Removal of residual VOCs in a collection chamber using decompression for analysis of large volatile sample

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Abstract: In order to measure the volatile organic compounds (VOCs) of a sample which is too large to use commercially available chamber, a stainless steel vacuum chamber (VC) (with an internal diameter of 205 mm and a height of 50 mm) was manufactured and the temperature of the chamber was controlled using an oven. After concentrating the volatiles of the sample in the chamber by helium gas, it was made possible to remove residual volatile substances present in the chamber under reduced pressure ($(2 \pm 1) \times 10^{-2}$ mmHg). The chamber was connected to a purge & trap (P&T) using a 6 port valve to concentrate the VOCs, which were analyzed by gas chromatography-mass spectrometry (GC-MS) after thermal desorption (VC-P&T-GC-MS). Using toluene, the toluene recovery rate of this device was 85 ± 2 %, reproducibility was 5 ± 2 %, and the detection limit was 0.01 ng L^{-1}. The method of removing VOCs remaining in the chamber with helium and the method of removing those with reduced pressure was compared using Korean drinking water regulation (KDWR) VOC Mix A (5 μL of 100 μg mL^{-1}) and butylated hydroxytoluene (BHT, 2 μL of 500 μg mL^{-1}). In case of using helium, which requires a large amount of gas and time, reduced pressure ($(2 \pm 1) \times 10^{-2}$ mmHg) only during the GC-MS running time, could remove VOCs and BHT to less than 0.1 % of the original injection concentration. As a result of analyzing volatile substances using VC-P&T-GC-MS of six types of cell phone case, BHT was detected in four types and quantitatively analyzed. Maintaining the chamber at reduced pressure during the GC-MS analysis time eliminated memory effect and did not affect the next sample analysis. The volatile substances in a cell phone case were also analyzed by dynamic headspace (HT3) and GC-MS, and the results of the analysis were compared with those of VC-P&T-GC-MS. Considering the chamber volume and sample weight, the VC-P&T configuration was able to collect volatile substances more efficiently than the HT3. The VC-P&T-GC-MS system is believed to be useful for VOCs measurement of inhomogeneous large sample or devices used inside clean rooms.

Key words: large volatile sample, vacuum chamber, residual VOCs, decompression, GC-MS

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1. Introduction

Concentration of semi-VOCs (SVOCs) in the clean room on the hardware, products and wafer surfaces is recognized as a source of processing problems and hardware failure.[1] SVOCs tend to be larger in molecular weight and have higher boiling points than VOCs, and the World Health Organization (WHO) classifies SVOCs as indoor organic pollutants with a boiling point range between 240-260 and 380-400 °C. They differ from volatile organic compounds (VOCs) and very volatile organic compounds (VVOCs) that present boiling point range of 50-100 to 240-260 °C and < 0 to 50-100 °C, respectively (US EPA, 2014b).[2] Light scattering method alone is not enough to evaluate the cleanliness of clean room and to manage particle numbers, and there are molecular contaminants (airborne molecular contaminants: AMCs) which cannot be removed by particle removal filters and cannot be measured by scattering light as particles.[3-5] AMCs can be originated from the raw materials used inside the clean room, as well as from the materials used outside the clean room, and there are a wide variety of types and can be divided into acids, bases, dopants, condensable vapors and etc.[4,6] Although AMCs appear to be a minimal amount under normal circumstances, they are known to affect quality, yield and performance as a result of the refinement of semiconductors, LCDs, and electronic devices,[3-5] and efforts are being made to track down and eliminate sources of contamination by AMCs in many ways. The problems associated with contamination from outside air can be effectively managed with the installation of high-efficiency chemical filters at the make-up air and recirculation of air compartments. However condensable organic compounds deposited on silicon wafers may make the wafer surfaces hydrophobic, which may affect etching, wetting, cleaning, and other wafer-processing steps.[1] The organophosphorustriesters (OPE), which are present in polymers as flame retardants, may migrate in the plastic material and can be emitted to the surroundings. They are not chemically bound to the plastic polymer and can migrate from the plastics to the clean room

environment and finally on the wafer.[7,8,9-16] The diethyl phthalate (DEP) and dibutyl phthalate (DBP) from the wafer carrier break-down the gate oxide performance,[17] dioctyl phthalate (DOP) is known to continue to be absorbed by wafers at low concentrations.[7,18] Aromatic hydrocarbon compounds (AHCs) such as butylated hydroxytoluene (BHT), toluene and etc. have been reported to cause haze in photomask by 193 nm laser.[19,20] Desorption and adsorption constants of volatile organic compounds (VOCs) (acetone, ethylacetate, xylene and propyleneglycolmethyletheracetate (PGMEA)) and semi-volatile organic compounds (SVOCs) were compared.[21] Authors found that the desorption rates of VOCs are approximately 100 times higher than SVOCs desorption rates. The later implies that once the SVOCs deposit on the wafer surface, they hardly desorb and the contamination will remain on the wafer surface in contrary to the VOCs that will rapidly desorb from the surface of the wafer.[22] The Institute of Environmental Sciences and Technology (IEST) reported data on the measurement of organic volatile substances that can be generated from substances used to construct clean rooms and materials used herein.[1] Medium- and low-vapor pressure organic compounds tend to adsorb on critical surfaces, including hardware, wafers, and optics may potentially lead to processing problems.[1] An extensive list of contaminating chemicals that may be of concern to products manufactured or processes carried out in any cleanroom environment is reported in ISO 14644-8:2006 (E), Annex B.

Sampling and analysis of volatile and semi-volatile organic contaminants in air has been well established and standardized.[1,3,23-25] Gaseous-phase contaminants are easily extracted by sorption tubes packed with sorbents of either polymeric or carbonaceous materials, or a mixture thereof, to selectively retain compounds of different chemical natures such as hydrophobicity and polarity.[1,3,26-30] In the case of wafers, organic materials adsorbed on the surface are known to be swept with carrier gas while heating the wafer, secured with a sampling tube filled with absorbents, then desorbed by heat and analyzed it with GC-MS.[3,4] In most cases, the equipment is optimized for

capturing and analyzing trace amounts of volatile substances (10 ng to 100 ng). The most common method of measuring VOCs in a uniform solid sample is to use a commercially available headspace. Samples are cut into a dedicated glass chamber (10 or 20 mL), sealed, concentrated in dynamic mode or static mode at the desired temperature, and analyzed by GC-MS. In the case of samples with large sample volumes, chambers of various sizes (50, 250, 500, 1000 mL) that can accommodate them, are sold. However, in order to measure volatile matter in a sample larger than the container sold, it must be manufactured. For example, the pellicle is used to protect the surface of the photomask from air pollution, and the size of a typical pellicle is about $115 \times 140 \times 5$ mm and 1000 mL chamber cannot be used. In this case, in order to measure the volatile matter of the pellicle, a suitable container must be manufactured to measure the volatile matter. Previously, pellicle containing BHT produced particles that formed on the surface of the mask, resulting in a process problem.[19] A large sample produces more volatile matter than a small sample, which is more likely to contaminate the inside of the chamber. In the case of samples that release a large amount of SVOC at a temperature higher than room temperature (< 50 °C), it is important to effectively remove residual volatile substances inside the chamber. In the case of removing with high purity inert gas such as nitrogen or helium while heating the collection chamber to a high temperature (< 250 °C) to remove residual volatile substances in the chamber, cool the chamber to the collection temperature after the removal work and wait for thermal equilibrium to be reached. When the chamber size is large, it takes a lot of time to achieve thermal equilibrium. If the chamber is severely contaminated with excess volatile substances, removing residual volatiles with an inert gas is very inefficient. In the manual of some commercially available chambers, it is stated that if severely contaminated with SVOCs, it should be washed with soapy water.

Among the most popular products used in everyday life, cell phone cases were chosen to test volatile substances using the VC-P&T-GC-MS system. Cell phones are one of the most common home appliances in the daily life of modern people, and in most cases, they are covered with cases for the purpose of protecting expensive cell phones or for decoration purposes. There are various types of cell phones such as protective bumper type, bar-type, flip cover type, and diary type. Materials used include silicone, thermoplastic polyurethane, polycarbonate, aluminum, leather, fiber, and eco-friendly materials, and some adhesives, paints, and pigments are also used. Cell phone cases are sometimes used as a single material, but in many cases, various materials, adhesives, and road pigments are mixed, making them inhomogeneous. When using the case, it comes into contact with hands or the body, and volatile substances released from the case may enter the human body through the respiratory system or skin. As a result of checking the types of cell phone cases currently on the market with a search engine, there are more than 800,000 units, and a large amount of new cases are being developed each time a new cell phone model is sold.

In this study, to analyze large volatile samples, the collection chamber is manufactured and a pressure reducer is connected to remove residual VOCs that may exist inside the chamber. The chamber was combined with P&T to concentrate the VOCs of the sample and analyze it with GC-MS (VC-P&T-GC-MS). The reliability and reproducibility of the VC-P&T-GCMS device was tested using toluene, and the method of removing the residual volatile substances inside the container with helium gas is compared with the method of removing them with decompression. Using the VC-P&T-GC-MS device, volatile substances in six types of cell phone case were analyzed and BHT in some cell phone cases were detected and quantitatively analyzed. Volatile substances in specific cell phone case were analyzed with dynamic headspace and GC-MS and compared to those obtained by VC-P&T-GC-MS.

2. Experimental

2.1. Chemicals and reagents
The standard material used in the experiment, toluene (certified reference material, 5000 mg mL^{-1}

in methanol, Merck, Germany), methanol (HPLC ≥ 99.9 %, J.T. Baker, USA), butylated hydroxytoluene (BHT, analytical basis, Merck, Germany), Korean drinking water regulation VOC mixture A (KDWR VOC Mix A, methanol ampule each component 100 mg mL^{-1}, components are benzene, bromodichloromethane, bromoform, carbon tetrachloride, chloroform, dibromochloromethane, 1,1-dichloroethylene, dichloromethane, ethylbenzene, phenol, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, toluene, *m*-xylene, *o*-xylene and *p*-xylene) were purchased from Merck, Germany. The cell phone cases used in the experiment were purchased in the local market.

2.2. Device configuration of VC-P&T-GC-MS and operational procedure

The stainless steel cylindrical chamber (with an internal diameter of 205 mm and a height of 50 mm) manufactured and the vacuum level (($2 \pm 1) \times 10^{-2}$ mmHg) can be maintained if necessary by connecting the vacuum pump to the chamber. Chamber was placed in an oven (room temperature to 300 °C) for temperature control (*Fig.* 1), it was connected to P&T device (Tekmar 3000, Mason, Ohio, USA) using a 6-port valve 1 (*Fig.* 2). The analysis specimen was
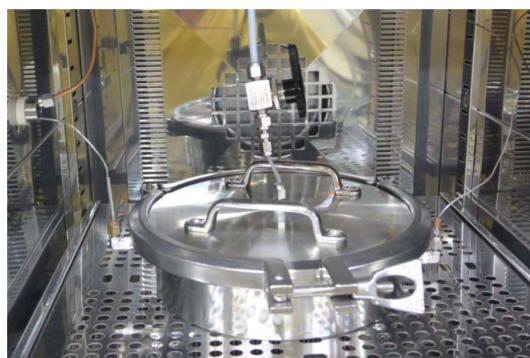

Fig. 1. Vacuum chamber manufactured in this study for decompression and nitrogen filling.

put in the chamber, concentrated the volatile substance in the trap of P&T, desorbed by heat, and analyzed with GC-MS (VC-P&T-GC-MS). The analysis conditions of typical P&T are summarized in *Table* 1 and the detailed sequence of operation is as follows. First, the chamber was put in an oven and heated to the temperature to be analyzed for 3 hours or more in order to stabilize the temperature of the chamber. Then the sample was put in the chamber and the lid was closed and it is sealed using the quick release V-clamp. The liquid sample was designed to be injected into the chamber using micro syringe. Second, helium gas was supplied to the chamber using 6-port valve
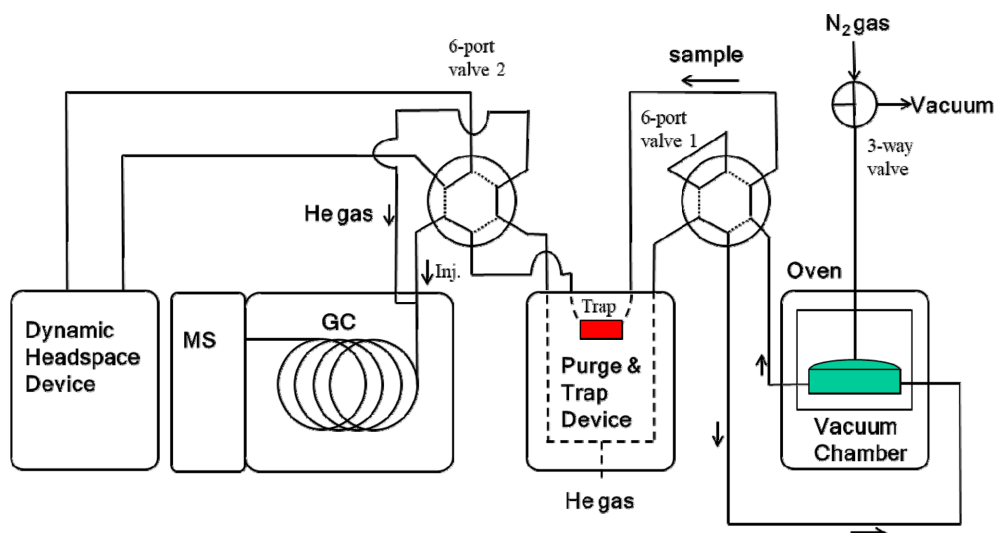

Fig. 2. Schematic diagram of the VOCs analysis system composed of vacuum chamber, purge & trap, GC-MS and dynamic headspace device.

and volatile substances were collected from samples in the chamber into P&T (*Fig.* 2). Third, the volatile substances collected in the trap were analyzed with GC-MS after thermal desorption. Fourth, after thermal desorption, 6-port valve was adjusted to block the connection between the chamber and the P&T, the samples was taken out in the chamber, and residual volatile substances was removed using the decompression ($(2 \pm 1) \times 10^{-2}$ mmHg) line connected to the chamber. Any volatile substances that can remain in the trap were removed using a Tekmar 3000 device, filled a decompression-conditioned chamber with nitrogen using a 3-way valve, and the next experiment was conducted.

2.3. Reliability and reproducibility of VC-P&T-GC-MS device by toluene

To determine linearity of VC-P&T-GC-MS system, the working solutions containing 5, 10, 30, 50, 100 mg mL^{-1} of toluene were prepared by diluting the 5,000 mg mL^{-1} with methanol. The working solutions were kept at -20 °C until use. The working solution (1 mL) was injected into the chamber, concentrated in the P&T trap using 3,300 mL of helium at 50 °C, analyzed with GC-MS. Using the peak area for concentrations of 5-100 μg mL^{-1}, the calibration curve was prepared and linearity was analyzed, and the correlation coefficient R^2 was obtained. Using ratio of peak areas obtained by the VC-P&T-GC-MS method (the swept volume of He was 3,300 mL at 50 °C) and by the direct injection for concentrations of 5-100 μg mL^{-1}, the recovery yield was calculated. All measurements were performed at least three times.

2.4. Removal of residual VOCs inside chamber

Performance of the analytical system should be checked to confirm that blanks of VC-P&T-GC-MS system are are clean down to a cleanliness level equivalent to the reporting limit level for the method. In particular, when a sample that emits a lot of volatile substances or a high boiling point volatile substance is concentrated using a chamber, the residual volatile substances must be sufficiently removed and the following analysis should be performed. The

method of using helium and the method of using reduced pressure as a method of removing residual volatile substances present in the chamber are compared below. KDWR VOC Mix A (5 mL of 100 mg mL^{-1}) was selected as a VOC specimen for testing memory effect removal efficiency using VC-P&T-GC-MS device, and BHT (1 mg of BHT applied on the PC (polycarbonate) plate was selected as a SVOC sample.

2.4.1. Removal of residual KDWR VOC Mix A by helium

KDWR VOC Mix A (5 mL of 100 mg mL^{-1}) was injected into the chamber, concentrated in the P&T trap using 1,650 mL of helium at 50 °C, analyzed with GC-MS. After GC-MS analysis, KDWR VOC Mix A remaining in the chamber was concentrated with 1,650 mL of helium at 50 °C and analyzed by GC-MS again. The P&T conditions are set out in *Table* 1 and this experiment were repeated to determine the number of sweep volume in which the residual concentration was less than 0.1 % of the concentration of the KDWR VOC Mix A injected.

2.4.2. Removal of residual KDWR VOC Mix A by reduced pressure

KDWR VOC Mix A (5 mL of 100 mg mL^{-1}) was injected into the chamber, concentrated in the P&T trap using 1,650 mL of helium at 50 °C, analyzed with GC-MS. After thermal desorption, remove residual volatile substances using the decompression ($(2 \pm 1) \times 10^{-2}$ mmHg) line connected to the chamber for the time of GC-MS analysis. The P&T conditions

Table 1. P&T conditions of VC-P&T-GC-MS method at 50 °C chamber temperature.

Purge & trap	Tekmar 3000 (Teledyne Tekmar)
Trap absorbent	Carbopack B/Carboxen 1000/ Carboxen 1001
Chamber temp.	50 °C
Transfer line temp.	150 °C
Valve temp. oven	140 °C
Desorption temp.	230 °C
Desorption time	3 min
Trap bake temp.	260 °C
Trap bake time	10 min

Table 2. P&T conditions of VC-P&T-GC-MS method at 100 ℃ chamber temperature

Purge & trap	Tekmar 3000 (Teledyne Tekmar)
Trap absorbent	Carbopack B/Carboxen 1000/ Carboxen 1001
Chamber temp.	100 ℃
Transfer line temp.	200 ℃
Valve temp. oven	190 ℃
Desorption temp.	230 ℃
Desorption time	3 min
Trap bake temp.	260 ℃
Trap bake time	10 min

are set out in *Table* 1. After GC-MS analysis, KDWR VOC Mix A remaining in the chamber was concentrated with 1,650 mL of helium at 50 °C again and analyzed by GC-MS.

2.4.3. Volatile substance inspection of PC (polycarbonate) plate

PC plate (3 cm × 3 cm × 0.3 cm) was put in the chamber and volatiles were concentrated in the P&T trap (3,300 mL of helium at 100 °C) and analyzed with GC-MS after thermal desorption. The P&T conditions are set out in *Table* 2.

2.4.4. Removal of residual BHT on PC plate by helium

The stock solution of BHT was prepared at a concentration of 2,000 μg mL^{-1} (methanol). The working solutions containing 500 mg mL^{-1} of BHT were prepared by diluting stock solution. The working solution of 2 mL was spiked on the PC plate (3 cm × 3 cm × 0.3 cm), methanol was removed by volatilization at room temperature and BHT was fixed to the plate surface. After putting the PC case in the chamber, volatiles were concentrated in the P&T trap (1,650 mL of helium at 50 °C), analyzed with GC-MS after thermal desorption. After thermal desorption, the PC plate was removed and the lid of the chamber was closed, remaining BHT in the chamber was concentrated with 1,650 mL of helium at 50 °C and analyzed by GC-MS again. These experiments were repeated to determine the sweep volumes of helium in which the residual BHT amount is less than 0.1 % of the initially

applied amount of BHT. The P&T conditions are set out in *Table* 1.

2.4.5. Removal of residual BHT on PC plate by reduced pressure

The working solution (2 mL of 500 mg mL^{-1} of BHT) prepared in the above section was spiked on PC plate (3 cm × 3 cm × 0.3 cm), methanol was removed by volatilization at room temperature and BHT was fixed to the PC plate surface. After putting the PC case in the chamber, volatiles were concentrated in the P&T trap (1,650 mL of helium at 50 °C), analyzed with GC-MS after thermal desorption. After thermal desorption, the PC plate was removed and the lid of the chamber was closed, remaining BHT in the chamber was removed using decompression ($(2 \pm 1) \times 10^{-2}$ mmHg) during GC-MS analysis. The P&T conditions are set out in *Table* 1.

2.5. Volatile analysis of cell phone by VC-P&T-GC-MS method

2.5.1. Volatile analysis of cell phone

The weight of the cell phone case was measured and placed in a chamber preheated to 50 °C and volatiles of the case were concentrated on P&T trap using 1,650 mL of helium and analyzed with GC-MS after thermal desorption. After thermal desorption, the chamber was isolated from P&T and cell phone case was taken out in the chamber and residual volatile substances were removed by the decompression ($(2 \pm 1) \times 10^{-2}$ mmHg) during GC-MS analysis. The P&T conditions are set out in *Table* 1. All measurements were performed at least three times.

2.5.2. Determination of BHT concentration of cell phone case

The stock solution of BHT was manufactured at a concentration of 2,000 μg mL^{-1} (methanol). To determine linearity, the working solutions containing 800, 920, 960 and 1,000 mg mL^{-1} of BHT were prepared by diluting the stock solution with methanol. The stock and working solutions were kept at -20 °C until use. The working solution (2 mL) was spiked on PC plate (3 cm × 3 cm × 0.3 cm), and methanol was

removed by volatilization at room temperature and BHT was fixed to the plate surface. After putting the PC case in the chamber, BHT was concentrated in the P&T trap (1,650 mL of helium at 50 °C), analyzed with GC-MS after thermal desorption. The P&T conditions are set out in *Table* 1. Using the peak area for these, the calibration curve was prepared and linearity was analyzed, and the correlation coefficient R^2 was obtained. All measurements were performed at least three times.

2.6. Methanol Soxhlet extraction of cell phone *case A*

Among the cases in which BHT was detected, *case A*, which had a simple distribution of volatile substances, was selected. Small pieces of *case A* of 2.06 g (approximate size: 5 mm × 1 mm × 1 mm) and methanol (160 mL) were added to the Soxhlet apparatus and extracted for 8 hours. The methanol extracts were moved into a flask (200 mL) and methanol was added to make 200 mL. The solution (2 mL) was injected to GC-MS and all measurements were performed at least three times.

2.7. Determination of BHT concentration of Soxhlet extract of *case A*

The stock solution of BHT for Soxhlet methanol extract was prepared at a concentration of 2,000 mg mL^{-1} in methanol. To determine linearity, the working solutions containing 1.0, 1.6, 2.0 and 3.0 mg mL^{-1} of BHT were prepared by diluting the stock solution (2,000 mg mL^{-1}) with methanol. The stock and working solutions were kept at -20 °C until use. The working solution (2 mL) was injected to GC-MS. Using the peak area for these, the calibration curve was prepared and linearity was analyzed, and the correlation coefficient R^2 was obtained. All measurements were performed at least three times.

2.8. Volatile Analysis of cell phone *case A* by dynamic headspace

2.8.1 Volatile analysis of cell phone *case A* at 50 °C and 75 °C

The cell phone *case A* was cut into about 1 cm × 2 cm in size, weighed (2.54 g), placed in a vial (20 mL), volatiles were concentrated with 1,650 mL of helium at 50 °C using HT3 (dynamic headspace, Teledyne Tekmar), analyzed with GC-MS after thermal desorption (HT3-50D). The HT3-50D conditions are set out in *Table* 3. The cell phone case was cut to about 1 cm × 2 cm in size, measured weight (0.254 g), put it in vial (20 mL), swept 400 mL of helium at 75 °C, concentrated, and desorbed with heat, and analyzed with GC-MS (HT3-75D). The conditions of HT3-75D are shown in *Table* 4. All measurements were performed at least three times.

2.8.2. Determination of BHT concentration of cell phone *case A*

To determine linearity, the working solutions containing 80, 120, 160 and 200 mg mL^{-1} of BHT were prepared by diluting the stock solution (2,000 mg mL^{-1}) with methanol. The stock and working

Table 3. Conditions of concentrating volatile substances in *case A* (2.54 g) using 1,650 mL of helium at 50 °C by HT3 (HT3-50D)

Dynamic head space	HT3-50D (Teledyne Tekmar)
Trap absorbent	Tenax, Silica Gel, Charcoal
Platen/sample temp.	50 °C
Transfer line temp.	150 °C
Valve oven temp.	140 °C
Desorb temp.	225 °C
Desorption time	3 min
Trap bake temp.	230 °C
Trap bake flow	450 mL min^{-1}
Trap bake Time	10 min

Table 4. Conditions of concentrating volatile substances in *case A* (0.254 g) using 400 mL of helium at 75 °C by HT3 (HT3-75D)

Dynamic head space	HT3-75D (Teledyne Tekmar)
Trap absorbent	Tenax, silica gel, charcoal
Platen/sample temp.	75 °C
Transfer line temp	175 °C
Valve oven temp.	165 °C
Desorb temp.	225 °C
Desorption time	3 min
Trap bake temp.	230 °C
Trap bake flow	450 mL min^{-1}
Trap bake Time	10 min

solutions were kept at -20 °C until use. The working solution (2 mL) was spiked on PC plate (3 cm × 1 cm × 0.3 cm), and methanol was removed by volatilization at room temperature and BHT was fixed to the plate surface. After putting the PC case in the 20 mL vial, volatiles were concentrated with 400 mL of helium at 75 °C using HT3, analyzed with GC-MS after thermal desorption. The HT3 conditions are set out in *Table* 4. Little volatiles in the PC plate had been detected when measured using HT3-75D-GCMS method. Using the peak area for these solutions, the calibration curve was prepared and linearity was analyzed, and the correlation coefficient R^2 was obtained. All measurements were performed at least three times.

2.9. GC-MS

The experimental conditions of GC-MS used in the above experiments are summarized in *Table* 5 and the component analysis in the TIC (total ion chromatogram) was determined by comparing the mass spectrum data of the GC-MS library (Wiley7Nist05) with the reported data.

3. Results and Discussion

3.1. Reliability and reproducibility of VC-P&T-GC-MS system

The reliability and reproducibility of the VC-P&T-GC-MS system were confirmed by using toluene. Toluene is widely used in daily life, including paints

Table 5. Conditions of GC-MS

Gas Chromatograph	Agilent 7890A
Column Temp.	45 °C for 2 min 5 °C min^{-1} to 80 °C for 1 min 12 °C min^{-1} to 300 °C for 5 min
Column	HP-5MSI (30 m × 0.25 mm × 0.25 μm film thickness) Split ratio: 1 : 10
Mass Spectrometer Ion source temp. Injector temp. Scan range	Agilent 5975C 230 °C 250 °C m/z 45 - 550

and adhesives[31] and is used to prepare a calibration curve when quantifying total volatile organic substances.[32-34] A standard toluene methanol solution was injected into the chamber, and analyzed by GC-MS and a calibration curve was prepared. Linearity (y = 55834x − 60797, R^2 = 0.9993) was shown in this concentration range, toluene recovery was 85 ± 2 %, which was calculated based on the area of toluene injected with the working solution into GC-MS. Reproducibility was 5 ± 2 %, and the detection limit was 0.01 ng L^{-1}. The proposed device was able to reproducibly analyze 5-100 ng of toluene.

3.2. Removal of residual VOCs in chamber

3.2.1. Removal of residual KDWR VOC Mix A by helium and reduced pressure

The experimental conditions were described at Experimental section 2.4.1 and 2.4.2. KDWR VOC Mix A was injected into the chamber and the volatile substances trapped in the P&T were analyzed with GC-MS. This experiment was repeated 9 times to indicate the volume of helium gas used on the horizontal axis, and the area of dibromochloromethane, tetrachloroethylene, ethylbenzene, tribromomethane, and 1,2-dimethlbenzene in KDWR VOC Mix A on the vertical axis (*Fig.* 3). As shown in the *Fig.* 3, 1,2-dimethylbenzene is removed the fastest, and tetrachloroethylene is removed most slowly. The concentrations of dibromochloromethane, ethylbenzene,
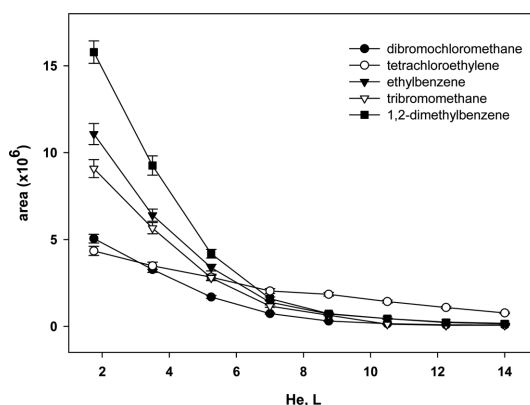

Fig. 3. Residual fractions of dibromochloromethane, tetrachloroethylene, ethylbenzene, tribromomethane and 1,2-dimethylbenzene by VC-P&T-GC-MS.

tribromomethane, and 1,2-dimethlbenzene seemed to decrease almost exponentially, while that of tetrachloroethylene appeared to decrease linearly, which seems to interact and remain more time with our lab-made chamber apparatus. In order for the residual concentration to be less than 0.1 % of the injected KDWR VOC Mix A concentration, 14,850 mL of helium (9 times the volume of the chamber) was required. To measure the memory effect by decompression under the same conditions, KDWR VOC Mix A was injected into the chamber and the materials trapped in the P&T were analyzed with GC-MS. After GC-MS analysis, KDWR VOC Mix A remaining in the chamber were removed for 35 minutes (GC-MS operating time) using reduced pressure $((2 \pm 1) \times 10^{-2}$ mmHg). After this, the residual KDWR VOC Mix A were concentrated with 1,650 mL of helium and analyzed by GC-MS. As a result, the concentrations of KDWR VOC Mix A were less than 0.1 % of the initial concentrations.

Therefore, the method of removing residual KDWR VOC Mix A by reduced pressure does not use expensive helium and it saves time because residual KDWR VOC Mix A can be removed during the operation time of GC-MS.

3.2.2. Removal of residual BHT by helium and reduced pressure

When using a chamber to measure volatile substances of plastic materials containing BHT, memory effect should be checked before next sample. For these samples, the PC plate and working solution of the BHT were used to measure the residual BHT concentration inside the chamber (see Experimental 2.4.3, 2.4.4 and 2.4.5). As a result of testing PC plate with VC-P&T-GC-MS system (3,330 mL of helium at 100 ºC), no volatile substances were detected. When removing residual BHT with helium using PC plate coated with BHT (1 mg) as above, in order for the residual amount of BHT to be less than 0.1 % of the applied BHT amount, 11,550 mL of helium (7 times the volume of the chamber) was required. However, in case of removing residual BHT using decompression, removing residual BHT by decompression

during GC-MS operation time, the residual BHT could be kept below 0.1 %. Therefore, the method of removing BHT (1 mg) on PC plate by decompression is an economical method because it does not use expensive helium, and it is considered as an efficient method for it can reduce the analysis time.

3.3. Cell phone case volatile analysis by VC-P&T-GC-MS

Among the cases on sale, six types of cellular phone case are randomly selected and the volatile materials were measured by the VC-P&T-GC-MS method. It revealed that BHT was detected in four types of case and volatile substances were hardly detected in two types of case. During the GC-MS operation time, the residual VOC in the chamber could be effectively removed using decompression, and little residual volatile substances were detected after decompression. *Case A* was selected and compared with the VC-P&T-GC-MS method and volatile substances concentrated by dynamic headspace. In addition, the BHT concentration in *case A* was measured in three different methods (VC-P&T method, Sohxlet extraction method, and dynamic headspace method) and the results were compared. *Case A* (weight = 21.0 g) was placed in a chamber, volatile substances were concentrated using helium at 50 °C, and then analyzed by GC-MS. For applications that are mainly used at room temperature (25 °C), it is desirable to set the outgassing temperature at 50 °C, and this is due to the suggestion that analysis can be performed at higher temperatures if necessary.[1] In the TIC obtained by the VC-P&T-GC-MS method, phenol, *N*-methylaniline, benzothiazole, 2,4,5-trimethyl benzaldehyde and BHT were detected as major substances (*Fig*. 4). As a result of analyzing four more of *cases A* under the same conditions, five volatile substances including BHT were detected as shown above, and the variations in peak areas of GC-MS were within ± 5.4 %. BHT is a material with a vapor pressure of 0.01 mmHg (20 ºC), and BHT has a tendency to decrease in use in recent years due to controversy over health risks.[35-38] In order to determine the BHT concentration of the case, a PC plate was used (see Experimental 2.4.3 and 2.5.2).
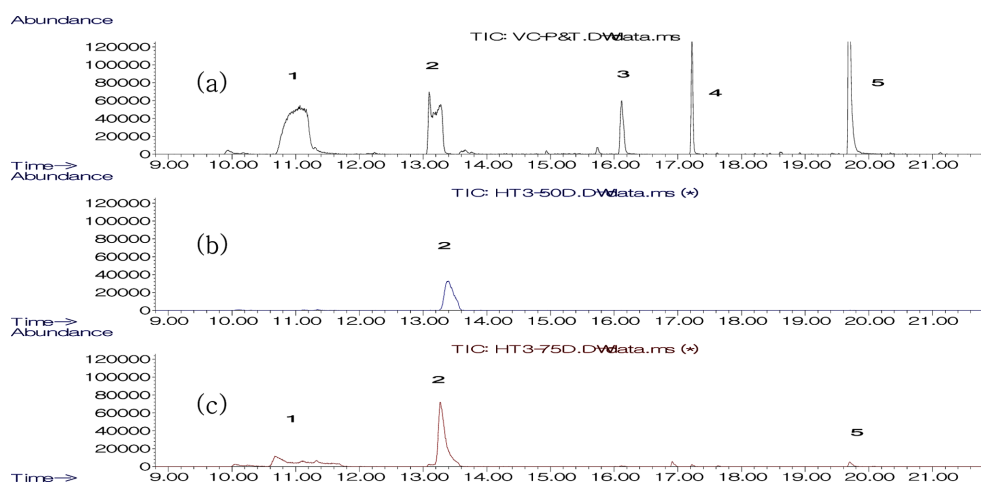
Fig. 4. Total ion chromatograms of different collection methods analyzed with GC-MS. (a) cell phone cases by VC-P&T (b) by HT3-50D (c) by HT3-75D; 1: phenol, 2: *N*-methylaniline, 3: benzothiazole, 4: 2,4,5-trimethyl benzaldehyde, 5: butylated hydroxytoluene (BHT).

Linearity (y = 8576x − 4557650, R^2 = 0.9913) was shown in the above narrow BHT concentration range. Using this, the BHT concentration in *case A* was measured as 0.091 (± 0.002) mg kg^{-1} and the BHT concentration in the other three types of case was in the range of 0.091-0.12 mg kg^{-1}. In general, BHT is known to be added to the resin at a level of about 0.05 to 1.0 (w/w)%, and there was a large difference from the BHT concentration of the case measured by the VC-P&T-GC-MS method. The recovery yield of BHT of *case A* obtained by the VC-P&T-GC-MS method was measured as follows using the methanol extract of the case separated by a Soxhlet apparatus (see 2.6 and 2.7). Linearity (y = 144146x + 26027, R^2 = 0.9935) was shown and the BHT concentration of *case A* methanol solution obtained by means of Soxhlet apparatus was 191 ± 6 mg kg^{-1}. Based on the BHT concentration obtained using the Soxhlet device, the BHT recovery rate of VC-P&T-GCMS was about 0.05 %. As a result of visual observation of the *case A* fragment after the Soxhlet experiment, it was not dissolved at all in methanol and was not swelled. This means that when extracting BHT using the Soxhlet device, only the BHT close to the surface of the case is dissolved and also that the concentration of BHT contained in *case A* may be higher than

191 ± 6 mg kg^{-1}. BHT concentration of *case A* was analyzed under the same conditions after 6 months, 9 months and 18 months at room temperature by method of VC-P&T-GCMS. The BHT concentration decreased only slightly 0.085 (± 0.002), 0.080 (± 0.002) and 0.071 (± 0.003) mg kg^{-1}, respectively and the physical properties of the case were not significantly different from observation with the naked eye. This is because BHT is gradually outgassed from the case surface and its concentration decreases, but it is judged that the physical properties are maintained by BHT acting as an antioxidant inside, and further research is needed on this part.

3.4. Volatile analysis of cell phone *case A* by dynamic headspace

The piece of *case A* was placed in a vial, and volatile substances were concentrated in a dynamic headspace and analyzed by GC-MS (HT3-50D method, see Experimental 2.8). Only *N*-methylaniline peak was detected, and no BHT peak was detected (*Fig.* 4). In order to quantify the BHT of *case A* with HT3, it was confirmed that the weight of the case should be 0.254 g or more, the sweep temperature should be at least 75 °C, and the sweep volume of helium should be 400 mL or more (*Fig.* 4, HT3-

75D). In the TIC of GC-MS analyzed by HT3-75D method, phenol and *N*-methylaniline were detected in addition to BHT. The BHT concentration was measured using a PC plate and BHT working solutios (see Experimental 2.8). Linearity (y = 1452x − 61999, R^2 = 0.9937) was shown in the range and using this, the BHT concentration in *case A* was measured as 0.82 (± 0.005) mg kg^{-1}. For the same *case A*, the results of measuring BHT concentration by VC-P&T, HT3-50D, HT3-75D and Soxhlet extraction method are summarized in *Table* 6. It is natural that the BHT concentration obtained by extracting BHT using a Soxhlet apparatus at the boiling point of methanol and injecting it directly into GC-MS is the largest. The value determined by concentrating the BHT concentration of *case* A by VC-P&T (21.0 g, 50 °C, 1,650 mL) method was 0.091 mg ± 0.002 mg kg^{-1}. However, BHT was not detected when concentrated by HT3-50D (2.54 g, 50 °C, 1,650 mL) method. To quantitatively analyze case A's BHT using HT3, the heating temperature of the case should be heated to 75 °C. These two methods (VC & PT and HT3-50D) have the same conditions for concentrating at 50 °C, but not only the concentrating device but also the weight of the sample, the volume of the chamber, and the volume of helium used to be concentrated are different, making it difficult to simply compare the analysis results. However, considering the chamber volume ratio (82.5 times larger in VC-P&T-GC-MS) and the sample weight ratio (8.25 times larger in VC-P&T) used in the two collection methods, it is judged that the VC-P&T-GC-MS method can more efficiently collect volatile substances than the HT3-50D method. In this study, volatile substances were tested using VC-P&T-GC-MS system and dynamic headspace for just six types of cell phone cases, and the volatile material test will be conducted on various types of cases in the future.

4. Conclusions

In order to measure the volatile organic compounds of a large sample, a stainless steel chamber was constructed and a decompression device was connected to remove residual volatile material in the chamber. A P&T was connected to concentrate volatile substances in a chamber, and the collected substances were configured to be analyzed by GC-MS (VC-P&T-GC-MS). Removal of residual KDWR VOC Mix A (5 mL of 100 mg mL^{-1}), BHT (1 mg) on PC plate and VOCs of some cellular cases inside of chamber were examined by method of washing helium or by using decompression. The VT-P&T system is a method of removing residual volatile substances inside the chamber by decompression at the collection temperature during the GC-MS operation time, reducing gas consumption and time, so it can be operated economically and efficiently. Volatile substances in six types of cell phone case were tested using VC-P&T-GC-MS system, and BHT was detected in some cases and quantitatively analyzed, and compared with the results of dynamic headspace analysis. It is difficult to compare the results simply because the analysis conditions are different, however, considering the chamber volume ratio (82.5 times) and the sample weight ratio (8.25 times) used in the two collection methods, it is judged that the VC-P&T method can more efficiently collect volatile substances than the

Table 6. BHT concentration of *case A* according to the method of VC-P&T, HT3-50D, HT3-75D and Soxhlet

Method	Case used, g	Temperature, °C	Chamber Volume, mL	Sweep volume, mL	BHT concentration, mg kg^{-1}
VC-P&T	21.0	50 °C	1,650	1,650	0.091 ± 0.002
HT3-50D	2.54	50 °C	20	1,650	ND[*]
HT3-75D	0.254	75 °C	20	400	0.82 ± 0.005
Soxhlet	2.06	64.7 °C[**]	-	-	191 ± 6

[*]: not detected
[**]: boiling point of methanol

HT3-50D method.

In the future, we plan to study and report on memory effect elimination studies for SVOC with high boiling point such diethyl phthalate and so on. It is expected to be useful for VOCs and SVOCs measurement of materials or devices used inside the clean room.

Acknowledgements

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