

CCP-TP-032

Revision 14

CCP

Single Sample Manifold Data Validation Procedure

EFFECTIVE DATE: 11/16/2006

J. R. Stroble

PRINTED NAME

APPROVED FOR USE

RECORD OF REVISION

Revision Number	Date Approved	Description of Revision
6	01/29/2002	Clarified Training Requirements, Independent Technical Review and references. Added trans-1,2-Dichloroethylene to Table 2.
7	09/20/2002	Added a place to put the Batch Number on all the attachment pages per SPQAO request, revised sections 4 and attachments in response to CBFO adequacy review and per SME request.
8	09/26/2002	Revised based on comments from NTS Certification Audit; revised step 4.1.16, moved step 4.1.32 to a substep to step 4.1.16, and revised Attachment 1 accordingly.
9	10/01/2002	Minor editorial change to line up the signature blocks in the ITR Checklist, Attachment 1.
10	02/03/2003	Changes made to implement the Drum Age Criteria (DAC) permit Modification.
11	12/03/2003	Revised sections 2.3, 4.1, 4.3 and 4.4, Table 4, and Attachments 1, 3 and 4. Added step 4.4.22. Eliminated redundancies in 4.1, 4.2, 4.3 and 4.4, as covered by the checklists in the attachments. Inserted Note after 4.4. Renumbered checklists in attachments. Added step to ITR checklist.
12	05/23/2006	Revised Attachment 4, QA Officer Checklist in response to New Mexico Environment Department (NMED) Observer Inquiry, Audit A-06-01.
13	05/25/2006	Minor revision to correct date error in header that occurred during issuance of Revision 12. The only change made during this minor revision was to correct dates.
14	11/16/2006	Revised to implement the Waste Isolation Pilot Plant Hazardous Waste Facility Permit requirements resulting from the Section 311/Remote-Handled (RH) Permit Modification Request (PMR).

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1.0 PURPOSE

This procedure describes the actions that must be performed for data generation level data review, verification, and validation for on-line, combined sampling and analytical batch data reports (BDRs). The BDRs are generated from operation of the Central Characterization Project (CCP) single sample manifold headspace gas (HSG) sampling and analysis equipment for gas volatile organic compounds (VOCs), hydrogen, and methane. Review, verification, and validation are performed in accordance with CCP-PO-001, *CCP Transuranic Waste Quality Assurance Project Plan (QAPjP)*.

Data review determines if raw data have been properly collected and ensures raw data are properly reduced. Data validation confirms that the data reported satisfy the requirements defined by CCP-PO-001 and is accompanied by signature release. Data verification authenticates that data as presented represent the sampling and analysis activities as performed and were subjected to the appropriate levels of data review.

1.1 Scope

This procedure applies to all personnel who review, validate, and perform verification of BDRs generated by the CCP single sample manifold HSG sampling and analysis equipment. These personnel are the HSG Operator, the Independent Technical Reviewer (ITR).

2.0 REQUIREMENTS

2.1 References

- CCP-PO-001, *CCP Transuranic Waste Characterization Quality Assurance Project Plan*
- CCP-QP-002, *CCP Training and Qualification Plan*
- CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control*
- CCP-QP-008, *CCP Records Management*
- CCP-TP-007, *CCP Single Sample Manifold Headspace Gas Sampling and Analysis Procedure*
- CCP-TP-009, *CCP Single Sample Manifold Data Handling Procedure*
- CCP-TP-029, *CCP Single Sample Manifold Headspace Gas Sampling and Analysis Methods and Equipment Calibration*

2.2 Training Requirements

2.2.1 Personnel performing this procedure will be trained and qualified in accordance with CCP-QP-002, *CCP Training and Qualification Plan* prior to performing this procedure.

2.3 Equipment

2.3.1 None.

2.4 Software

2.4.1 None.

2.5 Prerequisite Actions

2.5.1 None.

2.6 Definitions

2.6.1 None.

3.0 RESPONSIBILITIES

3.1 Independent Technical Reviewer (ITR)

3.1.1 Confirms that HSG raw data have been generated and reduced in a technically correct manner.

3.1.2 Ensure calculations are correct, deviations are documented.

3.1.3 Verify quality assurance (QA)/quality control (QC) results are complete, correctly documented, and compared to CCP-PO-001 criteria.

3.1.4 Verifies and validates all work performed by the HSG Operator.

3.1.5 Verifies the BDR is complete.

3.1.6 Confirms the instrument performance criteria have been met.

4.0 PROCEDURE

NOTE

If this procedure CAN **NOT** be implemented as written, CCP personnel shall notify the appropriate HSG LO. Work shall **NOT** be resumed until this procedure is modified or replaced by a new document that reflects the current work practice.

The HSG Operator will deliver the on-line BDR (in accordance with CCP-TP-009) to the ITR to begin the review process.

If any criteria is marked "Fail" or there are other deficiencies in the BDR, the person identifying the deficiency will initiate a nonconformance report (NCR) in accordance with CCP-QP-005, *CCP TRU Nonconforming Item Reporting and Control*.

4.1 ITR Review

- 4.1.1 Retrieve the BDR from the BDR holding file, **AND** locate Attachment 1, Independent Technical Reviewer Review Checklist.
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NOTE

The "Comment" block can be used as necessary to identify discrepancies, provide clarification, or state which page in the BDR contains the required information.

Discrepancies identified during the review, that do not impact DQOs or quality assurance objectives can be corrected by the data generator.

- 4.1.2 Record BDR number on each page of Attachment 1.

- 4.1.3 Review the BDR, **AND** record by checking PASS, FAIL, **OR** NA blocks as applicable on Attachment 1.

- [A] **IF** an item is checked PASS,
THEN GO TO step 4.1.4.

- [B] **IF** an item is checked FAIL,
THEN initiate an NCR in accordance with CCP-QP-005,
CCP TRU Nonconforming Item Reporting and Control.

- [C] **IF** an item is checked NA,
THEN provide explanation in the Comment block, as needed.

- 4.1.4 Repeat step 4.1.3 for each item on Attachment 1 until all items are complete.

4.1.5 Print name, sign and date Attachment 1.

4.1.6 Place the BDR in the BDR holding file.

4.2 ICAL/MDL ITR Review

4.2.1 **IF** this BDR contains an ICAL,
THEN obtain the BDR from the BDR holding file, **AND** locate
Attachment 2, ICAL/MDL Independent Technical Reviewer Review
Checklist.

4.2.2 Record BDR number on each page of Attachment 2.

4.2.3 Review the BDR, **AND** record by checking PASS, FAIL, **OR** NA
blocks as applicable on Attachment 2.

[A] **IF** an item is checked PASS,
THEN GO TO step 4.2.4.

[B] **IF** an item is checked FAIL,
THEN initiate an NCR in accordance with CCP-QP-005,
CCP TRU Nonconforming Item Reporting and Control.

[C] **IF** an item is checked NA,
THEN provide explanation in the Comment block, as
needed.

4.2.4 Repeat step 4.2.3 for each item on Attachment 2 until all items on
checklist are complete.

4.2.5 Print name, sign and date Attachment 2.

4.2.6 Place the BDR in the BDR holding file.

5.0 RECORDS

NOTE

Records generated in step 5.1.1 become part of the BDR that is generated in CCP-TP-009, *CCP Single Sample Manifold Data Handling Procedure*.

5.1 Records generated during the performance of this procedure are maintained as QA records in accordance with CCP-QP-008. The records are the following:

5.1.1 QA/Lifetime

- [A] Attachment 1 - Independent Technical Reviewer Review Checklist
- [B] Attachment 2 - ICAL/MDL Independent Technical Reviewer Review Checklist

Table 1. BFB Tune Criteria

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	Less than 2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% and <101% of mass 174
177	5 to 9% of mass 176

Table 2. Target Analyte List and QAOs

Compound	CAS No.	Precision ^a (%RSD or RPD)	Accuracy (%R)	MDL ^b (ng)	PRQL ^b (ppmv)	Completeness (%)
Benzene ^e	71-43-2	≤ 25	70-130	10	10	90
Bromoform	75-25-2	≤ 25	70-130	10	10	90
Carbon Disulfide ^h	75-15-0	≤ 25	70-130	10	10	90
Carbon tetrachloride ^d	56-23-5	≤ 25	70-130	10	10	90
Chlorobenzene ^e	108-90-7	≤ 25	70-130	10	10	90
Chloroform	67-66-3	≤ 25	70-130	10	10	90
Chloromethane ^h	74-87-3	≤ 25	70-130	10	10	90
1,1-Dichloroethane ^{d,e}	75-34-3	≤ 25	70-130	10	10	90
1,2-Dichloroethane ^e	107-06-2	≤ 25	70-130	10	10	90
1,1-Dichloroethylene ^e	75-35-4	≤ 25	70-130	10	10	90
cis-1,2-Dichloroethene ^e	156-59-2	≤ 25	70-130	10	10	90
trans-1,2-Dichloroethylene ^e	156-60-5	≤ 25	70-130	10	10	90
Ethyl benzene ^e	100-41-4	≤ 25	70-130	10	10	90
Ethyl ether ^e	60-29-7	≤ 25	70-130	10	10	90
Methylene chloride ^d	75-09-2	≤ 25	70-130	10	10	90
1,1,1,2-Tetrachloroethane	79-34-5	≤ 25	70-130	10	10	90
Tetrachloroethene	127-18-4	≤ 25	70-130	10	10	90
Toluene ^e	108-88-3	≤ 25	70-130	10	10	90
1,1,1-Trichloroethane ^d	71-55-6	≤ 25	70-130	10	10	90
Trichloroethene ^d	79-01-6	≤ 25	70-130	10	10	90
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	≤ 25	70-130	10	10	90
m-Xylene ^{c,e}	108-38-3	≤ 25	70-130	10	10	90
o-Xylene ^{d,e}	95-47-6	≤ 25	70-130	10	10	90
p-Xylene ^{c,e}	106-42-3	≤ 25	70-130	10	10	90
Acetone ^e	67-64-1	≤ 25	70-130	150	100	90
Butanol ^e	71-36-3	≤ 25	70-130	150	100	90
Methanol ^e	67-56-1	≤ 25	70-130	150	100	90
Methyl ethyl ketone ^e	78-93-3	≤ 25	70-130	150	100	90
Methyl isobutyl ketone ^e	108-10-1	≤ 25	70-130	150	100	90

a Criteria apply to PRQL concentrations.

b Values based on delivering 10 mL to the analytical system.

c These xylene isomers cannot be resolved by the analytical methods employed in this program and shall be reported as "m,p-xylene" (undifferentiated).

d Critical Target Compounds (CTCs)

e Flammable VOC

f Required only for Plutonium Finishing Plan (PFP) waste stream at Hanford.

NOTES:

%RSD Percent relative standard deviation

RPD Relative percent difference

%R Percent recovery

MDL Method Detection Limit (total number of nanograms delivered to the analytical system per sample)

PRQL Program required quantitation limit

Table 3. Hydrogen and Methane QAOs

Analyte	CAS Number	Precision (%RSD or RPD)	Accuracy ^a (%R)	MDL (vol%)	PRQL (vol%)	Completeness (%)
Hydrogen	1333-74-0	≤ 25	70-130	0.05	0.1	90
Methane	74-82-8	≤ 25	70-130	0.05	0.1	90

^a Criteria apply to PRQL concentrations

%RSD Percent relative standard deviation

RPD Relative percent difference

%R Percent recovery

MDL Method Detection Limit (total number of nanograms delivered to the analytical system per sample)

PRQL Program required quantitation limit

Table 4. Internal Standard Criteria

Instrument	Compounds	Response ¹	Retention Time ¹
GC/MS	Bromochloromethane	50% - 200% ²	±0.5 minutes ³
GC/MS	Chlorobenzene, d5	50% - 200% ²	±0.5 minutes ³
GC/MS	1,4-difluorobenzene	50% - 200% ²	±0.5 minutes ³

¹ Based on initial calibration

² Based on Method 8260B, Section 7.4.7

³ Based on Method 8260B, Section 7.4.6

Attachment 1 – Independent Technical Reviewer Review Checklist

BDR Number:					
Item	The Independent Technical Reviewer signature release must ensure the following:	Pass	Fail	NA	Comment
1.	Verify the current revision of CCP-TP-007.				Revision Number:
2.	Verify the current revision of CCP-TP-009.				Revision Number:
3.	Verify the current revision of CCP-TP-029.				Revision Number:
4.	Verify the current revision of CCP-TP-032.				Revision Number:
5.	Verify the Cover Page is attached.				
6.	Verify the Table of Contents is attached.				
7.	Verify the Case Narrative is attached.				
8.	Verify BFB Tune Report is attached.				
9.	Verify that the CCV is within 12-hours of the BFB.				
10.	Verify the CCV Report/QAO is attached and complete.				
11.	Verify that the OCS is within 12-hours of the BFB.				
12.	Verify the OCS Report/QAO is attached and complete.				
13.	Verify that the OCS Duplicate is within 12-hours of the BFB.				
14.	Verify that the Blank is within 12-hours of the BFB.				
15.	Verify that the Drum Duplicate is within 12-hours of the BFB.				
16.	Verify that all drum sample analysis are started within 12-hours of the BFB.				
17.	Verify drum age criteria (DAC) are acceptable in accordance with CCP-TP-007.				
18.	Verify the DAC and equilibrium calculations and times are acceptable.				
19.	Verify drum temperature $\geq 18^{\circ}$ C for 72 hrs.				
20.	Verify drum temperature $\geq 18^{\circ}$ C when sampling.				
21.	Verify ICAL is referenced.				
22.	Verify Blank Report/QAO is attached and complete.				
23.	Verify Drum Duplicate Report/QAO is attached and complete.				
24.	Verify Drum Duplicate is attached and complete.				
25.	Verify Drum Sample Report(s) is attached for each drum listed on the cover page and complete.				
26.	Verify TIC Report(s) is attached (if applicable) and complete.				

Attachment 1 – Independent Technical Reviewer Review Checklist (continued)

BDR Number:					
Item	The Independent Technical Reviewer signature release must ensure the following:	Pass	Fail	NA	Comment
27.	Verify MDL Spreadsheet is attached and complete.				
28.	Verify completed Attachments 1, 2, 3, 4, and 5 from CCP-TP-007 are attached.				
29.	Verify Dicksonware 99 Temperature Graph is attached and complete.				
30.	Verify Attachment 1, Data Generation Checklist, of CCP-TP-009, is attached and complete.				
31.	Verify copy of NCR(s) is/are attached and complete.				
32.	Verify the appropriate data qualifier flags were assigned to the CCV.				
33.	Verify the appropriate data qualifier flags were assigned to the OCS.				
34.	Verify the appropriate data qualifier flags were assigned to the OCS Duplicate.				
35.	Verify the appropriate data qualifier flags were assigned to the Blank.				
36.	Verify the appropriate data qualifier flags were assigned to the Drum Duplicate.				
37.	Verify the appropriate data qualifier flags were assigned to Drum samples.				
38.	Verify the impact of any qualifier flags is discussed in the Case Narrative.				
39.	Verify the impact of NCR(s) is discussed in the Case Narrative.				
40.	Verify that any quality affecting issues are discussed in the Case Narrative.				
41.	Verify that the data was generated in a technically correct manner and is reported in the proper units and significant figures.				
42.	Verify the BFB tune meets criteria, (see Table 1, BFB Tune Criteria).				
TICs					
43.	Verify that all ions present in the standard mass spectrum at a relative intensity > 10% are present in the sample compound spectrum.				
44.	Verify that the relative intensities of major ions agree within ±30 percent.				
45.	Molecular ions present in the reference spectrum should be present in the sample spectrum.				
46.	Verify integration of all identified peaks.				

Attachment 1 – Independent Technical Reviewer Review Checklist (continued)

BDR Number:					
Item	The Independent Technical Reviewer signature release must ensure the following:	Pass	Fail	NA	Comment
47.	Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.				
48.	Verify that the RT of the compound detected in the sample is within the RTW for that compound.				
49.	Verify RRT is plus or minus 0.06 RT units.				
50.	Verify the primary characteristic ion from Table 5 of CCP-TP-029 was used.				
51.	Examine the raw data and verify correct calculation by hand.				
TICs					
52.	Verify that the relative intensities of major ions in the reference spectrum (ions > 10 percent of the most abundant ion) should be present in the sample spectrum.				
53.	Verify that the relative intensities of major ions agree within ± 20 percent.				
54.	Verify that the molecular ions present in the reference spectrum are present in the sample spectrum.				
55.	Verify that the ions present in the sample spectrum but not in the reference are reviewed for possible subtraction because of background contamination or co-eluting peaks.				
56.	Verify that ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks.				
57.	Verify that a NIST/EPA mass spectral library search has been provided for all required peaks in the chromatograms for samples.				
58.	Verify that the concentration of TICs have been estimated using internal standard analytes nearest the retention time of the TIC (free of interferences).				
59.	Verify that the reference spectra library used for identifying TICs include, at a minimum, all of the available spectra for compounds that appear in the 20.4.1.200 NMAC Appendix VIII list.				

Attachment 1 – Independent Technical Reviewer Review Checklist (continued)

BDR Number:					
Item	The Independent Technical Reviewer signature release must ensure the following:	Pass	Fail	NA	Comment
60.	Verify CCV includes all Table 2 and 3 compounds.				
61.	Verify that the CCV is not from the same source as the ICAL.				
62.	Verify CCV was run after the BFB.				
63.	Verify the CCV %D for GC/MSD is $\leq 30\%$.				
64.	Verify the CCV %R for Hydrogen and Methane is within 70 - 130%.				
65.	Verify the %R for the internal Standard is within 50-200% (see Table 4, Internal Standard Criteria).				
66.	Verify the RT for the Internal standards are within ± 0.5 minutes of the initial calibration (see Table 4).				
67.	Verify noncompliant CCV data are flagged with a "Z" and a NCR initiated.				
68.	Verify the OCS includes 6 VOCs, H ₂ and CH ₄ .				
69.	Verify that the OCS is not from the same source as the ICAL.				
70.	Verify the OCS is the range of 10 to 100 ppmv (VOCs) 0.2% (H ₂ , CH ₄).				
71.	Verify OCS was run after the CCV.				
72.	Verify the OCS %R is within 70-130%.				
73.	Verify Blank was run after the OCS.				
74.	Verify the Blank is qualifier flagged "B" if contaminants are found above the MDL.				
75.	Verify the Blank is qualifier flagged "Z" if the compound is 3 times greater than the MDL.				
76.	Verify that any "Z" flagged data in the blank is addressed in the case narrative, and that there is an NCR addressing the issue.				
77.	IF the field blank failed, verify that an equipment blank was performed.				
78.	Verify that all Z and E qualifier flags are explained in the case narrative.				
79.	Verify compounds with concentrations exceeding the linear range are requantitated with an approved method that extends the linear range of the calibration curve.				
80.	Verify compounds with concentrations that exceed the highest linear range are "E" flagged.				

Attachment 1 – Independent Technical Reviewer Review Checklist (continued)

BDR Number:					
Item	The Independent Technical Reviewer signature release must ensure the following:	Pass	Fail	NA	Comment
81.	Verify that all detected compounds with concentrations <PRQL, and > MDL are correctly flagged as estimated "J".				
82.	Verify that a Drum Duplicate sample was collected once per batch.				
83.	Verify that the Drum Duplicate RPD is ≤ 25%.				
84.	Verify the Drum Duplicate noncompliant data are flagged with a "Z", an NCR was initiated, and is addressed in the case narrative.				
85.	IF the Drum Duplicate sample did not contain sufficient detected compounds to perform the duplicate comparison, THEN verify an OCS Duplicate was performed.				
86.	Ensure the OCS Duplicate was run to verify Hydrogen and Methane precision (TRAMPAC QAO).				
87.	Verify that the OCS Duplicate RPD ≤25%.				
88.	Verify the OCS Duplicate noncompliant data are flagged with a Z, an NCR was initiated, and is addressed in the case narrative.				
89.	Verify that the sample reports are signed by the headspace gas operator.				
90.	Verify the BDR for transcription errors.				
Sample Representativeness					
91.	Verify the PDPs are current.				
92.	Verify the standards are traceable and certified.				
93.	Verify PID calibration is current.				
94.	Verify sample equipment is clean per PID results.				
95.	Verify sample equipment leak tight per Manifold Leak Test results.				
96.	Verify pressure regulation is documented during sampling.				
97.	Verify the correct sampling scenario, waste packaging configuration, and DAC equilibrium times are met.				
98.	Verify manifold pressure sensor calibration is current.				

Attachment 1 – Independent Technical Reviewer Review Checklist (continued)

BDR Number:					
Item	The Independent Technical Reviewer signature release must ensure the following:	Pass	Fail	NA	Comment
99.	Verify temperature sensor and loggers calibration are current.				
100.	Verify calibration is met for ICAL R2 greater than or equal to 0.990 or referenced.				
101.	Verify batch completeness greater than or equal to 90 percent (E flag is not an invalid sample).				
ITR Printed Name		ITR Signature			Date

Attachment 2 – ICAL/MDL Independent Technical Reviewer Review Checklist

Note: This attachment is ONLY filled out if the Batch contains an ICAL and an MDL

BDR Number:					
Item	The ITR signature release must ensure the following:	Pass	Fail	NA	Comment
VOC ICAL					
1.	Verify the ICAL has all CCP-TP-032 Table 2 and Table 3 compounds.				
2.	Verify all VOCs target compounds %RSD<35.				
3.	Verify all VOC target compound $R^2 \geq 0.990$.				
4.	Verify a minimum of 5 concentration levels for a linear equation.				
5.	Verify a minimum of 6 concentration levels for a quadratic equation.				
6.	Verify one level is below PRQL.				
7.	Verify that the target compound was quantitated from the primary mass ion.				
8.	Verify VOC RT.				
9.	Verify VOC RT windows.				
10.	Verify three I.S. are used.				
Hydrogen ICAL					
11.	Verify the ICAL includes hydrogen.				
12.	Verify $R^2 \geq 0.990$ for hydrogen.				
13.	Verify a minimum of 3 concentration levels for a linear hydrogen calibration curve equation on the TCD.				
14.	Verify hydrogen units are in VOL%.				
15.	Verify one level below PRQL on the TCD.				
16.	Verify hydrogen RT windows.				
17.	Verify Hydrogen RT.				

Attachment 2 – ICAL/MDL Independent Technical Reviewer Review Checklist
(continued)

BDR Number:					
Item	The ITR signature release must ensure the following:	Pass	Fail	NA	Comment
Methane ICAL					
18.	Verify the ICAL includes methane.				
19.	Verify $R^2 \geq 0.990$ for methane.				
20.	Verify a minimum of 3 concentration levels for a linear methane calibration curve equation on the FID.				
21.	Verify methane units are in VOL%.				
22.	Verify one level below PRQL on FID.				
23.	Verify methane RT windows.				
24.	Verify methane RT.				
MDL					
25.	Verify that the MDL \leq PRQL, the %R is $< 130\%$ and $> 70\%$, and MDL \leq WAP required MDL.				
26.	Verify that the Target compounds are quantitated from the primary ion.				
27.	If a secondary ION was used, then verify that the standard was also quantitated from the same secondary quantitation ion.				
ICAL / MDL ITR Printed Name		ICAL / MDL ITR Signature			Date