

## Application Note

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### Introduction

The Korean Method ES 04601.2 requires static headspace with GC/MS to monitor 1,4-dioxane. The Minimum Quantitation Limit (MQL) must be less than 1 ppb. The method requires the calibration curve to have a correlation coefficient greater than 0.98, or a relative standard deviation of the response factors less than 25%.

The Teledyne Tekmar HT3 Automated Static and Dynamic Headspace Vial Sampler was used to meet these requirements for 1,4-dioxane in drinking water, by the static headspace GC/MS method.



### Standards

- 1 ppm Internal Standard (IS) containing 1,4-dioxane-d8
- 1 ppm Stock Standard containing 1,4-dioxane

### Calibration Curve and MQL

All standards and MQL samples were prepared similarly. 5 mL of deionized water was added to each headspace vial. All vials were spiked with 100 µL of the 1 ppm IS solution. A calibration curve and seven MQL standards were prepared according to [Table I](#).

Table I Calibration Curve and MQL Standard Dilution		
Standard Level (ppb)	Stock Standard	Sample Volume
0	0 µL	5 mL
1 and MQL	5 µL	5 mL
4	20 µL	5 mL
10	50 µL	5 mL
25	125 µL	5 mL
50	250 µL	5 mL

### Instrument Conditions

Table II Static (Loop) HT3 Headspace Instrument Parameters			
Variable	Value	Variable	Value
Constant Heat Time	On	Mixing Time	3.00 min
G.C. Cycle Time	20.00 min	Mixing Level	Level 9
Valve Oven Temp	140 °C	Mixer Stabilization Time	0.5 min
Transfer Line Temp	140 °C	Pressurize	15 psig
Standby Flow Rate	50 mL/min	Pressurize Time	1.00 min
Platen/Sample Temp	85 °C	Pressurize Equil. Time	0.20 min
Platen Temp Equil Time	0.10 min	Loop Fill Pressure	12 psig
Sample Equil Time	20.00 min	Loop Fill Time	1.00 min
Mixer	Off	Inject Time	2.00 min

Table III Agilent 7890B GC with 5977A MS Parameters	
Variable	Value
Column	Agilent DB-624UI, 20m, 0.18mm ID, 1µm; Constant Flow 1.0 mL/min: Average Velocity 44.32 cm/sec
Oven Program	36 °C for 7 min; 20 °C/min to 200 °C, hold for 0 min, run time 15.25 min
Inlet	Temp 200 °C; Helium Carrier Gas; Split Ratio 20:1, Septum Purge Flow 0.5 mL/min, 1 mm IP Deact. liner
MS	Source Temp 230 °C; Quad Temp 150 °C ; Solvent Delay 6.00 min; Atune; Scan/SIM Mode; Trace Ion Detection Off
Scan/SIM Mode	Scan - 35.0 m/z to 270.0 m/z, Threshold 10, Sampling Rate 3 SIM Scan Masses - 96.00 m/z, 88.00 m/z, 200 msec dwell; 64.00 m/z, 58.00 m/z, 46.00 m/z, 43.00 m/z, 50 msec dwell

## Results

The Selected Ion Monitoring (SIM) chromatograms were evaluated using the Agilent Environmental ChemStation™ software. [Figure 1](#) is the SIM chromatogram of a 1 ppb MQL standard by the static headspace method. The SIM ions that were used for the internal standard calculations are shown in [Table IV](#). The Response factor (Rf) of 1,4-dioxane was calculated versus the 1,4-dioxane-d8 internal standard.

The seven standards were evaluated for linearity and relative standard deviation of the Rf. The concentrations of the seven 1 ppb MQL samples were calculated by both the average Rf value and the linear calibration curve. The MQL was calculated by multiplying the standard deviation of the calculated amount of the seven MQL samples times 10. The %RSD of the Rf and its calculated MQL, and the linear correlation coefficient ( $r^2$ ) and its calculated MQL is presented in [Table IV](#).

**Figure 1** Static headspace SIM quantitation ion chromatogram 88 m/z of a 1 ppb standard.

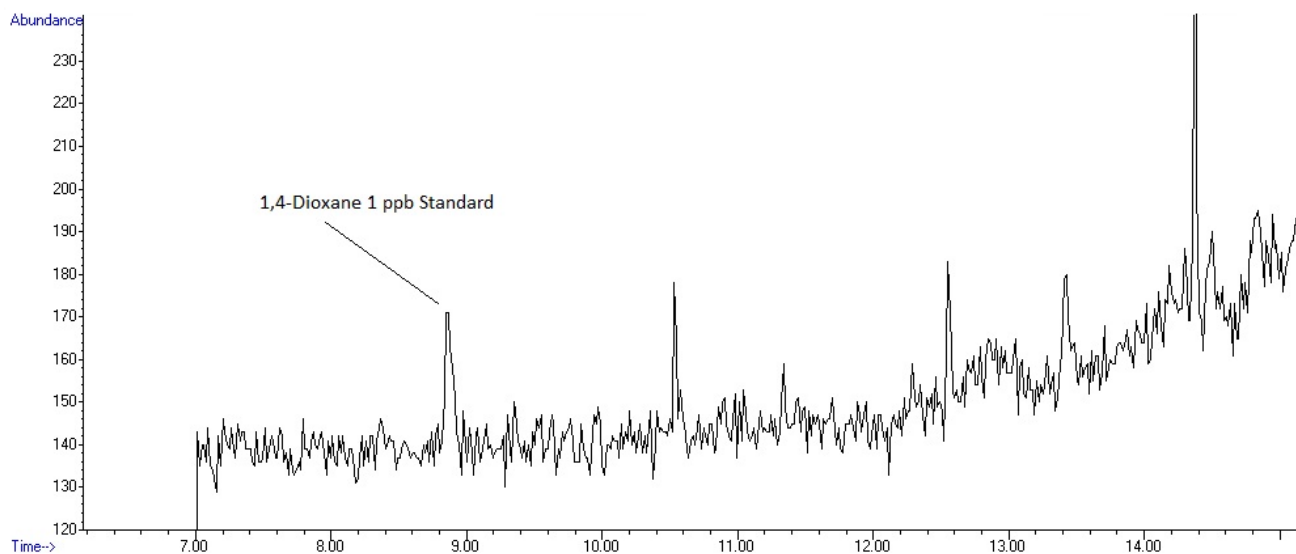


Table IV %RSD, Linearity and MQL Results with Static SIM GC/MS					
Compound	Quant Ion	Rf Calibration		Linear Calibration	
		% RSD	MQL (ppb)	r <sup>2</sup>	MQL (ppb)
1,4-Dioxane-d8 IS	96	8.3	NA	NA	NA
1,4-Dioxane	88	15.4	0.57	0.9991	0.47

## Conclusions

The HT3 static headspace method for the detection of 1,4-dioxane surpassed the method requirements for the response factor relative standard deviation, correlation coefficient and MQL as required by the Ministry of Environment.

- Korean: ES 04601.2, 1,4-다이옥산-퍼지-트랩/기체크로마토그래 피-질량분석법
- English: ES 04601.2, 1,4-Dioxane-Headspace/Gas Chromatography/Mass Spectrometry

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