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ANALYSIS OF 1,4-DIOXANE IN WATER BY GC/MS SIM (EPA/SW-846 Methods 8000B/8260B)

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1.0 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) outlines the analysis of 1,4-dioxane in water matrices using a gas chromatograph/mass spectrometer (GC/MS) by the Environmental Response Team/Scientific Engineering Response & Analytical Services (ERT/SERAS) Laboratory. This method is based on a modification of Environmental Protection Agency (EPA) Methods SW846/8000B/8260B and those requirements set forth in the latest approved version of the National Environmental Laboratory Accreditation Committee (NELAC) Quality Systems. This method uses the selective ion monitoring (SIM) mode with a 25-milliliter (mL) purge volume for water samples. The reporting limit (RL) is provided in Table 1, Appendix A. The ions used for 1,4-dioxane are listed in Table 3, Appendix A.

This method may not be changed without the expressed approval of the Quality Assurance/Quality Control (QA/QC) Officer and the Analytical Support Leader. Only those versions issued through the SERAS document control system may be used. Modifications made to the procedure due to interferences in the samples or for any other reason must be documented in the case narrative and on a nonconformance memo.

2.0 METHOD SUMMARY

1,4-Dioxane is purged from the sample matrix by bubbling an inert gas through a 25-mL sample in a sparging tube that is connected to a concentrator. The inert gas bubbling through the solution at 50 degrees Celsius (°C) transfers the purgeable 1,4-dioxane from the aqueous phase to the vapor phase. The vapor is then swept through a three-sorbent-bed trap where the 1,4-dioxane is trapped. When purging is complete, the sorbent trap is heated and backflushed with helium to desorb the trapped 1,4-dioxane onto a GC capillary column interfaced to a MS. The GC column is temperature programmed to separate the 1,4-dioxane, which is detected with the MS. The 1,4-dioxane eluting from the GC column is identified by comparing its measured mass spectra and retention time to reference spectra and the retention time for 1,4-dioxane in a database. Reference spectra (using ions 88 and 58 for 1,4-Dioxane) and the retention time for this analyte are obtained from the measurement of calibration standards under the same GC/MS operating conditions used for water samples. The concentration is measured by relating the MS response of the quantitation ion produced by 1,4-dioxane to the MS response of the quantitation ion produced by Bromochloromethane (BCM) is used as an internal standard. The surrogate compound 4-bromofluorobenzene (BFB), whose concentration is known, is measured with the same internal standard calibration procedure. To achieve the low RL for this compound that is very water soluble, the SIM mode is used.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

3.1 Sample Storage

Water samples must be collected in 40-mL Teflon[®]-lined septum vials. From the time of collection until after analysis, unused samples must be protected from light and refrigerated at less than or equal to (\leq) 6°C for the periods specified by SERAS Task Leader (TL) and/or the Work Assignment Manager (WAM) for the project.

Samples must be stored separately from standards in an atmosphere free of all potential contaminants.



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3.2 Holding Times

The analysis of water samples must be completed within 7 days of sample collection if unpreserved or 14 days if preserved with 1:1 hydrochloric acid (HCl) to pH less than (<) 2.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

The analytical system must be demonstrated to be contaminant free by analyzing laboratory blanks. The use of non-Teflon® tubing, non-Teflon® thread sealants or flow controllers with rubber components in the purging device is not allowed. Since the SIM method is used and selected ions of 1,4-dioxane are scanned for a certain period of time, other interferences are greatly diminished.

Carryover contamination may occur when samples containing high levels of target and non-target compounds are analyzed. A system blank should be analyzed after a sample with high target compounds or the sample with the carryover must be reanalyzed. If an unusually concentrated sample is analyzed, the inlet and column may be baked for approximately 10 minutes and blanks may be analyzed. If contamination still persists, the inlet may be changed and baked further.

The laboratory where 1,4-dioxane analysis is performed should be completely free of solvents. Any solvents or solvent waste containers, used or stored in the laboratory during the analysis, must be kept in a vented hood or vented storage area.

5.0 EQUIPMENT/APPARATUS

- Micro syringes, 1000-microliter (μL) or smaller, 0.006 inch inner diameter (ID) needle
- Syringes, 25- and 50-mL, gas tight with Luer end
- Vials - 40-mL, screw cap with Teflon®-lined septum
- Volumetric flasks - Class A with ground-glass stopper
- Vials - 2-mL, screw cap with Teflon®-lined septum
- Hewlett-Packard (HP) 6890 GC/5975 MS, interfaced with a HP CHEM STATION data system or equivalent
- Purge and Trap Unit, OI Eclipse 4660 concentrator equipped with an ARCHON Auto sampler
- Restek Column- Rtx-VOA 30 meter (m), 250 micron (μm) ID with a $3\mu\text{m}$ thickness



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6.0 REAGENTS

- Deionized (DI) water or equivalent, commercially available, suitable for VOC analysis
- Helium, ultra high purity (99.999%)
- Methanol (MeOH), purge and trap quality
- Calibration Stock 1,4-Dioxane Standard Solution, 2000 micrograms per milliliter ($\mu\text{g/mL}$), commercially available
- Calibration Intermediate 1,4-Dioxane Standard, 250 $\mu\text{g/mL}$ – Add 125 μL to 875 μL of MeOH.
- Secondary Stock Dioxane Standard Solution, 2000 $\mu\text{g/mL}$, commercially available, different source from calibration
- Secondary Working 1,4-Dioxane Standard, 250 $\mu\text{g/mL}$ – Add 125 μL to 875 μL of MeOH, used for the Laboratory Control Sample (LCS), Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Initial Calibration Verification (ICV).
- BCM Stock Internal Standard, 2000 $\mu\text{g/mL}$, commercially available
- BFB Stock Surrogate Standard, 2000 $\mu\text{g/mL}$, commercially available
- BCM/BFB Working Internal/Surrogate Standard, 250 $\mu\text{g/mL}$ – Add 125 μL of BCM Stock Internal Standard and 125 μL of Stock Surrogate Standard to 750 μL of MeOH.

NOTE: All of the above mentioned standard solutions must be stored at -4°C to -10°C (freezer section of the standards refrigerator) in tightly capped vials with Teflon® liners. Commercially prepared standard solutions that are received in sealed ampules may be stored in the shelf section of the standards refrigerator. Fresh mixtures should be prepared when the percent drift of 1,4-dioxane changes by more than 50 percent (%) or at least every six months.

NOTE: Premixed certified standards will be stored according to the manufacturer's documented storage requirements. These standards may be kept in storage up to the manufacturer's stated expiration date. Once the standard vials are opened, the standards will be stored with minimal headspace in the freezer for a period not to exceed six months or the manufacturer's expiration date, whichever is less.

NOTE: All calibration standards, internal standards, and spiking solutions will be prepared and documented in accordance with SERAS SOP #1012, *Preparation of Standard Solutions and Reagents*.



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7.0 PROCEDURE

7.1 GC/MS Operating Conditions

The conditions of the Electron Impact Ionization mass spectrometer are as follows:

Electron Energy:	70 volts (nominal)
Mass Range:	35 - 350 atomic mass units (amu)
Scan Time:	To give at least 5 scans per peak and not to exceed 3 seconds per scan.

The conditions of the GC HP 6890 GC system are as follows:

Helium carrier gas	Flow rate of 1.0 mL/minute (min)
Column temperature	Isothermal at 40 °C for 4 minutes Ramp at 9°C per minute to 165°C and hold for 2 minutes Ramp at 12°C per minute to 220°C and hold for 7 minutes
Inlet temperature	150°C
Source temperature	230°C
Total run time	~19 minutes
Time between injections	~45 minutes

GC/MS Interface, capillary direct with 1 mL/min helium carrier gas at 230°C.

The purge and trap conditions are as follows:

Purge	11 min at 50°C
Dry Purge	2 min at 50°C
Desorb preheat	180°C
Desorb	4 min at 190°C
Purge Flow Rate	40 mL/min
Bake	10 min at 210°C

Water Management Temp: Purge at 100°C, desorb at ambient and bake at 240°C

7.2 Bromofluorobenzene Tune

The autosampler adds 1 µL of the Working BCM/BFB solution to a 25-mL aliquot of reagent water equivalent to 10 nanograms (ng) per mL of BFB. The ion abundance criteria can be found in Table 2, Appendix A. The tune is acquired using either the apex or ± one scan. Background subtraction is required and must be accomplished using a single scan no more than 20 scans prior to the elution of the BFB. The BFB tune criteria must be met every 12 hours during sample analysis. If the software does not indicate what scan was subtracted, the analyst must document the scan number directly on the tune report.



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7.3 Initial Calibration

1. A 6-point initial calibration curve is prepared ranging from 1 µg/L to 50 µg/L as follows:

Standard Conc., µg/L	250 µg/mL Intermediate Calibration Standard, µL	250 µg/mL Working Internal/Surrogate Standard, µL	Final Volume, mL
50	10	2	50
30	6	2	50
20	4	2	50
10	2	2	50
5	1	2	50

The 1 µg/L working calibration standard is prepared by transferring 2 µL of the 250 µg/mL Intermediate Calibration Standard into a 500-mL volumetric flask and diluting to volume with DI water. Transfer 50 mL of the 1ppb working calibration standard into a syringe and add 2µL of the 250µg/mL working internal/surrogate standard. A 25-mL aliquot is transferred into a purge vessel and purged.

2. Calculate and tabulate the relative response factor (RRF) against the concentration for each compound by using the equation below. The primary ion from the internal standard must be used for quantitation. The average RRF and percent relative standard deviation (%RSD) must also be calculated and tabulated.

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:

A_x = Area of the characteristic ion for the compound to be measured
 A_{is} = Area of the characteristic ion for the specific internal standard
 C_{is} = Concentration of the internal standard, µg/L
 C_x = Concentration of the compound to be measured, µg/L

$$RRF = \frac{\sum_{i=1}^n RRF_i}{n}$$

where:

RRF_i = relative response factor for each initial calibration level
 n = total number of initial calibration levels

$$\%RSD = \frac{SD}{X} \times 100$$



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$$SD = \sqrt{\frac{\sum_{i=1}^n (\bar{X} - x)^2}{N - 1}}$$

The criterion for the %RSD can be found in Section 9.2. Due to the high solubility of 1,4-dioxane in water, a minimum RRF criterion has been set at 0.0010.

7.4 Initial Calibration Verification

The initial calibration curve must be verified immediately using the ICV standard. Add 4 μL of 250 $\mu\text{g}/\text{mL}$ of the secondary working 1,4-dioxane standard and 2 μL of the 250 $\mu\text{g}/\text{mL}$ working internal/surrogate standard to prepare a 20 ppb ICV.

7.5 Continuing Calibration

A check of the initial calibration curve must be performed every 12 hours after an acceptable BFB analysis. Sample analysis may begin only after a successful BFB tune and a continuing calibration check have been acquired.

1. Add 4 μL of 250 $\mu\text{g}/\text{mL}$ intermediate calibration standard and 2 μL of the 250 $\mu\text{g}/\text{mL}$ working internal/surrogate standard to prepare a 20 ppb midpoint calibration.
2. Calculate and tabulate the continuing calibration RRF for each compound.
3. Calculate the percent difference (%D) for the continuing calibration.

$$\%D = 100 - \left(\frac{\text{ActualConcentration}_{\text{Continuing}}}{\text{TrueConcentration}_{\text{Continuing}}} \times 100 \right)$$

4. The extracted ion current profile (EICP) area for each internal standard in the continuing calibration must be compared to the internal standard area in the mid-point standard of the current initial calibration. The criterion for comparison is found in section 9.4.

7.6 Sample Analysis

Prior to the analysis of calibration standards, blanks, and/or samples, it is necessary to verify that the GC/MS:

- Met the BFB ion abundance criteria listed in Table 2, Appendix A and in Section 9.1. The BFB tune criteria must be demonstrated every 12 hours by analyzing 10 ng of BFB.
- Successfully passed an initial six-point calibration and/or continuing calibration check. The continuing calibration check must be demonstrated every 12 hours during sample analysis by



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analyzing a 20 µg/L 1,4-dioxane standard.

The method blanks, LCS, MS/MSD and environmental samples must be analyzed with the same instrument conditions used for the calibration standards.

1. Method Blank(s) – Add 2µL of the working internal/surrogate standard mix to a 50 mL syringe containing organic free water and transfer to a 40-mL vial. Load this sample on the autosampler and analyze under the same conditions as the initial calibration and/or continuing calibration.
2. Undiluted Sample - Add 2µL of the working internal/surrogate standard mix to a 50 mL syringe containing the sample and transfer to a 40-mL vial. Load this sample on the autosampler and analyze under the same conditions as the initial calibration and/or continuing calibration.
3. Diluted Sample - If the analyst has reason (e.g., history or screening result) to believe that diluting the sample will be necessary, an undiluted run may not be required. If a target analyte exceeds the linear calibration range, use the appropriate dilution factor needed to bring the concentration within range. Ideally the concentration of the analyte should fall between midrange and the upper range of the curve after dilution.
4. MS/MSD Samples - Spike 4 µL of the secondary working 1,4-dioxane standard (250µg/mL) to 50 mL of a selected sample in duplicate for MS/MSD analysis. For water samples that require dilution, use appropriate diluted sample aliquots for the MS/MSD. Alternatively, spike 4 µL of MS intermediate solution (250µg/mL) to 50 mL of sample. Spike concentration is equivalent to 20µg/L.
5. LCS - Spike 4 µL of the secondary working 1,4-dioxane standard (250 µg/mL) to 50 mL of DI water for the LCS analysis. Spike concentration is equivalent to 20µg/L.

7.6 Identification of the Target Compound

Target compound identification will be made by comparison of the sample mass spectrum to the mass spectrum of a standard of the target compound. Two criteria must be satisfied to verify the identification:

- Elution of the sample component at the same GC relative retention time as the standard component
 - Correspondence of the sample component and standard component mass spectra
1. To establish correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the calibration standard must be analyzed within the same 12-hour time period as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.



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- For comparison of standard and sample component mass spectra, reference mass spectra must be obtained from the analysis of the 20 µg/L calibration standard. This standard spectrum may be obtained from the calibration run used to obtain reference RRT and daily relative response factor.
- The requirements for qualitative verification by comparison of mass spectra are as follows:

Because SIM analysis is being used and only two ions are being scanned, the compound will be identified first by its retention time. Both ions must be present but the relative abundances of each ion may vary at low concentrations.
- If a compound cannot be verified by the criteria in Step 3, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the analyst will report that identification and proceed with calculation in Section 8.0. The analyst must report in the case narrative that technical judgment was utilized.

8.0 CALCULATIONS

8.1 Target Compound

Identified target analytes must be quantitated by the internal standard method. The internal standard used must be the one nearest the retention time to that of a given analyte listed in Table 3, Appendix A. The extracted ion current profile (EICP) area of the characteristic ion of 1,4-dioxane listed in Table 3, Appendix A is used for quantitation.

Use the following equation to calculate the concentration of the identified analytes using the average RRF obtained from the initial calibration as described in Section 7.3.

A compound concentration will be calculated using the formula:

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_C)(I_{IS})(DF)}{(A_{IS})(RRF_{avg})(V_O)}$$

where:

C_c	=	Compound concentration, µg/L
A_c	=	Area of the characteristic ion for the compound
I_{is}	=	Amount of internal standard, ng
DF	=	Dilution factor
A_{is}	=	Area of the characteristic ion for the internal standard
RRF_{avg}	=	Average Relative Response Factor from the heated purge
V_0	=	Volume of water purged, mL



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The following EPA-defined flags will be used in the lab to qualify data:

U: This flag indicates that the compound was analyzed for but not detected

J: This flag indicates an estimated value above the limit of detection (LOD) and under the RL

B: This flag is used when the analyte is found in the associated method blank as well as in the sample

E: This flag identifies compounds whose concentrations exceed the upper calibration range of the instrument

All target concentrations are reported to three significant figures. For any concentrations reported from diluted runs, be sure to report the corresponding RL. For example, if a compound is run at a 10x dilution to bring the concentration within linear range, the RL must be reported at 10µg/L instead of 1.0µg/L.

8.2 Matrix Spike Recoveries

Accuracy (bias) is calculated from the MS/MSD recoveries. Precision is calculated from the relative percent difference (RPD) of the concentrations measured for the MS/MSD pair. Matrix spike recoveries and RPD will be calculated by the following equations:

$$\text{Matrix Spike Recovery (\%R)} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100$$

where:

SSR = Concentration of target analyte in spiked sample
SR = Concentration of target analyte in sample (unspiked)
SA = Concentration of spike added

and

$$\text{RPD} = \frac{(\text{MSR} - \text{MSDR})}{(\text{MSR} + \text{MSDR})/2} \times 100$$

where:

RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

Note: RPD is always expressed as a positive value.



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8.3 Laboratory Control Sample Recoveries

The recoveries of each of the compounds in the LCS solution will be calculated using the following equation:

$$LCS \text{ Recovery } (\%R) = \left(\frac{LCSR - B}{SA} \right) \times 100$$

where:

LCSR = Concentration of target analyte in LCS
B = Concentration of target analyte in blank
SA = Concentration of spike added

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 GC/MS Tuning and Performance Criteria

The GC/MS must be tuned with BFB and the ion abundance criteria listed in Table 2, Appendix A must be met prior to any standard, blank or sample analysis. In addition, the criteria must be achieved during every 12-hour period during which standards, blanks, and samples are analyzed. The 12-hour time period for GC/MS tuning begins at the time of injection of the BFB analysis that the laboratory submits as documentation of a compliant tune.

9.2 GC/MS Initial Calibration

The %RSD should be less than or equal to 50% for 1,4-dioxane.

Corrective action must be taken if the compound does not meet the criterion. Once this criterion has been met, blanks, samples and QC samples may be analyzed. Any deviations must be documented in the case narrative and on a nonconformance memo.

9.3 GC/MS Initial Calibration Verification

The initial calibration curve must be verified immediately using the ICV and prior to analyzing any blanks, samples or QC samples. The suggested acceptance limits for the ICV are 50-150% or until enough data are collected to generate control chart limits.

9.4 GC/MS Continuing Calibration

After 12 hours of sample acquisition have passed, the GC/MS must be re-tuned using BFB, and the initial calibration curve verified by the mid-level continuing calibration standard.

1. The BFB tune must pass the criteria in Table 2, Appendix A.
2. The 20 µg/L calibration standard must be used for the continuing calibration.



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3. The %D for 1,4-Dioxane must be $\pm 50\%$.
4. The EICP area for the internal standard in the continuing calibration must be between 50% and 200% of the respective internal standard EICP area in the mid-point standard of the current initial calibration. If this criterion is not met, re-analysis is required.
5. A maximum of two continuing calibrations may be run to meet the requirements in item 3 above. A new calibration curve must be reanalyzed if both continuing calibrations are unacceptable or instrument maintenance must be performed.
6. If any of the requirements listed in Step 3 are not met, notify the Analytical Support Leader.

9.5 Method Blank

A method blank is a volume of DI water, surrogate and internal standard carried through the entire analytical scheme. The method blank volume must be approximately equal to the sample volume.

1. A method blank analysis must be performed every 12 hours and must be analyzed immediately after calibration and prior to the analysis of any samples.
2. The 1,4-dioxane concentration must be less than the RL unless the concentration is ten times greater than the RL of 1.0 $\mu\text{g/L}$.

9.6 System Blank

A system blank may be run after any samples or dilutions that contain a level of target analyte exceeding the initial calibration range to ensure that there is no carryover from a previous sample. If samples are run after a system blank, the system blank must be free of the contaminants which are being quantitated in the subsequent samples.

9.7 Surrogate Spike Analysis

1. Each sample, LCS, MS, MSD and method blank are spiked with BFB prior to purging at a concentration of 10 $\mu\text{g/L}$. Deviations from the spiking protocol are not permitted.
2. The surrogate recovery limit for BFB is 86-115%. If the sample surrogate recovery does not meet the criterion, the affected sample must be reanalyzed to establish whether the nonconformance was due to the sample matrix or due to a laboratory problem.

If upon re-analysis of the sample the surrogate recovery falls within the QC limits, the problem was within the laboratory's control. Submit only the data from the analysis with the surrogate recovery within the QC limits. This will be considered the initial analysis and reported in the data package. If the analysis is outside the holding time, both sets of data will be submitted. Sample results will be evaluated based on the surrogate and the associated target compound.



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If upon re-analysis, the surrogate still falls outside QC limits, submit both sets of data. Distinguish between the initial and re-analysis in the data package.

3. If the method blank surrogate recovery does not meet the criterion, re-analysis of all affected samples is required.

9.8 Matrix Spike/Matrix Spike Duplicate

1. A MS/MSD must be analyzed every 20 samples. The MS/MSD must be associated with a method blank that meets the criteria in section 9.5, a calibration in sections 9.2 through 9.4 and a tune in section 9.1. The MS/MSD must be run on the same instrument that the sample was analyzed at the lowest dilution reported for the sample. The MS/MSD recovery limits are as follows:

Compound	% Recovery	RPD
1,4-Dioxane	50-150	20

2. State any deficiencies in case narrative and on a nonconformance memo if recoveries are outside the criteria. A matrix effect is indicated if the LCS recovery is within limits but the MS/MSD are outside the criteria. A similar pattern must be observed for both the MS and MSD.
3. If the lab fails to meet the QC recovery limits and/or the RPD on a routine basis, the Analytical Support Leader must investigate the cause and take corrective action. The MS/MSD must be prepared at the same dilution as the least diluted analysis from which sample results will be reported.

9.9 Internal Standard Area Evaluation

1. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate.
2. If samples, blanks, LCS or MS/MSDs are analyzed immediately following an initial calibration but before another BFB tune and a continuing calibration, evaluation will be conducted on the basis of the BCM internal standard area of the 20 µg/L initial calibration standard.
3. If samples, blanks, LCS or MS/MSDs are analyzed immediately following a BFB tune and a continuing calibration, evaluation will be conducted on the basis of the BCM internal standard area in the continuing calibration standard.
4. The EICP area for BCM in all samples, blanks, and matrix spike/matrix spike duplicates must be between 50% and 200% of the BCM internal standard EICP area in the appropriate calibration standard. In addition, the retention time of the BCM internal standard must be within "0.50 minutes (30 seconds)" of its retention time in the continuing calibration standard.



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5. If the internal standard EICP area does not meet the recovery criterion, the GC/MS system must be inspected for malfunctions and corrections made as appropriate. When corrections are made, re-analysis of all affected samples is required.
6. If after re-analysis, the EICP area for the BCM internal standard meet criteria (between 50% and 200%), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only data from the analysis with the EICP within the limits is required to be submitted. If re-analysis confirms matrix effects, submit both sets of data but report the initial run.

9.10 Manual Integrations

Because SIM analysis is being performed and the high water solubility of 1,4-dioxane, the peak will typically always have to be manually integrated due to its broad peak; therefore, a detailed quant report will be printed for all runs.

9.11 Laboratory Control Sample

1. A LCS must be analyzed every 20 samples. The LCS must be prepared at a concentration of 20µg/L using the second source standard. The LCS must be associated with a method blank that meets the criteria in section 9.5, a calibration in sections 9.2 through 9.4 and a tune in section 9.1.
2. The initial default QC criterion for the LCS recovery is 60-140%. Each time samples are analyzed, a LCS will be prepared and run that contains 1,4-dioxane. The above limits will be used until the sufficient data points are available to prepare a control chart. At that point, control and warning limits will be calculated every 10 to 20 points and updated at least quarterly. All LCS recoveries should be documented in the associated case narrative.
3. If the lab fails to meet the QC recovery limits and/or the RPD on a routine basis, the Analytical Support Leader must investigate the cause and take corrective action.

9.12 Demonstration of Capability

Prior to running a method or any time there is a change in instrument type, personnel or test method or any time a method or analyst has not performed a method in a twelve-month period, an analyst must demonstrate acceptable performance for that method. This is known as the initial demonstration of capability (DOC). Four aliquots of a QC standard (second source) must be prepared and analyzed according to the method over one or a period of days. If the method does not specify a concentration to be used for the DOC, then the concentration must be prepared at 1-4 times the RL. Using Excel, the analyst must provide a table containing the following: Results of the 4 replicates, Mean Concentration, Mean Recovery, Standard Deviation and %RSD with the LCS acceptance limits.

On-going demonstration of capability on an annual basis may be satisfied by the analyst successfully passing a performance testing (PT) sample or a minimum of 4 consecutive LCS samples with acceptable precision and accuracy levels or another initial DOC. Results of



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tabulated QC samples (i.e., control chart data) that are analyst-specific accompanied by precision and accuracy criteria agreed upon by the Analytical Task Leader and the QA/QC Officer may also be used.

9.13 Limit of Detection/Limit of Quantitation Studies

The LOD must be determined for each target analyte on every instrument that will be used for the analysis and reporting of samples. The LOD must be determined each time there is a change in the method that affects how the test is performed or when there is a change in instrumentation. The LOD must be verified annually for each matrix, method and analyte. The LOD will be run using a minimum of seven replicates of a sample prepared from the calibration source at 4 times the LOD for multiple analyte tests. Each of these 7 aliquots must be subjected to the entire analytical procedure. Calculate the mean, mean recovery, variance and standard deviation of the replicate measurements. The LOD is calculated by multiplying the standard deviation times the Students t-Value of 3.143. If more than 7 replicates are used, the Students t-Value must be adjusted accordingly.

The LOQ must be confirmed by the successful analysis of a secondary source QC sample containing each target analyte in each matrix at 1-2 times the claimed LOQ (typically the low standard). The recoveries must fall within the recoveries established for the LCS. Alternately, a control chart with recoveries established from previously analyzed LOQ samples may be used. The LOQ must be subjected to the entire analytical procedure. The LOQ must be verified annually for each matrix, method and analyte. The LOD/LOQ must be determined at the same time.

9.14 Nonconformance Memo

A nonconformance memo will be generated any time an employee notices a deficiency suspected of being a nonconformance. This nonconformance memo will be forwarded to the QA/QC Officer for verification of corrective action.

9.15 System Troubleshooting

Re-calibration must take place when performance changes are to the point when that the calibration verification criteria cannot be achieved. The following examples of maintenance do not require automatic re-calibration of the instrument with an initial calibration: changing compressed gas cylinders or syringes; transfer line or column; or flushing the system with multiple system blanks. If these types of maintenance rectify the problem, the instrument may be re-tuned and a new continuing calibration may be run. If the continuing calibration fails, then a new initial calibration must be run.

Maintenance activities that require automatic re-calibration of the instrument using an initial calibration include: changing, replacing or reversing the column; changing the entrance lens, draw out lens or repeller; changing the electron multiplier and ion source chamber.

All maintenance activities must be documented in the instrument-specific preventive maintenance log.



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10.0 DATA VALIDATION

Data will be assessed for usability in accordance with the guidelines set forth in the most current version of SERAS SOP #1015, *Data Validation Procedures for Routine Volatile Organic Analysis*. However, data are considered satisfactory for submission when *all* the requirements mentioned in Section 9.0 are met.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, refer to EPA, Occupational Safety and Health Administration (OSHA) and corporate health and safety practices. More specifically, refer to SERAS SOP #3013, *SERAS Chemical Hygiene Plan* and SERAS SOP #1501, *Hazardous Waste Management*.

12.0 REFERENCES

National Environmental Laboratory Accreditation Committee (NELAC), *Quality Systems*, current approved version.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste, SW-846, 3rd ed., Method 8000B*.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste, SW-846, 3rd ed., Method 8260B*.

U.S. Environmental Protection Agency. 1984. Federal Register, 40 Code of Federal Regulations (CFR) Part 136, Appendix B, *Definition and Procedure of the Determination of the Method Detection Limit - Revision 1.11*, October 26, 1984.

13.0 APPENDICES

A - Tables



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TABLE 1. Target Compound List (TCL)

Compound	RL, $\mu\text{g/L}$
1,4-Dioxane	1.00

TABLE 2. GC/MS Performance Standard

Bromofluorobenzene (BFB)

m/z	Ion Abundance Criteria
50	8.0 - 40% of mass 95
75	30 - 66% of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of mass 95
173	Less than 2.0% of mass 174
174	50.0 - 120% of mass 95
175	4.0 - 9.0% of mass 174
176	93 - 101% of mass 174
177	5.0 - 9.0% of mass 176

TABLE 3: Analytes of Concern and Quantitation Ions

Compound	Ions
Bromochloromethane (ISTD)	130, 128
1,4-Dioxane	88, 58
4-Bromofluorobenzene (BFB)	95, 174
