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DETERMINATION OF VOLATILE ORGANIC CONTENT
IN WATER-BASED PAINTS BY GAS-LIQUID CHROMATOGRAPHY

by
Troy R. Nichols

May 1981

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PREFACE

The work covered by this report was performed by Troy Nichols and was reviewed by Martha L. Adams under the supervision of Emil J. York, Chief, Material Technology Laboratory. The effort constitutes a part of the Army Materials and Mechanics Research Center's program to provide better procedures in chemical testing techniques to increase inspection efficiency for material/materiel procured by the US Army Materiel Development & Readiness Command.

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DETERMINATION OF VOLATILE ORGANIC CONTENT IN WATER-BASED PAINTS BY GAS-LIQUID CHROMATOGRAPHY

I. INTRODUCTION

1. **Subject.** The object of this investigation was to develop a method for the determination of the volatile organic content (VOC) of water-based paints being formulated to conform to air-pollution legislation.

2. **Background.** Analytical methods for determination of VOC¹ in protective coatings have received significantly increased emphasis since the enactment of pertinent air-pollution regulations. Recent approaches to the determination of VOC have utilized both gravimetric and gas-liquid chromatographic methods. One approach² determines total volatiles as a gravimetric weight loss at an elevated temperature. VOC is then calculated as the difference between the weight loss and the water content as determined by Karl Fischer titration or by gas-liquid chromatography (glc).

However, for purposes of quality control for Military protective coatings, an analytical method is essential for not only the determination of the total volatile organics but also the identity and the concentration of each component in the total.

The methods previously developed and proven satisfactory for the determination of volatile organics in solvent-based paints, now being replaced, were found unsatisfactory for water-based paints, partially because of the increased complexity of vehicle, solvent, and pigment separations.

The gas-liquid chromatographic method for volatile organic content presented here determines volatile organics independently of water content and is satisfactory for determining organic solvent components of water based paints used for Military application. Unlike previously used procedures, this one requires no distillation prior to injection into the gas-liquid chromatograph.

II. DETAILS OF TEST

3. **Gas-Liquid Chromatographic Column.** Prepare a 6-foot by 1/8-inch stainless steel column packed with chromosorb 101 30-100 mesh. Condition the column at 220°C for 4 hours with carrier (helium) flow of 30 milliliters per minute.

¹ Under the Society for Coatings Technology Technical Committee, "Test of Coatings Technology," 1/48 (1979).

² ASTM, "Standard Practice for Determining Volatile Organic Content of Paints and Related Coatings," to be published.

4. **Sample Preparation.** Accurately weigh approximately 0.2 gram of the resin or formulated paint into a 3-inch by 3/8-inch test tube containing two drops of a pre-selected dispersing solvent such as N,N dimethylformamide, n-decanol, or water. Add 0.03 gram, accurately weighed, of a suitable internal standard such as n-butyl alcohol or 1,4 butanediol. Add 4 drops of the dispersing solvent and mix thoroughly on a vortex-action shaker. Without centrifuging or filtering, inject 2 microliters of the dispersed material into the gas-liquid chromatograph and operate as described in paragraph 5.

5. **Chromatographic Conditions.** Program the instrument so that the initial column temperature is 150°C with an immediate increase of 3° per minute to 200°C; the column temperature is then held constant for 20 minutes. Use a thermal conductivity detector temperature of 300°C, injection port temperature of 220°C, and carrier (helium) flow rate of 30 milliliters per minute.

6. **Calculations.** Concentration Cx of a solvent component is calculated as

$$C_x = \frac{A_x}{A_{IS}} \times \frac{W_{IS}}{W_s} \times I \times 100$$

Where

A_x is the peak area of the solvent component.

A_{IS} is the peak area of the internal standard.

W_{IS} is the weight of the internal standard.

W_s is the weight of the resin or paint.

I is a predetermined correction factor.

III. DISCUSSION

7. **Results.** The screening of chromatographic columns indicated Chromosorb 101 to be one of the more suitable column packings from the severely limited number of stationary phases that are not degraded by the water present in the formulations of interest. This column, selected for this study, exhibits a retention time of less than 30 minutes for most solvents encountered here and requires only mild and infrequent reconditioning.

Table 1 shows retention times on the Chromosorb 101 column of the solvents which can be used in water-based coatings. Retention times of some dispersants are also shown. Water is eluted very early, about 0.4 minute, and generally causes no difficulty in peak area calculations for the organic solvents.

Table 1. Retention Times of Solvents and Dispersing Agents

Solvent or Dispersing Agent	Retention Time (min)
Water	0.4
Methanol	0.6
Isopropanol	1.2
Ethylene glycol monomethyl ether	3.0
n-Butyl alcohol	3.5
Benzene	3.9
Ethylene glycol	4.5
2-Nitropropane	4.6
Ethylene glycol monoethyl ether	4.9
Propylene glycol	5.0
Toluene	6.7
N,N Dimethylformamide (dispersing agent)	7.5
Propoxy propanol	9.0
Ethylbenzene	9.6
Xylenes	9.6, 9.8, 11.8
Dimethylsulfoxide (dispersing agent)	10.8
Ethylene glycol monoethyl ether acetate	11.0
Ethylene glycol monobutyl ether	12.4
1,4 Butanediol	13.2
Isopropylbenzene	13.4
Diethylene glycol	14.8
n-Heptanol	15.5
n-Butylbenzene	19.4
n-Octanol (dispersing agent)	21.0
n-Decanol (dispersing agent)	35.6

The method was demonstrated on as broad a range as possible of the currently available resins and water-based paints. Normally the supplier of the resin or paint used in this study gave insufficient data to evaluate the method for reliability. Therefore, to determine the capability of the method, the value obtained for percent of volatile organic content was compared to the value obtained by subtracting the percent water content by ASTM method D3792, from the percent weight loss at 105°C for 1 hour. Theoretically, the two values should be equal.

In the present method, neither a single internal standard nor a single solvent for dispersion prior to injection into the gas-liquid chromatograph could be adopted for all materials tested. Figures 1 through 4 illustrate the application of the method.

Figure 1 is the chromatogram of a commercially supplied dispersion of an aliphatic urethane resin. The material was satisfactorily diluted with water to facilitate injection into the gas-liquid chromatograph. The chromatogram for this resin dispersion indicates the presence of one original solvent, but its identity is unknown; its retention time matches none of those determined (Table I). Assuming a correction factor of one, the total volatile organic content was found to be 19.8 percent.

The acrylic resin emulsion represented in the chromatogram of Figure 2 was dispersed in water prior to injection into the chromatograph. The major solvent peak has the same retention time as ethylene glycol monobutyl ether. The peak near 33 minutes represents an unknown volatile organic. The total VOC for this water-based paint was calculated to be 16.8 percent.

The chromatogram in Figure 3 is the analysis of an acrylic modified alkyd resin dispersed in n-decanol for chromatograph injection. The major organic solvent was found to be ethylene glycol monobutyl ether. Total VOC was determined to be 23.3 percent.

Figure 4 shows the analysis of a water dispersion of a latex, alkd-resin paint. Ethylene glycol is present as the major organic solvent. Total VOC was found to be 2.0 percent.

The results of this investigation are summarized in Table 2. The description in column 2 was supplied by the manufacturer.

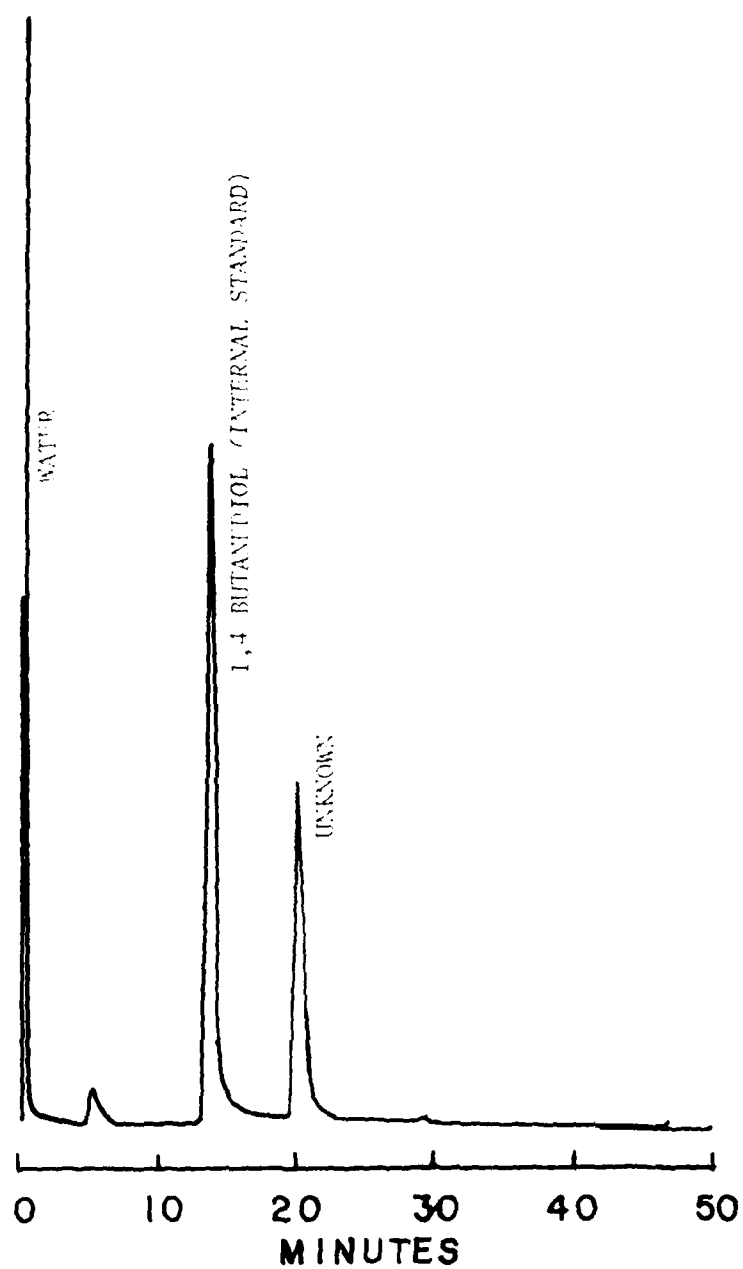


Figure 1. Analysis of a dispersion of an aliphatic urethane resin.

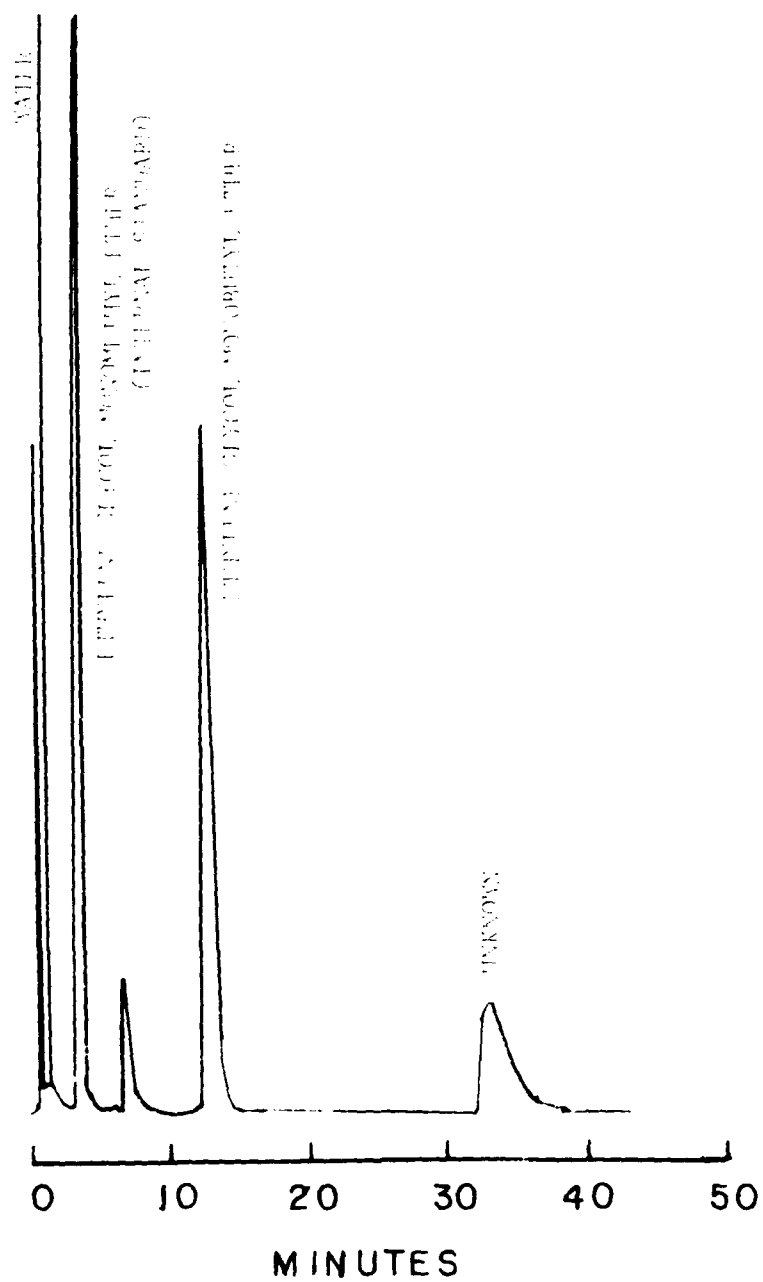


Figure 2. Analysis of an acrylic resin emulsion.

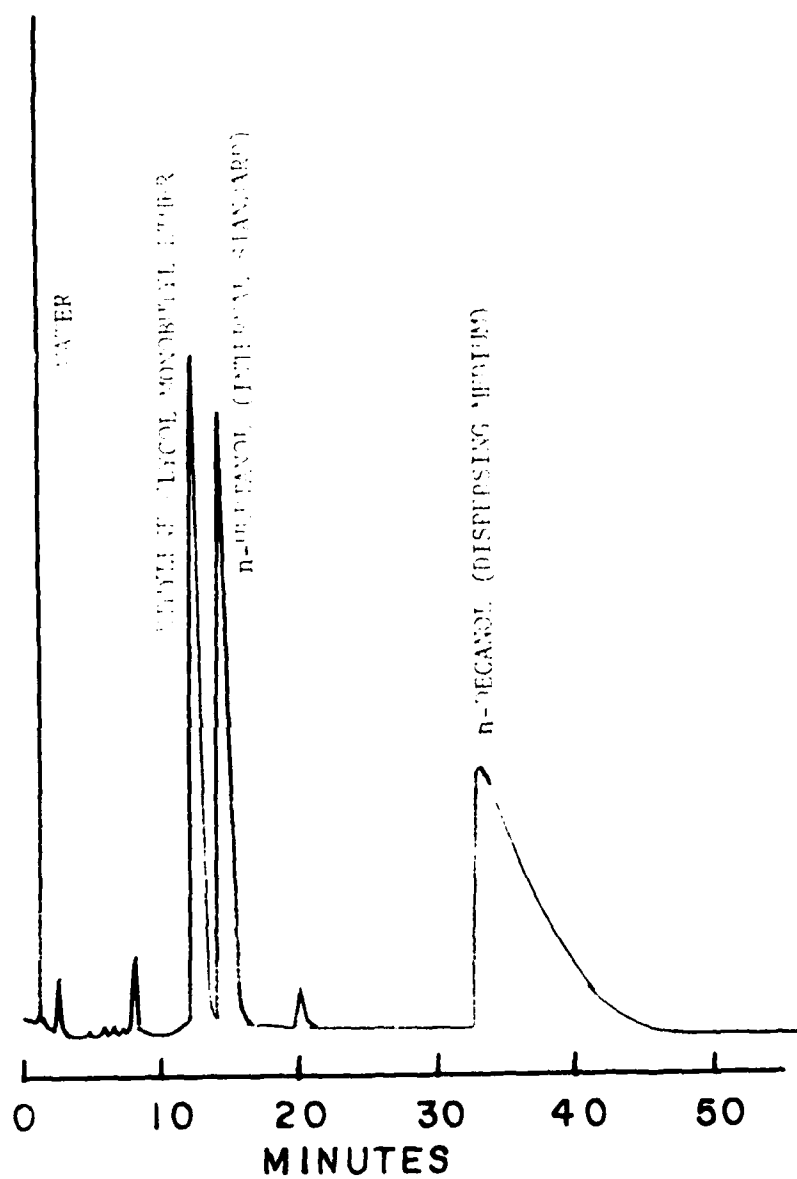


Figure 3. Analysis of an acrylic modified alkyd resin.

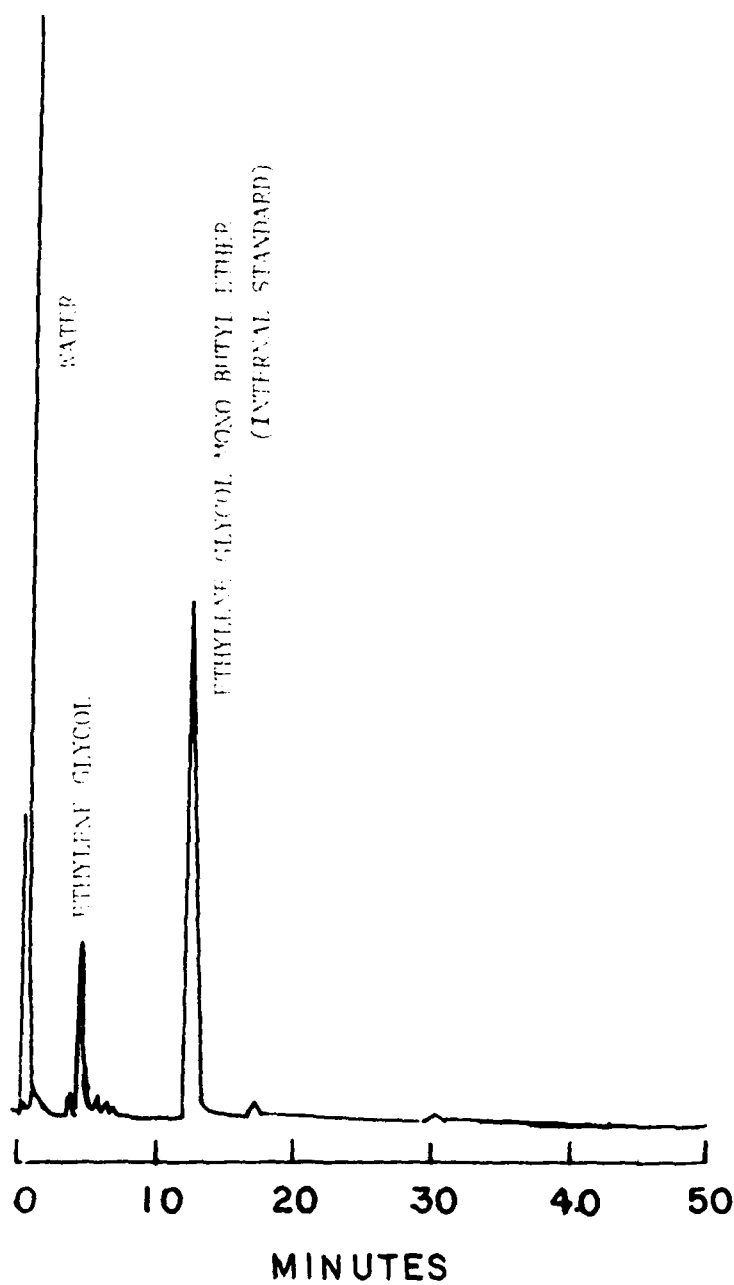


Figure 4. Analysis of a latex, alkyd-resin paint.

Table 2. VOC Values by the glc Method Compared to VOC Values Calculated as the Numerical Difference Between Total Volatiles and Water Content

No.	Description	Dispersant for VOC Determination	A		B		Percent VOC by glc Method
			Percent Volatiles 105 C./1 hour	Percent Water ASTM D3792	A-B =VOC		
1	Water-based primer in two parts Component 1: Pigmented Compound Component 2: Resin dispersion	n-Decanol	25.0	0.7	24.3	39.2	
		N,N-Dimethylformamide	21.3	1.0	20.3	18.0	
2	Acrylic resin paint	water	66.7	53.2	13.5	16.8	
3	Water-based urethane	water	44.5	34.8	9.7	7.6	
4	Acrylic modified alkyd resin	n-Decanol	21.4	7.8	13.6	23.3	
5	Latex, alkyd-resin paint	water	48.7	46.0	2.7	2.0	
6	Latex house paint, white	water	51.8	45.9	5.9	4.0	
7	Alkyd resin	n-Decanol	19.8	2.0	17.8	19.2	
8	Alkyd-acrylic resin	water	50.0	15.7	34.3	33.5	
9	Aqueous acrylic emulsion	water	42.7	27.5	15.2	16.8	
10	Aliphatic urethane resin	water	65.0	48.2	16.8	19.8	

Assuming the methods for water determination, total volatiles, and VOC by glc are valid, the numerical difference between the results of the first two methods should be equal to the value obtained by the third method. That is, corresponding values in the last two columns of Table 2 should be equal. Examination of Table 2 shows that VOC determined by difference between total volatiles and water content agrees well with the VOC determination by glc with the exception of two materials. Number 1, Component 1, and Number 4 do not show agreement between the two methods. The cause of the discrepancy is not known. Possibilities for the disagreement include resin degradation for the glc method or chemical reaction in the total volatiles determination.

In the instances where VOC value was in close agreement between the two methods, validation of the glc method was assumed. Where the results of the two methods disagreed, it was generally difficult to arrive at any firm conclusion regarding capability of the VOC by glc method because of the limited information on the proprietary materials.

IV. CONCLUSIONS

8. Conclusions. It is concluded that

a. A gas-liquid chromatographic method for the determination of volatile organic content was demonstrated for water based paints.

b. The method is also applicable to the determination of VOC in paint resins and their dispersions.

c. The results of this investigation support the recommendation that this method be incorporated into the Military Standards Paint Testing Handbook now being developed.

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