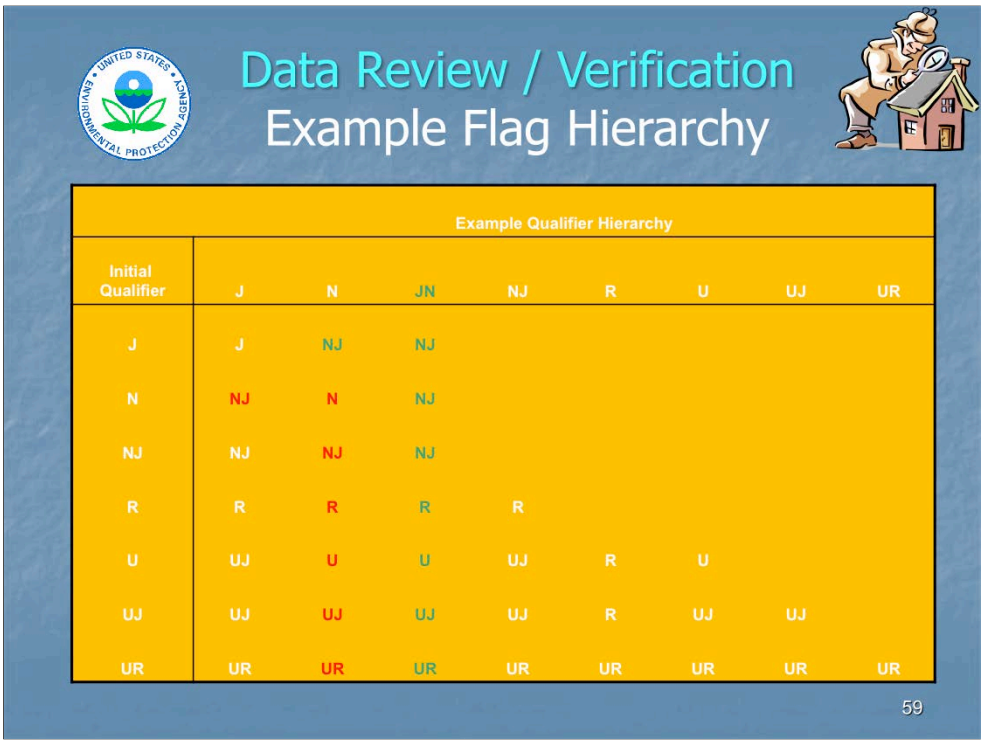
- **X** This qualifier applies to pesticide and Aroclor results when GC/MS analysis was attempted but was unsuccessful.
- **R** "Rejected" result, should not be used.
- **UJ** This is a combination of the "U" and "J" codes. The analyte is not detected and the value preceding "UJ" is an estimated MQL.

57

Data Review / Verification
Data Qualifiers Used by CLP

- **JN** This is a combination of the "J" and "N" codes. The analyte is tentatively identified and the value preceding the "JN" is estimated.
- **UR** This is a combination of the "U" and "R" codes. The analysis did not indicate the presence of the analyte. The data is rejected and the value preceding "UR" is the MQL. Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

58

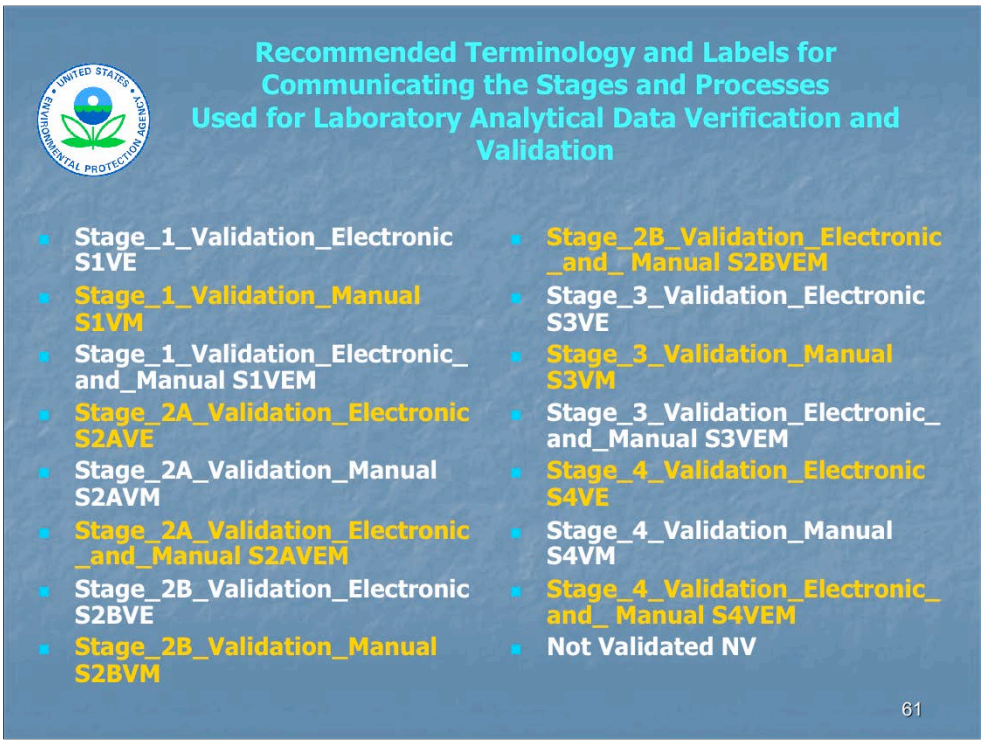


When more than one qualifier are applicable to a result, certain combinations make sense, but more than two applied to one result can be confusing. Therefore, we recommend establishing a hierarchy such as this.

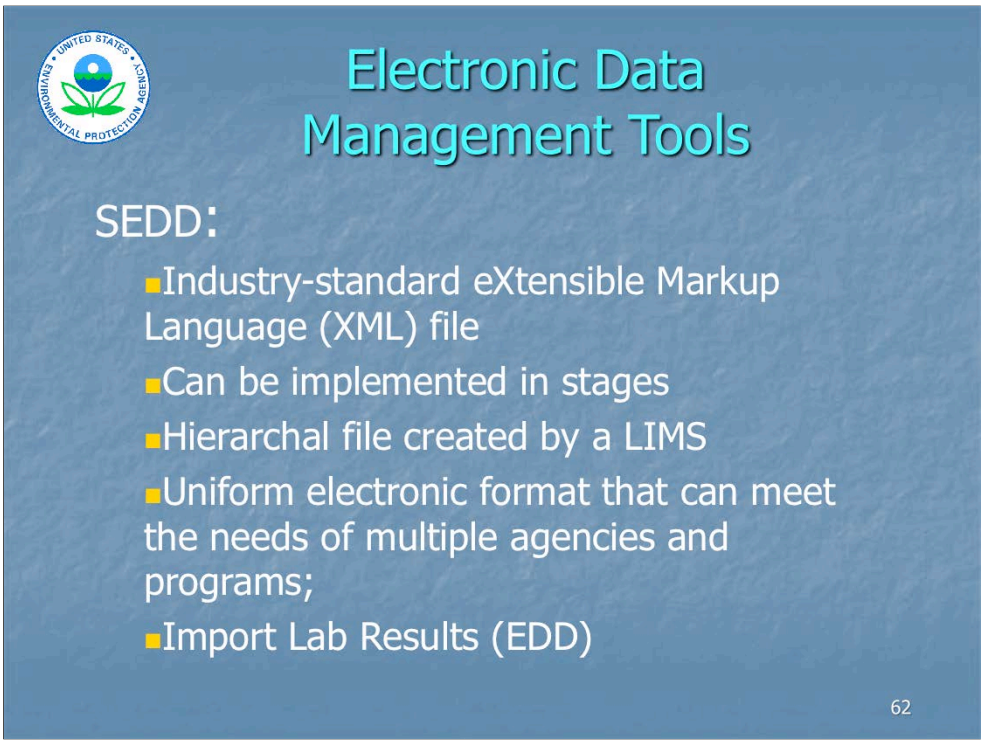
You have your qualified data and your data review narrative. I forgot to ask you whether you had a Standard Operating Procedure for what you did, or if you would reply that, "EPA told me to do it this way!" If you perform data review on any consistent basis, you should have an SOP. If you don't perform it, or until you have enough data coming in that it is a regular part of the routine, I recommend hiring third-party experts.

As a result of your review findings, there may be some follow-up items, such as missing documentation, a dilution that should have been done, or something like that. Typically the individual who is the POC for the lab should be the one to ask them to reconcile these issues. After reconciliation, you may need to revisit the review.

One last step in the review process is to let others know who may need to use your data in the future (i.e., as secondary data) what level of review was applied to the data. The following table was developed by a work group at EPA for this purpose.



A guidance document for this labeling scheme can be found on the Superfund CLP website at epa.gov.



Industry-standard eXtensible Markup Language (XML) file

Can be implemented in stages

Hierarchal file created by a LIMS

Uniform electronic format that can meet the needs of multiple agencies and programs;

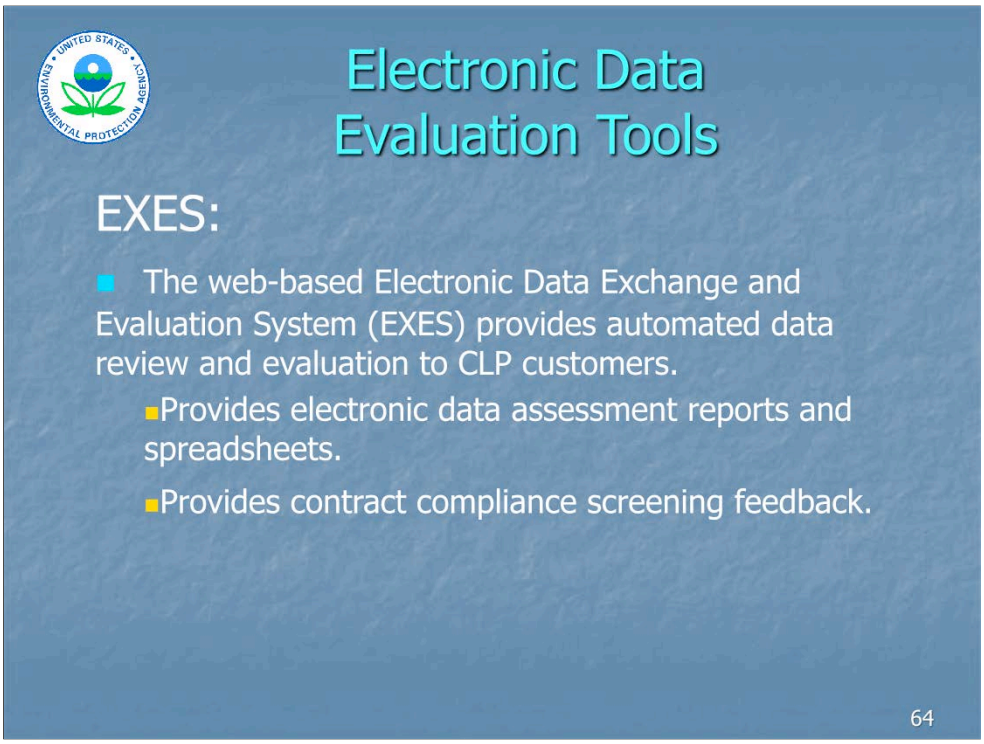
Import Lab Results (EDD)

Electronic Data Management Tools

SEDD Stages:

- Stage 1: minimum number of analytical data elements to convey results.
- Stage 2a and 2b: stage 1 plus method and instrument QC data, respectively.
- Stage 3: stage 1 and 2 plus data to allow for recalculation of reported results.
- Stage 4: stages 1, 2, & 3 plus raw instrument data files.

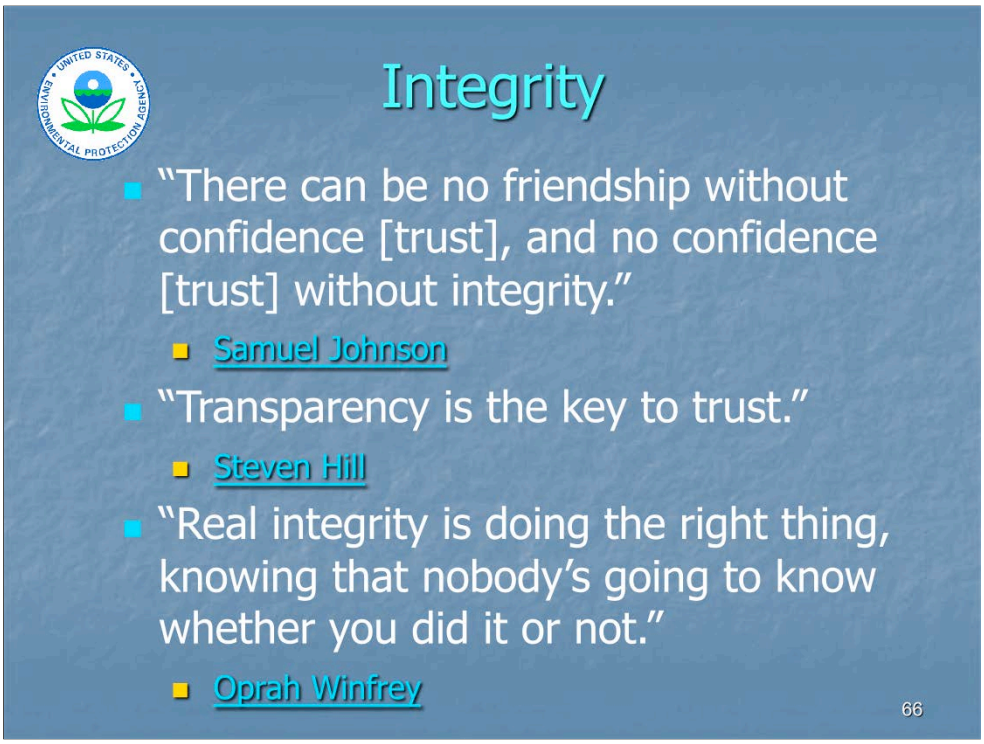
63



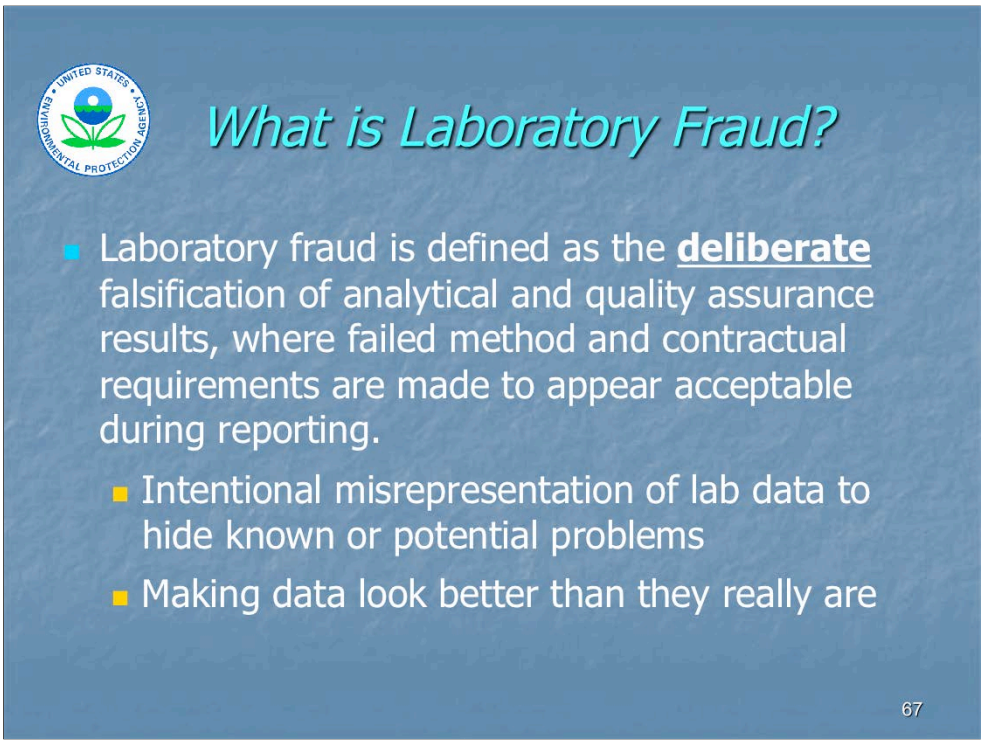
If you are interested in learning more about EXES, please register on the CLUin site for a webinar on March 24 by my co-worker, Sara Goehl, that will cover EXES in more detail, and she will answer your questions.

Improper Laboratory Practices

65



In order to help you to understand what I mean by the word integrity, let me share these three quotes.

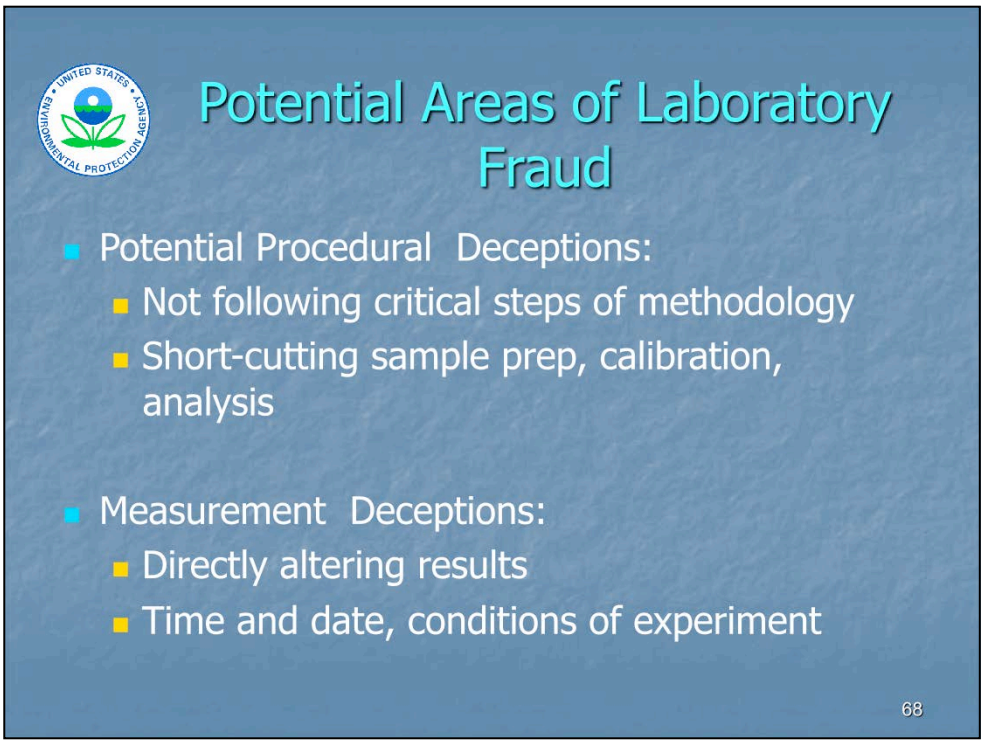


With that as a backdrop, what is laboratory fraud?

There can be no fraud without **intent**. Without intent, you have naivete or stupidity, or both.

Laboratory fraud is defined as the **deliberate** falsification of analytical and quality assurance results, where failed method and contractual requirements are made to appear acceptable during reporting.

> Intentional misrepresentation of lab data to hide known or potential problems
>
> Making data look better than they really are



Potential Procedural Deceptions:

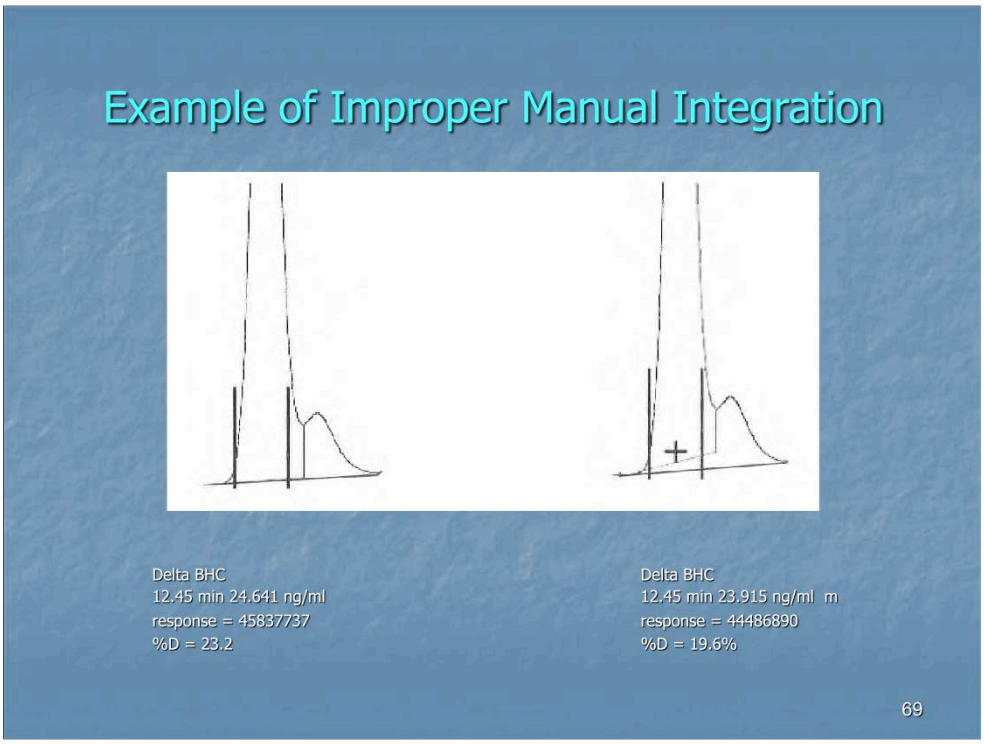
Not following critical steps of methodology

Short-cutting sample prep, calibration, analysis

Measurement Deceptions:

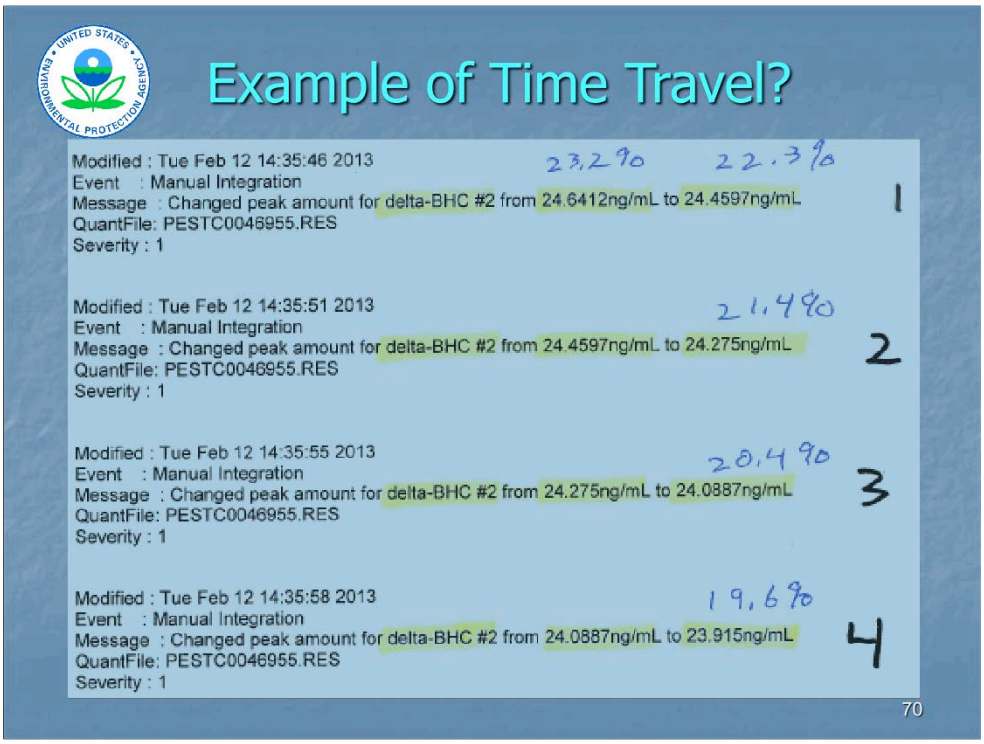
Directly altering results

Time and date, conditions of experiment



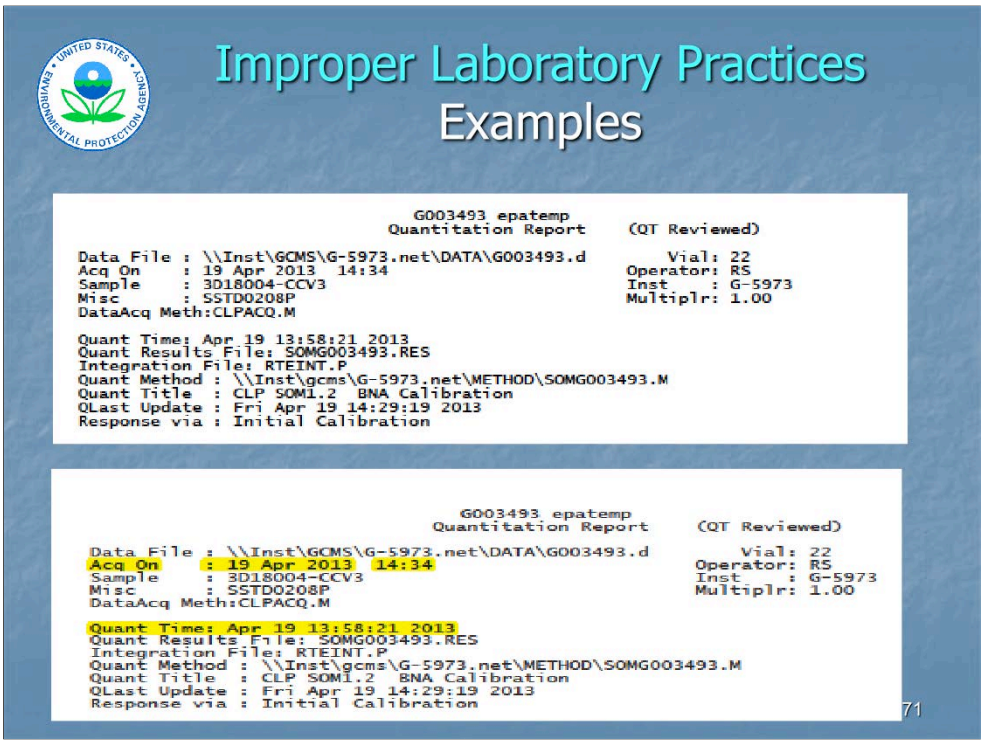
Here is what you may notice from looking at the data for a calibration verification standard. The peaks on the chromatogram are small, so perhaps you can look at a pdf of the data and blow it up to look for this. The typical chromatographic data system will sense a change in the slope of the detector response and integrate the peaks as shown on the left. But what you see is the one on the right, and you ask yourself, "why did they do that?" If it happens only once, you may be tempted to qualify the associated sample data for delta BHC as estimated and move on. But you should stay vigilant! When you see it repeatedly, only in standards or QC samples (which should be problem-free), and always with the result that the peak passed criteria when it otherwise would have failed, that is another story.

Other examples include: Selectively background subtracting spectra from other peaks to make tuning criteria pass in GC/MS analysis.

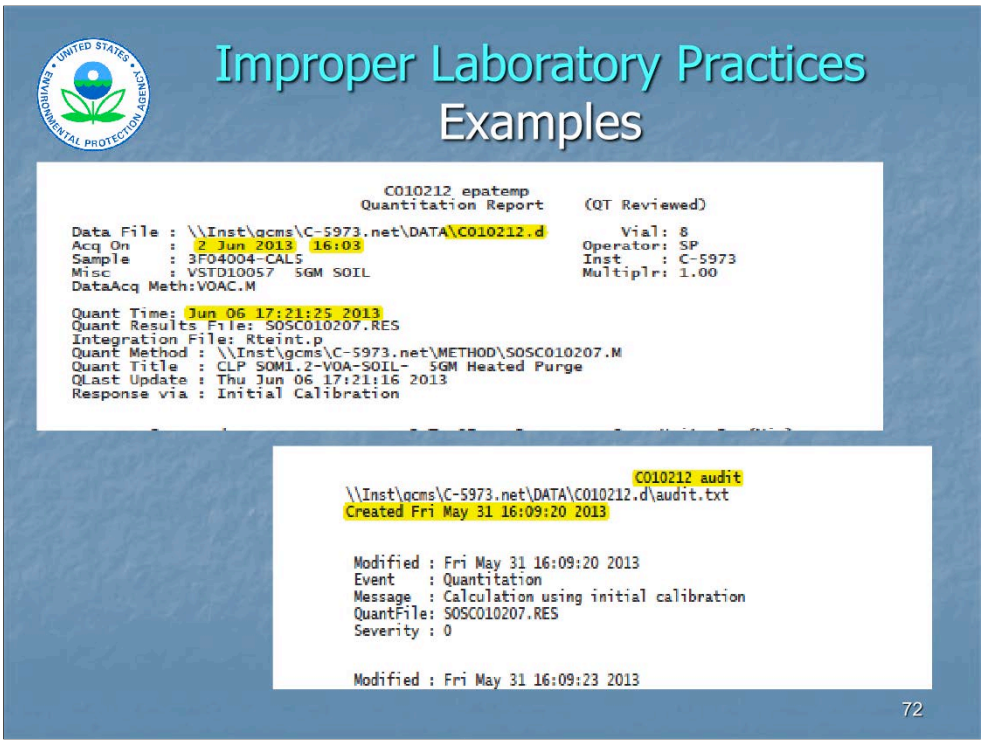


We are now looking at the audit trail for the peak we saw on the previous slide. You can obtain the audit trail by asking the lab for all raw and processed data files associated with the analysis. This is a text file that is associated with each injection on a GC or GC/MS instrument.

On slide 71, we saw that the initial percent difference between the delta-BHC peak and the initial calibration was 23.2%. The method performance criterion is < = 20%. From this trail, we can see that the peak was manually re-integrated four times in 12 seconds to create the result which meets the 20% criterion.

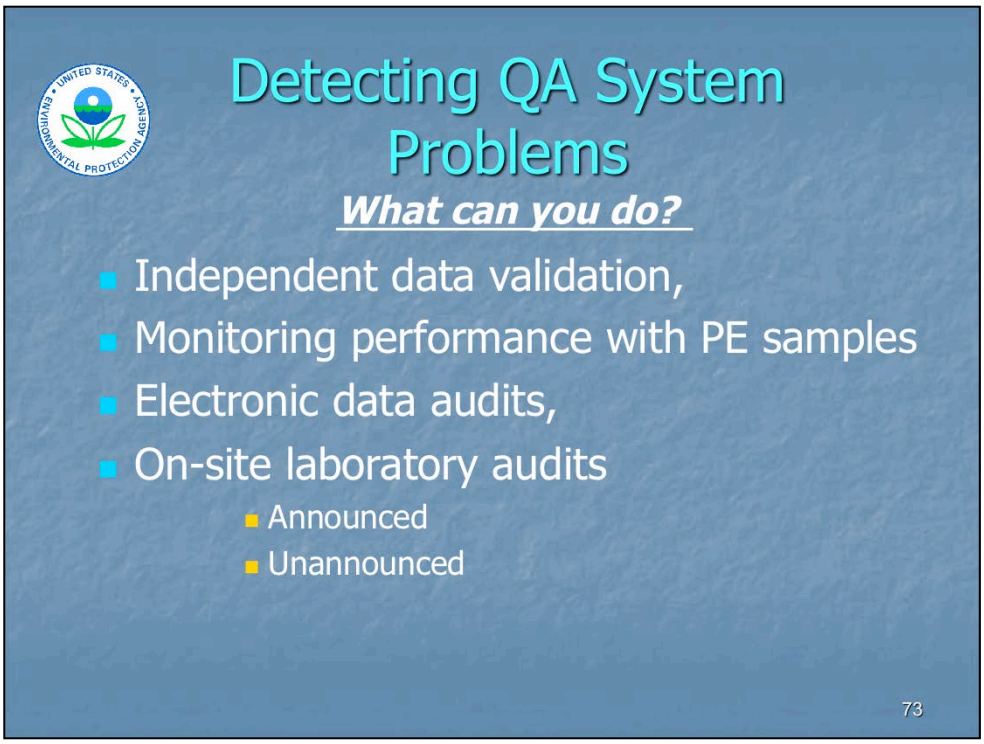


In this example, a CCV from a semivolatile GC/MS run, everything appears to be in order until you pay attention to the times. This analysis was quantitated before it was injected!



For this example, we obtained the audit trail text file. The quant report looks fine, the times make sense. However the reviewer, who was looking for the audit trail from the run on the previous slide, found that the audit trail file was created for this standard two days prior to the injection time!

If you do see something like this, you should not assume it is accidental, but you should investigate further, and consider providing it to someone who can open an official investigation. In the case of EPA, contact the Inspector General's office.



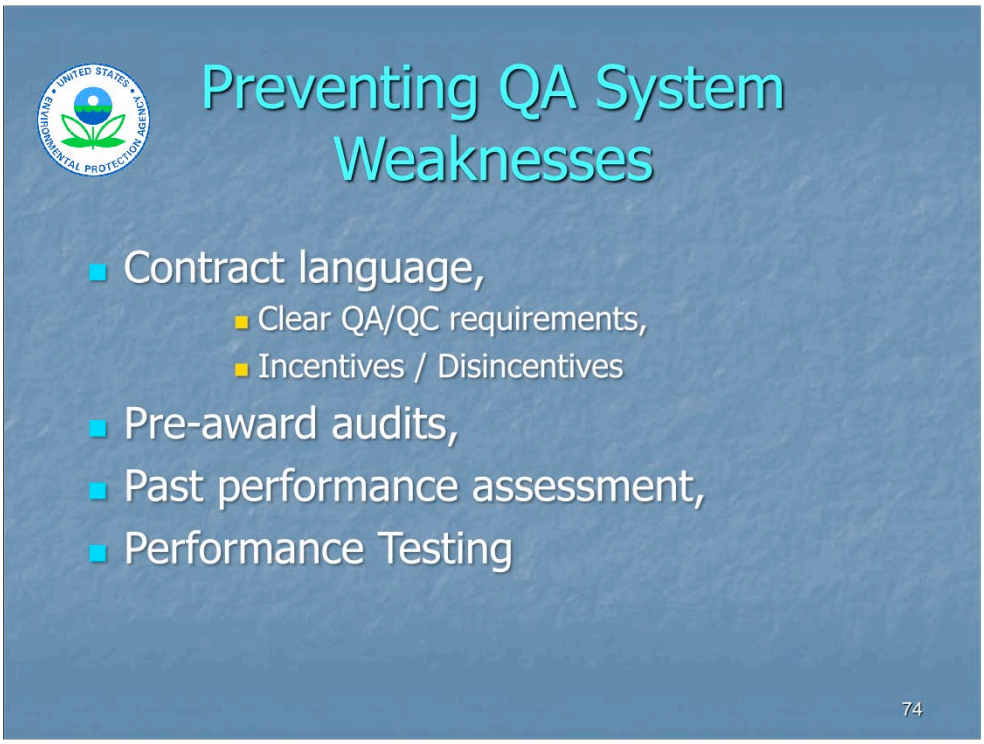
Independent data validation of all data, or of randomly selected data packages. If your project doesn't require enough raw data to detect these problems, periodically ask the lab to provide

you with a copy of everything that supports the data.

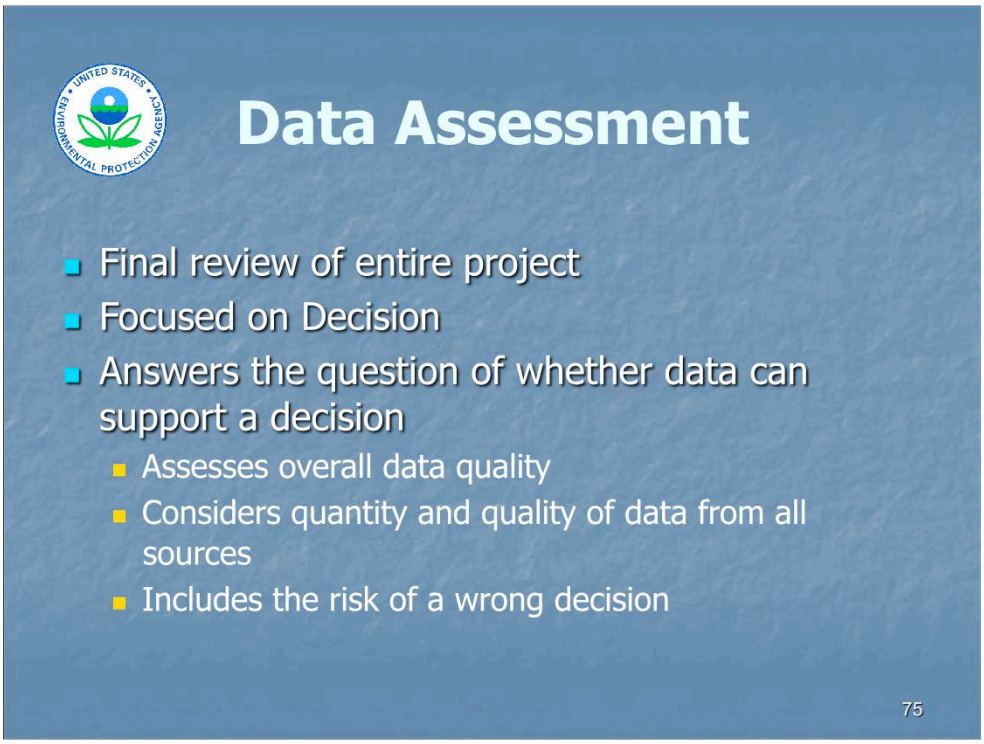
Monitoring performance with PE samples. Require that the PES be prepared and analyzed with the field samples.

Electronic data audits, done by the CLP on selected cases. This consists of requesting all hard copy (in pdf) and raw processed data and instrument files. We use the same software the laboratory has attached to their instruments to re-process their data.

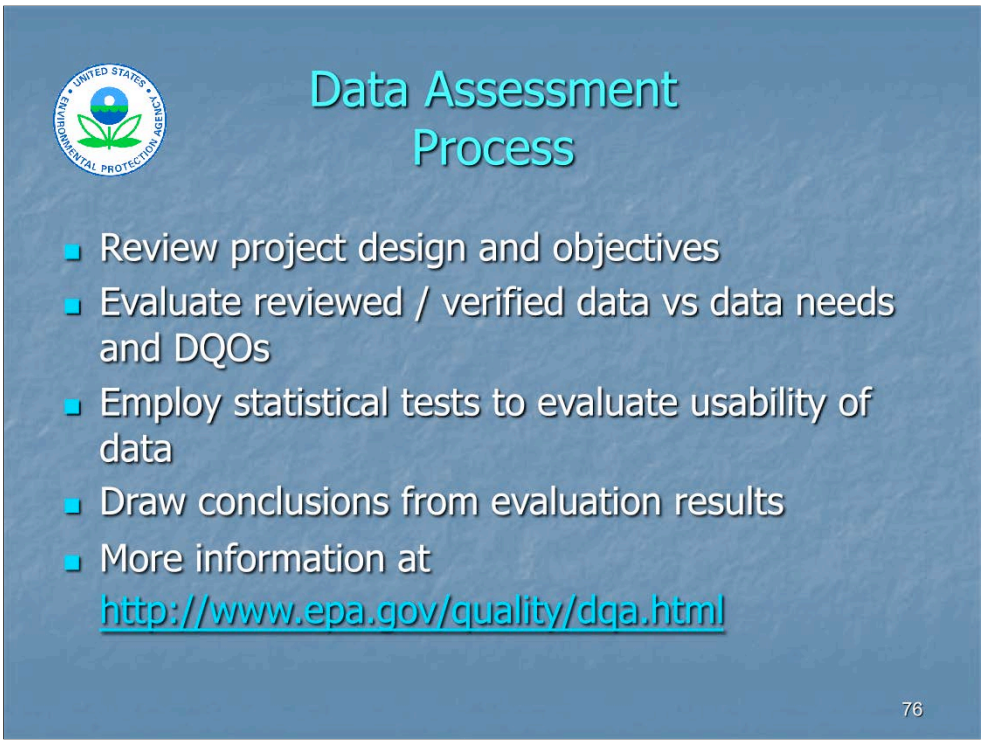
On-site laboratory audits: Mostly announced, but may be unannounced.



Backing up a step, what could you do prior to having a laboratory retained to test your samples? By building these conditions into your contracts for analytical services.



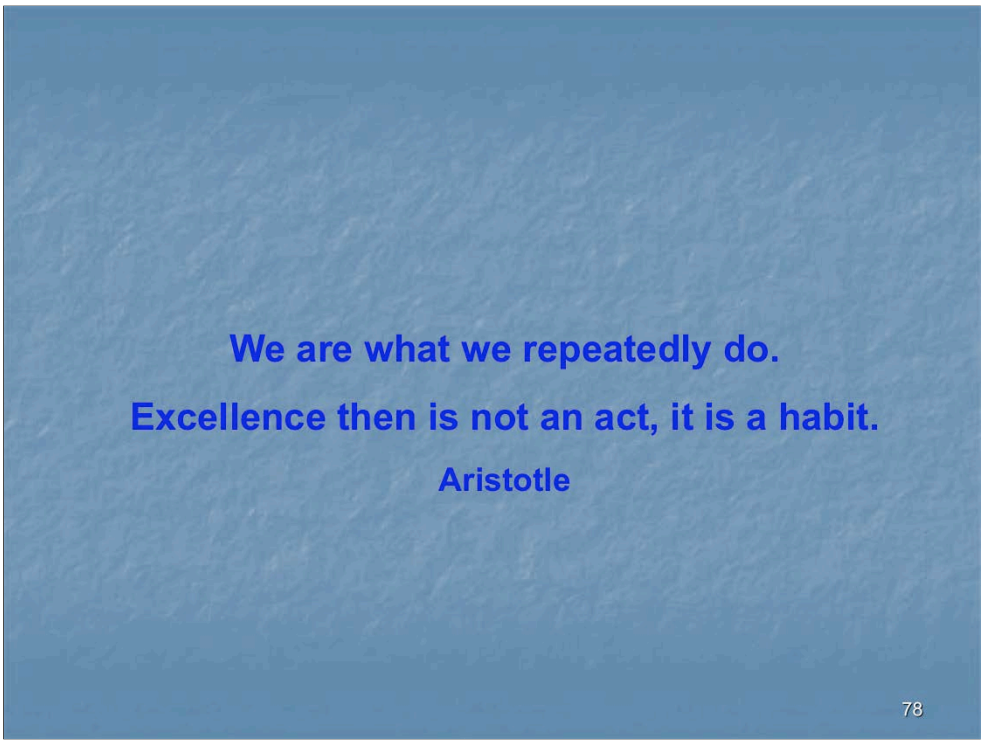
The last item on our agenda is slated for only limited discussion, but this is the step where it all comes together. All the planning, the implementation, documentation of what was done, right or wrong, and how problems were dealt with, the data obtained and its quality, are laid out on the table, and some clear-eyed person with plenty of experience asks the question, "Will all this support making a decision for this site and the population affected by it?"



If there are information gaps, either by lack of planning or oversight during implementation, what is the impact on supporting the decision? If there are qualified data, what is the impact of the qualification? If you have a result reported just under an action limit and ,due to calibration outliers, it is "J" flagged, what is the risk of making the wrong decision?

There are tools available to assist project managers in evaluating all the information needed to make that decision, including statistical tests, models, and step-by step procedures.

It's easy to get wrapped up in reviewing data, or writing QAPPS, or detecting improper practices, but each of those job descriptions provides a piece of a larger process. I'm pretty sure you could find a place for your own job description on this diagram as well. It's a lot like the scientific process, and not by accident, where a need arises and an experiment is designed based on a hypothesis or a null hypothesis. A plan is drawn up to obtain data to prove the hypothesis, and then it is implemented. Then the data is analyzed and processed and written up for peer review, and hopefully publication, after which it becomes available for the next researcher to build upon in a new experiment. This is how we clean up the environment, one experiment at a time, giving it the best effort we can. On that note, here is a final thought…



Thank you for attending this webinar. I want again to thank Jean Balent and Shari Myer for their support. The presentation will be posted on the Cluin website, including a bibliography and glossary, along with a podcast of this presentation. Now, Jean will have some closing administrative comments, and then we will take questions.

Charlie Appleby

U.S. Environmental Protection Agency
Office of Superfund Remediation and Technology Innovation
Analytical Services Branch
appleby.charlie@epa.gov

79

Bibliography

1. *Uniform Federal Policy for Quality Assurance Project Plans*, EPA-505-B-04-900A, 2005
2. *QAPP Requirements For Secondary Data Research Projects*, U.S. EPA internal guidance, NRMRL, 1999
3. *Using Data From Other Sources — A Checklist For Quality Concerns*, U.S. EPA internal guidance, EPA Quality Staff, 1999
4. *Guidance on Environmental Data Verification and Data Validation*, EPA QA/G-8, EPA/240/R-02/004, 2002

80

Bibliography

5. U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, EPA/R-014-002, 2014
6. U.S. EPA Analytical Services Branch National Functional Guidelines for Review and Validation of Dioxin/Furan Data, EPA-540-R-11-016, 2011
7. U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, EPA 540-R-013-001, 2014
8. Report of the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs, December, 2007

Bibliography

9. Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use, EPA 540-R-08-005, 2009

Glossary

- **Bias**: The constant or systematic distortion of a measurement process, different from random error, which manifests itself as a persistent positive or negative deviation from the known or true value. This can result from improper data collection, poorly calibrated analytical or sampling equipment, or limitations or errors in analytical methods and techniques.
- **Data Quality Assessment:** A statistical and scientific evaluation of the data set to determine the validity and performance of the data collection design and statistical test, and to determine the adequacy of the data set for its intended use.
- **Data Validation**: An analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance (i.e., data verification) to determine its usability for project objectives.
- **Data Verification**: The process of evaluating the completeness, correctness, and conformance or compliance of a specific data set against the method, procedural, or contractual requirements.
- **Defensibility**: The ability of a data set to withstand the scrutiny of the litigation process.
- **Definitive data**: analytical data suitable for final decision-making.
- **Confidence**: certainty, trust, as in level of confidence. See integrity.
- **Field vs laboratory measurements**: Generally portable equipment is used in field work whereas fixed equipment is used in a lab. Tighter control is possible in a laboratory setting.
- **Impartial or Third-Party Data Review**: The use of an independent, unbiased reviewer.
- **Integrity**: Adherence to an ethical code, unimpaired, complete, pure.

83

Quality Control Sample Types

- System Performance Check (SPC)
- Calibration Standard (CS, S)
- Interference Check Sample (ICS)
- Performance Check Sample (PCS)
- Performance Evaluation Sample (PES)
- Laboratory Reagent Blank (LRB, MB, PB)
- Instrument, Initial, Continuing Calibration Blank (ICB, CCB)
- Laboratory Fortified Blank (LFB, LCS)
- Laboratory Fortified Matrix (LFM, MS/MSD)
- Laboratory Duplicate (Dup)
- Serial Dilution Sample (Sdil)
- Initial Calibration Verification Standard (ICV)
- Continuing Calibration Verification Standard (CCV)
- Linear Range Standard (LRS)
- Reporting Limit Check Standard (CRI)

Glossary Cont'd

- **Sample Custody**: When a sample is either in one's possession or placed in a secure location with controlled access.
- **Screening data**: Analytical data that are of sufficient quality to support an intermediate or preliminary decision.
- **Standard Operating Procedure (SOP)**: Detailed description of a procedure. An SOP is specific to a particular workplace.
- **Statement of Work (SOW)**: Detailed description of work to be performed by a contractor.
- **Usability**: As applied to analytical chemistry data, usable data truly represent the object under study, i.e., the decision unit; are complete, and compliant with all quality criteria specified in the study plan.