Optimization of 1,4-Dioxane and Ethanol Detection Using USEPA Method 8260

Application Note

Environmental

Author

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Abstract

The United States Environmental Protection Agency (USEPA) Method 8260 has an extensive list of analytes that can be analyzed by purge and trap sampling. Two of the more troublesome compounds on this list are Ethanol and 1, 4-Dioxane. Both of these compounds are water miscible and Selective Ion Monitoring (SIM) is required in order to detect these compounds at lower levels. The advent of SIM/Scan monitoring has made it easier to analyze for these compounds by traditional purge and trap sampling. However, due to the miscibility of the compounds and their propensity to stick to the sparge vessel of the purge and trap, purge and trap sampling needs to be optimized. This application will compare linearity, method detection limits, precision and accuracy and carryover of several purge and trap sampling parameters.

Introduction:

During the manufacture of pharmaceuticals, 1, 4-Dioxane is used as a cleansing agent. It is also a byproduct of plastic manufacturing. The most likely exposure to 1, 4-Dioxane is at an industrial site. However, if any 1, 4-Dioxane is released into the environment during manufacturing there is a potential for it to migrate into ground water. The fact that 1, 4-Dioxane is so miscible in water makes degradation of the chemical challenging. Ethanol, on the other hand, has been a popular gasoline additive. Since it burns more quickly and completely than gasoline, emissions from car exhaust are decreased. The downside of this is underground storage tank leakage and fuel spills cause ground water and drinking water to be contaminated with both the fuel and the ethanol additive. Since ethanol is also very miscible in water, the detection of ethanol contamination in water can be difficult.

There have been several innovations that help overcome the obstacles of detecting 1, 4-Dioxane and Ethanol. The first one is the SIM mode of the mass spectrometer. This mode allows better detection of hard to extract compounds. Furthermore, mass spectrometers are now equipped to run SIM/Scan, this not only helps detect more difficult compounds, but also enables the detection of an extensive list of USEPA Method 8260 compounds without having to run the samples twice. Advancements in purge and trap sampling have also facilitated better detection of these compounds. Most effective in this has been the ability to heat the samples. However, there are drawbacks to better detection. The most problematic of these is the tendency of 1, 4-Dioxane and Ethanol to “stick” to the glass ware. This susceptibility has caused many headaches in environmental labs.

This application note will investigate seven variations of purge and trap sampling. The data will then be evaluated in order to recommend the optimum purge and trap sampling parameters for your lab.

Experimental:

The sampling system used for this study was the EST Analytical Evolution concentrator affixed with a Vocarb 3000 trap. The Centurion WS autosampler equipped with the syringe option was employed as the autosampler. The separation and analysis were performed by an Agilent 7890A Gas Chromatograph (GC) and 5975C inert XL Mass Spectrometer (MS). The GC was configured with a Restek Rxi-624 Sil MS 30m x 0.25mm x 1.4µm column. The purge and trap parameters used for this study are listed in Tables 1 and 2 while Table 3 shows the GC/MS parameters

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Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	150ºC
Transfer Line Temp.	150ºC
Trap Temp.	35ºC
Moisture Reduction Trap (MoRT) Temp.	39ºC
Purge Time	11 min
Purge Flow	40mL/min
Dry Purge Temp.	ambient
Dry Purge Flow	40mL/min
Dry Purge Time	1.0 min
Desorb Pressure Control	On
Desorb Pressure	5psi
Desorb Time	0.5 min
Desorb Preheat Delay	10 sec
Desorb Temp.	250ºC
Moisture Reduction Trap (MoRT) Bake Temp.	210ºC
Bake Temp	260ºC
Sparge Vessel Bake Temp.	40ºC for 3 min, ramp 100ºC to 110ºC hold for bake time
Bake Time	6
Bake Flow	85mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Type	Water
Water Volume	5 or 10ml
Internal Standard Vol.	5 µl

Table 1: Purge and Trap Parameters

Altered Parameters	Baseline Parameters A	Iteration B	Iteration C	Iteration D	Iteration E	Iteration F	Iteration G
Sparge Vessel Type	5ml Tradition	5ml Traditional	5ml Traditional	5ml Traditional	40ml Vial, 10ml purge volume	5ml Fritless Bulbless	5ml Fritless Bulbless
Purge Temperature (ºC)	Room Temp.	40	60	40	40	40	40
Sparge Bake Temperature (ºC)	110	110	110	Not Applied	Not Applied*	110	Not Applied

*For Iteration E, the patented Water/Soil prep mode was used.

Table 2: Purge and Trap Sampling Test Parameters

GC/MS	Agilent 7890A/5975C inert XL
Inlet	Split/Splitless
Inlet Temp.	220ºC
Inlet Head Pressure	12.153 psi
Mode	Split
Split Ratio	40:1
Column	Rxi-624Sil MS 30m x 0.25mm I.D. 1.4µm film thickness
Oven Temp. Program	45ºC hold for 1 min, ramp 15ºC/min to 220ºC, hold for 1.33 min, 14 min run time
Column Flow Rate	1mL/min
Gas	Helium
Total Flow	44mL/min
Source Temp.	230ºC
Quad Temp.	150ºC
MS Transfer Line Temp.	180ºC
Scan Range	m/z 35-300
Scans	5.2 scans/sec
SIM Ions (0.7min to 3.49min)	45, 46
SIM Ions (3.5min to 14min)	58, 88
Solvent Delay	0.7 min

Table 3: GC/MS Experimental Parameters

For each parameter iteration, see Table 2, a calibration curve was established with a linear range of 0.5 to 200ppb using standards from Restek. After each of the prescribed curves was determined; Method Detection Limits (MDLs), precision and accuracy and carryover studies were performed. A series of seven low level standards were run in order to establish MDLs per 40CFR Part 136, Appendix B. Next, seven replicate samples of the 50ppb standard were run in order to establish the precision and the accuracy of the experimental parameters. Finally, a series of four 50ppb standards were run with each standard followed by three blanks. The amount of carryover was then analyzed in the first blank. The data from each parameter variation was compiled and compared in order to determine the optimum conditions for this analysis. An average of the results for each analysis condition is listed in Table 4.

Averaged Results	Parameter Iteration						
	A	B	C	D	E	F	G
Curve Relative Standard Deviation	7.75	8.09	8.30	6.73	7.84	7.60	7.58
Curve Response Factor	1.10	1.06	1.09	1.02	1.15	1.03	1.11
Method Detection Limit	0.500	0.316	0.973	0.327	0.394	0.326	0.288
Precision at 50ppb	4.45	3.96	3.89	2.11	2.90	3.89	4.46
Accuracy at 50ppb	107.01	95.29	97.15	96.28	97.12	97.59	99.72

Results Summary

Table 4: Averaged Results Summary

The primary compounds of interest for the study were Ethanol and 1, 4-Dioxane. For this reason, the data for these compounds was compiled separately in order to better distinguish the benefits or detriment of each purge and trap parameter set. The experimental results of the precision and percent recovery studies are displayed in Tables 5 and 6.

Precision at 50ppb

Compound	Parameter Iteration						
	A	B	C	D	E	F	G
Ethanol	13.43	7.29	12.48	2.47	2.54	6.18	3.68
1,4-Dioxane	9.44	7.64	14.86	2.10	4.34	7.20	2.51

Table 5: Ethanol and 1, 4-Dioxane Precision at 50ppb

Percent Recovery at 50ppb

Compound	Parameter Iteration						
	A	B	C	D	E	F	G
Ethanol	170.24	108.45	125.90	110.68	93.71	80.05	96.53
1,4-Dioxane	148.44	128.01	122.49	110.95	101.55	80.27	97.45

Table 6: Ethanol and 1, 4-Dioxane Percent Recovery at 50ppb

For the carryover studies, Ethanol and 1, 4-Dioxane were examined along with the carryover of 1, 2, 4-Trichlorobenzene, Naphthalene and 1, 2, 3-Trichlorobenzene. The reason the heavier compounds were included in this study was a concern that changing the sampling parameters may help the Ethanol and 1, 4-Dioxane carryover, but harm the carryover of the heavier compounds of interest. Table 7 shows a listing of the carryover results, in parts per billion, while Figure 1 displays the percent carryover of the different purge and trap experimental parameters for just the Ethanol and 1, 4-Dioxane.

Average Carryover after 50ppb							
Compound	Iteration						
	A	B	C	D	E	F	G
Ethanol	63ppb	76ppb	38ppb	58ppb	ND	ND	ND
1,4-Dioxane	53ppb	60ppb	52ppb	44ppb	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND	0.50ppb	ND	ND	0.53ppb
Naphthalene	ND	ND	ND	0.59ppb	ND	ND	0.61ppb
1,2,3-Trichlorobenzene	ND	ND	ND	0.53ppb	ND	ND	0.57ppb

ND signifies Non Detect

Table 7: Carryover in First Blank after a 50ppb Standard

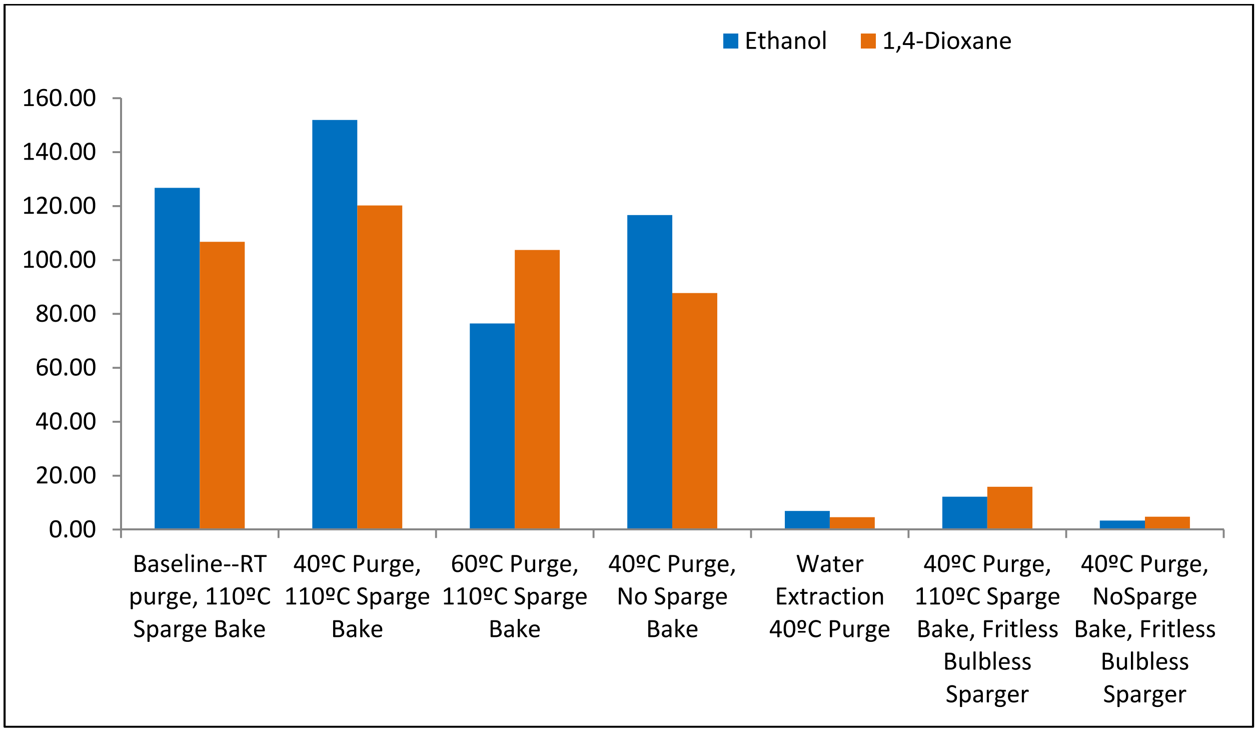

Figure 1: Ethanol and 1, 4-Dioxane Percent Carryover after a 50ppb Standard Graphic

After all the studies were completed, two purge and trap parameter variations showed the best precision, percent recovery, and carryover while meeting the USEPA Method 8260 linearity and response factor requirements. An abbreviated listing of the results for these two iterations are shown in Table 8.

Compound	Water Extraction 40ºC Purge (E)				Fritless Bulbless Sparge Vessel, 40ºC purge, Sparge Bake (F)			
	Curve Linearity	Response Factor	Precision (%RSD)	% Recovery	Curve Linearity	Response Factor	Precision (%RSD)	% Recovery
Dichlorodifluoromethane	3.3	0.543	5.03	96.45	7.73	0.42	6.62	100.91
Chloromethane	11.39	1.016	3.71	90.88	12.68	0.963	4.44	87.32
Vinyl Chloride	2.08	0.927	4.72	97.24	5.31	0.889	5.13	95.08
Bromomethane	11.04	0.547	3.2	89.98	14.45	0.568	5.25	90.29
Chloroethane	11.48	0.613	4.18	90.66	12.83	0.623	4.76	87.49
Ethanol	0.999*	0.012	2.54	93.71	14.71	0.009	6.18	80.05
Trichlorofluoromethane	3.86	0.614	4.8	98.25	7.91	0.54	6.45	98.41
1,1-Dichloroethene	4.26	0.611	3.99	98.96	6.46	0.517	5.73	101.07
Acetone	13.93	0.346	3.3	93.93	13.09	0.392	3.06	89.45
Carbon Disulfide	5.64	2.112	4.27	98.19	7.28	1.544	5.49	100.13
Methylene Chloride	13.51	0.786	2.12	91.85	9.99	0.728	2.31	92.19
MTBE	3.38	2.113	1.55	100.14	2.39	2.174	1.72	104.56
1,1-Dichloroethane	5.99	1.419	2.97	100.83	8.15	1.245	3.67	106.21
2-Butanone	5.86	1.574	1.21	93.14	9.97	1.901	4.7	95.12
Chloroform	10.6	1.33	2.6	92.31	5.51	1.211	3.06	99.47
Benzene	2.89	3.079	2.92	97.77	2.23	2.735	3.8	100.65
1,2-Dichloropropane	5.64	0.458	2.46	99.63	4.85	0.41	3.17	105.24
1,4-Dioxane	7.47	0.01	4.34	101.55	13.72	0.009	7.2	80.27
Toluene	12.28	1.136	3.5	92.8	4.15	0.958	4.79	102.29
2-Hexanone	6.69	0.367	1.64	98.85	5.14	0.448	1.81	106.37
Chlorobenzene	6.08	1.34	2.19	97.14	2.93	1.156	3.1	97.02
Ethylbenzene	7.62	2.321	3.45	98.97	6.16	1.994	4.27	97.77
Xylene (m+p)	7.87	1.804	3.18	97.64	5.89	1.527	4.06	98.29
Xylene (o)	7.56	1.819	2.45	99.5	5.6	1.614	3.62	98.74
Bromoform	14.45	0.259	1.52	116.43	13.74	0.286	1.42	109.97
1,1,2,2-Tetrachloroethane	6.15	1.266	1.09	94.79	4.33	1.213	2.06	100.72
1,2-Dibromo-3-chloropropane	7.97	0.245	0.91	104.86	4.89	0.271	1.19	104.47
1,2,4-Trichlorobenzene	7.68	1.291	2.6	98.69	5.61	1.02	2.71	98.64
Naphthalene	12.46	3.787	1.52	95.1	5.1	3.365	1.63	101.97
Hexachlorobutadiene	9.3	0.556	4.49	97.58	7.86	0.376	5.07	96.15
1,2,3-Trichlorobenzene	12.74	1.253	1.52	93.05	5.08	0.955	2.12	99.03

Table 8: Results of the Water Extraction and the Fritless/Bulbless Sparge Vessel With Sparge Bake Studies

Conclusions:

All seven purge and trap parameter iterations passed the USEPA Method 8260 requirements for linearity and method detection limits. The problem with some of the experimental parameters was found in the carryover and precision and accuracy studies. The carryover using the traditional sparge vessel showed a large amount of carryover for the Ethanol and 1, 4-Dioxane. Since the carryover was so high, the precision and accuracy data suffered. The Fritless/Bulbless sparge vessel, on the other hand, displayed much lower carryover for the Ethanol and 1, 4-Dioxane especially when the patented sparge bake was not used. However, the 1, 2, 4-Trichlorobenzene, Naphthalene and 1, 2, 3-Trichlorobenzene carryover after the 50ppb standard was above the lower limit of the curve. Thus, the sparge bake would be recommended in order to limit the carryover of the heavier compounds. The optimum purge and trap parameters proved to be the patented water extraction technique. This technique provided linearity and method detection limits that met the USEPA Method 8260 requirements, while providing excellent precision and accuracy data. During water extraction, the sample is transferred to an empty 40ml vial and then purged in the soil station of the Centurion. The “fresh” vial provides a clean sparge vessel for every sample thus limiting carryover for both the Ethanol and 1, 4-Dioxane and for the heavy compounds. This lack of carryover aided in providing optimum precision and accuracy and carryover results and would be the recommended method for examining these troublesome compounds.

References:

1. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); United States Environmental Protection Agency Method 8260C, Revision 3, August, 2006.

2. Jurek, Anne, “A Single Calibration Method for Water AND Soil Samples Performing EPA Method 8260”, https://www.estanalytical.com/a-single-calibration-method-for-water-and-soil-samples/, EST Analytical, published 3, 2015, Web 4, 2016.

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