

**VOLATILE ORGANIC COMPOUNDS (VOCs) in Air (Ambient Air/Soil Vapor/Stack Gas)
Samples Collected in Specially-Prepared Canisters and Analyzed by Gas
Chromatography/Mass Spectrometry (GC/MS)**

EPA Method TO-15 (January 1999)

Table 1A. Summary of Holding Times and Preservation for Volatile Organic Compounds (VOCs) in Air

Analytical Parameter ^a	Technical and Contract Holding Times	Preservation
Volatile Organic Compounds (VOCs) in SUMMA® canisters ^b	<u>Technical</u> : 14 days from collection; <u>Contract</u> : 10 days from receipt at laboratory	Ambient temperature
VOCs in tedlar bags	<u>Technical</u> : 48 hours from collection; <u>Contract</u> : 36 hours from receipt at laboratory	Ambient temperature

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

^b The laboratory must provide the following equipment certified as clean: Cleaned and evacuated 6-liter SUMMA® canisters with the manufacturer's serial number, or a unique permanent identification number attached. For cleaning and certification of SUMMA® canisters, follow the requirements specified in Section 8.4 of EPA Method TO-15 (January 1999). Cleaned and preset ultra-low flow orifices for each ambient air sample preset by the laboratory at a flow rate of 3.2 mL/min ±10% and digital flow meters capable of accurate measurements in the 3.2 mL/min range.

Leak test all canisters prior to sample collection according to Section 8.4 of Method TO-15 (January 1999).

Data Calculations and Reporting Units:

Calculate and report the sample results as specified in Section 10.8.4 of EPA Method TO-15 (January 1999). All records of analyses, dilutions and calculations must be legible and sufficient to recalculate all sample concentrations and QC results.

Perform sample quantitation using the relative response factor (RRF) from the daily continuing calibration standard. Report results for all target analytes in concentration units of parts per billion by volume (ppbv). Report tentatively identified compounds (TICs) with a response of <10% of the nearest internal standard. TIC values should be estimated in ppbv based on the response of the corresponding internal standard.

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 for VOCs by EPA Method TO-15

Analyte	CAS Number	MW	CRQL ppbv	CRQL ug/M3	CRQL ug/L	MDL ppbv	MDL ug/M3
Benzene	71-43-2	78.1	1.0	3.5	0.0035	0.2	0.7
Bromomethane	74-83-9	94.9	1.0	4.2	0.0042	0.2	0.8
Carbon Tetrachloride	56-23-5	153.8	1.0	6.9	0.0069	0.2	1.4
Chlorobenzene	108-90-7	112.6	1.0	5.0	0.0050	0.2	1.0
Chloroethane	75-00-3	64.5	1.0	2.9	0.0029	0.2	0.6
Chloroform	67-66-3	119.4	1.0	5.3	0.0053	0.2	1.1
Chloromethane	74-87-3	50.5	1.0	2.3	0.0023	0.2	0.5
1,1-Dichloroethane	75-34-3	99	1.0	4.4	0.0044	0.2	0.9
1,2-Dichloroethane	107-06-2	99	1.0	4.4	0.0044	0.2	0.9
1,1-Dichloroethene	75-35-4	96.9	1.0	4.3	0.0043	0.2	0.9
cis-1,2-Dichloroethene	156-59-2	96.9	1.0	4.3	0.0043	0.2	0.9
trans-1,2-Dichloroethene	156-60-5	96.9	1.0	4.3	0.0043	0.2	0.9
1,2-Dichloropropane	78-87-5	113	1.0	5.0	0.0050	0.2	1.0
cis-1,3-Dichloropropene	10061-01-5	111	1.0	5.0	0.0050	0.2	1.0
trans-1,3-Dichloropropene	10061-02-6	111	1.0	5.0	0.0050	0.2	1.0
Ethylbenzene	100-41-4	106.2	1.0	4.7	0.0047	0.2	0.9
Methylene Chloride	75-09-2	84.9	1.0	3.8	0.0038	0.2	0.8
Styrene	100-42-5	104.2	1.0	4.6	0.0046	0.2	0.9
1,1,2,2-Tetrachloroethane	79-34-5	167.9	1.0	7.5	0.0075	0.2	1.5
Tetrachloroethene	127-18-4	165.8	1.0	7.4	0.0074	0.2	1.5
Toluene	108-88-3	92.1	1.0	4.1	0.0041	0.2	0.8
1,1,1-Trichloroethane (TCA)	71-55-6	133.4	1.0	6.0	0.0060	0.2	1.2
1,1,2-Trichloroethane	79-00-5	133.4	1.0	6.0	0.0060	0.2	1.2
Trichloroethene (TCE)	79-01-6	131.4	1.0	5.9	0.0059	0.2	1.2
Vinyl Chloride	75-01-4	62.5	1.0	2.8	0.0028	0.2	0.6
p-Xylene & m- Xylene	106-42-3 & 108-38-3	106.2 106.2	2.0	9.5	0.0095	0.4	1.9
o-Xylene	95-47-6	106.2	1.0	4.7	0.0047	0.2	0.9

Table 2. Summary of Calibration Procedures for VOCs by EPA Method TO-15

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 3 of Method TO-15	1. Identify the problem. 2. MS tune criteria must be met before calibration
Initial Calibration (minimum blank + 5 points for each analyte) (ICAL) ^{a, b, c}	Initially; whenever required, due to failure of CCV	RRFs ≥ 0.05 for each analyte; RSD for RRFs $\leq 30\%$	1. Terminate analysis 2. Recalibrate and verify before sample analysis
Continuing Calibration Verification (CCV) (middle of the calibration range)	Following ICV, every 12-hour, and end of run	RRFs ≥ 0.05 for each analyte; %D between RRF of CCV and avg. RRFs from ICAL $\leq 30\%$	1. Recalibrate and verify 2. Reanalyze samples back to last good CCV
CRQL standard	Every 12 hour	65-135% of the expected value	1. Recalibrate and verify 2. Reanalyze samples back to last good CRQL standard
Internal Standards ^d	Every standard, sample, blank, and QC sample	IS area within $\pm 40\%$ of the IS area in the associated CCV	1. Investigate the system; 2. Re-analyze all samples analyzed during a system malfunction
Retention time evaluation	Each analysis	± 0.50 minute of the IS retention time in the associated CCV	1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV

^a The ICAL low standard must be at concentrations equivalent to the CRQL.

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

^c Report the retention time (RT) window for each analyte. Determine RT windows as $\pm 3 \times$ the standard deviation (SD) of the average initial calibration RT for each analyte.

^d Internal standards: Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5.

The standards must be traceable to known certified source. Humidify calibration standards when used.

Table 3. Summary of Internal Quality Control Procedures for VOCs by EPA Method TO-15

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Each 12-hour time period, minimum of one per SDG ^a	< CRQL for each compound	1. Investigate the source of contamination and document. 2. Reanalyze all samples processed with a blank that is out of control.
Blank Spike Blank Spike Duplicate (BS/BSD)	One BS/BSD set per batch or SDG (1 MS/MSD set per 20 samples minimum)	65-135% of expected value; ≤35% RPD between BS and BSD	1. Report in case narrative
Surrogate Spikes ^b	Every sample, standard and method blank	80-120% of expected value	1. Reanalyze all samples with non-compliant surrogate recoveries
Laboratory Duplicates	One per SDG	RPD ≤20 between duplicate results ≥5 times CRQL; ±CRQL for duplicate results ≤5 times CRQL	1. Reanalyze all samples with non-compliant results

^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 1,2-dichloroethane-d₄, Toluene-d₈, and 4-Bromofluorobenzene. If other surrogates are used the laboratory must demonstrate that the surrogates do not interfere with any target analytes. The laboratory must also notify the Region in advance.

Reanalyze samples containing target analytes at concentrations greater than the initial calibration range. Analyze a smaller aliquot of sample from the SUMMA® canister. If after analyzing a smaller aliquot, the concentration is still greater than the initial calibration range, then dilute the sample and reanalyze according to procedures outlined in EPA Method TO-15. If sample dilution is necessary, the dilution must be adjusted so that the target analyte is quantitated at a level in the upper half of the calibration range. Report the results and submit documentation for the analysis of both the diluted and undiluted sample.

Both the primary ions and the secondary ions must be present in the spectra. The acceptance level for relative abundance of the appropriate ions in all standards, method blanks, QC samples, laboratory duplicates and field samples is determined to be ±20% of the expected abundance observed in the most recent continuing calibration standard. All ions greater than 15% in the standard spectrum must be present in the sample spectrum.