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GAS-LIQUID CHROMATOGRAPHIC DETERMINATION OF NITRATE ESTERS, STABILIZERS AND PLASTICIZERS IN NITROCELLULOSE-BASE PROPELLANTS

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SUMMARY

A gas-liquid chromatographic method has been developed for determining nitrate esters as well as stabilizers and plasticizers in a wide variety of nitrocellulose-base propellants. Separations are performed on short columns containing light loadings of OV-101, -210, and -225. Retention data obtained for twenty-four components permit the selection of columns and identification of the components in unknown propellants. The precision and accuracy of determinations were evaluated by statistical procedures using HEN-12 double-base propellant and a simulated composite-modified double-base propellant. Semimicro calibration and extraction procedures substantially reduced analysis time. A special study was made of experimental factors that influence the reliability of nitrate ester determination.

INTRODUCTION

Controlling the quality of nitrocellulose-base propellants and monitoring chemical changes induced by storage requires determination of the nitrate esters, stabilizers, and plasticizers, which are usually the major ingredients outside of the nitrocellulose binder. The standardized wet-chemical and spectrometric methods¹ for determining these components are time-consuming and complex, in that they have to be adjusted for different combinations. The objective of this investigation was to devise a simpler and faster procedure that would be applicable to all three components and to the majority of nitrocellulose-base propellants.

Gas-liquid chromatography (GLC) offered the greatest potential for this role. Relatively straightforward GLC procedures had already been successfully used to determine stabilizers and plasticizers in single-base propellants, and plasticizers in double-base propellants. An analytical precision comparable to that of the standardized determination methods was obtained by KOHLBECK AND DALTON² for stabilizers and plasticizers in several single-base propellants. ALSTON *et al.*³ developed a GLC method for determining methyl centralite and diphenylamine in single-base 20-mm gun propellant. NORWITZ AND APATOFF⁴ reported a GLC method for determining dimethyl-, diethyl-, and dibutylphthalate plasticizers in small arms double-base propellants, and their method would present no problem in determining plasticizers

A GLC method has also been devised for determining stabilizers in double- and triple-base propellants, which is more difficult because nitrate ester decomposition products tend to react with the stabilizers to give anomalous results. TROWELL AND PHILPOT⁵ solved this problem by injecting samples "on column" and programming the column temperature to separate the nitrate ester from the stabilizer before reaction could take place. This procedure, however, does not provide for determination of the nitrate esters in nitrocellulose-base propellants, and no effective GLC method has been reported. Nitrate esters, particularly nitroglycerine (glyceryl trinitrate), are more difficult to determine than stabilizers and plasticizers because of their low thermal stability and their tendency to decompose on improperly prepared columns. The numerous GLC methods reported for determining nitrate esters in other materials⁶⁻¹¹ are not applicable to propellants because of the stabilizer interference.

The investigation reported here succeeded in developing a procedure for the determination of nitrate esters, as well as the plasticizers and stabilizers, in all types of nitrocellulose-base propellants. The basic approach was similar to that developed by TROWELL AND PHILPOT which used on-column injection and temperature-programming. The added features that permitted extension of the method to determination of nitrate esters included (1) careful control of the quality of the columns to preclude on-column decomposition; and (2) use of an electronic digital integrator, which provided more sensitive detection of the nitrate ester and precise measurement of its peak area. Also introduced into the procedure was the extraction of components by an ultrasonic cleaner, which greatly reduced the extraction time.

EXPERIMENTAL

Chemicals

The methylene chloride solvent used in this study was chromatography purchased from Matheson Scientific, and the 1,2-dichloroethane solvent was reagent-grade purchased from Eastman Organic Chemicals.

The nitrate esters were propellant-production-grade. The nitroglycerine (NG) was received as a desensitized solution of approx. 80% by weight in acetone, and was removed for calibration by evaporating the acetone at room temperature from a 1-ml or smaller aliquot. Since the nitrate esters are explosives, only small quantities were used and special safety precautions were taken in their weighing, handling, and storage.

The stabilizers and plasticizers were purchased from Fisher Scientific Co., Eastman Organic Chemicals, and K&K Laboratories, Inc. The isomeric dinitrotoluenes from K&K Laboratories were of unspecified purity. The other plasticizers and stabilizers were reagent grade or of comparable purity except for dimethyl sebacate, dibutyl phthalate, and dioctyl phthalate, which were practical grade. All of the chemicals were used without further purification.

The stationary phases were purchased from the following sources: OV-101, Pierce Chemical Co.; OV-210, Supelco, Inc.; and OV-225, Applied Science Laboratories, Inc. The Gas-Chrom Q and Chromosorb W-HP were purchased from Applied Science and Hewlett-Packard, respectively. The N.O-bis(trimethylsilyl)-acetamide

Apparatus and conditions

A Hewlett-Packard Model 7624A gas chromatograph was used. Eluted components were detected with a dual hydrogen flame ionization detector, and peak areas were measured with a Hewlett-Packard 3370A electronic digital integrator. All gases were high purity and were passed through drying tubes before entering the chromatograph. The helium carrier gas flow was set at 40 ml/min, and the air flow at 500 ml/min. The hydrogen flow was set at 32 ml/min to give maximum sensitivity.

The dual columns were $\frac{1}{8}$ -in. \times 2-ft. chromatographic-grade stainless steel (Hewlett-Packard). A $\frac{1}{8}$ -in. Swagelok brass "T" was installed in the column oven between the outlet of the standard injection block and the inlet to the "A" column to serve as an on-column injection port. A Teflon-faced silicone septum was mounted in the upper arm of the T. The stationary phases and solid supports, which were selected after investigation of a large number of both types of chemicals, are listed in Table I. The silicone stationary phases were chosen to cover a wide range of polarities.

TABLE I
COLUMN PARAMETERS

<i>Stationary phase</i>		<i>Solid support</i> ^a	<i>Packing weight</i> (mg/ft.)
<i>Type</i>	<i>Weight %</i>		
OV-101	3.8	Gas-Chrom Q	495
OV-210	2.5	Chromosorb W-HP	380
OV-225	1.1	Gas-Chrom Q	480

^a 80-100 mesh.

The packings were made by a filtration-fluidization procedure¹² in which the solid support was first slurried in a volatile solvent containing the stationary phase, and the excess solvent solution was then removed by filtration. The damp packing was then dried in a Hi-Eff fluidizer marketed by Applied Science. Special care was taken to prevent the breakage of particles, which would have produced active sites for the decomposition of the nitrate esters. The actual percentage of the stationary phase was determined by the weight loss measured after the packing was extracted in a Soxhlet extraction apparatus. To ensure solid packing of the column the packing material was added in small increments and the tubing was tapped during the process. The packed columns were preconditioned at 250° for 4-6 h while maintaining a helium flow of 10-15 ml/min.

All aliquot samples were injected on the column, after raising the oven door, at an initial temperature of 70°. The syringe was a 10- μ l Hamilton Type 701-N, and the normal aliquot size was 1 μ l. The column oven was then linearly temperature-programmed to elute the components.

PROCEDURE

Calibration. An internal standard procedure was used for the quantitative

standard is not critical — nitrate esters, stabilizers, plasticizers, and normal alkanes gave comparable results — but normal alkanes are preferred for ease of handling. After it was established that the detector response of each component as a function of its concentration was linear with zero or negligible intercept, a single calibration mixture was used to establish component calibration factors. The component percentages W_c (%) were calculated by the usual linear expression:

$$W_c(\%) = \frac{A_c \cdot F_c \cdot W_s \cdot 100}{A_s \cdot W_p}$$

where W and A are the weights and peak areas, respectively; the subscripts refer to the component (c), the internal standard (s), and the propellant (p), and the calibration factor F_c is the inverse of the relative response factor:

$$F_c = \frac{A_s \cdot W_c}{A_c \cdot W_s}$$

The F_c of each component was checked daily; the values for the stabilizers and plasticizers did not vary significantly over a period of several weeks, but those of the nitrate esters varied from day to day.

A semimicro procedure was used for the preparation of the calibration mixtures, which were made up of the components of the propellant extract to be analyzed, in approximately the same proportions, and the internal standard. In general the stabilizer and plasticizer weights ranged from 1 to 10 mg and the nitrate esters from 10 to 40 mg. The component and internal standard quantities, weighed to a precision of $\pm 1 \mu\text{g}$ by a Cahn Gram Electrobalance, were placed in separate differential scanning calorimeter (DSC) aluminium sample pans marketed by Perkin-Elmer Corporation. The pans were transferred to a dried 1-dram glass vial and 1–2 ml of solvent were added.

For most of the investigations, methylene chloride was used as the solvent for direct analysis of all mixtures except those containing resorcinol, in which case 1,2-dichloroethane was substituted because of resorcinol's greater solubility in this solvent. In the course of the experiment it was found that 1,2-dichloroethane is suitable for analysis of all components of interest, and is probably preferable to the methylene chloride because of its higher boiling point and greater solvent capabilities. When the silylation of resorcinol was desired, a 0.5-ml quantity of BSA was added to the completed calibration mixture in the vial. This procedure also silylates the impurities of NG containing hydroxyl groups¹³; the trimethylsilyl (TMS) derivative of resorcinol was formed immediately, but 10–20 min was required for quantitative conversion of the NG impurities to the TMS derivatives.

The vials containing the completed calibration mixtures were sealed with polyethylene stoppers and shaken vigorously to form homogeneous solutions. The solution was then poured into another 1-dram vial to separate it from the aluminium pans and thus preclude the possibility of metal catalysis of decomposition reactions.

Propellant samples. The propellant was cut into short, thin slices and for each test a 0.1–0.2-g sample weighed to $\pm 0.1 \text{ mg}$ was placed in a 12-mm \times 100-mm

also placed in the tube. A 2-ml quantity of methylene chloride was added and the tube was covered with aluminum foil. The sample tubes, in pairs, were suspended in the bath of a Beckman 977 ultrasonic cleaner and propellant components were extracted from the samples by a 15-min exposure to ultrasonic radiation. The extract was separated from the propellant residue and DSC pan, and 1- μ l aliquots of the extract were injected on the column and analyzed. The silylation procedure was the same as that used for the calibration mixture.

RESULTS AND DISCUSSION

Nitroglycerine (NG) analysis

The majority of the experimental work was concentrated on nitroglycerine and an extensive evaluation was made of the experimental factors that affect the precision and accuracy of its determination. Not only is NG the nitrate ester most commonly used in nitrocellulose-base propellants, but it is also the most unstable. Procedures developed for NG determination can be expected to apply equally well to other nitrate esters. The use of a high-quality column was found to be essential, and the filtration-fluidization method of preparing packings consistently resulted in acceptable columns. An attempt to improve column efficiency by sieving the packing, however, had a deleterious effect.

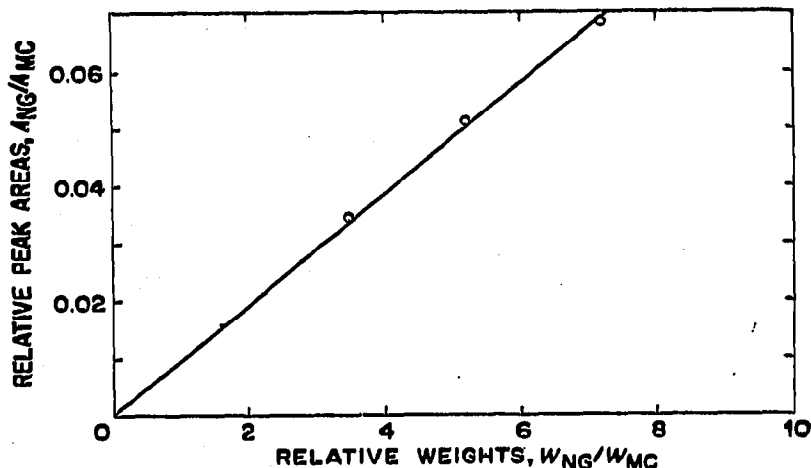


Fig. 1. Calibration curve for nitroglycerine (NG) with methyl centralite (MC) standard.

When the recommended procedure and an acceptable column were used, the NG detector response was a linear function of the NG concentration, as shown in Fig. 1, indicating that no detectable amount of decomposition occurred on the column. In this particular case the NG calibration factor was not affected by the sample size or the column temperature-programming rate. However, reproducible decomposition of NG did occur in the connecting tubing between the end of the column and the flame ionization detector jet, which was maintained at the detector temperature. As a consequence the NG calibration factor varied with the detector temperature: the relationship was linear up to 250°, as shown in Fig. 2, but at some point above that temperature the calibration factor deviated from linearity in an

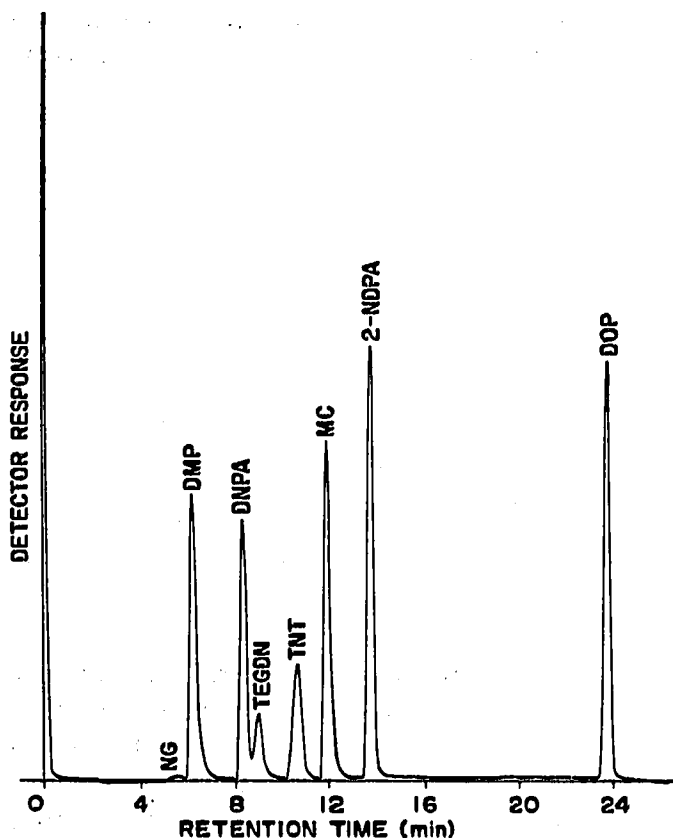


Fig. 3. Gas chromatogram of a mixture of nitrate esters, stabilizers, and plasticizers on 3.8% OV-101 column. Conditions: column temperature-programmed, from 70° to 220° at 6°/min; detector temperature, 225°; sensitivity, $4 \cdot 10^{-9}$ a.f.s.

TABLE III

NESTED EXPERIMENT AND RESULTS OF PROPELLANT SAMPLE ANALYSES

Propellant: HEN-12 containing the nitrate ester NG, the plasticizer DNPA, and the stabilizer 2-NDPA. Column: 3.8% OV-101.

Compound (symbol) ^a	GLC Condition 1 ^b				GLC Condition 2 ^c			
	Extraction 1		Extraction 2		Extraction 3		Extraction 4	
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
NG	40.86	40.04	39.06	39.90	39.82	39.83	39.15	40.02
	40.47	39.71	39.22	40.18	39.40	39.63	39.06	39.62
	39.72	39.53	39.26	39.68	39.59	39.61	39.10	38.85
DNPA	3.342	3.324	3.273	3.333	3.302	3.337	3.240	3.344
	3.334	3.314	3.322	3.337	3.344	3.352	3.272	3.311
	3.329	3.320	3.317	3.337	3.346	3.335	3.274	3.314
2-NDPA	2.018	2.016	1.987	2.018	1.969	1.974	1.929	1.984
	2.022	2.014	2.017	2.017	1.978	1.977	1.935	1.971
	2.018	2.008	2.028	2.017	1.986	1.967	1.936	1.978

^a For symbols explanation see text and Table II.

^b Described in Fig. 4.

^c Described in Fig. 5.

NG requires careful control of the detector temperature between calibration and analysis, and also more frequent calibration than is necessary in the case of stabilizers and plasticizers.

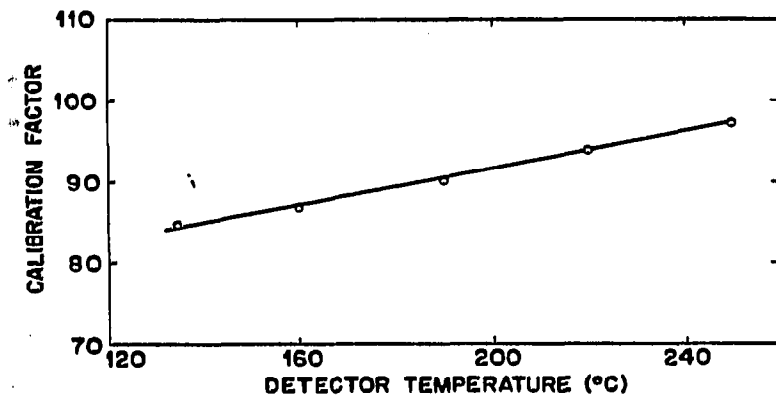


Fig. 2. Effect of flame ionization detector temperature on NG calibration factor.

Retention data

The retention data obtained for the most commonly used nitrate esters, stabilizers, and plasticizers are listed in Table II. The Kováts index of each component was determined by using normal alkanes with an even number of carbon atoms. The majority of nitrocellulose-base propellants can be analyzed for these components by using one or more of the columns shown. The chromatographic conditions can be varied to meet the speed and resolution requirements of a particular analysis; for example, for routine applications it might be preferable to use a single column with a mixed packing rather than multiple columns. The composition of this mixed packing for any given separation of components can be determined from the data in Tables I and II¹⁴.

In the chromatograms showing the results obtained, the sensitivity of the analyses is expressed in terms of ampères required for a recorder full-scale deflection (a.f.s.) of 1 mV. Those components separated by at least 70 Kováts-index units generally had a resolution greater than 1.5. The degree of resolution achieved is illustrated in Fig. 3 for a component mixture separated on the 3.8% OV-101 column. In this case the quantities injected were 20 μ g for the nitrate esters and 5-7 μ g for all other components.

Quantitative analysis: statistical precision and accuracy evaluation of the method

Double-base propellant analyses. Statistical methods were used to estimate the accuracy and overall precision of the method for double-base propellant analysis. The magnitude of the error variances associated with propellant extraction and sampling and the magnitude of the random error variances associated with the analyses of replicate extract aliquots were evaluated by a nested experiment¹⁵.

The propellant selected for this analysis was HEN-12, a double-base propellant manufactured in sheet form by Radford Army Ammunition Plant and containing NG as the nitrate ester, 2-nitrodiphenylamine (2-NDPA) as the stabilizer, and di-n-propyl adipate (DNPA) as the plasticizer. The experimental design and the

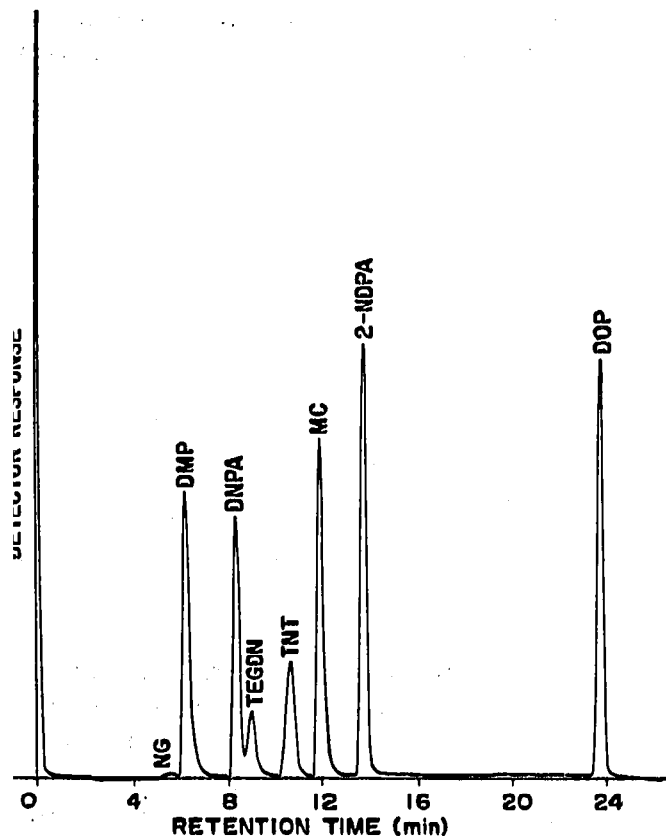


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Compound (symbol) ^a	GLC Condition 1 ^b				GLC Condition 2 ^c			
	Extraction 1		Extraction 2		Extraction 3		Extraction 4	
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
NG	40.86	40.04	39.06	39.90	39.82	39.83	39.15	40.02
	40.47	39.71	39.22	40.18	39.40	39.63	39.06	39.62
	39.72	39.53	39.26	39.68	39.59	39.61	39.10	38.85
DNPA	3.342	3.324	3.273	3.333	3.302	3.337	3.240	3.344
	3.334	3.314	3.322	3.337	3.344	3.352	3.272	3.311
	3.329	3.320	3.317	3.337	3.346	3.335	3.274	3.314
2-NDPA	2.018	2.016	1.987	2.018	1.969	1.974	1.929	1.984
	2.022	2.014	2.017	2.017	1.978	1.977	1.935	1.971
	2.018	2.008	2.028	2.017	1.986	1.967	1.936	1.978

^a For symbols explanation see text and Table II.

^b Described in Fig. 3.

Two chromatographic conditions, differing mainly in the flame ionization detector and column oven temperatures, were introduced primarily to evaluate the effect of the chromatographic condition on the repeatability or random error variances of replicate aliquot analyses. The specific conditions used and typical chromatograms obtained are given in Figs. 4 and 5. At the 200° detector temperature (Condition 2, Fig. 5) it was possible to reduce analysis time by a factor of two. This higher temperature also produced sharper peaks for the methyl centralite (MC) internal standard and for the 2-NDPA, providing a more favorable condition for precise measurement by the electronic integrator. The 135° detector temperature (Condition 1, Fig. 4) provided greater sensitivity and was more favorable for NG determination. Under both conditions the peak shape of NG was symmetrical with no evidence of decomposition on the column. The septum bleed was detectable at the high sensitivity used to record the NG peak and thus produced a slight positive slope in the baseline, but it had no significant effect on the precision and accuracy of the NG determination.

As indicated in the experimental design (Table III), two propellant extractions,

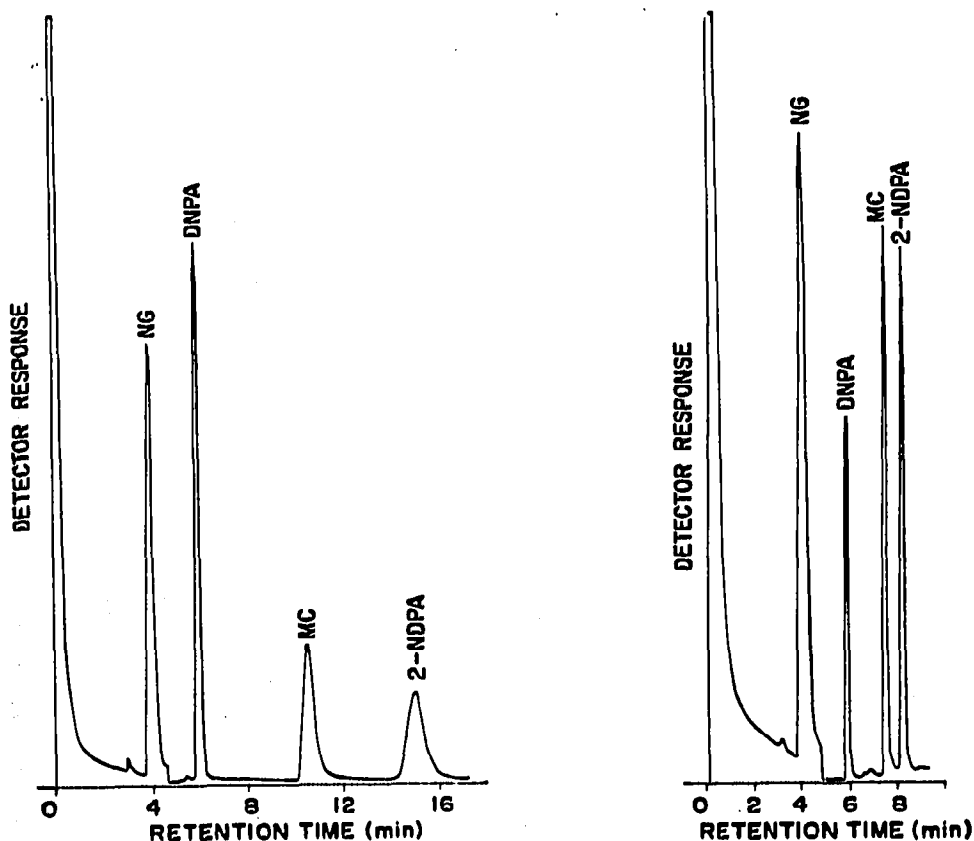


Fig. 4. Gas chromatogram of HEN-12 propellant extract on 3.8% OV-101 column (Condition 1). Conditions: column held at 70° for 1 min, then temperature-programmed to 130° at 15°/min, and held for 12 min; detector temperature, 135°; sensitivity, $1 \cdot 10^{-10}$ a.f.s. for NG, $1 \cdot 10^{-9}$ a.f.s. for other components.

Fig. 5. Gas chromatogram of HEN-12 propellant extract on 3.8% OV-101 column (Condition 2). Conditions: column held at 70° for 1 min, then temperature-programmed to 190° at 15°/min;

TABLE IV

CALIBRATION DATA FOR HEN-12 PROPELLANT ANALYSES

A separate calibration mixture was used for each condition.

Component (symbol)	Condition 1		Condition 2	
	Weight (mg/ml) ^a	F _c	Weight (mg/ml) ^a	F _c
NG	26.82	109.5	19.09	138.2
DNPA	2.608	1.318	2.930	1.333
MC	2.032	1.000 ^b	1.887	1.000 ^b
2-NDPA	2.101	1.057	2.281	1.047

^a Total volume = 1 ml.^b Integrator counts = 80,270 μ V sec/ μ g.

TABLE V

VARIANCE ANALYSES FOR NESTED EXPERIMENT

Obtained from results summarized in Table III.

DF = degrees of freedom; MS = observed mean square; SS = sum of squares; EMS = expected mean square.

Source of variation	DF	NG		DNPA		2-NDPA		EMS
		SS · 10 ²	MS · 10 ²	SS · 10 ²	MS · 10 ²	SS · 10 ²	MS · 10 ²	
Between GLC conditions	1	65.010	65.010	0.05133	0.05133	1.48006	1.48006 ^a	$\sigma_e^2 + 3\sigma_m^2 + 6\sigma_x^2 + 12\sigma_c^2$
Between extractions within conditions	2	112.560	56.280	0.58380	0.29190	0.11713	0.05861	$\sigma_e^2 + 3\sigma_m^2 + 6\sigma_x^2$
Between samples within extractions	4	158.687	39.672 ^a	0.76243	0.19060 ^a	0.31188	0.07797 ^a	$\bar{u}_e^2 + 3\sigma_m^2$
Within samples (error)	16	178.261	11.141	0.44028	0.02751	0.12576	0.00786	σ_e^2
Total	23	514.518		1.83784		2.03493		

^a Significant at 5% ($\alpha = 0.05$) or lower significance level.

each providing three aliquots of duplicate samples, were performed for each of the two chromatographic conditions. The two extractions for each condition were obtained on the same day, but there was a three-day lapse between Conditions 1 and 2.

A separate calibration mixture was used for each condition, and the mixture and propellant samples were analyzed on the same day. The resulting calibration data are listed in Table IV. As was expected, the NG analysis showed the lowest sensitivity among the components, and its calibration factor was particularly large under Condition 2 because of the effect of the higher detector temperature; however, under both conditions the detector response for NG exceeded that required for precise area measurement by the integrator. The calibration factors of the other components agreed between conditions within the experimental error.

In the variance analyses, summarized in Table V, the difference between the average results of the respective conditions was statistically significant only in the determination of 2-NDPA. The fact that there was no significant difference between extractions within conditions validates the semimicro extraction procedure. The sampling error, however, was significantly greater than the random error (repeatability) of replicate aliquot analyses. The primary contributor to this discrepancy was probably inhomogeneity of the propellant which was accentuated by storage in sheet form and the small size of the samples analyzed.

TABLE VI

ESTIMATED ERROR VARIANCES (S_e^2), VARIANCE COMPONENTS FOR SAMPLES (S_m^2), AND RELATIVE STANDARD DEVIATIONS (S_r) FOR NESTED EXPERIMENT

Calculations of S_e^2 and S_m^2 from MS and EMS values in Table V.

Component (symbol)	$S_e^2 \cdot 10^3$	$S_m^2 \cdot 10^3$	S_r (%)		
			Condition 1	Condition 2	Pooled ^a
NG	111.4	113.6	0.867	0.815	0.842
DNPA	0.2751	0.6562	0.425	0.565	0.495
2-NDPA	0.07855	0.2122	0.538	0.316	0.444

^a 16 degrees of freedom.

The estimated random error variances (S_e^2) and the variance components for samples (S_m^2) were calculated from the observed and expected mean squares in Table V. The calculated values and the estimated relative standard deviations (S_r) for the replicate aliquot analyses are given in Table VI. A more precise estimate of the sampling error mean square was obtained by pooling the mean squares for extractions within conditions with the mean squares for samples within extractions. The estimated relative standard deviations for individual aliquot analyses (injections) were all less than 1%, which is excellent repeatability for this type of analysis. Since no significant difference was found between the respective S_r values for Conditions 1 and 2, these values were likewise pooled for greater precision and the

TABLE VII

PRECISION OF THE GLC METHOD^a FOR HEN-12 PROPELLANT ANALYSIS

Number of samples (<i>k</i>)	$L_{1/2}$ at the 95 % confidence level		
	NG	DNPA	2-NDPA
1	0.895	0.0632	0.0360
2	0.729	0.0484	0.0274
3	0.665	0.0423	0.0238
4	0.630	0.0390	0.0218

^a Number of replicate injections per sample (*n*) = 2.

The overall precision of the method for HEN-12 propellant analysis (Table VII) was estimated by placing confidence limits ($X \pm L_{1/2}$) on a determination (X) at the 95 % level, where $L_{1/2}$ is half the length of the interval. The $L_{1/2}$ values were calculated from the expression

$$L_{1/2} = t_f S_d$$

where t_f is STUDENT'S t with f degrees of freedom and S_d is the positive square root of the total variance, which is

$$S_d^2 = \frac{S_e^2}{n} + \frac{S_m^2}{k}$$

for n aliquot analyses of each of k samples. The f degrees of freedom were estimated by SATTERTHWAITTE'S approximation¹⁶ and the S_e^2 and S_m^2 values were taken from Table VI. As could be predicted from the Table VI data, increasing the number of samples for $n = 2$ improves the precision of the determinations, to a slight degree in the case of NG and to a marked degree for DNPA and 2-NDPA.

The accuracy of the method was estimated by comparing the average GLC results with those of standardized chemical determinations supplied by the propellant manufacturer (Table VIII). Although two of the individual GLC determinations show a substantial variance at the 5 % significance level, the averages obtained by combining the results of Conditions 1 and 2 do not differ significantly from the chemical results.

TABLE VIII

COMPARISON OF CHEMICAL AND GLC ANALYSES OF HEN-12 PROPELLANT

Component (symbol)	Analysis result (wt. %)			
	Nominal	Chemical	GLC	
			Condition 1	Condition 2
NG	40.6	40.11	39.80	39.47 ^a
DNPA	3.3	3.30	3.32	3.31
2-NDPA	2.0	1.98	2.02 ^a	1.97

^a Significantly different from chemical analysis at 5 % significance level.

Composite-modified double-base propellant analyses. A simulated composite-modified double-base propellant (CMDB) containing triacetin (TA), NG, resorcinol, and 2-NDPA was analyzed to demonstrate applicability of the method to a mixture that is more difficult to separate and quantitatively determine. The column chosen for this experiment, based on the retention data in Table II, was the polar 1.1% OV-225. *n*-Eicosane was used as the internal standard.

The propellant extract was first analyzed directly as shown by the chromatogram in Fig. 6. The extract was then treated with BSA to form the trimethylsilyl (TMS) ether of resorcinol and the silylated mixture was analyzed (Fig. 7). Good separations and a high degree of analytical precision were achieved in both cases.

In the direct determination of resorcinol, it was found that a high quality packing with a minimum of active sites would prevent most of the adsorption and peak tailing that normally occur. The small amount of adsorption that could still take place was eliminated by conditioning the column with a 2- μ l injection of a 5-mg/ml solution of resorcinol in 1,2-dichloroethane prior to each series of resorcinol determinations. There was no evidence of NG decomposition on the column or interaction between the NG and the other components. The NG contained an

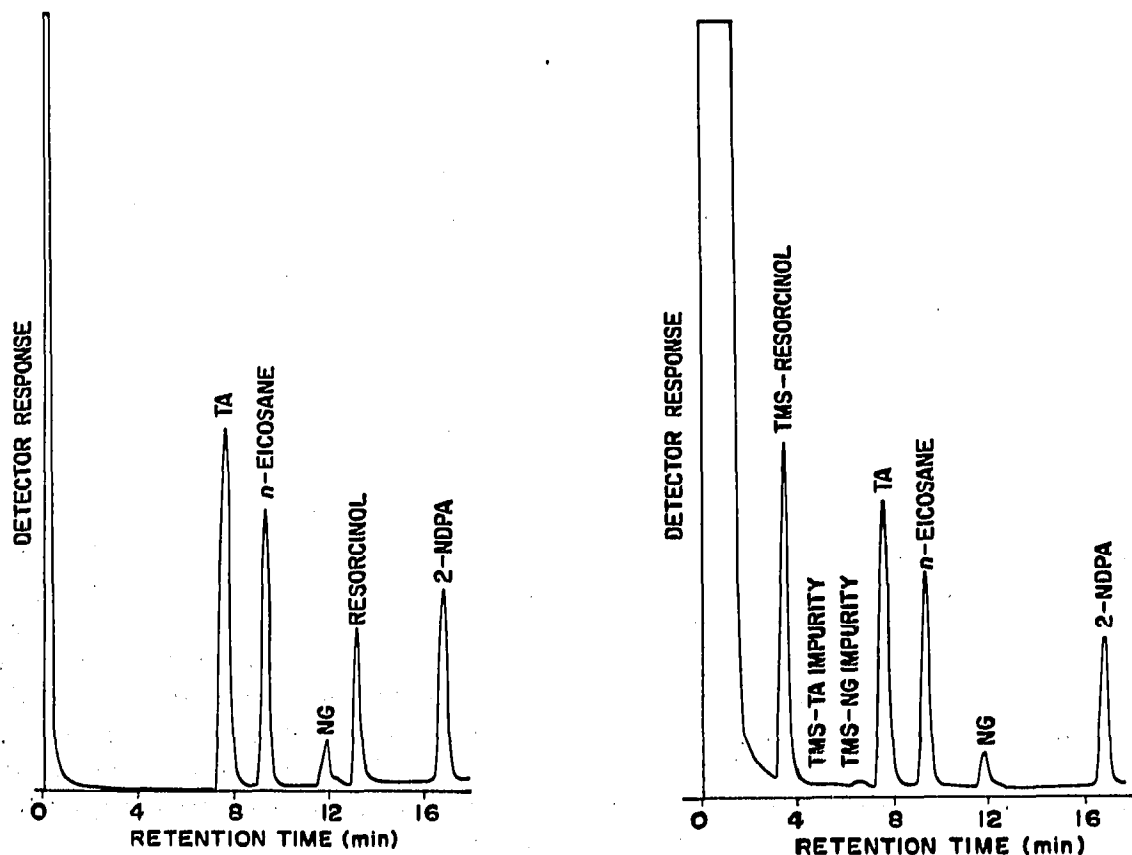


Fig. 6. Gas chromatogram of simulated CMDB propellant extract on 1.1% OV-225 column. Conditions: column temperature-programmed, from 70° to 190° at 6°/min; detector temperature 200°; sensitivity, $1 \cdot 10^{-9}$ a.f.s.

Fig. 7. Gas chromatogram of silylated (BSA) simulated CMDB propellant extract on 1.1%

impurity that was partially separated and appeared as a rear shoulder on the main peak (Fig. 6). This shoulder was included in the peak area measurement.

The TMS-resorcinol has a much shorter retention time than resorcinol itself, and its flame ionization detector response is greater by a factor of almost three. The TMS-resorcinol is ready for analyses immediately after the silylation mixture is shaken. The procedure silylated the impurities of TA as well as NG (Fig. 7).

Table IX outlines the composition of the simulated CMDB propellant mixture before silylation, and the calibration factors and relative standard deviations with and without silylation. The increase in TA and NG calibration factors after silylation is attributed to the removal of their impurities. The close agreement between the two factors for 2-NDPA shows that this component did not form a TMS derivative under the silylation conditions used. No explanation can be offered for the significant increase after silylation in the estimated relative standard deviation for the NG determination — from 0.654% to 2.12% — but the larger value is acceptable for NG determination.

TABLE IX

COMPOSITION AND REPEATABILITY DATA FOR SIMULATED CMDB PROPELLANT ANALYSIS

Component	Weight (mg/ml) ^a	Without silylation		With silylation	
		F_c	S_r (%) ^b	F_c	S_r (%)
TA	4.737	2.925	0.619	2.980	0.393
NG	29.70	139.7	0.654	169.2	2.12
<i>n</i> -Eicosane	1.015	1.000	—	1.000	—
Resorcinol	1.106	1.929	0.549	0.6971	0.259
2-NDPA	0.950	1.294	0.360	1.310	0.620

^a Total volume = 2 ml.

^b 10 degrees of freedom.

CONCLUSIONS

The GLC method described here is an attractive alternative to many of the standardized wet-chemical and spectrometric methods currently being used to determine the components of nitrocellulose-base propellants. The method is simple and rapid, and has been demonstrated to be very accurate and precise. The total time for quantitative determination on duplicate propellant samples is within two hours, and the estimated relative standard deviations for individual determinations are generally less than 1%. The three components of primary interest — nitrate esters, stabilizers, and plasticizers — can be determined by the same procedure, and the applicability of the method to double-base and to composite-modified double-base propellants has been demonstrated.

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