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DETERMINATION OF IMPURITIES IN 1,3,5-TRICHLOROBENZENE

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SUMMARY

A simple gas chromatographic method is described for the determination of dichloro-, trichloro-, and tetrachlorobenzene impurities in 1,3,5-trichlorobenzene samples. The sample is dissolved in carbon disulfide, and an aliquot is chromatographed on a 6-ft. long, 10% Bentone 34 column. The peak heights and peak areas are measured and related to concentration by means of calibration curves. 1,3,5-Trichlorobenzene samples were found to contain small amounts of *m*-dichlorobenzene and 1,2,4-trichlorobenzene. From these data and thin-layer chromatographic analyses of crude 1,3,5-trichloro-2,4,6-trinitrobenzene, an explanation is proposed for the origin of the 1,3-dinitro-2,4,5,6-tetrachlorobenzene impurity found in 1,3,5-triamino-2,4,6-trinitrobenzene samples. It is concluded that 1,3-dinitro-2,4,5,6-tetrachlorobenzene is produced during the nitration of 1,3,5-trichlorobenzene.

INTRODUCTION

The explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is made by nitrating 1,3,5-trichlorobenzene (*s*-TCB) and aminating the resulting trichlorotrinitrobenzene (TCTNB)¹. The product usually contains about 1% of chlorine, a major part of which is due to the presence of 1,3-dinitro-2,4,5,6-tetrachlorobenzene (DNtetraCB) in the TCTNB intermediate². As part of an investigation into the source of the DNtetraCB, a simple analytical procedure for determining the impurities in *s*-TCB was required.

Several methods are cited in the literature for the analysis of monochloro- and dichloroaromatic compounds³⁻⁵; however, the application of these methods to *s*-TCB samples was unsuccessful. The trichloro- and tetrachlorobenzene isomers could not be resolved for quantitative work. Consequently, a gas chromatographic method, capable of identifying and determining the dichloro-, trichloro-, and tetrachlorobenzene impurities in *s*-TCB samples, was developed.

REAGENTS AND EQUIPMENT

An Aerograph HY-FI gas chromatograph, Model 600-C, and a Varian recorder, Model G-14A-1, were used throughout this work.

A 6-ft. long × 1/8-in. O.D. (0.094-in. I.D.) stainless-steel tube was packed with 10% by weight of Bentone 34 coated on 80-90 mesh ABS Anakrom with a Matronic XL-300 column packer. The packed column was preconditioned at 165° for 24 h and 135° for an additional 24 h with helium carrier gas before use.

Various dichloro-, trichloro-, and tetrachlorobenzenes were purchased from Eastman Organic Chemicals, Aldrich Chemical Company, and Eastern Chemical Company, and they were purified to a purity of 99 % or better as shown by elemental and gas chromatographic analyses. A.R.-grade CS_2 purchased from Mallinckrodt Chemical Works was used as received. Helium and ultrapure hydrogen in H-size cylinders were obtained from the Matheson Company.

Volumetric pipettes (1-10 ml capacity), Hamilton microsyringes, and 10-ml volumetric flasks were used to transfer and prepare the solutions.

EXPERIMENTAL

In preliminary studies on the separation of the anticipated compounds, sixteen partitioning columns were prepared and tested on the flame-ionization gas chromatograph. A mixture consisting of nine components was employed as the test sample. In most cases the resolution of 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes was found to be poor, the latter appearing as a shoulder on the trailing edge of the 1,2,3,5-tetrachlorobenzene peak, presumably because of the similarity of the boiling points (246°) of these isomers. However, a partitioning column prepared with dimethyldioctadecylammonium bentonite (Bentone 34) as the stationary phase on acid-washed Chromosorb W separated all nine components sufficiently for identification work. Conservatively, each component can be detected at a level of $0.02 \mu\text{g}$.

Since the amount of stationary phase affects the column efficiency, varying amounts of Bentone 34 (5-30 % by weight) were coated on Chromosorb W and retested with the mixed sample. Peak symmetry, peak resolution, and the retention time of the last eluting compound (1,2,3,4-tetrachlorobenzene) indicated that a 6-ft. long \times 0.094-in. I.D. column packed with 10 % by weight of Bentone 34 coated on 80-90 mesh ABS Anakrom was the best compromise for our work. The ABS Anakrom was substituted for AW Chromosorb to improve the peak symmetry for area and peak-height measurements.

The selection of a solvent for introducing the sample into the gas chromatograph proved to be a problem. Common organic solvents produce large chromatographic peaks, which mask those of the impurities. CS_2 was chosen for our work as it produces a small and narrow peak that does not interfere with any of the other peaks.

A disadvantage of CS_2 is that it has a profound effect on the peak area and peak height of the dichloro-, trichloro-, and tetrachlorobenzenes, as shown in Fig. 1. To obtain acceptable calibration curves, a constant volume of CS_2 was used to introduce varying amounts of sample. In all cases, linear working curves were obtained.

The effect of column temperature and the flow-rate of the helium carrier gas were also investigated. The optimum conditions were found to be 135° and 30 cc/min, respectively. With these conditions calibration curves were determined for each of the eight impurities.

Procedure

A flame-ionization gas chromatograph is equipped with a 6-ft. long \times 0.094-in. I.D. stainless-steel column packed with 10 % by weight of Bentone 34 on 80-90 mesh ABS Anakrom. The column and inlet temperatures are maintained at 135° and

240°, respectively. The flow-rate of the helium carrier gas is adjusted to 30 cc/min, and the flow-rate ratio of helium:hydrogen:air is controlled at 1:1:10. The recorder is turned on, and, after the electrometer has been balanced, the flame ionization detector is ignited. With a Hamilton microsyringe, 1 μ l of a 5% *s*-TCB solution is introduced into the gas chromatograph. The peak heights or peak areas of the impurities are measured, and the concentrations are determined from calibration curves prepared previously with known standards.

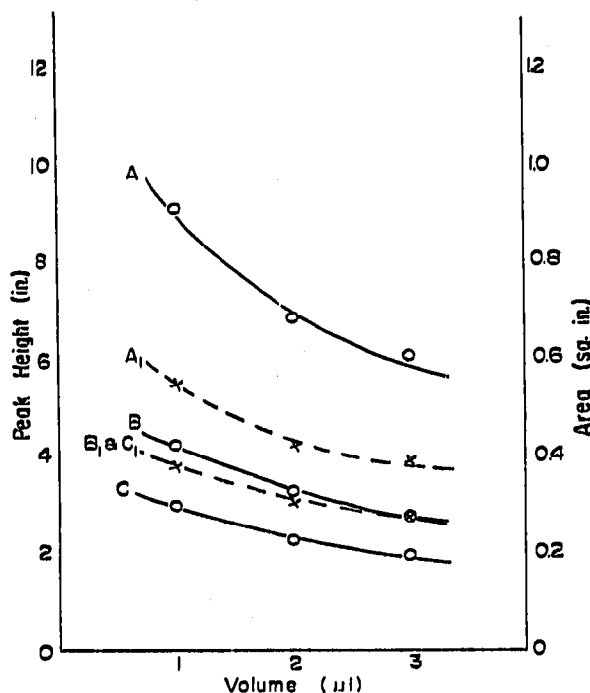


Fig. 1. Effect of solvent volume on peak area and peak height. Curves: A = peak height, 0.60 μ g *m*-dichlorobenzene; A₁ = peak area, 0.60 μ g *m*-dichlorobenzene; B = peak height, 0.51 μ g 1,2,4-trichlorobenzene; B₁ = peak area, 0.51 μ g 1,2,4-trichlorobenzene; C = peak height, 0.60 μ g 1,2,3,5-tetrachlorobenzene; C₁ = peak area, 0.60 μ g 1,2,3,5-tetrachlorobenzene.

RESULTS AND DISCUSSION

Several synthetic mixtures were analyzed to determine the precision and accuracy of the method, and the results are summarized in Table I. Within the concentration range of 0.10–1.50% impurity, excellent results were obtained, with the relative standard deviation (standard deviation divided by the mean) being ≤ 0.11 by both peak-height and peak-area measurements. The simplicity of the peak-height measurement makes it the method of choice. Fig. 2 shows tracings of the chromatograms obtained from these samples.

Two commercial samples of *s*-TCB were analyzed by this procedure. Surprisingly, these samples were found to be exceptionally good for production-grade chemicals. Sample D contained only 0.14% *m*-dichlorobenzene, while sample E, used in the TATB process, showed about 0.05% of 1,2,4-trichlorobenzene. Fig. 3 shows the chromatograms.

TABLE I
ANALYSIS OF s-TCB IMPURITIES
± indicates standard deviation.

Sample	No. of Dets.	% Impurity	p-DCB	m-DCB ^a	1,2,4- TCB	o-DCB	1,2,3,5- tetraCB	1,2,4,5- tetraCB	1,2,3- TCB	1,2,3,4- tetraCB
Sample A—syn mix	—	Contains	0.10	0.10	0.10	0.11	0.10	0.10	0.10	0.10
	4	Found (peak ht.)	0.10	0.26	0.11	0.11	0.10	0.09	0.10	0.09
	4	Found (area)	±0.00	±0.00	±0.01	±0.01	±0.00	±0.01	±0.01	±0.01
Sample B—syn mix	—	Contains	0.40	0.42	0.39	0.39	0.39	0.35	0.39	0.39
	4	Found (peak ht.)	0.40	0.57	0.41	0.42	0.39	0.33	0.40	0.40
	4	Found (area)	±0.00	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.00
Sample C—syn mix	—	Contains	0.40	0.60	0.40	0.44	0.40	0.34	0.40	0.38
	4	Found (peak ht.)	0.40	0.60	0.40	0.44	0.40	0.34	0.40	0.38
	4	Found (area)	±0.01	±0.03	±0.02	±0.01	±0.01	±0.01	±0.00	±0.01
1,3,5-Trichlorobenzene	—	Contains	1.41	1.46	1.42	1.53	1.43	1.29	1.41	1.45
	4	Found (peak ht.)	1.41	1.69	1.47	1.60	1.44	1.17	1.47	1.47
	4	Found (area)	±0.02	±0.05	±0.07	±0.03	±0.01	±0.04	±0.04	±0.02
Sample D	—	Contains	1.42	1.57	1.45	1.50	1.41	1.13	1.43	1.45
	4	Found (peak ht.)	1.42	1.57	1.45	1.50	1.41	1.13	1.43	1.45
	4	Found (area)	±0.00	±0.06	±0.09	±0.04	±0.03	±0.06	±0.03	±0.02
1,3,5-Trichlorobenzene	—	Contains	—	0.14	—	—	—	—	—	—
	4	Found (peak ht.)	—	0.14	—	—	—	—	—	—
	4	Found (area)	—	±0.00	—	—	—	—	—	—
1,3,5-Trichlorobenzene	—	Contains	—	—	~0.05	—	—	—	—	—
	4	Found (peak ht.)	—	—	~0.05	—	—	—	—	—
	4	Found (area)	—	—	~0.05	—	—	—	—	—

^a The 1,3,5-trichlorobenzene used to prepare the synthetic samples contains 0.14% m-DCB.

^b Used in the TATB process.

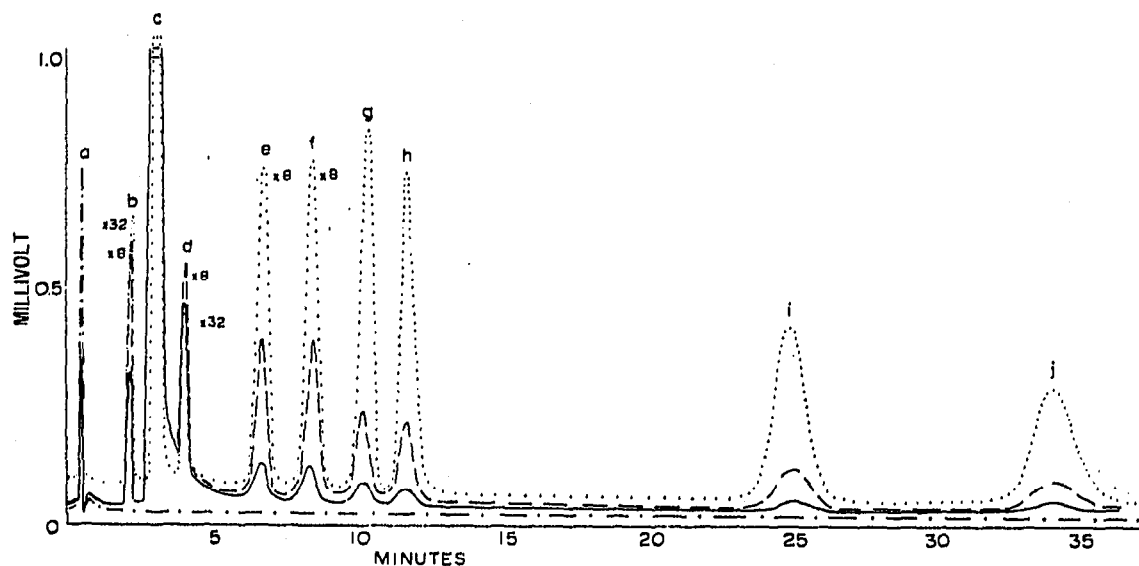


Fig. 2. Chromatograms of synthetic samples. Chromatographic conditions: column, 6-ft. long \times 1/8-in. O.D. (0.094-in. I.D.) 10% Bentone on 80-90 mesh ABS Anakrom; column temp., 135°; inlet temp., 240°; helium carrier gas flow-rate, 30 cc/min; hydrogen flow-rate, 30 cc/min; air flow-rate, \sim 300 cc/min; recorder speed, 16 in./h; Electrometer range, 10; attenuation, $\times 4$ - $\times 32$. (Sample size: 1 μ l of 5% *s*-TCB solution. Curves: - - - - , CS₂ solvent; ———, sample A — syn mix (composition, see Table I); - - - - , sample B — syn mix (composition, see Table I); ·····, Sample C — syn mix (composition, see Table I). Identification of products: a = CS₂; b = *p*-DCB; c = *s*-TCB; d = *m*-DCB; e = 1,2,4-TCB; f = *o*-DCB; g = 1,2,3,5-tetraCB; h = 1,2,4,5-tetraCB; i = 1,2,3-TCB; j = 1,2,3,4-tetraCB.

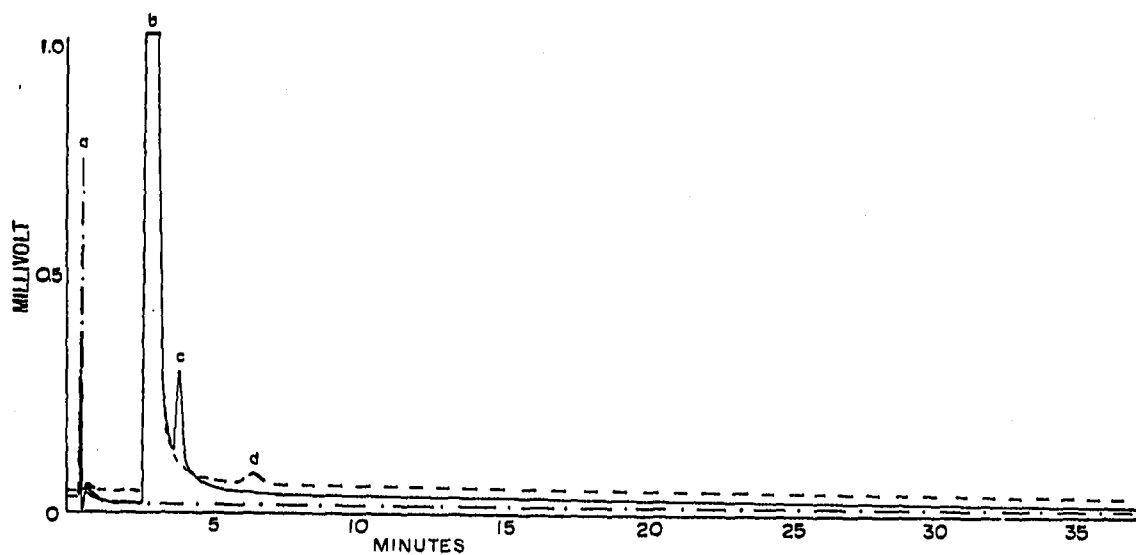


Fig. 3. Chromatograms of *s*-TCB samples. Chromatographic conditions: same as Fig. 2. Sample size: 1 μ l of 5% *s*-TCB solution. Curves: - - - - , CS₂ solvent; ———, *s*-TCB, Sample D; - - - - , *s*-TCB, Sample E. Identification of products: a = CS₂; b = *s*-TCB; c = *m*-DCB; d = 1,2,4-TCB.

These findings indicate that the DNtetraCB and DNTCB found in the crude TCTNB are formed in the nitration process. Partial nitration of *s*-TCB leads to DNTCB. As for the DNtetraCB, we can now rule out 1,2,3,5-tetrachlorobenzene as the source of this impurity, since no tetrachlorobenzene was found in the *s*-TCB used in the TATB process. Therefore, we conclude that DNtetraCB is produced during the nitration of *s*-TCB by "transchlorination". The origin of the DNtetraCB is of particular interest, since this impurity and its partially aminated products constitute half of the by-products found in production-grade TATB².

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