

Review Article

Time since last discharge of firearms and spent ammunition elements: state of the art and perspectives

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ABSTRACT

The estimation of the time since last discharge of firearms or spent ammunition elements (e.g., casings) may provide crucial information in the investigation of a shooting incident and, eventually, the following trial. Herein, an exhaustive review of the methods described in the literature is reported, with the aim to evaluate their potential and limitations from a forensic perspective. This work, in particular, highlighted the fact that a number of investigations have been carried out in the field during the last century (with an especially high rate in the last 30 years), but the implementation of related procedures in forensic laboratories is still rare. The situation has been discussed and a series of propositions have been forwarded, in order to overcome challenges and facilitate the implementation of dating approaches in real casework.

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Contents

1. Introduction	2
2. Uses in the criminal enquiry	2
3. General dating concepts and approach	3
4. Chemistry of the cartridge	3
4.1. Cartridge pre-discharge chemistry	3
4.2. General composition of GSR	4
4.3. Volatile GSR compounds	4
5. Approaches for black powder firearms/ammunition	5
5.1. Visual changes in solid GSR	5
5.2. Colourimetric tests	6
6. Approaches for smokeless powder firearms/ammunition	7
6.1. Visual changes in solid GSR	7
6.2. Deposition of dust/dirt and sooting	7
6.3. Formation of rust	8
6.4. Colourimetric tests on solid GSR	8
6.5. Colourimetric tests on volatile GSR	8
6.6. Thin-layer chromatography (TLC)	9
6.7. Solid-phase micro-extraction (SPME)	9
6.8. Headspace sorptive extraction (HSSE)	11
7. Interpretation of analytical findings	12
7.1. Inference based on qualitative data	12

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7.2.	Integration of quantitative data	12
7.3.	Assignment of an evidential value	14
8.	Influential factors	15
8.1.	Factors influencing the initial conditions	15
8.2.	Elements-related factors affecting the ageing kinetics	15
8.3.	Effects of the storage conditions	16
9.	Discussion: implementation of dating approaches in casework	16
9.1.	Selection of ageing parameters	16
9.2.	Analytical methods and related constraints	16
9.3.	Sampling of questioned material	18
9.4.	Reference material and analytical protocol	18
9.5.	Interpretation from a forensic perspective	19
9.6.	Data treatment and modelling	19
10.	Conclusion	19
	Acknowledgements	20
	References	20

1. Introduction

Violent crimes perpetrated through the use of firearms are still frequent today and claim the lives of many victims. For the sake of illustration, an international survey between the years 2010–2015 reported that an estimated 46 % of violent deaths worldwide (214,000 per year on average) were due to the use of firearms and that these were employed in about 50 % of homicides [1]. Consequently, the possibility to gain rapid knowledge on shooting dynamics (i.e., reconstruction), as well as to produce robust evidence for use at trial, are always of strong interest for law enforcement authorities and are continuously the subject of published research in the forensic literature.

The forensic investigation of shooting incidents is a very complex process that involves the collection, preservation and examination of numerous items. Shooting incidents, indeed, might consist of an intricate series of events that involve the interaction of a number of different elements amongst people and objects, including at least one shooter and one firearm. Because of that, many traces are usually produced during their commission, which cover all the main classical evidence categories, such as biological, pattern and chemical evidence [2]. For instance, fingermarks and DNA can be transferred from the shooter to the used gun and/or cartridge, blood can be (back-)scattered from the victim to the shooter, gunshot residue (GSR) can be deposited on the objects nearby, while physical marks can be impressed on the fired cartridges elements (i.e., bullets and casings). All these traces (and many others) might be helpful in the reconstruction of the crime itself and, later, as evidence at trial to assess the involvement of an arrested suspect [2]. Hence, they need to be collectively evaluated in order to answer several questions such as: which firearm was used to commit the crime? Who fired it? How many shots were fired? What were the trajectories of the projectiles? What was the firing distance? When did the firearm discharge occur? When were the collected elements fired?

While routine forensic analysis can help to address most of the relevant questions (especially, regarding the identification of the firearms and people involved) [3,4], establishing the temporal sequence or simultaneity of the events of the crime and, especially, situating the discharge of the different seized items in time, are still really challenging tasks. Indeed, few forensic laboratories so far have implemented methods to estimate the time since last discharge of firearms or spent cartridge elements (e.g., casings), even if this could be a significant added value for the criminal enquiry. The reason for that can be ascertained to the complexity of such kind of examinations, both in terms of analytical capability and findings interpretation. This paper has two main purposes. On one hand, to further highlight the importance of time-related

questions in the investigation of shooting incidents and, on the other hand, to outline and evaluate the methods proposed so far in the literature for the estimation of the time since last discharge of firearms and spent cartridge elements. The potential and limits of these methods, in particular, will be discussed in a forensic perspective and propositions will be made to further develop them for an application in casework situations. To the best of the authors' knowledge, this is the first comprehensive review published on time since discharge and related techniques.

The paper is organised as follows. Section 2 will present the main applications of time-since-discharge estimation in the investigation of shooting incidents with a specific focus on its utility, while Section 3 will introduce important concepts that will be useful for the subsequent discussions. As the chemistry of the cartridge is important to understand ageing phenomena occurring after discharge, this will be reviewed in Section 4. The approaches proposed in the literature for time-since-discharge estimation will be presented in Sections 5 and 6 for firearms using black and smokeless powder respectively, as well as related cartridge components. A specific focus will be put on analytical methods here. Section 7 will present the interpretative approaches proposed to interpret analytical findings and extract helpful information from analyses for use in a forensic context. Influential factors that could affect ageing phenomena and, therefore, also have a significant influence on inferred conclusions will be discussed in Section 8. Finally, a general discussion will make up Section 9.

2. Uses in the criminal enquiry

During a shooting event, several firearm-related items are usually left behind or abandoned by the shooter(s). These can include spent casings or shells, spent bullets or projectiles, and in some cases even the employed guns. Situating their discharge in time, i.e. to estimate the time since their discharge (or last discharge, in case of guns), can be a valuable piece of evidence that may serve different purposes depending on the actual stage of the criminal enquiry. In this regard, the criminal enquiry can generally be split into an investigative and a judicial (evaluative) stage [5].

During the investigative stage, the circumstances surrounding the incident are still not elucidated (e.g., a suspect might not be available yet) and the primary aim of the forensic scientist is to provide possible explanations on the facts [6]. Time-since-discharge estimation can thus be useful in this context for two main aims: situating the discharge of the different firearm-related elements in time in order to reconstruct the course of the events (i.e., sequencing), or identifying those elements that have most likely been used to commit the offence in order to focus further

analyses only on pertinent items. Typical examples where a selection is necessary are those situations where it is expected that spent cartridge elements from previous unrelated shooting activities may be present on the crime scene (e.g., murders in open fields known to be used from occasional shooters) or it is suspected that they were voluntarily imported by the true offenders to mislead investigation (i.e., fake evidence). Likewise, if multiple guns are discovered at the crime scene and/or seized from a suspect, dating their last discharge can be helpful to exclude some/all of them as reference elements. In this regard, Persin *et al.* [7,8] reported a case example where this kind of assessment was carried out on three shotguns seized from a suspect in order to identify those that have most likely been used during the alleged offence.

When a suspect has been identified, the crime investigation usually moves to its judicial (evaluative) stage. The role of the forensic scientist here is to assess the collected evidence in the light of alternative hypotheses on the proceedings of the events generally forwarded by the parties at trial (i.e., the prosecutor and the defence, respectively). Time-since-discharge estimation can thus be useful in this context in determining the relevance of the seized items. It is not uncommon at this stage, indeed, that items relevance is questioned by the suspect by bringing forth anachronisms. Numerous situations are imaginable. For instance, the suspect might admit that he fired the spent cartridge elements found at the crime scene using the seized firearm (so, he does not contest the source), but contest the time since discharge by placing the event before (or after) the crime for legitimate reasons. Examples where defence used similar questioning lines at trial were reported by Shanahan [9] and Bridgemon [10]. Andersson & Andrasko [11] reported a case where a two-barrel shotgun was used to discharge two shots onto a victim. In this case, the suspect did not deny having discharged his gun, but claimed that the two shots were discharged at the same time (through both barrels simultaneously) for self-defence while prosecution rather supported the hypothesis of voluntary homicide through shooting twice on the victim after recharging the same barrel. Estimating the relative time since discharge of both barrels provided support for the hypothesis that one barrel had been used more recently than the other.

3. General dating concepts and approach

The estimation of time since discharge involves the study of pre-selected ageing parameters, i.e. measurable changes that starts at the moment of discharge in or on the firearm-related element of interest and evolve over time due to the effect of one or multiple time-dependent phenomena (see Sections 5 and 6). These, in general, lead to modifications at physical or chemical levels in three main categories of materials, namely the exogenous materials deposited on the item surfaces (e.g., dust deposition), the post-discharge species produced during the discharge (e.g., GSR evaporation and degradation) or the endogenous materials composing the item surfaces themselves (e.g., rust formation). As a consequence, a number of different approaches have been proposed for time-since-discharge estimation, each one based on the following of different time-dependent phenomena and related ageing parameters.

Considering their large variability, all the identified time-dependent phenomena can occur simultaneously post-discharge and be useful for estimating the time since discharge. Some of them, nonetheless, were recognised to be more reproducible and/or easy to monitor than others, thus making the related ageing parameters more reliable and helpful from a dating perspective. In any case, two important characteristics for each ageing parameter of interest have to be known and taken into account in order to

reach a conclusion: its initial condition and its ageing kinetics. Together, they compose what is called the "expected ageing profile" of the selected parameter and, therefore, can strongly affect the interpretation of the results in a specific case. For the sake of illustration, consider the evaporation of volatile GSR compounds, which is a commonly exploited phenomenon for time-since-discharge estimation of firearms and spent casings (see Section 6). This usually involves the quantification of residual amounts for specific and pre-selected targeted analytes (e.g., naphthalene). It is easy to understand that the informative value associated to any observed measurement carried out in the context of a specific case can drastically change depending on the expected initial amounts and diffusion rates (and, so, the expected ageing profiles) for the targeted analytes.

The initial conditions and ageing kinetics for any given ageing parameter of interest are not universal or constant. Indeed, they may strongly vary amongst situations due to the effect of influential factors (See Section 8). Common influential factors in situations involving dating problems are the ammunition and/or firearms used and storage (environmental) conditions prior to crime scene investigation, such as the scene temperature. To allow an appropriate interpretation of results, therefore, all these influential factors have also to be assessed and taken into account during data interpretation.

4. Chemistry of the cartridge

A significant proportion of the time-dependent phenomena, which occur in or on any firearm-related element of interest after discharge, directly involves the materials that compose the ammunition/firearm themselves, or those that are released during the shot (e.g., GSR). Good knowledge of the chemistry of the cartridge before the discharge and immediately after it is, therefore, useful to understand them, as well as the range of ageing parameters available.

4.1. Cartridge pre-discharge chemistry

The ammunition consists of the primer cup (containing the primer mixture), the propellant and the bullet, all of which are contained in a cylinder-shaped cartridge case [3,12]. Bullets and cases are composed of metals. Indeed, bullets are generally formed by a lead core, which can be coated or jacketed with harder metals. Several coating and jacket materials exist, but they usually are alloys of copper, zinc and/or nickel. The same metals are also used in the fabrication of the cases, although the jacket and case compositions can differ in the final cartridge [12].

The primer mixture is essentially a highly percussion-sensitive, low-order explosive composed of initiators and oxidizers amalgamated to other supporting chemicals such as fuels and sensitizers [3,12]. Early priming compositions mainly consisted of mercury fulminate ($\text{Hg}(\text{CNO})_2$, initiator) and potassium chlorate (KClO_3 , oxidiser), but they were likely to cause the rapid rusting of the barrel and were thus substituted with other less corrosive formulations [12]. Today, two main categories of primer mixtures exist: Sinoxid-type (SX) and heavy metal free (HMF) [12,13]. Usually, SX primers are composed of lead styphnate (initiator), barium nitrate ($\text{Ba}(\text{NO}_3)_2$, oxidiser) and antimony sulfide (Sb_2S_3 , fuel). They are toxic because of the presence of heavy metals. This toxic hazard is decreased in HMF primers. The Sintox HMF primer mixture, for example, usually contains diazole (initiator) and a mixture of zinc peroxide and titanium metal powder (playing the roles of oxidiser and fuel, respectively). Sensitizers typically used in both SX and HMF formulations are tetracene and trinitrotoluene [12,13].

Finally, propellants are low-order explosive mixtures, which contain oxidisers along with other additives. The first propellant

used in firearms was black powder, a mechanical mixture of charcoal, potassium nitrate (KNO₃, a.k.a. saltpetre) and sulphur [12]. Charcoal and sulphur acted as fuel, and potassium nitrate supplied the oxygen necessary for the combustion. However, black powder was a very inefficient explosive as it gave a heavy and hygroscopic fouling, which accelerated the rusting of the barrel and created a smoke cloud that obscured the shooter's view [12]. Consequently, it was gradually replaced by smokeless powder in modern firearm ammunition. Smokeless powder is an extruded granular material, which can be subdivided into single- or double-base depending on the oxidiser it contains: pure nitrocellulose or a mixture of nitrocellulose and nitroglycerine, respectively [12,14]. Various other chemicals are also added for specific purposes. Amongst them are stabilisers (e.g., centralites and diphenylamines), plasticisers (e.g., phthalates, polyester adipate and urethane) and flame suppressors (e.g., dinitrotoluenes) [12,14]. The exact composition of smokeless powder can be very variable from ammunition to ammunition and many different formulations have been commercialised. Some of these compounds are shown in Fig. 1.

4.2. General composition of GSR

The stepwise ignition of the primer and propellant produces a large volume of incandescent gaseous materials, the rapid expansion of which accelerates the bullet [3,15]. A secondary effect of this process is the release of a chemical trace, which is known as GSR [12,16,17]. Several types of material make up the GSR (Table 1), and these can be classified with respect to their form/condition, physical state and chemical nature. Thus, we can differentiate between particulate and free materials, as well as between gaseous and condensate, or inorganic and organic, species. Generally, all the inorganic compounds found in GSR form what is called the "inorganic GSR" (IGSR), while organic compounds form the "organic GSR" (OGSR).

Particulate materials are generally composed of compounds in solid state and can be further divided into macro-particles (>50 μm) and micro-particles (<50 μm). The macro-fraction of particles found in GSR is mostly due to the residue of the propellant. The explosion yield of the propellant, indeed, is usually never complete and some unburnt and partially burnt grains/flakes are thus released during the discharge [18]. These carry the same

compounds as those found in the propellant, at least from a qualitative point of view. Micro-particles, on the contrary, mostly come from the re-condensation of metals, which vaporise during the discharge under the effect of the very high temperatures reached. The primary source of these metals is the primer mixture/cup and they are thus also collectively known under the name of "primer GSR" (pGSR) [17,19].

Free materials can be split into expanding gases, soluble inorganic salts and other organic compounds which are liquid or solid at environmental temperature and pressure. Soluble inorganic salts can have different origins depending on the type of propellant. Especially, older ammunition based on black powder is known to leave a wide variety of salts as main explosion products in addition to expanding gases [20,21]. These also come from stoichiometric reactions between propellant components and composed a very significant part of the remaining fouling. Main inorganic salts identified in GSR of black powder are those originating from carbonate (CO₃²⁻), sulphide (S²⁻), sulphate (SO₄²⁻), nitrite (NO²⁻) and thiocyanate (SCN⁻) [20,21]. On the contrary, modern ammunition based on smokeless powder mainly releases salts of nitrate (NO³⁻) and nitrite (NO²⁻) which rather originate from the spontaneous and thermal-induced decompositions of the propellant nitro-compounds [22–24]. Some minor traces of salts of sulphate (SO₄²⁻) are also usually found [20,21,25].

4.3. Volatile GSR compounds

Volatile compounds in GSR are of main interest for dating purposes. These include the remaining categories of free species in GSR, i.e. the hot expanding gases and condensed-phase organic compounds. As the production of high amounts of hot expanding gases is the intended result during the discharge of a cartridge, these are also the most abundant compounds found in GSR immediately after the shot. Hot expanding gases are generally produced through stoichiometric reactions taking place during the propellant explosion. For both black and smokeless powder, these are mainly carbon oxides (CO and CO₂), as well as molecular hydrogen (H₂) and nitrogen (N₂) [12]. Significant amounts of hydrogen sulphide (H₂S) and methane (CH₄) were additionally found in the GSR of black powder, while nitrogen oxides (NO_x) are more typical to the discharge of smokeless powder [12,26].

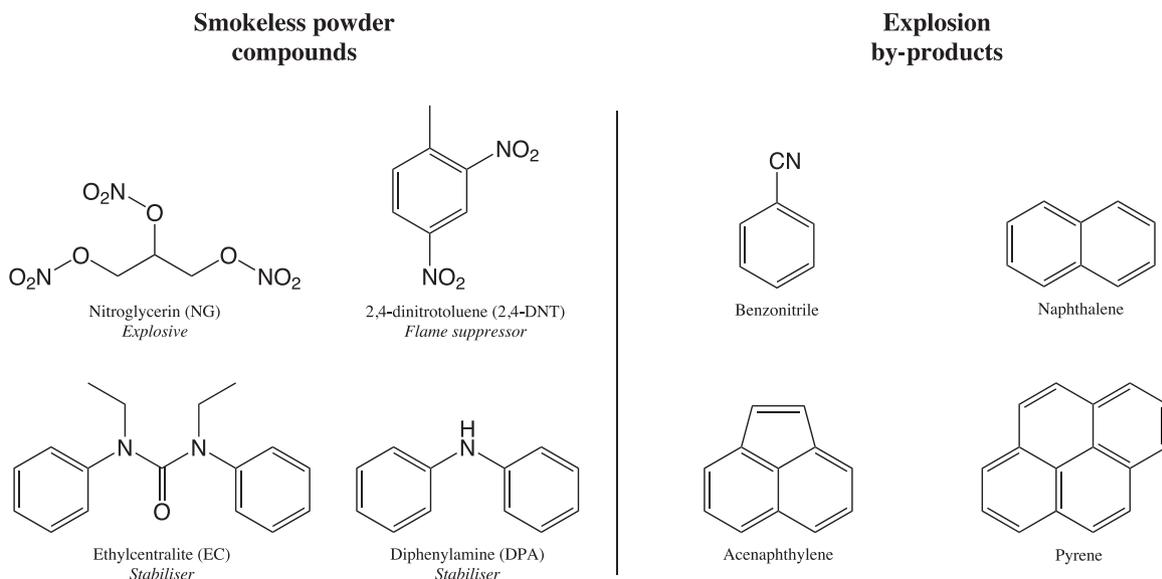


Fig. 1. Chemical structures of compounds typically found in modern smokeless powders and explosion products identified in GSRs of modern ammunition.

Table 1

Summary of the main categories of GSR components produced from modern ammunition, along with their mechanisms of formation and ageing.

Physical state		#	Chemical nature		Main source	Mechanism of formation	Main mechanisms of ageing
Class	Type		Organic (OGSR)	Inorganic (IGSR)			
Particulate materials	Macroscopic particles	I.	Explosives and additives (diphenylamine, etc.)		Propellant	Incomplete ignition	Falling off and/or chemical transformation
	Microscopic particles	II.		Metal oxides (PbO, etc.)	Primer mixture	Vaporisation followed by condensation	Falling off
		III.			Metallic elements (Pb, etc.)	Metallic surfaces	Surfaces wrenching
Free species	Gaseous-phase compounds	IV.		Light gaseous compounds (CO, NO _x , etc.)	Propellant	Stoichiometric combustion reaction	Diffusion
	Condensed-phase compounds	V.	Aromatic pyrolytic by-products (naphthalene, etc.)		Propellant	Pyrolysis and pyrosynthesis	Evaporation followed by diffusion
		VI.		Light condensed compounds (H ₂ O)	Propellant	Stoichiometric combustion reaction	Evaporation followed by diffusion
		VII.		Soluble salts (nitrites, nitrates)	Propellant	Propellant degradation	Chemical transformation
		VIII.	Explosives and additives (diphenylamine, etc.)		Propellant	Propellant vaporisation	Evaporation followed by diffusion, and/or chemical transformation

Free, condensed-phase organic compounds are mainly released by modern ammunition employing smokeless powder. Nonetheless, they have different sources as well. A large fraction comes from the rapid vaporisation of organic components inside the cartridge due to the high temperatures reached. This leads to the deposition of significant amounts of free unreacted compounds (especially from the propellant) on surfaces near and inside the firearm [14,27]. Another fraction is composed by pyrolytic by-products.

Pyrolytic by-products are those explosion products which do not result from stoichiometric combustion reactions between the different chemicals in the cartridge (Fig. 1). They rather come from pyrolysis and pyrosynthesis processes which can take place during the discharge because of the special oxygen-deficient and high-temperature conditions [28–30]. These lead to the creation of radicals, which add to other stable molecules and set in motion a waterfall mechanism resulting in the formation of larger compounds. Benzene, toluene and styrene are generally the first species formed by the stabilisation through cyclisation of unsaturated aliphatic radical species (independently from the starting molecules). Then, successive additions can lead (through further cyclisation phenomena) to naphthalene and from there to the synthesis of other heavier polycyclic aromatic hydrocarbons (PAHs). Branched or substituted derivatives of the previous compounds (e.g., methylnaphthalene) can be released as side-products; similarly, heteroatoms can take part in the reaction mechanism and be incorporated in the structure of the final products [7,31–33]. Hundreds of PAHs from 2 up to 6 rings, substituted derivatives of benzene and heterocyclic compounds resulting from these processes have been identified in GSRs [34–37].

5. Approaches for black powder firearms/ammunition

Several approaches to estimate the time since discharge have been suggested in the literature and their evolution has been directly correlated with the introduction of new propellant formulations, as well as the development of analytical techniques. In general, these can be classified into two main categories based on the strategy used for the assessment of the respective ageing parameters: those based on the visual inspection of macroscopic characteristics that change over time (e.g., rust and dust) and those

based on the quantification of residual amounts of target species (e.g., GSR) using either wet chemistry or instrumental methods. A general overview of these approaches that include the most influential ones is provided in Table 2. Those for firearms using black powder, as well as for related cartridge components, are reviewed in this Section.

5.1. Visual changes in solid GSR

Black powder was the first propellant used in ammunition. It yielded an abundant solid GSR composed by inorganic salts, which underwent chemical transformations over time (i.e., oxidation) influencing its colour and properties [25]. Thus, all the pioneering works in the field largely exploited these physical changes to estimate the time since discharge of firearms and cartridges employing black powder. In a first investigation published in the early 20th century, Sonnenschein (reported in [21]) observed that the inner surface of a recently used barrel looked black/blue in colour and successively developed rusty stains and white/green crystals when ageing. These were initially attributed to the formation of iron oxide (Fe₂O₃) and iron sulphate (FeSO₄), respectively. Exploiting these transformations, the author was able to discriminate a recent use (<24 h) from an older one (>24 h).

A more in-depth study was later carried out by Silveira (reported in [21,25]) in 1926, in an attempt to develop a methodology for estimating the time since discharge of rifles and related cartridges. He determined that the dark colour of inner surfaces of barrels and cartridges immediately after their discharge was due to the deposition of distinct traces of carbon and iron sulphide (FeS) in the form of a black/blue crystalline mass. This turned white/green after 24 h because of the oxidation of iron sulphide in iron sulphate (FeSO₄), supporting the observations of Sonnenschein. Being more hygroscopic, iron sulphate also absorbed moisture, which evaporated after 2–5 days turning the mass colour from white/green into grey. Finally, metallic iron oxidised into Fe₂O₃ and GSR crystals acquired a brown colour ca. 5 days after discharge. Over time, this rusty residue continued spreading until it covered the whole metallic surface. Thus, the author explicitly suggested to check the colour of the remaining fouling, the quantity of absorbed moisture and the size of the rust spread to estimate the time since discharge. The occurrence of particular odours was also considered an important observation,

Table 2

Most influential approaches suggested for the estimation of time since discharge of firearms and related spent elements, sorted by chronological order. The following abbreviations were used. For propellants, BP: black powder, SLP: smokeless powder. For calibres, HG: handguns, LG: long guns and rifles, SG: shotguns. For element types, FA: firearms, CR: cartridges, B: bullets. For analytical methods, GC: gas chromatography, GCxGC: comprehensive 2D gas chromatography, TEA: thermal energy analyser, FID: flame ionisation detector, qMS: single quadrupole mass spectrometry, ToF: time-of-flight mass spectrometry, SPME: solid-phase micro-extraction, HSSE: headspace sorptive extraction.

Authors	Year	Propellant	Calibre	Type	Analytical method	Approach	Conclusions
Sonnenschein (in [20])	1920	BP	All	FA	Visual inspection and colorimetric tests	Solid GSR appearance, metal appearance and ionic GSR composition	Case dependent. Typically: 0–24 h or >24 h
Silveira (in [21,25])	1926	BP	LG	FA + CR	Visual inspection and odour check	Solid GSR appearance, metal appearance and volatile GSR odour	Case dependent. Typically: 0–5 days or >10 days
Silveira (in [21,25])	1926	SLP	LG	FA + CR	Visual inspection and colorimetric tests	Solid GSR appearance, metal appearance and ionic GSR composition	0–24 h or >2 days
Lucas [20]	1935	BP	All	FA	Visual inspection and colorimetric tests	Solid GSR appearance and ionic GSR composition	Possible, but strongly case dependent
Sokol [21]	1939	BP	All	FA + CR	Visual inspection and colorimetric tests	Solid GSR appearance, metal appearance and ionic GSR composition	Case dependent. Typically: 0–3 days or >6 days
Price [42]	1968	SLP	All	FA	Colorimetric tests	Volatile GSR quantification	Possible, but strongly case dependent
Meier [38]	1970	SLP	All	FA + CR	Visual inspection and colorimetric tests	Dust deposition, metal appearance and ionic GSR composition	Possible, but strongly case dependent
Sinha [43]	1975	SLP	SG	CR	Colorimetric tests	Volatile GSR quantification	0–24 h, 2–5 days or 6–10 days
Shanahan [9]	1977	SLP	HG	CR	Visual inspection	Metal appearance	Possible, but strongly case dependent
Bridgemon [10]	1986	SLP	All	CR	Visual inspection	Dust/dirt deposition and metal appearance	Possible, but strongly case dependent
Voskertchian & Pavilova [47]	1994	SLP	All	FA	Colorimetric tests coupled to spectrophotometry	Volatile GSR quantification	±1 day between 0–5 days
Aginsky <i>et al.</i> [49]	1996	SLP	HG	FA + CR	Thin-layer chromatography	Solid GSR quantification	Possible, but strongly case dependent
Andrasko <i>et al.</i> [34]	1998	SLP	SG	FA	SPME coupled to GC/TEA	Volatile GSR quantification	2–3 days, 7–14 days or >21 days
Larrison [41]	2006	SLP	All	CR + B	Visual inspection	Metal appearance	None (physical mark study)
Persin <i>et al.</i> [7]	2007	SLP	SG + LG	FA	SPME coupled to GC/FID	Volatile GSR quantification	Case dependent. Typically: 0–5 days, 5–10 days or >10 days
Weyermann <i>et al.</i> [36]	2009	SLP	SG	CR	SPME coupled to GC/qMS	Volatile GSR quantification	None (characterisation study)
Schmidt [60]	2010	SLP	SG	CR	SPME coupled to GCxGC/ToF	Volatile GSR quantification	Not reliable results
Frère <i>et al.</i> [63]	2012	SLP	SG	FA	Cotton swab, followed by SPME coupled to GC/qMS	Volatile GSR quantification	Possible, but strongly case dependent
Kerkhoff <i>et al.</i> [40]	2014	SLP	HG	CR + B	Visual inspection	Metal appearance	None (exploratory study)
Chang <i>et al.</i> [61]	2015	SLP	SG	CR	SPME coupled to GC/FID	Volatile GSR quantification	<1 day, <5 days, <10 days, <20 days or <30 days
Gallidabino <i>et al.</i> [66,67]	2017	SLP	SG	CR	HSSE coupled to GC/qMS	Volatile GSR quantification	Case dependent. Typically: ±10 h between 0–2 days. Alternatively: 0–9 h or >24 h

given the presence of hydrogen sulphide (H_2S) in GSR during the first hours of ageing. Silveira stated that all these characteristics allowed discriminating recent shots (up to a maximum of 5–10 days, depending on the case) from older ones, but he also pointed out that obtaining more accurate time estimates would be very difficult in casework conditions.

Very similar results were obtained in more recent investigations by Sokol [21] and Lucas [20], further supporting the importance of visual inspection in estimating the time since discharge of firearms and cartridges employing this type of propellant. Sokol, in his work on small firearms and related cartridges was, nevertheless, less optimistic than Silveira about the possible ranges of conclusions. He suggested redefining the threshold of a “recent” discharge to less than 3–6 days. Similarly, he stated that recognising shots more recent than 24 h, as done by Sonnenschein, might be hazardous in real casework.

5.2. Colourimetric tests

All the early works on black powder highlighted the importance of exploiting changes in physical characteristics (and thus the role of visual inspection). Nonetheless, colourimetric reactions were also suggested as confirmatory techniques to improve the

confidence in the time-since-discharge estimates. In his pioneering work on the estimation of the time since discharge of firearms employing black powder, Sonnenschein (reported in [21]) suggested checking filtered GSR extracts (obtained by washing the barrels with distilled water after their visual inspection) for their colour, odour and presence of specific compounds. Particularly, he observed that the extracts from firearms discharged within 2 h, generally presented a characteristic smell of hydrogen sulphide (H_2S) and a pale yellow colour, while older ones were darker and did not smell. The use of lead acetate, barium chloride and potassium ferricyanide were recommended for testing the presence of sulphides (S^{2-}), sulphates (SO_4^{2-}) and ferrous ions (Fe^{2+}), respectively (Table 3). Indeed, the author noticed that sulphides totally disappeared in the first 2 h since discharge, while sulphates persisted up to 24 h. Detection of ferrous ions could be positive until 6 days.

Analogous approaches were later proposed by Lucas [20] and Sokol [21]. In particular, Lucas reported a thorough study on the gradual appearance/disappearance of sulphides (S^{2-}), sulphates (SO_4^{2-}), thiosulphates ($S_2O_3^{2-}$), thiocyanates (SCN^-), ferrous ions (Fe^{2+}), ferric ions (Fe^{3+}), nitrites (NO_2^-) and nitrates (NO_3^-) over time. Many of his results largely agreed with those of Sonnenschein. He thus observed that sulphides normally disappeared in

Table 3

Suggested ions and tests to estimate the time since discharge of firearms and cartridges employing black powder. "Temporal window" refers to the temporal window the ion can be detected.

Ion	Name	Suggested colorimetric test	Temporal window		Authors
			Min	Max	
S ²⁻	Sulphide	Lead acetate	0	2–5 h	Sonnenschein [21], Lucas [20]
SO ₄ ²⁻	Sulphate	Barium chloride	0	24 h	Sonnenschein [21], Lucas [20]
S ₂ O ₃ ²⁻	Thiosulphate	Silver nitrate	2–5 h	∞	Lucas [20]
SCN ⁻	Thiocyanate	Ferric chloride + mercury perchloride	No evolution		Lucas [20]
Fe ²⁺	Ferrous	Potassium ferricyanide	0	6 d	Sonnenschein [21], Lucas [20]
Fe ³⁺	Ferric	Potassium thiocyanate	28 h	∞	Lucas [20]
NO ₂ ⁻	Nitrite	Naphthylamine hydrochloride	2–5 h	∞	Lucas [20]
NO ₃ ⁻	Nitrate	Phenolsulphonic acid	Never detected		Lucas [20]

the first 4–5 h after discharge because of their gradual oxidation in sulphates (primary product) and thiosulphates (secondary product), the amount of which consequently increased over time. Furthermore, he observed that trace levels of ferrous ions were always present at the beginning, but oxidised to ferric ions during the first days after discharge. Nitrites only appeared after 4–5 h, as they decomposed in presence of alkaline sulphides. Nitrates were apparently never detected, contrary to thiocyanate which was initially present but did not show any reliable evolution. Tests used to semi-quantify all these ions are reported in Table 2. The author suggested to apply them on liquid extracts, obtained by pouring distilled water (20 mL for rifles and shotguns, and 10 mL for rifles for pistols and revolvers) down the barrel from the breech. An approach using cotton-wool swabs, which were then squeezed in order to obtain a test solution, was also proposed, but less satisfactory results were generally obtained.

6. Approaches for smokeless powder firearms/ammunition

From the beginning of the 20th century, smokeless powder has been gradually introduced to replace black powder in ammunition. As a consequence, approaches to estimate the time since discharge also evolved to adapt to this new type of propellant. This section reviews all the proposed approaches for firearms using smokeless powder, as well as for related cartridge components. The most influential amongst them are summarised in Table 2.

6.1. Visual changes in solid GSR

With the introduction of smokeless powders, early dating methods based on visual inspection became less important. This is because of the significantly lower amount of solid residue released by this type of propellant, and the fact that it does not form that intense black crystalline mass which is characteristic of black powder [20]. For these reasons, few reliable approaches based on the exploitation of physical changes in GSR of smokeless powder were reported. In one contribution, Silveira (reported in [21,25]) noted that the solid GSR left by smokeless powder had hygroscopic properties similar to that of black powder. Particularly, he noticed that it rapidly adsorbed moisture in the first hours after discharge, presenting a wet aspect 12–24 h after discharge. The moisture successively evaporated and totally disappeared after 2 days. Thus, he proposed to date the discharge of rifles and related cartridges employing smokeless powder through visual quantification of the humidity absorbed by the residue, in addition to the spreading of rust, which inevitably started developing 5 days after discharge.

Lucas [20] studied changes in composition and colour, and stated that no marked difference was found between fresh and (few days) older smokeless powder residues. Thus, he concluded that estimating the time of discharge using smokeless powders

was not feasible based on these features. Nonetheless, he noted that a characteristic smell was generally present after firing, which decreased in intensity over time, providing some evidence on the time since discharge. This smell could not be attributed to hydrogen sulphide (H₂S), because of the absence of sulphides in the GSR of this type of propellant. Contrary to Lucas, Sokol [21] observed that the GSR of smokeless powder slightly changed colour from light to dark grey ca. 3–5 days after discharge in barrels. However, he did not find this characteristic sufficiently reliable to provide indications of the time since discharge of both firearms and spent cartridges. He rather proposed to exploit residual humidity and rust, which he considered as the only characteristics which evolved in a sufficiently rapid and reliable way.

6.2. Deposition of dust/dirt and sooting

The possibility of exploiting additional visible physical changes to more reliably estimate the time since discharge was investigated in the following works. In 1968, Meier [38] presented in a conference report the general approach adopted by the *Wissenschaftliche Dienst* (WD) of Zürich to estimate the time since discharge of firearms and spent casings. A particularly important step of the latter involved the determination of the amount of dust deposited on external metallic surfaces, as its presence was recognised to help to determine whether a firearm or cartridge had been recently manipulated or not. Nonetheless, the author admitted that this type of examination was not always useful for firearms contrary to spent casings, given that no dust is usually deposited on guns stored in holsters (especially true for handguns). Furthermore, he also recognised that dust is a very delicate trace, which can be involuntarily removed during crime scene investigation. Thus, it is of little use if questioned specimens are not carefully handled and sampled.

Similarly to the approach documented by Meier, Bridgemon [10] investigated in 1986 the use of dirt accumulation and soot disappearance for dating the time since discharge of brass cartridges stored in desert sand. He thus observed that cartridges deposited at ground level were totally filled with soil within a month, mainly because of air movement. Furthermore, the amount of sooting was visibly reduced within a day. The latter mostly disappeared at the end of the first week, and never persisted more than a month. Thus, he concluded that an estimation of the time since deposition might be possible by exploiting these characteristics when studied together with rust formation (see next sub-Section 6.3). Nonetheless, he also admitted that all observations were case-related and examiners would have needed to duplicate the results for each casework circumstance, in order to provide reliable evidence in a particular case. The importance of factors influencing the ageing is thus acknowledged, adding complexity to the endeavour.

6.3. Formation of rust

Determining the onset time of corrosion products has been an important criterion in early dating approaches to estimate the time since discharge of firearms and cartridges using either black or smokeless powders (see the works of Sonnenschein, Sokol and Silveira reported above [21,25]). Despite that, rust formation and spreading have mainly been used as complementary evidence, and few systematic studies have been carried out. Faced with the raising challenges provided by smokeless powder, more extensive research based on these time-dependent phenomena was carried out in an attempt to develop more reliable dating approaches. Meier [38] explicitly mentioned that the possibility of exploiting rust formation and spreading for dating was studied at the WD in order to overcome the inherited practical issues of using dust only. However, this approach was not considered reliable, mainly because of a scarce case-to-case reproducibility and very slow formation rate in indoor environments.

Analogous conclusions were reported by other authors. In 1977, in an attempt to provide evidence in a murder case, Shanahan [9] investigated the corrosion behaviour of .22 calibre brass spent cartridges buried in 50 mm garden soil during 18 weeks. He thus found that cases coming from the same batch showed extremely variable spread and colour of corrosion products after ageing, even if they were buried side by side. Indeed, surface area coverage of rusting products ranged from a minimum of 5 % to a maximum of 100 %. Moreover, being superficial in nature, he noted that rust traces could be easily removed by handling. More recently, Wogan *et al.* [39] focused on evaluating the corrosion behaviour of handguns in aqueous environments to estimate their time since immersion. They noted that corrosion rate and rust properties could vary greatly between different firearms, even if all were made of stainless steel. This was mainly attributed to minor differences in alloys used for their production. Additionally, the authors observed that the composition of the ageing medium could significantly affect the rusting process because of the possible presence of different corroding agents. Thus, they concluded that rust formation and spreading are very complex phenomena which would be hardly helpful in real casework.

Other researchers were more encouraging on the use of corrosion phenomena for dating purposes. In his study of 1986 on the ageing of brass cartridges stored in desert sand, Bridgemon [10] studied the formation of rust in addition to dirt accumulation and sooting disappearance. He observed that no substantial difference was noted in the rate of tarnishing between various spent cases from a quantitative point of view, even belonging to different brands and calibres. Spent cartridges developed various colours after one month, but were almost totally covered by a characteristic olive-brown colouration after six months of ageing. He thus concluded that useful ageing information could actually be provided by exploiting rust formation and spreading. In this regard, dissimilarities between the studies of Bridgemon and Shanahan could partly be attributed to different characteristics of the soils used for experiments: in fact, while Shanahan carried out the ageing tests in garden soil, Bridgemon set his experiments in desert sand. Encouraged by these results, Kerkhoff *et al.* [40] tried to extend the work of Bridgemon by studying the development of corrosion products on cartridges and bullets made of metals other than brass (i.e., lead and steel). They thus noted that all elements generally corroded over time, but with different rates. Particularly, steel elements corroded very rapidly, while corrosion of lead ones was more slow to appear. This should be taken into account in the development of eventual dating approaches.

In addition to works directly related to the estimation of the time since discharge, some contributions studied corrosion effects on source identification and thus represent an alternative but

helpful source of information on these ageing processes. The most recent and exhaustive work is one by Larrison [41], who focused on the investigation of corrosion of copper-jacked bullets and brass cases in open air, soil, water and a dog carcass after their firing. Results showed that corrosion in water and the dog carcass was significantly quicker and that elements may no longer be identifiable after two years of ageing in these mediums.

6.4. Colourimetric tests on solid GSR

The introduction of smokeless powders significantly warranted the role of wet chemistry methods in comparison to visual inspection in order to provide time-since-discharge estimates. Nevertheless, their use was not yet fully established at the beginning of the 20th century, and few in-depth investigations were initially reported. Both Lucas [20] and Silveira (reported in [21,25]) recognised that the most important difference of smokeless powders compared to black powder was that the solid GSR was mainly composed by nitrites and nitrates. In his investigation on rifles and related cartridges, Silveira suggested brucine and/or diphenylamine tests to semi-quantify nitrates in scratched GSR samples. The decreasing intensity of reactions over time (a consequence of the diminution in nitrates content) could thus provide some evidence on the time since discharge and allow discriminating recent shots from older ones. Likewise, Lucas tried to exploit changes in GSR composition (i.e., nitrites, nitrates and sulphates) to date the discharge but, contrary to Silveira, he did not find any marked difference between fresh and a few days old residues. This might be explained by the use of a different sampling technique. Indeed, while Lucas preferred performing tests on a GSR solution obtained by washing the barrel with distilled water, Silveira applied them on solid GSR samples obtained by scratching. The latter actually seemed to be a more sensitive approach for colourimetric testing.

It was not until the late 1960s, and the widespread use of smokeless powders, that more systematic works on wet chemistry methods were proposed. Meier [38] published the results of an extensive study on the quantitative evolution of nitrites in barrels and spent cartridges after shooting. His method involved the sampling of GSR with water or dry tissues, followed by the application of (unspecified) colourimetric reactions. His experiences definitely demonstrated that the composition of solid residues of smokeless powders changed over time, but he did not recommend exploiting them for dating purposes because of reproducibility issues in their evolution.

6.5. Colourimetric tests on volatile GSR

Considering the low precision obtained when exploiting the evolution of nitrates and nitrites in smokeless powder residues, Price [42] opted for a totally different (and revolutionary) approach. Thus, instead of studying the different chemical transformations which take place in the solid GSR, he proposed to follow the evolution of the residual amounts of dissipating compounds in the volatile fraction of GSR. In his investigation, he focused on carbon monoxide (CO) remaining in firearms after the discharge. Barrel vapours were aspirated in tubes containing silica gel impregnated with potassium pallado-sulphite producing a colourimetric reaction in the presence of carbon monoxide. Through this procedure, the author stated that it was possible to differentiate recent discharges from less recent ones (particularly, the simple presence of carbon monoxide was found to be indicative of a recent shot).

Encouraged by these promising results, Sinha [43] later proposed a method to estimate the time since discharge of shotgun shells by quantifying the dissipation rate of nitrogen

oxides (NO_x). A filter paper containing a solution of 1-naphthylamine and sulphonic acid was placed over the mouth of the cartridge. The time taken by nitrogen oxides to escape through the hole and develop a pink colour was measured. This was found to be correlated to the time since discharge, and could thus be used as a metric for dating estimation. The author reported that this method allowed determining if a shotgun shell was last used within 24 h, 2–5 days, or 6–10 days before analysis. A very similar method, involving the same reagents and preparations steps, was later proposed by Heen [44] for the estimation of the time since discharge of pistols. Filter papers, in this case, were directly placed inside the pistol barrel, which was lay perpendicularly, without touching the internal walls. The author reported that the method allowed providing very useful information for dating purposes, but he did not provide any idea of the range of possible conclusions. Therefore, this specific application remains doubtful.

While the measurement of dissipating compounds was considered a very encouraging approach, early works were based on a subjective evaluation of the intensity of colourimetric reactions. This yielded time-since-discharge estimates affected by a low precision. Voskertchian & Pavilova suggested two instrumental approaches to solve the problem. The first was based on electron spin resonance [45,46] but did not receive much attention because of the limited availability of these devices in forensic laboratories. The second involved the use of a conventional spectrophotometer [47,48]. The latter consisted of the application of a nitronyl nitroxide solution on small squares of plastic-backed alumina plates, which were then exposed to the inner atmosphere of the questioned barrel (Fig. 2). In the presence of residual nitrogen monoxide (NO), a coloured product was developed and the intensity of the reaction was measured by spectrophotometry. Several plates were simultaneously inserted in the barrel and retrieved at different intervals. Thus, the reaction's kinetic rate could be measured and exploited as a metric to infer the time since discharge. The authors claimed a precision of ± 1 day on inferring times since discharge of recently used shotguns (up to 5–7 days).

6.6. Thin-layer chromatography (TLC)

While the introduction of instrumental methods by Voskertchian & Pavilova allowed for a more objective evaluation of the analytical results, the used of plastic-backed alumina plates still remained a tricky and lowly flexible sampling technique. Therefore, alternative approaches were developed using non-specific sampling methods instead of colourimetric reactions. Chromatographic steps were also generally implemented in the

analytical protocols to allow separation and quantification of the single extracted compounds. In a work of 1996, Aginsky *et al.* [49] first proposed monitoring the nitration of the diphenylamine, deposited on inner metallic surfaces after firing, for dating the discharge of pistols and spent cartridges. According to their procedure, residues were sampled by liquid extraction with dichloromethane. Cotton clothes wetted with the solvent were used to extract diphenylamine from pistol barrels, while cartridges were treated by immersion. Extracts were then analysed by gas chromatography (GC) coupled to mass spectrometry (MS), or by thin-layer chromatography (TLC). Results showed that several mono- and polynitrated diphenylamines were observable in aged residues, which were usually not found immediately after discharge. However, nitration is a slow reaction and only very old residues (1 year or older) could be differentiated from “fresh” ones, limiting the number of practical cases where this method would be useful.

6.7. Solid-phase micro-extraction (SPME)

More recently, Andrasko *et al.* [34,50–52] further developed the idea of analysing the volatile fraction of GSR, and proposed a new method based on the sampling of dissipating compounds by solid-phase micro-extraction (SPME). SPME is a solvent-free preparation technique which involves the use of a fused silica fibre coated with a small amount of extracting phase [53,54], such as polydimethylsiloxane (PDMS) or polyacrylate (PA). Behaving like high viscosity rubbery liquids, these fibres can interact with different kinds of analytes and simultaneously co-extract them. In their first work in 1998, Andrasko *et al.* [34] applied the technique to estimate the time since last discharge of shotguns. The method involved sampling volatile GSR compounds directly from the inner atmosphere of the barrels by inserting a SPME fibre at the muzzle position (Fig. 3). Polyacrylate was suggested as extraction coating and sampling was carried out for 30 minutes at laboratory temperature. The fibre content was then desorbed and analysed using GC. Many characteristic explosion by-products were identified by MS, particularly a large range of PAHs. The authors suggested naphthalene and an unidentified decomposition product of nitrocellulose (named “TEA2”) as target analytes, and followed their decreases using two GC systems coupled to flame ionization detector (FID) and thermal energy analyser (TEA), respectively. Partial ageing curves were thus constructed by daily analysis (i.e., multiple SPME extractions) of the barrels, until complete disappearance of any analytical response. This allowed estimating the time since last discharge by comparison with a complete reference curve obtained on analogous materials. The

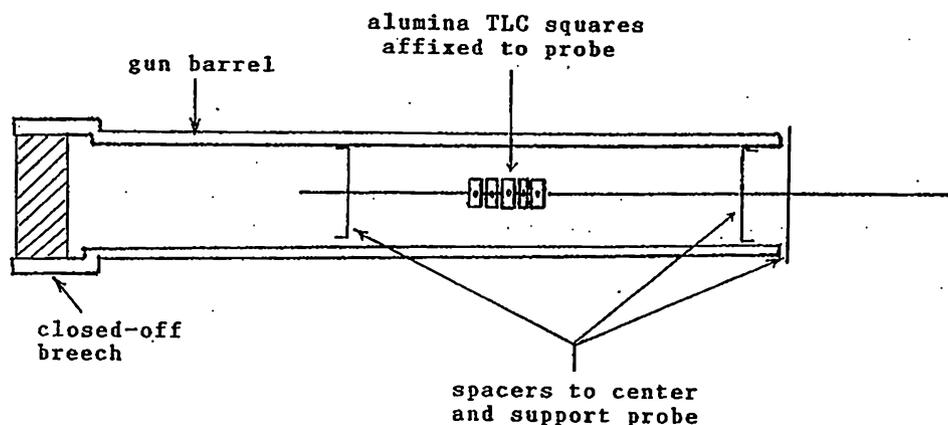


Fig. 2. Schematic diagram of the analytical approach proposed by Voskertchian & Pavilova [47,48] for estimating the time last discharge of shotguns. Adapted from [47], with permission.



Fig. 3. Sampling of a 9mm Parabellum pistol from the muzzle using SPME, as suggested by Andrasko *et al.* [34].

authors admitted that no exact estimation could be provided by this methodology (mainly because of the numerous variables affecting diffusion kinetics in real cases), but claimed a good precision in discriminating three time ranges for the last discharge: 2–3 days, 7–14 days, and beyond 21 days.

SPME has several advantages over earlier approaches. For example, being a non-specific sampling method, several volatile GSR compounds were simultaneously identified contrary to colourimetric reactions (which are usually selective for one class of compounds only). It also allowed the extraction of unreactive molecules (such as PAHs), which represent the major

class of investigated compounds amongst explosion products. These characteristics, together with instrumental detection, made it an efficient and promising technique for dating purposes. Indeed, a real case application was reported in a later contribution [11]. Furthermore, the possibility to transfer the method to other types of firearms was investigated by the same authors in a series of successive papers. In 2000, Andrasko & Stahling [51] reported an attempt to estimate the last discharge of sporting rifles, by testing the sampling of TEA2 from both the breech and muzzle. While most of the tested rifles showed highest compound concentrations in the breech position, systematically sampling both was recommended in order to achieve better precision. The authors, in particular, reported the possibility of discriminating between a recent discharge (2–3 days) from older ones of several weeks. The methodology was tested on pistols and revolvers from the muzzle position, even if just focusing on the sampling of TEA2 [52]. However, the peak could be followed only for a few days (max. 1–2 weeks) and inconsistent results were obtained. Finally, the same authors reported an attempt to apply the method to spent cartridges from different types of firearms [50]. A cork was fitted at the case opening and the SPME fibre was pushed through for sampling (Fig. 4a). TEA2 and naphthalene were chosen as target analytes. Nitroglycerin was additionally analysed using GC-TEA. The concentration of these molecules was found to be higher in spent shotgun shells, compared to rifle and handgun cartridges. Nonetheless, similarly to handguns, their escape was globally very rapid and could be followed only over a few days (up to 1–3 weeks, depending on the calibre) yielding generally unreproducible time-since-discharge estimates.



Fig. 4. Sampling of a 5.56 mm NATO spent casing using SPME, as suggested by (a) Andrasko *et al.* [34] (using a cork to stop the opening) and (b) Wilson *et al.* [55] (through putting the shell/cartridge in a vial).

In order to improve the robustness of the methodology and allow its application to a larger range of cases, Wilson *et al.* [55], in 2003, suggested some significant modifications to Andrasko & Stahling's method for the analysis of spent shotgun shells. Having recognised that the rapid disappearance of any compound is a major problem in the analysis of spent casings, they firstly recommended placing the latter in sealed vials, thus preventing volatile GSR compounds from escaping prior to laboratory analysis (Fig. 4b). This solution proved to be effective and, indeed, lately adopted by successive studies in the field. Furthermore, they suggested using MS instead of FID. In this way, they were able to follow naphthalene in spent 12/70 shells up to 4–5 weeks. Additional compounds were also investigated (i.e., diphenylamine, biphenylene and a fourth unidentified compound), but they were found unreliable as ageing parameters, at least for shotgun shells [55].

Successively, a research group from the Institut de Recherche Criminelle de la Gendarmerie National (IRCGN) published the results of their study on the estimation of the time since last discharge of shotguns [7,8,56]. The authors confirmed that the escape rate of volatile GSR compounds from barrels was affected by many factors. Nonetheless, they also found that more robust conclusions could be obtained by simultaneously exploiting multiple compounds in the same GC run instead of using single target analytes as done by previous works. 1-methylnaphthalene, 2-methylnaphthalene and acenaphthylene were thus exploited in addition to naphthalene, and the developed multi-residue GC-FID method allowed differentiating with enhanced confidence recently used shotguns of different calibres ranging from 12/70 to .22 LR (2–5 days), from those used in the last 5–10 days, and beyond 10 days [7]. Furthermore, strategies to prevent the escape of volatile GSR compounds from barrels prior to laboratory analysis were tested, and the use of lead stoppers or aluminium foils proved to be effective. The suggested improvements seemed promising, and an application to a real case was reported. The same research group also attempted to transfer the method to pistols and revolvers [56]. However, they confirmed that the analyte disappearance was too rapid to be followed over 24 h since discharge, at least using GC-FID. The possibility to follow the decrease of stabilisers (i.e., diphenylamine and ethyl centralite) and heavy PAHs (i.e., phenanthrene, acenaphthene and fluorene) using SPME coupled to GC/MS was additionally investigated, but the obtained results indicated that the developed methodology was insufficiently reliable to estimate the time since discharge of handguns in real cases.

Other research groups tried to replicate the previous results with little success [57,58]. A significant challenge reported was the low repeatability and sensitivity of SPME extraction. Major methodological changes were proposed more recently. Weyermann *et al.* [36,59] published the results of a study on the characterisation of the volatile GSR fraction in spent handgun cases using SPME coupled to GC/MS. Numerous new and potentially interesting analytes were identified. However, contrary to what was observed by Wilson *et al.* on shotgun shells, the authors found that SPME extraction affected the concentration of the residual volatile GSR amounts remaining in the cartridge. Thus, they concluded that a sequential sampling procedure was not applicable to estimate the time since discharge, at least for small calibres. A single-extraction procedure was tested as an alternative. However, poor reproducibility was observed between the measurements made on different cartridges. Hence, the authors concluded that further optimisation would be necessary to implement SPME for dating purposes. Very similar conclusions were reported by researchers of the *Bundeskriminalamt* (BKA) in an internal study [60]. The authors tried to upgrade the method by using comprehensive two-dimensional GCxGC hyphenated to

time-of-flight (ToF) MS, as well as to optimise SPME conditions by using a higher extraction temperature. They thus found that an extraction temperature of 55 °C was optimal for the targeted GSR compounds (i.e., 3-methyl-1-butanol, toluene, butyl acetate, hexyl acetate, cyclohexanone, benzonitrile, indene and naphthalene). Despite these improvements, low reliable ageing curves were again obtained.

More recently, Chang *et al.* [61] reported an attempt to estimate the time since discharge of spent handgun cartridges by exploiting diphenylamine, dibutyl phthalate and naphthalene. SPME extraction temperature was set to 66 °C, and a multi-residue GC-FID method was used. In controlled conditions, the authors were able to assess if cartridges were fired within 1 day, 5 days, 10 days, 20 days, 30 days or more. However, cartridges were aged in open vials, and this might have quenched their ageing kinetics and headspace concentrations, making the reported results not representative of real case scenarios [62]. Frère *et al.* from IRCGN proposed a modified SPME-based sampling strategy for shotguns [63]. They proposed to swab down the barrel with a dry cotton wad, and to preferentially extract the latter in a closed vial. The method was claimed to be simpler and less time-consuming. While promising preliminary results were reported, the method was more invasive (i.e., the specimen can be analysed only once) and further data should be acquired to evaluate if sufficient reliability can be achieved. A summary of the main analytical conditions adopted in the different works using SPME is reported in Table 4.

6.8. Headspace sorptive extraction (HSSE)

Starting from the premise that the low extraction capacity of SPME could be a contributing factor explaining the unreliable results obtained for handgun calibres, Gallidabino *et al.* [37,64] introduced a novel approach based on a more exhaustive extraction technique, i.e., headspace sorptive extraction (HSSE). While sharing the same principle as SPME, HSSE exploits a stir bar as an extraction support instead of a thin fibre. The stir bar is coated with a larger volume of PDMS (up to 220 times larger than a conventional SPME fibre), thus leading to generally higher recoveries for all classes of compound [65]. In order to implement this technique, the authors proposed to sample spent cartridges in 20 mL vials during several hours by suspending HSSE stir bars in their headspaces using special glass inserts (Fig. 5). Then, the stir bars were desorbed through a thermal desorption unit in GC/MS.

A preliminary version of this method was applied to the analysis of .45 ACP and .357 Magnum spent casings [37,64]. 166 compounds were identified in the headspace of 9 different types of ammunition. Many of them were reported for the first time, thus also proving the higher analytical performances, in terms of sensitivity and selectivity, of HSSE compared to SPME, which were promising for the development of a more reliable dating approach. A large proportion of the identified compounds was also showed to have significant decreases over time. This was especially true for explosion by-products such as PAHs, in contrast to residual unreacted propellant components that were found to be relatively stable over time. Starting from these findings, 29 analytes were then selected and the method further optimised for their targeted determination [66,67]. Optimal conditions for extraction time and temperature were found to be 24 h and 70 °C, respectively. This second method has been tested on 9 mm Parabellum cartridges, using multi-variate techniques based on machine learning for the data interpretation. The possibility to discriminate recently fired (0–9 h) from old cartridges (>24 h) was demonstrated, as long as the casing storage conditions before sampling are known.

Table 4

Published works using SPME-GC to estimate the date since discharge and corresponding experimental settings (T_{ext} and t_{ext} are the extraction temperature and time, respectively). AT stands for "ambient temperature". The following abbreviations were additionally used. For calibres, HG: handguns, LG: long guns and rifles, SG: shotguns. For target compounds, 1MNP: 1-methylnaphthalene, 2MNP: 2-methylnaphthalene, 3MB: 3-methyl-1-butanol, ACY: acenaphthylene, BIP: biphenylene, BNZ: benzonitrile, CYHONE: cyclohexanone, DBP: dibutyl phthalate, DPA: diphenylamine, EA: ethyl acetate, HA: hexyl acetate, IND: indene, NG: nitroglycerin, NPT: naphthalene, TOL: toluene, Unkn: unidentified compound. For detectors, TEA: thermal energy analyser, FID: flame ionisation detector, qMS: single quadrupole mass spectrometry, ToF: time-of-flight mass spectrometry.

Discharge of firearms						
Authors	Type	Coating	T_{ext}	t_{ext}	Detector	Targets
Andrasko <i>et al.</i> [34]	SG	PA	AT	30 min.	TEA, FID	TEA2, NPT
Andrasko <i>et al.</i> [11]	SG	PA	AT	20 min.	TEA, FID	TEA2, NPT
Persin <i>et al.</i> [7]	SG	PDMS	AT	30 min.	FID, qMS	NPT, 2-MNP, 1-MNP, ACY
Frère <i>et al.</i> [63]	SG	PA	50 °C	30 min.	qMS	NPT, 2-MNP, 1-MNP, ACY
Andrasko <i>et al.</i> [51]	LG	PA	AT	20 min.	TEA	TEA2
Andrasko <i>et al.</i> [52]	HG	PDMS/Carb.	AT	40 min.	TEA	TEA2
Discharge of cartridges						
Authors	Type	Coating	T_{ext}	t_{ext}	Detector	Targets
Andrasko <i>et al.</i> [50]	All	PA	AT	20 min.	TEA, FID	TEA2, NPT, NG
Wilson <i>et al.</i> [55]	SG	PA	AT	20 min.	qMS	NPT, BIP, DPA, Unkn
Weyermann <i>et al.</i> [36]	HG	PA	AT	40 min.	qMS	(characterisation study)
Schmidt [60]	HG	PDMS/DVB	55 °C	40 min.	ToF	3MB, TOL, EA, CYHONE, BNZ, HA, IND, NPT
Chang <i>et al.</i> [61]	HG	PA	66 °C	21 min.	FID	DPA, DBP, NPT
Bao <i>et al.</i> [58]	SG	PA	AT	20 min.	TEA	TEA2



Fig. 5. Sampling of cartridges using HSSE, as suggested by Gallidabino *et al.* [64]. The HSSE extraction bar is put in a special insert in the extraction vial, just above the cartridge to analyse.

7. Interpretation of analytical findings

Interpretation involves attaching a meaning to analytical observations, which is directly related to the expected ageing profiles and enables decisions to be made in a forensic context. Different approaches can be applied, depending on the situation and the stage of the criminal enquiry (i.e., investigative or evaluative phase), as previously discussed.

7.1. Inference based on qualitative data

Early dating approaches mainly relied on the evaluation of some qualitative ageing parameter, such as the colour of the solid

GSR or the presence of specific ions. Observed outcomes for these variables were mainly categorical (i.e., they could take only limited numbers of possible states). Thus, they were relatively difficult to be interpreted through statistical modelling, and times since discharge were estimated by the simple comparison of the assessments carried out on the questioned specimens with those of tabulated sets of reference data. A specific colour or smell was then interpreted as a sign of a recent shot. For example, it was inferred that the time since discharge using black powder was between 2 and 5 days if a white/green colour was observed [21,25]. However, conclusions were generally affected by low temporal resolution and precision, which essentially allowed placement of the discharge into wide time intervals.

The introduction of colourimetric and instrumental techniques made it possible to switch from discrete and qualitative to continuous and quantitative ageing indicators, such as the time taken to start a colourimetric reaction or the chromatographic peak area of target compounds. Potential advantages offered by this type of variable were multiple. In fact, on one hand, they allowed an improvement in the number of possible observable outcomes (with potential benefits to the resolution of time-since-discharge estimations). On the other hand, they were easier to implement into statistical (chemometric) interpretative models. Despite these added values, proposed interpretation approaches were generally similar to those previously employed, i.e., based on a comparison of assessments between the questioned specimen and a reference table. For example, Sinha [43] suggested to measure the time interval in which a visible colour was developed when a filter paper containing 1-naphthylamine was placed in contact with a headspace specimen, and to compare this measurement to a previously tabulated reference dataset. A time interval ($\leq 1, 2-5, \text{ or } 6-10$ days) could thus be inferred from the obtained results.

7.2. Integration of quantitative data

The first attempt to apply more formal statistical models to the estimation of the time since discharge was presented by Voskertchian & Pavilova [47,48] in their work on the quantification of the residual amount of nitrogen monoxide (NO) by colourimetric reaction with nitronyl nitroxide. Based on the fact that the

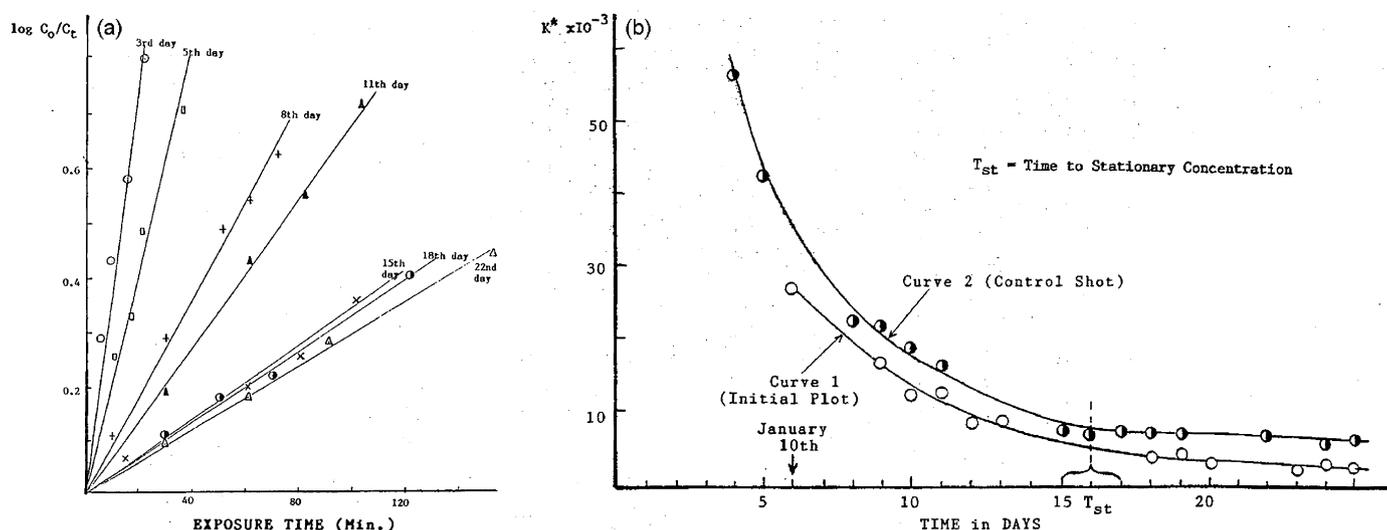


Fig. 6. Illustration of the data interpretation approach proposed by Voskertchian & Pavilova [47,48] for their spectrophotometric method. (a) Plot of $\log C_0/C_t$ versus exposure time in the barrel for different days of analysis after reception of the gun. C_0 is the initial concentration of the colorimetric reactive used in the probe while C_t is its concentration after reaction with NO in the barrel, determined at the exposure time t using a spectrophotometer. These plots help to determine the apparent reaction constant K^* for every day of analysis, which is dependent on the concentration of NO. (b) Plot of the measured K^* versus the day of analysis. These help to build a partial ageing curve (Curve 1) that can then be compared with a complete ageing curve obtained on control shots with the same gun (Curve 2), in order to estimate its time since last discharge at the beginning of the procedure. The data interpretation method proposed by Andrasko *et al.* [34] for their SPME method is based on a similar use of the plots in (b) where, however, K^* are substituted with the normalised peak areas I_n/I_{n-1} of naphthalene, determined by SPME-GC/MS. Adapted from [47], with permission.

approach involved multiple daily samplings of the same specimen, the authors suggested determining the within-day apparent reaction constants by using regression analysis between the intensity of the colour reaction and the relative exposure time. A set of constants corresponding to each day of analysis were thus obtained. As these were found to decrease with ageing, they were plotted against time in order to obtain a partial ageing profile, which could finally be compared to a complete reference curve (i.e., an ageing profile established using the same set of firearm/ammunition as the one used in the investigated case) (Fig. 6). This allowed obtaining a point instead of a range estimate of the time since discharge.

Andrasko *et al.* [34,50–52] adopted a similar approach for interpreting data using their SPME-based method. These authors, indeed, suggested to plot daily measurements as a function of time in order to obtain partial ageing profiles (and to compare the latter to a complete curve acquired from reference material). However, instead of apparent reaction constants, they suggested using chromatographic peak areas of specific target compounds after GC analysis. A major drawback encountered in the application of this methodology lay in the fact that peak areas are directly proportional to the residual amount of the measured compounds and, thus, the partial ageing profiles were strongly dependent on their initial quantity in the specimen. This was more particularly considered an issue in those situations where no case-related reference cartridges were available to obtain a complete ageing profile. Thus, the authors suggested applying the following data normalisation:

$$Q_n = I_n/I_{n-1} \quad (1)$$

where I_n and I_{n-1} are the naphthalene peak areas measured the day n and the day before ($n-1$), respectively. Thanks to this solution, the obtained partial ageing profiles were amount-independent and the authors claimed that a generic reference ageing profile could be used as a comparison.

In an attempt to adapt the SPME-GC method for systematic use in real casework, Persin *et al.* [7] suggested modifications to the

approach of Andrasko *et al.* by introducing a double-step and threshold-based evaluation. Following the latter, questioned firearms were analysed by SPME-GC at their arrival in the laboratory and four compounds were primarily targeted (namely, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and acenaphthylene). If these were simultaneously detected, the last discharge was considered very recent (generally, less than 5 days) and no further analysis was usually needed. Otherwise, the decrease of naphthalene was followed daily as suggested by Andrasko *et al.*, and the partial ageing profile was compared with a reference curve. Contrary to the latter authors, Persin *et al.* suggested to give conclusions considering previously defined decision thresholds and not as point time-since-discharge estimates. Particularly, the reference ageing curve was divided into three intervals depending on the naphthalene decrease rate. If the first point of the partial ageing profile fell inside a specific frame, it was thus inferred that the last discharge was between the related time limits. The use of time intervals makes the approach of Persin *et al.* very similar to early dating approaches. Nonetheless, the authors claimed that this is a more conservative way of expressing opinions about time since discharge, and stated systematic use in real cases. Furthermore, this approach is the first attempt (at least, in modern literature) to systematically interpreting multiple sources of information (i.e., different analytes) in a unique model in order to increase confidence in time-since-discharge estimation, as previous approaches were based on assessing single ageing parameters.

Schmidt [60] further studied the possibility of simultaneously interpreting multiple analytes to increase estimation accuracy. However, contrary to Persin *et al.*, she attempted to apply a more formal statistical approach by using multi-variate regression analysis. Partial least squares regression (PLS) was tested in order to model the relationship between time since discharge and the chromatographic peak areas of 8 target compounds (i.e., 3-methyl-1-butanol, toluene, butyl acetate, hexyl acetate, cyclohexanone, benzonitrile, indene and naphthalene) after single extraction of specimens by SPME. Good linearity between estimated and actual

times since discharge was obtained in the first 14 days of ageing for 9 mm spent cartridges, showing great potential for this kind of statistical techniques. However, the model was not trained using independent datasets and/or resampling, leaving doubt on the expected performance in real cases.

Gallidabino *et al.* [64,67] more systematically investigated the use of chemometrics and multi-variate techniques to interpret measurements obtained after application of single-extraction approaches using HSSE. Particularly, they compared 6 different multi-variate regression techniques in combination with diverse pre-treatment strategies to model the relationship between time since discharge and chromatographic peak areas of 21 target compounds. Regression methods included partial least squares regression (PLS), multi-variate adaptive regression splines (MARS), artificial neural networks (NN), random forests (RF), *k*-nearest neighbors (KNN) and support vector machines (SVM), while pre-treatments strategies included total sum normalisation (TSN), probabilistic quotient normalisation (PQN) and pairwise log-ratios normalisation (PLR). Particular attention was paid in attempting to estimate actual performance in real cases. Thus, models were trained by resampling and tested on independent datasets. A total of 381 models were compared. The authors remarked that PLR normalisation followed RF or PLS regression allowed obtaining the best results. Acceptable accuracy up to 48 h since discharge could be obtained on 9 mm spent cartridges and, beyond this limit, results could still be useful to differentiate a recently fired cartridge from an older one. Robustness of the models to three influence factors (i.e., temperature, relative humidity and cartridge position) was also tested. Model performances were not found to be significantly affected, as long as the reference dataset was acquired in similar conditions than the questioned cartridge.

7.3. Assignment of an evidential value

Alternative hypotheses on the course of the events are usually forwarded by the suspect following arrest. When multiple hypotheses are available, a preferential approach for the interpretation of analytical findings would be to provide preferential support for one of them rather than to directly infer a time since discharge. This is done through the assignment of what is called an “evidential value” to the analytical findings. To reach this purpose, probabilistic approaches based on the calculation of likelihood ratios (LRs) are nowadays recognised as a reliable strategy in forensic literature [68,69]. However, applications to time-since-discharge problems have been rare and late-appearing. Up to now, indeed, only two works reported the development of an LR-based approach for dating issues in this field, with the first formal model dating back to 2013 (see below).

An LR-based approach requires the formulation of at least two alternative hypotheses on the course of the events, which generally reflect the point of view of the prosecution and the defence in a judicial context. In cases where the time since discharge is contested, possible hypotheses could be, for instance [70]:

- T_p : the analysed specimen (firearm or cartridge) was lastly discharged at the same time as the commission of the crime (e.g., 9 h before sampling);
- T_d : the analysed specimen (firearm or cartridge) was lastly discharged prior to the commission of the crime (e.g., 24 h before sampling);

where the subscripts “p” and “d” indicate the hypotheses of the prosecution and defence, respectively. The role of the scientist is thus to assess the probability (*Pr*) of a given analytical outcome or set of analytical findings (say *q*) under both these hypotheses. Their

ratio is known as the LR:

$$LR = \frac{Pr(q|T_p)}{Pr(q|T_d)} \quad (2)$$

If $LR > 1$, the analytical results support the prosecutor hypothesis T_p , while they support the alternative hypothesis T_d if $LR < 1$; if $LR = 1$, the results are inconclusive. Differences in published approaches essentially lay in how these two probabilities are assigned.

For single extraction methods and continuous-quantitative ageing indicators, Gallidabino *et al.* [70] suggested to model the expected outcomes under each hypotheses $T_{p/d}$ using normal distributions. In this way, the LR of any measurement obtained on questioned material could be determined by dividing the densities of probability extracted by the respective normal curves (Fig. 7). This strategy, nonetheless, presupposed that the distribution parameters (i.e., mean and variance) for each of the two normal curves were known. To estimate them, fitting a least-squares regression model on reference data acquired at different times since discharge was suggested as an optimal solution. The latter, indeed, allows estimating the distribution parameters for each hypothetical time since discharge included in the range of the reference data without performing further analyses; an advantage that is particularly useful when hypotheses are redefined in the light of new information and a re-assessment of the evidence is necessary. Using this model, the authors presented the evidential assessment of naphthalene’s peak areas after analysis by SPME-GC/MS as an application example. A non-linear heteroscedastic least-squares regression model was specifically used for modelling decreasing in this case, and coherent results were observed. The possibility of adapting the same approach to multi-variate data (e.g., peak areas from more than one compound) has also been shown in an unpublished internal report [71].

More recently, Sauleau *et al.* [72] reported a proposition to extend the aforementioned interpretative methodology adopted by the IRCGN to evaluative frameworks through the use of a LR approach. The novel evaluative method was still based on fractionation of time into categorical frames (<5 days, 10–15 days, and 20–25 days). However, probabilities to observe the analytical outcomes were assigned under each time frame using Chebyshev’s inequality theorem and a large database of previous analyses carried out on different firearm/cartridge sets. Thus, probabilities

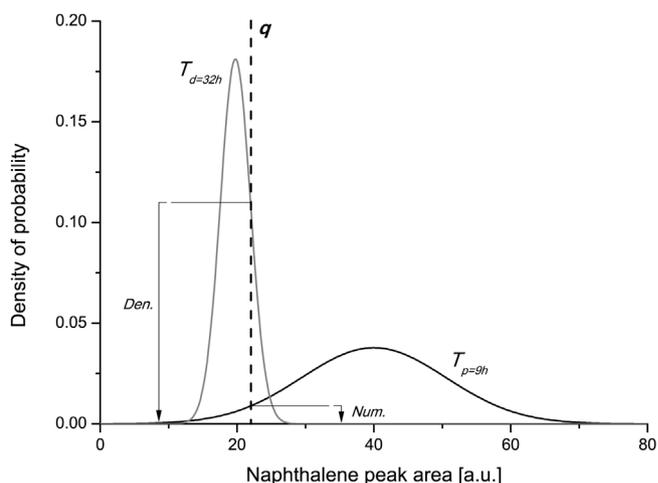


Fig. 7. Example of distributions for the expected amounts of a generic ageing parameter (in this case, the naphthalene peak area) under two forwarded hypotheses (T_p and T_d). The likelihood ratio (LR) for a specific value *q* measured after analysis of a questioned specimen is given by the ratio between the heights of the two curves at this value. Adapted from [70], with permission.

were estimated for each of the four targeted GSR compounds under each time-frame hypothesis and used to calculate analyte-related LR values. The latter were then multiplied together assuming independency in order to determine the global LR for the overall set of observations. The approach is straightforward and appealing, but it also relies on an assumption of independence between the decrease of the different compounds that has not been supported in other studies [71] and may lead to an overestimation of the assigned multi-variate LRs.

8. Influential factors

Independently of their nature or monitoring method, the expected profile of every ageing parameter of interest is characterised by two main elements: its initial conditions and its ageing kinetics, which specifically indicate the rate at which the initial conditions are going to change and how. Both of these elements are affected by a number of influential factors that can be classified into some general groups, such as the characteristics of the involved items/supports and the storage conditions during ageing [73]. Table 5 reports a summary of the main factors identified in the literature.

8.1. Factors influencing the initial conditions

Most of the suggested estimation approaches for time since discharge are based on the analysis of GSR. This is, thus, a trace of main interest for dating purposes, which has been particularly investigated against possible influential factors. In this regard, it has been observed that differences in the initial GSR composition, amount and/or concentration usually depend on variable characteristics of the firearm and ammunition used. Cartridges from different brands (and/or calibres), in particular, are usually loaded with different types and/or amounts of propellant, which thus might give markedly different residues, from both a qualitative and quantitative point of view [7,34,56]. Similar differences may also arise from cartridges from the same brand but different batches, as producers often change the materials used in ammunition manufacturing (from the alloys used for the metallic components to the propellant and primer mixture) to guarantee the same ballistic performance with the cheapest resources available on the market [7,34]. Nonetheless, no direct (linear) correlation has been identified between the composition and amount of propellant inside the cartridge with those of the GSR released. This relationship has recently been found to be much more complex and only investigable using non-linear techniques based on machine learning [74]. The casing alloy has also been proven to affect the composition of the residue released, even in cartridges loaded with the same smokeless powder [56]. The same is true for

the firearm working pressure, since it may significantly influence the ignition process [56].

The characteristics of the ammunition/firearm used are not the only factors that can affect the initial conditions of the ageing profiles of GSR. Cleaning the barrel and/or dismantling the firearm after the discharge, for example, proved to remove significant parts of the deposited residue and, consequently, modify the headspace concentrations of its different components [34,51,52]. New compounds may also be introduced if weapon oils are used, equally affecting the initial GSR composition [7]. In this regard, it seems reasonable to suppose that the use of weapon oil after the discharge may also reduce the propensity of the surface to corrode and form rust. This, however, has never been investigated in time-since-discharge literature. In addition to the previous observations, multiple shots proved to reduce the initial GSR amounts, as a result of an increase of the barrel temperature during the discharge [7,34]. Contradictory results, however, have often been reported on this subject by different authors [51,52]. Finally, the barrel or cartridge length, as well as their inner diameters (i.e., calibre), have been shown to directly affect the available surface for GSR deposition and, consequently, also its initial amounts [7,52].

8.2. Elements-related factors affecting the ageing kinetics

In addition to initial conditions, the characteristics of the seized elements themselves have also been proven to have a significant effect on the evaporation and diffusion rates of volatile GSR compounds. Amongst the intrinsic characteristics, the inner element geometries seem to be particularly important. Indeed, GSR evaporation was observed to be faster in short barrels compared to long ones [7,52,56]. This is likely due to the shorter diffusion pathways, which in turn provide fewer equilibration spots. Analogous observations were made in spent casings, where the persistence of volatile GSR compounds was found to be better in long casings or shells compared to short ones [50]. Openings in the weapon other than the muzzle (e.g., the barrel-cylinder gap in revolvers) also seemed to accelerate the diffusion process, as for the introduction of additional airways [56].

The specific composition of the alloys used for the manufacturing of the firearm and/or related cartridge elements have not been proven, so far, to have appreciable effects on the diffusion rates of volatile GSR. On the contrary, it was shown to be an important factor affecting the underlying ageing kinetics governing corrosion and rust formation [39]. Steel elements, indeed, showed more rapid corrosion than lead elements. Minor differences in the same type of alloy may also be important, as they were shown to cause variable corrosion rates. In addition to that, case-to-case inconsistencies for analogous specimens (e.g., casings from the same batch) have been reported [39], but it is unclear if these are due to minor differences in the alloy composition itself or rather to slight changes in environmental factors.

Regarding extrinsic characteristics, the item position showed to be a prominent (even if often ignored) influential factor to explain the evaporation and diffusion rates of volatile GSR compounds. Indeed, these were found to more rapidly decrease in spent casings laying horizontally than in those laying vertically [67]. It seems reasonable to suppose that a similar effect would be observable in firearms too, but no studies have been performed so far in this regard. The same is true for the effect of the item position on dust deposition and sooting disappearance. Analogously, no investigation has been carried out so far for the effect on ageing kinetics of the specific location of the investigated item of interest on the crime scene. This, however, could likely play a significant role, in a similar way to inhomogeneous storage conditions and slight differences in temperature, airflow and humidity (see below). More investigations, in general, seem necessary to assess the effect of extrinsic characteristics.

Table 5
Identified factors influencing the diffusion of volatile residues from barrels and spent casings.

Parameter	Reported influencing factors	
	Firearms	Firearms and casings
Initial conditions	1. Cleaning 2. Dismantling 3. Number of shots	4. Calibre 5. Ammunition brand 6. Cartridge batch 7. Alloy composition 8. Firearm working pressure
Ageing kinetics		9. Geometries of firearm/casing 10. Position 11. Temperature 12. Airflow (wind) 13. Humidity

8.3. Effects of the storage conditions

Ageing kinetics have generally been found to be significantly affected by the storage conditions. A particularly important variable, in this regard, seems to be the environmental temperature. A number of works, indeed, report that evaporation and diffusion kinetics of volatile GSR compounds slow down at low temperatures in both firearm barrels and spent casings [34,50–52], especially for those analytes with the lowest boiling points [67]. A temperature lower than 20 °C proved to quench the evaporation process, thus making them also appropriate to freeze the state of the specimens on the crime scene and safely transport them to the laboratory. The inverse is true for high temperatures, as decrease rates for volatile GSR compounds were shown to significantly accelerate at 40 °C compared to 25 °C [67]. No systematic study on the effect of the temperature on other time-dependent phenomena has been performed so far. Nonetheless, it seems strongly probable that similar effects would also be observable, at least, for the chemical transformations occurring in GSR after the discharge. This is supported by several works in the field of smokeless powder stability, which showed an increase in the nitration kinetics of diphenylamine at high temperature conditions [75,76].

Analogous to high temperatures, windy conditions also proved to enhance decrease rates of volatile GSR compounds, due to an acceleration of the diffusion process, at least in firearm barrels [7]. In a recent study, the effect of relative humidity was tested in handgun casings, which showed its significant effect on the decrease rates of some volatile GSR compounds [67]. Nonetheless, a non-linear trend was noticed, with the quickest decrease rates observed at 75 % relative humidity, in comparison to 60 and 90 %. In this regard, it is strongly probable that high relative humidity levels would accelerate metal corrosion and rust formation too, as these phenomena proved to be particularly rapid in outdoor locations, in comparison to indoor environments [40]. No systematic studies, however, have currently been published on this topic.

Although questioned items are usually discovered in non-confined and open environments in typical casework situations, it is not rare to find them in other media (e.g., water). As a consequence, some investigations have been reported addressing the effects of the nature and composition of different surrounding media on ageing kinetics. These have been proven to be very influential. Indeed, those media that promote the access of the specimens to corroding agents, such as chloride, were shown to lead to quick oxidation processes [39]. Metal corrosion and rust formation are thus generally quicker in water and biological media, such as dog carcasses, compared with open environments [41], or in seawater compared with freshwater [39,40], due to different concentrations of corroding agents. Specimen confinement can similarly affect ageing kinetics. Indeed, it has been reported that no dust deposition is generally observable on firearms stored in holsters [38]. Also, physically stopping the muzzle or cartridge opening with a cork or aluminium foil was proven to significantly slow down the diffusion rates of most volatile GSR compounds [7,50]. The latter strategy was actually suggested as an easier alternative to the use of low temperatures to freeze the age of the specimens at the arrival on the crime scene and safely transport them to the laboratory [7].

9. Discussion: implementation of dating approaches in casework

Implementation of dating methods in casework practice is a complex procedure which requires the consideration of many different aspects, from the initial crime scene investigation to the interpretation of evidence. Indeed, such methods should ideally be integrated within already existing forensic and investigation

procedures, with a low impact on routine protocols. All these aspects subject the acquisition of questioned and reference materials to practical constraints. Hence, application of best practices at the crime scene is essential to guarantee useful exploitation of the collected items. General guidelines can be extrapolated from published literature, in order to minimise problems in the sampling of both the questioned and reference materials, as well as in the sequencing of time-since-discharge estimation techniques with traditional forensic firearms examination. A general discussion is suggested in the next sections and a formal approach to address dating problems in shooting incidents is presented (Fig. 8).

9.1. Selection of ageing parameters

Several time-dependent phenomena have been identified in firearm-related elements, which can be studied using different examination and analytical approaches. As a consequence, a number of strategies are nowadays potentially available to tackle dating problems in shooting incidents. Despite this, every specific time-dependent phenomenon is characterised by its ageing kinetics, which makes it helpful according to the case situation. The choice of the most adequate (set of) examinations is, therefore, a step of considerable importance in the approach of a new case. From a general point of view, time-dependent phenomena can be ordered as follows (from the most to the least rapid): diffusion of light gases (minutes/hours) > diffusion of explosion by-products (days) > formation of rust \approx deposition of dust (weeks/months) > degradation of smokeless powder compounds (years).

While a few alternative applications have been reported in the literature (e.g., [49]), the main interest for the criminal justice system at both the investigative and evaluative stages is, usually, to recognise if the collected firearm-related items have been fired in the last few hours or days. Shooting incidents, indeed, are difficult to escape notice, as for the noise generated during a gunshot and/or its direct consequences on targets and people (in particular, serious wounds). This generally leads law enforcement authorities to be quickly informed of the event and, thus, enables rapid collection of evidence from the crime scene. Alternatively said, time-since-discharge estimation is more likely to be required in order to provide information on short temporal ranges. Applications to long temporal ranges, such as months or years, would be rare.

As for their compatible diffusion kinetics and ageing rates, the quantification of the residual amounts of explosion by-products (or, eventually, light gases) is surely a preferential approach for the estimation of short temporal ranges and, thus, also potentially helpful in real cases. Related methods should particularly be considered for integration in operational protocols, at least for investigation of the most serious crimes. Research in this specific field has been numerous and instrumental techniques based on the coupling of sorptive extraction methods (e.g., SPME and HSSE) with GC were shown to be the most promising, as for their lower extraction selectivity compared to colourimetric tests. Visual investigation of rust formation or dust/dirt deposition may be considered as complementary approaches, as they are easy to implement and only require largely available instruments (a low-power microscope is enough). Their usefulness, however, may be more limited, as for the slower ageing kinetics and the need for specific triggering conditions (i.e., humidity for rust and an open environment for dust).

9.2. Analytical methods and related constraints

While instrumental techniques for the analysis of volatile GSR (and especially, explosion by-products) seems to be the most promising up until now, every technique is different and has

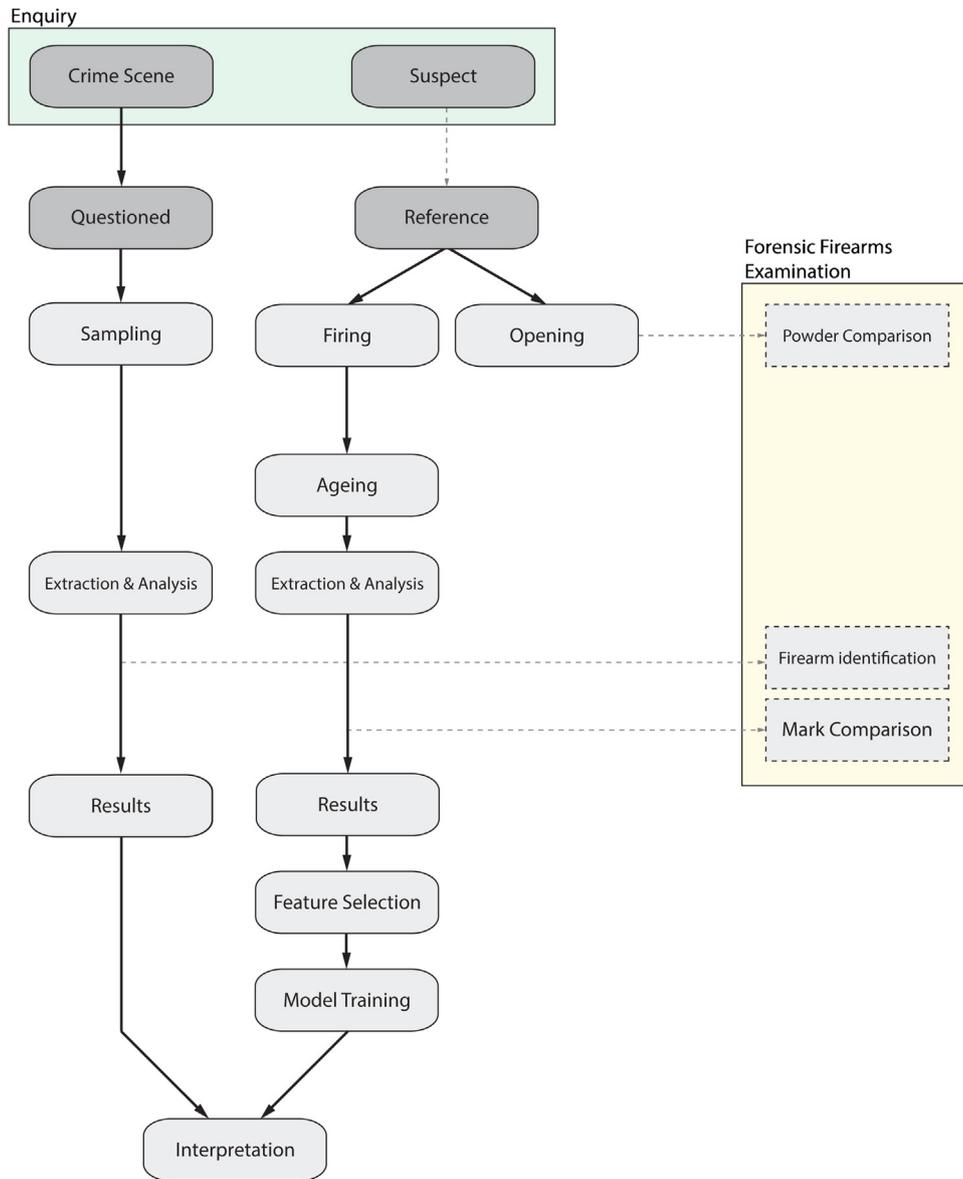


Fig. 8. Schema of the methodology suggested to approach time-since-discharge problems in real casework. Questioned firearm-related items (firearms, casings or bullets) are usually sampled on the crime scene using an appropriate strategy to avoid any alteration to fragile traces (e.g., GSR, dust or rust) and freeze their state. They are then sent to the laboratory. Here, chemical analyses need to be performed first, before transferring the sampled items to the forensic ballistic team for physical examination, as any subsequent handling may be destructive for chemical traces. Findings can then be interpreted using appropriate tools, such as ageing curves or statistical models. The latter have to be pertinent to the case, i.e. to be built or trained on case-related material. To reach this aim, the best strategy is to search the suspect for similar ammunition and/or firearm as those supposedly used to commit the crime. Using them, shooting tests can then be performed and specimens stored at the most similar conditions as those supposedly experienced by the questioned items before sampling. The reference specimens are analysed at different times since discharge, using the same methodology as for questioned items. Finally, results are pre-treated and filtered, in order to be used for curve or model training.

Table 6

Qualitative evaluation of the pros and cons of the main analytical techniques suggest to monitor ageing parameters in firearms and related elements. The symbols “+” and “-” indicate if the related characteristics is a strong or weak point of the approach, respectively. The following abbreviations were additionally used. LE: liquid extraction, CT: colorimetric tests, TLC: thin layer chromatography, SPME: solid-phase micro-extraction, HSSE: headspace sorptive extraction, cfSPME: cold-fibre solid-phase micro-extraction, ITEX: in-tube extraction by dynamic headspace, GC: gas chromatography.

Characteristics	Visual examination	LE-CT	LE-TLC	SPME-GC	HSSE-GC	cfSPME-GC or ITEX-GC
Sensitivity	-	-	-	-	+	+
Reproducibility	-	-	-	-	+	+
Selectivity	-	+	+	-	+	+
Invasivity	+	-	-	+	-	+
Simplicity	+	-	-	+	-	+
Availability	+	+	+	+	+	-

distinctive advantages and disadvantages, which should be known in order to allow a fruitful application to real cases. Particularly, analytical characteristics such as sensitivity, reproducibility and selectivity are critical characteristics to consider and assess. In addition to these, invasivity (of the selected extraction method), simplicity (in term of time and number of analytical steps) and availability (of the devices and instruments necessary to implement the method) are also important factors (Table 6).

Given its high extraction capacity, HSSE showed several advantages over non-exhaustive sorptive methods, such as SPME. Indeed, it allows for better sensitivity and reproducibility, as well as a lower selectivity which leads to the extraction of a broader range of compounds [64]. Because of this, HSSE has been an essential instrument in recent literature to comprehensively investigate GSR composition and ageing processes [37,67]. Nonetheless, it is an invasive and relatively complex technique. Principally, it does not allow analysis of an enclosed specimen without re-opening its transport vessel, an obvious drawback in forensic practice; also, it is not a method easily implementable for the estimation of time since last discharge in firearms. In this regards, SPME is a better alternative thanks to its needle-based design, but it is analytically less performant. Alternatives which combine the advantages of both techniques would be cold-fibre SPME (cfSPME) [77] or, eventually, in-tube extraction by dynamic headspace (ITEX) [78]. Both techniques offer better extraction efficiency than traditional SPME together with lower invasiveness than HSSE, thanks to their similar needle-based designs. While promising, cfSPME and ITEX applications are presently limited to very specific fields and related devices are difficult to obtain by common manufacturers. They could represent interesting solutions for future investigations.

The literature clearly showed the added benefits of multi-variate data analysis on the accuracy of the conclusions, i.e. of the simultaneous consideration of more than one ageing parameter at time [67]. In this regard, sorptive extraction techniques are advantageous over other approaches such as colourimetric tests as a broad range of compounds can be simultaneously detected and semi-quantified (i.e., they are lowly selective). This, indeed, allows an easier implementation of multi-residue methods, which can directly be used in a multi-variate data analysis framework. In general, exhaustive extraction techniques as those mentioned above are preferable, as for the larger number of co-extracted analytes. The different time-dependent phenomena are, in any case, not mutually exclusive between them and can happen simultaneously. An application in sequence of different approaches to studying different ageing parameters may thus also be convenient, in order to increase the accuracy on the inferred conclusions and/or to cross-validate them. This has been proved in early dating approaches (e.g., [20,21]), but it has not been investigated using more recent analytical approaches.

9.3. Sampling of questioned material

The sampling of questioned material on the crime scene is, probably, the most sensitive step in the examination procedure and should be carefully carried out. Usually, questioned firearm-related items (e.g., spent casing and bullets) are put in soft paper bags in order to preserve and transport them. While this type of packaging guarantees protection against alteration of physical marks, it is not fully satisfactory for dating purposes as it does not completely halt all ageing processes. This is especially true for the diffusion of light gases and explosion by-products, which are potentially the most helpful time-dependent phenomena for forensic dating purposes.

In cases where diffusive compounds must be analysed, freezing the state of the questioned specimens at the conditions they were

found on the crime scene is crucial, given that related ageing parameters could change very quickly, especially in the first hours after discharge. Transport in non-airtight conditions is likely to uncontrollably affect the ageing kinetics. In the specific case of spent casings, collecting them in closable glass vials should be systematically carried out if dating is expected. Caps with septa are strongly suggested if needle-like extraction techniques (e.g., SPME, cfSPME and ITEX) might be adopted, in order to enable analysis without re-opening the vials. For invasive extraction techniques (e.g., HSSE), an extraction device should be directly placed inside the vial before closing or more sophisticated capping methods should be developed for adequate subsequent extraction in laboratory. Regarding firearms, lowering their temperature and stopping the muzzle with a cork might be necessary, even if the literature is ambiguous about these topics.

As ageing kinetics is affected by many influential factors, the states of both the questioned items and crime scene must be well documented at the arrival, especially the item position and environmental conditions. Important details to register are whatever the questioned items lay horizontally or vertically, their specific orientation and relative location on the crime scene. Temperature, relative humidity and wind conditions (airflow) at the location of the questioned items are also fundamental parameters and should imperatively be measured and/or assessed (for example, using a thermometer). If these parameters might have changed previous to sampling (e.g., day/night cycles), conditions existing before the arrival on the crime scene should be reconstructed. In this regard, useful data could be obtained from meteorological records and/or direct *in-situ* measurements over several days after crime scene investigation. A similar methodology to collect this information as that used in forensic entomology could be used [79].

At the arrival to the laboratory, the chemical analysis should have the priority over the examination of physical marks because, once the vials are opened, concentrations of volatile compounds are modified and no useful analysis could be carried out anymore. Headspace extraction techniques are unlikely to alter physical marks. At the end of this procedure, question items can be transferred to the forensic firearm-marks examination section.

9.4. Reference material and analytical protocol

Basically, all published works recognised that the interpretation of the analytical findings obtained on questioned specimens is a comparative procedure, in which they are weighed against reference materials. Indeed, several factors influencing ageing profiles have been identified, which make them strongly case-related (Section 8). In addition to storage conditions, in particular, ageing profiles were proved to be strongly dependent on the ammunition type (brand and calibre), as for the probable differences in composition between the constituting elements. Other likely influential factors are the firearm (because of differences in working pressures and temperatures) and the ammunition production batch (because of the fact that smokeless powder formulations can change between batches).

In order to reach the most reliable conclusions, therefore, materials used to build reference models should be the most similar to those used during the alleged offence. In the case that a suspect has been apprehended, his personal belongings have to be searched for firearms and ammunition boxes, as they constitute the best reference material. Otherwise, the reference firearm and ammunition should be selected based on the physical and chemical characteristics of the question items. Independently from the situation, questioned and reference materials have to share comparable characteristics at both physical and chemical levels. Using case-unrelated reference materials and/or

interpretation models does not seem to be a reliable strategy, especially considering the multitude of factors that could have a significant impact on the ageing profiles. A case-by-case approach is strongly advised.

Providing evidence that supports the hypothesis that the seized firearm has been used to fire the questioned specimen(s) is a fundamental step in the investigation of firearm-related crimes. Thus, mark comparison between reference and questioned material is particularly important and reference cartridges should be collected to perform shooting tests. Besides, it is strongly suggested that at least one supplementary reference cartridge is opened and analysed in order to establish the smokeless powder composition (Fig. 8). The remaining reference cartridges can be used for the purpose of dating. In this regard, groups of cartridges should be aged over different times after discharge depending on the investigated timeframes (e.g., $t=0$ h; $t=1$ h; $t=5$ h; $t=9$ h; $t=24$ h, $t=48$ h).

As the variability of data is expected to be relatively high, genuine replica are very important and should be carried out. Independently from the type of case, it is essential that reference cartridges are submitted to the same manipulations and ageing conditions like those expected to have been experienced by the questioned specimens. A climatic chamber (as that used in [67]) can be used to simulate specific storage conditions (e.g., temperature, relative humidity, airflow, light, position). Furthermore, it is also suggested to schedule the analysis of all reference samples in the same analytical run. This suggested approach is more reliable than using "generic" reference curves. If reference curves using similar material (firearm/ammunition) exist, error rates must be tested, for example using blind tests, in order to evaluate their reliability.

9.5. Interpretation from a forensic perspective

Providing temporal information on the time since discharge can be helpful in a number of different situations, at both investigative and evaluative stages. However, depending on the final aim of the provided information (investigative vs. evaluative statements, respectively), distinct ways of interpreting analytical findings and providing conclusions are also needed and should be implemented in casework.

If no suspect is arrested or he does not release any declaration ("missing-man" and "no-comment" situations, respectively, as described by Jackson *et al.* [80]), the enquiry should be considered in its investigative stage. In this regard, the chemical analysis of specimens should allow a chronological placement of the discharge event in time, in order to reconstruct the course of the events or to identify those specimens that are more likely to have been fired during the alleged offence. Interpretation approaches that allow for a direct estimation of the time since discharge and, thus, provide the best explanation for the analytical findings, are surely the most appropriate at this stage. These include univariate models either based on the graphical superposition of ageing profiles as those suggested by Voskertchian & Pavilova [47,48] and Andrasko *et al.* [34], or based on regression analysis.

The consideration of only one ageing parameter at time, nonetheless, could be insufficient and/or particularly prone to estimation errors. Simultaneously considering multiple ageing parameters increases the reliability of the obtained time-since-discharge estimates and, thus, the adoption of a multi-variate model is preferable [66]. The use of random forest and partial least squares, for example, have previously been shown to be a more accurate alternative than traditional univariate approaches [60,66]. The implementation of classification methods in place of regression ones also seems promising and could be addressed in future works.

When a suspect is apprehended and provides an alternative hypothesis on the course of the events in addition to the one proposed by the prosecutor, the enquiry can move to its evaluate stage. Typically, the suspect might admit that the collected specimens were fired by the seized firearm and ammunition, but contest the time since discharge. From an interpretative point of view, these situations are different compared to those discussed above and, thus, they need the application of different interpretation strategies. Here, the examination should allow the assessment of the evidential value of the analytical findings under the different available hypotheses of the facts. Logical approaches based on the assignment of LR are promising to approach this type of situation [70,72]. In this regard, however, the use of multi-variate distributions seems to be necessary to account for correlations between compounds and, ultimately, provide more accurate evidential values. Models based on the multiplication of LR assigned on the single ageing parameters should be used with caution, as they are based on the assumption that parameter changes are independent on each other. This premise is not realised in this context and, thus, is prone to lead to over-estimations of the actual eventual values [71].

9.6. Data treatment and modelling

The development of relevant and reliable models to interpret data is an essential step for the development of a dating method and does not need to be under-estimated. Independently from the situation and/or the chosen modelling approaches, it is important to select ageing parameters that are (the most) informative for optimal results. A feature selection step before model training is thus strongly suggested (Fig. 8). In addition, as reproducibility of most quantitative ageing parameters was often found to be sub-optimal, the application of data normalisation approaches is also suggested in order to decrease sampling and analytical errors. In this regard, internal standards can be used [66], at least for chromatography-based techniques. Pairwise log-ratios normalisation (for example, between peak areas of different co-extracted analytes) was also found to be particularly useful in recent literature and can be used in conjunction or instead of internal-standard normalisation [67].

Model training needs to minimise overfitting, in order to maximise estimation performances. This is especially true for multi-variate models and it is usually reached through a correct and informed optimisation of their internal tuning parameters, such as the number of components for partial least squares regression or the number of hidden nodes for artificial neural networks. The best strategy for this purpose is statistical resampling. In particular, as for the very limited number of reference analysis usually available, bootstrap has been found to be a reliable approach. Finally, model performances should be determined before implementation, in order to validate the approach and determine its accuracy on newly submitted data. Both blind tests or leave-one-out cross-validation could be used here [67].

10. Conclusion

Time since discharge would be an important piece of information in the investigation of shooting incidents. As highlighted in this review, a number of approaches have been previously reported in the literature for this purpose, ranging from simple methods based on visual examination of the firearm-related elements of interest to more complex methods based on the analysis of gunshot residue (GSR) compounds by wet chemistry and/or instrumental techniques. In particular, the study of the diffusion of explosion by-products in volatile GSR using

sorptive extraction techniques coupled to gas chromatography – mass spectrometry (GC/MS) has been identified as one of the most promising approaches, mainly due to its compatibility with the temporal ranges usually investigated in shooting incidents. Other advantages include the capability to perform quantitative measurements of multiple analytes at the same time that can be used as semi-dependent ageing parameters. Statistical models have been suggested for the interpretation of findings and to correctly take into account all the sources of random variation linked to the samples and analyses.

While helpful information was repeatedly proved to be extractable from most firearm-related elements, the main challenge identified in the literature to efficiently reach this purpose in real casework lies in the numerous influential factors. Expected ageing profiles, indeed, were found to be strongly dependent on intrinsic and extrinsic characteristics, such as the ammunition/firearm used, their inner geometry and environmental conditions. All these characteristics have to be estimated in the specific case investigated, in order to properly be taken into account in data interpretation and provide accurate conclusions (e.g. time-since-discharge estimates or likelihood ratios). Based on the reported data, a case-by-case approach is suggested as the most reliable option to situate a discharge in time. This can be implemented by using relevant reference materials for ageing tests and model training, as well as by applying the same storage conditions during the ageing tests as those expected to be experienced by the studied firearm-related elements before sampling.

Further research should focus on the implementation of the proposed approaches in practice. This might require adapting less invasive extraction techniques, potentially for the use on-site by untrained personnel, as well as carrying out more in-depth studies about the effects of influential factors on data interpretation. A broader use of multi-residue and multi-variate methodologies is also strongly suggested for future works. In particular, statistical approaches based on multi-variate data analysis should be further investigated, as they proved to efficiently increase the accuracy of the extracted conclusions.

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