Verification and Review of Data for Volatile Organic Compounds by GC/MS

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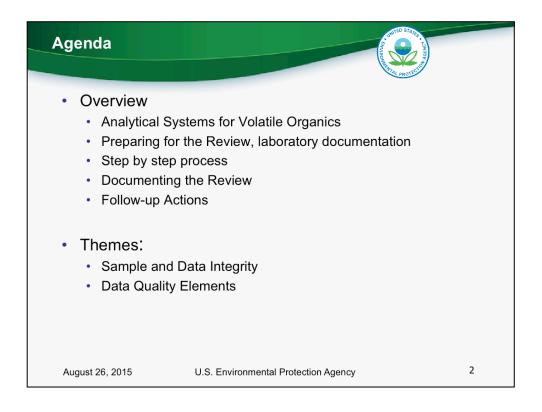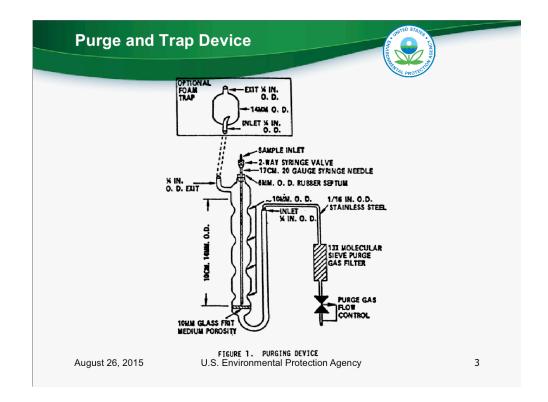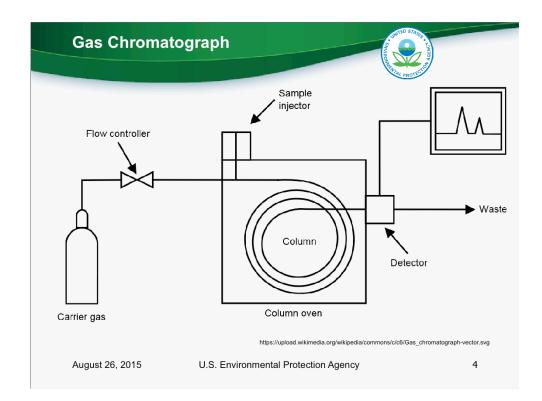Analytical Services Branch
August 26, 2015

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.

Agenda

- Overview
  - Analytical Systems for Volatile Organics
  - Preparing for the Review, laboratory documentation
  - Step by step process
  - Documenting the Review
  - Follow-up Actions

- Themes:
  - Sample and Data Integrity
  - Data Quality Elements

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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
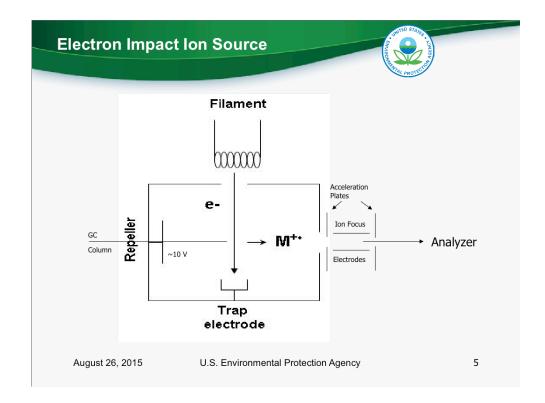
FIGURE 1. PURGING DEVICE

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?
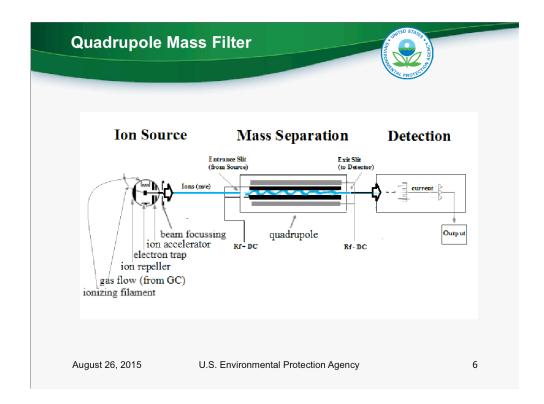
The separation and elution characteristics of a chromatographic column depend on the properties of the mobile and stationary phases and the interaction of the target analytes plus sample matrix that are introduced into the column with the mobile and stationary phases, and the length of the column. The 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.

Electron Impact Ion Source

Filament

e-

Acceleration Plates

Ion Focus

GC Column

Repeller

~10 V

M⁺·

Analyzer

Electrodes

Trap electrode

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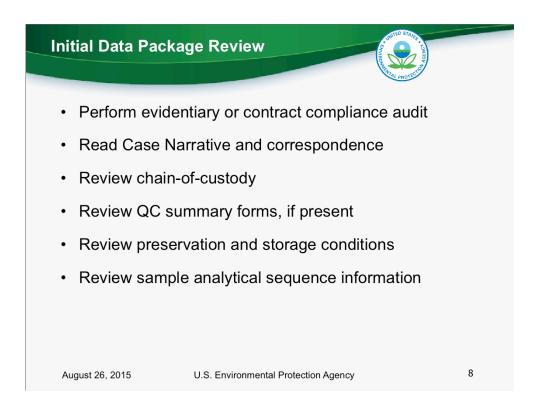
Here is the ion source, where molecules leaving the gas chromatograph are bombarded with electrons, which breaks some of them into characteristic fragments and gives them a positive charge (in most current configurations). These ions are then accelerated into the analyzer.

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

Quadrupole Mass Filter

Ion Source   Mass Separation   Detection

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?

- Perform evidentiary or contract compliance audit

- Read Case Narrative and correspondence

- Review chain-of-custody

- Review QC summary forms, if present

- Review preservation and storage conditions
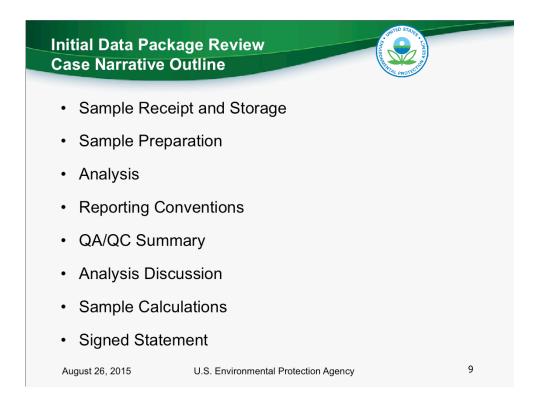
- Review sample analytical sequence information

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.

Initial Data Package Review
Case Narrative Outline

- Sample Receipt and Storage
- Sample Preparation
- Analysis
- Reporting Conventions
- QA/QC Summary
- Analysis Discussion
- Sample Calculations
- Signed Statement

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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.
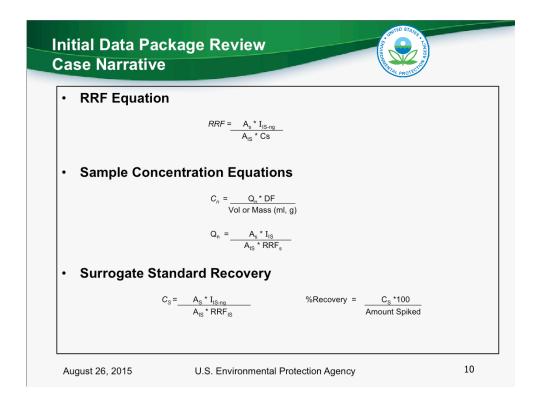
For example, if the laboratory decides to quantitate an analyte using different mass fragments, this should be described, and the calibration performance of the alternate ion should be documented as such. Yet we find upon checking that these things are done with no documentation, which does not serve 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.

- **RRF Equation**

$$RRF = \frac{A_s * I_{IS\text{-}ng}}{A_{IS} * Cs}$$

- **Sample Concentration Equations**

$$C_n = \frac{Q_n * DF}{\text{Vol or Mass (ml, g)}}$$

$$Q_n = \frac{A_s * I_{IS}}{A_{IS} * RRF_s}$$

- **Surrogate Standard Recovery**

$$C_S = \frac{A_S * I_{IS\text{-}ng}}{A_{IS} * RRF_{IS}} \qquad \%Recovery = \frac{C_S * 100}{\text{Amount Spiked}}$$

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.

Initial Data Package Review

Lab Name: ▮▮▮▮▮▮ Contract: ▮▮▮▮▮

Lab Code : ▮▮▮ Case No.: ▮441 MA No.: _____ SDG No.: ▮9954

Analytical Method: VOA Lab File ID: V1N6290.D

Instrument ID: V1 BFB/DFTPP: BFB

GC Column: DB 624 ID: 0.25 (mm)

Injection Date: 07/13/2015 Injection Time: 09:58

m/z	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
50	15.0 - 40.0% of mass 95	20.1
75	30.0 - 90.0% of mass 95	46.4
95	Base Peak, 100% relative abundance	100.0
96	5.0 - 9.0% of mass 95	8.6
173	Less than 2.0% of mass 174	0.1 (0.16) 1
174	50.0 - 120.0% of mass 95	61.4
175	5.0 - 9.0% of mass 174	4.5 (7.33) 1
176	95.0 - 101% of mass 174	61.3 (99.84) 1
177	5.0 - 9.0% of mass 176	3.9 (6.36) 2

EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED
VSTD0051Z	8800CAL01	V1N6291.D	07/13/2015	10:24
VSTD0101X	8801CAL02	V1N6292.D	07/13/2015	10:50
VSTD0501Z	8802CAL03	V1N6293.D	07/13/2015	11:17
VSTD1001Z	8803CAL04	V1N6294.D	07/13/2015	11:43
VSTD2001X	8804CAL05	V1N6295.D	07/13/2015	12:10
VSTD0501R	8807CCV	V1N6296.D	07/13/2015	13:03
VBLK1A	8805MB	V1N6297.D	07/13/2015	13:55
9957	501078506	V1N6313.D	07/13/2015	22:18
9953	501078510	V1N6315.D	07/13/2015	23:10
VSTD0501B	8808CCV	V1N6316.D	07/13/2015	23:36
VBLK1B	8859MB	V1N6317.D	07/14/2015	00:29
9954	501078501	V1N6323.D	07/14/2015	04:27
9955	501078502	V1N6324.D	07/14/2015	04:53
9956	501078503	V1N6325.D	07/14/2015	06:12
9958	501078507	V1N6326.D	07/14/2015	06:39
9959	501078508	V1N6327.D	07/14/2015	07:05
9961	501078509	V1N6328.D	07/14/2015	07:32
VSTD0501C	8861CCV	V1N6330.D	07/14/2015	09:43

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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.

Preservation / Holding Time

1. Technical holding time is determined from the date of sample collection to the date of sample analysis.
2. Samples should be in proper condition with shipping container temperatures at ≤ 6ºC upon receipt at the laboratory.
   1. Any unpreserved soil samples not received in field core sampling/storage containers shall be protected from light and stored at < -7ºC, from the time of receipt at the laboratory.
3. The EPA holding time for aqueous samples that are properly cooled but not acid preserved is 7 days. Aqueous samples with acid preservation can be held 14 days.
4. Samples received in field core containers must be transferred, immediately upon receipt, to a pre-prepared closed-system P/T vial, stored at < -7ºC, and analyzed within 14 days.
5. The technical holding time limit for non-aqueous samples, whether they are frozen, are preserved with bisulfite, or are preserved with methanol is 14 days.

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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.

Preservation / Holding Time

Preservation and Holding Time Actions for Trace Volatile Analysis

Criteria	Action	
	Detect	Non-detect
Sample temperature > 6°C upon receipt at the laboratory	Use professional judgment	Use professional judgment
Sample not preserved but analyzed within the 7-day technical holding time	No qualification	No qualification
Samples not preserved and analyzed outside the 7-day technical holding time	J-	R
Sample properly preserved and analyzed within the 14-day technical holding time	No qualification	No qualification
Sample properly preserved but analyzed outside the 14-day technical holding time	J*	R
Holding time grossly exceeded	J-	R

* The true direction of any bias may be unknown in this case. Use professional judgement based on knowledge of the chemistry of the analytes in the sample, or do not assign a direction to the bias.

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.
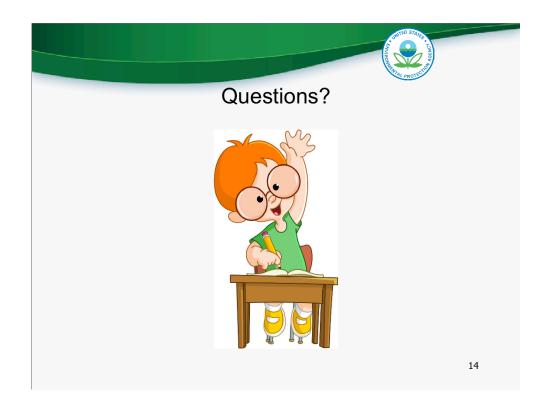
7. If aqueous samples are not properly preserved and are analyzed outside of the technical holding time of 7 days, qualify detects as estimated low (J-) and non-detects as unusable (R).
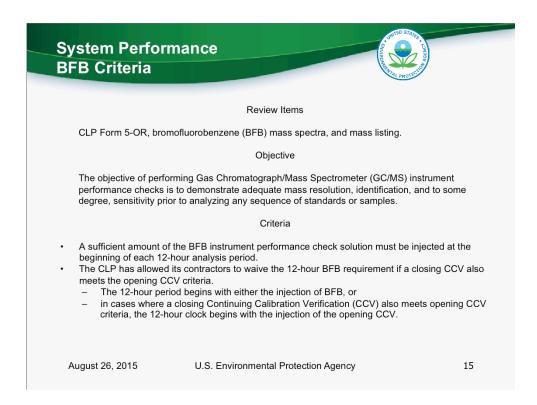
8. If aqueous samples are properly preserved and are analyzed within the technical holding time of 14 days, detects and non-detects should not be qualified.

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?

System Performance BFB Criteria

Review Items

CLP Form 5-OR, bromofluorobenzene (BFB) mass spectra, and mass listing.

Objective

The objective of performing Gas Chromatograph/Mass Spectrometer (GC/MS) instrument performance checks is to demonstrate adequate mass resolution, identification, and to some degree, sensitivity prior to analyzing any sequence of standards or samples.

Criteria

- A sufficient amount of the BFB instrument performance check solution must be injected at the beginning of each 12-hour analysis period.
- The CLP has allowed its contractors to waive the 12-hour BFB requirement if a closing CCV also meets the opening CCV criteria.
  - The 12-hour period begins with either the injection of BFB, or
  - in cases where a closing Continuing Calibration Verification (CCV) also meets opening CCV criteria, the 12-hour clock begins with the injection of the opening CCV.

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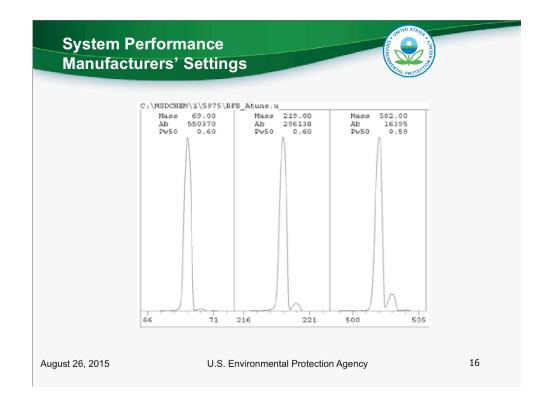

Verify that the BFB Instrument Performance Check solution is analyzed at the specified frequency
and sequence.

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).

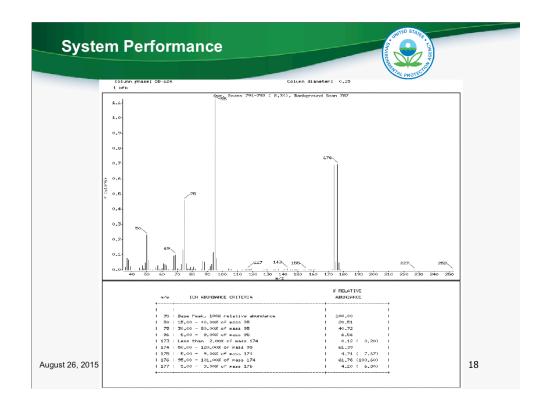Here are the results of the Agilent, formerly Hewlett Packard, "Autotune".

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

Ion Abundance Criteria for Bromofluorobenzene (BFB)

Mass	Ion Abundance Criteria
50	15.0 - 40.0% of mass 95
75	30.0 - 80.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of mass 95*
173	Less than 2.0% of mass 174
174	50.0% - 120% of mass 95
175	5.0 - 9.0% of mass 174
176	95.0 - 101% of mass 174
177	5.0 - 9.0% of mass 176

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).

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.

System Performance

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)

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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.

Data Review Action Summary for BFB Tune Check

Criterion	Action	
	Detects	Non-detects
Frequency		
Frequency not met and Qualitative characteristics optimum	No qualification	No qualification
Frequency not met and Qualitative criteria not achievable	R	R
BFB scan properly acquired	Professional Judgment	Professional Judgment
m/z assignments incorrect	R	R
Critical Ion Ratios out (95/96, 173-177)	R	R
Sensitivity requirements (25 ng Trace, 50 ng L/M)	J	R

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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.
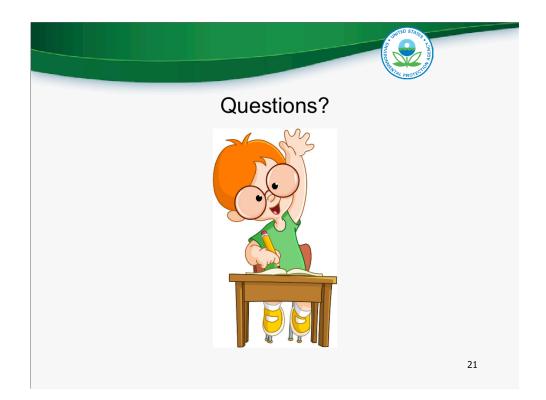
> 1. Retention times are not reproducible to within 0.06 RRT units.
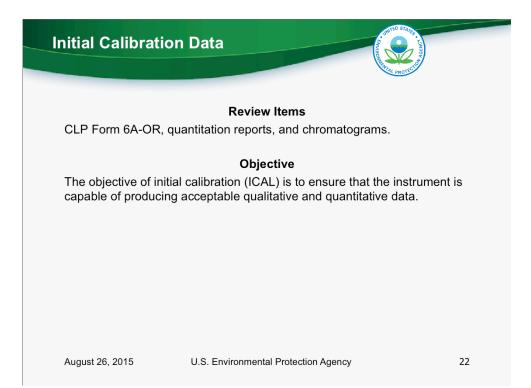
> 2. Chromatographic quality is degraded, with poor peak shapes, inconsistent shoulders or significant carry-over.
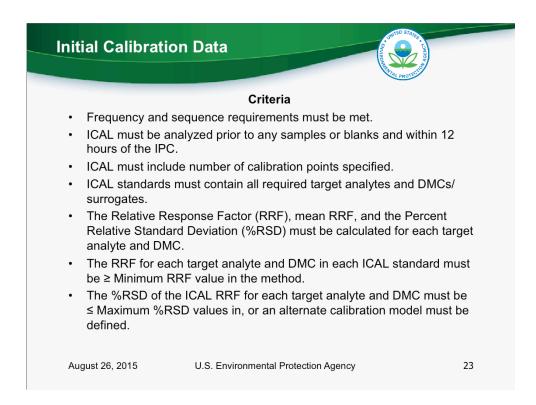
> 3. A valid tune check from the same instrument run at a different time and subsequent calibration standard data are not present in the package.

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.

Criteria

- Frequency and sequence requirements must be met.
- ICAL must be analyzed prior to any samples or blanks and within 12 hours of the IPC.
- ICAL must include number of calibration points specified.
- ICAL standards must contain all required target analytes and DMCs/ surrogates.
- The Relative Response Factor (RRF), mean RRF, and the Percent Relative Standard Deviation (%RSD) must be calculated for each target analyte and DMC.
- The RRF for each target analyte and DMC in each ICAL standard must be ≥ Minimum RRF value in the method.
- The %RSD of the ICAL RRF for each target analyte and DMC must be ≤ Maximum %RSD values in, or an alternate calibration model must be defined.

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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.
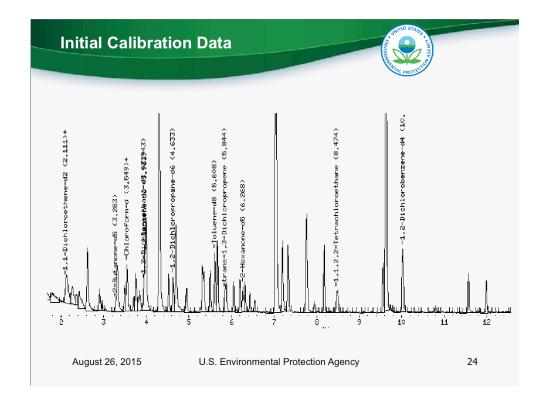
3. Verify that the RT for each target analyte and internal standard are within the specified RT windows, if equivalent columns to those specified in the method are used. If a different column has been used, examine the quant reports to evaluate whether there are any unacceptable co-elutions (i.e., with 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.

Initial Calibration Data

Initial Calibration Actions for Volatile Organic Analysis

Criteria	Action	
	Detected Compounds	Non-Detected Compounds
Initial calibrations are not performed	R	R
Initial calibration not at proper frequency	J professional judgment	UJ professional judgment
RRF < minimum in method	J+ or R professional judgment	R or professional judgment
GC Resolution inadequate	J	UJ
%RSDs outside limits, non-linear correlation not valid	J	UJ
Sensitivity inadequate to support low standard	J	Raise QL, J
RTs not reproducible		
	R	R

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.

Continuing Calibration Checks

Criteria

- Frequency and sequence requirements must be met.
- CCV must be analyzed prior to any samples or blanks and at end of the twelve-hour period.
- CCV must contain all target analytes at midpoint of Ical range.
- ICAL standards must contain all required target analytes and DMCs/ surrogates.
- The Relative Response Factor (RRF), and the Percent Difference (%D) calculations should be checked.
- The RRF for each target analyte and DMC in each CCV standard must be ≥ Minimum RRF value in the method.
- The %D of the CCV RRF for each target analyte and DMC must be ≤ Maximum %RSD values in, or an alternate calibration model must be defined.

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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.

Continuing Calibration Data

ANALYTE	$\overline{RRF}$	RRF 050	MIN RRF	%D	MAX %D
Dichlorodifluoromethane	0.435	0.360	0.010	-17.2	40.0
Chloromethane	0.832	0.830	0.010	-0.2	30.0
Vinyl chloride	0.589	0.580	0.010	-1.6	25.0
Bromomethane	0.258	0.291	0.010	12.5	30.0
Chloroethane	0.328	0.321	0.010	-2.1	25.0
Trichlorofluoromethane	0.398	0.384	0.010	-3.5	30.0
1,1-Dichloroethene	0.422	0.423	0.060	0.3	20.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.298	0.261	0.050	-12.3	25.0
Acetone	0.223	0.169	0.010	-24.4	40.0

ANALYTE	$\overline{RRF}$	RRF 050	MIN RRF	%D	MAX %D
Dichlorodifluoromethane	0.435	0.321	0.010	-26.0	40.0
Chloromethane	0.832	0.817	0.010	-1.8	30.0
Vinyl chloride	0.589	0.556	0.010	-5.6	25.0
Bromomethane	0.258	0.297	0.010	14.9	30.0
Chloroethane	0.328	0.323	0.010	-1.5	25.0
Trichlorofluoromethane	0.398	0.342	0.010	-14.0	30.0
1,1-Dichloroethene	0.422	0.399	0.060	-5.3	20.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.298	0.244	0.050	-18.1	25.0
Acetone	0.223	0.143	0.010	-36.0	40.0

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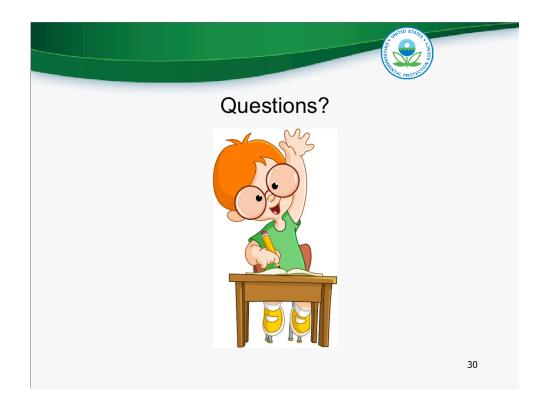
Now I would like to ask you to look at these two tables and tell me which one you think was done at the end of the 12-hour analysis period and why?
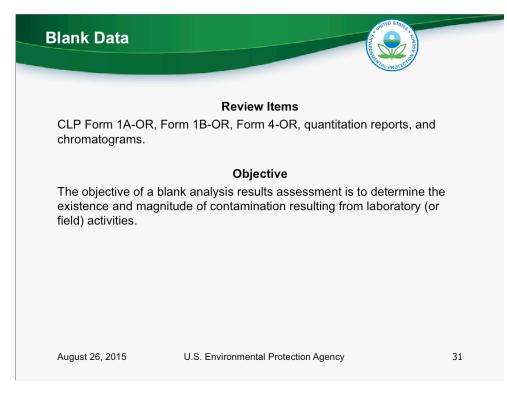
Continuing Calibration Data

CCV Actions for Volatile Organic Analysis

Criteria for Opening CCV	Criteria for Closing CCV	Action	
		Detect	Non-detect
CCV not performed at required frequency	CCV not performed at required frequency	Use professional judgment R	Use professional judgment R
CCV not performed at specified concentration	CCV not performed at specified concentration	Use professional judgment	Use professional judgment
RRF < Minimum RRF in the method or COD, $r^2 < 0.99$	RRF < Minimum RRF in the method or COD, $r^2 < 0.99$	Use professional judgment J or R	R
%D outside the Opening Maximum %D limits in the method for target analyte	%D outside the Closing Maximum %D limits in the method for target analyte	J	UJ

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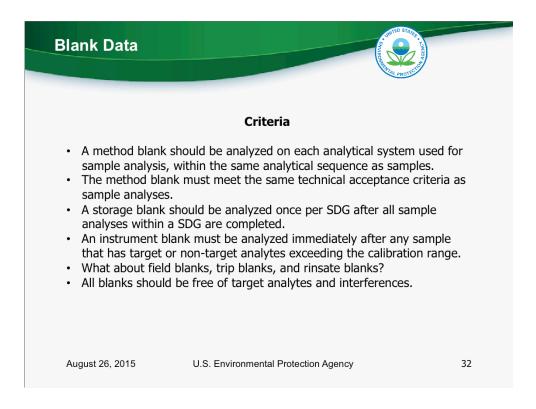
1. If the CCV standard was not analyzed at the specified frequency and sequence, use professional judgment to qualify detects and non-detects.

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.

Blank Data

Criteria

- A method blank should be analyzed on each analytical system used for sample analysis, within the same analytical sequence as samples.
- The method blank must meet the same technical acceptance criteria as sample analyses.
- A storage blank should be analyzed once per SDG after all sample analyses within a SDG are completed.
- An instrument blank must be analyzed immediately after any sample that has target or non-target analytes exceeding the calibration range.
- What about field blanks, trip blanks, and rinsate blanks?
- All blanks should be free of target analytes and interferences.

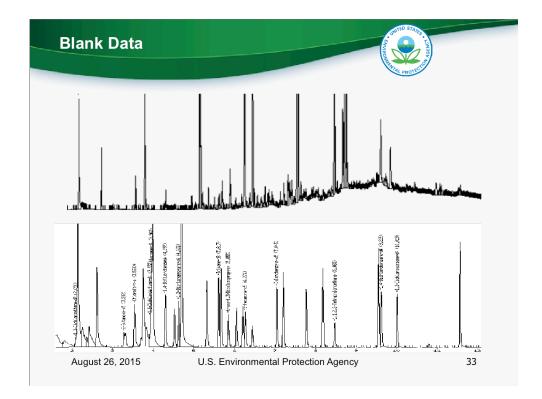August 26, 2015   U.S. Environmental Protection Agency   32

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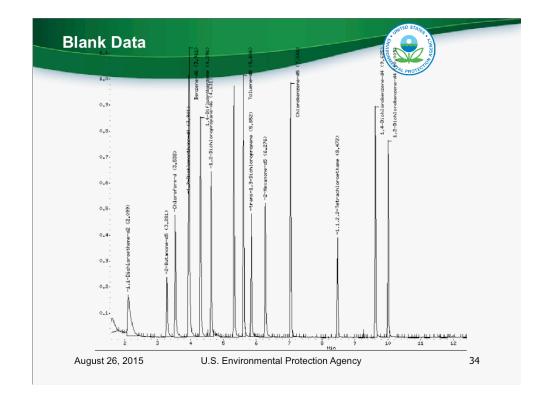
3. Verify that the instrument blank analysis has been performed following any sample analysis where a target analyte(s) is/are reported at high concentration(s).

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.

Blank Data

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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.

Method Blank

Method Blank Action

Method Blank Result	Sample Result	Action
< < CRQL or EDL	Not detected	No qualification
	≥CRQL and >> Blank Result	No qualification or use professional judgment to avoid false pos. or neg.
≥ CRQL or EDL	Not detected	No qualification
	≥CRQL and < Blank Result	U*
	> CRQL and ≥Blank Result	J or use professional judgment
Gross contamination	Positive	R

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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.
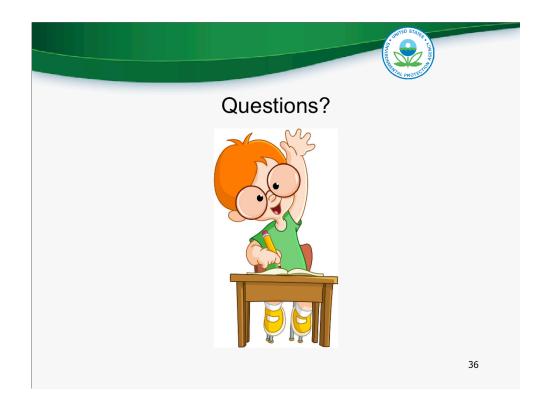
3. For a method blank or an instrument blank reported with results ≥ 1/2x CRQLs, non-detects should not be qualified. Report sample results that are < CRQLs at the CRQLs and qualify as non-detect (U). Report sample results ≥ CRQLs but < Blank Results at the blank results and qualify as non-detect (U.). Qualify sample results ≥ CRQLs and ≥ Blank Results as estimated (J).
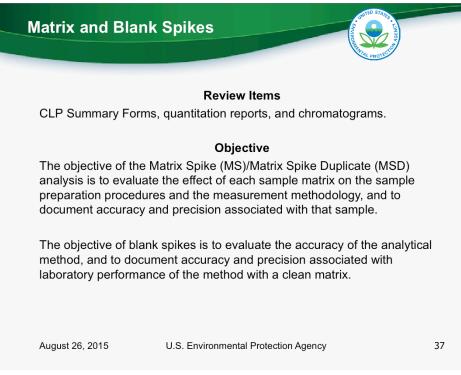
4. There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed appropriate. Use professional judgment to qualify sample results in these situations and provide an explanation of the rationale used for data qualifications in the Data Review Narrative.
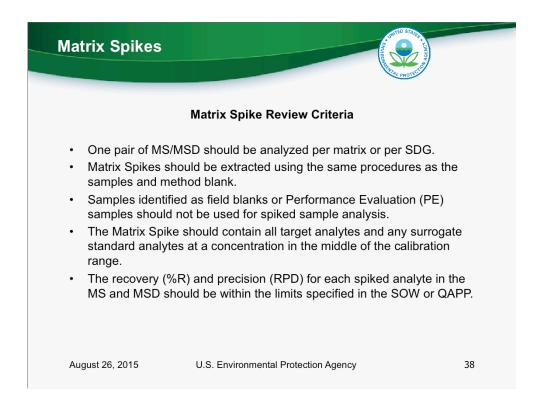
5. Blanks or samples analyzed after a PES sample, or a CCV should be carefully examined to evaluate the possible occurrence of instrument carry-over. Use professional judgment to determine whether sample or blank results are attributable to carry-over.

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.

Matrix Spikes

Matrix Spike Review Criteria

- One pair of MS/MSD should be analyzed per matrix or per SDG.
- Matrix Spikes should be extracted using the same procedures as the samples and method blank.
- Samples identified as field blanks or Performance Evaluation (PE) samples should not be used for spiked sample analysis.
- The Matrix Spike should contain all target analytes and any surrogate standard analytes at a concentration in the middle of the calibration range.
- The recovery (%R) and precision (RPD) for each spiked analyte in the MS and MSD should be within the limits specified in the SOW or QAPP.

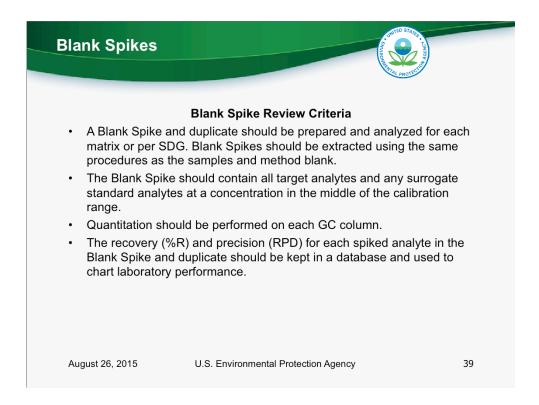August 26, 2015   U.S. Environmental Protection Agency   38

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.

Blank Spikes

Blank Spike Review Criteria
- A Blank Spike and duplicate should be prepared and analyzed for each matrix or per SDG. Blank Spikes should be extracted using the same procedures as the samples and method blank.
- The Blank Spike should contain all target analytes and any surrogate standard analytes at a concentration in the middle of the calibration range.
- Quantitation should be performed on each GC column.
- The recovery (%R) and precision (RPD) for each spiked analyte in the Blank Spike and duplicate should be kept in a database and used to chart laboratory performance.

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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.

Laboratory Control Spike

Spiked Sample Action

Blank Spike and MS/MSD Performance Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Spike not performed	J	Use professional judgment
Spike performed but not at required frequency	Use professional judgment	Use professional judgment
% R or RPD < lower limit	J -	R
%R or RPD > Upper Acceptance Limit	J +	No qualification

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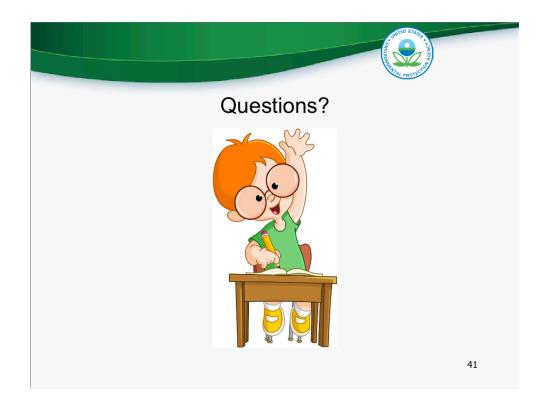
3. If the %R of any analyte is ≥ 10% but < lower acceptance limit, qualify detects as estimated low (J-) and non-detects as estimated (UJ).

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.
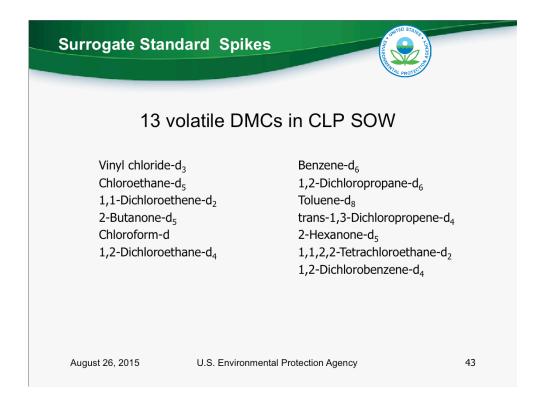
Objective

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.

13 volatile DMCs in CLP SOW

Vinyl chloride-d_3	Benzene-d_6
Chloroethane-d_5	1,2-Dichloropropane-d_6
1,1-Dichloroethene-d_2	Toluene-d_8
2-Butanone-d_5	trans-1,3-Dichloropropene-d_4
Chloroform-d	2-Hexanone-d_5
1,2-Dichloroethane-d_4	1,1,2,2-Tetrachloroethane-d_2
	1,2-Dichlorobenzene-d_4

- 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.
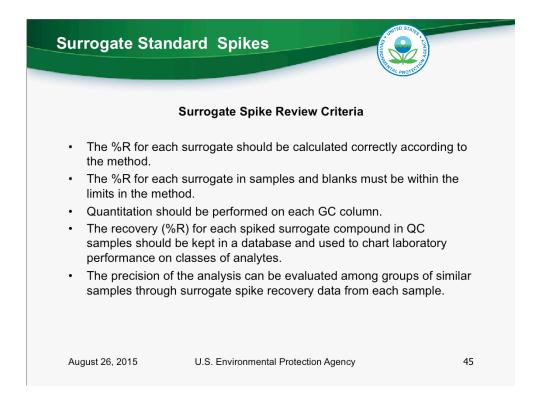

     Toxicity

     ➢ More toxic target analytes preferred.

  ✓ Accuracy and Precision of native analytes

     ➢ Poorly performing analytes preferred.

EPA SAMPLE NO.	DMC1	DMC2	DMC3	DMC4	DMC5	DMC6	DMC7	DMC8	DMC9
BLK1A	96	96	89	93	92	90	92	94	97
957	91	95	93	95	92	93	91	93	93
953	98	95	103	91	103	104	106	99	102

EPA SAMPLE NO.	DMC10	DMC11	DMC12	DMC13	DMC14	DMC15	DMC16	DMC17	TOT OUT
BLK1A	94	94	92	94					0
957	92	100	99	96					0
953	98	93	97	103					0

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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)

Surrogate Standard Spikes

Surrogate Spike Review Criteria

- The %R for each surrogate should be calculated correctly according to the method.
- The %R for each surrogate in samples and blanks must be within the limits in the method.
- Quantitation should be performed on each GC column.
- The recovery (%R) for each spiked surrogate compound in QC samples should be kept in a database and used to chart laboratory performance on classes of analytes.
- The precision of the analysis can be evaluated among groups of similar samples through surrogate spike recovery data from each sample.

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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.

Surrogate Standard Spikes

Surrogate Spike Data Review Action

Criteria	Action	
	Detect	**Non-detect**
%R < 10%	J-	R
10% ≤ %R < Lower Acceptance Limit	J-	UJ
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualification	No qualification
%R > Upper Acceptance Limit	J+	No qualification

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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:

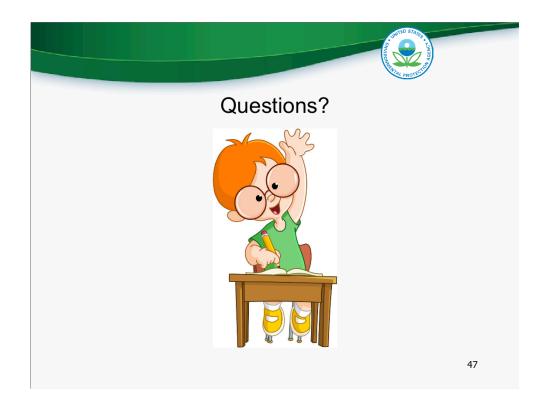a. If the DMC %R is < 10%, qualify detects as estimated low (J-) and non-detects as unusable (R).

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.

Internal Standards

FORM 8A-OR
INTERNAL STANDARD AREA AND RETENTION TIME STUDY

Lab Name: _____ Contract: _____

Lab Code : _____ Case No.: _____ MA No.: _____ SDG No.: 954

Analytical Method: VOA Level: LOW

EPA Sample No. (SSTD####)   0501B Lab File ID (Standard):   6316.D

Instrument ID   V1 Init. Calib. Date(s) 07/13/2015 07/13/2015

GC Column: DB-624   ID: 0.25   (mm) Date Analyzed: 07/13/2015

Heated Purge: (Y/N)   Y Time Analyzed: 23:36

	IS1 AREA	RT	IS2 AREA	RT	IS3 AREA	RT
12 HOUR STD	202026	9.630	581968	4.300	467846	7.050
UPPER LIMIT	404052	10.130	1163936	4.800	935692	7.550
LOWER LIMIT	101013	9.130	290984	3.800	233923	6.550
EPA SAMPLE NO.						
LK1B	214930	9.640	627541	4.310	519820	7.040
954	215774	9.640	680107	4.310	542161	7.050
955	150324	9.650	677766	4.310	478955	7.060
956	108535	9.630	663455	4.300	428311	7.050
958	134359	9.630	786516	4.300	505933	7.050
959	101575	9.630	515155	4.300	354855	7.050
961	131090	9.630	579169	4.300	411887	7.050

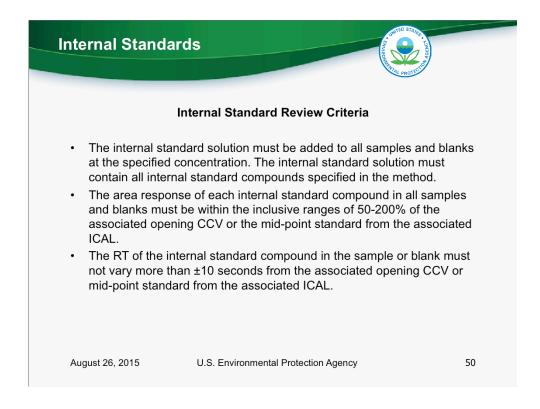August 26, 2015   U.S. Environmental Protection Agency   49

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

Internal Standards

Internal Standard Review Criteria

- The internal standard solution must be added to all samples and blanks at the specified concentration. The internal standard solution must contain all internal standard compounds specified in the method.
- The area response of each internal standard compound in all samples and blanks must be within the inclusive ranges of 50-200% of the associated opening CCV or the mid-point standard from the associated ICAL.
- The RT of the internal standard compound in the sample or blank must not vary more than ±10 seconds from the associated opening CCV or mid-point standard from the associated ICAL.

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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.

Surrogate Standard Spikes

Internal Standard Action

| Criteria	Action	
	Detect	Non-detect
Area response < 10 to 20% of the opening CCV or mid-point standard CS3 from initial calibration	J +	R
Area response > lower limit but < 40 to 50% of the opening CCV or mid-point standard CS3 from initial calibration	J +	UJ
40 - 50% ≤ area response ≤ 140 - 200% of the opening CCV or mid-point standard CS3 from initial calibration	No qualification	No qualification
Area response > 140 - 200% of the opening CCV or mid-point standard CS3 from initial calibration	J -	No qualification
RT shift between sample/blank and opening CCV or mid-point standard CS3 from initial calibration > 10.0 to 20 seconds	R	R
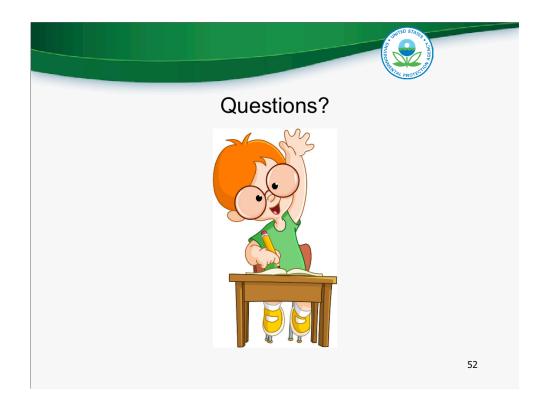
- **NOTE:** Apply the action to the target analytes in samples or blanks that are associated to the non-compliant internal standard compound.
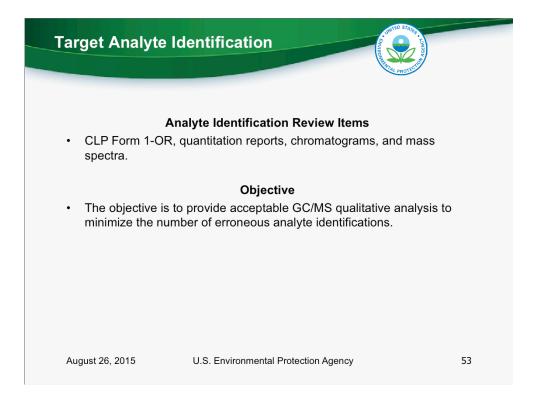
If there is a reanalysis for a particular sample, determine which analysis is the best data to report. Considerations include, but are not limited to:
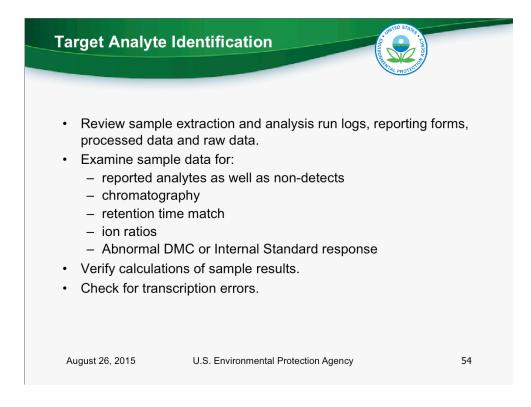
a. Magnitude and direction of the internal standard area response shift.

b. Magnitude and direction of the internal standard RT shift.
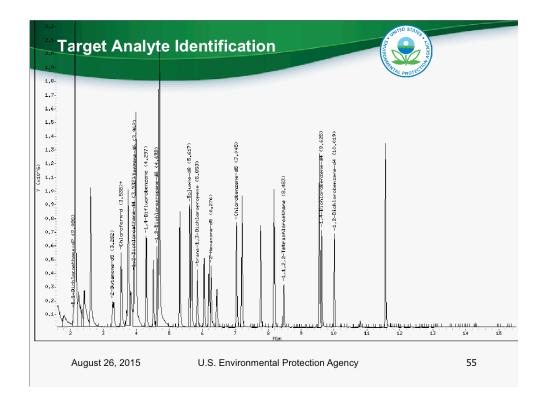
c. Technical holding times.

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.
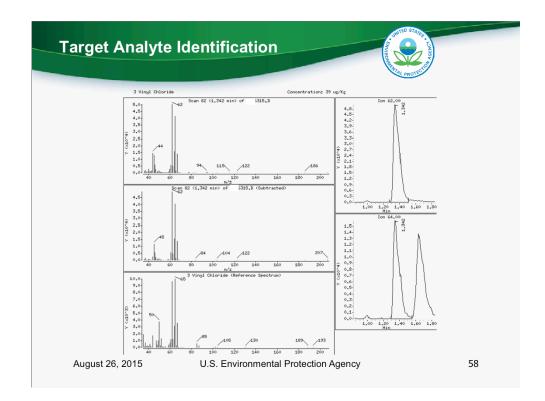
And the associated processed data report, page 1

Target Analyte Identification

	Compounds	QUANT SIG MASS	RT	EXP RT	REL RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ug/L)	FINAL (ug/Kg)
	=========================	====	====	========	========	========	=======	=======
	24 1,2-Dichloroethane	62	4.001	3.995	(0.929)	211925	43.9151	44
*	26 1,4-Difluorobenzene	114	4.306	4.300	(1.000)	568019	50.0000	
	27 Trichloroethene	95	4.523	4.527	(0.641)	177500	38.7271	39
$	85 1,2-Dichloropropane-d6	67	4.631	4.625	(0.657)	292046	49.6225	50
	28 Methylcyclohexane	83	4.700	4.694	(0.666)	536890	74.8101	75
	29 1,2-Dichloropropane	63	4.710	4.704	(0.668)	438828	70.8889	71
$	33 Toluene-d8	98	5.616	5.610	(0.796)	637499	51.1704	51
	34 Toluene	91	5.675	5.669	(0.805)	718705	40.0520	40
$	86 trans-1,3-Dichloropropene-d4	79	5.852	5.856	(0.830)	234853	48.8555	49
	36 1,1,2-Trichloroethane	97	6.059	6.053	(0.859)	170670	48.1116	48
	37 Tetrachloroethene	164	6.217	6.211	(0.881)	139366	48.7676	49
$	87 2-Hexanone-d5	63	6.276	6.270	(0.890)	166008	92.9768	93(Q)
	39 Dibromochloromethane	129	6.443	6.447	(0.913)	148412	38.6565	39
*	42 Chlorobenzene-d5	117	7.054	7.048	(1.000)	467117	50.0000	
	44 Ethylbenzene	91	7.212	7.206	(1.022)	766668	40.2045	40
	47 Styrene	104	7.773	7.777	(1.102)	405996	35.6886	36
	49 Isopropylbenzene	105	8.187	8.181	(1.161)	824325	49.0421	49
$	89 1,1,2,2-Tetrachloroethane-d2	84	8.482	8.476	(1.202)	209054	48.6355	49
	52 1,3-Dichlorobenzene	146	9.556	9.560	(0.992)	528110	79.3360	79
*	78 1,4-Dichlorobenzene-d4	152	9.635	9.629	(1.000)	188336	50.0000	
$	90 1,2-Dichlorobenzene-d4	152	10.019	10.013	(1.040)	178954	51.5814	52
	55 1,2-Dibromo-3-chloropropane	75	10.797	10.801	(1.121)	10107	18.1613	18(Q)
	56 1,2,4-Trichlorobenzene	180	11.565	11.569	(1.200)	384563	105.322	110

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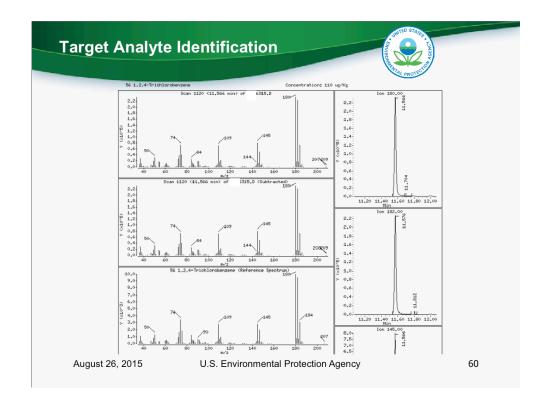
And page 2. Note the various notations automatically applied by the lab data system. One that was not needed here was the "m" flag, for manually integrated peaks. I'll talk more about that in a minute.
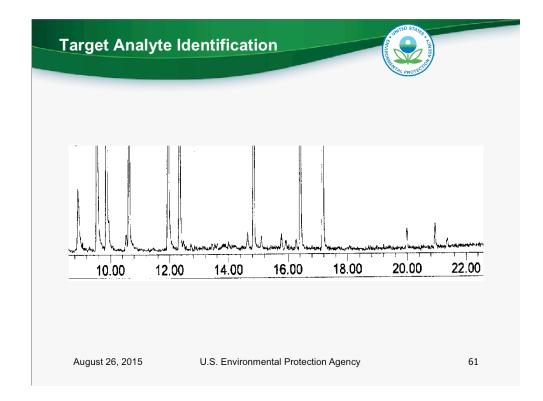
Here is an extracted ion current profile or EICP for target analyte Vinyl Chloride. Note the extra peak in the EICP for m/e 64. We'll learn what that is on the next slide. Chlorine patterns
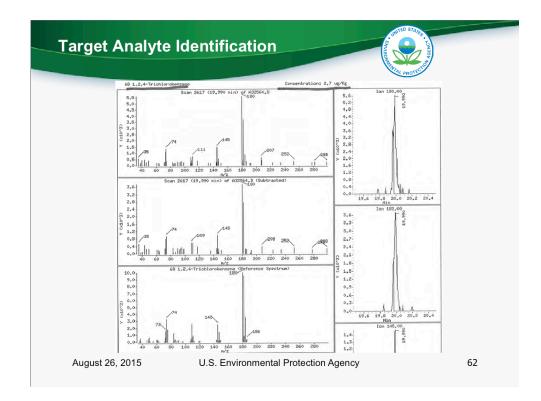
And here is chloroethane, about half a minute later, with its quantitation peak at 64.
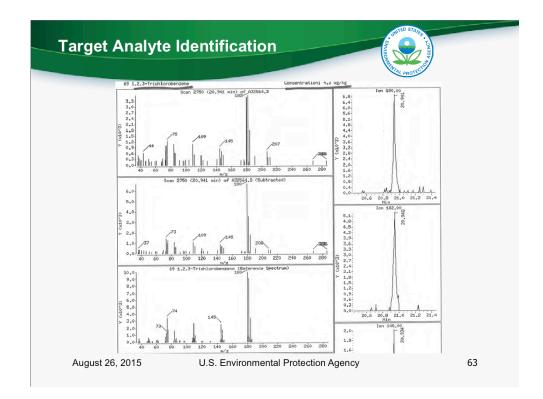
And one more; this is 1,2,4-trichlorobenzene. Chlorine patterns

Target Analyte Identification
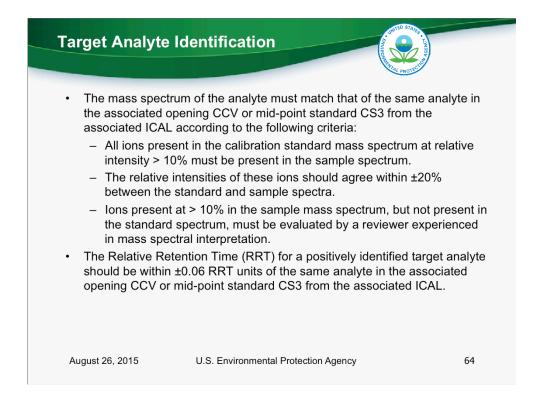
One of the elements of the CLP QA program is to periodically perform electronic media audits of data packages from our contract laboratories. The data packages are generally chosen at random, and the lab is required to submit the complete set of instrument-generated raw data files, processing method 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.

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

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.

Target Analyte Identification

- The mass spectrum of the analyte must match that of the same analyte in the associated opening CCV or mid-point standard CS3 from the associated ICAL according to the following criteria:
  - All ions present in the calibration standard mass spectrum at relative intensity > 10% must be present in the sample spectrum.
  - The relative intensities of these ions should agree within ±20% between the standard and sample spectra.
  - Ions present at > 10% in the sample mass spectrum, but not present in the standard spectrum, must be evaluated by a reviewer experienced in mass spectral interpretation.
- The Relative Retention Time (RRT) for a positively identified target analyte should be within ±0.06 RRT units of the same analyte in the associated opening CCV or mid-point standard CS3 from the associated ICAL.

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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.
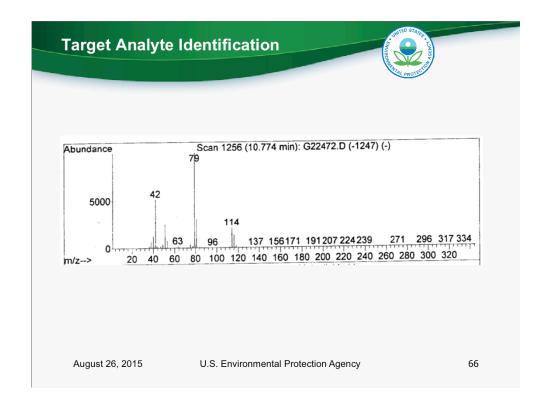
3. Be aware of situations when sample carryover is a possibility and use professional judgment to determine if instrument cross-contamination has affected any positive analyte identification. An instrument blank must be analyzed after a sample containing target analytes with concentrations exceeding 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: ▮▮▮▮▮▮▮▮   Contract: ▮▮▮▮▮

Lab Code: ▮▮   Case No.: ▮▮   Mod. Ref No.: _____   SDG No.: ▮▮▮▮

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

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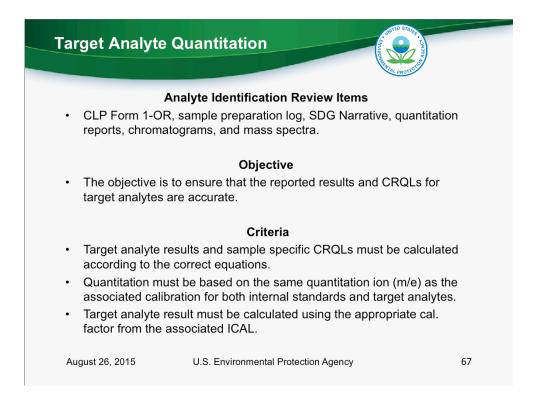
Here is a CLP reporting form for tentatively identified compounds (or non-target) compounds that was evaluated by the QATS team. This peak sparked their interest because it was found in all the blanks, it's tentative quantitation was above the CRQL without a good library match, and …

Target Analyte Identification

Abundance — Scan 1256 (10.774 min): G22472.D (-1247) (-)

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.

Target Analyte Quantitation

Analyte Identification Review Items
- CLP Form 1-OR, sample preparation log, SDG Narrative, quantitation reports, chromatograms, and mass spectra.

Objective
- The objective is to ensure that the reported results and CRQLs for target analytes are accurate.

Criteria
- Target analyte results and sample specific CRQLs must be calculated according to the correct equations.
- Quantitation must be based on the same quantitation ion (m/e) as the associated calibration for both internal standards and target analytes.
- Target analyte result must be calculated using the appropriate cal. factor from the associated ICAL.

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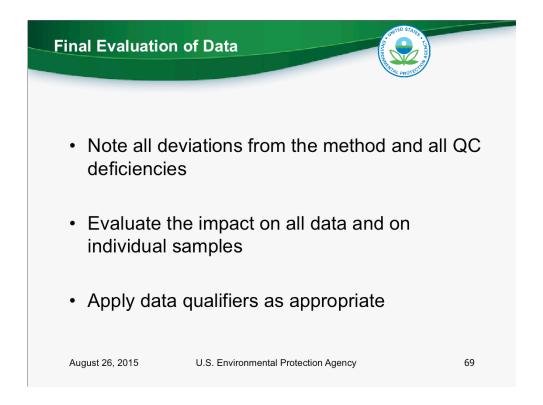
5. If any discrepancies are found, contact the Laboratory PO, who may contact the laboratory to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, use professional judgment to decide which value is the most accurate and whether qualification of data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

Target Analyte Quantitation

Manual integrations were performed for the following samples for the compounds listed against them.

Compound EPA Sample ID

Benzo (k) fluoranthene N0AB6, N0AB7, N41S1, N41S8.

Phenol-d5 N41S3, N41S8, SSTD0051I, SSTD0051I.

Caprolactam SSTD0809Y, SSTD0409Y, SSTD0109Y, SSTD0801I, SSTD0401I, SSTD0051I, SSTD0401I, SSTD0051I.

2,4-Dinitrophenol SSTD0809Y, SSTD0409Y, SSTD0209Y, SSTD0059Y,

SSTD0109Y, SSTD0201I, SSTD0101I, SSTD0401I, SSTD0201I, SSTD0801I, SSTD0101I, SSTD0401I, SSTD0209Y, SSTD0209Z, SSTD0201A, SSTD0201B, SSTD0201C, SSTD0201D, SSTD0201E, SSTD0201F, SSTD0201I, SSTD0201J, SSTD0201L, SSTD0201M, SSTD0201N, SSTD0201O, SSTD0201P, SSTD0201I, SSTD0201J, SSTD0201L, SSTD0201M, SSTD0201N, SSTD0201O, SSTD0201P.

Pentachlorophenol SSTD0109Y.

4,6-Dinitro-2-methylphenol SSTD0101I, SSTD0101I.

Dibenzo (a,h) anthracene SSTD0051I, SSTD0051I.

Benzo (g,h,i) perylene SSTD0051I, SSTD0051I.

These manual integrations were necessary because the software failed to accurately integrate the entire peak. In all the above instances, the quantitation reports are flagged with "m". A hard copy printout of the manual integration, the scan ranges, and initials of the analyst or manager is included in the data package.

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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?

- Note all deviations from the method and all QC deficiencies

- Evaluate the impact on all data and on individual samples

- Apply data qualifiers as appropriate

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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.

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