Volatile Organic Compounds in Water – PBM

Parameter

Volatile Organic Compounds (VOCs) in water.

Analytical Method

Purge and Trap, Headspace (Static or Dynamic) - GC/MS or GC/PID (PBM).

Introduction

This method is applicable to the quantitative determination of volatile organic compounds in water samples. Analysis for VHw6-10 is often conducted concurrently.

Method Summary

To minimize loss of VOCs during sampling and transport to the laboratory, samples must be collected with no headspace in glass vials containing preservative.

Purge and trap: The VOCs are purged from the sample with an inert gas, and are trapped on a solid sorbent trap. The trap is heated and the VOCs are directed into a gas chromatograph equipped with a mass spectrometric detector (GC/MS). GC/PID is acceptable for a subset of analytes, e.g. BTEX and styrene.

Headspace: A portion of the sample is transferred to a headspace vial. The vial is then sealed and heated to a pre-determined temperature for a given period. After equilibration, a portion of the headspace is introduced into a GC/MS. The sample may be focused onto a solid sorbent trap prior to being desorbed onto the GC column. GC/PID is acceptable for a subset of analytes, e.g. BTEX and styrene.

The analytical portion of this method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency if all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

The analytes listed below represent the volatile substances regulated in the 2017 Contaminated Site Regulations (CSR). Refer to EPA Method 8260C for a more complete list of applicable analytes. The MDLs listed below are achievable by GC/MS in a typical laboratory environment, but may vary by laboratory, and with the sample introduction technique used. Ensure that the detection limits reported by the laboratory are sufficient to meet any applicable regulatory standards.

Analyte	Approx. MDL (µg/L)	EMS Analyte Code
acetone	5	A005
acrolein	5	defined on request
acrylonitrile	5	defined on request
allyl alcohol	5	defined on request
allyl chloride	5	C056
benzene	0.5	B020
benzyl alcohol	5	defined on request
benzyl chloride	5	defined on request
1-bromo-2-chloroethane	1	defined on request
bromobenzene	1	B005
bromodichloromethane	1	B012
bromoform	1	B013
bromomethane	1	defined on request
1,3-butadiene	5	defined on request
2-butanol	5	defined on request
n-butanol	5	defined on request
n-butylbenzene	1	B034
sec-butylbenzene	1	B035
tert-butylbenzene	1	B036
carbon disulfide	2	defined on request
carbon tetrachloride	0.5	C034
chlorobenzene	1	C010

1-chlorobutane	1	defined on request
2-chloroethanol	5	defined on request
2-chloroethylvinyl ether	5	defined on request
chloroform	0.5	C032
chloromethyl methyl ether	5	defined on request
chloroprene	5	defined on request
2-chlorotoluene	1	2CLT
4-chlorotoluene	1	C047
trans-crotonaldehyde	5	defined on request
1,2-dibromo-3-chloropropane	0.5	B038
dibromochloromethane	1	C033
1,2-dibromoethane	0.5	B029
1,2-dichlorobenzene	0.5	defined on request
1,3-dichlorobenzene	0.5	defined on request
1,4-dichlorobenzene	0.5	defined on request
dichlorodifluoromethane	1	defined on request
1,1-dichloroethane	0.5	C021
1,2-dichloroethane	0.5	C022
1,1-dichloroethylene	0.5	C024
cis-1,2-dichloroethylene	0.5	C063
trans-1,2-dichloroethylene	0.5	C023
dichloromethane	2	M041
1,2-dichloropropane	0.5	C025
1,3-dichloropropane	0.5	defined on request
cis-1,3-dichloropropene	0.5	C027
trans-1,3-dichloropropene	0.5	C028
diethyl ether	5	defined on request
1,4-dioxane	5	defined on request
ethyl acetate	5	defined on request
ethyl acrylate	5	defined on request
ethylbenzene	0.5	B021
hexachlorobutadiene	1	HCBD
hexachloroethane	1	defined on request
2-hexanone	5	H024
isobutanol	5	defined on request
isopropanol	5	defined on request
isopropylbenzene	1	I008
methacrylonitrile	5	M028
methyl acetate	5	defined on request
methyl ethyl ketone (MEK)	5	B033
methyl methacrylate	5	M054
methyl-tertiary butyl ether (MTBE)	1	MTBE
alpha-methylstyrene	1	defined on request
1-propylbenzene	1	P030
pyridine	5	defined on request
styrene	0.5	S010
1,1,1,2-tetrachloroethane	0.5	defined on request
1,1,2,2-tetrachloroethane	0.5	C080
tetrachloroethylene	0.5	T030
tetrahydrofuran	5	defined on request
toluene	1	T001
1,2,3-trichloro-1,2,2-trifluoroethane	1	defined on request
1,1,1-trichloroethane	0.5	T016
1,1,2-trichloroethane	0.5	T017
trichloroethylene	0.5	T029
trichlorofluoromethane	1	T070
1,1,2-trichloropropane	1	defined on request
1,2,3-trichloropropane	1	T067
1,2,3-trichloropropene	1	defined on request

vinyl acetate	1	defined on request
vinyl chloride	1	C004
xylene, meta+para	1	X003
xylene, ortho	0.5	X002

Where appropriate, the method may be used for other compounds not listed here, if performance requirements and Quality Control requirements can be met.

EMS Method Code(s)

***Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes.

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 respect to methanol content (within ~20 µL 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 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 (NaHSO4) in aqueous solution or as a solid. Approximately 200 mg of NaHSO4 per 40 mL sample is recommended.

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 (3 mg Na2S2O3 per 40 mL sample is recommended, in aqueous solution or as a solid, and is sufficient for up to 5 ppm Cl2).

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 ¼" 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 H2SO4 are permitted as alternatives to the use of NaHSO4 to preserve non-chlorinated samples, but NaHSO4 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 as these analytes decompose over time. If analysis is required 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 volume has been removed, samples are quickly compromised. See interferences section regarding chemical incompatibilities of some analytes with preservatives.

Storage: Store at ≤6°C until dispensed to sealed analysis vessels.

Procedure

A summary of the analytical procedure follows. Detailed instrumental procedures are described in the following US Environmental Protection Agency methods:

Purge and Trap conditions:	SW846 Method 5030C
Static Headspace conditions:	SW846 Method 5021A
GC/MS conditions:	SW846 Method 8260C
GC/PID conditions:	SW846 Method 8021B

Headspace: An appropriate amount of sample is added to a clean headspace vial. Addition of salts to equalize aliphatic/aromatic headspace partitioning equilibria is recommended. Internal standards are added, either manually or automatically by the headspace system. Sample vials are sealed with a cap and Teflon-lined septum, and are introduced to the headspace heating system, where they establish a partition equilibrium. Mechanical vibration may be used to accelerate the process. The vial may be pressurized with an inert gas. A representative fraction of headspace is transferred to the analytical trap or directly to the GC column via a heated transfer line or syringe.

Purge and trap: An appropriate amount of sample is added to a clean purge and trap vial. Internal standards are added, either manually or automatically by the purge and trap system. Sample vials are sealed with a cap and Teflon-lined septum, and are loaded onto the autosampler. VOCs are purged from the samples with an inert gas, and are trapped on a solid sorbent trap. The trap is rapidly heated and the contents are transferred to the GC column via a heated transfer line.

GC/MS: Initial calibrations must be five points or more (no more than one point may be excluded). At least one Internal Standard is required for BTEX/Styrene/MTBE analysis. At least two Internal Standards must be used for the analysis of other multicomponent VOC lists. Continuing calibrations may be employed while Calibration Verification Standards meet acceptance criteria for all reported compounds.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual QC samples.

For Initial Validations, averages of at least 8 Lab Control Samples must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance

reviews) should assess QC data encompassing longer timeframes (e.g. 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Average accuracy must be between 80-120% for all routinely reported parameters.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Precision must be ≤ 15% relative standard deviation (%RSD) for all routinely reported parameters.

Where the laboratory's method does not meet these accuracy or precision requirements for specific parameters, the method may still be used, but reports must indicate that results are semi-quantitative or qualitative, and the established performance should be provided.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Internal Standard Area Checks	All samples and QC	Area counts must be 50-200% of the initial calibration CVS
Surrogate Compounds	All samples and QC	70-130% recovery
Calibration Verification Standard (CVS)	1 per initial calibration	80-120% recovery
Field Blank or Trip Blank	Strongly Recommended (1 per sampling event)	Less than reported DL
Method Blank (MB)	1 per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	1 per batch (max 20 samples)	70-130% recovery
Matrix Spike (MS) or Reference Material (RM)	1 per batch (max 20 samples)	60-140% recovery
Lab Duplicates (DUP)	1 per batch (max 20 samples)	≤ 30% RPD
Field Duplicates	Recommended	Not specified
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	80-120% recovery for mid-level standards
If DQOs are not met, repeat testing or report qualified test results.		

Internal Standards: Recommended internal standards include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs.

Surrogates: Appropriate Surrogate Compounds must be added to each sample prior to extraction. Recommended surrogates include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs (must differ from internal standards).

Calibration Verification Standard: Analysis of a second source VOC standard to ensure validity (accuracy) of the calibration. All calibrated and reported parameters must be included.

Continuing Calibration Verification (CCV): Calibration standards (typically a mid-point standard) must be re-analyzed periodically throughout the instrument run to monitor calibration drift.

Prescribed Elements

The following components of this method are mandatory:

a. Preservation as per the Sample Handling and Preservation section is mandatory.

b. Sample holding times must be adhered to. Samples analyzed beyond the stated holding time must be qualified.

c. When using GC/MS, at least two surrogates are required to be added to all samples prior to analysis. Stated calibration and internal standard requirements must be met.

d. Wherever possible, the same sample must be used for the analysis of both VHw6-10 and targeted VOC compounds, so that sub-sampling variability does not affect the calculated VPH result.

e. All target compound analysis must be conducted by GC/MS, except that BTEX, Styrene, and MTBE analysis may alternatively be conducted by GC-PID (Photoionization Detection). GC-PID is less selective than GC/MS, and is much more subject to false positives and false negatives than GC/MS.

f. Samples that exceed the calibration range must be diluted and re-analyzed, or reported as estimated or minimum values.

g. All stated Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

a. Test Methods for Evaluating Solid Wastes – Physical / Chemical Methods, SW-846, 3rd Edition, Method 8260C, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), August 2006, Final Update III. United States Environmental Protection Agency, Washington, D.C.

b. Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, SW-846, Method 5030C, Purge and Trap for Aqueous Samples, Revision 3, May 2003. United States Environmental Protection Agency, Washington, D.C.

c. Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, SW-846, Method 5021A, Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis, Revision 1, June 2003. United States Environmental Protection Agency, Washington, D.C.

d. Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, SW-846, Method 8021B, Aromatic and Halogenated Volatiles by Gas Chromatography using Photoionization and/or Electrolytic Conductivity Detectors, Revision 3, July 2014. United States Environmental Protection Agency, Washington, D.C.

e. 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.

f. 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

March 15, 2017	Updated to current method format. Where applicable, aligned with VOC in solids method, including use of headspace GC/MS and PID for selected analytes. Significantly expanded list of analytes to cover volatile substances in 2017 CSR. Deleted copper sulfate preservation option. Updated QC and internal standard acceptance criteria.
Jun 10, 2007	Preservation options modified to use sodium thiosulfate for chlorinated samples, and sodium bisulfate for non-chlorinated samples.
Apr 5, 2006	Additional analytes added to method as required for Hazardous Waste Leachate Quality Standards.
May 7, 2004	Revised. Additional analytes added. Updated to PBM format. Preservation options modified.

Dec 31, 2000	SEAM codes replaced by EMS codes.
Feb 14, 1994	Publication in 1994 Laboratory Manual.