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Analysis of Hazardous Air Pollutants (HAPs) in Coating Solvents via Capillary Gas Chromatography (GC)

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ARL-MR-321 July 1996

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13. ABSTRACT *(Maximum 200 words)*

This interim report covers the progress of the analytical work performed on the U.S. Army Research Laboratory (ARL) project entitled "Analysis of Class I Ozone Depleting Chemicals and Aromatic Solvents in Coating Related Materials Using Capillary Gas Chromatography." General background information is discussed and preliminary results of several gas chromatographic analyses of solvent mixtures are presented.

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1. INTRODUCTION

The analysis of solvent content in coating materials has always been an important determination when evaluating quality control of a given product formulation. However, with every tightening air pollution regulation, these analyses become even more critical in assuring product compliance to the proper volatile organic compound (VOC) emissions level.

More recently, environmental controls have broadened to target various groups of hazardous air pollutants (HAPs), including several common industrial paint solvents (i.e., toluene, methyl ethyl ketone, xylene(s), and trichloroethane). These compounds are also found in many of the solvent-based formulations referenced in various military and federal coating specifications. Additionally, these specifications most often refer to the federal standard test methods (FSTM) document for the analytical procedures in determining solvent content. For example, the Army's Chemical Agent Resistant Coatings, MIL-C-46168 and MIL-C-53039, references FSTM No. 7356, "Solvent Content of Enamels and Enamel Thinners (via Gas Chromatography)," for such analyses. This method calls for the use of a gas chromatograph (GC) equipped with an 8-ft stainless-steel column packed with 35% N, N-bis (2-cyanoethyl) formamide on 60–80 mesh chromosorb P support. This specialized, highly polar column is used for the determination of aromatic hydrocarbons (i.e., toluene, ethylbenzene, and xylene) found in the coating solvent blend.

Although the method is reliable, analysis time is lengthy. A single determination takes approximately 45 min to complete. And, although this column is well suited for aromatic hydrocarbons, it may not be the best overall choice when analyzing for the presence of other classes of VOCs. Additionally, today's new GCs are not designed for using the outdated packed column technology. For these reasons, a revision in methodology, using updated gas chromatographic columns, needs to be developed to increase analytical efficiency without sacrificing reliability.

2. METHOD

2.1 Instrumentation. For this study, a Hewlett-Packard 5890, Series II GC, with a flame ionization detector (FID) was used for the analyses. The GC was equipped with electronic pressure control and capillary inlet system designed for split/splitless operation. Additionally, a Hewlett-Packard G127A

Chemstation loaded with related application software was interfaced with the GC to control instrument parameters and data collection (chromatograms).

The column chosen for the initial screening of HAPs was a J&W Scientific DB-5 (1.5-mm) Megabore-fused silica capillary column (15 m x 0.53 mm). This easy-to-work-with, general-purpose column was selected as a practical alternative to the currently used 8-ft stainless-steel packed column. The Megabore column has good sample capacity, improved column efficiency, and excellent chemical and thermal stability.

Also, because the column's DB-5 stationary phase (a cross-linked diphenyldimethyl polysiloxane polymer) is relatively nonpolar, the separation of components occurs primarily due to dispersive effects.

This means that the elution order of many of the compounds under investigation is, in large part, a function of boiling-point differences (values which are readily available and easy to compare).

2.2 Sample Preparation. To be in the GC study, different classes of VOCs (ketones, aromatics, and chlorinated hydrocarbons) were analyzed to test the selectivity of the Megabore column. Samples were prepared by pipetting approximately 1 ml of the reference compound(s) into a 50-ml-volumetric flask and diluting to volume with dichloromethane. The reference compounds represent a cross section of various HAPs which might be found in solvent-based coatings. All of the chemicals used during this phase of the study were classified as either technical or American Chemical Society reagent-grade purities. Aliquots (1–2 ml) of the prepared solutions were manually injected into the GC using a standard borosilicate glass syringe with a removable 26-gauge needle.

3. RESULTS/DISCUSSIONS

The results of the GC analysis for each group of compounds are shown in the chromatograms (Figures 1–3). GC conditions are noted on each of the figures.

As expected, the selected column does well in separating compounds with different boiling points within the same chemical class. Additionally, no problems were encountered with sample overload (column capacity) or lack of detector response.

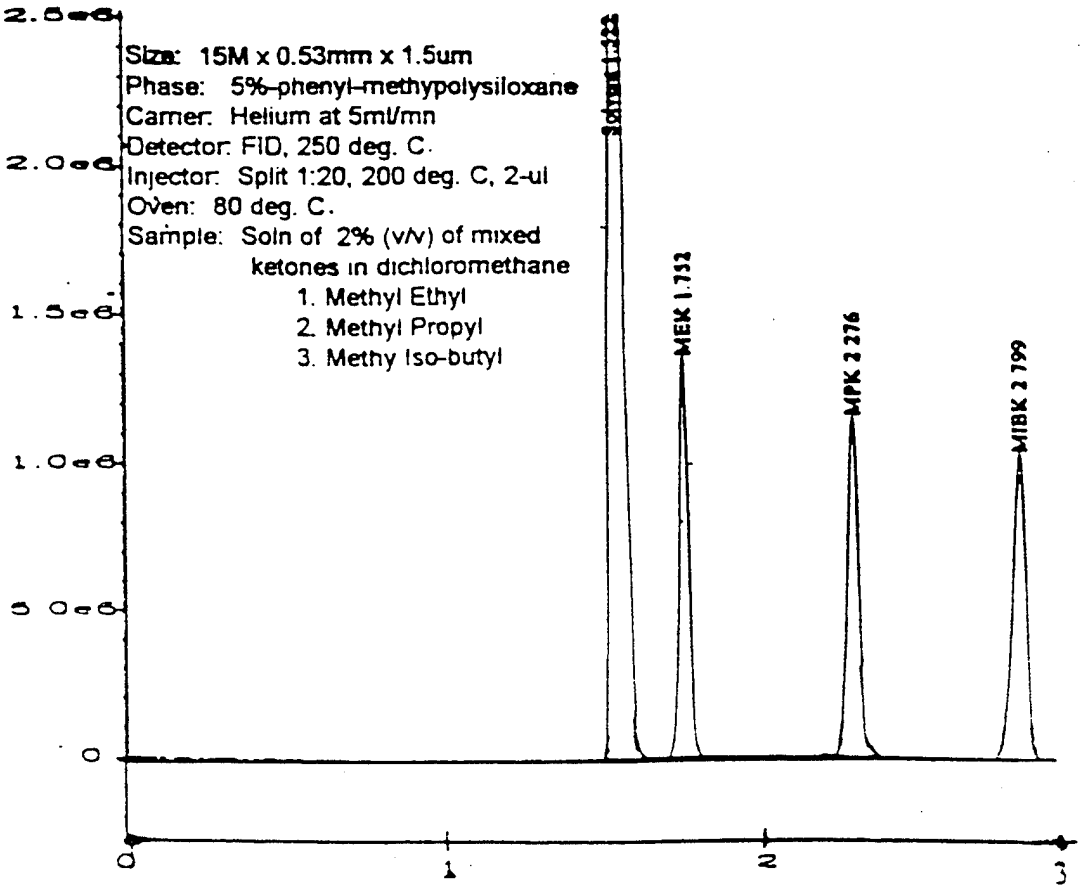

Figure 1. GC analysis of ketones.

4. CONCLUSION

The DB-5 Megabore (15-m x 0.53-mm) column can be successfully used for the screening of HAPs found in the solvent portion of organic coating materials. Separation of simple mixtures of similar compounds was easily performed within a very short time period (less than 5 min). However, if more complicated mixtures are encountered or quantitative analysis is required, a more efficient capillary column may be necessary (i.e., longer length or smaller diameter).

This issue, as well as the development of a final GC method, will direct the project work slated for continuance into FY96.

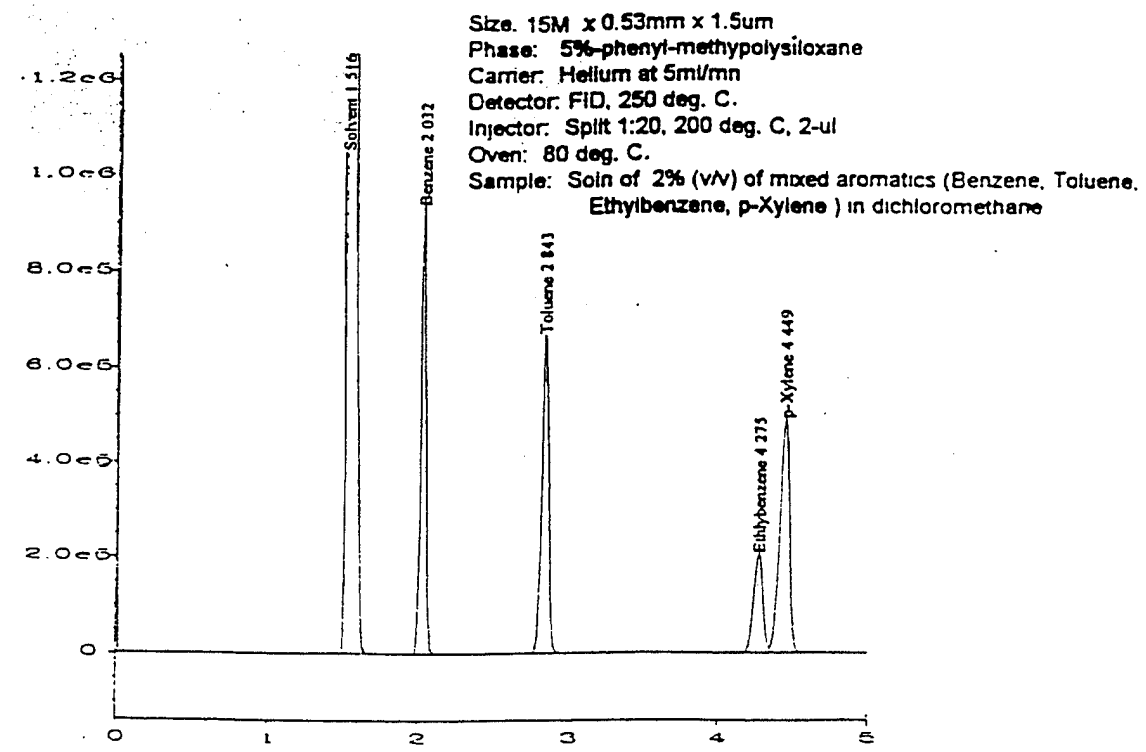

Figure 2. GC analysis of aromatics.

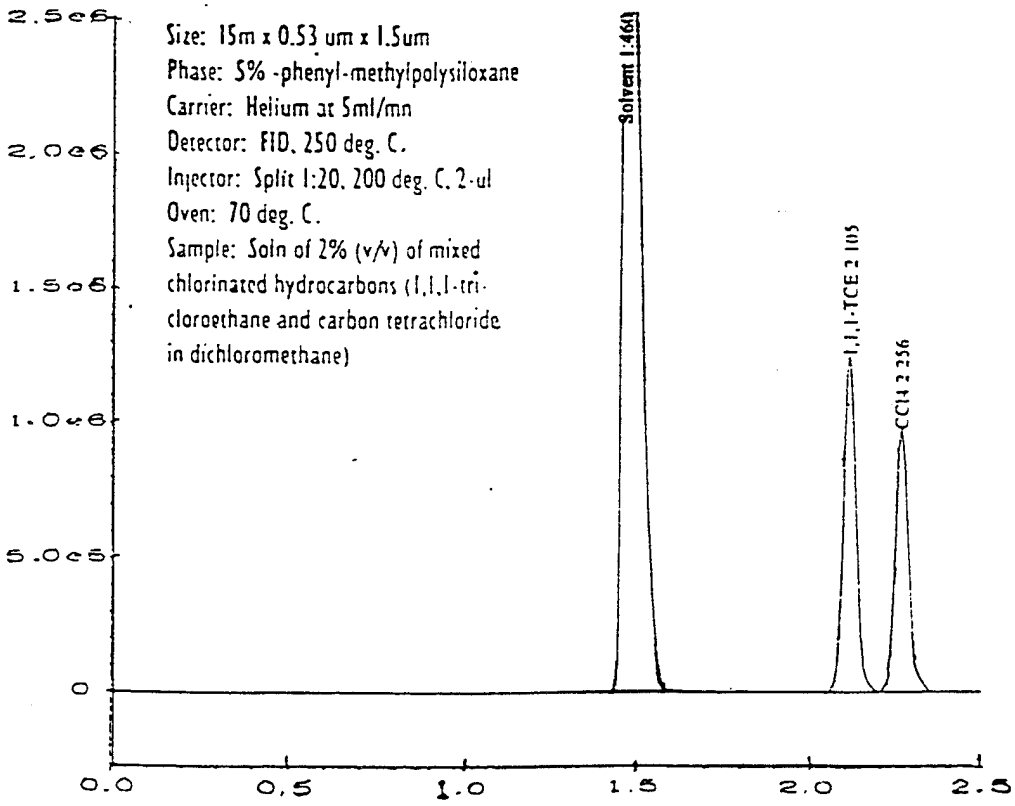

Figure 3. GC analysis of chlorinated hydrocarbons.

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