Low Level Analysis of 1,4-Dioxane by GC/MS SIM using Large Volume Injection

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Abstract

1,4-Dioxane is a manmade chemical used primarily as an industrial solvent or solvent stabilizer to prevent the breakdown of chlorinated solvents during manufacturing processes. In addition, 1,4-Dioxane can also be found in a host of household products, including shampoo, liquid and dishwashing soap, hair lotion, and cosmetic products.[1] Due to its volatility and solubility in water, 1,4-Dioxane has a high potential for entering the environment, and can facilitate the dispersal of spent chlorinated solvents into ground and surface water systems, as evidenced by its detection in surface waters throughout the United States. Also, due to its chemical properties, traditional remediation techniques for chlorinated solvents are ineffective in removing 1,4-Dioxane from contaminated waters. The USEPA has classified 1,4-Dioxane as a Group B2, probable human carcinogen of low carcinogenic hazard and, although a Federal drinking water standard or maximum contaminant level (MCL) for 1,4-Dioxane has not been established, exposure to small amounts of 1,4-Dioxane may lead to significant adverse health effects. A method for the detection of 1,4-Dioxane has been developed using a modified separatory funnel extraction technique designed to overcome both the water solubility and volatility issues associated with extraction of 1,4-Dioxane. The extracts are subsequently analyzed using a large volume injector in conjunction with gas chromatography and mass spectroscopy (GC/MS) running in the selected ion monitoring mode (SIM). Many state governments have set advisory action levels for this compound, with California having one of the lowest action levels at 3 µg/L. Using the modified extraction procedure combined with large volume injection GC/MS SIM, method detection levels in the part per trillion quantification range can be readily achieved, easily satisfying these requirements.

Introduction

Over the past few years, 1,4-Dioxane has garnered increased attention due to its presence in groundwater in several California locations and because there is little scientific data available on the long-term effects on human health. An additional concern is that traditional remediation technologies used for sites contaminated with chlorinated solvents are ineffective at removing 1,4-Dioxane. [1]

The traditional method for the analysis of 1,4-Dioxane is EPA Method 8260. However, the high water solubility of 1,4-Dioxane causes poor purging efficiency, resulting in relatively high reporting limits at 100 µg/L. Reproducibility can also be a problem when using this approach.[2]

Several different approaches have been used to achieve lower MRLs for 1,4-Dioxane including salting purge procedures, vacuum distillation, continuous liquid-liquid extraction, isotope dilution and selected ion monitoring.

Two of the primary problems affecting any method targeting 1,4-Dioxane are poor recovery due to high water solubility and volatility loss. Purge and trap methods are unaffected by volatility loss yet have significant problems with high water solubility. Conversely, extraction methods have problems with volatility loss due to heat during continuous liquid-liquid extractors and again during the solvent reduction phase of the extraction routinely yielding recovery of 30%.

By combining an efficient solvent extraction method with a large volume splitless injection, low levels of 1,4-Dioxane can be readily achieved.

Materials & Methods

Reagents and Standards

- VWR OmniSolv Dichloromethane, Gas Chromatography/Residual Analysis grade
- 1,4-Dioxane at 2000 µg/ml in methanol from Supelco
- 1,4-Dioxane at 10 mg/ml in methanol from AccuStandard
- 1,4-Dioxane-d8 neat from Cambridge Isotope Laboratories, Inc.
- 1,4-Dichlorobenzene-d4 at 2000 µg/ml in dichloromethane from Ultra Scientific

Calibration

- A calibration curve was prepared using a 100 µg/ml stock standard.
- Concentration levels were analyzed at 2,5,10,20,50,100 and 200 ng/ml.
- 1,4-Dioxane and 1,4-Dioxane-d8 were quanitiated using an internal standard model against 1,4-Dichlorobenzene-d4 at 50 ng/ml.

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Extraction

- Extraction based on a modified EPA 3510C approach.
- 100 ml sample size.
- 20 g NaCl added to each sample
- Samples were spiked with 100 µl of a 1.0 µg/ml 1,4-Dioxane-d8 standard.
- Serially extracted three times with 20/10/10 ml of dichloromethane.
- Extract was dried with 3-5 g of Na_2SO_4
- Brought to a final volume of 5ml.
- A Method Detection Limit (MDL) study was prepared by extracting eight replicates spiked with 100 µl of a 0.1 µg/ml 1,4-Dioxane standard.
- An initial precision and recovery (IPR) study was prepared by extracting four replicates spiked with 50 µl of a 5.0 µg/ml 1,4-Dioxane standard.

Instrument Conditions

System Configuration

- Agilent 6890 gas chromatograph
- ATAS Optic 2 Programmable injector
- 5973 Mass Selective Detector (MSD)
- 7683 Automatic Liquid Sampler (ALS) tray and autoinjector
- Restek Rtx-5Sil MS with Integra Guard column (30 m x 0.25 mm ID x 0.25 µm film)
- (5% phenyl 95% dimethyl polysiloxane)

GC Method Parameters

Initial Temp: 45° C
Initial Time: 4.0 minutes

Ramp:	Rate (°C/min)	Final Temp (°C)	Final time (min)
1	25	145	0.00
2	35	320	0.00

Run Time: 13.0 minutes

Injection Parameters

- ATAS Optic 2 Programmable Capillary Injector
- 20 µl injection volume

Temperature profile:
Initial temperature: 5°C

Ramp:	Rate(°C)	Final Temp(°C)	Isothermal time (min)
1	0	5	0.40
2	6	305	14.73

Pressure Ramps:

Ramp	Start Pressure (PSI)	Step Time(min)	Target Pressure(PSI)
1	5.00	0.40	5.00
2	20.00	1.6	20.00
3	9.08	2.00	9.08
4	9.08	12.00	33.70

Split State:

Time (min)	Split State
Initial	Vent
0.40	Closed/Splitless
2.00	Open/Split
13.00	Vent

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Mass Spectrometer Method Parameters

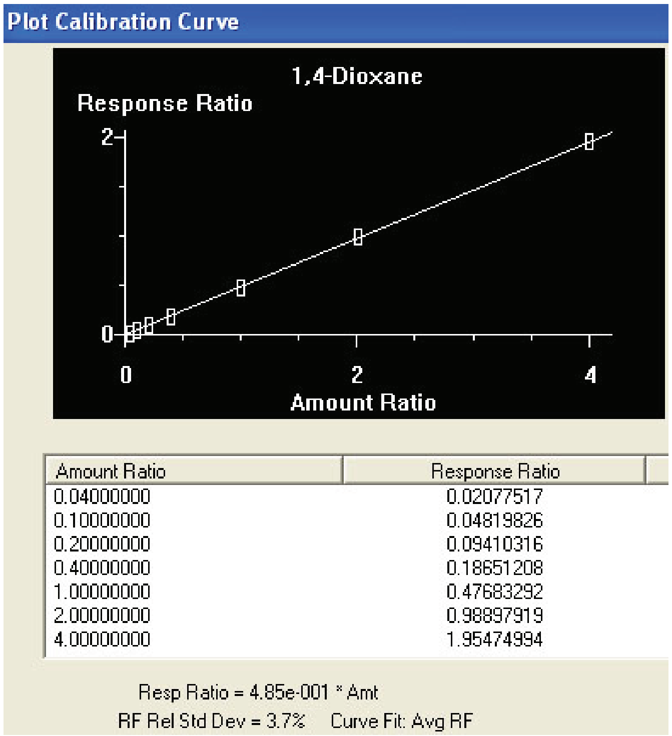
Solvent Delay: 4.20 minutes
Transfer line:
MS Quad: 150°C
MS source: 230°C
Acquisition mode: SIM
SIM groups: 1
Ions/Dwell: 43.0/20, 46.0/20, 58.0/20
64.0/20, 88.0/20, 96.0/20

SIM groups: 2
Ions/Dwell: 115.0/60, 150.0/60, 152.0/60

Results & Discussion

The calibration under the described method shows excellent linearity with the %RSD of 1,4-Dioxane and 1,4-Dioxane-d8 at 3.7% and 1.9% respectively (Figures 1 & 2).

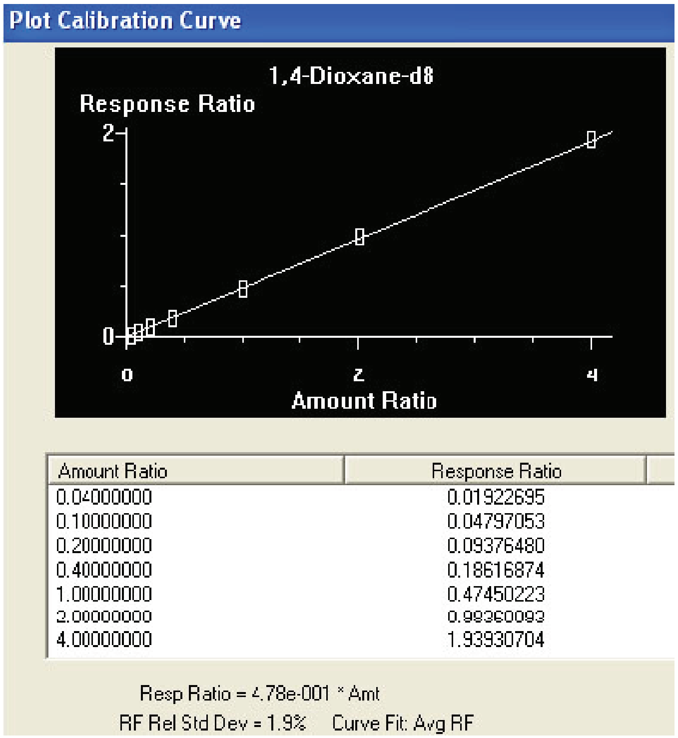
Figure 1. Calibration Curves of 1,4-Dioxane



Amount Ratio	Response Ratio
0.04000000	0.02077517
0.10000000	0.04819826
0.20000000	0.09410316
0.40000000	0.18651208
1.00000000	0.47683292
2.00000000	0.98897919
4.00000000	1.95474994

Resp Ratio = 4.85e-001 * Amt
RF Rel Std Dev = 3.7% Curve Fit: Avg RF

Figure 2. Calibration Curves of 1,4-Dioxane-d8

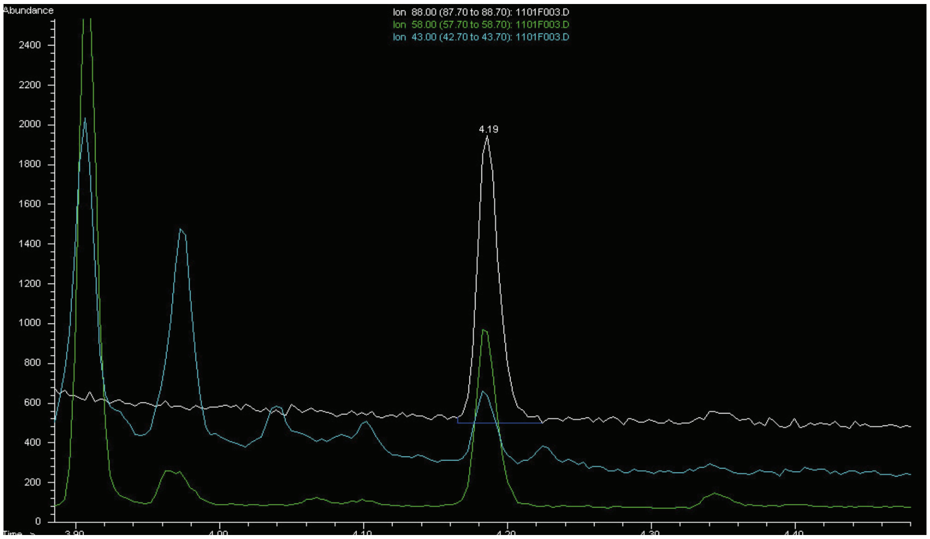


Amount Ratio	Response Ratio
0.04000000	0.01922695
0.10000000	0.04797053
0.20000000	0.09376480
0.40000000	0.18616874
1.00000000	0.47450223
2.00000000	0.99360093
4.00000000	1.93930704

Resp Ratio = 4.78e-001 * Amt
RF Rel Std Dev = 1.9% Curve Fit: Avg RF

The sensitivity of the large volume splitless injection technique is exceptional. The signal to noise ratio of 29 for the low calibration point of 2.0 ng/ml shows more than aqeduate response to support an MRL of 0.1 µg/L. (Figure 3)

Figure 3. EICP of 2.0 ng/ml Calibration Standard



Analysis of the IRP study produced the following results:

Analyte	True Value	Std Dev	MDL Value	%RSD	Avg Recovery
1, 4-Dioxane	0.1 µg/L	0.013	0.038 µg/L	12	100%

Analysis of the IRP study produced the following results:

Analyte	Spike Level PPB	Results IPR 1	IPR 2	IPR 3	IPR 4	Avg Percent Recovery	Percent RSD
1,4-Dioxane	2.5	1.91	2.03	1.97	1.97	78.8	2.5

Conclusions

- Columbia Analytical has set a Method Reporting Limit (MRL) of 0.1 µg/L.
- With a reporting limit of 1.0 µg/L final extract volume will be 50 ml.
- Modification to USEPA Method 3510C yields recoveries of about 80%.
- The accuracy and precision of the method meet USEPA requirements.
- Effectively eliminates the need for isotope dilution calculations while maintaining low reporting limits.
- The use of 1,4-Dioxane-d8 as a surrogate ensures performance of the method.

References

1. D. Grant Walson, Bruce Tunnicliffe, 1,4-Dioxane – A Little Known Compound, Environmental Science & Engineering, May 2002.
2. T. Mohr, Solvent Stabilizers White Paper, Santa Clara Valley Water District, June 2001.