Application News

No. AD-0074

GCMS-QP2010 Ultra

Determination of Volatile Organic Compounds in Water-based Paints and Varnishes Using GC-MS

❑ Introduction

Water-based paint has been increasingly gaining popularity in the recent years for some of its advantages, such as drying faster and being easier to clean off, over oil-based paint (aka solvent-based paint). Furthermore, the biggest advantage of water-based paint is that it does not pervade the room with the strong smell that solvent-based paint does[1]. Volatile organic compounds (VOCs) are responsible for the signature smell in paints, and are considered to be harmful to the environment, even more so for the people who work with them on a regular basis[2,3]. In many countries, governmental regulations, consumer demands and technological advances have led to the development of low-VOC and zero-VOC paints and varnishes which have significantly less impact on human and environmental health. Currently, regulations are still not available in many countries in the Asian region. This application news aims to provide a general model on using GC-MS to determine the amount of VOCs in water-based paints and varnishes, in anticipation of any emerging regulations in the near future. Referring to the method described in ISO 11890-2:2013, thirty-five commonly used solvents in water-based paints and varnishes are analyzed and quantified[4].

❑ Experimental

Instrument and Analytical Conditions

A single quadrupole GC-MS (Shimadzu Corporation, Japan) was employed in this work. The detailed conditions are shown in Table 1.

Thirty-five commonly used solvents in paint (see Table 2) were obtained from Sigma Aldrich, Merck and J.T. Baker, all of which have a minimum purity of 99%. Dimethyl glycol and dimethyl diglycol are used as internal standards for solvents which elute within their proximities.

Table 1: GC-MS analytical conditions for VOC determination

Instrumentation	
GC-MS	GCMS-QP2010 ultra
Auto Injector	AOC-5000 Plus
Column	Rxi-624 Sil MS (Restek Corp.) 30 m x 0.25 mm x 1.4 µm
Workstation	GCMS Solution Version 4
Gas Chromatograph	
Injection Condition	250 °C, split mode, split ratio 50
Injection Volume	0.3 µl
Carrier Gas	Helium, 99.9997% purity
Gas Flow Condition	Constant linear velocity mode linear velocity 35cm/s purge flow 3ml/min
Oven Temperature Programming	50°C (2min) →10°C/min to 70°C (0.5min) →36°C/min to 160°C →10°C/min to 170°C →36°C/min to 280°C (2min)
Mass Spectrometer	
Ion Source Temperature	250°C
Interface Temperature	300°C
Acquisition Mode	Scan mode (30 – 400 amu)

Diethyl adipate was used as the boiling point marker. The use of the marker is such that anything which elutes after this marker (bp 251°C) would not be regarded as a VOC, as indicated in ISO 11890-2.

Standard and Sample Preparation

A mixed stock solution of the 35 VOCs was prepared at 2.5% (w/w) using acetonitrile as solvent. Internal standards and boiling point marker were also prepared at 1% (w/w) with acetonitrile as diluent. A series of calibration standard solutions (10, 20, 50, 100, 200, 500, 1000 and 2000 ppm) was then prepared from the stock solution, spiked with 200 ppm of internal standards and boiling point marker each, and diluted with acetonitrile.

Paint samples were pre-treated according to the ISO method with some modifications as summarized in Figure 1. A 1ml-portion of the final clear solution was used as the sample solution for analysis.
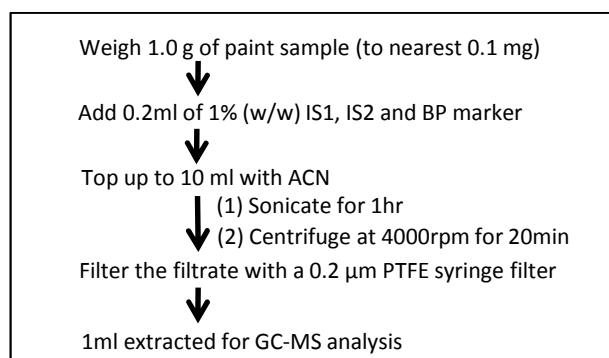
Weigh 1.0 g of paint sample (to nearest 0.1 mg)
↓
Add 0.2ml of 1% (w/w) IS1, IS2 and BP marker
↓
Top up to 10 ml with ACN
↓ (1) Sonicate for 1hr
(2) Centrifuge at 4000rpm for 20min
Filter the filtrate with a 0.2 µm PTFE syringe filter
↓
1ml extracted for GC-MS analysis

Figure 1: Flow chart of sample pre-treatment method
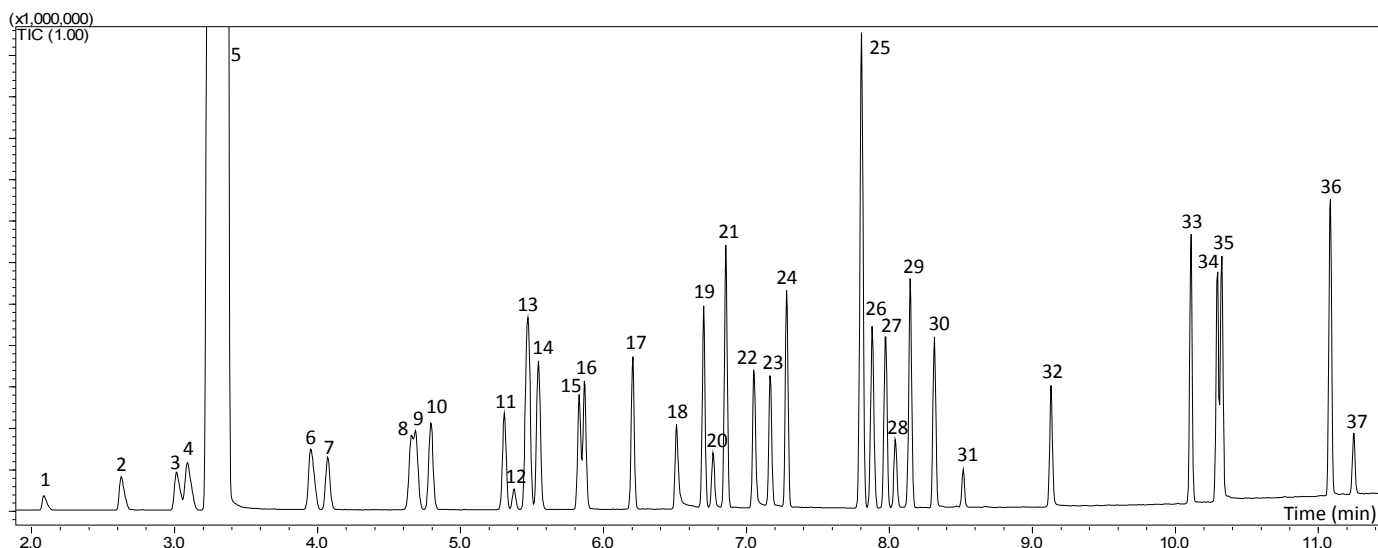
Figure 2: Chromatogram of 35 VOCs with internal standards and boiling point marker

❑ Results and Discussion

Method Development

A GC-MS method was developed for quantitation of the 35 VOCs. A fast gas chromatography separation was achieved and the result is depicted in Figure 2. It is noted that several peaks were not fully separated in this analysis. With reference to the chromatogram, the following compounds appeared in unresolved pairs: AcO and iPrOH (peaks 3 & 4, partial overlap), MEK and EtAc (peaks 8 & 9, complete overlap), iPrAc and Ben (peak 13, complete overlap), BuOH and MeO-PrOH (peaks 15 & 16, partial overlap), EtBen and MeO-PrAc (peak 25, complete overlap), m-Xyl and p-Xyl (peak 26, complete overlap), o-Xyl and Et-MEG-Ac (peak 29, complete overlap), and Bu-DEG and 2,2,4 (peaks 34 & 35, partial overlap).

It is however not an issue for GC-MS, because overlay peaks are distinguishable from their extract mass chromatograms. The only exception is the m- and p-xylenes pair (peak 26) due to their same mass and fragment pattern, which is normally unresolved. Nonetheless, it is considered as total xylenes along with the o-xylene in peak 29. Thus, separation for m-xylene and p-xylene is not necessary.
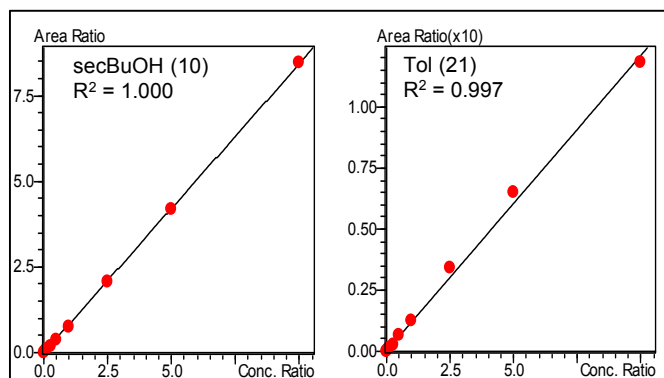
Table 2 shows the main fragments of the VOCs. The first fragment (in bold) was used as quantitation ion and the others as confirmation ions. It is noted that, because there are there many common fragments for acetone and isopropanol (peaks 3 & 4, partial overlap), only the molecular ion (m/z 58) was used for quantitation and confirmation of acetone.

Calibration curves of the 35 VOCs were established using mixed standard samples of concentrations from 10 ppm to 2000 ppm. Two calibration curves are illustrated in Figure 3, where secBuOH represents an average result and Tol represents the result with the least correlation coefficient. Linear calibration curves were obtained for all compounds ($R^2 > 0.997$) as shown in Table 2.

The precision of the system was evaluated and the %RSD (n=5) of peak areas obtained for 100 ppm concentration were below 5%, except for EtAc (5.21%), o-Xyl (5.64%), Et-MEG-Ac (5.69%) and Bu-DEG (5.33%) (See Table 2). A set of stacked mass chromatograms for some of the compounds used in the calibration curves are shown in Figure 4.

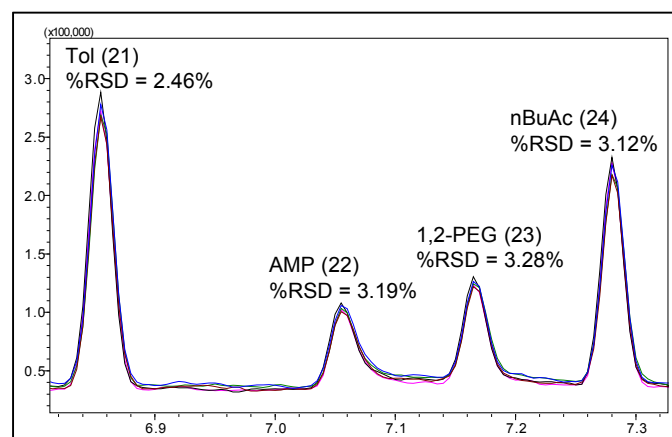Figure 3: Calibration curves of two select compounds from 10 to 2000 ppm

Figure 4: Overlapping of five mass chromatograms of 100 ppm for select compounds

Table 2: List of VOCs according to elution order with respective determining fragments (quantitative target ions in bold), calibration curve correlation coefficient and relative standard deviation of repeatability test.

Peak No	Name of VOC		Abbr.	Fragment (m/z)	R²	%RSD
1	methanol		MeOH	**31**, 32, 30	0.9997	2.4065
2	ethanol		EtOH	**45**, 31, 46	1.0000	1.8331
3	acetone		AcO	**58**	0.9997	3.5238
4	isopropanol		isoPrOH	**31**, 60	0.9999	4.0169
5	acetonitrile (solvent)		ACN	-	-	-
6	n-hexane		C6	**57**, 41, 43	0.9987	2.5037
7	n-propanol		PrOH	**31**, 42, 59	0.9997	3.7116
8	methyl ethyl ketone		MEK	**72**, 57	0.9999	2.9225
9	ethyl acetate		EtAc	**70**, 61	0.9999	5.2105
10	sec-butanol	Internal standard group 1	secBuOH	**45**, 59, 41	0.9999	2.4532
11	isobutanol		isoBuOH	**43**, 41, 42	0.9999	2.9513
12	dimethyl glycol		IS1	**45**, 60, 58	-	2.6277
13	isopropyl acetate		iPrAc	**61**, 41	0.9992	1.5892
13	benzene		Ben	**77**, 51	0.9999	2.4585
14	triethylamine		Et3N	**86**, 58, 101	0.9993	2.6981
15	n-butanol		BuOH	**56**, 41	0.9997	3.5991
16	methoxy propanol		MeO-PrOH	**47**, 45	0.9997	3.1786
17	n-propyl acetate		nPrAc	**43**, 61, 73	0.9993	2.5143
18	dimethyl ethanol amine		DMEA	**42**, 44	0.9980	4.8852
19	methyl isobutyl ketone		MIBK	**41**, 57, 85	0.9981	1.7366
20	ethylene glycol		MEG	**31**, 33, 32	0.9997	2.6619
21	toluene		Tol	**91**, 92, 65	0.9971	2.4593
22	2-amino-2-methyl-1-propanol		AMP	**58**, 41, 42	0.9992	3.1853
23	1,2-propanediol		1,2-PEG	**45**, 43, 31	0.9996	3.2800
24	n-butyl acetate		nBuAc	**43**, 56, 73	0.9983	3.1160
25	ethyl benzene		EtBen	**92**, 78	0.9971	3.5781
25	methoxy propyl acetate	Internal standard group 2	MeO-PrAc	**58**, 87	0.9981	0.8650
26	m,p-xylenes		m,p-Xyl	**91**, 106, 105	0.9991	2.9185
27	diacetone		diAcO	**43**, 59, 101	0.9996	3.3969
28	1,3-propanediol		1,3-PEG	**57**, 58, 31	0.9997	2.6721
29	o-xylene		o-Xyl	**105**, 77, 79	0.9999	5.6439
29	cellosolve acetate		Et-MEG-Ac	**45**, 41, 87	0.9995	5.6904
30	2-butoxy ethanol		Bu-MEG	**57**, 45, 41	0.9998	2.5816
31	dimethyl diglycol		IS2	**59**, 58, 45	-	2.3689
32	diethylene glycol		DEG	**45**, 75, 76	0.9981	3.0182
33	2-(2-ethoxyethoxy)ethyl acetate		Et-DEG-Ac	**43**, 87, 72	0.9984	3.1450
34	2-(2-butoxyethoxy)ethanol		Bu-DEG	**75**, 87, 101	0.9981	5.3309
35	2,2,4-trimethyl-1,3-pentanediol		2,2,4	**98**, 103	0.9995	4.2059
36	2-(2-butoxyethoxy)ethyl acetate		Bu-DEG-Ac	**43**, 57, 87	0.9981	2.7099
37	diethyl adipate (bp marker)		BP marker	**111**, 128, 157	-	2.3315

Total VOC content in samples

Two water-based paint samples of commercial products, one marketed for indoor usage and the other for outdoor, were analyzed using the method established in this work. The respective chromatograms are shown in Figure 5.

As shown in Table 3, four and three VOCs were found in the indoor and outdoor paint respectively. The individual concentration of the components in the samples were obtained by internal standard method. It ought to be noted that one component in the indoor paint sample was not listed in Table 2. This component was identified as toluenol, and had to be determined separately, based on the assumption that they have a response factor of 1.

Such component is 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 non-calibrated components)

m_s is the mass (in g) of paint sample used

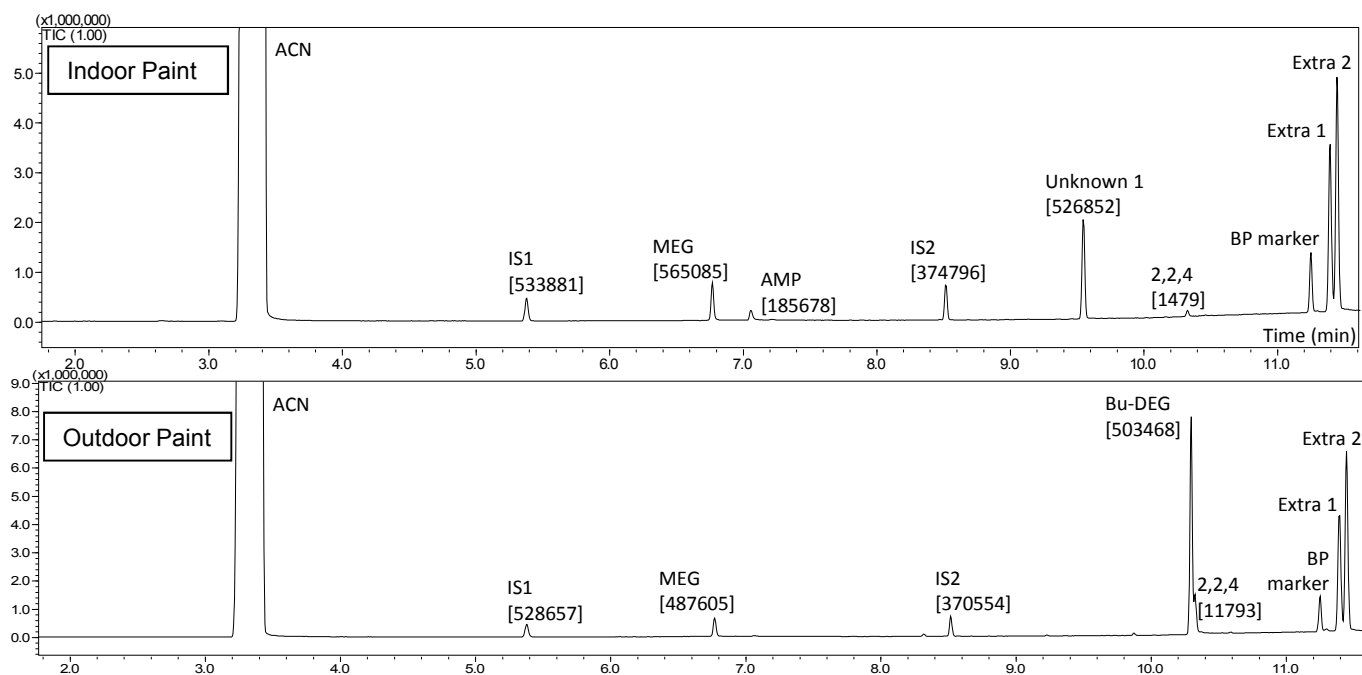A_i, A_{is} are the respective peak areas of component i, and internal standard (obtained from chromatogram)

Figure 5: Chromatograms of indoor and outdoor paint samples spiked with internal standards and boiling point marker, labelled with identified compound short names and peak areas (by fragment ions) in square brackets.

Determination of toluenol (labelled as unknown 1 in Figure 5), which was previously not calibrated, was done using mass fragments 108 (target ion), 79, and 107. By applying equation 1, its concentration was found to be 281.140 ppm in the sample solution.

In both indoor and outdoor paint samples, it can be seen that there are two peaks which elute after the boiling point marker (labelled as extra 1 and extra 2). In accordance to ISO 11890-2, these peaks need not be considered as VOCs, and hence their identities and amounts are not of concern.

The individual concentrations were then summed together and multiplied by 10 to give the total VOC content in paint samples (refer to workflow in Figure 1). The analysis results are listed in Table 3, in which the indoor paint contains 1.05% VOC, and the outdoor paint contains 2.58% VOC.

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

Sample	Component	Peak area	Concentration (ppm)	Total VOC content
indoor paint	MEG	565085	655.3	1.05%
	AMP	185678	75.5	
	Unknown 1 (Toluenol)	526852	281.1	
	2,2,4	1479	35.8	
	total		1047.7	
outdoor paint	MEG	487605	571.0	2.58%
	Bu-DEG	503468	1722.6	
	2,2,4	11793	288.9	
	total		2582.5	

❑ Conclusions

A general GC-MS method was developed, using the Shimadzu GCMS-QP2010 Ultra, for determination of 35 VOCs commonly found in water-based paints and varnishes. A wide range of calibration was established with good correlative coefficient, as well as good repeatability. The results even demonstrated the capability of using this instrument for the determination of compounds which were not calibrated, in preparation to fulfil the requirements of any possible future regulations.

❑ References

1. http://www.standox.co.uk/standox/uk/en/pdfs/Standotheks/THK_Standohyd_GB.pdf: *The future is water-based*, retrieved on 7 Mar 2014
2. G. Wieslander, D. Norback, C. Edling, Occupational and Environmental Medicine (1994) 51: 181-186
3. G. Wieslander, D. Norback, E. Bjornsson, Int Arch Occup Environ Health (1997) 69:115-124
4. ISO 11890-2:2013, *Paints and varnishes – Determination of volatile organic compound (VOC) content – Part 2: Gas-chromatographic method*

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