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## MICRODETERMINATION OF ESTANE IN EXPLOSIVE MIXTURES

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## SUMMARY

A microanalytical method based on pyrolytic gas chromatography is described for the determination of Estane 5740 X<sub>2</sub> in explosive mixtures. The explosive, octahydro-1,3,5,7-tetranitro-s-tetrazine, is separated from Estane in chloroform solution, and an aliquot is taken as a sample. The polymer is converted to cyclopentanone by controlled pyrolysis for gas chromatographic analysis. The peak area of the cyclic ketone is measured and related to Estane concentration by means of a calibration curve. Several PBX and synthetic samples were successfully analyzed by this method.

## INTRODUCTION

Plastic-bonded explosives (PBX's), which are usually mixtures of HMX (octahydro-1,3,5,7-tetranitro-s-tetrazine) or RDX (hexahydro-1,3,5-trinitro-s-triazine) with some thermoplastic binder, are an important class of contemporary explosives. Most such mixtures can be analyzed on a macro scale by relatively simple techniques, such as solvent extraction, and such techniques suffice for routine quality control. In research and development work, however, accurate analyses are frequently required on very small samples. In the present paper, we describe a procedure, based on pyrolytic gas chromatography (PGC), which is adaptable to the analysis of HMX-Estane mixtures on a semimicro scale.

Under controlled pyrolysis, Estane 5740 X<sub>2</sub> (B. F. Goodrich) was found to yield a distinctive product, cyclopentanone, in an amount which was proportional to the Estane concentration in the sample. In PBX samples, however, the cyclopentanone is susceptible to oxidation by the pyrolysis products of HMX, which leads to low results. It was found that this effect could be minimized by selectively dissolving the Estane in chloroform and taking an aliquot of the chloroform solution for pyrolysis. PBX and synthetic samples were successfully analyzed by this procedure with the standard deviation on synthetic samples being 0.12 % or less.

## EQUIPMENT AND REAGENTS

An Aerograph HY FI Model 600-D gas chromatograph, a Perkin-Elmer (PE) pyrolysis unit, and a Varian Model G-14 recorder were used.

A 6 ft. long  $\times$  1/8 in. O.D. (0.094 in. I.D.) stainless steel tube was packed with 25% (by wt.) of Carbowax 20 M coated on 60/80 mesh, acid-washed Chromosorb W, using a Mathtronic XL-300 column packer. The packed column was preconditioned at 125° with helium carrier gas before use.

Estane 5740 X2 (61.47% C, 7.53% H, 2.66% N, and 28.30% O by elemental analysis, empirical formula  $C_{27}H_{39}NO_9$ ) was dissolved in A.R. grade chloroform and used as standard. The standard Estane solution was prepared as needed.

Ultrapure hydrogen in H-size cylinders, purchased from The Matheson Company, was employed as the carrier gas for the PGC unit.

Three 25-ml and three 50-ml volumetric flasks, two Hamilton microsyringes (10- $\mu$ l capacity), and 12 microporcelain combustion boats (No. 00000) were needed for sample preparation.

An ultrasonic shaker was used to dissolve the PBX sample in chloroform. A centrifuge was used to separate the undissolved HMX granules.

## EXPERIMENTAL

The tricresyl phosphate partitioning column, used to identify the major pyrolysis products of Estane<sup>1</sup>, was unsuitable for quantitative work. Owing to excessive tailing of the cyclopentanone peak, the measurement of the peak area was difficult. A 6-ft. Carbowax column was found to separate the cyclic ketone as a symmetrical peak with a reasonable retention time from the other pyrolysis products. With this column, the pyrolysis and gas chromatographic conditions required to obtain a maximum conversion of Estane to cyclopentanone were determined.

Known amounts of Estane standards were pyrolyzed at different temperatures, and the pyrolysis products were separated on the Carbowax column. The peak area

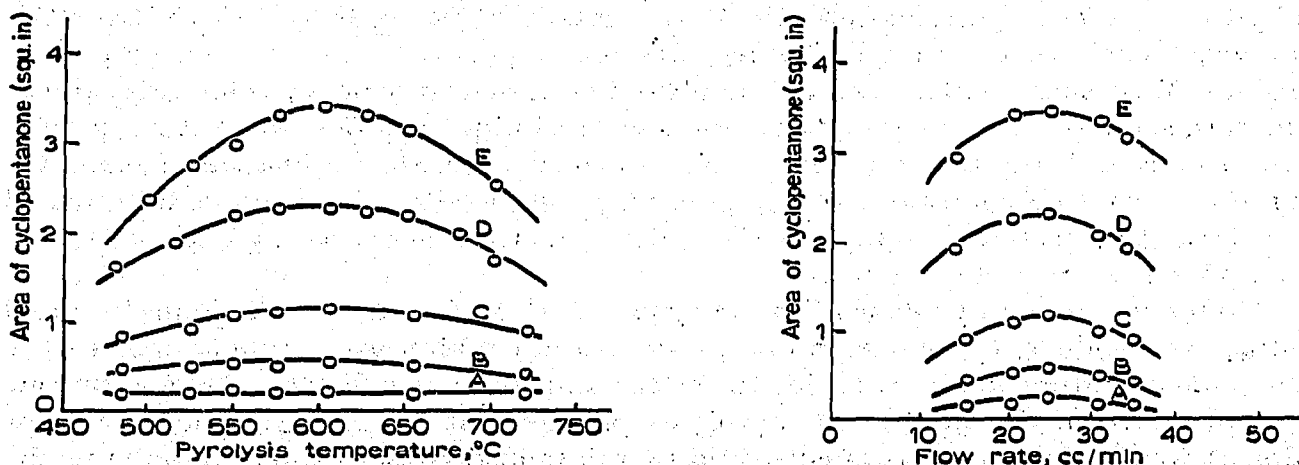


Fig. 1. Effect of pyrolysis temperature on Estane 5740 X2. Gas chromatographic conditions: Column, 6 ft. long  $\times$  1/8 in. O.D. (0.094 in. I.D.) 25% Carbowax 20 M on 60/80 mesh, acid-washed Chromosorb W; column temp., 85°; inlet temp., 100°; hydrogen carrier gas, flow rate 25 cc/min; recorder speed, 16 in./h; electrometer range, 1; attenuation  $\times$  4- $\times$  16. Sample size: curve A, 2  $\mu$ g Estane; curve B, 5  $\mu$ g Estane; curve C, 10  $\mu$ g Estane; curve D, 20  $\mu$ g Estane; curve E, 30  $\mu$ g Estane. Each point represents an average of duplicate runs.

Fig. 2. Effect of flow rate on Estane 5740 X2. Gas chromatographic and pyrolysis conditions: gas chromatographic conditions, same as Fig. 1, except variable flow rates; pyrolysis temp., 600°. Sample size: same as Fig. 1.

of cyclopentanone as a function of the pyrolysis temperature is shown graphically in Fig. 1. It can be seen that at 600° a maximum yield of cyclopentanone is obtained per given weight of polymer. At pyrolysis temperatures less than optimum, a measurable decrease in the cyclic ketone is noted.

With a pyrolysis temperature of 600° and the gas chromatographic conditions given in Fig. 1, the effect of the hydrogen flow rate on the cyclopentanone yield was determined. Fig. 2 shows that at between 24 and 25 cc/min of hydrogen the amount of cyclopentanone produced is a maximum.

It was anticipated that the pyrolysis of Estane in the presence of HMX would affect the yield of cyclopentanone. To establish the effect, a constant amount of Estane was mixed with varying amounts of HMX, and the mixed samples were subjected to pyrolysis. Fig. 3 shows that, with increasing amounts of HMX, the recovery of cyclopentanone decreases.

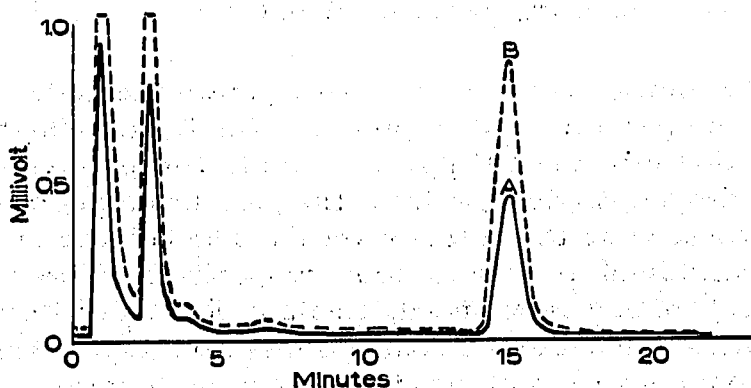
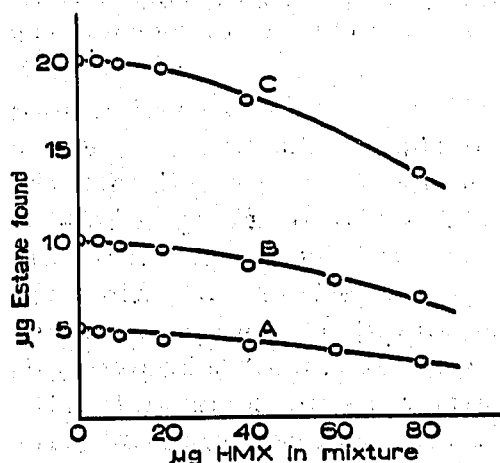


Fig. 3. Effect of mixed sample pyrolysis on Estane recovery. Chromatographic and pyrolysis conditions: column, 6 ft. long  $\times$  1/8 in. O.D. (0.094 in. I.D.), 25% Carbowax 20 M on 60/80 mesh, acid-washed Chromosorb W; column temp., 85°; inlet temp., 100°; hydrogen carrier gas, flow rate 24–25 cc/min; recorder speed, 16 in./h; electrometer range, 1; attenuation  $\times$  4– $\times$  16; pyrolysis temp., 600°. Sample size: curve A, varying amounts of HMX mixed with 5  $\mu$ g Estane 5740 X<sub>2</sub>; curve B, varying amounts of HMX mixed with 10  $\mu$ g Estane 5740 X<sub>2</sub>; curve C, varying amounts of HMX mixed with 20  $\mu$ g Estane 5740 X<sub>2</sub>. Each point on the curve represents an average value of two or more determinations.

Fig. 4. Pyrograms of Estane 5740 X<sub>2</sub>. Chromatographic and pyrolysis conditions: same as Fig. 3. Sample size: curve A (—), 5  $\mu$ g Estane 5740 X<sub>2</sub>; curve B (-----), 10  $\mu$ g Estane 5740 X<sub>2</sub>. Peaks A and B are cyclopentanone.

To eliminate the interference by HMX, chloroform was used as a selective solvent for the Estane. HMX is soluble to the extent of about 0.012 g per 100 ml of chloroform at 20°, while more than 0.200 g of Estane dissolves in the same amount of solvent. On the basis of these data, 1% PBX solutions and 10- $\mu$ l aliquot samples were selected for use. Figs. 4 and 5 are pyrograms of Estane 5740 X<sub>2</sub>, HMX, and PBX 9011, an HMX/Estane mixture. With chloroform, only a negligible amount of HMX appears in the sample, and it causes no interference with the analysis.

#### Procedure

An accurately weighed 0.5-g sample of PBX is dispersed in 50 ml of chloroform with the aid of an ultrasonic shaker until no large clusters of PBX granules are visible.

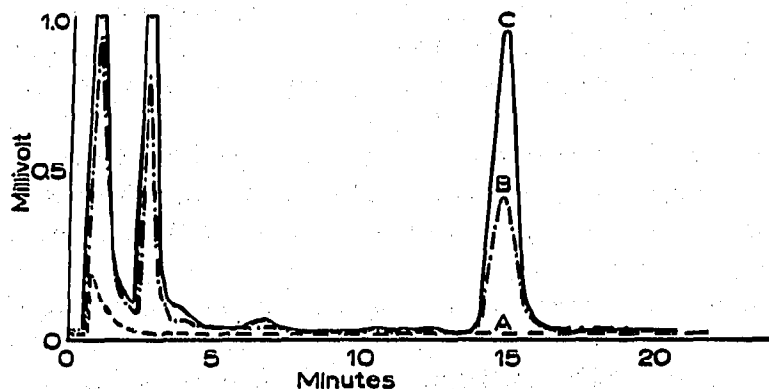


Fig. 5. Pyrograms of HMX, synthetic, and PBX 9011-06 samples. Chromatographic and pyrolysis conditions: same as Fig. 3. Sample size: curve A (-----), 10  $\mu$ l  $\text{CHCl}_3$  solution saturated with HMX; curve B (-·-·-·-), 10  $\mu$ l 1% synthetic sample (Estane-HMX, 5:95) = 5  $\mu$ g Estane; curve C (———), 10  $\mu$ l 1% PBX 9011-06 in  $\text{CHCl}_3$  = 10  $\mu$ g Estane. Peaks B and C are cyclopentanone.

The solution is centrifuged to separate the undissolved HMX crystals. A 10- $\mu$ l aliquot is pipetted into a microprocelain combustion boat. Six ceramic boats with samples are loaded into the PE pyrolysis unit. The pyrolysis unit is closed and purged with the hydrogen carrier gas from the gas chromatograph at a flow rate of 24–25 cc/min as measured at the detector outlet. The column and the sample inlet temperatures are maintained at 85 and 100°, respectively. The recorder is turned on, and, after the electrometer is balanced, the flame ionization detector is ignited. The sample is moved with a magnet and a boat pusher into the pyrolysis chamber set at 600°. The pyrolysis products are swept into the gas chromatograph by the carrier gas and separated on the 6-ft. 25% Carbowax column. The area of the cyclopentanone peak is measured by the peak height  $\times$  peak width at half-height method and is related to Estane concentration by means of a calibration curve previously prepared with Estane standards.

## RESULTS AND DISCUSSION

The procedure was applied to the analysis of several synthetic mixtures and PBX samples with the results shown in Table I. It is evident that the results are excellent. With synthetic mixtures, the standard deviation is about 0.1%; PBX 9011 shows slightly higher values, but they are within the acceptable limits.

TABLE I  
ANALYSIS OF ESTANE 5740 X<sub>2</sub>

Sample	Nominal composition	No. of determinations	Percent estane found	S.D.
Synthetic mix	HMX-Estane 5740 X <sub>2</sub> , 95:5	5	4.9	0.07
Synthetic mix	HMX-Estane 5740 X <sub>2</sub> , 90:10	5	9.8	0.12
PBX 9011-02	HMX-Estane 5740 X <sub>2</sub> , 90:10	10	9.8	0.18
PBX 9011-06	HMX-Estane 5740 X <sub>2</sub> , 90:10	10	9.8	0.27

The origin of cyclopentanone from the pyrolysis of Estane 5740 X2 was briefly investigated. Although the exact chemical composition of this polymer is not available, a closely related polymer, Estane 5740 X1, involves the condensation of 4,4'-diphenylmethane diisocyanate, 1,4-butanediol, and adipic acid<sup>2</sup>. If similar reactants are used in different proportions to prepare Estane 5740 X2, one of the reactants must be responsible for the formation of cyclopentanone. Each reactant was pyrolyzed in the same manner as the PBX samples, and adipic acid and its *n*-butyl ester produced the cyclic ketone as shown in Fig. 6. Therefore, the adipate group in Estane 5740 X2 yields the cyclopentanone product.

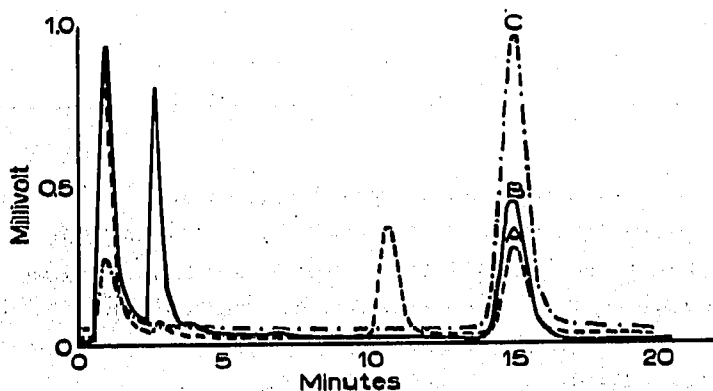


Fig. 6. Pyrograms of adipic acid, *n*-butyl adipate, and Estane 5740 X2. Chromatographic and pyrolysis conditions: same as Fig. 3. Sample size: curve A (-----), 20  $\mu$ g *n*-butyl adipate, attenuated  $\times$  16; curve B (—), 5  $\mu$ g Estane 5740 X2, attenuated  $\times$  4; curve C (-·-·-·-), 20  $\mu$ g adipic acid, attenuated  $\times$  16. Peaks A, B, and C are cyclopentanone.

#### ACKNOWLEDGEMENT

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