

## Application Note

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### Introduction

The Korean Standard Method for Drinking Water ES 04605.3 requires static headspace with Gas Chromatograph/Mass Spectrometer (GC/MS) to monitor formaldehyde. The method is based on the derivatization of formaldehyde with O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) to form the pentafluorobenzyl oximine compound within a static headspace vial.

The method requires that the Minimum Quantitation Limit (MQL) must be less than 10 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 formaldehyde in drinking water by the static headspace GC/MS method.



### Standards

- 10 ppm p-bromofluorobenzene Internal Standard (IS)
- 5 ppm formaldehyde Stock Standard
- PFBHA solution, 1 mg/mL O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) in water

### 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 20  $\mu$ L of the 10 ppm IS solution. 1 mL of the PFBHA solution was added. The HT3 was equipped with an optional sample loader/mixer assembly with triangular head (Part No 14-9440-079) to provide vigorous mixing of the sample.

A calibration curve and seven MQL samples were prepared according to [Table I](#). Seven 5 ppb standards were prepared for the MQL calculation.

| Table I Calibration Curve and MQL Standard Dilution |                |               |
|---|----------------|---------------|
| Standard Level (ppb)                                | Stock Standard | Sample Volume |
| 0   | 0 $\mu$ L      | 10 mL         |
| 5 and MQL   | 10 $\mu$ L     | 10 mL         |
| 10 and MQL  | 20 $\mu$ L     | 10 mL         |
| 20  | 40 $\mu$ L     | 10 mL         |
| 50  | 100 $\mu$ L    | 10 mL         |
| 100   | 200 $\mu$ L    | 10 mL         |

## Instrument Conditions

| Table II Static (Loop) HT3 Headspace Instrument Parameters |           |                          |           |
|--|-----------|--------------------------|-----------|
| Variable   | Value     | Variable                 | Value     |
| Constant Heat Time   | Off       | Mixing Time              | 20.00 min |
| G.C. Cycle Time  | NA        | Mixing Level             | Level 10  |
| Valve Oven Temp  | 140 °C    | Mixer Stabilization Time | 3.00 min  |
| Transfer Line Temp   | 180 °C    | Pressurize               | 14 psig   |
| Standby Flow Rate  | 50 mL/min | Pressurize Time          | 1.00 min  |
| Platen/Sample Temp   | 80 °C     | Pressurize Equil Time    | 0.20 min  |
| Platen Temp Equil Time                                     | 0.10 min  | Loop Fill Pressure       | 10 psig   |
| Sample Equil Time  | 2.00 min  | Loop Fill Time           | 1.00 min  |
| Mixer  | On        | Inject Time              | 1.00 min  |

| Table III 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  | 40 °C for 2 min; 10 °C/min to 210 °C, hold for 5 min  |
| Inlet   | Temp 200 °C; Helium Carrier Gas; Septum Purge Flow 0.5 mL/min, 1 mm IP Deact. Liner Split Ratio - 15:1                        |
| MS  | Source Temp 230 °C; Quad Temp 150 °C ; Solvent Delay 0.50 min; Atune; Transfer Line 225 °C ;Scan Mode; Trace Ion Detection On |
| Scan Mode   | Scan - 35.0 m/z to 270.0 m/z, Threshold 10, Sampling Rate N=3   |

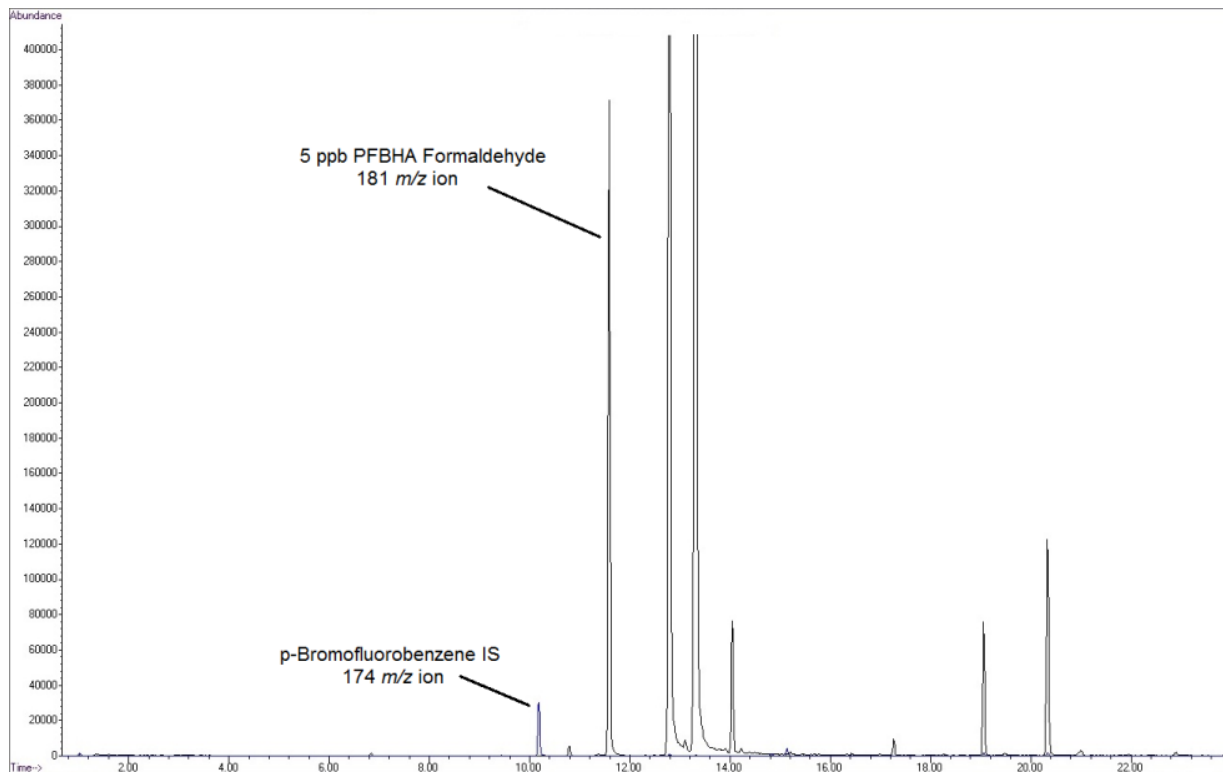
## Static (Loop) Headspace Mass Spectrometry Results

The chromatograms were evaluated using the Agilent Environmental ChemStation™ software. [Figure 1](#) is the quantitation ion chromatogram of a 5 ppb MQL standard by the static headspace method. The quantitation ions that were used for the IS calculation are shown in [Figure 1](#), [Table IV](#) and [Table V](#). The RF of formaldehyde was calculated versus the p-bromofluorobenzene IS.

The six standards were evaluated for linearity and RSD of the Relative RF (RRF). The method has a significant PFBHA formaldehyde background peak from the formaldehyde present in methanol. The RSD of the RRF was greater than the allowable 25% due to the background peak. The RRF was also calculated with this background peak subtracted.

The concentrations of the seven 5 ppb MQL samples were calculated by the linear calibration curve, the RRF and the RRF less the background area. The MQL was calculated by multiplying the standard deviation of the calculated amount of the seven MQL samples times 10. [Table IV](#) presents the RSD of the RRF and its calculated MQL including the background subtracted data. [Table V](#) presents the linear correlation coefficient ( $r^2$ ) and its calculated MQL data.

**Figure 1** Static headspace quantitation ion chromatogram of a 5 ppb PFBHA formaldehyde standard with p-bromofluorobenzene internal standard.



| Table IV %RSD and MQL Results with Static Headspace and Scan GC/MS |           |                 |           |               |          |                                 |           |               |          |
|--|-----------|-----------------|-----------|---------------|----------|---------------------------------|-----------|---------------|----------|
| Compound   | Quant Ion | RRF Calculation |           |               |          | RRF Calculation Less Background |           |               |          |
|  |           | % RSD           | MQL (ppb) | Calc Recovery | % Theory | %RSD                            | MQL (ppb) | Calc Recovery | % Theory |
| p-Bromofluorobenzene IS  | 174       | 3.7             | NA        | NA            | NA       | 3.7                             | NA        | NA            | NA       |
| PFBHA Formaldehyde   | 181       | 27.9            | 11.7      | 7.8 ppb       | 156      | 16.0                            | 9.8       | 5.2 ppb       | 105      |

| Table V Linearity and MQL Results with Static Headspace and Scan GC/MS |           |                    |           |               |          |
|--|-----------|--------------------|-----------|---------------|----------|
| Compound   | Quant Ion | Linear Calculation |           |               |          |
|  |           | r <sup>2</sup>     | MQL (ppb) | Calc Recovery | % Theory |
| p-Bromofluorobenzene IS  | 174       | NA                 | NA        | NA            | NA       |
| PFBHA Formaldehyde   | 181       | 0.9968             | 9.3       | 5.9 ppb       | 118      |

## Conclusions

The Teledyne Tekmar HT3 Automated Static and Dynamic Headspace Vial Sampler and the method used for the detection of formaldehyde by the derivatization with PFBHA, surpassed the method requirements for the correlation coefficient and MQL as required by the Ministry of Environment. The %RSD requirement for the calibration curve passed when the background formaldehyde was subtracted. The linear calibration method provided a better calculation of the sample concentration without the need for subtracting the background formaldehyde present.

- Korean: ES 04605.3, 폼알데하이드-헤드스페이스/기체크로마토그래피-질량분석법
- English: ES 04605.3, Formaldehyde-Headspace/Gas Chromatography-Mass Spectrometry

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