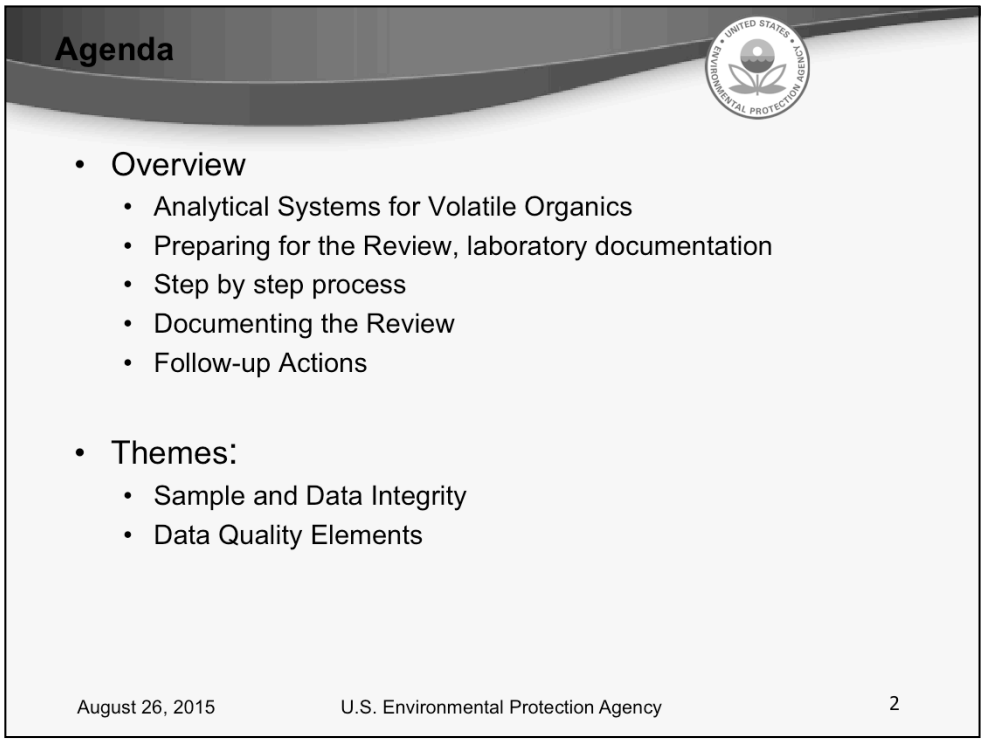
During this webinar, I will refer quite often to the National Functional Guidelines for Organic Data Review, which are currently posted on the U.S. EPA Superfund/CLP website. I will talk about review of volatile organic data, whether it is from aqueous, solid, or gaseous matrices. I will speak from the context of GC/MS analysis, but if you have any questions about a GC application for VOAs, ask away.



In my approach to this topic, I will generally not assume anything about your understanding of these methods, and will try to take it at a fairly slow pace. I will pause after each section and take a few questions, and depending on how much time we have at the end, I will then try to answer the remainder of your questions. I will begin with a description of the analytical system, similarly to my previous talk on high-res GC/MS data review, because I think it is important to have an understanding of the process used to obtain the data you are reviewing.

Purge and Trap Device

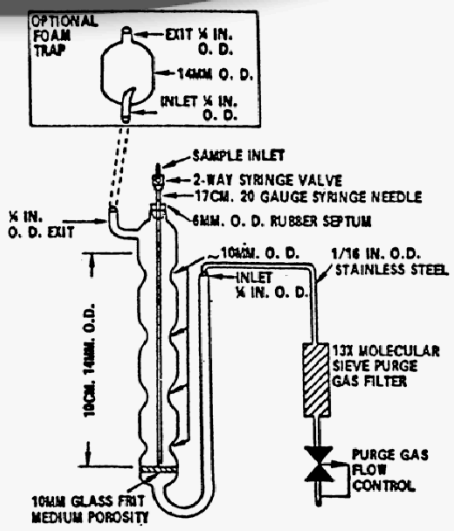
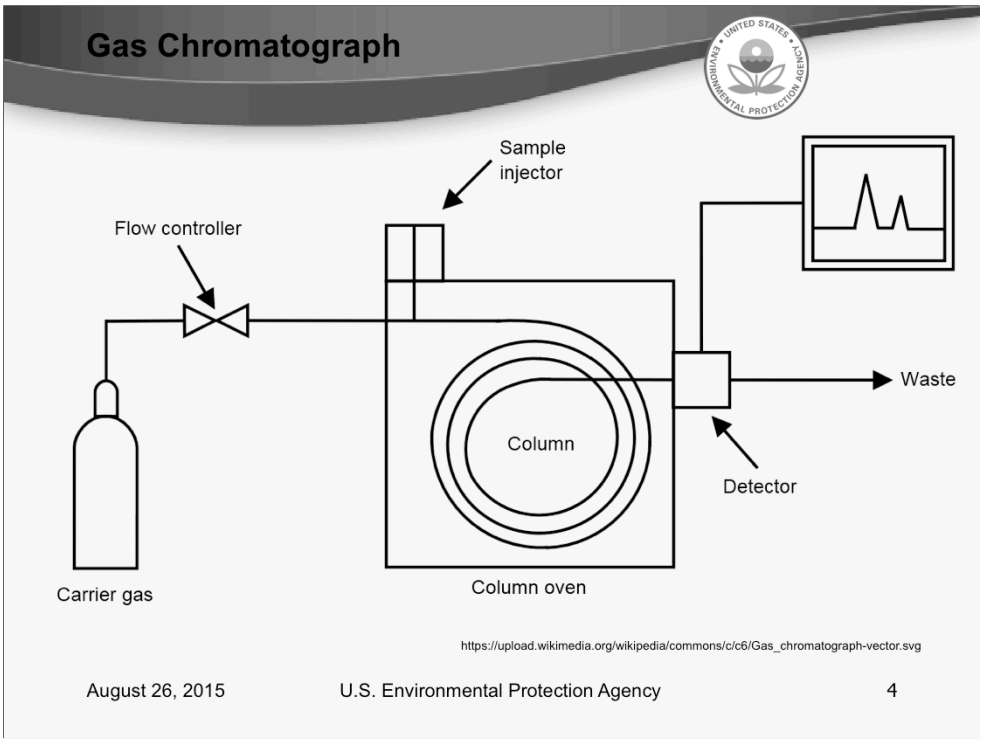


FIGURE 1. PURGING DEVICE

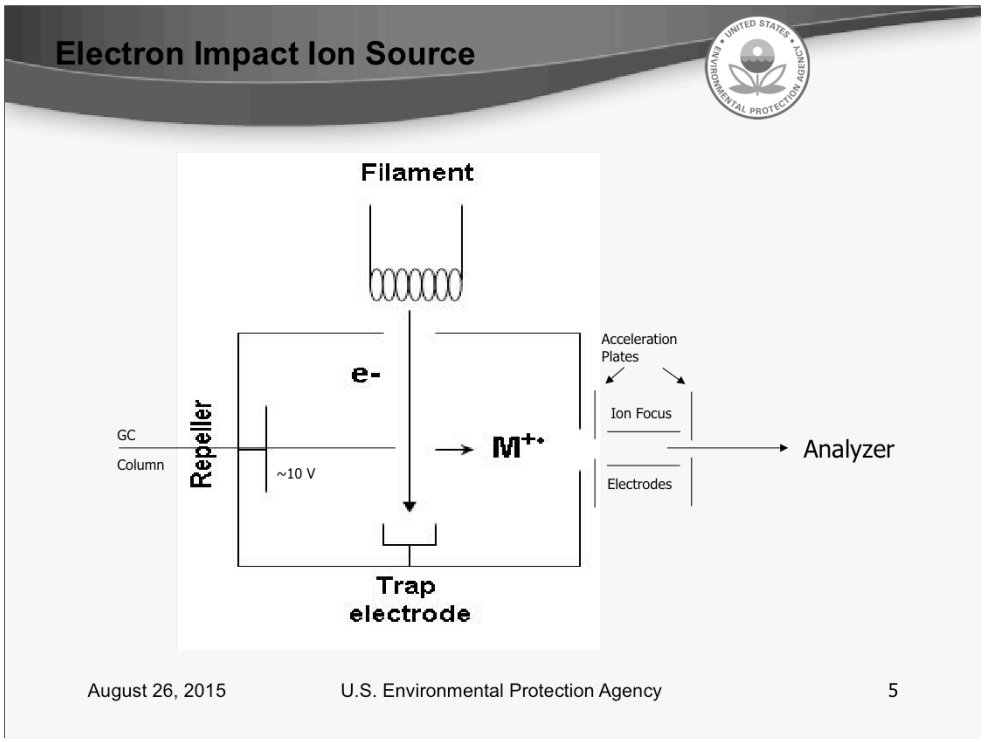
The technology used to separate volatile compounds from the matrix has come a long way since this unit was used, but the principle is the same. An aliquot of a liquid sample is added to the sparger. The sample is taken directly from the sample vial in most modern units, and water is added directly to the sample vial for solids. A gas is bubbled through the sample in the sparger or sample vial, which then flows through a trap. Air samples are sampled and the air sample flows directly to the trap. The trap is then heated and a valve is switched, so the trapped volatiles can then be desorbed onto the analytical column.



Chromatography was invented by a Russian pigments chemist, Mikhail Semenovich Tswett in 1903 (I don't know whether he coined the term "chromatography"). Modern chromatography came about in the early 1940s.

Question: How many people in attendance today have packed their own column for gas chromatography?

The separation and elution characteristics of a chromatographic column depend on the properties of the mobile and stationary phases and the interaction of the target analytes plus sample matrix that are introduced into the column with the mobile and stationary phases, and the length of the column. The injector plays a vital role, and there are many options for that step. The choice of detector is also very important, because it provides the quantitative (and sometimes also qualitative) dimensions to the analysis.

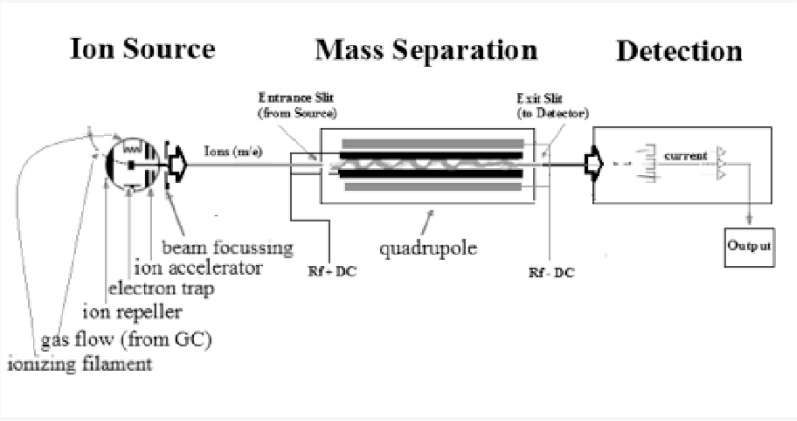


For methods that use gas chromatography or GC/mass spectrometry, the analytes elute from the GC column, ideally one at a time, and enter the ion source of the mass spectrometer.

Here is the ion source, where molecules leaving the gas chromatograph are bombarded with electrons, which breaks some of them into characteristic fragments and gives them a positive charge (in most current configurations). These ions are then accelerated into the analyzer.

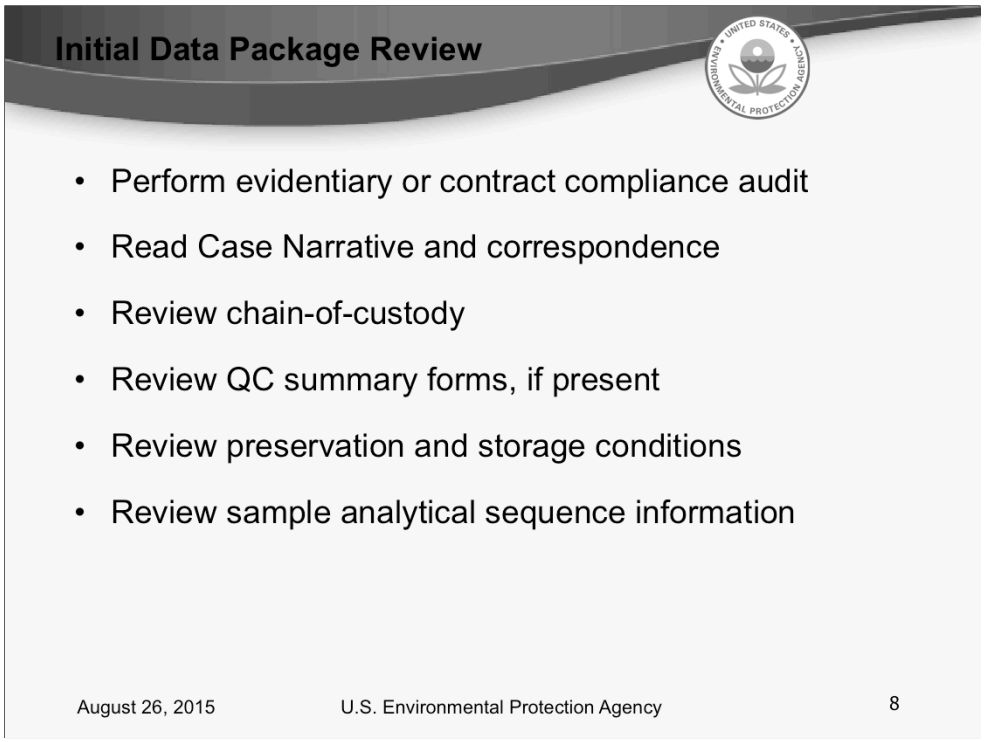
Why do we then begin to describe the ionization products as "m/e or m/z"?

Quadrupole Mass Filter



In a quadrupole mass filter, the quadrupole is the component of the instrument responsible for filtering sample ions, based on their mass-to-charge ratios (m/e or m/z). The quadrupole consists of four parallel metal rods. Each opposing rod pair is connected together electrically, and a radio frequency (RF) voltage is applied between one pair of rods and the other. A direct current voltage is then superimposed on the RF voltage, and the resulting electrical field affects the trajectory of the ions traveling down the quadrupole between the rods. Only ions of a certain mass-to-charge ratio will reach the detector for a given ratio of voltages: other ions have unstable trajectories and will collide with the rods and be drawn out of the system by the vacuum pumps. This permits selection of an ion with a particular *m/z* or allows the operator to scan for a range of *m/z*-values by continuously varying the applied voltage.

Questions?



The first step in data review is to conduct an Evidentiary Audit, or we could say to take a high-level tour of the package to find whether all data elements called for in the SOW or the QAPP are present.

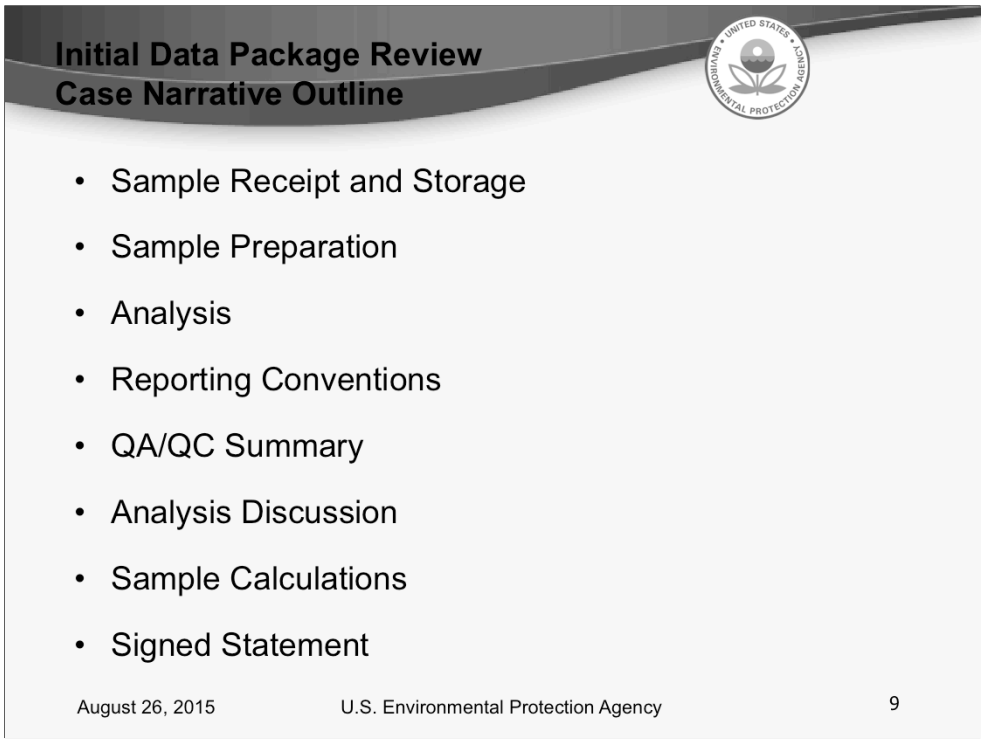
Are data present for all samples? Were there problems with sample delivery? Did all samples arrive intact and properly preserved at the lab? Was this the lab scheduled to receive these samples? Was the COC signed? If custody seals are typically used to protect evidentiary integrity of the samples, were they intact?

If hard copy package, lab should be identified on all documentation and pages should be numbered in case they get dropped or misplaced.

Case narrative, (more later);

Laboratory correspondence (typically at end of package) should further document any logistical problems or attempts to get information. If the laboratory was to follow a particular approved method or SOW, is it referenced in the documentation (including on the prep sheets)?

Will talk more about preservation/storage.



The case narrative should describe any problems with receipt and handling, analysis, and data processing of the samples, any deviations from the required method of analysis and reporting, example calculations, and any QC deficiencies. There should be a statement as to the completeness and authenticity of the data and signed by the lab manager.

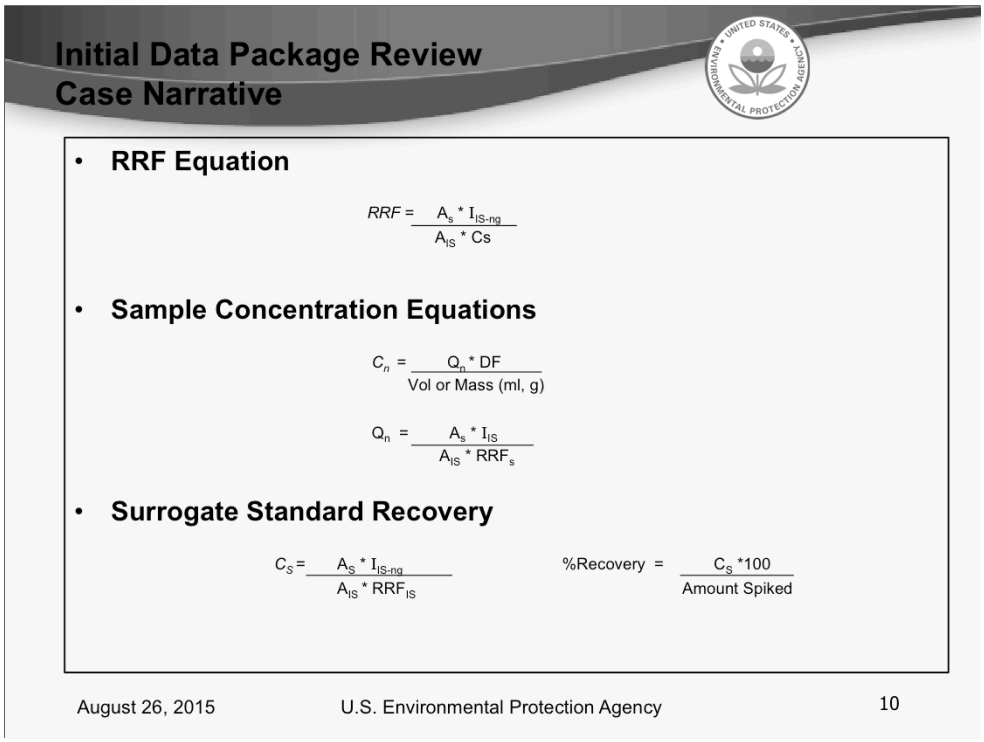
For example, if the laboratory decides to quantitate an analyte using different mass fragments, this should be described, and the calibration performance of the alternate ion should be documented as such. Yet we find upon checking that these things are done with no documentation, which does not serve to document data quality. However, these things will go unidentified in the data unless you look at all of the package.

The CLP requires laboratories to provide a list of manual integrations in the SDG Narrative. However, there are times when this list has been hastily prepared and the reviewer finds that some manual integrations have been incorrectly completed, such as:

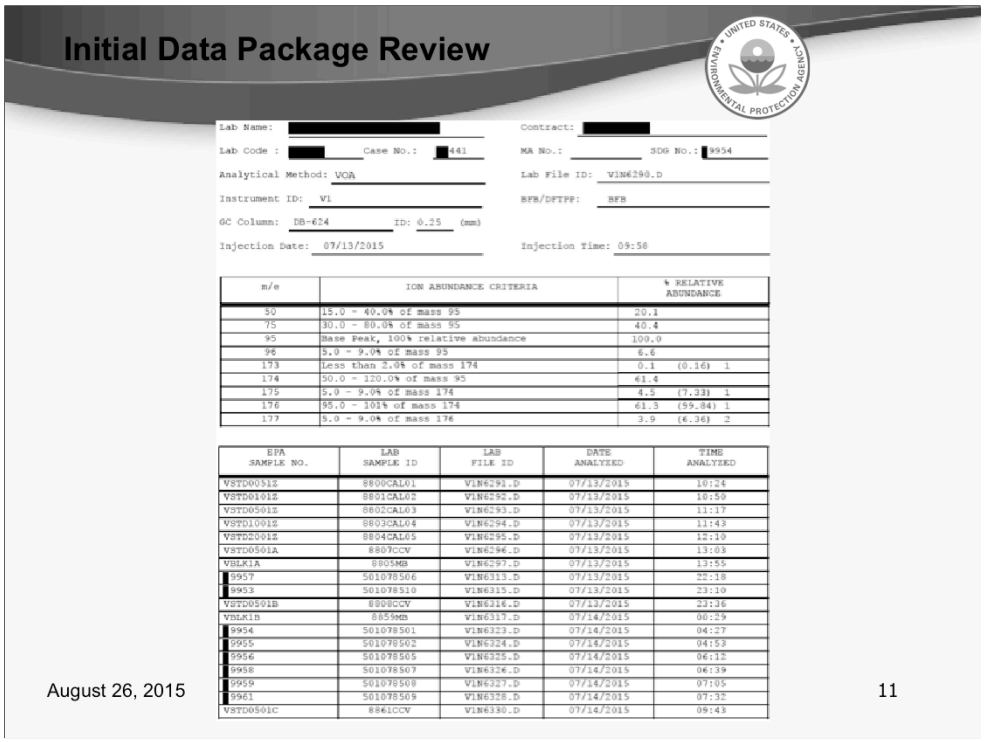
o Sample IDs incorrectly listed,

o omitting some of the manual integrations,

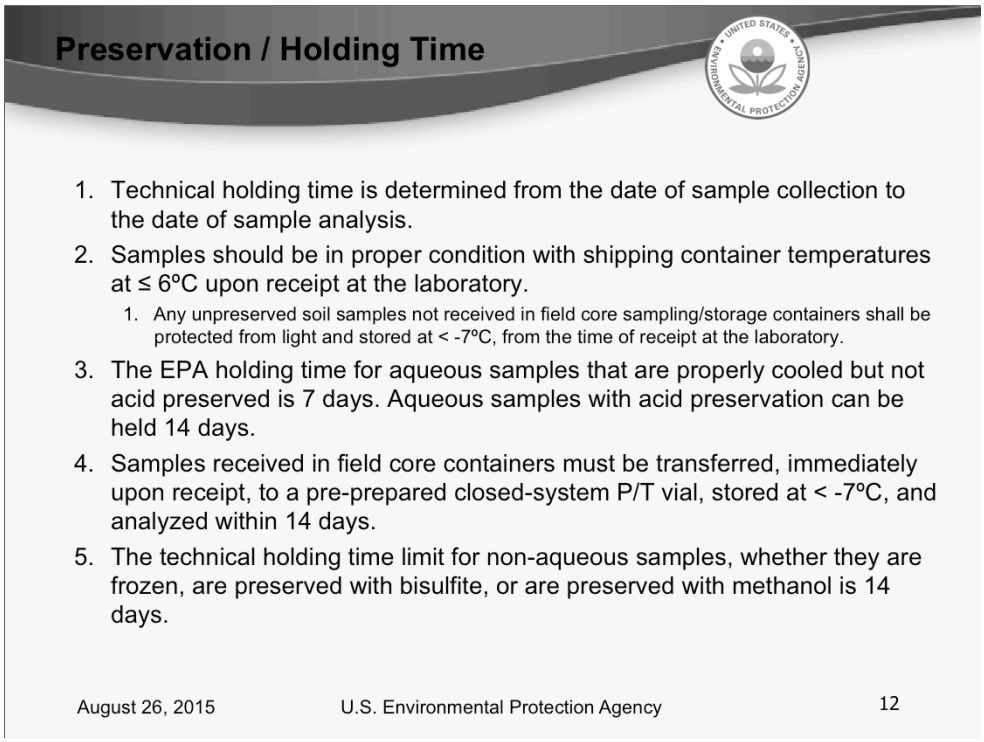
o Reporting manual integration of a standard that was not part of the SDG.



Sample calculations are typically generic like these, but they would be more useful if they showed specific data from the package, used to duplicate the reported results. Often labs introduce a slight twist, incorporating steps and not showing all their math. Also, is very important that the lab does not round any numbers until the final result. If they show all their steps, you can fully evaluate how the results were determined. Note that the methods don't require this, you have to ask for it.



Here is an example of the types of information that should be reviewed with regard to the analytical sequence summary (this from Form 5, BFB). The reviewer should note the start and end times of the sequence and look for blanks being included after calibration standards, and after any samples with high contamination.



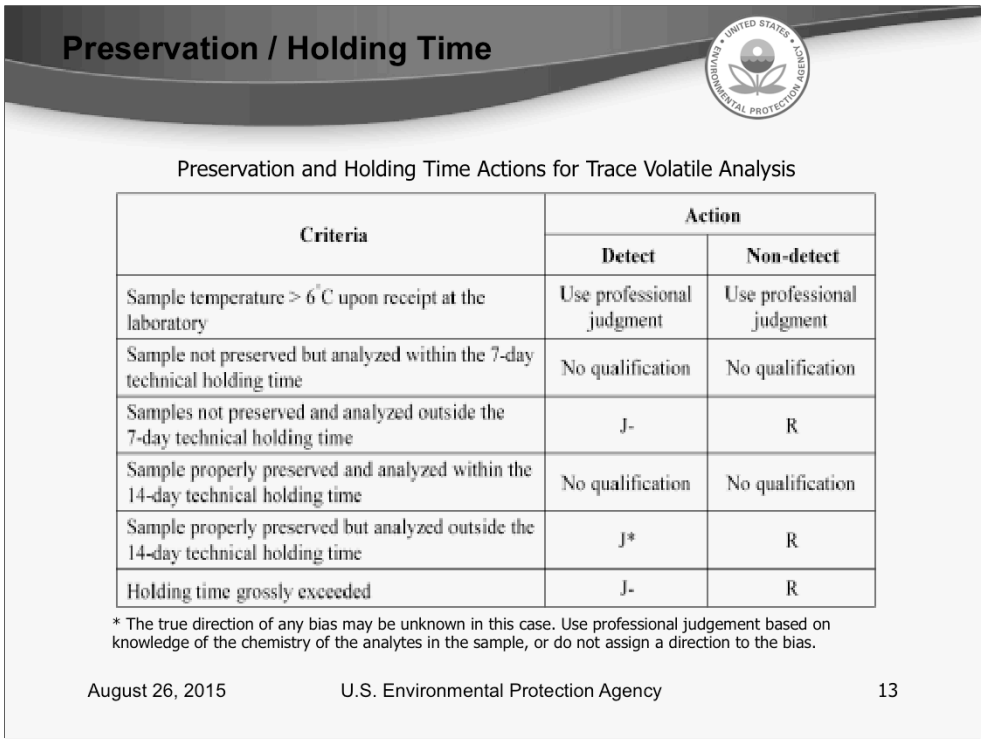
1. Review the SDG Narrative to determine if the samples were properly preserved and arrived at the

laboratory in proper condition (e.g., received intact, appropriate sample temperature at receipt, pH, and absence of air bubbles or detectable headspace). If there is an indication of problems with the samples, the sample integrity may be compromised.

2. Verify that technical holding times have been met by comparing the sample collection dates on the TR/COC documentation with the dates of analysis on Form 1A-OR and Form 1B-OR. Also consider information contained in the CSF as it may be helpful in the assessment.

3. Establish the TCLP/SPLP ZHE procedure technical holding times by comparing the sample collection dates on the TR/COC documentation with the dates of extraction in the preparation sheet. Also consider information contained in the Complete SDG File (CSF) as it may be helpful in the assessment.

4. Establish technical holding times for TCLP/SPLP leachate samples by comparing the dates on the extraction sheet with the dates of analysis on Form 1A-OR and Form 1B-OR.



1. If samples are received with shipping container temperatures > 6ºC, use professional judgment to qualify detects and non-detects.

2. Soil samples can typically be held under refrigeration for up to 14 days prior to analysis.

3. Ambient air samples collected in Suma cannisters may be held up to 30 days prior to analysis.

4. If the TCLP/SPLP ZHE procedure is performed within the extraction technical holding time of 14 days, detects and non-detects should not be qualified.

5. If a discrepancy between the sample analysis date and that on raw data is found, perform a more comprehensive review to determine the correct date for establishing holding time.

6. If aqueous samples are not properly preserved, but the samples are analyzed within the technical holding time of 7 days, detects and non-detects should not be qualified.

7. If aqueous samples are not properly preserved and are analyzed outside of the technical holding time of 7 days, qualify detects as estimated low (J-) and non-detects as unusable (R).

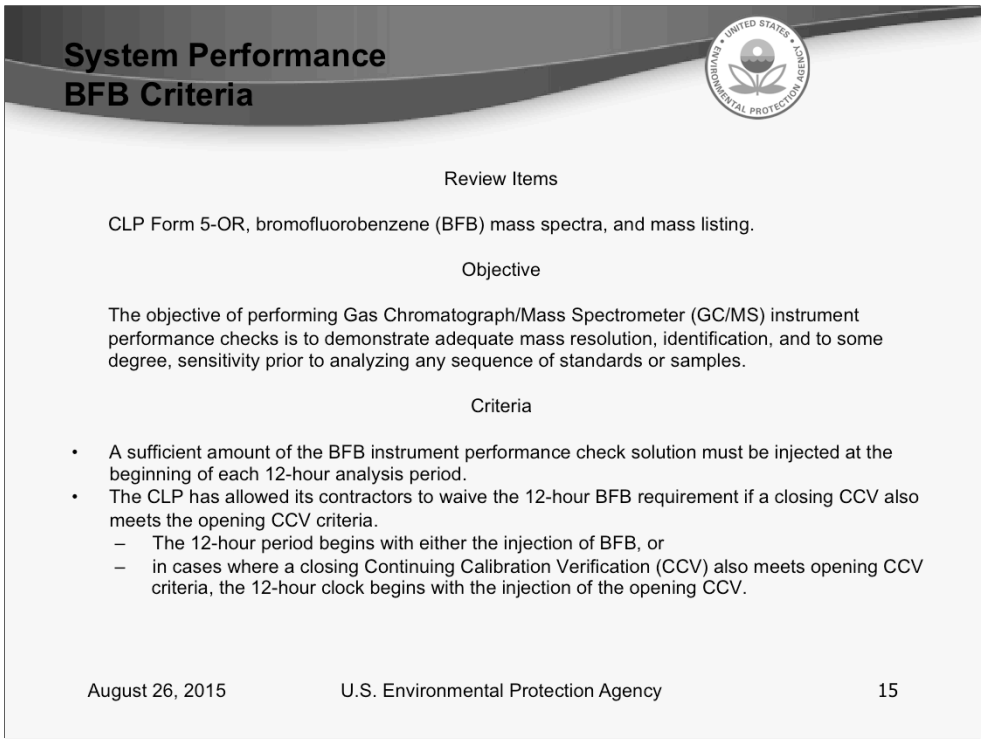
8. If aqueous samples are properly preserved and are analyzed within the technical holding time of 14 days, detects and non-detects should not be qualified.

9. Soil samples received in coring samplers should have been transferred immediately to pre-prepared (and tared) vials, should be kept frozen, but be aware of the actual shipping vessels used. The lab should be aware of what they are receiving and report any situation that could compromise sample integrity (sediment sample situation).

10. Annotate the effect of the holding time exceedance on the resulting data in the Data Review Narrative, whenever possible.

11. If samples are received with shipping container temperatures > 10°C, use professional judgment to determine the reliability of the data or qualify detects as estimated low (J-) and non-detects as estimated (UJ).

Questions?



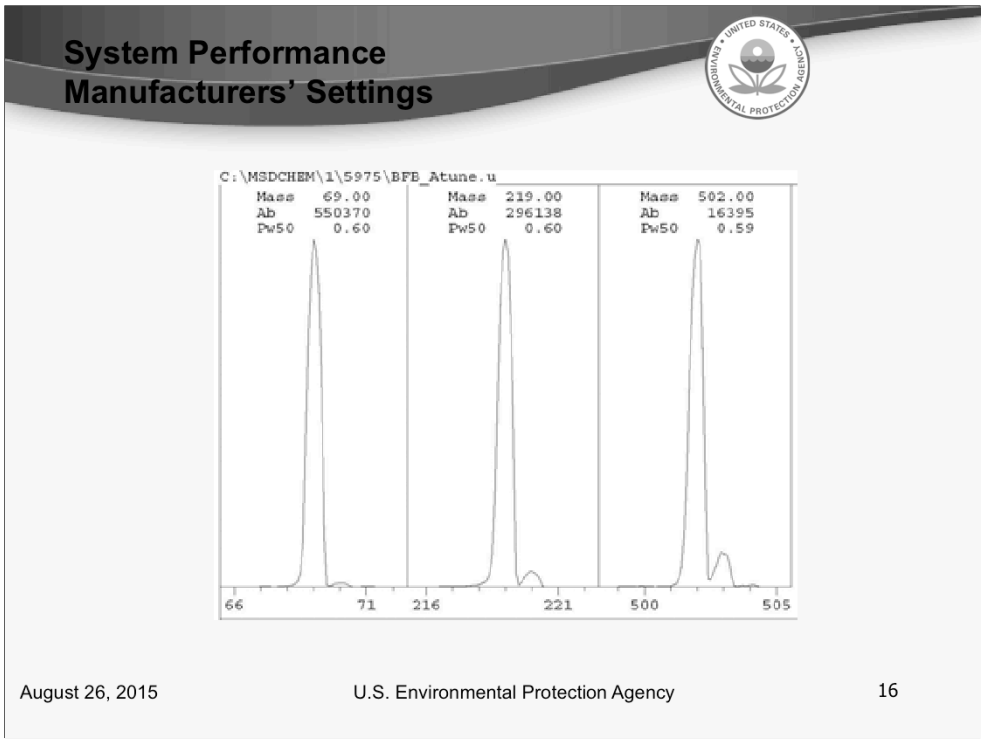
Verify that the BFB Instrument Performance Check solution is analyzed at the specified frequency and sequence.

Compare the data presented on Form 5-OR for each Instrument Performance Check with each mass listing submitted to ensure the following:

1. Form 5-OR is present and completed for each required BFB at the specified frequency.
2. The laboratory has not made transcription errors between the data and the form. If there are major differences between the mass listing and Form 5-OR, a more in-depth review of the data is required. This may include obtaining and reviewing additional information from the laboratory.
3. The appropriate number of significant figures has been reported (number of significant figures given for each ion in the ion abundance criteria column) and that rounding is correct.
4. The laboratory has not made any calculation errors.

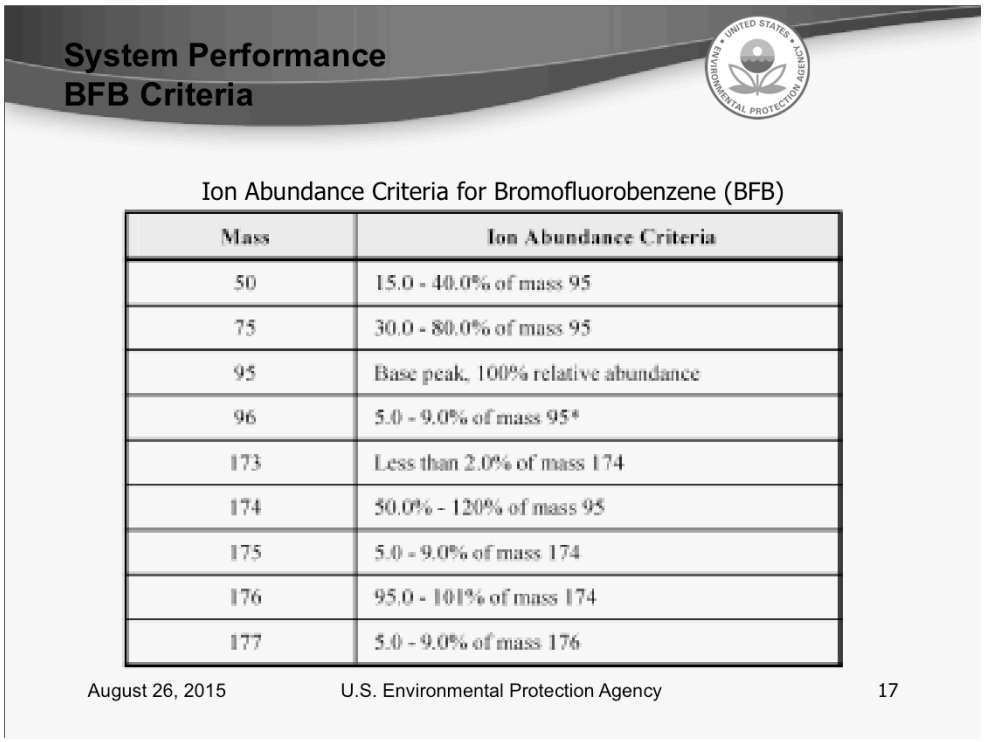
Verify from the raw data (mass listing) that the mass assignments are correct and that the mass listing is normalized to m/z 95.

Verify that the ion abundance criteria are met. The criteria for m/z 173, 175, 176, and 177 are calculated by normalizing to the specified m/z. The critical ion abundance criteria for BFB are the relative abundance ratios of m/z 95/96, 174/175, 174/176, and 176/177. The relative abundance ratios of m/z 50 and 75 are of lower importance for target analytes than for Tentatively Identified Compounds (TICs).



Here are the results of the Agilent, formerly Hewlett Packard, "Autotune".

Who can tell me the cause for the small peaks after each of these mass profiles?



Verify that the BFB Instrument Performance Check solution is analyzed at the specified frequency

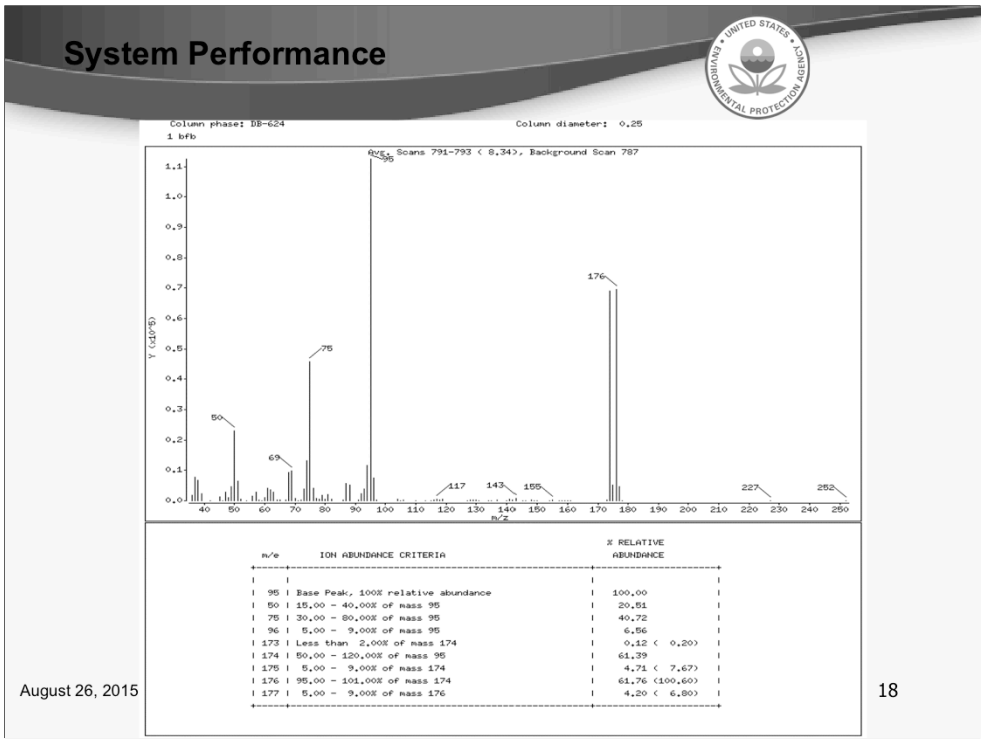
and sequence.

Compare the data presented on Form 5-OR for each Instrument Performance Check with each mass listing submitted to ensure the following:

1. Form 5-OR is present and completed for each required BFB at the specified frequency.
2. The laboratory has not made transcription errors between the data and the form. If there are major differences between the mass listing and Form 5-OR, a more in-depth review of the data is required. This may include obtaining and reviewing additional information from the laboratory.
3. The appropriate number of significant figures has been reported (number of significant figures given for each ion in the ion abundance criteria column) and that rounding is correct.
4. The laboratory has not made any calculation errors.

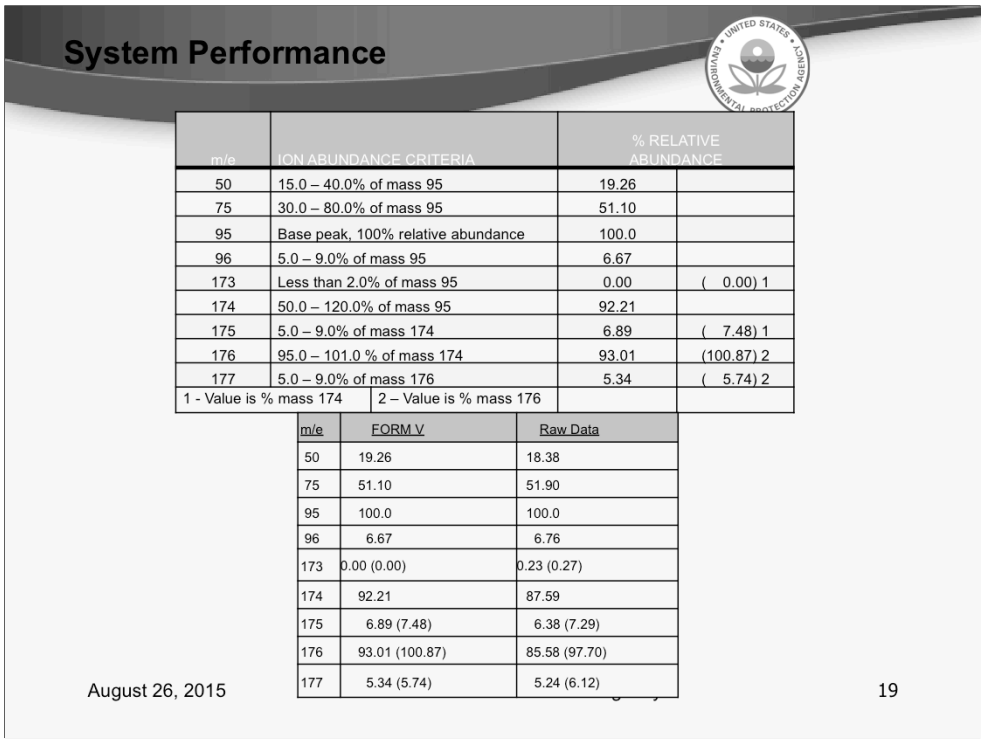
Verify from the raw data (mass listing) that the mass assignment is correct and that the mass listing is normalized to m/z 95.

Verify that the ion abundance criteria are met. The criteria for m/z 173, 175, 176, and 177 are calculated by normalizing to the specified m/z. The critical ion abundance criteria for BFB are the relative abundance ratios of m/z 95/96, 174/175, 174/176, and 176/177. The relative abundance ratios of m/z 50 and 75 are of lower importance for target analytes than for Tentatively Identified Compounds (TICs).



m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
95	Base Peak, 100% relative abundance	100.00
50	15.00 - 40.00% of mass 95	20.51
75	30.00 - 80.00% of mass 95	40.72
96	5.00 - 9.00% of mass 95	6.56
173	Less than 2.00% of mass 174	0.12 (0.20)
174	50.00 - 120.00% of mass 95	61.39
175	5.00 - 9.00% of mass 174	4.71 (7.67)
176	95.00 - 101.00% of mass 174	61.76 (100.60)
177	5.00 - 9.00% of mass 176	4.20 (6.80)

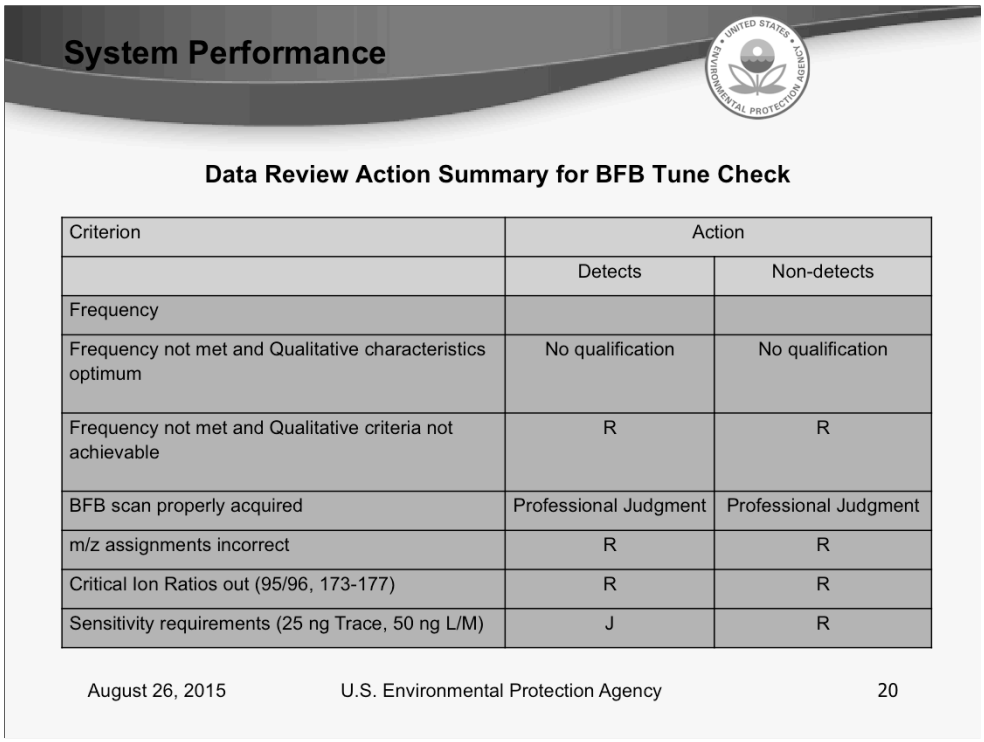
EPA acknowledges that the BFB criteria have become a limitation on the capabilities of newer GC/MS systems due to enhanced electronic features. But what we and others who require evidentiary proof of performance need, is documentation of the basis for the system's ability to consistently identify not only the reference standards, but also the compounds in the reference library which were obtained using the same criteria. The identification of emerging contaminants relies heavily on the regular surveillance provided by the routine TIC searches.



m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE	
50	15.0 – 40.0% of mass 95	19.26	
75	30.0 – 80.0% of mass 95	51.10	
95	Base peak, 100% relative abundance	100.0	
96	5.0 – 9.0% of mass 95	6.67	
173	Less than 2.0% of mass 95	0.00	(0.00) 1
174	50.0 – 120.0% of mass 95	92.21	
175	5.0 – 9.0% of mass 174	6.89	(7.48) 1
176	95.0 – 101.0 % of mass 174	93.01	(100.87) 2
177	5.0 – 9.0% of mass 176	5.34	(5.74) 2
1 - Value is % mass 174	2 – Value is % mass 176		

m/e	FORM V	Raw Data
50	19.26	18.38
75	51.10	51.90
95	100.0	100.0
96	6.67	6.76
173	0.00 (0.00)	0.23 (0.27)
174	92.21	87.59
175	6.89 (7.48)	6.38 (7.29)
176	93.01 (100.87)	85.58 (97.70)
177	5.34 (5.74)	5.24 (6.12)

Here is a case where there was a discrepancy between the BFB tune percent relative abundance data on the CLP FORM V report form versus the raw data (bar graph, mass listing, and RIC) for a BFB tune check. Here you can see the FORM V VOA report and the raw data vs the Form V results are given in the table below. Note that both sets of percent relative abundance data meet the ion abundance criteria.



1. Action to be taken may depend upon whether sample re-analysis can be done. In the event the samples cannot be reanalyzed, examine all calibrations associated with the sequence to evaluate whether proper qualitative criteria were achievable. If so, it may be possible to salvage usable data from the sequence. Otherwise, qualify the data as unusable (R).

2. The reviewer should consider that qualitative criteria have not been met if one or more of the following are observed, in addition to the lack of a valid BFB check.

    1. Retention times are not reproducible to within 0.06 RRT units.

    2. Chromatographic quality is degraded, with poor peak shapes, inconsistent shoulders or significant carry-over.

    3. A valid tune check from the same instrument run at a different time and subsequent calibration standard data are not present in the package.

3. If the BFB peak was improperly acquired (too many scans averaged, background taken from wrong part of peak), the lab should be contacted to reprocess and resubmit. If this is not an option, the reviewer must use their professional judgement to qualify the data.

4. If mass assignments or critical ion ratios are incorrect in the tune check, check the standards to assess the extent of the problem. Data rejection may be the only option.

Questions?

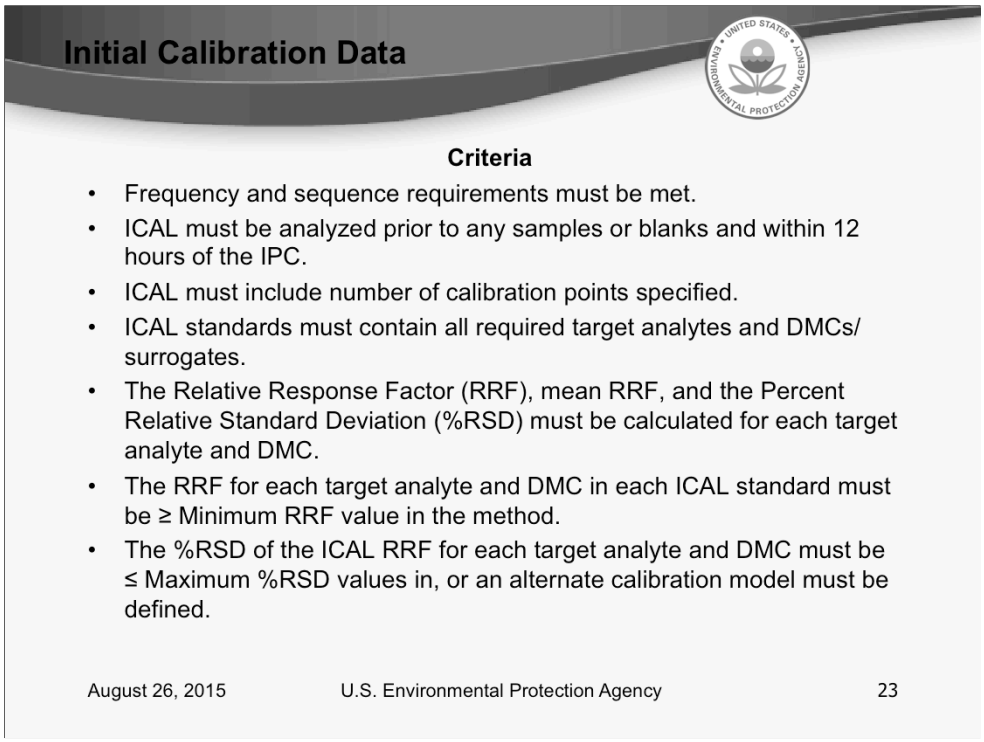
Initial Calibration Data

Review Items

CLP Form 6A-OR, quantitation reports, and chromatograms.

Objective

The objective of initial calibration (ICAL) is to ensure that the instrument is capable of producing acceptable qualitative and quantitative data.



1. Verify that the initial calibration was performed at the specified frequency and sequence. Verify that all target analytes and labeled compounds are present at the correct concentrations in all initial calibration standards.

2. If you have spectra for each target analyte and labeled compound in the calibration standards, check to make sure they are the right spectra, or match them to your own reference spectra if you have any.

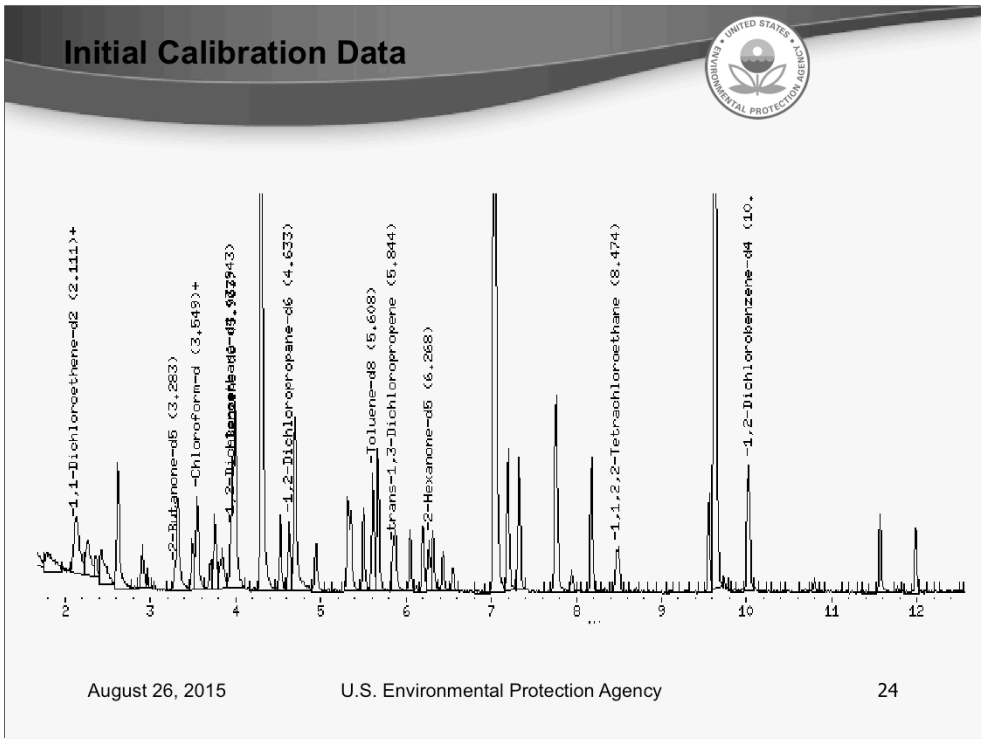
3. Verify that the RT for each target analyte and internal standard are within the specified RT windows, if equivalent columns to those specified in the method are used. If a different column has been used, examine the quant reports to evaluate whether there are any unacceptable co-elutions (i.e., with the same m/zs), or multiple co-elutions. Only the meta and para xylene co-elute on the recommended column.

4. Verify that RTs are consistent between the calibration standards, and between the calibration standards and any subsequent samples.

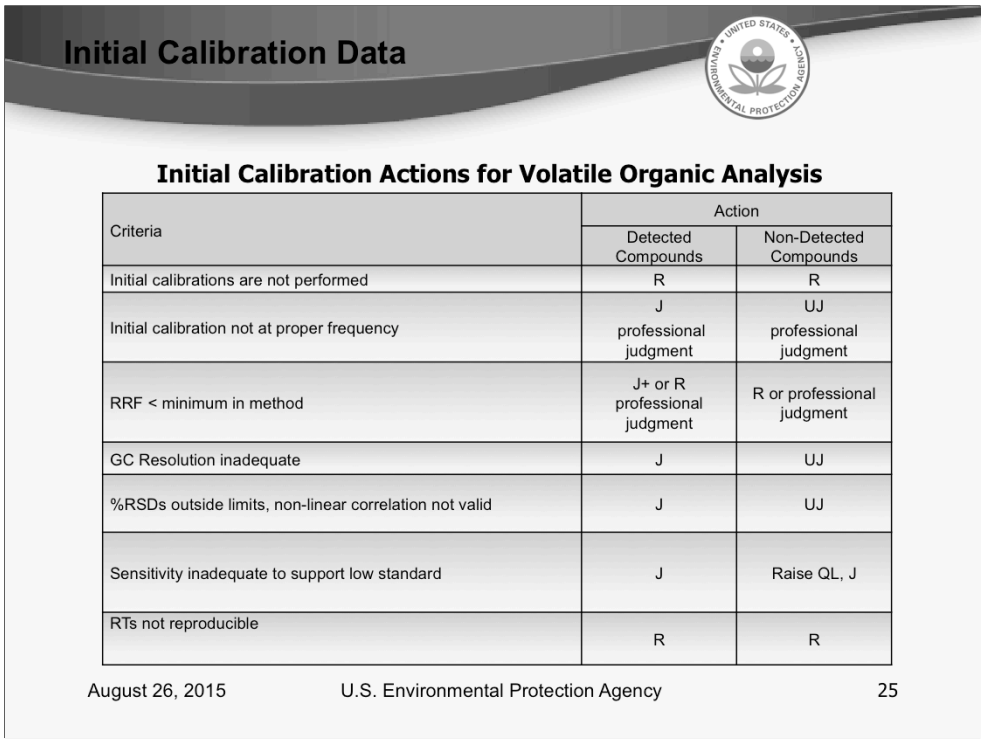
• If an alternate column has been used, the laboratory should have included sufficient information in the SDG narrative to evaluate column performance, ideally a table of retention time windows, as well as information on the optimum resolution of closely eluting analytes, and a table of relative retention times.

5. Verify that the %RSD of the RRF for each target analyte, and the %RSD of the RRF for each labeled compound are within method limits.

6. Recalculate the RRFs, mean RRF and %RSD for at least one target analyte and DMC associated with each internal standard, and verify that the recalculated values agree with the laboratory reported values on Form 6A-OR.



It is a good idea to check the lowest standard in the calibration to see if system conditions are causing problems with peak shapes or resolution.



1. If no initial calibration was performed, the data should not be considered definitive; qualify detects and non-detects as unusable (R). If the specified calibration concentration levels were not used, it may be necessary to modify the linear range for reporting (with approval of the data user). If an otherwise compliant initial calibration was performed, but not at the specified frequency, qualify detects and non-detects as estimated.

2. Non-compliant IAR for any analyte is cause for concern. It may indicate that the MS was not tuned correctly, that the ion source was dirty, or that other electronic problems existed. If there was a systemic problem resulting in failed ion ratios in the calibration, qualify detects and non-detects in the associated samples as unusable (R), or report all identifications as tentative.

3. If the RTs are outside the specified windows, qualify non-detects as unusable (R). Consider ordering reanalysis of the initial calibration and all associated samples.

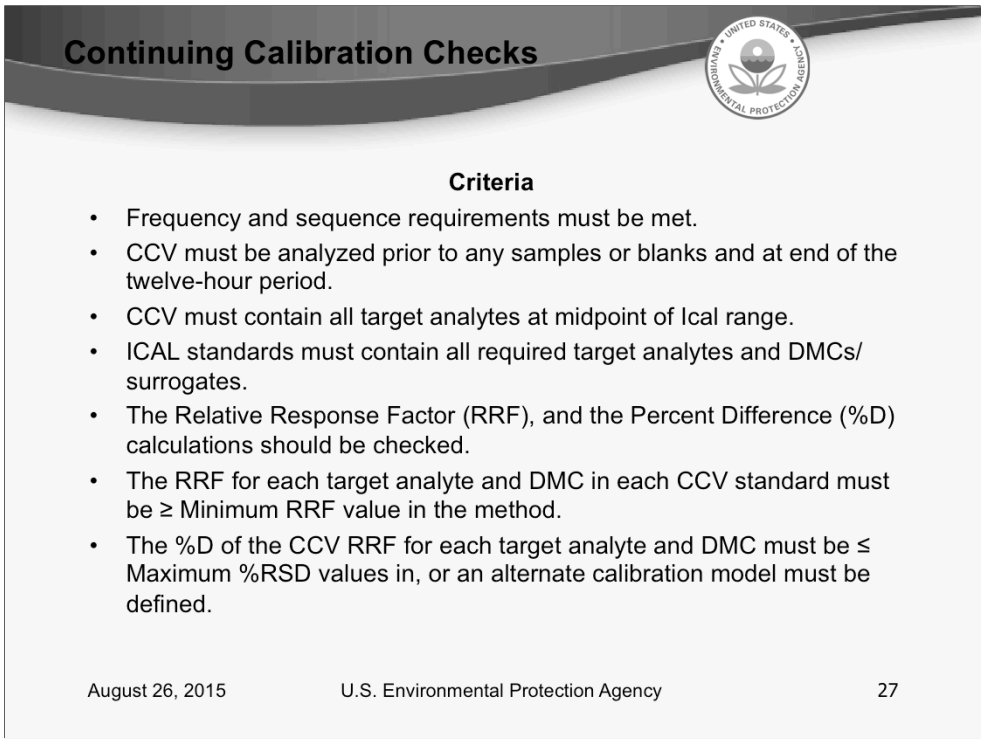
Continuing Calibration Checks

Review Items

CLP Form 7A-OR, quantitation reports, and chromatograms.

Objective

The objective of continuing calibration (CCV) is to ensure that the instrument has remained stable since the initial calibration was performed, and that it remains so throughout each analytical sequence.



Evaluation

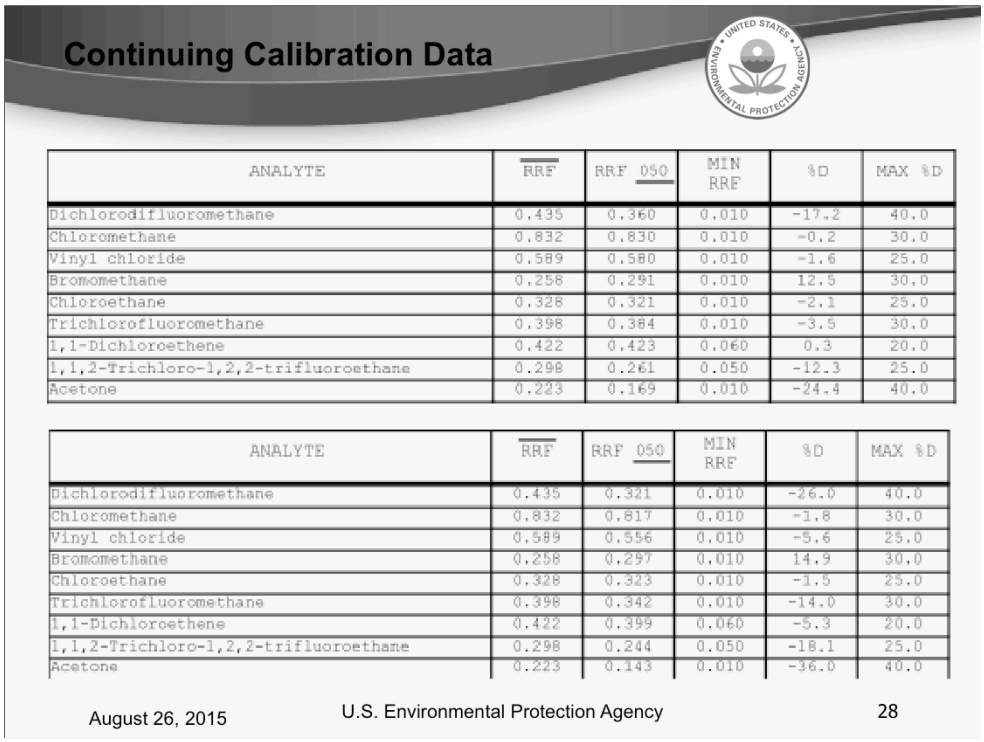
1. Verify that the CCV is performed at the specified frequency and sequence.

2. Verify that the correct concentrations of the target analytes and DMCs are used in each CCV standard.

3. Verify that the RRF, mean RRF and %D for each target analyte and DMC are reported in Form 7A-OR. Recalculate the RRFs, mean RRF and %D for at least one target analyte and DMC associated with each internal standard, and verify that the recalculated values agree with the laboratory reported values on Form 7A-OR.

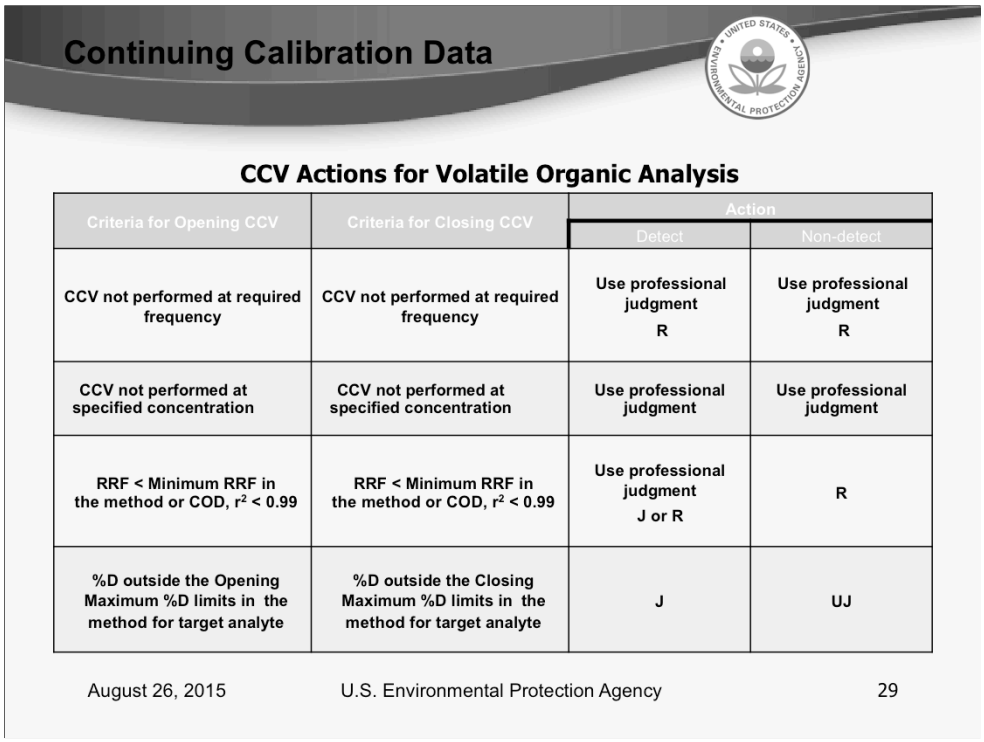
4. Verify that RRF is ≥ Minimum RRF values in the method for each target analyte and DMC.

5. Verify that %Ds are ≤ Maximum %D values in the method for each target analyte and DMC.



A large part of the review process is verifying the information upon which other decisions are made. Here we have two processed summary tables with the first nine analytes, calculated RRF for the CCV, the mean response factors from the Ical, the calculated %D, and %D limits. I recommend checking a few of the calculated values, all of which are determined by the data system, but to verify most of the other values. I have seen pages like this that actually used values from the wrong Ical for the evaluation. This table would normally have a header that includes information on which Ical, and when the CCV was analyzed, what instrument, etc.

Now I would like to ask you to look at these two tables and tell me which one you think was done at the end of the 12-hour analysis period and why?



1. If the CCV standard was not analyzed at the specified frequency and sequence, use professional judgment to qualify detects and non-detects.

2. If the RRT of each target analyte and labeled compound is outside the specified limits in the method, use professional judgment to qualify detects and non-detects.

3. If the %D of analytes or labeled compounds in the CCV standard are not within QC limits, qualify detects as estimated (J) and non-detect as estimated (UJ), or verify the correlation coefficients for alternate calibration models.

Questions?

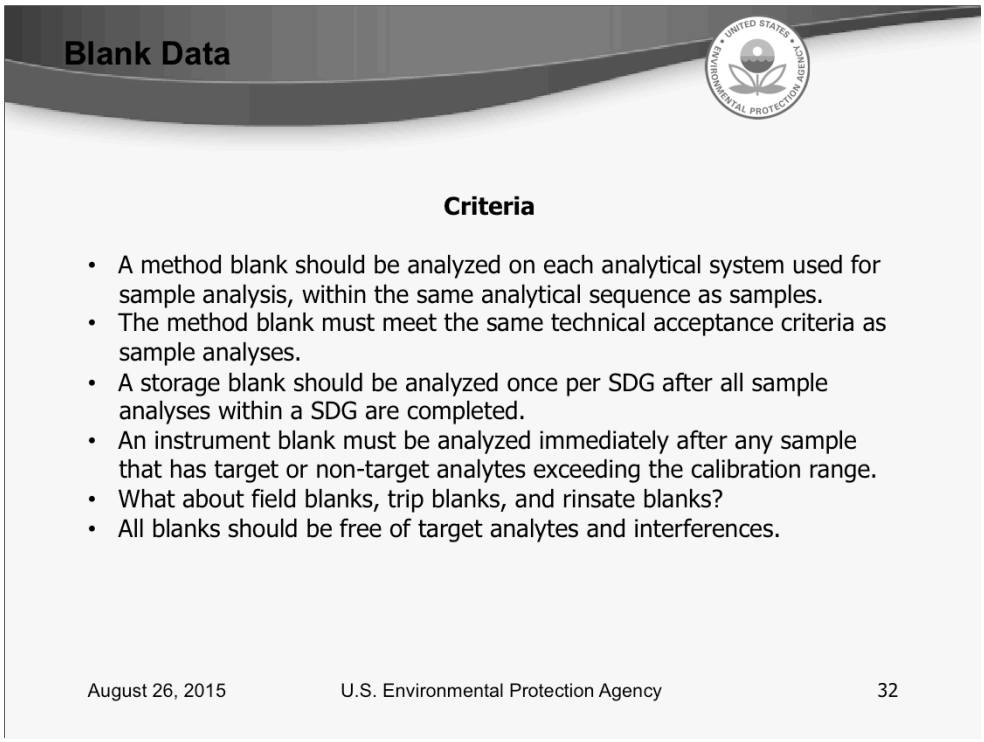
Blank Data

Review Items

CLP Form 1A-OR, Form 1B-OR, Form 4-OR, quantitation reports, and chromatograms.

Objective

The objective of a blank analysis results assessment is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities.



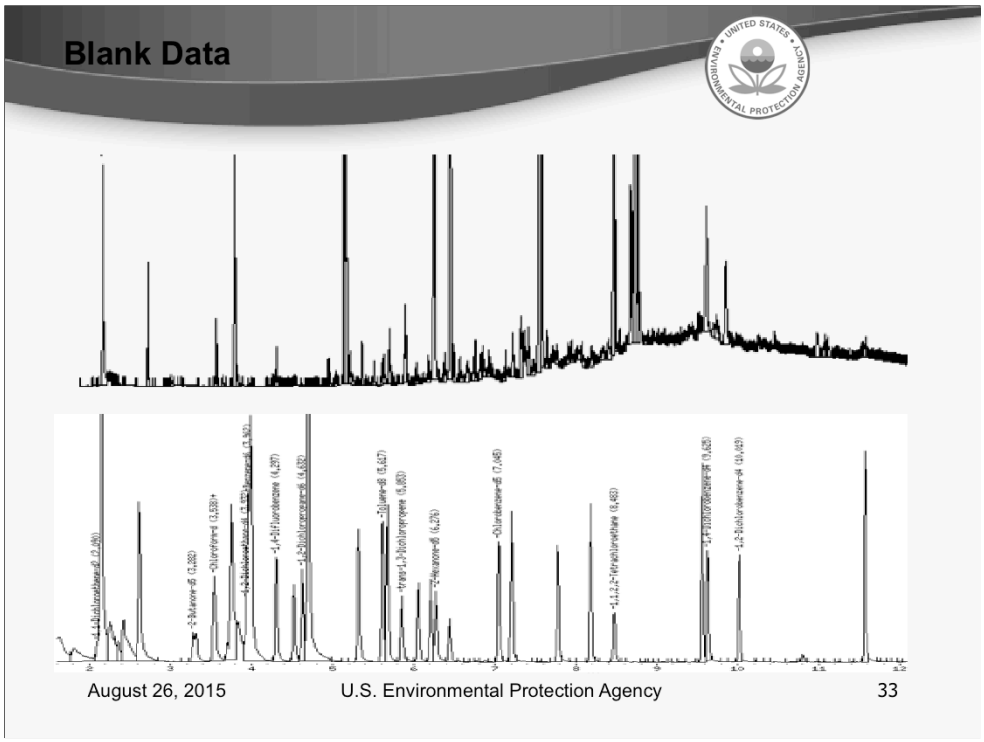
1. Verify that method blanks are analyzed at the specified frequency and sequence. The Method Blank Summary (Form 4-OR) may be used to identify the samples associated with each method blank.

2. Verify that a storage blank has been analyzed at the specified frequency and sequence.

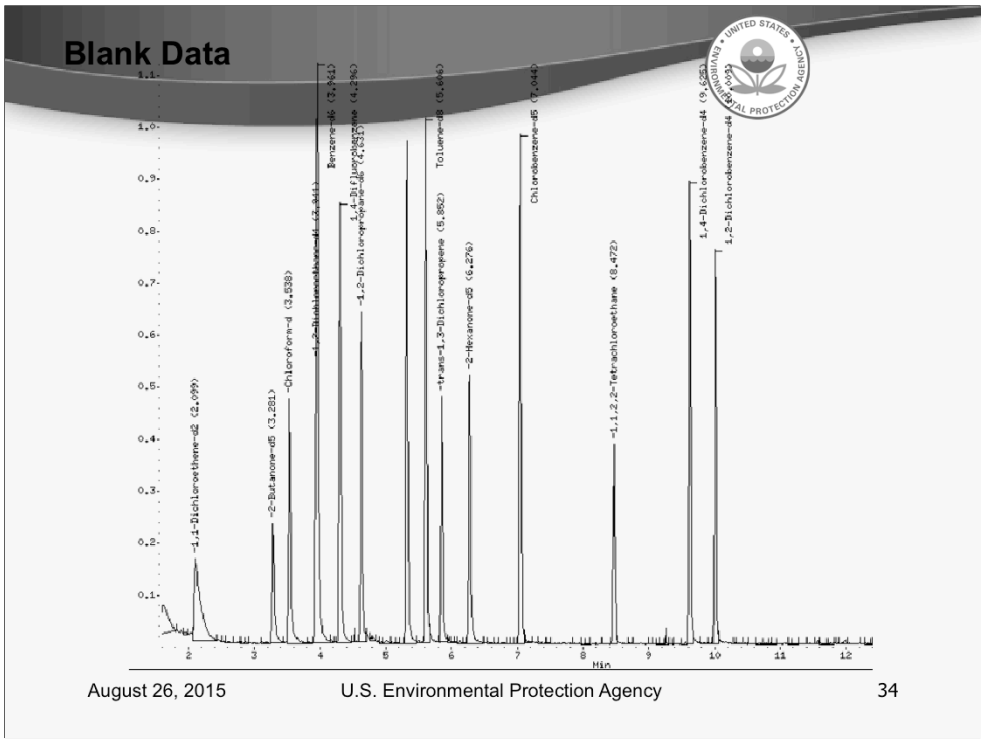
3. Verify that the instrument blank analysis has been performed following any sample analysis where a target analyte(s) is/are reported at high concentration(s).

4. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target analytes and non-target compounds in the blanks.

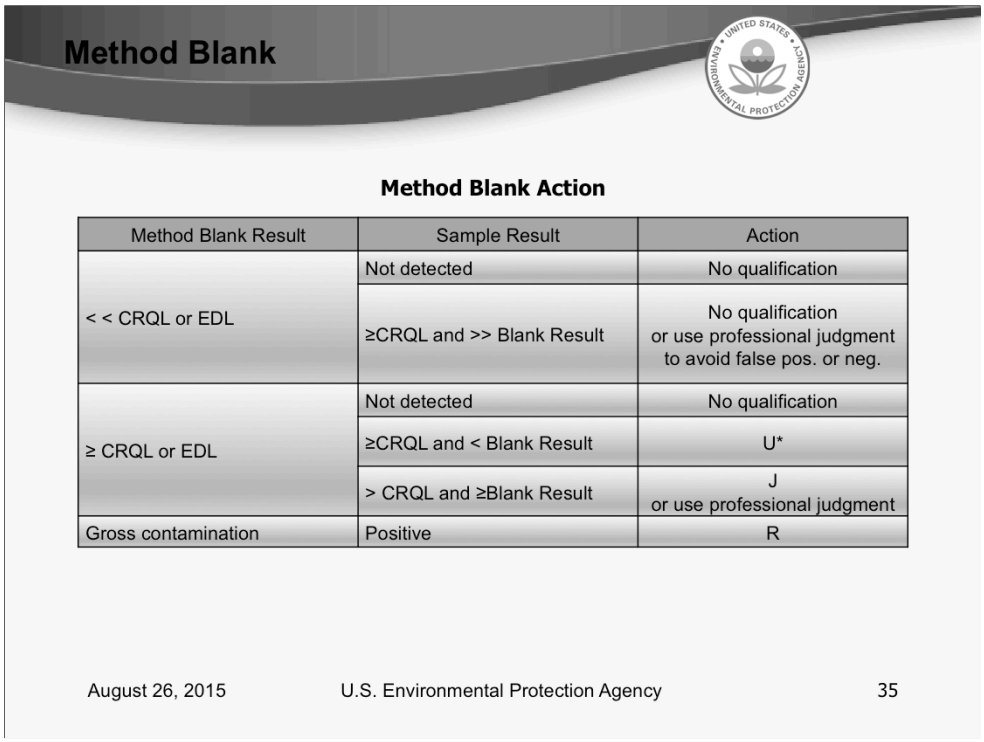
5. Evaluate field or trip blanks in a manner similar to that used for the method blanks and note findings for action as required in the QAPP.



Here are tow examples of problematic method blanks. If blanks show carryover, elevated baselines, significant tailing, or RT excursions in the surrogates and ISTDs, carefully check the performance in the associated samples, and potentially flag for re-analysis.



Here is what a VOA blank should look like.



1. *If a method blank or an instrument blank is not prepared and analyzed at the specified frequency, use professional judgment to determine if the associated sample data should be qualified. It may be necessary to obtain additional information from the laboratory. Record the situation in the Data Review Narrative.*

2. For a method blank or an instrument blank reported with results < 1/2x CRQLs, non-detects should not be qualified. Report sample results that are < CRQLs at the CRQLs and qualify as non-detect (U). Use professional judgment to qualify sample results ≥ CRQLs or ≥ Blank Results.

3. For a method blank or an instrument blank reported with results ≥ 1/2x CRQLs, non-detects should not be qualified. Report sample results that are < CRQLs at the CRQLs and qualify as non-detect (U). Report sample results ≥ CRQLs but < Blank Results at the blank results and qualify as non-detect (U.). Qualify sample results ≥ CRQLs and ≥ Blank Results as estimated (J).

4. There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed appropriate. Use professional judgment to qualify sample results in these situations and provide an explanation of the rationale used for data qualifications in the Data Review Narrative.

5. Blanks or samples analyzed after a PES sample, or a CCV should be carefully examined to evaluate the possible occurrence of instrument carry-over. Use professional judgment to determine whether sample or blank results are attributable to carry-over.

6. When there is convincing evidence that contamination is isolated to a particular instrument, matrix, or concentration level, use professional judgment to determine if qualification should only be applied to certain associated samples (as opposed to all of the associated samples).

7. If gross contamination exists (i.e., saturated peaks), qualify detects and non-detects as unusable (R). The laboratory should have taken corrective action prior to reporting the data.

Questions?

Matrix and Blank Spikes

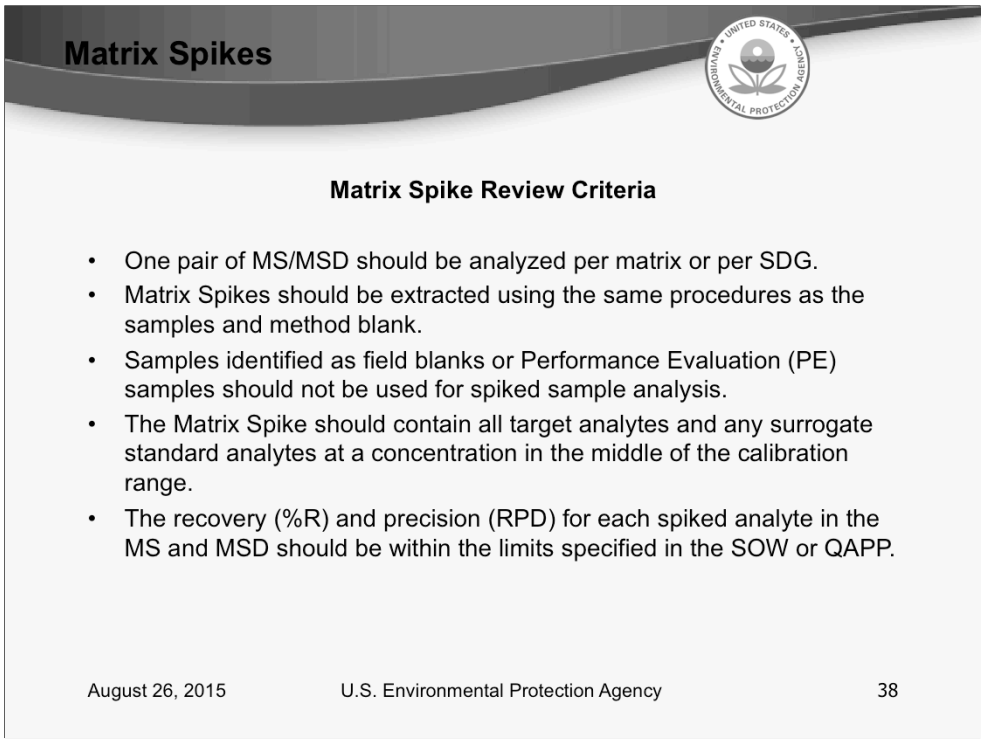
Review Items

CLP Summary Forms, quantitation reports, and chromatograms.

Objective

The objective of the Matrix Spike (MS)/Matrix Spike Duplicate (MSD) analysis is to evaluate the effect of each sample matrix on the sample preparation procedures and the measurement methodology, and to document accuracy and precision associated with that sample.

The objective of blank spikes is to evaluate the accuracy of the analytical method, and to document accuracy and precision associated with laboratory performance of the method with a clean matrix.

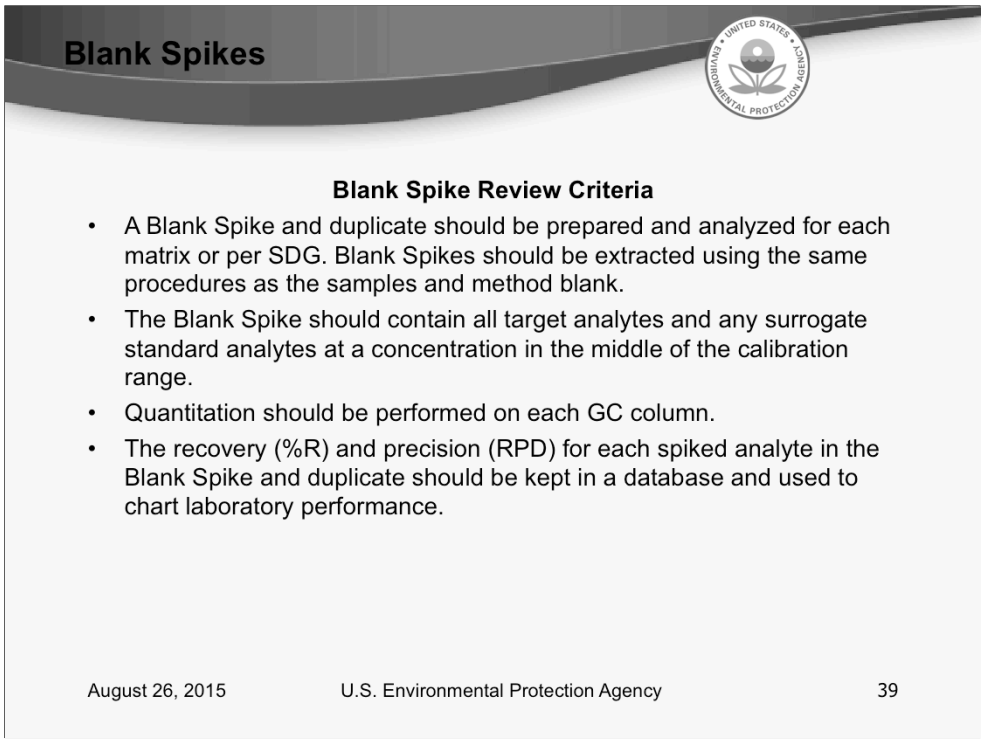


1. Verify that requested MS/MSD samples were analyzed at the required frequency, if applicable to the method and requested.

2. Verify that a field blank or PE sample was not used for MS/MSD analysis.

3. Verify that the recalculated MS/MSD %R and RPD values agree with the laboratory reported values on Form 3A-OR.

4. Inspect the MS/MSD %R and RPD on Form 3A-OR and verify that they are within the limits in the method.



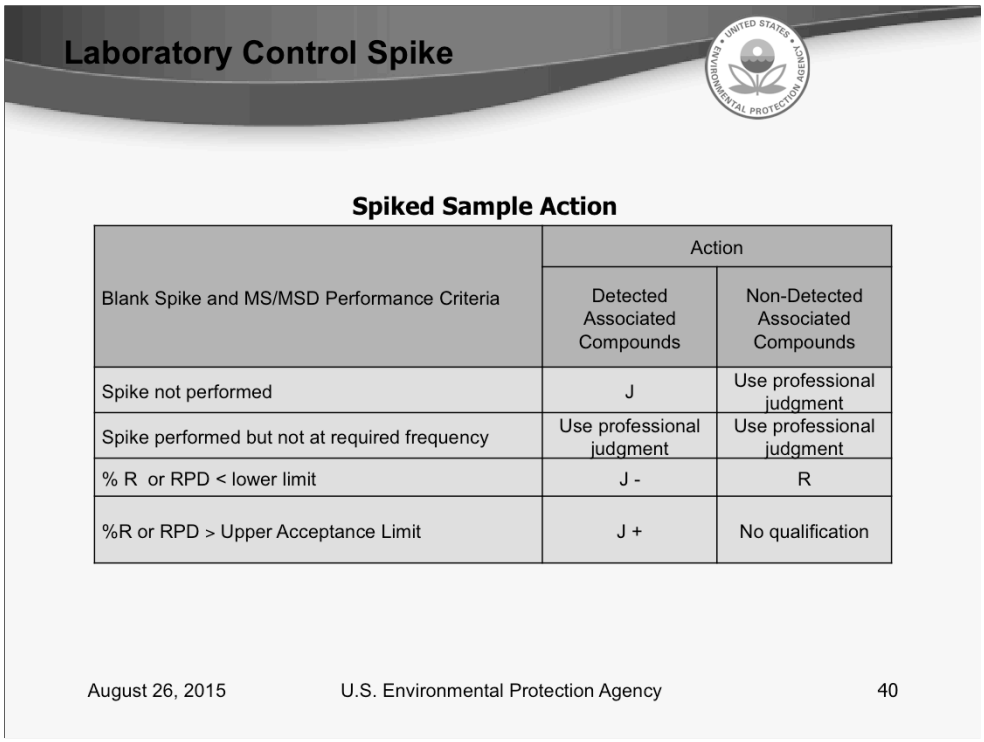
1.Verify that LCS is prepared and analyzed at the specified frequency.

2.Check the raw data (e.g., chromatograms and data system printouts) to verify that the LCS is spiked with the specified target analytes at the method specified concentrations.

3.Check the raw data (e.g., chromatograms and data system printouts) to verify that %R of each target analyte in LCS is calculated correctly and that the recalculated %R values agree with that reported on Form 3B-OR.

4.Verify that %R of each target analyte in LCS is within the specified acceptance limits.

NOTE: If an LCS sample is not analyzed at the specified frequency, use professional judgment to determine the impact on sample data; obtain additional information from the laboratory, if necessary. Record the situation in the Data Review Narrative.



1. If the spike analyses were not performed, or not performed at the required frequency, be sure to note this in the Data Review Narrative. Qualify detects as estimated (J) and use professional judgment to qualify non-detects.

Note: I recommend the establishment of performance windows at the 90% or 95% confidence interval (which we have found is typically 20 – 30%) for initial data qualification, and then if that is greater than 10% recovery, to also set a lower limit, for data rejection.

2. If the %R of any spiked analyte is < 10%, qualify detects as estimated low (J-) and non-detects as unusable (R). re-extraction and reanalysis are necessary.

3. If the %R of any analyte is ≥ 10% but < lower acceptance limit, qualify detects as estimated low (J-) and non-detects as estimated (UJ).

4. If the %R of any spiked analyte is ≥ lower acceptance limit and ≤ upper acceptance limit, detects and non-detects should not be qualified.

5. If the %R of any spiked analyte is > upper acceptance limit, qualify detects as estimated high (J+). Non-detects should not be qualified. re-extraction and reanalysis may be adviseable.

6. If the RPD of any spiked analyte is > 30%, use professional judgment to qualify detects and non-detects. This limit is only advisory.

7. %R and/or RPD failure, in conjunction with other performance factors, may indicate that the laboratory performance is unacceptable. In this case, use professional judgment to qualify detects and non-detects.

Questions?

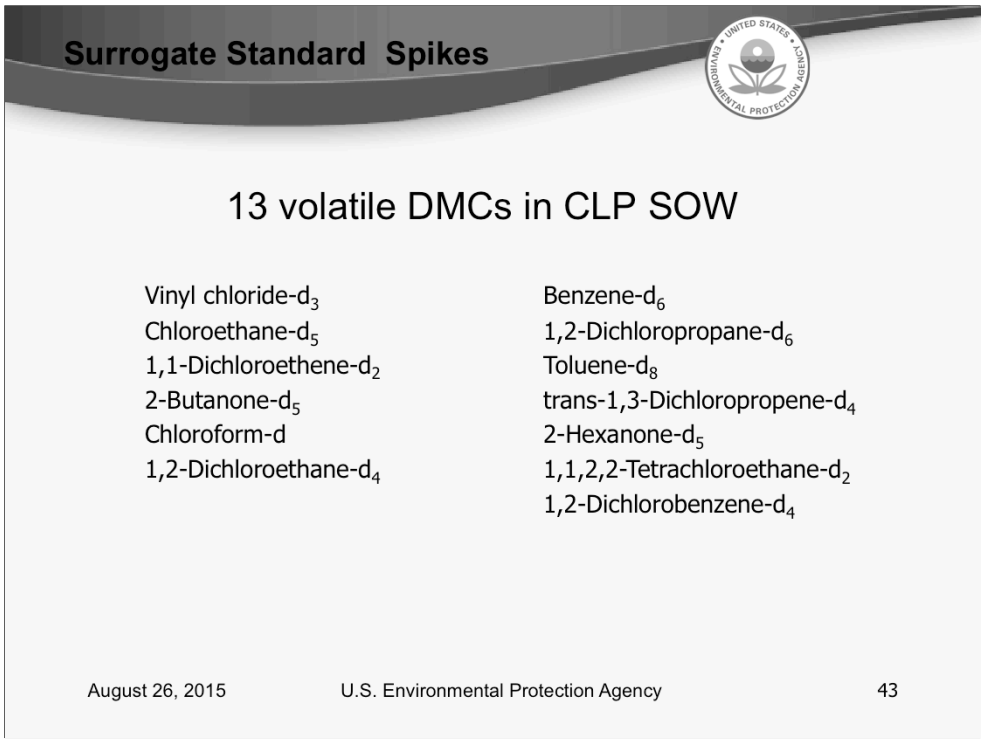
Surrogate Standard Spikes

Review Items

CLP Form 2-OR, calibration summary information, quantitation reports, and chromatograms for QC and field samples.

Objective

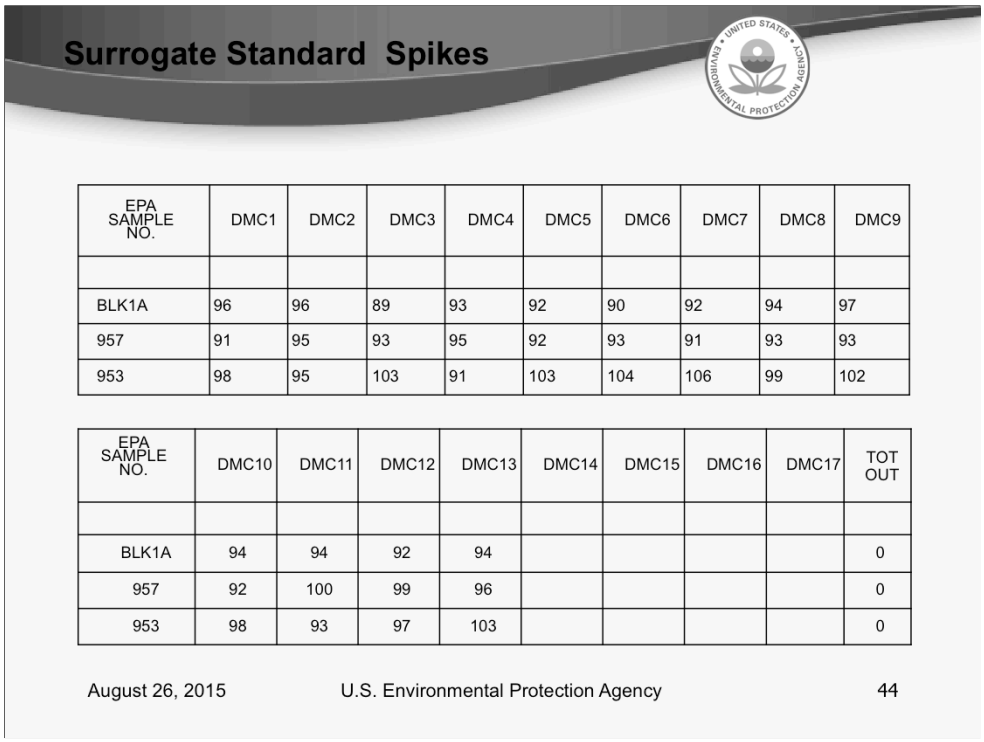
The objective of monitoring surrogate standards is to gain information about method performance of as many analyte types as are represented by the choice of surrogates in blank matrices as well as in field samples.



- The CLP uses deuterated compounds for surrogates in its GC/MS methods, and has expanded the list to 13 DMCs, to simulate the chemical behavior of all classes of compounds covered by the method.

- DMCs proposed and selected based on:
  - ✓ Characteristics and availability
    - ➢ All levels of deuteration investigated.
    - ➢ Stability
  - ✓ Cost
    - ➢ $0.90/VOC sample, approximately $2.85-$5.70/SVOC sample.
  - ✓ Chemical Representativeness
    - ➢ All 5 chemical groups of VOCs.

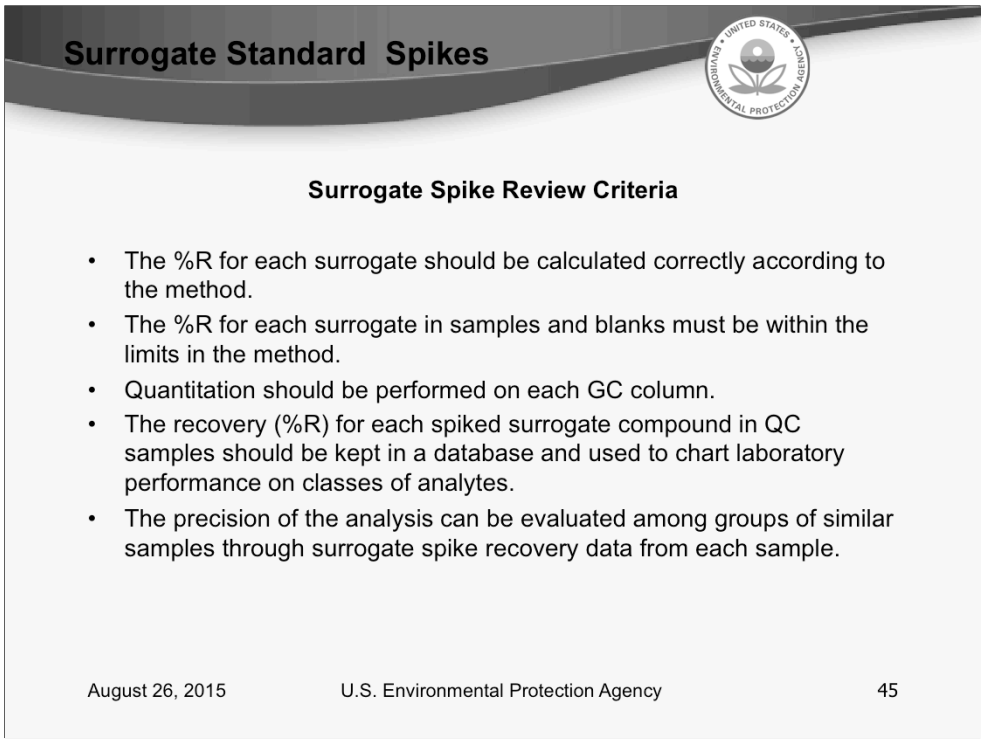
    Toxicity
    - ➢ More toxic target analytes preferred.
  - ✓ Accuracy and Precision of native analytes
    - ➢ Poorly performing analytes preferred.



Here is a CLP Form 2-OR for the DMC recovery summary for an SDG.

Now who can give me an idea of what we could do with the data we get by putting all these analytes in every sample (besides recovery – or accuracy of measurement - of each chemical class in each sample)?

DMC1 (VCL) = Vinyl chloride-d3 (30 - 150)
DMC2 (CLA) = Chloroethane-d5 (30 - 150)
DMC3 (DCE) = 1,1-Dichloroethene-d2 (45 - 110)
DMC4 (BUT) = 2-Butanone-d5 (20 - 135)
DMC5 (CLF) = Chloroform-d (40 - 150)
DMC6 (DCA) = 1,2-Dichloroethane-d4 (70 - 130)
DMC7 (BEN) = Benzene-d6 (20 - 135)
DMC8 (DPA) = 1,2-Dichloropropane-d6 (70 - 120)
DMC9 (TOL) = Toluene-d8 (30 - 130)
DMC10 (TDP) = trans-1,3-Dichloropropene-d4 (30 - 135)
DMC11 (HEX) = 2-Hexanone-d5 (20 - 135)
DMC12 (TCA) = 1,1,2,2-Tetrachloroethane-d2 (45 - 120)
DMC13 (DCZ) = 1,2-Dichlorobenzene-d4 (75 - 120)



1. Check raw data (e.g., chromatograms and quantitation reports) to verify the recoveries on the Deuterated Monitoring Compound Recovery Form 2A-OR and Form 2B-OR.

2. Check for any calculation or transcription errors. Verify that the DMC recoveries were calculated correctly using the equation in the method and that the recalculated values agree with the laboratory reported values on Form 2A-OR and Form 2B-OR.

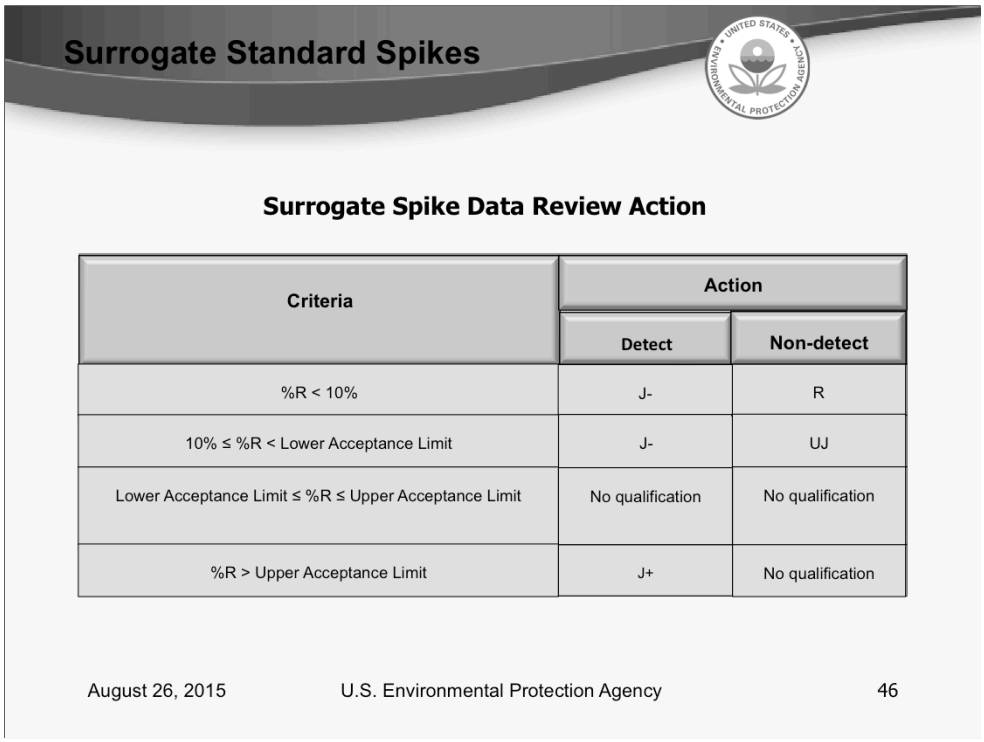
3. Whenever there are two or more analyses for a particular sample, use professional judgment to determine which analysis has the most acceptable data to report. Considerations include, but are not limited to:

a. DMC recovery (marginal versus gross deviation).

b. Technical holding times.

c. Comparison of the target analyte results reported in each sample analysis.

d. Other QC information, such as performance of internal standards.



1. If a DMC is not added in the samples and blanks or the concentrations of DMCs in the samples and blanks are not as specified, use professional judgment to qualify detects and non-detects. The project lead should be contacted to arrange for reanalysis, if possible.

2. If errors are detected in the calculations of %R, perform a more comprehensive recalculation. It may be necessary to have the laboratory resubmit the data after making corrections.

3. If any DMC %R is outside the limits in samples, qualify the associated analytes considering the existence of interference in the raw data. Considerations include, but are not limited to:

a. If the DMC %R is < 10%, qualify detects as estimated low (J-) and non-detects as unusable (R).

b. If the DMC %R is ≥ 10% and < the lower acceptance limit, qualify detects as estimated low (J-) and non-detects as estimated (UJ).

c. If the DMC %R is ≥ lower acceptance limit and ≤ upper acceptance limit, detects and non-detects should not be qualified.

d. If the DMC %R is > upper acceptance limit, qualify detects as estimated high (J+). Non-detects should not be qualified.

4. *If any DMC %R is outside the limits in a blank, special consideration should be taken to determine the validity of the associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process.*

For example, if one or more samples in the analytical sequence show acceptable DMC %Rs, the blank problem may be considered as an isolated occurrence. However, even if this judgment allows some use of the affected data, note analytical problems for further discussions with the lab.

Questions?

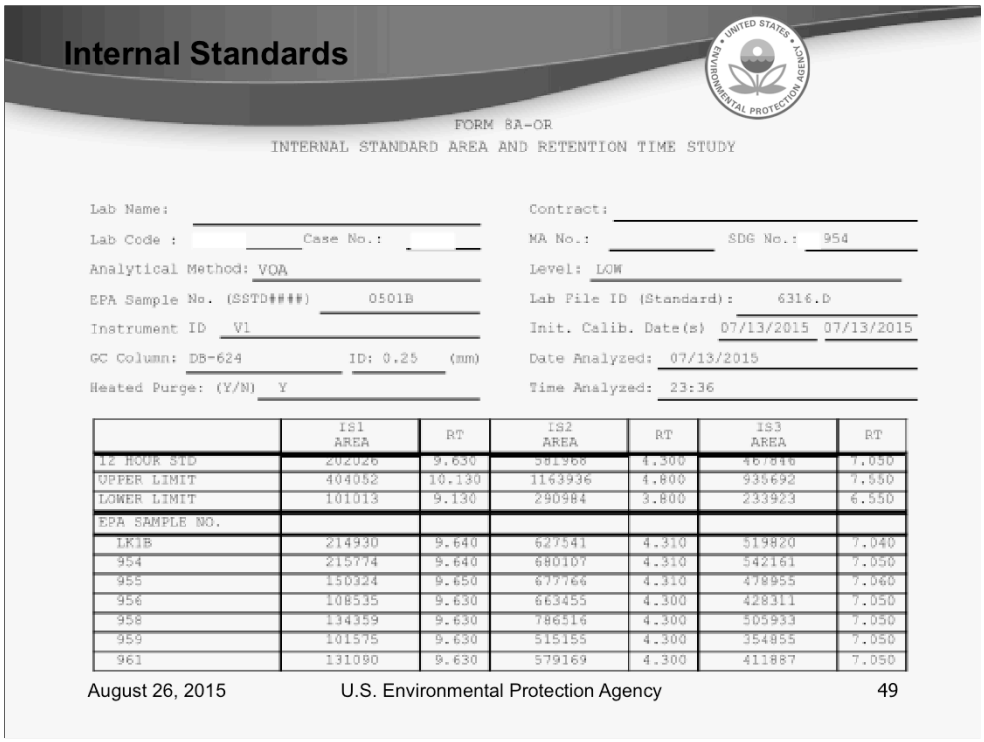
Internal Standards

Internal Standard Review Items

- CLP Form 8A-OR, quantitation reports, and chromatograms, GC/MS run-log.

Objective

- The objective is to evaluate the internal standard performance to ensure that GC/MS sensitivity and response are stable during each analysis.



Here is a CLP Form 8, listing the three ISTDs for VOA.

IS1 (CBZ)

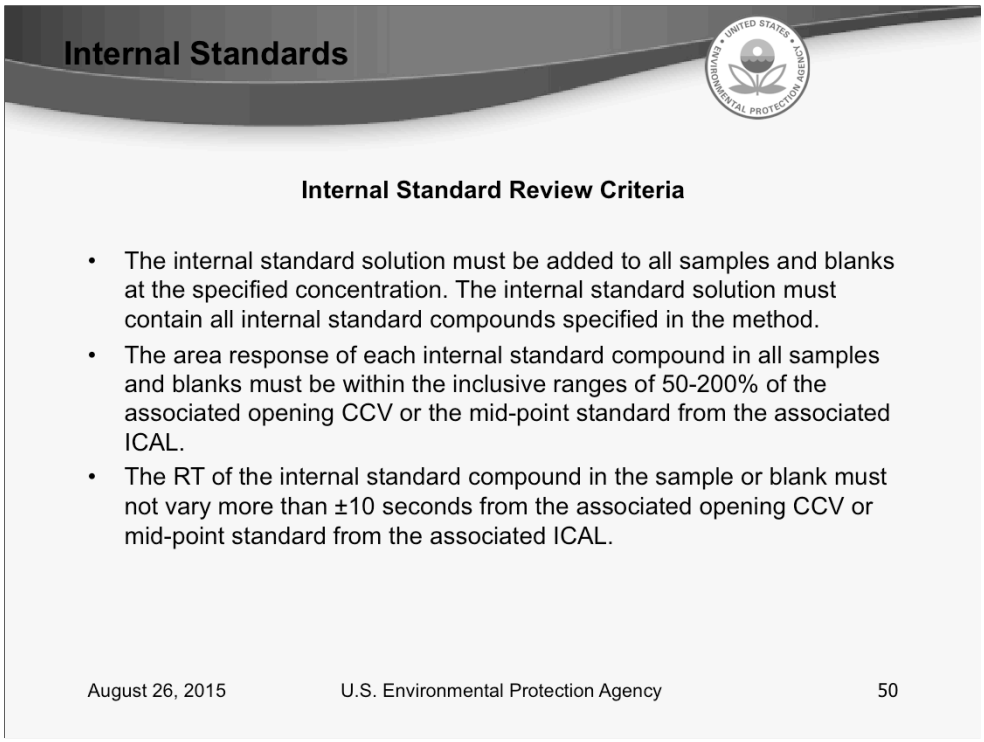
IS2 (DFB)

IS3 (DCB)

= Chlorobenzene-d5

= 1,4-Difluorobenzene

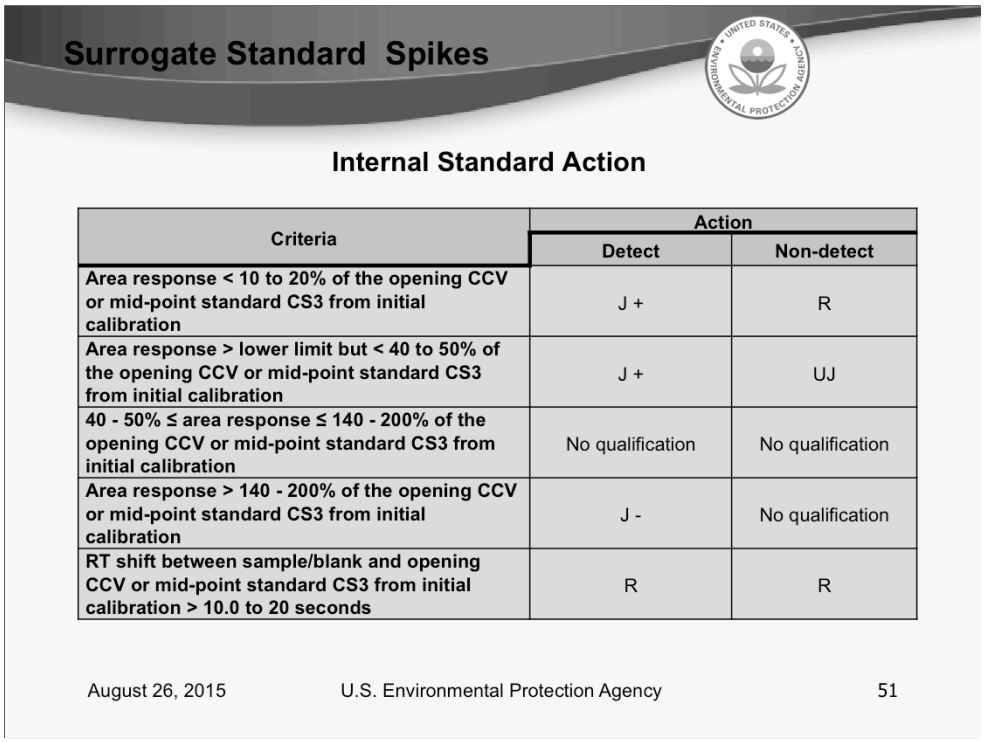
= 1,4-Dichlorobenzene-d4



1. Verify that all required internal standard compounds were added to sample and blank analyses at the specified concentrations.

2. Check raw data (e.g., chromatograms and quantitation reports) to verify that the RT and area response of each internal standard compound in a sample or blank are reported on the Internal Standard Area and Retention Time Summary Form 8A-OR.

3. Verify that the RTs and area responses for all internal standard compounds are within the specified criteria. If internal standard RTs are significantly different from the associated CCV or ICAL midpoint, i.e., more than 10 seconds, the internal standard peak may have been misidentified, but most likely a change in the chromatographic system should be suspected. This could be an improper desorb/injection cycle, a leak in the purge/trap/GC system, or the effect of a highly contaminated matrix. Normally, the area counts will also suffer in this situation, but even if they appear unaffected, both quantitative and qualitative results should be considered highly suspect.



- **NOTE:** Apply the action to the target analytes in samples or blanks that are associated to the non-compliant internal standard compound.

If there is a reanalysis for a particular sample, determine which analysis is the best data to report. Considerations include, but are not limited to:

a. Magnitude and direction of the internal standard area response shift.

b. Magnitude and direction of the internal standard RT shift.

c. Technical holding times.

d. Comparison of the values of the target analytes reported in each analysis of a sample,

e. Other QC information.

Questions?

Target Analyte Identification

Analyte Identification Review Items

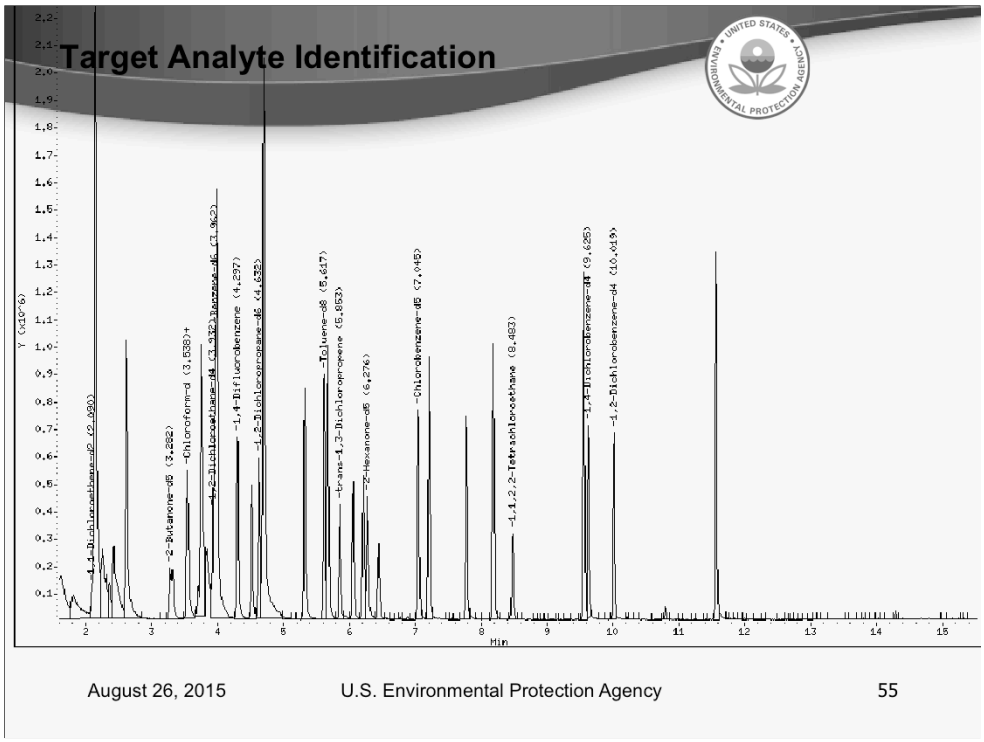
- CLP Form 1-OR, quantitation reports, chromatograms, and mass spectra.

Objective

- The objective is to provide acceptable GC/MS qualitative analysis to minimize the number of erroneous analyte identifications.

Target Analyte Identification

- Review sample extraction and analysis run logs, reporting forms, processed data and raw data.
- Examine sample data for:
  - reported analytes as well as non-detects
  - chromatography
  - retention time match
  - ion ratios
  - Abnormal DMC or Internal Standard response
- Verify calculations of sample results.
- Check for transcription errors.

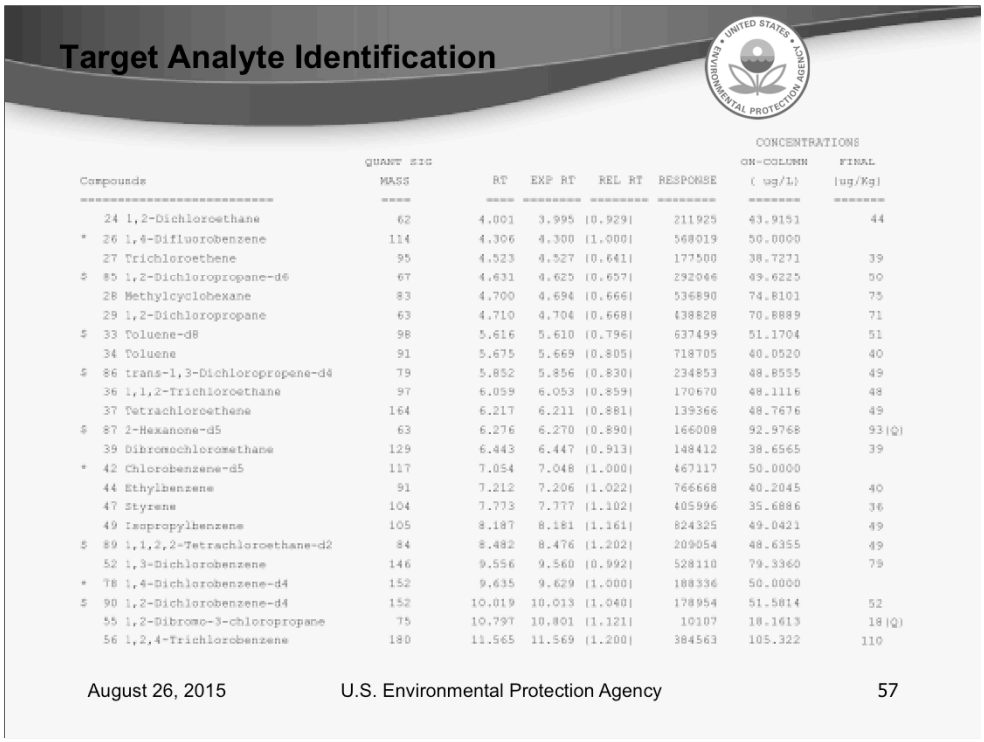


Here is one of the samples in the example data package that is posted on the Clu-In website.

Target Analyte Identification

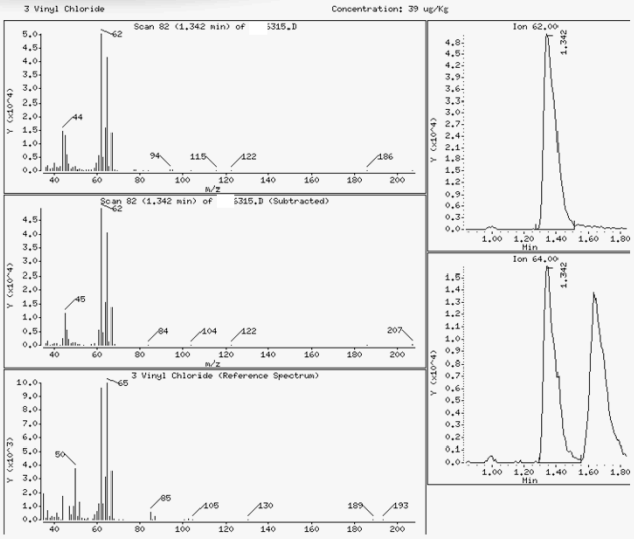
	Compounds	QUANT SIG MASS	RT	EXP RT	REL RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ug/L)	CONCENTRATIONS FINAL (ug/Kg)
$	79 Vinyl Chloride-d3	65	1.331	1.345	(0.309)	228150	48.7519	49
	3 Vinyl Chloride	62	1.341	1.335	(0.312)	263841	39.4133	39
	4 Bromomethane	94	1.568	1.582	(0.364)	86803	29.5887	30(Q)
$	80 Chloroethane-d5	69	1.627	1.621	(0.378)	165259	47.5187	48
	5 Chloroethane	64	1.627	1.650	(0.378)	91485	24.5549	25
$	81 1,1-Dichloroethene-d2	65	2.090	2.104	(0.485)	99923	51.5849	52(Q)
	9 Acetone	43	2.129	2.133	(0.495)	240807	94.9768	95
	10 Carbon Disulfide	76	2.257	2.261	(0.524)	684203	37.9046	38
	11 Methyl Acetate	43	2.356	2.360	(0.547)	102571	20.7469	21
	12 Methylene Chloride	84	2.425	2.419	(0.563)	237504	42.3206	42
	13 trans-1,2-Dichloroethene	96	2.612	2.616	(0.607)	171362	35.7416	36
	14 Methyl tert-Butyl Ether	73	2.612	2.616	(0.607)	671704	61.8046	62
$	82 2-Butanone-d5	46	3.282	3.285	(0.762)	290147	91.0967	91
$	83 Chloroform-d	84	3.538	3.542	(0.822)	349759	51.4730	51
	19 Chloroform	83	3.548	3.551	(0.824)	203453	27.0169	27
	20 1,1,1-Trichloroethane	97	3.705	3.709	(0.525)	98337	25.3185	25
	21 Cyclohexane	56	3.754	3.758	(0.532)	903249	93.9321	94
	22 Carbon Tetrachloride	117	3.833	3.837	(0.543)	46303	13.3410	13
$	23 1,2-Dichloroethane-d4	65	3.932	3.936	(0.913)	179496	51.8563	52
$	84 Benzene-d6	84	3.961	3.965	(0.562)	925893	52.7560	53
	25 Benzene	78	3.991	3.995	(0.566)	1000211	50.0804	50

And the associated processed data report, page 1

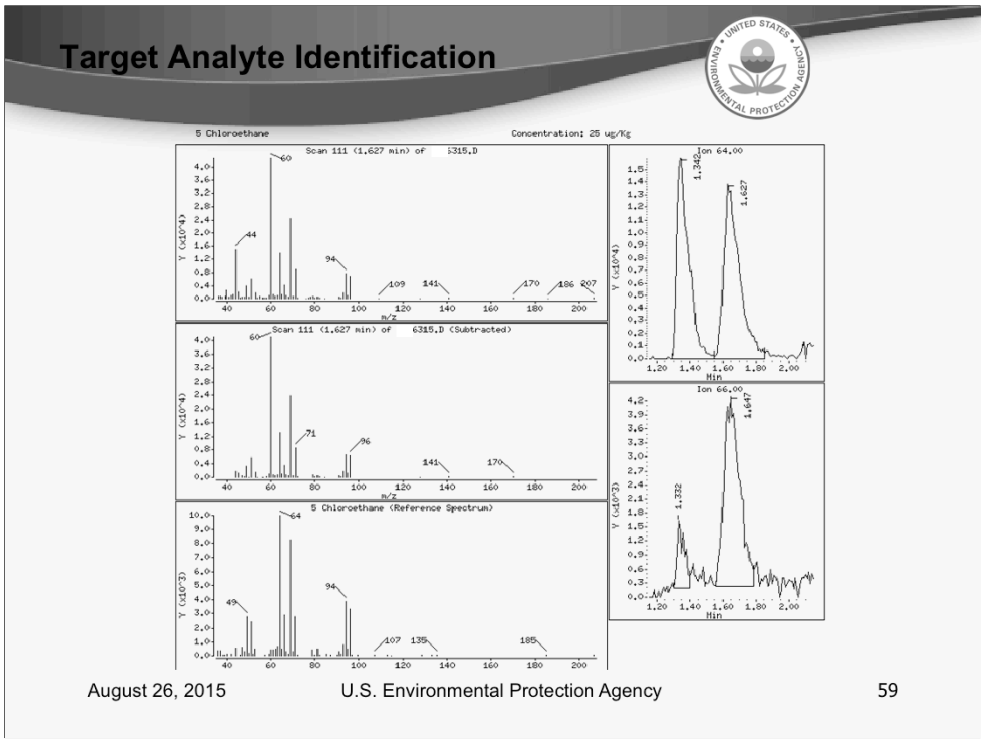


And page 2. Note the various notations automatically applied by the lab data system. One that was not needed here was the “m” flag, for manually integrated peaks. I’ll talk more about that in a minute.

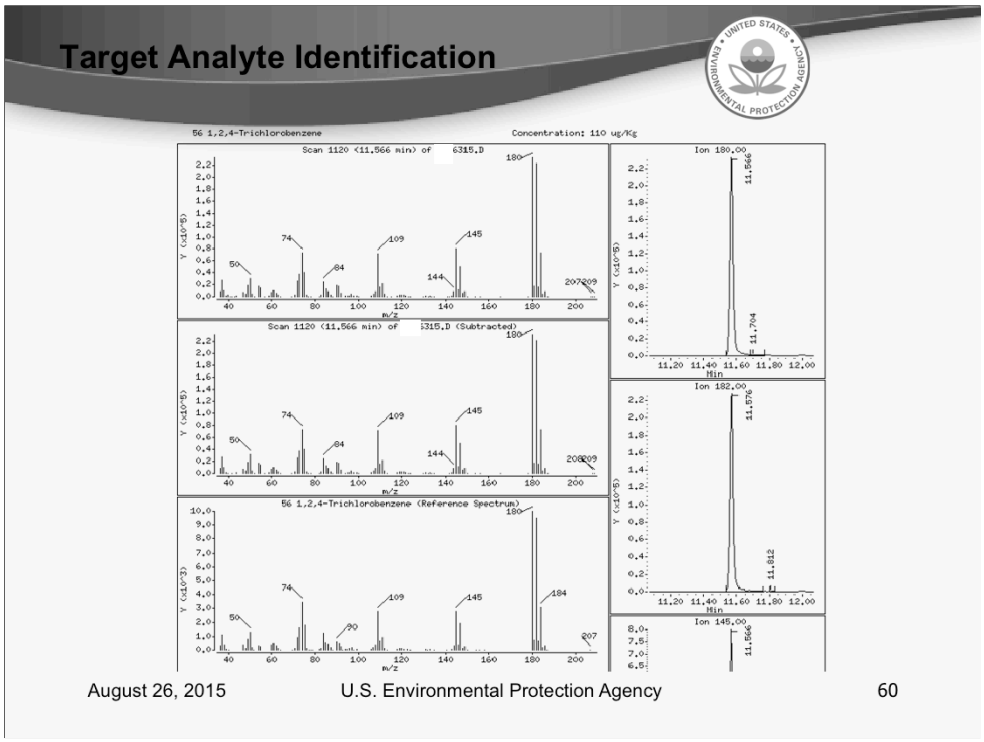
Target Analyte Identification



Here is an extracted ion current profile or EICP for target analyte Vinyl Chloride. Note the extra peak in the EICP for m/e 64. We'll learn what that is on the next slide. Chlorine patterns

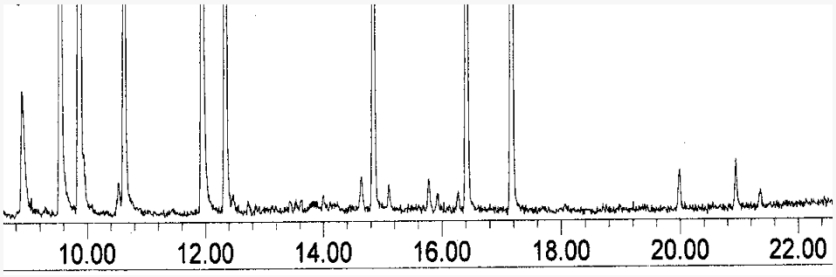


And here is chloroethane, about half a minute later, with its quantitation peak at 64.



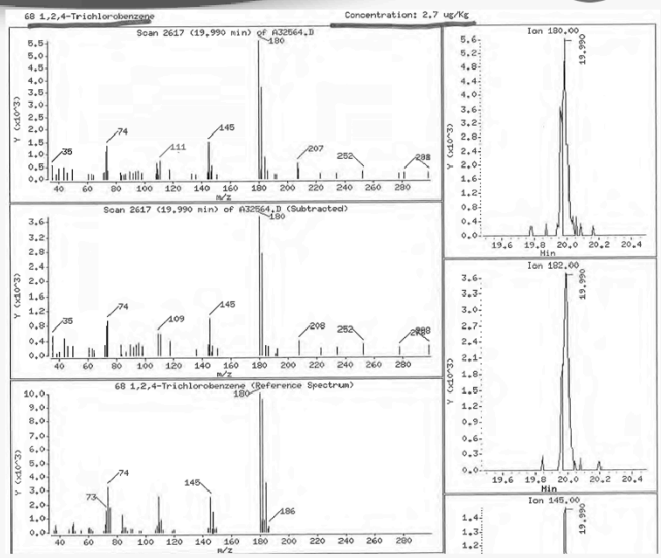
And one more; this is 1,2,4-trichlorobenzene. Chlorine patterns

Target Analyte Identification



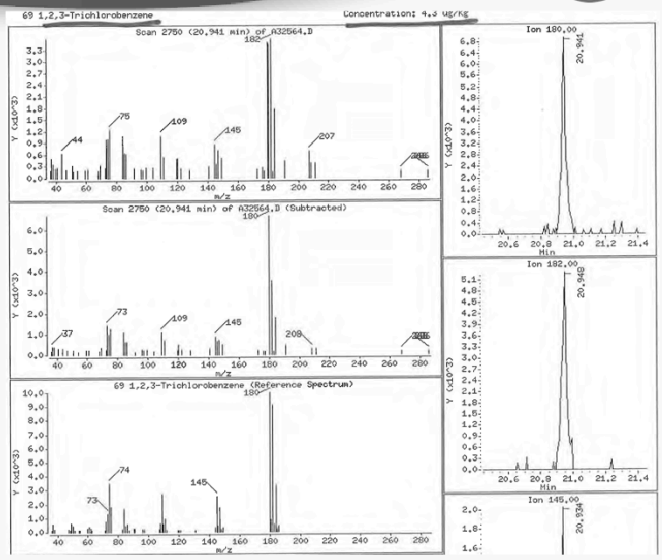
One of the elements of the CLP QA program is to periodically perform electronic media audits of data packages from our contract laboratories. The data packages are generally chosen at random, and the lab is required to submit the complete set of instrument-generated raw data files, processing method files, and processed data files. CLP's Quality Assurance and Technical Support contractor then uses the same software used by the labs to examine how the data were processed. So, if they observe peaks like these in the TIC of a GC/MS VOA run, they can access the mass spectra as the next slides will show. Here, the peaks at 20 and 21.94 min match the RT of the trichlorobenzenes, which were not reported by the lab. Peak on left is deuterated 1,4-Dioxane at 8.91 min, which was processed by the lab.

Target Analyte Identification

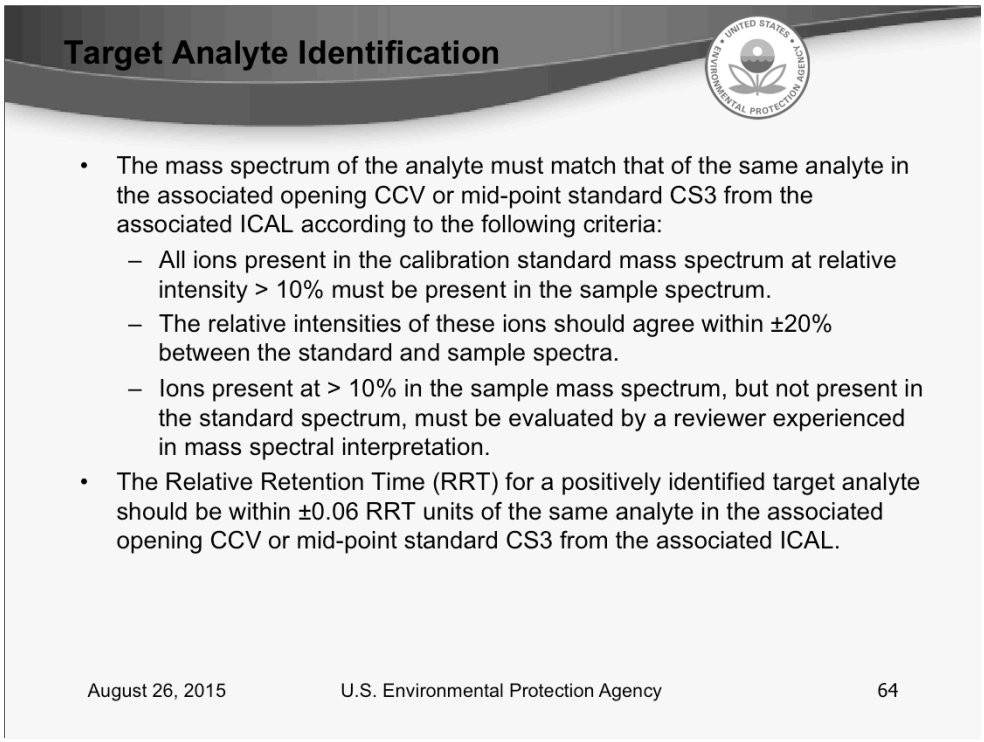


EICP of the GC peak at 19.99 min, and spectra matching it with 1,2,4-TCB.

Target Analyte Identification



The here is the QATS-produced EICP of the peak at 21.94 min, which is a RT and spectral match for 1,2,3-TCB. As a data reviewer, you should be on the look-out for unprocessed peaks like these that match the RT of target analytes. When you observe them, you should be able to ask the lab to re-process the data to determine whether they should be reported.



1. Verify that the positively identified target analyte mass spectrum meets the specified criteria. If not, examine the sample target analyte spectra for the presence of interference at one or more mass fragment peaks. Although the presence of a co-eluting interferent may preclude positive identification of the analyte, the presumptive evidence of its presence may be useful information to include in the Data Review Narrative.

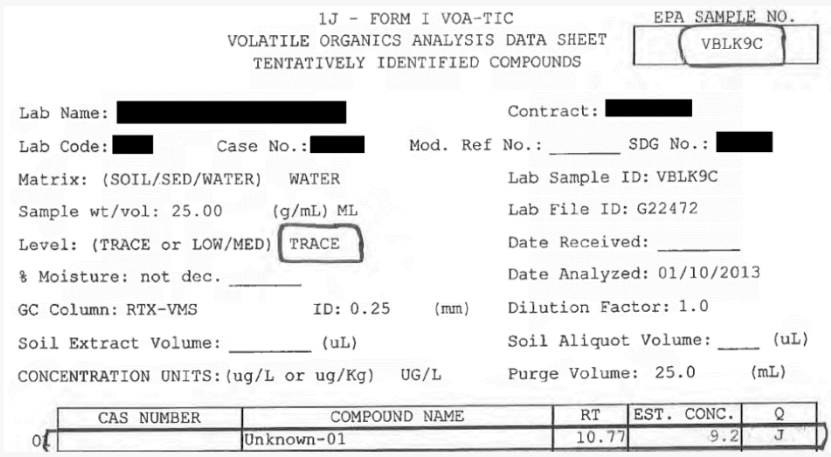
2. Verify that the RRT of the positively identified target analyte is within an acceptable range (i.e., ±0.06 RRT units) of the same analyte in the associated opening CCV or mid-point standard CS3 from the associated ICAL.

3. Be aware of situations when sample carryover is a possibility and use professional judgment to determine if instrument cross-contamination has affected any positive analyte identification. An instrument blank must be analyzed after a sample containing target analytes with concentrations exceeding the ICAL range (200 µg/L for non-ketones, 400 µg/L for ketones), non-target compounds at concentrations > 200 µg/L, or saturated ions from an analyte (excluding the analyte peaks in the solvent front).

4. Verify that peaks are correctly identified as target analytes, non-target chemicals that may be of interest, surrogate standards, or internal standards on the chromatogram for samples and blanks.

5. Verify that there is no erroneous analyte identification, either false positive or false negative, for each target analyte. The positively identified target analytes can be more easily detected for false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Non-detected target analytes, on the other hand, are more difficult to assess. One example of the detection of false negatives is reporting a target analyte as a TIC.

Target Analyte Identification



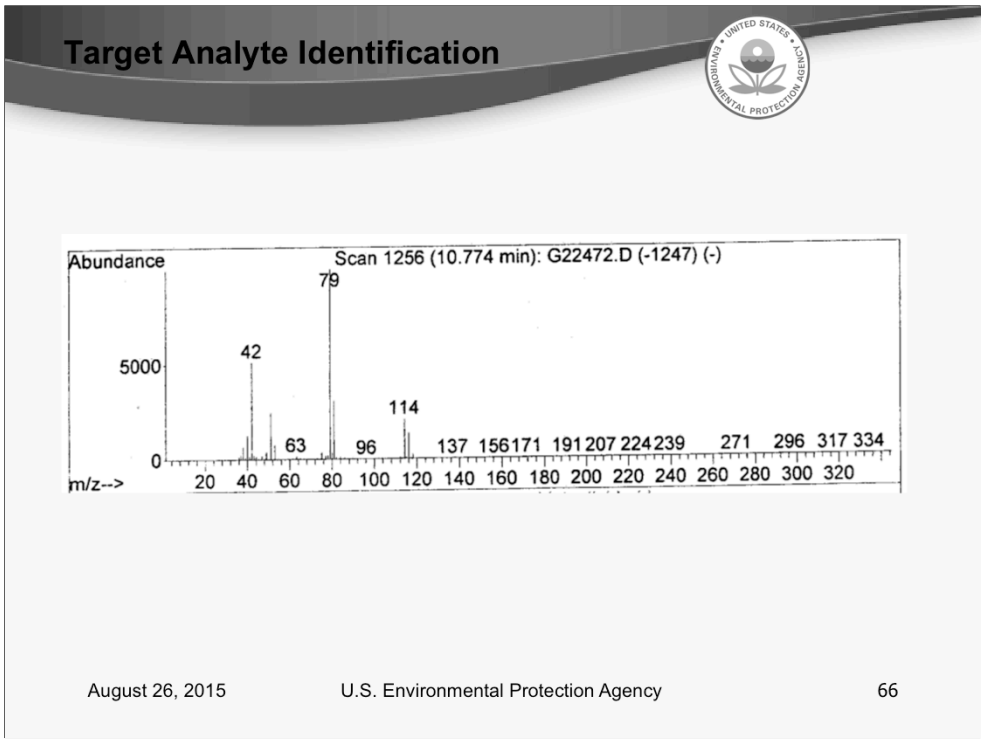
1J - FORM I VOA-TIC
VOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO.: VBLK9C

Lab Name: [redacted] Contract: [redacted]
Lab Code: [redacted] Case No.: [redacted] Mod. Ref No.: _____ SDG No.: [redacted]
Matrix: (SOIL/SED/WATER) WATER Lab Sample ID: VBLK9C
Sample wt/vol: 25.00 (g/mL) ML Lab File ID: G22472
Level: (TRACE or LOW/MED) TRACE Date Received: _____
% Moisture: not dec. _____ Date Analyzed: 01/10/2013
GC Column: RTX-VMS ID: 0.25 (mm) Dilution Factor: 1.0
Soil Extract Volume: _____ (uL) Soil Aliquot Volume: ____ (uL)
CONCENTRATION UNITS: (ug/L or ug/Kg) UG/L Purge Volume: 25.0 (mL)

	CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
01		Unknown-01	10.77	9.2	J

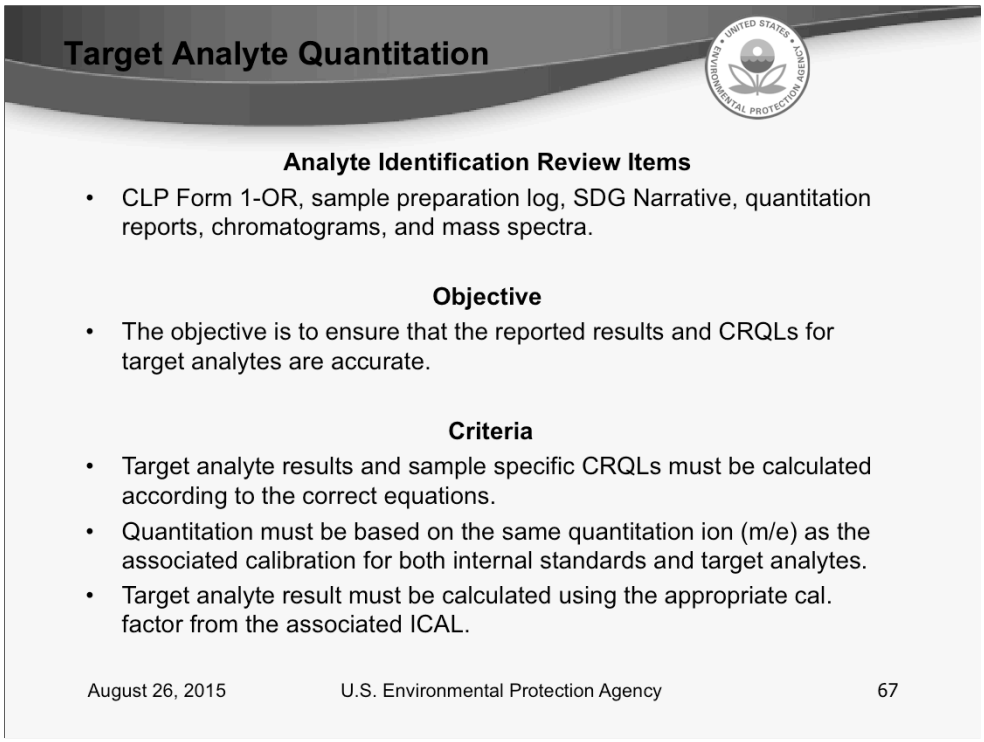
Here is a CLP reporting form for tentatively identified compounds (or non-target) compounds that was evaluated by the QATS team. This peak sparked their interest because it was found in all the blanks, it's tentative quantitation was above the CRQL without a good library match, and …



Its mass spectrum showed a chlorine pattern as you can see on the clusters at m/e 79 (one chlorine atom) and m/e 114 (2 chlorine atoms).

<u>Can anyone identify a likely empirical formula for this unknown?</u>

The compound was reported as “unknown-01”, but was identified by the QATS team as the cis-isomer of the trans-1,3-Dichloropropene-d4, which is an impurity of the manufacturing of the volatiles DMC spiking solution added to the blanks and samples and should not have been reported on the blanks and samples report forms.



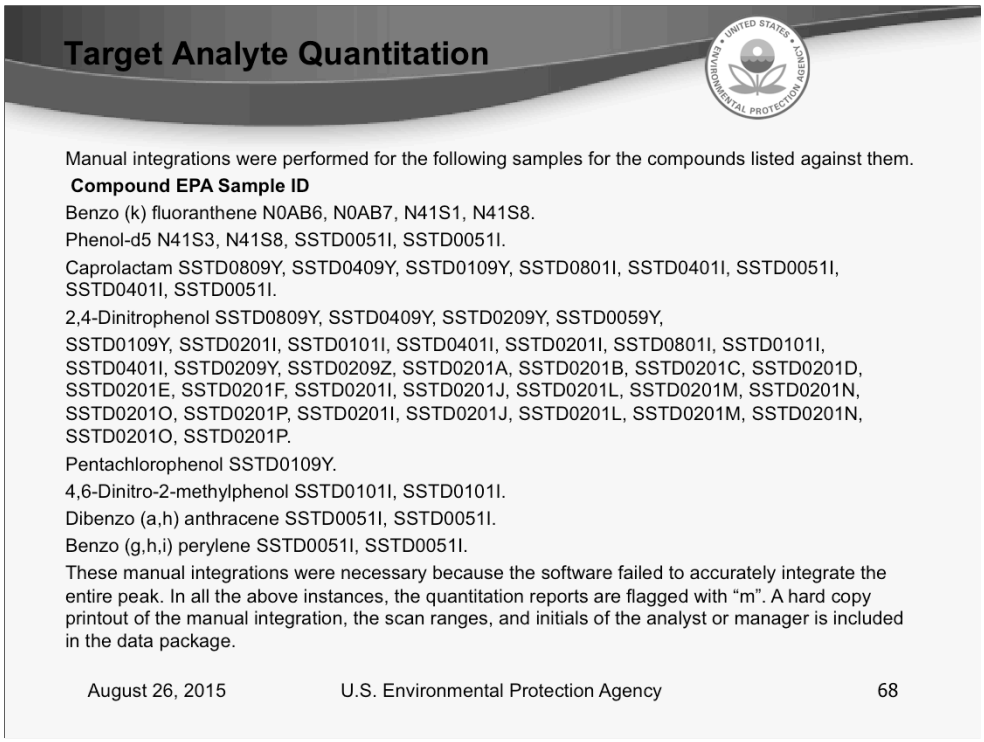
1. Verify that the results for all positively identified analytes are calculated and reported by the laboratory. Verify that the CRQLs are calculated for the non-detects and reported accordingly.

2. Verify that the correct internal standard, quantitation ion, and proper calibration factor are used to calculate the reported results.

3. Verify that the same internal standard, quantitation ion, and proper calibration factor are used consistently.

4. Verify that the sample specific CRQLs have been calculated and adjusted to reflect Percent Solids (%Solids), original sample mass/volume, and sample dilutions.

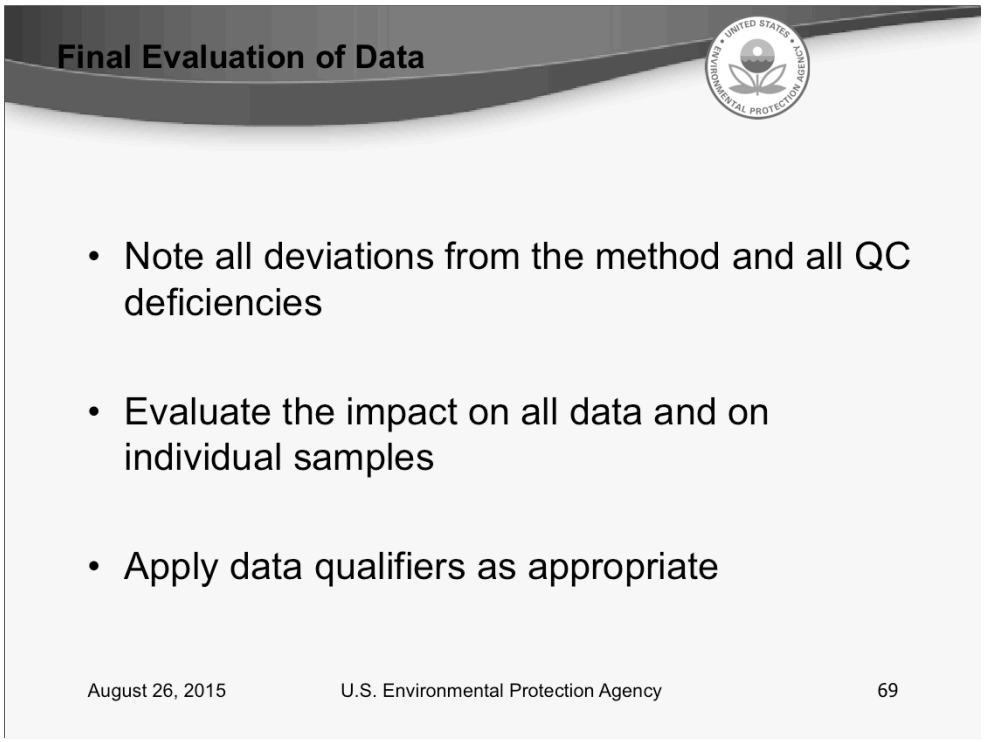
5. If any discrepancies are found, contact the Laboratory PO, who may contact the laboratory to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, use professional judgment to decide which value is the most accurate and whether qualification of data is warranted. Annotate the reasons for any data qualification in the Data Review Narrative.



Documentation of manual integrations is extremely important for organic data. If left unchecked, this practice leaves the door open for a dishonest scientist to maximize their profit at the expense of data usability.

Using the tools available to ASB's QATS contractors, we have been able to detect and pursue likely instances of the improper use of manual integration and other data processing practices. However, careful eyes can detect the tell-tail signs and take action.

Can you see the potential problem in the list above of the manual integrations performed for one SDG?



1. Check qualifiers applied by the laboratory before finalizing data qualification.

2. The amount of moisture in a solid sample may have an impact on data representativeness (i.e., if there is >70% moisture in a solid sample), depending on the nature of the equilibria between the two phases, and analyte solubility characteristics. The reviewer should be aware of any local standard operating procedures (SOPs) and/or concerns of the data user and evaluate the data on this basis.

3. If any discrepancies are found, the Region's designated representative may contact the laboratory to obtain additional information that could provide a resolution. If a discrepancy remains unresolved, the reviewer must use professional judgment to decide which value is the most accurate. Under these circumstances, the reviewer may determine that qualification of data is warranted. Note in the Data Review Narrative a description of the reasons for data qualification and the qualification that is applied to the data.

4. Note, for follow-up action, numerous or significant failures to accurately quantify the target compounds, homologue totals, or toxic equivalent quantities (TEQs), or to properly evaluate and adjust quantitation limits.

5. Apply appropriate qualification to the data, considering all QC criteria discussed in this webinar or in the National Functional Guidelines, to which there is a link on the CLU-IN website. It is recommended that a Data Review Narrative be developed to document the review process, including the impact on data quality of any anomalies found.

6. It is highly recommended that the data review process applied to each analyte, sample, sample delivery group (SDG), and/or project be characterized for the benefit of those who may subsequently review or use the data. Some terminology and labels for communicating the stages and processes used for laboratory analytical data verification and validation have been developed by an EPA workgroup and are published in *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use*, posted on the EPA Superfund CLP website, in the guidance documents folder.

I am available to answer any questions. Please feel free to contact me.