

Time since Discharge of Spent Cartridges

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ABSTRACT: A method for estimation of the time since discharge of spent cartridges is presented. This method is based on SPME (Solid Phase Microextraction) sampling from the atmosphere inside cartridges. Either naphthalene or an unidentified compound designated as the TEA2-compound were detected in most of the cartridges. These combustion products are the same as those measured in firearm barrels, but in cartridges the detected amounts are lower. The estimation of time since discharge is based on the rate of escape of the volatile combustion compounds from the cartridge as a function of time. Three categories of cartridges were studied separately—shotgun shells, cartridges from sporting rifles, and cartridges from pistols/revolvers. For shotgun shells the decay of the naphthalene peak is measured. At room temperature, naphthalene is detectable in shotgun cartridges for 2-3 weeks after the discharge. In cartridges from sporting rifles, only the TEA2-peak is detectable and observable for about 2 weeks after the discharge. The technique presented failed to detect any combustion product in pistol/revolver cartridges, with the exception of longer cartridges, such as Magnum and in small caliber cartridges (caliber .22) where the TEA2-peak was observed for several days after the discharge. Nitroglycerin (NG) was detectable in cartridges from some manufacturers, but the reproducibility of its detection was rather poor. Moreover the decay of NG was too slow at temperatures below room temperature. The repetitive SPME sampling did not disturb the system. Attempts to prevent the volatile compound from escaping from cartridges was unsuccessful. Some experiments were performed with cartridges stored outdoors, exposed to wind, rain, and snow.

KEYWORDS: forensic science, firearms, time since discharge, SPME, GC, GC-TEA, firearm discharge residues, spent cartridges

Estimation of the time elapsed 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. Also when spent cartridges are found at the scene of a crime, it is desirable to know when these were fired.

Several gas-escape methods have been proposed to estimate time since the latest discharge of a firearm (1–4). One of these studies deals with quantitative analysis of nitrogen oxides escaping from fired shotgun shells (2).

Recently, Solid Phase Microextraction (SPME) was employed for detection and quantitative analysis of various combustion products formed in shotgun barrels (5). This rather new extraction technique was found useful and particularly suited for headspace sampling from narrow spaces like weapon barrels. The disturbance to the system is minimal, because the adsorption process is passive. Repetitive samplings are easy to perform and the precision of a quantitative analysis is good.

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In this study, the SPME technique was used to detect similar combustion products deposited in fired cartridges. Various types of cartridges, including cartridges from shotguns, sporting rifles, pistols and revolvers, were investigated. The escape of the combustion products from cartridges with time after shooting was monitored.

Materials and Methods

Solid Phase Microextraction

Fused silica fibers with a 85 μm polyacrylate coating were purchased from Supelco and used in all the experiments. The conditioning, desorption temperature and time were the same as in our previous study (5).

Sampling from Cartridges

The cartridge was placed horizontally and fitted with a suitable cork in the open end. The needle of the SPME holder was pushed through the cork. The coated fiber on the top of the SPME needle was exposed to the atmosphere inside the cartridge for 20 min. The sampling was performed at room temperature. The fiber position inside the same type of cartridge was kept constant at about in the middle of the space available. This procedure was applied for cartridges longer than about 2.5 cm. The lengths of shorter cartridges were extended with suitable adapters (plastic tubing) to prevent breaking of the SPME fiber inside the cartridge. Figure 1 illustrates the method of SPME sampling from three different cartridges.

Gas Chromatographic Analyses

Two GC systems were used for quantitative analysis of compounds adsorbed by headspace SPME from inside the cartridges: the GC-TEA system and the GC-FID (or MS) system as described in the previous study (5). To improve the detection of the TEA2-peak (5), the temperature program used for the GC-TEA system was slightly modified. The starting temperature was changed from 60°C to 35°C, otherwise both of the temperature program and all the other settings were the same.

Results and Discussion

Generally, the compounds detected in shotgun barrels (5) are also detected inside spent cartridges. In addition to the TEA2-peak (the GC-TEA system) and the naphthalene peak (representing compounds detected with the GC-FID system) nitroglycerin (NG) was also observed in some ammunitions (the GC-TEA system). However, the amount of combustion products inside the fired cartridges was considerably lower compared with that observed in shotgun barrels (5). The escape rates for these compounds from cartridges were higher compared with those from the barrels of the



FIG. 1—SPME sampling from a shotgun shell, from a sporting rifle cartridge and from a pistol cartridge. The pistol cartridge was too short for direct insertion of the SPME fiber and was therefore prolonged with a plastic tubing. The sampling time was 20 min in all experiments.

firearms they were fired. This is not surprising because weapon barrels are much longer compared with cartridges and the opening area for diffusion out from the inner space is about the same. The modification of the temperature program in the GC-TEA system resulted in a better separation of the TEA2-peak from the TEA1-peak. The retention time for the TEA2-peak was between 3 to 4 min depending on the amount present. The peak was, however, still very broad showing a considerable tailing.

The major difference in the estimation of the time since discharge of firearms and spent cartridge, respectively, is the fact that

the manufacturer of the latter is known. If the manufacturer produces ammunition of uniform quality, test shooting with the same kind of ammunition should give results suitable as reference values for the suspect cartridge.

The results obtained in many experiments with different kinds of cartridges and manufacturers were divided into three categories, which will be treated separately—cartridges from shotguns, sporting rifles, and pistols/revolvers, respectively.

Shotgun Cartridges

A number of experiments with fired shot shells from different manufacturers (caliber 12/70) was carried out. The TEA2-peak, usually very strong in shotgun barrels, was hardly detected in fired cartridges. On the other hand, the naphthalene peak was observed in all the shootings and easily quantified. The area of the naphthalene peak decreased with time since discharge in a similar way as in shotgun barrels. Figure 2 shows this decrease measured for FN Légia Star fired shells. The decays were measured at three different temperatures: 7°C, 12°C and at room temperature (about 23°C). The escape of naphthalene from shot shells is temperature dependent and for more accurate estimation of the time since discharge, the temperature of storage should be known. As observed for decays of various compounds from shotgun barrels, even the decay of naphthalene from spent shot shells is nonexponential, as illustrated in Fig. 2 where the vertical axis has a logarithmic scale.

Some shotgun ammunition contains nitroglycerin (NG) which will be deposited in spent shells. The decay of NG is slower than that of naphthalene and might be used to identify cartridges fired more than about two weeks earlier (the upper time limit of naphthalene decay at room temperature). However, NG is a very unstable compound, which often shows poor reproducibility between different shootings and the quantitative analysis is not as precise as that for other detectable compounds. In addition, when stored at temperatures below room temperature, the NG peak may be detected after many months storage and will almost never disappear. Figure 3 shows the decay of NG from Winchester shot shell at room temperature and at 7°C, respectively.

The reproducibility on shooting with cartridges from the same production lot was studied for two manufacturers - Fiochi and Federal US 6 ammunition. Figure 4 shows the excellent reproducibility of the GC/FID chromatograms obtained in test shootings with Fiochi ammunition. The chromatograms were recorded 24 h after the shooting. Table 1 summarizes some quantitative results of repetitive shootings with Federal US 6 ammunition. The reproducibility for naphthalene is much better than that for NG. The nitroglycerin peak was detected and quantified by the GC/TEA system. The reproducibility on shooting with different production lots was tested for nine different manufacturers. Two batches from each of the manufacturer were used and the peak areas for the naphthalene peak measured 24 h after the shooting. Eight of the manufacturers showed good reproducibility with the differences between the batches less than 20%. For one of the manufacturers (Hubertus, Germany), however, the results differed by a factor of four. It must be noted here, that the cartridge with four times higher content of naphthalene was seriously damaged after the shooting. Shooting with another cartridge from the same batch gave results in agreement with the second batch. Even when the manufacturer of the actual ammunition may be known, the production lot is normally unknown. Several batches from the same manufacturer should be testfired and care must be taken not to draw too hasty conclusion concerning the exactness in the estimation of time since discharge.

Shot shell - FN Légia Star

stored at different temperatures

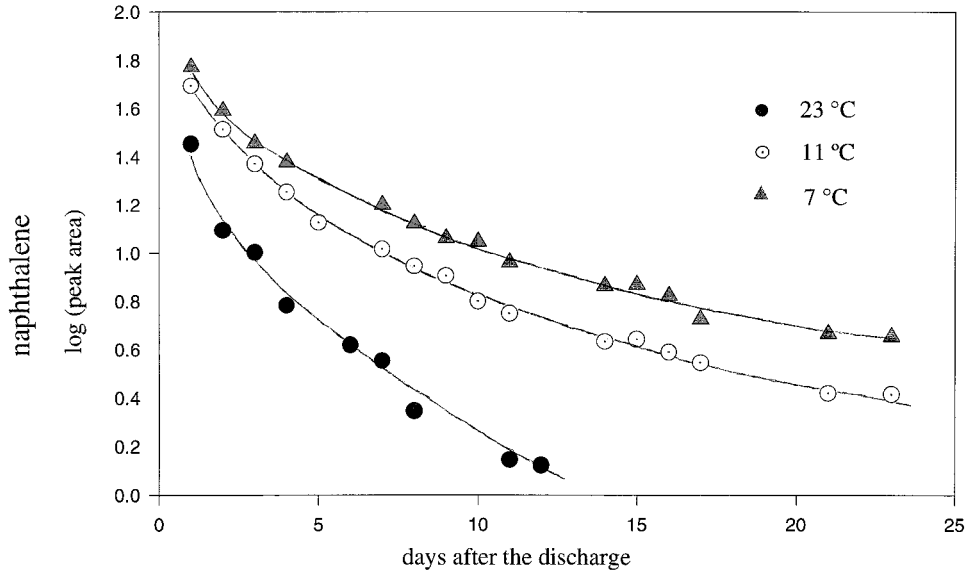


FIG. 2—Decrease in the amount of naphthalene detected inside FN Légia Star cartridges with time after the discharge. The shot shells were stored at three different temperatures, at 7°C, 11°C and at room temperature (23°C).

Shot shells

Winchester (SKEET 100)

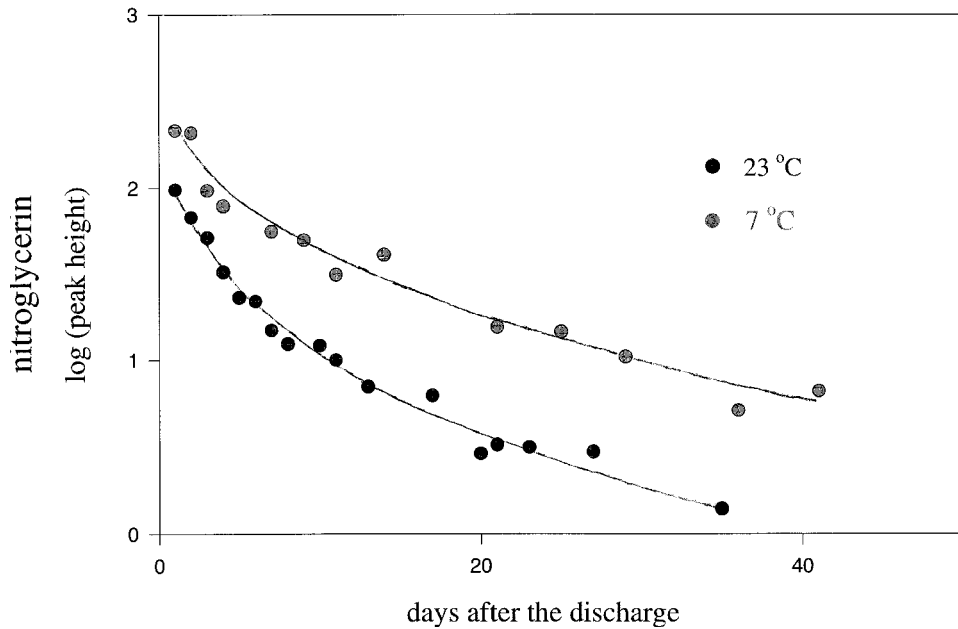
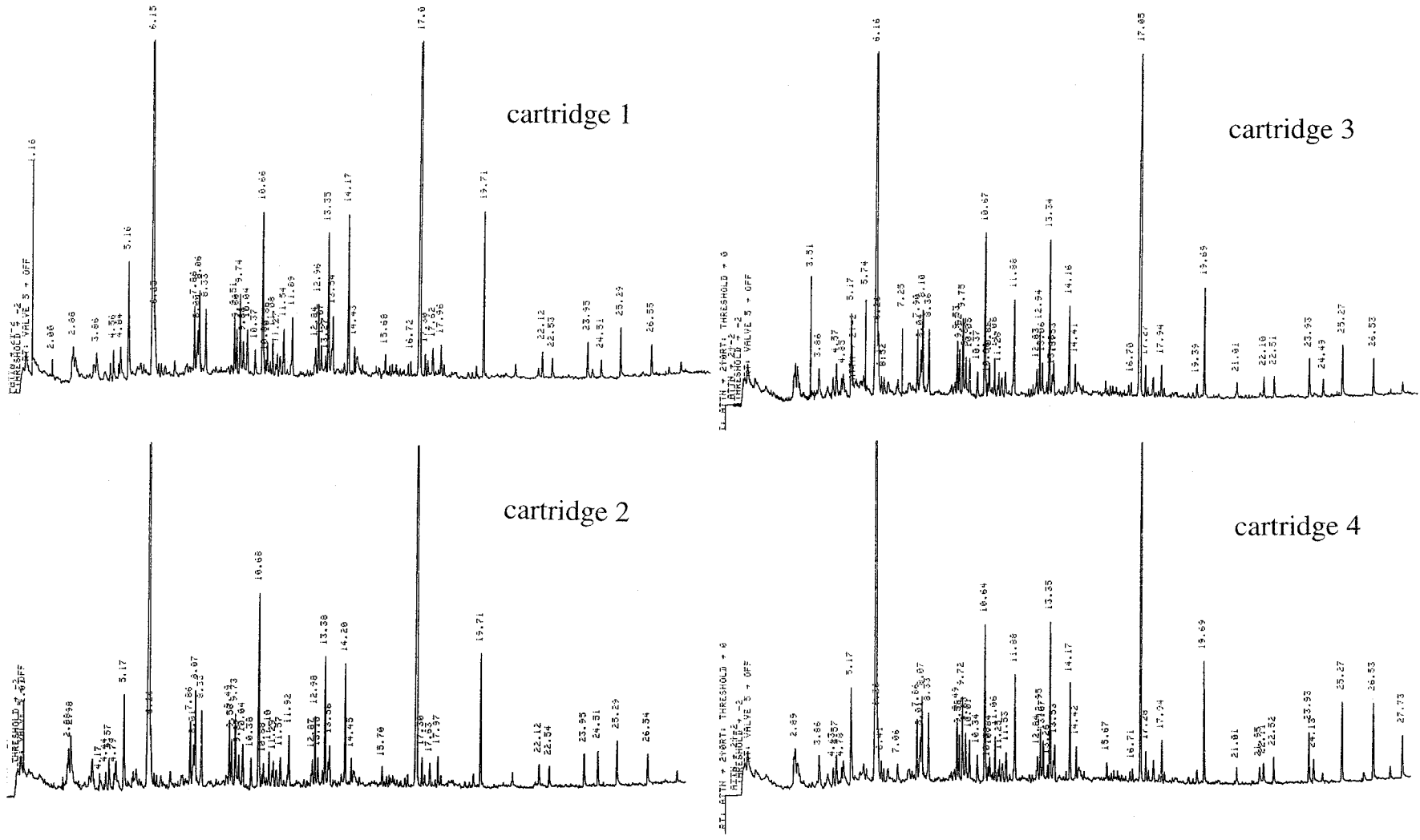


FIG. 3—Decay of the nitroglycerin peak measured by the GC/TEA system at two different temperatures. At 7°C, this decay was so slow, that NG could be detected inside the shell several months after the shooting. Ammunition: Winchester SKEET 100, caliber 12/70.



Spent shotgun cartridges

FIG. 4—The GC/FID chromatograms obtained after SPME sampling from shot shells (Fiocchi ammunition, batch 3615TIF5). For this ammunition, the reproducibility between the results for cartridges from the same batch and even between two different batches was excellent.

TABLE 1—The reproducibility of peak areas of naphthalene and biphenyl obtained by the GC/FID system and of the peak height of nitroglycerin by the GC/TEA system.

Shell No.	Naphthalene (Peak Area)	Biphenyl (Peak Area)	Nitroglycerin (Peak Height)
1	19.4	20.8	369
2	18.5	21.0	498
3	17.8	24.0	516
4	16.9	20.4	508
5	16.1	25.0	356
6	17.3	24.7	434
average:	17.6 ± 1.15	22.6 ± 2.1	447 ± 71.5

NOTE: Shot shells—Federal ammunition (cal. 12/70, US 6, copper-plated shots). Test of reproducibility. Shells from the same ammunition box (Batch No. LOT - 0119). The cartridges were stored at room temperature for one day after the shooting.

Cartridges from Sporting Rifles

In these cartridges, neither naphthalene nor NG were detected with the GC/FID and the GC/TEA systems one day after the shooting. The TEA2-peak was weak, with a peak height between 2–30 mV one day after the shooting for the ammunition types and manufacturers investigated. As the detection limit of our GC/TEA system is about 0.1 mV, the decrease in the TEA2-peak height can be followed for several days after the shooting. This decay is rapid and the TEA2-peak becomes undetectable 1–2 weeks after the firing (for cartridges stored at room temperature). Figure 5 illustrates the changes in the chromatograms obtained by the GC/TEA system on sampling from sporting rifle cartridges (caliber 9.3 × 62, Norma ammunition). Figure 6 shows the decay of the TEA2-peak in three different cartridges, caliber .222, 9.3 × 62 and .30-06, manufactured by Norma. The vertical axis uses a logarithmic range and the detection limit is around the y-value of -1.0. The decay of the TEA2-peak is temperature dependent, but even at temperatures lower than room temperature, the TEA2-compound escapes from the cartridge within about 2–3 weeks. A rather surprising feature of Fig. 6 is that the decrease in the peak height of the TEA2-peak is slowest for the largest caliber (9.3 × 62) despite the largest free area for diffusion out from the cartridge. Obviously, the free diffusion space is not the most important factor for the escape of the TEA2-compound from shotgun cartridges.

When investigating a spent cartridge from a sporting rifle, the manufacturer of the ammunition is known. On the other hand, there may be several types of bullets associated with this cartridge. With the same cartridge, different burning characteristics and possibly somewhat different propellants might be used. In Table 2 we summarize the results obtained for various types of caliber .30-06 cartridges, Norma manufacture, one day after the shooting. The date of purchase of the ammunitions is noted in Table 2, and the ammunition was clearly of different age. With the exception of Silberblitz ammunition, the results are in good agreement. The TEA2-compound escapes rapidly from sporting rifle cartridges, making the uncertainty in the determination of the time since discharge for an unknown production batch (the differences reported in Table 2) not very large, this uncertainty is within a couple of days for Norma ammunition.

Cartridges from Pistols/Revolvers

This type of cartridge is the most difficult to obtain a reliable estimation of the time since discharge. The cartridges are too short to

retain enough of combustion products from the shooting and also the amount of propellant is low. In this study we testfired a number of pistol cartridges from two manufacturers—Norma (which usually deposits low amount of combustion products) and Winchester (which usually deposits large amounts of combustion products). This series of firings should show us if there are possibilities to detect products of propellant decomposition at least in some cases. Norma does not produce caliber .22 ammunition, thus other manufacturers were chosen. The results obtained for SPME sampling from spent cartridges 1 day after the firing are shown in Table 3. No naphthalene was detected in these cartridges. The TEA2-peak was detected in many cartridges, but often at too low amounts (the peak height below 0.5 mV). Only relatively long cartridges (magnum type) and those with small opening diameter are suitable for following its decay with time after shooting. Because the TEA2-compound escapes rapidly from the cartridges, only very recently fired cartridges may be identified. Figure 7 shows the decay of the TEA2-peaks for .357 and .44 Magnum cartridges manufactured by Norma and Winchester.

It can be seen in Table 3 that nitroglycerin may be detected inside spent cartridges after shooting with certain kinds of ammunition. Indeed, the concentration of NG was sometimes very high. However, in our experiments using CCI .22 Magnum ammunition, the reproducibility in the amount of NG detected 1 day after the shooting was very poor.

Preventing the Escape of Volatile Compounds from the Cartridge

Our experiments indicate that estimation of time since discharge is often possible only for very recently fired cartridges (1–2 weeks after shooting). It would be a definite advantage to keep the concentration of volatile compounds inside the cartridge the same as that when the suspect cartridge was found until investigation of the forensic laboratory can be started. In our study with shotguns, we tried to prevent these compounds escaping from firearms by sealing the muzzle with a cork. This procedure failed to prevent the disappearance of, e.g., the TEA2-compound from the barrel (5). In this work we tested two kinds of plastic films—sealing films Nescofilm and Seal View, respectively. Two .30-06 Winchester made cartridges were sealed each with one of these films, the third cartridge was left opened. The results were disappointing. The content of the TEA2-compound decreased significantly more in the sealed cartridges than in the unsealed, probably because of adsorption of the TEA2-compound on the sealing film.

Cartridges Stored Outdoors

The most likely place of finding a suspect cartridge is outdoors, close to the scene of a crime. The results obtained after storage indoors may not be so easily applied to outdoor storage conditions. Rain, wind, and snow may eliminate the possibility of detection of combustion products even very shortly after the shooting. We have performed two tests with cartridges stored outdoors. In the first test, the cartridges were outdoors in a storehouse, exposed to an outdoor atmosphere, but protected from rain, wind and snow. In the second test, the cartridges were exposed to these atmospheric phenomena in the open air. The tests were carried out during the winter, with a lot of rain and strong wind almost every day. Some snow appeared also during that time period and the temperature was between -5 and +8°C. Figure 8 shows the results obtained for .30-06 cartridges of Norma manufacture. A comparison with results indoors at room temperature (Fig. 6, Norma ammunition), the escape of the TEA2-compound from the cartridge stored at the storehouse

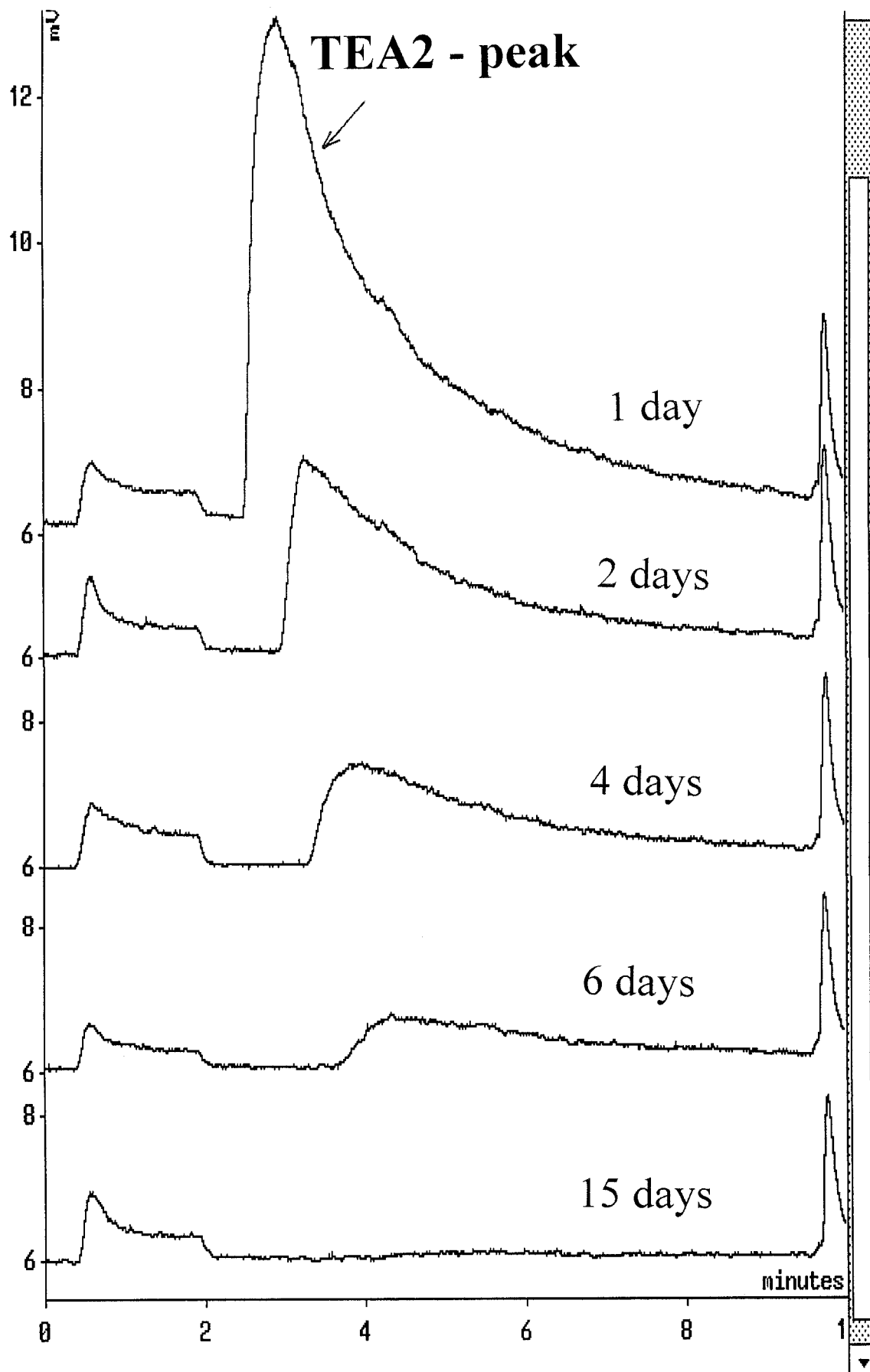


FIG. 5—The appearance of the TEA2-peak detected inside cartridges from sporting rifles by the GC/TEA system. This peak decreases with the time after discharge. Norma ammunition, caliber 9.3×62 was used. Note that the retention time of this peak increases with decreasing amount of this compound. The peak has seriously tailing. The peak with the retention time of about 10 min originates from the SPME fiber.

Spent cartridges from sporting rifles

SPME sampling from the inside of cartridges, 20 minutes

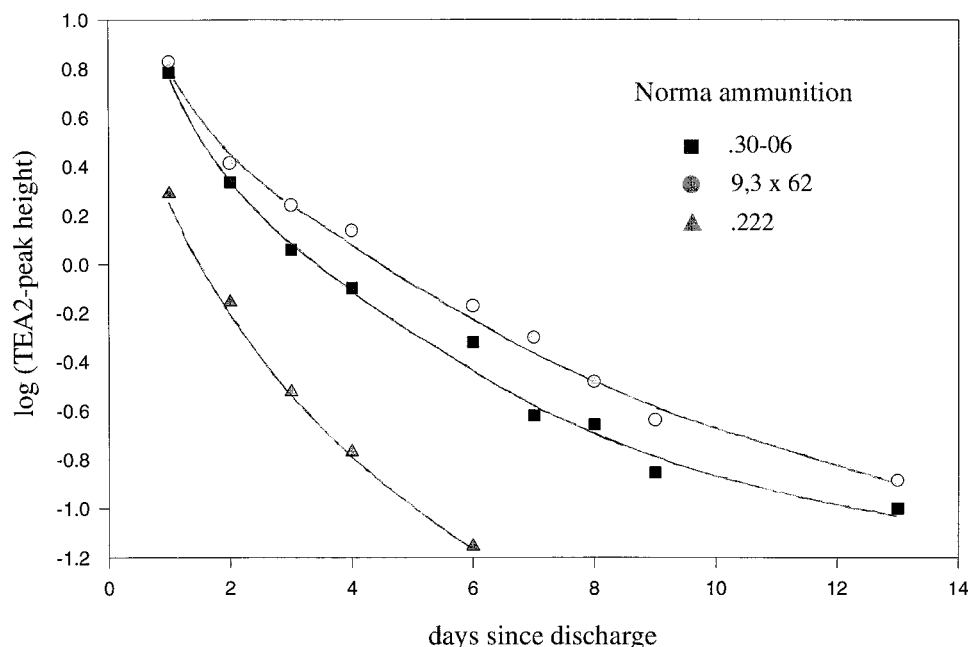


FIG. 6—Decay of the TEA2-peak with time after discharge of three types of cartridges from sporting rifles. This decay is rapid and the TEA2-peaks are only detected for 1–2 weeks after the shooting (the detection limit of the GC/TEA system is about 0.1 mV for the height of the TEA peak, it means about -1.0 on the logarithmic scale employed in this figure). Norma ammunition was used and the temperature was at room temperature.

TABLE 2—Comparison of TEA2 peak height for cartridges from sporting rifles, caliber .30-06, manufactured by Norma.

Type of Ammunition	Date of Purchase	TEA2-Peak Height
9,7 gram Nosler	July 1969	6,2
11,6 gram Nosler	??	6,6
Jaktmatch	1989	5,05
11,6 gram Silverblitx	August 1977	10,2
11,6 gram PRJ 80	September 1981	6,0
180 grains BS	July 1962	6,2
8,4 gram BS	July 1962	7,2
13 g Vulcan	October 1984	6,2

NOTE: The peak heights were measured 1 day after the discharge. The cartridges were stored at room temperature. Different types of ammunition, different production lots.

is somewhat slower, as expected for a storage at lower temperature. On the other hand, the decay of the TEA2-peak from the cartridge exposed to wind, rain etc. is even more rapid than that measured at room temperature indoors.

Test of Eventual Disturbance to the System by the SPME Sampling

The slower decay in Fig. 8 includes two series of measurements. The black triangles represent measurements performed repeatedly on the same cartridge, which was after sampling placed again in the storehouse. The circles were obtained by sampling of different cartridges, fired at the same time as the first cartridge and stored together with that cartridge. Each of these cartridges was only sampled once, e.g., 4 days after the shooting. On comparison between

the results, there is no observable tendency for the repeatedly sampled cartridge to show lower concentration of the TEA2-compound. The influence of the SPME sampling on the system is seemingly negligible.

Conclusions

The SPME technique is suitable for detection of various volatile compounds inside spent cartridges. The escape of these compounds from cartridges is used to estimate the time since discharge. The analytical systems and the compounds analyzed are the same as those for shotgun barrels (5). The volatile compounds escape rapidly from cartridges and an estimation of the time since discharge is generally possible only for a short time after the shooting (1–2 weeks). So far we have not found a method for preventing the volatile compounds from escaping from spent cartridges prior to the laboratory analysis.

In contrast to suspect firearms, the manufacturer of the actual ammunition is generally known when a suspect cartridge is found. Test shooting with the same type of cartridge may thus give a good estimation of the time since discharge if the storage conditions are known. Caution is necessary in the interpretation of the results, since the day of production of the actual cartridge is not known and we found variations in the amount of combustion products in fired cartridges between different production batches of some manufacturers. For most manufacturers, the differences between different batches were low.

For shotgun shells and cartridges from sporting rifles, the method can be used for time period up to about 2–3 weeks after the shooting. In cartridges from pistols and revolvers, an estimation of the time after discharge was only possible for longer cartridges (Magnum type) or small caliber cartridges (.22) and only for a short

TABLE 3—Detection of the TEA2-peak and the naphthalene peak by the GC/TEA system after SPME sampling 1 day after the shooting from various pistol/revolver cartridges.

Caliber	Manufacturer	Batch	TEA2-Peak	Nitroglycerin
9 mm P	Norma Winchester	04129 26KH20(76)	— (+)	— —
7,65 mm B	Norma Winchester	6005051 76LM02(26)	— +	— ++
6,35 B	Norma Winchester	2205005 83KC60(49)	— (+)	— ++
9 mm BK	Norma Winchester	06905 26LB72(76)	(+) (+)	— +
.45 ACP	Norma Winchester	02926 74LF30(62)	(+) (+)	— +
.44 Magnum	Norma Winchester	12920 72MM03(73)	+ +	— —
.357 Magnum	Norma Winchester	01413 29WL90(2)	+ +	— —
.22 lr	RWS Standard Fiocchi Winchester	61MF10 2807014B 1VL81N	+ + +	+ — (+)
.22 Magnum	RWS CCI Winchester	70ST C27U10 E51RD42	++ ++ +	+ +++ —

+++ A very strong peak (the peak height of TEA2 > 100 mV, of nitroglycerin > 500 mV).

++ A strong peak (the peak height of TEA2 > 10 mV, of nitroglycerin > 50 mV).

+ A clearly detectable peak which decrease can be measured for several days. (TEA2 > 0,5 mV, NG > ca. 5 mV).

(+) A hardly detectable peak (TEA2 < 0,5 mV, NG < 2 mV).

— A non-detectable peak.

Cartridges from pistols/revolvers

room temperature

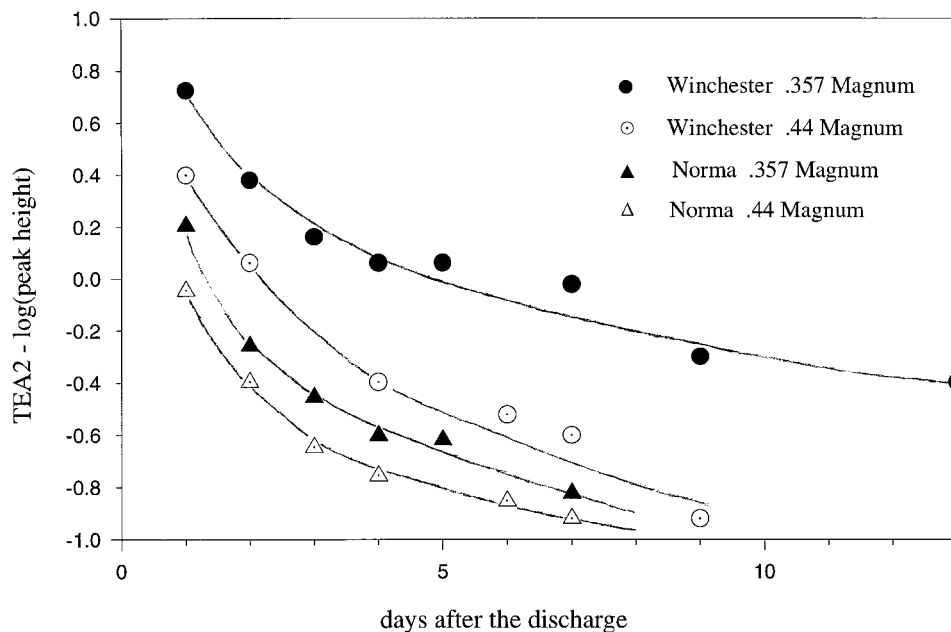


FIG. 7—The peak height of the TEA2-peak as a function of time since discharge for .357 Magnum and .44 Magnum pistol/revolver cartridges. Two manufacturers of ammunition were studied: Winchester, which usually deposits large amounts, and Norma, which usually deposits small amounts of combustion products inside weapons or cartridges.

Cartridges from sporting rifles
 .30-06 Winchester ammunition
 (stored outdoors)

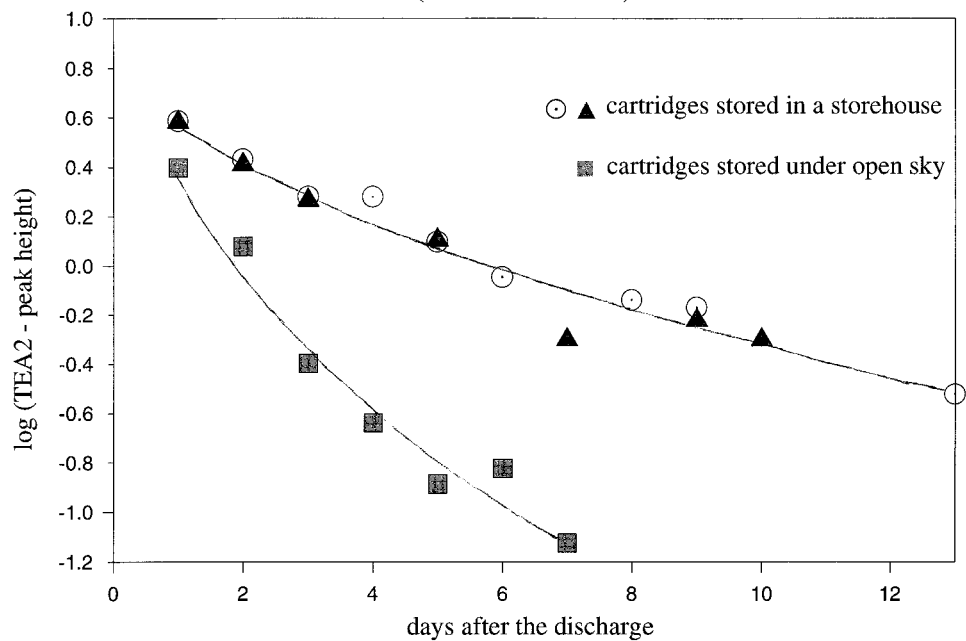


FIG. 8—The influence of atmospheric conditions on the decay of the TEA2-peak from sporting rifle cartridges stored outdoors. Ammunition used was Winchester, caliber .30-06. The two decay curves were obtained for cartridges stored during winter in a storehouse (○,▲) and under open sky (■), respectively. The cartridges stored in the storehouse were exposed to the same temperature and humidity but protected from rain and strong wind. The rate of decay for the cartridge exposed to wind, rain and snow was considerably faster.

time after the firing (about 1–2 weeks).

If a suspect cartridge is found outdoors and the weather had been rainy and windy, the decay of the volatile compounds is very rapid and these compounds will not be detected about 1 week or more after the shooting.

In its simplest application, if the proposed method detects naphthalene in shotgun shells or the TEA2-peak in other types of cartridges, the cartridge has recently been fired. It could not have been fired 3 to 4 month ago.

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