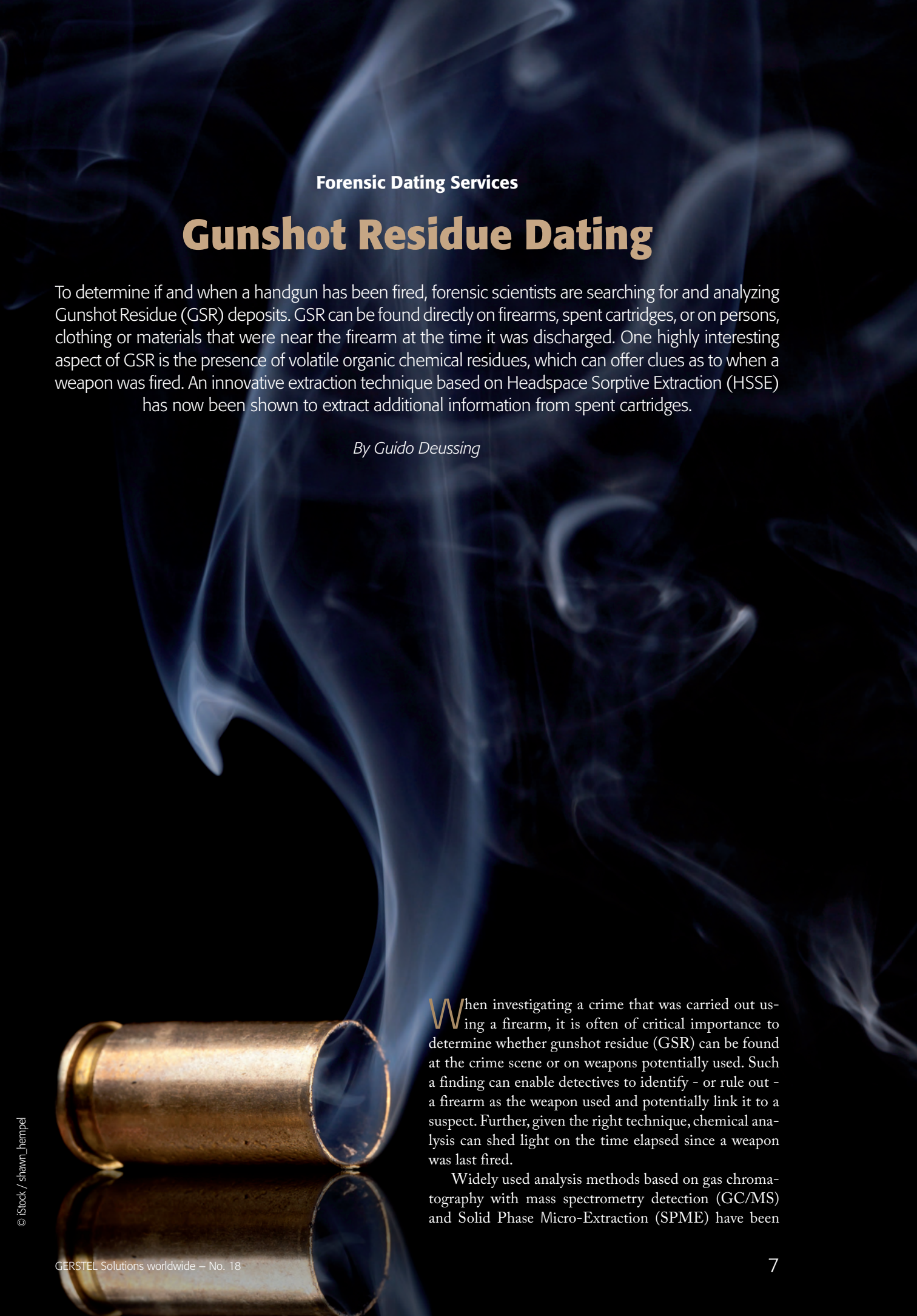
Forensic Dating Services

Gunshot Residue Dating

To determine if and when a handgun has been fired, forensic scientists are searching for and analyzing Gunshot Residue (GSR) deposits. GSR can be found directly on firearms, spent cartridges, or on persons, clothing or materials that were near the firearm at the time it was discharged. One highly interesting aspect of GSR is the presence of volatile organic chemical residues, which can offer clues as to when a weapon was fired. An innovative extraction technique based on Headspace Sorptive Extraction (HSSE) has now been shown to extract additional information from spent cartridges.

By Guido Deussing



When investigating a crime that was carried out using a firearm, it is often of critical importance to determine whether gunshot residue (GSR) can be found at the crime scene or on weapons potentially used. Such a finding can enable detectives to identify - or rule out - a firearm as the weapon used and potentially link it to a suspect. Further, given the right technique, chemical analysis can shed light on the time elapsed since a weapon was last fired.

Widely used analysis methods based on gas chromatography with mass spectrometry detection (GC/MS) and Solid Phase Micro-Extraction (SPME) have been

evaluated by collaborating scientists at the University of Lausanne, Switzerland; the Sapienza University in Rome, Italy; and King's College in London, England. In addition, a novel method using Headspace Sorptive Extraction (HSSE) followed by thermal desorption-GC/MS (TD-GC/MS) was compared with the SPME based method. The scientists were pleased with the results. [1].

The Content of Gunshot Residue

Every firearm emits gunshot residue when discharged. The compounds involved are released at explosive speed and deposited or adsorbed on the hand, body and clothing of the shooter. Depending on the distance to the firearm, residue can also be found on the victim and, obviously, on the weapon used and on spent cartridges that were ejected.

Sources of GSR are the ignition- and propellant charge powders in the cartridge. In addition, metallic powder is formed by abrasion from the bullet and cartridge and added to the mix. GSR consists of various inorganic and organic chemicals. Due to aging processes and volatilization, changes in the concentrations and amounts of organic chemicals as well as certain compound to compound ratios of amounts can be helpful in determining the time of discharge of a weapon according to Gallidabino et al. as reported in their paper in Analytical Chemistry [1].

To perform Headspace Sorptive Extraction (HSSE), a GERSTEL Twister is suspended inside a sealed vial placed in the headspace above the sample. In the case shown here, a spent handgun cartridge (left) is being analyzed. During extraction, volatile and semi-volatile organic compounds (VOCs and SVOCs) are concentrated in the sorption phase of the Twister. The Twister shown here is the Polydimethylsiloxane (PDMS) version. Following the extraction period, the Twister is removed, placed in a glass liner, and analyzed by thermal desorption-GC/MS. The GERSTEL Thermal Desorption Unit combined with a GC/MS-System (Agilent Technologies) was used in the work reported here.

The compounds identified as GSR from literature references are, among others, nitroglycerine, diphenylamine, ethylcentralite, dibutylphthalate and 3-Ethyl-1-Hexanol as well as organic reaction byproducts, especially derivatives of benzene, and polycyclic aromatic hydrocarbons (PAHs). To determine these, the SPME technique has been widely used in combination with GC/MS. To perform GSR-based dating, Gallidabino et al. performed repeat extractions of analytes from the interior of a firearm and/or spent ammunition with the aim of establishing an aging profile, which can be compared with reference profiles. Naphthalene and decomposition products of nitrocellulose were proposed as target reference compounds.

The problem with handguns – and the solution

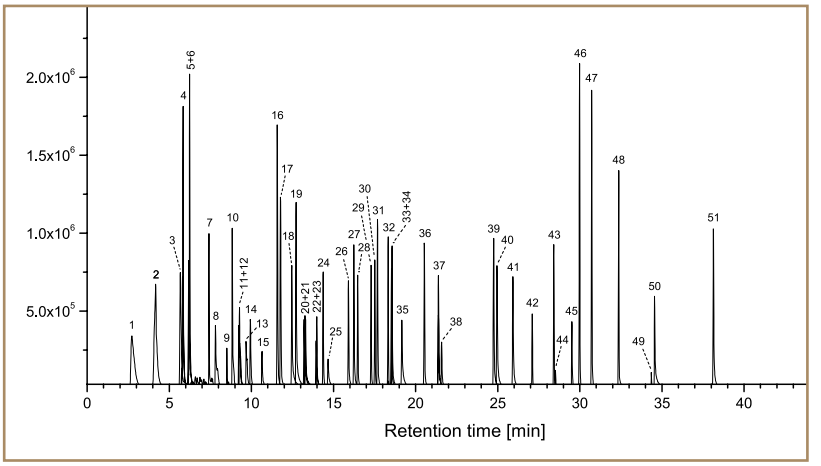
SPME is an established technique for time estimates concerning discharge of ammunition from rifles and other larger firearms. However, its usefulness for forensic dating of firing of smaller handguns is more limited. The repeatability is insufficient, as reported by the scientists, and degradation curves for the target analytes quickly fall below their limits of detection with SPME, as Gallidabino et al. [1] report. For these reasons, SPME is not the ideal technique for the investigation of GSR in combination with handguns.

In their search for an alternative extraction and analysis method with significantly higher sensitivity for the target analytes, the scientists' attention was caught by Headspace Sorptive Extraction (HSSE). HSSE is based on the GERSTEL Twister, a glass coated magnetic stir bar with a PDMS sorption phase. The Twister is most often used for Stir Bar Sorptive Extraction (SBSE) of aqueous samples. In HSSE, the Twister is suspended in the Headspace above the sample inside a sealed 20 mL headspace vial. HSSE is thus very similar in principle to Headspace Solid Phase Micro-Extraction (HS-SPME). The main difference is that the Twister offers a much larger sorption phase volume than SPME fibers which consist of a thin sorption phase coating on a metal or glass fiber contained within a syringe needle. Consequently, SBSE provides better recovery, better repeatability, and lower limits of detection. After the extraction step, analytes are released from the Twister by thermal desorption in the GERSTEL Thermal Desorption Unit (TDU 2) immediately followed by GC/MS determination of the analytes. These steps are fully automated using the GERSTEL MultiPurpose Sampler (MPS) under MAESTRO software control. "The Twister can provide up to 1000 times higher sensitivity than SPME, depending on the application", says Oliver Lerch, Ph.D., Application Scientist from GERSTEL.

SBSE can be performed with different Twisters to cover a wide range of analytes from non-polar to polar. Desorption can be performed by thermal desorption – as is most often the case - or by liquid desorption combined with either GC/MS or LC/MS.

Preparing the GSR analysis

To determine whether HSSE is a suitable extraction technique for the analysis of GSR, different types of cartridges were inserted into a semi-automatic pistol, discharged, and the spent cartridges placed in sealed HS vials with GERSTEL Twisters suspended in the headspace above the sample. The cartridges contained propellant charges based on either nitrocellulose or a combination of nitrocellulose and nitroglycerine. The results from the HSSE-TD-GC/MS analysis were compared with results from the analysis of a reference mixture based on 55 selected substances, identified as GSR compounds. This is how Gallidabino et al. approached the analysis: In the headspace above the spent cartridge to be analyzed, a perforated glass insert containing a conditioned Twister was positioned and the headspace vial was sealed. Different Twister techniques enable different sampling approaches along with the use of different phases to collect a wider range of analytes. In this case, the analytes were extracted at 80 °C for 72 hours. The Twisters were removed from the vial and placed in individual sealed glass tubes ready for Thermal Desorption-GC/MS analysis. The glass tubes were fitted with individual transport adaptors, which seal the tubes and enable the MultiPurpose Sampler (MPS) gripper to transfer them to the Thermal Desorption Unit (TDU) for temperature programmed desorption. The released analytes are focused in the GERSTEL Cooled Injection System (CIS) PTV type GC inlet at -80 °C. The CIS is then heated using a temperature program and the analytes transferred to the GC column in splitless mode using a helium carrier gas flow of 1.3 mL/min for highly sensitive GC/MS determination. The CIS was installed in a gas chromatograph (Agilent GC 7890A) connected to an Agilent 5975 Mass Selective Detector (MSD). The column used was an Agilent HP-5MS (30 m x 0.25 mm x 0.25 µm). The GC oven initial temperature was 40 °C, the program progressing to a final temperature of 280 °C. The GC run including cool-down and equilibration lasted 46 minutes. Mass Selective Detection (Agilent 5975C MSD) was performed in EI mode in full scan mode across a range of m/z 40 to 500.



Extracted Ion Chromatogramm (EIC) of the standard solution containing 55 substances injected by Gallidabino et al. Using HSSE-GC/MS, the researchers were able to determine 51 of the 55 compounds in GSR. The "missing compounds" were thermally labile substances including nitroglycerine and N-nitrosophenylamine.

HSSE delivers

The results of their study clearly showed that by using HSSE, the scientists were able to determine and track the concentration degradation curves of 51 of the selected 55 GSR target analytes from discharged cartridges. HSSE proved to be significantly more sensitive while delivering better reproducibility than SPME. Among the 4 compounds not found were thermally labile compounds such as nitroglycerine that are decomposed during thermal desorption. Further studies are to be performed to optimize the analysis method parameters with the aim of increasing the number of target analytes that can be determined.

As part of their project, Gallidabino et al. generated aging curves in order to develop a method for determining the approximate time of discharge including determining whether the firearm was discharged at all. These aging curves are based on GSR compound concentrations on spent cartridges from handguns and their degradation curves. The scientists report that based on the use of HSSE on aged samples, several GSR compounds have shown significant aging profiles. In addition, compound-to-compound ratios can be used to extend the time periods that can be covered. This approach also contributes to making the determination more rugged and to reducing variability, making the method more useful for the forensic scientist entrusted with the case. Gallidabino and his colleagues concluded that their results were very encouraging for the development of a new and complete forensic dating technique based on GSR.

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Reference

[1] M. Gallidabino, F. S. Romolo, K. Bylenga and C. Weyermann, Development of a Novel Headspace Sorptive Extraction Method to Study the Aging of Volatile Compounds in Spent Handgun Cartridges, Analytical Chemistry 86 (2014) 4471-4478