METHOD 522 DETERMINATION OF 1,4-DIOXANE IN DRINKING WATER BY SOLID PHASE EXTRACTION (SPE) AND GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS) WITH SELECTED ION MONITORING (SIM)

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DETERMINATION OF 1,4-DIOXANE IN DRINKING WATER BY SOLID PHASE EXTRACTION (SPE) AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) WITH SELECTED ION MONITORING (SIM)

1. SCOPE AND APPLICATION

1.1 This is a gas chromatography/mass spectrometry (GC/MS) method for the determination of 1,4-dioxane (CASRN 123-91-1) in drinking water. Accuracy and precision data have been generated in reagent water, finished ground and surface waters. Although this method was developed and demonstrated using selected ion monitoring (SIM) GC/MS for maximum sensitivity, it can also be used with full scan GC/MS if the sensitivity achieved meets the user's data requirements.

1.2 The Minimum Reporting Level (MRL) is the lowest analyte concentration that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method. Two single laboratory Lowest Concentration Minimum Reporting Levels (LCMRLs) of 0.036 and 0.047 µg/L have been determined in reagent water. The single laboratory LCMRL is the lowest true concentration for which the future recovery is predicted to fall, with high confidence (99%), between 50 and 150% recovery. The procedure used to determine the LCMRLs is described elsewhere.[1]

1.3 Laboratories using this method will not be required to determine the LCMRL for this method, but will need to demonstrate that their laboratory MRL for this method meets the requirements described in Section 9.2.4.

1.4 Determining the Detection Limit (DL) for analytes in this method is optional (Sect. 9.2.6). Detection limit is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero.[2] The DL is compound dependent and is dependent on extraction efficiency, sample matrix, fortification concentration, and instrument performance.

1.5 This method is intended for use only by analysts skilled in solid phase extraction (SPE), the operation of GC/MS instruments, and the interpretation of the associated data.

1.6 METHOD FLEXIBILITY – In recognition of technological advances in analytical systems and techniques, the laboratory is permitted to modify the GC column, GC conditions and MS conditions (Sect. 9.4). Changes may not be made to sample collection and preservation (Sect. 8), the quality control (QC) requirements (Sect. 9), or to the sample extraction steps (Sect. 11). Method modifications should be considered only to improve method performance. Modifications that are introduced in the interest of reducing cost or sample processing time, but result in poorer method performance, should not be used. For example, modifications should not sacrifice

chromatographic separations in the interest of method turnaround time. Because the method analyte, surrogate analyte (SUR) and internal standard (IS) have only very low mass ions in their mass spectra, and SIM is being used, it is important to strive for chromatographic separation from potential interferences. In all cases where method modifications are proposed, the analyst must perform the procedures outlined in the initial demonstration of capability (IDC; Sect. 9.2), verify that all QC acceptance criteria in this method (Sect. 9) are met, and demonstrate that method performance can be verified in a real sample matrix (Sect. 9.3.7 and 9.4).

NOTE: The above method flexibility section is intended as an abbreviated summation of method flexibility. Method Sections 4-12 provide detailed information of specific portions of the method that may be modified. If there is any perceived conflict between the general method flexibility statement in this section and specific information in Sections 4-12, Sections 4-12 supersede Section 1.6.

2. <u>SUMMARY OF METHOD</u>

2.1 A water sample that has been dechlorinated and preserved with a microbial inhibitor is fortified with the isotopically labeled SUR, 1,4-dioxane-d_8. The sample is extracted by one of two SPE options. In option 1, a 500-mL sample is passed through an SPE cartridge containing 2 g of coconut charcoal to extract the method analyte and SUR. In option 2, a 100-mL sample is extracted on a Waters AC-2 Sep-Pak or Supelco Supelclean ENVI-Carb Plus cartridge. In either option, the compounds are eluted from the solid phase with a small amount of dichloromethane (DCM), approximately 9 mL or 1.5 mL, respectively. The extract volume is adjusted, and the IS, tetrahydrofuran-d_8 (THF-d_8), is added. Finally, the extract is dried with anhydrous sodium sulfate. Analysis of the extract is performed by GC/MS. The data provided in this method were collected using splitless injection with a high-resolution fused silica capillary GC column that was interfaced to an MS operated in the SIM mode. The analyte, SUR and IS are separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical GC/MS conditions. The concentration of the analyte is determined by comparison to its response in calibration standards relative to the IS. Although the performance data presented in Section 17 of this method were obtained in the SIM mode for maximum method sensitivity, the sample extract analysis may also be performed in full scan mode if the sensitivity achieved meets the data user's requirements.

3. <u>DEFINITIONS</u>

3.1 ANALYSIS BATCH – A set of samples that is analyzed on the same instrument during a 24-hour period that begins and ends with the analysis of the appropriate Continuing Calibration Check (CCC) Standards. Additional CCCs may be required depending on the length of the analysis batch and/or the number of Field Samples.

3.2 CALIBRATION STANDARD (CAL) – A solution prepared from stock standard solution(s) and the ISs and SURs. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 CONTINUING CALIBRATION CHECK (CCC) STANDARD – A calibration standard containing the method analyte, IS and SUR which is analyzed periodically to verify the accuracy of the existing calibration for those analytes.

3.4 DETECTION LIMIT (DL) – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. This is a statistical determination (Sect. 9.2.6), and accurate quantitation is not expected at this level.[2]

3.5 EXTRACTION BATCH – A set of up to 20 Field Samples (not including QC samples) extracted together by the same person(s) during a work day using the same lot of SPE devices, solvents, SUR solution, and fortifying solutions. Required QC samples include Laboratory Reagent Blank (LRB), Laboratory Fortified Blank (LFB), Laboratory Fortified Sample Matrix (LFSM), and either a Field Duplicate (FD1 and FD2) or Laboratory Fortified Sample Matrix Duplicate (LFSMD).

3.6 FIELD DUPLICATES (FD1 and FD2) – Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.7 INTERNAL STANDARD (IS) – A pure analyte, which is extremely unlikely to be found in any sample, which is added to an extract or standard solution in a known amount and used to measure the relative responses of the method analyte and SUR. The IS must be an analyte that is not a sample component.

3.8 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water or other blank matrix to which known quantities of the method analyte and all the preservation compounds are added. The LFB is processed and analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – An aliquot of a Field Sample to which known quantities of the method analyte and all the preservation compounds are added. The LFSM is processed and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analyte in the sample matrix must be determined in a separate aliquot or duplicate sample and the measured values in the LFSM corrected for background concentrations.

3.10   LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) – A Field Sample Duplicate of the Field Sample used to prepare the LFSM, which is fortified, extracted and analyzed identically to the LFSM. The LFSMD is used instead of the Field Duplicate to access method precision and accuracy when the occurrence of the method analyte at a concentration greater than the MRL is infrequent.

3.11   LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, sample preservatives, ISs, and SURs that are used in the extraction batch. The LRB is used to determine if the method analyte or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.12   LOWEST CONCENTRATION MINIMUM REPORTING LEVEL (LCMRL) – The single-laboratory LCMRL is the lowest true concentration for which the future recovery is predicted to fall, with high confidence (99%), between 50 and 150% recovery.[1]

3.13   MATERIAL SAFETY DATA SHEET (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.14   MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported by a laboratory as a quantitated value for a target analyte in a sample following analysis. This defined concentration must meet the criteria defined in Section 9.2.4 and must not be any lower than the concentration of the lowest calibration standard for that analyte. A laboratory may be required to demonstrate a specific MRL by a regulatory body if this method is being performed for compliance purposes.

3.15   QUALITY CONTROL SAMPLE (QCS) – A sample or standard prepared using a Stock Standard Solution (SSS) of the method analyte that is obtained from a source external to the laboratory and different from the source of calibration standards. The second source SSS is used to fortify the QCS at a known concentration. The QCS is used to check calibration standard integrity.

3.16   SELECTED ION MONITORING (SIM) – A GC/MS technique where only one or a few ions are monitored. When used with gas chromatography, the set of ions monitored is usually changed periodically throughout the chromatographic run, to correlate with the characteristic ions of the analyte, SUR and IS as they elute from the chromatographic column.

3.17   STOCK STANDARD SOLUTION (SSS) – A concentrated solution containing the method analyte prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.18   SURROGATE ANALYTE (SUR) – A pure analyte, which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in a known amount before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SUR is to monitor method performance with each sample.

4.   **INTERFERENCES**

4.1   All glassware must be meticulously cleaned. Wash glassware with detergent and tap water, rinse with tap water, followed by reagent water. Non-volumetric glassware should be heated in a muffle furnace at 400 °C for 2 hours. Volumetric glassware should be solvent rinsed with DCM or purge and trap grade methanol after washing, and dried in a low temperature oven (<120 °C) or air dried.

4.2   Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles and caps, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All items such as these must be routinely demonstrated to be free from interferences (less than $^1/_3$ the MRL for the method analyte) under the conditions of the analysis by analyzing LRBs as described in Sections 9.2.1 and 9.3.1. **Subtracting blank values from sample results is not permitted.**

4.3   **Purge and trap grade methanol must be used for all steps where methanol is used in this method. Other grades of methanol contain numerous low molecular weight compounds that contain interfering ions which may prohibit accurate identification and quantitation of the analyte, SUR and IS.**

4.4   Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water.

4.5   Preservatives (Sect. 8.1) are added to samples to ensure sample stability during shipping and storage prior to analysis. The potential exists for trace-level organic contaminants in these reagents. Interferences from these sources should be monitored by analysis of LRBs, particularly when new lots of reagents are acquired.

4.6   Solid phase extraction cartridges may be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

4.7   Analyte carry-over may occur when a relatively "clean" sample is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a

LRB should be analyzed to ensure that accurate values are obtained for the next sample. During automated GC/MS analyses, extracts with positive results that were analyzed immediately following a sample with high concentrations of the analyte, should be reanalyzed after analyzing an acceptable LRB. If the analyte is not detected in extracts analyzed immediately after a high concentration extract, no reanalysis is necessary.

4.8   Silicone compounds may be leached from punctured autosampler vial septa, particularly when particles of the septa sit in the vial. This can occur after repeated injections from the same autosampler vial. If this method is performed in full scan mode, these silicone compounds may appear as regularly spaced chromatographic peaks with similar fragmentation patterns. They can unnecessarily complicate the total ion chromatogram and may cause interferences at high levels.

4.9   High laboratory background levels of 1,4-dioxane have been reported to be associated with air contamination. If 1,4-dioxane is detected in LRBs, room air should be considered as a possible source.[3,4]

5. SAFETY

5.1   The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. 1,4-Dioxane is classified as a class B2 or probable human carcinogen.[5] Each laboratory is responsible for maintaining an awareness of OSHA regulations regarding safe handling of chemicals used in this method. A reference file of MSDSs should be made available to all personnel involved in the chemical analysis. Additional references on laboratory safety are available.[6-8]

5.2   Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin and eyes, and care should be taken not to breathe the vapors or ingest the materials.

5.3   Sodium bisulfate is used as a sample preservative to inhibit microbial growth and potential decay of 1,4-dioxane. Sodium bisulfate is highly acidic and should be used with appropriate caution.

6. EQUIPMENT AND SUPPLIES (References to specific brands or catalog numbers are included for illustration only, and do not imply endorsement of the product.)

6.1   SAMPLE CONTAINERS – Glass bottles fitted with polytetrafluoroethylene (PTFE) lined screw caps. Although samples do not need to be collected headspace free, the size of the sample bottle should be selected based upon the sample volume to be extracted.

6.2   VIALS – Various sizes of glass vials with PTFE-lined screw caps for storing standard solutions and extracts, including glass 2-mL autosampler vials with PTFE-faced septa.

6.3   VOLUMETRIC FLASKS – Class A, various sizes, including 1, 5, and 10 mL for preparation of standards. A 2-mL volumetric collection tube may also be used for the collection of the extract when SPE Option 2 is used (Sect. 11.5.3).

6.4   GRADUATED CYLINDERS – Glass, various sizes, including 100 and 500 mL for measurement of sample volumes.

6.5   MICRO SYRINGES – Suggested sizes include 10, 25, 50, 100, 250, 500, and 1000 μL.

6.6   CONICAL CENTRIFUGE TUBES – 15 mL, glass, with graduations at 0.1 mL and PTFE-lined screw caps (KIMAX #45166 or equivalent), suitable for collection of the eluent from the 2-g solid phase cartridge after extraction.

6.7   ANALYTICAL BALANCE – Capable of weighing to the nearest 0.0001 g.

6.8   SOLID PHASE EXTRACTION (SPE) APPARATUS

   6.8.1   SPE CARTRIDGES – SPE carbon cartridges acceptable for use in this method are made of either coconut charcoal or synthetic carbon as described in Sections 6.8.1.1 and 6.8.1.2 below. Graphitized carbon does not retain 1,4-dioxane and may not be used in this method.

      6.8.1.1   Option 1 (for use with sample volumes of ≤ 500 mL) – 6-mL polypropylene tubes packed with 2 g coconut charcoal (80-120 mesh, approximately 150 μm). At the time of method development, pre-packed cartridges were obtained from Restek Corporation (cat. # 26032) and United Chemical Technologies (UCT; cat. # EU52112M6). Equivalent brands of coconut charcoal SPE cartridges with the specified particle size and whose performance meets all QC criteria in Section 9 may be used.

      6.8.1.2   Option 2 (for use with samples volumes of ≤ 100 mL) – Waters AC-2 Sep-Pak 400-mg activated carbon SPE cartridge (cat. # JJAN20229; 85 μm particle size) or Supelco Supelclean ENVI-Carb Plus 400-mg synthetic carbon SPE cartridge (cat. # 54812-U).

   6.8.2   VACUUM EXTRACTION MANIFOLD – Equipped with flow/vacuum control (Supelco cat. # 57250-U or equivalent).

   6.8.3   SAMPLE DELIVERY SYSTEM – Use of a transfer tube system (Supelco "Visiprep", cat. # 57275 or equivalent), which transfers the sample directly from the sample container to the SPE cartridge, is recommended. Sample reservoirs

(Varian, cat. #12131012 or equivalent), which attach to the cartridge, may be used, although they hold only a limited volume of sample.

6.8.4 An automatic or robotic system designed for use with SPE cartridges may be used if all QC requirements discussed in Section 9 are met. Automated systems may use either vacuum or positive pressure to process samples and solvents through the cartridge. **All extraction and elution steps must be the same as in the manual procedure. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system**.

6.9 LABORATORY OR ASPIRATOR VACUUM SYSTEM – Sufficient capacity to maintain a vacuum of approximately 15 to 25 inches of mercury.

6.10 GAS CHROMATOGRAPH/MASS SPECTROMETER (GC/MS) SYSTEM

6.10.1 FUSED SILICA CAPILLARY GC COLUMN – Data presented in this method were obtained with a column typically used for volatiles analysis: Varian CP Select 624, 30 m x 0.25-mm i.d. with a 1.4 μm film thickness, or equivalent. Other types of columns may be used. However, use of shorter or thinner film columns is not recommended because this will result in loss of resolution and very short retention times. Because the method analyte, SUR and IS have only very low mass ions in their spectra, and SIM is being used, it is important to strive for chromatographic separation from any potential interferences. See Section 9.4 regarding the use of alternate GC columns.

CAUTION: If a GC column and/or temperature program different than that described in this method is used, **the analyst must verify that the temperature program and subsequent column bake-out is sufficient to remove all injected material from the column.** Although the retention times of the method analyte, IS and SUR are short, many chemicals may be co-extracted by carbon SPE and these need to be eluted from the GC column to prevent them from appearing as interferences in subsequent analyses.

6.10.2 GC INJECTOR AND OVEN – The performance data in Section 17 were obtained using hot, splitless injection. Other injection techniques such as temperature programmed injections, cold on-column injections and large volume injections may be used if the QC criteria in Section 9 are met. Equipment designed appropriately for these alternate types of injections must be used if these options are selected.

6.10.3 GC/MS INTERFACE – The interface should allow the capillary column or transfer line exit to be placed within a few millimeters of the ion source. Other interfaces, such as jet separators, are acceptable as long as the system has adequate sensitivity and QC performance criteria in Section 9 are met.

6.10.4 MASS SPECTROMETER (MS) – Any type of mass spectrometer may be used (i.e., quadrupole, ion trap, time of flight, etc.), although the SIM option may not provide enhanced sensitivity, or be an available option on all instruments. The spectrometer must produce a mass spectrum that meets all criteria in Table 1 when a solution containing approximately one to two nanograms of bromo-fluorobenzene (BFB) is injected into the GC/MS. This test must be performed in the full scan mode. Use a single spectrum at the apex of the BFB peak, an average spectrum of the three highest points of the peak, or an average spectrum across the entire peak to evaluate the performance of the system. Appropriate background subtraction is permitted. The scan time should be set so that there is a minimum of five scans across the chromatographic peak. Ten scans across chromatographic peaks are recommended.

6.10.5 DATA SYSTEM – An interfaced data system is required to acquire, store, and output MS data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within a given retention time window. The software must allow integration of the ion abundance of any specific ion between specified times or scan number limits. The software must be able to construct linear regressions and quadratic calibration curves, and calculate analyte concentrations.

6.11 N, N-DIETHYL-P-PHENYLENEDIAMINE (DPD) CHLORINE TEST KIT – Used to verify sample dechlorination when samples are received at the analytical laboratory (Hach model CN-66; cat. # 2231-01 or equivalent).

7. <u>REAGENTS AND STANDARDS</u>

7.1 REAGENTS AND SOLVENTS – Reagent grade or better chemicals should be used in all steps. Unless otherwise indicated, it is intended that all reagents will conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used, provided it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the quality of the determination. During method development, only purge and trap grade methanol was found to be sufficiently free from low molecular weight interferences (as described in Sect. 4.3). Therefore that grade **must** be used.

7.1.1 HELIUM – 99.999 % or better, GC carrier gas.

7.1.2 REAGENT WATER – Purified water which does not contain any measurable quantities of the method analyte or interfering compounds at or above $^1/_3$ the MRL for 1,4-dioxane. In addition, there must be no interferences with the SUR or IS.

7.1.3 METHANOL (CASRN 67-56-1) – **<u>Purge and trap grade only (see Section 4.3)</u>**.

7.1.4 DICHLOROMETHANE (DCM) (CASRN 75-09-02) – High purity, demonstrated to be free of analytes and interferences (B&J Brand GC[2], Capillary GC or GC/MS Grade or equivalent).

7.1.5 SODIUM SULFATE, ANHYDROUS (CASRN 7757-82-6) – Soxhlet extracted with DCM for a minimum of four hours or heated to 400 °C for two hours in a muffle furnace. An "ACS grade, suitable for pesticide residue analysis", or equivalent, of anhydrous sodium sulfate is recommended.

7.1.6 SAMPLE PRESERVATION REAGENTS

7.1.6.1 SODIUM SULFITE (CASRN 7757-83-7) – Reduces free and combined chlorine in samples that have been disinfected with chlorine and/or chloramine.

7.1.6.2 SODIUM BISULFATE (CASRN 7681-38-1) – Anhydrous, technical grade. It is added to acidify the samples to pH < 4 to act as a microbial inhibitor during sample shipping and storage.

7.2 STANDARD SOLUTIONS – When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Solution concentrations listed in this section were used to develop this method and are included as examples. Alternate concentrations may be used as necessary depending on instrument sensitivity and the calibration range used. Standards for sample fortification generally should be prepared in the smallest volume that can be accurately measured to minimize the addition of excess organic solvent to aqueous samples. During method development, standard solutions were stored in a freezer at about -15 to -20 °C for several months. Experience indicates that the most likely cause of standard deterioration for this method is solvent evaporation. Therefore, it is recommended that standard solutions be stored at 0 °C or less, with minimal headspace. Laboratories should use standard QC practices to determine when standards need to be replaced. Standard QC practices, such as monitoring area counts and recovery percentages of CCCs, would help to determine if a standard requires replacement. As mentioned above, the major form of "standard deterioration" is solvent evaporation, which would result in a continuous increase in area counts, and in some cases, target and SUR recoveries. During method development, SSSs and dilutions of SSSs of 1,4-dioxane, THF-d_8, 1,4-dioxane-d_8, and BFB were valid for at least 6 months after opening/preparation. Expiration dates provided by the vendor should be used as an indicator of SSS shelf life prior to opening.

NOTE: Only purge and trap grade methanol may be used in the preparation of standards and sample fortification solutions.

7.2.1 STOCK STANDARD SOLUTIONS (SSS) – Stock standard solutions of the method analyte, SUR and IS are commercially available from multiple commercial sources. It is recommended that these solutions be purchased from

commercial sources. However, they may be prepared from neat materials. Utilizing stock standards prepared in methanol allows the same stock standard to be used to prepare both calibration standards and sample fortification solutions. The concentrations of the stock standard solutions used during method development were 1000-2000 µg/mL.

7.2.1.1 PREPARATION OF STOCK STANDARD SOLUTIONS (SSS) FROM NEAT MATERIALS

7.2.1.1.1 Place about 9.8 mL of methanol in a 10-mL volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol wetted surfaces have dried. Weigh to the nearest 0.1 mg.

7.2.1.1.2 Using a 100 µL-syringe, quickly add two or more drops of the neat standard material to the flask. Be sure that the standard falls directly into the alcohol, without contacting the neck of the flask.

7.2.1.1.3 Quickly reweigh, dilute to volume and mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight.

7.2.1.1.4 Store SSS in 12-15 mL glass vials with PTFE lined screw caps.

7.2.2 CALIBRATION STANDARD SOLUTIONS (CAL) – Prepare a series of calibration standards to encompass the desired calibration range. Calibration standards must contain varying amounts of 1,4-dioxane, and a fixed amount of both the SUR and the IS, and be prepared in DCM. The number of standards required is determined by the calibration range. Three standards are required for one order of magnitude, six standards for two orders of magnitude and nine standards for three orders of magnitude. The calibration curve associated with the demonstration data in Section 17 contained nine standards with concentrations of 1,4-dioxane ranging from 0.002 µg/mL to 1.0 µg/mL. (This corresponds to a concentration range of 0.04-20 µg/L in the drinking water samples.) The concentrations of both 1,4-dioxane-d_8 (SUR) and the THF-d_8 (IS) were 0.500 µg/mL in each standard.

7.2.3 SAMPLE FORTIFICATION SOLUTIONS

7.2.3.1 ANALYTE FORTIFICATON SOLUTION – Prepare one or more solutions in methanol for use in preparing LFBs and LFSMs (Sect. 11.3.5). The number of solutions needed depends upon the calibration range and/or sample volume. During method development, two solutions at concentrations of 20 µg/mL and 200 µg/mL were used to fortify 100-mL and 500-mL samples, respectively.

7.2.3.2 SURROGATE ANALYTE (SUR) FORTIFICATION SOLUTION – Prepare one or more solutions of 1,4-dioxane-d_8 in methanol to be used for fortification of the SUR into samples, LFBs, LRBs and LFSMs (Sect.11.3.4). The concentrations used during method development were 200 μg/mL and 2000 μg/mL (STOCK) to fortify 100-mL and 500-mL samples, respectively.

7.2.3.3 INTERNAL STANDARD (IS) FORTIFICATION SOLUTION – Prepare one or more solutions of THF-d_8 in DCM to be used to add the IS to all extracts (Sect. 11.4.4 and 11.5.4). During method development, the concentrations of these solutions were 100 μg/mL and 1000 μg/mL (STOCK), used to fortify 2-mL and 10-mL extracts, respectively.

7.2.4 GC/MS TUNE CHECK SOLUTION – Stock standard solutions of BFB (CASRN 460-00-4) are available commercially. Prepare a BFB solution at a concentration of 1-2 μg/mL in DCM by dilution of the stock standard. Store this solution in an amber glass screw cap vial at 0 °C or less. To prepare a SSS of BFB from neat material, see Section 7.2.1.1.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE PRESERVATIVES – Preservation reagents, listed in the table below, are added to each sample at the time of sample collection. Sodium sulfite must be added first and may be placed as a dry material in the sample bottles prior to shipment to the field. Aqueous solutions of sodium sulfite may not be added to sample bottles prior to shipment to the collection site because these solutions are unstable and cannot be relied upon to completely dechlorinate the samples. Sodium bisulfate is added only after the sodium sulfite has been dissolved in the aqueous sample. See Section 8.2.2 and 8.2.3 for complete instructions.

Compound	Amount	Purpose
Sodium sulfite	50 mg/L	Reduce chlorine/chloramine residual
Sodium bisulfate	1 g/L (approx)	Microbial inhibitor

8.2 SAMPLE COLLECTION

8.2.1 Open the tap and allow the system to flush until the water temperature has stabilized (approximately three to five min). Collect samples from the flowing system.

8.2.2 Fill sample bottles, taking care not to flush out the sample dechlorination reagent. Samples do not need to be collected headspace free.

8.2.3 After collecting the sample, cap the bottle and agitate by hand until the sodium sulfite is dissolved. Add enough sodium bisulfate such that the final

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concentration will be 1 g/L. Cap the bottle and mix until dissolved. Unless field verification of pH is to be performed, keep the sample sealed until just prior to extraction.

8.2.4 Field verification of pH 4 (optional). It is anticipated that 1 g/L of sodium bisulfate will be sufficient to acidify most samples to < pH 4. If there is reason to suspect that more may be needed, the pH can be verified with narrow range pH paper at the time of sample collection. After acidification and mixing, pour a small amount of sample over a strip of the pH paper (do not dip the strip in the sample). Read the result as instructed on the pH paper package. If the pH is ≥ 4, add additional sodium bisulfate until pH < 4 is obtained. Seal the bottle, and keep the sample sealed until extraction.

8.3 SAMPLE SHIPMENT AND STORAGE – Samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Sample temperature must be confirmed to be at or below 10 °C when they are received at the laboratory. Depending upon the water temperature at the time of collection, samples may need to be refrigerated to reduce their temperature before being packed on ice for shipment. Samples stored in the lab must be held at or below 6 °C until extraction, but should not be frozen. Freezing samples may compromise the sealed cap or result in sample bottle breakage.

8.3.1 Verification of sample dechlorination – Upon the receipt of samples at the laboratory, verify that Field Samples were dechlorinated at the time of collection. The absence of total chlorine can be verified with a DPD chlorine test kit (Sect. 6.11).

8.4 SAMPLE AND EXTRACT HOLDING TIMES – Aqueous samples may be stored as described above for up to 28 days from collection. Sample extracts, as prepared in Section 11, may be stored at -5 °C and protected from light for an additional 28 days.

9. QUALITY CONTROL

9.1 QC requirements include the Initial Demonstration of Capability (IDC) and ongoing QC requirements that must be met when preparing and analyzing Field Samples. This section describes each QC parameter, its required frequency, and the performance criteria that must be met in order to meet USEPA quality objectives. The QC criteria discussed in the following sections are summarized in Section 17, Tables 6 and 7. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs. If method modifications are under consideration by the laboratory, refer to Sect. 9.4 for detailed requirements.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) – The IDC must be successfully performed prior to analyzing any Field Samples. Prior to conducting the

IDC, the analyst must first generate an acceptable Initial Calibration following the procedure outlined in Section 10.2.

9.2.1 INITIAL DEMONSTRATION OF LOW BACKGROUND – Before any samples are analyzed, or any time a new lot or brand of SPE materials or solvents are received from a supplier, it must be demonstrated that a LRB is reasonably free of any contamination that would prevent the identification or quantitation of 1,4-dioxane, the IS or SUR.

9.2.1.1 A source of potential contamination is the SPE materials which may contain phthalate esters, silicon compounds, and other contaminants that could interfere with the determination of the method analyte, SUR or IS. Although extraction media are generally made of inert materials, they may still contain extractable organic material. If the background contamination is sufficient to prevent accurate and precise measurements, the condition must be corrected before proceeding with the IDP (Sect. 9.2.2).

9.2.1.2 Other sources of background contamination are solvents, reagents (including reagent water), room air and glassware. Background contamination must be reduced to an acceptable level before proceeding with the IDP (Sect. 9.2.2). Background from 1,4-dioxane and interferences must be ≤ 1/3 the MRL. If background contamination is an on-going or intermittent issue, the analyst must not attempt to verify an MRL less than the mean LRB concentration + 3σ, or three times the mean LRB concentration, whichever is greater.

NOTE: Although quantitative data below the MRL may not be reliably accurate enough for data reporting, such data are useful in determining an MRL cut off for the method analyte if it is found in the LRB. Therefore, blank contamination levels may be estimated by extrapolation, when the concentration is below the lowest calibration standard. This also applies to estimating LRB concentrations for daily low background verification.

9.2.2 INITIAL DEMONSTRATION OF PRECISION (IDP) – Prepare, extract, and analyze four to seven replicate LFBs fortified near the midrange of the initial calibration curve according to the procedure described in Section 11. Sample preservatives as described in Section 8.1 must be added to these samples. The relative standard deviation (RSD) of the results of the replicate analyses must be less than 20%.

9.2.3 INITIAL DEMONSTRATION OF ACCURACY (IDA) – Using the same set of replicate data generated for Section 9.2.2, calculate average recovery. The average recovery of the replicate values must be within ± 20% of the true value.

9.2.4 MINIMUM REPORTING LEVEL (MRL) CONFIRMATION – Establish a target concentration for the MRL for 1,4-dioxane based on the intended use of the method. In some cases, the MRL may be dictated by USEPA or another

regulatory body. Establish an Initial Calibration following the procedure outlined in Section 10.2. The lowest calibration standard used to establish the Initial Calibration (as well as the low-level CCC) must be at or below the concentration of the MRL. Establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements. Validate the MRL following the procedure outlined below.

9.2.4.1 Fortify, extract, and analyze seven replicate LFBs at the proposed MRL concentration. These LFBs must contain all method preservatives described in Section 8.1. Calculate the mean (*Mean*) and standard deviation for these replicates. Determine the Half Range for the prediction interval of results (*HR$_{PIR}$*) using the equation below

$$HR_{PIR} = 3.963S$$

where *S* is the standard deviation, and 3.963 is the constant value for seven replicates.[1]

NOTE: The mass spectrum (either SIM or full scan) for the method analyte in the LFBs must meet all the analyte identification criteria in Sections 12.1 and 12.2, i.e., the MRL verification may not be performed on LFBs where only the base peak is observed. If during MRL confirmation all identification ions are not observed, the MRL selected is too low.

9.2.4.2 Confirm that the upper and lower limits for the Prediction Interval of Result (*PIR = Mean ± HR$_{PIR}$*) meet the upper and lower recovery limits as shown below.

The Upper PIR Limit must be ≤ 150% recovery.

$$\frac{Mean + HR_{PIR}}{FortifiedConcentration} \times 100\% \leq 150\%$$

The Lower PIR Limit must be ≥ 50% recovery.

$$\frac{Mean - HR_{PIR}}{FortifiedConcentration} \times 100\% \geq 50\%$$

9.2.4.3 The MRL is validated if both the Upper and Lower PIR Limits meet the criteria described above (Sects. 9.2.4.2). If these criteria are not met, the MRL for 1,4-dioxane has been set too low and must be re-evaluated at a higher concentration.

9.2.5 CALIBRATION CONFIRMATION – Analyze a QCS as described in Section 9.3.9 to confirm the accuracy of the standards and calibration curve.

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9.2.6 DETECTION LIMIT (DL) DETERMINATION *(optional) – While DL determination is not a specific requirement of this method, it may be required by various regulatory bodies associated with compliance monitoring. It is the responsibility of the laboratory to determine if DL determination is required based upon the intended use of the data.*

Replicate analyses for this procedure should be done over at least three days (i.e., both the sample extraction and the GC analyses should be done over at least three days). Prepare at least seven replicate LFBs containing 1,4-dioxane at a concentration estimated to be near the DL. This concentration may be estimated by selecting a concentration at two to five times the noise level. The appropriate fortification concentrations will be dependent upon the sensitivity of the GC/MS system used. All preservation reagents listed in Section 8.1 must also be added to these samples. Analyze the seven replicates through all steps of Section 11.

NOTE: If an MRL confirmation data set meets these requirements, a DL may be calculated from the MRL confirmation data, and no additional analyses are necessary.

Calculate the *DL* using the equation

$$DL = s \times t_{(n-1, 1-\alpha=0.99)}$$

where:

s = standard deviation of replicate analyses
$t_{(n-1, 1-\alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates.

NOTE: There are no precision and accuracy requirements for the DL replicates. Do not subtract blank values when performing DL calculations.

9.3 ONGOING QC REQUIREMENTS – This section summarizes the ongoing QC criteria that must be followed when processing and analyzing Field Samples.

9.3.1 LABORATORY REAGENT BLANK (LRB) – An LRB is required with each extraction batch to confirm that potential background contaminants are not interfering with the identification or quantitation of the method analyte, SUR or IS. If the LRB produces a peak within the retention time window of any analyte that would prevent the identification or quantitation of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding.

NOTE: Absence of interferences must be verified for 1,4-dioxane at both the quantitation ion (QI) (*m/z* 88) and the confirmation ion (*m/z* 58). Background from contaminants that interfere with the measurement of 1,4-dioxane must be below $^1/_3$ of the MRL. Blank contamination may be estimated by extrapolation, if the concentration is below the lowest calibration standard. This procedure is not allowed for sample results as it may not meet data quality objectives. If the method analyte is detected in the LRB at concentrations equal to or greater than this level, then all data for the analyte must be considered invalid for all samples in the extraction batch.

9.3.2   CONTINUING CALIBRATION CHECK (CCC) – CCC Standards are analyzed at the beginning of each analysis batch, after every ten Field Samples, and at the end of the analysis batch. See Section 10.3 for concentration requirements and acceptance criteria.

9.3.3   LABORATORY FORTIFIED BLANK (LFB) – An LFB is required with each extraction batch. The fortified concentration of the LFB must be rotated between low, medium, and high concentrations from batch to batch. The low concentration LFB must be as near as practical to, but no more than two times the MRL. Similarly, the high concentration LFB should be near the high end of the calibration range established during the initial calibration (Sect. 10.2). Results of the low-level LFB analyses must be 50-150% of the true value. Results of the medium and high-level LFB analyses must be 70-130% of the true value. If the LFB results do not meet these criteria for 1,4-dioxane, then all data must be considered invalid for all samples in the extraction batch.

9.3.4   MS TUNE CHECK – A complete description of the MS Tune Check is found in Section 10.2.1. Acceptance criteria for the MS Tune Check are summarized in Section 17, Table 1. The MS Tune Check must be performed each time a major change is made to the mass spectrometer, and prior to establishing and/or re-establishing an initial calibration (Sect.10.2). In this method, daily BFB analysis is not required.

9.3.5   INTERNAL STANDARDS (IS) – The analyst must monitor the peak area of the IS in all injections during each analysis day. The IS response (peak area) in any chromatographic run must not deviate from the response in the most recent CCC by more than 30%, and must not deviate by more than 50% from the mean area measured during initial analyte calibration. If the IS area in a chromatographic run does not meet these criteria, inject a second aliquot of that extract.

9.3.5.1   If the reinjected aliquot produces an acceptable IS response, report results for that aliquot.

9.3.5.2   If the reinjected extract fails again, the analyst should check the calibration by reanalyzing the most recently acceptable calibration standard. If the calibration standard fails the criteria of Section 10.3, recalibration is in order

per Section 10.2. If the calibration standard is acceptable, extraction of the sample may need to be repeated provided the sample is still within the holding time. Otherwise, report results obtained from the reinjected extract, but annotate as "suspect/IS recovery." Alternatively, collect a new sample and re-analyze.

9.3.6 SURROGATE (SUR) RECOVERY – The SUR standard is fortified into the aqueous portion of all samples, LRBs, LFBs, CCCs, LFSMs and LFSMDs prior to extraction. It is also added to the calibration standards. The SUR is a means of assessing method performance from extraction to final chromatographic measurement. Calculate the percent recovery (%R) for the SUR using the equation

$$\%R = \left(\frac{A}{B}\right) \times 100$$

where:
A = calculated SUR concentration for the QC or Field Sample
B = fortified concentration of the SUR.

9.3.6.1 SUR recovery must be in the range of 70-130% of the true value. When SUR recovery is less than 70% or greater than 130%, check the 1) calculations to locate possible errors, 2) standard solutions for degradation, 3) contamination, and 4) instrument performance. Correct the problem and reanalyze the extract.

9.3.6.2 If the extract reanalysis meets the SUR recovery criterion, report only data for the reanalyzed extract.

9.3.6.3 If the extract reanalysis fails the 70-130% recovery criterion, the analyst should check the calibration by injecting the last CCC that passed. If the CCC fails the criteria of Section 9.3.6.1, recalibration is in order per Section 10.2. If the calibration standard is acceptable, extraction of the sample should be repeated provided the sample is still within the holding time. If the re-extracted sample also fails the recovery criterion, report all data for that sample as "suspect/SUR recovery" to inform the data user that the results are suspect due to SUR recovery. Alternatively, collect a new sample and re-analyze.

9.3.7 LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) – Analysis of an LFSM is required in each extraction batch and is used to determine that the sample matrix does not adversely affect method accuracy. If the occurrence of 1,4-dioxane in the samples is infrequent, or if historical trends are unavailable, a LFSMD must be prepared, extracted, and analyzed from a duplicate Field Sample to assess method precision (Sect. 9.3.8). Extraction batches that contain LFSMDs do not require the analysis of a Field Duplicate. If a variety of different sample

matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, method performance should be established for each. Over time, LFSM data should be documented by the laboratory for all routine sample sources analyzed.

9.3.7.1   Within each extraction batch, a minimum of one Field Sample is fortified as an LFSM for every 20 samples extracted. The LFSM is prepared by spiking a sample with an appropriate amount of the Analyte Fortification Solution (Sect. 7.2.3.1). Select a spiking concentration that is greater than or equal to the matrix background concentration, if known. Use historical data and rotate through low, medium and high concentrations when selecting a fortifying concentration.

9.3.7.2   Calculate the percent recovery (%R) for the analyte using the equation

$$\% R = \frac{(A - B)}{C} \times 100$$

where:
> A = measured concentration in the fortified sample
> B = measured concentration in the unfortified sample
> C = fortification concentration.

NOTE: Field Samples that have native analyte concentrations above the DL but below the MRL, and are fortified at concentrations at or near the MRL, should be corrected for the native levels in order to obtain meaningful %R values. This example and the LRB (Sect. 9.3.1) are the only permitted use of analyte results below the MRL.

9.3.7.3   Analyte recoveries may exhibit matrix bias. For samples fortified at or above their native concentration, recoveries should range between 70-130%, except for low-level fortification near or at the MRL (within a factor of two times the MRL concentration) where 50-150% recoveries are acceptable. If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled "suspect/matrix" to inform the data user that the results are suspect due to matrix effects.

9.3.8   FIELD DUPLICATE (FD) OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) – Within each extraction batch, a minimum of one Field Duplicate (FD) or Laboratory Fortified Sample Matrix Duplicate (LFSMD) must be analyzed. Duplicates check the precision associated with sample collection, preservation, storage, and laboratory procedures. If method analytes are not routinely observed in Field Samples, an LFSMD should be analyzed rather than an FD.

9.3.8.1 Calculate the relative percent difference (*RPD*) for duplicate FD measurements (*FD1* and *FD2*) using the equation

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2)/2} \times 100$$

9.3.8.2 RPDs for FDs should be ≤ 30%. Greater variability may be observed when FDs have analyte concentrations that are within a factor of two of the MRL. At these concentrations, FDs should have RPDs that are ≤ 50%. If the RPD of the analyte falls outside the designated range, and the laboratory performance for the analyte is shown to be in control in the CCC, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled "suspect/matrix" to inform the data user that the results are suspect due to matrix effects. Failure to meet the FD criteria is a reflection of the performance of the method for that individual sample, and does not constitute analysis or extraction batch failure.

9.3.8.3 If an LFSMD is analyzed instead of a FD, calculate the relative percent difference (RPD) for duplicate LFSMs (LFSM and LFSMD) using the equation

$$RPD = \frac{|LFSM - LFSMD|}{(LFSM + LFSMD)/2} \times 100$$

9.3.8.4 RPDs for duplicate LFSMs should be ≤ 30% for samples fortified at or above their native concentration. Greater variability may be observed when LFSMs are fortified at analyte concentrations that are within a factor of two of the MRL. LFSMs fortified at these concentrations should have RPDs that are ≤ 50% for samples fortified at or above their native concentration. If the RPD of the analyte falls outside the designated range, and the laboratory performance for the analyte is shown to be in control in the CCC, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled "suspect/matrix" to inform the data user that the results are suspect due to matrix effects. Failure to meet the LFSM/LFSMD criteria is a reflection of the performance of the method for that individual sample, and does not constitute analysis or extraction batch failure.

9.3.9 QUALITY CONTROL SAMPLES (QCS) – As part of the IDC (Sect. 9.2), each time new calibration standards are prepared, and at least quarterly, analyze a QCS sample from a source different from the source of the calibration standards. The QCS should be prepared and analyzed just like a CCC (Sect. 10.3). The calculated amount for the analyte in the QCS must be ± 20% of the expected value. If measured analyte concentrations are not of acceptable accuracy, check

the entire analytical procedure to locate and correct the problem, or obtain another QCS.

9.4   METHOD MODIFICATION QC REQUIREMENTS – The analyst is permitted to modify the GC injection technique, GC column and conditions, and MS conditions.

9.4.1   Each time method modifications are made, the analyst must repeat the procedures of the IDC (Sect. 9.2) and verify that all QC criteria can be met in ongoing QC samples (Sect. 9.3).

9.4.2   The analyst is also required to evaluate and document method performance for the proposed method modifications in real matrices that span the range of waters that the laboratory analyzes. This additional step is required because modifications that perform acceptably in the IDC, which is conducted in reagent water, can fail ongoing method QC requirements in real matrices. This is particularly important for methods subject to matrix effects. If, for example, the laboratory analyzes finished waters from both surface and groundwater municipalities, this requirement can be accomplished by assessing precision and accuracy (Sects. 9.2.2 and 9.2.3) in a surface water with moderate to high Total Organic Carbon (TOC) (e.g., 2 mg/L or greater) and a hard groundwater (e.g., 250 mg/L or greater as calcium carbonate).

9.4.3   The results of Sections 9.4.1 and 9.4.2 must be appropriately documented by the analyst and should be independently assessed by the laboratory's Quality Assurance (QA) officer prior to analyzing Field Samples.

9.4.3.1   When implementing method modifications, it is the responsibility of the laboratory to closely review the results of ongoing QC, and in particular, the results associated with the LFBs (Sect. 9.3.3), LFSMs (Sect. 9.3.7), FDs or LFSMDs (Sect. 9.3.8), CCCs (Sect. 9.3.2), and the IS area counts (Sect. 9.3.5). If repeated failures are noted, the modification must be abandoned.

10. CALIBRATION AND STANDARDIZATION

10.1   Demonstration and documentation of acceptable mass spectrometer (MS) tune and initial calibration is required before any samples are analyzed. After the initial calibration is successful, a CCC is required at the beginning and end of each period in which analyses are performed, and after every tenth Field Sample. Verification of mass spectrometer tune must be repeated each time a major instrument modification is made or maintenance is performed, and prior to establishing or re-establishing an initial calibration.

10.2   INITIAL CALIBRATION

10.2.1   MS TUNE/MS TUNE CHECK – Operate the MS in the electron ionization (EI) mode. Calibrate the mass and abundance scales of the MS with calibration

compounds and procedures prescribed by the manufacturer with any modifications necessary to meet tuning requirements. Inject 2 ng or less of the BFB solution (Sect. 7.2.4) into the GC/MS system. Acquire a mass spectrum that includes data for *m/z* 45 to 180. The GC and MS parameters must be set such that a minimum of five scans (10 scans are recommended) are obtained during the elution of the BFB chromatographic peak   Use a single spectrum of the BFB peak, an average spectrum of the three highest points of the peak, or an average spectrum across the entire peak to evaluate the performance of the system. Appropriate background subtraction is permitted. If the BFB mass spectrum does not meet all criteria in Table 1, the MS must be re-tuned and adjusted to meet all criteria before proceeding with the initial calibration.

10.2.2   ANALYTE CALIBRATION – Operating conditions used during method development are described below. Data were obtained using SIM on a quadrupole MS system using the GC column described in Section 6.10.1. Conditions different from those described may be used if QC criteria in Section 9 are met. Different conditions include alternate GC columns, temperature programs, MS conditions, and injection techniques and volume, such as cold on-column and direct injection port liners and/or large volume injection techniques. Equipment specifically designed for alternate types of injections must be used if these options are selected. Full scan MS data may be used if the sensitivity achieved meets the data user's needs.

10.2.2.1   GAS CHROMATOGRAPH (GC) CONDITIONS – Inject a 1-µL aliquot of each CAL prepared as in Section 7.2.2 into a hot, splitless injection port held at 200 °C with a split delay of 0.5 min. Temperature program the GC as follows: initial oven temperature of 30 °C, hold for 1.0 min, ramp at 7 °C/min to 90 °C, ramp at 20 °C/min to a final temperature of 200 °C and hold for 3.0 min, for a total run time of 18.07 min. Begin data acquisition at 6.0 min. During method development, the GC was operated in a constant flow rate mode at a rate of 1.0 mL per min. The MS ion source and the GC injector were both maintained at 200 °C.

NOTE: Using these conditions, all compounds of interest eluted before 9 min. However, it is important to complete the GC temperature program to ensure that co-extracted materials have eluted from the GC column prior to initiating the next analysis.

10.2.2.2   MASS SPECTROMETER (MS) CONDITIONS – Any type of MS may be used as detailed in Sect. 6.10.4. Data shown in Section 17 (Tables 2-5) were obtained in the SIM mode. Operation of the MS in this mode enhances sensitivity. However, less mass spectral data are obtained for all peaks including the method analyte, SUR, IS and any potential interferences. Because of this, and because the selected ions for the compounds of interest are very low masses that are likely to occur more frequently in interferences than most higher mass ions, the analyst should also rely on chromatography

to reduce the possibility of false positives. It is highly recommended that a GC column at least 30 m in length with a film thickness of at least 1.4 μm be used to provide adequate separation of the compounds of interest from possible interferences. During method development, the MS was scanned in SIM mode for m/z 46, 78, and 80 (IS) at a rate of 0.36 s/scan in Segment 1 (6 to 8 min). Segment 2 (8 to 18 min) was set to scan for m/z 58 and 88 (TARGET), as well as 62, 64, and 96 (SUR) at 0.60 s/scan, resulting in at least nine scans across each chromatographic peak. A minimum of five scans during the elution of each GC peak are required. Ten scans across each GC peak are recommended. This requirement is applicable to both full scan and SIM analysis. Timing of the SIM segments must be set such that no chromatographic peak of interest begins or ends within 5 s of the beginning or end of the segment. An example chromatogram obtained during method development using the instrumental conditions described in this section is shown in Figure 1.

10.2.3 CALIBRATION CURVE – Use the GC/MS software to create a calibration curve for 1,4-dioxane using the IS technique. Concentrations may be calculated through the use of a linear or quadratic calibration curve. A weighted curve is permitted at the discretion of the analyst. Because the SUR is added to all samples and standards at a single concentration, calibrate for the SUR using the average response factor.

10.2.4 CALIBRATION ACCEPTANCE CRITERIA – When quantitated using the calibration curve, each calibration point, except the lowest point, should calculate to be within 80-120% of its true value. The lowest point should calculate to be within 60-140% of its true value. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. It is recommended that corrective action be taken to re-analyze the CALs, restrict the range of calibration, or select an alternate method of calibration.

10.3 CONTINUING CALIBRATION CHECK (CCC) – The CCC verifies the initial calibration at the beginning and end of each group of analyses, and after every tenth sample during analyses. In this context, a "sample" is considered to be a Field Sample. The LRBs, LFBs, LFSMs, LFSMDs, FDs and CCCs are not counted as samples. The beginning CCC for each analysis batch must be at or below the MRL in order to verify instrument sensitivity prior to any analyses. Subsequent CCCs must alternate between medium and high concentration CALs.

10.3.1 Inject an aliquot of the appropriate concentration CAL solution and analyze with the same conditions used during the initial calibration.

10.3.2 Determine that the absolute area of the QI of the IS has not changed by more than ± 50% from the average area measured during initial calibration, or more than ± 30% from the most recent CCC. If the IS area has changed by more than this

amount, remedial action must be taken (Sect. 10.3.4). Control charts are useful aids in documenting system sensitivity changes.

10.3.3 Calculate the concentration of 1,4-dioxane and the SUR in the check standard. The calculated amount for 1,4-dioxane for medium and high level CCCs must be ± 30% of the true value. The calculated amount for the lowest calibration level for 1,4-dioxane, which must be at a concentration less than or equal to the MRL, must be within ± 50% of the true value. If these criteria are not met, then all data for the problem analyte must be considered invalid, and remedial action (Sect. 10.3.4) should be taken. This may require recalibration. Any Field Sample extracts that have been analyzed since the last acceptable calibration verification should be re-analyzed after adequate calibration has been restored, with the following exception: if the CCC fails at the end of an analytical sequence because the calculated concentration of the target compound or SUR is greater than 130% (150% for the low-level CCC), and Field Sample extracts show no detection for the target compound, non-detects may be reported without re-analysis.

10.3.4 REMEDIAL ACTION – Failure to meet CCC QC performance criteria may require remedial action. Major maintenance such as cleaning the ion source, cleaning the mass analyzer, replacing filament assemblies, replacing the GC column, etc., require returning to the initial calibration step (Sect. 10.2).

11. PROCEDURE

11.1 This procedure may be performed manually or in an automated mode (Sect. 6.8.4) using a robotic or automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but all extraction and elution steps must be the same as in the manual procedure. **Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system.**

11.2 Important aspects of this analytical procedure include proper preparation of laboratory glassware and sample containers (Sect. 4.1), as well as sample collection and storage (Sect. 8). This section details the procedures for sample preparation, SPE using 2-g coconut charcoal or 0.4-g carbon cartridges as described in Sect. 6.8.1, and extract analysis.

NOTE: The SPE cartridges and sodium sulfate drying materials described in this section are designed as single use items and must be discarded after use. They may not be refurbished for re-use in subsequent analyses.

NOTE: Only purge and trap grade methanol may be used in this extraction (see Sect. 4.3).

11.3 SAMPLE PREPARATION

11.3.1 All Field and QC samples (LRBs and LFBs) must contain the dechlorinating agent, sodium sulfite. Verify that Field Samples were checked for total chlorine upon sample receipt at the laboratory, and that no chlorine was present (Sect. 8.3.1). Add sodium sulfite to all LRBs and LFBs according to the instructions in Section 8, prior to fortification with the SUR and analyte.

11.3.2 All Field and QC samples (LRBs and LFBs), must contain the anti-microbial agent sodium bisulfate. Verify that Field Samples were acidified to < pH 4 at the time of collection by checking with narrow range pH paper (this verification may take place at sample receipt if preferred by the laboratory). Add sodium bisulfate to all LRBs and LFBs according to the instructions in Section 8, prior to fortification with the SUR and analyte.

11.3.3 If the sample bottles used contain a sample volume close to the sample volume to be extracted (± 10%), mark the sample level on the outside of the sample container for subsequent measurement of the sample volume. After the sample has been extracted, determine the exact sample volume by filling the bottle to the mark with water and transferring to an appropriately sized graduated cylinder. Measure to within ± 5 mL for 100 mL samples, and to within ± 25 mL for 500-mL samples. If a much larger sample has been collected than will be extracted, transfer either 100 mL or 500 mL of the sample to a clean glass container with a clean graduated cylinder. The sample volume will depend upon the SPE being used (Sects. 11.4, 11.5).

Alternatively, the sample volume may be calculated by weighing the sample bottle before and after extraction (or sample transfer) and using a density of 1.0 g/mL.

11.3.4 ADDITION OF SURROGATE (SUR) ANALYTE – Add an aliquot of the Surrogate Analyte Fortification Solution (Sect. 7.2.3.2) to all samples and mix by swirling the sample. Addition of 2.5 μL of a 2000-μg/mL solution to a 500-mL sample will result in a concentration of 10 μg/L. Addition of 5 μL of a 200-μg/mL solution to a 100-mL sample will also result in a concentration of 10 μg/L.

11.3.5 FORTIFICATION WITH METHOD ANALYTE – If the sample is an LFB, LFSM, or LFSMD, add the necessary amount of Analyte Fortification Solution (Sect. 7.2.3.1). Swirl each sample to ensure all components are properly mixed. Addition of 2.5 μL of a 200-μg/mL solution to a 500-mL sample will result in a concentration of 1 μg/L. Addition of 5 μL of a 20-μg/mL solution to a 100-mL sample will also result in a concentration of 1 μg/L.

11.3.6 Proceed with sample extraction Option 1 (Sect. 11.4) or Option 2 (Sect. 11.5).

11.4 SPE PROCEDURE OPTION 1; EXTRACTION OF 500-ML SAMPLES – Proper conditioning of the solid phase sorbent can have a marked effect on method precision and accuracy. This section describes the SPE procedure using 2-g coconut charcoal cartridges and the transfer tube system and SPE manifold as described in Section 6.8.

  11.4.1 CARTRIDGE CONDITIONING

    11.4.1.1 Fill the cartridge with approximately 3 mL of DCM, turn on the vacuum, and pull the solvent through, aspirating completely.

    11.4.1.2 Fill the cartridge with approximately 3 mL of methanol, turn on the vacuum, and pull the solvent through, aspirating completely.

    11.4.1.3 Fill the cartridge with approximately 3 mL of methanol and elute with vacuum to just above the top frit - not allowing the cartridge to go dry at the end. From this point forward, do not allow the cartridge to go dry.

    11.4.1.4 Fill the cartridge with approximately 3 mL of reagent water, turn on the vacuum, and pull the water through, repeat five times, without allowing the cartridge to go dry in between washes or at the end.

  11.4.2 SAMPLE EXTRACTION – Attach a transfer tube from each sample bottle to each cartridge and then turn on the vacuum. Adjust the vacuum so that the approximate flow rate is 10 mL/min. After all the sample has passed through each SPE cartridge, detach the transfer tube and draw air through the cartridge for 10 min at full vacuum. Turn off and release the vacuum. Proceed immediately with cartridge elution.

  11.4.3 CARTRIDGE ELUTION – Lift the extraction manifold top and insert a rack with collection tubes into the vacuum manifold tank to collect the extracts as they are eluted from the cartridges. Fill each cartridge with DCM. Pull enough of the solvent into the cartridge at low vacuum to soak the sorbent. Turn off the vacuum and vent the system. Allow the sorbent to soak in DCM for approximately 1 min. Apply a low vacuum and pull the DCM through the cartridge in a dropwise fashion into the collection tube. Continue to add DCM to the cartridge as it is being drawn through until the volume of extract is about 9 mL, determined by the markings on the side of the collection tube.

  11.4.4 Remove collection tubes containing the extract from the vacuum manifold. Adjust the final volume as closely as possible to 10 mL with DCM. Small amounts of residual water from the sample container and the SPE cartridge may form a small immiscible layer with the extract. Read the volume on the collection tube at the level of the DCM layer. Add the IS. Addition of 5 μL of a 1000-μg/mL IS solution to a 10-mL extract will result in an IS concentration of 500 ng/mL. Mix well. A vortex mixer is recommended. To eliminate residual water, add approximately 2 g of anhydrous sodium sulfate. Mix well. Transfer

aliquots of the extract to autosampler vials, or other glass vials, for storage until analysis.

NOTE: Experiments during method development indicated that this extract cannot be reliably concentrated by nitrogen evaporation because of the volatility of the method analyte. Therefore, extract concentration to enhance sensitivity is not permitted.

11.5   SPE PROCEDURE OPTION 2; EXTRACTION OF 100-ML SAMPLES – Proper conditioning of the solid phase sorbent can have a marked effect on method precision and accuracy. This section describes the SPE procedure using Waters AC-2 Sep-Pak or Supelco Supelclean ENVI-Carb Plus cartridges with 60-mL reservoirs and the SPE manifold as described in Sect. 6.8.

   11.5.1 CARTRIDGE CONDITIONING

       11.5.1.1 Fill the cartridge with approximately 1 mL of DCM, turn on the vacuum, and pull the solvent through, aspirating completely.

       11.5.1.2 Place a reservoir over each cartridge and fill the cartridge with approximately 2 mL of methanol, turn on the vacuum, and pull the solvent through, aspirating completely.

       11.5.1.3 Fill the cartridge with approximately 2 mL of methanol and elute with vacuum to just above the top of the cartridge - not allowing the cartridge to go dry at the end. From this point forward, do not allow the cartridge to go dry.

       11.5.1.4 Fill the cartridge with approximately 3 mL of reagent water, turn on the vacuum, and pull the water through, without allowing the cartridge to go dry.

   11.5.2 SAMPLE EXTRACTION – Fill each reservoir with sample. Adjust the vacuum so that the approximate flow rate is 10 mL/min. A 60-mL reservoir will require a second filling to complete sample loading. After all the sample has passed through each SPE cartridge, detach the reservoir and draw air through the cartridge for 10 min at full vacuum. Turn off and release the vacuum. Proceed immediately with cartridge elution.

   11.5.3 CARTRIDGE ELUTION – Lift the extraction manifold top and insert a rack with 2-mL volumetric collection tubes into the extraction tank to collect the extracts as they are eluted from the cartridges. (It is not necessary to reverse the ENVI-Carb Plus cartridge as described in the manufacturer's literature.) Fill each cartridge with DCM. Pull enough of the solvent into the cartridge at low vacuum to soak the sorbent. Turn off the vacuum and vent the system. Allow the sorbent to soak in DCM for approximately 1 min. Apply a low vacuum and pull the DCM

through the cartridge in a dropwise fashion into the collection tube. Continue to add DCM to the cartridge as it is being drawn through until the volume of extract is about 1.5 mL, estimated by the volumetric mark on the side of the collection tube.

11.5.4   Remove collection tubes containing the extracts from the vacuum manifold. Adjust the final volume as closely as possible to 2 mL with DCM. Small amounts of residual water from the sample container and the SPE cartridge may form a small immiscible layer with the extract. Read the volume on the collection tube at the level of the DCM layer. Add the IS. Addition of 10 µL of a 100-µg/mL IS solution to a 2-mL extract will result in an IS concentration of 500 ng/mL. Mix well. A vortex mixer is recommended. To eliminate residual water, pass the 2-mL extracts through a small column containing a minimum of 0.4 g of dry anhydrous sodium sulfate. A fritted 3-mL polypropylene column or a 5-8 mm diameter disposable pipette with a small piece of glass wool may be used. Collect the extracts from the drying column directly in 2-mL autosampler vials for storage until analysis.

NOTE: Experiments during method development indicated that this extract cannot be reliably concentrated by nitrogen evaporation because of the volatility of the method analyte. Therefore, extract concentration to enhance sensitivity is not permitted.

11.6   Analyze an aliquot of the sample extract prepared using Option 1 or 2, with the GC/MS system under the same conditions used for the initial and continuing calibrations (Sect. 10).

12. DATA ANALYSIS AND CALCULATIONS

12.1   IDENTIFICATION OF ANALYTES – At the conclusion of data acquisition, use the same software that was used in the calibration procedure to identify peaks in predetermined retention time windows of interest. Use the data system software to examine the ion abundances of components of the chromatogram. Identify a sample component by comparison of its SIM (or full scan) mass spectrum to a SIM (or full scan) reference spectrum in the user-created database. The GC retention time of a method analyte should be within one to two sec of the retention time observed for that same compound in the most recently analyzed CCC standard. Ideally, the width of the retention time window should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for an analyte. However, the experience of the analyst should weigh heavily in the interpretation of the chromatogram. When this method is performed in the SIM mode, verification of retention times is particularly important because less mass spectral information is being collected.

12.2 IDENTIFICATION VERIFICATION USING ION RATIOS – When the QI of 1,4-dioxane (*m/z* 88) is observed at the correct retention time, verify that it is truly present by verifying that the ratio of the confirmation ion (*m/z* 58) to the QI (*m/z* 88) is within an absolute ±20% of the ratio observed in a mid-range calibration standard. For example, if the ratio in the standard is 70%, then the ratio in a Field Sample must be within 50-90%. **Ratios must be determined using the integrated areas for the QI and confirmation ion from their respective mass chromatograms.** Using relative abundances obtained directly from the mass spectrum, whether or not it has undergone background subtraction, is not acceptable. Variations in system software and analyst subjectivity in selecting background spectra for subtraction can affect the validity of the ratio calculation when the relative abundance from the spectrum is used. Using a raw spectrum (not corrected for background) can also affect the validity of the ratio calculation.

Use similar procedures for identification of the IS and SUR. Suggested QIs and confirmation ions for these compounds may be found in Table 2 (Sect. 17).

12.3 Calculate analyte and SUR concentrations using the multi-point calibration established in Section 10.2. Do not use daily CCC data to quantitate 1,4-dioxane or the SUR in samples. The integrated abundances of the QIs of the analyte, SUR and IS should be used for all calculations. Adjust the final analyte concentrations to reflect the actual sample volume as determined in Sect.11.3.3. Field Sample extracts that require dilution should be treated as described in Section 12.4.

12.4 EXCEEDING CALIBRATION RANGE – An analyst must not extrapolate beyond the established calibration range. If an analyte result exceeds the range of the initial calibration curve, the extract may be diluted with DCM, with the appropriate amount of IS added to match the original concentration, and the diluted extract injected. Acceptable SUR performance (Sect. 9.3.6.1) should be determined from the undiluted sample extract. Incorporate the dilution factor into final concentration calculations. The resulting sample should be documented as a dilution, and the MRL adjusted accordingly.

12.5 Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

NOTE: Some data in Section 17 of this method are reported with more than two significant figures. This is done to better illustrate the method performance data.

13. <u>METHOD PERFORMANCE</u>

13.1 Method performance data presented in Section 17 were obtained with a Thermo Finnigan Trace DSQ GC/MS system. Any GC/MS system that meets all of the QC requirements of the method may be used.

13.2 PRECISION, ACCURACY, AND MINIMUM REPORTING LEVELS – Single laboratory DLs and LCMRLs are presented in Table 3. Single laboratory accuracy and precision data from both fortified reagent water and fortified drinking water matrices are presented in Tables 4 and 5, respectively. Two of the matrices tested were selected specifically as potentially difficult matrices because of either their relatively high TOC or high mineral content (hardness). There was no apparent difference in method performance when results from reagent water studies were compared to these drinking water matrices.

13.3 METHOD PERFORMANCE IN SAMPLES WITH HIGH CONCENTRATIONS OF 1,1,1-TRICHLORETHANE – Because of its widespread use as a chlorinated solvent stabilizer, 1,4-dioxane may be found in the presence of high concentrations of 1,1,1-trichloroethane. The method was tested in a high TOC water matrix with up to 500 µg/L of 1,1,1-trichloroethane added as a co-contaminant. No adverse affect was observed, and the method performed well within QC limits (data not shown).

13.4 SAMPLE STORAGE STABILITY STUDIES

13.4.1 AQUEOUS SAMPLES – Chlorinated drinking water samples from a surface water source were fortified with 1,4-dioxane and preserved and stored as required in Section 8. Samples were extracted and analyzed in replicate (n=7) on day 0, and at five additional times points up to and beyond 28 days. Data from these analyses validate the 28 day holding time, and are presented in Figure 2.

13.4.2 EXTRACTS – Sample extracts stored at -5 °C and protected from light were analyzed in replicate (n=7) on day 0, and at three additional time points up to and beyond 28 days. Data from these analyses validate the 28 day holding time, and are presented in Figure 3.

13.5 MULTIPLE LABORATORY DEMONSTRATION – The performance of this method was demonstrated in two additional laboratories, with results similar to those reported in Section 17. The authors wish to acknowledge the assistance of the analysts and laboratories listed below for their participation in the multi-lab demonstration.

13.5.1 Mr. Alan Zaffiro of Shaw Environmental and Infrastructure, Inc. under contract to the USEPA Office of Ground Water and Drinking Water Technical Support Center, Cincinnati, OH.

13.5.2 Dr. Peggy Knight and Ms. Megan Pickett of the USEPA Region 10 Laboratory, Port Orchard, WA.

14. POLLUTION PREVENTION

14.1 This method utilizes SPE to extract the analyte from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analyte, thereby minimizing the potential hazards to both the analyst and the environment as compared

to the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036 or on-line at http://membership.acs.org/c/ccs/pub_9.htm. (accessed September 2008).

15. WASTE MANAGEMENT

15.1 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents and solvents are used. The matrices of concern are finished drinking water or source water. Waste management practices must be conducted consistent with all applicable rules and regulations, and laboratories must protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16. REFERENCES

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6. *Carcinogens - Working With Carcinogens.* Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.

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8. *Safety in Academic Chemistry Laboratories.* American Chemical Society Publication, Committee on Chemical Safety, 7th Edition. Information on obtaining a copy is available at http://membership.acs.org/C/CCS/pub_3.htm. (accessed September 2008). Also available by request at OSS@acs.org

17.TABLES, DIAGRAMS, FLOWCHARTS AND DEMONSTRATION DATA

Table 1.   Bromofluorobenzene (BFB) Tune Verification Criteria

Mass (m/z)	Relative Abundance Criteria
50	15-40% of mass 95
75	30-80% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5-9% of mass 174
176	>95% but <101% of mass 174
177	5-9% of mass 176

Table 2.   Retention Times and Quantitation Ions (QIs)

Compound	Retention Time (min)	SIM Ions (m/z)
1,4-dioxane	8.85	58[a], **88**
1,4-dioxane-d_8 (SUR)	8.77	62, 64, **96**
THF-d_8 (IS)	6.68	**46**, 78, 80

Note: Suggested quantitation ion in bold.

a. Ion traps may give a confirmation ion of m/z 57 for 1,4-dioxane instead of the typical m/z 58 in quadrupole spectra and in many mass spectral libraries. If the instrument has been calibrated and passes bromofluorobenzene (BFB) criteria, then m/z 57 may be used as the confirmation ion on ion trap instruments.

Table 3.   Lowest Concentration Minimum Reporting Level (LCMRL) and Detection Limit (DL) Calculated for Each Extraction Option

Compound/Extraction Option	LCMRL (μg/L)	DL (μg/L)
1,4-dioxane (500 ml w/2-g Coconut charcoal)	0.047	0.026[a]
1,4-dioxane (100 ml w/Waters AC-2 Sep-Pak cartridge)	0.036	0.020[b]

a. Calculated from replicates fortified at 0.040 µg/L, n=7.
b. Calculated from replicates fortified at 0.030 µg/L, n=8.

Table 4. Demonstration of Method Performance in Reagent Water Fortified with 1,4-Dioxane at Three Concentrations

Compound/Extraction Option	Reagent Water Fortified at 0.030 or 0.040 µg/L (n=7 or 8) [a]	
	Mean % recovery	RSD (%)
1,4-dioxane (500 ml w/2-g Coconut charcoal)	110	19
1,4-dioxane-d_8 (SUR) (500 ml w/2-g Coconut charcoal)	92	3.5
1,4-dioxane (100 ml w/Waters AC-2 Sep-Pak cartridge)	110	20
1,4-dioxane-d_8 (SUR) (100 ml w/Waters AC-2 Sep-Pak cartridge)	102	3.8
	Reagent Water Fortified at 1.0 µg/L (n=6)	
	Mean % recovery	RSD (%)
1,4-dioxane (500 ml w/2-g Coconut charcoal)	98.0	6.2
1,4-dioxane-d_8 (SUR) (500 ml w/2-g Coconut charcoal)	97.1	5.2
1,4-dioxane (100 ml w/Waters AC-2 Sep-Pak cartridge)	101	4.2
1,4-dioxane-d_8 (SUR) (100 ml w/Waters AC-2 Sep-Pak cartridge)	105	4.8
	Reagent Water Fortified at 10.0 µg/L (n=7)	
	Mean % recovery	RSD (%)
1,4-dioxane (500 ml w/2-g Coconut charcoal)	93.9	2.8
1,4-dioxane-d_8 (SUR) (500 ml w/2-g Coconut charcoal)	90.1	2.8
1,4-dioxane (100 ml w/Waters AC-2 Sep-Pak cartridge)	95.2	2.9
1,4-dioxane-d_8 (SUR) (100 ml w/Waters AC-2 Sep-Pak cartridge)	99.3	3.0

a. Samples (500 mL) extracted on 2-g Coconut charcoal cartridges were fortified at 0.040 µg/L, n=7. Samples (100 mL) extracted on Waters AC-2 Sep-Pak cartridges were fortified at 0.030 µg/L, n=8.

Table 5. Demonstration of Method Performance in Drinking Water Matrices Using Each of the Solid Phase Extraction (SPE) Options; Matrix Samples Fortified at 1.0 µg/L (n=7 for each matrix)

Compound/Extraction Option	Surface Water	
	Mean % recovery	**RSD (%)**
1,4-dioxane (500 ml w/2-g Coconut charcoal)	99.0[a]	4.9
1,4-dioxane-d_8 (SUR) (500 ml w/2-g Coconut charcoal)	100	2.5
1,4-dioxane (100 ml w/Waters AC-2 Sep-Pak cartridge)	97.0[b]	4.6
1,4-dioxane-d_8 (SUR) (100 ml w/Waters AC-2 Sep-Pak cartridge)	98.5	2.5
	Surface Water (high in TOC)[c]	
	Mean % recovery	**RSD (%)**
1,4-dioxane (500 ml w/2-g Coconut charcoal)	102	3.5
1,4-dioxane-d_8 (SUR) (500 ml w/2-g Coconut charcoal)	99.8	2.4
1,4-dioxane (100 ml w/Waters AC-2 Sep-Pak cartridge)	98.5	5.6
1,4-dioxane-d_8 (SUR) (100 ml w/Waters AC-2 Sep-Pak cartridge)	101	4.2
	Groundwater (high in mineral content) [d]	
	Mean % recovery	**RSD (%)**
1,4-dioxane (500 ml w/2-g Coconut charcoal)	95.9[e]	2.1
1,4-dioxane-d_8 (SUR) (500 ml w/2-g Coconut charcoal)	98.2	2.5
1,4-dioxane (100 ml w/Waters AC-2 Sep-Pak cartridge)	101[f]	3.3
1,4-dioxane-d_8 (SUR) (100 ml w/Waters AC-2 Sep-Pak cartridge)	104	5.9

a. Percent recovery after correction for matrix background of 0.66 µg/L.
b. Percent recovery after correction for matrix background of 0.42 µg/L.
  Note: Groundwater used for these Laboratory Fortified Blanks (LFBs) was collected from the same source as the 500 mL LFBs using coconut charcoal, but was collected on different days, thus the difference in matrix background concentration.
c. TOC measured at 4.950 mg/L.
d. Hardness measured at 289 mg/L as calcium carbonate.
e. Percent recovery after correction for matrix background of 0.070 µg/L.
f. Percent recovery after correction for matrix background of 0.080 µg/L.

Table 6.   Initial Demonstration of Capability (IDC) and Quality Control (QC) Requirements (Summary)

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.2.1	Initial Demonstration of Low Background	Analyze LRB prior to any other IDC steps. When a new lot of SPE media is obtained, verify that background is at acceptable limits.	Demonstrate that the method analyte is $\leq 1/3$ the MRL, and that possible interferences from extraction media do not prevent the identification and/or quantification of the method analyte, SUR or IS. **Note:** This includes the absence of interferences at both the QIs and confirmation ions at the RTs of interest.
Sect. 9.2.2	Initial Demonstration of Precision (IDP)	Analyze 4-7 replicate LFBs fortified near the midrange calibration concentration.	%RSD must be $\leq 20\%$
Sect. 9.2.3	Initial Demonstration of Accuracy (IDA)	Calculate average recovery for replicates used in IDP.	Mean recovery $\pm 20\%$ of true value
Sect. 9.2.4	Minimum Reporting Limit (MRL) Confirmation	Fortify, extract and analyze 7 replicates at the proposed MRL concentration. Calculate the mean, standard deviation and HR_{PIR}. Confirm that the upper and lower limits for the Prediction Interval of Result (Upper PIR, and Lower PIR, Sect. 9.2.4.2) meet the recovery criteria.	Upper PIR $\leq 150\%$ Lower PIR $\geq 50\%$
Sect. 9.2.5 & 9.3.9	Calibration Confirmation, Quality Control Sample (QCS)	Analyze a standard from a second source (QCS) to verify the initial calibration curve.	$\pm 20\%$ of the expected value.

NOTE: Table 6 is intended as an abbreviated summary of QC requirements provided as a convenience to the method user. Because the information has been abbreviated to fit the table format, there may be issues that need additional clarification, or areas where important additional information from the method text is needed. In all cases, the full text of the QC in Section 9 supersedes any missing or conflicting information in this table.

**Table 7. Ongoing Quality Control (QC) Requirements (Summary)**

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 8.3	Sample Holding Time	28 days with appropriate preservation and storage as described in Sections 8.1-8.3.	Sample results are valid only if samples are extracted within sample hold time.
Sect. 8.4	Extract Holding Time	28 days stored at -5 °C and protected from light	Sample results are valid only if extracts are analyzed within extract hold time.
Sect. 9.3.1	Laboratory Reagent Blank (LRB)	One LRB with each extraction batch of up to 20 Field Samples.	Demonstrate that the method analyte concentration is $\leq \frac{1}{3}$ the MRL, and confirm that possible interferences do not prevent quantification. If the background concentration exceeds $\frac{1}{3}$ the MRL, results for the extraction batch are invalid.
Sect. 9.3.3	Laboratory Fortified Blank (LFB)	One LFB is required for each extraction batch of up to 20 Field Samples. Rotate the fortified concentrations between low, medium, and high amounts.	Results of LFB analyses at medium and high fortifications must be 70-130% of the true value for the analyte and SUR. Results of the low-level LFB must be 50-150% of the true value.
Sect. 9.3.5	Internal Standard (IS)	Compare IS area to the average IS area in the initial calibration and the most recent CCC.	Peak area counts for all injections must be within $\pm$ 50% of the average peak area calculated during the initial calibration and $\pm$ 30% from the most recent CCC. If the IS does not meet this criterion, target analyte results are invalid. Consult Sect. 9.3.5 for further information.
Sect. 9.3.6	Surrogate(SUR) Standards	The SUR standard added to all calibration standards and samples, including QC samples. Calculate SUR recoveries.	SUR recovery must be 70-130% of the true value. If a SUR fails this criterion, report all results for sample as suspect/SUR recovery.
Sect. 9.3.7	Laboratory Fortified Sample Matrix (LFSM)	Analyze one LFSM per extraction batch (of up to 20 Field Samples) fortified with the method analyte at a concentration close to but greater than the native concentration. Calculate LFSM recoveries.	See Sect. 9.3.7.3 for instructions on the interpretation of LFSM results.

Table 7.Ongoing Quality Control (QC) Requirements (Summary) (Continued)

|			
Sect. 9.3.8	Laboratory Fortified Sample Matrix Duplicate (LFSMD) or Field Duplicates (FD)	Extract and analyze at least one FD or LFSMD with each extraction batch of up to 20 Field Samples. A LFSMD may be substituted for a FD when the frequency of detects for 1,4-dioxane are low. Calculate RPDs.	Method analyte RPDs for the LFSMD or FD should be ≤ 30% at mid and high levels of fortification and ≤ 50% near the MRL. Failure to meet this criterion may indicate a matrix effect.
Sect. 9.3.9	Quality Control Sample (QCS)	Analyze QCS during the IDC, each time CAL solutions are prepared. A QCS must be analyzed at least quarterly.	Results must be 80-120% of the expected value.
Sect. 10.2	Initial Calibration	Use IS calibration technique to generate a linear or quadratic calibration curve. The number of standards required is determined by the calibration range (Sect. 7.2.2). Check the calibration curve as described in Section 10.2.4.	When each calibration standard is calculated as an unknown using the calibration curve, the result should be 80-120% of the true value for all except the lowest standard, which should be 60-140% of the true value. If this criterion is not met, reanalyze CALs, select a different method of calibration or recalibrate over a shorter range.
Sects. 10.1 and 10.2.1	MS Tune Check	Analyze BFB to verify MS tune each time the instrument is calibrated.	Criteria are given in Table 1.
Sect. 10.3	Continuing Calibration Check (CCC)	Verify initial calibration by analyzing a calibration standard at the beginning of each analysis batch prior to analyzing samples, after every 10 samples, and after the last sample. The first CCC daily must be at or below the MRL. Subsequent CCCs alternate between medium and high concentrations. Low CCC – at or below the MRL concentration Mid CCC – near midpoint in initial calibration curve High CCC – near the highest calibration standard.	Low: ± 50% of true value Mid: ± 30% of true value High: ± 30% of true value

Note: Table 7 is intended as an abbreviated summary of QC requirements provided as a convenience to the method user. Because the information has been abbreviated to fit the table format, there may be issues that need additional clarification, or areas where important additional information from the method text is needed. In all cases, the full text of Sections 8-10 in the method supersedes any missing or conflicting information in this table.
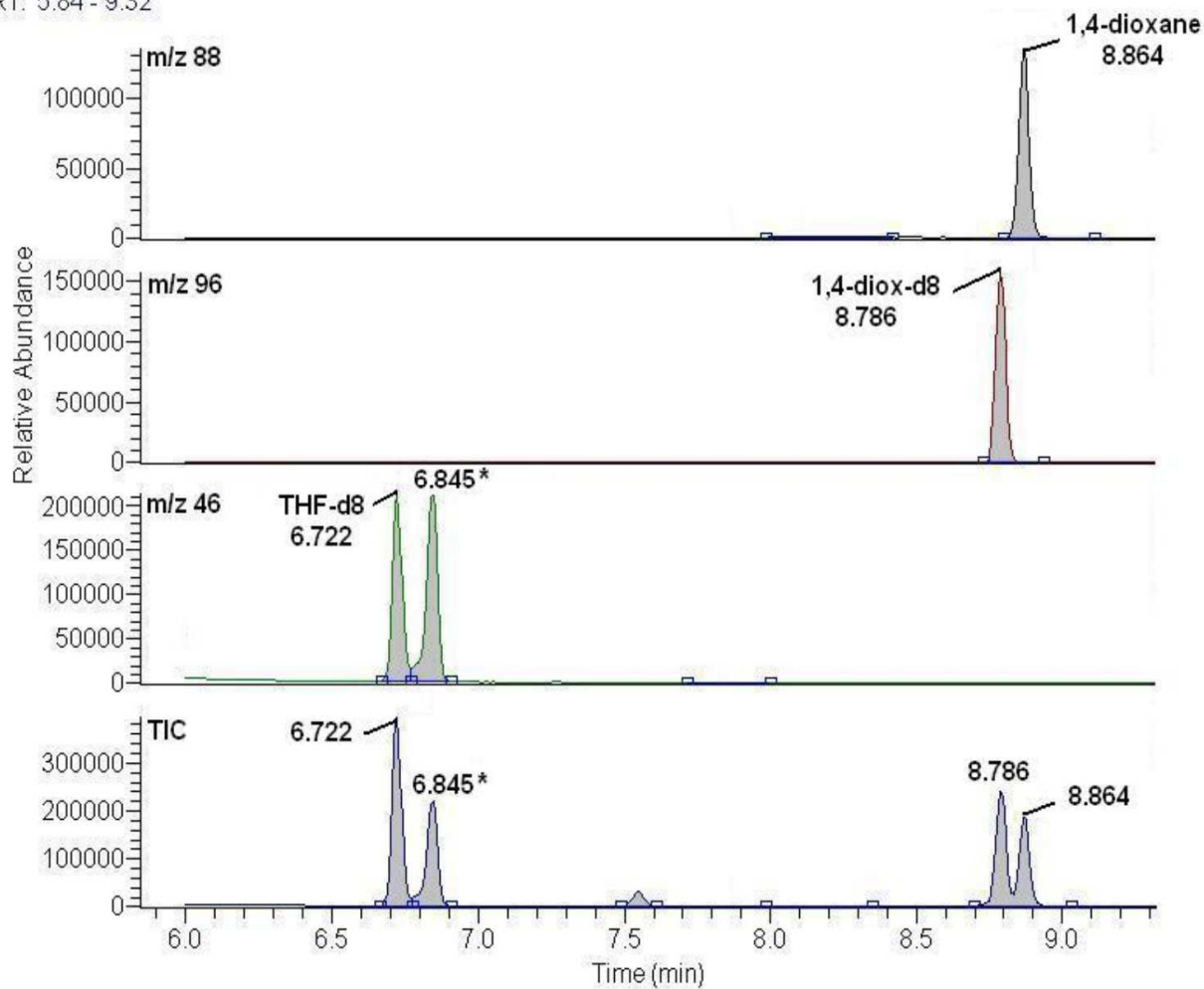
Figure 1. Reconstructed total ion current chromatogram and mass chromatograms for THF-d_8 (IS), 1,4-dioxane-d_8 (SUR), and 1,4-dioxane at 0.5 µg/mL each (the standard is equivalent to an extract of a 10 µg/L aqueous sample). * Peak at 6.845 min is chloroform, a chemical present in DCM.
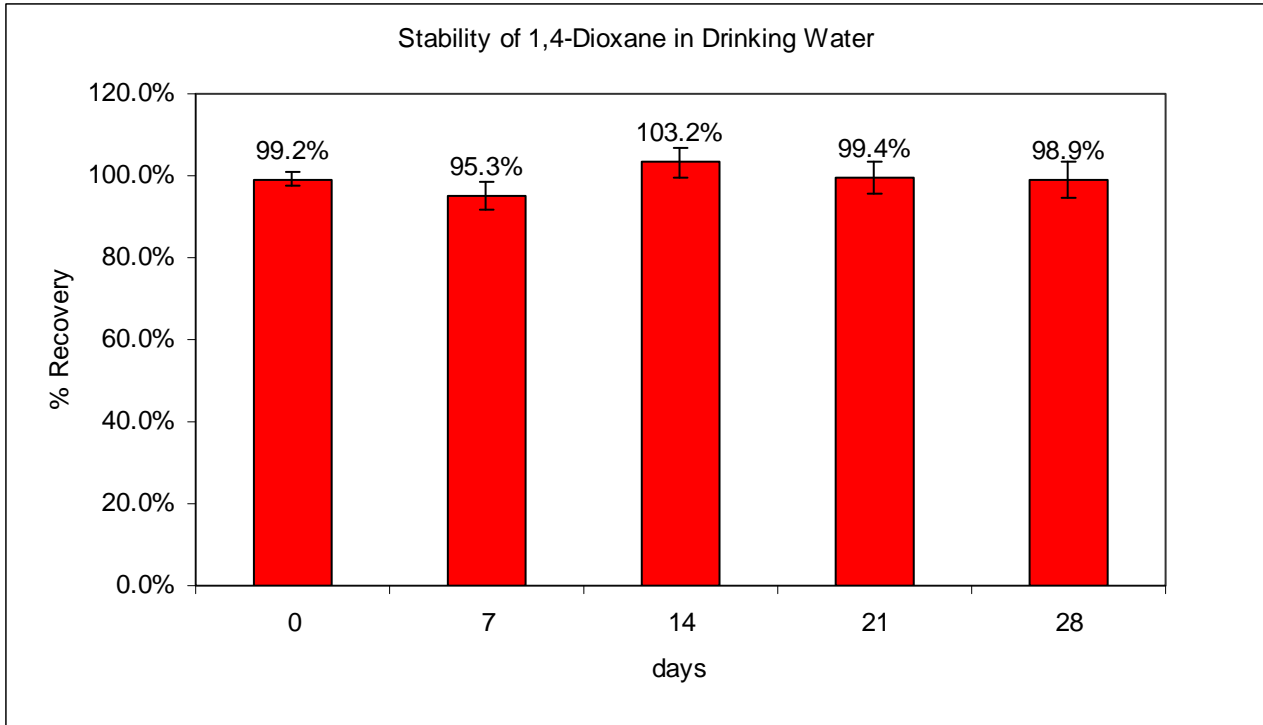
Figure 2. Stability of 1,4-dioxane in preserved drinking water stored at 4°C in the dark, over a 35-day time period. Replicate samples (*n* = 7) were fortified to a concentration of 1 μg/L 1,4-dioxane. Matrix blank data were used to correct for native analyte concentrations.
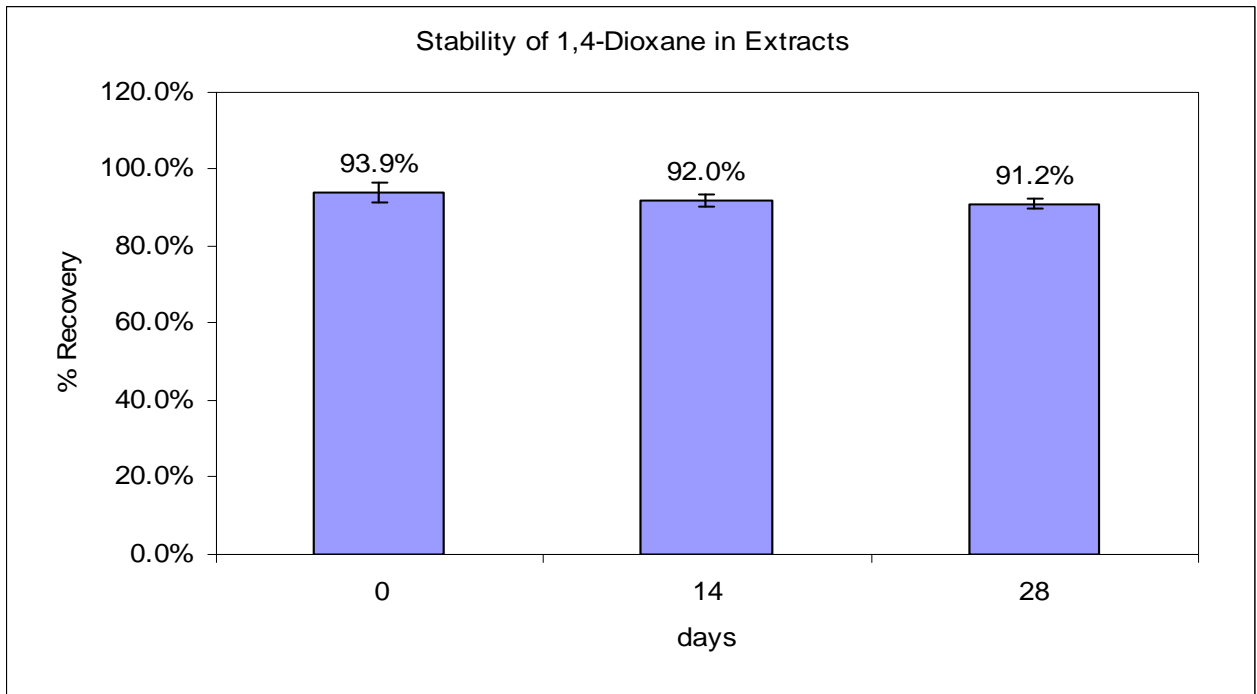
Figure 3. Stability of 1,4-dioxane in sample extracts stored at -5°C, in the dark, over a 42-day time period. Replicate samples (*n* = 7) were fortified to a concentration of 10 μg/L 1,4-dioxane.