Determination of 1,4-Dioxane in Drinking Water by Gas Chromatography/Mass Spectrometry (GC/MS) with Selected Ion Monitoring (SIM)

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Key Words
ISQ Single Quadrupole GC-MS, TRACE GC Ultra, TriPlus RSH autosampler, PTV inlet, Sequential SIM/Full Scan, EPA Method 522, Environmental

Introduction
1,4-Dioxane is used mainly as a stabilizer for 1,1,1-trichloroethane for transport in aluminum containers. It is an irritant to eyes and respiratory system and suspected of causing damage to nervous system, liver, and kidneys.[1] In 2008, testing sponsored by the U.S. Organic Consumers Association found dioxane in almost half of tested organic personal-care products.[1] Of the total 1.163 million pounds of 1,4-dioxane released into the U.S. environment in 1992, as reported to the Toxics Release Inventory, 680 thousand pounds (58.5%) were released into the atmosphere, 450 thousand pounds (38.7%) were released into surface waters, and 33 hundred pounds (2.8%) were released onto the land (TRI92 1994).[2] In 2005, the New Hampshire Department of Environmental Services Waste Management Division started enforcement of an Ambient Groundwater Quality Standard reporting limit of 3 µg/L and trending towards a detection limit of 0.25 µg/L. 1,4-Dioxane has been detected in drinking water in the U.S. at a concentration of 1 µg/L. This application highlights the use of SIM/Full Scan to identify unknowns with a NIST library, while producing accurate results that meet EPA Method 522 requirements.

Experimental Conditions
Data was collected using a Thermo Scientific ISQ single quadrupole mass spectrometer utilizing the Thermo Scientific TriPlus RSH autosampler and a PTV inlet (CT-Splitless mode) on a Thermo Scientific TRACE GC Ultra gas chromatograph. The mass spectrometry data was collected in Full Scan (FS), selected ion monitoring (SIM), and SIM/Scan modes. A Thermo Scientific TraceGOLD TG-624 column (30 m × 0.25 mm ID, 1.4 µm film thickness; p/n 26085-3320) was used with a Siltek® deactivated baffle liner (p/n 453T2120). Table 1 lists the GC parameters. The ion source temperature of the mass spectrometer was set to 230 °C. The instrument was tuned to meet the bromofluorobenzene (BFB) criteria for this method. See Figure 1.

1,4-Dioxane calibration standards were prepared in dichloromethane as per the method to provide a range from 0.05 ppb to 40 ppb of dioxane.

Table 1. GC parameters

GC Oven Ramp		
Ramp	**Temp**	**Hold**
	30 °C	1 min
7 °C/min	90 °C	0 min
20 °C/min	200 °C	3 min
PTV Inlet		
Temperature	200 °C	
Split Flow	30 mL/min	
Splitless Time	0.50 min	
Solvent Valve Temp	100 °C	

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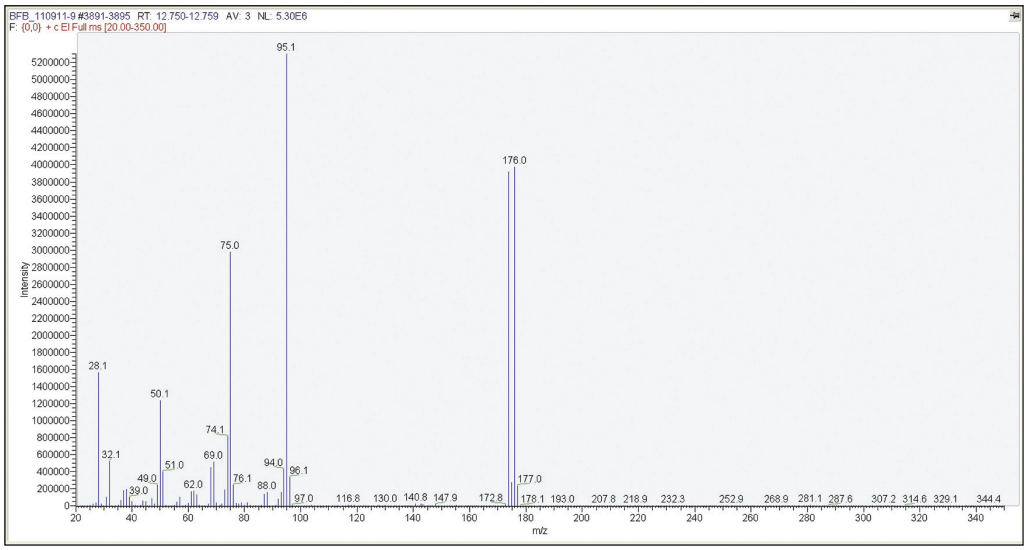

m/z	Criteria	Ion Intensity	TIC %	Criteria %	Pass/Fail
50	15%-40% of mass 95	871150	23.88	23.88	Pass
75	30%-80% of mass 95	1759792	48.25	48.25	Pass
95	Base peak	3647589	100.00	100.00	Pass
96	5%-9% of mass 95	240562	6.60	6.60	Pass
173	<2% of mass 174	21386	0.59	0.71	Pass
174	>50% of mass 174	2993264	82.06	82.06	Pass
175	5%-9% of mass 174	206831	5.67	6.91	Pass
176	>95% but <101% of mass 174	3003238	82.33	100.33	Pass
177	5%-9% of mass 176	173848	4.77	5.79	Pass

Figure 1. BFB and EPA Method 522 criteria

Full Scan Results

A calibration curve was created in Full Scan mode from 0.05 to 40 ppb of 1,4-dioxane. Figure 2 demonstrates the peak shape and S/N ratio at 0.1 ppb. The Full Scan calibration curve with an R^2 value of 0.9998 is presented in Figure 3.

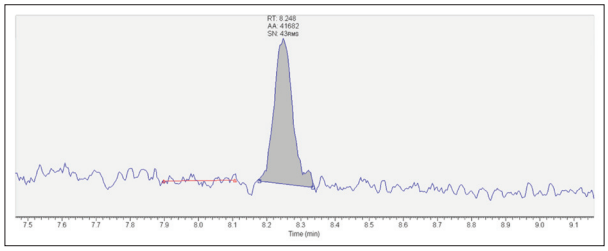

Figure 2. 1,4 -Dioxane at a concentration of 0.1 ppb with S/N = 43 in Full Scan

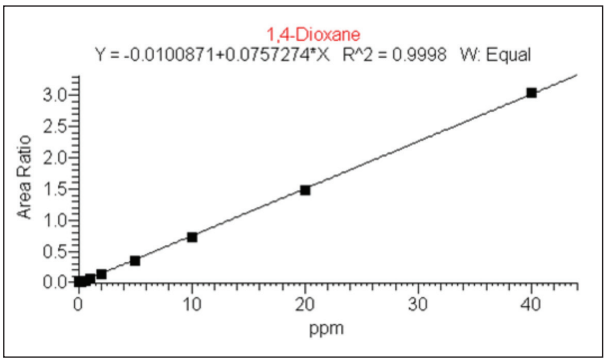

Figure 3. Full Scan calibration curve 0.05 to 40 ppb of 1,4-dioxane

SIM Results

A calibration curve was created in SIM mode from 0.05 to 40 ppb of 1,4-dioxane by monitoring three ions for the internal standard (46, 78, and 80), three ions for the surrogate (62, 64, 96), and two for the target compound (58, 88). Figure 4 shows the resulting calibration curve with an R^2 value of 0.9998. The chromatogram of the 0.05 ppb standard is depicted in Figure 5. At half the concentration of the full scan the S/N ratio is twice as high, highlighting the power of selected ion monitoring.

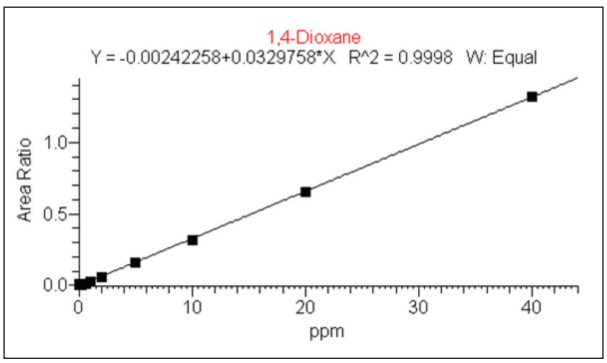

Figure 4. SIM mode calibration curve 0.05 to 40 ppb of 1,4-dioxane

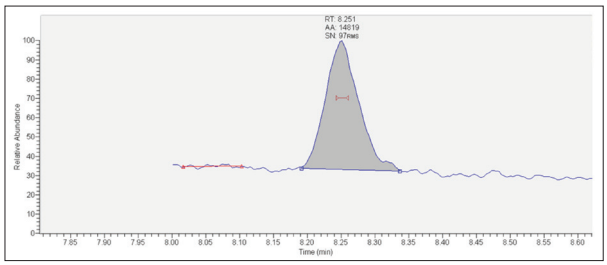

Figure 5. SIM analysis of 1,4-dioxane at 0.05 ppb with S/N = 97. Note the two-fold improvement in the S/N ratio in the SIM mode at one-half the concentration of 1,4-dioxane shown in the full scan in Figure 2.

Sequential SIM/Full Scan

The advantage of the SIM/Full Scan mode (tandem Full Scan/SIM) is the ability to identify additional peaks in unknown samples using a NIST or other library. Figure 6 provides the setup parameters for the SIM/Full Scan method in the software. Each scan segment contains both the SIM ions and scanning from 45 to 450 amu (Full Scan). SIM and the Full Scan alternate during the data collection. This is visualized in Figure 7, where the shorter scans are the SIM scans and the taller scans are the Full Scans. 1,4-Dioxane standards were analyzed from 0.05 to 40 ppb (Figure 8). According to EPA Method 522, each point on the curve must be within ± 20% of the true value, except the lowest point on the curve, which must be within ± 40%.[3] Even though the calibration curve is linear (R^2 = 0.9999), the curve only meets this criteria down to 0.5 ppb. By weighting the curve 1/x, the curve meets the criteria down to 0.05 ppb (Figure 9). Weighting the curve 1/x places more importance on the lower concentrations and has less influence in skewing the results, providing better accuracy at lower levels.

Time (min)	Mass List or Range (amu)	Dwell or Scan Times (sec)	Tune File Name
5.00	20-350	0.096	(Last Saved)
	46, 78, 80	0.03, 0.03, 0....	(Last Saved)
8.00	20-350	0.096	(Last Saved)
	58, 88, 62, 64, 96	0.03, 0.03, 0....	(Last Saved)

Figure 6. MS Method Parameters page from software showing SIM/Full Scan. Note that each segment can have its own specific tune file.

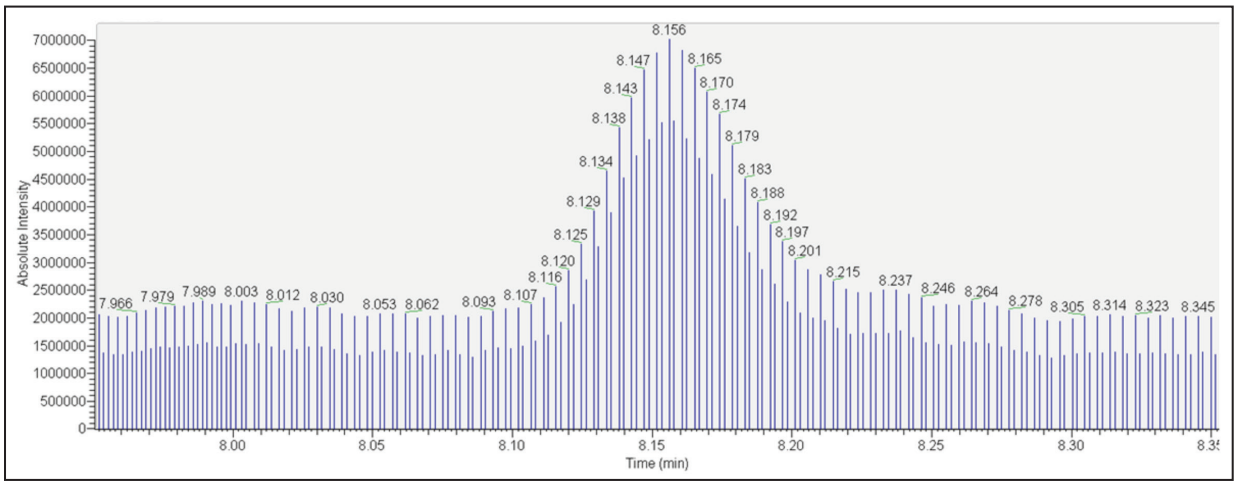

Figure 7. Chromatogram demonstrating the alternating SIM/Full Scan mode of data collection

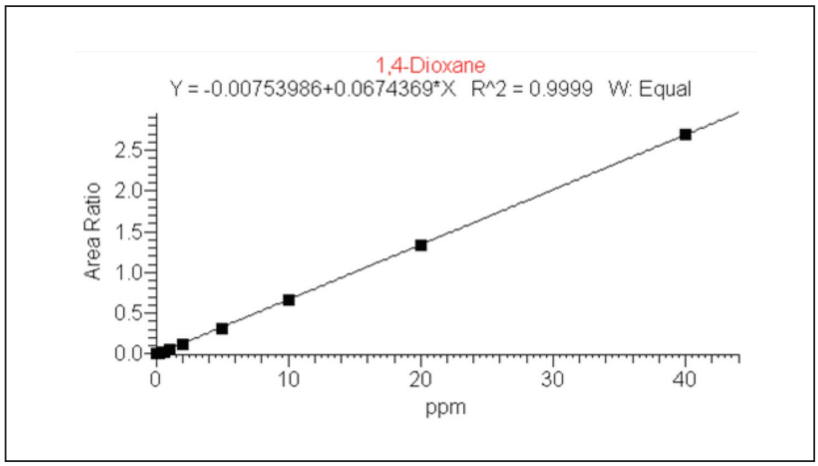

Figure 8. Sequential SIM/Full Scan calibration curve 0.05 to 40 ppb of dioxane

Specified Amount	Calculated Amount	Specified Amount	Calculated Amount
0.050	0.157	0.050	0.061
0.070	0.176	0.070	0.081
0.100	0.199	0.100	0.103
0.200	0.287	0.200	0.193
0.500	0.514	0.500	0.423
1.000	0.980	1.000	0.896
2.000	1.940	2.000	1.869
5.000	4.757	5.000	4.724
10.000	9.840	10.000	9.877
20.000	19.997	20.000	20.172
40.000	40.074	40.000	40.523

Figure 9. Equal weighting (left) vs. 1/x weighting (right) results for calibration curves. 1/x weighting provides better accuracy at lower concentrations

Comparison

Figure 10 is a comparison of the peak shape of 0.05 ppb in Full Scan, SIM and sequential SIM/Full Scan modes. No loss of precision or accuracy results from using SIM/Full Scan vs. SIM alone. However, by using the SIM/Full Scan mode additional compounds can be identified using a NIST or other library.

Reproducibility of the SIM/Full Scan mode was tested by injecting seven replicates from the same vial at concentrations of 0.07 and 2.0 ppb. The results are reported in Figure 11.

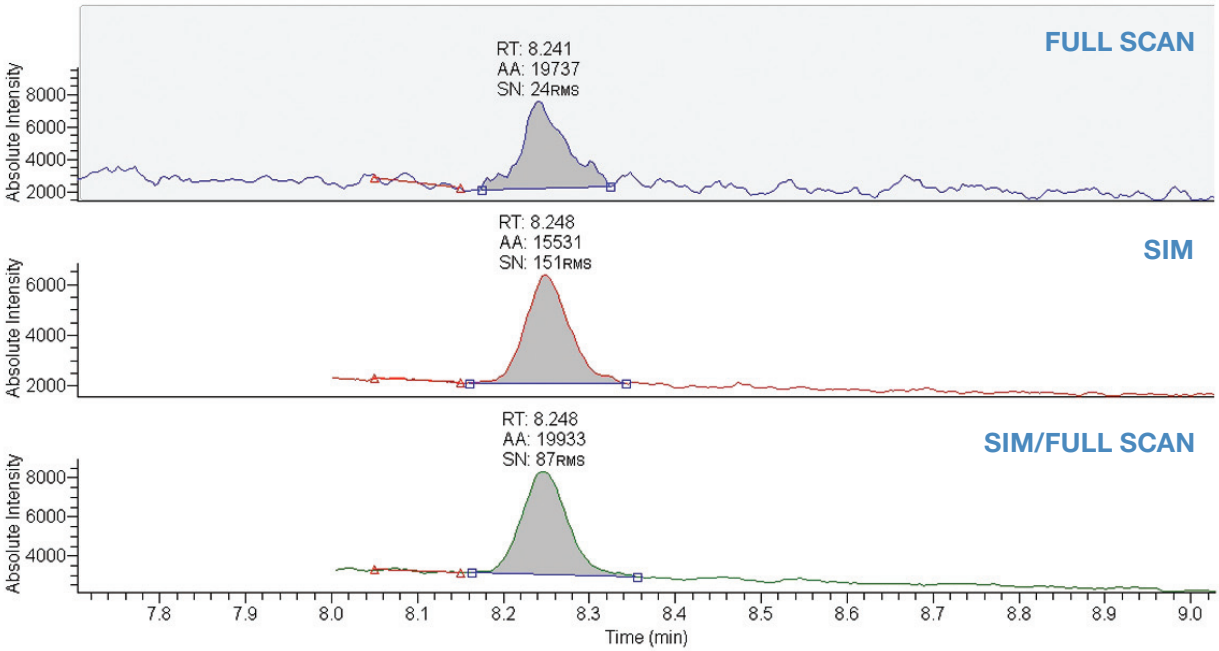

Figure 10. 0.05 ppb of 1,4-dioxane in Full Scan (S/N = 24), SIM (S/N = 151), and SIM/Full Scan (S/N = 87) modes

Sample Name	Area	ISTD Area	Area Ratio	Amount	RT
70ppt_Rep_2	28,335	14,060,852	0.002	0.069	8.236
70ppt_Rep_3	34,444	14,363,502	0.002	0.081	8.243
70ppt_Rep_4	31,241	13,625,849	0.002	0.078	8.234
70ppt_Rep_5	27,271	14,377,709	0.002	0.066	8.235
70ppt_Rep_6	31,189	14,662,503	0.002	0.073	8.234
70ppt_Rep_7	32,470	15,052,986	0.002	0.074	8.244
70ppt_Rep_8	38,823	15,153,194	0.003	0.086	8.240
Avg	*31,967*	*14,470,942*	*0.002*	*0.075*	*8.238*
StDev	*3,868*	*539,063*	*0.000*	*0.007*	*0.004*
%RSD	*12.10*	*3.73*	*10.33*	*9.13*	*0.05*

Sample Name	Area	ISTD Area	Area Ratio	Amount	RT
2ppm_Rep_2	823,612	15,064,599	0.055	1.655	8.238
2ppm_Rep_3	843,990	15,169,091	0.056	1.684	8.235
2ppm_Rep_4	857,227	15,163,169	0.057	1.711	8.231
2ppm_Rep_5	866,259	15,280,099	0.057	1.715	8.227
2ppm_Rep_6	822,302	14,467,495	0.057	1.720	8.239
2ppm_Rep_7	858,037	14,998,817	0.057	1.731	8.246
2ppm_Rep_8	839,242	14,638,036	0.057	1.735	8.236
Avg	*844,381*	*14,968,758*	*0.056*	*1.707*	*8.236*
StDev	*17,202*	*301,550*	*0.001*	*0.029*	*0.006*
%RSD	*2.04*	*2.01*	*1.68*	*1.67*	*0.07*

Figure 11. Precision in SIM/Full Scan mode at 0.07 and 2.0 ppb

Conclusion

The ISQ™ single quadrupole GC-MS system utilizing the TriPlus™ RSH autosampler and a PTV inlet (CT-Splitless mode) demonstrated its capability to analyze 1,4-dioxane according to EPA Method 522. It easily met the criteria for tuning with BFB and for calibration down to a level of 0.05 ppb. For better accuracy at the lower end of the curve, 1/x weighting was used to meet all of the criteria of the initial calibration of EPA Method 522. SIM analysis gave excellent results at low concentrations. The added advantage of the SIM/Full Scan mode is the ability to identify unknowns with a NIST or other library, while producing accurate results for 1,4-dioxane.

References

1) International Chemical Safety Card: 1,4-Dioxane. National Institute for Occupational Safety and Health. http://www.cdc.gov/niosh/ipcsneng/neng0041.html. Retrieved 15 May 2012.

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3) "1, 4-Dioxane Fact Sheet: Support Document". OPPT Chemical Fact Sheets. United States Environmental Protection Agency. February **1995**.

4) EPA/600/R-08/101, Method 522 Determination of 1,4-Dioxane in Drinking Water by Solid Phase Extraction (SPE) and Gas Chromatography/Mass Spectrometry (GC/MS) with Selected Ion Monitoring (SIM), Version 1.0, September, **2008**, Jean W. Munch and Paul E. Grimmett.

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