

CHROM. 3485

MICRODETERMINATION OF POLYSTYRENE IN EXPLOSIVE MIXTURES BY PYROLYTIC GAS CHROMATOGRAPHY

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(Received March 4th, 1968)

SUMMARY

A simple pyrolytic gas chromatographic method, capable of determining 0-40 micrograms of polystyrene in a plastic-bonded RDX explosive, is described. The polystyrene is converted to the monomer by controlled pyrolysis. The styrene monomer is determined by gas chromatography and related to polymer concentration by means of a calibration curve. Synthetic mixtures and explosive samples were successfully analyzed by the method, and the method has been applied to the study of composition variations in small PBX granules.

INTRODUCTION

Pyrolytic gas chromatography (PGC) has been used extensively as an analytical technique for the identification of polymers, but very few attempts have been made to use it for quantitative polymer determination¹⁻³. The simplicity and rapidity of the method make it attractive for quantitative work. Because of our interest in the analysis of plastic-bonded explosives (PBX), we investigated the application of PGC to the determination of polystyrene in a mixture with hexahydro-1,3,5-trinitro-s-triazine (RDX).

PBX presents a set of analytical conditions unlike those encountered with simple polymer or copolymer samples. In PBX, the polymer is a minor component, and the major component, RDX, provides a reactive environment during pyrolysis which may alter the products from polystyrene. In the work reported here, it was found that good results could be obtained either by removing most of the RDX before pyrolysis or by suitably distributing the sample in the pyrolysis boat. PBX and synthetic samples were successfully analyzed by the developed procedure with an indicated standard deviation (synthetic mixtures) of about 0.1 %.

EQUIPMENT AND REAGENTS

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

used throughout this work. The PE pyrolysis unit was connected to the gas chromatograph by a heated connector.

A 2 ft. long \times 1/8 in. O.D. (0.094 in. I.D.) stainless steel tube was packed with 30% tricresyl phosphate (TCP) coated on 40/60 mesh, acid-washed C-22 firebrick, using a Mathronic XL-300 column packer. The packed column was preconditioned at 100° for 24 h with helium carrier gas before use.

Polystyrene with an indicated purity of 100% (carbon-hydrogen analysis) was dissolved in AR grade benzene and employed as standard.

Ultrapure hydrogen in H-size cylinders was purchased from the Matheson Company.

Twelve micro porcelain combustion boats, No. 00000 (17 mm long \times 6 mm wide \times 4 mm high), two Hamilton microsyringes (10 μ l capacity), and five 10 ml volumetric flasks were necessary to contain, transfer, and prepare the samples.

The dissolution of the PBX sample in benzene was accomplished with an ultrasonic shaker.

EXPERIMENTAL

The selection of the TCP column for the separation of polystyrene pyrolysis products is based on the work recently published by the author⁴. The 2 ft. column, operated at 85° with hydrogen carrier gas at a flow rate of 30 cc/min, was the best compromise for maintaining a reasonable retention time for the styrene monomer without interference from the pyrolysis products of RDX and dioctyl phthalate (DOP).

The temperature of the pyrolysis furnace was calibrated under dynamic conditions to ensure that the pyrometer registered the true temperature of the pyrolysis chamber. A 30-gauge chromel-alumel thermocouple was threaded through a No. 0 rubber stopper and placed inside the pyrolysis chamber normally occupied by the ceramic boat. The rubber stopper replaced the knurled nut used to keep the chamber leak-tight. The flow rate of the hydrogen carrier gas was varied from 22–35 cc/min, and the furnace temperature was set between 400° and 700°. The readings of the thermocouple and the pyrometer were compared at each temperature and flow-rate setting. The pyrometer was adjusted to read the inside temperature of the pyrolysis chamber directly. At the specified flow rates, no effect of flow rate on the temperature was noted.

A systematic study of several variables important in the analysis of PBX samples was made. Known amounts between 1–40 μ g of polystyrene were pyrolyzed at different temperatures, and the products were separated on the 2 ft. TCP column. A plot of the data and the chromatographic conditions used to separate the products are presented in Fig. 1. Inspection of the figure reveals that the optimum pyrolysis temperature is between 500° and 525°. A maximum yield of styrene monomer is obtained within this narrow range.

The effect of the hydrogen carrier gas flow rate on the monomer yield was studied at a pyrolysis temperature of 510° with the gas chromatographic conditions given in Fig. 1. Between 20 and 30 cc/min, no effect was noted; however, at 40 cc/min, a drastic decrease in the formation of styrene monomer was found. This is attributed to the rapid removal of large polymer fragments from the heated zone before complete pyrolysis occurs.

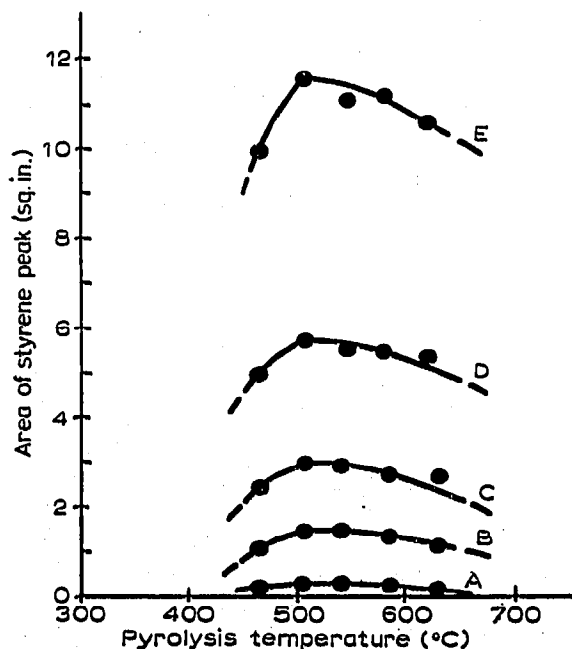


Fig. 1. Effect of pyrolysis temperature on polystyrene. Chromatographic conditions: Column, 2 ft. long \times 1/8 in. O.D. (0.094 in. I.D.), 30% TCP on 40/60 mesh, acid-washed C-22 firebrick; column temp., 85°; inlet temp., 100°; hydrogen carrier gas, flow rate, 30 cc/min; recorder speed, 16 in./h; electrometer range, 1; attenuation \times 8- \times 64. Sample size: curve A, 1 μ g polystyrene; curve B, 5 μ g polystyrene; Curve C, 10 μ g polystyrene; curve D, 20 μ g polystyrene; curve E, 40 μ g polystyrene.

Polystyrene is a minor component in PBX samples, and the possible effects of interference by the RDX on the pyrolysis of the polymer had to be determined. Solid granules of PBX were selected at random and analyzed for polystyrene. The results were erratic, varying from 4 to 10% polymer. There are two possible explanations for these results: (1) the polymer distribution may vary from grain to grain, and (2) the diffusion of the pyrolysis products through grains of varying size may lead to secondary reactions in varying proportions. The latter explanation is substantiated by the increase in by-products, particularly toluene and ethylbenzene. Therefore, we dissolved a large sample of PBX in benzene and took an aliquot as a sample.

With aliquot samples, we found no effect of mixed-sample pyrolysis on the styrene yield. Owing to the limited solubility of RDX in benzene (about 0.05 g RDX/100 g of benzene at 25°), a partial separation of RDX from polystyrene is obtained in solution. A 10 μ l aliquot of a PBX sample, normally used for analysis, contains only negligible RDX, which causes no interference. Likewise, the amount of DOP present in PBX as a plasticizer does not interfere with the analysis. Pyrograms of polystyrene and mixed samples are shown in Fig. 2.

The effect of the sample holder on the pyrolysis of polystyrene was also investigated. Ceramic and platinum-rhodium boats, commonly used in microanalysis, were tested with polystyrene samples. The results from the Pt-Rh boat showed a marked decrease in styrene monomer with a considerable increase in benzene, toluene, and ethylbenzene products, as compared to the data from the ceramic boat. Possible explanations are: (1) the Pt-Rh boat may serve as a catalyst during pyrolysis, and (2) the high thermal conductivity of the Pt-Rh boat may heat the sample to the

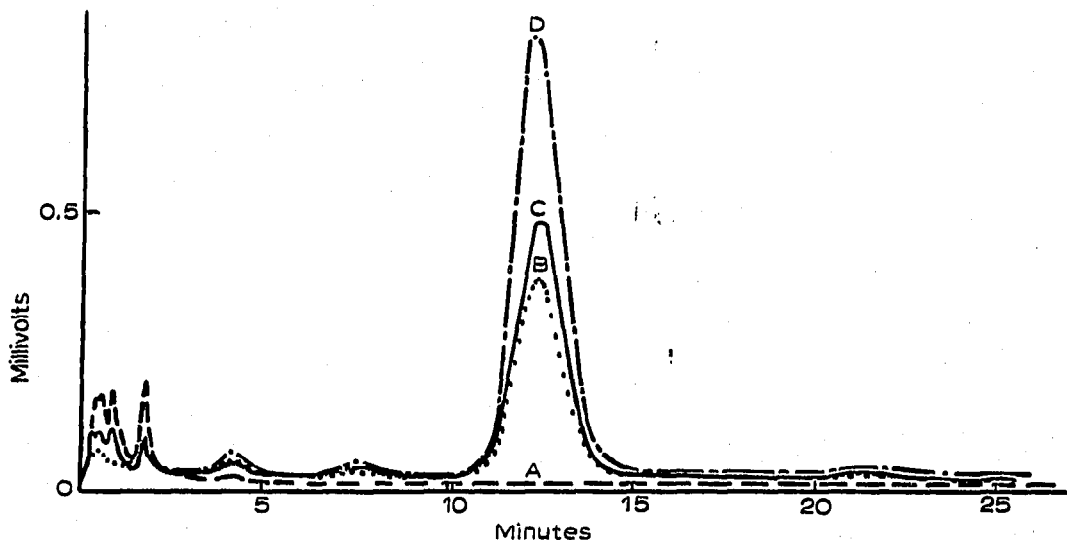


Fig. 2. Pyrograms of polystyrene (PS), RDX/DOP and PBX 9205. Chromatographic and pyrolysis conditions: column, 2 ft. long \times 1/8 in. O.D. (0.094 in. I.D.), 30% TCP on 40/60 mesh, acid-washed C-22 firebrick; column temp., 85°; inlet temp., 100°; hydrogen carrier gas, flow rate, 30 cc/min; recorder speed, 16 in./h; electrometer range, 1; attenuation: \times 16; pyrolysis temp., 510°. Sample size: curve A, 20 μ l 1% RDX and 0.02% DOP in benzene; curve B, 5 μ l 0.1% PS in benzene = 5 μ g PS; curve C, 10 μ l 1% PBX 9205 in benzene = 6 μ g PS; curve D, 10 μ l 0.1% PS in benzene = 10 μ g PS. The major peak is the styrene monomer.

preset pyrolysis temperature more rapidly and cause greater fragmentation of the polymer than does the ceramic boat. Therefore, the ceramic boat was chosen for our work.

Procedure

An accurately weighed 0.1 g sample of PBX is dispersed in 10 ml of benzene with the aid of an ultrasonic shaker. With a Hamilton microsyringe, 10 μ l of the solution is pipetted into porcelain boat. The solvent is allowed to evaporate at room temperature, then the boat is placed in the pyrolysis unit. Up to six samples can be stored in the unit. The pyrolysis unit is closed and purged with the hydrogen carrier gas from the gas chromatograph at a flow rate of 30 cc/min as measured at the detector outlet. With the TCP column operated at 85°, the flame ionization detector is ignited and the recorder is turned on, allowing about 15 min for the detector and the recorder to stabilize. With the aid of a magnet and a boat pusher, the porcelain boat is moved into the pyrolysis chamber maintained at 510°. The pyrolysis products are swept into the gas chromatograph by the carrier gas and separated on the TCP column. The peak area of the styrene monomer is measured and related to polymer concentration via a calibration curve previously prepared under identical conditions with polystyrene standards.

RESULTS AND DISCUSSION

Several PBX samples and synthetic mixtures were analyzed by this method, and the results are summarized in Table I. It can be seen that excellent results were obtained, with standard deviations within acceptable limits.

TABLE I
ANALYSIS OF POLYSTYRENE

Sample	Ratio of composition	No. of determinations	Polystyrene found			
			Disc integration (%)	Std. dev.	Peak ht. \times peak width at half-ht. (%)	Std. dev.
Synthetic mix	93.7:6.3, RDX-PS	6	6.4	0.03	6.3	0.20
PBX 9205	92.0:6.0:2.0, RDX-PS-DOP	5	6.2	0.17	6.1	0.11
PBX 9007 with graphite	90.9:8.2:0.5:0.4, RDX-PS-DOP-Rosin + 0.8% graphite	5	8.0	0.16	8.1	0.23

TABLE II
DETERMINATION OF POLYSTYRENE IN SINGLE PBX GRANULE

Sample	Wt. of granule (μ g)	No. of determinations	Polystyrene found (%)	Av. (%)	Std. dev.
PBX 9205	68-141	17	5.0-6.9	6.0	0.51
PBX 9007 with graphite	72-151	17	6.2-8.9	7.9	0.84
Synthetic mix	105	6	4.7-4.8	4.8	0.08

Two methods for area measurements were evaluated. The disc integration and peak height \times peak width at half-height methods gave similar results. This is, in part, due to the symmetry of the styrene peak.

To determine the extent to which the composition varies from grain to grain in a plastic-bonded explosive, we also applied the PGC method to the analysis of polystyrene in individual PBX granules. Since sample distribution was found to have a profound effect on the degradation of polystyrene, as has already been noted, the weighed granule, selected at random, was treated with three 30 μ l volumes of benzene, followed by four 30 μ l volumes of acetone, to distribute the granule as a thin layer on the inside walls of the porcelain boat. The solvent was allowed to evaporate completely after each addition before repeating the solvent treatment. In like manner, synthetic mixtures were treated with benzene-acetone and analyzed by the PGC method. The data are summarized in Table II.

It is evident from Table II that the amount of polystyrene varies significantly from grain to grain. For PBX 9205, the range is from 5.0 to 6.9% polystyrene, while PBX 9007 with graphite shows 6.2 to 8.9% polymer. However, the data from the synthetic samples analyzed in the same manner are excellent. Therefore, the variations of polymer content in the granular samples must be real. The average values of polystyrene in Table II agree very well with those in Table I for the respective PBX samples, in spite of the different sampling techniques.

ACKNOWLEDGEMENTS

The author thanks L. C. SMITH for helpful suggestions and D. L. UPHAM for designing special parts for the pyrolysis unit. This work was done under the auspices of the U.S. Atomic Energy Commission.

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