

## Time Since Discharge of Rifles

**REFERENCE:** Andrasko J, Ståhling S. Time since discharge of rifles. *J Forensic Sci* 2000;45(6):1250–1255.

**ABSTRACT:** The estimation of time since the latest discharge of rifles has been achieved by the SPME sampling technique and the GC-TEA analytical system. An unidentified compound, designated as the TEA2 compound, was detected in all the rifles investigated. The same compound was observed in shotguns and spent cartridges in our previous work. This compound escapes rapidly from the inside of rifle barrels, but can still be detected there one to two months after the shooting. The decrease of the TEA2 peak with time after shooting is non-exponential, and the curve-fitting procedure proposed for the estimation of time since discharge of shotguns can be applied also for rifles.

**KEYWORDS:** forensic science, firearms, time since discharge, SPME, GC, GC-TEA, firearm discharge residues, rifles

The solid phase micro-extraction (SPME) technique has been used successfully for detection of various volatile compounds inside firearm barrels as well as inside spent cartridges for the estimation of the time since the latest discharge of the firearms and the cartridges (1–3). In shotguns and shotgun shells, naphthalene is the compound whose escape from the barrel or the shell is most suitable for monitoring the time since the latest discharge. Additionally, an unidentified compound, designated as TEA2 compound, and detected with the TEA detector in the GC-TEA system is suggested for this purpose. These volatile decomposition products of smokeless powder can generally be detected for weeks after the shooting in spent cartridges and for months in shotgun barrels.

In this study, the SPME technique was applied for the detection of the escape of the TEA2 compound from rifle barrels.

### Materials and Methods

#### *Solid Phase Micro-Extraction*

Fused silica fibers with an 85  $\mu\text{m}$  polyacrylate coating were purchased from Supelco and used in all the experiments. Conditioning, desorption temperature, and time were the same as in our previous studies (1). New fibers were conditioned at 270°C for 2–3 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 at room temperature for an additional 7 min. Blank analyses were per-

formed to make sure that the fiber and the chromatographic system were clean and free from interfering substances.

#### *Sampling from Rifles*

The rifle was placed horizontally. As the size of the SPME holder exceeded the caliber of the firearms investigated, sampling in the middle of the rifles could not be achieved. The SPME sampling was performed by pushing the needle of the SPME holder inside the barrel as far as possible. Two samplings were carried out on each rifle, one from the muzzle side and another from the breech side. The coated fiber on the top of the SPME needle was exposed to the atmosphere inside the barrel for 20 min. The samplings were performed at room temperature. The fiber positions inside the same type of firearms were kept constant. Figure 1 illustrates the two SPME samplings from rifles. The sampling from the breech position starts by opening the breech, removing the adjustable depth gage from the SPME holder, and pushing the holder inside the barrel by the use of tweezers. In this way, the SPME fiber reaches as far as possible inside the barrel.

#### *Gas Chromatographic Analyses*

The GC-TEA system was used for quantitative analysis of compounds adsorbed by headspace SPME from inside the rifle barrels. This system was described in the previous study (1) and the temperature program was modified to improve the detection of the TEA2 peak (3). The thermal desorption of the SPME fiber (polyacrylate) was performed at 170°C in the splitless mode of injection. The liner used was purchased from Supelco (SPME Injection Sleeve for Hewlett Packard), especially designed for desorption of volatile compounds from SPME fiber. The inner diameter is only 0.75 mm, which means that the desorption volume inside the liner is very small. The peak broadening of the most volatile compounds is thus minimized. The liner was used empty.

### Results and Discussion

#### *Decomposition Products of Smokeless Powder Detected Inside Rifle Barrels*

The only compound detected in rifle barrels after shooting, escaping from the barrel with time after shooting, and suitable for estimation of time since the latest discharge of the firearm was the TEA2 compound. No naphthalene or related compounds, often detected inside shotgun barrels, were observed on SPME sampling from rifles. In comparison with shotguns, the TEA2 peak detected in rifles was very much weaker, approximately two orders of magnitude weaker. The amount of TEA2 detected one day after the shooting (a peak height of only some millivolts) is comparable with the amount detected inside spent cartridges. Differences in burning

<sup>1</sup> Associate professor and firearm investigator, respectively, SKL, National Laboratory of Forensic Science, S-58194 Linköping, Sweden.

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FIG. 1—Sampling from rifle barrels. The SPME fiber is exposed to the atmosphere inside the barrel for 20 min at room temperature. The rifle shown is of .30–06 caliber: (a) sampling at the muzzle position; (b) sampling at the breech position. Note that the bolt of the rifle must be removed as well as the adjustable depth gage from the SPME holder. The SPME device is pushed inside the barrel using tweezers.

characteristics and different cartridge material between rifles and shotguns should be the explanation to the observed discrepancies in the amount and kind of combustion products. Particularly, the material in shotgun cartridges is different and should explain the presence of naphthalene and similar combustion products in shotgun barrels.

Rifles of various calibers charged with ammunition from a number of various manufacturers have been subjected to SPME sampling. All the experiments resulted in the detection of the TEA2 peak inside rifle barrels one day after the shooting, which was the shortest studied time after discharge. This represents normally the shortest possible time since discharge achieved in casework. The amount of combustion products detected inside a firearm immediately after firing will be, of course, much higher. The amount of the TEA2 compound decreased with time after discharge in a manner similar to that observed for shotguns and spent cartridges. Like in shotguns, there are differences in the amount of the TEA2 com-

pound deposited in firearm barrels on shooting with ammunition from different manufacturers. However, these differences are lower for rifles. The difference between the propellant depositing the lowest respective and the highest amount of TEA2 compound in the same weapon is about a factor of three (when sampled in the breech position). Table 1 shows the results of SPME sampling from the barrel of a Browning rifle, calibre .30–06. The sampling was performed both from the muzzle position and the breech position one day after the shooting with various kinds of ammunition. For comparison, the results obtained for the spent cartridges are shown as well. The amount detected inside the spent cartridges seems to be related closely to that in the firearm. This implies that the combustion characteristics and the efficiency of various propellants are clearly different. The distribution of the TEA2 inside the barrels was found to be different in different rifles of the same caliber. There is a clear difference in the amount of the TEA2 compound detected in the two sampling positions (Table 1). Most of the rifles

TABLE 1—The height of the TEA2 peak detected on SPME sampling from a sporting rifle Browning, caliber .30–06, with stainless steel barrel.

Manufacturer of Ammunition	Spent Cartridge	Rifle	
		Sampling from the Muzzle Position	Sampling from the Breech Position
Federal	6.15	0.85	6.0
Prvi Partizan	5.65	2.05	5.70
Kynoch	6.50	1.35	9.30
Lapua	3.65	0.80	5.90
PMC	5.2	1.55	8.55
Remington	3.15	0.80	5.45
RWS	2.0	0.30–35	4.70
Svenska Metallverken	7.0	2.90	≥9.25
Samson (IMI)	5.05	2.10–15	≥7.40
Winchester	11.8	1.60	14.5

NOTE: The sampling from the rifle and the cartridges was performed one day after the shooting. The sampling time was 20 min. The peak height values are in millivolts.

showed the highest concentration in the breech position. We found, however, rifles where the concentration was highest in the muzzle position. The explanation is probably the various types of breech constructions, possible leaks in the breech, and also different sampling geometry in the breech position of different firearms.

The decay of the TEA2 peak with time since discharge was non-exponential in similarity to its decay in shotguns. Figure 2 shows this decay measured for three rifles of different caliber: .222, .30-06, and  $9.3 \times 62$ . Norma ammunition was used for these shootings. The y-axis is logarithmic, which clearly shows that the decay is non-exponential. It seems that the rate of escape of the TEA2 compound is faster for rifles of coarser caliber (e.g.,  $9.3 \times 62$ ) compared to smaller caliber (.222). It is normally expected to be like that, but to our surprise, the results, obtained for spent cartridges of various calibers (3), were inconsistent with this assumption. Comparison of the escape of the TEA2 compound from the barrel of a rifle, caliber .30-06, sampled at the muzzle and the breech position, respectively, is shown in Fig. 3. The weapon investigated here was of the type where more TEA2 compound is detected at the muzzle position. Winchester ammunition was used.

The detection limit for the TEA2 peak in our GC-TEA system was estimated to about 0.1 mV as peak height. This value corresponds to  $-1.0$  on the y-axis of Figs. 2 and 3. In spite of the fact that the amount of the TEA2 compound inside rifle barrels is much lower compared with shotgun barrels, the TEA2 peak may be

detected for a relatively long period after the shooting—generally for one to two months.

When the ammunition used in the latest shooting is unknown, the procedure suggested for the estimation of the time since discharge of shotguns (1) may be used for rifles as well. According to this procedure, the ratio  $I_n/I_{n-1}$  is calculated, where  $I_n$  is an intensity of the TEA2 peak day  $n$  and  $I_{n-1}$  day  $(n - 1)$ . The ratio  $I_n/I_{n-1}$  is then plotted against time since discharge. The resulting curves will not be influenced by the amount of TEA2 detected, only by the shape of its decay. Figures 4 and 5 show plots of the normalized function  $I_n/I_{n-1}$  against the time since discharge for rifles of different caliber. The ratio  $I_n/I_{n-1}$  in Fig. 4 was calculated for sampling in the breech position, where the amount of the TEA2 compound detected was larger and the reproducibility of the measurements was better compared to the muzzle position. The sampling in Fig. 5 was carried out in the muzzle position, because the bolt of the weapon investigated, the .222 rifle, was not easily removed for sampling in the breech position. The function  $I_n/I_{n-1}$  was not exactly the same in Figs. 4 and 5, but quite similar. Due to the much weaker detected TEA2 peak, the estimation of time since the latest discharge for rifles is expected to be less exact in comparison to that of shotguns. In both cases, the accuracy of this estimation decreases with the time elapsed after the shooting. Nevertheless, it should be quite possible to distinguish between a rifle used a few days ago and one used several weeks ago.

## Rifles of different calibre SPME sampling in the muzzle position

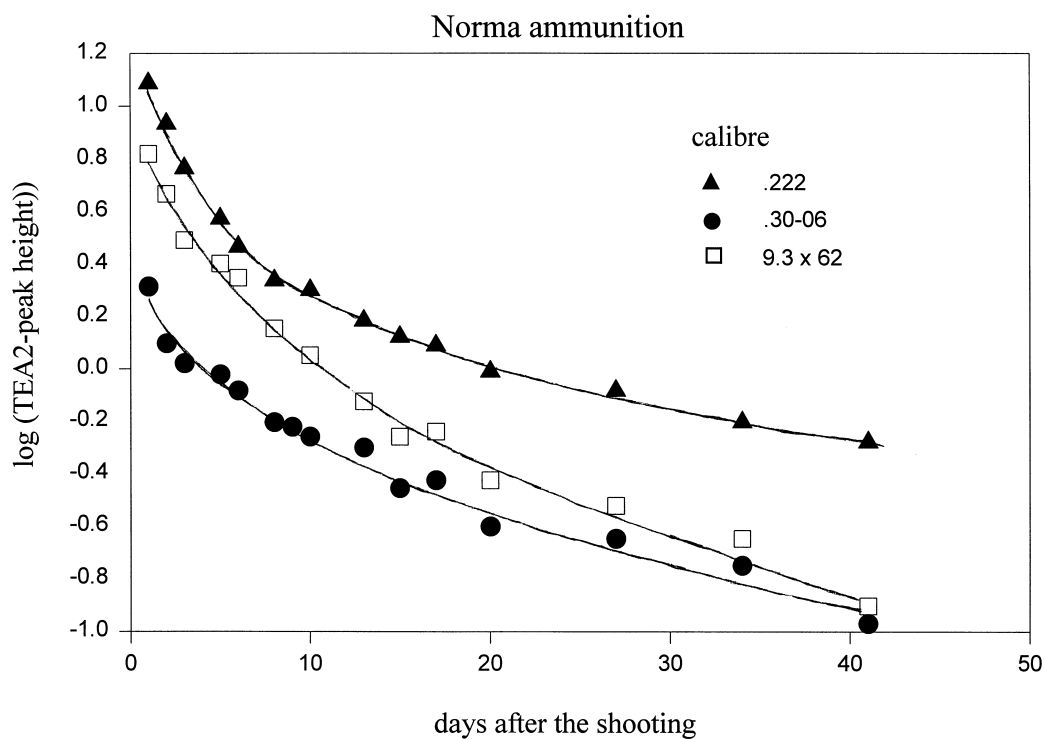


FIG. 2—The decay of the TEA2 peak with time after firing one shot with Norma ammunition. The results for rifles of three different calibers are shown. Note that the y-axis uses a logarithmic scale and the decays are thus non-exponential. The curves have been drawn only tentatively through the measured points. The SPME samplings were performed in the muzzle positions of these firearms. The sampling time was 20 min at room temperature. The detection limit for the TEA2 peak in our GC/TEA system was estimated to 0.1 mV, which corresponds to the value of  $-1.0$  on the logarithmic scale.

## Sporting rifle, calibre .30-06

### Winchester ammunition

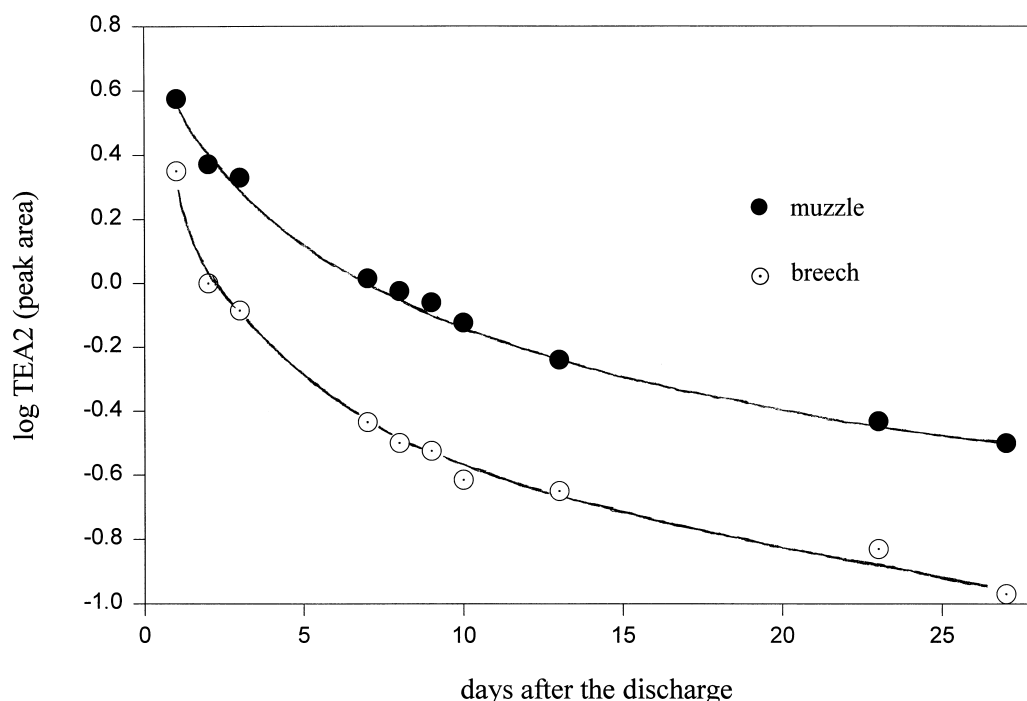


FIG. 3—The decay curves observed on sampling from the muzzle and the breech position of the same rifle, respectively. The firearm used was a FFV Husquarna sporting rifle, caliber .30-06, and the ammunition manufactured by Winchester. This rifle deposited higher concentration of the TEA2 compound in the muzzle position.

So far we have not succeeded in identifying the chemical nature of the TEA2 compound. By using GC/MS in the EI mode we have obtained the mass spectrum of this compound, and the same spectrum was obtained independently of us by our colleagues in Italy (Romolo, FS, personal communication). Unfortunately, no compound with this spectrum is present in our library of mass spectra. The use of positive chemical ionization to obtain the molecular ion of the TEA2 compound has so far been unsuccessful.

#### Number of Shots Fired and the Effect of Cleaning

Some of the results and tests performed with shotguns may be used for rifles as well. Thus, e.g., the rate of escape of the TEA2 compound from weapon barrels decreases with temperature of storage. In a rifle stored at about  $-20^{\circ}\text{C}$ , the TEA2 peak may still be detected after several months. Such outdoor temperatures are not common in every country, but are normal during wintertime in the northern part of Sweden.

The surface of the inside of rifles is different from that of shotguns. The surface is smooth in shotguns, but grooved in rifles. Thus, soot particles may not be removed so easily from rifle barrels by cleaning, and the number of shots may influence the results in a manner different from that observed for shotguns. Table 2 shows the results obtained for a Browning rifle, caliber .30-06, after shooting with Lapua ammunition. After firing five shots with this firearm, the amount of the TEA2 compound increased approximately by a factor of two compared to firing a single shot.

TABLE 2—Influence of the number of fired shots and of cleaning the weapon.

	Sampling from the Muzzle	Sampling from the Breech
1 shot	1.50 mV	9.60 mV
5 shots	3.60 mV	19.9 mV
5 shots + cleaning of the weapon by cloth	1.80 mV	10.6 mV

NOTE: Twenty-minute SPME sampling in the barrel of a Browning sporting rifle, caliber .30-06, 18–20 h after the activity shown in the table. Shooting with Lapua ammunition.

Cleaning the firearm afterwards with cloth removed part of the decomposition products from the barrel to a level close to that detected after a single shot. In shotguns, the amount of TEA was constant for a few shots and decreased on firing five shots or more.

We have carried out several experiments where rifle barrels were cleaned with weapon oil and found that normal cleaning did not remove the TEA2 compound entirely from the barrel. However, a careful cleaning with brushes and some weapon oil resulted in TEA-detectable nitro-compounds that interfered with the detection of the TEA2 peak. As for shotguns, a careful cleaning of the firearm with oil seriously restricts the possibility of estimation of time since the latest discharge of the firearm.

# Sporting rifles

SPME sampling in the breech position

NORMA ammunition

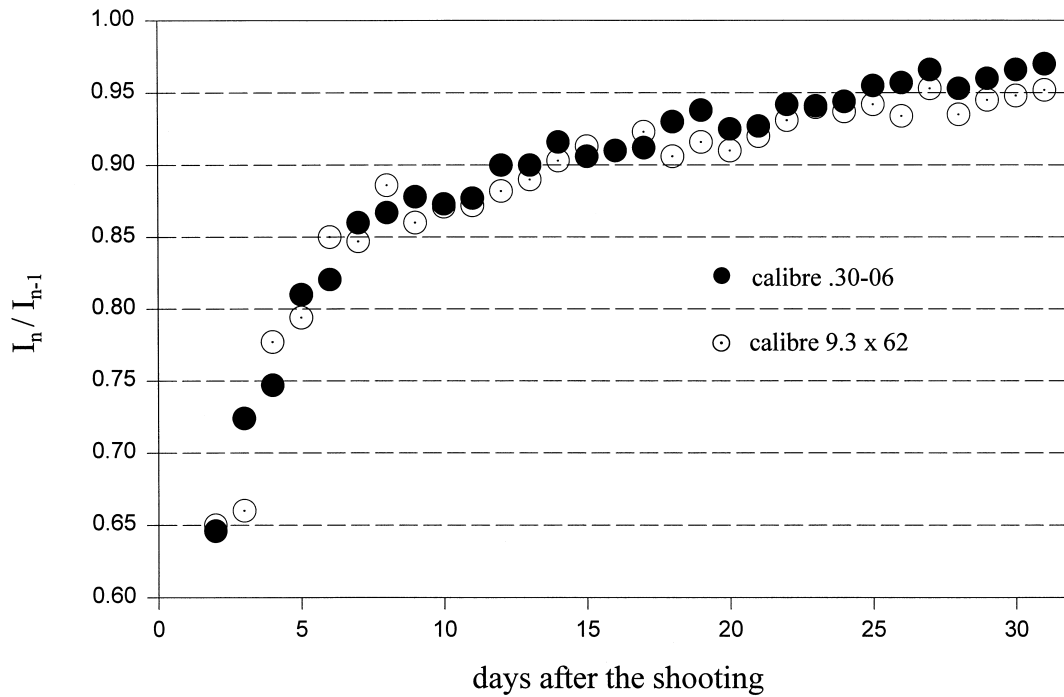


FIG. 4—The function  $I_n/I_{n-1}$  calculated for the decay of the TEA2 peak. The shooting was the same as shown in Fig. 2, but the sampling was performed in the breech position. Norma ammunition was used. Two rifles of caliber .30-06 and  $9.3 \times 62$  are presented. The  $I_n/I_{n-1}$  function obtained is similar for both two firearms.

# Sporting rifle, calibre .222

SPME sampling in the muzzle position

Norma ammunition

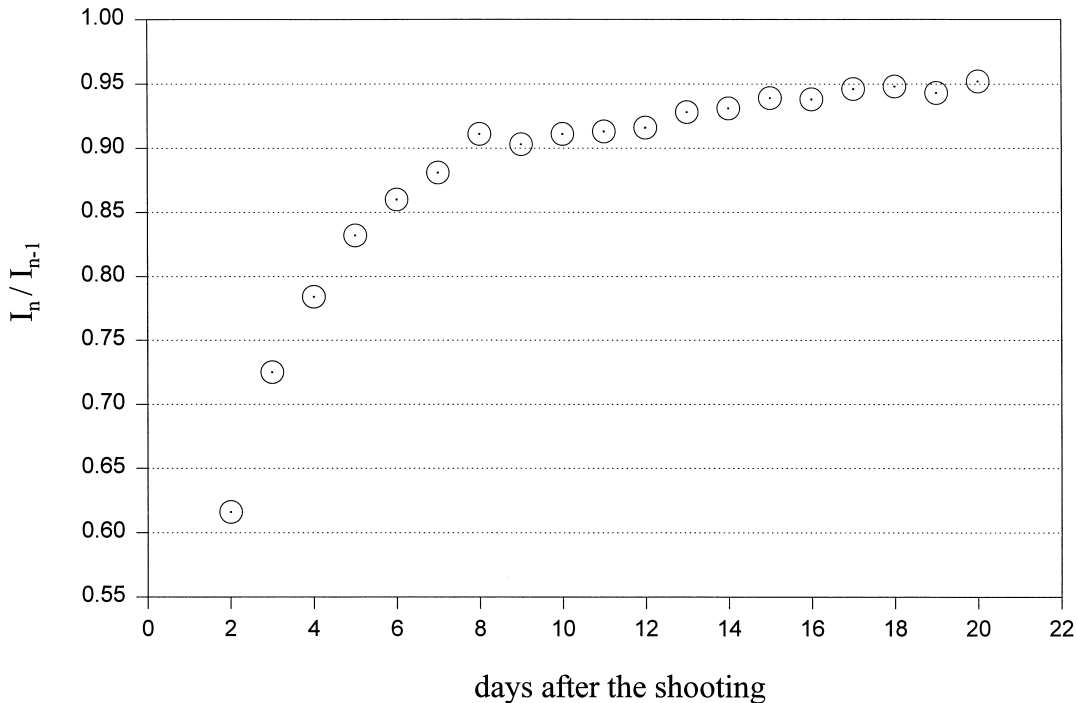


FIG. 5—The ratio  $I_n/I_{n-1}$  calculated for the decay of the TEA2 peak observed on SPME sampling from the muzzle position of a rifle, calibre .222. Even this curve resembles those obtained on SPME sampling from other types of weapons with long barrels.

## Conclusion

The GC-TEA system can be used for detection of the TEA2 compound inside rifle barrels. The escape of this compound from the barrel with time is suitable for the estimation of time since the discharge of rifles. It can generally be detected for one to two months after the latest discharge. On comparison with shotguns, the TEA2 peak detected in rifles is much weaker. Due to this low amount, the accuracy of the estimation of time since the latest discharge achieved for rifles is poorer compared with that for shotguns. To achieve a better precision, the sampling in both the muzzle position and the breech position is recommended.

## References

1. Andrasko J, Norberg T, Ståhling S. Time since discharge of shotguns. *J Forensic Sci* 1998;43(5):1005–15.
2. Andersson C, Andrasko J. A novel application of time since the latest discharge of a shotgun in a suspect murder. *J Forensic Sci* 1999;44(1):209–11.
3. Andrasko J, Ståhling S. Time since discharge of spent cartridges. *J Forensic Sci* 1999;44(3):487–95.

Additional information and reprint requests:

Jan Andrasko, Ph.D.

SKL, National Laboratory of Forensic Science

S—581 94 Linköping, Sweden