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Title **1,4-Dioxane Determination**	Document No. **ELS-105**	Revision **D**
Approved By (signature) Not valid unless signed WJ Schultz Lab Manager	Effective Date 01/14/09	Pages **1 of 38**

1,4-Dioxane Determination

By signing this, I certify that I have received a copy of the above-mentioned document. I have read and understood it, and agree to perform the procedures in accordance with the document until such time that it is superseded by a more recent approved revision.

Name	Signature	Date
WENDY SCHULTZ	WJ Schultz	01/20/09

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SECTION 1 - SCOPE AND APPLICATION

The purpose of this *Standard Operating Procedure (SOP)* is to establish written guidelines for the method used in the identification, quantification and reporting of 1,4-Dioxane (CAS Number 123-91-1).

1.1 Scope of Testing

This procedure is applicable for 1,4-Dioxane in reagent water, ground water, treated water, drinking water, wastewater and surface water matrices.

1.2 Reporting Limits

The Reporting Limit (RL) for 1,4-Dioxane is not less than the lowest calibration concentration used during routine laboratory analysis, and is dependant on possible matrix interference.

Results below the RL are reported as not detected (nd).

1.3 Concentration Range

The concentration range for this method is generally between 0.5 ppb and 200 ppb. This range is dependant on each calibration. Samples with concentrations above the highest calibration level will be reanalyzed either in a diluted form or with an appropriate calibration range.

1.4 Test Method

This SOP is based on USEPA Method 1624 Revision B: Volatile Organic Compounds by Isotope Dilution GC/MS.

SECTION 2 – SUMMARY OF TEST METHOD

The autosampler removes 25 mL of water from the sample vial and transfers it to a sample concentrator. A solution of two internal standards and one surrogate is added during the transfer step. The sample is heated and purged with helium and the compounds are concentrated on an adsorbent trap. The trap is then heated and flushed with helium, which carries the compounds to a capillary column within the Gas Chromatograph (GC). The GC utilizes a temperature program to separate the compounds, which are then transferred to the Mass Spectrometer (MS). A computer system records and stores all sample analytical data. The compounds are identified by comparing their retention times and mass spectra to those previously obtained from known standards. The quantitation of the identified compounds is calculated by comparing the MS response of selected ions of that compound to those of the internal standard used.

SECTION 3– DEFINITIONS, ACRONYMS and ABBREVIATIONS

Definitions can be found in *Lab Glossary*, document number ELS-122, or in the applicable section of this SOP.

Acronyms and Abbreviations

A list of acronyms used in this document and their definitions are:

A/S	–	Autosampler
C	–	Celsius
CAS	–	Chemical abstracts number
CD	–	Compact disk
COC	–	Chain of Custody
CVS	–	Calibration Verification Standard
DI	–	Deionized
DOC	–	Demonstration of Capability
DVD	–	Digital video disk
GC/MS	–	Gas Chromatograph/Mass Spectrometer
HDPE	–	High-density polyethylene
IDOA	–	Initial Demonstration of Ability
IDOC	–	Initial Demonstration of Capability
L	–	Liter
LCS	–	Laboratory Control Sample
LFB	–	Laboratory Fortified Blank
LIMS	–	Laboratory Information Management System
LOD	–	Limit of Detection
LOQ	–	Limit of Quantitation
MB	–	Method Blank
m/z	–	mass to charge ratio
MDL	–	Method Detection Limit
mg	–	milligram
Min	–	minutes
mL	–	milliliter
MΩ	–	mega ohms
MRL	–	Minimum reporting level
MS	–	Matrix Spike
MSD	–	Matrix Spike Duplicate
MSDS	–	Material Safety Data Sheet
NELAC	–	National Environmental Laboratory Accreditation Conference
nd	–	not detected
PE	–	Proficiency Evaluation
p/n	–	part number
PPE	–	Personal protective equipment
PPB	–	Parts per billion
PPM	–	Parts per million
Psi	–	Pounds per square inch
PT	–	Proficiency Test
QC	–	Quality Control
QCS	–	Quality Control Sample
Rev	–	Revision
RF	–	Response Factor
RL	–	Reporting Limit
RRF	–	Relative response factor
RSD	–	Relative standard deviation
SD	–	Standard deviation
SOP	–	Standard Operating Procedure
USEPA	–	United States Environmental Protection Agency
µg	–	microgram
µL	–	microliter

SECTION 4 – INTERFERENCES

Method interferences may be caused by contamination or impurities in reagent water, solvents, reagents, glassware, or the laboratory equipment.

Policy

At least one method blank is analyzed per analysis batch prior to actual sample analysis. This is done to demonstrate the equipment is free from interferences that may affect sample analysis.

When potential interfering peaks are noted in method blanks, the analyst should consider possible sources and eliminate the contamination.

Subtracting blank values from sample results is not permitted.

*Sample dilution due to interferences will affect the MRL by an equal dilution.

4.1 Carryover Contamination

CARRYOVER: Analytes transferred from one sample to the following sample, when a sample containing low concentrations of analytes is analyzed immediately after a sample containing relatively high concentrations.

To eliminate or reduce the possibility of carryover contamination from a high-level sample, the following guidelines are followed:

1. One or more blanks are analyzed after any sample with known high levels of analytes present and after check standards. If contamination of the next sample is suspected, then the sample should be reanalyzed to determine if any carryover contamination occurred. If the sample immediately following the high-level sample does not contain any of the target compounds, that sample is considered free from carryover.

2. The purge and trap system is rinsed and baked, and the GC system is baked after every sample.

3. During initial calibration standard analysis, blanks follow all standards higher than 20 ppb to determine the amount of carryover expected from samples of known high concentrations.

4.2 Matrix Interference

Matrix interference may be caused by contaminants within the sample that co-elute with the target compounds or otherwise interfere with the analysis.

Sample dilution can also be used to eliminate any matrix interference. Sample dilution to correct this will affect the MRL by an equal dilution.

4.3 Glassware

Glassware should be cleaned following *Labware Cleaning*, document number ELS-109.

SECTION 5 – HEALTH AND SAFETY

Treat each chemical as a potential health hazard. Reduce exposure to the lowest possible level. Use a fume hood when using or preparing standards, solvents, or reagents.

Chemical resistant gloves, such as nitrile, a lab coat and safety glasses should be worn while handling samples and standards.

Reagent water is the primary solvent used in the preparation of working standards; standard laboratory hygiene practices should be used when handling reagent water.

1,4-Dioxane is a suspected carcinogen. Chemical resistant gloves and safety glasses should be worn while handling samples and standards. Use a fume hood when using or preparing standards containing concentrated stock standards.

Methanol is the primary solvent used in the preparation of dilution standards. Methanol is a flammable solvent and must be stored and handled accordingly. It is harmful or toxic if inhaled or ingested.

A reference file of MSDS sheets for all chemicals contained in the laboratory is located in the binder labeled "MSDS" and should be consulted before use of this or any laboratory procedure.

5.1 Personal Protective Equipment (PPE)

1. Safety glasses
2. Nitrile gloves (see MSDS)
3. Good ventilation
4. Fume hood

SECTION 6 – LABORATORY ENVIRONMENT

The laboratory facilities should be clean, have adequate temperature control, and have adequate lighting and bench space.

There are no technical requirements for environmental conditions for this method.

SECTION 7 - SUPPLIES

7.1 Glassware

1. 40 mL glass sample container vials, preserved with HCl acid, Scientific Specialties p/n 276710-1/2 HCl-V
2. 40 mL glass sample container vials, unpreserved, Environmental Sampling Supplies p/n 4050-0300PC
3. Class "A" Volumetric Flasks and stoppers. (Various sizes).
4. 25 mL fritted sparge vessel, O.I. Analytical p/n 322998
5. Gas-Tight syringes. (Various sizes).
6. 25 mL sample loop, O.I. Analytical p/n 259507

7.2 Ultra High Purity Helium (99.999%) Airgas p/n UHP300

Regulator outlet set at 100 psi.

7.3 Strip pH Paper VWR p/n 60777-242

7.4 Vocarb 3000 trap, Supelco p/n: 24940-U

Precondition according to manufacturers instructions

SECTION 8 – STANDARDS AND REAGENTS

8.1 Reagents

Purchased reagents are marked with an ID number, the date of receipt and recorded in the Reagent Logbook.

1. Methanol (CAS Number 67-56-1): ACS, GC/MS grade or equivalent.
2. Reagent Water: Organic Free water

8.2 Standards

Purchased standards are marked with an ID number, the date of receipt or preparation, and recorded in the Standards Logbook. Daily standards are not recorded.

8.2.1 Primary Stock Standards

PRIMARY STOCK STANDARDS are purchased as certified solutions in sealed ampoules. They are used to prepare the working standards.

1. 1, 4-Dioxane (CAS Number 123-91-1): 100 ppm, Absolute Standards p/n X9097
2. 1, 4-Dioxane (CAS Number 123-91-1): 2000 ppm, Restek p/n 30287
3. 1, 4-Dioxane-d8 (CAS Number 123-91-1): 99%, Sigma Aldrich p/n 308803
4. Toluene-d8 (CAS Number 02037-26-5): 200 ppm, Absolute Standards p/n 70282
5. 524 Internal Standard/Surrogate Mix: 2000 ppm, Restek p/n 30201 containing:
   a. Fluorobenzene (CAS Number 462-06-6)
   b. Bromofluorobenzene (CAS Number 460-00-4)
   c. 1,2-Dichlorobenzene-d4 (CAS Number 2199-69-1)

8.2.2 Secondary Stock Standards

SECONDARY STOCK STANDARDS are stock standards purchased as certified solutions in sealed ampoules, from a lot other than the Primary Stock Standards. They are used to prepare the quality check working standards.

1. 1, 4-Dioxane (CAS Number 123-91-1): 100 ppm, AccuStandard p/n APP-9-096

8.2.3 Working Standards

WORKING STANDARDS are standards prepared from the Primary or Secondary Stock Standards diluted with methanol.

8.2.3.1 1,4-Dioxane Dilution Standards

Procedure

In a Class "A" 2 mL volumetric tube, place approximately 1.8 mL of methanol.

Using a gas-tight syringe, add a sufficient amount of 1,4-Dioxane Stock Standard under the methanol level to prepare the standard at the desired concentration.

Dilute to the mark with methanol, cap, and invert gently three times. Pour the standard into a 2 mL glass container.

8.2.3.2 Internal Standard Fortification Solution (ISFS)

Procedure

In a Class "A" 50 mL volumetric flask, place approximately 48 mL of methanol.

Using a gas-tight syringe, add a sufficient amount of Toluene-d8, 1,4-Dioxane-d8, and 524 Internal Standard/Surrogate Mix under the methanol level to prepare concentrations of 12.5 ppm, 2500 ppm, and 25 ppm respectively.

Dilute to the mark with methanol, cap, and invert the flask gently three times. Pour the standard into labeled glass containers and cap tightly. Keep in the freezer until transfer to the pressurized SAM vial.

8.2.4 Daily Standards

DAILY STANDARDS are standards prepared from Stock or Working standards diluted in water.

8.2.4.1 Initial Calibration Standards

Procedure

In a Class "A" 100 mL volumetric flask, place approximately 99 mL of reagent water.

Using a gas-tight syringe, add a sufficient amount of Primary Stock Standard under the water level to prepare the standard at the desired concentration. (See Table 8.3)

Dilute to the mark with reagent water, cap, and invert the flask gently three times. Pour each standard into two 40 mL vials preserved with HCl acid.

8.2.4.2 Calibration Verification Standards and Laboratory Fortified Blanks

Procedure

In a Class "A" 100 mL volumetric flask, place approximately 99 mL of reagent water.

Using a gas-tight syringe, add a sufficient amount of Secondary Stock Standard under the water level to prepare the standard at the desired concentration. (See Table 8.3)

Dilute to the mark with reagent water, cap, and invert the flask gently three times. Pour the standard into 40 mL vials preserved with HCl acid.

8.2.4.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

Procedure

Prepare the MS and MSD samples by injecting sufficient Secondary Stock Standard with a gas-tight syringe through the edge of the sample vial septa to achieve a 10 ppb spike. (See Table 8.3)

8.3 Standard Preparation

Table 8.3 Standards Preparation				
Standard	**Final Concentration**	**Stock Amount**	**Stock Concentration**	**Total Volume**
Calibration Std 1	0.5 ppb	0.5 µL	100 ppm	100 mL
Calibration Std 2	1.0 ppb	1.0 µL	100 ppm	100 mL
Calibration Std 3	2.0 ppb	2.0 µL	100 ppm	100 mL
Calibration Std 4	5.0 ppb	5.0 µL	100 ppm	100 mL
Calibration Std 5	10.0 ppb	10.0 µL	100 ppm	100 mL
Calibration Std 6	20.0 ppb	20.0 µL	100 ppm	100 mL
Calibration Std 7	50.0 ppb	2.5 µL	2000 ppm	100 mL
Calibration Std 8	100.0 ppb	5.0 µL	2000 ppm	100 mL
Calibration Std 9	200.0 ppb	10.0 µL	2000 ppm	100 mL
CVS	10.0 ppb	10 µL	100 ppm	100 mL
LFB	10.0 ppb	10 µL	100 ppm	100 mL
MS/MSD	10 ppb + Sample	4.3 µL	100 ppm	43 mL

8.4 Standard Storage and Hold Times

Table 8.4 Standard Storage and Hold Times			
Item	**Container**	**Storage**	**Hold Time**
Opened Stock Standard	Amber, PTFE-sealed screw cap vials or Mininert vials	Freezer ≤ 0°C	Within 12 months of opening*
Sealed ampoules	Original ampoule	Freezer ≤ 0°C	Until expiration date provided by manufacturer.*
Working Standards in methanol	Amber, PTFE-sealed screw cap vials or Mininert vials	Freezer ≤ 0°C	Within 3 months of preparation*
Dilution Standards in water	40 mL VOA preserved with HCl acid	Refrigerator ≤4°C	14 days*

*or sooner if degradation or evaporation is suspected

SECTION 9 – EQUIPMENT

9.1 O.I. Analytical 4660 Purge and Trap Device

9.1.1 Instrument Operating Conditions

1. Purge Temperature: 40°C
2. Desorb Temperature: 190°C
3. Bake Temperature: 210°C
4. Valve Temperature: 110°C
5. Transfer Line Temperature: 120°C
6. Sample Temperature: 40°C
7. Sparge Mount Temperature: 40°C
8. Water Management Temperatures:
   a. Purge: 120°C
   b. Desorb: ambient(set at 0°C)
   c. Bake: 240°C
9. Purge Time: 11 minutes
10. Desorb Time: 0.50 minutes
11. Bake Time: 10 minutes
12. Pre-purge: 0
13. Pre-heat: 0
14. Dry Purge: 1 minute
15. Desorb Preheat: 125°C
16. Total Time: 22.50 minutes
17. Purge flow: 40 mL/minute, ±2 mL/min

9.2 O.I. Analytical 4551-A Autosampler with Standard Addition Module

9.2.1 Instrument Operating Conditions

1. Number of Washes: 2
2. Wash station fill time: 0.28 minutes *
3. Wash station empty time: 0.28 minutes *
4. Sparge Volume: 25 mL
5. 25 mL Fill Time: 0.30 minutes *
6. 25 mL Transfer Time: 0.75 minutes *
7. Needle Depth: ~94%

*These times may vary due to pump wear, line lengths, or flow restrictions.

9.3 Agilent 6890 Gas Chromatograph

9.3.1 Instrument Operating Conditions

1. Inlet: 15:1 Split, 200°C
2. Oven: 40°C for 3 minutes, 10°C/minute to 100°C, 25°C/min to 225°C.
3. Total Run Time: 14 minutes
4. Column: DB-VRX, 20 m: J and W p/n 121-1524
5. Flow: 1.0 mL/minute constant pressure
6. Average Velocity: 45 cm/sec
7. Pressure: 20.69 psi

9.4 Agilent Mass Spectrometer (5973n or i)

9.4.1 Instrument Operating Conditions for 1,4-Dioxane method

1. MS Inlet: 200°C
2. MS Quad: 150°C
3. MS Source: 230°C
4. Acquisition Mode: SIM
5. Solvent Delay: 4 minutes
6. Scan Settings
   a. Fluorobenzene: 50,70,96
   b. Dioxanes: 46,58,64,88
   c. Toluene-d8: 98,100
7. Electron Multiplier Offset: 400
8. Tune file: lowmass.u

9.4.2 Instrument Operating Conditions for BFB method

1. MS Inlet: 200°C
2. MS Quad: 150°C
3. MS Source: 230°C
4. Acquisition Mode: Scan
5. Solvent Delay: 4.20 minutes
6. Scan Range : 35-350
7. Threshold: 50
8. Sample #: 3
9. Electron Multiplier Offset: 0
10. Tune file: bfb.u

9.5 Data System

The computer system allows continuous data acquisition and storage of all data obtained during the analytical run.

Agilent ChemStation software version D.03.00.611 is used to process the obtained data, record, and maintain lists of response factors and generate multi-point calibration curves.

A printer is used to print out hard copies of data and associated files.

A DVD/CD storage device is used to backup all data files and methods for long-term storage.

9.6 Equipment Maintenance

Equipment maintenance should be performed when operating problems arise and on a scheduled basis. Follow the manufacturer's guidelines and instructions for specific maintenance procedures.

All maintenance performed is documented in the logbook that accompanies each instrument.

9.6.1 As Needed

1. Clean the Ion Source
2. Replace worn parts
3. Lubricate MSD side plate and o-rings
4. Replace/trim the GC column
5. Replace the GC ferrules, inlet liner, gold seal and septa
6. Clean the 4551-A sample filter
7. Clean/change the 4551-A sample loop
8. Clean/change the 4660 sparge vessel
9. Replace the 4660 trap
10. Change the helium tank
11. Refill the 4660 DI water container
12. Empty the 4660 waste container
13. Refill the ISFS vial

9.6.2 Daily

1. Tune the MSD

9.6.3 Monthly

1. Backup data files onto CD
2. Check helium tank levels

9.6.4 Every 6 months

1. Replace the foreline pump fluid
2. Check the calibration vial fluid (PFTBA)

SECTION 10 – SAMPLE MANAGEMENT

Prior to analysis, the laboratory staff assumes custody of the samples and inspects them following the laboratory sample acceptance policies and procedures.

The laboratory sample acceptance policy and sample management procedures covering sample receipt, acceptance, identification, transport, storage and disposal can be found in the *Sample Receipt and Handling* SOP, Document Number ELS-113.

10.1 Sample Collection and Preservation

Samples must be collected in HCl acid preserved glass vials with a septa and open-top screw caps, with the exception of the Pall ozone treatment samples. (See Section 10.3) Two vials should be collected for each sample with each vial having a total volume of at least 40 mL.

No air bubbles >5 mm should be trapped inside the sample vials.

10.2 Sample Shipment

Samples that are transported under the responsibility of the laboratory, where necessary, are done so safely and according to storage conditions. This includes moving bottles within the laboratory. Specific safety operations are addressed outside of this document.

10.3 Sample Storage and Preservation

Samples are collected in HCl acid-preserved vials to a pH of ≤2, with the exception of the Pall ozone treatment samples. These samples have chemicals that, when mixed with the HCl acid, cause interferences and trap damage. Every attempt is made to analyze these samples within 24 hours of receipt.

All samples are iced or refrigerated at 4°C (±2°C) from the time of collection until sample preparation or analysis. Samples and standards are stored separately.

Samples that are delivered to the laboratory the same day as they are collected are likely not to have reached a fully chilled temperature. This is acceptable as long as there is evidence that chilling has begun.

10.4 Sample Hold Time

1,4-Dioxane has a 14-day hold time. Samples analyzed after the hold time must have it noted in the sample data report or case narrative.

10.5 Sample Dilution

If the background data suggests or laboratory staff has suspicion that a sample may contain high concentrations of 1,4-Dioxane, dilutions may be necessary.

Procedure

Determine the lowest dilution factor required to get the analyte concentration within the initial calibration range. Suggested dilution factors would keep the concentration in the upper half of the calibration curve range.

Dilutions should be made just prior to sample analysis, when possible.

Using an appropriate sized volumetric flask, fill the flask ¾ full with reagent water, then add the calculated amount of sample using a syringe when possible.

Dilute to the mark with reagent water, cap, and invert the flask gently three times.

Pour the dilution into one 40 mL vial preserved with HCl acid. The vial cap should be labeled with the sample name, sample date and sample time as well as the dilution factor.

SECTION 11 – CALIBRATION AND STANDARDIZATION

11.1 Instrument Tuning

Frequency

The GC/MS system is calibrated with PFTBA to adjust the sensitivity and to allow the software to set the instrument parameters for optimal analysis. The tune is performed before analysis of any blanks, samples, or standards.

Procedure

Follow the manufacturer's procedures to perform the Low Mass Autotune, Autotune, or BFB tune.

Acceptance Criteria/Corrective Action

Once the tune is completed, a copy of the tune will print. Review the printout and check that the air and water levels (m/z 28 and 18) are less than 5% of m/z 69. If air or water is present at higher levels, system maintenance may be required.

Data

The tune printout is kept with the applicable batch data.

11.2 Instrument Performance Check (BFB Tune)

BFB acceptance criteria must be met prior to the analysis of any samples, blanks or standards.

Frequency

Once at the beginning of each 12-hour period and prior to the analysis of any samples, blanks or standards, the GC/MS system must produce a mass spectrum that meets all BFB mass-intensity criteria listed in Table 11.2.

Procedure

Analyze a blank under the BFB method settings and evaluate the BFB peak using the system software.

Acceptance Criteria

Table 11.2 BFB Mass Intensity Criteria

m/z	Ion Abundance Criteria
50	15 to 40 % of m/z 95
75	30 to 60 % of m/z 95
95	Base peak, 100 %
96	5 to 9 % of m/z 95
173	Less than 2 % of m/z 174
174	Greater than 50 % of m/z 95
175	5 to 9 % of m/z 174
176	95 to 101 % of m/z 174
177	5 to 9 % of m/z 176

Corrective Action

If intensity specifications in Table 11.2 are not met, re-tune the system. It may be necessary to clean the source, change the column, prepare new standards, service the purge and trap or take other corrective actions to achieve the acceptance criteria.

When possible, samples analyzed when the BFB acceptance criteria are not met will be reanalyzed.

Data

A BFB tune report is printed showing "pass" or "fail" for each criterion, and is kept with the data packet.

11.3 Initial Calibration

Prior to the analysis of samples and after the Instrument Performance Check (BFB Tune) acceptance criteria have been met, the GC/MS system must undergo Initial Instrument Calibration using a minimum of five calibration standards. The actual number of standards used should be based upon the necessary working range.

Frequency

Initial Calibration is performed when beginning a method, whenever a corrective action (source cleaning, trap change, column replacement) or other circumstance affects any of the method acceptance criteria, or when the quality control method acceptance criteria have not been met.

Procedure

Prepare the initial calibration standards (See Table 8.3). Place blanks after any standard higher than 20 ppb to evaluate possible carryover. Analyze the standards in order of increasing concentration using the same methodology as a sample.

Once analysis is complete, the analyst reviews all chromatograms to ensure proper baseline integration and peak identification before continuing. For each of the initial calibration standards the software will calculate the Response Ratio and the Amount Ratio for 1,4-Dioxane and Toluene-d8 relative to the associated internal standards, and will generate a calibration curve for these compounds.

Calibration points are not dropped from the curve unless the cause is determined, technically justifiable, and documented.

Points can be discarded at the upper end of the curve if the linear range of the detector has been exceeded. Dilute any sample that exceeds the highest standard of the calibration curve.

Points can be discarded at the lower end of the curve if the detector is not producing a response, but the reporting limit must then be adjusted accordingly.

Calculations

Calculate the Relative Response Factor (RRF), the Mean RRF, and the Percent Relative Standard Deviation (%RSD) of the RRF values for 1,4-Dioxane and Toluene-d8 using the calculations listed in Section 14.

Quantitate the Initial Calibration Standards using the new calibration curve (as if they were unknowns) and then calculate the Percent Difference (%DIFF) for 1,4-Dioxane and Toluene-d8 using the calculations listed in Section 14.

Acceptance Criteria

Initial calibration standards are considered acceptable if all of the following criteria are met:

1. The initial calibration must be analyzed on a GC/MS system meeting the BFB and method blank acceptance criteria.
2. Calibration Curve Correlation Coefficient (R^2) ≥ 0.995
3. Compound RRF ≥ 0.10
4. Compound RSD from -20% to +20%
5. The percent difference of 1,4-Dioxane and Toluene-d8 concentrations from the true values ≤ 20%.

Corrective Action

Initial calibration standards that do not meet acceptance criteria will be reanalyzed.

It may be necessary to perform maintenance or take other corrective actions to meet the acceptance criteria.

Data

Initial calibration data packets include:

1. Original data printout for all files (quantitated under the old calibration curve),
2. New data printout for all files (quantitated under the new calibration curve),
3. BFB tune acceptance printout,
4. Calibration curve printout,
5. Calibration check sheet,
6. Updated run log cover sheet,
7. QA-QC Check report,
8. Batch printout, and
9. Tune file printout (Autotune, BFB, Lowmass as applicable)

Any manual integration changes are stamped and signed on the quantitation report.

11.4 Calibration Verification Standard

Before the analysis of samples and after BFB and initial calibration acceptance criteria have been met, the validity of the initial calibration is verified by use of a Calibration Verification Standard (CVS). Calibration is verified for any compound being reported in the analytical batch.

Frequency

Calibration verification is performed prior to any sample analysis and:

1. at the beginning of each analytical batch;
2. whenever it is expected that the analytical system may be out of calibration or might not meet verification acceptance criteria; and
3. every 12-hour analytical shift.

Procedure

Prepare the 10 ppb CVS (See Table 8.3) and analyze it using the same methods and procedures as a sample.

Calculations

The data system software calculates the concentration of 1,4-Dioxane and Toluene-d8 in the CVS.

Using the data system software, evaluate the sample as a continuing calibration standard and print a Continuing Calibration Report for the CVS.

Acceptance Criteria

1. The CVS must be analyzed on a GC/MS system meeting the BFB and initial calibration acceptance criteria.
2. The 1,4-Dioxane concentration in the CVS must be within 80-120% of the true value.
3. The Toluene-d8 concentration in the CVS must be within 70-130% of the true value.
4. The minimum RRF for all compounds must be ≥0.10.
5. The percent difference (% DIFF) between the RRF for 1,4-Dioxane and Toluene-d8 in the CVS and the average RRF for the initial calibration standards must be ≤20%.
6. The area of 1,4-Dioxane-d8 has not changed by more than 50% from the average areas measured during the initial calibration.
7. The retention times of the compounds have not deviated more than 0.33 min from the expected retention times.

Corrective Action

For results outside established criteria, data are evaluated to determine the impact. If routine corrective action for calibration verification fails to produce a second consecutive (immediate) calibration verification within acceptance criteria, then a new calibration is performed or acceptable performance is demonstrated after corrective action with two consecutive calibration verifications.

Continuing calibration acceptance criteria must be met before any samples, standards or blanks are analyzed. Any sample, standard or blank analyzed when the continuing calibration acceptance criteria have not been met will require reanalysis.

Data

Quantitation and Continuing Calibration reports for each CVS are kept with the corresponding data packet.

SECTION 12 – ANALYSIS

All samples, blanks, and standards should be allowed to come to room temperature before analysis.

12.1 Sample Preparation

1. Dilute any samples that are suspected to contain 1,4-Dioxane in levels higher than the calibration curve, where interferences may be present, or at levels that may cause carryover. Write the sample name, date and time collected and the dilution amount on the cap of the new vial.
2. Samples that contain large amounts of soil, sand or silt may need to be consolidated and the water transferred to another vial.

12.2 System Preparation

1. Load the vials on the autosampler carrousel following the sample sequence (batch) below and, once ready, start the autosampler to run.
2. Type the vial names into the ChemStation software and save the batch under the date the run began on, in the format of mmddyy.
3. Once the GC/MS system is ready, start the batch to run.

Table 12.2.1 Example Short Sample Batch

Vial	Name
1	BFB Tune
2	CVS
3	MB
4-21	Samples 1-18
22	Sample 18 MS
23	Sample 18 MSD
24	LFB

Table 12.2.2 Example Long Sample Batch

Vial	Name
1	BFB Tune
2	CVS
3	MB
4-21	Samples 1-18
22	Sample 18 MS
23	Sample 18 MSD
24	LFB
25	BFB
26	CVS
27	MB
28-45	Samples 19-36
46	LFB

Table 12.2.3 Example Initial Calibration Batch

Vial	Name
1	BFB
2	MB
3-8	Std 1- Std 6
9	Rinse Blank
10	Std 7
11	Rinse Blank
12	Std 8
13	Rinse Blank
14	Rinse Blank
15	Std 9
16	Rinse Blank
17	Rinse Blank

12.3 Data Acquisition

Data acquisition is performed according to specified method and equipment parameters listed in Section 9.

One µL of ISFS solution is delivered by the SAM into each 25 mL sample aliquot as it is transferred to the sparge vessel. This creates a final concentration of Toluene-d8, 1,4-Dioxane-d8, and Fluorobenzene of 0.5 ppb, 100 ppb, and 1 ppb respectively.

After the analysis is complete, remove the vials from the carrousel and inspect the remaining volume of sample in each one. Any vials that have a larger than usual amount of water in them should be reanalyzed.

Before discarding the used vial, open the cap of each vial and insert a strip of pH paper into the remaining sample. Make note of any sample with a pH >2 on the run log cover page.*

*Samples that have been treated in the Pall ozone treatment systems are purposely not preserved and thus are not marked on the run log cover page if their pH is >2.

12.4 Qualitative Identification

The data system software automatically performs peak integration and identification based on the parameters set by the analyst. Positive identification of method analytes occurs when a sample peak:

1. falls within the expected retention time window, and
2. qualifier ions (Table 12.4) and their ratios match those of the reference spectrum in the calibration database.

Table 12.4 Qualifier Ions

Compound	CAS No.	Qual Ion 1	Qual Ion 2	Qual Ion 3
Fluorobenzene	462-06-6	96	70	50
Toluene-d8	2037-265	98	100	-
1,4-Dioxane-d8	17647-74-4	64*	46	-
1,4-Dioxane	123-91-1	88	58	-

*m/z 96 is not used due to frequent interference caused by halogenated alkenes containing this ion.

12.5 Quantitative Assessment

Identified target compounds will be quantified by the internal standard method using the calculation in Section 14.3 and factoring the dilution factor. Once analysis is complete, the analyst reviews all chromatograms to ensure proper baseline integration and peak identification.

Results less than the lowest calibration standard or the client specified reporting limit are considered to have increased uncertainty, and are reported as "not detected" or "nd". Results greater than the highest calibration standard are either diluted to within the calibration range and reanalyzed, or are considered to be an estimate and are reported with a qualifier code and explained in the case narrative.

12.6 Acceptance Criteria

Sample acceptance criteria must be met before data are reported.

1. The sample must be analyzed on a GC/MS system meeting the BFB, initial calibration, CVS and method blank acceptance criteria.
2. The sample must be analyzed within the allowed holding time.
3. The Toluene-d8 concentration in the sample must be within 70-130% of the true value.
4. The area of the internal standards in the blank must be within ±30% of their areas in the most recent CVS.
5. The retention time for each internal standard must be within 0.33 minutes of its retention time in the most recent CVS.

12.7 Corrective Action

For results outside the acceptance criteria, the difficulty must be investigated and measures taken to minimize or eliminate the problem. Corrective actions include reanalysis, qualified data, and documentation of the event as appropriate.

12.8 Data

Quantitation reports for each sample are kept with the corresponding data packet.

SECTION 13 – QUALITY CONTROL

The laboratory quality assurance/control program for this method consists of an initial demonstration of laboratory capability, and subsequent analysis in each analysis batch of a method blank, calibration verification standard, laboratory fortified blank, and matrix spike and duplicate analyses.

13.1 Initial Demonstration of Ability or Demonstration of Capability

An INITIAL DEMONSTRATION OF ABILITY (IDOA) is a procedure used to establish the ability of the analyst to generate data of acceptable accuracy and precision. It is also called a demonstration of capability (DOC).

An initial demonstration of ability must be conducted before any sample analysis takes place.

Policy

The laboratory confirms that it is capable of generating data of acceptable accuracy and precision on all methods before employing them.

An IDOA/DOC is performed for 1,4-Dioxane whenever the method, analyst, analyte, or instrument type is changed, and at least annually.

Procedure

Three levels of QC samples are to be analyzed, with at least four aliquots per level. Prepare the QC samples in reagent water spiked with a Second Source standard at concentrations at the lowest calibration level, the highest calibration level and a mid-range concentration for 1,4-Dioxane. (See Table 8.3) Other matrices may be used if there are no target analytes or interferences present at concentrations that impact the results of the analysis.

Analyze the aliquots either concurrently or over a period of days using the same procedures and methods for sample analysis.

Calculation

Using all of the results from these analyses, calculate the mean recovery and the standard deviation of the population sample (% RSD) for 1,4-Dioxane using the calculations in Section 14.

Acceptance Criteria

1. The aliquots must be analyzed on a GC/MS system meeting the BFB, initial calibration, and method blank acceptance criteria.
2. The mean recovery must be within ± 20%.
3. The % RSD must be from -20% to +20%.

Analysis of actual samples begins only after all parameters meet the acceptance criteria.

Corrective Action

Locate and correct the source of the problem and repeat the analyses for all analytes.

Data

The IDOA/DOC is documented on the *Demonstration of Capability Certification Statement* form, document number ELS-118, and signed by the Laboratory Manager. These completed forms are kept in the training files for each analyst.

13.2 Method Detection Limit (MDL) or Limit of Detection (LOD)

A method detection limit study must be conducted before any sample analysis takes place, when a new analyst begins work, when there is a significant change in the background or instrument response, and at least once per year.

The METHOD DETECTION LIMIT (MDL) for 1,4-Dioxane is used as the LOD and is determined for the compounds of interest in each test method in clean quality system matrix or reagent water.

Procedure

The MDL is determined according to Code of Federal Regulations 40, Part 136 Appendix B.

Prepare seven replicate aliquots of reagent water fortified at a concentration of 1 to 5 times the estimated detection limit. Analyze using the same methods and procedures as sample analysis, and over a period of at least three days.

Calculation

Using all the results from these analyses, calculate the MDL using the equation found in Section 14.

Data

Transfer the 1,4-Dioxane concentrations from the quantitation reports to the MDL data sheet. Print out the MDL sheet and keep a copy in the data packet.

13.3 Limit of Quantitation (LOQ) or Minimum Reporting Level (MRL)

The LIMIT OF QUANTITATION (LOQ) is the minimum concentration of an analyte or category of analytes in a specific matrix that can be identified and quantified above the LOD and within specified limits of precision and bias during routine analytical operating conditions. The LOQ is equal to the lowest calibration standard. Data are not reported below the LOQ.

The LOQ is verified using a quality systems matrix sample spiked at 1-2 times the determined LOQ that returns a concentration within the acceptance criteria for accuracy, according to the requirements of the test method or client data quality objectives.

13.4 Blanks

Blanks are used to detect contamination during sample collection, handling, preparation, and/or analysis. There are many types of blanks, each with a specific purpose including:

1. EQUIPMENT BLANKS: A reagent water sample used to monitor for potential contamination from decontamination procedures of field gear or from other sources of equipment contamination like oil or other lubricants.
2. FIELD BLANK: A reagent water sample used to provide information about contaminants that may be introduced during sample collection, storage, and transport. A clean sample, carried to the sampling site, exposed to sampling conditions, returned to the laboratory, and treated as an environmental sample.
3. INSTRUMENT BLANK OR LABORATORY RINSE BLANK: A reagent water sample that is used to provide a rinse step in the analytical process.
4. LABORATORY BLANKS: A reagent water sample used to identify potential sources of contamination generated during the processing and analysis of samples in the laboratory.
5. METHOD BLANK: A blank prepared to represent the sample matrix as closely as possible and analyzed exactly like the calibration standards, samples, and quality control (QC) samples. Results of method blanks provide an estimate of the within-batch variability of the blank response and an indication of bias introduced by the analytical procedure. Method blanks are created using Reagent Water.
6. TRIP BLANK: A blank that is taken to the sampling site and transported to the laboratory for analysis without having been exposed to sampling procedures.

Policy

At least one method blank (MB) must be analyzed once every 12-hour period, after the CVS, but before any samples are analyzed.

Samples associated with a contaminated method blank are evaluated as to the appropriate corrective action for the samples (e.g. reprocessing or data qualifying codes).

Rinse blanks are placed after samples or standards of known or suspected contamination or carryover.

Field blanks, trip blanks and equipment blanks are analyzed when requested and submitted by the client.

Procedure

To prepare a method blank, fill a pre-preserved VOA vial with reagent water and cap.

Analyze all blanks using the same methods and procedures as sample analysis.

Calculation

The data system software calculates the concentration of 1,4-Dioxane in the blanks and will print out a quantitation report.

Acceptance Criteria

1. The blank must be analyzed on a GC/MS system meeting the BFB, initial calibration, and CVS acceptance criteria.
2. The method blank is not contaminated with 1,4-Dioxane.**
3. The area of the internal standards must be within ±30% of their areas in the most recent CVS.
4. The Toluene-d8 concentration be within 70-130% of the true value.
5. The retention time for each internal standard must be within 0.33 minutes of its retention time in the most recent CVS.

**The laboratory identifies a method blank as contaminated when 1,4-Dioxane results are greater than the MRL, or where the contamination affects the sample results according to client objectives.

Rinse blanks, field blanks, trip blanks or equipment blanks are evaluated like samples.

Corrective Action

When a method blank is considered contaminated, the cause must be investigated and measures taken to minimize or eliminate the problem.

Data that are unaffected by the method blank contamination (non-detects or other analytes) are reported unqualified.

Sample data that are suspect due to the presence of a contaminated method blank are reanalyzed or qualified.

Data

Quantitation reports for each blank are kept with the corresponding data packet.

13.5 Laboratory Fortified Blanks (LFB)

LABORATORY FORTIFIED BLANKS (LFB): An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory, verifies previously established calibration curves, and confirms the accurate quantitation for the previous 20 (maximum, including matrix spikes) field samples analyzed.

Frequency

Laboratory fortified blanks are analyzed at least every 12 hours and at the end of each analytical batch. If a new 12-hour batch is started, this requirement is satisfied by using the CVS from the new batch as the LFB.

Procedure

Prepare a 10 ppb LFB following Section 8.2.4.2. Analyze the LFB using the same methods and procedures as a sample.

Calculation

The data system software calculates the concentration of 1,4-Dioxane in the LFB and will print out a quantitation report.

Acceptance Criteria

1. The LFB must be analyzed on a GC/MS system meeting the BFB, initial calibration, CVS and method blank acceptance criteria.
2. The 1,4-Dioxane concentration is within 80-120% of the true value.
3. The area of the internal standards must be within ±30% of their areas in the most recent CVS.
4. The Toluene-d8 concentration must be within 70-130% of the true value.
5. The retention time for each internal standard must be within 0.33 minutes of its retention time in the most recent CVS.

Corrective Action

For results outside established criteria, the difficulty must be investigated and measures taken to minimize or eliminate the problem. Corrective actions include reanalysis, qualified data, and documentation of the event as appropriate.

When possible, all samples following the last acceptable LFB are reanalyzed. If the LFB fails repeatedly, the source of the error is located and corrective action is taken.

Repeated failure may require the analysis of new Initial Calibration Standards.

Data

Quantitation reports for each LFB are kept with the corresponding data packet.

13.6 Duplicate Samples

LAB DUPLICATES: Two aliquots of a sample taken in the laboratory from a single sample bottle and analyzed separately, but under the same conditions; used to measure precision associated with laboratory procedures.

FIELD DUPLICATES: Two separate samples collected at the same time and place under identical circumstances and treated the same throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

BLIND DUPLICATES: Two separate samples collected at the same time and place under identical circumstances and treated the same throughout field and laboratory procedures. The identification of one of the samples is unknown to the laboratory. Analysis of blind duplicates indicates the precision associated with sample collection, preservation and storage, as well as with laboratory procedures and serves as a indicator of non-homogeneity.

Frequency

A duplicate sample is analyzed when requested or submitted by the client.

Procedure

Analyze the duplicate using the same methods and procedures as a sample. Calculate the relative percent difference (RPD) between 1,4-Dioxane concentration in the original sample and in the duplicate, if the identity is known.

Calculation

Calculate the RPD using the equations found in Section 14.

Acceptance Criteria

1. The duplicates must be analyzed on a GC/MS system meeting the BFB, initial calibration, CVS and method blank acceptance criteria.
2. The area of the internal standards must be within ±30% of their areas in the most recent CVS.
3. The Toluene-d8 concentration must be within 70-130% of the true value.
4. The retention time for each internal standard must be within 0.33 minutes of its retention time in the most recent CVS.
5. The RPD must be from -20% to +20%.

Corrective Action

For RPD results outside established criteria the data of both the sample and the duplicate are reported with a qualifier identifying the sample analysis result as yielding a poor duplicate RPD.

Data

Quantitation reports for each duplicate are kept with the corresponding data packet.

13.7 Matrix Spike and Duplicate Samples

MATRIX SPIKE SAMPLES (MS) AND MATRIX SPIKE DUPLICATE SAMPLES (MSD) are environmental samples fortified with a known amount of 1,4-Dioxane to help assess the affect of the matrix on method performance.

The results from the MS sample compared to the duplicate MS are used to assess the effect of sample matrix on precision and accuracy of analytical results.

Frequency

MS and MSD samples are analyzed when requested or submitted by the client.

Procedure

Prepare the MS/MSD following Section 8.2.4.3. Analyze the MS and MSD using the same methods and procedures as a sample.

The data system software calculates the concentration of 1,4-Dioxane in the MS and MSD, and will print out a quantitation report.

Calculation

Calculate the analyte percent recovery (% R) for 1,4-Dioxane in the MS and MSD, corrected for the concentration measured in the original unspiked sample.

Calculate the relative percent difference (RPD) between the 1,4-Dioxane concentration in the MS and in the MSD.

Acceptance Criteria

1. The MS/MSD must be analyzed on a GC/MS system meeting the BFB, initial calibration, CVS and method blank acceptance criteria.
2. The percent recovery of 1,4-Dioxane is within 80-120% of the true value.
3. The relative percent difference must be from -20% to +20%.
4. The area of the internal standards must be within ±30% of their areas in the most recent CVS.
5. The Toluene-d8 concentration must be within 70-130% of the true value.
6. The retention time for each internal standard must be within 0.33 minutes of its retention time in the most recent CVS.

Corrective Action

If the acceptance criteria are not met and there is sufficient sample, the analyses may be repeated, corrective action is documented or the data reported with appropriate data qualifying codes.

Data

Quantitation reports for each MS and MSD are kept with the corresponding data packet.

13.8 Proficiency Test Samples

Policy

Proficiency test samples (PT) are analyzed at least 4 times per year.

Procedure

Proficiency Testing (PT) or Proficiency Evaluation (PE) samples are treated as typical samples in the normal production process where possible, including the same preparation, calibration, quality control and acceptance criteria, sequence of analytical steps, and number of replicates. PT samples are not analyzed multiple times unless routine environmental samples are analyzed multiple times.

Corrective Action

Whenever a PT study is failed, the cause for the failure is determined and corrective action is taken if necessary. The documentation of this is maintained and made available to the accrediting authority. If two out of the three most recent studies for a given field of proficiency testing are failed, performance is considered unacceptable under the NELAC PT standard for that field. The requirements of initial accreditation as described in NELAC Section 2.7.2 must then be met.

Data

Quantitation reports for each PT set are kept with the corresponding data packet.

SECTION 14 – CALCULATIONS

14.1 Response Factor (RF)

$$RF_x = \frac{A_X}{C_X}$$

Where:
A = Peak area or height
C = Concentration
x = Analyte of interest

14.2 Relative Response Factor (RRF)

$$RRF_x = \frac{A_X}{A_{IS}} \times \frac{C_{IS}}{C_X}$$

Where:
A = Peak area or height
C = Concentration
x = Analyte of interest
IS = Internal Standard

14.3 Concentration (C)

$$C_x = \frac{A_X}{A_{IS}} \times \frac{C_{IS}}{RF_x}$$

Where:
RF_x= Response Factor
A = Peak area or height
C = Concentration
x = Analyte of interest
IS = Internal Standard

14.4 Mean ($\overline{X}$)

$$\overline{X} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Where:
n = Total number of values
x_i = Each value used to calculate mean

14.5 Standard Deviation (SD)

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(x_i - \overline{x} \right)^2}{(n-1)}}$$

Where:
n = Total number of values
$\overline{x}$ = Mean of n values
x_i = Each value used to calculate mean

14.6 Percent Relative Standard Deviation (% RSD)

$$\%\,RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

Where:
SD = Standard Deviation
$\overline{RRF}$ = Mean Relative Response Factor
RRF = Relative Response Factor

14.7 Percent Difference (%D) for Response Factor or Relative Response Factor

$$\%\,D = \frac{\overline{RF_i} - RF_v}{RF_i} \times 100$$

Where:
RF = RF (or RRF)
$\overline{RF}$ = Mean RF (or RRF)
$_i$ = Initial Calibration
$_v$ = Initial Calibration Verification Standard

14.8 Percent Difference for Values (%D)

$$\%\,D = \frac{T - F}{T} \times 100$$

Where:
T = True Value
F = Found Value

14.9 Percent Recovery (% R)

$$\%\,R = \frac{F}{T} \times 100$$

Where:
T = True Value
F = Found Value

14.10 Percent Recovery for MS (% R)

$$\%\,R = \frac{|MS - SP|}{MSA} \times 100$$

Where:
MS = Matrix Spike Result
SP = Sample Result
MSA = Matrix Spike Added

14.11 Relative Percent Difference for MSD (%RPD)

$$\%\,RPD = \left(\frac{(MS - MSD)}{(MS + MSD)/2} \right) \times 100$$

Where:
MS = Matrix Spike Result
MSD = Matrix Spike Duplicate Result

14.12 Relative Percent Difference for Sample Duplicates (%RPD)

$$\%\,RPD = \left(\frac{(SP - DP)}{(SP + DP)/2} \right) \times 100$$

Where:
SP = Sample Result
DP = Duplicate Result

14.13 Method Detection Limit (MDL)

$$MDL = t \times SD$$

Where:
SD = Standard Deviation
t = Student's t value for a 99% confidence level and a SD estimate with n-1 degrees of freedom (t = 3.14 for seven replicates)

SECTION 15 – METHOD PERFORMANCE

15.1 Precision and Bias

PRECISION is the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms.

BIAS is the systematic error that contributes to the difference between the mean of a significant number of test results and the accepted reference value.

Procedure

Precision and bias are determined for standard methods through the performance of a DOC.

Precision and bias using non-standard, modified standard or laboratory-developed methods are compared to the criteria established by the client (when requested), the method, or the laboratory.

Replicate spikes in a quality system matrix are analyzed according to the procedures outlined in Section 12 or the 2003 NELAC Standard, Appendix C.3.3.b. where applicable.

15.2 Selectivity

SELECTIVITY is the capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances.

The laboratory evaluates selectivity through use of chromatography retention time windows and mass spectral interpretation.

15.3 Estimation of Uncertainty

ESTIMATION OF UNCERTAINTY consists of the sum (combining the components) of the uncertainties of the numerous steps of the analytical process, including, but not limited to, sample plan variability, spatial and temporal sample variation, sample heterogeneity, calibration/calibration check variability, extraction variability, and weighing variability.

Procedure

The laboratory estimates uncertainty using the standard deviation calculated from routine quality control samples.

SECTION 16 – DATA AND RECORDS MANAGEMENT

16.1 Data Package Contents

1. GC/MS run log cover page
2. Sequence (analysis batch) list
3. Autotune printout
4. Calibration curve and RRF values printout
5. BFB Tune printout
6. QA-QC Check report
7. Continuing Calibration Check report
8. Sample analysis reports and chromatograms

16.2 Data Review

All data review is documented.

Before, during and after sample analysis, the analyst reviews the data for acceptability of quality control measures and accuracy of the results. This includes the checking of general instrument conditions, instrument performance criteria such as blank evaluation, calibration checks, and analyte and surrogate recoveries and retention times.

The information from each analysis batch is stored in individual folders. Each folder contains the printed analytical results (raw data) of the entire batch, as well as supporting documentation.

Each folder has a summary cover sheet that guides the analyst to record the information required for traceability of the analysis. The cover sheet includes space for recording quality control measurements and lists the acceptance criteria for the QC parameters, as well as space for notes.

Data are recorded on the cover sheet, in ink, promptly during analysis, and the cover sheet is completed before the folder is submitted for second review. When the analyst has finished the primary review, the cover sheet is signed and dated. Proper documentation procedures must be used.

A second reviewer, when available, checks the data packet for the following items:

1. All required information has been recorded on the cover sheet and is included in the folder;
2. QC criteria have been met or exceptions are documented in the comments section of the cover sheet;
3. Manual calculations, if any, are checked for accuracy;
4. Any non-conformances have been identified.

When these checks have been completed, the second reviewer signs and dates the cover sheet to document that the review has been performed. Additional data audit checklists may be filled out and signed. Signed checklists are kept with the data packet.

The results are taken directly from the raw data files and entered into the LIMS system by the laboratory staff.

The COCs are compared to the printed reports to verify that all samples received were analyzed and reported, and to check for any typographical errors.

The results are reviewed against previous trends and background data and samples are scheduled for reanalysis if significant deviations are noted.

Corrective action is taken if a problem is found at any stage in the review process. The QA system and review of data packets and reports is designed to catch errors and problems prior to data being reported in a final report. However, when corrective action affects previously reported data, the appropriate persons are notified in writing describing the problem, resolution and any result changes.

16.3 Data Storage

Printed data is stored in individual data packets in folders labeled with the analysis date. Electronic data is backed up onto compact disks or other media.

SECTION 17 – POLLUTION PREVENTION

All employees are responsible for reducing the amount of waste produced in the laboratory and actively seeking new methods of pollution prevention.

Employees are encouraged to read *Less Is Better: Guide to Minimizing Waste in Laboratories*, 2002, American Chemical Society.

SECTION 18 – WASTE MANAGEMENT

The samples from this method are disposed of in the treatment facility or by a licensed professional.

Excess and expired ISFS and stock standards are collected for disposal by a licensed professional.

The empty sample vials and caps are disposed of in the trash.

SECTION 19 – REFERENCES

USEPA Method 1624 "*Volatile Organic Compounds by Isotope Dilution GC/MS*", Revision B

USEPA Method 524.2 "*Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*", Revision 4.1, 1995

Code of Federal Regulations 40, Chapter 1, Part 136, Appendix B.

2003 NELAC Standard

SECTION 20 – APPENDICES

20.1 Code of Federal Regulations 40, Part 136, Appendix B

Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit. The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample. The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:
(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.
(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.
(c) That region of the standard curve where there is a significant change in sensitivity, *i.e.* , a break in the slope of the standard curve.
(d) Instrumental limitations.
It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.
(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.
If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.
If the measured level of analyte is greater than five times the estimated detection limit, there are two options.
(1) Obtain another sample with a lower level of analyte in the same matrix if possible.
(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.
(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower

method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:
(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.
(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} X_i\right)^2}{n}\right] \qquad S = \left(S^2\right)^{\frac{1}{2}}$$

where:
Xi; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=l to n.

6. (a) Compute the MDL as follows:
MDL = t(n-1,1-α=0.99) (S)
where:
MDL = the method detection limit
t(n-1,1-α=.99)= the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.
S = standard deviation of the replicate analyses.
(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2 /df).
LCL = 0.64 MDL
UCL = 2.20 MDL
where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.
(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.
(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.
(c) Use the S_{pooled} as calculated in 7b to compute The final MDL according to the following equation:
MDL=2.681 (S_{pooled})
where 2.681 is equal to t(12,1−α=.99).
(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.
LCL=0.72 MDL
UCL=1.65 MDL
where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

Tables of Students' t Values at the 99 Percent Confidence Level

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title ald the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]