Meeting the Korean Method ES 04602.1b for Vinyl Chloride, Acrylonitrile, and Bromoform (염화비닐, 아크릴로니트릴, 브로모포름) with Static and Dynamic Headspace GC/MS

Application Note

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Introduction

The Korean Method ES 04602.1b requires either static or dynamic headspace with GC/MS to monitor vinyl chloride, acrylonitrile, and bromoform. 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 vinyl chloride, acrylonitrile and bromoform in drinking water by the static and dynamic headspace GC/MS method.

Standards

- 2 ppm Internal Standard (IS) containing Fluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4
- 5 ppm Stock Standard containing acrylonitrile, vinyl chloride and bromoform

Calibration Curve and MQL

All standards and MQL samples were prepared similarly. Each headspace vial contained 3 g of sodium chloride, 10 mL of deionized water and 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 Standards and MQL Standard Dilution

Standard Level (ppb)	Stock Standard	Sample Volume
0	0 µL	10 mL
5 and MQL	10 µL	10 mL
10	20 µL	10 mL
25	50 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	60 °C	Pressurize Equil Time	0.20 min
Platen Temp Equil Time	0.10 min	Loop Fill Pressure	7 psig
Sample Equil Time	30.00 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 0 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; Trace Ion Detection Static - On Dynamic - Off; Gain Factor: Static - 10 Dynamic - 5
Scan/SIM Mode	Scan - 35.0 m/z to 270.0 m/z, Threshold 10, Sampling Rate 3 SIM Group 1 - 0.75 min; 62.00 m/z, 64.00 m/z, 200 msec dwell - Vinyl Chloride Group 2 - 2.20 min; 51.00 m/z, 52.00 m/z, 53.00 m/z, 200 msec dwell - Acrylonitrile Group 3 - 4.50 min; 62.00 m/z, 64.00 m/z, 200 msec dwell - Fluorobenzene Group 4 - 7.50 min; 117.00 m/z, 171.00 m/z, 173.00 m/z, 175.00 m/z ,200 msec dwell – Chlorobenzene-d5, Bromoform Group 5 - 9.90min; 115.00 m/z, 150.00 m/z, 152.00 m/z, 200 msec dwell - 1,4-Dichlorobenzene-d4

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 5 ppb MQL sample by the static headspace method. The SIM ions that were used for the Internal Standard calculation are shown in Figure 1 and Table V. The Response factor (Rf) of vinyl chloride and chlorobenzene were calculated versus both the fluorobenzene and the chlorobenzene-d5 Internal Standards. The Rf of bromoform was calculated versus the 1,4-dichlorobenzene-d4 internal standard.

The four standards were evaluated for linearity and RSD of the Rf. The concentrations of the seven 5 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 data are presented in Table V.

Figure 1 Static headspace SIM quantitation ion chromatogram of a 5 ppb vinyl chloride, chlorobenzene and bromoform standard with fluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4 Internal Standard.

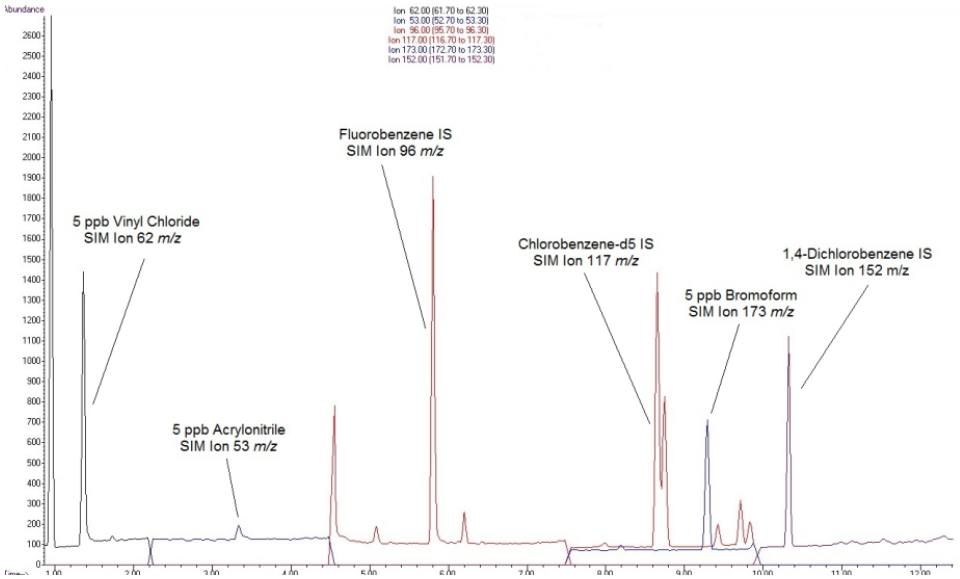

Table V %RSD, Linearity and MQL Results with Static SIM GC/MS

Compound	Quant Ion	Rf Calibration		Linear Calibration	
		%RSD	MQL (ppb)	r^2	MQL (ppb)
Fluorobenzene IS	96	11.8	NA	NA	NA
Vinyl Chloride	62	2.4	2.1	0.9998	2.2
Acrylonitrile	53	2.1	4.9	0.9999	5.0
Chlorobenzene-d5 IS	117	11.8	NA	NA	NA
Vinyl Chloride	62	11.7	2.0	0.9917	1.8
Acrylonitrile	53	9.1	3.5	0.9948	3.2
1,4-Dichlorobenzene-d4 IS	152	9.1	NA	NA	NA
Bromoform	173	4.4	1.2	0.9988	1.3

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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 of a 5 ppb MQL sample by the dynamic headspace method displaying the quantitation ion (quant ion) for each compound. The quant ions used for calculations are shown in Figure 2 and Table VI. The Response factor (Rf) of vinyl chloride and acrylonitrile were calculated versus both the fluorobenzene and the chlorobenzene-d5 internal standards. The Rf of bromoform was calculated versus the 1,4-dichlorobenzene-d4 internal standard.

The four standards were evaluated for linearity and RSD of the Rf. The concentrations of the seven 5 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 data are presented in Table VI.

Figure 2 Dynamic headspace TIC quantitation ion of a 5 ppb vinyl chloride, acrylonitrile and bromoform standard with fluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4 Internal Standard.

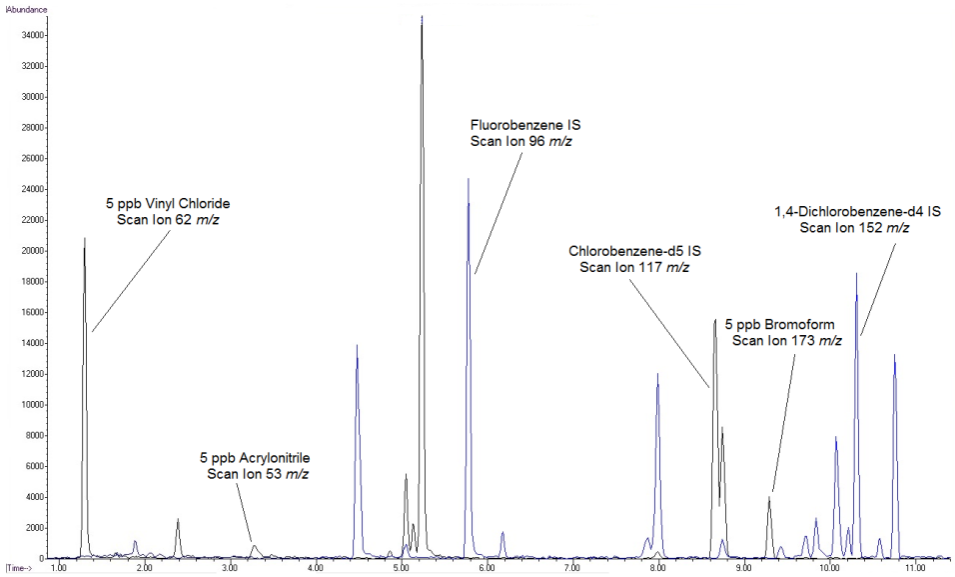

Table VI %RSD, Linearity and MQL Results with Dynamic Full Scan GC/MS

Compound	Quant Ion	Rf Calibration		Linear Calibration	
		%RSD	MQL (ppb)	r^2	MQL (ppb)
Fluorobenzene IS	96	8.7	NA	NA	NA
Vinyl Chloride	62	0.5	1.8	1.0000	2.0
Acrylonitrile	53	16.0	5.7	0.9992	5.2
Chlorobenzene-d5 IS	117	5.8	NA	NA	NA
Vinyl Chloride	62	3.8	2.4	0.9997	2.5
Acrylonitrile	53	14.9	3.5	0.9998	4.9
1,4-Dichlorobenzene-d4 IS	152	7.7	NA	NA	NA
Bromoform	173	2.8	3.2	0.9993	3.3

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 5 ppb MQL sample by the dynamic headspace method. The SIM ions that were used for the internal standard calculation are shown in Figure 3 and Table VII. The Response factor (Rf) of vinyl chloride and acrylonitrile were calculated versus both the fluorobenzene and the chlorobenzene-d5 internal standards. The Rf of bromoform was calculated versus the 1,4-dichlorobenzene-d4 internal standard.

The four standards were evaluated for linearity and RSD of the Rf. The concentrations of the seven 5 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 data are presented in Table VII.

Figure 3 Dynamic headspace SIM quantitation ion chromatogram of a 5 ppb vinyl chloride, acrylonitrile and bromoform standard with fluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4 Internal Standard.

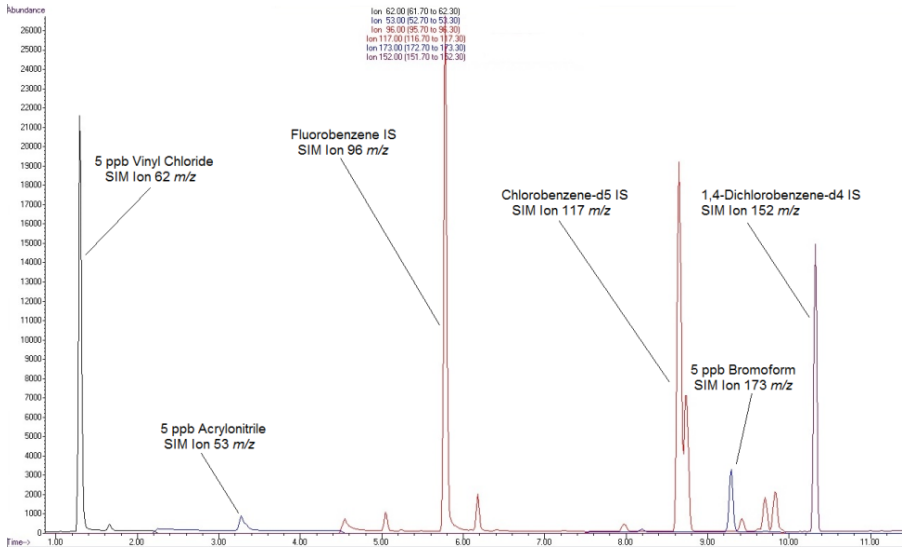

Table VII %RSD, Linearity and MQL Results with Dynamic SIM GC/MS

Compound	Quant Ion	Rf Calibration		Linear Calibration	
		%RSD	MQL (ppb)	r^2	MQL (ppb)
Fluorobenzene IS	96	6.2	NA	NA	NA
Vinyl Chloride	62	3.6	2.1	0.9996	1.8
Acrylonitrile	53	4.7	1.7	0.9998	1.7
Chlorobenzene-d5 IS	117	2.4	NA	NA	NA
Vinyl Chloride	62	2.2	1.7	0.9999	1.6
Acrylonitrile	53	2.3	1.3	0.9997	1.3
1,4-Dichlorobenzene-d4 IS	152	4.1	NA	NA	NA
Bromoform	173	6.5	1.8	0.9992	2.0

Conclusion

The HT3 static and dynamic headspace method for the detection of vinyl chloride, acrylonitrile and bromoform surpassed the method requirements for the response factor Relative Standard Deviation, correlation coefficient and MQL as required by the Ministry of Environment. Acrylonitrile detection is greatly improved when determining the concentration using SIM GC/MS analysis with the dynamic capability of the HT3.

References

- Korean: ES 04602.1b, 염화비닐, 아크릴로니트릴, 브로모포름-드스페이스/기체크로마토그래피-질량분석법
- English: ES 04602.1b, Vinyl Chloride, Acrylonitrile, Bromoform-Headspace/Gas Chromatography/Mass Spectrometry

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