

Comparison between Head Space Gas Sampling and Purge & Trap Sampling in Water Analysis

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Abstract : The two main methods to prepare water samples for analyzing volatile organic compounds(VOC's) were investigated. One is the purge and trap(PT) method and another is the head space(HS) sampling method. Both methods were effective to transfer the low boiling point components from the water sample onto the capillary column. The cryo-focusing at the top of the main capillary column was an effective way to obtain the sharpness of the chromatographic peaks but could be avoided when a semi-wide bore column was used. The recovery from the same amount of the sample was better in PT than in HS but a larger sample volume in HS method could compensate the lower efficiency. Therefore PT is suitable to the analysis of drinking water where the very low concentration must be determined. HS is suitable to waste water analysis because of the easiness of the operation. The repeatability was good and similar in both methods. For the contamination of the former sample, both methods were tough and could be used without any problems. The matrix effect which could change the equilibrium parameters in HS method was found negligible in many components. The actual samples such as tap water and river water were analyzed with both methods concerning 16 components regulated in Korea..

Keywords : VOC, Purge & Trap Sampling, Head Space Gas Sampling, GC/MS Drinking Water, Waste Water, Matrix effect.

1.Introduction

Volatile organic compounds(VOC) in water are regulated in many countries. In USA, EPA(Environmental Protection Agency) has specified many organic compounds as purgeable components[1]. In Japan, 23 compounds are regulated in drinking water. In Korea, 16 compounds including two internal standards are

regulated. The analysis of VOC in waste water is also important. The details of the analytical method are discussed in a review[2]. In this paper the two main methods of sample pre-treatment are compared each other from the practical view points. Head space gas sampling (HS hereinafter) method is based on the equilibrium between the liquid and gas

phases at the constant temperature. When the components has low boiling points, they will mostly exist in the gaseous phase. Because the liquid is not injected into the column, this method provides a convenient and clean way in the gas chromatographic analysis. Purge and Trap (PT hereinafter) method, on the other hand, is based on the concentration procedures of purging out by the carrier gas into a trap column, which will be heated afterward to transfer the concentrated components onto the column.

In this paper these two pretreatment methods for water sample are compared and discussed to find the suitable method to the specified purpose.

2. Experimental

A gas chromatography with quadrupole mass spectrometer, Shimadzu QP-5000

with 151 l/sec turbo-molecular vacuum pump was used throughout this paper. A head space gas sampler, Perkin-Elmer HS-40 was used as the HS method and Tekmar LSC-3000 was used as PT method. DB-624 column made by J&W, which had 0.32mm i.d., 60m in length and 1.8 micrometer in film thickness, was used mostly as the main column. All the standard components are obtained from Tokyo Kasei Co.Ltd in Japan.

3. Results and Discussion

3-1 Separation and peak shape

When the gaseous sample in large volume is introduced onto the main capillary column, it takes normally some minutes, which causes the peak broadening especially for low volatile components. In PT method,

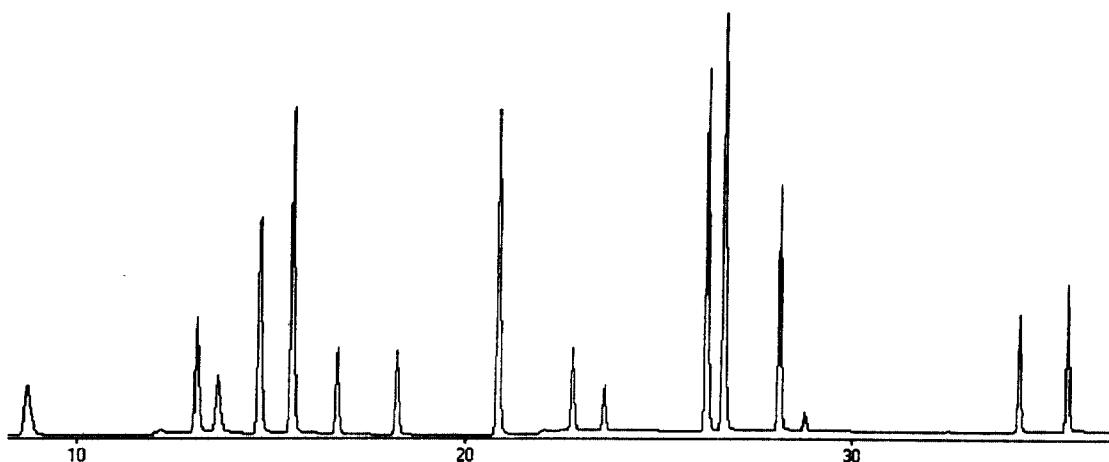


Fig. 1 Peak Shape of VOC with PT by using a semi wide bore (0.32mm i.d.) column

Conditions:

Column: DB624 0.32mm i.d. 60m in length, 1.8 micrometer in film thickness

Column Temperature($^{\circ}$ C): 40(6min.)-4/min-120-5/min-190-20/min-200

Column Inlet Pressure: 100kPa(Helium)

Interface Temperature for GC/MS: 250 $^{\circ}$ C

The elution order is as follows: (1)dichloromethane, (2)chloroform, (3)1,1,1-trichloroethane, (4)benzene, (5)fluorobenzene(IS1), (6)trichloroethylene, (7)bromodichloromethane, (8)toluene, (9)tetrachloroethylene, (10)dibromochloromethane, (11)ethylbenzene, (12)m,p-xylene, (13)o-xylene, (14)bromoform, (15)1,4-dichlorobenzene, (16)1,2-dichlorobenzene(IS2)

cryogenic re-focusing is recommended to prevent it. But practically it is preferred to operate without cryo-focussing because it is very time consuming and also costly to use the coolant such as liquid nitrogen or liquid carbon dioxide. As *Fig. 1* shows, peak shape is good enough when the column has a large inner diameter as 0.32mm in PT method.

Fig. 2 shows similar peak shapes in HS method. In both methods, a capillary column with the larger inner diameter provides the

shorter time for sample introduction and results in the good peak shape.

In *Figs. 1* and *2*, the chromatographic responses were indicated in total ion as the total sum of the measured mass number.

Each ion for individual mass number can be used for each quantitation. One component could be identified by measuring several mass numbers and comparing their ratio to that of the standard component. Thus even with SIM(selected ion monitoring)

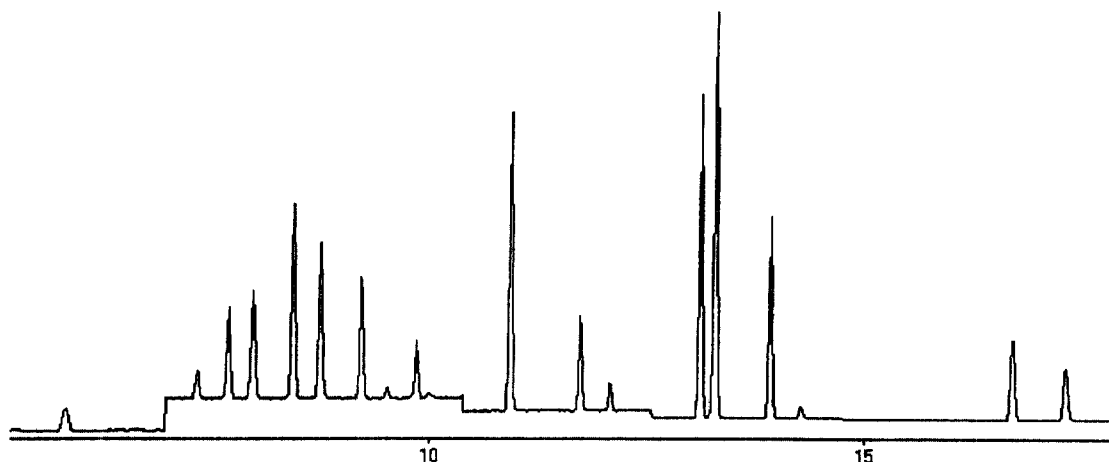


Fig. 2 Peak Shape of VOC with HS by using semi wide bore (0.32mm i.d.) column

Column Temperature($^{\circ}$ C): 40-10/min-200

Other conditions are equal with those in *Fig. 1*

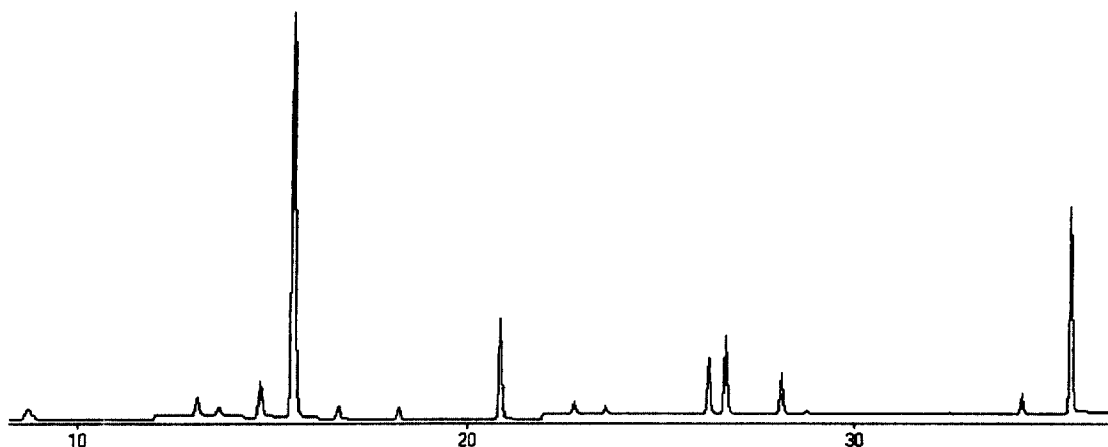


Fig. 3 Chromatogram for low concentration (0.1ppb) with PT.

Conditions are equal to those in *Fig. 1*.



Fig. 4 Chromatogram for low concentration (0.2ppb) with HS. Conditions are equal to those in *Fig. 2*.

mode, each component is identified with good confidence.

In *Fig. 3* typical chromatogram with HS method without cryo-focusing obtained for the standard mixture of 16 components which are regulated in Korea, was shown where the semi-wide bore capillary column works well to prevent the peak broadening. In any cases, the initial temperature of the column oven should be as low as possible. Concerning the liquid phase of the main column, the difference between Vocol and DB-624 was small. But the film thickness was important to prevent the peak broadening.

3-2 Lowest detectable concentration

In principle, PT method recovers the total amount of volatile components from the water sample. The lowest concentration is determined by the total volume of the sample put in the purge bottle and also the detector sensitivity. Normally 5ml of water sample is enough to detect the concentration of one order magnitude lower than that of the most of the regulation.

HS method has lower recovery of the components from the water than PT because of the limitation of the gas sampling volume

from the bottle, but the initial volume of the water sample can almost compensate it when approximately 15ml of the water sample is used. Consequently the regulated concentration level can be determined with both methods.

Fig. 3 and *4* show the chromatograms for 0.2ppb standard mixture with both methods.

3-3 Repeatability

Though the concentrations of the components were quite low, the repeatability was good in both methods as shown in the *Tables I and II*. Most important factors are the contamination of the sample during the sample treatment. The contaminants come mainly from air during the sample treatment. The frequently used solvents such as dichloromethane and chloroform are easily found in the blank water. So the ventilation of the laboratory is quite important to obtain good blank data. The method to provide a blank water based on the heating of the de-ionized water, is quite time consuming. One of the practical way to obtain a blank water is to use mineral water sold in the food shop.

Table I Repeatability of peak area with PT in 0.2ppb.

Conditions are equal to those in Fig. 1.

$n=7$

components	C.V.(%)
dichloromethane	3.90
chloroform	3.84
1,1,1-trichloroethane	8.72
trichloroethylene	7.55
bromodichloromethane	1.37
toluene	4.12
tetrachloroethylene	7.95
dibromochloromethane	3.17
m,p-xylene	6.13
o-xylene	4.22
bromoform	6.40
1,4-dichlorobenzene	1.19

Table II Repeatability of peak area with HS in 0.2ppb.

Conditions are equal to those in Fig. 2.

$n=5$

components	C.V.(%)
dichloromethane	4.86
chloroform	5.79
1,1,1-trichloroethane	4.15
trichloroethylene	6.41
bromodichloromethane	7.22
toluene	5.61
tetrachloroethylene	2.80
dibromochloromethane	5.74
m,p-xylene	7.50
o-xylene	5.24
bromoform	9.17
1,4-dichlorobenzene	5.35

3-4 Total analysis time

In HS analysis, it takes around 30 minutes before the equilibrium between the gas and the liquid phases is stabilized. But in actual automatic analysis system, this time is well scheduled in the programmed sequence and no significant difference exists between both methods. The total analysis time is mainly controlled by the analysis time of the gas

chromatography.

3-5 Carry-over

When the sample is the drinking water there are no problem of the contamination of the former sample because all of the components are normally in low concentration. But in waste water analysis some components could be very high in the

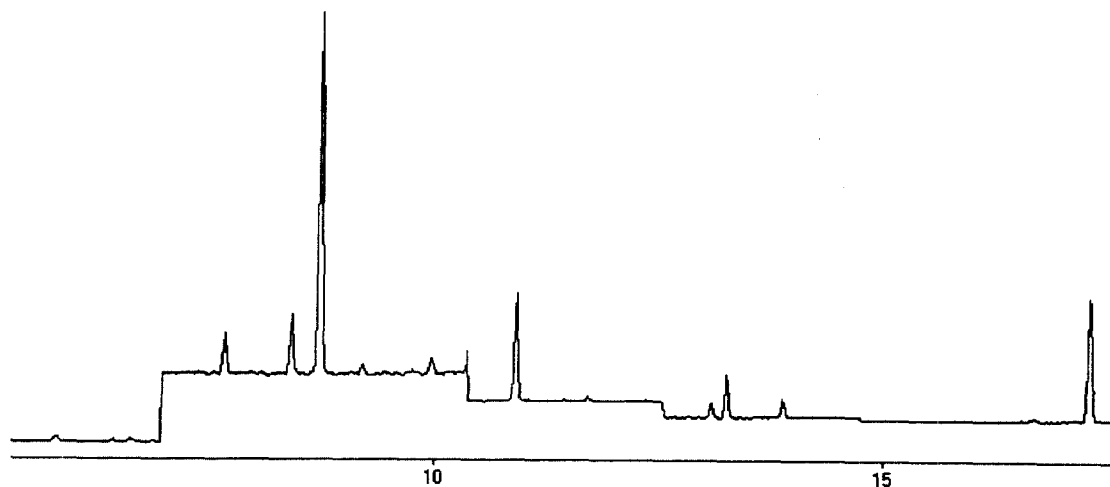


Fig.5 Analysis of waste water with HS.

Table III Matrix effects in HS method

As matrix components, 100ppb chloroform, 40ppb 1,1,1-trichloroethane, 150ppb trichloroethylene, 25ppb bromodichloromethane, 40ppb tetrachloroethylene, 40ppb dibromochloromethane and 200ppb bromoform are added.

component	measured conc.(ppb) in dilute mixture	measured conc.(ppb) in matrix solution with X
dichlorometane	1.998	2.221
benzene	2.180	2.157
toluene	2.496	2.521
m,p-xylene	4.904	4.909
o-xylene	2.158	2.178
1,4-dichlorobenzene	1.929	2.006

concentration and will remain in the following analysis. This "carry-over" effect was negligible in both methods. When the waste water which is suspected to contain some components in high concentration, the control sample will be useful to be analyzed before the next actual sample is analyzed, in order to check the contamination of the system. In Fig.5 an example of waste water is shown, which is measured with HS method.

3-6 Matrix effect in HS

HS method depends on the equilibrium of the gas and liquid phases. When some of the components exist in large concentrations, the equilibrium could be different from that in low concentrations. *Table III* shows the results for such cases and normally it is not necessary to consider such effect. When such effect is still suspected, the special calibration method called "standard addition method" will be effective.

3-7 Maintenance and Easiness of operation

Maintenance for PT method is normally only to keep the performance of the trap column in constant conditions. Maintenance for HS method is mainly to keep the flow-line as clean as possible.

Both methods were fully automated and the easiness of the operation was not so different. But the trap column in PT makes the flow line and the time sequence slightly complicated. The operation with HS is simpler.

Conclusion

PT and HS have their own suitability for the sample. Generally speaking PT is preferred in the drinking water analysis because of the sensitivity to the low concentration. HT is preferred in the waste water analysis because of the easiness of the operation. There were no significant problem for the contamination from the former sample in both methods.

References

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