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Report 2223

QUANTITATIVE DETERMINATION OF AROMATICS IN PAINT THINNERS

September 1977

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The continuing investigation to develop analytical methods for solvents used in organic coatings has resulted in a proposed gas chromatographic method for complementary use in the quantitative determination of the aromatic hydrocarbon content of the organic coatings.

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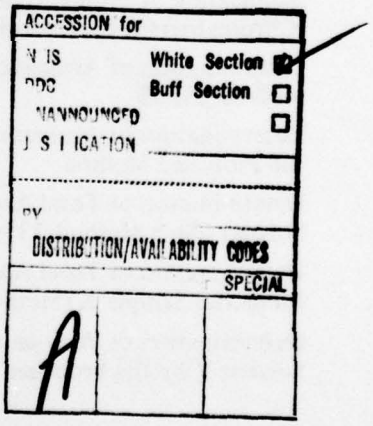
PREFACE

Authority for the work covered by this report is contained in Project 1L162105AH84.

The period covered is 1975 to 1976.

The investigation was performed by T. Nichols and reviewed by M. Adams under the supervision of E. J. York, Chief, Material Technology Laboratory, MERADCOM, Fort Belvoir, Virginia.



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QUANTITATIVE DETERMINATION OF AROMATICS IN PAINT THINNERS

I. INTRODUCTION

1. **Subject.** The object of this investigation was to develop an improved method for determination of aromatics in the volatile portion of organic coatings.

2. **Background.** The quantitative analysis of aromatic compounds in paint thinners is complex. Various analytical methods for aromatics have been reported.[1] [2] These were not shown to be applicable to organic coatings. Methods which were adequate for earlier solvent formulations are often deceptively inaccurate for some of the newer solvent systems.[3] [4]

Aromatics enhance solvency and, therefore, have been widely used as solvents for organic coatings. However, their use is now limited in various localities by pollution legislation. An example of such legislation is Los Angeles Rule 102 (previously, Rule 66). Military specifications for coatings require composition L solvents which are restricted much as are those covered by Rule 102 (Table 1).

Table 1. Composition L Requirements

Type	Aromatic	Amount
a.	Toluene + Ethylbenzene	20% max.
b.	Aromatics with 8 or more carbon atoms excluding ethylbenzene	8% max.
c.	a + b	20% max.

Reformulation of solvents to meet pollution legislation requirements has introduced compositions with higher concentrations of oxygenated compounds. These oxygenated compounds – alcohols, esters, and ketones – have introduced difficulties in the application of method 7356, *Solvent Content of Enamels and Enamel Thinners (Gas Liquid Chromatography), Federal Test Method Standard No. 141*, a method which is now often inadequate because it can produce falsely high results due to undetectable interference from residual, oxygenated solvents.

This report details a complementary method for the determination of aromatics and is recommended for use in those cases where high concentrations of

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1 Charles L. Stuckey, J. of Chromatographic Science 7, 177-181 (1969).

2 Stanley P. Wasik and Robert L. Brown, Analytical Chem. *48*, 2218 (1976).

3 George G. Esposito, J. of Paint Technology *40*, 214-221 (1968).

4 ASTM Method D3257-3.

oxygenated solvents are known to be present or where the solvent blend apparently fails to meet compositional requirements when tested by method 7356.

II. EXPERIMENTAL

3. **Instrumental Analysis.** The method employs a gas chromatograph (GC) utilizing a flame-ionization detector and a stainless steel column, 6 feet long by 1/8 inch inside diameter, packed with 5% SP 1200-1.75% Bentone 34 on 100-120 mesh supelcoport.

The GC operating parameters are as follows: carrier (helium) flow, 20 ml/minute; injection port temperature, 250° C. The column oven temperature is maintained at 32° C for 12 minutes after injection and is then increased at the rate of 2°/minute to a temperature of 90° C at which it is isothermally maintained for 10 minutes.

4. **Calculations.** Chromatogram peaks are identified in the usual way by relative retention times. Correction factors are determined from compositions of known solvents. Concentrations in percent by volume are calculated from the commonly used equation.

$$C = \frac{ADF}{B}$$

where A is the area under the peak in question, B is the area under the internal standard peak, D is the concentration of the internal standard, and F is the correction factor.

5. **Preparation of Sample.** Isolate the solvent from the organic coatings according to method 7355, Federal Test Method Standard No. 141A. In order that a suitable internal standard may be selected, a chromatogram is first obtained omitting any internal standard (Figure 1). This locates a suitable area having no interfering peaks. Possible internal standards include cumene, cymene, undecane, and dodecane.

Pipette 3.0 ml of the solvent and 0.3 ml of the internal standard into a small, glass-stoppered flask. Dilute a suitable aliquot 100 fold with hexane. Transfer 3.0 ml of the diluted solution to a 25-ml volumetric flask. Add 15 ml of 85% (by volume) sulfuric acid, and shake vigorously for 2 minutes. After the layers have separated, add sufficient 85% sulfuric acid to force the upper layer into the neck of the flask. Transfer about 1 ml of the upper layer to a 10-ml, glass-stoppered volumetric cylinder containing 5 ml of distilled water. Shake gently and let stand until the upper layer clears. With a syringe, inject 0.2 μl of the sample into the injection port of the gas chromatograph operated as described above.

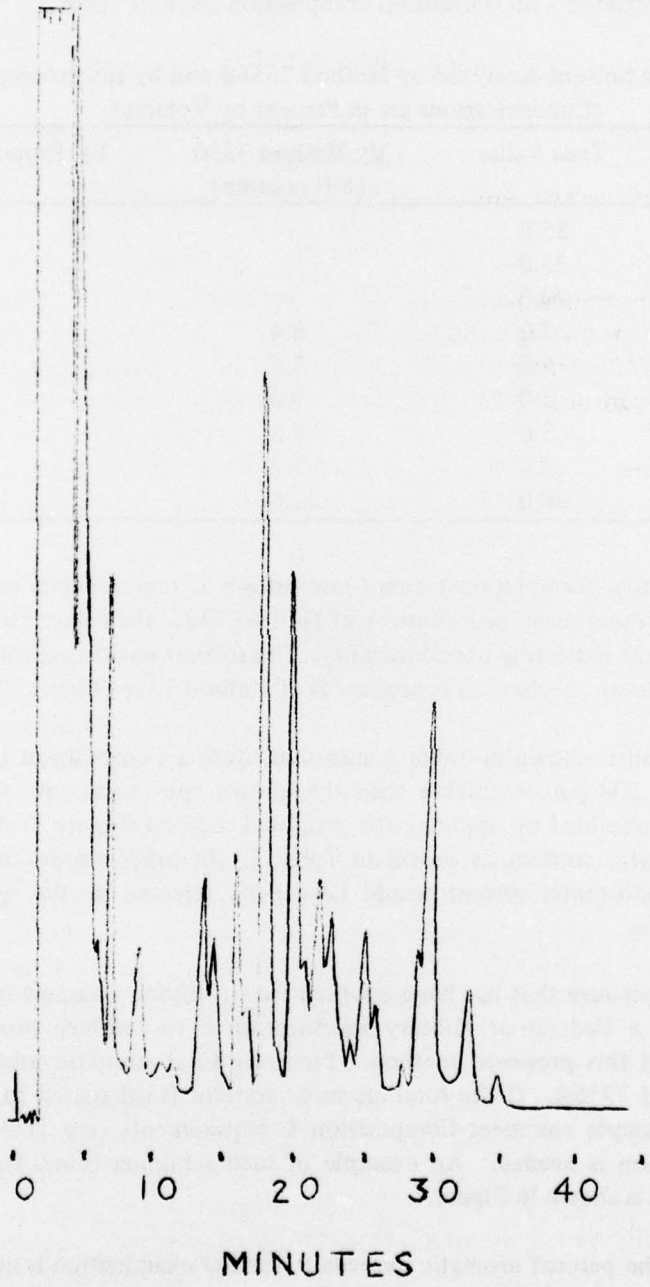

Figure 1. Application of proposed method to industrial sample X. (Chromatogram for choosing suitable internal standard.)

6. **Results.** The inadequacy of method 7356 of Federal Test Method Standard 141 can be demonstrated with the solvent composition given in Table 2.

Table 2. Known Solvent Analyzed by Method 7356B and by the Proposed Method (Concentrations are in Percent by Volume)

Ingredient	True Value	By Method 7356 (18-ft column)	By Proposed Method
Hexane	35.0	–	–
n-Butanol	25.0	–	–
sec-Butanol	20.0	–	
Toluene	7.0	8.4	6.8
Ethylbenzene	5.0	5.5	4.6
p-Xylene	3.0	9.0	2.8
m-Xylene	3.0	6.5	3.1
o-Xylene	2.0	3.2	1.9
Total aromatic	20.0	32.6	19.2

This blend by actual formulation meets Composition L requirements (see Table 1), but when it was tested using procedure A of Method 7356, the percent total aromatic exceeded 20 percent indicating nonconformity. This solvent was then chromatographed on the 18-foot column specified in procedure B of Method 7356 (Figure 2).

The results, shown in Table 2, also constitute a Composition L failure; the results are 10 to 200 percent higher than the known concentrations. On the other hand, the results obtained by applying the proposed method (Figure 3) closely reflect the known aromatic content as shown in Table 2. In other words, this particular Composition-L-conforming solvent would have been rejected by the application of Method 7356 alone.

The procedure that has been adopted for qualifying a sample submitted for evaluation under a Federal or Military specification is to combine procedure A of method 7356 and this proposed method. First, the total aromatic content is determined by method 7356A. If the total aromatic content is calculated to be less than 8 percent, the sample has meet Composition L requirements (see Table 1) and no further examination is needed. An example of such a thinner found to contain 3.9 percent aromatics is shown in Figure 4.

When the percent aromatic exceeds 8, further examination is necessary. An example is industrial solvent X which is found to contain 19.4 percent total aromatic. The percent toluene can be calculated from this chromatogram, but the ethylbenzene and p-, m-xylene peaks are not resolved. Consequently, the calculations obtained

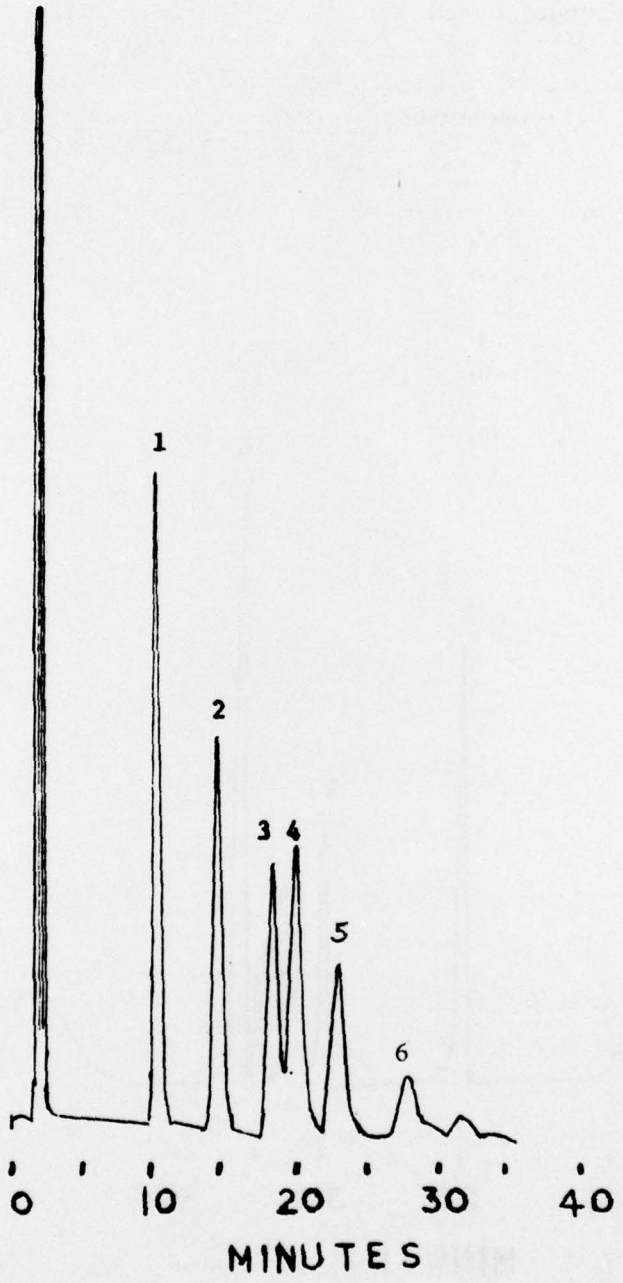

Figure 2. Determination of aromatics in a known solvent by method 7356B. Peaks: 1, internal standard (benzene); 2, toluene; 3, ethylbenzene; 4, para-xylene; 5, meta-xylene; 6, ortho-xylene.

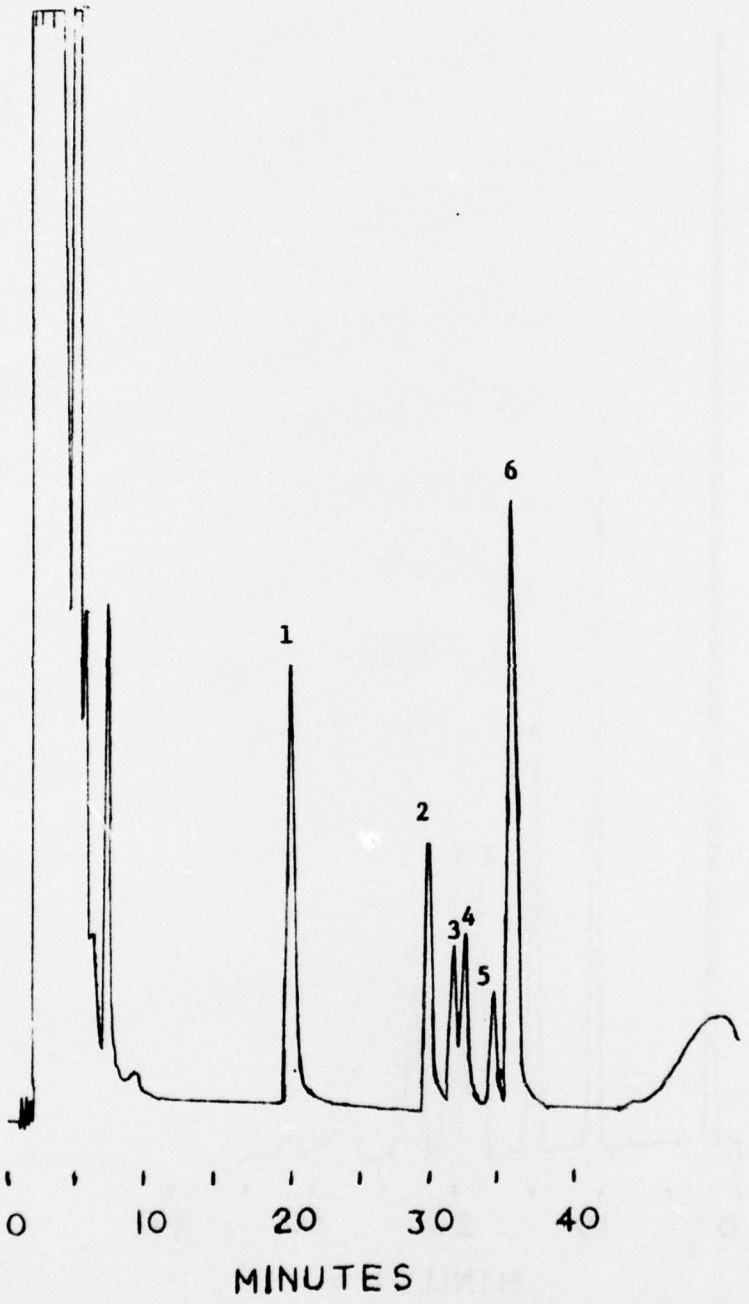

Figure 3. Determination of aromatics in the known solvent using the proposed method. Peaks: 1, toluene; 2, ethylbenzene; 3, para-xylene; 4, meta-xylene; 5, ortho-xylene; 6, internal standard (cumene).

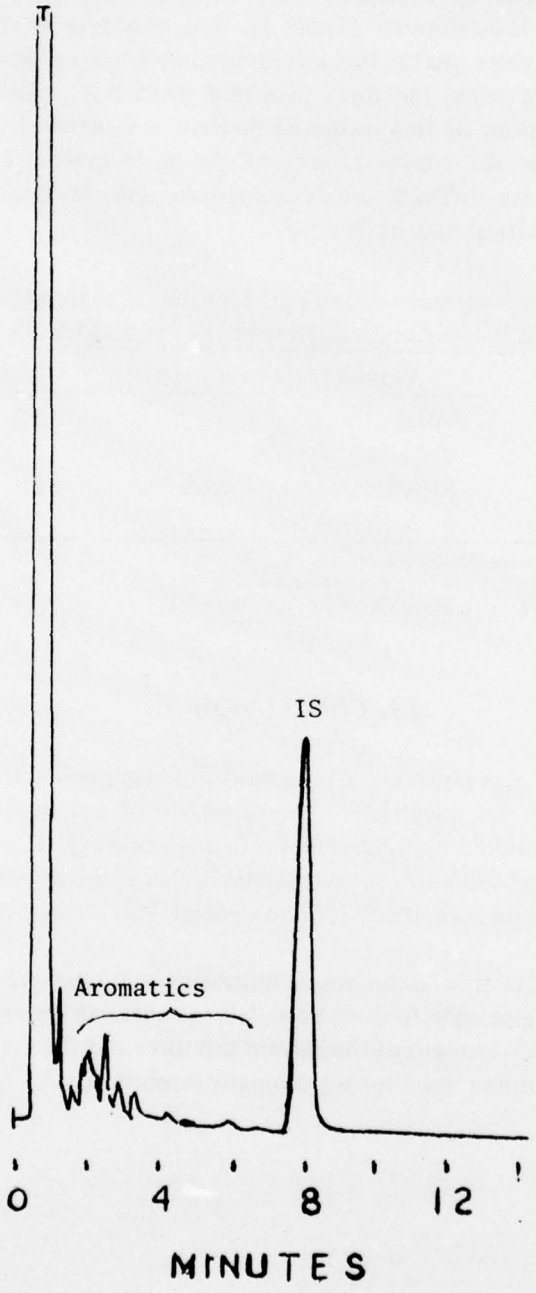

Figure 4. Determination of total aromatics in an industrial coatings solvent using Method 7356A. The internal standard (IS) is phenylcyclohexane.

from the Figure 5 chromatogram give percent toluene, 9.4; percent ethylbenzene plus the p-, m-xylenes, 8.6; and by difference, percent other aromatics, 1.4. In order to check for Composition L conformity (Table 1), it is necessary to resolve the ethylbenzene and the two xylene peaks; this can be accomplished by determining the p-, m-xylene concentrations using the new, proposed procedure. The chromatogram obtained by the application of this proposed method is illustrated in Figure 6, and from this chromatogram the concentrations of the p-, m-xylenes can be obtained. Table 3 shows how these methods are combined to give the final analysis of the aromatic content of industrial solvent X.

Table 3. Aromatic Content of Industrial Solvent X as Determined by Method 7356A in Conjunction with the Proposed Method

Figure	Method	Aromatic(s) Determined	Peak(s)	%
5	7356A	Total	1-3	19.4
5	7356A	Toluene	1	9.4
5	7356A	Ethylbenzene + p-, m-xylene	2	8.6
6	Proposed	p-, m-xylene	1 and 2	1.8

Calculations (see Table 1 for Composition L conformity):
a. Toluene + ethylbenzene (EB) = 9.4 + (8.6 - 1.8) = 9.4 + 6.8 = 16.2
b. Aromatics with 8 or more carbons excluding EB = 19.4 - 6.8 - 9.4 = 3.2
c. a + b = 19.4.

III. CONCLUSION

7. **Conclusion.** A complementary method utilizing gas-liquid chromatography has been developed for the quantitative determination of aromatic hydrocarbons in paint solvents. The proposed method is useful in analyzing highly oxygenated solvent blends and in monitoring unknown solvent mixtures that show apparently high aromatic contents when analyzed by method 7356 in Federal Test Method Standard 141.

Future work in this continuing investigation will examine other techniques by which potential interference from oxygenated solvents can be eliminated or minimized such as better pretreatment of the solvent mixtures and the use of a highly polar column preceding the column used for the aromatic resolution.

Figure 5. Determination of total aromatics (exceeds 8 percent) in industrial solvent X. Method 7356A. Peaks: 1, toluene; 2, ethylbenzene, para-xylene, and meta-xylene; 3, other aromatics; 4, internal standard (phenylcyclohexane).

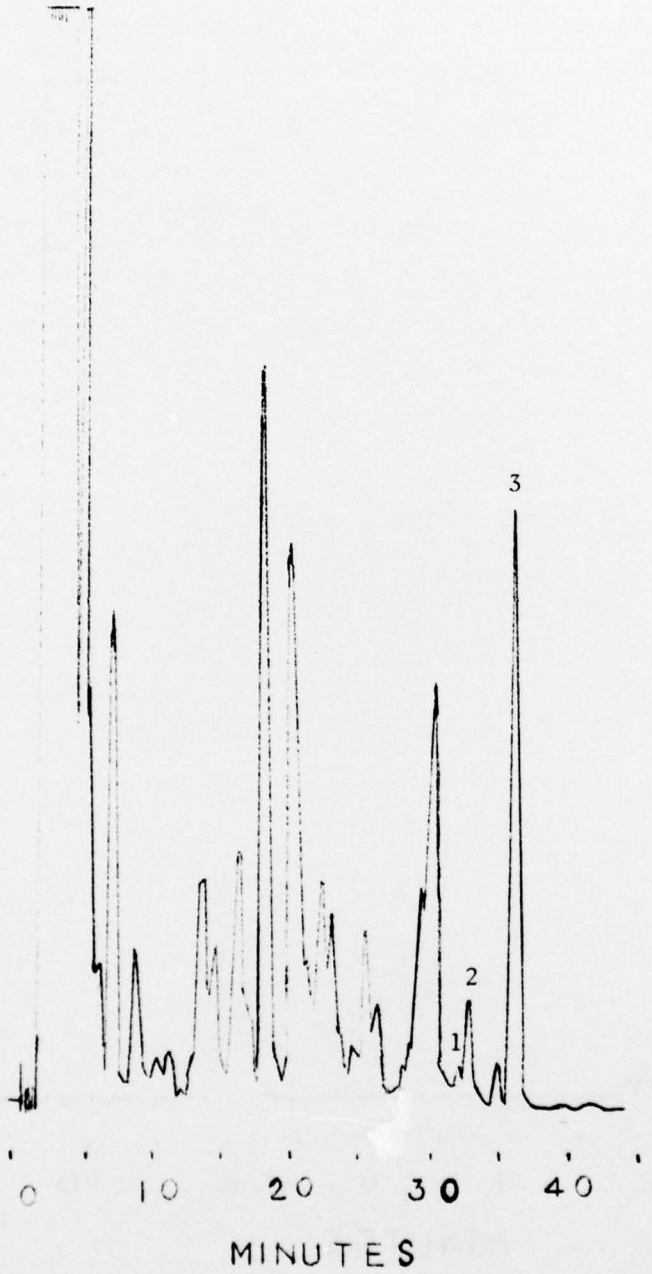

Figure 6. Determination of para- and meta-xylene in industrial solvent X by the proposed method. Peaks: 1, p-xylene; 2, m-xylene; 3, internal standard (cumene).

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