

# Measurement of SVOCs emitted from building materials and electric appliances using thermal desorption test chamber method

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## ABSTRACT

Many reports have been published on the emission test chamber method for measuring volatile organic compounds (VOCs) emitted from materials. However, there are very few reports on the measurement of semi-volatile organic compounds (SVOCs) emitted from materials. Because SVOCs emitted from materials are adsorbed on the internal surface of the test chamber under actual room temperature, it is extremely difficult to measure the emission amount from materials by the emission test chamber method. Therefore, the authors develop a Thermal Desorption test Chamber method (TDC method) that can measure correctly the emission rate of SVOCs released from materials<sup>1)</sup>. On the other hand, it is worried that indoor air quality will be affected by the emission from electric appliances. In this paper, the authors analyzed the emissions from a notebook computer using the TDC method. As a result, the emission rate of SVOCs increased sharply by turning on a power supply.

## INDEX TERMS

SVOCs, VOCs, Adsorption, Emission, TDC method

## INTRODUCTION

With regard to measurement of SVOCs emitted from materials using the test chamber, there is a screening test in which the materials are heated at 60 to 100°C in the test chamber and which is possible to measure of SVOCs emitted to some extent. However, the result does not reflect the indoor environmental conditions and since the amount of SVOCs emitted increased by raising temperature, the amount of adsorption on the internal surface of the test chamber also increased (Figure 1).

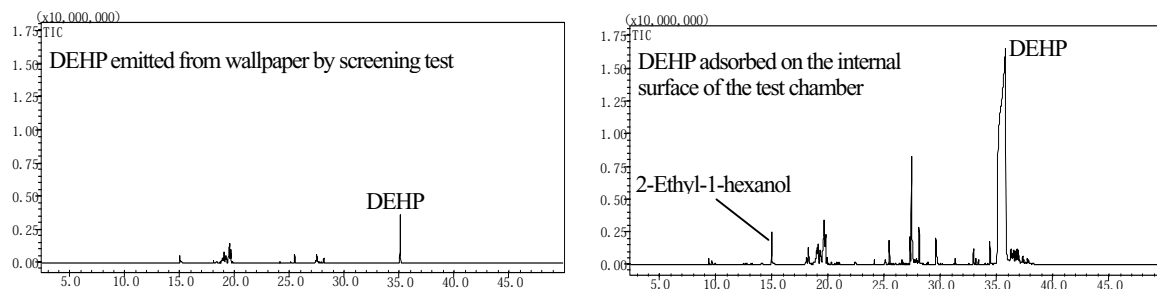
E. Uhde et al. measured SVOCs in polyvinyl chloride (PVC) wallpaper using the fogging test method, and proposed a method for measuring SVOCs in building materials at room temperature.<sup>2)</sup> Based on this research, the present authors proposed the TDC method, by which building materials, etc. are removed from the chamber after measurements by the emission test chamber method, and the chamber is filled with inert gas (He) while the chamber is heated to high temperature. The SVOC components adsorbed on the internal surface of the test chamber would undergo thermal desorption through this procedure, and can be measured. This method was reported at "Indoor Air 2002" as a method for accurate measurement of the amount of SVOCs emitted from building materials at room temperature. This paper focuses on electric appliances, which are feared to be a major source of indoor air contamination other than building materials. Specifically, measurement of the amount of SVOCs emitted from notebook computer was reported.

In this study, a glass (pyrex) chamber of the capacity of 6.5L was used. The notebook computer was put into the glass (pyrex) chamber. Clean air of RH 50±5% was supplied in to the chamber at room temperature. VOCs emitted from the notebook computer were sampled on Tenax TA tube. After the notebook computer was removed, the chamber was heated to 200°C in He atmosphere in order to desorb SVOCs from the chamber. Tenax TA tube was also used to sample SVOCs. The system flow of the measurement is shown in Figure 2. Each Tenax TA tubes were analyzed by the thermal desorption auto-sampler (TD, GL Sciences Inc. TMD-253H) connected to the gas chromatography/mass spectrometry (GC/MS, JEOL Auto Mass50). Measurements were conducted for the emission from notebook computer (when not in operation) at room temperature and at 35 °C, and from notebook computer in both operating and non-operating states at room temperature, and the results were

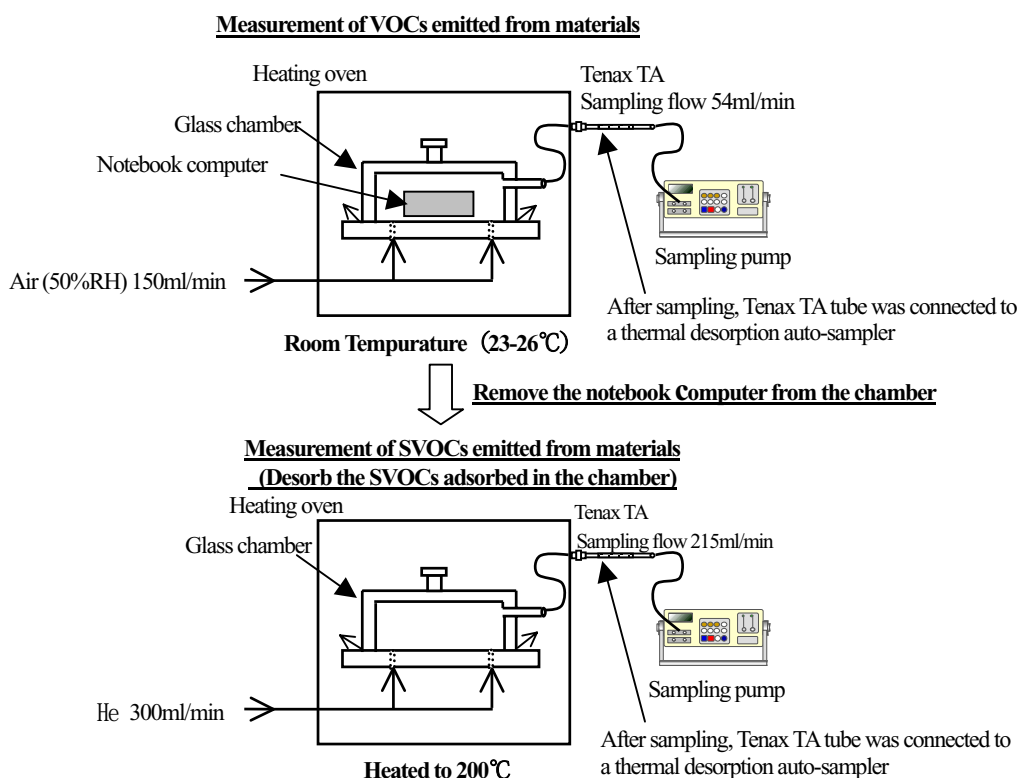
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examined.



**Figure 1.** TIC of DEHP emitted from wallpaper by screening test at 80°C and TIC of DEHP adsorbed on the internal surface of the test chamber after screening test



**Figure 2.** System flow of the TDC method

## METHODS

### Confirmation of the recovery of SVOCs from the chamber

To Confirm of the recovery of SVOCs from the chamber, each 250ng of standard SVOCs mixture sample of Phthalate esters (DBP(Dibutyl phthalate), DEHP(Di(2-ethylhexyl) phthalate)), Adipate (DOA(Di(2-ethylhexyl) adipate)), Phosphoric esters (TBP(Tributyl phosphate), TCEP (Tris(2-chloroethyl) phosphate)), BHT (Butylated hydroxytoluene) and D6 (Dodecamethyl Cyclohexasiloxane) and hydrocarbon mixture sample of Hexadecane and Eicosane were spiked inside the chamber. And the chamber was heated to 200 °C, after which sampling was carried out using a Tenax TA tube, followed by analysis by TD-GC/MS.

### Calibration

When carrying out quantitative analysis of the emissions, calibration curves are required to be created in advance. The calibration curve for VOCs emission measurement was analyzed by TD-GC/MS of standard VOCs mixture sample of Toluene, Ethylbenzene, o,m,p-Xylene, Styrene, p-Dichlorobenzene, Nonanal and Tetradecane in a Tenax TA tube (10 to 500 ng of each component) after dry purging with nitrogen for 5 min. To generate a calibration curve for measurement of SVOCs adsorbed in the chamber, standard SVOCs mixture sample and hydrocarbon mixture sample were spiked to a 90° wall surface through the chamber sampling

inlet (100 to 1,500 ng of each component), and the chamber was heated to 200 °C, after which sampling was carried out using a Tenax TA sampling tube, followed by analysis by TD-GC/MS.

### Measuring the equipment blank and operation blank

Before carrying out actual measurement, equipment and operation blank were measured. The equipment blank measurement served as background when measuring VOCs emission and SVOCs adsorbed in the chamber without opening and closing the chamber. The operation blank served as background taking into consideration that the air of the laboratory would get into the chamber when the notebook computer was placed in the chamber. In other words, other than placing the notebook computer in the chamber, operation blank measurement was carried out in the same way as the actual measurement.

### Measurement of the notebook computer

The entire surface of a new, commercially available notebook computer was lightly wiped with wiper which was immersed in pure water, and then the notebook computer was placed in the chamber, as shown in Figure 2. The chamber volume was  $6.50 \times 10^{-3} \text{ m}^3$ , air flow rate was  $32.4 \times 10^{-4} \text{ m}^3/\text{h}$  (54 ml/min) with clean air (RH50±5%) and air exchange rate was 0.5/h.

1) The power supply to the notebook computer was turned off, and the emission amount at room temperature (22 to 29°C with the heater off) and at 35 °C were measured. VOCs emitted were sampled after 1 h and then again after 23 h using a Tenax TA tube (sampling volume: 3 L). The sample in the Tenax TA tube was analyzed by TD-GC/MS. After VOCs emitted were sampled, the notebook computer was removed from the chamber. Helium gas was supplied to the empty chamber, then it was heated to 200°C. SVOCs adsorbed in the chamber were desorbed from the chamber, and the desorbed gases were sampled on Tenax TA tube to 19.5L. Analysis was carried out by TD-GC/MS, and the amount of adsorption in the chamber was measured. The amounts of SVOCs emitted from the notebook computer under room-temperature conditions and at 35 °C were measured through this series of measurements.

2) The heater of the heating oven was turned off, and the emission amount at room temperature (23 to 26 °C) were measured. VOCs emitted were sampled after 1 h and then again after 3.2 h using a Tenax TA tube (sampling volume: 1 L). The sample in the Tenax TA tube was analyzed by TD-GC/MS. After VOCs emitted were sampled, the notebook computer was removed from the chamber. Helium gas was supplied to the empty chamber, then it was heated to 200 °C. SVOCs adsorbed in the chamber were desorbed from the chamber, and the desorbed gases were sampled on Tenax TA tube to 19.5L. Analysis was carried out by TD-GC/MS, and the amount of adsorption in the chamber was measured. This measurement was conducted with the notebook computer in the non-operating state and in the operating state.

These measurement conditions are shown in Table 1, and the TD-GC/MS analysis conditions are listed in Table 2.

**Table 1.** Measurement condition of TDC method

Chamber dimension	$\phi 235 \times H150 \text{ mm}$		
Chamber volume	$6.50 \times 10^{-3} \text{ m}^3$ (6.5L)		
Temperature	measuring SVOCs adsorbed in the chamber: Room temp.-200°C		
	measuring VOCs emission : Room temp., 35°C		
Supply gas to the chamber	measuring SVOCs adsorbed in the chamber : He 300ml/min		
	measuring VOCs emission : clean air 50%±5%RH 150ml/min		
Air exchange rate	0.5/h	Sampling material	Tenax TA, mesh25/35, 100mg
Sampling flow rate	measuring SVOCs adsorbed in the chamber : 215ml/min		
	measuring VOCs emission : $32.4 \times 10^{-4} \text{ m}^3/\text{h}$ (54ml/min)		
Sampling volume	measuring SVOCs adsorbed in the chamber : 19.5L		
	measuring VOCs emission : 3L, 1L		

**Table 2.** TD-GC/MS analysis condition

Desorption Temp.	250°C, 15min	Cold Trap Temp.	-130°C
Column	TC-1 0.25mm I.D. $\times$ 60m, df=0.25 $\mu\text{m}$		
Temperature Programming	40°C (5min) - 10°C/min - 280°C (21min)		
Scan mode	m/z 35-450		

## RESULTS

The value obtained by adding a 250 ng of standard SVOCs mixture sample and hydrocarbon mixture sample directly to the Tenax TA tube was taken as 100%. The recovery obtained when the sample were spiked inside the chamber is shown in Table 3. When compared with the quartz chamber having a volume of 233.5 mL shown for reference, the overall recovery is lower. In particular, the recovery for TBP, TCEP, and DEHP are low. This indicates a tendency for the recovery to decrease as the chamber volume increases.

**Table 3.** recovery of SVOCs from the chamber (%)

	Spot A	Spot B	Spot C	Spot D	quartz chamber
Hexadecane	49.2	67	49.5	47.7	60.9
Eicosane	49.2	62	49.5	48	77.1
D6	53.4	79.5	54.2	48.4	82.6
DEP	45.3	62.1	49.2	46.4	67.9
TBP	4.4	14.3	4.3	4.3	34.8
TCEP	7.6	17.5	8	8.3	28.4
DBA	27.7	44.7	30.2	29	67.3
DBP	42.9	60.5	48.7	43.9	75.2
DEHP	16.8	34.3	20.4	20.1	62.4

\* Spot A : added to a 90° wall surface through the chamber sampling inlet

Spot B: added to a just below chamber sampling inlet

Spot C : added to a 180° wall surface through the chamber sampling inlet

Spot D : added to a chamber base

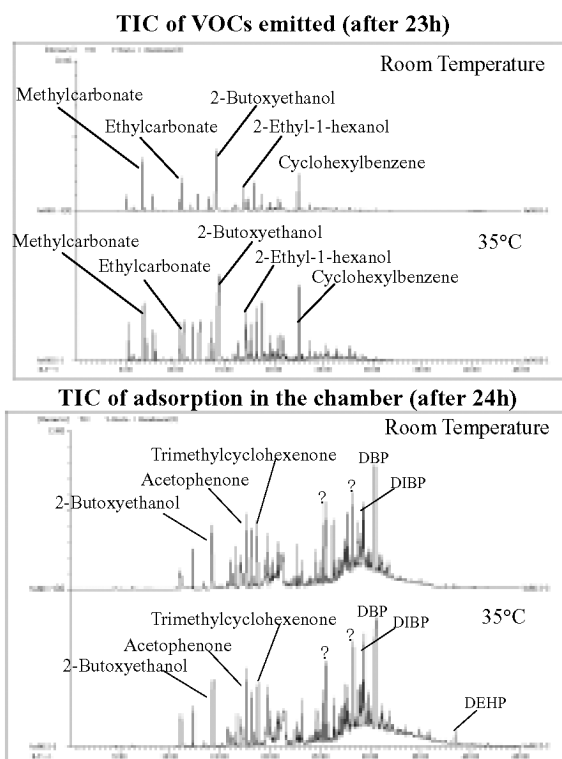
\* quartz chamber : recovery from the chamber, each 100ng of standard mixture sample spiked

Good linearity was obtained for the calibration curves for each of the components in the VOCs emission measurement. For example  $r^2$  of toluene was 0.9967. Good linearity was also obtained for the calibration curves used to measure the SVOCs adsorbed in the chamber. For example  $r^2$  of Hexadecane, DBP and DEHP were 0.9995, 0.9925 and 0.9637.

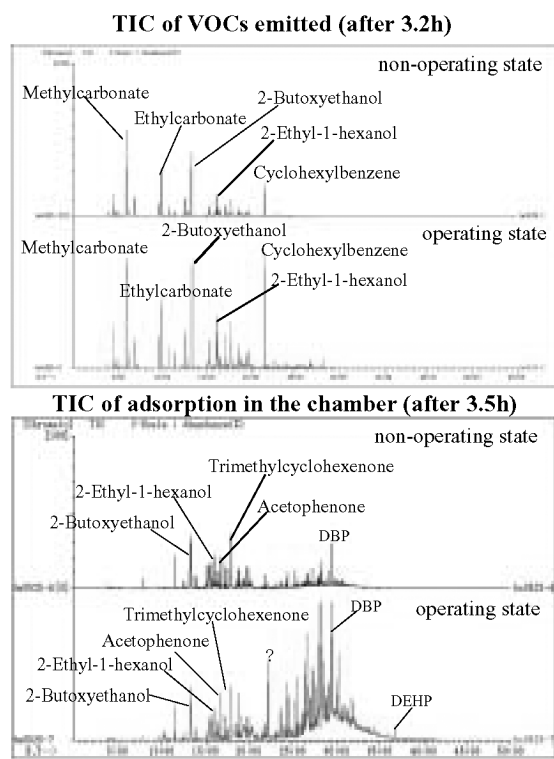
The total VOC value for the VOCs emission measurement for the equipment blank was approximately  $3.4 \mu\text{g}/\text{m}^3$  (toluene conversion), which was sufficiently low not to affect the analysis to any great extent. Eliminating the blank component judged to originate from the equipment blank of SVOCs adsorbed in the chamber, the total component value for the adsorption in the chamber is approximately 200 ng (Hexadecane conversion). For the operation blank, because the measurements were carried out after the lid of the chamber had been left off in the laboratory for approximately 5 min, the blank value increased because of contamination with laboratory air. 2-(2-Methoxyethoxy)ethanol, 2-(2-Ethoxy-ethoxy)ethanol and 2-Ethyl-1-hexanol were confirmed as the operation blank components from the VOCs emission measurement. The total value of the three components sampled after 1 h was  $13 \mu\text{g}/\text{m}^3$  (toluene conversion), but when sampled after 3.2 h, the value had dropped significantly to  $1.9 \mu\text{g}/\text{m}^3$  (toluene conversion). This is thought to be because the components were diluted by the clean air supplied into the chamber. The adsorption values of the three components in the chamber noted above were confirmed to be 233ng, 400ng, and 20ng, respectively (Hexadecane conversion). It was thus confirmed to be necessary to subtract these components from the actual measured values.

Figure 3 shows the total ion chromatogram (TIC) for the measurement of VOCs emitted from the notebook computer (23 h after being placed in the chamber) and TIC for the measurement of components adsorbed in the chamber 24 h after the notebook computer was placed in the chamber in the non-operating state at room temperature and at 35 °C. It was found that the amount of VOCs emitted had increased by approximately under three times at 35°C in comparison to that at room temperature. 2-Butoxyethanol, Toluene, Methylcarbonate, Ethylcarbonate, 2-Ethyl-1-hexanol, Cyclohexylbenzene, Trimethylcyclohexenone were confirmed as the measurement of VOCs emitted. Overall, no significant differences were observed in the amount of components adsorbed in the chamber between room temperature and 35 °C. DBP, a Phthalate ester, was confirmed as the major adsorption component. DEHP was also detected in the measurements at 35 °C, although in very small amounts. Table 4 lists the amount of components absorbed in the chamber and emission rate (ER,  $\mu\text{g}/\text{unit}/\text{h}$ ) of the various components.

Figure 4 shows the TIC for the measurement of VOCs emitted from the notebook computer (3.2 h after being placed in the chamber) and TIC for the measurement of components adsorbed in the chamber 3.5 h after the notebook computer was placed in the chamber at room temperature, in the non-operating state and the operating state. It was found that the amount of VOCs emitted had increased by approximately under three times in the operating state in comparison to that in the non-operating state. 2-Butoxyethanol, Methylcarbonate, Ethylcarbonate, Cyclohexylbenzene, 2-Ethyl-1-hexanol were confirmed as the measurement of VOCs emitted. 2-Butoxyethanol, 2-Ethyl-1-hexanol, Cyclohexylbenzene were significant increase in the operating state. It was found that the amount of components adsorbed in the chamber approximately three times in the operating state. The increase in the amount of adsorption of the SVOC component, which has a high boiling point, was particularly noticeable (approximately 6 times in the case of DBP). DEHP was also detected in the measurements in the operating state. Table 5 lists the amount of components absorbed in the chamber and ER of the various components.



**Figure 3.** TIC for the measurement of VOCs emitted from the notebook computer and SVOCs absorbed in the chamber(24 h placed in the chamber) in the non-operating state



**Figure 4.** TIC for the measurement of VOCs emitted from the notebook computer and SVOCs absorbed in the chamber at room temp. in the non-operating state and operating state

**Table 4.** ER of VOCs and SVOCs from notebook computer(24 h placed in the chamber) in the non-operating state at room temperature and at 35 °C

	Concentration of emission gas [ $\mu\text{g}/\text{m}^3$ ]		Adsorption in the chamber [ng]		Emission rate(ER) [ $\mu\text{g}/\text{unit}/\text{h}$ ]	
	Room Temp.	35°C	Room Temp.	35°C	Room Temp.	35°C
Methylcarbonate	138.9	233.6	-	-	0.45	0.76
Toluene	13.6	50.3	-	-	0.04	0.16
Ethylcarbonate	70.5	139.9	-	-	0.23	0.45
2-Butoxyethanol	227.6	614.6	699.9	803.5	0.77	2.03
2-Ethyl-1-hexanol	35.2	97.8	-	-	0.11	0.32
Acetophenone	14.8	71.2	559.0	618.8	0.07	0.26
Trimethylcyclohexenone	26.4	95.0	435.5	407.2	0.11	0.33
Cyclohexylbenzene	51.7	140.3	-	-	0.17	0.46
DIBP (Diisobutylphthalate)	-	-	209.3	534.0	0.01	0.02
DBP	-	-	1134.7	1572.7	0.05	0.07
Total	578.7	1442.7	3038.4	3936.2	2.01	4.86

**Table 5.** ER of VOCs and SVOCs from notebook computer(3.5 h placed in the chamber) at room temperature in the non-operating state and operating state

	Concentration of emission gas [ $\mu\text{g}/\text{m}^3$ ]		Adsorption in the chamber [ng]		Emission rate(ER) [ $\mu\text{g}/\text{unit}/\text{h}$ ]	
	non-operating	operating	non-operating	operating	non-operating	operating
Methylcarbonate	223.4	393.2	-	-	0.73	1.28
Toluene	12.5	45.6	-	-	0.04	0.15
Ethylcarbonate	112.1	240.1	-	-	0.37	0.78
Cyclohexanone	22.8	64.6	-	-	0.07	0.21
2-Butoxyethanol	217.0	618.4	408.1	463.4	0.82	2.14
2-Ethyl-1-hexanol	33.9	150.0	106.7	102.2	0.14	0.52
Acetophenone	-	-	172.1	379.1	0.05	0.11
Trimethylcyclohexenone	18.4	86.3	242.2	213.8	0.13	0.34
Cyclohexylbenzene	50.1	250.2	-	-	0.16	0.81
DBP	-	-	370.3	2267.3	0.11	0.65
Total	690.2	1848.4	1299.4	3425.8	2.62	6.99

## DISCUSSION

For the TDC method, it is necessary to know in advance the recovery of SVOCs from the chamber. It was found, through this experiment, that the recovery changes depending on the chamber size and the differences in components. Particular attention is required because a tendency has been seen for the recovery of organic components (SVOCs) adsorbed in the chamber to decrease as the chamber volume is increased. The reliability of this method can be improved by determining the calibration curve for the target SVOC component. It is necessary to understand beforehand that the blank value for the adsorption component in the chamber increases when air in the laboratory is allowed to enter the chamber when the chamber is opened and closed. It is therefore necessary to subtract the blank component from the measured value in actual measurement.

It was found that while the amount of VOCs emitted from the notebook computer increased from room temperature to 35°C and in the operating state at room temperature, adsorption components in the chamber (most of which were SVOCs) increased only in the operating state. This means that turning on the power supply at this point causes the temperature inside the notebook computer to rise and increases not only the amount of VOC components emitted, but also the amount of SVOC components emitted. Conversely, it was found that the amount of SVOC components emitted in the non-operating state did not increase. DBP was the principal SVOC component, but a number of SVOC components other than DBP were confirmed as well. It was not possible, however, to achieve sufficient identification of these minor components. Consequently, actual ER at which the total SVOC component is predicted to be higher than that indicated by the values shown in Tables 4 and 5.

Because the measurement conditions (the time taken to place the notebook computer and sample the volume of emitted gases) differed in the two experiments conducted in our research, it is important to note that it is not possible to directly compare ER for 1) measurement of the amount of VOCs/SVOCs emitted at room temperature and at 35 °C, and 2) measurement of the amount of VOCs/SVOCs emitted in the non-operating state and in the operating state.

## CONCLUSION AND IMPLICATIONS

With the current emission test chamber method, most SVOC components from building materials and other materials are adsorbed on the internal surface of the test chamber, making it difficult to measure them. With screening tests, as well, raising the heating temperature causes the amount of SVOCs emitted to increase, but also increases the amount of adsorption on the internal surface of the test chamber. As such, there is a fear that the amount of SVOCs emitted will be underestimated. In order to solve those problems, the TDC method was proposed for measuring the amount of SVOCs emitted from building materials, electric appliances and other items under actual room temperature. It was confirmed that the amount of SVOCs emitted could be accurately measured using this method.

By the present method, the ER of SVOCs from a notebook computer, several µg/unit/h, was quite low. In comparison to screening tests, such low ER allow emission levels to be evaluated more precisely, allowing for more strict conditions.

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