

VOLATILE ORGANIC COMPOUNDS (VOCs)

EPA Contract Laboratory Program (CLP) Statement of Work (SOW) and Superfund Analytical Methods for Low Concentration Water for Organics Analysis (SAMLCO)

Table 1A. Summary of Holding Times and Preservation for Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry

Analytical Parameter ^a	Technical and Contract Holding Times	Preservation
Low concentration Volatile Organic Compounds (VOCs) in Water ^b	<u>Technical</u> : 7 days from collection; <u>Contract</u> : 5 days from receipt at laboratory	Cool to 4°C ±2°C;
VOCs in Water ^b	<u>Technical</u> : 14 days from collection; <u>Contract</u> : 10 days from receipt at laboratory	HCl to pH <2; Cool to 4°C ±2°C

^a Individual target compounds are listed in Table 1B.

^b 25-mL Purge volume

Data Calculations and Reporting Units:

Calculate the relative response factor (RRF) and the concentration of individual analytes according to the equations specified in Exhibit D, Sections 9.3.4.1 and 11.2.1 of the CLP SOW (OLM03.1).

Report water sample results in concentration units of micrograms per liter (µg/L).

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

Table 1B. Target Compound List, CAS Numbers, and Contract Required Quantitation Limits (CRQLs) for VOCs by EPA CLP SOW and SAMLCO

Analyte	CAS Number	(CRQL) $\mu\text{g/L}$
Chloromethane	74-87-3	1
Bromomethane	74-83-9	1
Vinyl chloride	75-01-4	0.5
Chloroethane	75-00-3	1
Methylene chloride	75-09-2	1
Acetone	67-64-1	10
Carbon disulfide	75-15-0	1
1,1-Dichloroethene	75-35-4	1
1,1-Dichloroethane	75-34-3	1
1,2-Dichloroethene (total)	540-59-0	1
Chloroform	67-66-3	1
1,2-Dichloroethane	107-06-2	0.5
2-Butanone	78-87-5	10
1,1,1-Trichloroethane	71-55-6	1
Carbon tetrachloride	56-23-5	0.5
Bromodichloromethane	75-27-4	1
1,2-Dichloropropane	78-87-5	1
<i>cis</i> -1,3-Dichloropropene	10061-01-5	0.5
Trichloroethene	79-01-6	1
Dibromochloromethane	124-48-1	1
1,1,2-Trichloroethane	79-00-5	1
Benzene	71-43-2	1
<i>trans</i> -1,3-Dichloropropene	10061-02-6	0.5
Bromoform	75-25-2	1
4-Methyl-2-pentanone	108-10-1	10
2-Hexanone	591-78-6	10
Tetrachloroethene	127-18-4	1
1,1,2,2-Tetrachloroethane	79-34-5	1
Toluene	108-88-3	1
Chlorobenzene	108-90-7	1

Ethylbenzene	100-41-4	1
Styrene	100-42-5	1
Xylenes (total)	1330-20-7	1
1,3-Dichloropropane	142-28-9	1
1,2-Dibromoethane	106-93-4	1
1,2-Dibromo-3-chloropropane	96-12-8	1
1,2,3-Trichloropropane	96-18-4	1
Methyl-t-butyl ether	163-40-44	1
Dichlorofluoromethane	75-43-4	1
Trichlorofluoromethane	75-69-4	1
Dichlorodifluoromethane	75-71-8	1

Table 2. Summary of Calibration Procedures for VOCs by EPA CLP SOW and SAMLCO

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
GC/MS Tuning with 4-bromofluorobenzene (BFB)	Beginning of each 12 hour period during which standards and samples are analyzed	Ion abundance criteria in Table 1 of Exhibit D, Section 17.0 of the CLP SOW (OLM03.1)	1. Identify the problem. 2. MS tune criteria must be met before any calibration standards, samples, blanks, or QC samples are analyzed
Initial Calibration (minimum blank + 5 points for each analyte) (ICAL) ^{a, b, c}	Initially; whenever required, due to failure of CCV	Minimum RRFs for all analytes in the ICAL must meet the acceptance criteria specified in Table D-3 of Exhibit D, Section V and Section III, Item 14.5.4 of SAMLCO (10/92). The %RSD of RRFs across the ICAL #30% except as noted in Section III, Item 14.5.4.	1. Terminate analysis 2. Re-calibrate and verify before sample analysis Corrective action as specified in Exhibit D, Section III, Part C, Items 14.6 of SAMLCO (10/92)
Sixth ICAL containing carbon tetrachloride, 1,2-dichloroethane, <i>cis</i> -1,3-dichloropropene, <i>trans</i> -1,3-dichloropropene, and vinyl chloride at a concentration of 0.5 µg/L to verify that the requested CRQLs can be achieved	Initially; whenever required, due to failure of CCV	Minimum RRF requirement for these analytes is 0.05	1. Terminate analysis 2. Re-calibrate and verify before sample analysis

Continuing Calibration Verification (CCV)	Every 12 hour period before samples are analyzed and at the end of the analytical run	<p>Minimum RRFs for all analytes in the CCV must meet the acceptance criteria specified in Table D-3 of Exhibit D, Section V and Section III, Item 15.5.4 of SAMLCO (10/92).</p> <p>%D between the RRFs from the CCV and average RRFs from the ICAL #30% except as noted in Section III, Item 15.5.4.</p>	<p>1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV</p> <p>Corrective action as specified in Exhibit D, Section III, Part C, Items 15.6 of SAMLCO (10/92)</p>
Internal Standards: bromochloromethane, chlorobenzene-d ₅ , and 1,4-difluorobenzene	Each analysis of CCV	<p>Internal standard area counts -50% to +100% from the area counts of the associated CCV.</p> <p>Internal standard RT within ±30 seconds from the RT of the CCV</p> <p>Refer to Exhibit D, Sections 11.3.5 and 11.3.6 of the CLP SOW (OLM03.1) for acceptance criteria</p>	<p>1. Re-analyze the affected sample</p> <p>2. If re-analysis of the sample does not solve the problem, then submit data from both the initial analysis and the re-analysis.</p>

^a The ICAL low standard must be above but near the CRQL. The low ICAL standard must have a signal to noise ratio \$5:1. If this requirement cannot be met, the laboratory must submit a MDL study as part of the data package.

^b ICAL and continuing CAL standards must contain all target analytes listed in Table 1B.

^c Report the retention time window for each analyte. Determine retention time windows as ±3 x the standard deviation of the average initial calibration retention time for each analyte.

Table 3. Summary of Internal Quality Control Procedures for VOCs by EPA CLP SOW and SAMLCO

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Beginning of each 12-hour time period, minimum of one per SDG ^a	< CRQL for each compound MB must meet the requirements specified in Exhibit D, Section 12.1.4.5 of OLM03.1	1. Investigate the source of contamination and document. 2. Reanalyze all samples processed with a blank that is out of control. Corrective action procedures outlined in Exhibit D, Section 12.1.5 of the CLP SOW (OLM03.1)
Instrument Blank (IB)	After the analysis of a sample containing target analytes at concentration exceeding the ICAL range	IB and storage blanks must meet the requirements specified in Exhibit D, Section V, Item 26.4 of SAMLCO	1. Investigate the source of contamination and document. 2. Reanalyze all samples processed with an instrument blank out of control. Corrective action procedures outlined in Exhibit D, Section V, Item 26.5 of SAMLCO
Matrix Spike and Matrix Spike Duplicate (MS/MSD)	One MS/MSD set per batch or SDG (1 MS/MSD set per 20 samples minimum)	MS/MSD recoveries, and RPDs between MS/MSD recoveries, within the limits specified in Table 8 of Exhibit D, Section 17.0	1. Report in case narrative

System monitoring compounds (SMCs): toluene-d ₈ , 4-bromofluorobenzene (BFB), and 1,2-dichloroethane-d ₄	Every sample, standard and method blank	SMC recoveries within the limits specified in Table 7 of Exhibit D, Section 17	1. Re-analyze all samples with non-compliant SMC recoveries. 2. If re-analysis of the sample does <i>not</i> solve the problem, then submit data from both the initial analysis and the re-analysis.
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^a SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

^b SMC: Toluene-d₈, BFB, and 1,2-dichloroethane-d₄

Dilute and reanalyze samples which contain one or more target analytes at concentrations above the initial calibration range. Results for such reanalyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.