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Using the Teledyne Tekmar HT3™ Headspace Analyzer to Meet the Requirements of the New Korean Standard Method for Water Pollution, ES04602.1, for Bromoform, Vinyl Chloride and Acrylonitrile

Application Note

Abstract

The Ministry of Environment of the Republic of Korea recently updated the Korean Standard Method for Water Pollution to include seven new harmful substances to the list of compounds subject of wastewater discharge standards from 35 to 42. One of the methods specified in this update for three of the seven new compounds, bromoform, vinyl chloride and acrylonitrile is ES04602.1 utilizing either static or dynamic headspace with GC/MS.

The Teledyne Tekmar HT3™ Headspace Analyzer was used to perform the method for the quantitation of bromoform, vinyl chloride and acrylonitrile in wastewater by both the static and dynamic headspace method.

The method requires the correlation coefficient to be greater than 0.98 for the 3 point calibration curve and the MDL be less than 5 ppb. The Teledyne Tekmar HT3 surpassed these requirements of the Korean Standard Method.

Introduction

In October of 2010, the Ministry of Environment of the Republic of Korea added seven harmful substances to their list of 35 compounds that are required to be monitored in wastewater discharge by 2012. The Korea Standard Method for Water Pollution, Method ES04902.1[1] is specific for the detection and quantitation of three of these compounds: bromoform, vinyl chloride and acrylonitrile, by headspace/gas chromatography/mass spectrometry in wastewater.

The method requires a calibration curve from 5ppb to 50ppb for the three compounds. These calibration curves must have a correlation coefficient (r squared) greater than 0.98. The minimum detection limit (MDL) must be less than 5 ppb for bromoform, vinyl chloride and acrylonitrile.

A Teledyne Tekmar HT3 Headspace Analyzer was used in the both the static and the dynamic mode along with an Agilent Technologies 7890 GC with 5975 inert XL MSD with triple-Axis detector for the detection and quantification of the target compounds. A Teledyne Tekmar proprietary #9 trap was used for the dynamic portion of the headspace assay. The instrument conditions are listed in Table 1 for the HT3 and Table 2 for the GC/MS. Bromoform, vinyl chloride and acrylonitrile standards were prepared from two Restek environmental standards that contain more than 75 compounds related to environmental compound of concern in water.

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Experimental-Instrument Conditions

Teledyne Tekmar HT3 Headspace Analyzer Parameters			
Static		Dynamic	
Variable	Value	Variable	Value
Valve Oven Temp	150°C	Valve Oven Temp	150°C
Transfer Line Temp	150°C	Transfer Line Temp	150°C
Platen/Sample Temp	60°C	Platen/Sample Temp	60°C
Standby Flow Rate	150mL/min	Trap Standby Temp	30°C
Sample Equil Time	30.00 min	Trap Sweep Temp	0°C
Mixing Time	5.00 min	Sample Preheat Time	0.10 min
Mixing Level	Level 9	Preheat Mixer	On
Mixer Stabilization Time	0.5 min	Preheat Mixing Level	Level 5
Pressurize	15 psig	Preheat Mixing Time	5.00 min
Pressurize Time	2.00 min	Preheat Mixer Stabilize Time	3.00 min
Pressurize Equil Time	0.20 min	Sweep Flow Rate	100mL/min
Loop Volume	1 mL	Sweep Flow Time	5.00 min
Loop Fill Pressure	10 psig	Dry Purge Time	3.00 min
Loop Fill Time	2.00 min	Dry Purge Flow	100mL/min
Inject Time	2.00 min	Dry Purge Temp	25°C
		Desorb Preheat	245°C
		Desorb Temp	250°C
		Desorb Time	2.00 min
		Trap Bake Temp	280°C
		Trap Bake Time	6.00 min
		Trap Bake Flow	200mL/min
		Trap Material	#9

Table 1: Static and Dynamic HT3™ Parameters

Agilent 7890 GC with 5975C XL MSD with Triple-Axis Detector Parameters	
Column	Restek Rtx® VMS, 20m, 0.18mm ID, 1µm; Constant Flow 0.8mL/min: Average Velocity 39.631 cm/sec
Oven Program	35°C for 1 min; 10°C/min to 230°C, hold for 5 min, run time 25.5 min
Inlet:	Temperature 200°C; Helium Carrier Gas; Split Ratio - Dynamic 60:1, - Static 10:1
MS	Source and Transfer Line Temp 230°C; Quad Temp 150°C ; Solvent Delay 0.50 min; Atune; Full Scan 35.0 *m/z* to 270.0 *m/z;* Threshold 25; Sample # 3; Trace Ion Detection ON

Table 2: Agilent GC/MS with iTAD Parameters

Standard Preparation

The method uses a 2ppm (mg/L) internal standard (IS) solution of fluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4. Vinyl chloride and acrylonitrile can use either fluorobenzene or chlorobenzene-d5 as the IS for quantitation. Bromoform uses 1,4-dichlorobenzene-d4 as the IS for quantitation.

The IS solution was prepared by adding 8µL of a 2,500 g/mL standard containing chlorobenzene-d5 and 1,4-dichlorobenzene-d4 and 10µL of a 2,000g/mL standard containing fluorobenzene into a total volume of 10mL of purge and trap methanol.

The method uses a 5ppm (mg/L) stock standard (SS) of bromoform, vinyl chloride and acrylonitrile to prepare a calibration curve of 5ppb, 10ppb and 50ppb of each compound. The stock calibration standard was prepared by adding 25µL of two 2,000g/mL Restek standards, Catalog # 30601[2] and # 30042[3], into a total volume of 10mL of purge and trap methanol.

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Sample Preparation

The method procedure utilizes sodium chloride to assist volatile compounds into the headspace. Certified ACS crystalline sodium chloride from Fisher Scientific was used. All standards and minimum detection limit (MDL) samples were prepared similarly. 3.0g of sodium chloride was weighed into 22mL headspace vials. 10.0mL of deionized water was added to each vial. All vials were spiked with 10µL of the 2 ppm IS solution.

The calibration curve was prepared by adding 10µL (5ppb Final), 20µL (10ppb Final) and 100µL (50ppb Final) of the SS to separate vials. The MDL was prepared by adding 10µL (5ppb Final) of the SS into 7 separate vials. All vials including blank samples were capped with Teflon lined silicon septa and aluminum crimp seals. Once sealed the vials were shaken to dissolve the sodium chloride.

All of the samples and standard were tested with Teledyne Tekmar HT3 with both dynamic and static headspace methods and the Agilent GC/MS. The test parameters for the HT3 are listed in Table 1 and for the Agilent GC/MS are listed in Table 2.

Results

The total ion current (TIC) chromatograms from both the dynamic and static headspace methods were evaluated using the Agilent Environmental ChemStation software. Figure 1 is the TIC of a 5 ppb MDL standard by the static headspace method. Figure 2 is the TIC of a 5ppb MDL standard with the dynamic headspace method.

The peak areas of the primary ions were determined for each of the compounds. The response factor of vinyl chloride, acrylonitrile and bromoform were calculated for each internal standard as allowed by the method. All three standards for each compound were evaluated for linearity.

MDLs were established for the compounds by analyzing seven replicates at a concentration of 5ppb. The MDL of the seven replicate samples were calculated by multiplying the relative standard deviation of the calculated amount times 3.14. The linear correlation coefficient (r squared) and the calculated MDL data for each compound and its corresponding internal standard are presented in Table 3.

		Loop Linear		Trap Linear	
VOCs	Primary Ion	r^2	MDL	r^2	MDL
Fluorobenzene IS	96				
Vinyl Chloride	62	0.9998	1.03	0.9986	1.73
Acrylonitrile	53	0.9998	2.26	0.9999	1.61
Chlorobenzene-d5 IS	117				
Vinyl Chloride	62	1.0000	1.30	0.9996	0.77
Acrylonitrile	53	0.9966	4.42	0.9978	1.23
1,4-Dichlorobenzene-d4 IS	152				
Bromoform	173	1.0000	1.50	0.9976	1.50

Table 3: Linear Correlation Coefficient (r squared) and MDL Data for Vinyl Chloride, Acrylonitrile and Bromoform with the Corresponding Internal Standard used for Calculation.

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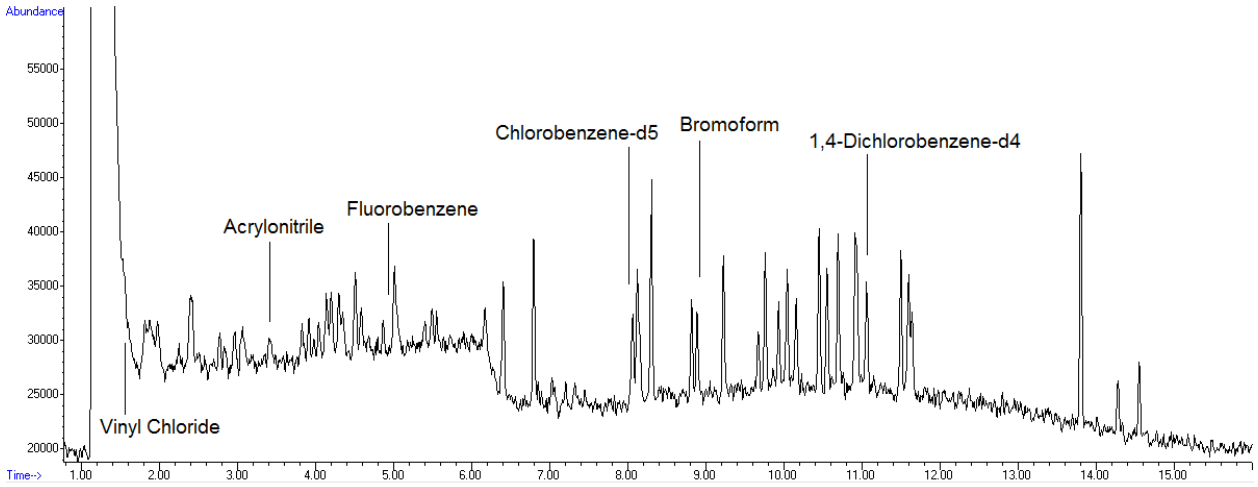

Figure 1: Total Ion Chromatogram of a 5ppb Standard with the Static HT3 Headspace Parameters. The compound retention times are located on the chromatogram.

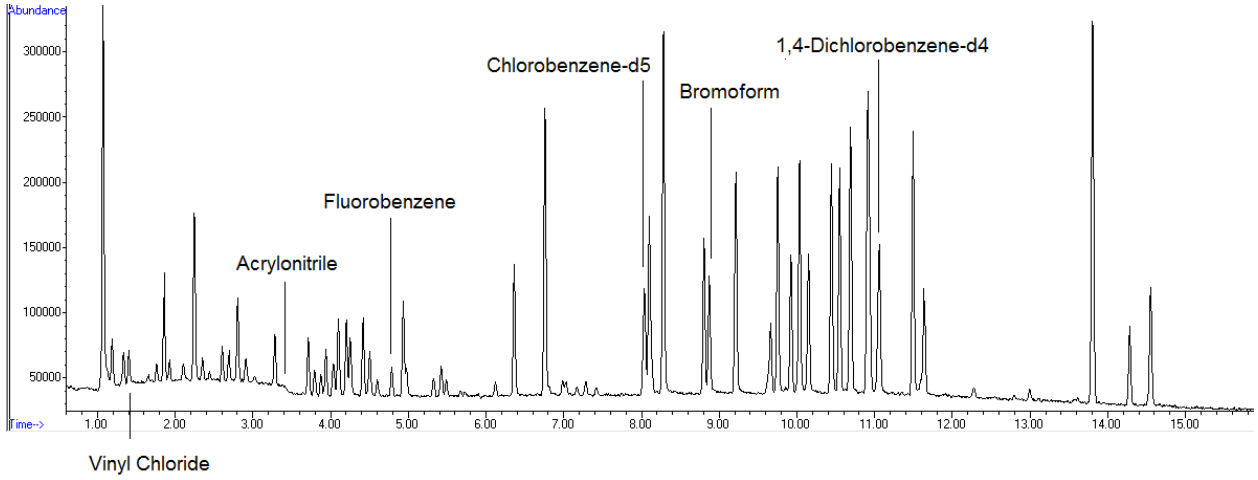

Figure 2: Total Ion Chromatogram of a 5ppb Standard with the Dynamic HT3 Headspace Parameters. The compound retention times are located on the chromatogram.

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Conclusions

The Ministry of the Environment of the Republic of Korea recently added vinyl chloride, acrylonitrile and bromoform to the list of compounds in wastewater that must be monitored by 2012. The allowable method is headspace GC/MS in either the static or dynamic method. The method requires that the linear correlation (r squared) of a 3 point curve consisting of a 5ppb, 10 ppb and 50ppb standard must be greater than 0.98. The minimum detectable limit (MDL) of the three compounds must also be less than 5ppb.

The Teledyne Tekmar HT3 innovative headspace instrument following the method parameters was used to determine its suitability for this method. The HT3 surpassed the method requirements for the correlation coefficient and the MDL as required by the Ministry of Environment.

References

1: **Korean:** 환경부, 대한민국, 수질오염공정시험기준, ES04602.1, 염화비닐, 아크릴로니트릴, 브로모포름-헤드스페이스/기체크로마토그래피/질량분석법, 2010

English: Ministry of Environmental, Republic of Korea, The Korean Standard Method for Water Pollution, ES04602.1, Bromoform, Vinyl Chloride, Acrylonitrile-Headspace/Gas Chromatography/Mass Spectrometry, 2010

Special thanks to Young-Min, Kim of Young-In Scientific Co Ltd of Seoul Korea for translation of the method and the method requirements.

2: Drinking Water VOA MegaMix®, 524.2 Rev 4.1, Catalog # 30601, www.restek.com for the most current listing of Restek distributors.

3: 502.2 Calibration Mix #1 (gases), Catalog # 30042, www.restek.com for the most current listing of Restek distributors.

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