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SIMULTANEOUS DETERMINATION OF 1,3-DINITRO-2,4,6-TRICHLORO-
BENZENE AND 1,3-DINITRO-2,4,5,6-TETRACHLOROBENZENE IN
1,3,5-TRICHLORO-2,4,6-TRINITROBENZENE

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SUMMARY

A gas chromatographic method is described for the determination of 1,3-dinitro-2,4,6-trichlorobenzene (DNTCB) and 1,3-dinitro-2,4,5,6-tetrachlorobenzene (DNtetraCB) in production-grade 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) samples. An aliquot is chromatographed on a 6-ft. long, 20% Dexsil 300 GC column, and the peak areas of the impurities are measured. The concentration of each component is determined from the calibration curves. Crude and recrystallized TCTNB's contain 2.1% DNTCB and 7.8% DNtetraCB, and 2.0% DNTCB and 4.8% DNtetraCB respectively.

INTRODUCTION

1,3,5-Trichloro-2,4,6-trinitrobenzene (TCTNB) is an intermediate in the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) by ammonolysis¹. The final product is relatively pure; however, various by-products that remain in the TATB alter its physical and chemical properties. To a large extent, the quality of the TCTNB controls the amount of contaminants found in the TATB. Hence a convenient method for TCTNB analysis would be of practical value in studying an important aspect of the TATB process.

Earlier work by the author² revealed that two predominant impurities are found in TCTNB, namely, 1,3-dinitro-2,4,6-trichlorobenzene (DNTCB) and 1,3-dinitro-2,4,5,6-tetrachlorobenzene (DNtetraCB). Although thin-layer chromatography (TLC) proved to be an acceptable method for identification work, quantitative analysis for these impurities could not be achieved because of the lack of a sensitive spray reagent.

In this article we describe a gas chromatographic (GC) method for the determination of DNTCB and DNtetraCB in TCTNB samples.

REAGENTS AND EQUIPMENT

An Aerograph Hy-Fi gas chromatograph, Model 600-C, and a Varian recorder, Model G-14A-1, were used in this investigation.

A 6-ft. long \times $\frac{1}{8}$ -in. O.D. (0.094-in. I.D.) stainless-steel tube was packed with 20% by weight of Dexsil 300 GC on 80-90 mesh ABS Anakrom with a Matronic XL-300 column packer. The packed column was preconditioned at 300° for 24 h with helium before use.

DNTCB was purchased from Eastman Organic Chemicals; DNtetraCB and TCTNB were synthesized and purified by TLC.

A.R.-grade CS₂ was purchased from Mallinckrodt Chemical Works; helium and hydrogen in H-size cylinders were obtained from Matheson Company.

Hamilton microsyringes (10- μ l capacity), volumetric pipettes, and 10-ml volumetric flasks were used to prepare the solutions. The dissolution of the sample was accomplished with the aid of an ultrasonic shaker.

EXPERIMENTAL

Various analytical parameters were investigated to optimize conditions for the GC analysis. After screening a variety of partitioning columns, Dexsil 300 GC, a carborane polymer, coated on ABS Anakrom was found to separate DNTCB, DNtetraCB, and TCTNB. By varying the amount of liquid phase from 5% to 30% by weight, drastic changes in the resolution of the three components were observed. With less than 10% of Dexsil 300 sharp and symmetrical peaks were obtained, but the TCTNB and DNtetraCB peaks partially overlapped so as to make the column unacceptable for quantitative work. At 30% of Dexsil 300, acceptable resolution was

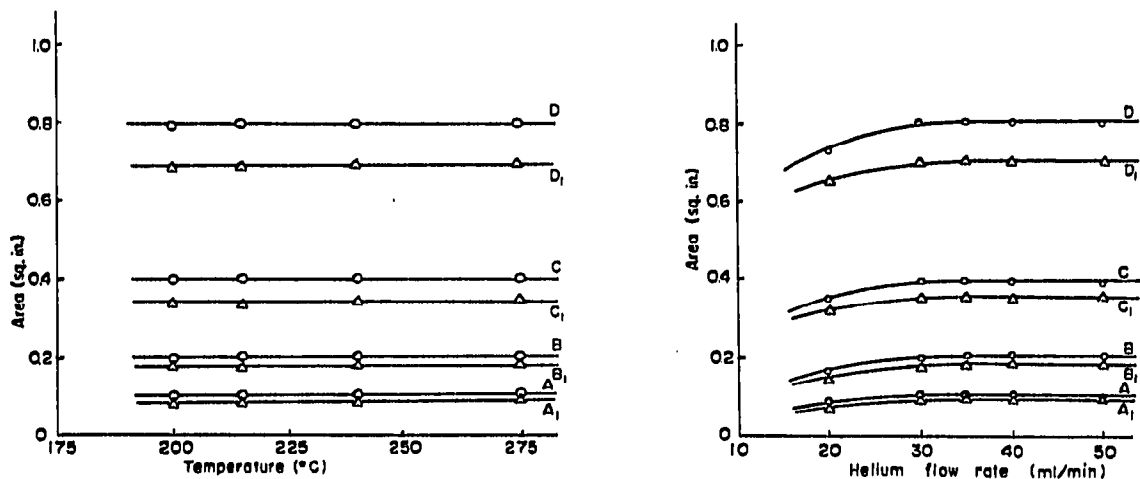


Fig. 1. Effect of column temperature on peak area measurements. Curves: A = 0.25 μ g DNTCB; A₁ = 0.25 μ g DNtetraCB; B = 0.50 μ g DNTCB; B₁ = 0.50 μ g DNtetraCB; C = 1.00 μ g DNTCB; C₁ = 1.00 μ g DNtetraCB; D = 2.00 μ g DNTCB; D₁ = 2.00 μ g DNtetraCB.

Fig. 2. Effect of helium flow-rate on the peak areas of DNTCB and DNtetraCB. Curves: A = 0.25 μ g DNTCB; A₁ = 0.25 μ g DNtetraCB; B = 0.50 μ g DNTCB; B₁ = 0.50 μ g DNtetraCB; C = 1.00 μ g DNTCB; C₁ = 1.00 μ g DNtetraCB; D = 2.00 μ g DNTCB; D₁ = 2.00 μ g DNtetraCB.

achieved, but this was accompanied by peak broadening. Therefore, a 6-ft. long \times 0.094-in. I.D. column packed with 20% by weight of Dexsil 300, coated on 80-90 mesh ABS Anakrom, was selected for our work.

The solvent, CS_2 , has a profound effect on the peak area of DNTCB and DNtetraCB with the flame-ionization detector. By using a constant volume of CS_2 with varying amounts of sample, the solvent effect is completely eliminated.

The effect of column temperature on the peak area of the impurities was investigated. Fig. 1 shows that the peak area for a given concentration is independent of the column temperature, showing that there is a negligible sample loss through decomposition or column interaction. However, inspection of the chromatograms shows that the resolution of the TCTNB and DNtetraCB peaks gradually decreases with increase in temperature above 230°. Below 200°, the retention time of the last eluting compound, DNtetraCB, becomes too long. Thus the optimum column temperature lies between 200 and 225°.

With a column temperature of 215°, the influence of helium flow-rate on the peak areas of DNTCB and DNtetraCB was also investigated. From the data shown in Fig. 2, it can be seen that an optimum flow-rate exists between 30 and 50 ml/min. However, at flow-rates greater than 40 ml/min, the resolution of the TCTNB and DNtetraCB peaks decreases, and the noise level becomes appreciable. Consequently, a helium flow-rate of 35 ml/min was chosen for our work.

Since complete resolution of the TCTNB and DNtetraCB peaks could not be accomplished at a reasonable column temperature and flow-rate without increasing the retention time, it was necessary to determine the error contributed by the TCTNB peak on the peak area of DNtetraCB. Calibration curves were prepared with standards containing DNTCB and DNtetraCB, and with standards containing all three components. The working curves were found to be identical, indicating that the slight overlap of the TCTNB and DNtetraCB peaks causes negligible change in the area measurement of the DNtetraCB peak. DNTCB presents no problem since it is a completely resolved peak.

The relative retention times of several related compounds were measured with respect to TCTNB for identification purposes. Table I summarizes these values. In

TABLE I

RELATIVE RETENTION TIMES OF TCTNB AND RELATED COMPOUNDS

<i>Compound</i>	<i>Relative retention time</i>
1,3,5-Trichlorobenzene	0.10
1,2,3,5-Tetrachlorobenzene	0.20
1-Nitro-2,4,6-trichlorobenzene	0.34
1-Nitro-2,4,5-trichlorobenzene	0.42
1-Chloro-2,4-dinitrobenzene	0.55
1-Nitro-2,3,4,6-tetrachlorobenzene	0.62
1,3-Dinitro-2,4,6-trichlorobenzene (DNTCB)	0.77
1,3-Dinitro-2,4,5-trichlorobenzene	0.92
1,3,5-Trichloro-2,4,6-trinitrobenzene (TCTNB—reference compound)	1.00
1,3-Dinitro-2,4,5,6-tetrachlorobenzene (DNtetraCB)	1.18
1,3-Dichloro-2,4,6-trinitrobenzene	1.25

particular, DNTCB and DNtetraCB can be identified at a concentration of about 0.01 μg , which represents 50–80 times the sensitivity of the TLC method.

Procedure

A 6-ft. long \times 0.094-in. I.D. stainless-steel column packed with 20% by weight of Dexsil 300 GC on 80–90 mesh ABS Anakrom is installed on a flame-ionization gas chromatograph. The column and inlet temperatures are maintained at 215 and 240°, respectively. The flow-rate of the helium carrier gas is adjusted to 35 ml/min, and the flow-rate ratio of helium–hydrogen–air is controlled at 1:1:10. After balancing the electrometer, the detector is ignited. A 1- μl sample of 1 or 2% TCTNB dissolved in CS_2 is introduced into the gas chromatograph with an Hamilton microsyringe. The peak areas of the impurities are measured, and the concentration of each component is determined from the calibration curves.

TABLE II
GC ANALYSIS OF SYNTHETIC AND TCTNB SAMPLES

Sample	Composition	Det'ns (No.)	DNTCB		DNtetraCB	
			Found (%)	S.D.	Found (%)	S.D.
Synthetic mix A	DNTCB–DNtetraCB–TCTNB 2.1:2.4:95.5	5	2.10	0.02	2.46	0.09
Synthetic mix B	DNTCB–DNtetraCB–TCTNB 5.1:5.5:89.4					
Crude TCTNB	—	5	5.12	0.13	5.34	0.11
Recryst. TCTNB	—	5	2.07	0.04	7.82	0.07
		5	0.20	0.00	4.78	0.08

RESULTS AND DISCUSSION

The precision and accuracy of the method were established with the analysis of synthetic mixtures. Excellent results were obtained, as shown in Table II, with the standard deviation being less than 0.13%. In all cases the compounds used in the mixes were purified by TLC, and the purity was established to be 99.5% or better by elemental and GC analyses.

Crude and recrystallized TCTNB used in the TATB synthesis were analyzed, and the results are included in Table II. As previously indicated by TLC, these samples contain appreciable quantities of DNTCB and DNtetraCB. From GC analysis, the purity of crude and recrystallized TCTNB's is 90.1% and 95.0%, respectively. Figs. 3 and 4 show the tracings of the chromatograms.

Since DNTCB and DNtetraCB are as susceptible to amination as TCTNB, the amount of 1,3-dinitro-2,4,6-triaminobenzene (DNTAB) and 1-chloro-3,5-dinitro-2,4,6-triaminobenzene (CDNTAB) that could be derived from the respective TCTNB samples was calculated. These values are of interest in indicating the maximum amount of aminated impurities to be expected in crude TATB. Crude TCTNB yields a product containing 1.62% DNTAB and 6.33% CDNTAB, while recrystallized TCTNB yields a product containing 0.16% DNTAB and 3.8% CDNTAB. Complete amination of DNtetraCB to the corresponding dinitro-tetraaminobenzene is unlikely

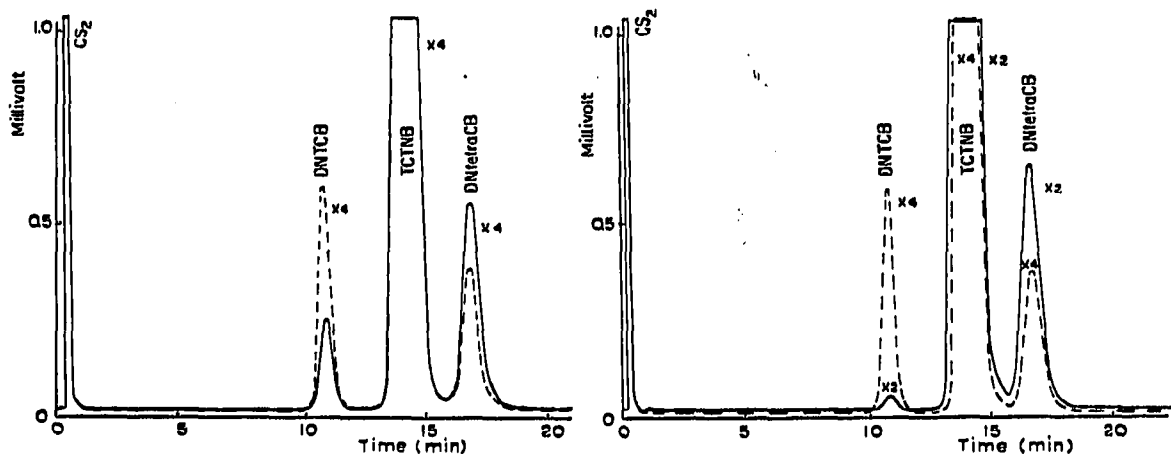


Fig. 3. Chromatogram of crude TCTNB sample. — = 1 μ l of 2% crude TCTNB solution; --- = 1 μ l of 2% synthetic mix B.

Fig. 4. Chromatogram of recrystallized TCTNB sample. — = 1 μ l of 2% recrystallized TCTNB solution; ---, = 1 μ l of 2% synthetic mix B.

to occur because the initial substitution of 3 amino groups deactivates the last chloro group on the aromatic ring, thus leading to the CDNTAB product.

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