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# Determination of Volatile Organic Compounds in Waste Water using Headspace/GC Analysis

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The HS-GC(Headspace-Gas Chromatography) method was performed to analyze the volatile organic compounds in waste water. This study was performed to eastablish the basic data by studying the effects of salt addition, equilibrium temperature and time in the volatile organic compounds(VOCs) analysis. The presence of salts have been found to increase the sensitivity of NaCl, $Na_2SO_4$ and $Na_2CO_3$. The peak area is increased from 1.19 to 2.73 times by adding the salts to the water sample, compared with a salt free sample. At equilibrium temperature of 90℃, the recoveries of target compounds have been found between 92% and 120%. This HS-GC method can be applied to analyze the volatile organic compounds and organohalo compounds in the environmental matrix.

**Key words** : Headspace/GC method, VOCs, Organohalo compounds

## 1. Introduction

The organic compounds which are discharged to the stream have affected to the human life, animal, and plant growth. Volatile organic compounds(VOCs) are the primary pollutant of environments. These chemicals are widely used as solvents, cleaning agents, and fuels in the large number of industrial and commercial applications. As the results, the contamination of VOCs are widespread in the environments. The most commonly identified problems are the contamination of soil, various aqueous environments such as groundwater, surface water and wastewater.

HS-GC(Headspace-Gas Chromatography) analysis was a quantitative analysis technique, which is carried out by heating the sample to carefully controll the temperature until equilibrium reached and then transferring the headspace samples from the vial to gas chromatography column. Organic volatile impurities can be extracted from various matrices and analyzed directly without the use of solvents as extractants. When using headspace analysis, involatile sample material is prevented from entering the separation system, which means that chromatography time is shortened considerably and the analysis system is kept clean and stable over an extended period of time. Since large volumes can be employed for VOCs analysis, very low detection limits can be achieved compared with other techniques.

The headspace can be applied to analyze the VOCs in the environmental media directly without pretreating the samples which contained slurry and particles. The samples preparing is very simple and many samples can be loaded in headspace, simultaneously. The headspace is based on the principle that the volatile organic compounds from liquid or solid matrix will be distributed between sample phase and headspace gas.[1-3] The volatile organic compounds between vapor phase and liquid phase are reached the

equilibrium. When the equilibrium is reached at given temperature, the concentration of components in the vapor phase are proportional to that in the samples.[4-6] In this research, a new analytical method for VOCs was performed using HS-GC. The ratio of component peak area to the operation solution without containing the salt is tested at each calibration level and the calibration curve plotted to find the effect of salt addition, equilibrium temperature, and equilibrium time in the waste water samples contaminated by VOCs.

## 2. Materials and Methods

### 2.1. Preparation of Samples

Table 1 represented the physical properties of the analytes employed in this research. Analytial standards and matrix spiking solutions were prepared using procedure specifically developed to minimize volatilization losses. Pure compounds were transferred with a microliter syringe to a volumetric flask which had been chilled to prepare a stock solution. The further diluted solution was used the second chilled flask, and the remainder was stored to 2 mL vial which is remainded the minimal headspace. The fresh vial was used to prepare the working standard solutions using a microliter syringe inserted through the teflon-lined septum. New working standards were prepared weekly from the stock solution and new stock solution vial was opened monthly.

Two environmental samples are prepared as follows. These samples were prepared by spiking chilled water(4℃) in 22.3 mL headspace vials for static headspace analysis. The headspace vials were immediately capped with teflon-lined septa and aluminum seals and then loaded into a headspace sampler for analysis. The 5 g of salts(NaCl, $Na_2SO_4$, $Na_2CO_3$) were added to 10 mL headspace water samples to investigate the salt effect to increase the sensitivity.

### 2.2. Analytical Instrumentation

The Perkin-Elmer Auto System GC which equipped with 60-m×0.32-㎜ DB-624 column and phtoionization detector(PID) and electron capture detector(ECD) were connected in series. The headspace sampler was used after heating the sample to 60~120℃ for 30~120 minutes and the carrier gas was the 99.999 vol% grade nitrogen. Analytical conditions are shown in Table 2.

**Table 1.** Physical properties of the compounds studied in this research.

| Components | Molecular Weight (g/mol) | Boiling point (℃) | Aqueous Solubility (at 25℃ M: -log $C_w^{sat}$) | Log octanol-water partition coefficient: (log $K_{ow}$) |
|---|---|---|---|---|
| Benzene | 78.1 | 80.1 | 1.64 | 2.13 |
| Toluene | 92.1 | 110.6 | 2.25 | 2.69 |
| Ethylbenzene | 106.2 | 136.2 | 2.80 | 3.15 |
| Xylene | 106.2 | 138.0 | 2.76 | 3.12 |
| Chloroform | 119.4 | 61.5 | - | 1.90 |
| 1,1,1-Trichloroethane | 133.4 | 74.1 | 2.70 | 2.48 |
| Trichloroethylene | 131.4 | 87.0 | 2.04 | 2.42 |
| Bromodichloromethane | 162.0 | 90.1 | - | 1.90 |
| Tetrachloroethylene | 165.8 | 121.0 | 3.04 | 2.88 |
| Chlorodibromomethane | 206.5 | 199.5 | - | 2.10 |
| Bromoform | 252.8 | 149.5 | - | 2.30 |

**Table 2.** Conditions for environmental water analysis.

| Parameters | Conditions |
|---|---|
| **Headspace sampler for BTEX** | Perkin Elmer HS-40 |
| - Sample Volume | 5, 10 mL |
| - Salt Addition(NaCl, $Na_2SO_4$, $Na_2CO_3$) | 5 g |
| - Sample Heating(equilibration) Temp. | 60~90 ℃ |
| - Heating Time | 30~120 min |
| - Sample Introduction Time | 0.15 min |
| - Transfer Line Temp. | 120 ℃ |
| - Pressurization Time | 3 min |
| **Gas Chromatograph** | Auto System GC |
| - Injector Temp. | 200 ℃ |
| - Colume | DB-624 60m×0.32mm ID |
| | 50 ℃(5 min) ------→ 140 ℃(5 min) |
| | 5 ℃/min |
| - Detector | PID(220 ℃) |
| - Carrier Gas | $N_2$, 21psi |
| - Injection Mode | Splitless |
| **Headspace sampler for Organohalogen compounds** | Perkin Elmer HS-40 |
| - Sample Volume | 10 mL |
| - Sample Heating(equilibration) Temp. | 80 ℃ |
| - Heating Time | 30 min |
| - Sample Introduction Time | 0.15 min |
| - Transfer Line Temp. | 120 ℃ |
| - Pressurization Time | 3 min |
| **Gas Chromatograph** | Auto System GC |
| - Injector Temp. | 200 ℃ |
| - Colume | DB-624 60m×0.32mm ID |
| | 50 ℃(10 min) ------→ 140 ℃(5 min) |
| | 5 ℃/min |
| - Detector | ECD(230 ℃) |
| - Carrier Gas | $N_2$, 21psi |
| - Injection Mode | Split(10:1) |

## 3. Results and Discussion

Table 3 shows the minimum detection limits (MDL) and area reproducibility data in the analytes. As shown in Table 3, the minimum detection limit was achieved from 0.21 μg/L to 0.27 μg/L with relative standard deviation of 2.4~7.4% in benzene, toluene, ethylbenzene, and xylenes(BTEX) and from 0.01 μg/L to 0.08 μg/L with relative standard deviation of 2.2~8.1% in organohalogen compounds. These detection limits in the headspace analysis were satisfied with quantitation limit in prescribing the Korean offical testings of water. The minimum detection limit of each component was calculated with 2.5 of the signal to noise ratio and containing the salt of 5 g NaCl. The method linearity was determined over 5-point calibration curve and the results are listed in Table 3. The concentration range selected was 0.175 μg/ℓ to 400 μg/ℓ for benzene, toluene, ethylbenzene, and xylene and 0.02 μg/ℓ to 200 μg/ℓ for organohalo compounds.

**Table 3.** MDL, linearity, reproducibility and recovery for various Components using 10㎖ Liquid sample volume(S/N=2.5).

| Analytes | Minimum Detection Limit(㎍/ℓ) | Correlation Coefficient $R^2$ | Reproducibility at 20 ㎍/ℓ (% RSD) | Average Recovery (N=3, %) |
|---|---|---|---|---|
| Benzene | 0.27 | 0.99 | 6.0 | 98 |
| Toluene | 0.25 | 0.99 | 4.6 | 103 |
| Ethyl benzene | 0.23 | 0.99 | 6.4 | 92 |
| m-, p-Xylene | 0.42 | 0.99 | 7.4 | 113 |
| o-Xylene | 0.21 | 0.99 | 2.4 | 95 |
| Chloroform | 0.04 | 0.98 | 4.6 | 120 |
| 1,1,1-Trichloroethane | 0.02 | 0.99 | 4.2 | 98 |
| Trichloroethylene | 0.07 | 0.99 | 6.7 | 105 |
| Bromodichloromethane | 0.08 | 0.99 | 2.2 | 96 |
| Tetrachloroethylene | 0.01 | 0.99 | 5.3 | 92 |
| Chlorodibromomethane | 0.02 | 0.99 | 7.4 | 102 |
| Bromoform | 0.02 | 0.99 | 8.1 | 95 |

Reproducibility was determined at the 20 ㎍/ℓ level using the standard solution which saturated with 5 g NaCl and the range surveyed between 2.2 and 8.1% of the relative standard deviations (RSDs). The average recovery was obtained from 92% to 120% on three separated samples.

## 3.1. Effect of Equilibrium Temperature and Time

The equilibrium temperature and time were taken from 60℃ to 120℃ for 30, 60 and 90 minutes to see their effects. The effects of equilibrium time and temperature on the sensitivity of the analytes in 10 mL samples was showed in Figure 1. The peak area was increased from 30 to 60 minutes and then the area was slightly decreased from 60 to 90 minutes for all experimental compounds at 90℃. The peak area was also increased from 60 to 9 0℃ and then slightly decreased from 90 to 120℃. The effect of temperature of analytes showed the same tendency of equilibrium time effects. From these results the higher sensitivity of analytes was observed at 60 min. For applying the headspace techiques to analyze the volatile organic compounds, we have to set up the experimental conditions such as equilibrium time and temperature for each compound.

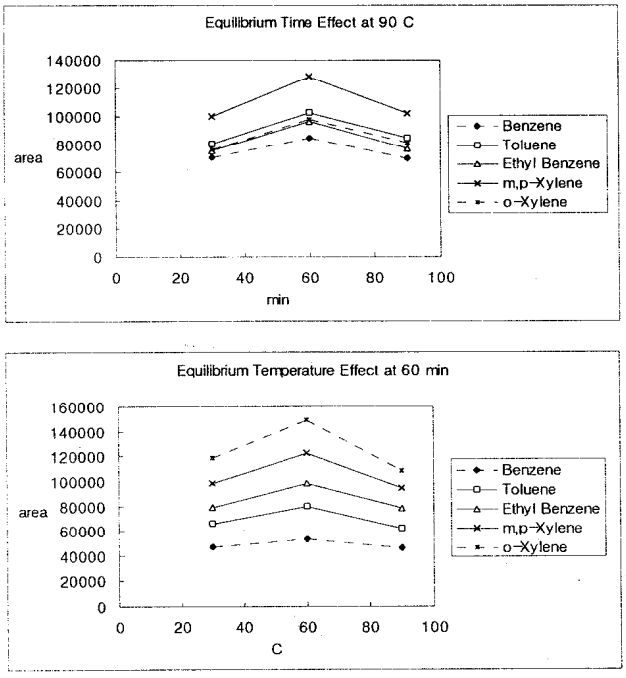


**Fig. 1.** Effects of equilibration time and temperature in headspace analysis.

### 3.2. Effect of Salt Addition

Table 4 represented the VOCs recovery effect using three different salts. For this purpose 5 g of NaCl, $Na_2SO_4$ and $Na_2CO_3$ are added to the VOCs samples. The peak area is increased from 1.19 to 2.73 times by adding the salt to the water sample, compared with a salt free sample. Adding the salt reduces the solubility of the components in water by breaking up the structure of the aqueous phase. Reducing the solubility leads to increase concentration of analytes in the headspace of the sample.

**Table 4.** Effect of salt addition on response(10mL Sample Used).

| Component | No Salt | NaCl | $Na_2SO_4$ | $Na_2CO_3$ |
|---|---|---|---|---|
| Benzene | 1.0 | 1.73 | 2.40 | 1.21 |
| Toluene | 1.0 | 1.86 | 2.40 | 1.26 |
| Ethyl Benzene | 1.0 | 1.97 | 2.40 | 1.34 |
| m-, p-Xylene | 1.0 | 2.03 | 2.45 | 1.33 |
| o-Xylene | 1.0 | 2.00 | 2.73 | 1.19 |

### 3.3. Analysis of waste water

This study was applied to analyze the waste-water. The samples were prepared with salt addition to increase the amount of analyte in the gas phase.

Chromatograms of a high level standard and a wastewater using the PID are shown in Fig. 2. In this case, the response for benzene(peak 1 at 1.63 min), toluene(peak 2 at 16.44 min), ethyl benzene(peak 3 at 20.71 min), m- and p-xylene (peak 4 at 21.06 min), and o-xylene(peak 5 at 22.23 min) are above that of calibration standards and these target compounds are also detected in wastewater. Chromatograms are obtained with the ECD for a low level standard and an aqueous sample are shown in Fig. 3. The responses of the analytes detected in wastewater sample were below the response of the standard.

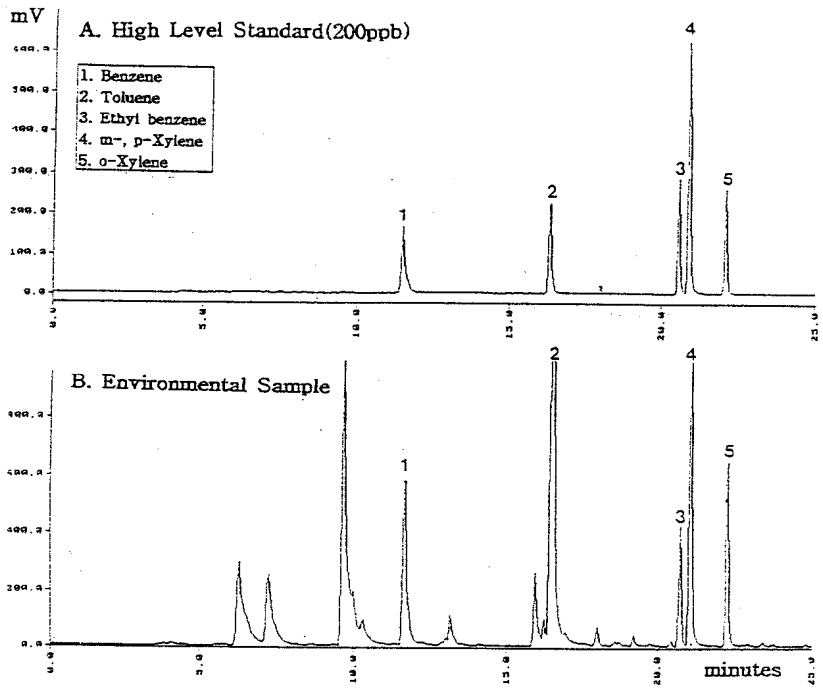


**Fig. 2.** Chromatograms obtained with the PID for analysis of a high level standard and a sample of environmental untreated wastewater.

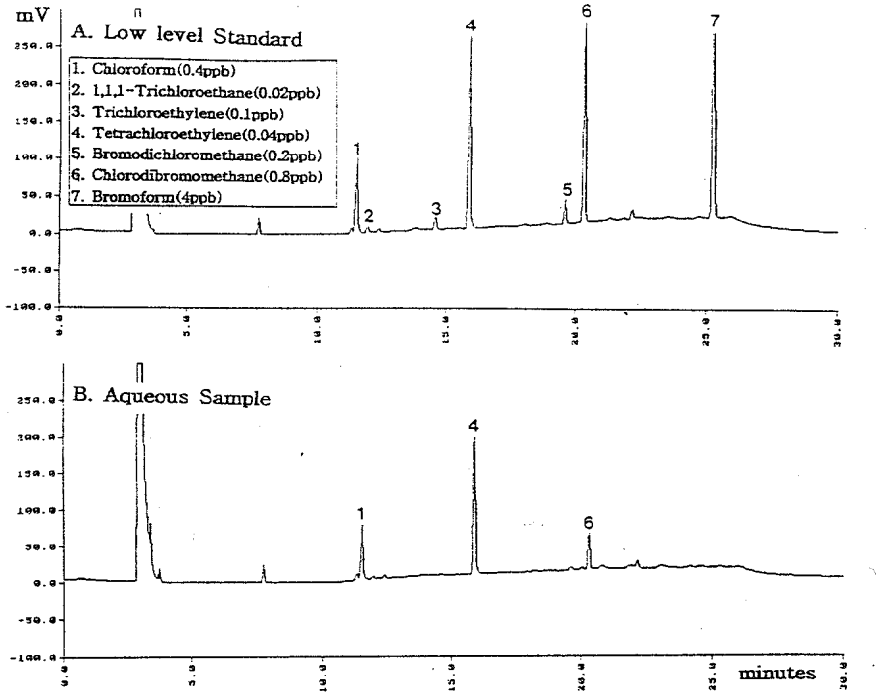


**Fig. 3.** Chromatograms obtained with the ECD for analysis of a low level standard and an aqueous sample.

## 4. Conclusion

The new analytical method of headspace/GC approaches to the analysis of VOCs and organhalogen compounds has been discussed to establish the analytical method in waste water samples. The effects of salt, equilibrium temperature and equibrium time are studied. The presence of salts have been found to increase the sensitivity of VOCs. The recoveries of target compounds have been found between 92% and 120% at sample temperature of 90℃. This headspace/GC method can be applied to analyze the VOCs and organohalogen compounds.

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