Appendix C
CLP/SOW OLC02.1/Low Concentration Volatile Organic Analysis
Method QC criteria, Equations, and Definitions

APPENDIX C

The following method QC criteria, equations, and definitions apply to data generated according to the **USEPA CLP Statement of Work for Organic Analysis, Low Concentration Water, OLC02.1, Exhibit D Volatiles**.

Note: MS/MSD are not applicable. MS/MSDs are not required for work under this SOW.

Capillary GC columns are mandatory. Packed columns cannot be used.

SECTION I: PRESERVATION & TECHNICAL HOLDING TIME CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-I-B for preservation and technical holding time data validation criteria.

SECTION II: GC/MS INSTRUMENT PERFORMANCE CHECK (TUNING) CRITERIA

Refer to the following method GC/MS instrument performance (tuning) QC criteria for data validation:

The analysis of the instrument performance (tuning) check solution (50 ng BFB on column) must be performed at the beginning of each **12-hour** period during which samples or standards are analyzed. The tuning check, bromofluorobenzene (BFB), for volatile analysis must meet the ion abundance criteria given below:

m/z	ION ABUNDANCE CRITERIA
50	8.0 - 40.0% of m/z 95
75	30.0 - 66.0% of m/z 95
95	Base Peak, 100% Relative Abundance
96	5.0 - 9.0% of m/z 95 (see note)
173	Less than 2.0% of m/z 174
174	50.0 - 120.0% of m/z 95
175	4.0 - 9.0% of mass 174
176	93.0 - 101.0% of m/z 174
177	5.0 - 9.0% of m/z 176

Note: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Part of the BFB peak must not be background subtracted.

SECTION III: INITIAL CALIBRATION CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-III-B for initial calibration data validation criteria and the following method initial calibration QC criteria:

The initial calibration standards must be analyzed upon contract award, whenever corrective action is taken which may change or affect the initial calibration criteria or if the continuing calibration acceptance criteria have not been met. Initial calibrations must be analyzed after the analysis of a compliant instrument performance check.

The initial calibration standards must include the target compounds listed in the Target Compound List (TCL) in Section XIII of this Appendix, as well as the internal standards and the system monitoring compound.

All initial calibration standards must be analyzed at the following concentration levels; 1.0, 2.0, 5.0, 10, and 25 ug/L except for the ketones which are analyzed at 5.0, 10, 25, 50, and 125 ug/L.

RELATIVE RESPONSE FACTOR (RRF) - A measure of the relative mass spectral response of an analyte compared to its internal standard. The RRF is calculated using the following equation:

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where,

A_x = Area of primary quantitation ion response (EICP) for the compound to be measured
A_{is} = Area of primary quantitation ion response (EICP) for the internal standard
C_{is} = Concentration of the internal standard
C_x = Concentration of the compound to be measured

AVERAGE (MEAN) RELATIVE RESPONSE FACTOR (RRF) - The average or mean RRF is determined by the analysis of five different standard concentrations and is used in calculating a compound concentration in samples. The RRF is calculated using the following equation:

$$\overline{RRF} = \sum_{i=1}^{n} \frac{RRF_i}{n}$$

Where,

RRF_i = The individual RRFs for various concentration levels
n = The number of RRFs

PERCENT RELATIVE STANDARD DEVIATION (%RSD) - The % RSD for each compound is a measure of the linearity of the calibration curve. The % RSD is calculated using the following equation:

$$\%RSD = \frac{Standard\ Deviation}{Mean} \times 100$$

Where,

$$Standard\ Deviation = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{(n-1)}}$$

$\bar{x}$ = Mean
n = total number of values
x_i= each individual value used to calculate the mean

SECTION IV: CONTINUING CALIBRATION CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-IV-B for continuing calibration data validation criteria and the following method continuing calibration QC criteria:

The continuing calibration standard must be analyzed once every 12 hours, following the analysis of a compliant instrument performance check and initial calibration, and prior to the analysis of field samples, QC samples and blanks.

The continuing calibration standard must include the target compounds listed in the Target Compound List (TCL) in Section XIII of this Appendix, as well as the internal standards and the system monitoring compound.

Continuing calibrations must be analyzed at a final concentration of 5 ug/L for non-ketone compounds and at a final concentration 25 ug/L for the ketones.

Note: The low concentration method % Difference for continuing calibration differs from the Region I Functional Guidelines continuing calibration % Difference criteria (± 25.0 %). The low concentration method requires that the continuing calibration % Difference for most target compounds and surrogates be less than or equal to ± 30.0%. The following compounds do not have a minimum % D requirement but must meet a minimum RRF criterion of 0.010: carbon disulfide, chloroethane, chloromethane, cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,2-dichloropropane, and methylene chloride. Furthermore, OLC02.1 does not specify RRF or % D criteria for the following compounds: acetone, 2-butanone, 1,2-dibromo-3-chloropropane, 2-hexanone, 4-methyl-2-pentanone, and 1,2,4-trichlorobenzene. (If data quality objectives allow for greater variability of data, then expanded %D and minimum response factor criteria should be documented in the EPA-approved site-specific QAPjP or amendment to the QAPjP. If response factors less than 0.05 are allowed, then the validator should ensure that there is sufficient QC data to support the use of low RFs in sample calculations.

PERCENT DIFFERENCE (%D) - The % D is used to compare the initial calibration mean RRF with the continuing calibration RRF5. The % Difference indicates both the direction and the magnitude of the comparison, i.e., the % Difference may be either negative, positive or zero.

$$\%\ Difference = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where,

$\overline{RRF_i}$ = Mean relative response factor from the most recent initial calibration meeting technical acceptance criteria

RRF_c = Relative response factor from continuing calibration standard

SECTION V: BLANK CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-V-B for blank data validation criteria and the following method QC criteria.

Method Required Blanks

1. Method Blank - A 25.0 mL aliquot of reagent water that is carried through the entire analytical process to determine the levels of contamination associated with the processing and analysis of samples. All blanks are spiked with internal standards and surrogate compounds and blank analysis must meet internal standard and surrogate compound criteria. The method blank must be analyzed at least once during every 12 hour time period on each GC/MS system used for volatile analysis.

2. Storage Blank - Consists of two 40 mL VOA vials filled with reagent water prepared by the laboratory when the first samples in the SDG are received. The vials are stored, under the same conditions, with the field samples. After all the samples in the SDG are analyzed, a 25.0 mL aliquot of the storage blank is analyzed to determine whether contamination was introduced during storage of the samples. All blanks are spiked with internal standards and surrogate compounds and blank analysis must meet internal standard and surrogate compound criteria. A minimum of one storage blank must be analyzed per SDG after all samples for that SDG have been analyzed.

3. Instrument Blank - A 25.0 ml aliquot of reagent water that is carried through the entire analytical procedure and is analyzed following highly contaminated samples containing target compounds that exceed the initial calibration range. The instrument blanks are used to determine if contamination is introduced from a previous sample and the level associated with the analytical instrument. All blanks are spiked with internal standards and surrogate compounds and blank analysis must meet internal standard and surrogate compound criteria. Instrument blanks are analyzed after a sample/dilution which contains a target compound at a concentration greater than 25 ug/L (ketones 125 ug/L) or a non-target compound at a concentration greater than 100 ug/L or saturated ions from a compound (excluding peaks in the solvent front).

SECTION VI: SURROGATE COMPOUND CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-VI-B for surrogate compound data validation criteria and the following method surrogate compound QC criteria:

The proper surrogate compounds must be quantified using the correctly assigned internal standards and the correct primary quantitation ions.

The surrogate compound, 4-Bromofluorobenzene, is added to all samples, standards, QC samples, and blanks for a final concentration of 5 ug/L.

Table App.D.VI-1 - CHARACTERISTIC IONS FOR SURROGATE COMPOUNDS

Surrogate	Characteristic Ions		
	Primary Quantitation Ion	Secondary Ion(s)	Internal Standard
4-Bromofluorobenzene	174	95, 176	1,4-Difluorobenzene

The surrogate % recovery is calculated using the following equation:

$$Surrogate\ Percent\ Recovery = \frac{Q_d}{Q_a}\ x\ 100\%$$

Q_d = Quantity of surrogate determined by analysis

Q_a = Quantity of surrogate added to sample/blank

Table App.D.VI-2 - SURROGATE RECOVERY LIMITS

Surrogate	Method QC Criteria
	Percent Recovery (Water)
4-Bromofluorobenzene	80-120

Sample reanalysis is required for samples that do not meet the surrogate recovery acceptance criteria.

SECTION VII: INTERNAL STANDARDS CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-VII-B for internal standard data validation criteria and the following method internal standard QC criteria:

The correct internal standard must be used for sample compound quantitation and the correct internal standard primary quantitation ion must be used for quantitation.

The internal standards Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d_5 are added to all samples, standards, QC samples, and blanks for a final concentration of 5.0 ug/L.

Table App.D.VII-1 - LOW CONCENTRATION VOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SURROGATES ASSIGNED FOR QUANTITATION

IS 1,4-Difluorobenzene	IS Chlorobenzene-d_5	IS 1,4-Dichlorobenzene-d_4
Acetone	Benzene	Bromoform
Bromochloromethane	Bromodichloromethane	1,2-Dibromo-3-chloropropane
Bromomethane	Carbon tetrachloride	1,2-Dichlorobenzene
2-Butanone	Chlorobenzene	1,3-Dichlorobenzene
Carbon disulfide	Dibromochloromethane	1,4-Dichlorobenzene
Chloroethane	1,2-Dibromoethane	1,2,4-Trichlorobenzene
Chloroform	1,2-Dichloropropane	
Chloromethane	cis-1,3-Dichloropropene	
1,1-Dichloroethane	trans-1,3-Dichloropropene	
1,2-Dichloroethane	Ethylbenzene	
1,1-Dichloroethene	2-Hexanone	
cis-1,2-Dichloroethene	4-Methyl-2-pentanone	
trans-1,2-Dichloroethene	Styrene	
Methylene chloride	1,1,2,2-Tetrachloroethane	
Vinyl chloride	Tetrachloroethene	
	Toluene	
	1,1,1-Trichloroethane	
4-Bromofluorobenzene (surr)	1,1,2-Trichloroethane	
	Trichloroethene	
	Xylenes (total)	

Table App.D.VII-2 - CHARACTERISTIC IONS FOR INTERNAL STANDARDS FOR LOW CONCENTRATION VOLATILE COMPOUNDS

Internal Standard	Characteristic Ions	
	Primary Quantitation Ion	Secondary Ion(s)
1,4-Difluorobenzene	114	63, 88
1,4-Dichlorobenzene-d4	152	115, 50
Chlorobenzene-d5	117	82, 119

Internal standard area counts for each of the internal standards must be within the inclusive range of ± 40% of the response of internal standards in the associated daily continuing calibration standard.

The retention time of the internal standard must not vary by more than ± 20 seconds from the retention time of the associated daily continuing calibration standard.

Sample reanalysis is required for samples that do not meet the internal standard acceptance criteria.

SECTION VIII: MATRIX SPIKE/MATRIX SPIKE DUPLICATE CRITERIA

The Low Concentration method does not require MS/MSD analysis therefore, no method-specific criteria are available for MS/MSD. Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-VIII-B for MS/MSD validation criteria if MS/MSD analyses are performed.

SECTION IX: FIELD DUPLICATE CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-IX-B for field duplicate data validation criteria.

SECTION X: SENSITIVITY CHECK CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-X-B for sensitivity check data validation criteria.

SECTION XI: PE SAMPLES - ACCURACY CHECK CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-XI-B for accuracy check data validation criteria and the following method accuracy check QC criteria:
The LCS is a method-required internal laboratory quality control sample that must be prepared, analyzed and reported once per SDG. It must be prepared and analyzed concurrently with the samples in the SDG using the same instrumentation as the samples.

Compound	Final Concentration ug/L	Method Required QC % Recovery Limits
Vinyl chloride	5.0	60 - 140
1,2- Dichloroethane	5.0	60 - 140
Carbon tetrachloride	5.0	60 - 140
1,2-Dichloropropane	5.0	60 - 140
Trichloroethene	5.0	60 - 140
1,1,2-Trichloroethane	5.0	60 - 140
Benzene	5.0	60 - 140
cis-1,3-Dichloropropene	5.0	60 - 140
Bromoform	5.0	60 - 140
Tetrachloroethene	5.0	60 - 140
1,2-Dibromoethane	5.0	60 - 140
1,4-Dichlorobenzene	5.0	60 - 140

SECTION XII: TARGET COMPOUND IDENTIFICATION CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-XII-B for target compound identification data validation criteria.

SECTION XIII: COMPOUND QUANTITATION AND REPORTED QUANTITATION LIMITS CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-XIII-B for compound quantitation and reported quantitation limit data validation criteria and the following method quantitation QC criteria:

Volatile target compounds must be quantitated using the internal standard method with the internal standards assigned in Appendix A, Section VII. The daily RRF5 must be used for sample quantitation. The sample target compounds must be quantified using the following primary quantitation ions and must be reported to the CRQLs listed below:

Table App.D.XIII-1 - TARGET COMPOUND LIST (TCL), PRIMARY QUANTITATION AND SECONDARY IONS, AND CONTRACT REQUIRED QUANTITATION LIMITS (CRQLs) FOR OLCO2.0 SOW VOLATILE ORGANIC COMPOUNDS

		Quantitation Limits			
		Low Water	On Column	Characteristic Ions	
Volatiles	CAS Number	ug/L	(ng)	Primary	Secondary
Chloromethane	74)87)3	1	(25)	50	52
Bromochloromethane	74-97-5	1	(25)	128	49,130
1,2-Dibromoethane	106-93-4	1	(25)	107	109,188
Bromomethane	74)83)9	1	(25)	94	96
Vinyl Chloride	75)01)4	1	(25)	62	64
Chloroethane	75)00)3	1	(25)	64	66
Methylene Chloride	75)09)2	2	(50)	84	86,49
Acetone	67)64)1	5	(125)	43	58
Carbon Disulfide	75)15)0	1	(25)	76	78
1,1)Dichloroethene	75)35)4	1	(25)	96	61,63
1,1)Dichloroethane	75)34)3	1	(25)	63	65,83
cis-1,2)Dichloroethene	156)59)2	1	(25)	96	61,98
trans-1,2-Dichloroethene	156-60-5	1	(25)	96	61,98
Chloroform	67)66)3	1	(25)	83	85
1,2)Dichloroethane	107)06)2	1	(25)	62	98
2)Butanone	78)93)3	5	(125)	43	72*
1,1,1)Trichloroethane	71)55)6	1	(25)	97	99,61
Carbon Tetrachloride	56)23)5	1	(25)	117	119
Bromodichloromethane	75)27)4	1	(25)	83	85,127
1,2)Dichloropropane	78)87)5	1	(25)	63	112
cis)1,3)Dichloropropene	10061)01)5	1	(25)	75	77
Trichloroethene	79)01)6	1	(25)	95	130,132
Dibromochloromethane	124)48)1	1	(25)	129	127
1,1,2)Trichloroethane	79)00)5	1	(25)	97	83,85,99,132,134
Benzene	71)43)2	1	(25)	78	--
trans)1,3)Dichloropropene	10061)02)6	1	(25)	75	77
Bromoform	75)25)2	1	(25)	173	175,254
4)Methyl)2)pentanone	108)10)1	5	(125)	43	58,100
2)Hexanone	591)78)6	5	(125)	43	58,57,100
Tetrachloroethene	127)18)4	1	(25)	166	168,129
Toluene	108)88)3	1	(25)	91	92
1,1,2,2)Tetrachloroethane	79)34)5	1	(25)	83	131,85
1,2,4-Trichlorobenzene	120-82-1	1	(25)	180	182,145
1,2-Dichlorobenzene	95-50-1	1	(25)	146	111,148
1,3-Dichlorobenzene	541-73-1	1	(25)	146	111,148
1,4-Dichlorobenzene	106-46-7	1	(25)	146	111,148
Chlorobenzene	108)90)7	1	(25)	112	77,114
Ethylbenzene	100)41)4	1	(25)	91	106
Styrene	100)42)5	1	(25)	104	78
Xylenes (Total)	1330)20)7	1	(25)	106	91
1,2-Dibromo-3-chloropropane	96-12-8	1	(25)	75	155,157

* - m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

SAMPLE CONCENTRATION - The amount of analyte present in a sample is calculated using the RRF5 of the continuing calibration standard in the following equation:

Sample concentration for water:

$$ug/L = \frac{(A_x)(IS)(Df)}{(A_{is})(RRF)(V_o)}$$

Where,

A_x = Area of the primary quantitation ion response (EICP) for the compound to be measured
A_{is} = Area of the primary quantitation ion response (EICP) for the specific internal standard
IS = Amount of internal standard added in nanograms (ng)
RRF = The Relative Response Factor from the most recent continuing calibration standard
V_o = Total volume of water purged in milliliters (mL)
Df = Dilution Factor - The dilution factor for analysis of water samples for volatiles by this method is defined as the ratio of the number of milliliters (mL) of water purged (i.e., V_o above) to the number of mL of the original water sample used for purging. If no dilution is performed , Df=1.

CRQL CALCULATIONS

Water:

$$Adjusted\ CRQL = Contract\ CRQL\ x \frac{(V_x)}{(V_o)}\ x\ (Df)$$

Where,

V_o and Df are defined in the sample concentration equation above
V_x = Contract sample volume (5 to 25 mL)

SECTION XIV: TENTATIVELY IDENTIFIED COMPOUND CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-XIV-B for tentatively identified compound (TIC) data validation criteria and the following method TIC QC criteria:

The validator is required to report up to 30 TICs in the Data Validation Memorandum.

TENTATIVELY IDENTIFIED COMPOUND CONCENTRATION - the estimated concentration for non-target compounds tentatively identified shall be determined by the internal standard method using the following equations:

Sample concentration for water:

$$ug/L = \frac{(A_x)(IS)(Df)}{(A_{is})(RRF)(V_o)}$$

Where,

A_x = Area of the primary quantitation ion response (EICP) for the non-target compound to be measured
A_{is} = Area of the primary quantitation ion response (EICP) for the specific internal standard
IS = Amount of internal standard added in nanograms (ng)
RRF = Relative Response Factor assumed to be 1
V_o = Total volume of water purged in milliliters (mL)
Df = Dilution Factor - The dilution factor for analysis of water samples for volatiles by this method is defined as the ratio of the number of milliliters (mL) of water purged (i.e., V_o above) to the number of mL of the original water sample used for purging. If no dilution is performed , Df=1.

SECTION XV: SEMIVOLATILE CLEANUP CRITERIA

Not applicable to low concentration volatile analysis.

SECTION XVI: SYSTEM PERFORMANCE CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-XVI-B for system performance data validation criteria.

SECTION XVII: OVERALL ASSESSMENT CRITERIA

Refer to Region 1, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, Section VOA/SV-XVII-B for overall assessment data validation criteria.