4. Sampling and Analysis

The objectives of this section are as follows:

- Describe potential sampling concerns when sampling for 1,4-dioxane.
- Identify the common analytical methods available for 1,4-dioxane in different matrices, including water, solids, and air.
- Highlight the benefits and limitations of the available analytical methods.
- Discuss concerns of historical data usability.
- Describe the impact of quality control (QC) parameters (e.g., blanks, laboratory control samples) on data usability.

4.1 1,4-Dioxane Sampling

Conventional equipment and/or sampling methods are generally acceptable when sampling for 1,4-dioxane in different matrices and are summarized in Figure 4-1. Proper quality control (e.g., collection of field blanks) should always be in place to monitor potential issues. This section provides information for groundwater and soil sampling and equipment decontamination procedures when 1,4-dioxane is a contaminant of concern.

MEDIUM	Solid Samples		Water Samples[1]		Air Samples
MATRIX	Soils	Sediments	Groundwater	Surface Water	Air
SAMPLING EQUIPMENT AND TECHNIQUES	Hand augers Direct push Split spoon En Core™ Terra Core™	Spade/shovel Eckman dredge Ponar grab Bucket or tube auger	Low-flow submersible pumps No purge passive or grab sampler[2] Bailers Volume purging Peepers	Dip samplers Direct fill Discrete-depth sampler Peristaltic pump	Canister Sorbent tubes

1 Drinking water samples are obtained directly from the faucet.

2 Limitations summarized in section 4.1.2.

Figure 4-1. Conventional sampling equipment and techniques.
Source: ITRC 1,4-Dioxane Team, 2020.

4.1.1 How Physical Characteristics Affect Water and Solid Sampling Techniques

Based on 1,4-dioxane's physical characteristics, groundwater sampling procedures for either subsequent VOC or semivolatile organic compound (SVOC) analyses can be used. Ultimately, the choice of procedures will depend on the data quality objectives and regulatory requirements. Soil sampling procedures for either subsequent VOC or SVOC analysis can also be used, but if the soil contains little to no moisture, soil sampling procedures for USEPA SW-846 Method 5035A/8260 (En Core™/Terra Core™ type samplers) should be used.

Background

In aqueous matrices, 1,4-dioxane exhibits strong polar compound-like characteristics similar to both VOCs and SVOCs, such that specific considerations should be made when selecting a sampling or analytical method. Sampling for 1,4-dioxane can be impacted by its polar-like characteristic, vapor pressure, boiling point, and partitioning coefficient (see Tables 3-1 for information on 1,4-dioxane's chemical and physical properties). These characteristics present challenges to the sampling and the analysis (see Section 3 and Section 4.2.1). Section 4.1.5 discuss the various analytical methods that may be used in different matrices. USEPA SW-846 Method 8270 and USEPA Method 522 (a drinking water method) are designed for the analysis of SVOCs and are not generally appropriate for VOCs due to the loss of chemicals caused by volatilization [(USEPA 2008b); (USEPA 2018d)]. In contrast, sampling methods associated with USEPA SW-846 Method 8260 are designed for VOCs and are intended to minimize the volatilization of chemicals from the sample (USEPA 2018c). Where benzene and toluene are always analyzed as a VOC, 1,4-dioxane can be analyzed as a VOC (e.g., by Methods 8260, 624, and 1624) or as a SVOC (e.g., by Methods 8270 and 522). As a pure product, 1,4-dioxane acts as a VOC, with a vapor pressure between that of benzene and toluene. **Table 4-1** shows the vapor pressure of 1,4-dioxane compared to some other common VOCs and SVOCs.

Table 4-1. Vapor pressure comparison

Compound	**Vapor pressure[1] (mm Hg)**
Benzo(a)pyrene	5.49E-9
PCB-Congener 47	8.63E-5
Naphthalene	8.50E-2
Tetrachloroethylene	18.5
Toluene	28.4
1,4-Dioxane	**38.1**
Benzene	94.8
Vinyl chloride	2.98E3

[1] *https://comptox.epa.gov/dashboard*

Source: https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID4020533

Groundwater

Volatilization from an aqueous sample would depend on the Henry's law constant rather than the vapor pressure (see Section 3.1 for further information). Because its Henry's law constant is low, 1,4-dioxane has a volatilization potential similar to polycyclic aromatic hydrocarbons (PAHs; e.g., benzo[a]pyrene) and polychlorinated biphenyls (PCBs). **Table 4-2** shows the Henry's law constant of 1,4-dioxane compared to some other common VOCs and SVOCs.

Table 4-2. Comparison of Henry's law constants

Compound	Henry's law constant[1] (atm-m^3/mole)
Benzo(a)pyrene	4.57E-7
1,4-Dioxane	**4.8E-6**
PCB-Congener 47	1.90E-4
Naphthalene	4.40E-4
Benzene	5.55E-3
Toluene	6.64E-3
Tetrachloroethylene	1.77E-2
Vinyl chloride	2.78E-2

[1] *https://comptox.epa.gov/dashboard*

Source: https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID4020533

Because of 1,4-dioxane's low Henry's law constant, following typical groundwater sampling procedures for SVOCs is appropriate for 1,4-dioxane. No precautions to prevent volatilization would be needed beyond those that would be used for other chemicals analyzed by a SVOC analytical method. While not required, sampling procedures for VOCs may be equally acceptable.

Soil

For soil samples, if any soil moisture is present, the high solubility and very low sorptive characteristics would result in any 1,4-dioxane primarily being contained in the soil moisture. Volatilization from the soil moisture would again be controlled by the Henry's law constant, and sampling techniques used for SVOCs (i.e., homogenization and collection in 4–8 oz. glass jars) would be appropriate. In arid climates, such as those found in the desert Southwest or potentially under structures, samples that have little to no soil moisture could potentially contain nonaqueous 1,4-dioxane. In these cases, volatilization potential would be a function of the vapor pressure, and soil sampling procedures for USEPA SW-846 Method 5035A/8260 (En Core™/Terra Core™ type samplers) should be used.

4.1.2 General Groundwater Sampling Considerations for 1,4-Dioxane

Passive Diffusion Sampling

Practitioners have evaluated and used various methods and devices for sampling 1,4-dioxane in groundwater. The following properties of 1,4-dioxane do not create any special concerns for groundwater sampling:

- Does not adhere strongly to sampling equipment
- Is not expected to be introduced from sampling equipment
- Is not strongly sorbed to suspended particles
- Is not expected to be lost to volatilization

While some passive diffusion bags (PDBs) work well for groundwater sampling [(ITRC 2004); (ITRC 2006)], PDBs that are not water permeable have been found to be ineffective in sampling for 1,4-dioxane. In particular, PDBs using a single low-density polyethylene (LDPE) membrane for VOCs do not diffuse the 1,4-dioxane molecule and should not be used for 1,4-dioxane sampling. This is a limitation of the membrane and not of the underlying diffusion or passive sampling technology. This limitation may be overcome using different membrane materials or pore sizes that facilitate diffusion of 1,4-dioxane into the sampler. Two examples of commercially available passive diffusion samplers that employ membranes that facilitate the

diffusion of 1,4-dioxane into the sampler are the following:

- Rigid Porous Polyethylene (RPP) Passive Diffusion Sampler
- Dual Membrane Passive Diffusion Sampler

Check with the manufacturer and regulatory authorities before using PDBs for 1,4-dioxane sampling.

Low-Yield Formations

Note that, typically, when 1,4-dioxane analyses of water samples are performed using USEPA SW-846 Method 8270, a higher volume (potentially 2 L) of water is required than when 1,4-dioxane analyses of water samples are performed using USEPA SW-846 Method 8260 (120 mL). As discussed in Section 4.2 , analysis of 1,4-dioxane in water samples by USEPA SW-846 Method 8270 may be preferred, but if samples are collected in low-yield formations, analysis using USEPA SW-846 Method 8260 may need to be considered if other project objectives (e.g., low enough RLs) will still be achieved [(USEPA 2018c); (USEPA 2018d)].

4.1.3 General Soil Sampling Considerations for 1,4-Dioxane

Volatilization in Dry Soil

As described above in Section 4.1.1 , 1,4-dioxane can volatilize from dry soil samples, so these soils should be sampled using the sampling procedure described in USEPA SW-846 Method 5035A with subsequent USEPA SW-846 Method 8260 for analysis to reduce the potential for volatilization. No specific soil moisture levels have been identified as a cut-off for this consideration, so when in doubt, the VOC sampling procedures should be considered. The presence of dry soils may only be an issue in certain geographies (e.g., southwest United States) or specific site conditions (e.g., under structures). If any soil moisture is present, sampling techniques used for SVOCs (i.e., homogenization and collection in 4-8 oz. glass jars) may be equally appropriate.

VOC Preservation Methods

Most investigations will be evaluating direct exposure of 1,4-dioxane from soil and in general, direct exposure standards do not require low RLs. Therefore, when USEPA SW-846 Method 8260 is used, low-level preservation, as described in **Table 4-3**, likely will not be required, and samples can be preserved in methanol only (medium-level preservation). However, if migration to groundwater is being evaluated, low-level preservation likely will be required due to the need for lower RLs.

4.1.4 Equipment Decontamination Precautions

1,4-Dioxane is a common impurity in detergents (see Section 1). In early 2014 (DiGuiseppi et al. 2015), 1,4-dioxane was detected at elevated concentrations in leachate from a widely used decontamination detergent. Because manufacturing processes can introduce 1,4-dioxane into cleaning products through ethoxylation, care should be taken to prevent residual detergents or surfactants from remaining on sampling equipment. In studying the potential presence of 1,4-dioxane in detergents used for decontamination of sampling equipment, researchers demonstrated that some common products were free of 1,4-dioxane if used in accordance with the manufacturer's instructions (DiGuiseppi et al. 2015). The collection of equipment blanks is useful for the detection of any residual 1,4-dioxane on the sampling equipment.

Disposable sampling equipment reduces the likelihood of cross contamination and reduces the need for equipment decontamination.

4.1.5 Sampling Containers, Preservation Requirements, and Holding Times

Table 4-3 provides a summary of the typical sampling containers, preservation methods, and holding times when sampling for 1,4-dioxane in different matrices.

Table 4-3. Containers, preservation, and holding times for 1,4-dioxane

Matrix	Analytical method	Typical collection volumes and containers & Containers	Preservative	Holding time (Schep et al. 2009)

Aqueous	USEPA SW-846 Method 8260 (ambient and heated purge) (full-scan and SIM)	Three 40-mL VOA vials with PTFE-lined screw caps (one 40 mL for analysis; remaining vials for screening and backup)	No headspace; HCl to pH < 2; Cool to 0°C–6°C. If residual chlorine is present, pre-preserve vials with sodium thiosulfate (3 g/40 mL).	***Analysis:***7 days from collection if pH ≥ 2 ***Analysis***: 14 days from collection if pH < 2
Aqueous	USEPA Method 624	Three 40-mL VOA vials with PTFE-lined screw caps (one 40 mL for analysis; remaining vials for screening and backup)	No headspace; HCl to pH < 2; Cool to 0°C–6°C. If residual chlorine is present, pre-preserve vials with sodium thiosulfate (3 g/40 mL).	***Analysis:*** 7 days from collection if pH ≥ 2 ***Analysis***: 14 days from collection if pH < 2
Aqueous	USEPA SW-846 Method 8270 (full-scan and SIM)	Two 1-L amber glass bottles with PTFE-lined screw caps (1 L for extraction and 1 L for backup)*	Cool to 0°C–6°C.	***Extraction:*** 7 days from collection ***Analysis:*** 40 days from extraction. Extract may be frozen for up to 1 year to arrest HT.
Drinking Water	USEPA Method 522	Two 500-mL glass bottles with PTFE-lined screw caps (1 container for extraction and the other for backup)	Sodium sulfite (50 mg/L) and sodium bisulfate (~ 1 g/L); pH < 4; Cool to ≤ 10°C.	***Extraction:*** 28 days from collection ***Analysis:*** 28 days from extraction if extracts are stored in the dark at –5^{0}C
Aqueous	USEPA Mehtod 1624	Three 40-mL VOA vials with PTFE-lined screw caps (40 mL for analysis; remaining vials for screening and backup)	No headspace, HCl to pH < 2; Cool 0°C–4°C. If residual chlorine is present, pre-preserve vials with sodium thiosulfate (10 mg/40 mL).	***Analysis***: 14 days from collection
Solid	USEPA SW-846Method 8260 (ambient and heated purge) (full-scan and SIM)	Terra Core™ sampler with three 40-mL VOA vials with PTFE-lined screw caps (two 40 mL for low-level analysis; one 40 mL for medium-level analysis) or three En Core™ samplers	VOA vials are preweighed and pre-preserved prior to addition of sample. ***Low-level preservative*** = 1 g sample: 1 mL water (with or without sodium bisulfate). ***Medium-level preservative*** = 1 g sample: 1–2 mL methanol (typically 5 g of soil in 5–10 mL methanol). Sample extruded from Terra Core™ sampler into pre-preserved vials on site; preservative must cover sample; Cool to 0°C–6°C; low-level vials stored at <–7°C within 48 hours and medium-level vials stored at 0°C–6°C. ***En Core™ samplers***: Must be preserved as described above within 48 hours.	***Analysis (low-level):*** 48 hours from collection if not frozen ***Analysis (low-level):*** 14 days from collection if frozen within 48 hours of collection ***Analysis (medium-level):*** 14 days from collection

Solid	USEPA SW-846Method 8270 (full-scan and SIM)	One 4- to 8-oz glass jar with PTFE-lined screw cap	Cool to 0°C–6°C. May be frozen at lab to <–10°C.	***Extraction:*** 14 days from collection. If sample is frozen to arrest HT, HT extends to up to 1 year from collection ***Analysis:*** 40 days from extraction. Extract may be frozen for up to 1 year to arrest HT.
Air	USEPA TO-15	One 1-L to 6-L evacuated, passivated stainless-steel canister	None	***Analysis:*** 30 days from collection
Air	USEPA TO-17	Two sorbent tubes	Sealed tubes wrapped in aluminum foil (uncoated side facing tube) and placed in clean amber glass container. Store at <4°C.	***Analysis:*** 30 days from collection
*Check with the laboratory on whether a reduced volume option is available for the 8270 analysis. HCl: hydrochloric acid; PTFE: polytetrafluoroethylene; SIM: selective ion monitoring; VOA: volatile organic analyte. Preservation and HT requirements are standard VOC/SVOC requirements from the listed method references. Analytical laboratories should be consulted for proper containers and preservatives for all matrices.				

4.2 1,4-Dioxane Analysis

4.2.1 How Physical Characteristics Affect Analytical Techniques

Due to its chemical properties, 1,4-dioxane is particularly difficult to purge or extract from water matrices. Its vapor pressure, boiling point, and partitioning coefficient make it preferentially favor being in aqueous solutions, limiting its susceptibility to extraction, resulting in low recovery. These characteristics present challenges to the analytical chemist in making accurate and precise measurements of the analyte at low levels in aqueous matrices. This is particularly challenging at levels now considered relevant (i.e., regulatory limits). Detection at levels approximating 0.2 micrograms per liter (µg/L) (or 0.2 parts per billion [ppb]) necessitates analytical procedures that are either optimized specifically for overcoming these characteristics, and/or designed to mitigate their effects on analyte recovery. Refer to Section 3 for more information of the unique properties of 1,4-dioxane (e.g., isotope dilution techniques; see Section 4.2.3.1).

4.2.2 Sample Preparation Method Summary

The methods detailed in **Table 4-4** use one of four principle techniques of sample preparation: purge-and-trap, organic solvent extraction, solid-phase extraction (Alvarez-Cohen and Speitel 2001), or solid sorbent trapping. Each employs some form of target analyte extraction and concentration prior to instrumental analysis.

Table 4-4. Method techniques

Analytical Method	**Preparation technique**
Methods 8260, 624, and 1624	Water: Purge-and-trap (Method 5030)
	Solid: Purge-and-trap (Method 5035)

Method 8270	Water: Organic solvent extraction (Methods 3510, 3520) Solid phase extraction (Alvarez-Cohen and Speitel) (Method 3535)
	Solid: Organic solvent extraction (Methods 3540, 3546, 3550)
Method 522	Drinking water: SPE Solid: Not applicable
Methods TO-15 and TO-17	Air: Solid sorbent trapping

Subsequent to sample extraction and concentration, each of these techniques employ a gas chromatography (GC) coupled to a mass spectrometer (MS) detector for instrumental analysis. GC allows for separation of the individual sample constituents (i.e., target analytes), and the MS detector is used for constituent detection and identification. Each analytical method is discussed in detail in Section 4.2.3. The ultimate analytical method selected will depend on the project objectives.

4.2.3 Analytical Method Summary

There are several analytical methods for the detection of low levels of 1,4-dioxane covering a variety of environmental matrices and reporting to different detection levels (as shown in Table 4-5). The matrices typically evaluated for the presence of 1,4-dioxane include aqueous samples; solid samples; and ambient air, indoor air, or soil gas samples.

Analytical methodologies that use a combination of an extraction preparation, GC/MS with selective ion monitoring (Simonich et al. 2013), and isotope dilution generate accurate low-level measurements of 1,4-dioxane. SIM offers greater sensitivity (lower RLs) than GC/MS analyses operated in full-scan electron impact (EI) mode. Using 1,4-dioxane-d8 for isotope dilution yields a “recovery-corrected” final result that can compensate for the analyte’s poor recovery characteristics at low levels as well as correct for potential extraction/analysis losses or sample matrix interferences. For this reason, the isotope dilution analytical approach typically improves accuracy and precision. However, the ultimate analytical method selected will depend on the project objectives.

It is important to review the applicable regulatory agency’s required action levels and to contact the laboratory to ensure the following:

- Ability to achieve the required sensitivity (e.g., RLs low enough to meet project action limits)
- Ability to perform the desired method
- Possession of the appropriate certifications required by the regulatory agency

Table 4-5 lists comments and additional considerations for each method to assist users in choosing the best analytical approach for their project. In addition, Figure 4-2 provides a flow chart that can help users select the appropriate analytical method in the absence of regulatory requirements.

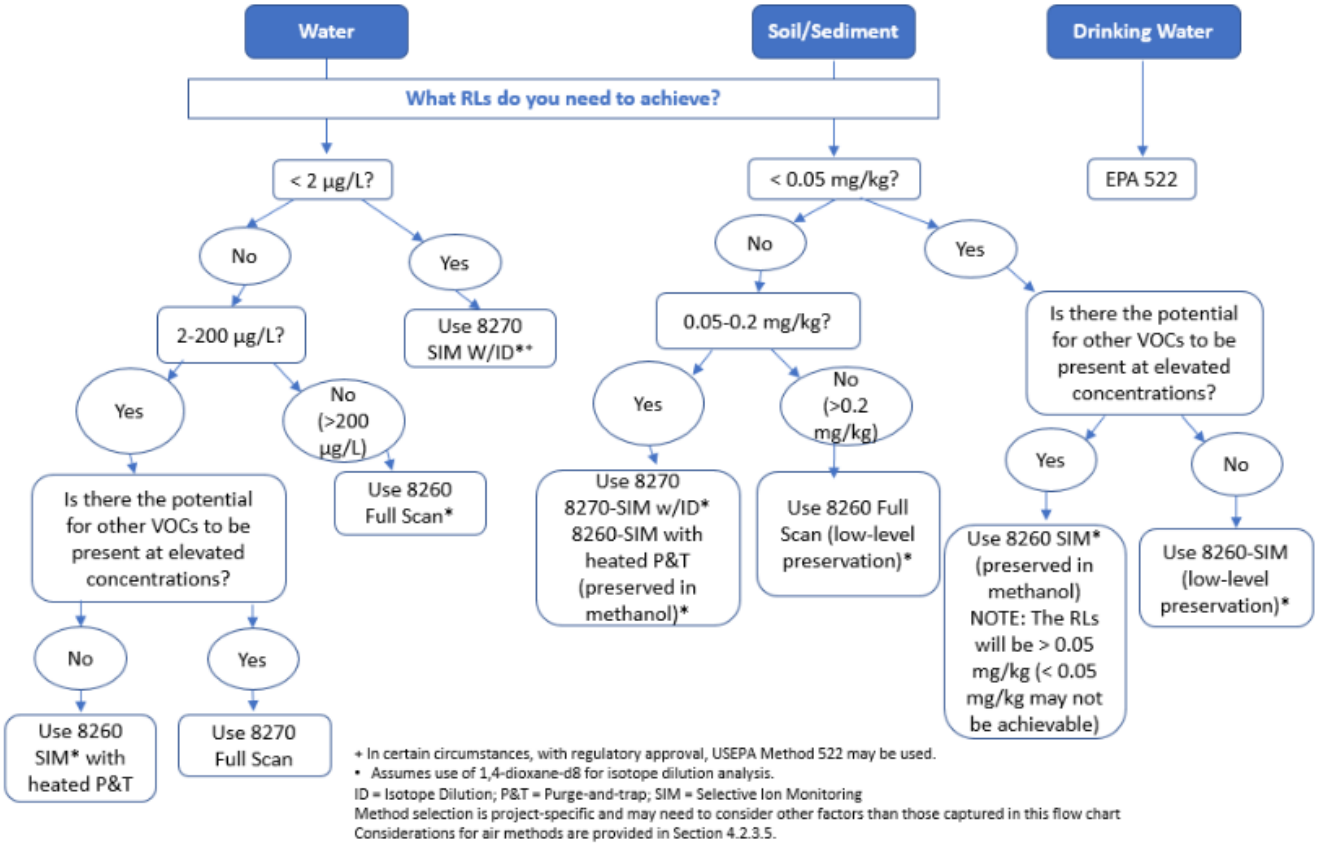


Figure 4-2. Flow chart for selecting an analytical method for 1,4-dioxane in the absence of regulatory requirements.

Source: ITRC 1,4-Dioxane Team, 2020.

Table 4-5. Commonly used analytical methodologies for 1,4-dioxane

Analytical Method Reference	Typical RLs	Approximate cost	Comments/additional considerations
WATER MATRICES			

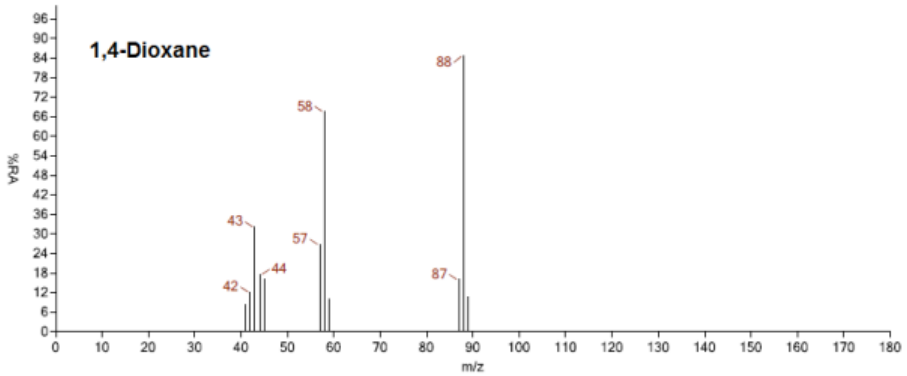
USEPA SW-846Method 8260: VOC	200–500 µg/L	$	Ambient purge-and-trap with full-scan GC/MS (1)Due to poor purging efficiency, RLs may be too high to achieve regulatory standards. (2)1,4-Dioxane-d8 should be used as internal standard.[a] (3)Isotope dilution method compensates for poor purge efficiency. (4)Improved precision and accuracy through isotope dilution (i.e., recovery correction).
	2–5 µg/L	$	Heated purge-and-trap (40°C–80°C) with SIM GC/MS (1) RLs may be too high to achieve regulatory standards. (2) Interferences can result in dilutions due to potential contamination of the instrument, resulting in elevated RLs for 1,4-dioxane. (3) 1,4-Dioxane-d8 should be used as internal standard.[a] (4) Interferences may also cause elevated recoveries of the internal standard, 1,4-dioxane-d8. (5) Isotope dilution method compensates for poor purge efficiency. (6) Improved precision and accuracy through isotope dilution (i.e., recovery correction).
USEPA SW-846Method 8270: SVOC (USEPA 2018d)	5–10 µg/L	$$	Full-scan GC/MS (1) RLs may be too high to achieve regulatory standards. (2) May result in low-biased data and poor recoveries of 1,4-dioxane due to poor extraction efficiency.
	0.15–0.4 µg/L	$$	SIM with isotope dilution GC/MS (1) Suggested isotope for internal standard, 1,4-dioxane-d8. (2) Isotope dilution method compensates for poor extraction efficiency. (3) Improved precision and accuracy through isotope dilution (i.e., recovery correction).
USEPA Method 522 (USEPA 2008b)	0.05–0.1 µg/L	$$	Used for drinking water SPE and SIM GC/MS (1) Generally required method for analysis of drinking water samples.
USEPA Method 624 (USEPA 2016b)	200–500 µg/L	$	Ambient purge-and-trap with full-scan GC/MS (1) Due to poor purging efficiency, RLs may be too high to achieve regulatory standards.

USEPA Method 1624 (USEPA 1990)	50–200 µg/L	$$	Ambient or heated purge-and-trap with isotope dilution (1) RLs may be too high to achieve regulatory standards. (2) Interferences can result in dilutions due to potential contamination of the instrument, resulting in elevated RLs for 1,4-dioxane. (3) Interferences may also cause elevated recoveries of the internal standard, 1,4-dioxane-d8. (4) Isotope dilution method compensates for poor purge efficiency. (5) Improved precision and accuracy through isotope dilution (i.e., recovery correction).
SOLID MATRICES			
USEPA SW-846 Method 8260: VOC (USEPA 2018c)	0.2–0.5 mg/kg[b,c]	$	Ambient purge-and-trap with full-scan GC/MS (1) 1,4-Dioxane-d8 should be used as internal standard.[a] (2) Elevated RLs due to poor purging efficiency.
	0.002–0.005 mg/kg[b,c] 0.05–0.1 mg/kg[c,d]	$	Heated purge-and-trap (40°C–80°C) with SIM GC/MS (1) Not routinely needed for solid samples. (2) 1,4-Dioxane-d8 should be used as internal standard.[a]
USEPA SW-846 Method 8270: SVOC	0.05–0.2 mg/kg[c]	$$	Full-scan GC/MS (1) May result in low-biased data and poor recoveries of 1,4-dioxane due to poor extraction efficiency.
	0.00067 mg/kg[c]	$$	Full-scan with isotope dilution GC/MS (1) Suggested isotope for internal standard, 1,4-dioxane-d8. (2) Isotope dilution method compensates for poor extraction efficiency. (3) Improved precision and accuracy through isotope dilution (i.e., recovery correction).
AIR MATRICES			
USEPA TO-15: VOC	0.7–1.0 µg/m3	$$$	Full-scan GC/MS
	0.4–1.0 µg/m3	$$$	SIM GC/MS
USEPA TO-17: VOC	1.1–11 ng/tube	$$$	Thermal desorption/full-scan GC/MS

GC/MS: Gas chromatography/mass spectrometry RL: Reporting limit SIM: Selective ion monitoring SPE: Solid-phase extraction SVOC: Semivolatile organic compound VOC: Volatile organic compound a. When 1,4-dioxane-d8 is used as an internal standard in 8260 analyses, this is comparable to isotope dilution. b. Assumes samples preserved using low-level preservation method in Table 4-3. c. RLs assume 100% solids content; RLs and results should be corrected for percent solids. d. Assumes samples preserved using medium-level preservation method in Table 4-3. $–$$$: Relative costs of analysis	Notes: • Other analytical methods may be available but are not commonly used on environmental samples. • Check with the appropriate regulatory agency for any state-specific requirements. • See Section 4.2.3.1 for further explanation of the isotope used as an internal standard. • Listed RLs are based on consultation with commercial laboratories and represent typical RLs that can be readily achieved; project-specific RLs may be different.

4.2.3.1 Gas Chromatography—Mass Spectrometry

This section discusses GC/MS methods and different calibration models. Constituent detection and identification are accomplished by measurement of the compound retention time (the time at which the compound elutes from the GC column) and evaluation of the analyte's ionization fragmentation pattern (mass spectrum) as compared to that compound's retention time and mass spectrum from an authentic standard. Mass spectral measurements rely on the compound's ionization fragmentation pattern, or mass spectrum, for identification and quantification. The mass spectrum generated by the detector is specific to the analyte's chemical structure and yields positive constituent identification of the analyte by comparison of its spectral pattern to that of a verified spectrum of the analyte. The mass spectrum also provides a basis for quantification by using the response measurement of one or more mass fragments specific to that analyte. **Figure 4-3** shows an example of the mass spectra for 1,4-dioxane and the internal standard 1,4-dioxane-d8. These spectra exhibit the characteristic mass fragments of 88, 58, and 43 for 1,4-dioxane and 96, 64, and 46 for 1,4-dioxane-d8. Typically, analyte response and quantification is based on the most intense mass fragment in the spectral pattern. In this instance, mass 88 is commonly used for quantification of 1,4-dioxane, and mass fragment 96 is commonly used for the quantification of 1,4-dioxane-d8.



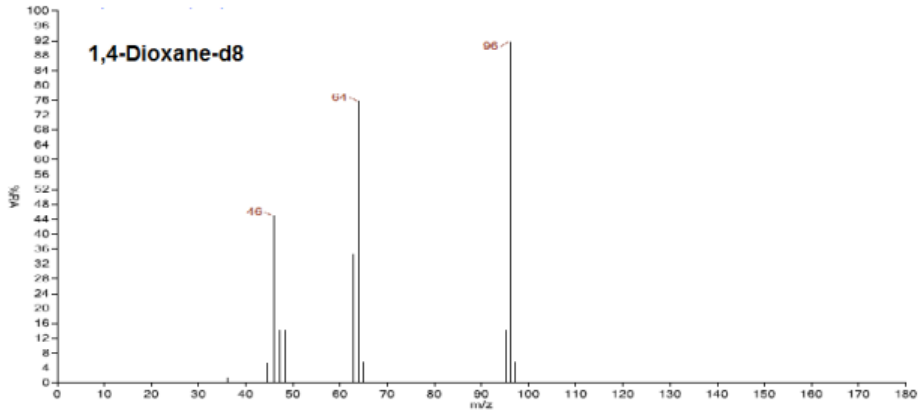


Figure 4-3. Mass spectra: 1,4-dioxane and 1,4-dioxane-d8.

Source: Developed by the ITRC 1,4-Dioxane Team, courtesy of Eurofins.

GC/MS methodologies commonly employ an internal standard (ISTD) technique for analyte quantification. This technique employs the use of a compound, which is not found in nature, that is added to each sample or extract just prior to instrumental analysis and is used in calculating the amount of the target analyte present. The compound(s) chosen for internal standards are often deuterium labeled analogs of one or more of the target analytes. The internal standard(s) are also used to monitor ongoing instrument performance.

When using the internal standard quantification technique, a known amount of the internal standard compound is added to each sample and the ISTD measured response is used in calculating the concentration of the target compound using the formula in Equation 4-1. The internal standards also provide the analyst with a mechanism to monitor instrument performance of the analysis by evaluating the sample's ISTD measured response versus the expected response.

For 1,4-dioxane, the labeled isotope, 1,4-dioxane-d8, is the recommended internal standard. 1,4-Dioxane-d8 can variably be used as an internal standard (added to samples or extracts just prior to instrumental analysis) or for isotopic dilution analyses (IDAs), where the labeled compound is added to the sample prior to any preparation or extraction procedure. (The labeled compound used in an IDA is sometimes called the extracted internal standard [EIS], or simply the surrogate). When IDA is used, the labeled compound is subjected to all of the same procedural biases and extraction inefficiencies that affect the target analyte 1,4-dioxane (see the IDA callout box in Section 4.2.3.3 for more details on IDA). Whether ISTD or IDA analysis is used, 1,4-dioxane-d8 will have a slightly shorter retention time than that of the undeuterated 1,4-dioxane, which also aids in the qualitative identification of 1,4-dioxane in a sample.

Equation 4-1. Internal Standard Formula

$$Analyte\ Concentration = \frac{Area\ Response\ of\ Analyte}{Area\ Response\ of\ ISTD} \times \frac{Amount\ of ISTD}{Analyte\ RRF}$$

RRF (relative response factor) = average of initial calibration response factors

During instrumental analysis, the MS can be operated in one of two mass spectral data collection modes: full-scan or SIM mode. Full-scan mode acquires mass spectral data across a continuous range of masses, typically from mass 35 to 500 daltons. In SIM mode, the MS is configured to acquire spectral data for only a selected number of mass fragments specific to the analyte(s) under investigation.

In SIM mode, the MS is configured to monitor and collect mass intensity data on only a small number of select masses versus acquiring spectral data across an extended range of masses (full scan). This allows the MS to spend more time monitoring each selected mass, thereby increasing sensitivity. Since the MS is acquiring only select spectral data, some specificity may be lost due to the reduced amount of spectral information being collected. In **Figure 4-4**, only masses 58 and 88 are being monitored for 1,4-dioxane, significantly increasing the instrument's dwell time on these two masses, but at the cost of some spectral data used for positive identification.

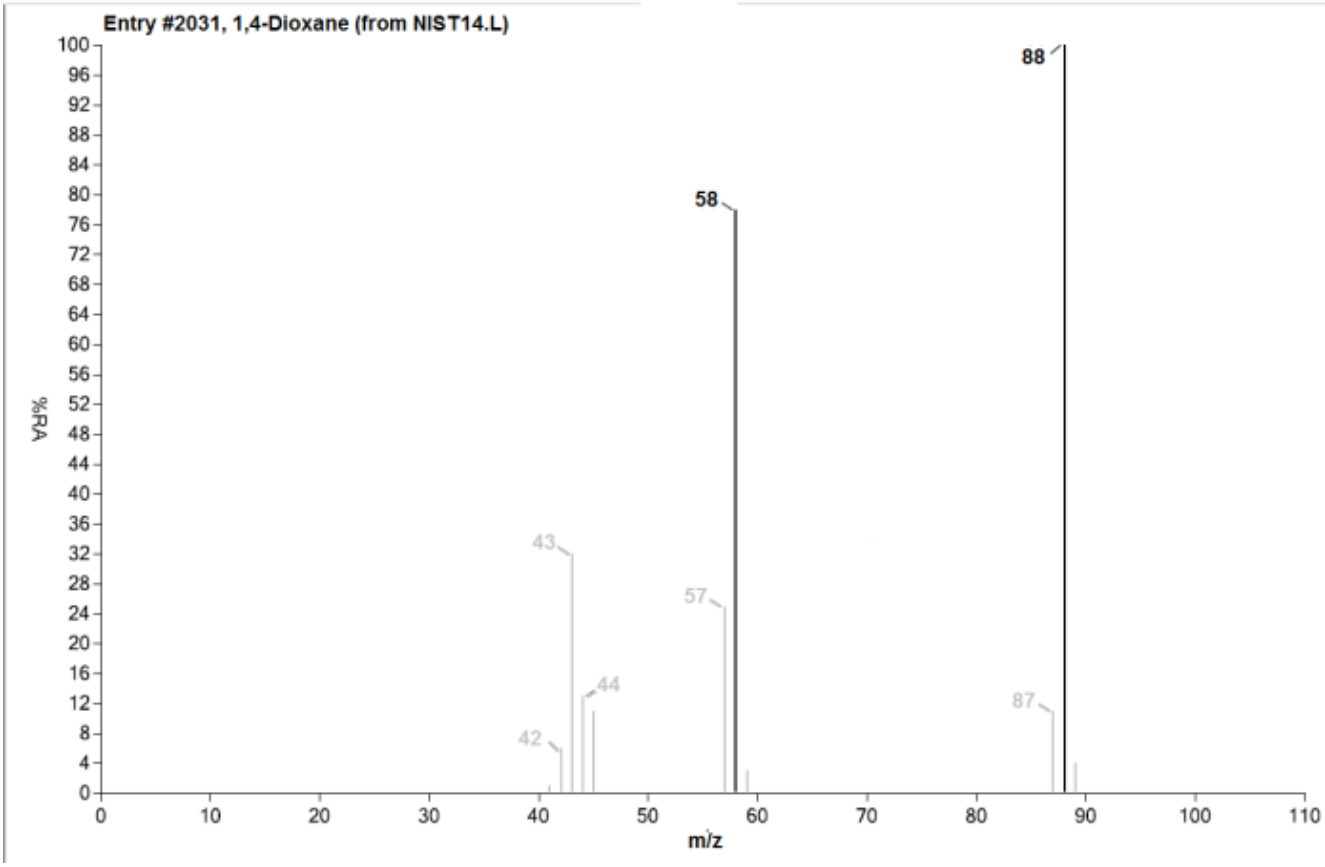


Figure 4-4. Example SIM spectra.
Source: Developed by the ITRC 1,4-Dioxane Team, courtesy of Eurofins.

4.2.3.2 Volatile Methods 8260, 624, and 1624 (Preparation Methods 5030 and 5035)

Methods 8260, 624, and 1624 employ a purge-and-trap sample preparation and concentration technique in which an aliquot of the sample matrix is purged with an inert gas to extract the analyte(s) of interest (**Figure 4-5**). These methods are suitable for VOCs in water and solid/preserved samples per USEPA SW-846 Method 5035A. As the inert gas passes through the sample, it strips (purges) the target analytes from the sample matrix. The gas stream is then directed through a solid sorbent trap where the target analyte(s) are collected (trapped). Once the purge-and-trap step is completed, the sorbent trap is heated and the collected target analyte(s) are transferred to the GC/MS system where they are separated and detected (**Figure 4-6**).

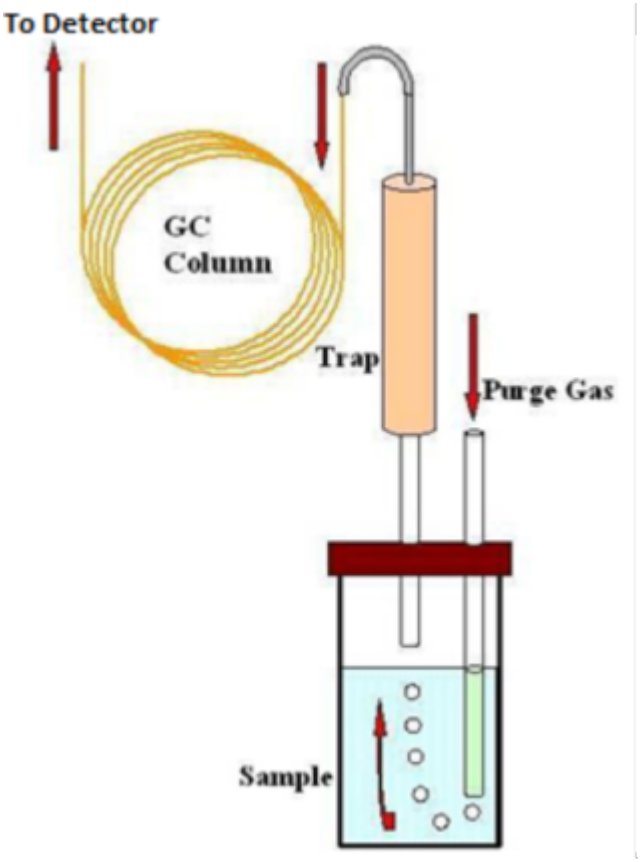


Figure 4-5. Purge-and-trap.
Source: http://departments.agri.huji.ac.il/zabam/Agilent-5975.html

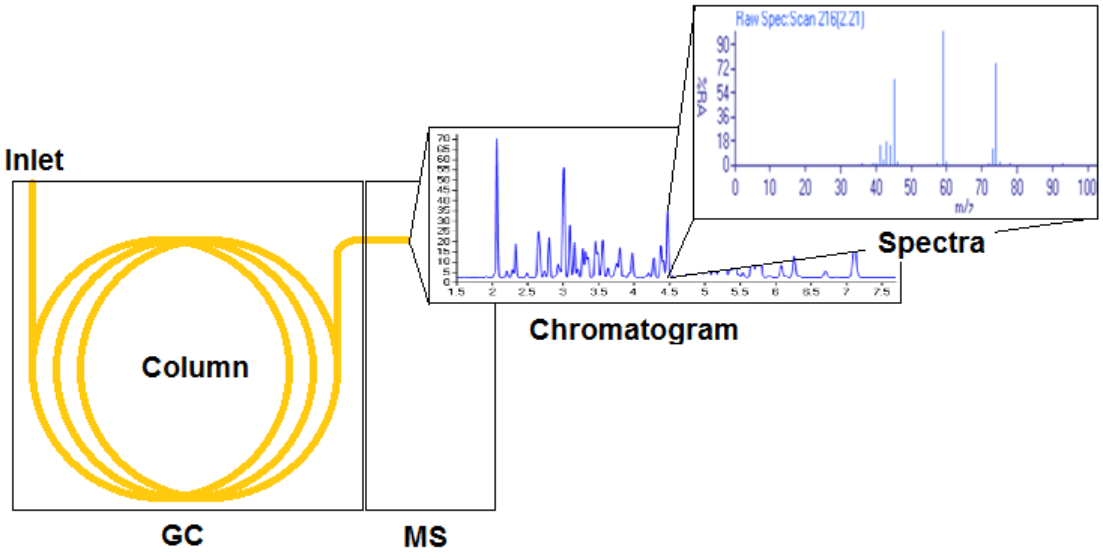


Figure 4-6. GC/MS system diagram.
Source: Developed by the ITRC 1,4-Dioxane Team, courtesy of Eurofins.

For each of these methods, the MS can be operated in either full-scan or SIM mode, depending on the level of sensitivity needed. Note that the SIM mode is not typically used for Method 624.

For analytes with poor recovery characteristics, it is advisable to use an internal standard analyte with properties similar to those of the target compound. Matching the polarity of the target analyte with its internal standard increases the target analyte's RRF, improving the accuracy and sensitivity in quantification.

For the analysis of 1,4-dioxane, it is strongly recommended that the labeled analog, 1,4-dioxane-d8, be used as the internal

standard. Since there is no extraction process prior to the purge-and-trap, use of 1,4-dioxane-d8 in the VOC analysis is an isotopic dilution technique that can help mitigate analyte losses or biases incurred during sample purging and analysis procedures. See the IDA callout box in Section 4.2.3.3.

Customarily, Method 8260 uses ambient purge temperatures for water samples and a heated purge temperature for soils, although either sample type (soil or water) may be purged at an elevated temperature to increase the purge efficiency for the analyte(s) under investigation. The use of heated purge is particularly helpful when evaluating polar constituents in aqueous matrices, like 1,4-dioxane. Analytes with polar-like characteristics tend to remain in the aqueous phase during the purge step, resulting in inefficient extraction and poor recovery. This, in turn, can result in elevated RLs.

All purge-and-trap methods will experience the same low recovery of analytes with poor purging characteristics unless modifications are made to optimize the extraction performance during the purge step. The primary modification used to improve recovery is through the use of elevated purge temperatures. Although heated sample purging can be used in either GC/MS operating mode (full scan or SIM), it may be particularly important to use heated purging in SIM mode to achieve sufficient analyte recovery to support detection and RLs at regulatory levels. An additional strategy for improving purge efficiency is to decrease the water sample's ionic strength using a matrix modifier such as NaCl (salt). However, this technique is less common and has potential drawbacks in increased sample manipulation and possible contamination. If a matrix modifier is employed, the entire analytical batch, including the method blank and laboratory control sample, should also contain the matrix modifier so that the accuracy of using the matrix modifier may be evaluated. Note that the GC/MS SIM analysis can be performed without heated purge, but this would not be effective in achieving low RLs.

Analytical Considerations

- Due to 1,4-dioxane's poor purge efficiency and low recovery characteristics, it is important to ensure that the analytical system (GC/MS) has sufficient spectral signal-to-noise response for all monitored mass fragments to support accurate analyte integration and identification. **Figure 4-7** illustrates what might be characterized as a minimum amount of peak signal response to background noise (3:1) needed for positive confirmation of the analyte's presence. This has been an issue with both full-scan and SIM VOC analyses.

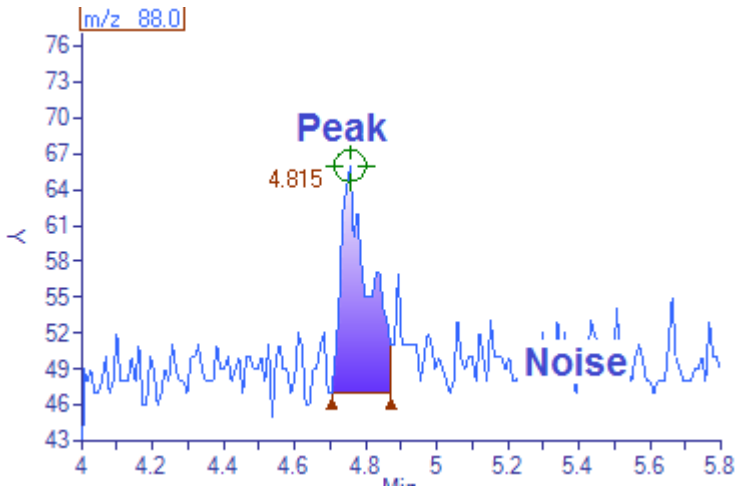


Figure 4-7. Minimum signal-to-noise example.
Source: Developed by the ITRC 1,4-Dioxane Team, courtesy of Eurofins.

- Development of initial calibration RRFs for 1,4-dioxane without the use of 1,4-dioxane-d8 as its internal standard reference may result in the generation of unacceptably low response factors (e.g., RRFs <0.01). Often, these RRFs will exhibit good precision in the initial calibration (i.e., acceptable percent relative standard deviations) because the standard deviation of these low response factors is low, but the subsequent results for 1,4-dioxane can be questionable. Other internal standards may help improve 1,4-dioxane's RRF, but unless these other internal standards act chemically like 1,4-dioxane, the analyses may yield questionable results.

- Due to 1,4-dioxane's solubility, there is an increase in its potential for carryover (the process in which a high-level sample may contaminate subsequent sample analyses). Thus, the laboratory analyst should closely monitor sample analyses for carryover. The purge-and-trap or GC system may become contaminated by a high-level sample, which could result in low levels of 1,4-dioxane carrying over into the next sample analysis. Although this is an issue with any potential contaminant, there are other issues associated with carryover for 1,4-dioxane. The purge-and-trap's internal plumbing is coated with water at all times. 1,4-Dioxane's solubility

means that it can indirectly contaminate the purge-and-trap lines, because it may not be completely removed from the water in these lines during a typical analysis, depending on the laboratory's parameters for desorbing and baking out the purge-and-trap equipment. This is a concern when high-concentration samples are analyzed but also a concern for systems that are not well maintained or optimized. It may be helpful to inform the laboratory on the chain of custody (Chu et al. 2018) when it is known that samples will have elevated concentrations to help prevent carryover issues.

- Achieving the lowest possible detection limit for 1,4-dioxane may not be feasible in instances where sample dilutions are needed due to the presence of comingled target or nontarget analytes. In some instances, it may be necessary for the laboratory to preemptively perform dilutions on samples containing high concentrations of nontarget constituents to protect sensitive instrumentation. This can result in nondetects with elevated reporting and detection limits for 1,4-dioxane. Sample analysis for low levels of 1,4-dioxane can be particularly challenging when evaluating samples from sites heavily impacted by chlorinated solvents, particularly those historically impacted by 1,1,1-TCA or TCE.
- Interferences from other target or nontarget constituents can impact the laboratories' ability to accurately identify or quantify 1,4-dioxane if the interference co-elutes chromatographically with 1,4-dioxane or 1,4-dioxane-d8 and has a mass spectrum or fragmentation masses similar to these compounds. Co-eluting interferences typically result in a positive contribution to the response of one or more critical mass fragments used for identification or quantification. Positive interference to the quantification mass of 1,4-dioxane would result in a high biased result for the analyte, whereas a positive interference to the quantification mass of its ISTD 1,4-dioxane-d8 would result in a low-biased result for 1,4-dioxane (see Equation 1).
- If TCE is present at high enough concentrations, or if it is insufficiently resolved from 1,4-dioxane-d8, it could contribute a significant response to the m/z 96 quantification mass used for 1,4-dioxane-d8, resulting in generation of low-biased values for 1,4-dioxane. As **Figure 4-8** shows, both 1,4-dioxane-d8 and TCE have m/z 96 as part of their fragmentation pattern. Samples should be closely monitored for the presence of high concentrations of TCE and other possible co-eluting interferences, and close attention paid to the relative recovery of the labeled analog and the spectral signatures of both analytes for indications of possible interference. The laboratory may need to use an alternative quantitation ion for 1,4-dioxane-d8 if TCE is present.

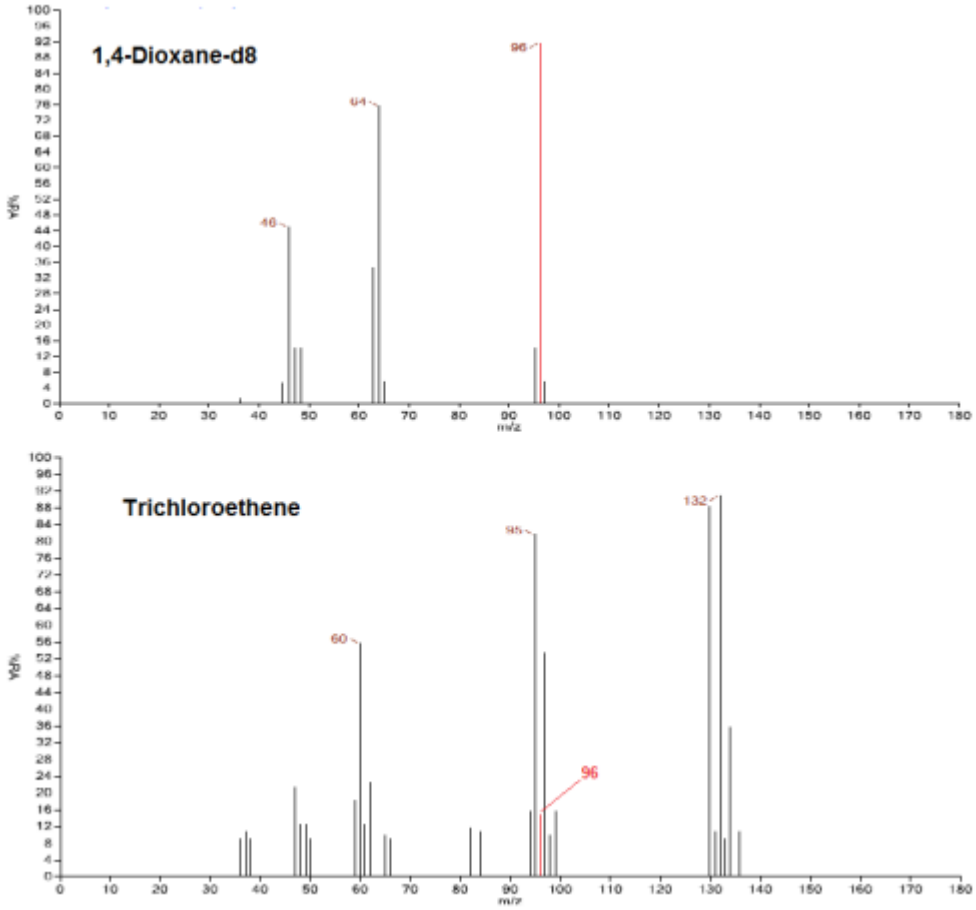


Figure 4-8. 1,4-Dioxane-d8/TCE m/z 96 spectral interference.
Source: Developed by the ITRC 1,4-Dioxane Team, courtesy of Eurofins.

- Methods 8260 and 624 are readily available, whereas Method 1624 is not widely offered. Method 624 is typically used for wastewater and analyses associated with NPDES permits (USEPA 2016b).

4.2.3.3 Semivolatile Method 8270 (Preparation Methods 3510, 3520, 3535, 3540, 3546, and 3550)

Method 8270 incorporates an initial sample preparation technique in which 1,4-dioxane is isolated from the sample matrix through extraction by an organic solvent. This method is suitable for SVOCs in water and solid samples. Extraction is accomplished through the preferential partitioning of the target analyte from the sample matrix into an organic solvent with extraction techniques designed for either water samples (e.g., 3510, 3520; **Figure 4-9**) or soil samples (e.g., 3540, 3550). Aqueous samples may also be extracted using SPE, as described in Section 4.2.3.4. Once extracted, the volume of the organic solvent is reduced through evaporation to a smaller volume, yielding a concentrated sample extract that facilitates analyte detection. Once the sample is extracted and concentrated, an aliquot of the extract is injected into the GC/MS system for component separation and detection. Method 8270 can be operated in full-scan or SIM mode, depending on the level of detection needed.

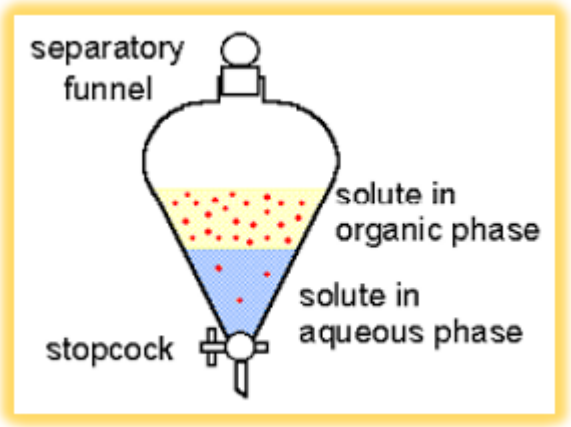


Figure 4-9. Separatory funnel process.
Source: B.M. Tissue, SciMedia, 1996.

Due to its chemical properties, 1,4-dioxane exhibits poor extraction efficiency from water matrices, and as such, it is important to implement strategies to mitigate recovery losses to achieve accurate measurement of the actual amount of 1,4-dioxane in the water sample. It is strongly recommended that the labeled analog, 1,4-dioxane-d8, be used as the EIS, which is also sometimes referred to as the surrogate, to achieve isotope dilution quantification for the target analyte 1,4-dioxane. The isotope dilution form of quantification is identified here as the preferred strategy for improving the accuracy of quantification.

For Method 8270, if isotope dilution is being performed, a known amount of 1,4-dioxane-d8 is added to each sample at the beginning of the extraction procedure prior to the addition of the organic solvent. In this way, the labeled analog is subjected to, and experiences, all of the same process losses and biases as the target analyte 1,4-dioxane. Once the sample is analyzed on the GC/MS system, quantification of 1,4-dioxane using the isotope dilution technique will yield a “recovery-corrected” concentration, minimizing extraction and analysis efficiency related losses. See the IDA callout box in Section 4.2.3.3.

Some regulations require detection of 1,4-dioxane at low levels (e.g., 0.4 µg/L or lower); therefore, analysis by Method 8270-SIM may be required.

Refer to Table 4-4 for a summary of preparation methods. Preparation methods commonly used with Method 8270 include Method 3510 separatory funnel, Method 3520 continuous liquid-liquid, and Method 3535 SPE for water samples; and Method 3540 soxhlet extraction, Method 3546 microwave extraction, and Method 3550 sonication for solid samples. These preparation methods use between 250 and 1,000 mL of samples for waters and typically 30 g for soils and sediments.

IDA is a form of analyte quantification whereby the final analyte amount is adjusted proportionally to that of the recovery of a known and measured amount of an EIS. The labeled analog is added to the sample just prior to sample preparation and is similarly impacted by process losses and biases. In this instance, the deuterium labeled analog 1,4-dioxane-d8 is added to the sample and is used as the basis for quantification of 1,4-dioxane, yielding, in effect, a “recovery-corrected” amount of 1,4-dioxane in the native sample (**Figure 4-10**). In Equation 1, the amount and response of 1,4-dioxane-d8 is used in place of the ISTD.

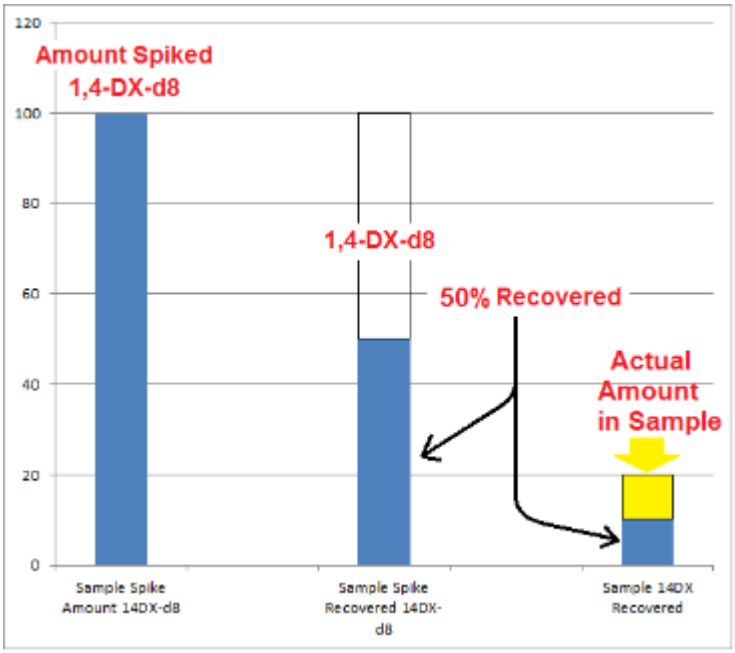


Figure 4-10. IDA recovery.
Source: Developed by the ITRC 1,4-Dioxane Team, courtesy of Eurofins.

Analytical Considerations

- Large dilutions cannot be accommodated by methods employing isotope dilution (diluting out the isotope standard will prevent the ability to perform the quantitation); options would include extracting a smaller amount or volume, using a method with a higher RL, or using a different technique.
- Extraction processes should be optimized to minimize evaporative losses of 1,4-dioxane and the labeled isotope during the sample extract concentration step. However, it should be noted that the use of 1,4-dioxane-d8 and isotope dilution will compensate for any potential evaporative losses of 1,4-dioxane, as their potential for evaporation is similar.
- Solid samples do not typically exhibit the same low-biased recoveries as water samples.

4.2.3.4 Semivolatile Method 522

Method 522 is an SPE procedure that employs column chromatography, whereby target constituents are trapped on a granular solid sorbent material as the sample is passed through. This method is suitable for SVOCs in aqueous samples. Once collected, the target analyte(s) are eluted off of the sorbent using an appropriate organic solvent and the eluent is collected as the sample extract (**Figure 4-11**). The sample extract can then be reduced through evaporation to a smaller volume, yielding a concentrated sample extract that is subsequently analyzed via GC/MS. Method 522 is specific to drinking water samples and uses volumes of 100–500 mL (USEPA 2008b).

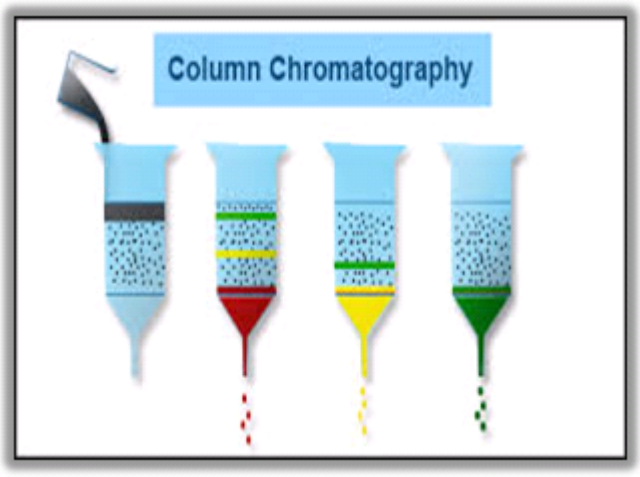


Figure 4-11. Solid-phase extraction.

Source: https://lab-training.com/2013/09/13/what-is-chromatography/

The instrument is operated in SIM mode. However, the method does not use the isotope dilution form of quantification but instead relies on the labeled form of THF (tetrahydrofuran-d8) for conventional internal standard quantification. In addition, Method 522 uses 1,4-dioxane-d8 as a surrogate control, added to samples prior to extraction, for assessing extraction efficiency. Typical recoveries of 1,4-dioxane in laboratory control spikes approximate 80%–90% recoveries. Method 522, normally used only for drinking water samples, is not typically exposed to high concentrations of nontarget constituents or significant matrix interferences, which may indirectly facilitate improved analyte recovery from the matrix allowing for lower detection and RLs. Due to the absence of interferences in most drinking water samples, the use of isotope dilution is less important for this method.

Analytical Considerations

- Interferences could include heavy sediment or suspended solid loads.

4.2.3.5 Air Methods TO-15 and TO-17

Ambient air, indoor air, or soil vapor samples can be evaluated for 1,4-dioxane using Methods TO-15 and/or TO-17, which use GC/MS instrumentation for separation and detection. These methods are suitable for VOCs in air samples. Each method employs specialized sample collection equipment comprising either evacuated sampling canisters (**Figure 4-12**) or solid sorbent collection tubes (**Figure 4-13**) for Methods TO-15 and TO-17, respectively.



Figure 4-12. Summa canister.

Source: Courtesy of Eurofins – https://www.eurofinsus.com/media/161448/guide-to-air-sampling-analysis-2014-06-27_revised-logos.pdf



Figure 4-13. Thermal desorption tubes.
Source: Courtesy of Markes International – https://www.markes.com/land/EN/Sorbent-sampling-tubes-for-thermal-desorption.aspx

Samples can be collected in 1– to 6 L sample canisters, which can be analyzed by Method TO-15. Samples for Method TO-15 can be collected as grab or time-averaged whole air samples (USEPA 1999a). The canister is hooked up to a special sampling manifold on the GC/MS, which employs a multisorbent trap that retains and concentrates the analytes of interest for subsequent transfer (desorption) to the GC/MS system (similar to the process described for the purge-and-trap procedure).

Method TO-17 uses solid sorbent sampling tubes through which the air sample is drawn, capturing the analytes under investigation. Tubes are analyzed using a tube desorption system that is interfaced to a GC/MS system. Method TO-17 sorbent tubes typically require the use of a pump during sample collection.

The use of TO-15 versus TO-17 in the assessment of indoor air and soil gas will likely be based on regulatory requirements; in general, regulators typically prefer TO-15.

Analytical Considerations

- Methods TO-15 and TO-17 can be operated in full-scan or SIM mode.
- Multiple aliquots can be withdrawn from sample canisters; however, if after collection the canister's vacuum is low, accuracy and precision may be poor if the canister is subsampled multiple times. Overpressurization of the canister with zero-grade air at the laboratory may improve subsampling precision but will increase RLs.
- TO-17 sample tubes are typically single assay devices unless the particular tube desorption system is capable of multiple assays from the same tube. Breakthrough of contaminants of concern may occur, which should be monitored.
- Canister and sample collection tubes are reused and must be cleaned and certified prior to use.
- Method TO-17 provides specific guidance on the selection of sorbents and tubes to be used in the collection and analysis of target constituents. Method TO-17 should be consulted prior to sample collection to ensure the appropriate sorbent and sampling volumes are used for 1,4-dioxane.

4.2.4 Emerging Analytical Options

Several emerging analytical techniques are available when 1,4-dioxane is a contaminant of concern.

Phytoscreening (qualitative/semi-quantitative): Phytoscreening can be used for preliminary delineation of 1,4-dioxane in shallow groundwater. The data can also be used to guide the groundwater investigations, improve the efficiency of the data collection, and provide insight into data gaps that may appear after the groundwater investigations. This involves the collection of tree core samples (typically 3 inches long and 0.2 inches in diameter) from the area of interest, with subsequent laboratory analysis for 1,4-dioxane by GC/MS.

Phytoscreening also involves the sampling of plant tissues to assess the distribution of pollutants in the subsurface. As plants have tremendous potential for mass transfer from soil, vapor, and groundwater with the transpiration stream, novel sampling and analysis of the aboveground plant tissues can delineate the below-ground plumes. The chemical properties of 1,4-dioxane are amenable to uptake, and multiple methods have been developed for analyzing plant tissues efficiently via

solid-phase microextraction (SPME) GC [(Bagheri et al. 2019); (Limmer and Burken 2014); (Limmer and Burken 2015)]. It is important to work with the laboratory to determine the best approach.

Environmental molecular diagnostic (EMD) techniques may assist in evaluating distinct 1,4-dioxane sources and the extent of natural or enhanced degradation. These techniques include CSIA, stable isotope probing (SIP), and quantitative polymerase chain reaction (qPCR) amplification of key genes of interest. Each of these techniques is discussed in detail in ITRC'sTechnical and Regulatory Guidance on EMDs. EMDs are specialty analyses that are performed by a limited number of laboratories and by methods that are less standardized than those applied to measure constituent concentrations. Furthermore, the science behind and application of EMDs continues to rapidly evolve. In general, EMDs are best applied with the support of an expert in the field and with adequate preplanning with the laboratory that will perform the analysis. Key sampling and analysis considerations associated with the application of EMDs for 1,4-dioxane include the following:

- **CSIA:** This technique measures stable isotope ratios of elements within contaminants in groundwater, soil, and vapor for evidence of fractionation. CSIA may also be used to estimate degradation rates over the impacted plume, provided that relevant fractionation factors are known and/or groundwater flow characteristics (including the magnitude of dilution) are well defined.

For 1,4-dioxane, CSIA evaluates the stable isotopes of carbon (C^{12} and C^{13}) and hydrogen (H^{1} and H^{2}). Depending on the specific mechanism of degradation, the isotopic effect may be more pronounced in one isotope (see the ITRC CSIA Fact Sheet). Further, using two pairs of stable isotopes provides a two-dimensional aspect to better describe the relationships between analyzed samples, with or without the occurrence of biodegradation.

CSIA analysis requires a minimum mass of the constituent of interest for analysis. In general, larger volume samples are required for CSIA than for analysis of concentrations. There are minimum concentrations required to use CSIA. For the isotopes in 1,4-dioxane—carbon and hydrogen—the minimum concentrations of 1,4-dioxane needed are 10 ppb for the carbon isotope and 100 ppb for the hydrogen isotope. A best practice for CSIA is to confirm with the laboratory what concentrations are needed to perform the analysis. The specific sample volume required may vary by laboratory and should be discussed during project planning. Samples must also be collected concurrently to measure 1,4-dioxane concentrations by standard analytical methods. See Section 6.5.1.1 for additional information on CSIA and limitations.

Because CSIA methods for 1,4-dioxane are evolving and are not standardized, it is important to work with the laboratory to confirm that results will be comparable between relevant data sets and will be presented in reference to accepted international standards.

- **SIP:** This technique uses isotopically labeled contaminants and examines the incorporation of stable isotopes into molecules generated during biodegradation processes (see ITRC's Technical and Regulatory Guidance on EMDs for more information). SIP is a powerful tool for directly and conclusively demonstrating biodegradation. However, because application of this EMD can be costly, a well-designed sampling program developed in consultation with an expert is critical for achieving the full value of the method. Additionally, due to 1,4-dioxane's solubility and nonsorptive nature, additional measures may need to be taken to ensure retention of 1,4-dioxane on the sampler during deployment. For example, in one study conducted at Vandenberg Air Force Base in California, a predeployment leaching of the most labile 1,4-dioxane was conducted prior to sampler deployment (Bell et al. 2016). Additionally, the change in concentration of 1,4-dioxane over the deployment period should be interpreted with caution because the full extent of the loss of isotopically labeled 1,4-dioxane may not be attributable to biodegradation. Notably, the amount of isotopically labeled 1,4-dioxane that is impregnated on (and therefore may be lost from) SIP sampling devices is well below regulatory concentration thresholds.
- **qPCR analysis:** This technique can be used to detect and quantify the genes responsible for degradation of 1,4-dioxane. It can provide information on whether a sample contains microorganisms responsible for biodegradation of 1,4-dioxane. This method simply quantifies the specific genes that are targeted; it may miss microbial community members that facilitate biodegradation but that are not yet recognized or for which appropriate gene targets have not yet been developed or commercialized. Because the state-of-knowledge of microorganisms responsible for 1,4-dioxane biodegradation is rapidly evolving, genetic targets that are commercially available are unlikely to cover all potentially relevant microorganisms. As such, the potential for false negative results must be considered and expectations managed during the planning stage for the sampling program.

qPCR-based identification of broad gene classes (e.g., monooxygenases) that have been implicated in cometabolic biodegradation does not necessarily imply that this process is occurring. This determination must be made based on

multiple lines of evidence. Building multiple lines of evidence should be considered in development of the sampling and analysis strategy.

Collecting representative microbiological samples can be a challenge. This challenge can be mitigated by careful consideration of sampling methods within the context of the questions that these samples are intended to help answer. The most successful application of microbiological tools is often based on direct comparison of identically collected samples—for instance, between sampling locations with distinct characteristics or before and after treatment.

4.3 1,4-Dioxane Data Evaluation

It is imperative that the usability of the analytical data, as discussed in the sections below, be evaluated before the data are used for project objectives and ultimately risk assessment. It is also important to remember that data quality and data usability issues may exist even when laboratories are certified and follow all method-required procedures.

Combining or comparing data sets for 1,4-dioxane from one sampling event to another or from data generated by two laboratories can be complicated. For example, historical data may have RLs for 1,4-dioxane that are quite high so that the presence or absence of 1,4-dioxane in these data might be uncertain relative to data generated using newer methods (e.g., isotope dilution techniques) with better sensitivity. Therefore, the data user should understand the limitations of the data sets with respect to the project objectives before using results to make project decisions; this includes understanding the differences between methods used to generate the data and the impact of quality control deviations on the results. The guidance given in **Table 4-6** may aid in this determination.

4.3.1 Analytical Method Sensitivity

Determining Analytical Method Sensitivity in Comparison to Project Objectives

1,4-Dioxane's analytical method sensitivity requirement is determined by the relevant and applicable regulatory limit (often called the Project Action Limit [PAL]) for this compound based on the matrix analyzed and the data's intended use (e.g., the PAL for a drinking water evaluation may differ from an ecological risk assessment PAL). The method of analysis should be chosen so that the RL (also called the quantitation limit [QL], practical quantitation limit [PQL], or limit of quantitation [LOQ]) is at or below the PAL. The RLs (and not the method detection limits [MDLs]) for each method should be evaluated versus the PAL prior to submitting samples to the laboratory. The RLs should be below the project screening criteria to ensure project objectives are achieved. Table 4-5 lists typical RLs for 1,4-dioxane.

For each matrix and preparation and analysis method, the laboratory must determine the MDL, which is the lowest concentration for 1,4-dioxane that can be detected for the matrix and method where there is confidence that the signal observed is for 1,4-dioxane and not due to background. The MDL is generally 2–5 times below the RL. The RL must be at or above the lowest concentration standard analyzed during the initial calibration of the instrument on a sample-specific basis (i.e., accounting for all sample preparation and analytical factors, such as moisture content, dilutions, sample size), so that the RL is accurate and supported by the calibration. Results reported between the MDL and RL are considered estimated data and are qualified "J" due to uncertainty in quantitation below the instrument calibration range. Nondetect data should be reported at the RL and qualified "U" to indicate that 1,4-dioxane was not detected at or above the RL concentration.

Determining Usability of Nondetect Results

The method's sensitivity is most important for nondetect data and cannot be evaluated without also taking into consideration the accuracy of the measurement. If 1,4-dioxane is reported accurately at a level exceeding the PAL, sensitivity is considered acceptable even if the RL is above the PAL since there is no uncertainty that the PAL was exceeded. However, if 1,4-dioxane is nondetect at a level below the PAL, but there is an indication that the result may be biased low (e.g., QC such as surrogates, laboratory control sample [LCS], or matrix spike [MS] are recovered below criteria), the sample concentration may exceed the PAL and the sensitivity objective may not be achieved. Therefore, sensitivity of results (detected results and nondetects) is judged relative to the PAL, taking into consideration whether 1,4-dioxane is detected and whether the result has a bias that would make the 1,4-dioxane uncertain relative to the PAL. If the sensitivity objective is not achieved, the data may or may not be usable.

4.3.2 Evaluation of Potential Biases/Uncertainty from Laboratory QC Data

Many components to the data quality assessment can affect the usability of 1,4-dioxane data in all matrices. There are three evaluation categories used in the assessment of data: laboratory performance, field performance, and matrix interferences. QC results for laboratory data should always be evaluated with respect to the intended use of the data and the project-specific objectives that were established for the types of decisions that will be made using the data. Note that data evaluation or validation guidelines do not currently exist for 1,4-dioxane methods. However, USEPA and DOD guidance for

evaluating VOC and SVOC data may be applicable to 1,4-dioxane: specifically, ***USEPA National Functional Guidelines for Organic Superfund Methods Data Review* (EPA-540-R-2017-002),** January 2017 (USEPA 2017g), and *Data Validation Guidelines Module 1: Data Validation Procedure for Organic Analysis by GC/MS*, May 11, 2020.

The most important goal of data usability is to ensure that the 1,4-dioxane data generated are usable to meet the data needs and that the data user understands any limitations in the use of the data due to potential uncertainty or bias.

Table 4-6 summarizes the typical QC parameters that will be evaluated for 1,4-dioxane analyses. This table provides the following details for each QC parameter: frequency, how the QC parameter is evaluated, the data quality indicator, typical measurement performance criteria, and the ultimate impact on the data's usability, including potential biases, potential uncertainty, or potentially unusable data. Other documents—such as quality assurance project plans (QAPPs), sampling and analysis plans (SAPs), and state-specific criteria (e.g., Massachusetts Department of Environmental Protection Compendium of Analytical Methods)—may take precedence over the recommendations in this table.

Table 4-6. Evaluation of data usability for 1,4-dioxane

QC Check	Frequency	How is QC generated or evaluated?	Data quality indicator	Measurement performance criteria	Impact on data usability
Sample collection*	Every sample	Ensure proper sample collection techniques and proper containers are used. Ensure COC is properly executed.	Sampling accuracy	Sample/LD or FD precision may indicate error in collection. ***Refer to Table 4-3 for container requirements.*** ***TO-15*:** Canisters must be at >25″ Hg vacuum prior to filling and should be ~5″ Hg after collection.	• If water VOCs have headspace, 1,4-dioxane may be biased low. • If soil VOCs are not covered by preservative prior to analysis, 1,4-dioxane may be biased low. • If dry soil is homogenized for 8270, 1,4-dioxane may be biased low. • If TO-15 canister vacuum at lab differs by more than ±5″ Hg from field final vacuum, 1,4-dioxane may have indeterminate bias.

Preservation*	Every sample	Chemical preservative added by lab to containers prior to shipment to the field; water and soil samples transmitted to the lab cooled to method-required temperature (e.g., <6°C)	Sampling accuracy	***Refer to Table 4-3 for preservation requirements.*** VOC sample pH <2, no headspace and Method 522 sample pH <4 at time of lab analysis. ***VOCs:*** If pH ≥ 2, analysis should occur within 7 days of sample collection.	• If cooler temperature > method or project criteria, 1,4-dioxane may be biased low. • Water VOCs: If pH≥ 2 and sample analyzed >7 days from collection, 1,4-dioxane may be biased low. • If soil VOCs not preserved, nondetects may not be usable (false negatives) and detects may be biased low. • Method 522: If pH >4, 1,4-dioxane may be biased low.
Holding time	Every sample	Time from collection to analysis (VOC methods) or time from collection to extraction and from extraction to analysis (SVOC methods)	Analytical accuracy	Extraction and/or analysis within HT. ***Refer to Table 4-3 for holding time requirements.***	• If HT exceeded by ≤2x HT specified in Table 4-3, 1,4-dioxane may be biased low. • If HT exceeded by >2x HT given in Table 4-3, 1,4-dioxane detects may be biased low and nondetects may not be usable.
Method blank	***Waters and soil*****:** 1 per preparation/analytical batch of up to 20 field samples. ***Air*****:** 1 for each 24 hrs of analysis.	***Waters and soil*****:** Analyte-free matrix processed in the lab in the same manner as samples. ***TO-15:*** Lab-pressurized canister with ultra-pure zero air. ***TO-17*****:** Two sorbent tubes conditioned as per tubes for sampling and stored at lab from time tubes sent to field until field sample analysis.	Analytical accuracy	1,4-dioxane < RL	• If 1,4-dioxane detected in MB, 1,4-dioxane in all samples in the affected batch may be biased high or may be false positives.

Field blank*	1 per day of sample collection for waters per SAP or QAPP requirements	***Waters and soil*:** Analyte-free water sent from lab to field, bottle opened during sample collection, resealed, and sent back to the lab with samples. ***TO-17*:** Sorbent tubes sent to field, uncapped, and immediately recapped and sent back with samples.	Analytical and field collection accuracy	1,4-dioxane < RL	• If 1,4-dioxane detected in FB, 1,4-dioxane in samples associated with FB may be biased high or may be false positives.
Equipment blank*	1 per type of equipment used in collecting samples per SAP or QAPP requirements	***Waters and soil*:** Analyte-free water sent from lab to field, poured through equipment after decontamination, and sent back to the lab. ***TO-15*:** Ultra-pure zero air used to fill precleaned canister in the field.	Analytical and field collection accuracy	1,4-dioxane < RL	• If 1,4-dioxane detected in EB, 1,4-dioxane in samples collected using the same equipment as EB may be biased high or may be false positives.
Trip blank*	1 per cooler for VOC analysis per SAP or QAPP requirements	Analyte-free water in preserved VOA vials accompanying samples back from the field to the lab	Analytical and field collection accuracy	1,4-dioxane < RL	• If 1,4-dioxane detected in TB, 1,4-dioxane in samples received in the same cooler as the TB may be biased high or may be false positives

Laboratory control sample	1 per preparation/analytical batch of up to 20 field samples	***Waters and soils*:** Analyte-free matrix spiked with 1,4-dioxane and processed in the lab in the same manner as samples. ***TO-15:*** Second source calibration gas cylinder.	Analytical accuracy	Recovery within method and/or lab SOP criteria	LCS results affect all the samples in the batch. • If LCS recovery is high, no effect on nondetects, but 1,4-dioxane detects may be biased high. • If LCS recovery is low but >10%, all 1,4-dioxane data may be biased low. • If LCS recovery <10%, nondetects may not be usable (false negatives) and detects may be biased low.
Surrogate (non-isotope dilution)	Every sample	***VOCs*:** Surrogate spiked into sample prior to analysis. ***SVOCs*:** Surrogate spiked into sample prior to extraction and analysis. ***TO-15 and TO-17:*** Surrogate spiked through transfer lines as the sample volume is transferred to the preconcentrator (optional for TO-15).	Analytical accuracy	Recovery within method and/or lab SOP criteria	Use professional judgment to determine the impact of a non-isotope dilution surrogate on 1,4-dioxane. • If recovery is high, no effect on nondetects, but 1,4-dioxane detects may be biased high in affected sample. • If recovery is low but >10%, 1,4-dioxane may be biased low in affected sample. • If recovery <10%, nondetects may not be usable (false negatives) and detects may be biased low in affected sample.

EIS (isotope dilution)	Every sample	***VOCs*:** 1,4-Dioxane-d8 spiked into sample prior to analysis. ***SVOCs*:** 1,4-Dioxane-d8 spiked into sample prior to extraction and analysis. ***TO-15 & TO-17:*** Not applicable.	Analytical accuracy	Recovery within method and/or lab SOP criteria	Since isotope dilution is used, recovery outside criteria may not affect sample data, so overall bias is indeterminate: • If recovery is high, no effect on nondetects, but 1,4-dioxane detects may have indeterminate bias in affected sample. • If recovery is low but >10%, all 1,4-dioxane data may have indeterminate bias in affected sample. • If recovery <10%, nondetects may not be usable (false negatives) and detects may have indeterminate bias in affected sample.
Instrument tunes	Every 12 hours (24 hours for TO-15) prior to calibration and analysis of samples	Tuning compound introduced to GC/MS	Analytical accuracy	Per analytical method (e.g., 8260C, 8270D, 522, TO-15)	• If sample analyzed outside 12-hour tune window, use professional judgment. • If instrument fails tune criteria, sample data associated with the tune are generally not usable.
Initial calibration	Initially and when CCV fails after tune	Minimum of five concentration levels of 1,4-dioxane, with lowest level standard at concentration ≤ RL	Analytical accuracy	Lowest concentration standard and average RRF >0.01; %RSD or correlation coefficient per method criteria	• If 1,4-dioxane RRF <0.01, associated nondetects may not be usable (false negatives), and detects may be biased low. • If 1,4-dioxane %RSD > method criteria, associated results may have indeterminate bias.

Continuing calibration verification	Every 12 hours (24 hours for TO-15) following tune	Standard near mid-level concentration	Analytical accuracy	RRF > 0.01; %D ± method criteria	• If %D indicates enhanced sensitivity to detection of 1,4-dioxane, no effect on nondetects, but associated detected results may be biased high. • If %D indicates loss in sensitivity, associated detects, and nondetects may be biased low. • If 1,4-dioxane RRF <0.01, associated nondetects may not be usable (false negatives), and associated detects may be biased low.
Lab duplicate	***Waters/soil*:** 1 per preparation/analytical batch of up to 20 field samples. ***Air*:** 1 for each 24 hrs of analysis.	***VOCs*:** Second aliquot of a sample analyzed. ***SVOCs*:** Second aliquot of a sample extracted and analyzed. ***TO-15***: Second analysis of a canister performed.	Analytical accuracy and precision	***In absence of method-specific criteria:*** ***Water*:** RPD ≤30% for values >2x RL ***Soil:*** RPD ≤50% for values >2x RL ***Air:*** RPD ≤25% for values >5x RL	• If sample/LD RPD > criteria for values >2x RL (or 5x RL for air), sample result may have indeterminate bias.
Field duplicate*	1 per 20 field samples collected of the same matrix per SAP or QAPP requirements	Second sample collected in the field using the same techniques as required for other samples	Sampling precision	***Water:*** RPD ≤30% for values >2x RL ***Soil:*** RPD ≤50% for values >2x RL ***Air:*** RPD ≤50% for values >5x RL	• If sample/FD RPD > criteria for values >2x RL (or 5x RL for air), sample and FD results may have indeterminate bias.

Matrix spike/ matrix spike duplicate	1 MS/MSD per preparation/analytical batch	***VOCs*:** 1,4-Dioxane spiked into aliquots of sample prior to analysis. ***SVOCs*:** 1,4-Dioxane spiked into aliquots of sample prior to extraction and analysis. ***Air:*** Not applicable.	Sampling and analysis accuracy and precision	Recovery and precision (RPD) within method and/or lab SOP criteria when spike amount is >4x the concentration of 1,4-dioxane in the unspiked sample.	Actions affect the unspiked sample only: • If recovery is high, no effect on nondetects, but detected results may • If recovery is low but >10%, detects and nondetects may be biased low. • If recovery is <10%, nondetects may not be usable (false negatives) and detects may be biased low. • If MS/MSD RPD > criteria, detects may have indeterminate bias.
Analytical internal standards	Every sample	***VOCs and SVOCs:*** Spiked into sample or extract prior to analysis. ***TO-15 and TO-17:*** Spiked through transfer lines as the sample volume is transferred to the preconcentrator.	Analytical accuracy	IS area and retention time within method criteria	• ***Isotope dilution methods:*** IS used only to quantitate recovery of isotope, so if isotope recovery is OK, no impact on data usability. • ***Non-isotope dilution methods:*** If IS outside criteria, it is unclear if this is an IS spike issue or problem with the matrix, so 1,4-dioxane data may have indeterminate bias in affected sample.

Quantitation and general reporting issues	Every sample	• Average RRF from internal calibration (Dow) used to quantitate results. • QI and CI must be present. • Soils must be reported on a dry-weight basis. • Medium-level VOCs must have results (including RLs) corrected for moisture contribution of sample to extract volume per Method 5035A. • Results reported < RL qualified "J" by the lab. • Samples with 1,4-dioxane reported above the calibration range should be diluted to bring response with the calibration range.	Analytical accuracy	Characteristic ions (QI 88 and CI 58) must maximize at the same RRT; RRT of 1,4-dioxane in sample within ±0.06 RRT of 1,4-dioxane RRT in CCV; ***Method 522*:** ion ratio (QI/CI) within ±20% of ratio from last CCV.	• If VOC methanol-preserved soil 1,4-dioxane results are not moisture corrected per Method 8000C/D, all results, including RLs, may be biased low. • If a lab result is qualified "E" or "J" by the lab indicating quantitation outside the calibration range, the result is uncertain with indeterminate bias.
*May be dictated by SAP or QAPP requirements. CCV: continuing calibration verification; CI: confirmation ion; COC: chain of custody; EB: equipment blank; EIS: extraction internal standard; FB: field blank; FD: field duplicate; GC/MS: gas chromatography/mass spectrometer; HT: holding time; IS: internal standard; LCS: laboratory control sample; LD: lab duplicate; MB: method blank; MS/MSD: matrix spike/matrix spike duplicate; %D: percent difference; %RSD: percent relative standard deviation; QAPP: quality assurance project plan; QI: quantitation ion; RL: reporting limit; RPD: relative percent difference; RRF: relative response factor; RRT: relative retention time; SAP: sampling and analysis plan; SOP: standard operating procedure; SVOC: semivolatile organic compound; TB: trip blank; VOA: volatile organic analyte;VOC: volatile organic compound.					

4.3.3 Examples Where Data May Be Rendered Potentially Unusable

Several issues may cause data to be unusable for an intended purpose. Some examples are as follows:

- Exceedances of holding times
- Contamination introduced during the sampling and analysis process
- Improper sampling techniques or nonrepresentative sampling methodology (e.g., lack of preservation or En Core™ samplers not used for soil samples collected for volatile methods)
- Sample labeling, custody, and identification issues (e.g., switched samples)
- Analysis performed at too high of a dilution, causing target compounds to be reported with RLs exceeding PALs
- Significantly low RRFs (<0.01) for 1,4-dioxane in calibration
- Poor signal-to-noise ratio of 1,4-dioxane peak (may occur in VOC analyses with and without SIM)
- Significantly low EIS or surrogate recoveries (<10%)
- Significant or gross violations of QC sample results

All of these potential problems have to be addressed in the beginning of a project through description of acceptance criteria and corrective actions. Whether data are usable or not should be determined based on the comparison of these criteria (i.e., Data Quality Objectives [DQOs]) to QC sample results. If data should be rejected based on severe QC issues, this does not automatically indicate that resampling or reanalysis is required. Rather, the entire data set and other lines of evidence should be evaluated to determine whether the data gap is critical, thereby requiring corrective action.