

分析水性室内建筑油漆中的挥发性有机化合物

Application Note

Gas Chromatography/Mass Spectrometry

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Abstract

本文描述了如何使用安捷伦 J&W DB-1701 GC 色谱柱分析水性油漆中的挥发性有机化合物 (VOC)。通过 Agilent 7890 GC 进行分析并用安捷伦 GC/MS 确认分析结果。结果表明该方法快速、经济而可靠，并且符合室内建筑涂料中挥发性有机化合物的检测要求。

Introduction

Indoor air pollution has become a serious issue with an increase in the airtight nature of houses. Many governments introduced draft regulations to place stricter limits on the allowable level of volatile organic compounds (VOCs) in interior architectural coatings including indoor decorating and refurbishing materials. Therefore, paints for construction and household use have been rapidly changing from solvent-type (oil-based) paints emitting many volatile organic compounds (VOCs) to waterborne paints [1].

There are several definitions of VOCs because volatility depends on many different parameters such as boiling point, vapor pressure, molecular weight, and size. EU directive 2004/42/EC defines VOCs as any organic compound having an initial boiling point less than or equal to 250 °C measured at standard pressure of 101.3 kPa [2]. The directive states that the VOC should be determined by analytical test method ISO 11890-2 [3], which specifies a method for the determination of waterborne paint products that have an expected VOC content between 0.1 and 15% by mass.

U.S. EPA Method 24 is widely accepted for testing the VOC content of coatings, but it is not reliable for the analysis of low VOC waterborne paints. Headspace as a technique for analyzing VOCs in waterborne paints is often limited by the need to



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analyze antifreeze agents such as glycols, as a result of their high boiling point and “stickiness”. As in the EU regulation, diethyl adipate (B.P. 251 °C) was used as the internal boiling point marker in Chinese regulation GB 18582-2008. The VOCs were identified and quantified using GC/FID with an internal standard method [4].

This application note demonstrates a direct method for the analysis of 24 VOC components used in waterborne interior architectural paints by gas chromatography- flame ionization detection (GC-FID) and GC/MSD according to the VOC definition in the EU directive.

Experimental

Chemicals and standards

All standard chemicals including methanol, ethyl alcohol, isopropyl alcohol, 1-propanol, triethylamine, benzene, 2-methyl-1-propanol, 1-butanol, N,N-dimethyl-2-aminoethanol, toluene, 2-amino-2-methyl-1-propanol, 1,2-ethanediol, ethylbenzene, p-xylene, m-xylene, 1,2-propanediol, o-xylene, 2-butoxyethanol, 1,3-propanediol, diethylene glycol, 2-(2-ethoxyethoxy)ethyl acetate, 2-(2-butoxyethoxy)ethanol, 2,2,4-trimethyl-1,3-pentanediol, 2-(2-butoxyethoxy)ethyl acetate and Diethyl adipate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). These chemicals have a minimum purity level of 99%. 2-butoxyethanol was used as internal standard and diethyl adipate (B.P. 251 °C) was used as the internal boiling point marker in this experiment.

Acetonitrile (Honeywell Burdick & Jackson, U.S.A) used as dilution solvent has a purity of 99.99% by mass.

Standard solution was prepared from aliquots of pure compound diluted with dilution solvent to a concentration of 5 g/L, and served as a stock solution.

Internal standard solution was prepared from aliquots of pure compound diluted with dilution solvent to a concentration of 5 g/L, and served as a stock solution.

Sample preparation

Weigh, to the nearest 0.1 mg, approximately 1.0 g of waterborne paint sample and an amount of internal standard that is of the same order of magnitude as the analytes. Add these to a sample vial. Dilute the test sample with 10 mL of acetonitrile; seal the vial and homogenize the contents. The extract of 1.0 g waterborne paint sample contained 0.02 g of 2-butoxyethanol as the internal standard.

Waterborne paint spiked with target standard chemicals was treated according to the procedure described above.

Instrumentation

The GC/FID and GC/MS systems used for these experiments are described in Tables 1 and 2.

Table 1. Instrumentation and Analytical Conditions for the GC/FID System

GC chromatograph:	Agilent 7890A Series GC System
Autosampler:	Agilent 7683 Injector and Sample Tray
Column:	Agilent J&W DB-1701, 30 m × 0.25 mm, 0.25 μm (p/n 122-0732)
GC Inlet:	250 °C, split ratio 30:1
Carrier gas:	Helium, constant flow mode, 37 cm/s
Oven temperature program:	60 °C (2 min), 15 °C/min to 130 °C (0 min), 30 °C/min to 240 °C (1 min), 20 °C/min to 280 °C (5 min)
Detector:	FID at 260 °C
Detector Gas:	H ₂ 30 mL/min, air 400 mL/min, makeup (N ₂) 25 mL/min
Inlet liner:	Split liner, tapered deactivated, (p/n 5188-5398)
Injection volume:	1 μL

Table 2. Instrumentation and Analytical Conditions for the GC/MS system

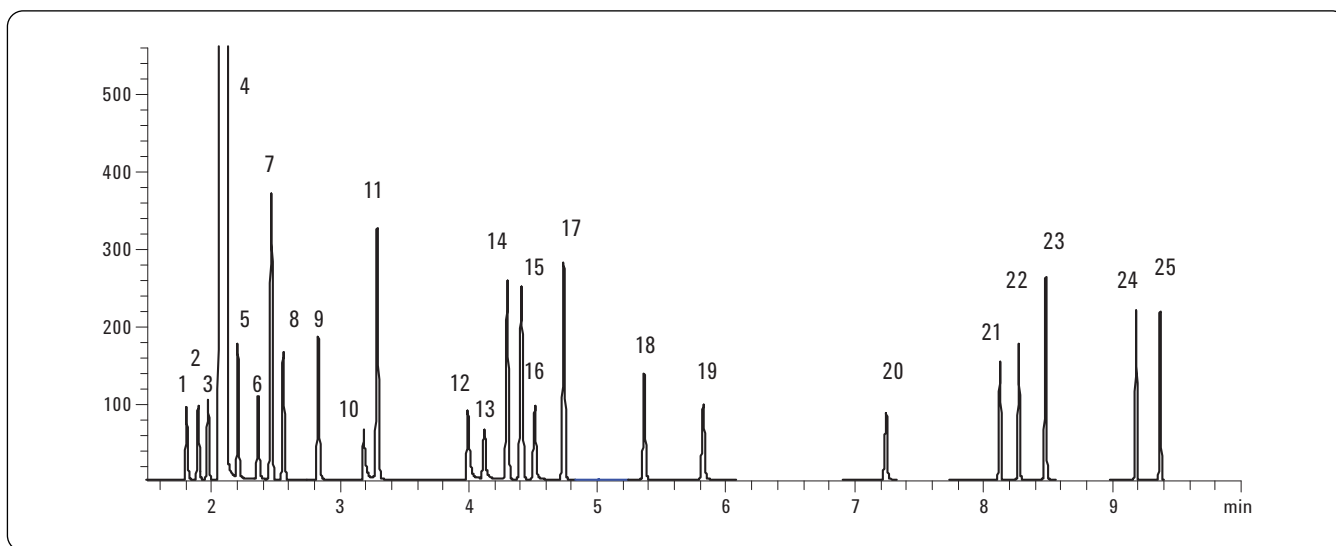
GC chromatograph:	Agilent 7890A Series GC System
Autosampler:	Agilent 7683 Injector and Sample Tray
Column:	Agilent J&W DB-1701, 30 m × 0.25 mm, 0.25 μm (p/n 122-0732)
GC Inlet:	250 °C, split ratio 30:1
Carrier gas:	Helium, constant flow mode, 37 cm/s
Oven temperature program:	60 °C (2 min), 15 °C/min to 130 °C (0 min), 30 °C/min to 240 °C (1 min), 20 °C/min to 280 °C (5 min)
Inlet liner:	Split liner, tapered deactivated, (p/n 5188-5398)
Injection volume:	0.2 μL
Mass selective detector:	Agilent 5975 Series GC/MSD
Transfer line:	280 °C
Acquisition mode:	Scan (30-400 amu)

Results and Discussion

GC/FID Method

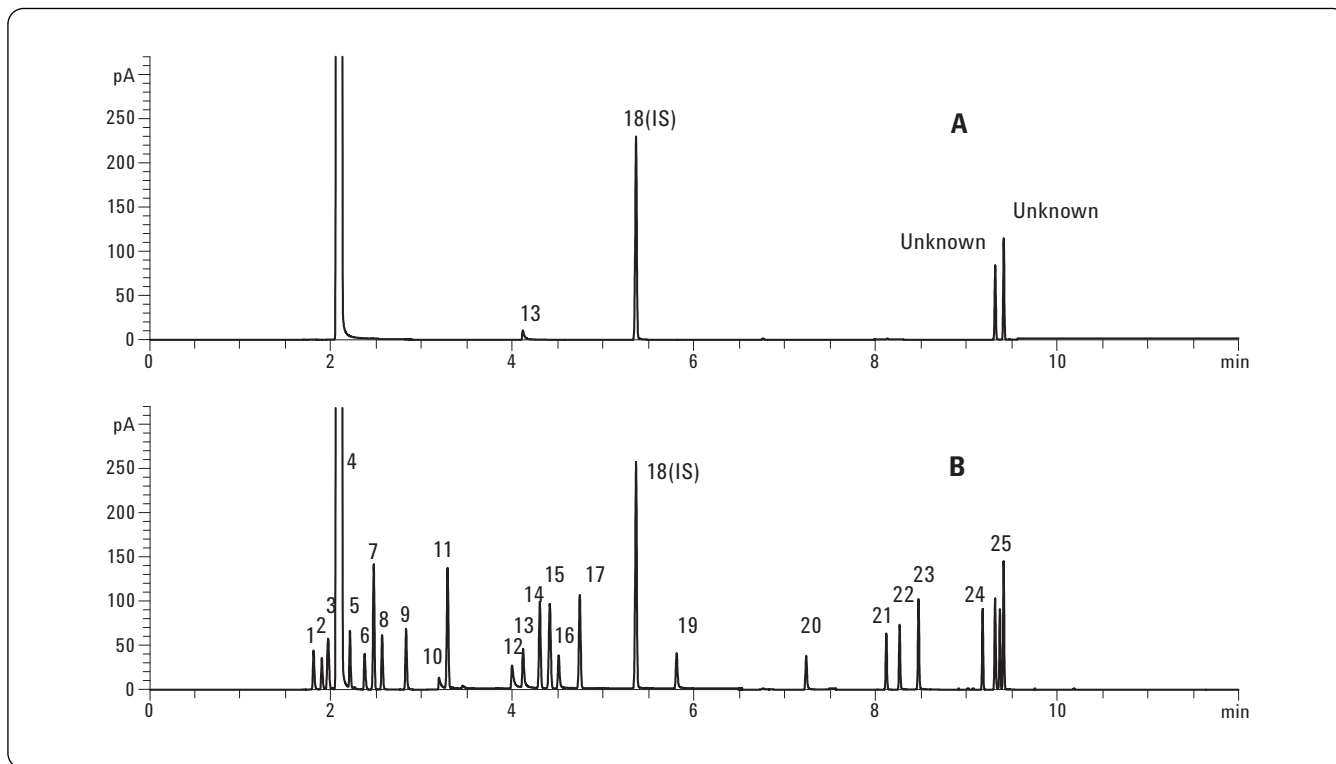
The described GC/FID method is used for quality control of waterborne paints. Figure 1 shows the GC/FID chromatogram for the compounds of interest. As indicated in the chromatogram, there are many active compounds in the standards, but most of the target compounds can be baseline separated by an Agilent J&W DB-1701 GC column with excellent peak shapes. One compound pair is an exception: p-xylene and m-xylene. This pair of compounds was also not resolved in many original regulations and, along with o-xylene was reported as total xylene. Therefore, this should not present a problem.

The extract and matrix spiked extract for one example of waterborne interior paint are both shown in Figure 2. Peaks in the GC chromatogram can be identified based on retention times. The top chromatogram shows separation of one paint extract. 1,2-ethanediol was detected in this sample, and there are two unknown compounds in this chromatogram. Compared with the chromatograms of spiked extract and VOC standards of interest, (Figure 3), Unknown 1 elutes out of the DB-1701 column at 9.322 min. Diethyl adipate as the boiling point marker elutes at 9.376 min, but retention time of Unknown 2 is 9.415 min. According to EU directive 2004/42/EC, compounds eluting after this marker are not considered to be VOCs.



- | | | | |
|---------------------------|---------------------------------|-------------------------------------|--|
| 1. Methanol | 8. 2-Methyl-1-propanol | 15. m,p-Xylene | 22. 2-(2-Butoxyethoxy)ethanol |
| 2. Ethyl alcohol | 9. 1-Butanol | 16. 1,2-Propanediol | 23. 2,2,4-Trimethyl-1,3-pentanediol |
| 3. Isopropyl alcohol | 10. N,N-Dimethyl-2-aminoethanol | 17. o-Xylene | 24. 2-(2-Butoxyethoxy)ethyl acetate |
| 4. Acetonitrile (solvent) | 11. Toluene | 18. 2-Butoxyethanol (IS) | 25. Diethyl adipate (boiling point marker) |
| 5. 1-Propanol | 12. 2-Amino-2-methyl-1-propanol | 19. 1,3-Propanediol | |
| 6. Triethylamine | 13. 1,2-Ethanediol | 20. Diethylene glycol | |
| 7. Benzene | 14. Ethylbenzene | 21. 2-(2-Ethoxyethoxy)ethyl acetate | |

Figure 1. Chromatogram of 24 VOCs using an Agilent 7890 GC/FID system and an Agilent J&W DB-1701 30 m × 0.25 mm , 0.25 μm column.



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|---------------------------|---------------------------------|-------------------------------------|--|
| 1. Methanol | 8. 2-Methyl-1-propanol | 15. m,p-Xylene | 22. 2-(2-Butoxyethoxy)ethanol |
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| 3. Isopropyl alcohol | 10. N,N-Dimethyl-2-aminoethanol | 17. o-Xylene | 24. 2-(2-Butoxyethoxy)ethyl acetate |
| 4. Acetonitrile (solvent) | 11. Toluene | 18. 2-Butoxyethanol (IS) | 25. Diethyl adipate (boiling point marker) |
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| 6. Triethylamine | 13. 1,2-Ethanediol | 20. Diethylene glycol | |
| 7. Benzene | 14. Ethylbenzene | 21. 2-(2-Ethoxyethoxy)ethyl acetate | |

Figure 2. GC/FID chromatograms of one paint extract (A) and matrix spiked extract (B) using Agilent J&W DB-1701 30 m × 0.25 mm × 0.25 μm column.

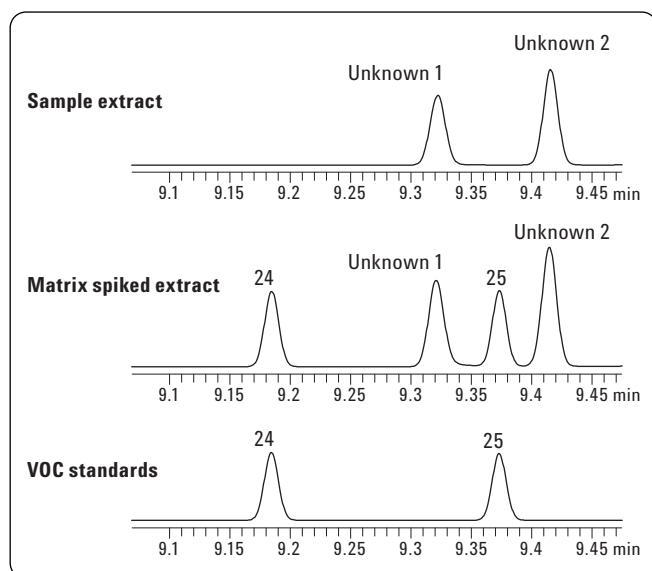
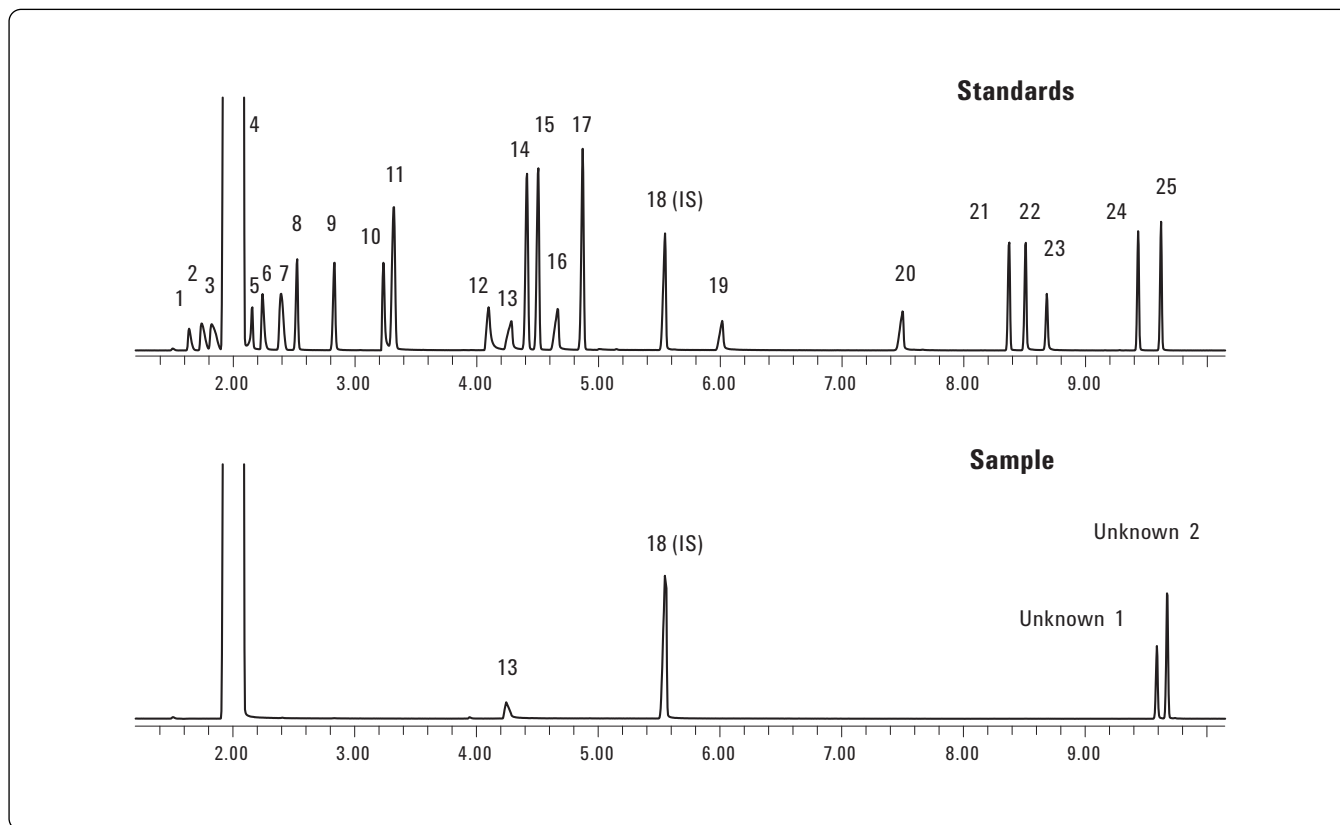


Figure 3. Expanded view from Figure 2 and the chromatogram of VOC standards.

GC/MS Method

For confirmation of solute identities and identification of unknown peaks, the waterborne interior paint was analyzed by GC/MS to reduce the risk of incorrectly identifying compounds as VOCs. The total ion chromatograms (TICs) obtained for VOC standards of interest and sample extract are given in Figure 4. The same separation was achieved in this method as with GC-FID. Confirmation of 1,2-ethanediol detected in the sample by GC/MS was shown in Figure 5. Unknown 2 elutes out of the column after diethyl adipate. The MS spectrum of Unknown 2 in the sample shows it is one of the 2,2,4-trimethyl-1,3-pentanediol derivatives. Normally 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol) or 2,2,4-trimethyl-1,3-pentanediol diisobutyrate can be used as film-forming agents for paints. Texanol has an initial boiling point > 250 °C. The boiling point of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate is 280 °C. Therefore, it confirms that Unknown 2 is not considered to be a VOC.



- | | | | |
|---------------------------|---------------------------------|-------------------------------------|--|
| 1. Methanol | 8. 2-Methyl-1-propanol | 15. m,p-Xylene | 22. 2-(2-Butoxyethoxy)ethanol |
| 2. Ethyl alcohol | 9. 1-Butanol | 16. 1,2-Propanediol | 23. 2,2,4-Trimethyl-1,3-pentanediol |
| 3. Isopropyl alcohol | 10. N,N-Dimethyl-2-aminoethanol | 17. o-Xylene | 24. 2-(2-Butoxyethoxy)ethyl acetate |
| 4. Acetonitrile (solvent) | 11. Toluene | 18. 2-Butoxyethanol (IS) | 25. Diethyl adipate (boiling point marker) |
| 5. 1-Propanol | 12. 2-Amino-2-methyl-1-propanol | 19. 1,3-Propanediol | |
| 6. Triethylamine | 13. 1,2-Ethanediol | 20. Diethylene glycol | |
| 7. Benzene | 14. Ethylbenzene | 21. 2-(2-Ethoxyethoxy)ethyl acetate | |

Figure 4. TICs of VOC standards and sample using Agilent J&W DB-1701 30 m × 0.25 mm, 0.25 μm column.

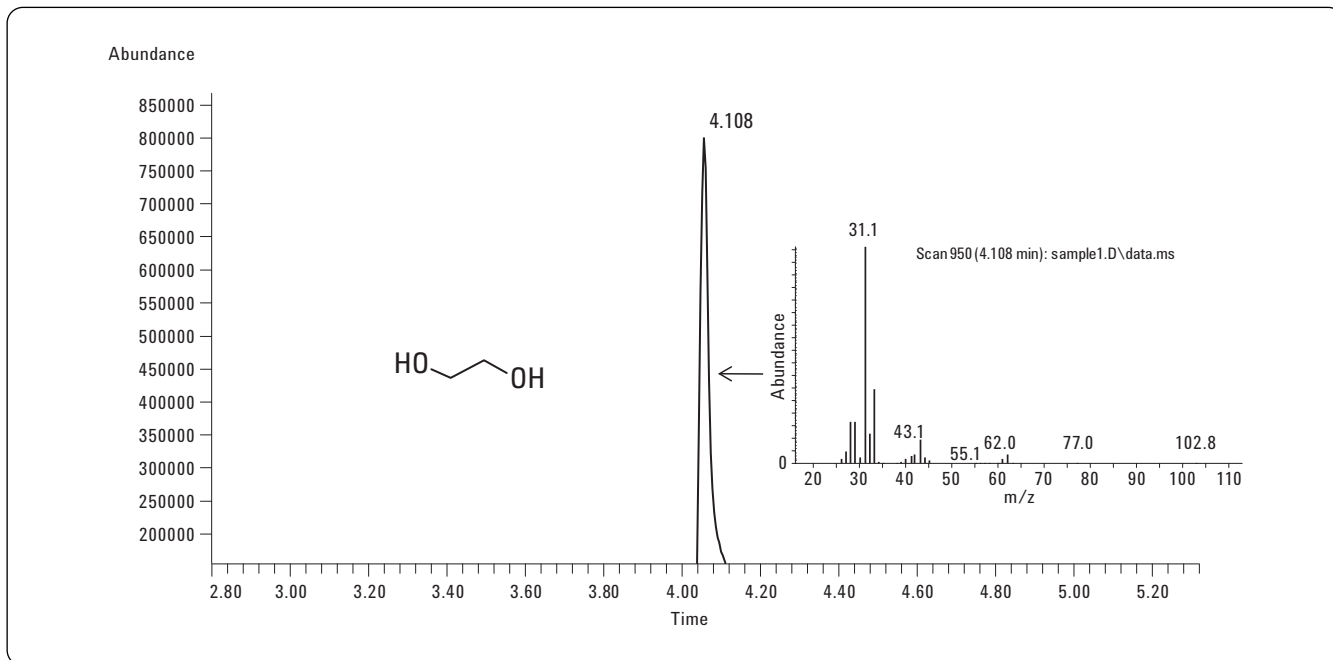


Figure 5. TIC of 1,2-Ethanediol in sample using DB-1701 column by GC/MS.

VOC content in samples

Two of the waterborne paint products that had an expected VOC content of between 0.1 and 15% by mass were tested.

The peak areas for all compounds with retention times lower than that of diethyl adipate (the marker compound) were determined. The response factor of 1.0 was assumed where unidentified peaks were found.

VOCs are calculated according to the following formula:

$$\text{VOC}_{\text{lw}} = \left[\frac{\sum_{i=1}^{i=n} m_i}{1 - \rho_s \times \frac{m_w}{\rho_w}} \right] \times \rho_s \times 1000$$

where

- VOC_{lw} is the VOC content, in grams per liter;
- m_i is the mass, in grams, of compound i in 1 g of the test sample;
- m_w is the mass, in grams, of water in 1 g of the test sample;
- ρ_s is the density, in grams per milliliter, of the test sample at 23 °C;
- ρ_w is the density, in grams per milliliter, of water at 23 °C (= 0.997 537 g/mL);
- 1000 is a conversion factor.

The water content was determined by the Karl Fischer method. The results of VOC analysis in waterborne points are shown in Table 3.

Table 3. Analysis Results of VOCs in Waterborne Paint

Sample No.	m_i (g/g)	Density of sample ρ_s (g/mL)	Water in the test sample ρ_w (g/g)	VOC_{lw} g/L
Sample 1	0.01806	1.5084	0.4337	79
Sample 2	0.02205	1.4358	0.4046	76

Analysis results are listed in Table 3. The VOC content of two samples are 79 g/L and 76 g/L, respectively, which are well below the regulatory limits. Allowable limits range from 100 to 800 g/L depending on the product.

Matrix spikes with targeted VOCs at the 1% and 3% level by mass were determined. All data were based on five replicates of matrix spikes with targeted VOCs. Good recoveries were achieved for VOCs, ranging from 71.01% to 101.78%, satisfying both Chinese and EU regulatory requirements.

Conclusion

This application demonstrates the use of an Agilent J&W DB-1701 GC column to analyze VOCs in interior waterborne paints by GC/FID and GC/MS. The Agilent J&W DB-1701 GC column can effectively separate the 24 VOCs with excellent peak shape, delivers reliable results, and meets the requirements of regulatory methods.

References

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