# Using the Teledyne Tekmar HT3™ Headspace Analyzer to Meet the Requirements of the Korean Standard Method for Drinking Water, ES05602.3, for 1,4-Dioxane

**Application Note**


## Abstract

The Ministry of Environment of the Republic of Korea recently updated the Korean Standard Method for Drinking Water 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 drinking water is ES05602.3 utilizing static headspace with GC/MS to monitor 1,4-dioxane, one of the seven new compounds.

The Teledyne Tekmar HT3™ Headspace Analyzer was used to perform the method for the quantitation of 1,4-dioxane in drinking water by the static headspace GC/MS method.

The method requires the correlation coefficient to be greater than 0.98 for the 5 point calibration curve and the MDL be less than 1ppb. The 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 drinking water by 2012. The Korea Standard Method for Drinking Water, Method ES05602.3[1] is specific for the detection and quantitation of one of these compounds: 1,4-dioxane, by headspace/gas chromatography/mass spectrometry in drinking water.

The method requires a 5 point calibration curve from 2ppb to 50ppb for 1,4-dioxane. The calibration curve must have a correlation coefficient (r squared) greater than 0.98 or a response factor relative standard deviation of less than 25%. The minimum detection limit must be less than 1 ppb for 1,4-dioxane.

A Teledyne Tekmar HT3™ Headspace Analyzer was used in the static 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. The instrument conditions are listed in Table 1 for the HT3 and Table 2 for the GC/MS. The 1,4-Dioxane standard was prepared from a Restek environmental standard that contains more than 75 compounds related to environmental compounds of concern in water.




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## Experimental-Instrument Conditions

| Teledyne Tekmar HT3™ Headspace Instrument Parameters | |
|---|---|
| **Static** | |
| **Variable** | **Value** |
| Valve Oven Temp | 140°C |
| Transfer Line Temp | 140°C |
| Platen/Sample Temp | 85°C |
| Standby Flow Rate | 150mL/min |
| Sample Equil Time | 20.00 min |
| Mixing Time | 3.00 min |
| Mixing Level | Level 9 |
| Mixer Stabilization Time | 0.5 min |
| Pressurize | 15 psig |
| Pressurize Time | 2.00 min |
| Pressurize Equil Time | 0.20 min |
| Loop Volume | 1 mL |
| Loop Fill Pressure | 12 psig |
| Loop Fill Time | 2.00 min |
| Inject Time | 2.00 min |

*Table 1: Static 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 39.631cm/sec |
| Oven Program | 36°C for 7 min; 20°C/min to 200°C, hold for 0 min, run time 15.25 min |
| Inlet: | Temperature 200°C; Helium Carrier Gas; Split Ratio - 10:1 |
| MS | Source and Transfer Line Temp 230°C; Quad Temp 150°C ; Solvent Delay 0.50 min; Atune; Scan/SIM Mode; Trace Ion Detection ON |
| Scan/SIM Mode | Scan - 35.0*m/z* to 270.0*m/z*, Threshold 25, Sampling Rate 3<br>SIM Scan Masses - 96.00*m/z*, 88.00*m/z*, 64.00*m/z*, 58.00*m/z*, 46.00*m/z*, 43.00*m/z*, 100 msec dwell |

*Table 2: Agilent GC/MS with iTAD Parameters*

## Standard Preparation

The method uses a 1ppm (mg/L) internal standard (IS) solution of 1,4-dioxane-d8. The IS solution was prepared by adding 5µL of a 2,000µg/mL standard containing 1,4-dioxane-d8 into a total volume of 10mL of purge and trap methanol.

The method uses a 1ppm (mg/L) stock standard (SS) of 1,4-dioxane to prepare a calibration curve of 2ppb, 10 ppb, 20ppb, 40ppb and 50 ppb. The stock calibration standard was prepared by adding 5µL of a 2,000µg/mL Restek standards, Catalog # 30633[2], into a total volume of 10mL of purge and trap methanol.



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## Sample Preparation

All standards and minimum detection limit (MDL) samples were prepared similarly. 5.0mL of deionized water was added to each vial. All vials were spiked with 50µL of the 1ppm IS solution.

The calibration curve was prepared by adding 10µL (2ppb Final), 50µL (10ppb Final), 100µL (20ppb Final), 200L (40ppb Final), and 250L (50ppb Final) of the SS into separate vials. The MDL was prepared by adding 10µL (2ppb Final) of the SS into 7 separate vials. All vials including blank samples were capped with Teflon lined silicon septa and aluminum crimp seals

All of the samples and standard were tested with Teledyne Tekmar HT3$^{TM}$ Headspace Analyzer with the 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 selected ion monitoring (SIM) chromatograms from the static headspace methods were evaluated using the Agilent Environmental ChemStation software. Figure 1 is the TIC chromatogram from the SIM scan of a 2ppb MDL standard by the static headspace method.

The peak area of the primary ions for 1,4-dioxane were determined for each standard or MDL sample. The response factor of 1,4-dioxane was calculated versus the 1,4-dioxane-d8 internal standard. The five standards were evaluated for linearity and relative standard deviation of the response factor.

MDLs were established for the compounds by analyzing seven replicates at a concentration of 2ppb. The MDL of the seven replicate samples were calculated by multiplying the relative standard deviation of the calculated amount times 3.143. 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 RSD | | Loop Linear | |
|---|---|---|---|---|---|
| VOC | Primary Ion | % RSD | MDL | $r^2$ | MDL |
| 1,4-Dioxane-d8 IS | 96 | | | | |
| 1,4-Dioxane | 88 | 10.8 | 0.65 | 0.9957 | 0.81 |

Table 3: Relative Standard Deviation, Linear Correlation Coefficient (r squared, $r^2$), and MDL Data for 1,4-Dioxane.

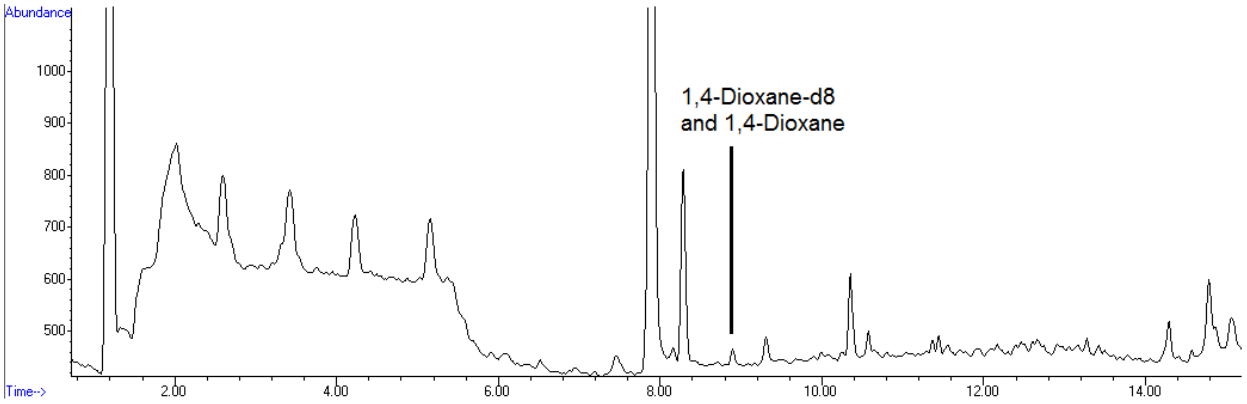


Figure 1: SIM Scan of a 2ppb Standard with the Static HT3 Headspace Parameters. The retention times of 1,4-dioxane and 1,4-dioxane-d8 are located on the chromatogram.



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## Conclusions

The Ministry of the Environment of the Republic of Korea recently added 1,4-dioxane to the list of compounds in drinking water that must be monitored by 2012. The allowable method is headspace GC/MS by the static method. The method requires that the linear correlation (r squared) of a 5 point curve consisting of 2ppb, 10 ppb, 20ppb, 40ppb and 50ppb standards must be greater than 0.98. The minimum detectable limit (MDL) must also be less than 1ppb.

The Teledyne Tekmar HT3™ Headspace Analyzer following the method parameters was used to determine its suitability for this method. The HT3 surpassed the method requirements for the relative standard deviation, the correlation coefficient and the MDL as required by the Ministry of Environment.


1. Korean: 환경부, 대한민국, 먹는물수질공정시험기준, ES05602.3, 1,4-다이옥산-헤드스페이스/기체크로마토그래피/질량분석법, 2010

   English: Ministry of Environmental, Republic of Korea, The Korean Standard Method for Drinking Water, ES05602.3, 1,4-Dioxane-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. 8260M MegaMix® Calibration Mix, Catalog # 30633, www.restek.com for the most current listing of Restek distributors.





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