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TECHNICAL NOTE

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Time Since Discharge of Shotgun Shells

ABSTRACT: A technique for the estimation of time since discharge of a given class of spent shotgun shells is presented. The technique involved the use of SPME (Solid Phase Microextraction) sampling from the atmosphere inside spent shotgun shells. Compounds absorbed on the SPME fiber were desorbed and analyzed with GC-MS. The decrease in concentration of the combustion product naphthalene was monitored in all shells over a two-month period. Three conditions were examined to prevent naphthalene from escaping prior to testing the shells. A glass vial was successfully incorporated to halt the dissipation of naphthalene. At room temperature the naphthalene peak can be measured for several months and the curve-fitting data can lead to an estimation of time since discharge.

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

Background

Determining the time since discharge of firearms is an important aspect of firearms investigations. Spent cartridges found at a crime scene may provide information for determining the approximate time that a firearm was discharged. A spent cartridge can often be linked to a firearm through comparison of fire pin impression, breech face, or extractor markings.

The solid phase microextraction (SPME) technique has been used to detect volatile compounds from firearms and spent cartridges (1–5). In these studies, difficulties had been observed in preserving the condition of a spent cartridge. In the present experiment, the volatile compound, naphthalene, was monitored because of the reproducibility and detection limit of the peaks produced with GC-MS. The escape of naphthalene can be measured several weeks after the cartridge has been fired. The ideal situation involves a forensic scientist finding a spent cartridge and preserving it in a condition that allows the concentration of the volatiles to remain constant until the laboratory testing can be accomplished.

In the present study, the method of placing a shotgun shell in a vial prevented the escape of the volatile compounds. The concentration of the naphthalene remained constant prior to laboratory analysis. The naphthalene peak height produced a curve-fitting line that was used to estimate time since discharge.

Materials and Methods

Test Shootings

All test fires were performed with a Remington Model 870 Express 12 gauge shotgun. All ammunition used was Federal Cartridge Brand Gold Medal 2¾ in. shot shells (product number T115 8), which originated from the same lot. The shells were divided into four groups. They were held at 21°C immediately after firing. The first group was stored as open shells. The second group was sealed by placing a cork in the end of the shell. Corks wrapped in Teflon were used to seal the shells from the third group. The fourth group was placed as open shells into a vial slightly larger than the shotgun shell. A hole was drilled through the center of the lid but not through the Teflon inner lining of the cap. This allowed for easy sampling with SPME without opening the vial or disturbing the shell. Sampling from the corked and the vial samples is shown in Fig. 1.

Solid Phase Microextraction

Silica fibers with an 85 μm polyacrylate coating were purchased from Supelco and used in all of the experiments. The fibers were initially conditioned prior to use in a GC injection port at 300°C for 3 h. The fiber was conditioned daily before sampling at 200°C for 10 min. Blank runs were performed between samples to ensure that the fiber and GC injection port were free of residues.

Sampling from Shotgun Shells

The shotgun shells that were stored in open air were corked just prior to sampling. The SPME needle was pushed through the cork for the first three groups of shells and through the Teflon lining of the cap on the vial in the fourth group. Each silica fiber was centered and exposed to the atmosphere inside the shell for 20 min at room temperature.

Gas Chromatographic and Mass Spectrometric Analysis

In this experiment, a Varian Saturn 200R 3800 gas chromatograph in splitless mode was connected in series to a Varian Saturn 2000R mass spectrometer was used. The GC separations were achieved on a 29 m 250 μm CP-S18 CB low bleed/MS fused silica

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capillary column. The injection port temperature was 200°C, helium gas flow of 1 mL/min, in splitless mode. The analytical conditions were: initial temperature 70°C held for 1.0 min, ramp 8°C/min to 280°C and held for 5 min. The compounds on the SPME fiber were fully desorbed within 10 min of starting the temperature program.

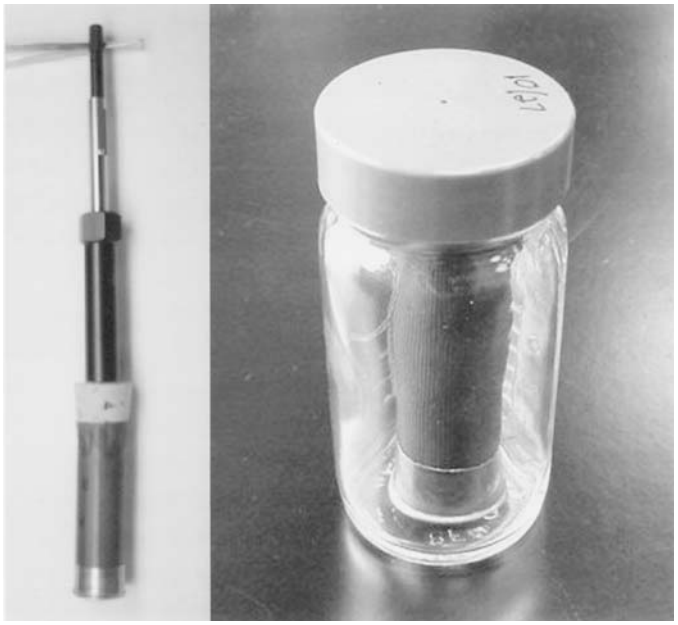

FIG. 1—*SPME sampling from shotgun shells in two different conditions. The picture on the left represents the technique used to test corked shells and prepared open shells. The picture on the right shows how the shotgun shells were placed in a vial that had a small hole drilled at the top that allowed SPME sampling.*

Results and Discussion

Detected Combustion Compounds

The SPME sampling of the shotgun shells was very reproducible as seen in other ammunition cartridges in previous papers (3). A typical gas chromatogram is shown in Fig. 2.

Many of the peaks were identified using the MS detector. The heights of four of the larger peaks were measured over the time frame of this experiment. These peaks were naphthalene (8.3 min), an unidentified peak (10.9 min), biphenylene (12.7 min), and diphenylamine (15.2 min). These four peaks were monitored because of their large size and noticeable decrease in intensity over time. Both biphenylene and diphenylamine were found not to be a good measure of the time since discharge as there was a greater variance in the concentration of the compounds. The unidentified peak had a satisfactory variance, but did not have a great decrease in concentration during the first four weeks after firing. Naphthalene provided the most consistent information for this experiment. The measured concentrations were highly reproducible from sample to sample. Three separate shells were fired and sampled two days later; these yielded a 1.3% and 12.9% relative standard deviation for the peak area and peak height, respectively. The naphthalene concentrations had a measurable decrease during the first four to five weeks after discharge.

Estimation of Time Since Discharge

The shotgun shells that were left open to the air in this experiment were sampled over 63 days (~9 weeks). A new shell was sampled for each data point. The decrease of naphthalene concentration over the first seven weeks is shown in Fig. 3.

The log of the peak heights was plotted against time and is shown in Fig. 4.

The logarithmic dissipation of naphthalene is nonlinear. A curve fitting line indicates that the peak height of naphthalene can

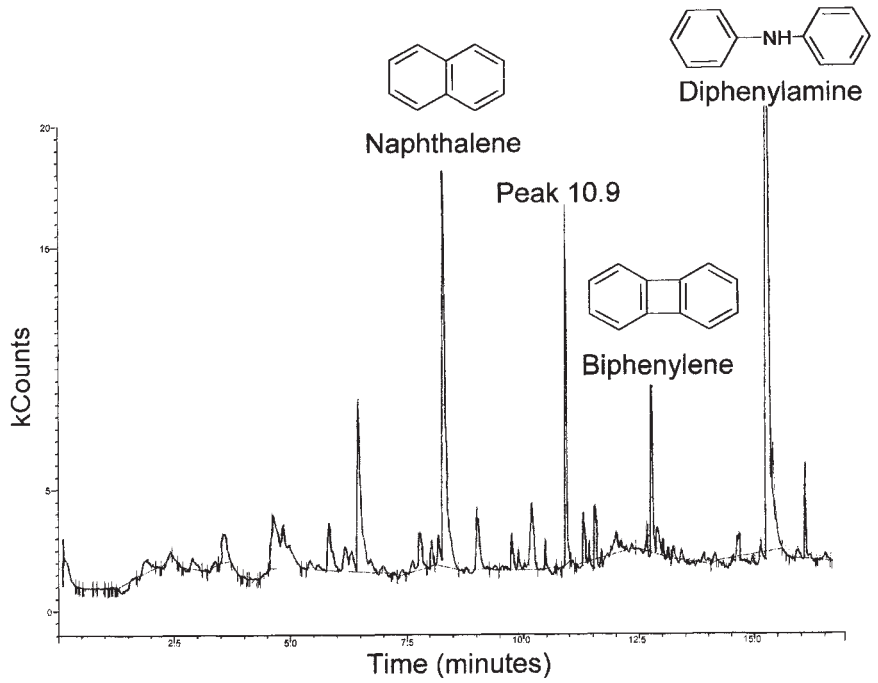

FIG. 2—*Gas chromatogram produced using SPME sampling of a shotgun shell 1 day after discharge. Four peaks have been labeled: naphthalene (peak 8.3), an unidentified peak (10.9), biphenylene (peak 12.7), and diphenylamine (peak 15.2).*

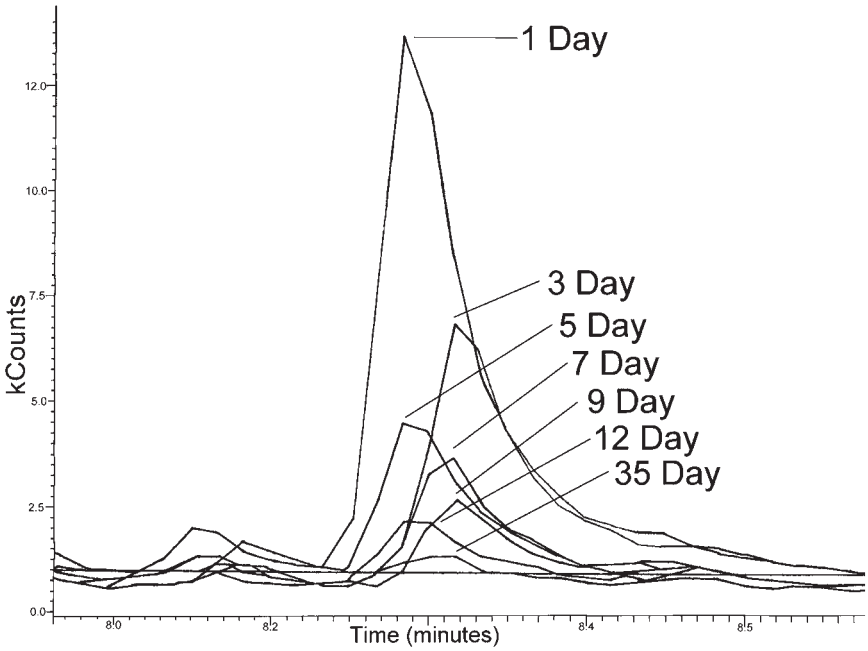

FIG. 3—*Overlaid GC plots showing the decrease of the naphthalene peak over the first 35 days from an open shell. The decrease is rapid near the time of the firing but levels off weeks later.*

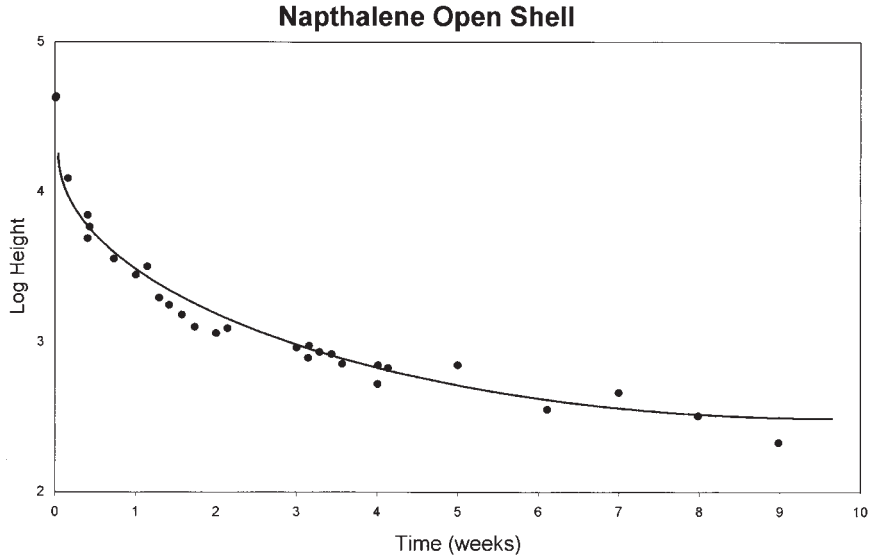

FIG. 4—*The disappearance of naphthalene from a shotgun shell after firing. The curve has been drawn tentatively through the measured points. The data show little variation around this line over the first four weeks.*

be used to estimate time since discharge for nearly four to five weeks after the shell has been fired under laboratory conditions. The data points have a slight variation around the line at greater time points.

Sampling from Corked Shell Conditions

Shotgun shells were capped with corks or Teflon-wrapped corks immediately after firing with the intention of preventing the naphthalene from escaping from the shell. The goal was to preserve the condition of the shell until it could be tested. A Teflon-wrapped cork was implemented with the idea that the naphthalene may have been slightly absorbed by the wooden cork.

The corked and Teflon corked shells were unsuccessful at preventing the disappearance of naphthalene. The dissipation of naphthalene is shown in Fig. 5.

Naphthalene continued to disappear from both cork and Teflon corked conditions over the several weeks monitored. There was no detectable difference between the two types of corks, which indicated that the naphthalene was not being absorbed into the corks.

Sampling from Vial Condition

Glass vials with SPME-compatible lids were found to prevent the naphthalene from dissipating. Shells were placed in the vials after firing and were sampled over 31 days. The curve-fitting line for

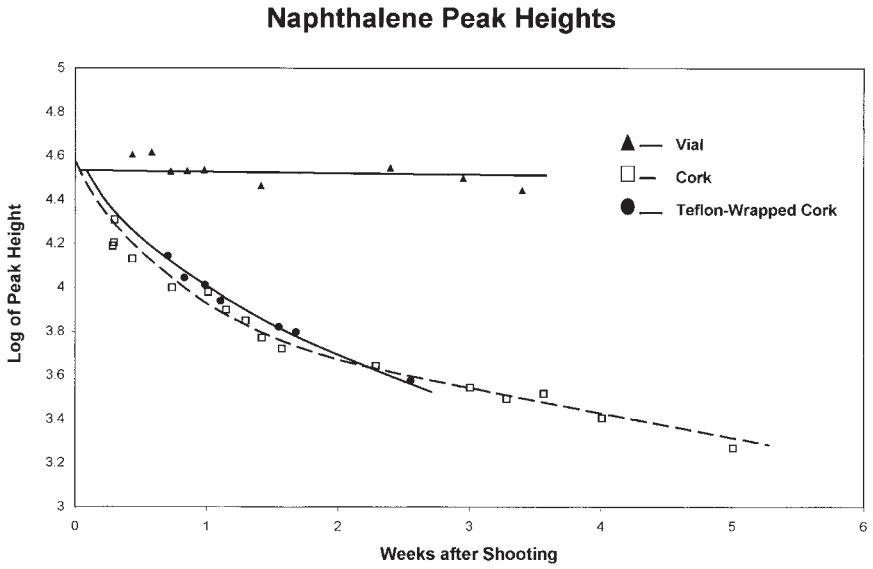

FIG. 5—*Comparison of three conditions that shotgun shells were exposed to in order to prevent the disappearance of naphthalene. The cork and Teflon-wrapped cork had nearly the same results. The shell in the vial was successfully used to prevent naphthalene from escaping.*

the data is shown in Fig. 5. The peak height of the naphthalene does not decrease over time. The glass vial system was the most successful method of preserving the naphthalene. This system would be beneficial to a forensic lab that may not be able to test a suspect shell for many days after it was found. The concentration of the shell the day it was found at a crime scene would be nearly identical to the day that it was tested in the lab.

The concentration of the naphthalene in the vial fell slightly in the first two days after the shell had been placed in the vial. This was thought to be due to the equilibration of the naphthalene throughout the volume of the vial as the vial used was slightly larger than the shell. The data were normalized to correct for this factor by multiplying the peak height by the ratio of the volume of the vial outside the shell divided by the volume of the vial. After equilibration had been achieved, the concentration remained constant. The dimensions of the ideal vial would be just large enough to fit a shell and minimize the initial decrease in the naphthalene concentration.

Repeated Sampling from Vial

Repeated sampling from the same vial over time was compared with the results of individual vials for each data point. A piece of Teflon was placed over the sampling hole in order to prevent naphthalene escape between tests. Repeated sampling with SPME did not show a significant difference from the vials that were only sampled once. This is beneficial to a crime lab because it permits multiple samples to be taken from the same shell.

Conclusions

The SPME technique combined with GC-MS was used to detect several volatile combustion compounds in shotgun shells after they had been fired. The volatile compound naphthalene proved to be a suitable peak to monitor because of its reproducibility and noticeable decrease in concentration over time. The decrease in concentration of the naphthalene could be used to estimate time since discharge.

A glass vial system was found to have the ideal conditions to preserve the condition of a spent cartridge in that the concentration of the naphthalene did not significantly decrease prior to laboratory analysis. It was also determined that repeated SPME sampling could be performed on the shell without a significant decrease in the naphthalene concentration. The vial system also included other evidence valuable to a forensic crime lab. A shotgun shell as a piece of evidence needs to be placed in a sealed container. The vial provides this condition and also allows testing without disturbing the shell. SPME sampling can be performed through the top of the vial and the fiber will not come in contact with the shell. This nondestructive method will not disturb any other evidence on the shell such as latent fingerprints or blood. The vial can be passed on to other sections of the lab unopened.

An important use of these data is being able to identify if a shell is a part of a crime scene. If the shell was found at the scene of a crime that had taken place recently, this technique could be used to determine whether the shell was recently fired. It could rule out a shell that had been fired months ago or an old shell that had been planted on a scene.

Future work will involve examining this system with other types of ammunition cartridges, and examination of other types of SPME fibers that may be more suitable for monitoring volatile compounds.

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 discharge of a shotgun in a suspect murder. J Forensic Sci 1999;44(1):211–3.
3. Andrasko J, Ståhling S. Time since discharge of spent cartridges. J Forensic Sci 1999;44(3):487–95.
4. Andrasko J, Ståhling S. Time since discharge of rifles. J Forensic Sci 2000;45(6):1250–5.
5. Andrasko J, Ståhling S. Time since discharge of pistols and revolvers. J Forensic Sci 2003;48(2):307–11.

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