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GAS CHROMATOGRAPHIC DETERMINATION OF METHYLENE CHLORIDE IN EXTRACTED PROPELLANTS

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Franford Arsenal

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In connection with a nitrocellulose recovery process that involves extraction of the "solvent-extractable" materials from scrap nitrocellulose-base propellant, it was necessary to develop a method for determining residual methylene chloride in the extracted propellant. A method is proposed for this determination whereby the methylene chloride is extracted with benzene and is determined by gas chromatography using a Silicone Rubber UC W98 column at 50°C and toluene as an internal standard. About

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20. ABSTRACT: (continued)

15% of the methylene chloride is lost in the Soxhlet extraction due to volatilization, so it is necessary to divide by the empirical factor 0.85 in calculating the result. The method was checked with actual and synthetic samples.

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INTRODUCTION

An improved nitrocellulose recovery process is being used that involves extraction of the "solvent-extractable" materials (nitroglycerin, dinitrotoluene, phthalates, stabilizers, etc.) from scrap nitrocellulose-base propellants with methylene chloride, leaving essentially nitrocellulose.[1] After the extraction, most of the methylene chloride is eliminated from the nitrocellulose by a special technique and the nitrocellulose while still moist is incorporated with other ingredients in the manufacture of new propellant.[1] In connection with this process, it was necessary to develop a method for determining methylene chloride in the moist residue. It was found that this could be done by gas chromatography after extracting the methylene chloride with benzene.

EXPERIMENTAL

Apparatus

Hewlett-Packard Model 5750 gas chromatograph with a flame detector and a column of 10% Silicone Rubber UC W98 on acid washed Chromosorb W (80-100 mesh). The column dimensions were 1/8 inch (o.d.) x 4 feet. The carrier gas was helium (35 ml/minute). The operating temperatures were: column, 50°C; injector, 75°C; detector, 75°C. An attenuation of 2 and a chart speed of 0.25 inch/minute were used.

Hamilton syringe 701-NCH, 10 µl.

Extraction apparatus consisting of a Soxhlet extractor with a 3.9 x 11.5 cm chamber (A. H. Thomas 4406-E34), a 2.2 x 8.0 cm cellulose thimble (A. H. Thomas 4390-C15), 125-ml extraction flask (A. H. Thomas 4846-J13), an Allihn condenser with a jacket 60 cm long and a 29/42 ground glass joint (A. H. Thomas 3216-C65), and an adapter to connect the Soxhlet extractor to the condenser (29/42 to 34/45) (A. H. Thomas 5732-E66). A glass rod, 0.5 x 2.0 cm, was placed flat under the thimble to facilitate drainage. The heating operation was performed using a steam bath.

Special powder funnel with stem 1.2 cm in diameter and 10 cm long.

Weighing bottles, 4 cm in diameter and 5 cm high.

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[1] J. M. Goldman and J. A. Sipia, Jr., communications from and to various arsenals.

Reagents

Reagent grade methylene chloride, benzene, and toluene.

Standard methylene chloride solution (1%), prepared by weighing 10.000 g of methylene chloride in a 50-ml volumetric flask, diluting to the mark with benzene, pipetting 5 ml into a 100-ml volumetric flask, and diluting to the mark with benzene.

Standard toluene solution (1%), prepared by weighing 10.000 g of toluene in a 50-ml volumetric flask, diluting to the mark with benzene, pipetting 5 ml into a 100-ml volumetric flask, and diluting to the mark with benzene.

Preparation of Calibration Curve

Add about 50 ml of benzene to five 100-ml volumetric flasks and then add 0, 5.00, 10.00, 15.00, and 20.00 ml of standard methylene chloride solution (1%). Add 5.00 ml of standard toluene solution (1%) and dilute to 100 ml with benzene. Adjust the gas chromatograph to the proper operating conditions and inject 3 µl. The peaks for methylene chloride, benzene, and toluene emerge in about 1-1/4, 3-1/2, and 7 minutes, respectively. Measure the peak heights of the methylene chloride and toluene and deduct the blank (which is ordinarily not significant). Plot the ratios of the peak heights of methylene chloride and toluene against mg of methylene chloride (per 100 ml).

Method

Quickly transfer a portion of the specimen (approximately 5 g) to a covered tared weighing bottle, weigh the bottle and sample, and calculate the exact weight of sample. Add about 10 ml of benzene to the bottle and wash the contents into a thimble (set into the Soxhlet attached to the extraction flask) with about 10 ml of benzene from a wash bottle, using the special powder funnel. Add 40 more ml of benzene to the extraction flask and connect the Soxhlet to the condenser, through which is flowing a fairly rapid stream of water. Extract for 2 hours. After the extraction, raise the extraction flask a few inches and allow it to cool to room temperature. Add 10 ml of benzene through the condenser and detach it. Allow the benzene to flow from the chamber and rinse with about 10 ml of benzene. Transfer the solution to a 100-ml volumetric flask with benzene. For samples containing less than 4 0% methylene chloride use the entire solution; for samples containing more than 4.0% methylene chloride dilute to the mark and transfer a 10-ml aliquot to a 100-ml volumetric flask. Add 5.00 ml of standard toluene solution (1%), dilute to the mark with benzene, inject the sample, and determine the ratio of the peaks as described under preparation of the calibration curve. Determine the mg of methylene chloride (per 100 ml) by referring to the calibration curve, and calculate the percent methylene chloride as follows:

% methylene chloride =

$$\frac{\text{mg of methylene chloride as read from curve}}{\text{g of sample in vol. flask from which 3 }\mu\text{l was taken} \times 10 \times 0.85}$$

DISCUSSION AND RESULTS

The choice of a solvent for extracting the methylene chloride from the propellant in the method was limited. Alcohols, esters, and ketones could not be used since they would attack the nitrocellulose significantly. Chlorinated solvents (for example, carbon tetrachloride, chloroform, and trichlorethylene) were undesirable since they contain appreciable amounts of methylene chloride. Petroleum ether was found to produce too many interfering peaks (with the Silicone Rubber UC W98 column at 30°C 6 large peaks were produced by reagent petroleum ether over the interval 1/2 to 4 minutes and the methylene chloride peak was completely obscured). The use of ethyl ether was rejected because of the hazards caused by its low flash point and tendency to form explosives peroxides on evaporation to dryness (this arsenal does not sanction the use of this solvent as an extractant for propellants in view of past accidents). Another disadvantage of ethyl ether is that it attacks the nitrocellulose somewhat, probably due to impurities or preservatives.

It was found that benzene was a satisfactory solvent in that it readily extracted the methylene chloride and did not affect the nitrocellulose or produce interfering peaks. However, it had a disadvantage in that its relatively high boiling point (80°C as compared with 40°C for methylene chloride) caused the loss of about 15% of the methylene chloride during a 2 hour extraction, as ascertained by experiments with standard methylene chloride solution in benzene. Therefore, it was decided to divide the calculation result by the empirical factor 0.85.

To minimize volatilization losses, a long condenser (60 cm) was used. Also, the extraction flask and Soxhlet were allowed to cool to room temperature before being disconnected.

Obviously, the benzene solutions cannot be evaporated to a smaller volume prior to the gas chromatographic determination because this would cause a loss of methylene chloride.

It was necessary to use a Soxhlet to extract the methylene chloride from the propellant. Merely digesting the extracted propellant with benzene (hot or cold) removed only a portion of the methylene chloride. Apparently, much of the methylene chloride is absorbed into the propellant. All the methylene chloride was extracted from the propellant by the Soxhlet in 2 hours. This was established by the fact that no further methylene chloride was recovered on subjecting propellants that had contained several percent methylene chloride to a second 2-hour extraction period.

Toluene was chosen as the internal standard because it gave a peak that was fairly close to the methylene chloride peak and did not produce interfering peaks.

The peak height ratio method[2] was found to give excellent results. Essentially the same results were obtained by the peak area measurement as determined by multiplying height x width at half-peak height;[2] however, such area measurements are troublesome.

Small amounts of water had no effect on the extraction and produced no peaks (the solubility of water in benzene is very low).

Typical peaks obtained in the method are shown in Figure 1. The calibration curve is shown in Figure 2. The calibration curve was a straight line for 0 to 150 mg methylene chloride, then deviated slightly over the range 150 to 200 mg.

The accuracy of this method was checked by transferring 5-g samples of propellant (previously extracted with benzene to remove any methylene chloride) to weighing bottles and adding 5.00, 10.00, 15.00, and 20.00 ml of standard methylene chloride solution (1%). The solutions and samples were then transferred to the thimbles in the Soxhlet extraction apparatus with benzene. A total of 60 ml of benzene (counting the benzene in the standard methylene chloride solution) was added and the methylene chloride was determined and calculated as in the method. The methylene chloride recoveries (Table I) were satisfactory.

The methylene chloride was determined on nine extracted propellants. The results varied over the range 0.32 to 5.98% methylene chloride.

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[2] S. Dal Nogare and R. S. Juvet, Jr., "Gas-Liquid Chromatography," Interscience Publishers, New York, 1962, p. 254 to 257.

SUMMARY

In connection with a nitrocellulose recovery process that involves extraction of the "solvent-extractable" materials from scrap nitrocellulose-base propellant, it was necessary to develop a method for determining residual methylene chloride in the extracted propellant. A method is proposed for this determination whereby the methylene chloride is extracted with benzene and is determined by gas chromatography using a Silicone Rubber UC W98 column at 50°C and toluene as an internal standard. About 15% of the methylene chloride is lost in the Soxhlet extraction due to volatilization, so it is necessary to divide by the empirical factor 0.85 in calculating the result. The method was checked on actual and synthetic samples.

RECOMMENDATIONS

It is recommended that the method in this report be adopted by interested arsenals.

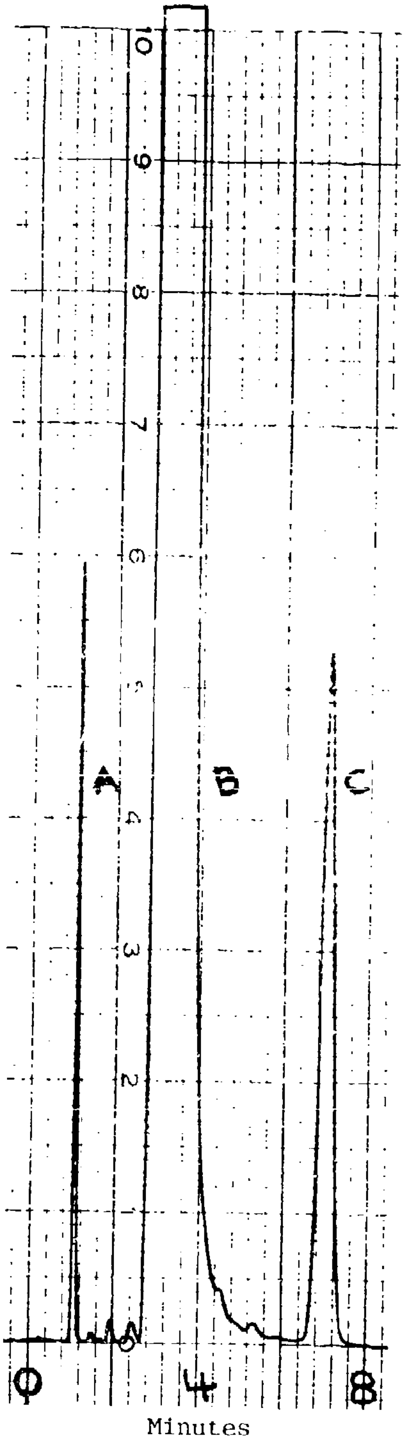

Figure 1. Chromatogram of Benzene Solution Containing Methylene Chloride and Toluene (Internal Standard): A, Methylene Chloride; B, Benzene; C, Toluene.

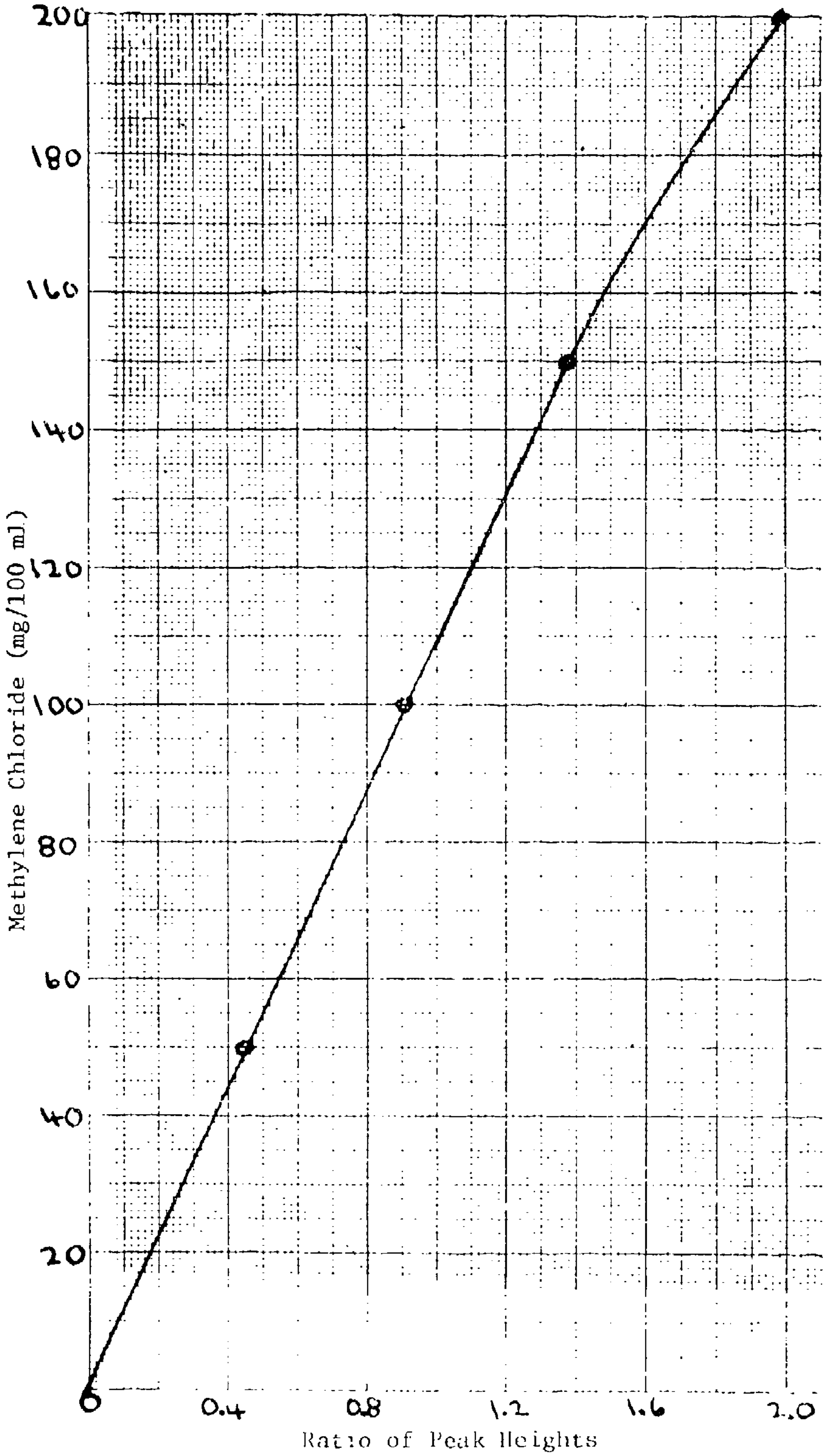

Figure 2. Calibration Curve Prepared by Plotting Ratio of Peak Heights of Methylene Chloride and Toluene against Concentration of Methylene Chloride.

Table I.

Recoveries of Methylene Chloride from Synthetic Samples Prepared Using Standard Methylene Chloride Solution

Methylene Chloride Added (mg)	Methylene Chloride Recovered (mg)
50	56
50	52
50	45
100	106
100	105
100	100
150	138
150	153
150	156
200	191
200	194
200	211