Meeting the Korean Method ES 04607.1 for Naphthalene (나프탈렌) with Static and Dynamic Headspace GC/MS

Application Note

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Introduction

The Korean Standard Method for Drinking Water ES 04607.1 requires static headspace with GC/MS to monitor naphthalene. The Minimum Quantitation Limit (MQL) must be less than 3 ppb. The method requires the calibration curve to have a correlation coefficient greater than 0.98 or a Relative Standard Deviation (RSD) of the Response factors (Rf) less than 25%.

The Teledyne Tekmar HT3 Automated Static and Dynamic Headspace Vial Sampler was used to meet these requirements for naphthalene in drinking water by both the static and dynamic headspace GC/MS method.

Standards

- 2 ppm chlorobenzene-d5 Internal Standard (IS)
- 5 ppm naphthalene Stock Standard

Calibration Curve and MQL

All standards and MQL samples were prepared similarly. 10 mL of deionized water was added to each headspace vial containing 3 g of sodium chloride. All vials were spiked with 10 µL of the 2 ppm IS solution. A calibration curve and seven MQL samples were prepared according to Table I.

Table I Calibration Curve and MQL Standard Dilution

Standard Level (ppb)	Stock Standard	Sample Volume
0	0 µL	10 mL
1 and MQL	2 µL	10 mL
5	10 µL	10 mL
10	20 µL	10 mL
50	100 µL	10 mL
100	200 µL	10 mL

Instrument Conditions

Table II Static (Loop) HT3 Headspace Instrument Parameters

Variable	Value	Variable	Value
Constant Heat Time	On	Mixing Time	5.00 min
G.C. Cycle Time	20.00 min	Mixing Level	Level 5
Valve Oven Temp	120 °C	Mixer Stabilization Time	0.5 min
Transfer Line Temp	180 °C	Pressurize	11 psig
Standby Flow Rate	50 mL/min	Pressurize Time	1.00 min
Platen/Sample Temp	60 °C	Pressurize Equil Time	0.20 min
Platen Temp Equil Time	0.10 min	Loop Fill Pressure	7 psig
Sample Equil Time	10.00 min	Loop Fill Time	2.00 min
Mixer	Off	Inject Time	1.00 min

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Table III Dynamic (Trap) HT3 Headspace Instrument Parameters			
Variable	**Value**	**Variable**	**Value**
Valve Oven Temp	180 °C	Sweep Flow Rate	75 mL/min
Transfer Line Temp	180 °C	Sweep Flow Time	5.00 min
Standby Flow Rate	100 mL/min	Dry Purge Time	2.00 min
Trap Standby Temp	30 °C	Dry Purge Flow	50 mL/min
Trap Sweep Temp	0 °C	Dry Purge Temp	25 °C
Platen/Sample Temp	45 °C	Desorb Preheat	245 °C
Sample Preheat Time	0.00 min	Desorb Temp	260 °C
Preheat Mixer	On	Desorb Time	1.00 min
Preheat Mixing Level	Level 10	Trap Bake Temp	265 °C
Preheat Mixing Time	5.00 min	Trap Bake Time	5.00 min
Preheat Mixer Stabilize Time	0.50 min	Trap Bake Flow	150 ml/min
		Trap	K

Table IV Agilent 7890B GC with 5977A MS Parameters	
Variable	**Value**
Column	Agilent DB-624UI, 20 m, 0.18 mm ID, 1 µm; Constant Flow 0.9 mL/min: Average Velocity 42.02 cm/sec
Oven Program	35 °C for 3 min; 13 °C/min to 85 °C, 25 °C/min to 225 °C, hold for 1 min
Inlet	Temp 200 °C; Helium Carrier Gas; Septum Purge Flow 0.5 mL/min, 1 mm IP Deact. Liner Static Headspace Split Ratio - 30:1 Dynamic Headspace Split Ratio - 100:1
MS	Source Temp 230 °C; Quad Temp 150 °C ; Solvent Delay 7.00 min; Atune; Transfer Line 225 °C ;Scan/SIM Mode; Static Headspace - Trace Ion Detection On Dynamic Headspace - trace Ion Detection Off
Scan/SIM Mode	Scan - 35.0 m/z to 270.0 m/z, Threshold 10, Sampling Rate 3 SIM - 7.00 min, 182.00 m/z, 117.00 m/z, 200 msec dwell; 9.5 min 128.00 m/z, 200 msec dwell, 129.00 m/z, 400 msec dwell

Static (Loop) Headspace SIM Mass Spectrometry 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 IS calculation are shown in Figure 1 and Table V. The Response factor (Rf) of naphthalene was calculated versus the chlorobenzene-d5 IS.

The six standards were evaluated for linearity and RSD of the Rf. The concentrations of the seven 1 ppb MQL samples were calculated by both the 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. Table V presents the %RSD of the Rf and its calculated MQL and the linear correlation coefficient (r^2) and its calculated MQL data.

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Figure 1 Static headspace SIM quantitation ion chromatogram of a 1 ppb naphthalene standard with chlorobenzene-d5 internal standard.

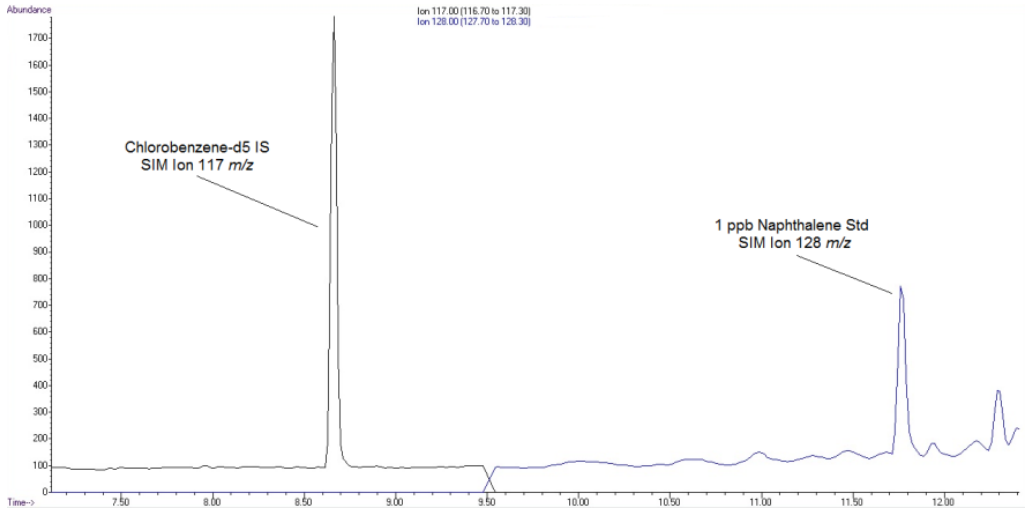

Table V %RSD, Linearity and MQL Results with Static SIM GC/MS					
Compound	Quant Ion	Rf Calculation		Linear Calculation	
		% RSD	MQL (ppb)	r^2	MQL (ppb)
Chlorobenzene-d5 IS	117	8.8	NA	NA	NA
Naphthalene	128	5.3	1.1	0.9993	1.1

Dynamic (Trap) Headspace Full Scan Mass Spectrometry Results

The Total Ion Chromatograms (TIC) were evaluated using the Agilent Environmental ChemStation™ software. Figure 2 is the TIC chromatogram of a 1 ppb MQL standard by the dynamic headspace method displaying the quantitation ion (quant ion) for each compound. The quant ion used for calculations is shown in Figure 2 and Table VI. The Response factor (Rf) of naphthalene was calculated versus chlorobenzene-d5 IS.

The six standards were evaluated for linearity and RSD 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. Table VI presents the %RSD of the Rf and its calculated MQL and the linear correlation coefficient (r^2) and its calculated MQL data.

Figure 2 Dynamic headspace TIC quantitation ion of a 1 ppb naphthalene standard with chlorobenzene-d5 internal standard.

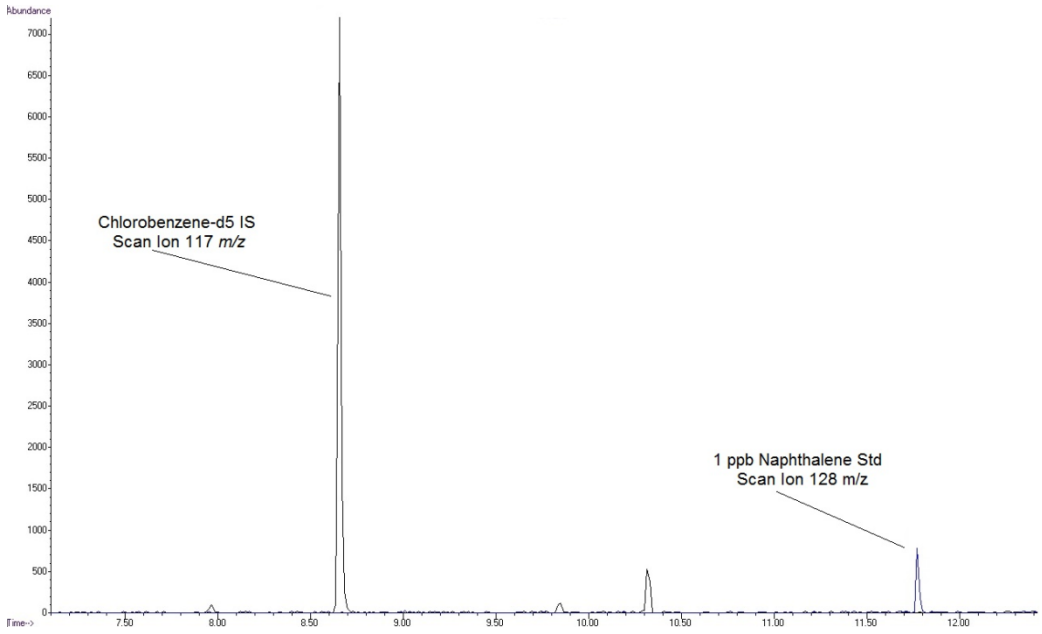

Table VI %RSD, Linearity and MQL Results with Dynamic Full Scan GC/MS					
Compound	Quant Ion	Rf Calculation		Linear Calculation	
		% RSD	MQL (ppb)	r^2	MQL (ppb)
Chlorobenzene-d5 IS	117	8.8	NA	NA	NA
Naphthalene	128	22.7	0.7	0.9884	0.6

Dynamic (Trap) Headspace SIM Mass Spectrometry Results

The Selected Ion Monitoring (SIM) chromatograms were evaluated using the Agilent Environmental ChemStation™ software. Figure 3 is the SIM chromatogram of a 1 ppb MQL standard by the dynamic headspace method displaying the quantitation ion (quant ion) for each compound. The quant ion used for calculations is shown in Figure 3 and Table VII. The Rf of naphthalene was calculated versus chlorobenzene-d5 IS.

The six 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. Table VII presents the %RSD of the Rf and its calculated MQL and the linear correlation coefficient (r^2) and its calculated MQL data.

Figure 3 Dynamic headspace SIM quantitation ion chromatogram of a 1 ppb naphthalene standard with chlorobenzene-d5 internal standard.

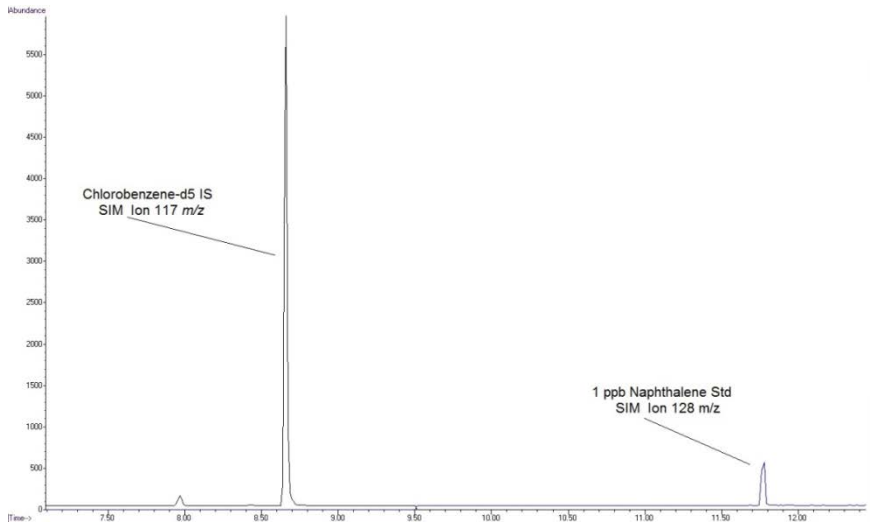

Table VII %RSD, Linearity and MQL Results with Dynamic SIM GC/MS					
Compound	Quant Ion	Rf Calculation		Linear Calculation	
		% RSD	MQL (ppb)	r^2	MQL (ppb)
Chlorobenzene-d5 IS	117	8.8	NA	NA	NA
Naphthalene	128	22.7	0.7	0.9884	0.6

Conclusions

The Teledyne Tekmar HT3 Automated Static and Dynamic Headspace Vial Sampler and the methods used for the detection of naphthalene, surpassed the method requirements for the Response factor (Rf) Relative Standard Deviation (RSD), correlation coefficient and MQL as required by the Ministry of Environment.

- Korean: ES 04607.1, 나프탈렌-헤드스페이스/기체크로마토그래피-질량분석법
- English: ES 04607.1, Naphthalene-Headspace/Gas Chromatography-Mass Spectrometry

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