

## Time Since Discharge of Shotguns

**REFERENCE:** Andrasko J, Norberg T, Ståhling S. Time since discharge of shotguns. *J Forensic Sci* 1998;43(5):1005–1015.

**ABSTRACT:** A method for estimation of the time since the latest discharge of a shotgun is presented. This method is based on SPME (Solid Phase Micro-Extraction) sampling from the atmosphere inside the shotgun barrel. Two analytical systems were used in parallel, the GC/TEA and GC/FID(MS) system. These two systems detect various combustion products and the estimation of time since the latest discharge is based on the rate of escape of the volatile discharge residues from the barrel as a function of time. If the ammunition used in the suspect firearm is known, the use of decay curves for the actual firearm and the actual ammunition is fairly straightforward. For unknown ammunition, repetitive samplings must be performed and the results fitted to decay curves obtained for other ammunition types according to the proposed procedure. Generally, the method presented in this study can give an indication whether a weapon was fired, e.g., 2 to 3 days, 1 to 2 weeks, or more than 3 weeks ago. Some factors that may impact data interpretation were studied, such as the effect of cleaning the barrel, the number of shots fired, the eventual disturbance to the system by SPME sampling and the effect of temperature of the storage.

**KEYWORDS:** forensic science, firearms, time since discharge, SPME, gas chromatography (GC), GC-TEA, firearm discharge residues

Estimation of the lapsed time since a firearm or a cartridge was fired is an important aspect of firearm investigations. A frequently occurring task is to decide if a firearm was fired recently or a long time ago.

When a modern firearm is discharged, the nitrocellulose based propellant (smokeless gunpowder) generates various firearm discharge residues of both gaseous and solid compounds. The amount of gases and other firearm discharge residues remaining inside the barrel after firing depends on the type and manufacturer of propellant used, type of firearm, length of barrel, and many other factors. After firing, the gaseous and other volatile discharge residues escape from the barrel with time and the measurement of this escape phenomenon is a basis for estimating the time since discharge of the weapon. The rate of escape is influenced by many factors such as the temperature of storage, the treatment given to the firearm after firing, type of weapon and the amount of discharge residues formed on shooting.

The effect of type of firearm causes no problem to the investigator, since the weapon itself is a subject of examination and can be test fired. The other factors are more difficult to deal with and are not always known to the investigator.

The complexity of this problem is presumably the reason that

<sup>1</sup> SKL, National Laboratory of Forensic Science, S-58194 Linköping, Sweden.

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only few efforts to estimate time since the latest discharge of a firearm have so far appeared in the literature. Most studies deal with quantitative analyses of gases escaping from firearms or cartridges, namely carbon monoxide (1), nitrogen oxides (2) and nitric oxide (3,4). Unfortunately, these studies comprised only a limited number of experiments and used only one type of ammunition. Generally, the gas escape methods should be suitable for answering the question if a firearm has recently been fired, since gases escape relatively quickly from the barrel. Treatment of the firearm such as opening of the breech after firing might, however, clearly influence the results.

Some other methods for detection of variations of the combustion products in the weapon's barrel with time have been reported (5,6). These experiments included barrel washings or dry swabs pushed through the barrel. The problem with these methods is a difficulty to extract the total quantity of combustion products (for correct quantitative analyses) and that repetitive sampling is not possible. Recently, changes in the composition of organic gunshot residues with time after firing were reported (7).

In this study, solid phase microextraction (SPME) was employed for detection and quantitative analysis of various combustion products deposited in weapon barrels. SPME is a rather new extraction technique (8–10) which has attracted increasing attention in different analytical fields for its simplicity, efficiency, good precision and low detection limits. SPME uses a fine fused silica fiber coated with a polymeric coating to extract organic compounds from their matrix and direct transfer into the injector of a gas chromatograph (GC) for thermal desorption and analysis. This technique is particularly suited for headspace samplings from limited (narrow) spaces like weapon barrels. The adsorption process is passive (diffusional), thus the disturbance to the system is minimal and repetitive sampling easy to perform.

Our efforts to estimate the time lapse since the latest discharge of a firearm were in this study focused on shotguns. The long barrels and large amount of propellant used means that the amount of discharge residues is significant. A number of partially burnt powder flakes as well as soot is deposited inside the shotgun barrels after shooting.

We are presently extending our studies on other types of weapons with long barrels as well as on fired cartridges.

### Materials and Methods

#### Test Shootings

All the test shootings were carried out using double-barreled shotguns, caliber 12/70, and various types of ammunition. To simplify some studies (e.g., effect of storage temperature) the barrels were removed from the shotguns after the shooting and the breech ends sealed by corks of suitable size.

### Solid Phase Microextraction

The SPME device was purchased from Supelco. Fused silica fibers with an 85  $\mu\text{m}$  polyacrylate coating were used in all the experiments. New fibers were conditioned at 270°C for 2 to 3 h by heating in a GC injector. Prior to sampling the fiber was conditioned for 7 min at 200°C and then allowed to cool down at room temperature for an additional 7 min. Blank analyses were performed to make sure that the fiber and the chromatographic system were clean and free from interfering substances.

### Sampling from Firearms

The double barrel was placed horizontally. SPME sampling was performed by pushing the SPME holder inside the barrel from the muzzle side. The coated fiber on the top of the SPME needle was exposed to the atmosphere inside the barrel for 30 min. The fiber position inside the shotgun barrel was always the same at a distance of 20 cm from the muzzle.

### Gas Chromatographic Analyses

Two GC systems for quantitative analysis of compounds adsorbed by headspace SPME from inside of the barrels were used in parallel.

**GC-TEA Analysis**—In this system a Hewlett-Packard 5890 Series II Plus gas chromatograph connected to a TEA Model 610 Analyzer (Thermedics Detection Inc.) was used. The TEA detector operated in nitroso mode and the pyrolysis temperature of 850°C. With these parameters nitro-, nitroso-compounds and nitrate esters (e.g., nitroglycerin) are selectively detected. The detection is sensitive and based on chemiluminescence reaction of nitrosyl radical (formed by pyrolysis of these compounds) with ozone. The GC separations were achieved on a 15 m 0.25 mm DB-5MS fused silica capillary column (J&W Scientific). The thickness of the bonded phase was 0.25  $\mu\text{m}$ . Injector temperature was 170°C,

helium gas flow 1 mL/min. The analytical conditions were: initial temperature 60°C held for 1 min, ramp 10°C/min to 200°C then 25°C/min between 200 and 250°C, final time 2 min.

**GC-FID (or MS) Analysis**—A Hewlett-Packard 5880A gas chromatograph equipped with flame ionization detector (FID) and a 0.25 mm by 15 m DB-5MS fused silica capillary column (J&W Scientific). The average linear gas flow rate was 40 cm/s of helium. Injector temperature was 200°C, detector temperature was 300°C. The thickness of the bonded phase was 0.25  $\mu\text{m}$ . The analytical conditions were: initial temperature 70°C held for 1 min, ramp 8°C/min to 280°C, final time 5 min.

Some analyses were performed on a gas chromatograph connected to a MSD detector (Hewlett-Packard 5972 series) for identification of compounds detected by the GC-FID system.

After the sampling, the SPME fiber was thermally desorbed in the injector for 7 min in splitless mode in both analytical systems described above.

## Results and Discussion

### Detection and Identification of Combustion Products Inside the Shotgun Barrel

**GC/TEA**—SPME analysis carried out one day after firing a single shot from a shotgun resulted in a number of peaks detected by this system. The TEA detector does not permit an identification of the detected compounds, but its high selectivity for nitro- and nitroso-groups means that some of the compounds may be identified on the basis of their retention times and the knowledge of their occurrence in propellants. Thus trinitroglycerin (NG), dinitroglycerin (diNG), 2,6- and 2,4-dinitrotoluene (2,6- and 2,4-DNT) have been recognized. Some other peaks, presumably representing various decomposition products of nitrocellulose, are so far unknown to us, but can easily be measured and quantified.

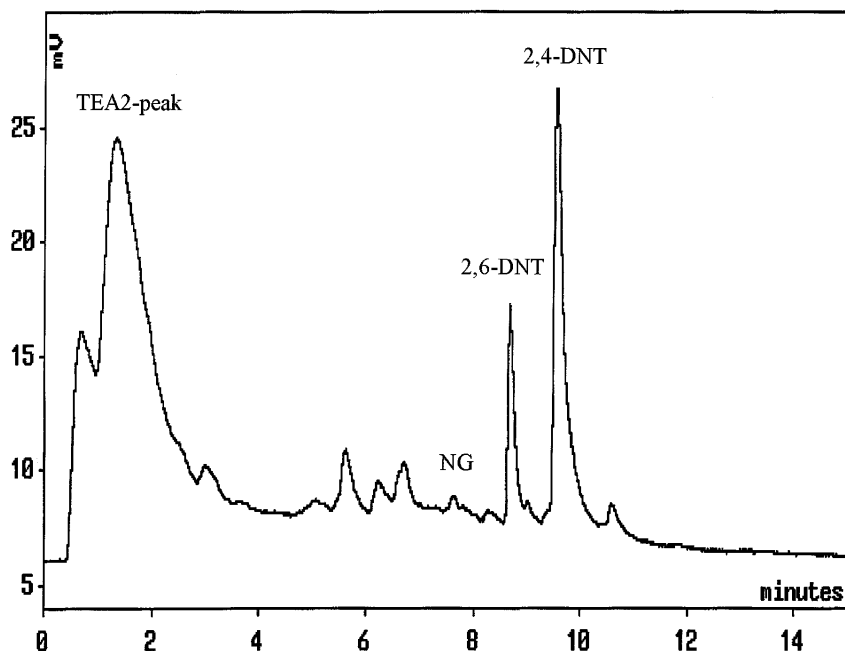


FIG. 1—The GC/TEA chromatogram obtained by SPME sampling from inside a shotgun barrel. DanArms was the ammunition used in the latest firing, which occurred eight days before the sampling. Only some of the peaks could be identified on the basis of their retention times—nitroglycerin (NG), 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT). The broad peak at the beginning of the chromatogram, designated as TEA2, is an unknown decomposition product of nitrocellulose, but in this study was used for monitoring the time lapse since the latest discharge.

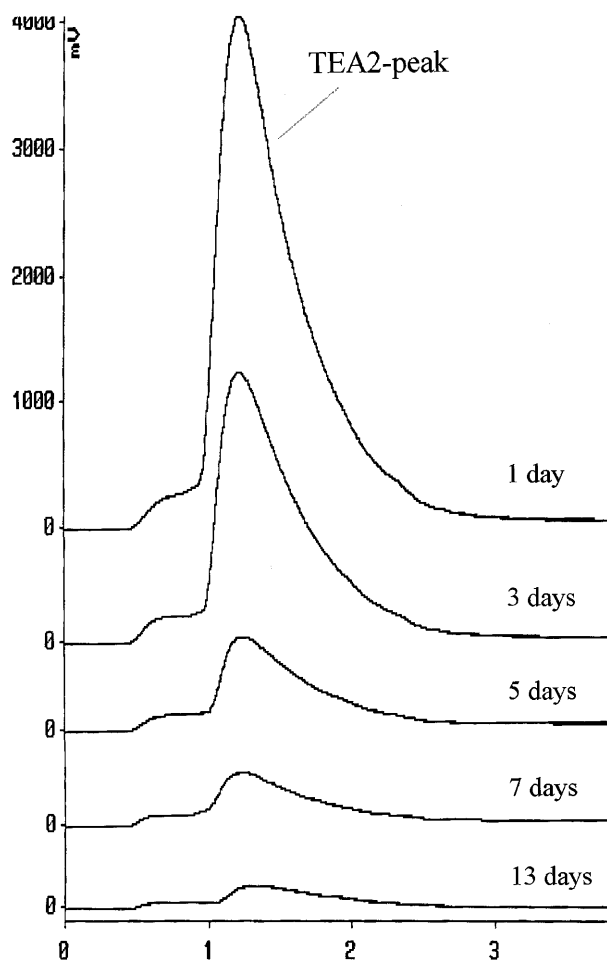


FIG. 2—The decrease of the TEA2-peak with time since discharge. Only the initial parts of the chromatograms are shown. A single shot with Bajkal ammunition was fired.

Figure 1 shows the chromatogram obtained on SPME sampling eight days after shooting with DanArms ammunition. One of the two broad peaks in the initial part of the chromatograms (designated as TEA2-peak in Fig. 1) was found to decrease with time since discharge. This decrease is rapid enough to be monitored daily, as shown in Fig. 2, and suitable for dating of the firing. The peak is not well resolved and is presumably a result of some decomposition of nitrocellulose. The TEA2-peak is not detected in unburned propellant, but was observed in SPME sampling from burned propellant. Figure 3 shows the GC/TEA chromatogram obtained from a single grain of Eley shotgun propellant burned inside a glass vial by focused light beam (using magnifying glass).

Other peaks detected by this system, such as NG and 2,4-DNT can be useful in cases when the manufacturer of the propellant used in the latest shooting has to be investigated. Volatility of these compounds is lower and thus the mean residence time inside the barrel increases. Actually, 2,4-DNT (if present in the propellant) can still be detected one year after the shooting in a shotgun stored at room temperature.

*GC/FID and GC/MS*—SPME analysis carried out one day after firing a shotgun (single shot) resulted in a large number of peaks detected by this system (Fig. 4). Many of the peaks were identified using GC/MS. The majority of the peaks represents compounds which are not present in propellants. The only strong peak originating from the propellant is diphenylamine (DPA), used as a stabilizer (Fig. 4). The other strong peaks detected, such as naphthalene, biphenyl, indol, acenaphthylene, etc., have thus been formed on burning of propellant and/or cartridge. The chromatographic profile changes with time since discharge. Generally, the peaks with short retention times decrease faster than the peaks with longer retention times, due to their higher volatility, as shown in Fig. 5.

#### Decrease of Peak Areas with Time Since Discharge

To study the rate of escape of various compounds from a shotgun barrel quantitatively we used Eley ammunition and the weapon was stored at room temperature (about 23°C). The concentration of the

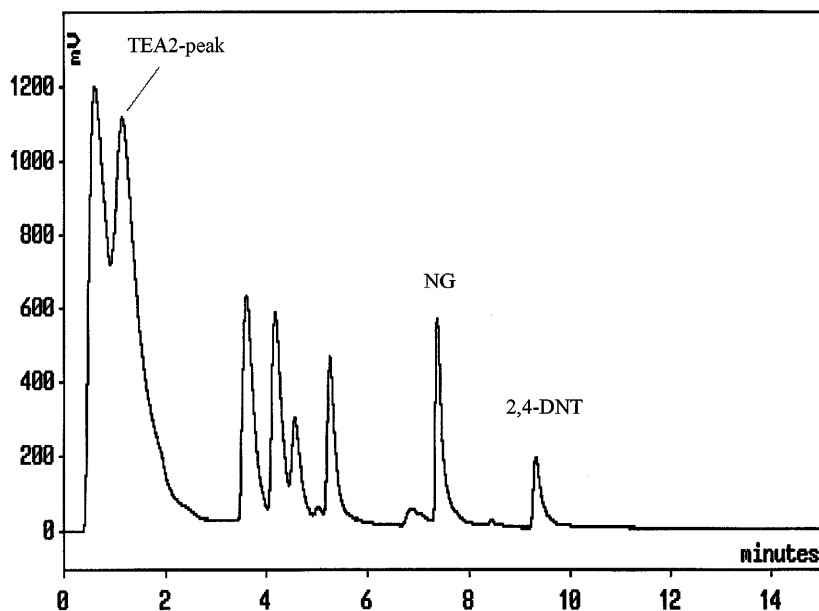


FIG. 3—The GC/TEA chromatogram obtained by SPME sampling from a single grain of burned propellant (Eley). The grain was placed inside a 1.5 mL glass vial, the vial sealed and the propellant burned by focused light beam using a magnifying glass.

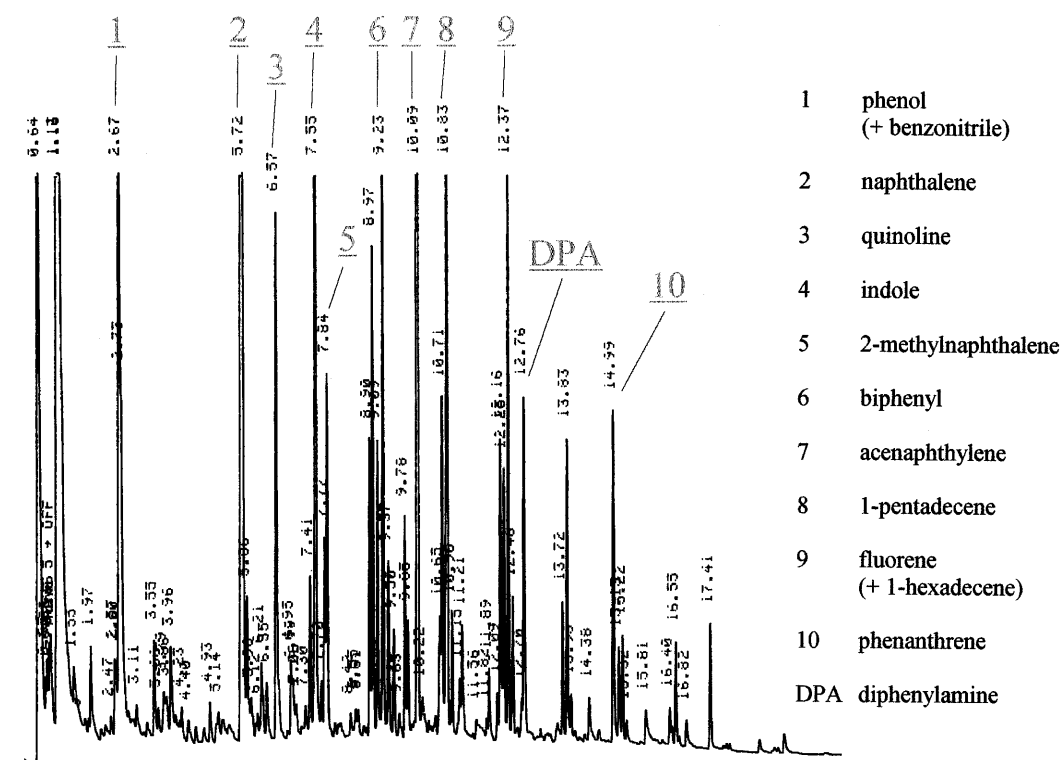


FIG. 4—The GC/FID chromatogram obtained by SPME sampling inside a shotgun barrel one day after shooting with Federal ammunition. Most of the peaks were identified by the GC/MSD system, some identifications are presented in this figure. The only stronger peak present in unburned propellant and detected after shooting was diphenylamine (DPA), which is used as stabilizer.

volatile compounds in the shotgun barrel decreased rapidly with time during the first days after shooting, followed by successively slower decreases thereafter. The decays are nonexponential, as illustrated by Fig. 6, which shows the decay of the initial broad peak no. 2 detected by GC/TEA system (designated as TEA2) as well as the decay of some selected peaks from GC/FID chromatograms. The y-axis in this figure has logarithmic scale. The observed values in Fig. 6 can roughly be fitted by double exponential decays, but for times longer than those showed in this figure, the decays were even slower. The diffusional processes involved in the escape of volatile compounds from a barrel are certainly complicated and include the diffusion from a specific position inside the barrel towards the muzzle and the equilibrium between compounds in vapor phase and adsorbed on the walls and particles (soot particles of varying size distribution, heavily burned propellant flakes, etc.). Additional continued decomposition of propellant traces in a barrel cannot be excluded.

#### Shooting with Ammunition from Different Manufacturers

The decays in peak area presented in Fig. 6 were all obtained using the same kind of ammunition (Eley). Similar decays for other types of ammunition can be plotted and used for estimation of time since latest discharge, if the ammunition and conditions of storage are known.

We performed a number of shooting experiments to investigate the influence of ammunition type on compounds detected in the barrel after the shooting and their escape from the barrel. For five different manufacturers, the decays of various compounds were studied in detail for a time period of at least three weeks after the discharge. For an additional ten ammunition types, quantitative SPME analyses were only carried out one day after the discharge to obtain information about the range of concentrations and/or types of compounds detected.

The GC/TEA system detected the broad TEA2 peak in all the shootings. Also the chromatograms recorded by the GC/FID system were similar (qualitatively the same)—all the main peaks (naphthalene, biphenyl, indol, acenaphthylene, etc.) were present and independent of the ammunition used. There were, however, quantitative differences between various manufacturers as well as in ratios between different peaks. Most of the ammunitions gave TEA2 peaks with peak heights between 1000 and 2000 mV and naphthalene peaks with peak areas between 500 and 1000 (one day after the discharge). For simplicity only the naphthalene peak is given here as a representative for the GC/FID system. If the ammunition used in the latest shooting is unknown and mean values for decays of naphthalene or TEA2 peaks are used for the estimation of time lapse since discharge, the error in this estimation will only be two to three days for recently discharged weapons, since the decrease of the peaks is initially very rapid (e.g., approximately 40% from day 1 to day 2). The observation of a TEA2 peak with height of 500 mV or higher and/or naphthalene peak with area of 500 or higher is a clear indication of a very recently discharged shotgun. For longer time periods since discharge, the error in time estimation for an unknown ammunition increases as the the slopes of the decays decrease with time and the vertically values at the start of these decay curves vary greatly (more details are given in the next paragraph).

#### Curve Fitting as a General Method for Estimation of Time Since Discharge When the Ammunition is Unknown

When the ammunition used in the latest shooting is unknown, the estimation of time since the discharge by a single SPME measurement and associated decays shown in Fig. 6 may involve significant errors. In some cases, as mentioned above, it may give useful information.

Among the shotgun ammunitions we investigated in this study, there were two kinds which on firing gave TEA2 peaks in quantities significantly different from the others, namely Bajkal which caused an extremely strong peak and S&B which gave a relatively weak TEA2 peak (Bajkal peak was about 40 times stronger than S&B peak one day after shooting). Figure 7 shows the decay of the TEA2 peak with time since discharge for these two ammunition types. It seems from this figure that, e.g., the peak height of TEA2 peak detected 40 days after shooting with Bajkal ammunition is the same as that detected after only three days of shooting with S&B ammunition.

Despite their large quantitative differences the decay curves in Fig. 7 have similar shapes. This shape was observed also for the other ammunition types studied. It is clear that some kind of curve fitting would be valuable to make use of these similarities for estimation of time since discharge. We tested a simple method by calculating the ratio  $I_n/I_{n-1}$ , where  $I_n$  is an intensity of the TEA2 peak day  $n$  and  $I_{n-1}$  day  $(n - 1)$ , and plotted this ratio against time since discharge ( $n$ ). The resulting curves will not be influenced by the amount of TEA2 detected, only by the shape of its decays. For decays observed in this study, the ratio  $I_n/I_{n-1}$  gives low values

for short times (where the amount of TEA2 detected decreases rapidly) and increases with time until asymptotically reaching the value of 1. Figure 8 shows the measurements from Fig. 7 after this modification. Within experimental errors, the function  $I_n/I_{n-1}$  seems to be the same for both kinds of ammunition. We have applied this function also for naphthalene peaks and obtained similar time dependent results (Fig. 9).

Figure 10 illustrates the theoretical appearance of the function  $I_n/I_{n-1}$ . For exponential decays,  $I_n/I_{n-1}$  will be a constant independent of time and thus unsuitable for time estimation. For double exponential decays, this function increases with time as in our measurements, but it reaches asymptotically a value lower than 1. Our observations for longer time periods after firing indicate that the decays are not double exponential.

The ratios calculated in Figs. 8 and 9 are strongly influenced by experimental errors in single measurements. Therefore these figures were constructed from experimentally measured decays of the TEA2 and naphthalene peaks but using values from fitting curves drawn through the experimental points.

The curves in Figs. 8 and 9 cannot be used for estimation of time since discharge after a single measurement. The firearm must

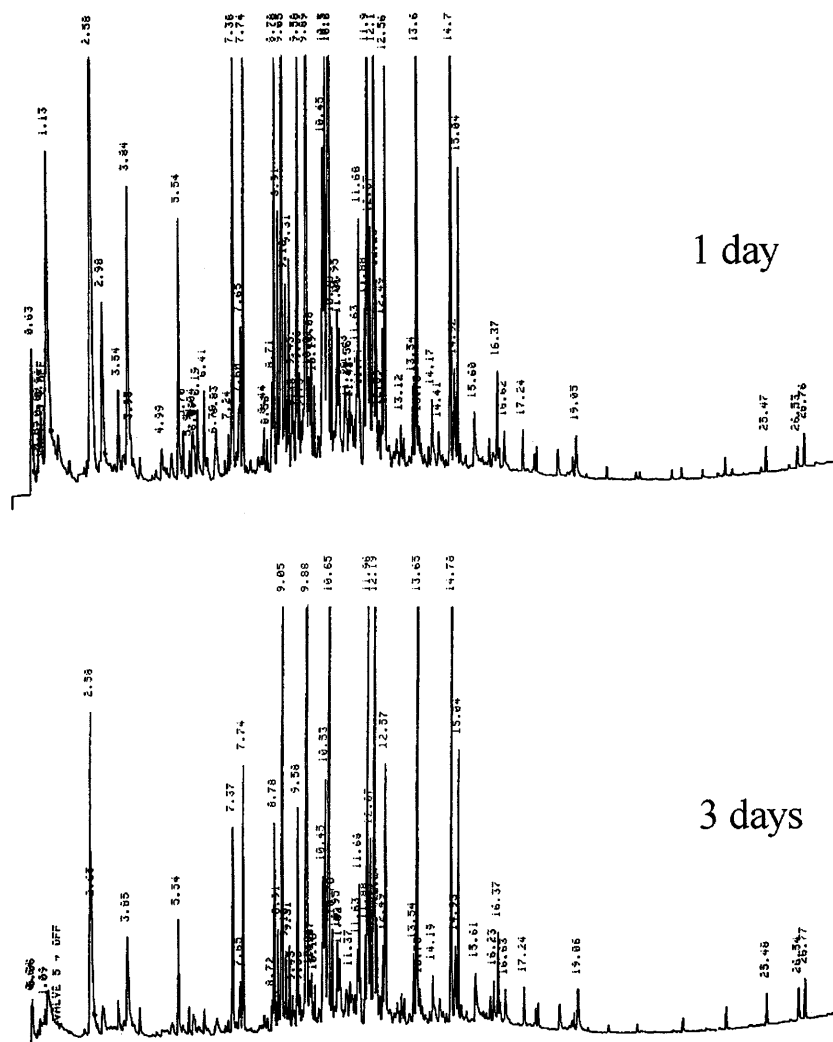


FIG. 5—Changes in GC/FID chromatograms with time after shooting. The ammunition used was Eley. Note that the rate of escape of the various compounds from the barrel is dependent on their retention time (and thus their volatility).

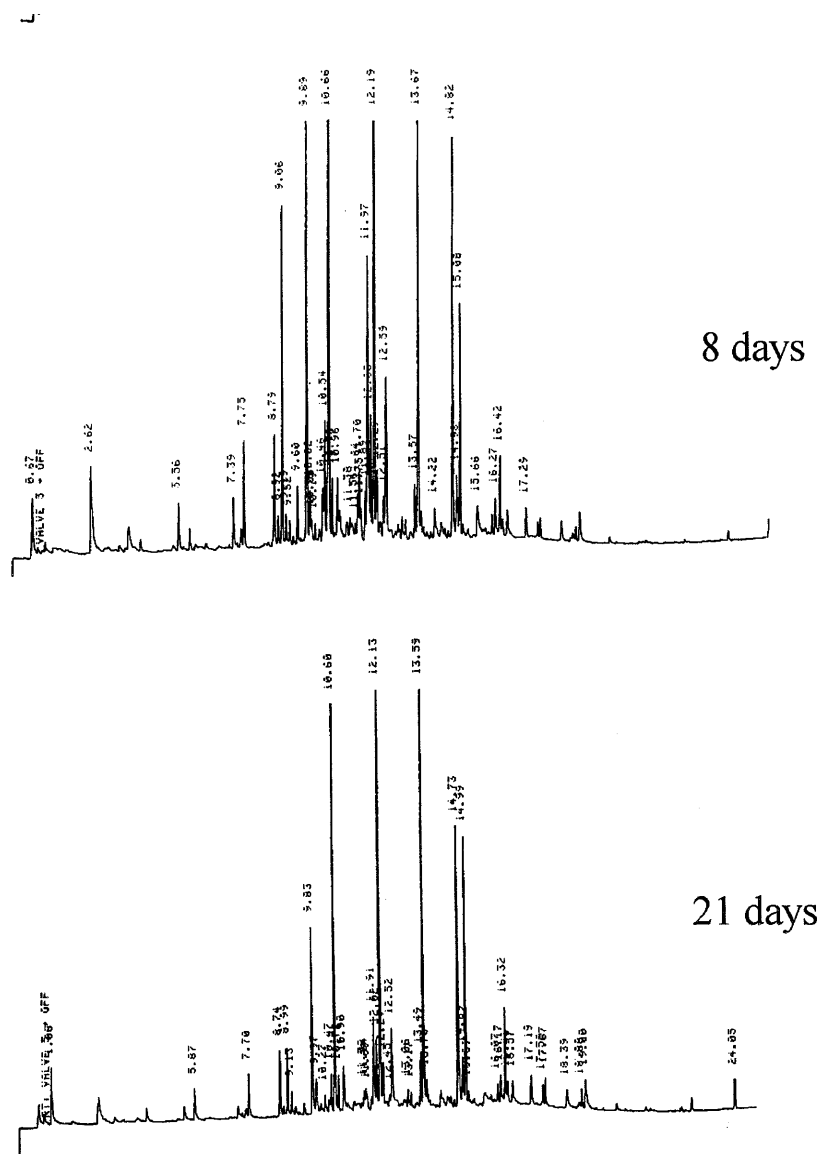


FIG. 5—Continued

be sampled once a day for several days to obtain several values of the function  $I_n/I_{n-1}$ . The use of two parallel systems as in our study and plotting the decays for several compounds detected should improve the accuracy in the estimation of time. For very recently fired weapons, the time lapse since discharge may be estimated accurately, the function  $I_n/I_{n-1}$  increases at first rapidly with time. After approximately five days the function for the naphthalene peak (Fig. 9) reaches the value of 0.8, and after an additional five days the value of 0.9. In about 20 days the function reaches the value of 0.95 and the accuracy in the time estimation is low. Values of 0.95 or more indicate that the firearm was not so recently fired. The ratio  $I_n/I_{n-1}$  for the TEA2-peak increases somewhat slower with time (Fig. 8), but the precision in those measurements is not as good as for naphthalene. In some experiments we followed the decay of the TEA2 and naphthalene peaks in detail for more than two months after the discharge. The calculated functions  $I_n/I_{n-1}$  were very close to the value of 1, if the peaks were still detected at all.

#### *Reproducibility of Shooting with the Same Type of Ammunition*

The reproducibility of shooting with the same type of ammunition was tested with shotgun ammunition from two different manufacturers. Four to six shots were made using the same firearm and both barrels were fired. SPME sampling was performed 24 h after each shot with the firearm left at room temperature all the time. For one of the manufacturers, ammunition from two different production lots was used. The amount of naphthalene or TEA2 detected on shooting with ammunition from the same production lot was not exactly the same, but reasonably close with the standard deviation for the naphthalene peak area about 11% for both ammunitions tested. On testing with ammunition from the same manufacturer but from different production lots, the results could differ much more (as much as for ammunition from different manufacturers).

In cases when the ammunition used in the latest shooting is known, the estimation of time since discharge can be improved considerably, provided that the storage conditions are known and

the ammunition employed in the test shooting in the laboratory is from the same ammunition box as the suspect one. The reproducibility test performed in this study is, however, limited to two manufacturers and a few batches. The limited data cannot exclude that some brands of cartridges, although from the same batch, may deposit different amounts of combustion products on shooting.

#### Factors That May Influence the Results and Interpretation

*The Effect of Cleaning the Barrel*—If a firearm after shooting is cleaned, it can be expected that the amount of combustion products detected inside the barrel will be significantly decreased or completely eliminated.

We have carried out a test with single shots, SPME sampling 24 h after the shooting, on cleaned and uncleaned barrels. Three types of cleaning were used:

- cleaning with paper,
- cleaning with paper followed by treatment with weapon grease no. 101 (aluminum hydrolysate of fat from mineral oil), and
- cleaning with paper followed by treatment with weapon oil

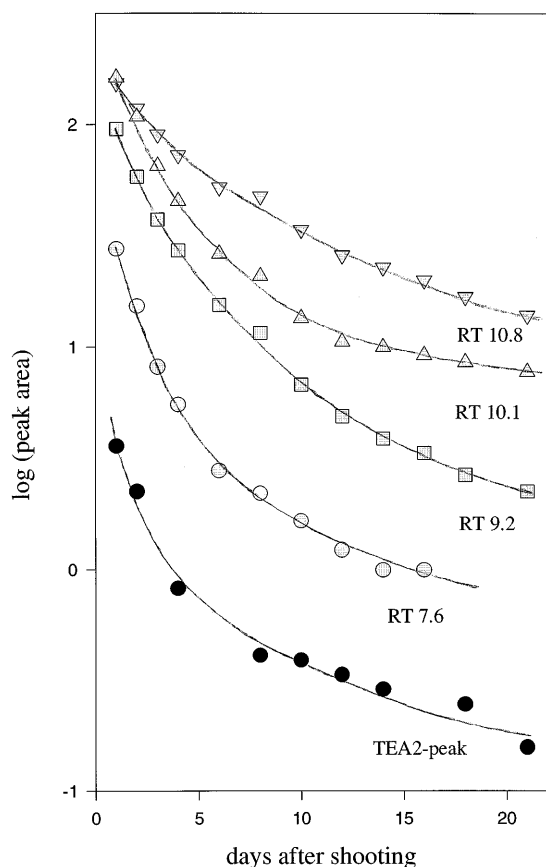


FIG. 6—Decays of the TEA2-peak and some of the peaks detected by the GC/FID system with time after shooting. A single shot with Eley shotgun ammunition was fired. Note that the y-axis uses a logarithmic scale and the decays are thus non-exponential. Indol, biphenyl, acenaphthylene and 1-pentadecene are the compounds represented by the peaks with their retention time (in increasing order) indicated in the figure. The curves were drawn only tentatively through the measured points. The values of the peak height of the TEA2-peak were divided by 100 and thus moved in parallel down in this figure to avoid overlapping.

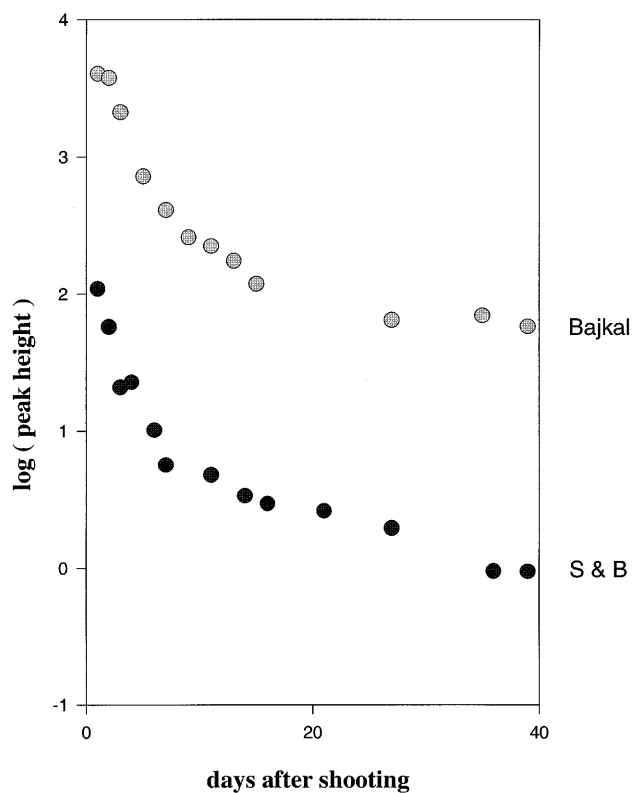


FIG. 7—The decays of the TEA2-peaks for shooting with Bajkal and Sellier & Bellot ammunition.

Hessa (petroleum distillate containing solvent refined mineral oil, propane and butane, Hessa Industries AB, Enköping, Sweden).

Federal Classic 12/70 US No. 5 was the ammunition employed in these experiments. Cleaning with paper did not have any noticeable effect on the amount of naphthalene detected inside the barrel. The height of the TEA2 peak decreased, however, whereas nitroglycerin and diphenylamine detected in significant amounts in the uncleaned barrel were almost completely eliminated by the cleaning procedure. A reasonable explanation for this observation is that the cleaning procedure removes predominately the large partially burned propellant flakes from the barrel. These flakes can easily be seen in the barrel after shooting and, if present, indicate that the barrel was not cleaned. The compounds present in unburned propellant can still be detected after shooting in the partially burned flakes and their concentration will decrease drastically when the flakes are removed. The compounds produced on shooting, like naphthalene, are presumably deposited on the barrel walls, adsorbed on the microscopic soot particles which will not be removed by cleaning with paper.

Cleaning with grease or oil did not influence the height of the TEA2 peak. However, the analysis of naphthalene and other volatile compounds by the GC/FID system was seriously influenced by numerous additional peaks originating from the cleaning media, especially from the oil.

To summarize, the cleaning of the shotgun barrel does not prevent the estimation of time since discharge, but the use of grease and particularly of weapon oil will make it more uncertain when the GC/FID system is used for the measurements. The use of only paper for the cleaning has no significant effect on the measurements.

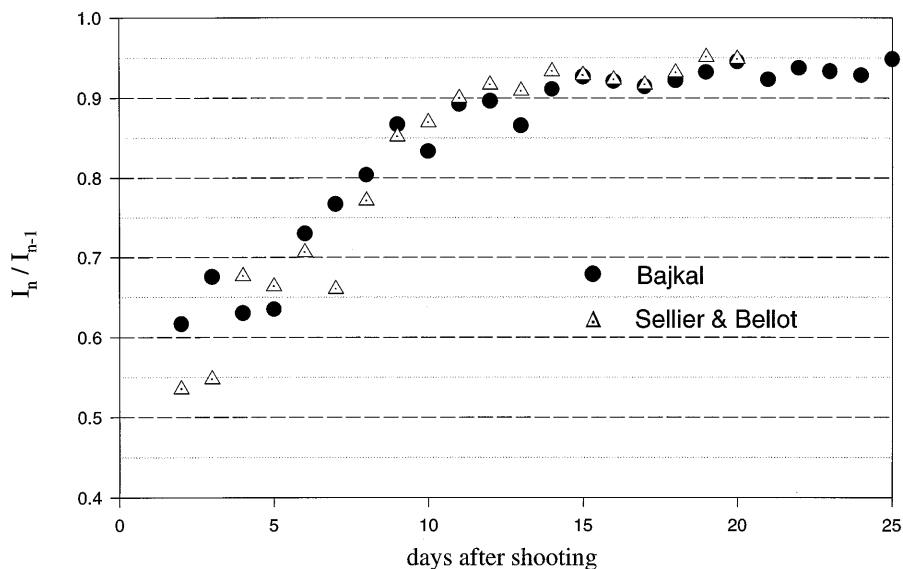


FIG. 8—The function  $I_n/I_{n-1}$  calculated for the decays in Fig. 7 and plotted against  $n$  (days since discharge). This function is useful for estimation of time since discharge when the ammunition used in the latest shooting is unknown.

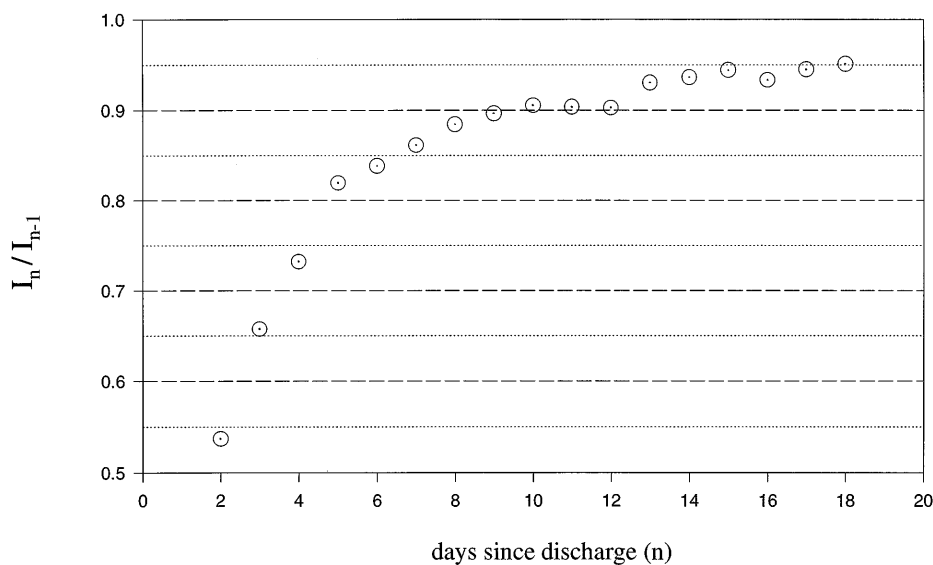


FIG. 9—The function  $I_n/I_{n-1}$  calculated for decay of naphthalene peak. One shot with Eley ammunition.

*The Effect of Number of Shots Fired*—One of the unknown variables in this type of investigation is how many shots were fired when the weapon was last used. The assumption is that the number of shots should not influence the results, because every new shot will destroy residues from previous shootings. We performed a single series of test shootings using the same batch of ammunition. The number of shots was 1, 2, 5 and 10. The repetitive shootings were carried out at the shortest possible intervals, by replacing the fired cartridge immediately with a new one. As a result of these repetitive shootings the shotgun barrels become very hot, particularly after a series with 10 shots. SPME sampling were performed 24 h after each of the shooting tests. There was no difference in either the TEA2 peak nor the naphthalene peak between 1 and 2 shots. The TEA2 peak height decreased to 50% after 5 repetitive shots and to only about 10% after 10 shots, compared to the height

after 1 shot. We believe that the increased heating of the barrels on repetitive shootings is the explanation.

On the other hand, the amount of naphthalene detected was not noticeably influenced by the number of shots in this experiment.

*Test of Eventual Disturbance to the System by SPME Sampling*—Compared with other headspace sampling techniques, SPME with its passive diffusional sampling should not cause any serious disturbance to the system it was applied to in this study. We have tested the eventual systematic errors of the sampling procedure. One shot in each barrel of a double-barreled shotgun was carried out. One of the barrels was sampled every day after the shooting, the second barrel was sampled only every fifth day. No marked difference between the results obtained for both barrels was observed (the difference was less than 15%).



*Preventing the Escape of Volatile Compounds from the Barrel*—Our experiments indicate that accuracy in the estimation of time since the latest discharge is highest for very recently fired shotguns, when the rate of escape of volatile compounds from the firearm is greatest. In one experiment we tested if there was a simple way to prevent these compounds from escaping the firearm. It would be a definite advantage to keep the concentration of these compounds inside the barrel at the same level as that when the suspect firearm was found until the investigation of the forensic laboratory can be started.

In this experiment one shot in each barrel of a double-barreled shotgun was fired. One day after the shooting, both barrels were sampled by SPME. After this sampling, one of the muzzles was sealed with a cork. SPME samplings were then continued at certain time intervals from both barrels to study the escape of the various compounds from the barrels. The cork was removed only during the sampling procedure. The sealing of the barrel with a cork had no detectable effect on the decay of the TEA2 peak. The decays from both barrels were indistinguishable. The rate of escape of naphthalene from the sealed barrel was slightly reduced, particularly during the first few days after the shooting. By calculating the function  $I_n/I_{n-1}$  for naphthalene escaping from the sealed and unsealed barrel, respectively, there was only a difference in the values obtained for days 2 to 5, and on longer storage, the values were indistinguishable. We conclude that sealing shotgun barrel with a cork does not prevent the volatile compounds from escaping from the barrel and that the estimation of the time lapse after the shooting is made more complicated by this procedure.

*The Effect of Temperature of the Storage*—The effect of storage temperature on decay curves of the naphthalene and TEA2 peaks was studied. In addition to room temperature shotgun barrels were stored at lower temperatures, 12°C and 7°C. We had no possibility for sampling directly from the barrels at these temperatures. Therefore, and also for comparison with the results obtained on storage at room temperature, the samplings from barrels were performed

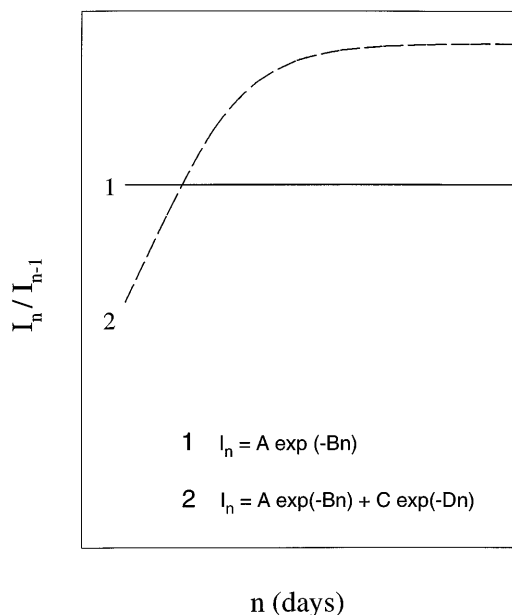


FIG. 10—The ratio  $I_n/I_{n-1}$  plotted against time for (1)—exponential and (2)—double-exponential decays.

in the following way. For each SPME sampling, the barrels were exposed to room temperature for 30 min, followed by sampling for 20 min. Afterwards, the barrels were brought back to the temperature of storage. This procedure causes disturbance to the investigation of temperature dependence, but with the knowledge about the decay curves measured at room temperature previously, the results might be recalculated and corrected for 50 min exposure to room temperature at the sampling occasions. In casework, the weapon sent for examination may be exposed to various temperatures during postal delivery before it can be sampled at a forensic science laboratory. At the laboratory the SPME sampling should be done as soon as possible and at room temperature.

Figure 11 shows the decay of the naphthalene peak from shotgun barrel at different temperatures and sampling as described above. The decay measured at room temperature is also included in this figure. Figure 12 illustrates in a similar way the temperature dependence for the TEA2 peak. The escape of naphthalene from the barrel of a shotgun is not greatly affected by temperature as the escape of the compound represented by the TEA2 peak. The decay curves in Fig. 11 for 7°C respective 12°C are almost identical. We investigated the dependence of temperature on volatility of naphthalene and the TEA2-compound by SPME sampling at room temperature and 7°C, respectively. For naphthalene, the amount detected at these two temperatures differed by a factor of 2, but for TEA2 by a factor of 5 to 6. This explains the more pronounced temperature dependence in Fig. 12 in comparison with Fig. 11. The stronger temperature dependence of the TEA2-compound also presumably explains why the decay curves for the TEA2 peak exhibit greater experimental errors observed as deviations from the fitted lines. The measurements at various times after the discharge were in this study performed at room temperature; this temperature in reality was found to vary from day to day between about 21.5 and 24°C. The decay curves for naphthalene do not deviate from the fitted lines to the same extent as those for the TEA2.

Figure 13 shows the function  $I_n/I_{n-1}$  calculated for the decay of the naphthalene peak at three different temperatures, according to the data in Fig. 11. Only the initial part of this function seems to vary significantly with temperature. After approximately five days of storage the temperature does not seem to influence the function noticeably.

## Conclusions

The method proposed in this study can generally not give an exact determination of time since discharge of shotguns. The type of weapon is a factor that may influence the results. This uncertainty is eliminated in the practical case, because the suspect firearm is available for the investigation and can be test-fired. There are, however, too many other variables, some of them studied in this work, that can influence the exactness of this determination. As many of these variables are probably unknown to the investigator, the exact determination of the time since discharge is generally not possible. Not only does the type of ammunition, the temperature of storage, the cleaning of the barrel after the shooting and the number of shots fired influence the results, but even using the same type of ammunition can give significant differences in amount of decomposition compounds detected inside the barrel at a certain time after the shooting. Nevertheless, this method can give a good estimation of the time since discharge, particularly when the temperature of storage and the ammunition type (even the production lot) are known. Generally the method presented in

this study can give an indication whether a weapon was fired, e.g., 2 to 3 days ago, 1 to 2 weeks ago, or more than 3 weeks ago.

The two systems used in this study, the GC/TEA and the GC/FID system, detect different types of compounds, and are thus complementary to each other and may both be used in parallel in the same investigation. The GC/TEA system detects nitro- and nitroso-compounds present originally in the propellant or formed on shooting. (The compound represented by the TEA2 peak is so far not known, but the peak can easily be measured.) The GC/FID system detects all the different combustion products formed on shooting, originating from the propellant, the wad or from the cartridge. We have not noticed any particular difference in the combustion products between different types of ammunition with plastic or paper cartridges and wads, respectively.

The two analytical systems should give approximately the same results which are satisfactory for investigatory purposes.

The GC/FID system, with detection of naphthalene as a compound suitable for quantitative determination of its escape with time from the barrel, is otherwise preferable. Naphthalene has several advantages compared with the TEA2-compound. The detection of naphthalene by SPME is not so strongly influenced by variations in sampling (room) temperature. The rate of escape of naphthalene from the shotgun barrel is less dependent on the temperature of storage. The detection of naphthalene is not disturbed by dry cleaning of the barrel with paper or by the number of repetitive shots fired.

For estimation of time since the latest discharge, a single SPME sampling is not sufficient, when the ammunition is unknown.

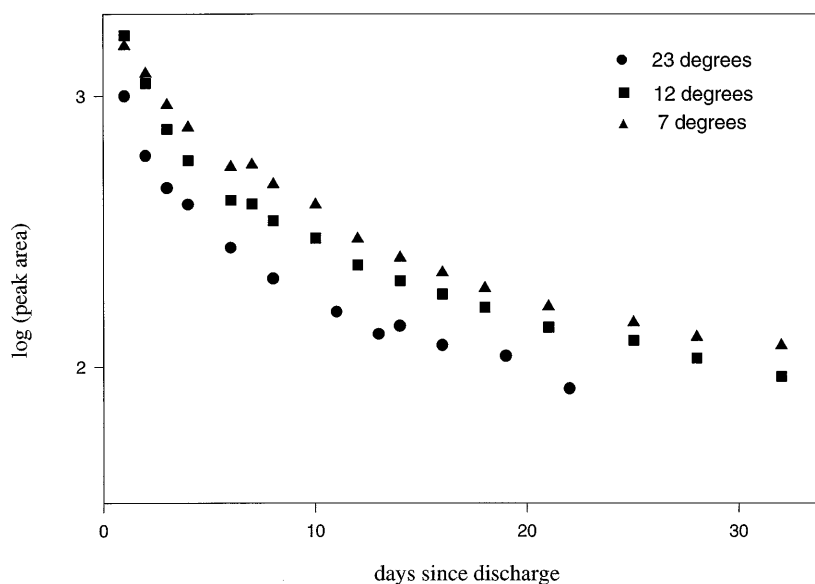


FIG. 11—The decay of naphthalene peak with time after firing one shot with Federal premium shotgun ammunition. The weapons were stored at three different temperatures after the shooting.

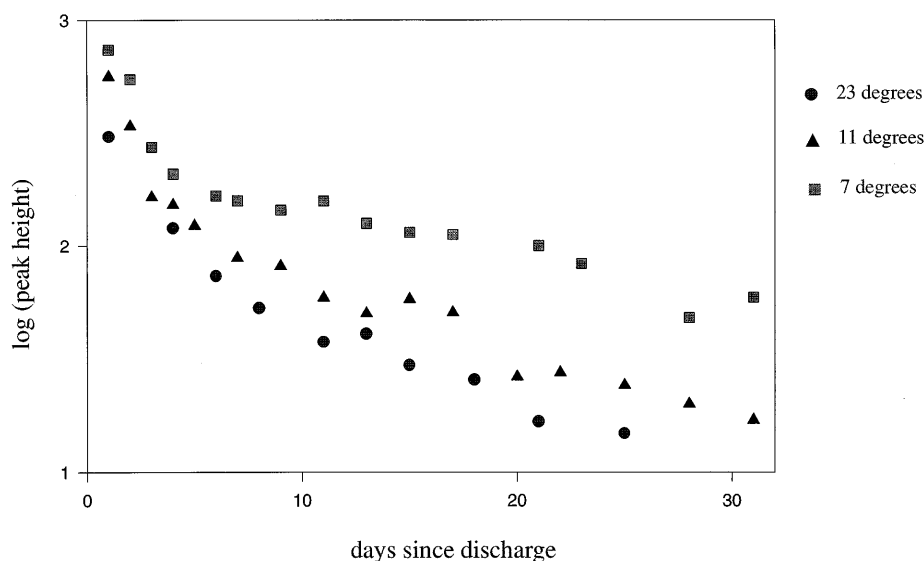


FIG. 12—The decay of the TEA2-peak with time after shooting for weapons stored at three different temperatures. The ammunition used was the same as that in Fig. 11.

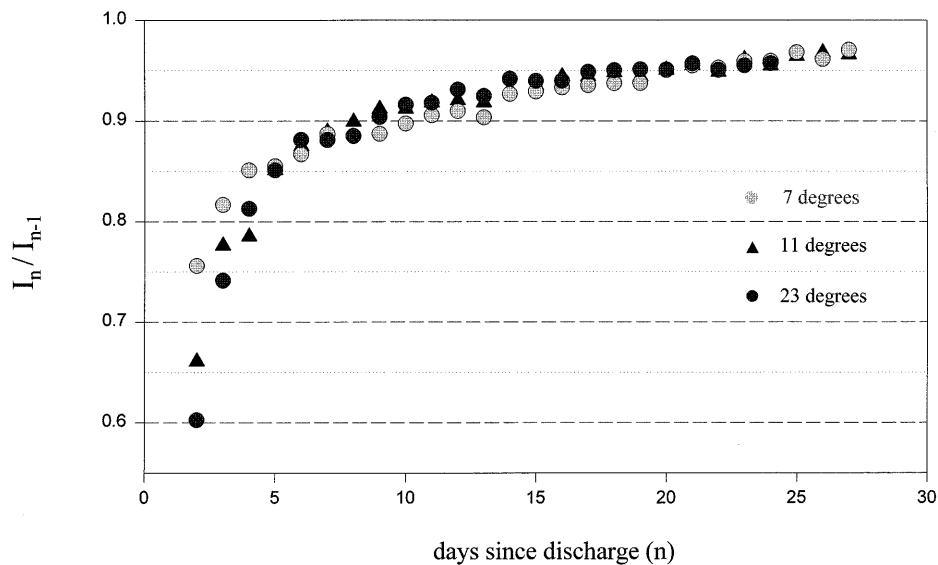


FIG. 13—The function  $I_n/I_{n-1}$  for decay of naphthalene peak at different temperatures of storage (conditions in Fig. 11). Temperature seems to influence noticeably only the initial part of this function.

Before the firearm is test-fired, several samplings should be performed, e.g., one sampling every day. The measurements are then fitted to the decay curve obtained in test-firing, preferably using the function  $I_n/I_{n-1}$ . This procedure is recommended even when the ammunition is known. However, single sampling can give sufficient information in some cases. The absence of the TEA2 peak or the absence of a very low concentration of naphthalene and other volatile compounds detected by the GC/FID system indicates that the firearm was not recently fired. On the other hand, the detection of naphthalene with the peak area over 500 or the TEA2 peak with the peak height more than 500 mV indicates a very recently fired shotgun.

The estimation of the time lapse since discharge depends very much on the type of weapon used. The amount of propellant used and the nature of the cartridges (organic material) make shotguns the most suitable object for this type of investigation. We have carried out some measurements on other types of weapons with long barrels and have obtained results which we hope indicate when they were recently fired. The SPME sampling has also been found useful when applied to several types of fired cartridges.

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Additional information and reprint requests:  
Jan Andrasko, Ph.D.  
SKL  
National Laboratory of Forensic Science  
S-58194 Linköping  
Sweden