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GAS CHROMATOGRAPHIC DETERMINATION OF METHYL CENTRALITE AND DIPHENYLAMINE IN 20-MM GUN PROPELLANT

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FOREWORD

This report presents the results of gas-liquid chromatographic determinations of methyl centralite and diphenylamine in 20-mm gun propellant as of 15 October 1966. These results may be modified by future work. The Naval Ordnance Station, Indian Head, performed this work, which was done for the Ships Parts Control Center, Mechanicsburg, Pennsylvania.

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ABSTRACT

This report presents a rapid procedure for precise determinations of both methyl centralite (MC), also known as dimethyldiphenylurea, and diphenylamine (DPA). The sample is extracted with methylene chloride, removing the MC and DPA. The extract is blown to dryness with dry air, dissolved in ethylene dichloride, and analyzed on a Perkin-Elmer 226 Flame Chromatograph.

INTRODUCTION

Gas-liquid chromatography (GLC) separates similar substances by a process of differential migration. An inert, mobile gas phase carries the sample to be separated and analyzed through a thermostated column containing a liquid phase held immobile by a solid. Either gases or the vapors of liquids may comprise the sample carried by the inert carrier gas.

DISCUSSION

The 20-mm gun propellant presently contains both methyl centralite (MC), also known as dimethyldiphenylurea, and diphenylamine (DPA). MC reduces gun-barrel corrosion, thereby increasing the barrel life of the gun. DPA stabilizes the propellant and increases its storage life by absorbing the gaseous oxides of nitrogen formed as the propellant decomposes naturally. For these reasons appropriate amounts of both MC and DPA are required.

Since experience shows that 5.0% to 15.0% MC (by weight) and 0.50% ± 0.05% DPA (by weight) give optimum propellant performance for 20-mm guns, the amounts of MC and of DPA should fall within these limits.

Presently the 65° C oven surveillance method is used to test the stability of gun propellants. A 45-gram sample is tightly closed in a bottle and placed in a 65° C oven; emission of nitrous oxide fumes indicates that the propellant is no longer stable. This surveillance method results in accelerated aging and is now used to predict the safe life of gun propellants. However, in addition to this qualitative surveillance method, the propellant industry desires a quantitative surveillance method which is both reliable and accurate. Since the available method of ultraviolet analysis does not meet the desired standards, this laboratory investigated quantitative analysis by GLC. Infrared analysis for MC was also studied, but it does not analyze for both components as does GLC.

Since MC melts at 120° C, and since DPA melts at 53° C and boils at 302° C, GLC analysis for these compounds should be carried out at a minimum column temperature of 250° C. An Apiezon L column was chosen to withstand this temperature. A helium pressure of 40 pounds was chosen empirically. A column of 5-foot length and 1/8-inch diameter packed with 15% Apiezon L on Chromasorb W was chosen for optimum reproducibility and resolution.

The experimental procedure is simple. Weigh accurately a 5.0 ± 0.1-gram sample of 20-mm gun propellant and transfer the sample to an extraction thimble. Using a Soxhlet extraction apparatus on a steam bath, extract the sample for 24 hours with methylene chloride. Evaporate the extract to dryness with a stream of dry air. Transfer the residue with ethylene dichloride to a 25-ml volumetric flask and dilute to volume.

Prepare standards in 25-ml volumetric flasks containing both MC and DPA diluted with ethylene dichloride where the MC concentrations are ten times greater than those of the DPA (Table I). Inject the standards and samples into the chromatograph using the conditions given below.

Apparatus: Perkin-Elmer 226 Flame Chromatograph (or equivalent)
Helium pressure: 40 lb
Flow rate: 5.0 cc He/min
Column: 5-ft length, 1/8-in. diameter, packed with 15% Apiezon L on Chromasorb W
Temperatures:
- Block: 300° C
- Column: 250° C
- Detector: 190° C

Attenuation:
- DPA: 1000×
- MC: 5000×

Sample size: 4 μl
Stream splitter: Open position with a restrictor ratio of 1:300
Graphical treatment of data: Peak height plotted versus concentration for a standard curve
Retention times:
- Ethylene dichloride: 10 sec
- DPA: 2 min
- MC: 2.5 min

Both GLC and infrared analyses for MC were conducted on six samples of an actual 20-mm gun propellant (the six "plant" samples). These same samples were also analyzed for DPA by GLC. In addition, to test the applicability of GLC to these analyses over a range of MC and DPA compositions, a series of compounds (the synthetic samples) having varying amounts of MC and DPA were prepared and analyzed.

Table I

CONCENTRATIONS OF MC AND DPA IN STANDARD SOLUTIONS

Standard solution no.	MC (mg MC/ml)	DPA (mg DPA/ml)
1	4	0.4
2	6	0.6
3	8	0.8
4	10	1.0
5	12	1.2

RESULTS

Infrared and GLC analyses of MC in the six duplicate plant samples agree within experimental error (Table II). GLC analysis of the DPA in the same six plant samples showed that the DPA composition of these samples was within specification (Table II). Since DPA cannot be analyzed by the infrared method, the accuracy of the GLC analysis for DPA cannot be supported as is that for the MC.

However, the GLC analysis for both MC and DPA in the synthetic samples verifies the accuracy of the GLC analysis (Table III). The percent by weight of MC and DPA found by the GLC analysis in the synthetic samples agrees with the known percentage of these samples.

CONCLUSIONS AND RECOMMENDATIONS

These studies indicate that GLC is sufficiently precise, accurate, and simple to quantitatively determine MC and DPA in oven surveillance studies. In addition, usefulness of GLC in general surveillance studies should increase, since it can be adapted for routine use on other smokeless powders.

In future work, amounts of DPA and MC degradation products will be determined by GLC.

Table II

ANALYSIS OF METHYL CENTRALITE AND DIPHENYLAMINE IN SIX PLANT SAMPLES

Sample no.	MC analysis		DPA analysis	
	Infrared analysis (% MC by wt)	GLC analysis (% MC by wt)	Infrared analysis (% DPA by wt)[1]	GLC analysis (% DPA by wt)
4900 A	5.50	5.45	None	0.48
4900 B	5.45	5.50	"	0.49
4998 A	5.00	5.20	"	0.47
4998 B	4.90	5.30	"	0.48
4999 A	5.00	4.85	"	0.50
4999 B	5.00	5.00	"	0.51
5024 A	4.95	4.70	"	0.46
5024 B	4.95	5.05	"	0.45
5025 A	4.65	4.70	"	0.46
5025 B	4.70	4.80	"	0.47
5073 A	5.00	5.10	"	0.50
5073 B	5.05	5.30	"	0.51

[1] No infrared method available for DPA analysis.

Table III

ANALYSIS FOR METHYL CENTRALITE AND DIPHENYLAMINE IN THE MC-DPA SYNTHETIC SAMPLES

Sample no.	% MC (by wt) added	% MC (by wt) found by GLC analysis	% DPA (by wt) added	% DPA (by wt) found by GLC analysis
Synthetic 1	6.33	6.12	0.47	0.43
Synthetic 2	9.28	8.92	0.90	0.85
Synthetic 3	11.22	11.40	0.59	0.56
Synthetic 4	7.00	7.30	0.73	0.73
Synthetic 5	11.70	11.70	0.80	0.80

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