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Analysis and Characterization of Military-Grade Trinitrotoluene by Gas Chromatography

Military grade trinitrotoluene (TNT), manufactured by complex nitration and purification procedures [1], contains over 99% α-2,4,6-trinitrotoluene and trace amounts of precursors, isomers, and oxidation by-products. The detection and determination of TNT and other explosives by gas chromatography (GC) has been reported by a number of authors and summarized in a recent review [2]. Impurities in TNT have been identified by thin-layer chromatography [3], nuclear magnetic resonance [4], and GC [5–7]. The major impurities in commercial TNT were found to be 2,4-dinitrotoluene (DNT); 2,3,4-TNT; 2,3,5-TNT; and 2,4,5-TNT in reported concentrations of 0.1 to 0.4%, with traces of other DNT isomers detected. A novel method for characterizing TNT origins by means by variation in $^{13}C/^{12}C$ ratios has been reported [8].

We wish to report improved GC procedures for the separation of isomers and other impurities present in military-grade TNT. These procedures, when combined with standardized extraction techniques for concentration of the impurities, permit detection and semiquantitative measurement of up to 20 impurities in typical samples. This combined extraction–GC procedure determines impurities present in commercial samples of TNT at levels as low as 0.001%.

Although we have not identified many of these impurities, they may be used as a "fingerprint" to characterize a given sample as to its probable source as well as to estimate its overall purity.

Materials and Methods

Gas Chromatography

The GC was a Becker Model 420 equipped with hydrogen flame and electron capture (^{63}Ni source) ionization detectors and a 1-mV recorder. A 10-μl Terumo microsyringe was used for sample injections.

Solvents were analytical or reagent grade. Pure (99.9%) TNT was prepared by repeated extraction of commercial TNT with boiling hexane followed by two crystallizations from isopropanol to a melting point of 80.4°C. The DNT isomers were purchased commercially and consisted essentially of one isomer by GC analysis.

Chromatographic glass columns, 6.35 mm (0.25 in.) outside diameter by 1.5 m were packed with 60-80 mesh Chromosorb-W, acid-washed, treated with dimethyldichlorosilane, and coated as indicated below. Carrier gas (nitrogen) flow rates were optimized for

each column and achieved 2600 to 2900 theoretical plates for TNT. Peak areas were measured as the products of retention time, peak height, and attenuation factor [9]. Temperatures for the injection port and detector were 225 and 260°C, respectively. The following stationary phases were used:

(1) Column 1, 10% OV-225 at 220°C;

(2) Column 2, 1.8% OV-225 and 10.2% OV-101 at 200 to 230°C; and

(3) Column 3, 2.4% polyphenylether (Convalex 10, Bendix Corp.) and 0.6% OV-225 at 185°C.

Extraction Procedures

1. Weigh 100 ± 2 mg finely ground TNT into a 3-ml vial or test tube. Add 1 ml hexane and heat to boiling. Cool to ambient temperature and decant into a second test tube. Repeat the extraction with a second portion of boiling hexane and evaporate the combined extracts virtually to dryness. Dissolve the residue in 20 to 50 μl of chloroform and inject 2 μl into the gas chromatograph.

2. Extract twice with 1-ml portions of boiling hexane as in Procedure 1. Add 100 mg silica gel (Merck, chromatographic grade, 35-70 mesh) to the combined extracts, mix, decant, and discard the hexane. Wash the silica gel twice with 1-ml portions of hexane and discard the washings. Extract the silica gel with two 1-ml portions of chloroform and concentrate to about 50 μl. Inject 2 μl into the gas chromatograph.

Results and Discussion

Gas Chromatography

The reference materials examined and their retention times relative to 2,4-DNT are listed in Table 1. Although lightly coated columns achieved satisfactory separations of test mixtures, a 10% coating was found necessary to avoid gross overloading of the liquid phases in Columns 1 and 2, with resultant skewing of the 2,4,6-TNT peak and masking of

TABLE 1—*Retention times of DNT and TNT isomers and impurities relative to 2,4-DNT.*

Compound	Relative Retention Times		
	Column 1	Column 2[a]	Column 3
2,6-DNT	0.669	0.750	0.640
2,5-DNT	0.818	0.861	0.860
2,4-DNT	1.00	1.00	1.00
2,3-DNT	1.18	1.08	0.940
3,4-DNT	1.72	1.44	1.39
2,4,6-TNT	2.65	2.19	3.14
2,4,5-TNT	3.04	2.42	2.89
Trinitrobenzene[b]	3.27	2.50	3.95
2,3,5-TNT[c]	4.92	3.77	5.03
2,3,4-TNT[d]	5.52	4.17	4.58

[a]At 200°C.

[b]Synthesized by S. Zitrin of Israel Police Headquarters laboratories according to the procedure of Davis [10]; authenticated by infrared and mass spectra.

[c]Identity not proven; present as a major impurity in a sample of 2,4,5-TNT from K&K Laboratories.

[d]Isolated from commercial TNT by preparative TLC and identified by its infrared spectrum.

the 2,4,5-TNT peak. The low dynamic range of the electron capture detector precluded its use in this study; it was not possible to measure the main TNT peak as well as impurity peaks from a single injection even after extraction and concentration of the impurities. All determinations were therefore made with the flame detector.

Column 1 gave the best separations, both of the compounds listed in Table 1 and of other impurities detected but not identified in commercial TNT samples. However, long-term baseline instability indicated that substances from some samples were not being eluted within reasonable times and thus escaped detection. Column 2, whose superior stability permitted temperature programming (to 230°C) at high sensitivity, afforded detection of several peaks in addition to those observed with Column 1 and increased the characterization specificity. Column 3, with its different order of elution for some of the impurities, was useful in identifying peaks whose identity was doubtful. Column 1 was preferred for routine screening and analysis and was used in all of the determinations reported in this study.

Concentration of Impurities

Despite the excellent separations achieved by Column 1, the low levels of many of the impurities present in military-grade TNT precluded their routine detection and quantitative estimation. The enrichment afforded by the extraction procedures raised these impurities to a convenient measurement level at reasonable instrument sensitivity. The degree of impurity enrichment was estimated by spiking pure TNT with weighed amounts of DNT isomers and analyzing the extracts and the extract residues. The results (Table 2) indicate an *apparent* enrichment factor of about 22, which would raise an impurity present at a level of 0.001% to a concentration of 0.02%.

To assess the true enrichment factor, relative detector responses were established by analyzing the known mixture and calculating the factors needed to adjust the measured peaks to the component concentrations. The results (Table 3) show that the flame ionization detector is about equally sensitive to the various DNT isomers, but only about 60% as sensitive to TNT. When the response factors are used to correct the peak areas a real

TABLE 2—*Efficiency of extraction of DNT isomers from TNT.*

Compound	Original Mixture, %	Extract, %	Residue, %	Enrichment Factor
2,6-DNT	0.16	3.1	0.06	19.4
2,5-DNT	0.38	9.0	0.10	23.7
2,4-DNT	0.58	12.8	0.18	22.1
2,3-DNT	0.51	12.6	0.17	24.7
3,4-DNT	1.07	23.4	0.37	22.3
2,4,6-TNT	97.30	38.6	99.12	...
			avg, 22.4 ± 2.0	

TABLE 3—*Relative sensitivities of the flame ionization detector.*

Compound	Sensitivity
2,6-DNT	1.14
2,5-DNT	1.05
2,4-DNT	1.00
2,3-DNT	1.13
3,4-DNT	1.04
2,4,6-TNT	0.616

extraction enrichment factor of 17.8 is obtained. This additional calculation is superfluous if only comparative data for different samples are required.

Removal of Hydrocarbon Impurities

Several of the TNT samples investigated contained traces of hydrocarbon oils, easily identified by the constant increments of the logarithms of their peak retention times. These oil peaks, which mask to a large extent the true impurity peaks, are virtually removed by extraction Procedure 2 and can be separately analyzed from the hexane phase. The TNT and its impurities are retained by the silica gel and reextracted into the chloroform. This fact was established by analyzing a typical sample by both extraction procedures and comparing the results obtained (Table 4).

The combination of extractive impurity enrichment and efficient chromatographic separation makes it possible to analyze and characterize even samples whose α-TNT content is greater than 99.5%. In most cases visual comparison of chromatograms is sufficient to distinguish between samples of differing purity or origin. A quantitative comparison can be made by calculating the percentages of the impurities. Greater sensitivity can be achieved by excluding the TNT peak from the calculations and calculating instead the relative distribution of the impurities. Apparently similar materials show highly significant differences by this technique. It is not necessary to include all of the impurity peaks for this purpose; calculation of seven to ten of the largest peaks is adequate. Typical analyses of several military-grade TNT samples are presented in Table 5, including two samples (1 and 2) from the same source manufactured in different years.

The reproducibility of the total procedure is of course dependent on the peak size and can be expected to be poorer for very small peaks. We have found that an average relative precision of 10% is routinely achieved, which is quite satisfactory for substances present in concentrations of 0.002 to 0.4% in the original TNT.

Summary

A method has been developed for the GC detection and semiquantitative estimation of impurities present in military-grade TNT. The impurities are concentrated approximately 20-fold by extraction with hexane and chromatographed on OV-225 with a flame ionization detector. Typical TNT samples contain 10 to 20 detectable impurities, including DNT

TABLE 4—*Analysis of TNT by extraction Procedures 1 and 2.*

	Extract Composition, %	
Compound	Procedure 1	Procedure 2
2,6-DNT	0.3	0.4
2,5-DNT	0.5	0.6
2,4-DNT	5.2	5.9
3,4-DNT	0.1	0.2
RRT 2.06[a]	0.1	...
2,4,6-TNT	90.1	90.2
2,4,5-TNT	1.0	0.8
Trinitrobenzene	0.3	0.3
2,3,5-TNT	0.3	0.2
2,3,4-TNT	2.2	1.4

[a]Unidentified component; retention time relative to 2,4-DNT.

TABLE 5—*Relative distributions (%) of impurities in TNT after extraction.*[a]

Component	Samples					
	1	2	3	4	5	6
2,6-DNT	...	...	3.4	...	...	...
2,5-DNT	15.6	15.5	5.7	28.1	11.4	8.2
2,4-DNT	56.2	46.6	56.8	56.6	9.0	5.5
RRT 1.34[b]	...	...	...	1.5	...	...
RRT 1.64[b]	8.2	5.4	...	...	10.0	11.0
3,4-DNT	9.1	7.3	...	2.7	...	...
RRT 2.06[b]	...	0.9	...	1.2	...	...
2,4,5-TNT	...	...	9.0	...	13.1	8.2
Trinitrobenzene	4.0	18.8	2.8	1.7	21.8	30.1
RRT 3.54[b]	...	...	...	...	...	2.7
2.3.5-TNT	6.9	5.6	2.4	8.2	8.3	6.8
2,3,4-TNT	...	...	18.3	...	18.9	...
RRT 6.77[b]	...	...	...	...	7.6	27.4
2,4,6-TNT[c]	(98.4)	(96.4)	(90.4)	(96.1)	(98.0)	(99.3)

[a]Results not corrected for detector sensitivity.
[b]Identity unknown; retention time relative to 2,4-DNT.
[c]Absolute percentage of 2,4,6-TNT in extract.

and TNT isomers and trinitrobenzene. Contaminants present in concentrations as low as 0.002% in the original TNT can be measured and used to characterize it.

References

[1] Urbanski, T., *Chemistry and Technology of Explosives*, Vol. 1, Macmillan, New York, 1969.
[2] Kaplan, M. A. and Zitrin, S., "Identification of Post-Explosion Residues," *Journal of the Association of Official Analytical Chemists*, Vol. 60, No. 3, 1977, pp. 619–624.
[3] Yasuda, S. K., "Identification of Impurities in α-Trinitrotoluene by Thin-Layer Chromatography," *Journal of Chromatography*, Vol. 13, No. 1, 1964, pp. 78–82.
[4] Ghering, D. G., "Identification of Impurities in α-Trinitrotoluene by Nuclear Magnetic Resonance Spectrometry," *Analytical Chemistry*, Vol. 42, No. 8, July 1970, pp. 889–902.
[5] Etienne, L. and Tranchart, J., "Gas Phase Chromatography: Analysis of Aromatic Nitro Derivatives," *Memorial des Poudres*, Vol. 47, 1965, pp. 167–189.
[6] Ghering, D. G. and Shirk, J. E., "Separation and Determination of Trinitrotoluene Isomers by Gas Chromatography," *Analytical Chemistry*, Vol. 39, No. 11, Sept. 1967, pp. 1315–1318.
[7] Murrmann, R. P., Jenkins, T. F., and Leggett, D. C., "Composition and Mass Spectra of Impurities in Military Grade TNT Vapor," S.R. 158, Cold Regions Research and Engineering Laboratory, U.S. Army Corps of Engineers, Hanover, N.H., May 1971.
[8] Nissenbaum. A., "The Distribution of Natural Stable Isotopes of Carbon as a Possible Tool for the Differentiation of Samples of TNT," *Journal of Forensic Sciences*, Vol. 20, No. 3, July 1975, pp. 455–459.
[9] Pecsok, R. L., *Principles and Practice of Gas Chromatography*, Chapman and Hall, London, 1959.
[10] Davis, T. L., *Chemistry of Powder and Explosives*, Wiley, New York, 1953.

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