

Analysis of 1,4-Dioxane by Purge and Trap and Gas Chromatography/Mass Spectrometry

Introduction

1,4-Dioxane is a heterocyclic molecule that belongs to a class known as ethers. This compound has been used in the past as a stabilizer for different types of chemicals and is a component of many consumer products such as paint strippers, dyes and waxes. 1,4-Dioxane can also be found as a contaminant in anything from groundwater to cosmetics. Exposure to this contaminant has been shown to have negative health effects and has led to its characterization as a Group 2B carcinogen. Recently, 1,4-Dioxane has become of increasing concern in the environment due to its presence in groundwater at several California sites.¹ Although it is short-lived in the atmosphere due to its hygroscopic nature, it readily leaches from soil to groundwater and is known to migrate rapidly.² Although there is currently no maximum contaminant level established by the U.S. EPA, California recommends the drinking water notification level to be less than or equal to 1 µg/L.³

One of the challenges for analysis of this compound is that 1,4-Dioxane is extremely miscible in water. This level of miscibility in water makes it difficult to detect at trace levels. It can be so difficult to detect that it has historically been known to be almost “invisible” in laboratory samples.⁴ Looking for this compound in ultra-low levels utilizing a standard GC-MS method yields unsatisfactory results and a specialized approach is needed. A low level method using heated purge and trap (P&T) concentration and gas chromatography/mass spectrometry (GC/MS) with Selective Ion Monitoring (SIM) is presented here.

Instrumentation

Instrumentation used for this study included an **OI Analytical 4760 Purge and Trap, 4100 Sample Processor**, and an Agilent 7890A GC with 5975C mass spectrometer. Purge and Trap is a well-established technique used by analytical and environmental labs to help quantitate volatiles that are in solution. To start, a liquid sample is purged with an inert gas. This purging acts to essentially extract the volatiles from the liquid which are then concentrated onto a sorbent trap. Once they have been collected in this trap, it is heated and the volatiles are desorbed and sent into the GC for chromatographic separation and mass spectrometric detection. Purge and trap instruments, also known as concentrators, increase the sensitivity of these dissolved species for the GC and are essential to identifying trace amounts of certain analytes. The OI Analytical **Eclipse 4760 Purge and Trap** was designed to maximize detection efficiency without a loss in throughput. The 4760 also has a patented cyclone water management system that removes excess moisture which can have a detrimental effect on the chromatographic performance of the system. This technology allows for the detection of traditionally difficult compounds. In conjunction with the 4760, a 4100 autosampler equipped with OI Analytical's VOA Constrictor™ gripper technology and high speed injection valves was employed to introduce our samples into the purge and trap and to maximize throughput.



Figure 1. Eclipse 4760 P&T and 4100 Autosampler

Experimental

Modified USEPA Method 8260C was used with selective ion monitoring (SIM) instead of full scan and a 10 ml purge volume to achieve low concentration detection. Elevated heated purge was used to increase purging efficiency. A longer trap bake time was used along with an increased GC final temperature time to minimize the amount of water injected into the GC/MS. A calibration from 0.25-50ppb was analyzed using 0.25ppb Fluorobenzene as the internal standard and 0.25ppb Toluene-d8 as the surrogate standard. Method detection limit (MDL) studies were performed at 0.2ppb and initial demonstration of capability (IDOC) at 10ppb.

Please see Table 1 for instrument configuration and operating parameters.

Table 1. Instrument Configuration and Operating Conditions

Purge-and-Trap	Eclipse 4760 P&T Sample Concentrator
Trap	#10 trap; Tenax® / Silica gel / CMS
Purge Gas	Zero grade Helium at 40 mL/min
Purge Time	11 min
Sparge Mount Temperature	60 °C
Sample Temperature (purge)	60 °C
Sample Temperature (bake)	60 °C
Desorb Time	0.5 min
Bake Time	10 min
OI #10 Trap Temperature	Ambient during purge 180 °C during desorb pre-heat 190 °C during desorb 210 °C during bake
Water Management	120 °C during purge Ambient during desorb 240 °C during bake
Transfer Line Temperature	140 °C
Six-port Valve Temperature	140 °C
Autosampler	4100 Water/Soil Sample Processor
System Gas	Zero grade nitrogen
Purge Gas	Zero grade helium
LV20 Pressure	8.0 psi
Loop-based Time Settings	Default
Rinse Water	80 °C
Soil Sample Transfer	150 °C
Soil Oven	150 °C
Soil Lift Station	45 °C
Loop Size	10 mL

4100 Sample Processor Methods	
Sample Type	Waters
Needle Rinses	1
SAM A (µL)	5
SAM B (µL)	0
SAM C (µL)	0
SAM D (µL)	0
Purge Time (min)	11.0
Desorb Time (min)	0.5
P&T Rinses	3
Rinse Water	Hot
Water Stir Time (min)	0.0
Water Settle Time (sec)	0
Gas Chromatograph	Agilent 7890A
Column	Restek Rtx - VMS 30 meter, 0.25 mm ID, 1.4 µm
Carrier Gas	Zero grade helium
Inlet Temperature	240 °C
Inlet Liner	Agilent Ultra Inert, 1 mm straight taper
Column Flow Rate	0.8 mL/min
Split Ratio	30:1
Oven Program	Hold at 40 °C for 1.5 min 16 °C/minute to 180 °C 40 °C/minute to 220 °C Hold at 220 °C for 10 min Total GC Run is 20.75 min
Mass Spectrometer	Agilent 5975C
Mode	SIM
SIM Compounds	
Group 1	Fluorobenzene m/z 70,96 start time 3.5
Group 2	1,4-Dioxane m/z 58,88 start time 5.6
Group 3	Toluene-d8 m/z 98,100 start time 6.0
Dwell Time	100 ms
Solvent Delay	3.50 min
Transfer Line Temperature	250 °C
Source Temperature	300 °C
Quadrupole Temperature	200 °C
Draw Out Plate	6 mm

Results

Data generated met Method 8260 criteria of $\leq 20\%$ RSD. The IDOC results show excellent % recovery and % RSD and the MDL is well below current action levels.

See Table 2 and 3 for analytical results.

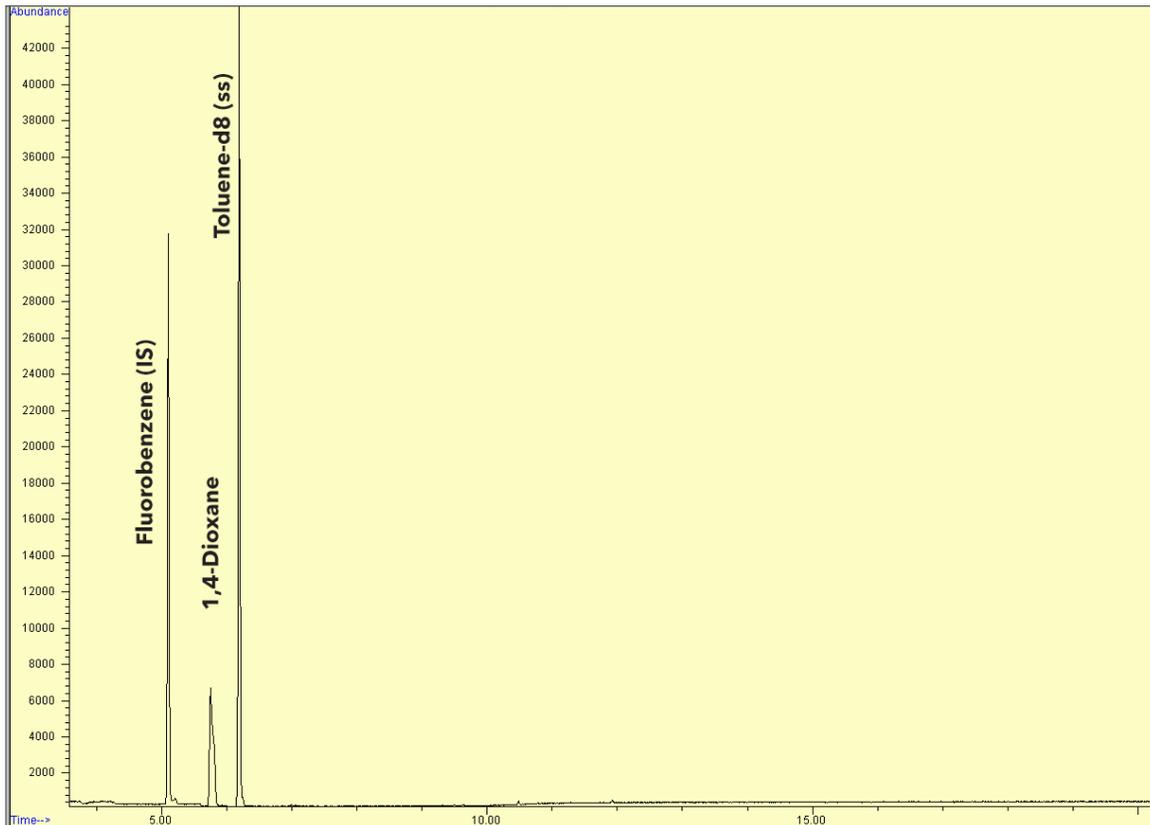
Table 2. Calibration Data

Analyte	Compound	Avg Response Factor	% RSD
1	Fluorobenzene	N/A	N/A
2	1,4-Dioxane	0.002	9.81
3	Toluene-d8	1.061	2.49

Table 3. Results

Analyte	Compound	IDOC % RSD	IDOC % Recovery	MDL Avg	MDL Std Dev	MDL
1	1,4-Dioxane	4.19	101.7	0.245	0.027	0.075

Figure 2. Chromatogram of 25 ppb 1,4-Dioxane



Conclusions

As mentioned previously, 1,4-Dioxane is notoriously difficult to analyze due to its solubility in water. Using elevated purge temperature along with SIM offers a reasonable analysis time along with the ability to detect very low concentrations of 1,4-Dioxane without sacrificing laboratory throughput.

References

1. "Groundwater Information Sheet 1,4-Dioxane". California Water Resources Board. April 2009.
2. "Technical Fact Sheet-1,4-Dioxane". USEPA Office of Solid Waste and Emergency Response. January 2014.
3. "1,4-Dioxane". California State Water Resources Board. February 2016.
4. "Analytical Methods and Recommendations for the Analysis of 1,4-Dioxane". Florida Department of Environmental Protection". October 2010.
5. "Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry(GC/MS)" . Revision 3. USEPA SW846 August 2006.



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