ESTIMATING THE TIME SINCE DISCHARGE OF SPENT CARTRIDGES: A LOGICAL APPROACH FOR INTERPRETING THE EVIDENCE

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Abstract

Estimating the time since discharge of a spent cartridge or a firearm can be useful in criminal situations involving firearms. The analysis of volatile gunshot residue remaining after shooting using solid-phase microextraction (SPME) followed by gas chromatography (GC) was proposed to meet this objective. However, current interpretative models suffer from several conceptual drawbacks which render them inadequate to assess the evidential value of a given measurement. This paper aims to fill this gap by proposing a logical approach based on the assessment of likelihood ratios. A probabilistic model was thus developed and applied to a hypothetical scenario where alternative hypotheses about the discharge time of a spent cartridge found on a crime scene were forwarded. In order to estimate the parameters required to implement this solution, a non-linear regression model was proposed and applied to real published data. The proposed approach proved to be a valuable method for interpreting aging-related data.

Keywords: forensic science, firearms, solid phase microextraction, gunshot residue, dating, time since discharge, interpretation, likelihood ratio

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1. Introduction

Determining the time since discharge of firearms or spent cartridges would be very useful in the forensic investigation of firearm-related cases [1, 2]. For this purpose, several methods were previously proposed in the literature. Simpler approaches focused on the evaluation of physical characteristics like the thickness of the rust or dust layer on the inner surface of firearm barrels [3-5]. Modern techniques, on the other hand, are based on the chemical analysis of the gaseous and volatile compounds composing the organic gunshot residue (GSR) [3-13].

The GSR is the residue formed during the discharge of a firearm. It is a complex and heterogeneous mixture composed of a variety of chemical species, the majority of which are gaseous and volatile products generated by the cartridge explosion [14, 15]. After the shot, these products stay mainly in the inner atmosphere of barrels and cartridges, and they quantitatively decrease over time due to physicochemical processes, such as diffusion through air and adsorption on metallic surfaces. Knowing that the residual quantity could be very informative for dating purposes, recent developments proposed to sample organic GSR compounds by solid phase microextraction (SPME) and analyze them using gas chromatography (GC) [10-13]. These methods showed promising results to follow compound diminution in a wide range of firearms and spent cartridges [1, 2, 16-19] and was even applied in casework [1, 2].

Although several works reported the analysis of organic GSR compounds for dating purposes, the issue of age inference from the obtained analytical results was only superficially addressed. In simple terms, SPME/GC analyses of barrels and cartridges provide qualitative and semi-quantitative data (in the form of chromatograms) about the compounds remaining in their inner atmosphere at the moment of extraction. Information about the time that has elapsed since discharge can be evaluated from some selected aging indicators such as the presence and/or the residual quantity of specific compounds (e.g.: naphthalene). In literature, the present trend is to incorporate these indicators in investigative frameworks and then infer temporal propositions about the discharge time. However, this typical approach suffers from several statistical and conceptual drawbacks.

The main objective of this paper is therefore to develop an innovative and reliable framework for assessing the evidential value of organic GSR analyses in discriminating between temporal propositions regarding the discharge. To reach this objective, a logical approach based on the assessment of likelihood ratios (LRs) was proposed as recently suggested by different authors [20-23], and its use to discriminate between competitive hypotheses on discharge time will be shown. The paper is organized as follows. Sections 2 and 3 will introduce the hypothetical scenario and the analytical background which will be the core of the subsequent discussion. In Section 4, current interpretative

approaches will be discussed in more detail. Section 5 will present the proposed evaluative method based on the LR approach. The application of this model will be shown in Section 6. Empirical problems concerning the estimation of some relevant parameters needed for implementation will also be presented. Section 7 will develop statistical solutions to overcome these difficulties. Discussion and conclusion will be presented in Sections 8 and 9, respectively.

2. Hypothetical scenario

One evening in the woods, the body of a young man was found in a pool of blood with a gunshot-compatible wound. A spent cartridge (caliber 9mm Parabellum) was discovered close to the dead body. The autopsy estimated the time of death at about 8 hours before the discovery. The cause of death was a heavy hemorrhage due to the gunshot wound, and a bullet was extracted from the thorax. After some time, a suspect was arrested. A 9mm Parabellum pistol and some cartridges were seized at the suspect's apartment. According to the examination of the firearm experts, the observations carried out between the questioned and the comparison cartridge cases strongly support the hypothesis that the questioned cartridge was fired with the suspect's weapon rather than with another, unknown pistol; however, the bullet was too damaged, and no useful comparison could be undertaken. With regard to the results, the suspect did not deny that he fired the questioned cartridge; he claimed however that it was already at the scene due to a shooting game the morning before the discovery of the corpse (i.e., about 32 hours earlier).

3. Organic GSR analysis of the spent cartridge

In the situation presented, the main issue for the court is to determine if the cartridge discharge was or was not simultaneous with the commission of the crime so as to support or reject its relevance and, indirectly, the culpability of the suspect. In order to carry out useful analyses, we assume that, before sending the questioned cartridge to firearm experts, it was immediately sealed in a hermetic vial preventing gas escape [18, 19]. A single analysis was immediately performed in the laboratory using SPME/GC [11, 17]. The chromatogram of the extracted analytes yielded the quantitative data on several organic GSR compounds including naphthalene, a polycyclic aromatic hydrocarbon which is often produced by the incomplete combustion of gunpowder [2, 24-26] and previously proposed for dating purposes [2, 10, 11, 19]. The peak area of naphthalene was therefore selected as

a suitable aging indicator, and a specific value (say q = 28.00 a.u.[1]) was observed. The question that should be asked now is: how can we use this result to help the court make a decision?

4. Current methodologies for the interpretation

In the literature on discharge dating, the interpretation of organic GSR analyses has always been treated as a comparative process in which the measurements on the questioned cartridge are weighed against a reference calibration curve [2, 10, 16]. In this way, a particular observation can be correlated to a discharge time. The use of arbitrary pre-established thresholds was previously proposed in order to define intervals in which the real discharge time is most likely to have occurred [2, 10]. This solution was given mainly for dealing with the variability due to factors influencing the aging kinetics (i.e., the temperature). Considering the previous scenario (q = 28.00) and the hypothetical aging profile reported in Figure 1, the calibration method would lead to the inference that "the cartridge discharge dates back to 13.7 hours before the discovery of the body", while the threshold method allows to conclude that "the discharge time is older than 8 hours".

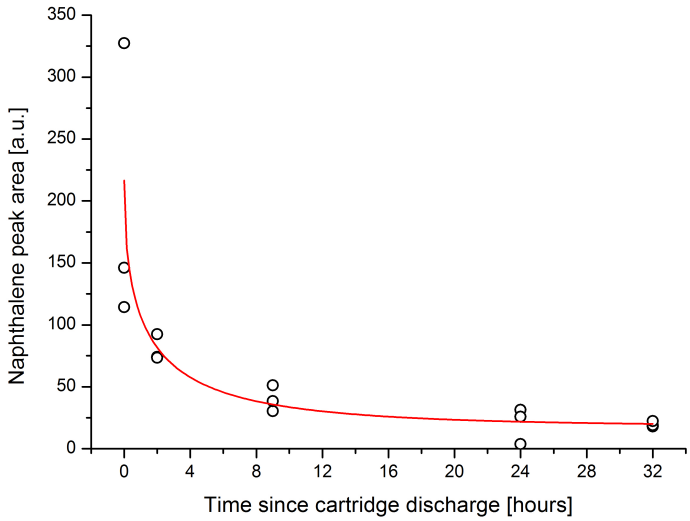

Figure 1 – Decrease of the naphthalene peak area measured through the SPME/GC analysis of some reference cartridges (data from Table 1). The scale of the vertical axis is the chromatographic peak area divided by 1000. The central line represents the mean tendency curve.

[1] In this work, peak areas are expressed as the absolute ion count divided by 1000. Units are thus arbitrary.

However, these are considered inadequate from both a statistical and a conceptual point of view. Firstly, no work considered the measurement errors in their interpretative models. This is particularly problematic because the discharge time estimation is an inductive inferential process which is naturally uncertain [27, 28]. Secondly, some ambiguities still exist about the collection of the reference data. Although almost all the authors agreed that they should be acquired from case-related material (i.e., the same firearm/ammunition system stored in the same conditions as the one used for perpetuating the investigated crime), few solutions were proposed in case the relevant comparison material and/or sufficient circumstantial information about storage conditions are not available. In these situations the use of a "standard" set of data (i.e., a set of analyses performed on arbitrarily predetermined cartridges at laboratory conditions) is generally proposed with a "prudent interpretation" [2]. Finally, it should be noted that the proposed interpretative methodologies are actually investigative frameworks whose implicit purpose is to infer the best explanation from the observations on the questioned cartridge [29, 30]. However, information on the lapse of time since discharge are rarely used for investigative purposes: contextualizing the discharge on a time scale usually becomes an issue when the relevance of the evidence is contested by the suspect during his defense [20]. At this trial stage, different scenarios explaining the facts have already been formulated by the parties, and it would be of the greatest interest to test them rather than advance new propositions. An impartial approach may therefore be preferred [31].

5. A logical approach for interpreting analytical results

The LR-based logical approach has gained considerable importance in the interpretation of forensic data [32-34], and applications in firearm-related [35-42] as well as dating-related domains [20-23] have been reported. Under an LR-based interpretative framework, the role of the scientist is to assess the probability of a given evidential element under different alternative hypotheses: the ratio between these probabilities is known as the LR. From a conceptual point of view, this approach is thus a balanced, robust and transparent method for the assessment of the evidential value [31]. The LR is also a useful metric because it gives information about which hypothesis is supported by the observations on the questioned material as well as the force of this inference [32, 33].

The formulation of the hypotheses depends on the circumstances of the case. In this paper, we focus on the case where a suspect admits to having fired the questioned cartridge but he contests the proposed discharge time. In such a situation, two hypotheses about the course of the events (one from

the prosecutor and one from the defense, named respectively T_p and T_d) can therefore be suggested as follows:

- T_p: the questioned cartridge was fired at the same time as the commission of the crime with the suspect's firearm and ammunitions.
- T_d: the questioned cartridge was fired prior to the commission of the crime with the suspect's firearm and ammunitions.

The expert's role is therefore to assess the probability of observing q (i.e., the naphthalene peak area observed on the questioned cartridge) given respectively the prosecutor and the defense hypotheses; the LR (defined with the letter V) is given by the ratio of these two likelihoods:

$$V = \frac{p(q|T_p)}{p(q|T_d)} \quad (1)$$

If V is greater than 1, it can be said that the value q (based on analytical results) supports the prosecutor's hypothesis T_p. If V is smaller than 1, the evidence supports the defense proposition T_d. It should be noted that it is not necessary that one of the advanced propositions perfectly explains the measurement q: each probability composing the LR can assume values smaller than 1. In order to quantify V, the determination of the relative magnitude between numerator and denominator is thus sufficient [37].

Consider now that q is a particular observation of Q: the unknown quantity of naphthalene. This variable is continuous because q can assume any value between the limits delimited by the definition of the aging parameter. For the sake of simplicity, it is assumed that Q is normally distributed, so $Q \sim N(\mu;\sigma^2)$. Therefore, if the values of the distribution parameters (the mean μ and the variance σ^2) are known, the density for a given $Q = q$ is provided by the following density function:

$$f_Q(q|\mu,\sigma^2) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(q-\mu)^2}{2\sigma^2}\right] \quad (2)$$

From a practical point of view, it should be noted that the more recent is the discharge time, the greater is the amount of organic GSR compounds remaining in the spent cartridge (and vice-versa for longer intervals). Consequently, the distribution parameters for Q depends on the hypothesis that has been put forth, and the formula in equation (1) can be substituted by the following definition [37, 43]:

$$V = \frac{f_Q(q|\mu_p, \sigma_p^2)}{f_Q(q|\mu_d, \sigma_d^2)} \quad (3)$$

where μ_p, μ_d, σ_p^2 and σ_d^2 are the parameters characterizing the distribution of the chosen aging parameter under each of the two given propositions.

6. Estimation of the distribution parameters in an ideal situation

Parameter estimation

From a general point of view, the exact values of the different parameters which are needed to implement a specific probabilistic model are unknown, and their determination is the main practical problem. The easiest way is to estimate them from a set of reference data is through conventional frequentist methods [37, 40, 44, 45]. In this case, attention must be given to the fact that, by using point estimates of the true parameters, the obtained value for *V* shall also be treated as a point estimate of the likelihood ratio (hereafter, $\hat{V}$) [45, 46].

Considering the definition (3), two sets of estimates are needed in order to calculate $\hat{V}$, ($\hat{\mu}_p$ and $\hat{\sigma}_p^2$; $\hat{\mu}_d$ and $\hat{\sigma}_d^2$), both defining the distribution of *Q* under a given hypothesis. Two series of experiments can thus be planned with the reference firearm and ammunition[2]: the spent cartridges belonging to the two groups are then analyzed after the intervals defined by the propositions T_p and T_d, respectively. The estimates $\hat{\mu}_p$, $\hat{\mu}_d$, $\hat{\sigma}_p^2$ and $\hat{\sigma}_d^2$ are provided by determining the sample means and variances of the two groups of measurements.

Case scenario example

In the previous scenario, the victim's death occurred about 8 hours before the discovery of the body: consequently, assuming that the cartridge was sampled one hour after the discovery, the prosecutor's proposition would be that the suspect's firearm and ammunition were used to shoot the spent cartridge 9 hours before its seizure on the crime scene ($T_{p=9h}$). However, the suspect pretended that cartridge discharge occurred 32 hours before the discovery of the corpse in a situation uncorrelated with the crime ($T_{d=32h}$). For the present discussion, we neglected the effect of the environmental conditions at the crime scene, as well as the certainty about the suspect testimony and the

[2] If hypotheses are formulated as above, it is very important to use the correct comparison material given that the cartridge batch and the employed firearm are supposed to be known. Anyway, it is acknowledged that it is not always so in real casework. Evaluation of the evidence when firearm and ammunition are treated as stochastic variables is not treated in this paper, but it is possible and will be discussed in future works.

medico-legal conclusions[3]. Estimates for the distribution of *Q* under each hypothesis can thus be inferred from two series of shots (analyzed 9 hours and 32 hours, respectively, after the discharges of the cartridges) with the firearm and ammunition seized from the suspect's apartment. Considering that naphthalene peak area was selected as a reliable aging indicator, shooting experiences for the considered scenario are summarized in Table 1 (data are provided by the work of Weyermann *et al.* on 9mm Parabellum ammunition [17]).

Time after discharge [h]	*Observed naphthalene peak area [a.u.]*			***Estimates [a.u.]***	
	Cart. #1	*Cart. #2*	*Cart. #3*	$\hat{\mu}$	$\hat{\sigma}^2$
0	327.26	114.23	146.10	**195.86**	**13202.42**
2	92.36	73.97	73.35	**79.89**	**116.68**
9	30.30	51.26	38.43	**40.00**	**111.70**
24	31.33	25.83	3.65	**20.27**	**214.66**
32	18.01	19.05	22.23	**19.76**	**4.85**

Table 1 – Naphthalene peak areas measured through the SPME/GC analysis of some reference cartridges at different times after discharge. These data are drawn from the work of Weyermann *et al.* [17]. Values represent integrated peak areas of the corresponding chromatographic peaks divided by 1000.

Remember that the analysis of the questioned cartridge cases produced a naphthalene peak area of *q* = 28.00 a.u. It is possible to calculate the LR associated with this observation by using the function (2) in definition (3) and the estimates calculated in Table 1:

$$V = \frac{f_Q(q = 28.00 \mid \hat{\mu}_{p=9h} = 40.00, \hat{\sigma}^2_{p=9h} = 111.70)}{f_Q(q = 28.00 \mid \hat{\mu}_{d=32h} = 19.76, \hat{\sigma}^2_{d=32h} = 4.85)} = \frac{1.98 \cdot 10^{-2}}{1.65 \cdot 10^{-4}} \approx 120 \quad (4)$$

Given the measurements on the reference material, this result means that the naphthalene peak area *q* observed on the SPME/GC chromatogram of the questioned cartridge is estimated to be about 120 times more likely if the discharge occurred 9 hours before its sampling on the crime scene rather than if it occurred 32 hours before, thus supporting the prosecutor's hypothesis that the discharge of the questioned cartridge is approximately at the same time as the commission of the crime. It is im-

[3] Clearly, these variables will represent additional sources of uncertainty which should be considered in the evaluation of the measurements in real cases. However, more research is actually needed in order to model their effects.

portant to note that a lower q value would have supported the defense proposition. For example, with q = 17.00 a.u., a $\hat{V}$ of about 0.043 is obtained, which indicates that the observation is approximately 23 times (=1/$\hat{V}$) more likely under $T_{d=32h}$ than under $T_{p=9h}$. Figure 2 provides a graphical representation of the two estimated density distributions exploited in the assessment of the present scenario. It should be noted that, from a geometrical point of view, the $\hat{V}$ associated to a particular observation q actually corresponds to the relative height of the two curves at this value. In this case, it is moreover evident that, for q values greater than about 25.00 a.u., the height of the distribution of Q given $T_{p=9h}$ is always greater than its height given $T_{d=32h}$: thus, the prosecution's proposition is always supported with regard to the defense's alternative for q > 25.00 a.u.

Practical issues

Estimating parameters from the direct analysis of comparison material at the given discharge times could be a good approach in ideal situations. However, two problems could arise in real cases. First, on the basis of some new pieces of information gathered during an intermediate investigative stage, it is possible that both parties change their explanations about the events, requiring a further evaluation of the evidence under new revised hypotheses. For instance, the validity of the lapse of time after the victim's death may be questioned, and the defense may ask to evaluate the measurements on the questioned cartridge under another prosecutor's proposition. Secondly, many environmental factors may influence the GSR aging kinetics in real cases (e.g., the temperature and the rate of air flow) and the actual state of these factors may be uncertain. Both of these issues would need further comparison shots and analyses to be conducted in order to estimate the distribution parameters for different intervals after discharge and/or different environmental conditions. However, one must also take into account the actual limitations of a real case:

- the case-related comparison material is never unlimited (i.e., comparison cartridges seized from the suspect may be insufficient to perform all the required analyses);
- the available time and money to produce expert opinion is also limited (i.e., manipulations shall be selected as a function of their relevance).

A statistical tool to manage these difficulties is therefore necessary. For this purpose, a parametric regression model is proposed in the following sections.

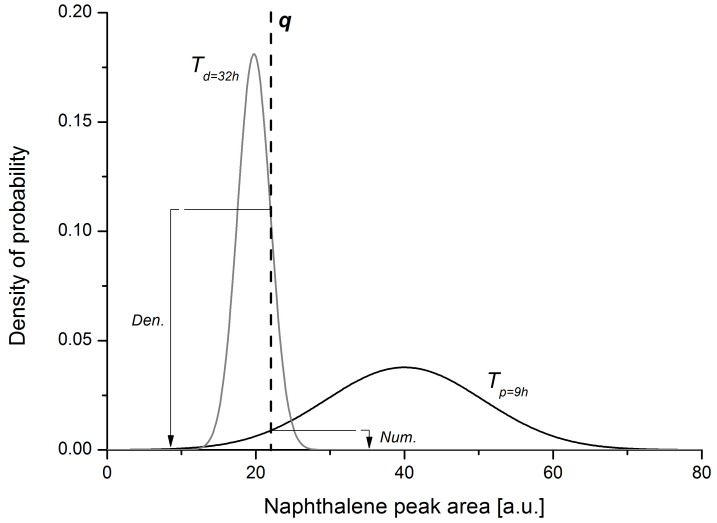

Figure 2 – Example of density distributions for the naphthalene peak area at different intervals after discharge. These distributions were inferred from the data summarized in Table 1. From a geometric point of view, the estimated likelihood ratio ($\hat{V}$) associated to a particular measurement q is the ratio between the heights of the two curves at this value ($\hat{V}$ = num./den.).

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7. A regression model for the estimation of parameters

Parametric non-linear regression model

In general, a parametric regression model is a statistical tool which describes the relationship between two or more variables through parametric equations [47]. In its simple univariate form, the model is composed of a stochastic response variable (in this case, the selected aging parameter Q) and a non-stochastic predictor variable (the time interval, say t, after the discharge of the cartridge). Assuming a true regression relationship between these variables, it is presumed that the response Q is the sum of a systematic part (described by the mean response μ_t) and a random part (the measurement's random error ε_t on the mean response), whose magnitudes depend on t [48, 49]; formally:

$$Q = \mu_t + \varepsilon_t \tag{5}$$

Assuming moreover that the error ε_t is normally distributed, that is $\varepsilon_t \sim N(0;\sigma_t^2)$, it is deductible that $Q \sim N(\mu_t;\sigma_t^2)$ for any time interval t after the discharge. Thus, using such a model, it is virtually pos-

sible to estimate the mean and the variance of Q at any t if the relationship between these variables is known.

The mean response μ_t and the variance of the measurement error σ_t^2 are two unspecified functions of t. Yet, the mean response μ_t can be approximated by a regression function $f(t,\theta)$ which depends on a series of regression parameters $\theta = \{\theta_1, \theta_2, ..., \theta_n\}$, so that $\mu_t = f(t,\theta)$. Regarding the variance of the measurement's error σ_t^2, it is generally assumed to be homogeneous throughout the considered domain of the predictor variable (a situation called homoscedasticity) [50]. Nevertheless, a preliminary observation of Table 1 (which reports real data obtained from the SPME/GC analysis of spent cartridges) already offers contrary observations to this assumption. Thus, it is more rigorous to approximate σ_t^2 by a variance function $g(t,\theta,\tau)$ that depends on the generic parameters θ as well as on the specific regression parameters $\tau = \{\tau_1, \tau_2, ..., \tau_m\}$ (a situation called heteroscedasticity), so that $\sigma_t^2 = g(t,\theta,\tau)$ [50]. Regression parameters θ and τ involved in the definition of the model are still undetermined but they can be estimated on the basis of some analyses carried out on a set of comparison cartridges. The main difficulty lies in the fact that the functions $f(t,\theta)$ and $g(t,\theta,\tau)$ must be specified *a priori*.

The definition of an effective set of functions may depend on the chosen aging parameter. For the sake of demonstration, Figure 1 shows the evolution of the naphthalene peak area as a function of time for a 9mm Parabellum ammunition. It is obvious that the relationship between Q and t is non-linear: in fact, the decrease of the peak area is particularly rapid in the first period after discharge, and then it becomes stable. On the basis of the published literature, this seems to be the case for all organic GSR compounds in a spent cartridge or firearm, regardless of the caliber [2, 10-13, 17, 19]. The disappearance of these compounds is a complex process, which involves different phenomena. The diffusion is however the largest contributor, and a reliable equation to approximate naphthalene decrease may be derived from the diffusion theory. Inspired by several works studying the diffusion of volatile molecules [23, 51-54], the following equation was used as a regression function:

$$f(t,\theta) = \theta_1 + \theta_2 \cdot e^{-\theta_3\sqrt{t}} \qquad (6)$$

where θ_1 and θ_2 are two size constants (for $t \to \infty$, θ_1 represents the minimal value of the considered aging parameter; for $t = 0$, the sum $\theta_1 + \theta_2$ represents its maximal value), and θ_3 is a characteristic curve constant which is proportional to the rate of decrease of the aging parameter. It should be noted that this function is intrinsically non-linear [47].

Furthermore, it could be observed from Figure 1 that the measurement error fundamentally decreases over time, and this indicates the heteroscedasticity of the data. The literature reported similar trends for several organic GSR compounds in small gun cartridges [17]. For other situations however, the behaviors are unknown because of the general lack of error bars on the published aging profiles. For modeling variance inhomogeneity, a power-of-the-mean function is generally used [49, 50]:

$$g(t,\theta,\tau) = \tau_1^2 \cdot (\mu_t)^{\tau_2} = \tau_1^2 \cdot f(t,\theta)^{\tau_2} \quad (7)$$

θ_1, θ_2, θ_3, τ_1 and τ_2 are parameters whose real values are unknown but estimable. Starting from a series of comparison shots carried out at different times after discharge (such as those represented in Figure 1), the parameter estimation can easily be performed by the maximum likelihood method and a computerized iterative resolution algorithm [47, 49, 50][4].

Case scenario example

To illustrate the utility of this statistical model, suppose that the investigators of the previous example were interested in the evaluation of the observed q with regard to several pairs of hypotheses. In fact, the hypotheses that the discharge occurred 4 hours and 20 hours before the discovery of the body were additionally forwarded by the parties after the presentation of new circumstantial information. Additional analyses were conducted with the available reference material at adequate times after the discharges, and the naphthalene peak areas were measured (Table 1 and Figure 1). The estimation of the regression parameters was performed using "R" statistical software and the above definitions. The following equations were obtained for the regression model $Q = \mu_t + \varepsilon_t$, where $\varepsilon_t \sim N(0;\sigma_t^2)$:

$$\hat{\mu}_t = 17.945 + 198.641 \cdot e^{-0.805\sqrt{t}}$$
$$\hat{\sigma}_t^2 = 0.321^2 \cdot \hat{\mu}_t^{\,2.037} \quad (8)$$

where t is expressed in hours. Although no analysis was performed at 4 hours and 20 hours after the discharge of the reference cartridges, using (8) it is possible to interpolate distribution parameters

[4] For this purpose, the library "NLREG" developed by Brazzale & Bellio [55-57] for the mathematical software "R" is an interesting solution because it implements high-order asymptotic methods for estimating regression parameters of non-linear, heteroscedastic models for small samples.

for Q at those times. Table 2 shows the interpolated estimates corresponding to all the hypotheses forwarded by the parties ($T_{p=4h}$, $T_{p=9h}$, $T_{d=20h}$, $T_{d=32h}$), as well as the corresponding densities for the previous measurement q = 28 a.u. carried out on the questioned cartridge. For the sake of illustration, other hypothetical measurements are also reported (q = 17.00 a.u., 39.00 a.u. and 50.00 a.u.). Table 3 summarizes the $\hat{V}$ obtained through the analysis of different pairs of propositions (scenarios I to IV). We observe that, for a given measurement q, the magnitude of $\hat{V}$ clearly depends on the considered pair of hypotheses. Generally, greater discrimination is obtained for the propositions in scenario I ($T_{p=4h}$ vs. $T_{d=32h}$). This is normal considering that the estimated distributions for q given $T_{p=4h}$ and $T_{d=32h}$ are only slightly overlapping in comparison with other scenarios (Figure 3) and thus less "similar". In fact, for the scenario where the distributions are the most overlapping (i.e., scenario IV, $T_{p=9h}$ vs. $T_{d=20h}$), the discrimination between hypotheses is globally weaker.

Time after discharge [h]	*Hypothesis*	***Estimates [a.u.]***		*Densities*			
		$\hat{\mu}$	$\hat{\sigma}^2$	*q = 17.00 a.u.*	*q = 28.00 a.u.*	*q = 39.00 a.u.*	*q = 50.00 a.u.*
4	$T_{p=4h}$	**57.69**	**398.76**	2.50 x 10^{-3}	6.61 x 10^{-3}	1.29 x 10^{-2}	1.85 x 10^{-2}
9	$T_{p=9h}$	**35.73**	**150.24**	1.01 x 10^{-2}	2.67 x 10^{-2}	3.14 x 10^{-2}	1.65 x 10^{-2}
20	$T_{d=20h}$	**23.39**	**63.38**	3.63 x 10^{-2}	4.24 x 10^{-2}	7.32 x 10^{-3}	1.88 x 10^{-4}
32	$T_{d=32h}$	**20.04**	**46.30**	5.31 x 10^{-2}	2.96 x 10^{-2}	1.21 x 10^{-3}	3.62 x 10^{-6}

Table 2 – Interpolated estimates for the mean and variance of Q (i.e., the distribution of the naphthalene peak area) given different intervals after discharge. These estimates were obtained by applying the non-linear regression model (8). The right side of the table shows the probability densities associated with some selected measurements q at the different intervals after discharge.

Scenarios	***I*** $T_{p=4h}$ ***vs.*** $T_{d=32h}$		***II*** $T_{p=9h}$ ***vs.*** $T_{d=32h}$		***III*** $T_{p=4h}$ ***vs.*** $T_{d=20h}$		***IV*** $T_{p=9h}$ ***vs.*** $T_{d=20h}$	
Measurements	$\hat{V}$	$log_{10}\hat{V}$	$\hat{V}$	$log_{10}\hat{V}$	$\hat{V}$	$log_{10}\hat{V}$	$\hat{V}$	$log_{10}\hat{V}$
q = 17.00 a.u.	0.05	-1.33	0.19	-0.72	0.07	-1.16	0.28	-0.55
q = 28.00 a.u.	0.22	-0.65	0.90	-0.04	0.16	-0.81	0.63	-0.20
q = 39.00 a.u.	10.66	1.03	25.98	1.41	1.76	0.25	4.29	0.63
q = 50.00 a.u.	5124.79	3.71	4564.41	3.66	98.89	2.00	88.07	1.94

Table 3 – Estimated likelihood ratios ($\hat{V}$) and related logarithmic values associated with some selected measurements q under different scenarios. $\hat{V}$ was obtained by applying the definition (3) and the data in Table 2.

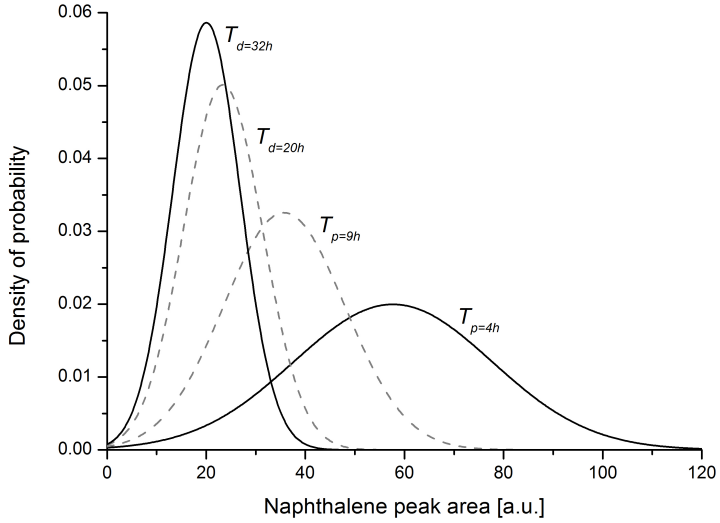

Figure 3 – Examples of density distributions for Q (i.e., the chromatographic peak area of naphthalene) estimated with the regression model (8) at four intervals after discharge. It is evident that the distributions for $T_{p=4h}$ and $T_{d=32h}$ are less overlapped with respect to the distributions for $T_{p=9h}$ and $T_{d=20h}$.

8. Discussion

The proposed approach allows the analysis of any scenario forwarded by the parties on the basis of the same set of reference data. This is possible because distribution parameters for the naphthalene peak area are estimated by the regression model. Thus, it is no longer necessary to perform specific analyses for any new hypothesis. However, it should be noted that distribution parameters at a specific time after discharge estimated with the regression model may not perfectly match the same parameters directly estimated from a group of measurements at the same time. For example, we can observe that the parameters estimated from three individual measurements carried out 9 hours after the discharge are $\hat{\mu}$ = 40.00 and $\hat{\sigma}^2$ = 111.70 (Table 1), while the same estimates calculated with the corresponding regression model are slightly different: $\hat{\mu}$ = 35.72 and $\hat{\sigma}^2$ = 150.49 (Table 2). Anyway, assuming that the regression functions are correctly specified, the latter values shall be considered more valid as a consequence of the fact that the model is estimated on the basis of a larger number of contributing measurements.

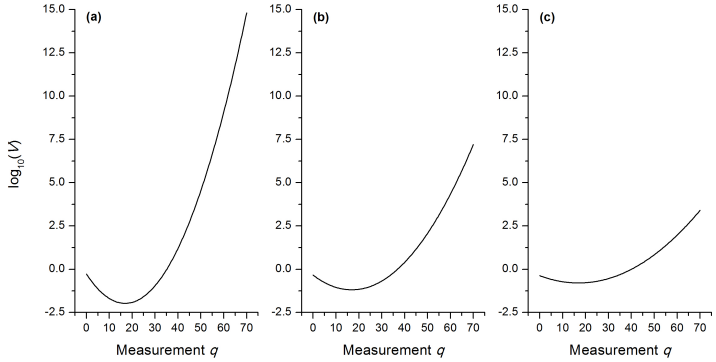

Figure 4 – Estimated likelihood ratio ($\hat{V}$, $T_{p=4h}$ vs. $T_{d=20h}$) as a function of different observed measurements q (in this case, the chromatographic peak area of naphthalene) assuming respectively a low (a), an average (b) and a high (c) expected variability of the observations. $\hat{V}$ is reported as its logarithmic value. These simulations were performed by modifying the estimated regression parameter τ_1^2 in the model (8).

By plotting $\hat{V}$ as a function of q, as in the different cases depicted in Figure 4, other interesting observations could be drawn. Firstly, it should be noted that $\hat{V}$ always reaches a minimum value for which the evidence maximally support the defense hypothesis T_d. However, it never has a well-defined maximum, and very large values supporting the prosecutor's hypothesis T_p are theoretically possible. Secondly, the probative force associated to a large q value in favor of T_p is generally greater than the contribution of a small q value in favor of T_d. In fact, the increase of $\hat{V}$ over the neutral value of 1 ($\log\hat{V} = 0$) is more rapid than its decrease below this threshold (see also Table 3). These observations are coherent since they reflect the intrinsic uncertainty about the weaker extracted quantities of organic GSR compounds. In fact, small q values have two reasonable explanations: a sufficiently long time has passed between discharge and analysis (the small extracted quantity is thus due to a true decrease of naphthalene) or the shot is recent but only a small quantity of compounds was produced (the small extracted quantity is due to a large deviation from the mean, which is still probable considering the large distributions of q for the shorter discharge times). On the contrary, large q values are fundamentally explained only by a short interval since discharge. This shows that an LR-based approach easily allows one to proportionally weigh all the possible explanations in the final result. Anyway, it should be pointed out that very high residual amounts of compounds are always very improbable under any hypothesis, and the probability of obtaining a large value for $\hat{V}$ is thus greatly limited.

A further investigation of the current model reveals that, for a given pair of propositions, the final magnitude of V mainly depends on the measurement q carried out on the questioned material (evidence characteristics), the expected aging profile of the selected indicator (mean tendency) and the expected variability of the observations (deviation from the mean). This last factor merits further discussion. In fact, it is demonstrable that a better discrimination between the given hypotheses is obtained for a smaller expected variability of the observations. Figure 4 simulates an increasing variability of the observations, and the evidence value is obviously higher when the standard deviation is minimized. This factor thus has a large influence on the evaluation of the evidence. However, up to now, few works have shown error bars on the aging profiles, and even fewer performed systematic studies to establish what its real range is. This is because the variability of the observations is often assimilated to the measurement variance (i.e., the precision of the analytical method), which is merely perceived as a validation parameter unrelated to the interpretation of the evidence. In addition to the measurement variance, the variability of the GSR's initial composition also contributes to the total variability of the observations, and further studies are thus essential. Several replicas of the same reference analyses are generally needed to correctly assess the evidence in a particular case. It is also interesting to note that, while the expected variability of the observations is moderate (i.e., the analytical method is not very repeatable and/or the GSR's initial composition is highly variable), the given hypotheses could always be discriminated to a certain degree. A low variability is thus not necessarily needed to assist the court in its decision, even if they would allow maximizing the contribution of the physical evidence.

Finally, note that the considered case is a very simple scenario, merely elaborated to introduce the possibility of applying a LR-based perspective in the interpretation of dating-related data. There is no claim of generalization of the proposed model. In fact, real cases are generally more complex. Particularly, serious problems affect the evaluation of organic GSR compound analyses found in real casework, such as uncertainties about storage conditions and/ the circumstances surrounding the discharge, as well as the inaccessibility to relevant reference material. All of these factors actually constitute additional sources of uncertainty and were not addressed in this contribution. However, a further benefit of applying a probabilistic evaluative perspective is that all of these factors could be treated as additional stochastic variables and implemented in the model. Future works should consider this objective. Moreover, completely Bayesian inferential methodologies can be adopted instead of frequentist parametric estimation methods [46, 58] and this would be particularly useful to statistically learn parameters from previous experiments and cases [36, 59, 60]. Applications to other dating-related forensic fields should also be promising.

9. Conclusion

Estimating the time since the last discharge of a firearm or of a spent cartridge can be useful in specific situations. A novel, logical approach to interpret the data obtained by SPME/GC using likelihood ratios was thus proposed in this contribution. A probabilistic model was developed and applied to a hypothetical scenario where the discharge time of a questioned cartridge found on the crime scene was questioned.

The parameters needed for the implementation of the model can easily be estimated from comparison shots carried out with seized reference material. A regression model was proposed for interpolating such estimates on the basis of a limited number of comparison data. This solution is adapted to the constraints of real casework (i.e., the limited availability of comparison cartridges).

The proposed approach proved to be a valuable method for interpreting aging-related data, and further developments are promising.

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References

[1] C. Andersson, J. Andrasko, A novel application of time since the latest discharge of a shotgun in a suspect murder, Journal of forensic sciences, 44 (1999) 211.

[2] B. Persin, P. Touron, F. Mille, G. Bernier, T. Subercazes, Évaluation de la date d'un tir, Canadian society of forensic science journal, 40 (2007) 65.

[3] J. Meier, Détermination du temps écoulé depuis le tir, Revue internationale de police criminelle, 234 (1970) 22.

[4] J. Sokol, Die Bestimmung des Zeitpunktes, wann eine Waffe das letztemal beschossen und eine Patrone verfeuert wurde, Buchdruckerei Friedli & Co, Bern, CH, 1931.

[5] A. Lucas, Forensic chemistry and scientific criminal investigation, 3th ed., Edward Arnold & Co., London, 1935.

[6] G. Price, Recent advances in ballistics laboratory methods, Journal of forensic science society, 8 (1968) 83.

[7] J.K. Sinha, Time of firing of shot shells, Journal of forensic sciences, 21 (1976) 171.

[8] G.P. Voskertchian, G.V. Pavilova, Spectrophotometric determination of time since discharge of firearms, AFTE journal, 26 (1994) 216.

[9] G.P. Voskertchian, G.V. Pavilova, Spectrophotometric determination of time since discharge of firearms, Crime laboratory digest, 22 (1995) 4.

[10] J. Andrasko, T. Norberg, S. Stahling, Time since discharge of shotguns, Journal of forensic sciences, 43 (1998) 1005.

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

[12] J. Andrasko, S. Stahling, Time since discharge of rifles, Journal of forensic sciences, 45 (2000) 1250.

[13] J. Andrasko, S. Stahling, Time since discharge of pistols and revolvers, Journal of forensic sciences, 48 (2003) 307.

[14] J.S. Wallace, Chemical analysis of firearms, ammunition, and gunshot residue, CRC Press, Boca Raton, FL, 2008.

[15] W.F. Rowe, Residues, in: J.A. Siegel, P.J. Saukko, G.C. Knupfer (Eds.) Encyclopedia of forensic sciences, Academic Press, San Diego, CA, 2000.

[16] O. Rigal, Analyse des résidus de tir par arme à feu en SPME GC/MS: caractérisation d'un tir, University of Paris-Sud, 2007.

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

[18] V. Belaud, Identification par SPME-GC-MS des résidus de tirs volatils retrouvés dans les douilles: étude du vieillissement de composés cibles, University of Lausanne, 2008.

[19] J.D. Wilson, J.D. Tebow, K.W. Moline, Time since discharge of shotgun shells, Journal of forensic sciences, 48 (2003) 1298.

[20] P. Margot, A question of time, Science & justice, 40 (2000) 64.

[21] C. Weyermann, Dating: document, in: A. Jamieson, A. Moenssens (Eds.) Wiley encyclopedia of forensic science, John Wiley & Sons, Chichester, UK, 2009.

[22] C. Weyermann, B. Schiffer, P. Margot, A logical framework to ballpoint ink dating interpretation, Science & justice, 48 (2008) 118.

[23] C. Weyermann, J. Almog, J. Bügler, A.A. Cantu, Minimum requirements for application of ink dating methods based on solvent analysis in casework, Forensic science international, (2011) In press.

[24] D.M. Cropek, P.A. Kemme, J.M. Day, J. Cochran, Use of pyrolysis GC/MS for predicting emission byproducts from the incineration of double-base propellant, Environmental science & technology, 36 (2002) 4346.

[25] D.M. Cropek, P.A. Kemme, J.M. Day, Pyrolytic decomposition studies of AA2, a double-base propellant, US Army Corps of Engineers, 2001.

[26] D.M. Cropek, P.A. Kemme, J.M. Day, Incineration by-products of AA2, NC fines, and NG slums, US Army Corps of Engineers, 2001.

[27] I.W. Evett, Expert evidence and forensic misconception of the nature of exact science, Science & justice, 36 (1996) 118.

[28] D.A. Stoney, What made us ever think we could individualize using statistics?, Journal of forensic science society, 31 (1991) 197.

[29] G. Jackson, S. Jones, G. Booth, C. Champod, I.W. Evett, The nature of forensic science opinion - a possible framework to guide thinking and practice in investigations and in court proceedings, Science & justice, 46 (2006) 33.

[30] I.W. Evett, G. Jackson, J.A. Lambert, More on the hierarchy of propositions: exploring the distinction between explanations and propositions, Science & justice, 40 (2000) 3.

[31] G. Jackson, The scientist and the scales of justice, Science & justice, 40 (2000) 81.

[32] C.G.G. Aitken, F. Taroni, Statistics and the evaluation of evidence for forensic scientists, 2nd ed., John Wiley & Sons, Hoboken, NJ, 2004.

[33] B. Robertson, G.A. Vignaux, Interpreting evidence: evaluating forensic science in the courtroom, John Wiley & Sons, Chichester, UK, 1995.

[34] F. Taroni, C.G.G. Aitken, P. Garbolino, A. Biedermann, Bayesian networks and probabilistic inference in forensic science, John Wiley & Sons, Hoboken, NJ, 2006.

[35] A. Biedermann, S. Bozza, F. Taroni, Probabilistic evidential assessment of gunshot residue particle evidence, part 1: likelihood ratio calculation and case pre-assessment using Bayesian networks, Forensic science international, 191 (2009) 24.

[36] A. Biedermann, S. Bozza, F. Taroni, Probabilistic evidential assessment of gunshot residue particle evidence, part 2: Bayesian parameter estimation for experimental count data, Forensic science international, 206 (2010) 103.

[37] A. Biedermann, F. Taroni, A probabilistic approach to the joint evaluation of firearm evidence and gunshot residues, Forensic science international, 163 (2006) 18.

[38] J.S. Buckleton, R.G. Nichols, C.M. Triggs, G. Wevers, An exploratory Bayesian model for firearm and tool mark interpretation, AFTE journal, 37 (2005) 352.

[39] C. Champod, D. Baldwin, F. Taroni, J.S. Buckleton, Firearm and tool marks identification: the Bayesian approach, AFTE journal, 35 (2003) 307.

[40] B. Cardinetti, C. Ciampini, S. Abate, C. Marchetti, F. Ferrari, D. Di Tullio, C. D'Onofrio, G. Orlando, L. Gravina, L. Torresi, G. Saporita, A proposal for statistical evaluation of the detection of gunshot residues on a suspect, Scanning, 28 (2006) 142.

[41] S.G. Bunch, Consecutive matching striation criteria: a general critique, Journal of forensic sciences, 45 (2000) 955.

[42] F.S. Romolo, P. Margot, Identification of gunshot residue: a critical review, Forensic science international, 119 (2001) 195.

[43] R. Royall, On the probability of observing misleading statistical evidence, Journal of the american statistical association, 95 (2000) 760.

[44] I.W. Evett, A Bayesian approach to the problem of interpreting glass evidence in forensic science casework, Journal of forensic science society, 26 (1986) 3.

[45] A. Nordgaard, T. Höglund, Assessment of approximate likelihood ratios from continuous distributions: a case study of digital camera identification, Journal of forensic sciences, 56 (2011) 390.

[46] F. Taroni, S. Bozza, A. Biedermann, P. Garbolino, C.G.G. Aitken, Data analysis in forensic science: a Bayesian decision perspective, John Wiley & Sons, Chichester, UK, 2010.

[47] N.R. Draper, H. Smith, Applied regression analysis, 3rd ed., John Wiley & Sons, New York, 1998.

[48] R.A. Johnson, D.W. Wichern, Applied multivariate stastistical analysis, 5th ed., Prentice-Hall, Upper Saddle River, NJ, 2002.

[49] S. Huet, A. Bouvier, M.-A. Poursat, E. Jolivet, Statistical tools for nonlinear regression: a practical guide with S-Plus and R examples, 2nd ed., Springer, New York, 2004.

[50] C. Ritz, J.C. Streibig, Nonlinear regression with R, Springer, New York, 2008.

[51] S. Lociciro, L. Dujourdy, W.D. Mazzella, P. Margot, E. Lock, Dynamic of the ageing of ballpoint pen inks, quauntification of phenoxyethanol by GC-MS, Science & justice, 44 (2004) 165.

[52] C. Weyermann, Mass spectrometric investigation of the aging processes of ballpoint ink for the examination of questioned documents, University of Giessen, 2005.

[53] C. Weyermann, D. Kirsch, C. Costa Vera, B. Spengler, A GC/MS study of the drying of ballpoint pen ink on paper, Forensic science international, 168 (2007) 119.

[54] B. Guerrier, C. Bouchard, C. Allain, C. Bénard, Drying kinetics of polymer films, AlChE journal, 44 (1998) 791.

[55] R. Bellio, A.R. Brazzale, Higher order asymptotics unleashed: software design for nonlinear heteroscedastic regression, Journal of computational and graphical statistics, 12 (2003) 682.

[56] A.R. Brazzale, Pratical small-sample parametric inference, University of Lausanne, 2000.

[57] A.R. Brazzale, "hoa": an R package bundle for higher order likelihood inference, Rnews, 5 (2005) 20.

[58] A. Gelman, J.B. Carlin, H.S. Stern, D.B. Rubin, Bayesian data analysis, 2nd ed., Chapman & Hall / CRC, Boca Raton, FL, 2004.

[59] A. Biedermann, F. Taroni, S. Bozza, Implementing statistical learning methods through Bayesian networks, part 1: a guide to Bayesian parameter estimation using forensic science data, Forensic science international, 193 (2009) 63.

[60] A. Biedermann, F. Taroni, S. Bozza, W. Mazzella, Implementing statistical learning methods through Bayesian networks, part 2: Bayesian evaluations for results of black toner analyses in forensic document examination, Forensic science international, 204 (2010) 58.