

## 9.8 Methods of Analyzing Toxic Airborne Compounds (Volatile Organic Compounds)

### 9.8.1 Introduction

Volatile organic compounds are separated into aldehydes and benzene and chlorine-based hydrocarbons (hereinafter called VOCs), depending on their collection method. Moreover, I would like to refer to particulate matter concerning metallic toxic substances.

### 9.8.2 Methods of analyzing benzene and other volatile organic compounds (VOCs)<sup>1)-3)</sup>

#### (1) Sample collection

Generally, following electrolytic polishing of the inside, the specimen is collected (see Fig.9.8.1) using a system container (canister) that employs a special inert processing to create an even purer thin chrome/nickel oxidant membrane. In addition, there is also the solid absorption and solvent extraction method<sup>4)</sup>.

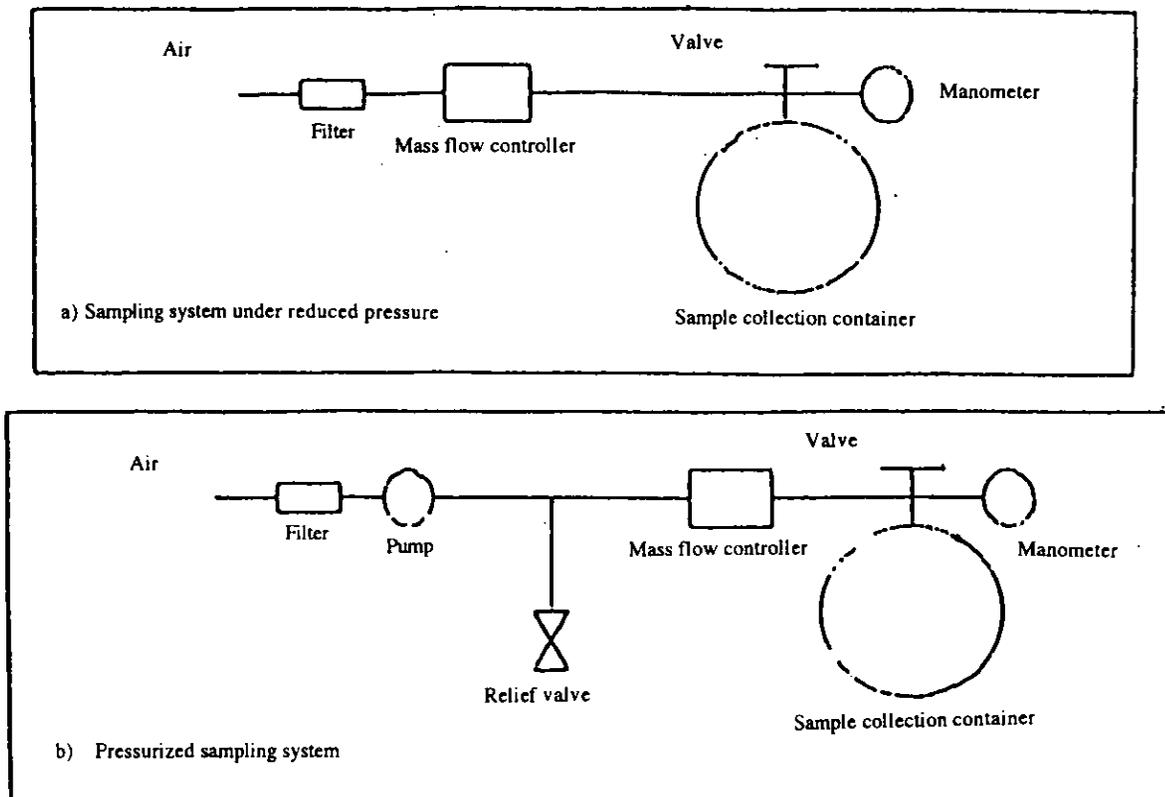


Fig.9.8.1 Overview of the sample collection container<sup>3)</sup>

#### ① Subatmospheric pressure sampling method (Standard atmospheric pressure collection method)

The tip of the sample collection container is connected to the sample collection equipment. The sample

collection container valve is opened, and collection begins to a previously determined flow volume, then after 24 hours the valve is closed and the tip of the sample collection container is stoppered. The sample collection start time, finishing time, and the pressure within the sample collection container are all recorded.

② Pressurized sampling system

The tip of the sample collection container is connected to the sample collection equipment. The valve is opened while the sample collection equipment pump is running, and collection begins to a previously determined flow volume, then after 24 hours the valve is closed and the tip of the sample collection container is stoppered. The sample collection start time, finishing time, and the pressure within the sample collection container are all recorded.

(2) Analysis operation

① The GC/MS analysis conditions are set and the equipment is adjusted.

The GC/MS analysis conditions are set as appropriate with reference to the following items:

- Column used : Methyl silicon uncovered capillary column  
Internal diameter 0.25 mm, length 60 m, membrane thickness 0.25  $\mu$  m
- Column temperature : 40°C (kept for 5 mins.)  $\rightarrow$  4°C/min  $\rightarrow$  140°C
- Interface temperature : 220°C
- Carrier gas : Helium 1 to 3 ml/min
- Ion source temperature : 200°C
- Ionization voltage : 70 eV
- Detection method : SIM or scan

Either PFTBA (Perfluorotri-n-butyl amine) or PFK (Perfluoro kerosine) is introduced to MS as a control substance for calibrating the volume, and using the subatmospheric, specific values are calibrated such as mass balance and analysis function (one unit of volume or more is taken to be in the range of volume (m/z) = 18 to 300), depending on the measurement objectives. The measurement results following calibration are also stored.

② Test concentration

If collecting is done using the sampling system under reduced sub atmospheric pressure, pressure is added to the sample collection container until it reaches approximately 200 kPa ( $1.5 \times 10^3$  mmHg), and the pressure  $P$  (kPa) within the sample collection container is read accurately. The dilution rate ( $n$ ) caused by the additional pressure is given by Eq. (1).

$$(n) = \frac{P}{p} \dots\dots\dots (1)$$

Here,  $p$  is the pressure (kPa) in the container following collection.

Specimens collected using either added pressure with zero gas following sampling system under reduced pressure or specimens collected using the pressurized sampling system are concentrated by a fixed flow of sample during dehumidification, with the sample collection container collected to the sample introduction equipment. Control of the flow volume is done using a mass flow controller, and concentration is completed in a fixed amount

of time. At this juncture, a fixed volume of control gas, the same as for when the calibration curve was compiled, is also concentrated within the concentrator.

The concentrator is heated (the adsorption concentration tubes are heated for one minute to 250°C, and the low temperature concentration tubes are heated to 90°C), and the target measurement substance is removed, and reconcentrated in the cooled cryofocusing trap using liquid nitrogen.

### ③ Sample introduction

In equipment which uses an air tube as a cryofocuser, the air tube is heated for a fixed period and the VOCs removed, an analysis column is introduced, and the GC temperature program is started.

The column tank is cooled, and analysis is started using equipment to cool the tip of the analysis column, by starting the GC column tank temperature increase program.

### ④ SIM method

- The measured flow volume (see Table 9.8.1 for reference examples) is set for each target measurement substance.
- The chromatogram is recorded to both confirm quantitative mass fragment and fix characteristic mass fragment for each of the target measurement substances that were set in a), and a comparison between the two is sought.
- The peak surface area or peak height of the target measurement items detected, and either the peak surface area or peak height of the internal standard are measured, a comparison between the two is sought and, using the previously compiled ⑥, the volume of the target measurement substances in the specimen (As: ng) is determined.

Table 9.8.1 Volume for measuring GC/MS in VOCs

Compound	Primary key Ion	Secondary Key Ion
Acrylnitril	52	53
Vinyl chloride monomer	62	64
Dichloromethane	84	86, 49
1, 2-Dichloromethane	62	64
Tetrachloroethylene	166	164, 129
Trichloroethylene	130	132, 95
Benzene	78	77
1, 3-Butadiene	54	53, 51
internal standard	98	
Toluene d8	96, 70	
Fluorobenzene	117	
Chlorobenzene d5		

### ⑤ Scan method

- Set the measurement parameters.
- Record a total ion chromatogram (TIC) for the conditions set in a).
- Either the peak surface area or the height corresponding to both the internal standard and each target measurement substance on the TIC are determined. Either the peak surface area or the height is compared for both the internal standard and each target measurement substance and, using the calibration curve compiled in advance by the ⑥, the volume of each target measurement substance in the sample (As: ng) is determined.

⑥ Compiling the calibration curve

- a) After directly introducing a fixed volume of both the mixed control gas and the control gas to the condenser on the sample introducer, an operation is conducted from ② to either ④ or ⑤, and the chromatograph for each target measurement substance is recorded. The volume of the mixed control gas introduced is made to correspond with the volume range, and changed to five or more stages (including zero), after which the above operation is repeated.
- b) The volume infused into the GC/MS for each target measurement substance from the mixed control gas that was used for the calibrations in a) select the midrange of the calibration curve, and both target ion and the secondary ion chromatograms are recorded for each target measurement substance. Using either the peak surface area or the peak height for each, a comparison of the strength is determined between the target ion and the secondary ion for each substance.
- c) The relative strength of either the peak surface area or the peak height for both the target ion and the secondary ion are determined for each target measurement substance at each of the concentrations, and the fact that they agree with the relative strengths of each target measurement substance as sought in b) is checked. The difference between the peak surface area or the peak height for both each target measurement substance and the internal standard is determined, and the calibration curve is compiled by comparing the volume of each target measurement substance and either the peak surface area or the peak height of each target measurement substance.

⑦ For the blank test, in accordance with ②, following the introduction of a humidified zero gas to the container, both the sample and the same quantity of humidified zero gas are concentrated by the concentrator, operations are performed from ② to either ④ or ⑤, and the blank value ( $A_b$ : ng) is measured.

(3) Calculating the concentration

From the results obtained in (2) in the preceding paragraph of ④ and either ⑤ or ⑦, the concentration of each target measurement substance within the sample is calculated using Eq. (2).

$$C = \frac{n(A_s - A_b)}{V \times \frac{293}{273 + t} \times \frac{P}{101.3}} \dots\dots\dots (2)$$

Here,

$C$  = Concentration of each airborne target measurement substance at 20°C ( $\mu$  g/m<sup>3</sup>)

$n$  = Dilution rate (in the case of reduced pressure collection)

$A_s$  = Volume of each target measurement substance in the sample gas determined by the calibration curve (ng)

$A_b$  = Volume of each target measurement substance in the blank gas determined by the calibration curve (ng)

$V$  = Sample gas volume supplied for analysis (ℓ)

$t$  = Temperature during sample analysis (°C)

$P$  = Air pressure during sample analysis (kPa)

### 9.8.3 Formaldehyde and acetaldehyde analysis methods <sup>1)-3)</sup>

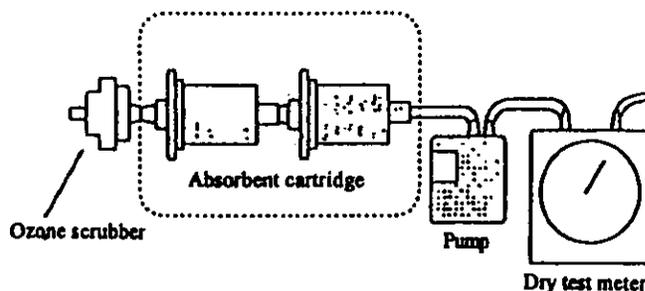
#### (1) Sample collection and sample solution adjustment

A fixed volume of about 1 mg of 2, 4-DNPH (2, 4-Dinitrophenyl hydrazine) is placed in a resin tube (internal diameter 10 mm, length 20 mm) and covered with 350 mg silica gel with particles of 50 to 250  $\mu$  m in diameter. This is then designated the specimen collection tube. In addition, in the case of a comparatively high concentration, the specimen is trapped in a 2, 4-DNPH solution and, following extraction with carbon tetrachloride, is subjected to either gas chromatography or the fixed volume method <sup>1) 2)</sup>.

##### ① Collection method

Fig.9.8.2 shows a typical collector. The absorbent cartridge tube and the ozone scrubber are both opened, and the ozone scrubber, absorbent cartridge, pump, and gas meter are connected, and collection is continued at 0.1  $\ell$ /min flow for 24 hours. After the sample has been collected, the absorbent cartridge is stoppered tightly.

The contents of the absorbent cartridge should be sent for extraction as fast as possible. The ozone scrubber should not be reused.



Source: Shimadzu catalogue No. G179

Fig.9.8.2 Sampling of aldehydes

##### ② Test solution adjustment

The absorbent cartridge is removed from the storage container and, following removal of the stoppers at both ends, the top end is connected to a solution syringe (10 ml) holding 5 ml of acetonitril, which is then passed gently into the absorbent cartridge at a flow rate of 1 ml/min, and subsequently allowed to flow into a (graded) full volume flask containing 5 ml of the aldehyde hydrozone conductor  $\ell$ .

The acetonitril is added to the end solution, brought into line with the standard curve for the full flask, stoppered tightly, and shaken well to mix it. This solution is then separated into two vials, and one vial is used as the HPLC (High Performance Liquid Chromatograph) test solution. The remaining vial is stored in a refrigerator until its analysis values can be checked.

③ For the blank test, the ② operation is carried out on a absorbent cartridge from the same lot, but in which no specimens have been collected, and the blank test solution is thereby adjusted.

#### (2) Test operation

① Set the HPLC analysis conditions and adjust the equipment.

The HPLC analysis conditions should be set appropriately with reference to the following:

Separation column : ODS, 5  $\mu$  m

4.6 mm  $\times$  50 mm + 4.6 mm  $\times$  250 mm

Mobile phase: Acetonitril: water/ 60 : 40

Flow volume: 1.0 ml/min.

Sample injection volume: 20  $\mu$  l

Column temperature: 40°C

Detector: UV (360 nm)

② Sample solution measurements

(1) ② Approximately 20  $\mu$  l of the sample solution, which was adjusted by ② in (1), is extracted using a microsyringe, infused into the HPLC, and its chromatogram recorded, and either the peak surface area or the peak height is determined for the FA-2, 4-DNPHz, and AA-2, 4-DNPHz sustainable peak period.

Using either the peak surface area or the peak height for the FA-2, 4-DNPHz, and AA-2, 4-DNPHz, the substance volume ( $A_s$ ; ng), which was converted as formaldehyde and acetaldehyde from the calibration curve that was compiled earlier, is determined.

③ Compiling the calibration curve

- a) 0 to 2 ml of the prototype control solution mix (each 10  $\mu$  g/ml) of formaldehyde and acetaldehyde are removed in steps to a total container flask (10 ml), adjusted to a fixed volume using acetonitril, and the control series for compiling the calibration curve is compiled. The control series has five stages, including zero.
- b) The ② operation is carried out, and either the peak surface area or peak height is determined equivalent for both the formaldehyde and the acetaldehyde.
- c) The calibration curve is then compiled from the peak surface area or peak height and the flow volume (ng) for both the formaldehyde and the acetaldehyde.

④ The blank test solution is infused into the HPLC, the ② operation is carried out, and the blank value ( $A_b$ ; ng) is determined.

⑤ As for the fluctuation sensitivity test, a control solution close to the middle of the calibration curve is infused into the HPLC, and the ② operation is carried out. This operation is carried out at least once for every 10 sample measurements.

(3) Calculating the concentration

The concentration of each airborne target measurement substance is calculated using Eq. (3) from the ② and

④ Obtained in (2).

$$C = \frac{(A_s - A_b) \times E \times 1,000}{V \times V \times \frac{293}{273 + t} \times \frac{P}{101.3}} \dots \dots \dots (3)$$

Here,

$C$  = Concentration of for maldehyde and acetaldehyde the atmosphere at 20°C ( $\mu \text{ g/m}^3$ )

$A_s$  = Volume of each target measurement substance in the sample solution determined by the calibration curve (ng)

$A_b$  = Volume of each target measurement substance in the blank solution determined by the calibration curve (ng)

$E$  = Test solution volume (mℓ)

$V$  = Solution volume infused into HPLC ( $\mu \text{ ℓ}$ )

$V$  = Absorbed air volume measured by the gas meter ( $\text{ℓ}$ )

$t$  = Mean air temperature during sample collection (°C)

$P$  = Mean atmospheric pressure during sample collection (kPa)