

Application News

No. AD-0079

GC-2025

Determination of Volatile Organic Compounds in Water-based Paints and Varnishes Using Gas Chromatography

□ Introduction

Organic solvents in solvent-based paints allow easy paint application and fast drying. However, in the process of drying, Volatile Organic Compounds (VOCs) which are harmful to health will be emitted into the environment [1]. Solvent-based paint is one of the main contributors to indoor environmental pollution according to U.S. Environmental Protection Agency [2]. Water-based paints with near zero VOC content have been steadily used as a substitute, making up to 80% of the residential market [3]. This increase in popularity triggers the need to verify the stated amount of VOCs in water-based paints, in order to ensure that they adhere to regulations. The aim of this work is to develop a fast and efficient method for the quantitative determination of the amount of VOCs in water-based paints and varnishes using GC. Thirty solvents commonly used in water-based paints and varnishes were analyzed and quantified in reference to the method described in GB 18582-2008 by China [4].

□ Experimental

Analytical Conditions and Chemicals

A gas chromatograph GC-2025 (Shimadzu Corporation, Japan) was utilized in this work. The detailed analytical conditions are shown in Table 1. Thirty commonly used solvents in paint (see Table 2) were obtained from Sigma Aldrich, Merck and J.T. Baker. All the chemicals used in this study have a minimum purity of 99%. Dimethyl glycol and dimethyl diglycol were used as internal standards for paint solvents which elute within their proximities. Diethyl adipate was used as the boiling point marker. As indicated in GB 18582-2008, any compound eluting after the boiling point marker (bp 251°C) will not be regarded as a VOC.

Table 1: GC analytical conditions for VOC determination

Auto-injector	AOC-20i
Gas Chromatograph	GC-2025
Column	J&W DB-1701, 30m x 0.25mm x 0.25µm
Injection Condition	200°C, split mode, split ratio 20
Injection Volume	0.5µl
Carrier Gas	Helium, 99.9997% purity
Gas Flow Condition	Constant linear velocity mode, linear velocity 37.5cm/s, purge flow 3ml/min
Oven Temperature	35°C (1min)
Programming	→ 20°C/min to 60°C (1.5min) → 30°C/min to 90°C (1min) → 35°C/min to 150°C (0.5min) → 20°C/min to 240°C
Detector	FID-2010
FID Temperature	280°C
Gas Flow Condition	Hydrogen flow 30ml/min Air flow 400ml/min Makeup gas flow (Nitrogen) 40ml/min

Preparation of Standard and Sample

Stock solutions of thirty VOCs, internal standards and boiling point marker (1%, w/w) were prepared using acetonitrile as the diluent. For standards, the amount prepared varied with respect to the sample for the one-point calibration curve. Hence, the amount of VOC content in the paint should be roughly known beforehand. An example of the preparation is illustrated in the Results and Discussion section.

Paint samples were weighed and spiked with the internal standards and boiling point marker according to the GB 18582-2008 method, then topped up to 10ml with acetonitrile, as summarized in Figure 1. As paint samples may be pigmented or otherwise difficult for direct analysis, a clean-up step with centrifugation and filtration was added to the workflow. Finally, a 1ml-portion of the clear solution was used as the sample solution for GC analysis.

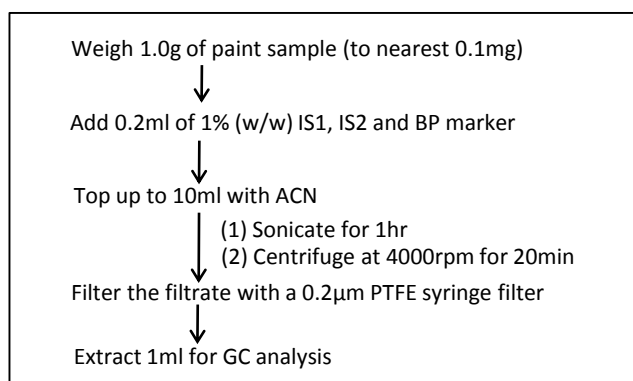


Figure 1: Flow chart of sample pre-treatment method

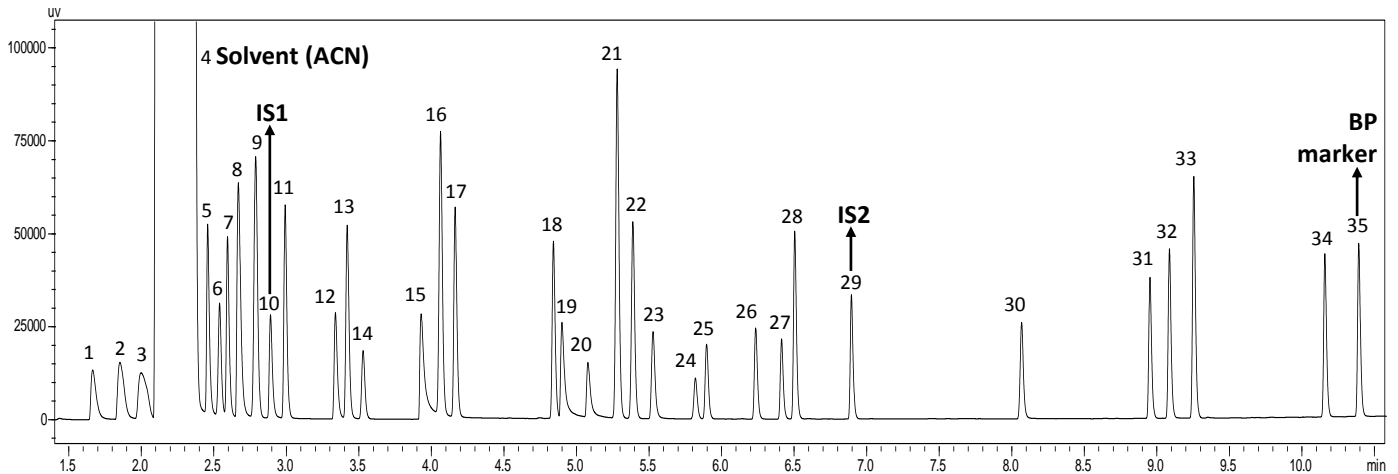


Figure 2: GC-FID chromatogram of the 30 VOCs with internal standards and boiling point marker

Table 2: List of VOCs according to elution order with relative standard deviation of repeatability test (n=5) for concentrations 300mg/L and 30mg/L. The abbreviated names are used in this work. Compounds listed in bold are aromatics, whose total concentration in paint should not exceed 300mg/L. The summed concentration of other VOCs should not exceed 120g/L.

Peak no.	Name of VOC	Abbr.	Retention time (min)	%RSD (300mg/L)	%RSD (30mg/L)
1	methanol	MeOH	1.67	0.24	0.57
2	ethanol	EtOH	1.85	0.30	1.24
3	isopropanol	isoPrOH	2.00	0.22	0.83
4	acetonitrile (<i>solvent</i>)	ACN	2.33	-	-
5	n-propanol	PrOH	2.46	0.18	0.99
6	ethyl acetate	EtAc	2.54	0.22	0.83
7	methyl ethyl ketone	MEK	2.60	0.28	0.61
8	triethylamine	Et3N	2.67	0.25	0.45
9	benzene	Ben	2.79	0.19	0.89
10	dimethyl glycol (<i>internal standard 1</i>)	IS1	2.89	0.27	0.31
11	isobutanol	isoBuOH	2.99	0.28	0.72
12	methoxy propanol	MeO-PrOH	3.34	0.26	1.06
13	n-butanol	BuOH	3.42	0.21	0.69
14	n-propyl acetate	nPrAc	3.53	0.26	1.71
15	dimethyl ethanol amine	DMEA	3.93	0.35	Not detected
16	toluene	Tol	4.06	0.28	0.48
17	methyl isobutyl ketone	MIBK	4.16	0.35	0.49
18	n-butyl acetate	nBuAc	4.84	0.29	0.72
19	2-amino-2-methyl-1-propanol	AMP	4.90	0.21	2.22
20	ethylene glycol	MEG	5.08	0.34	0.47
21	ethylbenzene	EtBen	5.28	0.31	0.73
22	m,p-xylenes	m,p-Xyl	5.39	0.44	0.87
23	1,2-propanediol	1,2-PEG	5.53	0.28	1.52
24	o-xylene	o-Xyl	5.82	0.30	0.41
25	methoxy propyl acetate	MeO-PrAc	5.90	0.37	0.78
26	diacetone	diAcO	6.24	0.36	1.04
27	cellosolve acetate	Et-MEG-Ac	6.41	0.27	0.91
28	2-butoxyethanol	Bu-MEG	6.51	0.26	0.74
29	dimethyl diglycol (<i>internal standard 2</i>)	IS2	6.90	0.34	0.27
30	diethylene glycol	DEG	8.07	0.36	0.89
31	2-(2-ethoxyethoxy)ethyl acetate	Et-DEG-Ac	8.95	0.42	0.64
32	2-(2-butoxyethoxy)ethanol	Bu-DEG	9.09	0.41	0.49
33	2,2,4-trimethyl-1,3-pentanediol	2,2,4	9.26	0.30	0.45
34	2-(2-butoxyethoxy)ethyl acetate	Bu-DEG-Ac	10.16	0.41	0.55
35	diethyl adipate (<i>boiling point marker</i>)	BP marker	10.39	0.32	0.78

□ Results and Discussion

Method Development

The GC method described in GB 18582-2008 is 31 minutes long, encompassing 24 different VOC solvents. The method was redeveloped in this work for the quantitation of the 30 VOCs. A fast and efficient gas chromatography separation was achieved within 10.5 minutes, with the result illustrated in Figure 2. Base peak separation for 35 peaks was achieved. As observed in the chromatogram, xylene was eluted out as two separate peaks. The m-Xyl and p-Xyl are completely overlapping in peak 22, while o-Xyl was eluted out as a single peak in peak 25. The quantitation of xylenes is considered as total xylenes of all the three isomers. Hence, it is not necessary to separate m-Xyl and p-Xyl.

The precision of the system was evaluated and the %RSD (n=5) of the peak areas obtained for the 35 peaks at 300mg/L were all below 0.5% (See Table 2). A set of stacked chromatograms for some of the compounds used are shown in Figure 3a.

Stacked chromatograms of these compounds obtained at 30mg/L are depicted in Figure 3b for comparison. The %RSDs at this concentration were below 2% (See Table 2). It is noted that DMEA peak (#15) was not detectable in the 30mg/L mixture. The sole purpose of the dilution is to certify this method's capability to fulfill the GB requirement of measuring total aromatic content to be below 300mg/L. Thus, as a non-aromatic compound, DMEA can be omitted.

Total VOC Content in Samples

One commercial indoor and one outdoor water-based paint samples, with known amount of solvents used, were analyzed using the developed method. The chromatograms of the indoor and outdoor paint samples are shown in Figure 4.

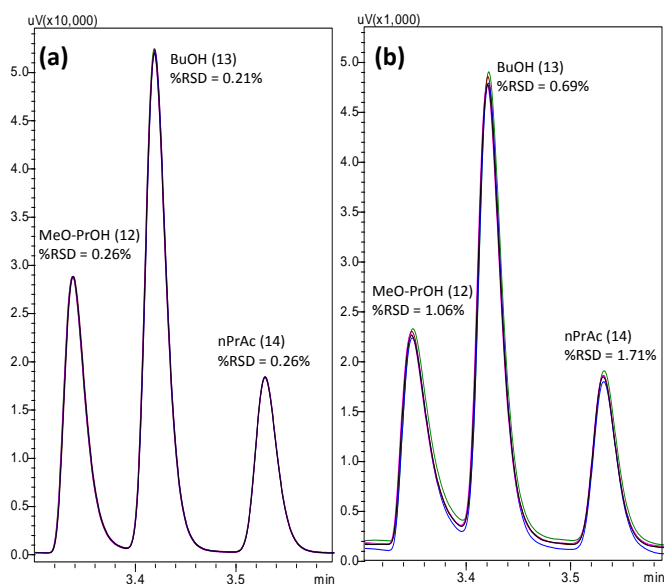


Figure 3: Overlapping of five chromatograms of select compounds at 300mg/L (a) and 30mg/L (b).

A one-point (internal standard method) calibration curve was established for each of the paint samples according to the GB 18582-2008 method. The calibration standard was prepared according to the previously known concentrations, as listed in Table 3. Internal standards were spiked according to the highest concentration compound within its group. For instance, 1700mg/L of IS2 was spiked for the outdoor paint calibration standard, with respect to that of Bu-DEG.

The individual concentrations of the VOC present in each commercial paint sample were determined according to the respective standard calibration curves using internal standard method (Table 3).

Concentrations of compounds which were not calibrated for, but eluted out before the boiling point marker, had to be taken into account separately. Such compounds were labeled as unknowns and calculated using the formula:

$$m_i = \frac{r_i \times A_i \times m_{is}}{m_s \times A_{is}} \quad (1)$$

Where

- m_i, m_{is} are the mass (in g) of component i and the internal standard in the sample solution (which also represent the concentrations of the respective components in w/w format)
- r_i is the response factor of the component i (assumed to be 1 for components not calibrated)
- m_s is the mass (in g) of paint sample used
- A_i, A_{is} are the respective peak areas of component i , and internal standard (obtained from chromatogram)

As seen in Figure 4, indoor paint sample has one unknown compound (labelled as Unknown 1) and outdoor paint sample has two (Unknown 2 and Unknown 3). Applying Equation 1, the concentrations were calculated to be 807mg/L, 178mg/L and 425mg/L for Unknown 1, 2 and 3 respectively.

Table 3: Results of total VOC content in two paint samples

Sample	Component	Calibration Conc. (mg/L)	Peak area	Actual Conc. (mg/L)	Total VOC content
Indoor	MEG	650	89205	882.1	32.8g/L
	AMP	100	20134	183.9	
	DEG	2000	133943	1359.1	
	2,2,4	50	10986	48.1	
	Unknown 1	-	127888	806.6	
	total concentration				
Outdoor	MEG	600	116930	1186.2	50.2g/L
	Unknown 2	-	23232	177.7	
	Bu-DEG	1700	485925	2886.7	
	2,2,4	300	78378	342.5	
	Unknown 3	-	63603	424.7	
	total concentration				

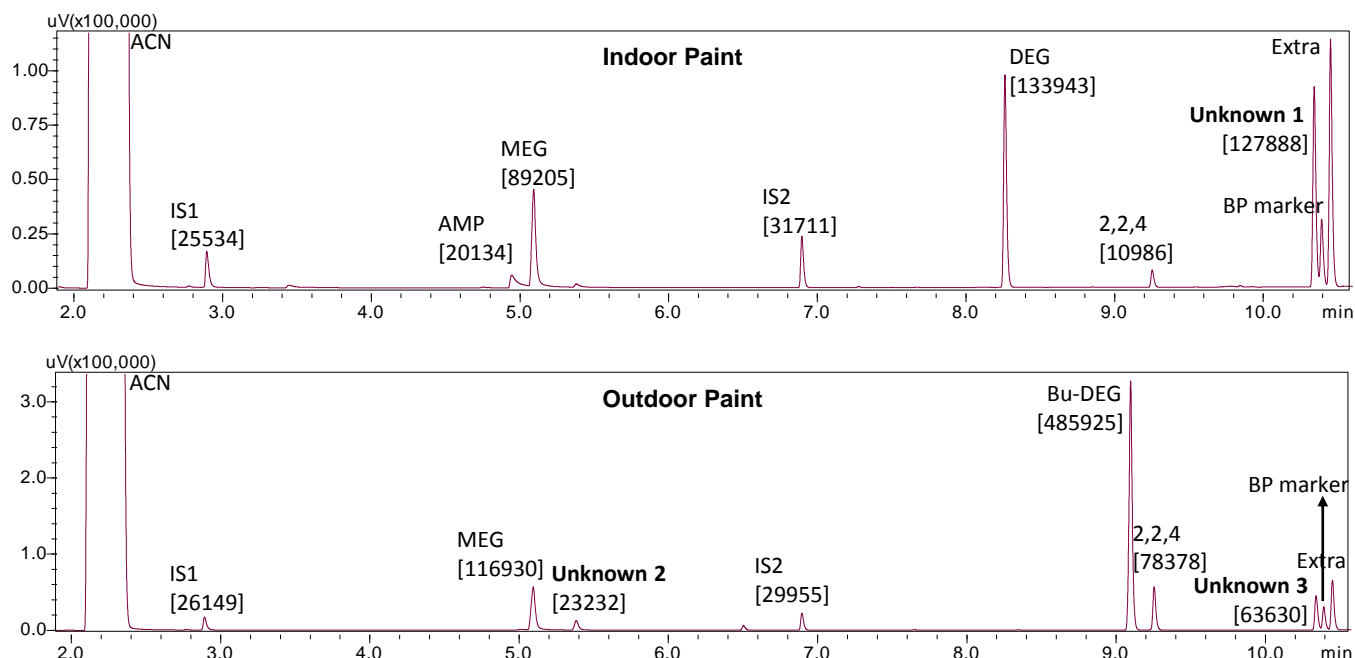


Figure 5: Chromatograms of indoor and outdoor paint samples spiked with internal standards and boiling point marker. The identified compounds are labelled with abbreviated names and peak areas in brackets.

Both indoor and outdoor paints contain an extra peak each that elute after the boiling point marker. As the GB method states that compounds eluting after the boiling point marker are not VOCs, their amounts are not of concern.

The concentrations of the individual compounds in each paint sample were summed up and multiplied by 10 to give the total VOC content (refer to workflow in Figure 1). As summarized in Table 3, the indoor and outdoor paint contain 32.8g/L and 50.2g/L of VOC respectively. The total VOC content in each paint does not exceed the 120g/L limit as stated in the China's regulation.

A final verification on the precision of the method was carried out, where the absolute difference between two single test results obtained by one operator in one laboratory within a short time interval had to be less than 10% (20% when done in different laboratories) [5]. Good repeatability was obtained for this verification (Table 4).

Table 4: Repeatability test for indoor and outdoor paint samples

Sample	Indoor Paint		Outdoor Paint	
	1 st run	2 nd run	1 st run	2 nd run
total VOC	32.80g/L	32.77g/L	50.18g/L	50.09g/L
absolute difference	0.03g/L \equiv 0.003%		0.09g/L \equiv 0.009%	

Conclusions

A fast, precise and efficient GC method was optimized using Shimadzu GC-2025 for the quantitative determination of 30 VOCs commonly found in water-based paints and varnishes. It is a simple method which employs one-point calibration to determine the total VOCs content in real paint samples. The precision of the system was illustrated by the excellent repeatability of the results obtained. The results also demonstrated the feasibility of this method to quantitate the amount of compounds which were not calibrated using standard solutions.

References

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