Post-refereeing version
Final version published in: Journal of Forensic Sciences, Vol. 61(5), 1409-1410.
doi:10.1111/1556-4029.13167

Commentary on: Chang KH, Yew CH, Abdullah AFL. Study on the behaviors of gunshot residues from spent cartridges by headspace solid-phase microextraction-gas chromatographic techniques. J Forensic Sci 2015;60(4);869-877.

Matteo Gallidabino*, Céline Weyermann

University of Lausanne, École des Sciences Criminelles, Institut de Police Scientifique, Bâtiment Batochime, 1015 Lausanne-Dorigny, Switzerland

Abstract

Commentary on: Chang KH, Yew CH, Abdullah AFL. Study on the behaviors of gunshot residues from spent cartridges by headspace solid-phase microextraction-gas chromatographic techniques. J Forensic Sci 2015;60(4);869-877.

* Corresponding author: matteo.gallidabino@unil.ch

Sir,

we would like to comment on the paper by Chang et al. [1], "Study on the behaviors of gunshot residues from spent cartridges by headspace solid-phase microextraction-gas chromatographic techniques". In this paper, the authors applied a previously optimized headspace solid phase micro-extraction (SPME) method to study the disappearance over time of several common smokeless powder compounds from 9 mm spent cartridges. They discussed the possibility of estimating the time since discharge, and stated that: *"[the global interpretation of the results] could be used to predict the elapsed time after a gunshot, whether it was fired 1 day, 2 – 4 days, < 5 days, 10 days, 20 days, or more than 30 days ago. (see "Conclusion", p. 876)"*

We wish to emphasize that such a possibility would be very useful in the investigation of firearm-related crimes and, in this regard, new contributions are particularly welcome to increase knowledge in the field. However, we would also like to address issues in the experimental methodology adopted by Chang et al., which, in our opinion, could affect the final interpretation of the results and the application of the methodology itself to real cases.

Figures 4 to 7 show ageing curves for reliable analytes identified by the authors to estimate the time since discharge, i.e., diphenylamine (DPA), dibutyl phthalate (DBP) and naphthalene. Decrease was followed up to 30 days, and level-off for the three target analytes occurred only after 15 days of ageing. This is a surprising result compared to previous works on handgun cartridges [2-4]. As described in the experimental part, cartridges were extracted in 10 mL vials, and the authors further explained that: *"Spent cartridges were left open in the headspace vials to allow exposure to the atmosphere for up to 30 days in an air-conditioned room (about 20 °C) without environmental disturbances, for example, wind and direct sunlight exposure (see "Kinetic study", p. 870)."*

It should be noted that, additionally to environmental disturbances, other factors can play a significant role in decrease kinetics, such as the cartridge position and its confinement. In this regard, the experimental methodology adopted by Chang et al. is not comparable to real casework situations. On one hand, the spent cartridges were left aged in a vertical position, and, on the other hand, they were confined in open vials during ageing. Both these experimental choices are, unfortunately, susceptible to introduce strong bias between the observed decrease rates and those actually met in real-life situations. We found, for example, that the decrease rate of GSR compounds is significantly influenced by the cartridge position, and is usually slower when spent cases are placed vertically. This may be explained by a smaller evaporation surface. Regarding confinement in open vials, 9 mm spent cases are significantly smaller than conventional 10 mL vials, and the latter also present a smaller opening in comparison to their body (i.e., they are bottlenecked). Consequently, it is likely

that a fraction of the compounds dissipating from the cartridge is conveyed into the internal headspace of the vial, making the observed decrease rate slower than that one would actually encounter during ageing in an open space. Thus, we have good reasons to believe that the ageing curves showed by Chang et al. are not representative of real ones. Ageing curves acquired by the same authors after direct exposure to environmental conditions (Figure 7 and 8) confirm this conclusion as they presented significantly quicker decreases in comparison to those acquired during the main kinetic study. In this case, level-off seemed to occur already after a few hours of ageing, which is actually comparable to previously published works [3, 4]. Therefore, we feel that the possibility to classify the discharge amongst temporal classes such as "2 – 4 days old" or "5 – 10 days old", as proposed by the authors, may be too optimistic and more realistic investigations should be performed to clarify potential time ranges.

Another result we would like to comment on concerns the effect of storage in the measurement of GSR from single spent cartridges (Figure 3). Chang et al. stated that: *"The experimental results showed no significant change in peak areas of tested compounds from the extraction of headspace GSR except for DPA which showed a decreasing trend in the spent cartridge samples. (see "Interday measurement of GSR from spent cartridges", p. 872)"* and that: *"Extended study up 2 months suggested the integrity for the samples collected in the headspace vials allow their analysis even at 2 months period after sampling [at the exception of DPA]. (see "Interday measurement of GSR from spent cartridges", p. 872)"*

From observation of Figure 3, we would like to challenge these conclusions. We find that even naphthalene had an appreciable decrease over the first months of storage and that waiting may actually be an issue. It can be noted that chemical transformation of compounds is not the only phenomenon which can modify the GSR concentrations during storage. In fact, for apolar analytes, adsorption on the glass vial walls was previously reported (as, for example, in [5]), and we fear that the concentration of naphthalene was affected by this phenomenon. As a consequence, we would like to stress the importance of immediate analysis or suggest to test alternative conservation means in order to avoid irreversible loss of analytes and guarantee the comparability between questioned and reference analyses.

The estimation of the time since discharge of handgun cartridges is a very complex topic, which needs to take into account several variables in order to develop reliable methods for the application in casework. The research of Chang et al. is a very useful step toward a better understanding of the GSR ageing kinetics, and we advise to adopt a more systematic and realistic experimental approach in future works.

References

[1] K.H. Chang, C.H. Yew, A.F.L. Abdullah, Study of the behaviors of gunshot residues from spent cartridges by headspace solid-phase microextraction–gas chromatographic techniques, Journal of Forensic Sciences, 60 (2015) 869.

[2] J. Andrasko, S. Stahling, Time since discharge of spent cartridges, Journal of forensic sciences, 44 (1999) 487.

[3] C. Weyermann, V. Belaud, F. Riva, F.S. Romolo, Analysis of organic volatile residues in 9mm spent cartridges, Forensic science international, 186 (2009) 29.

[4] M. Gallidabino, F.S. Romolo, K. Bylenga, 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.

[5] Y. Qian, T. Posch, T.C. Schmidt, Sorption of polycyclic aromatic hydrocarbons (PAHs) on glass surfaces, Chemosphere, 82 (2011) 859.