Volatile Organic Compound (VOC) Analysis and Anti-VOC Measures in Water-based Paints

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We developed an analytical method for volatile organic compounds (VOCs) used as film-forming agents or anti-freeze agents in water-based paints by flame ionization detection (FID-GC) and gas chromatography mass spectrometry (GC/MS). Twelve VOC components were separated using 2 types of column that differ in polarity. In addition, a pretreatment method by ethyl acetate-water partition was evaluated, and a survey of the use of VOCs in commercially available water-based paints was performed. For indoor paints, the anti-VOC measures included changes from VOC solvents to semi-VOC (SVOC) solvents such as those from 2,2,4-trimethyl-1,3-pentanediol-monoisobutyrate (TMPMIB) to 2,2,4-trimethyl-1,3-pentanediol diisobutyrate and from ethylene glycol (EG) to triethylene glycol. However, in multipurpose paints for both indoor and outdoor use, VOCs such as EG, TMPMIB, diethyleneglycol dibutyl ether, and diethyleneglycol monobutyl ether were detected. Since these products may be also used for indoor painting, indications of VOC components and caution for use on products are necessary.

Key words —— volatile organic compounds, water-based paints, flame ionization detection, gas chromatography mass spectrometry, film-forming agents, anti-freeze agents

INTRODUCTION

With an increase in the airtight nature of houses, indoor air pollution has become a serious issue. Therefore, paints for construction and household use have been rapidly changing from solvent-type (oil-based) paints emitting many volatile organic compounds (VOCs) to water-based paints.[1,2] For water-based paints, anti-volatile organic compound (VOC) measures such as a reduction in VOC components and a change to solvents with a high boiling point began to be taken.[1,2] VOCs used in water-based paints include film-forming agents (such as texanol and cellosolve) and anti-freeze agents (such as glycols).[1] There have been many studies on VOC measurement in air,[3–8] but few studies that directly analyzed VOCs in paints.[9] To investigate the present status of the use of VOCs in water-based paints and anti-VOC measures, we developed a method for the analysis of 12 VOC components used in paints by flame ionization detection (FID-GC) and gas chromatography mass spectrometry (GC/MS), and performed an analysis survey by this method.

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MATERIALS AND METHODS

Samples —— Fifteen water-based paint products were used as test samples.

Reagents —— Chemical names used here and terms of abbreviations are shown in Table 1. Table 1 shows the manufacturers and boiling points of the standards of 12 VOCs analyzed. All standards were of analytic grade or better. Eight VOCs from No. 1 to No. 8 are used as film-forming agents while 4 VOCs from No. 9 to No. 12 are used as anti-freeze agents. Ethyl acetate was used for pesticide residue analysis produced by Wako Pure Chemical Indus-

Table 1. Analyzed VOCs

Abbreviation	Chemical Name	B.P.	Manufacturer
1. CA	Ethyleneglycol monoethyl ether acetate (Cellosolve Acetate)	156°C	Tokyo Chemical Industry Co., Ltd.
2. BC	Ethyleneglycol butyl ether (Butyl Cellosolve)	171°C	Tokyo Chemical Industry Co., Ltd.
3. BCA	Ethyleneglycol butyl ether acetate (Butyl Cellosolve Acetate)	188°C	Tokyo Chemical Industry Co., Ltd.
4. DEGDB	Diethyleneglycol dibutyl ether	256°C	Wako Pure Chemical Industries Co., Ltd.
5. DEGMB	Diethyleneglycol monobutyl ether	230°C	Wako Pure Chemical Industries Co., Ltd.
6. TMPMIB-1	2,2,4-trimethyl-1,3-pentanediol-1-monoisobutyrate	250°C	Tokyo Chemical Industry Co., Ltd.
7. TMPMIB-3	2,2,4-trimethyl-1,3-pentanediol-3-monoisobutyrate		
8. TMPDIB	2,2,4-trimethyl-1,3-pentanediol diisobutyrate	280°C	Tokyo Chemical Industry Co., Ltd.
9. PG	Propylene glycol	187°C	Wako Pure Chemical Industries Co., Ltd.
10. EG	Ethylene glycol	197°C	Wako Pure Chemical Industries Co., Ltd.
11. DEG	Diethylene glycol	245°C	Tokyo Chemical Industry Co., Ltd.
12. TEG	Triethylene glycol	285°C	Tokyo Chemical Industry Co., Ltd.

No. 1–8 Film-forming agents, No. 9–12 Anti-freeze agents, Texanol: TMPMIB-1 and TMPMIB-3.

tries, Co., Ltd. (Osaka, Japan).

FID-GC Conditions —— As an FID-GC apparatus, a Hewlett Packard 5890 Series II Plus GC model with a Hewlett Packard FID detector was used. Samples (1 μl) were automatically injected by the splitless method using a Hewlett Packard 7673 model. The following 2 types of column that differ in polarity were used. (1) GL Science TC-WAX (0.25 mmϕ × 30 m; film thickness, 0.25 μm)—Operating conditions: carrier gas flowrate, He 1 ml/min; injection temperature, 250°C; detector temperature, 280°C; and column temperature, 50°C (3 min)–6°C/min–100°C (0 min)–10°C/min–250°C (3 min). (2) GL Science Inert CAP 5 MS (0.25 mmϕ × 30 m; film thickness, 0.25 μm)—Operating conditions: carrier gas flowrate, He 1 ml/min; injection temperature, 200°C; detector temperature, 280°C; and column temperature, 60°C (1.5 min)–10°C/min–280°C (10 min).

GC/MS Conditions —— As a GC/MS apparatus, a Hewlett Packard 5890 Series II Plus GC model with a Hewlett Packard MS detector (MSD 5972) was used. The columns (2 types) for GC and operating conditions were the same as those in FID-GC. Samples (1 μl) were injected by the splitless method using a Hewlett Packard 7673 model. The ionization voltage was set at 70 eV (EI method). MS spectra were scanned in the range from m/z 20 to 450 and quantified by SIM.

Preparation of Test Samples —— Paint samples (0.5 g) were put into 50 ml centrifugation tubes containing 15 ml distilled water, which were adjusted with distilled water to a volume of 20 ml. After the addition of 20 ml of ethyl acetate, the tubes were shaken and centrifuged at 3000 rpm. The ethyl acetate phase was dehydrated with sodium sulfate, and substances with low polarity were determined by FID-GC and GC/MS. In addition, 0.1 ml of the water phase was obtained and mixed with ethyl acetate to obtain a volume of 5 ml, and dehydrated with sodium sulfate. This solution was applied to FID-GC and GC/MS, and 4 types of glycol with high polarity [ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG), and triethylene glycol (TEG)] were determined.

RESULTS AND DISCUSSION

Evaluation of Measurements by FID-GC and GC/MS

To analyze the 12 VOCs by GC (FID-GC, GC/MS), mutual separation was evaluated using various columns. First, using a TC-WAX column with high polarity, mutual separation was evaluated. Figure 1 shows an FID-GC of 11 VOCs measured using TC-WAX, and Fig. 2 shows a total ion chromatogram (TIC) obtained by GC/MS. This column did not allow the mutual separation of 2,2,4-trimethyl-1,3-pentanediol-monoisobutyrate (TMPMIB-1 and -3) and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TMPDIB). The total ion chromatogram of TMPDIB is shown in Fig. 3.

Next, the conditions of the mutual separation of these VOC components were evaluated using Inert CAP 5 MS columns with very low polarity. Figure 4 shows an FID-GC of 10 VOCs measured using Inert CAP 5MS, and Fig. 5 shows a total ion chromatogram obtained by GC/MS. In this column, PG and EG could not be detected due to absorption and/or degradation. In addition, the mutual separation

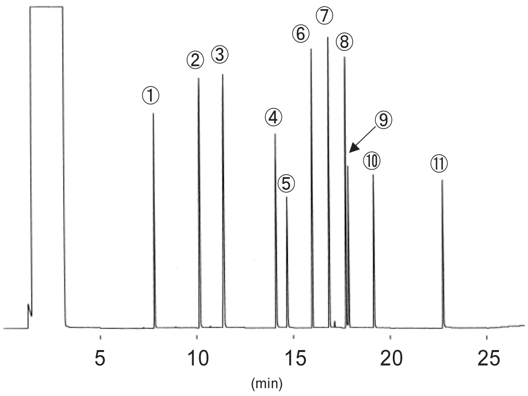


Fig. 1. FID Gas Chromatogram of 11 Types of VOCs Using TC-WAX Column

Operating Conditions for FID-GC are given in text. ①CA: Ethyleneglycol monoethyl ether acetate, ②BC: Ethylenglycol butyl ether, ③BCA: Ethyleneglycol butyl ether acetate, ④PG: Propylene glycol, ⑤EG: Ethylene glycol, ⑥DEGDB: Diethyleneglycol dibutyl ether, ⑦DEGMB: Diethylene glycol monobutyl ether, ⑧TMPMIB-1: 2,2,4-trimethyl-1,3-pentanediol-1-monoisobutyrate, ⑨TMPMIB-3: 2,2,4-trimethyl-1,3-pentanediol-3-monoisobutyrate, ⑩DEG: Diethylene glycol, ⑪TEG: Triethylene glycol.

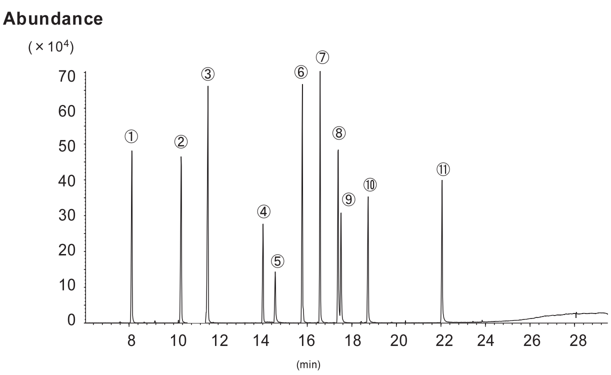


Fig. 2. Total Ion Chromatogram of 11 Types of VOCs Using TC-WAX Column

Operating Conditions for GC/MS are given in text. ①CA: Ethyleneglycol monoethyl ether acetate, ②BC: Ethylenglycol butyl ether, ③BCA: Ethyleneglycol butyl ether acetate, ④PG: Propylene glycol, ⑤EG: Ethylene glycol, ⑥DEGDB: Diethyleneglycol dibutyl ether, ⑦DEGMB: Diethylene glycol monobutyl ether, ⑧TMPMIB-1: 2,2,4-trimethyl-1,3-pentanediol-1-monoisobutyrate, ⑨TMPMIB-3: 2,2,4-trimethyl-1,3-pentanediol-3-monoisobutyrate, ⑩DEG: Diethylene glycol, ⑪TEG: Triethylene glycol.

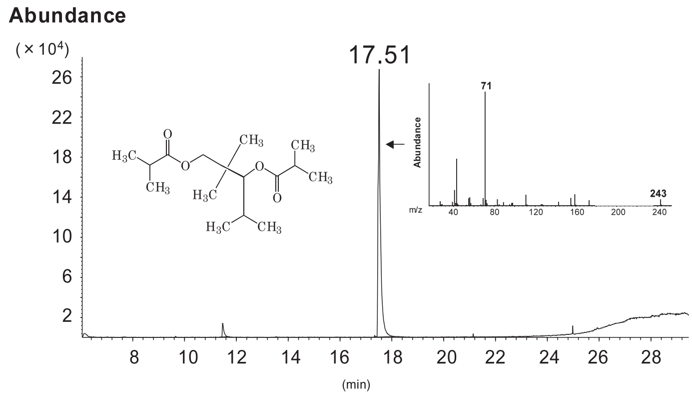


Fig. 3. Total Ion Chromatogram of TMPDIB Using TC-WAX Column

Operating Conditions for GC/MS are the same as those in Fig. 2.

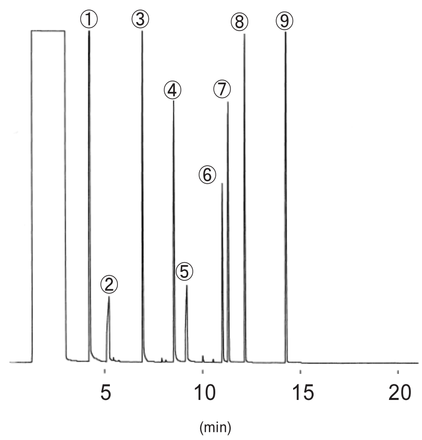


Fig. 4. FID Gas Chromatogram of 10 Types of VOCs Using Inert Cap 5MS Column

Operating Conditions for FID-GC are given in text. ①CA and BC: Ethyleneglycol monoethyl ether acetate and Ethylenglycol butyl ether, ②DEG: Diethylene glycol, ③BCA: Ethyleneglycol butyl ether acetate, ④DEGMB: Diethylene glycol monobutyl ether, ⑤TEG: Triethylene glycol, ⑥TMPMIB-3: 2,2,4-trimethyl-1,3-pentanediol-3-monoisobutyrate, ⑦TMPMIB-1: 2,2,4-trimethyl-1,3-pentanediol-1-monoisobutyrate, ⑧DEGDB: Diethyleneglycol dibutyl ether, ⑨TMPDIB: 2,2,4-trimethyl-1,3-pentanediol diisobutyrate.

of ethyleneglycol monoethyl ether acetate (CA) and ethyleneglycol butyl ether (BC) was poor. However, good separation of TMPMIB and TMPDIB could be achieved.

Therefore, each VOC was measured using TC-WAX, and when peaks of the retention time close to those of TMPMIB and TMPDIB appeared, these VOCs were quantified using Inert CAP 5 MS.

Figure 6 shows MS spectra of the VOCs, and Table 2 shows the monitor ions and quantification ions for the VOCs. Each calibration curve showed good linearity in the range from 0.1 to 100 μg/ml, and the reproducibility was high. The detection limit was 0.6–0.03 μg/ml (S/N = 5).

TMPMIB (Texanol) is a mixture of TMPMIB-1, which is formed by ester bonding between isobutyric acid and the hydroxyl group at position 1 of 2,2,4-trimethyl-1,3-pentanediol, and TMPMIB-3, which is formed by ester bonding between isobutyric acid and the hydroxyl group at position 3. Therefore, the TMPMIB standard showed 2 peaks. The peak areas of FID-GC were compared to confirm the ratio of the two isomers. In the standard

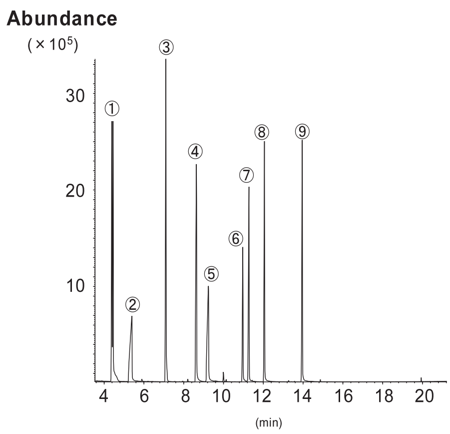


Fig. 5. Total Ion Chromatogram of 10 Types of VOCs Using Inert Cap 5MS Column

Operating Conditions for GC/MS are given in text. ①CA and BC: Ethyleneglycol monoethyl ether acetate and Ethyleneglycol butyl ether, ②DEG: Diethylene glycol, ③BCA: Ethyleneglycol butyl ether acetate, ④DEGMB: Diethylene glycol monobutyl ether, ⑤TEG: Triethylene glycol, ⑥TMPMIB-3: 2,2,4-trimethyl-1,3-pentanediol-3-monoisobutyrate, ⑦TMPMIB-1: 2,2,4-trimethyl-1,3-pentanediol-1-monoisobutyrate, ⑧DEGDB: Diethyleneglycol dibutyl ether, ⑨TMPDIB: 2,2,4-trimethyl-1,3-pentanediol diisobutyrate.

Table 2. Monitor Ions for SIM Measurement

VOCs	Monitor ions (m/z)
CA	43, 59, 187
BC	57, 87
BCA	57, 87
DEGDB	57, 75
DEGMB	57, 75
TMPMIB-1	71, 89
TMPMIB-3	71, 89
TMPDIB	71, 243
PG	31, 43, 45
EG	31, 43
DEG	45, 75
TEG	45, 75

The underlined number is the m/z of the ion used for quantification. Chemical names and terms of abbreviations are given in Table 1.

used in this study, the indicated 1-monoisoburyrate : 3-monoisobutyrate was 6 : 4. Using a TC-WAX column, the area ratio of the peak appearing first to that appearing later was 4 : 6 (Fig. 1). Therefore, using this column, the peak of 3-monoisobutyrate was detected first. Conversely, the ratio was 6 : 4 using an Inert CAP 5 column (Fig. 4). Thus, the retention times of the two isomers using the former column were the reverse of those using the latter column. The MS spectrum of 1-monoisobutyrate slightly differed from that of 3-monoisobutyrate, but both spectra showed high m/z 71 ion intensity (Fig. 6). Therefore, in SIM measurement, m/z 71 of the ion was used for quantification, and TMPMIB was quantified as the total of the peak areas of the two isomers.

Preparation of Test Solutions and Recovery Experiments

Water-based solutions of the 12 VOCs at concentrations of 100, 1000, and 10000 μg/ml were prepared. Each solution was mixed with the same volume of ethyl acetate. Evaluation of the liquid-liquid partition rate showed the transfer of 97–101% or more of 7 VOCs [CA, BC, ethyleneglycol butyl ether acetate (BCA), diethyleneglycol dibutyl ether (DEGDB), TMPMIB-1, TMPMIB-3, and TMPDIB] and 75–85% of diethyleneglycol monobutyl ether (DEGMB) to the ethyl acetate phase, and the remaining of 98–100% or more of glycols in the water phase. Therefore, the compounds that were transferred to the ethyl acetate phase were dehydrated and applied to GC and GC/MS. Glycols remaining in the water phase were mixed with 50-volume ethyl acetate, dehydrated, and ethyl acetate solution was measured. For DEGMB, the total of the values in both phases was used. For products in which each VOC was not detected, recovery experiments (n = 3) were performed, and good recovery rates (94–105%) were obtained.

Analysis of Commercially Available Products

VOC analysis was performed in 15 commercially available water-based paint products by the above method. The results are shown in Table 3. Four samples (No. 1–4) were paints for business use with consideration paid to the indoor environment, and 5 products (No. 5–9) were commercially available indoor paints for household use. Six products (No. 10–15) were commercially available multipurpose paints for household use that can also be used for outdoor painting.

Figure 7 shows the TIC in the ethyl acetate phase of Sample No. 3 in which TMPDIB and TMPMIB could be quantified using Inert CAP 5 MS. Figure 8 shows the TIC of the water phase of No. 6 in which TEG was detected using TC-WAX while Fig. 9 shows the TIC of the ethyl acetate phase of Sample No. 8 in which BC was detected using TC-WAX. Figure 10 shows the TICs (ethyl acetate and water phases) of Sample No. 13 in which 5 VOCs were detected using TC-WAX and the TIC of its ethyl acetate phase using Inert CAP 5 MS. As shown in these figures, there were only a few in-

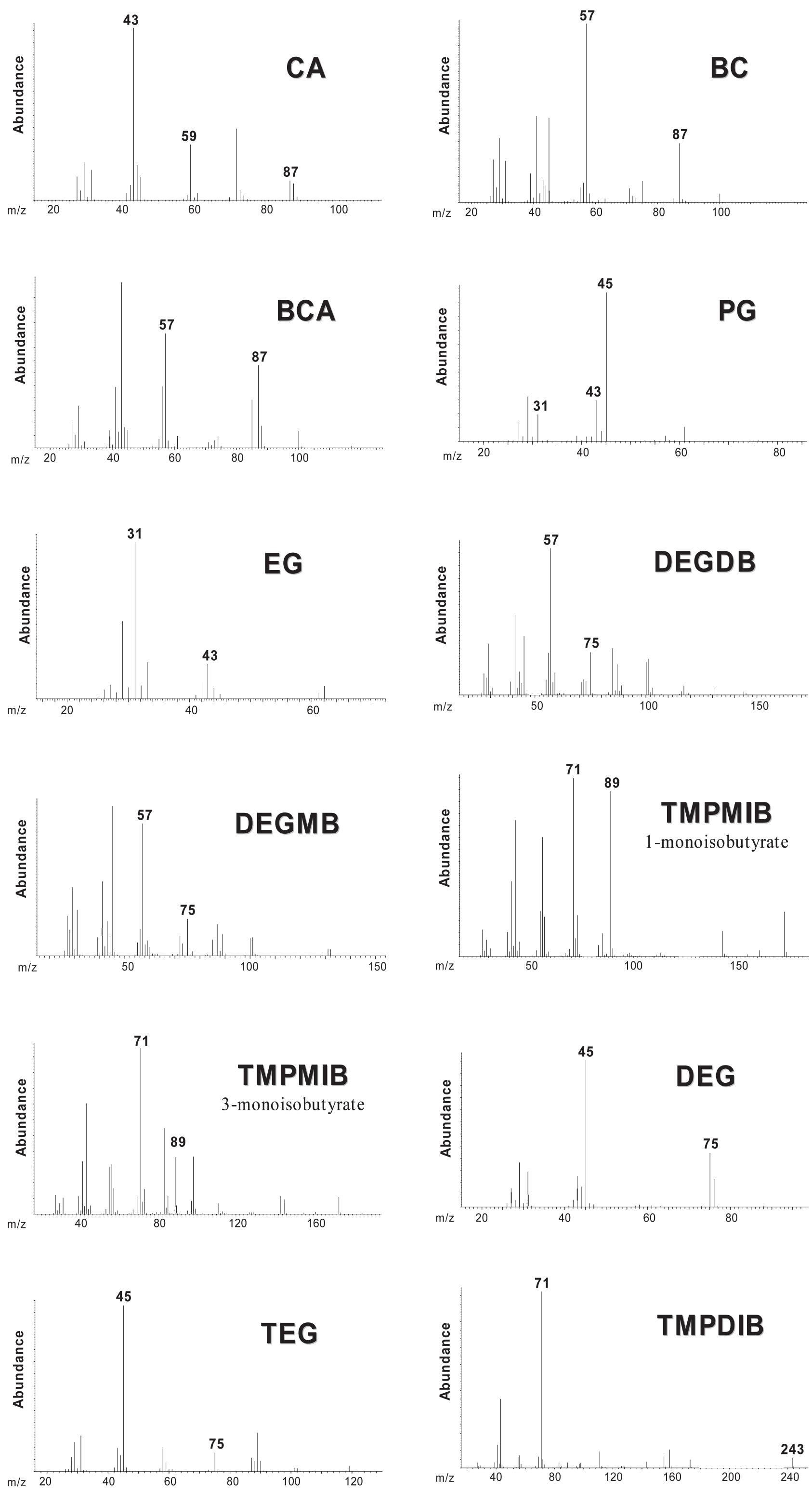


Fig. 6. Mass Spectra of 12 Types of VOCs

Chemical names and terms of abbreviations are given in Table 1.

terfering peaks.

There have been many studies on VOC measurement in air.[3–8] Since the collection efficiency from the air differs among substances, the values of VOC measurement are not always consistent with the actual diffusion values. Therefore, the VOC

Table 3. Analytical Results of VOCs in Water-based Paint

Sample No.	Use	Manufacturer	Concentration of VOCs	
1	Paint for business use (indoor)	A	TMPMIB	0.003%
2	Paint for business use (indoor)	A	N.D.	
3	Paint for business use (indoor)	B	EG	0.07%
			DEGMB	0.11%
			TMPMIB	0.03%
			TMPDIB	1.52%
4	Paint for business use (indoor)	B	TEG	0.13%
5	Paint for household use (indoor)	C	EG	0.03%
			TMPMIB	0.013%
			TMPDIB	4.39%
6	Paint for household use (indoor)	C	TEG	0.20%
7	Paint for household use (indoor)	D	TMPMIB	0.013%
			TMPDIB	2.96%
8	Paint for household use (indoor)	E	BC	0.03%
9	Paint for household use (indoor)	D	EG	0.14%
			TMPMIB	0.026%
			TMPDIB	1.31%
10	Paint for household use (multipurpose)	D	EG	0.17%
			DEGDB	0.87%
			DEGMB	0.38%
			TMPMIB	3.69%
			TMPDIB	0.006%
11	Paint for household use (multipurpose)	D	EG	0.53%
			DEGDB	0.37%
			DEGMB	1.24%
			TMPMIB	1.33%
12	Paint for household use (multipurpose)	C	EG	0.14%
			TMPMIB	0.015%
			TMPDIB	3.30%
13	Paint for household use (multipurpose)	D	EG	0.32%
			DEGDB	0.73%
			DEGMB	0.60%
			TMPMIB	5.91%
14	Paint for household use (multipurpose)	D	EG	0.34%
			DEGDB	0.56%
			DEGMB	0.51%
			TMPMIB	4.69%
15	Paint for household use (multipurpose)	F	EG	0.40%
			TMPMIB	3.98%
			TMPDIB	0.72%

BC: Ethylenglycol butyl ether, EG: Ethylene glycol, DEGDB: Diethyleneglycol dibutyl ether, DEGMB: Diethylene glycol monobutyl ether, TMPMIB-1: 2,2,4-trimethyl-1,3-pentanediol-1-monoisobutyrate, TMPMIB-3: 2,2,4-trimethyl-1,3-pentanediol-3-monoisobutyrate, TMPDIB: 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, TEG: Triethylene glycol, N.D.: Not detected.

content of the source should also be measured. VOC analysis in water solution by the headspace method or the solid-phase micro extraction (SPME) method has been frequently reported.[10–12] These methods differ in the recovery rate of each substance and reproducibility, and their procedures are complicated. In this study, VOCs in water-based paints could be quantified by a simple method using only liquid-liquid distribution. There have been studies on the analysis of VOCs in water-based paints[9, 13, 14] but no studies on the simultaneous analysis of 12 VOCs that differ in polarity from polar substances to nonpolar substances such as TMPDIB by GC/MS. Therefore, this method is applicable to the measurement of VOCs used in water-based paints.

As indoor anti-VOC measures, solvents with a

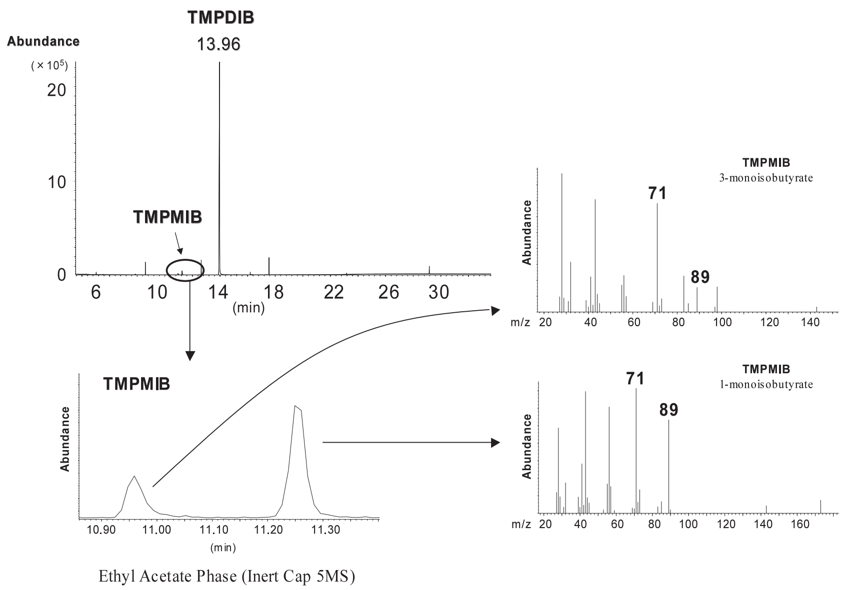


Fig. 7. Total Ion Chromatograms of Sample No. 3

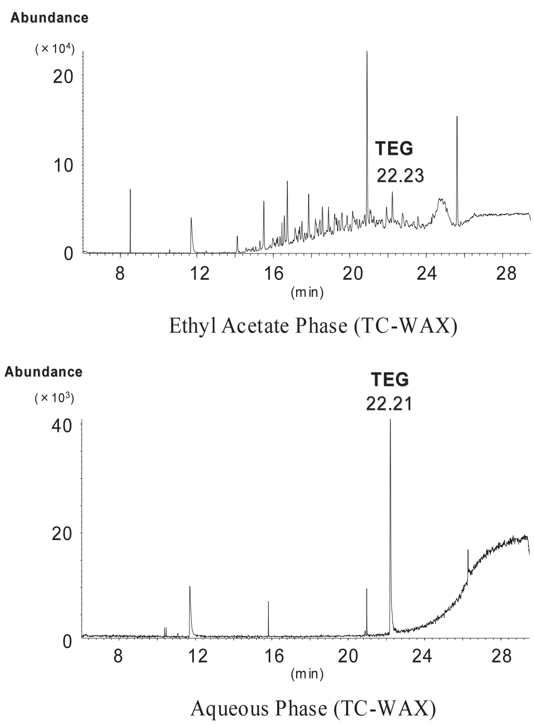


Fig. 8. Total Ion Chromatograms of Sample No. 6

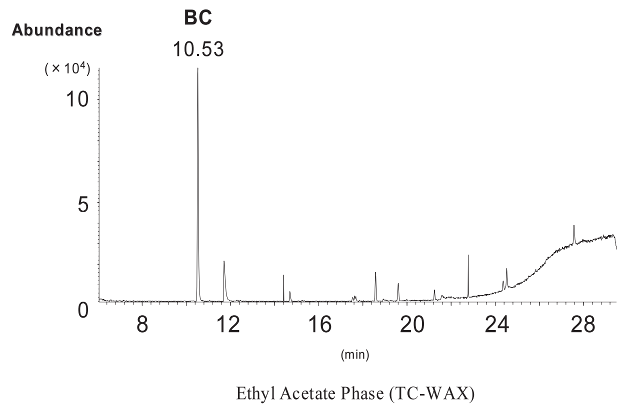
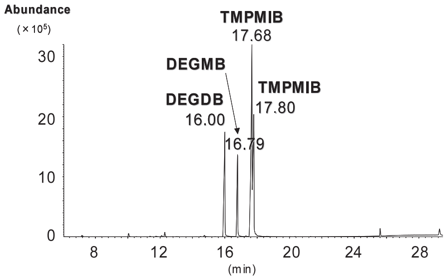
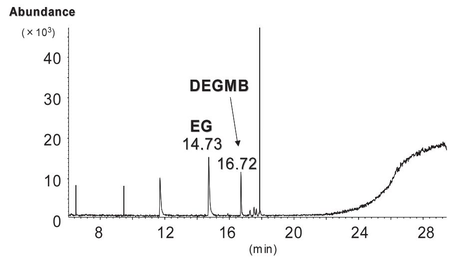


Fig. 9. Total Ion Chromatogram of Sample No. 8

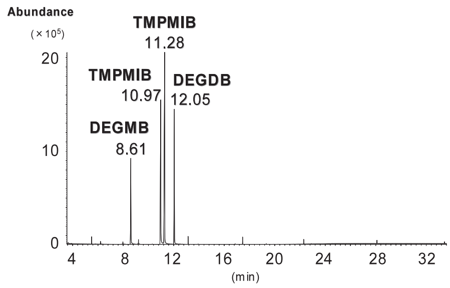
high boiling point were used in the indoor water-based paints evaluated in this study. As film-forming agents, TMPMIB with a low boiling point (250°C) was changed to TMPDIB (280°C). Concerning anti-freeze agents, EG with a low boiling point (197°C) was reduced (No. 3, 5) or changed to TEG with a high boiling point (285°C) (No. 4, 6). Thus, changes to SVOCs with a boiling point higher than the WHO's VOC criteria (260°C) were observed. Both TMPMIB and TMPDIB irritate the eyes and skin, but the LD_{50} of TMPDIB is higher.[15–17] Some studies on TMPDIB toxicity have shown that this compound is relatively safe.[18–21] EG and DEG not only irritate the eyes and skin but also affect the kidneys and central nervous system, sometimes inducing renal failure and brain injury.[22–25] TEG has been reported to be safer than EG.[26,27] Therefore, in terms of toxicity also, the components have been changed to less toxic substances. However, in 1 commercially available indoor paint for household use (No. 8), BC with a low boiling point (171°C) was detected. BC irritates the eyes and skin and affects the central nervous system,



(1) Ethyl Acetate Phase (TC-WAX)



(2) Aqueous Phase (TC-WAX)



(3) Ethyl Acetate Phase (Inert Cap 5MS)

Fig. 10. Total Ion Chromatograms of Sample No. 13

kidneys, and the liver.[28, 29] Since there is a possibility that evaporated BC reaches a toxic level, caution for use should be indicated.

In the multipurpose (indoor and outdoor) paints, TMPMIB and EG were detected. In 4 products, DEGDB (256°C) and DEGMB (230°C) as film-forming agents were detected. DEGMB irritates the eyes and may reach toxic levels after evaporation.[30] These products are also used for indoor painting, but the indications on the products do not show differences between their solvents and those of paints only for indoor use. In addition, there were no indications of solvents used in paints for household use. VOC components and items requiring caution for use should be indicated clearly on products.

In consideration of the possible use of TMPDIB and TMPMIB as plasticizers, we analyzed plasticizers in 26 commercially available vinyl chloride products.[31] TMPDIB was detected but not TMPMIB.

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