Meeting the Korean Method ES 04603.2b for 12 VOC (휘발성유기화합물) with Static and Dynamic Headspace GC/MS

Application Note

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Introduction

The Korean Standard Method for Drinking Water ES 04603.2b requires static headspace with GC/MS to monitor 12 Volatile Organic Compounds (VOCs). The Minimum Quantitation Limit (MQL) must be less than 5 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 these 12 VOCs in drinking water by both the static and dynamic headspace GC/MS methods.

Standards

- 1 ppm Internal Standard (IS) containing fluorobenzene and 1,2-dichlorobenzene-d4
- 1 ppm Stock Standard containing the following 12 VOCs: 1,1-dichloroethylene; dichloromethane; chloroform; 1,1,1-trichloroethane; 1,2 dichloroethane; benzene; carbon tetrachloride; trichloroethylene; toluene; tetrachloroethylene; ethylbenzene and xylenes.

Calibration Curve and MQL

All standards and MQL samples were prepared similarly. 10 mL of deionized water was added to each headspace vial. All vials were spiked with 10 µL of the 2 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	10 mL
1 and MQL	10 µL	10 mL
2	20 µL	10 mL
5	50 µL	10 mL
10	100 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	150 °C	Mixer Stabilization Time	0.5 min
Transfer Line Temp	150 °C	Pressurize	11 psig
Standby Flow Rate	50 mL/min	Pressurize Time	1.00 min
Platen/Sample Temp	65 °C	Pressurize Equil Time	0.20 min
Platen Temp Equil Time	0.10 min	Loop Fill Pressure	7 psig
Sample Equil Time	20.00 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	150 °C	Sweep Flow Rate	150 mL/min
Transfer Line Temp	180 °C	Sweep Flow Time	6.00 min
Standby Flow Rate	100 mL/min	Dry Purge Time	4.00 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	5.00 min	Desorb Temp	260 °C
Preheat Mixer	On	Desorb Time	2.00 min
Preheat Mixing Level	Level 5	Trap Bake Temp	265 °C
Preheat Mixing Time	2.00 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, 20m, 0.18mm ID, 1µm; 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 – 80:1
MS	Source Temp 230 °C; Quad Temp 150 °C ; Solvent Delay 7.00 min; Atune; Transfer Line 225 °C ;Scan/SIM Mode; Trace Ion Detection On
Scan/SIM Mode	Scan - 35.0 m/z to 270.0 m/z, Threshold 10, Sampling Rate 3 SIM: Group 1- 1.05 min; 61.00 m/z, 96.00 m/z, 98.00 m/z, 200 msec dwell – 1,1-Dichloroethylene Group 2 – 2.78 min; 49.00 m/z, 84.00 m/z, 86.00 m/z 200 msec dwell - Dichloromethane Group 3 – 4.16 min; 47.00 m/z, 49.00 m/z, 61.00 m/z, 62.00 m/z, 77.00 m/z, 78.00 m/z, 83.00 m/z, 85.00 m/z, 97.00 m/z, 98.00 m/z, 99.00m/z, 117.00 m/z, 119.00 m/z,121.00 m/z, 90 msec dwell – Chloroform, Carbon Tetrachloride, 1,1,1-Trichloroethane, Benzene, 1,2-Dichloroethane Group 4 – 5.68 min; 70.00 m/z, 96.00 m/z, 200 msec dwell - Fluorobenzene Group 5 – 6.04 min; 95.00 m/z, 130.00 m/z, 132.00 m/z, 200 msec dwell - Trichloroethylene Group 6 – 7.00 min; 91.00 m/z, 92.00 m/z, 200 msec dwell - Toluene Group 7 – 7.75 min;129.00 m/z, 166.00 msec, 168.00 m/z, 200 msec dwell - Tetrachloroethylene Group 8 – 8.50 min; 77.00 m/z, 91.00 m/z, 106.00 m/z, 200 msec dwell – Ethylbenzene, Xylenes Group 9 – 9.70 min; 115.00 m/z, 150.00 m/z, 152.00 m/z, 200 msec dwell – 1,2-Dichlorobenzene-d4

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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 ion that was used for calculation is shown in Figure 1 and Table V. The Rf of the various VOCs were calculated versus both the fluorobenzene and 1,2-dichlorobenzene-d4 Internal Standard (IS).

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

Figure 1 Static headspace SIM quantitation ion chromatogram of a 1 ppb VOC Standard with Fluorobenzene and 1,2-Dichlorobenzene-d5 Internal Standards.

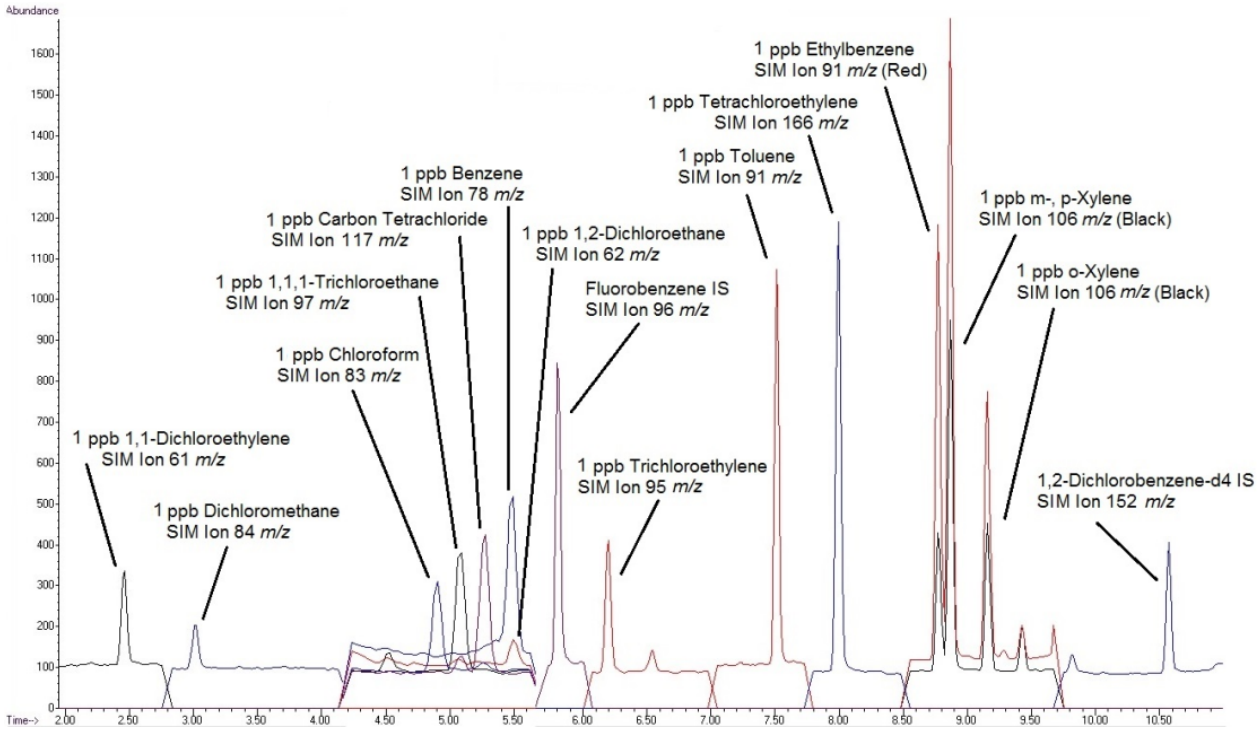

Table V %RSD, Linearity and MQL Results with Static SIM GC/MS					
Compound	Quant Ion	Rf Calculation		Linear Calculation	
		% RSD	MQL (ppb)	r^2	MQL (ppb)
Fluorobenzene IS	96	Calculated with Fluorobenzene values			
1,1-Dichloroethylene	61	19.29	0.7	0.9987	0.7
Dichloromethane	84	6.56	1.0	0.9991	1.2
Chloroform	83	13.19	1.3	0.9796	1.4
Carbon Tetrachloride	117	12.82	1.1	0.9976	1.0
1,1,1-Trichloroethane	97	14.88	1.0	0.9880	1.1
Benzene	78	16.2	0.8	0.9883	0.8
1,2-Dichloroethane	62	13.77	1.0	0.9845	1.2
Trichloroethylene	95	14.08	0.8	0.9989	0.9
Toluene	91	12.29	0.6	0.9950	0.6
Tetrachloroethylene	166	15.55	0.9	0.9992	0.8
Ethylbenzene	91	11.53	0.9	0.9953	0.7
m-, p-Xylene	106	12.15	1.4	0.9964	1.1
o-Xylene	106	9.73	0.7	0.9957	0.6
Total Xylenes (Sum)			2.1		1.7
1,2-Dichlorobenzene-d5 IS	152	Calculated with 1,2-Dichlorobenzene-d5 values			
1,1-Dichloroethylene	61	17.28	0.6	0.9949	0.6
Dichloromethane	84	3.92	0.6	0.9982	0.6
Chloroform	83	10.81	1.3	0.9919	1.3
Carbon Tetrachloride	117	9.96	1.0	0.9994	1.0
1,1,1-Trichloroethane	97	9.66	1.0	0.9973	1.0
Benzene	78	14.08	0.9	0.9948	0.5
1,2-Dichloroethane	62	13.05	0.9	0.9914	0.9
Trichloroethylene	95	13.71	0.9	0.9978	0.9
Toluene	91	9.93	0.7	0.9995	0.6
Tetrachloroethylene	166	15.33	1.2	0.9973	1.1
Ethylbenzene	91	13.82	0.8	0.9988	0.7
m-, p-Xylene	106	8.19	1.2	0.9994	1.2
o-Xylene	106	7.22	0.5	0.9991	0.6
Total Xylenes (Sum)			1.7		1.8

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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 the various VOCs were calculated versus both the fluorobenzene and 1,2-dichlorobenzene-d4 IS.

The five 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 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 VOC Standard with Fluorobenzene and 1,2-Dichlorobenzene-d5 Internal Standards.

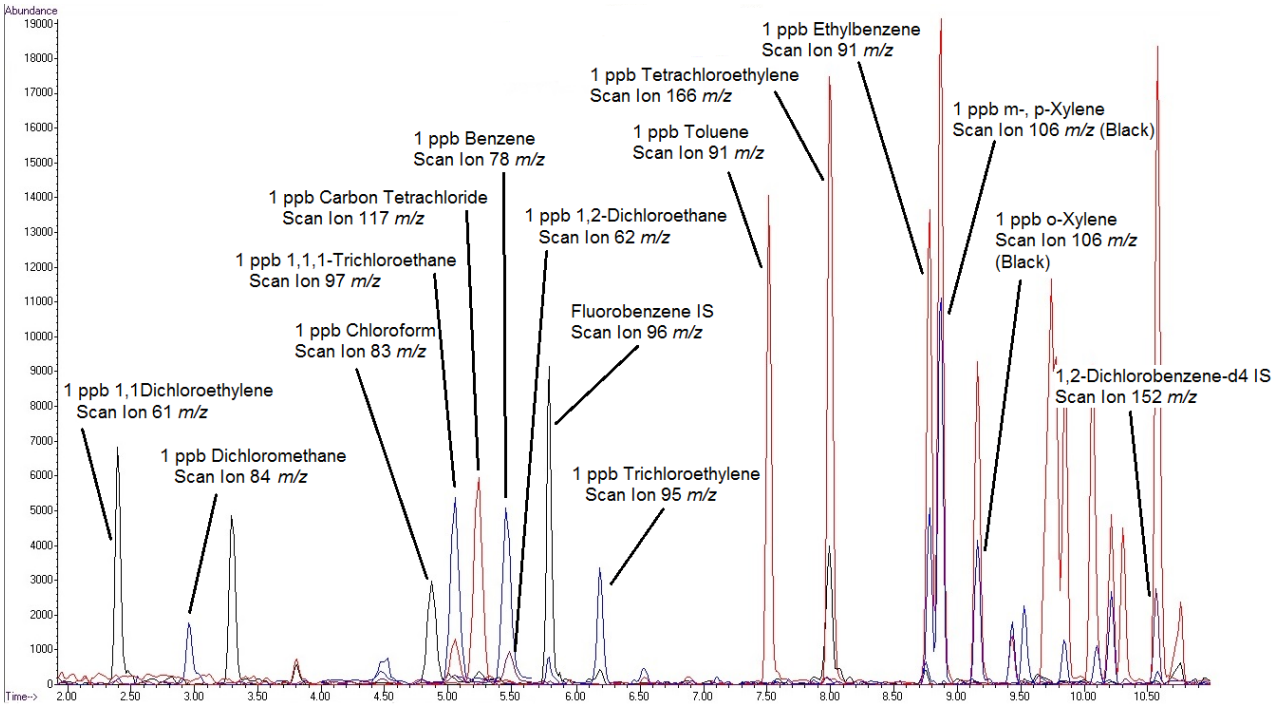

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Table VI %RSD, Linearity and MQL Results with Dynamic Full Scan GC/MS					
Compound	Quant Ion	Rf Calculation		Linear Calculation	
		% RSD	MQL (ppb)	r^2	MQL (ppb)
Fluorobenzene IS	96	Calculated with Fluorobenzene values			
1,1-Dichloroethylene	61	11.2	1.6	0.9971	1.4
Dichloromethane	84	2.6	1.3	0.9995	1.3
Chloroform	83	18.2	1.7	0.9984	1.5
Carbon Tetrachloride	117	16.3	1.4	0.9986	1.2
1,1,1-Trichloroethane	97	14.8	1.3	0.9988	1.1
Benzene	78	24.6	1.7	0.9957	1.4
1,2-Dichloroethane	62	15.3	1.8	0.9982	1.6
Trichloroethylene	95	14.9	1.5	0.9947	1..2
Toluene	91	12.7	1.3	0.9982	1.2
Tetrachloroethylene	166	10.5	1.5	0.9990	1.5
Ethylbenzene	91	14.0	1.6	0.9960	1.4
m-, p-Xylene	106	18.9	2.9	0.9939	2.3
o-Xylene	106	13.9	1.4	0.9983	1.2
Total Xylenes (Sum)			4.3		3.5
1,2-Dichlorobenzene-d5 IS	152	Calculated with 1,2-Dichlorobenzene-d5 values			
1,1-Dichloroethylene	61	9.5	1.4	0.9903	1.4
Dichloromethane	84	20.3	1.7	0.9924	1.9
Chloroform	83	3.2	1.2	0.9996	1.2
Carbon Tetrachloride	117	4.4	1.3	0.9985	1.3
1,1,1-Trichloroethane	97	4.8	1.0	0.9961	1..0
Benzene	78	13.0	1.5	0.99972	1.3
1,2-Dichloroethane	62	6.8	1.8	0.9936	1.7
Trichloroethylene	95	11.3	1.0	0.9885	0.9
Toluene	91	8.0	1.1	0.9924	1.0
Tetrachloroethylene	166	13.1	1.4	0.9951	1.6
Ethylbenzene	91	8.9	1.1	0.9885	1.0
m-, p-Xylene	106	9.4	2.3	0.9877	2.1
o-Xylene	106	8.9	0.6	0.9966	0.6
Total Xylenes (Sum)			2.9		2.7

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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 the various VOCs were calculated versus both the fluorobenzene and 1,2-dichlorobenzene-d4 IS.

The five 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 VOC Standard with Fluorobenzene and 1,2-Dichlorobenzene-d5 Internal Standards.

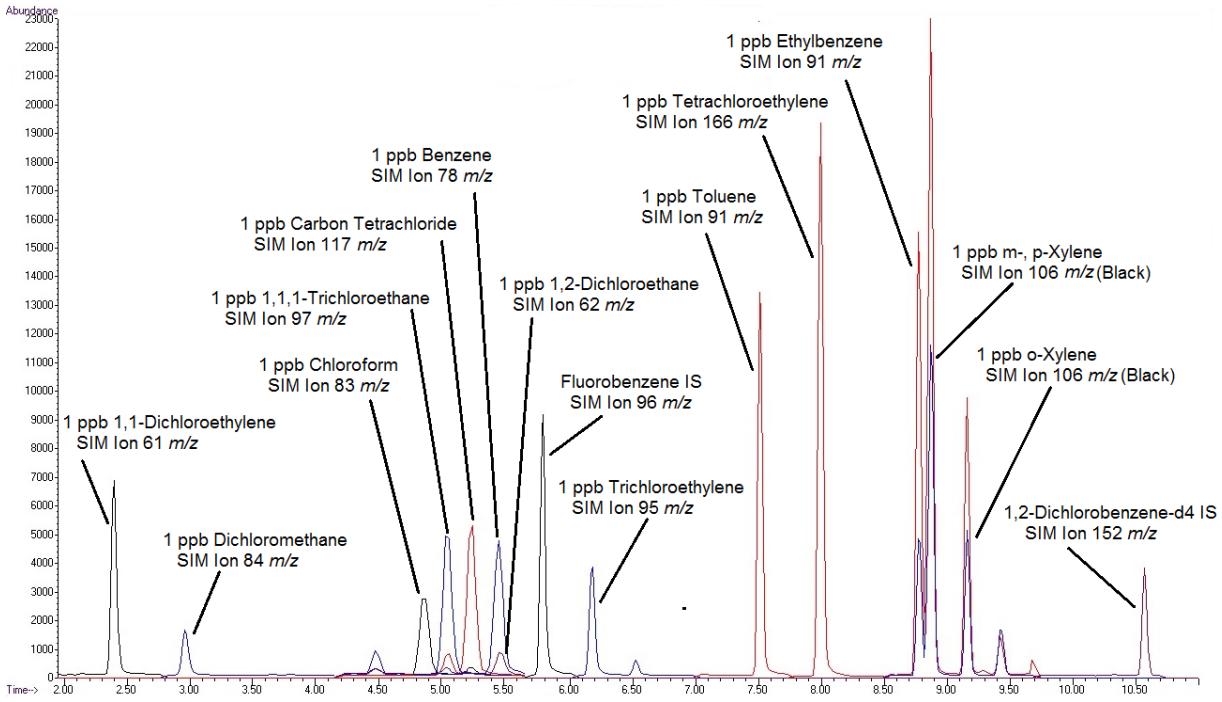

Table VII %RSD, Linearity and MQL Results with Dynamic SIM GC/MS					
Compound	Quant Ion	Rf Calculation		Linear Calculation	
		% RSD	MQL (ppb)	r^2	MQL (ppb)
Fluorobenzene IS	96	Calculated with Fluorobenzene values			
1,1-Dichloroethylene	61	13.9	1.3	0.9954	1.1
Dichloromethane	84	7.8	0.9	0.9973	0.8
Chloroform	83	9.0	1.0	0.9962	0.9
Carbon Tetrachloride	117	8.0	1.0	0.9927	0.8
1,1,1-Trichloroethane	97	15.4	1.0	0.9937	0.8
Benzene	78	17.9	1.0	0.9979	0.8
1,2-Dichloroethane	62	12.2	0.69	0.9977	0.7
Trichloroethylene	95	19.0	1.2	0.9963	0.9
Toluene	91	11.8	1.1	0.9962	0.9
Tetrachloroethylene	166	10.1	1.4	0.9970	1.3
Ethylbenzene	91	14.3	1.1	0.9955	0.9
m-, p-Xylene	106	18.5	2.1	0.9923	1.6
o-Xylene	106	17.4	1.0	0.9932	0.8
Total Xylenes (Sum)			3.1		2.4
1,2-Dichlorobenzene-d5 IS	152	Calculated with 1,2-Dichlorobenzene-d5 values			
1,1-Dichloroethylene	61	8.3	1.2	0.9997	1.1
Dichloromethane	84	3.0	0.8	0.9999	0.8
Chloroform	83	4.0	1.0	0.9996	0.9
Carbon Tetrachloride	117	02.9	0.9	0.9979	0.8
1,1,1-Trichloroethane	97	10.4	0.9	0.9985	0.8
Benzene	78	11.2	0.9	0.9998	0.8
1,2-Dichloroethane	62	4.9	0.7	0.9998	0.7
Trichloroethylene	95	14.1	1.3	0.9996	1.1
Toluene	91	7.5	0.9	0.9994	0.9
Tetrachloroethylene	166	8.5	1.2	0.9987	1.2
Ethylbenzene	91	9.9	1.0	0.9993	0.9
m-, p-Xylene	106	14.0	1.8	0.9969	1.5
o-Xylene	106	12.4	0.9	0.9981	0.8
Total Xylenes (Sum)			2.7		2.3

Conclusions

The HT3 static and dynamic headspace methods for the detection of 12 volatile organic compounds surpassed the method requirements for the response factor relative standard deviation, correlation coefficient and MQL as required by the Ministry of Environment.

- Korean: ES 04603.2b, 휘발성유기화합물-헤드스페이스/기체크로마토그래피-질량분석법
- English: ES 04603.2b, Volatile Organic Compounds/Gas Chromatography/Mass Spectrometry

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