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GAS CHROMATOGRAPHIC ANALYSIS OF TRINITROTOLUENE
FROM THE CONTINUOUS PROCESS

R. W. DALTON, J. A. KOHLBECK AND W. T. BOLLETER

Hercules Incorporated, Radford Army Ammunition Plant, Radford, Va. (U.S.A.)

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SUMMARY

A rapid gas chromatographic method has been developed for determining the composition of the organic phase of the continuous TNT process. The method provides analyses for isomers of mono-, di-, and trinitrotoluenes in samples from nitration phases and for residual dinitrotoluenes and asymmetrical trinitrotoluenes from the TNT purification process and in the final product. The column used for separation was 10% UC-W98 silicone rubber on 80-100 Diatoport-S. Detector response factors were determined and used to calculate relative percent components to eliminate time-consuming calibration and achieve better reproducibility.

INTRODUCTION

During 1968, the first continuous process plant in the U.S. for the manufacture of trinitrotoluene (TNT) began operation at Radford Army Ammunition Plant (RAAP), Radford, Va. In the continuous process, toluene is fed to the first nitrator and mixed nitrating acids to the latter nitrators. Nitric acid is fed at various stages of nitration to replenish acid used in the process. The flow is countercurrent and the toluene is nitrated to the mono-, di-, and trinitro products in a series of eight nitration vessels while the acid becomes progressively more dilute as the result of nitration. As TNT leaves the last nitrator, it enters the purification section of the process where the *meta* TNT isomers are removed by treatment with aqueous sodium sulfite. Following purification, the TNT is water-washed, dried, and flaked.

Rapid analytical methods were required to study the continuous change in composition of the organic phase throughout the process. GEHRING AND SHIRK¹ showed that gas chromatographic techniques could be applied to analyzing crude and refined TNT for TNT and DNT isomers of 0.02 to approximately 3.00%. However, their method requires the availability of high-purity isomers for preparation of external standards and frequent checks on instrument calibration. The procedure also does not indicate that isomers of mononitrotoluene and other nitration components can be determined.

Others have reported methods on thin-layer chromatography^{2,3}, paper chroma-

tography⁴, and infrared spectrometry^{5,6}. Although these methods may be satisfactory for a specific purpose, none of the methods were satisfactory for samples taken throughout the continuous TNT process. Therefore, this paper describes a single, rapid, and accurate gas chromatographic procedure for the determination of toluene, trinitrobenzene, and isomers of mono-, di-, and trinitrotoluene throughout the continuous process. Flame ionization detector response factors were determined and used in calculating relative percentages thus eliminating daily time-consuming calibrations.

EXPERIMENTAL

Apparatus

All work was performed using a Hewlett-Packard Model 5750 dual-column gas chromatograph equipped with a flame ionization detector and a 1-mV recorder. The analytical columns were stainless steel, 12-ft. \times 1/8-in. O.D. containing 10% UC-W98 silicone gum rubber on 80-100 mesh Diatoport-S. (One was used as a reference column.) The columns were preconditioned at 280° for 18 h with a helium flow of 60 cc/min.

Reagents

The 2,5-, 2,3-, and 3,5-DNT isomers and the 2,3,5-, 2,3,4-, and 2,3,6-TNT isomers were furnished by Picatinny Arsenal, Dover, N.J. The 2,6- and 3,4-DNT isomers were purchased from K & K Laboratories Incorporated. The 2,4-DNT was military grade per MIL-D-204A from Joliet Army Ammunition Plant, Joliet, Ill. The 2,4,5-TNT was laboratory synthesized and purified by selective solvent extraction⁷. The 2-, 3-, and 4-MNT isomers were purchased from Aldrich Chemical Company, Incorporated, Milwaukee, Wisc. High-purity 2,4,6-TNT was received from Volunteer Army Ammunition Plant, Chattanooga, Tenn. and the 1,3,5-trinitrobenzene (TNB) from Eastman Organic Chemicals. All reagents were first tested individually by gas chromatography, thin-layer chromatography, and infrared to identify any traces of impurities and moisture was removed prior to use. Toluene was reagent grade.

Detector response factors

Since detector response will vary for each compound, it was necessary to determine correction factors for each component to be analyzed. The method used for this determination was as follows: Standard solutions were prepared containing a known weight (w) of each compound (approximately 4 mg/ml in acetone). Two microliters were injected into the gas chromatograph and a chromatogram was obtained. The area " A " of each peak was measured using the height of the peak times width at half height. The ratio A/w was calculated for each peak. The correction factor " F " was calculated by dividing the A/w of each peak by 2,4,6-TNT A/w thus arbitrarily setting 2,4,6-TNT equal to 1.00 and all other components relative to 2,4,6-TNT.

When separation interference occurred between components, each was prepared in individual standards with 2,4,6-TNT. Since 2,3,6-TNT elutes with 2,4,6-TNT, this comparison was made with 2,3-DNT which was previously standardized against 2,4,6-TNT. The relationship between 2,3,6-TNT and 2,4,6-TNT was then determined. Since 1,3,5-TNB does not completely separate from 2,4,6-TNT, its response factor was calculated two ways: (1) In direct comparison with 2,4,6-TNT and (2) in comparison with 3,4-DNT which was previously standardized against 2,4,6-TNT.

In sampling organic material from separator vessels, 1 ml was pipetted into a 25-ml volumetric flask containing approximately 5 ml of distilled water, hence quenching the reaction. The flask was then diluted to volume with reagent grade acetone. When nitrators were sampled, the acid and organic materials were allowed to first separate.

For analysis of organics in the acid phase, the organic material was separated by ether extraction. After the ether was evaporated, 1 g of organic material was dissolved in acetone and diluted to volume in a 25-ml volumetric flask.

Two microliters of the prepared samples were injected into the gas chromatograph at conditions given below. The instrument was attenuated prior to elution of each peak to obtain a satisfactory peak measurement.

Injection port: 230°
 Detector: 260°
 Column: (A) 200° for samples containing only DNT and TNT isomers
 (B) 150° to 240° at 6°/min when toluene, MNT, DNT, and TNT isomers are present
 Helium carrier gas flow: 60 cc/min
 Hydrogen gas flow: 30 cc/min
 Air flow: 500 cc/min

In calculating results, the area of each peak was obtained by multiplying instrument attenuation times peak height times width of peak at half height times "1/F". Total area was thus obtained, and percent by weight was calculated for each component by multiplying each individual area by 100 and dividing by total area.

TABLE I
 FLAME IONIZATION DETECTOR RELATIVE RESPONSE FACTORS

<i>Compound</i>	<i>Weight factors (I/F)</i>	<i>Mole factors^a</i>
Toluene	0.275	1.475
2-MNT	0.46	1.313
3-MNT	0.45	1.342
4-MNT	0.47	1.285
2,6-DNT	0.72	1.114
2,5-DNT	0.72	1.114
2,4-DNT	0.76	1.055
2,3-DNT	0.66	1.215
3,5-DNT	0.71	1.129
3,4-DNT	0.72	1.114
2,4,6-TNT	1.00	1.000
2,3,6-TNT	0.99	1.010
2,3,5-TNT	1.13	0.885
2,4,5-TNT	1.12	0.893
2,3,4-TNT	1.03	0.971
1,3,5-TNB	1.18 ^b	0.795 ^b
	1.53 ^c	0.614 ^c

^a [(F) (molecular weight)] ÷ [(F for 2,4,6-TNT) (molecular weight for 2,4,6-TNT)].

^b In the absence of 2,4,6-TNT.

^c In the presence of large amounts of 2,4,6-TNT. This value is used for estimating TNB content in actual samples.

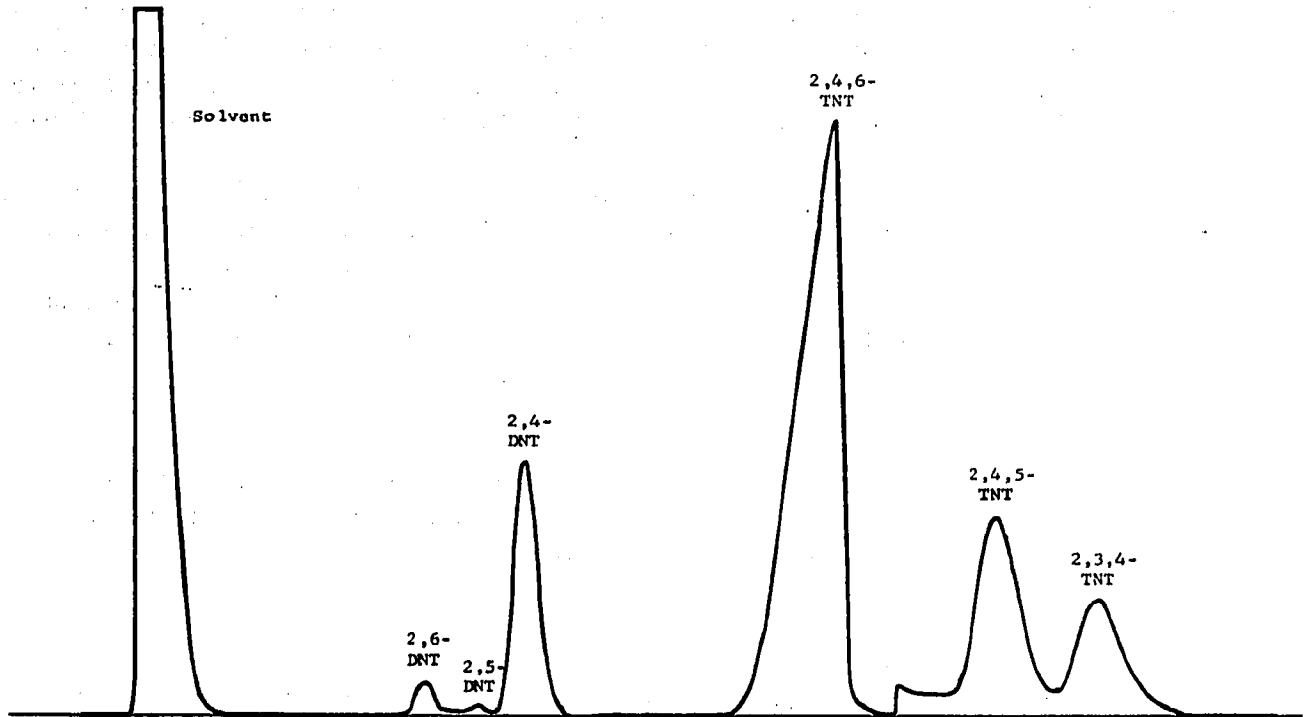


Fig. 1. Chromatogram of material from the last nitrator.

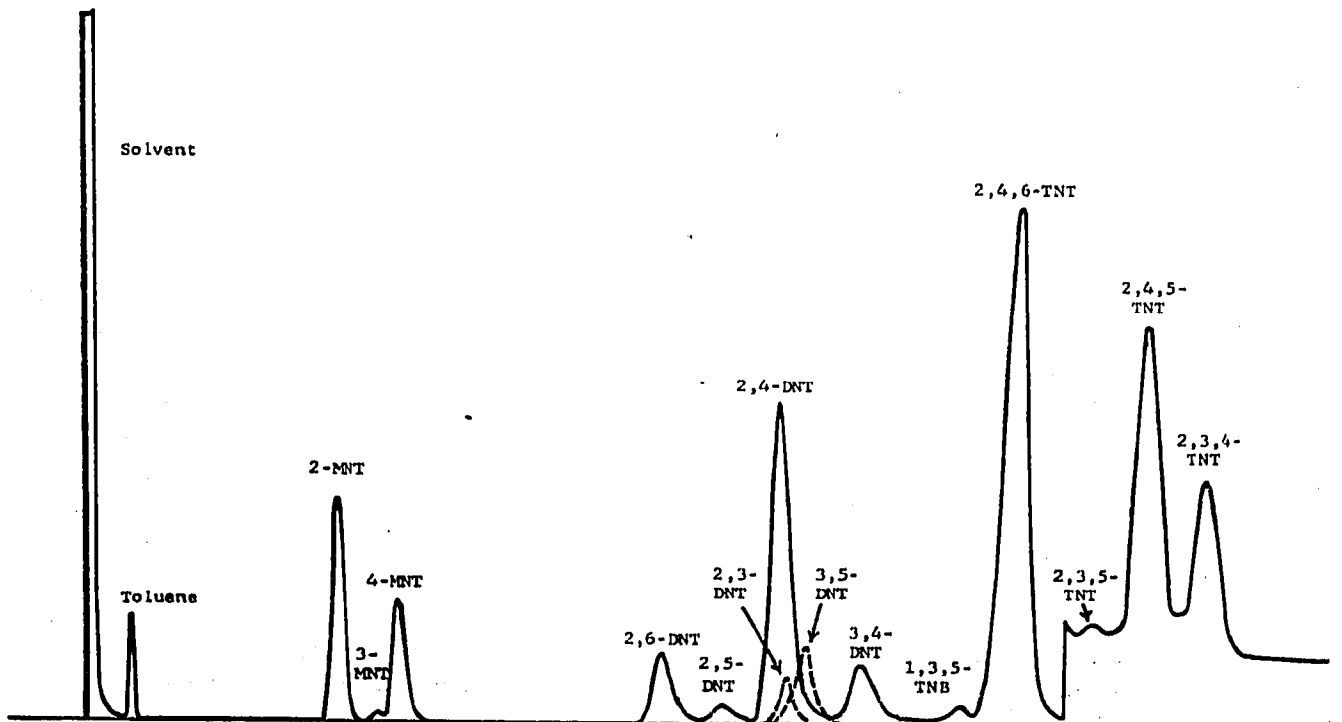


Fig. 2. Chromatogram of a synthetic mixture.

RESULTS AND DISCUSSION

Response factors were determined for nitration products found in various stages of nitration from the continuous process. These are shown in Table I. As might be expected, a relationship exists between the response factors and the number of unnitrated carbons. Fig. 3 shows this relationship where the average molar response factor is plotted against the number of unnitrated carbons in toluene.

During the course of this investigation, both programmed and isothermal gas chromatographic operating conditions were used. Chromatograms for these conditions are shown in Figs. 1 and 2 for isothermal and programmed, respectively. Isothermal conditions can be used to decrease the analysis time on samples containing only di- and trinitrotoluenes, whereas programming was required to get adequate separation of the various components when the samples contained aromatics with all degrees of nitration.

A number of the samples analyzed contained 2,4,6-trinitrobenzoic acid (TNBA) in addition to the nitrotoluenes. The TNBA is an oxidation product of 2,4,6-TNT.

TABLE II
PERCENT RECOVERY EVALUATION

Sample No.	Components	Actual percent	Measured percent	Percent recovery
I ^a	2-MNT	16.37	16.00	97.7
	3-MNT	0.05	—	—
	4-MNT	16.25	16.51	101.6
	2,6-DNT	16.83	17.06	101.4
	2,4-DNT	16.86	17.31	102.7
	2,4,6-TNT	16.66	16.85	101.1
	2,4,5-TNT	16.98	16.24	95.6
II ^a	2-MNT	17.40	17.89	102.8
	3-MNT	17.42	17.30	99.3
	4-MNT	0.03	—	—
	2,6-DNT	16.14	15.58	96.5
	2,4-DNT	17.08	16.94	99.2
	2,4,6-TNT	16.59	16.59	100.0
	2,4,5-TNT	15.34	15.67	102.2
III ^b	2,6-DNT	25.00	24.59	98.4
	2,4-DNT	25.05	24.89	99.4
	2,4,6-TNT	24.74	24.64	99.6
	2,4,5-TNT	25.21	25.88	102.7
IV ^b	2,6-DNT	24.77	24.26	97.9
	2,4-DNT	26.22	26.30	100.3
	2,4,6-TNT	25.46	25.95	101.9
	2,4,5-TNT	23.55	23.49	99.8
V ^b	2,6-DNT	24.77	25.59	103.3
	2,4-DNT	26.22	26.37	100.6
	2,4,6-TNT	25.46	24.92	97.9
	2,4,5-TNT	23.55	23.13	98.2

^a Gas chromatographic oven programmed from 150° to 240° at 6°/min.

^b Gas chromatographic oven operated isothermally at 200°.

With the injection port at 230°, the TNBA was converted to 1,3,5-TNB which shows up as a poorly resolved peak adjacent to the peak for 2,4,6-TNT, thus allowing only an estimation of total TNB content. The 3,5- and 2,3-DNT peaks are poorly resolved from the 2,4-DNT peak. However, the major DNT isomer present in all samples was the 2,4; therefore, the presence of the very small amounts of 2,3- and 3,5-DNT caused very little error in the determination of the 2,4-DNT; they were included as 2,4-DNT. The 2,3,6-TNT has the same retention time as 2,4,6-TNT; however, the amount of 2,3,6-TNT is so small as to cause a negligible error in the determination of the 2,4,6-TNT. The major unsymmetrical isomers produced in the continuous process are the 2,3,4- and 2,4,5-TNT. Both of these components are well resolved from 2,4,6-TNT permitting accurate analysis for these components.

Synthetic mixtures containing all of the nitration products were prepared to evaluate the GC method. The data for this study are shown in Table II. The results show very good recoveries for all components using the separation techniques described above and response factors in the calculations.

To further evaluate the method, duplicate samples were taken from several of

TABLE III

REPRODUCIBILITY STUDY OF SAMPLES FROM NITRATORS

	Average (%)		
	Nitrator No. 1	Nitrator No. 3	Nitrator No. 6
I. Components			
2-MNT	48.94	0.0023	
3-MNT	1.71	0.063	
4-MNT	27.86		
Total MNT	78.51	0.066	
2,6-DNT	2.47	2.37	0.0042
2,5-DNT	0.032	0.16	0.0010
2,4-DNT	13.55	19.81	0.058
3,4-DNT	0.114	0.28	
Total DNT	16.17	22.62	0.064
2,4,6-TNT	5.32	75.00	96.42
2,4,5-TNT	<0.01	1.60	2.19
2,3,4-TNT	0.018	0.72	1.31
Total TNT	5.34	77.32	99.92
	$S/\sqrt{\bar{X}}$		
	Nitrator No. 1	Nitrator No. 3	Nitrator No. 6
II. Variability			
Testing variability	0.075	0.043	0.060
Sample variability	0.093	0.055	0.047
Process variability	0.175	0.080	0.070

the nitrators at 10-min intervals. These samples were then analyzed in replicate to obtain a measure of testing, sampling, and process variability. The results of this study are given in Table III. Several methods were attempted for treating the data to obtain a measure for variability. As might be expected, the standard deviation was not constant for the different components at the various levels. This was also true of the coefficient of variation. A value for variability was obtained by dividing

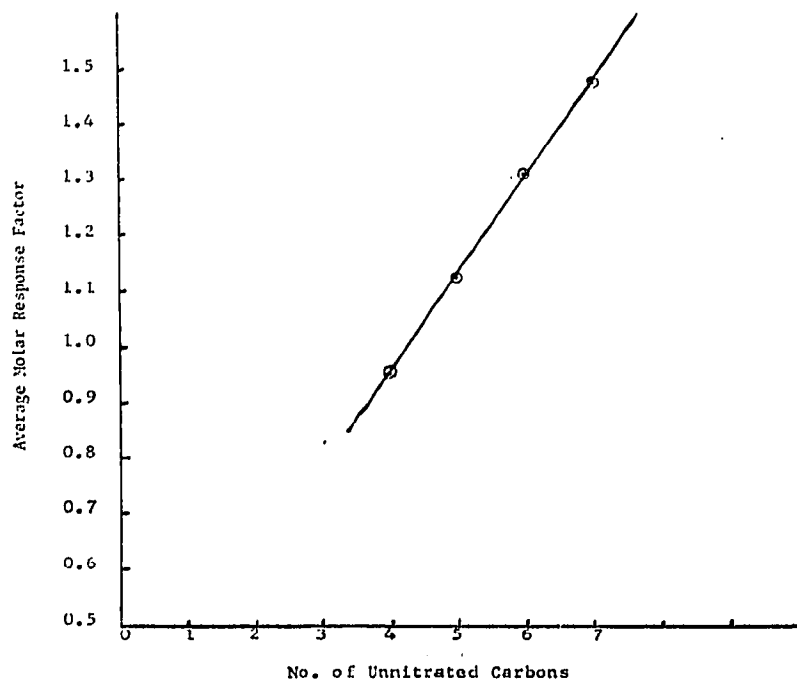


Fig. 3. Relationship between the response factors and the number of unnitrated carbons.

the standard deviation by the square root of the average value or the square root of 100 minus the average value for minor (< 50 %) and major (> 50 %) components, respectively. This value was found to be fairly constant for all components in a given nitrator and is also given in Table III for each of the nitrators for the three types of variability. The value for testing represents the reproducibility in the analysis of replicate aliquots from a given sample solution. The value for sampling includes the error involved in taking duplicate samples and in testing these samples. The value for process variability serves as a measure of the change in the process over a 30-min period. As can be seen from the data, there is very little difference in the testing and sampling variability indicating that a single sample provides an adequate measure of the composition of the organic phase at any given time. The values for process variability show that there is essentially no change in the composition of the organic phase in the No. 6 nitrator over a 30-min period. There is some change in the composition of the organic phase at nitrator No. 3, and a marked change in the composition of the organic phase in the No. 1 nitrator. Thus, by treating the data in the indicated fashion, it is possible to determine if changes in the composition of the organic phase as a result of changes in operating parameters are statistically significant.

Table III shows the types of nitration products present in several of the nitra-

tion vessels. In the first nitrator, toluene is nitrated to MNT with some DNT and TNT also being found. The presence of the TNT, and to some extent DNT, results from entrainment of these species in the acid being fed to the first nitrator rather than being a reaction product in this vessel. As the organic phase proceeds through the higher nitrators, the concentration of the MNT is reduced to nil. The concentration of TNT increases continuously while the concentration of DNT increases to a maximum in nitrator No. 2 and then decreases continuously through the higher nitrators.

From nitrator No. 6, the organic phase is washed with water to remove most of the entrained nitrating acids and is then reacted with a sodium sulfite solution in two successive vessels called sellite washers to remove the asymmetrical TNT isomers. A study of the purification process revealed that the extent of isomer removal was

TABLE IV

EFFECT OF pH IN THE NO. 2 SELITE WASHER ON PURIFICATION

pH	Percent by weight (2,4,5- plus 2,3,4-TNT)
7.0	0.64
7.6	0.18
8.0	0.08
9.0	0.07

dependent upon pH. Table IV gives results on samples taken from the No. 2 sellite washer under different operating conditions. As can be seen, there is a marked difference in the amount of *meta* isomers remaining as a function of pH.

Table V shows another example of the application of the GC method in process studies. In this study, the temperature in nitrator No. 5 was adjusted from a low of 86.5° to a high of 99.0° to determine the magnitude of the effect of nitration temperature on the conversion of DNT to TNT. As can be seen, this roughly 10° increase in

TABLE V

EFFECT OF TEMPERATURE IN NO. 5 NITRATOR

Component	86.5°	99.0°
2,6-DNT	0.18	0.08
2,5-DNT	0.05	0.03
2,4-DNT	2.26	1.16
3,4-DNT	0.03	<0.01
Total DNT	2.52	1.27
2,4,6-TNT	94.75	95.99
2,3,5-TNT	0.01	0.02
2,4,5-TNT	1.72	1.78
2,3,4-TNT	0.98	0.90
Total TNT	97.46	98.69

reaction temperature reduced the concentration of residual DNT by approximately 50 %.

In another study, the concentration of the nitrating acid was varied to determine the magnitude of the effects of degree of nitration as a function of total acidity. Results from this study are given in Table VI. The results from this study show that the nitration products leaving the first nitration vessel are highly dependent upon total acidity.

TABLE VI
EFFECT OF SPENT ACID STRENGTH IN NO. 1 NITRATOR

	<i>Normal total acidity (73.4%)</i>	<i>High total acidity (78.1%)</i>
2-MNT	60.26	14.66
3-MNT	2.44	0.76
4-MNT	29.81	9.12
Total MNT	92.51	24.54
3,4-DNT	0.04	0.67
2,5-DNT	0.03	0.23
2,6-DNT	0.81	6.92
2,4-DNT	4.51	40.27
Total DNT	5.39	48.09
2,3,4-TNT		0.19
2,4,5-TNT	0.01	0.40
2,4,6-TNT	2.08	26.76
Total TNT	2.09	27.35

These are but a few examples of the information provided by the GC analysis of TNT samples in a process variable study. The results from these and other investigations will be used to optimize the process. Other process variables to be investigated are the ratio of nitrating acid to organic material in the various nitrators; the composition of the nitrating acid, *i.e.*, relative amounts of sulfuric and nitric acid and water; the temperature of nitration in all nitrators; and the rate of agitation.

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