

Volatile Organic Compounds (VOC) in Water by Purge and Trap GC/MS - PBM

Parameter Volatile Organic Compounds (VOC).

Analytical Method Purge and Trap GC/MS (PBM).

Introduction This method is applicable to the qualitative and/or quantitative determination of VOCs in water samples.

Method Summary Samples are analyzed by purge and trap gas chromatography / mass spectrometry. Volatile organic compounds are purged from a water sample with an inert gas, trapped on a solid carbon-based sorbant, and then thermally desorbed to a capillary GC/MS system.

This method is performance-based. Sample introduction techniques other than purge and trap are permitted if performance requirements are met, but GC/MS detection is a requirement of this method.

MDL and EMS Codes The analytes listed below represents only a partial list of compounds which may be analyzed by this method. Refer to EPA Method 8260B for a more complete list of applicable analytes. The MDLs listed below are achievable for this method in a typical laboratory environment. Ensure that the detection limits reported by the laboratory are sufficient to meet any applicable regulatory standards.

<u>Compound</u>	<u>Approximate MDL (ug/L)</u>	<u>EMS Code</u>
benzene	0.5	B020 X384
bromodichloromethane	1	B012 X384
bromoform	1	B013 X384
bromomethane	2	defined on request
carbon tetrachloride	1	defined on request
chlorobenzene	1	C010 X384
chloroethane	2	C003 X384
2-chloroethylvinyl ether	5	defined on request
chloroform	1	C032 X384
chloromethane	2	C070 X384
dibromochloromethane	1	C033 X384
1,2-dichlorobenzene	1	defined on request
1,4-dichlorobenzene	1	defined on request
dichloromethane	5	M041 X384
1,1-dichloroethane	1	C021 X384
1,2-dichloroethane	1	C022 X384
1,1-dichloroethylene	1	C024 X384
1,2-dichloroethylene	1	C023 X384
1,2-dichloropropane	1	C025 X384
cis-1,3-dichloropropene	1	C027 X384
trans-1,3-dichloropropene	1	C028 X384

ethylbenzene	0.5	B021 X384
hexachlorobutadiene	1	defined on request
iso-octane	1	defined on request
meta/para-xylenes	0.5	defined on request
methyl ethyl ketone	20	defined on request
methyl-tertiary butyl ether (MTBE)	1	defined on request
nitrobenzene	1	defined on request
styrene	1	S010 X384
1,1,2,2-tetrachloroethane	1	C080 X384
tetrachloroethene	1	T030 X384
1,1,1-trichloroethane	1	T016 X384
trichloroethene	1	T029 X384
trichlorofluoromethane	1	T070 X384
toluene	1	T001 X384
vinyl chloride	2	defined on request

Matrix

Fresh Water
Wastewater
Marine Water
Sludge

Interferences and Precautions

Preservation is necessary to prevent microbial degradation of VOC analytes, notably some aromatic compounds (BTEX), and/or to prevent reactions with residual chlorine. Residual chlorine reacts with organic matter to produce trihalomethanes, and can react with and degrade some VOC analytes, notably styrene.

Use extreme caution to prevent losses due to evaporation. Keep samples cold until they are dispensed. Avoid the application of vacuum to VOC water samples prior to analysis (syringes with restrictive inlets or needles are not recommended for sub-sampling). Anytime a second analysis is required for dilution purposes, a second sample vial which has not been opened should be used.

Calibration standards are prepared using methanolic standard solutions. Ensure that samples and standards are matrix-matched as closely as possible with regard to methanol content (within ~20uL methanol).

Samples can potentially be contaminated during storage by diffusion of volatile organics through the septum (particularly fluorocarbons and dichloromethane).

A transportation blank can be prepared from reagent water and carried through the sampling and handling protocol as a check on contamination from external sources.

Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree of carryover that occurs on their instrument system, and should take appropriate steps to prevent the occurrence of false positives.

2-chloroethylvinylether often decomposes on purge and trap systems, sometimes completely. It also rapidly decomposes under acidic conditions, so acid preservation is may not be used for this analyte. Non-detect analyses for the 2-chloroethanol breakdown product may be sufficient to demonstrate the absence of this compound in samples.

Cis- and trans-1,3-dichloropropene and bromomethane decompose over time in the solutions containing sodium thiosulfate. Analysis of these analytes is not recommended from samples preserved with sodium thiosulfate.

Sample Handling and Preservation

Use 40 mL clear or amber glass VOC vials with Teflon-lined septa.

If no residual chlorine is present, preserve to a pH of less than 2 with sodium bisulfate (NaHSO_4) in aqueous solution or as a solid. Approximately 120mg of NaHSO_4 per 40mL sample is recommended. Alternatively, treat with copper sulfate, adding 0.5 mL of 10% by weight $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(\text{aq})}$ per 40mL vial. Each of these procedures have been demonstrated to prevent the microbial degradation of VOCs.

If the sample is recently chlorinated, and is likely to contain residual chlorine (e.g. freshly sampled chlorinated water supplies), add sodium thiosulfate to reduce the chlorine to unreactive chloride (10 mg $\text{Na}_2\text{S}_2\text{O}_3$ per 40 mL sample is recommended, in aqueous solution or as a solid, and is sufficient for up to 5 ppm Cl_2).

Do not pre-rinse the vial with sample (to avoid loss of preservative). Collect the sample with as little aeration as possible, filling to just overflowing. Cap the vial and try to ensure that no bubbles are present. A small air bubble of up to 1/4" diameter may appear after sampling, and is acceptable.

It is recommended that all VOC samples be collected in triplicate to allow for re-analyses or dilutions.

HCl or H_2SO_4 are permitted as alternatives to the use of NaHSO_4 to preserve non-chlorinated samples, but NaHSO_4 is recommended. Degradation of styrene by HCl preservative has been reported, and other unsaturated VOCs may react similarly.

Acid preservative may not be used for the analysis of 2-chloroethylvinylether. This analyte rapidly decomposes in acidic solution. For this analyte, collect unpreserved samples, or preserve with sodium thiosulfate.

Sodium thiosulfate preservation is not recommended for cis- and trans-1,3-dichloropropene and bromomethane. These analytes decompose over time in sodium thiosulfate solution. If analysis is required for these analytes in sodium thiosulfate preserved samples, analyze as soon as possible and verify potential decomposition losses with field spikes or lab studies.

One investigator has reported the formation of bromomethane artifacts in some groundwater samples where preservation with copper sulfate had been used.

For a full discussion of the merits of various VOC preservation techniques, refer to Appendix A of Draft EPA Method 5035A, entitled "The Collection and Preservation of Aqueous and Solid Samples for Volatile Organic Compound (VOC) Analysis".

Stability

Holding Time - Analyze samples as soon as possible, but within 14 days of sampling. The 14 day holding time applies to correctly preserved, unopened samples with essentially zero headspace. After any significant sample volume has been removed, samples are quickly compromised. See interferences section regarding chemical incompatibilities of some analytes with preservatives.

Storage - Store at 4°C until dispensed to sealed analysis vessels.

Procedure

Detailed instrumental procedures are not provided in this method. The procedures described in following US Environmental Protection Agency methods are recommended as general guidelines:

Purge and Trap conditions: SW846 Method 5030b (Dec, 1996 or newer).

GC/MS conditions: SW846 Method 8260b (Dec, 1996 or newer).

Whenever possible, the use of internal standards are strongly recommended for this method. Internal standards can vastly improve the precision of the method. Deuterium labeled VOCs, fluorinated VOCs, and brominated VOCs are recommended (see Quality Control - Surrogates for examples).

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below. Achievement of these requirements is to be demonstrated during method validation. Acceptance criteria for routine Quality Control samples are to be determined by the laboratory:

Accuracy Requirement: This method should not be subject to any significant positive or negative bias. Any instrumental conditions selected should achieve average recoveries of (100±20)% on clean matrix spikes, at concentrations above ten to twenty times the MDL.

Precision Requirement: The method must generate precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten to twenty times the MDL.

Selectivity Requirement: The use of gas chromatography with mass spectrometric detection assures optimum selectivity.

Sensitivity Requirement: The method must be capable of achieving MDLs as listed, or alternatively must be less than or equal to one-half of the relevant regulatory standard value.

Quality Control

Blanks: Analyze at least one Method Blank with each sample batch. Method Blank results should be below reported detection limits, or data must be qualified. A transportation blank may be carried along with the samples to check for contamination during handling.

Duplicates: Sample duplicate analyses are recommended at a frequency of about 5-10%.

Spikes: At least one Clean Matrix Method Spike must be analyzed with each batch.

Control Standard: If the Spike sample is prepared from a secondary source from calibration standards, it can also function as a Control Standard. Otherwise, a separate Control Standard is required.

Surrogates: Appropriate Surrogate Compounds must be added to each sample. Recommended surrogates include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs. Examples include:

- deuterium labeled BTEX compounds
- 4-bromofluorobenzene
- d5-chlorobenzene

Laboratories should establish suitable control limits and corrective actions for all Quality Control steps. Warning and Control Limits based on a statistical process control model, and in keeping with the specified Performance Requirements are recommended.

Prescribed Elements

1. Preservation as per the Sample Handling and Preservation section is mandatory.
2. Analysis must be by GC/MS. Purge and Trap is the recommended sample introduction system, but other mechanisms are permitted if performance requirements are met (Examples include Static Headspace, Solid Phase Micro Extraction - SPME).

References

Test Methods for Evaluating Solid Wastes – Physical / Chemical Methods, SW-846, 3rd Edition, Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), December 1996, Final Update III. United States Environmental Protection Agency, Washington, D.C.

Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, SW-846, Method 5035A, Closed System Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples, Draft Revision 1, July 2002. United States Environmental Protection Agency, Washington, D.C.

Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, SW-846, 3rd Edition, Method 5030B, Purge and Trap for Aqueous Samples, December 1996, Final Update III. United States Environmental Protection Agency, Washington, D.C.

American Public Health Association, 1998. Standard Methods for the Examination of Water and Wastewater (20th Edition), Introduction Section 6010 B, Sample Collection and Preservation, Volatile Organic Compounds.

CPPI (Canadian Petroleum Products Institute), 1992. Inter-Laboratory Study #3 to Evaluate the Analytical Variability of Volatile Organics, Phenol, and Sulfide Procedures, CPPI Report No. 92-1. (Reference for copper sulfate preservation of BTEX).

Ontario MOE. Practices for the Collection and Handling of Drinking Water Samples, version 1.0. June 2003. Reference for preservation of chlorinated water samples with sodium thiosulfate alone.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.
May 7, 2004:	Revised. Additional analytes added. Updated to PBM format. Preservation options modified.
April 5, 2006:	Additional analytes added to method as required for Hazardous Waste Leachate Quality Standards.
June 10, 2007:	Preservation options modified to use sodium thiosulfate for chlorinated samples, and sodium bisulfate for non-chlorinated samples.