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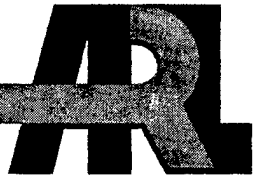

Determining the Exempt Solvent Content of Coatings Using Gas Chromatography

by Philip Patterson and William Lum

ARL-TN-194 December 2002

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Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

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Philip Patterson and William Lum
Weapons and Materials Research Directorate, ARL

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Contents

List of Figures ii

List of Tables ii

1. Background 1

2. Approach 1

2.1 Instrumentation....1

2.2 Procedure....2

2.3 Calibration....2

2.4 Analysis/Determination....2

3. Results and Discussion 3

4. Conclusion 3

Appendix. Exempt Solvent (ES) Content Calculations 5

Report Documentation Page 6

List of Figures

Figure 1. Typical GC analysis for exempt solvent content.....4

List of Tables

Table 1. Exempt solvent content (% by weight).....3

1. Background

The Coatings Technology Team at the Polymers Research Branch, U.S. Army Research Laboratory (ARL) is responsible for the development and testing of multifunctional coatings to be applied on U. S. Army tactical equipment and vehicles. While efforts are made to keep these coatings environmentally friendly, some of the solvent-based coatings supplied for military use exceed the volatile organic compound (VOC) limits as established by State and Federal environmental agencies. Additionally, these limits are expected to become tighter in the future as new air quality standards are imposed. Therefore, these coatings must be reformulated, with an emphasis on changing the organic solvent content, in order to become VOC compliant. One successful approach currently employed by coating's formulators is to replace the non-compliant solvents with VOC exempt solvents.[1] These exempt compounds have been determined by the Environmental Protection Agency to have negligible contribution to tropospheric ozone formation and therefore are excluded as VOCs. Acetone, t-butyl acetate (TBAC), methyl acetate, and parachlorobenzotrifluoride (PCBTF) are examples of exempt solvents. Once these exempt solvents have been used, an analytical test method must be developed to verify their presence, thereby ensuring that the reformulated coating is indeed meeting the established VOC regulations. The test method presented in this report provides a relatively simple and direct way to separate and quantitate the percentage of exempt solvent found within a coating. The method uses the principles of gas chromatography (GC) to perform the analyses.

2. Approach

2.1 Instrumentation

Used in this study was a Hewlett-Packard (HP) 5890 Series II Gas Chromatograph equipped as follows:

- Column Size/Phase: 30 m × 0.53 mm × 3.0 μm /6%-cyanopropylphenyl-94% dimethyl polysiloxane (cross-linked).
- Oven: Programmable, set at 90 °C.
- Detector: Thermal Conductivity, set at 225 °C.
- Carrier Gas: Helium, set at 8 ml/mn.

[1] Pourreau, D. B., G. B. Kelly, L. J. Junker, R. T. Wojcik, S. L. Goldstein, and M. L. Morgan. "Formulating VOC-Compliant Coatings With Exempt Solvents." *Paint and Coatings Magazine*, pp. 65–77, November 1999.

- Injector: Split 1:20, set at 200 °C.
- Data Acquisition: Agilent GC-MSD ChemStation Application software.
- Printer: HP Desk Jet 560.

2.2 Procedure

A modified version of American Society for Testing and Materials (ASTM) D 4457[2] was followed for the sample preparation and GC analysis. This ASTM method was chosen because it is used industry wide as an authoritative test procedure in determining the amount of VOC-exempt halocarbon solvents in coatings. In this instance, the ASTM method and related instrument set-up was tailored specifically to analyze the exempt solvents previously mentioned. However, most of the modifications were relatively minor. For example, the exempt solvent standards (American Chemical Society [ACS] Reagent Grade) and coating samples were prepared by diluting with methyl ethyl ketone (MEK), instead of dimethylformamide.

2.3 Calibration

Weigh ~0.1 g of exempt solvent and 0.1 g of the selected internal standard (toluene) to the nearest 0.1 mg into a disposable micro-centrifuge tube and mix well. Dilute this mixture with ~1.25–1.30 g of MEK. Shake well and inject a 1-µl aliquot into the gas chromatograph (note: MEK and/or toluene should not interfere/coelute with any of the analytes. However, if interferences do occur, substitutions must be made). Record the integrated peak areas of the exempt solvent and the internal standard. Repeat the injection and record the peaks areas as before. Compare them to the first. The values should be within 3% of each other. Report the weights and the averaged peak areas for the response factor (RF) calculation. The equation is given in the Appendix. Once the RF has been derived, the exempt content within the coating sample can be determined.

2.4 Analysis/Determination

Weigh 5–10 g of paint (note: actual weight is dependent upon the exempt solvent content of the coating) and 0.1 g of the selected internal standard to the nearest 0.1 mg into a disposable glass vial with a septum-lined cap. Dilute the mixture with ~10 ml of MEK. If the coating's solvent composition is unknown, it will be necessary to run an undiluted sample to make sure no peak interferences will occur. Cap the vial tightly and shake well for a few minutes. To facilitate the settling of solids, allow the samples to stand for at least 5 min. Low-speed centrifuging may also be used. Inject a 1-µl aliquot into the gas chromatograph. Record the peak areas and repeat the injection when all compounds have eluted. It may be necessary to raise the oven temperature between injections to allow the elution of all of the solvents in the sample.

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[2] American Society for Testing and Materials. "Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection Into a Gas Chromatograph." ASTM D 4457, May 1997.

Compare the integrated peak areas for the compounds of interest. The values obtained from the two injections should be within 5% of each other. Report the weights and the averaged peak to calculate the exempt solvent content. The final equation is presented in the Appendix.

3. Results and Discussion

Three solvent-based coatings were selected for a trial study. The composition of each of the coatings was different, but each contained at least one of the following exempt solvents: methyl acetate, t-butyl acetate, and/or PCBTF. The total exempt solvent content of the samples ranged from 5%–35% by weight. Duplicate determinations were made for each sample with the averaged value reported as the final determinate. Results are provided in Table 1.

Table 1. Exempt solvent content (% by weight).

Sample No.	Theoretical Value (Wt. % of Coating)	Determined Value (Wt. % of Coating)
1	34.3	32.9
2	19.8	19.2
3	5.1	4.9

As shown in Table 1, the determined results agree well (within 4.5% relative difference) to the theoretical values reported by the manufacturer for each coating product. The calibration runs (not tabulated) also agreed well—with the averaged results within 2.5% of each other. A chromatogram depicting a typical exempt solvent coating analysis is shown in Figure 1.

4. Conclusion

A gas chromatograph interfaced with a polymeric cross-linked, megabore (30 m × 0.53 mm) column has been successfully used for the direct determination of VOC-exempt solvents. The instrumental method is well suited for the qualitative and quantitative analysis of VOCs in most solvent-based coating products. The analysis time is short, generally requiring no longer than 10 min per sample. The established working range for the procedure was ~5%–35% exempt solvent by weight of the whole paint. However, it is believed that higher or lower percentages could also be determined using this method.

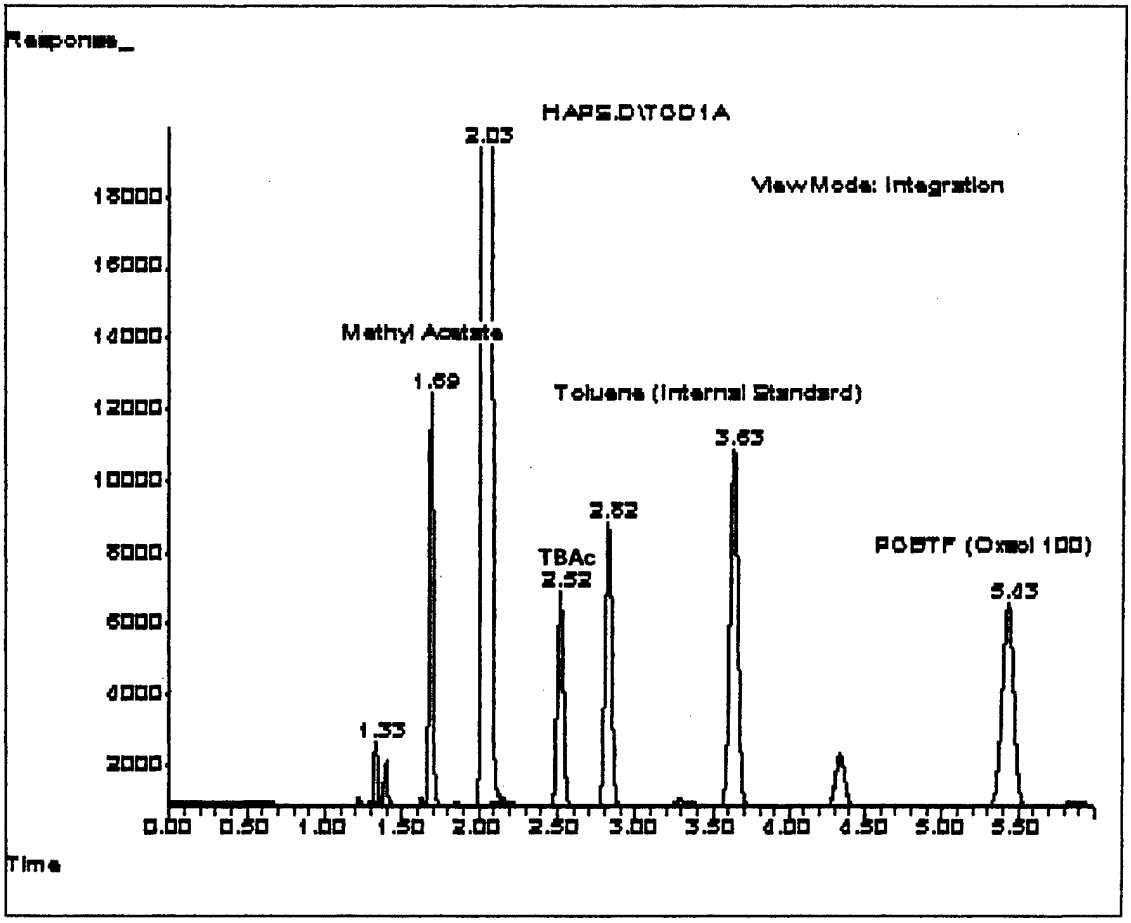

Figure 1. Typical GC analysis for exempt solvent content.

Appendix. Exempt Solvent (ES) Content Calculations

Calculate the exempt solvent content of each sample using the following equations:

$$\%ES = \frac{A_{ES} \chi W_{TOL} \chi 100}{ATOL \chi Wc \chi R}, \quad \text{(A-1)}$$

where

A_{ES} = integrated area of exempt solvent,
W_{TOL} = weight of toluene added,
A_{TOL} = integrated area of the toluene peak,
W_C = weight of coating, and
R = detector response factor from the standard (ES) analysis, calculated as follows:

$$RF = \frac{W_{TOL} \chi A_{STD}}{W_{STD} \chi A_{TOL}}, \quad \text{(A-2)}$$

where

A_{STD} = integrated area of exempt solvent, and
W_{STD} = weight of exempt solvent standard.

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14. ABSTRACT
The Coatings Team of the Polymers Research Branch has developed a method for the analysis of the exempt solvent content in pigmented coating materials using gas chromatography. This technical note outlines the instrument parameters and the sampling procedures established to perform the determinations. A typical analysis is graphically presented with a brief explanation summarizing the tabulated results.

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