Study on the quantitative evaluation method of SVOC in a vehicle cabin using the passive method

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Abstract

In order to lower vehicle interior VOC concentration, Japan Automobile Manufacturers Association (JAMA) is announced self-imposed control of vehicle interior VOC concentration. Although high boiling point substances, such as phthalate ester, are contained in the substances for self-imposed control, these quantity boiling point substances are difficult to measure with sufficient accuracy in the collection by the conventional tube (Tenax-TA). In this research, we studied the plate material suitable for adsorbing SVOC. Solvent extraction method was found to be suitable for desorption method of SVOC adsorbed on plate. Quartz plate was the best for SVOC adsorption performance on plate and desorption performance of SVOC adsorbed on plate. In the actual vehicle measurement, DOA and DEHP were able to detect more efficiently than conventional active sampling.

Keywords: SVOC, VOC, passive sampling, active sampling

1. Introduction

In February 2005, operating from the viewpoint that the interior of the passenger compartment of an automobile is part of a person’s living space and using the same approach concerning chemical substances in the air as that used for housing, the Japan Automobile Manufacturers Association announced a self-imposed goal of reducing the concentrations of volatile organic compounds (VOCs) in the passenger compartment of passenger cars1. The objective of this voluntary initiative is to reduce the concentrations of indoor VOCs while satisfying the vehicle interior concentration guidelines established for nine substances (formaldehyde, acetaldehyde, toluene, xylene, ethylbenzene, styrene, tetradecane, di-n-butylphthalate (DBP), and di-2-ethylhexyl phthalate (DEHP)) by the Ministry of Health, Labor and Welfare for new vehicle models produced in 2007. p-Dichlorobenzene (p-DCB), diazinon, chlorpyrifos, and fenobucarb are substances peculiar to houses and are not used for parts in the passenger compartment of

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cars; thus, these compounds were not targeted. In March 2006, an additional announcement was made to start voluntary initiatives similar to those for passenger cars for new models of trucks and buses produced in 2008 or later.

In response to this effort, in April 2007, standard JASO M 902, “Automotive Parts: Interior Parts and Materials–Measurement Methods of Diffused Volatile Organic Compounds (VOC)”, was issued by the VOCs Measurement Subcommittee of the Automobile Interior Part Public Interest Corporation of the Association of Automotive Engineers as a quantitative method for evaluating VOCs released from the parts of automobile interiors. Furthermore, the standard JASO Z125, “Automobile: Car, Indoor Volatile Organic Compound Measurement Methods,” was issued in 2009 as a quantitative evaluation method for VOCs in passenger compartments, establishing a passive method (referred to as the “plate method” hereafter to distinguish it from the general passive method) and evaluated the amount of SVOCs transferred once adsorbed to identify the optimum method for storage, etc. We evaluated the desorption from the plates with a recovery rate by dropping a reagent onto plates made of different materials (glass, quartz, and stainless steel, with silane and polydimethylsiloxane (PDMS) treatments) and then heating for desorption. As a result, we found that the recovery rate is low for stainless steel. Assessing the adsorptivity requires reproducing the actual SVOC emission from parts inside the vehicle compartment in real space. Therefore, the recovery rate was evaluated using parts of the SVOC inclusion that had already been confirmed. Accordingly, the largest amount was adsorbed onto the plate made of quartz. In addition, the collected components will clearly desorb (migrate) from the plate to the storage container, etc. when the collected plates are left untouched. Thus, if the analysis recovery rate is low for stainless steel.

The SVOCs emitted from automobile parts are quantitatively evaluated using the aforementioned approaches, because only active sampling methods have been developed for evaluating SVOCs in passenger compartments, establishing a passive method is necessary. In this research, we investigated the materials properties (i.e., the SVOC adsorption–desorption properties) of plates used for the passive method (referred

| Type       | Target | Reference standard | Apparatus                        |
|------------|--------|--------------------|----------------------------------|
| Vehicle    | VOCs   | JASO Z125          | Bag                              |
|            |        | ISO 12219-1        | Bag                              |
| Material   | VOCs   | JASO M902          | Small chamber                    |
|            |        | ISO 12219-2        |                                 |
|            |        | ISO 12219-3        |                                 |
| Odor       |        | ISO 12219-7        |                                 |
| Components | VOCs   | VDA276             | Small chamber                    |
|            |        | ISO 12219-4        | Static                           |
|            |        | ISO 12219-5        |                                 |
|            | SVOC   | ISO 12219-6        |                                 |

Fig. 1. Research work flow

Table 1. Measuring methods of reference standard

Study of SVOC desorption method from plate
- Procedure comparison between solvent extraction and thermal desorption method

Selection of plate material
- Blank evaluation of plate
- SVOC desorption (recovery with reagents)
- SVOC adsorptivity (adsorption of emitted SVOCs)

Storability of collecting plate
- Quantitative evaluation of migration from the collecting plate and examination of the countermeasure proposals

Measurement of SVOC in vehicle interior using the plate method
- Measurement evaluation by plate (comparison with conventional method)
2. Experimental method

2.1 Selection of plate materials

2.1.1 Study of the SVOC desorption method

Two methods for desorbing the SVOC components adsorbed onto the plates were investigated: desorption using a solvent and desorption by heating.

In the solvent extraction method, 1 μL of a mixed standard reagent (each containing 1000 ng/μL of 2-ethyl-1-hexanol [2E1H], dodecamethylcyclohexasiloxane [D6], dibutylphthalate [BHT], hexadecane [C16], diethyl phthalate [DEP], tributylphosphate [TBP], dibutyladipate [DBA], triphenyl phosphate [TPP], and bis (2-ethylhexyl)phthalate [DEHP]) was added dropwise to a glass plate, which was subsequently dried for 5 min. From a test tube containing 1 mL of ethanol, 300 μL was dropped onto the glass plate; the surface of the plate was then wiped with washed-and-dried glass wool. The glass wool was placed in a test tube and subjected to ultrasonic extraction for 15 min; the SVOC in the extract was subsequently quantitatively analyzed by gas chromatography–mass spectrometry (GC–MS). One of the plates is shown in Fig. 2.

In the thermal desorption method, 1 μL of the mixed standard reagent was dropped onto a glass plate, which was allowed to dry for 5 min; the temperature was then increased from 30 to 250°C using a generated-gas concentrating and sampling device (MSTD 258). The desorbed gas was collected in Tenax-TA adsorbent resin (Fig. 3) and quantitatively analyzed by GC–MS. The analytical conditions are shown in Table 2.

2.1.2 Blank evaluation of plates

For quantitative evaluation, the components desorbed from the plates were captured. The plate materials used in the blank test of the single plate were glass, quartz glass, and stainless steel; a silane treatment and a PDMS treatment were applied as surface treatments, providing five kinds of plates (φ80 mm × 2 mm). The procedure included cleaning each plate in ethanol, aging each plate at 250°C for 30 min, and then subjecting each plate to the SVOC desorption method described in section 2.1.1. Figure 4 shows the appearance of a PDMS and a stainless steel plate.

2.1.3 Evaluation of SVOC desorptivity from plates

To each plate, 1 μL of the mixed standard reagent described in section 2.1.1 was added dropwise; after the plates were allowed to dry for 5 min, evaluation was conducted using the SVOC desorption method described in section 2.1.1.

2.1.4 Evaluation of SVOC adsorptivity on plates

To evaluate the SVOC adsorption performance of
the plates, we used our previously developed method for releasing the materials.

A floor mat (50 mm × 50 mm) made of polyvinyl chloride (PVC) was used as an SVOC emission source, the heating temperature of the chamber was 65°C, and the emission time was 1 h. The evaluation method using a microchamber is shown in Fig. 5. The amounts of SVOCs adsorbed onto the plate were evaluated using the SVOC desorption method described in section 2.1.1.

2.2 Storability of collecting plates

Previous research has already confirmed that SVOC components transfer from the collecting plates to the storage container, etc. Thus, in the present work, the upper and lower surfaces of the collecting plate were sandwiched between plates of the same material and subjected to a surface treatment. The plates were allowed to stand for three days at 40°C and 40% relative humidity and were quantitatively evaluated with the collecting plate to check storability. The plate selected in section 2.1.4 was used for the evaluation.

2.3 Measurement of SVOCs in vehicle interiors by the plate method

In this study, SVOC measurement conditions in the passenger compartment were set assuming summer season when SVOC emissions increased. In the past research, the evaluation is carried out under the condition that the vehicle is left outdoors. Since the temperature and humidity conditions depend on the weather conditions at that time, it is impossible to evaluate by fixing the temperature and humidity. Under such test conditions, quantitative comparison of results is difficult. Therefore, in this study, we decided the conditions so that the measurement results can be compared quantitatively.

For SVOC measurements in the interior of a vehicle, two evaluation scenarios were performed: one case where a new light truck was installed in an environmental test room with controllable solar radiation and temperature (infrared lamp) and another case of outdoor exposure. We investigated these two cases to check whether the SVOC components could be similarly detected under temperature-controlled conditions in the environmental test room and under outdoor conditions. The detailed conditions are shown in Fig. 6. The test conditions for measuring VOCs in the passenger compartment were individually selected with reference to temperatures measured outdoors because standard JASO Z 125 has not yet been introduced. The temperature shown in the figure is the temperature set inside the cabin. The temperature and relative humidity in the test chamber were constant at 23°C and 50%, respectively. The conditions for collecting Tenax were 100 mL/min × 100 min = 10 L. By contrast, the plate was installed in the passenger compartment on the precondition of an opened door. Table 3 shows the setting conditions. The plate in the environmental test room was evaluated together with the collecting effect (generally used in evaluating condensed components) in the case of cooling the plate. The cooling device used for the evaluation is shown in Fig. 7. We preliminarily confirmed that the surface temperature could be controlled to 20–25°C when the passenger compartment temperature was 65°C; however, because the dew point at 65°C and 20% relative humidity is approximately 32°C, the temperature of the cooling device was set to 40°C to prevent condensation. The collection position was the exposed part of the human body in the vicinity of the face, which is the most exposed part.
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3. Results and Discussion

3.1 Results of selection of plate material

3.1.1 Results of our study of the SVOC desorption method

A comparison of the recovery rates by thermal desorption and solvent extraction is shown in Fig. 9. These results show that the recovery ratio by solvent extraction of 2E1H, D6, BHT, DEP, and C16 was found to be as low as 40%. Consequently, we presumed that the components that disappeared easily dissipated during the procedure after the reagent was dropped onto the plates. In addition, the recovery ratio of the thermal desorption was greater than that of the solvent extraction for the other components. The low recovery ratio of the solvent extraction is likely due to the solvent wiping process, etc. However, the authors of a previous paper reported that not only the solvent type but also the extraction temperature is related to the recovery rate; thus, room for further improving the recovery rate in future investigations exists. In the present study, we decided to use the thermal desorption method for desorbing SVOCs collected on the plates.

3.1.2 Blank evaluation results of plates

The measurement results for the plate blank are shown in Fig.10. Hexamethyldicyclosiloxane(D3) and octamethyldicyclosiloxane (D4) were detected from the PDMS-treated plate. The corresponding amounts of SVOCs obtained from the other plates were less than 1 ng. Therefore, we decided to exclude the PDMS-treated plate from the experiments conducted in the remainder of this study.

![Fig. 7 Outline of cooling unit](image)

![Fig. 8 Outline of vehicle test](image)

(a) Chamber test (b) Sampling pump for Tenax (c) Outdoor test (d) Plate was set in cabin

Table 3 Evaluation conditions on SVOC into vehicle interior

| Index   | condition          | Sampling point | Flow rate(mL/min) | Sampling volume(L) |
|---------|--------------------|----------------|-------------------|--------------------|
| Vehicle type Light truck | Chamber | Tenax | 100 | 10 |
| chamber | Plate/Cooling Unit/40°C | Driver’s Face | 100 | 10 |
| Out door | Tenax | Plate | 100 | 10 |

Outline of vehicle test is shown in Fig.8.

![Fig. 9 Compare of recovery rate between solvent extraction and thermal desorption](image)

![Fig. 10 Chromatograph of plate blank (upper: PDMS lower: Glass)](image)
3.1.3 Evaluation of SVOC desorption ability using plates
The recovery rates of SVOC components from various plates are shown in Fig. 11. These results indicate that the recovery rate of certain components (e.g., DEHP) from the stainless steel plate was low, suggesting that stainless steel is not a suitable material for collecting plates. The poor recovery rate from stainless steel is likely associated with the oxidative decomposition of DEHP on its surface. The recovery rate from the other plates was good (approximately 80% or greater).

3.1.4 Evaluation of SVOC adsorption ability on plate
The results of our evaluation of the adsorption efficiency of DEHP emitted from the parts on each plate are shown in Fig. 12. From these results, we found that the quartz plate exhibited the highest adsorptivity among the investigated plates. Shinohara et al. \(^9\) have reported that the degree of adsorption varies with the adsorbent. This variation is speculatively attributed to differences in the surface area, electric charge, and functional groups among adsorbents. In this case, the efficiency is assumed to be enhanced by the interaction between the hydroxyl groups on the quartz glass surface and carbonyl groups of the phthalic acid ester. Given the results presented in section 3.1.3, we decided to use quartz plates in our study, which enables the efficient evaluation of SVOCs.

3.2 Storability of collecting plates
The results of our evaluation of storability, where DEHP emitted from parts was adsorbed onto the plates, are shown in Fig. 13. These results show that approximately 57% of the DEHP emitted from the parts was adsorbed onto the chamber wall. Furthermore, the amount transferred from the collecting plate was trapped in the storage plate and the total amount was the same as that before storage (DEHP amount before storage: 2601 ng). For storing the collecting plate, a sandwich method of shielding the upper and lower surfaces of the collecting plate with a quartz plate was applied.

3.3 Measurement of SVOCs in the interior of a vehicle by the plate method
The results of SVOC determination in the interior of a vehicle are shown in Fig. 14. 2E1H and BHT were more efficiently captured by active sampling using
Tenax than with the plate method. However, for DOA and DEHP, the efficiency of the plate method was good. The results for DBP were dispersed because of its low concentration.

The ability to efficiently collect the components by the passive method can be said to be easy to adhere to the skin etc. That is why components such as DEHP are regarded as a problem concerning absorption toxicity (dermal toxicity) of the skin.

Furthermore, DBP, DOA, and DEHP could be more efficiently collected in a device equipped with a cooling unit, which likely facilitated condensation because of the temperature difference. The results obtained via outdoor and environmental-test-room active sampling and those obtained with plates were similar. The results show that an environmental test room equipped with an infrared lamp can reproduce outdoor storage conditions. The temperature and humidity during the outdoor test are shown in Fig. 15.

The influence of humidity in each method will be described. Active sampling using Tenax has been reported\(^{10}\) to be less sensitive to humidity. On the other hand, regarding the plate method, the efficiency may differ depending on the components to be collected. In other words, in the case of a hydrophilic component, the efficiency is considered to be improved when the humidity is high. In order to reduce the influence of humidity, it is important to prevent dew condensation from occurring on the plate surface, so the plate may be stored at the evaluation temperature before being used for evaluation.

Next, the influence of ultraviolet rays will be described. Although it is reported\(^{11}\) that general VOC is a cause to generate photochemical oxidant by sunlight, there is no actual measurement case in the passenger compartment. Also, since ozone is required for this reaction, it is considered that ozone is hardly generated because short wavelength ultraviolet rays are cut when sunlight passes through the glass. I think that it is better to distinguish properly using active sampling and plate method by the route of toxicity of the target ingredient (inhalation, transdermal).

4. Conclusion

(1) Thermal desorption was found to be a suitable method for desorbing SVOCs adsorbed onto the plate.

(2) Among the investigated plates, the quartz plate exhibited the best desorption ability of an SVOC reagent dropped onto the plate and the best adsorption ability of DEHP released from the automobile parts.

(3) By sandwiching the collecting surface of the plate after collection with a quartz plate, we could assess the total amount of trapped SVOCs by quantitatively analyzing the sandwiched plate at the same time as the collecting plate.

(4) SVOCs in the interior of a vehicle were quantitatively evaluated using a quartz plate. The results showed that evaluation could be conducted more efficiently than with active sampling.

(5) SVOCs emitted from the vehicle interior were evaluated using a quartz plate. The results confirmed that the assessment is more efficient than that with conventional active sampling. In particular, DEHP could not be detected by active sampling but was detected by the plate method.

On the basis of the aforementioned results, we examined the procedure using quartz plates to evaluate SVOCs. Although some components were difficult to evaluate because of their low concentration, we successfully evaluated components such as DOA and DEHP, which are difficult to evaluate by conventional methods. We believe that this method can be used for evaluating transdermal exposure to DEHP because the passive method does not use a pump and readily enables long-term evaluation.

In addition, in order to evaluate the occupant’s exposure, it is necessary to carry out the measurement according to the riding time of the occupant using this method.

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