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The Identification of Smokeless Powders and Their Residues by Pyrolysis Gas Chromatography

The identification and characterization of smokeless powders by means of gas chromatographic examination of their pyrolysis products is possibly the most significant method of selective identification available to the forensic examiner. Minor constituent analysis has been established as a rapid and accurate means of distinguishing various powders from each other [1], but the inherent limitations resulting from the amount of sample necessary for examination and the chemical changes associated with the burning of surface coatings restrict the utility to situations where grains of virtually unaltered powder can be obtained. The examination of powders by thermoanalytical methods [2,3] introduces the advantage of reduced sample size, but these techniques are not so selective and have limitations when partially burned powder is being examined. Pyrolysis gas chromatography, on the other hand, is advantageous in that it requires only small samples and the examination is primarily of homogeneous constituents that exhibit considerable variations among different lots of powder.

Equipment and Chemicals

All smokeless powders examined were obtained by retail purchase of reloading powders or by removing the unfired powder charges from various cartridges (Table 1). Many of the powders examined were those previously examined for minor constituents [1].

Pyrolysis gas chromatography was performed by using a Varian Model 2400 gas chromatograph with flame ionization detectors and a Chemical Data Systems Model 150 Pyroprobe. A 1.8-m (6-ft) long, 6.35-mm (¼-in.) diameter (2-mm inside diameter) glass column packed with 0.4% Carbowax 1500 on 60-80 mesh Carbopak A was used. Each sample was pyrolyzed by heating ("ramp off") to 500 °C for 10 s. The operating conditions for the gas chromatograph were these: column, 3 min at 60 °C with linear temperature increase at a rate of 20 °C/min for 4½ min to a final temperature of 150 °C, which was held for 15 min; injector temperature, 140 °C; detector temperature, 250 °C; and carrier gas, nitrogen at 30 ml/min. Chromatograms were recorded with a linear recorder at 2 cm/min.

Fired powder residues were collected on fine muslin cloth. Weapon residues were obtained from the barrels of weapons that had been thoroughly cleaned and then fouled with one shot of ammunition charged with the powder being examined.

Procedure

Samples of each powder to be examined were weighed; 0.1 to 0.2 mg of each was then

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TABLE 1—*Reloading powders and unfired powder charges tested.*

Reloading Powders	Pistol Powders
Hercules "Bullseye"	Remington .357 Magnum
Hercules "Unique"	Winchester .44 Special
Dupont "SR4756"	Federal .38 Special wad cutter
Hercules "2400"	Federal .38 Special round nose
Dupont "IMR 3031"	Winchester .357 Magnum
Dupont "IMR 4895"	Rem-UMC .32 Colt new police
Dupont "IMR 4320"	Western .38 long
Winchester "760-BR"	Peters .38 Special
Hodgdon "4831"	Canadian 9-mm military
Rifle Powders	U.S. .45 (1943)
Remington .38/55	U.S. .45 (1926)
Norma 6.5-mm Japanese	German 9-mm military
Winchester 7-mm Magnum	Russian 7.5-mm military
Superspeed .222	Japanese 8-mm military
Winchester 30/30	French 8-mm military
Russian 7.62-mm army	Shotgun Powders
.22 Rimfire Powders	Wanda 12 gauge
CCI	Winchester 16 gauge
Sinoxide	Sears 20 gauge, field
Remington	Peters 16 gauge, high velocity
Eley	Peters .410, 76 mm (3 in.) high velocity
Winchester	Federal .410, 63 mm (2½ in.)
Federal	

placed in a quartz capillary tube inserted into the Model 150 Pyroprobe. Peak areas were computed as the product of peak height and peak width at half-height.

Results and Discussion

This method of analysis was examined to determine its applicability to the examination of smokeless powders. The following criteria were considered during its development: sensitivity, reproducibility with unfired powders, correlation between fired and unfired powders, ability to characterize individually various lots of powder, cost, and time.

This method is several orders of magnitude more sensitive than the previously described method for the examination of minor constituents. Sub-milligram samples that approach the sensitivity limit for minor constituent determinations represented an optimum sample size for pyrolysis gas chromatography. Increasing the sensitivity allows one to detect peaks attributed to minor constituents, such as deterrent coatings, stabilizers, and their reaction products, but increases the total number of peaks on the chromatogram from the number normally observed (approximately 10 to 20) to 50 or more. (A peak is defined as being a reproducible response having an amplitude greater than four times the ambient noise.) The overall effect of sensitivity increase is to abandon simple chromatograms for chromatograms showing an unrelieved clutter of indistinguishable peaks.

The chromatogram of a single-base rifle powder (shown in Fig. 1) is illustrative of the characteristics obtained from all of the powders examined. Most of the fragments have retention times of less than 2 min and between 8 and 15 distinctive fragments usually appear during this relatively short period. Virtually all the chromatograms could be separated based on the differences noted among these peaks.

Fewer fragments had retention times greater than 2 min and less than 10% of the total material detected by the gas chromatograph was eluted after this time. Most of these

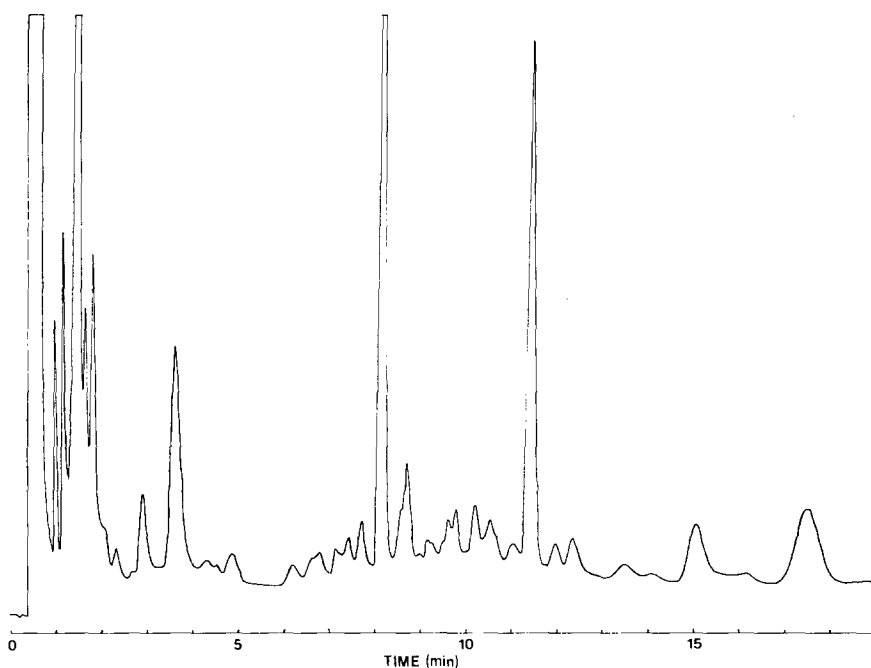


FIG. 1—*Chromatogram of a single-base smokeless powder.*

peaks may be attributed to fragments originating from the stabilizers and deterrent coatings and from incompletely nitrated anhydroglucose units in the cellulose polymer. This explanation is supported by experimental data: nitrocellulose (collodion) that is less nitrated than that used in smokeless powder yields more fragments eluting after 2 min, and all of the pyrolysis fragments of unnitrated cellulose elute after 2 min. The highly nitrated monomeric nitroglycerine yields only one fragment; that fragment elutes within the first 40 s. Diphenylamine also yields one fragment, but its retention time is 10½ min.

The time required for the examination including sample preparation was less than ½ h and no costs above the normal operating expenses for the equipment were encountered.

Forty different powders were examined during the development of this method. The chromatogram of each was individually distinguishable from the others, and in most instances significant detail such as the presence of peaks or the gross variation in the relative peak areas of two or more peaks could readily be found to characterize each individual powder. The only instance in which similarities sufficient to confuse the observer were found was in the comparison of samples of two lots of "Bullseye" powder manufactured 50 years apart. Other lots of this same powder were quite distinguishable from these two and from each other, and these two lots of powder were easily separated on the basis of their minor constituents. Several .22-caliber rimfire cartridges manufactured by Remington were used to obtain powder samples for comparison and no difficulty was encountered in readily distinguishing one powder charge from another. Table 2 illustrates the degree of dissimilarity noted. Figures 2 and 3 show two of the powders from the Remington cartridges (equal weights at similar sensitivities).

Numerous samples of powder from a single lot invariably gave reproducible chromatograms. The comparison of the chromatograms of partially burned powder granules to those of unaltered powder granules from the same lot showed no detectable changes in the chromatograms. This was true not only of the powder grains having complete homogeneity

TABLE 2—Comparison of retention times and relative peak areas for the powder charges from four Remington .22 cartridges.^a

Sample A	Sample B	Sample C	Sample D
0.41/48.7	0.41/42.8	0.41/49.4	0.41/46.1
0.53/24.3	0.53/32.8	0.61/ 9.9	0.53/ 9.2
0.66/ 2.4	0.76/ 3.7	0.64/17.3	0.61/12.3
0.79/ 1.0	0.87/ 1.2	0.66/ 5.2	0.74/ 4.4
0.98/ 5.4	1.04/14.6	0.90/ 0.8	1.02/ 2.0
1.12/16.1	1.14/ 1.3	1.08/ 0.5	1.18/ 0.4
1.78/ 0.9	1.27/ 1.8	1.36/12.3	1.57/11.0
6.48/ 1.2	1.97/ 0.5	1.49/ 1.2	1.70/ 1.7
	6.83/ 1.1	1.61/ 1.6	1.97/ 2.3
		2.54/ 0.2	2.41/ 0.9
		6.60/ 0.4	3.11/ 0.4
		7.32/ 1.2	6.92/ 1.0
			7.49/ 7.6
			9.25/ 0.4

^aRetention times (min)/relative peak area (%).

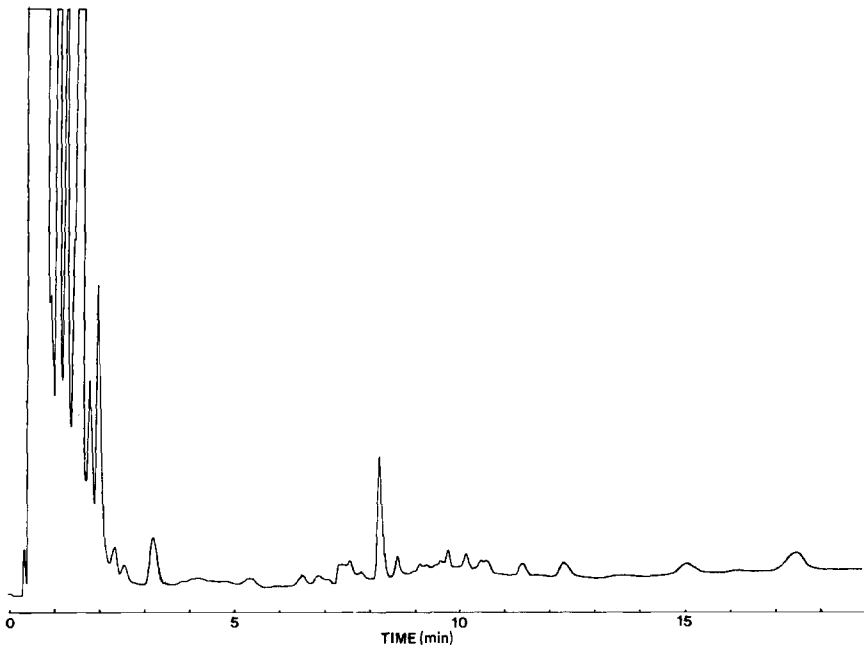


FIG. 2—Chromatogram of powder removed from a Remington .22-caliber rimfire cartridge.

but also of the powder grains having surface coatings. It may well be expected that some variance in this latter type of comparison might be found at higher sensitivities, but where the samples could be removed as discrete particles no problem was encountered. Similarly, the two rifle powders previously reported to be indistinguishable on the basis of their minor constituent analysis were readily separated on the basis of their pyrolysis gas chromatograms. It appears, therefore, that an examination of either the major or the

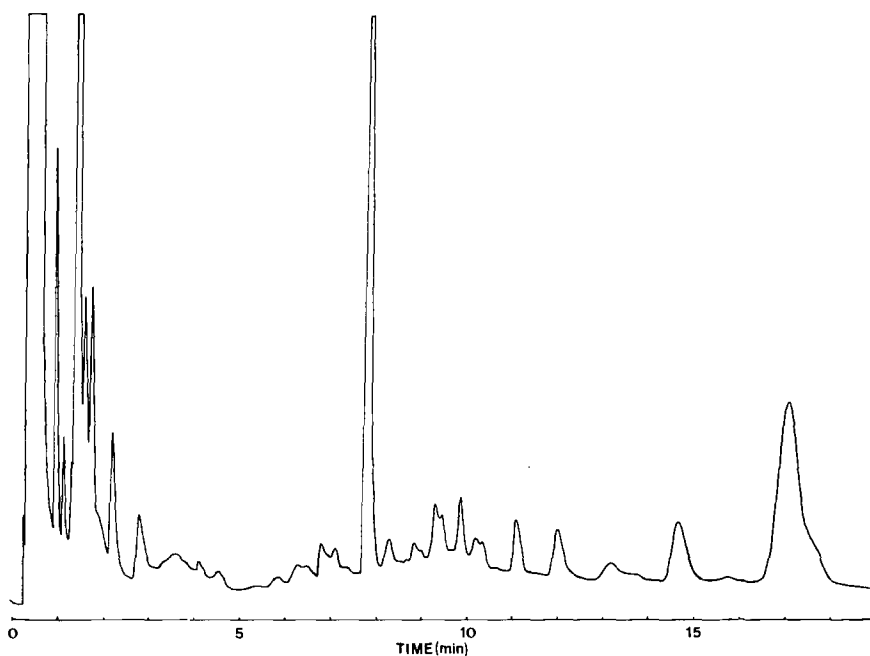


FIG. 3—Chromatogram of powder removed from a second Remington .22-caliber rimfire cartridge.

minor constituents of a smokeless powder can be used to obtain highly individual characteristics and that a combination of the two examinations can be of even more value in limiting the number of possible sources of a powder sample.

Summary

The examination of the major constituents of smokeless powders by examining chromatograms of their pyrolysis fragments is the most sensitive method of characterizing these propellants. By thermally degrading milligram and sub-milligram samples at 500°C characteristic chromatograms have been obtained from 40 different brands and lots of smokeless powder. This method is more rapid than previously reported methods of examination and greatly reduces the quantity of sample necessary for testing.

References

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