Jan Andrasko, Ph.D.[1]

Characterization of Smokeless Powder Flakes from Fired Cartridge Cases and from Discharge Patterns on Clothing

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ABSTRACT: Shooting experiments over short distances (30 to 50 cm) deposited apparently non-burnt and partially burned flakes of smokeless powder propellants on clothing around the bullet holes. An approach was made to compare the propellant particles recovered from the clothing with those from a particular cartridge. Evidence of this kind may help the police to identify a shooter in cases when weapon or bullet or both are not found. Gas chromatography and high-pressure liquid chromatography were the analytical techniques used.

A series of shooting tests with various types of ammunition produced by different manufacturers was performed. The analyses were expected to reveal which of the shootings used the same kind of ammunition. Predictions were correct in all these experiments.

The analyses of propellant particles collected from clothing or from fired cartridges could also distinguish between a number of different production lots from the same manufacturer.

KEYWORDS: criminalistics, firearm investigations, propellant analysis, smokeloss powder, high pressure liquid chromatography, gas chromatography

The need to analyze smokeless powders in forensic science has been stressed in two main areas. First, smokeless powders are encountered in connection with improvised explosive devices (IED)—both exploded and unexploded. Numerous analytical methods have been reported for identification of propellants. A review of these methods has recently appeared [*1*]. Secondly, after the discharge of a firearm, traces of propellants are deposited on the hands and clothing of the shooter. These traces can be analyzed to determine whether a suspect has fired a gun. Generally, two different systems have been developed for this type of analysis, the same systems are also used for the detection of trace amounts of explosives. The first system uses high pressure liquid chromatography (HPLC) equipped with some kind of electrochemical detector [*2–5*]. The second system consists of a gas chromatograph (GC) connected to the thermal energy analyzer (TEA) [*6–8*]. Both systems have the sensitivity and the specificity required for trace analyses, where ng quantities of nitroglycerine and other explosives are found in complex matrixes.

In this study, another application of smokeless powder analysis has been investigated. The flakes of smokeless powder were collected from the clothing, surrounding the area of the bullet hole. Such flakes, partially burned or apparently non-burnt, can usually be found on clothing when the shooting distance is sufficiently short (less than 50 cm). An

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[1]Research associate, The National Laboratory of Forensic Sciences, Linköping, Sweden.

approach was made to compare the propellant particles recovered from clothing and those from a particular cartridge or ammunition box found in a suspect's possession. The aim of such an analysis is to help the police to identify a shooter in case when weapon or bullet or both are not found. This analysis can be combined with the measurement of lead isotope ratios of bullet fragments [*9*,*10*] recovered from the same clothing.

In our laboratory, we have performed the measurements of lead isotope ratios on different production lots of .357 Winchester Magnum ammunition in connection to a homicide case [*10*]. At the same time, we analyzed smokeless powder from these production lots to investigate the possibilities of differentiating between the different production lots by combining these two methods.

Only visible flakes of smokeless powder were analyzed in this work. No trace-analysis equipment was necessary. The analytical methods used were HPLC and GC for the analysis of organic constituents of propellants.

Materials and Methods

Propellant Composition

Smokeless powders are grouped into three basic categories—single, double, and triple base. Single-base powders consist mainly of nitrocellulose (NC). A powder containing nitroglycerine (NG) in addition to NC is classified as double base. Triple-base powders contain NC, NG and nitroguanidine salts. Most smokeless propellant powders for small arms are either single or double-base types. Triple-base powders are used in rockets and military ordnance.

In addition to major constituents, smokeless powders also contain stabilizers, such as diphenylamine (DPA), ethyl centralite (EC), 2-nitro diphenylamine (2-nitroDPA), burning modifiers, such as 2,4- and 2,6-dinitrotoluenes (2,4-DNT, 2,6-DNT), plasticizers, such as dibutylphtalate (DBP), coating ingredients etc. [*1*].

Stabilizers (the most common is DPA) are added to prolong the safe storage time of smokeless powders. Different nitrogen oxides liberated in the degradation of NC on storing react with DPA to form various nitro- and nitrosoderivatives. Thus 2-nitroDPA, 4-nitroDPA, N-nitrosoDPA and sometimes even dinitro- and trinitroderivatives of DPA are found in smokeless powder. An analysis of these decomposition products together with that of other additives should be valuable to differentiate between propellants from different production lots.

HPLC Analysis

HPLC chromatograms were run on a Varian Model 5000 liquid chromatograph equipped with a variable wavelength detector (Model 100). The detector wavelength was set to 385 nm. This wavelength was chosen for rather selective detection of the various nitroso- and nitrocompounds present in propellant extracts. These compounds exhibit absorption maxima in the range 350 to 450 nm and give the extract yellow color. A fixed wavelength UV-detector operating at 254 nm was connected in series with this detector. The various constituents in propellant extracts, including NG, were detected. The sensitivity for NG was low because NG shows UV absorption at shorter wavelengths.

The HPLC column used was a 5-μm Spherisorb ODS-2 (4.0 by 250 mm) reversed phase column (Pharmacia LKB) equipped with 5 μm 4.0 by 30 mm guard cartridge. The temperature was 25°C. The injections were made by means of a valve injector (Rheodyne type 7125) with 10-μL sample loop. The amount injected corresponded to about 50 to 100 μg propellant. The mobile phase consisted of 70% methanol and 30% water, and the flow rate was 0.9 mL/min. The analyzes were carried out under isocratic conditions.

The methanol was of ordinary HPLC grade. This HPLC system was found adequate for the analysis of stabilizers and their derivatives used for comparison of propellants in this study. More sophisticated HPLC systems may be applied.

Propellant samples were extracted using methylene chloride. The solvent was added to the propellant samples in glass test tubes and left to stand overnight in darkness. After extraction, the solvent was evaporated using flow of nitrogen and the dry sample dissolved in methanol. This procedure may cause some loss of NG, but NG was not not used for quantitative comparison of propellants. The injections were made with 10 μl portions of this extract.

GC Analysis

GC analyses were performed on a Hewlett-Packard 5880A gas chromatograph equipped with flame ionization detector and a 0.22-mm by 15 m DB-5 fused silica capillary column (J&W Scientific). The thickness of the bonded phase was 1.0 μm. The average linear gas flow rate was 40 cm/s of helium. The split ratio was 20 to 1. The analytical conditions were: initial temperature 50°C, ramp 8°C/min to 280°C, final time 5 min. Injector temperature was 200°C and detector temperature was 280°C. The relatively low injector temperature was chosen to detect some thermally labile compounds, particularly NG. The amount injected corresponded to about 50 to 100-μg propellant.

Propellant samples were extracted using 20% methanol in toluene. The solvent was added to the propellant sample and the samples were left to stand overnight (in darkness).

Shooting Experiments

All the experiments described in this study were conducted in a laboratory. White laboratory coats hanging on the walls in the test shooting room of our laboratory served as clothing. The test shooting was carried out with various weapons and different types of ammunition. The shooting distance was generally 30 to 50 cm. The fired cartridges were taken for examination.

Collection of Propellant Samples

Samples of unburnt propellant were taken from unfired cartridges after removing the bullet.

Flakes of smokeless powder were removed from the fired cartridges using tweezers and cotton wool.

Propellant flakes on clothing were examined with a light microscope at low magnification ($\times 10$). The flakes were removed from the clothing mechanically, using tweezers. In some experiments (the experiments with Winchester .357 Magnum ammunition) three groups of flakes were collected separately—apparently non-burnt flakes, partly burnt flakes (flakes slightly deformed on comparison with the unburnt powder) and heavily burnt flakes (small fragments with variable shape, not resembling the original powder). In other experiments, only the best looking flakes were chosen for analysis.

Data Comparison

The comparison of two chromatograms obtained from the analysis of propellants of qualitatively different composition did not need any data manipulation.

The comparison of chromatograms obtained for propellants from different production lots from the same manufacturer is more complicated. Ratios between various peaks in the chromatograms may vary from lot to lot, but there are no qualitative differences.

Some data manipulation is also needed when the chromatograms obtained for the fired propellant (collected from clothing or fired cartridge) are compared with those from the unfired propellant. The question is whether the propellant flakes found on clothing can originate from the suspect ammunition box.

To compare this kind of chromatograms we have used a correlation analysis described by Keto [*11*] for comparison of smokeless powder by pyrolysis gas chromatography. For any two chromatograms A and B, the correlation function C is defined as

$$C = \frac{\sum_{1}^{n} (A_i B_i)^2}{\sum_{1}^{n} A_i^2 \sum_{1}^{n} B_i^2} * 100$$

where A_i and B_i are peak areas (or peak heights, as we have used) for peak number i in the Chromatogram A and B. In total, n peaks are taken for comparison. The correlation value C is 100 times the value of square of the cosine of the angle between the chromatograms A and B when plotted as vectors in n-dimensional space. Each dimension represents the area of one chromatographic peak. The value of C is 100 for identical chromatograms and this value decreases with increasing dissimilarity between the chromatograms. The use of correlation values is an advantage in the comparison of chromatograms obtained for fired propellants, since its value is independent of sample size.

We have also used the Euclidean distance between the points in n-dimensional space. In this calculation, the data must be normalized. The data were divided into three groups—GC peaks in one group, HPLC peaks detected at 254 nm in one group and HPLC peaks detected at 385 nm in one group. The data were then normalized so that the sum of the values in each group was set to 100. If only HPLC chromatograms were taken for comparison, the data were similarly divided into two groups.

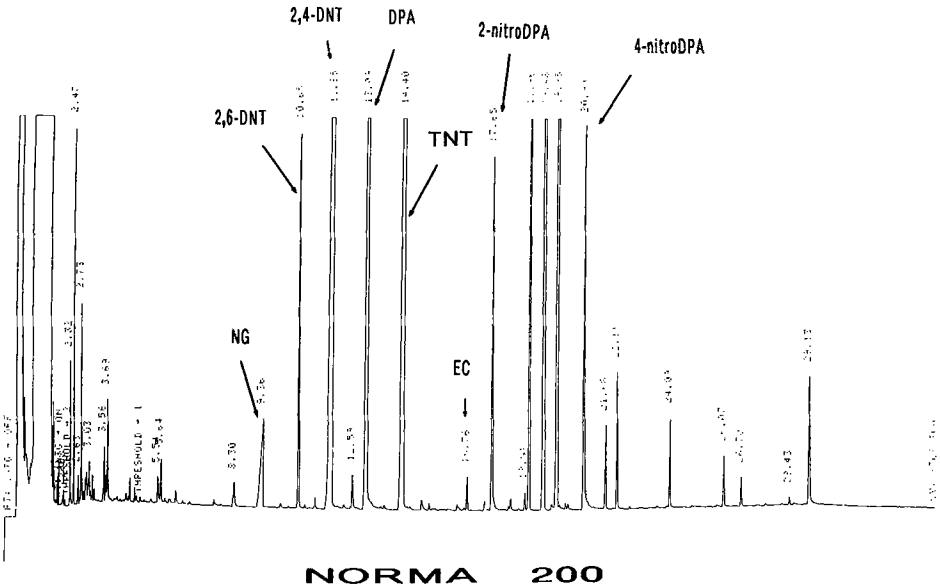
To calculate the correlation value C according to the expression above, the peak areas A_i and B_i should be weighted in some manner. Without weighting, only the strongest peaks influence the value of C. Thus, two chromatograms exhibiting a similar composition of strong peaks, but showing serious dissimilarity in small peaks will give high values of C. We have tested several weighting functions in our data manipulation—logarithmic, standard deviation, square root and also the division of each peak area by the mean value of the area of the corresponding peak within the group of chromatograms taken for comparison. The best results were achieved when standard deviation was used for data weighting. The values of standard deviations were calculated for each of the peaks taken for comparison from repeated analyses of non-burnt propellant samples from the same ammunition cartridge. Each value of the peak area was divided by the corresponding standard deviation calculated for this peak.

It must be emphasized that only some of the GC and HPLC peaks were used for comparison.

Results and Discussion

Unburnt Smokeless Powder

Gas Chromatography—Gas chromatography is a valuable method for propellant analysis [*12*]. Capillary GC can resolve and detect most of the chemical compounds in smokeless powders, except the main component—nitrocellulose. An example of GC-analysis of Norma 200 (rifle propellant) is shown in Fig. 1. Components of low volatility (such as di- and trinitrodiphenylamines) and thermally labile compounds are not suitable for



NG—trinitroglycerine **TNT**–2,4,6-trinitrotoluene
DNT—dinitrotoluene **EC**—ethylcentralite
DPA—diphenylamine **nitroDPA**—nitrodiphenylamine
The amount injected corresponded to about 50 μg propellant. Split: 20:1.

FIG. 1—*An example of GC analysis of unfired smokeless powder (Norma 200). The identification of the various compounds in this chromatogram is based on the comparison of retention time with the actual compound.*

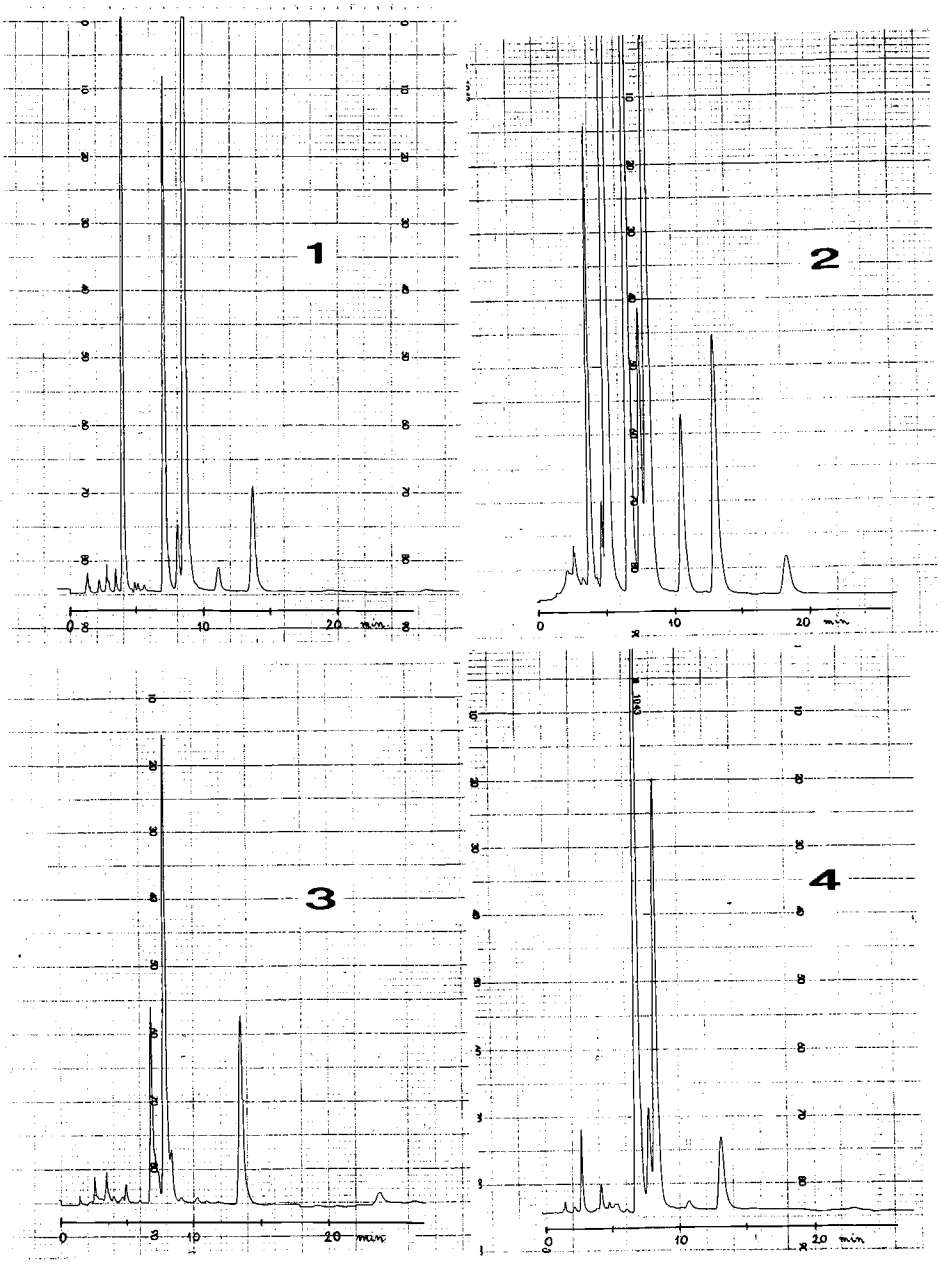
GC analysis. It is possible to detect nitroglycerine but this cannot be analyzed quantitatively by conventional fused silica capillary columns. Diphenylamine, centralites, dinitrotoluenes and dibutylphthalate formed well shaped GC peaks, whereas 2-nitroDPA and 4-nitroDPA peaks exhibited some tailing, which became more pronounced on repeated injections of sample.

More than 20 propellant samples from various manufacturers were analyzed by this technique. All these samples could be distinguished, the differences being of qualitative character.

GC analysis is sufficiently sensitive to analyze single propellant flakes, even for ammunitions with small size particles, such as .357 Winchester Magnum ammunition.

HPLC—HPLC was found to distinguish between many manufacturers of smokeless powder. This agrees with previously published data [*13*]. The sensitivity of this method is sufficient to analyze single propellant flakes. The thermally unstable and non-volatile constituents of smokeless powders may be analyzed by HPLC. Compounds such as N-nitroso-DPA, various dinitro- and trinitroDPAs and NG can be determined quantitatively. In our experimental arrangement, the detection sensitivity for NG is low, because NG shows weak absorbance at 254 nm and no absorbance at 385 nm. Some examples of the chromatograms obtained for smokeless powder from 4 different manufacturers of .22 rimfire ammunition are shown in Fig. 2.

The resolution of this method is lower than that of capillary GC. Thus, GC analysis is preferred for analyses of unburnt propellants to distinguish between different manufacturers. The advantage of HPLC is that this method can distinguish between various production batches from the same manufacturer. HPLC analyzes the degradation prod-



1—Eley 3—RWS
2—Winchester 4—Sellier & Bellot
The amounts injected corresponded to about 100 μg propellants.

FIG. 2—*HPLC-chromatograms obtained at 254 nm for propellant extracts. Four different manufacturers of .22 rimfire ammunition are represented.*

ucts in smokeless powders—many nitro- and nitrosoderivates of the stabilizers are formed on storing or are intentionally added in the production of propellants. These products are detected rather selectively using the detection wavelengths of 385 nm.

Smokeless powder from 16 cartridges of .357 Winchester Magnum metal piercing ammunition, produced at different periods between 1975 and 1982, was analyzed. About 50 powder flakes were taken for each analysis. Two or more cartridges were selected from each ammunition box. We found no qualitative differences in composition of propellant from these different production lots. The analyses suggested quantitative differences in the relative concentrations of the various constituents of the smokeless powder. These differences were much greater between different production lots than between cartridges from the same ammunition box. All 16 production lots investigated could be distinguished by HPLC, although two of the lots showed similar composition. Figure 3 shows the chromatograms obtained at 385 nm for three of the lots. We have not attempted to identify all the compounds represented by the various peaks in the chromatograms. Some of the peaks in Figs. 1 and 3 were identified only by their retention times as compared with authentic standards. Some peaks were identified from the FTIR spectra recorded on the fractions eluted from the HPLC column. The FTIR spectra of some nitro- and dinitroDPAs have been published [*14*]. The month and the year of production of ammunition boxes are also shown in Fig. 3.

Inhomogeneity in Composition of Smokeless Powder—GC and HPLC analyses performed with relatively large amounts of propellant did not show any noticeable differences on repeated analyses of the propellant from the same cartridge or from the same ammunition box. Both methods are sufficiently sensitive to be applied when only single flakes of smokeless powder are available. Such analyses would be valuable if the composition of every single powder flake from one cartridge was the same.

We obtained information about the production details of smokeless powder from the main manufacturer of propellant in Sweden. According to that source, the propellant is produced in smaller sub-batches. Samples taken from each of these sub-batches are tested in shooting experiments. The final production lot is then obtained by mixing the sub-batches in certain proportions to obtain the best product. Also, according to this source, interpretations of origin based on the analysis of single propellant flakes is not recommended, at least not when trying to distinguish between various production lots from the same manufacturer.

We have performed some analysis of single propellant particles from Norma ammunition. The samples were taken from boxes containing between 275 and 500 g of propellant. Between six and eleven particles were selected at random for HPLC analysis from each of the boxes. Five different products from FFV Norma AB were represented: rifle powders 200 (N-200), 202 (N-202), 204 (N-204), Magnum Rifle Powder (N-MRP)

1—2,4-dinitrotoluene
2—unknown
3—unknown
4—unknown
5—N-nitroso-diphenylamine
6—4-nitro-diphenylamine
7—unknown
8—2,2'-dinitro-DPA
9—2,4-dinitro-DPA (?)
10—2-nitro-diphenylamine

The injected amount: about 100 μg propellant.

FIG. 3—*HPLC-chromatograms detected at 385 nm for three boxes of unfired propellant (.357 Winchester Magnum). The year and the month of production is shown in the figure. The wavelength of 385 nm detects mainly the different nitroso- and nitroderivatives of DPA—the degradation products formed from DPA on aging of propellant, or during the production. The detection of other constituents of smokeless powder was achieved simultaneously by another UV-detector, operating at 254 nm. The identification of the various compounds in these chromatograms is based on the comparison of retention times with the actual compound and/or from FTIR spectra of the fractions collected from the HPLC column.*

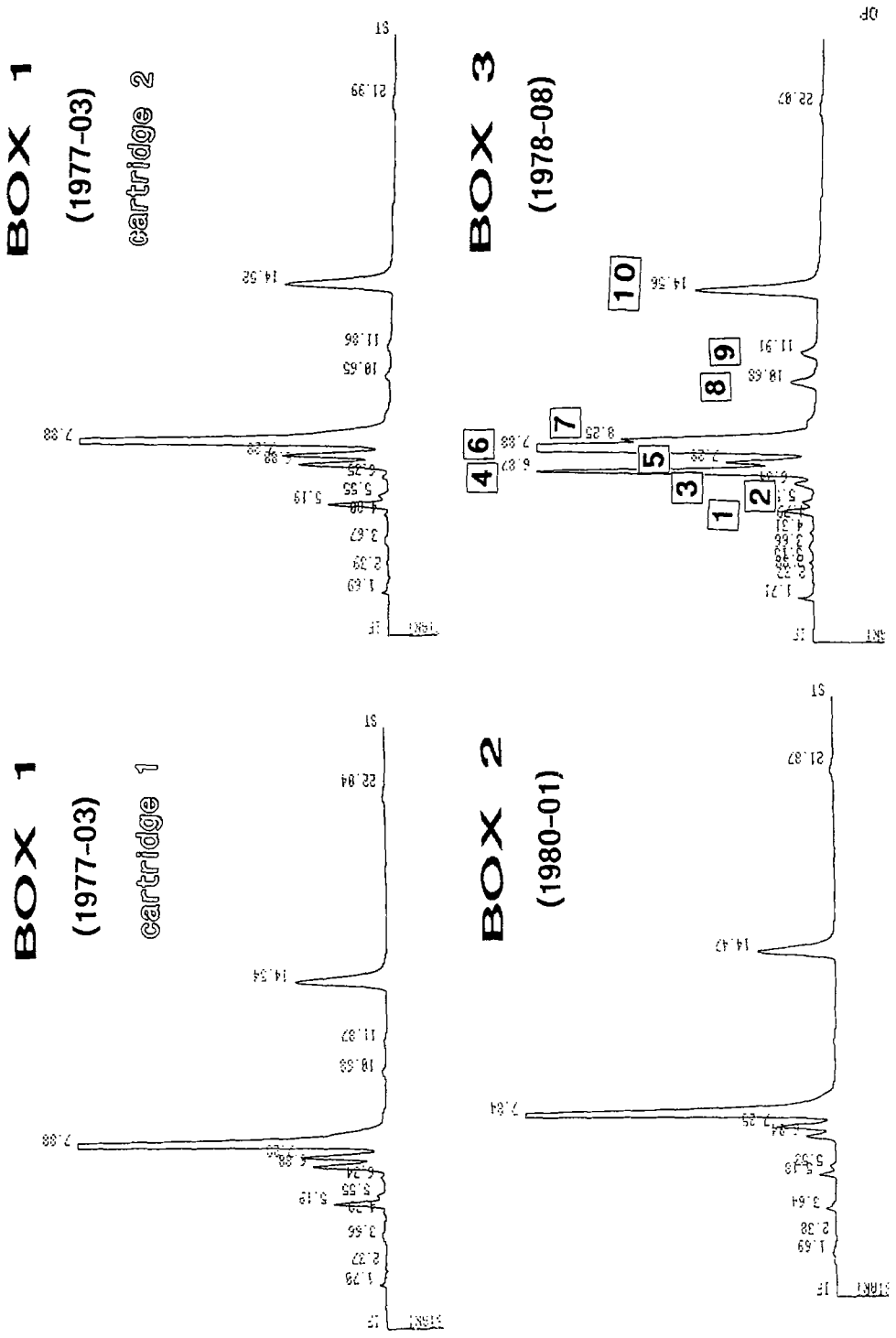

BOX 1
(1977-03)
cartridge 2
BOX 3
(1978-08)
BOX 1
(1977-03)
cartridge 1
BOX 2
(1980-01)

FIG. 3

and small gun powder R 1 (N-RP). Two boxes of the propellant 204 (N-204A and N-204B) were examined, the date of production was unknown. Thirteen relatively strong chromatographic peaks (seven peaks detected at 254 nm and six peaks detected at 385 nm) were used for comparison. The calculation of correlation values and of Euclidean distances was carried out. The composition of single flakes of the smokeless powders studied was compared with the mean value of the composition calculated for each group. The mean standard deviations were calculated for each of the chromatographic peaks to weight the data. Note that the chromatograms lacking some of the peaks were not included in the calculation of the mean standard deviation of that peak. The calculated correlation values are shown in Table 1.

Table 1 illustrates that the correlation for single flakes in each group of smokeless powder was very high—exceeding 99.6 with one exception. N202-5 exhibited somewhat different composition from its group but it still showed the best correlation with this group. The correlation based on the calculation of Euclidean distances showed the same feature.

The results in Table 1 indicate that the variation in composition of single flakes of Norma ammunition powders is not very great. The particle size of Norma smokeless powders, particularly that of rifle ammunition, is rather large (the weight of one flake is about 1 mg). Some of our experiments with small particle size ammunition (.357 Winchester ammunition) showed a greater variation in the composition of single flakes from the same cartridge. When only a single flake is available for analysis, the amount is still sufficient for distinguishing between different manufacturers because different propellants show qualitative differences in composition. Analyses of single propellant particles are generally not reliable for distinguishing between different production lots from the same manufacturer. The more propellant particles available for analysis the greater is such a possibility.

Burnt Smokeless Powder

Test Shooting with Different Types of Ammunition—We have performed a number of test shooting experiments in which the analyses of propellant flakes found on clothing around bullet hole should distinguish between different manufacturers of the propellants. Two aspects were studied, not only the possibility of identifying the ammunition used, but also possible contamination by propellant particles deposited inside the weapon used in previous shootings.

The test shootings were arranged so that five shots with four different types of ammunition of the same caliber were fired with the same weapon in each experiment. The analysis should establish, which two of the shots were from the same ammunition. In two experiments (with calibers 7.65 mm and 6.35 mm) the weapons were carefully cleaned after each shot to remove the residue from inside of the weapons. In the two additional experiments (calibers 7.65 mm and 9 mm) the weapons were not cleaned between the shots. The intervals between subsequent shots were only a few seconds.

We observed large differences between the different types of propellant in the number of particles deposited on clothing. Some of these powders, Lapua and Norma for example, deposited only a few fragments (only three in one test), whereas Winchester, Geco, and Fiocchi deposited hundreds of apparently non-burnt flakes of smokeless powder (shooting distance 30–50 cm).

Both HPLC and GC analyses were performed on the material recovered from clothing. Whenever possible, twenty of the best looking flakes were picked up for analysis. Predictions were correct in all these experiments, both with cleaned and noncleaned weapons. Qualitative differences were observed between different types of smokeless powder. There was no indication of contamination by powder particles from previous shootings

TABLE 1—*The correlation values calculated for single flakes of smokeless powder from Norma.*[a]

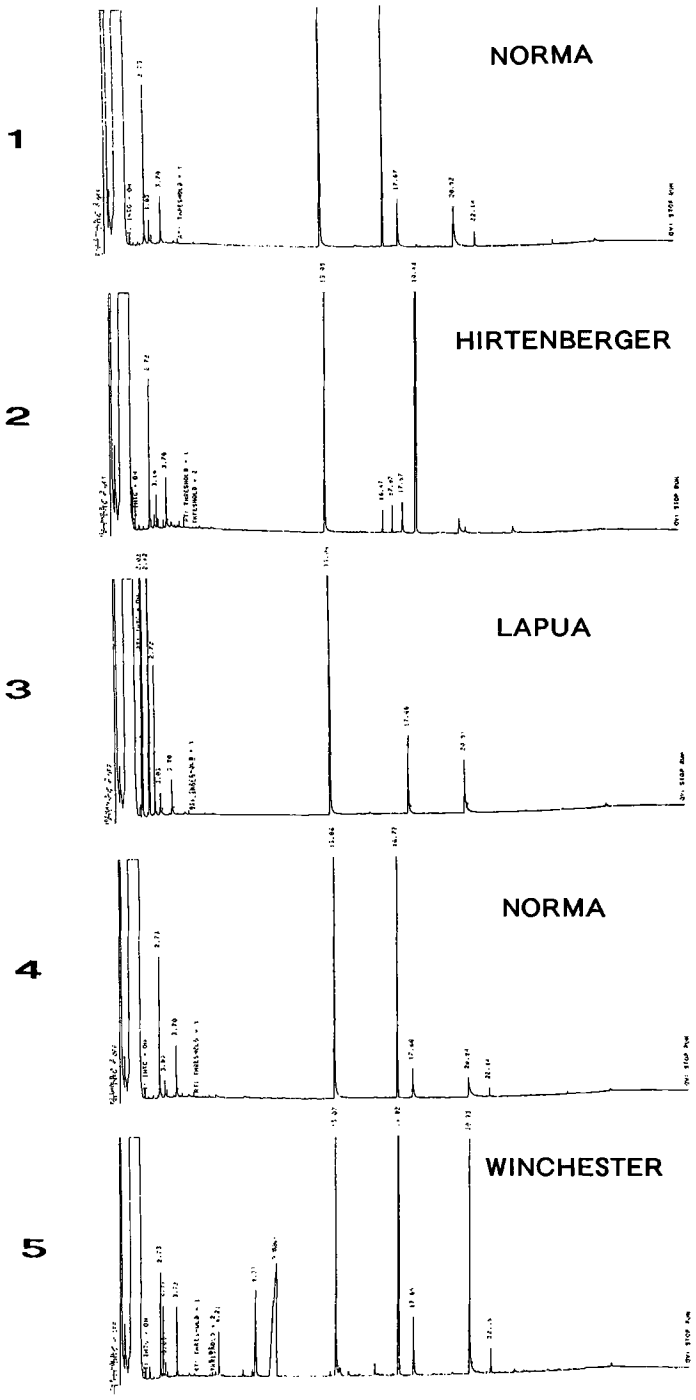
	N-200	N-202	N-204A	N-204B	N-MRP	N-RP
N 200-1	**99.96**	92.86	69.18	74.40	83.96	53.64
N 299-2	**99.87**	94.59	69.38	76.41	85.66	51.59
N 200-3	**99.85**	95.15	70.17	77.37	86.68	50.79
N 200-4	**99.70**	94.93	71.19	76.87	86.71	50.71
N 200-5	**99.98**	93.35	69.43	74.96	84.43	53.31
N 200-6	**99.93**	94.04	70.05	76.39	85.94	52.19
N 200-7	**99.89**	93.25	66.74	73.90	84.79	52.85
N 200-8	**99.91**	93.00	69.36	76.09	84.44	53.69
N 200-9	**99.82**	91.98	67.07	72.42	82.91	55.11
N 200-10	**99.75**	91.79	67.28	73.40	83.13	54.54
N 200-11	**99.91**	92.43	69.62	74.84	83.90	53.77
N 202-1	91.17	**99.78**	72.05	88.74	96.77	33.15
N 202-2	92.58	**99.88**	72.37	86.61	95.42	34.79
N 202-3	94.11	**99.86**	75.06	86.12	95.54	36.52
N 202-4	92.63	**99.79**	70.51	87.64	95.68	35.38
N 202-5	97.79	**98.72**	72.86	82.85	92.89	42.85
N 202-6	90.74	**99.60**	73.83	89.41	97.76	32.30
N 204A-1	69.74	72.67	**99.92**	76.30	71.20	22.21
N 204A-2	68.82	73.29	**99.98**	78.63	72.18	20.29
N 204A-3	64.64	68.29	**99.71**	74.20	67.14	19.03
N 204A-4	71.58	76.10	**99.81**	80.67	75.10	21.50
N 204A-5	70.12	74.66	**99.94**	79.51	73.59	20.72
N 204A-6	69.73	73.29	**99.97**	77.75	72.01	21.44
N 204B-1	73.91	86.52	78.06	**99.96**	86.51	18.64
N 204B-2	74.03	87.08	77.97	**99.90**	86.95	18.48
N 204B-3	75.83	87.12	77.94	**99.97**	86.62	20.18
N 204B-4	78.17	88.95	78.71	**99.87**	88.19	21.80
N 204B-5	76.23	87.43	77.66	**99.96**	86.91	20.55
N 204B-6	73.29	86.01	76.63	**99.94**	86.20	18.22
N MRP-1	84.34	96.04	71.45	87.23	**99.97**	27.81
N MRP-2	85.93	96.64	72.21	87.05	**99.97**	28.65
N MRP-3	84.13	96.03	71.67	88.08	**99.92**	26.69
N MRP-4	84.87	96.02	72.27	86.88	**99.97**	27.94
N MRP-5	83.69	95.52	71.64	86.89	**99.97**	26.64
N MRP-6	86.03	95.77	71.79	85.30	**99.84**	29.35
N RP-1	54.09	36.55	21.25	19.95	28.17	**99.94**
N RP-2	56.63	38.14	22.30	20.94	29.31	**99.61**
N RP-3	53.51	36.19	21.03	19.80	28.02	**99.99**
N RP-4	52.73	35.76	20.91	19.63	28.00	**99.98**
N RP-5	52.04	35.18	20.22	19.13	27.03	**99.96**
N RP-6	49.79	33.94	19.83	18.58	26.86	**99.66**
N RP-7	52.47	35.56	20.68	19.51	27.75	**99.97**
N RP-8	52.69	35.65	20.65	19.47	27.59	**100.00**

[a]Five different products from Norma are represented: rifle powders 200 (N–200), 202 (N-202), 204 (N-204), Magnum Rifle Powder (N-MRP) and small gun powder R 1 (N-RP). The comparison is based on HPLC analyses. The composition of single flakes is compared with the mean composition of each of the products. Two boxes of the propellant 204 (N-204A and N-204B) were examined.

in the experiments with uncleaned weapons. Figure 4 depicts the GC analyses of the collected propellants in one of the shooting experiments with uncleaned weapons, caliber 7.65 mm. The four different smokeless powders used were Norma, Lapua, Winchester, and Hirtenberger. The agreement between the chromatograms 1 and 4 (both Norma) as well as the disagreement between the different products is clearly seen in this figure.

FIVE SHOTS WITH FOUR DIFFERENT AMMUNITIONS

(Pistol - caliber 7.65 mm)



The agreement in composition between burnt and unburnt smokeless powder was generally very good. Some changes in the composition of smokeless powder on firing the gun have been noted. Dibutylphthalate and some small peaks in the GC chromatograms obtained for Winchester ammunition almost disappeared on shooting. These compounds are presumably added only to the surface of the propellant and are not a part of the bulk material.

It might be possible to identify the manufacturer of unknown propellant by the analysis of propellant flakes from clothing. To achieve this, many analyses of propellant from various manufacturers produced over several years must be carried out under the same analytical conditions. Identifying the caliber of the ammunition used is not always possible, because the same kind of propellant may be used in several calibers from the same manufacturer.

The chromatograms presented in Fig. 4 were obtained when analyses were performed immediately after the test shootings. The clothing with the fired propellants of Hirtenberger and Winchester manufacture was stored inside the laboratory about 2 m from the window, exposed occasionally to sunshine. After 12 days, new samples of propellant flakes were collected and analyzed by GC. The resulting chromatograms were virtually the same as those obtained for fresh samples.

Test Shootings with Ammunition from the Same Manufacturer, Produced at Different Occasions—A number of shooting experiments were performed using different ammunition boxes with .357 Winchester Magnum ammunition. The year, the month and the day of production was known. The boxes were taken from our collection of this type of ammunition. Bullet samples from each of these boxes were also analyzed for lead isotope ratios [*10*].

A minimum of five samples were collected in each of the shootings—three types of samples from the clothing (apparently non-burnt flakes, slightly burnt flakes and heavily burnt flakes), one sample from the fired cartridge case and one sample of unfired propellant from another cartridge from the same ammunition box. To obtain the best flakes according to the categories mentioned above, separate shootings were performed for GC and HPLC analyses, respectively. The particle size of Winchester smokeless powder is very small. Twenty or more flakes of smokeless powder were collected for each analysis to avoid uncertainties in the analyses because of variations in composition from particle to particle. Twenty is also the approximate number of particles of smokeless powder that were generally recovered from fired cartridge cases. The number of particles recoverable from clothing was much higher for the shooting distance used in this work.

Smokeless powder from Winchester ammunition (.357 Magnum) consists of many different compounds. Among others, nitroglycerine (NG), diphenylamine (DPA), dinitrotoluenes (2,4-DNT and 2,6-DNT), dibutylphthalate (DBP) and many nitroso- and nitroderivatives of DPA. However, another stabilizer frequently present in propellants, ethylcentralite (EC), was found only in trace amounts.

Figure 5 depicts the dual-wavelength HPLC analysis of .357 Winchester Magnum propellant and the compounds that were taken for comparison between different production lots. Some of these compounds were detected at two wavelengths, and both peaks were taken for comparison independently, as two different compounds. HPLC did not achieve baseline separation between the peaks detected and also, it is not always certain that the peak detected at single wavelength represents only one compound. Thus,

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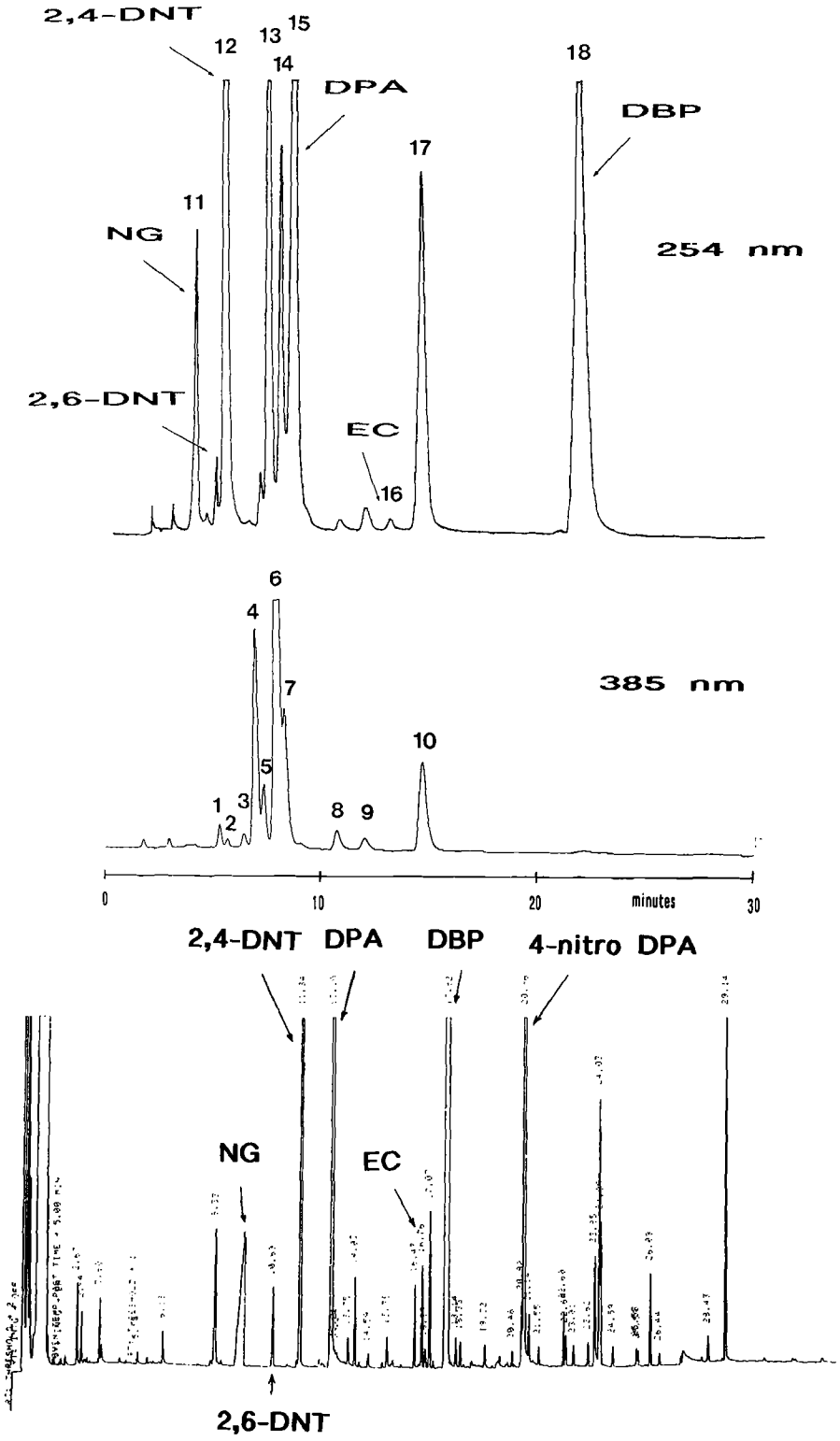
◄ FIG. 4—*GC analyses of propellant flakes collected from clothing in a series of test shootings. Five single shots were fired with the same weapon (pistol—caliber 7.65 mm) with four different ammunitions. The analyses should indicate, in which two of the shots the same kind of ammunition was used. The weapon was not cleaned between the firings. The injected amounts corresponded to about 50 to 100 μg propellants.*


2,4-DNT
12
13
15
14
DPA
18
DBP
17
11
NG
254 nm
2,6-DNT
EC
16
6
4
7
385 nm
10
5
1
3
2
8
9
0
10
20
minutes
30
2,4-DNT
DPA
DBP
4-nitro DPA
NG
EC
2,6-DNT

counting some peaks twice in data comparison improved the reliability in the analysis of stabilizer derivatives. Standard deviation was calculated for each of the peaks independently and used the data weighting. The lowest part of Fig. 5 shows the chromatogram obtained for the same sample by GC.

Our analyses showed some general changes in the composition of smokeless powder on firing the gun. The concentration of DBP decreased to below 10% of its original value. Also, the NG content of the fired propellant decreased significantly. These changes were noted for every recovered particle, even for particles apparently non-burnt. The content of some other constituents of smokeless powder was influenced by the shooting. This phenomenon was more pronounced in the analyses of heavily burnt flakes and affected mostly some of the compounds detected at 385 nm. In summary, the following effect of shooting was found:

No change	Peaks 1, 10, 12, 16, 17
Slight increase	5, 6, 8, 9, 13, 14
Slight decrease	15
Increase	2, 3, 4
Decrease	11
Large decrease	18

The effect of slight decrease or increase of peaks was in reality observed only for heavily burnt flakes. On the basis of these observations, the areas under the peaks 2, 3, 4, 7, 11, and 18 were not used for the correlation analysis carried out on .357 Winchester magnum propellant.

Figure 6 illustrates the use of HPLC analysis to distinguish between different production lots from the same manufacturer after firing. Five different production lots were analyzed. Four of these production lots (1977-03, 1980-01, 1978-08, and 1979-10) were found indistinguishable by lead isotope measurements. The ratios between the peak areas for four of the most stable (on shooting) compounds were used in this figure. The clusters for the different production lots are naturally larger in this figure, compared with the corresponding figure for unfired propellants. Nevertheless, the lots found indistinguishable by measurements of lead isotope ratios are found clearly distinguishable by HPLC analysis of the fired propellant.

The results of correlation analysis carried out on the production lots presented in Fig. 6 are shown in Table 2. The correlation values for fired propellants and propellants from the discharged cartridges on comparison with the unfired propellants have been calculated. The composition of the unfired propellants used for comparison was a mean value of several independent analyses. The mean standard deviations for the peaks taken for comparison were also obtained from these analyses.

◄ **NG**—nitroglycerine **EC**—ethylcentralite
DNT—dinitrotoluene **DBP**—dibutylphthalate
DPA—diphenylamine
Some of the peaks detected at 385 nm are identified in Fig. 3.
Lower part: *GC chromatogram obtained for the same sample. The amounts injected corresponded to about 100 μg propellant in each of the analyses.*

FIG. 5—Upper part: *Dual-wavelength HPLC analysis of unfired .357 Winchester Magnum propellant (1980-01). The numbered peaks were considered for comparison between different production lots of the same manufacturer. Some of these peaks were, however, found unsuitable for the calculation of correlation values between fired and unfired propellants.*

HPLC - ANALYSIS

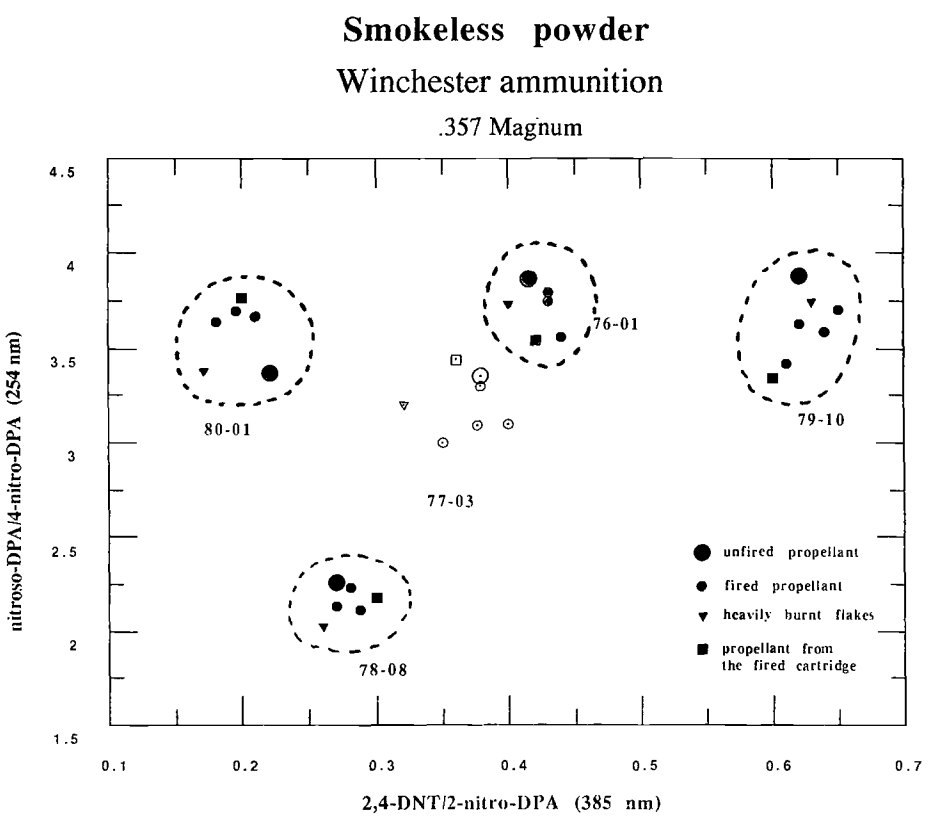


FIG. 6—*An illustration of the possibility of HPLC-analysis to distinguish between different production lots from the same manufacturer (.357 Winchester Magnum) after firing. The analyses of unfired propellant, fired propellant (apparently non-burnt, slightly burnt or heavily burnt flakes) and also propellant recovered from the fired cartridge, are shown in this figure. The bullets from four of these five production lots (1977-03, 1980-01, 1978-08, and 1979-10) were found indistinguishable by lead isotope measurements. All the groups depicted in this figure were found distinguishable by correlation analysis (Table 2).*

It can be seen in Table 2 that the highest correlation values are those between fired and unfired propellants from the same production lot. These values were generally higher than 99.0, with some exceptions for heavily burnt flakes. Correlation analysis can thus distinguish between these five production lots. The best correlation with unfired propellant was obtained for apparently non-burnt flakes and flakes recovered from the fired cartridges.

The calculation of Euclidean distances was performed in parallel with that of correlation values. Also this type of comparison correlated fired propellant to unfired propellant from the same production lot.

The correlation analysis was also carried out using GC chromatograms. GC analysis could distinguish between some but not all the production lots investigated.

TABLE 2—*The correlation analysis carried out on some of the samples in Fig. 4. The samples of fired propellants are compared with corresponding samples of unfired propellant. Five different production lots of Winchester .357 Magnum are compared at this table.*[a]

	77-03	80-01	78-08	79-10	76-01
77-03 f1	**99.65**	81.62	78.90	94.16	98.13
77-03 f2	**99.62**	79.40	75.23	92.38	97.76
77-03 1b	**99.17**	82.04	80.12	94.97	97.98
77-03 hb	**98.59**	79.42	79.32	93.68	96.81
77-03 c	**99.03**	82.32	79.87	94.82	97.58
80-01 f1	76.03	**99.61**	84.54	93.00	85.22
80-01 f2	78.07	**99.85**	86.89	94.22	87.05
80-01 1b	82.41	**99.13**	83.85	94.92	90.60
80-01 hb	73.58	**98.01**	90.46	92.63	82.99
80-01 c	79.76	**99.80**	86.67	95.02	88.14
78-08 f1	74.58	83.96	**99.88**	89.43	80.21
78-08 f2	76.57	85.78	**99.77**	90.87	82.28
78-08 1b	67.65	81.91	**99.70**	85.23	74.35
78-08 hb	68.10	81.46	**99.38**	85.42	74.58
78-08 c	76.32	85.39	**99.89**	90.48	81.85
79-10 f1	91.64	94.43	91.01	**99.94**	95.88
79-10 f2	91.84	93.25	91.48	**99.85**	96.06
79-10 lb	89.97	94.72	91.97	**99.81**	94.79
79-10 hb	88.81	93.86	92.81	**99.33**	93.98
79-10 c	90.92	94.93	90.27	**99.87**	95.63
76-01 f1	97.33	89.49	83.71	97.45	**99.84**
76-01 f2	97.59	85.97	79.17	94.32	**99.88**
76-01 1b	97.29	89.30	83.60	97.78	**99.70**
76-01 hb	96.85	85.42	76.32	93.30	**99.11**
76-01 c	96.57	90.01	85.35	97.04	**99.26**

[a]The experimental data were obtained from HPLC-analyses at 254 and 385 nm. In total, 12 HPLC peaks were taken for comparison (some of these peaks are detected at both wavelengths but considered as two different peaks). Nitroglycerine, dibutylphthalate and the Peaks 2, 3, 4, and 7 from Fig. 4 were not used for this comparison, because the concentration of these compounds was found to change significantly on shooting.

Explanations to this table:

1977-03	Unfired propellant from another cartridge but the same box
1977-03 f	Fired propellant, apparently non-burnt
1977-03 1b	Fired propellant, lightly burnt
1977-03 hb	Heavily burnt propellant
1977-03 c	Propellant recovered from the fired cartridge

Summary and Conclusions

In this study, flakes of smokeless powder collected from clothing round the bullet holes were analyzed using two analytical techniques—gas chromatography (GC) and high pressure liquid chromatography (HPLC). The aim of these analyses was to help the police to find a shooter in cases when the weapon or the bullet or both are not found. The composition of propellant particles recovered from the clothing can be compared with that of unfired propellant from a particular cartridge (from the same ammunition box).

Propellant flakes were generally found on clothing in our shooting experiments for shooting distances shorter than about 50 cm. The amount of propellant recoverable from clothing was sufficient for the analytical techniques used. Subsequent shootings with the

same weapon using ammunition from various manufacturers did not indicate any contamination from the propellant flakes from previous shootings.

GC and HPLC analyses could distinguish between the propellants from different manufacturers. A series of test shootings with various types of ammunition produced by different manufacturers were performed. These results suggest that the analyses of the propellant flakes collected from clothing should reveal which of the shootings used the same kind of ammunition. Four such shootings with different weapons and calibers were carried out. Predictions were correct in all these experiments.

GC analyses were better than HPLC analyses in distinguishing between various manufacturers of smokeless powder. It might be possible to identify the manufacturer of unknown propellant by the GC analysis of propellant flakes from clothing.

On the other hand, HPLC analysis detects the various degradation products in smokeless powder—many nitro- and nitrosoderivatives of diphenylamine—formed on storing or in the production of propellant. Such an analysis can distinguish between various production lots from the same manufacturer. In the shooting experiments performed in this study, HPLC analysis was successful in distinguishing between different production lots of .357 Winchester Magnum ammunition after firing. The correlation between fired and unfired propellants from the same ammunition box was very high.

Although similar information is derived from HPLC and GC analyses of smokeless powders, it is not completely redundant and thus it is advantageous to combine both methods in the analyses of fired propellants recovered from clothing.

To compare the GC and the HPLC chromatograms the calculations of correlation functions and Euclidean distances were performed in this study.

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Address requests for reprints or additional information to
Jan Andrasko, Ph.D.
The National Laboratory of Forensic Sciences
S-581 01 Linköping
Sweden