

A nationwide survey of volatile organic compounds including volatile methylsiloxanes in indoor air from Japanese residential houses using sorbent tube/thermal desorption GC/MS

Takekuma M¹, Horii Y², Motegi M², Kikuta K³, Hasegawa K⁴, Takeuchi J⁴, Honma Y⁵, Yan S⁵, Yamada H⁶, Hayashi M⁷

¹Saitama Prefectural Institute of Public Health, Japan, 355-0133, takekuma.mikiko@pref.saitama.lg.jp; ²Center for Environmental Science in Saitama, Japan, 347-0115, ³Hokkaido University, Japan, 060-8628, ⁴Akita Prefectural University, Japan, 015-0055, ⁵Miyagi Gakuin Women's University, Japan, 981-8557, ⁶Nagasaki Institute of Applied Science, Japan, 851-0193, ⁷National Institute of Public Health, Japan, 351-0197.

Introduction: Silicone products such as building materials, electronic devices, medical supplies, kitchen supplies, and cosmetics are made of volatile methylsiloxanes (VMS), and are excellent in heat and cold resistance, electrical insulation, water repellency, and defoaming properties. On the other hand, persistence in the environment, bioaccumulation, and toxicity of VMS have been reported recently.^{1, 2, 3} Octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) have been registered on the REACH SVHC candidate list in 2018. However, very limited information is reported on VMS in Japanese indoor air. To investigate occurrence and behavior of VMS in residential house, in this study, sampling method including sample transportation and storage and determination of VMS in indoor air using sorbent tube/thermal desorption (TD)-GC/MS were examined. Moreover, we investigated the occurrence of cyclic and linear VMS along with 45 common volatile organic compounds (VOCs) in indoor air collected from Japanese residential houses.

Materials and methods: *Chemicals and equipment:* Hexamethylcyclotrisiloxane (D3), D4, D5, and D6 standards were purchased from Tokyo Chemical Industry Co., Ltd. Tetradecamethylhexasiloxane (L6) and 50 Component Indoor Air Standard were from Fluorochem Ltd. and Sigma-Aldrich Inc., respectively. All standards were diluted with methanol (phthalate ester analysis grade, Kanto Chemical Co., Ltd.). High purity nitrogen gas (99.99995% purity, N₂ gas) was used for conditioning of a sorbent tube and preparation of calibration curve. Air sampling was performed using mass flow controlled diaphragm pumps (SP208-20 Dual II, SP208-100 Dual II, SP208-1000 Dual (GL Sciences Inc.), and GSP-400 FT (Gastec Co., Ltd.).

Sorbent tube and conditioning method: An inert stainless tube filled with Tenax TA (200 mg, 60/80 mesh, Camsco Inc.) was used as sorbent tube. Graphite vespel ferrule was precleaned by ultrasonication with methanol for 10 min, and then heating from 40°C (1 min) to 320°C (120 min) at 10°C/min in a thermostat. The conditioning of a sorbent tube was performed using a sample tube conditioner (STC-4000, GL Science Inc.). The gas flow rate was adjusted to 30 mL/min of N₂ gas. The temperature program was set from 40°C (30 min) to 100°C (30 min) at 10°C/min, and subsequently to 310°C (360 min) at 10°C/min for a new sorbent tube, and was held for 60 min at 310°C for a reused tube.

Sample analysis: Five VMS and 45 VOCs were analyzed by sorbent tube/thermal desorption (TD) GC-MS using *d*₈-toluene (Takachiho Chemical Industrial Inc.) as an internal standard gas (Table 1). Target compounds were summarized in Table 2. Calibration curve was prepared using VMS standards at 1, 5, 10, 50, 100 and 200 ng with the internal standard. Ranges of calibration curve were optimized based on the linearity test. The lowest calibration standard (1 ng) was analyzed five times to determine the method detection limit (MDL; $t(n-1, 0.05) = 2.132$).

Breakthrough test: When preparing a calibration curve, two sorbent tubes were connected in series, and 20 ng (1.0 µL methanol) and 200 ng (2.0 µL methanol) of VMS standards were added severally while supplying N₂ gas of 50 mL/min for 2 min. To check any breakthrough of the target compounds in each sorbent tube was analyzed separately. Living room air was collected under different conditions at a flow rate of 100 mL/min for 30 min and 2 mL/min for 24 hours, using three sorbent tubes deployed tandem. Furthermore, the living room air after using hair conditioner containing D5 (wash-off type) was collected at a flow rate of 100 mL/min for 30 min.

Comparison of sampling method: In order to investigate variance of VMS concentrations influenced by the different sampling volumes, flow rates, and sampling times, several sampling conditions were tested (Tables 3 and 4), including (1) flow rate: 100 mL/min (30 min), sampling volume: 3.00 L, (2) flow rate: 100 mL/min (60 min), sampling volume: 6.00 L, (3) Flow rate: 10 mL/min (24 hours), sampling volume: 14.40 L, (4) flow rate: 2 mL/min (24 hours), sampling volume: 2.88 L.

Storage and transport method: The sorbent tube was stored in the TDS³ Storage Container (Sigma-Aldrich Inc.) immediately after conditioning. The several sorbent tubes for sampling and for checking the travel blank were stored in an aluminum zipper bag (Lamizip, SeisanNipponsha Ltd.) with activated carbon granule (Fujifilm Wako Pure Chemical Co.) and were shipped nationwide by mail or courier.

Sample collection: Indoor air was collected twice in the living rooms of 12 residences (a total of 41 houses) at a flow rate of 100 mL/min (30 min) during September 2018 to March 2019. The indoor air samples were analyzed for 5 VMS and 45 VOCs.

Results and discussion: *Preparation of calibration curve:* In six-point calibration curve (1, 5, 10, 50, 100 and 200 ng) of D3, D4, D5, D6 and L6, good linearity with $R^2 = 0.999$ was obtained for all VMS, except for D3 ($R^2 = 0.998$). The linearity of the calibration curve up to 200 ng was confirmed. Calibration curves for upper concentrations of D5 and D6 were additionally prepared, if concentrations were higher than the maximum (200 ng). Relative standard deviations in the replicate analysis of 1 ng injection were 0.88%, 1.5%, 2.2%, 0.81% and 7.1%, respectively for D3, D4, D5, D6 and L6. The MDL were calculated at 0.023 ng, 0.086 ng, 0.056 ng, 0.024 ng and 0.084 ng, respectively for D3, D4, D5, D6 and L6.

Breakthrough test: No breakthrough of VMS to the second sorbent tube was observed in the calibration curve preparation (20 ng and 200 ng). Furthermore, no breakthrough of D3, D4, D5, and D6 to the second and third sorbent tubes were confirmed for the indoor air sampling in several different conditions (Tables 3 and 4), and in the highest concentration samples for D5 at 125 $\mu\text{g}/\text{m}^3$.

Comparison of sampling method: VMS concentrations in the different sampling conditions were shown in Tables 3 and 4. Low concentration of VMS can be detected with increasing the sampling volume. 24-hour sampling is effective to monitor a daily average concentration of VMS. It was confirmed that the flow rates of 10 mL/min and 2 mL/min using the Tenax TA were applicable for 24-h sampling without any breakthrough. In addition, small sample volume (3L) at the flow rate of 100 mL/min was found to be sufficient to detect VMS in indoor air.

Storage and transport method: No target compounds were detected in the travel blank samples, which had been sampled and transported until two weeks after conditioning of the sorbent tube. TDS³ Storage Container and Lamizip with activated carbon were suitable for the storage and transport of samples.

Occurrence in indoor air: The concentrations of VMS and VOCs were shown in Fig. 1. D4, D5, and D6 were detected at relatively high concentrations in the living rooms with the ranges of <0.33 -30 $\mu\text{g}/\text{m}^3$, 0.60-1,042 $\mu\text{g}/\text{m}^3$ and <0.33 -158 $\mu\text{g}/\text{m}^3$, respectively. The maximum concentration of VMS was in the order of $\text{D5} > \text{D6} > \text{D4} > \text{D3} > \text{L6}$ (Table 5). In some cases, the ratio of VMS to total volatile organic compounds (TVOC, the provisional target value of Japan: 400 $\mu\text{g}/\text{m}^3$), which is an indicator of indoor air quality level, tended to increase. The guideline value for the sum of D3-D6 in indoor air in Germany was set at 4 mg/m^3 (the guideline value I; health hazard value) and 0.4 mg/m^3 (the guideline value II; precautionary value). In this study, several indoor air with the maximum concentration at 1,201 $\mu\text{g}/\text{m}^3$ exceeded the precautionary value, but lower than the health hazard value (Fig. 1). Previous study⁴ reported that the concentrations of D4 and D5 in indoor air collected in 10 houses in Tokyo, Japan were <2.5 -5.4 $\mu\text{g}/\text{m}^3$ and <2.5 -67.5 $\mu\text{g}/\text{m}^3$, respectively. Average concentrations of D5 in European indoor air ranged from 4.0 to 250 $\mu\text{g}/\text{m}^3$ for D5.⁵ In addition, the concentrations of D5 in indoor air after use of D5 containing conditioners were reported 2.7-156 times higher than before use, with the ranging from 1.7 to 266 $\mu\text{g}/\text{m}^3$.⁶ We also found that the concentrations of D5 in living room after shower increased to 2.8-125 $\mu\text{g}/\text{m}^3$, it was 45 times higher than the concentration before shower. Fromme et al., 2019 reported that the concentrations of cyclic-VMS in indoor air increased distinctly after baking with silicone moulds.⁵ The VMS measured widely varied in each house depending on the sampling date and time, even in the same house, suggesting the concentrations of VMS were influenced by the lifestyle and use of personal care products in each residence. Further investigations including daily variation of VMS in indoor air with the application of personal care products are needed.

Exposure rates: Residents spend most of their lifetime in their house and can be exposed by indoor air. Based on the average staying time (15.8 h/day⁷) and corresponding inhalation volume (11.4 m^3/day ⁸) for Japanese people and median concentrations of VMS, daily exposure rates of VMS in indoor air were preliminary estimated (Table 6). Assuming 50 kg body weight for adult, the exposure rates of D4, D5, D6, and sum of VMS were 0.10, 4.1, 0.12 and 5.3 $\mu\text{g}/\text{kg}$ body weight per day, respectively. It should be noted that the exposure rates estimated here were based on a short sampling time of 30 min. Further investigation is needed to estimate exposure rate to VMS in steady-state by indoor air.

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References:

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Table 1. Operating conditions for TD-GC/MS.

Thermal Desorber: Turbo Matrix 650 (Perkin Elmer Inc.)	
Desorption temp.	300 °C
Desorption flow	30 mL/min
Desorption time	10 min
Cold trap inlet split flow	30 mL/min
Cold trap temp.	4 °C
Cold trap desorp. temp.	300 °C
Cold trap desorp. time	30 min
Cold trap outlet split flow	10 mL/min
GC: 7890B GC System, MS: 5977A MSD (Agilent Technologies Inc.)	
Column	InertCap 1MS 0.25 mm × 60 m, df: 1.00 µm (GL Sciences Inc.)
Oven	40 °C (8 min) → 10 °C/min → 120 °C (0 min) → 20 °C/min → 220 °C (4 min) → 20 °C/min → 280 °C (2 min)
Carrier gas	helium, 1.2 mL/min
MS source temp.	260 °C
MS quad temp.	180 °C
MS mode	SIM / SCAN (m/z 33-450)

Table 2. Target and qualifier ions of volatile organic compounds including volatile methylsiloxanes.

No.	Compound	Target ion (m/z)	Qualifier ion (m/z)	No.	Compound	Target ion (m/z)	Qualifier ion (m/z)
1	2-Propanol	45	59	26	o-Xylene	91	106
2	Dichloromethane	84	86	27	Nonane	57	85
3	1-Propanol	59	60	28	α -Pinene	93	136
4	2-Butanone	43	72	29	3-Ethyltoluene	105	120
5	Ethylacetate	61	70	30	4-Ethyltoluene	105	120
6	Hexane	57	56	31	1,3,5-Trimethylbenzene	105	120
7	Trichloromethane	83	85	32	2-Ethyltoluene	105	120
8	1,2-Dichloroethane	62	64	33	Octamethylcyclotetrasiloxane (D4)	281	133
9	1-Butanol	56	41	34	β -Pinene	93	136
10	Benzene	78	77	35	1,2,4-Trimethylbenzene	105	120
11	1,2-Dichloropropane	76	63	36	Decane	57	85
12	Bromodichloroethane	83	85	37	1,4-Dichlorobenzene	146	148
13	Trichloroethene	130	132	38	1,2,3-Trimethylbenzene	105	120
14	Heptane	71	100	39	Limonene	68	93
15	4-Methyl-2-pentanone	43	100	40	Nonanal	82	57 114
16	Toluene	91	92	41	Undecane	57	85 156
17	Dibromochloromethane	129	127	42	Decamethylcyclopentasiloxane (D5)	355	267
18	n-Butylacetate	43	56	43	Decanal	57	82 112
19	Octane	85	114	44	Dodecane	57	85 170
20	Tetrachloroethene	166	164	45	Tridecane	57	85
21	Hexamethylcyclotrisiloxane (D3)	207	96	46	Dodecamethylcyclohexasiloxane (D6)	341	429
22	Ethylbenzene	91	106	48	Tetradecamethylhexasiloxane (L6)	221	443
23	m-Xylene	91	106	47	Tetradecane	57	85
24	p-Xylene	91	106	49	Pentadecane	57	85
25	Styrene	104	78	50	Hexadecane	57	85

Table 3. Concentrations of volatile methylsiloxanes in indoor air in different sampling volumes.

Flow rate (mL/min)	Sampling time	Sampling volume (L)	Quantity (ng)					Concentration (µg/m ³)				
			D3	D4	D5	D6	L6	D3	D4	D5	D6	L6
100	30 min	2.98	9.08	1.98	3.85	<1.0	<1.0	3.05	0.66	1.29	<0.33	<0.33
100	60 min	5.98	13.18	4.01	7.94	1.46	<1.0	2.20	0.67	1.33	0.24	<0.17
10	24 hr	14.396	34.53	10.92	15.48	3.28	<1.0	2.40	0.76	1.08	0.23	<0.07

Table 4. Concentrations of volatile methylsiloxanes in indoor air in different sampling times.

Flow rate (mL/min)	Sampling time	Sampling volume (L)	Quantity (ng)					Concentration ($\mu\text{g}/\text{m}^3$)				
			D3	D4	D5	D6	L6	D3	D4	D5	D6	L6
100	30 min	2.98	<1.0	1.68	6.28	1.21	<1.0	<0.33	0.56	2.11	0.41	<0.33
2	24 hr	2.879	<1.0	1.32	3.12	<1.0	<1.0	<0.33	0.46	1.09	<0.33	<0.33

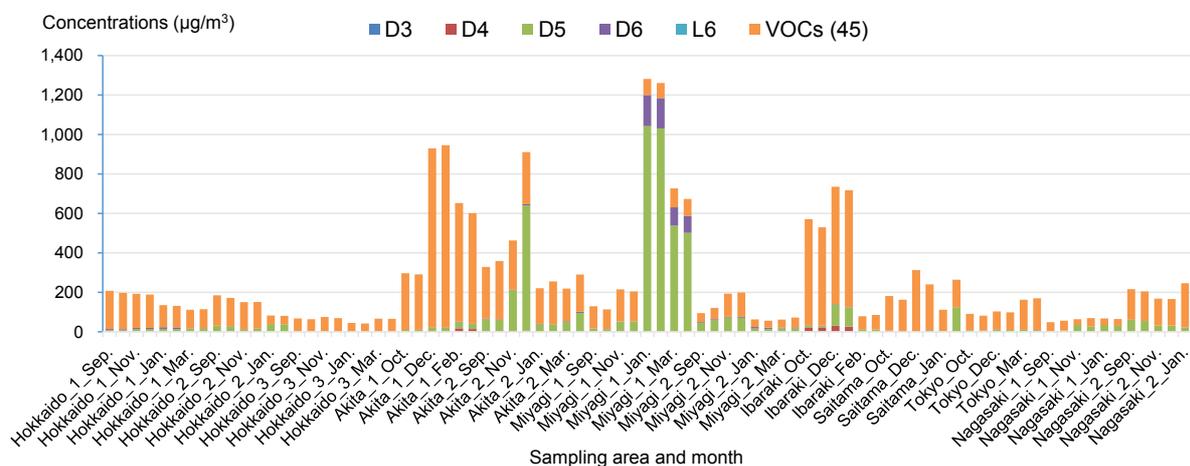


Figure 1. Concentrations of volatile methylsiloxanes and 45 volatile organic compounds (VOCs) in indoor air from Japanese residential houses ($\mu\text{g}/\text{m}^3$).

Table 5. Concentrations of volatile methylsiloxanes (VMS) and 45 volatile organic compounds (VOCs) ($\mu\text{g}/\text{m}^3$), composition rates and sample conditions in indoor air from Japanese residential houses.*

Compounds	Mean	Median	Minimum	Maximum	Standard deviation
D3	1.2	1.1	<0.33	4.3	1.1
D4	2.2	0.45	<0.33	30	5.6
D5	72	18	0.60	1,042	186
D6	7.5	0.54	<0.33	158	27
L6	0.022	<0.33	<0.33	0.77	0.12
VMS (5 compounds)	83	23	0.60	1,201	212
VOCs (45 compounds)	176	128	28	924	179
TVOC (50 compounds)	258	170	42	1,283	271
The rate of VMS per TVOC (%)	22	15	1.1	94	22
Temperature ($^{\circ}\text{C}$)	22	23	15	30	3.4
Relative humidity (%)	47	47	20	81	15

* 12 places, a total of 41 houses and 82 samples.

Table 6. Daily exposure rates of volatile methylsiloxanes in indoor air from Japanese residential houses ($\mu\text{g}/\text{kg}$ body weight per day).*

Compounds	Mean	Median	Minimum	Maximum	Standard deviation
D3	0.28	0.26	0	0.97	0.26
D4	0.50	0.10	0	6.8	1.3
D5	16	4.1	0.14	238	43
D6	1.7	0.12	0	36	6.3
L6	0.0050	0	0	0.18	0.027
VMS (5 compounds)	19	5.3	0.14	274	48

* 12 places, a total of 41 houses and 82 samples.