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Case report

USE OF SODIUM RHODIZONATE IN FIREARM USE CASES: CAN IT BE USEFUL IN IDENTIFYING THE SHOOTER?

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ABSTRACT

The sodium rhodizonate test is a simple colorimetric technique used to identify traces of lead and barium. A positive test provides rapid and photographically documentable results for shots fired at distances not exceeding 50 cm. Usually, this method is not used for identification of the firing hand, which is detected by electron microscopy with energy dispersive analysis (SEM-EDX), requiring the removal of any particles on the surface to be analyzed by STUB. The use of Sodium Rhodizonate, which is undoubtedly less selective, has the disadvantage of target element solubilization (lead and barium) and thus the loss of the preliminary morphological investigation of the particles. The purpose of this paper is to demonstrate that the two indicated methods can be considered complementary in the following order: 1. buffer sampling for electron microscopy investigation (STUB); 2. and subsequent performance of the Sodium Rhodizonate Test. In some special cases, when it is necessary to obtain the result more quickly, with regards to respecting the chronology of the aforementioned tests, it may be useful to carry out the Sodium Rhodizonate Test first, especially when particular and perhaps antiquated weapons were used for suicidal purposes causing considerable gas dispersion and shot residues from the mechanisms. This research illustrates how significant results were obtained substantiating the suicide hypothesis, following the use of an old revolver (year of manufacture around 1915-1920).

1. Introduction

It is well known and well described in the Scientific Literature that during the explosion of a firearm, not only the bullet, but also the combustion products of the gunpowder, such as the primer, as well as minute metal fragments produced by the friction of the bullet with the barrel, escape from the barrel of the firearm: the residues of the shot are commonly called Gun Shot Residues (GSR) [1]; these are mainly composed of three elements: lead (Pb), barium (Ba) and antimony (Sb) combined and in varying proportions [2]. Once fired from the weapon, trace amounts of these GSRs are distributed in the surrounding environment by depositing on nearby surfaces, the shooter's hands, and objects near the shooter, while another amount of these particles are entrained by the projectile and, when the distance to the target is not excessive, are deposited on the impact surface.

An important factor, which should not be overlooked, concerns the difference in the distribution of GSRs that varies depending on the weapon used: if automatic and semiautomatic pistols are used, GSRs are ejected immediately after firing and concomitantly with case ejection from the breech face of the weapon. If, on the other hand, drum guns are used, GSRs may also be ejected from the space between the drum and the barrel [3-7].

When deflagration occurs inside the chamber of a weapon, three phases occur in a very short time:

1. Pirostatic phase, characterized by combustion of the launch powder at constant volume being the projectile stationary. In this phase the temperature reaches 2,000°C and the pressure 1,400 PSI (pound square inch=pound x square inch).
2. Pirodynamic phase, characterized by simultaneous combustion at constant volume and varying pressures. Temperature and pressure reach maximum levels: about 3,600°C and about 40,000 PSI.
3. Expansion phase, characterized by the expansion of the gas and the motion of the projectile. The next three phases occur almost simultaneously with the detonation of the ignition.

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As mentioned earlier, metallic elements such as lead, antimony and barium (GSR), which are part of the chemical composition of the ignition powders during firing, as well as other metallic elements that are part of the chemical composition of the launching powder. Subsequently, the projectile and the cartridge case, due to the high thermal and mechanical energy and high pressure to which they are subjected, undergo a process of fusion and subsequent vaporization, thus sometimes assuming the form of molten droplets (aerosol) that cool immediately and taking-on a characteristic spheroidal appearance, analogous to the phenomenon of volcanic lapilli, hence, they have been called “Fireballs”.

It is evident that the area of the hand holding the firing weapon is inevitably contaminated by the aforementioned gunshot residues, which appear denser in the area of the hand closest to the firearm.

It is no coincidence that certain areas of the hand, called elective zones, were chosen by researchers, namely: the dorsal surface of the index finger, the thumb, and the interdigital fold that extends between the lateral and medial surfaces of the thumb [8].

If the gunshot residues are observed in areas that are not compatible with so-called elective areas, or if their distribution is not compatible with what it should be following the projection of gunshot residues from the weapon that fired the shot, it could be ruled out that the individual suspect fired the gun and that any traces detected are attributable to a case of a self-inflicted shot [9].

Indeed, it is not always the case that a "positive" draw means that the individual has fired a gunshot, nor does a "negative" draw necessarily prove, on the contrary, that the individual is unrelated to a gunshot.

One must first consider the place where the event took place: the behavior of GSRs escaping from the weapon and diffusing into the surrounding environment, deposit on nearby surfaces differently depending on whether the firing took place outdoors or indoors. Studies have shown that during firing in an enclosed environment, significant amounts of GSRs are deposited not only on the hands of the person holding the weapon, but also on those of other people present, even at a relatively large distance [10]-[12]. A gunshot in an enclosed environment, especially if it is cramped, can therefore result in positivity of samples taken on people who, although without firing gunshots, were present at the event, as well as on the victim himself [13].

Therefore, the search for residues is influenced by the purpose of the investigation: generally, judges ask the medical examiner questions regarding whether a suspect used weapons or explosives, to ascertain the firing distance, whether or not a particular injury is produced by ballistic agent and to identify the type of cartridge used.

Indeed, the differential diagnosis between suicide event and simulated suicide homicide is not always easy for the forensic scientist who is not skilled in forensic ballistics. Confounding elements, such as atypicality of entry and exit wounds, type of weapon, and conditions under which the victim was found, can confuse counselors.

Often, alterations to the crime scene can also be maliciously made by the murderer, precisely to confuse investigators.

The investigations currently carried out to solve the first two problems are mainly aimed at identifying the residues of the priming mixtures or the launch powders, since high amounts of metal salts are present in the former and very stable organic residues in the latter.

On the other hand, to ascertain the type of cartridge used, or to determine whether damage to a substrate is from a ballistic agent, the investigation is directed toward looking for metal fragments that may have detached from the cartridge case, projectile, or originated from barrel delamination particles projected on the contour of the entrance holes or along the obstructions.

Analytical investigations of these metal traces can provide advantageous indications [14].

First of all, it is important to point out that several studies have shown that there is a different behavior, following firing, of the smoky compared to the corpusculated residues: the former arrange themselves-immediately after firing, forming a cone with the apex facing the muzzle of the weapon and apex in the direction of the target; the corpusculated particles, on the contrary, once they come out of the muzzle of the weapon immediately after the projectile, follow its trail for about 1.5 meters, projecting forward.

In automatic and semiautomatic weapons, in the final stage of slide retraction and immediately after case ejection, powder particles at various stages of combustion are projected from the breech of the barrel in various directions depending on the type of weapon. In those with an uncovered slide (e.g., Beretta mod. 70), the granules are directed back toward the arm and body of the shooter, as well as laterally; while in weapons with a covered slide, (Walter PPK type), which have a side ejection window, the residue is projected mostly upward and laterally.

After briefly illustrating the arrangement of GSRs immediately after firing, it is easy to understand how, through different methods of detection (colorimetric tests; chromatography; gas chromatography; atomic absorption spectrophotometry, photoluminescence, SEM-EDX association, neutron activation analysis; etc.), it is possible to search for the presence of GSRs. Each of these search methods is chosen from time to time according to the specific needs and requirements of the case [15], [16].

Today, the most widely method is SEM-EDX, which has the main advantage of simultaneously carrying out accurate morphological surveys and qualitative-quantitative investigations on traces; this has made its use for the search and identification of micro-traces of a ballistic nature highly significant [17].

Sampling from skin surfaces is done with a swab covered with adhesive tape, which is used in the "stub" of the electron microscope employed later for direct observation.

The main advantages of this method are speed and ease of execution, as well as the very low risk of contamination and the great merit of being nondestructive.

The drawbacks of surveying are the absence of trace topography and the long analysis time required [18].

There are also colorimetric methods based on the use of different detector chromatic solutions, which are generally easy to perform, but have the disadvantage of being nonspecific. However, for the most part they are nondestructive and therefore allow the continuation of the investigation with other techniques.

The chromogenic (i.e., color-producing) methods are based on analysis of the shape and size (the morphology) of the halo of residue deposited by firing. They represent an amplified level of visual examination. The chemical reactions chromatically enhance (with color) specific elements or compounds present on the area under examination [19]. The targeted application of reagents makes the presence of otherwise invisible traces, visible to the naked eye and to understand what elements are involved. The use of these methods is not complicated and, if performed according to established protocols, can provide much important information without resorting to more expensive instrumental examinations [19].

The purpose of this manuscript is not to claim that one method can replace another, but to show that there are cases that may benefit from one method rather than another.

Indeed, sometimes there are special urgent reasons that may make it necessary to perform tests for "orientation" purposes, such as conservative colorimetric tests, which, however, influence the type of subsequent analysis because the sample would be previously treated with acid solutions [20].

Identification of gunshot residues should be carried out directly on the suspect substrate to preserve the original topographic arrangement of any particles present, while avoiding possible contamination. The Sodium Rhodizonate Test is useful in such cases because allows for an extemporaneous, simple and rapid analysis.

In conclusion, while the investigation performed with the SEM-EDX should be credited with the undoubted merit of allowing both morphological and microanalytical examination, the other methods that are still valid (and in some respects perhaps even more reliable) for solving numerous forensic ballistics problems that cannot be overlooked.

2. Material and Methods

The Sodium Rhodizonate Test is a colorimetric reaction, which recognizes the presence of gunshot residue. Specifically, a colorimetric change occurs if lead and/or barium is detected [21]. It represents a preliminary and qualitative investigation and, moreover, is carried out through an easily transportable "kit." It is a "topographic" test, in the sense that it is positive only at the anatomical area where any lead and/or barium residues are present, showing very precisely where such residues were deposited after firing [22].
The test is performed directly on the target to be analyzed by spraying the following reagents in succession:

1) Solution A: 0.2% hydrochloric acid.
2) Solution B: 5% sodium rhodizonate, possibly decanting the non-solubilized reagent particles (the reagent should be prepared shortly before use).
3) Solution C: 5% hydrochloric acid.

The target should be photographed as soon as possible because of the color instability of the complex "metal-rhodizonate" salts.
The first solution is intended to solubilize the metals on the target in the form of chlorides and to create the optimum pH for the first stage of the reaction. Upon application of Reagent B, most of the metals turn orange red (excluding tin) against a light orange background due to the excess of the reagent (Table I). Reagent C enables the color change of the formed "metal-rhodizonate" complex salts, and thus the sharp detection of lead and barium, which are colored blue-violet and bright red, respectively. The results of the color reactions of metals with the rhodizonate reagent are shown in Table 1. The use of dilute nitric acid, recommended by other Authors, is equally satisfactory, but prevents the eventual assay of nitrate ions (which we performed with a selective electrode pH-meter) useful to better define the nature of the gunshot residue. The use of acetic acid (as a metal solubilizer) and ethyl alcohol (to dissolve the reagent) is also less suitable because they somewhat depress the lead-rhodizonate color reaction [5].

IONI	SODIUM RHODIZONATE	
	+ HCl 0,2%	+ HCl 5%
Pb^{++}	Red	Blue violet
Ba^{++}	Bright red	Bright red
Cu^{++}	Pale orange	Lightens
Fe^{++}	Red brown	Lightens
Hg^{+}	Orange red	Lightens
Hg^{++}	Red brown	Lightens
Ag^{+}	Violet	Lightens
Sn^{++}	Violet	Lightens
NO_2^{-}	Pale orange	Lightens
S^{--}	Black	Lightens
SO_3^{--}	Orange	Lightens
$S_2O_3^{--}$	Red	Lightens

Table 1. Results of color reactions of metals with rhodizonate reagent

The possibility of formation of two main colors (red and blue violet) depending on pH also facilitates observation on colored substrates as well, for which the transfer of the color reaction, immediately after spraying solution C onto Whatman No. 41 paper, is always possible anyway. Finally, the presence of blood stains on the analyzed objects (clothing, body parts), as is often the case in daily practice, staining brick red with the addition of 5 percent hydrochloric acid, does not prevent the perception of the blue-violet coloration of lead-rhodizonate.
Specifically, the great advantages of this method are: speed of execution; representation of the exact arrangement of residues topographic method; easily transportable.
In addition, the possibility of photographing, and thus making the test results immediately visible, offers the enormous advantage of being able to illustrate, even at trial, and thus in courtrooms, the actual presence of GSR at the investigated site. This makes the obtained results more "impactful", allowing even those who are not technicians to fully understand the findings of the investigations carried out.

3. Case presentation

A 72-year-old man was found dead on an armchair in the living room of his home with a revolver in his right hand.
The body was positioned with the head bent over the chest, tilted to the right, the right arm adducted over the chest. A 7.65-cal revolver was held in the right hand, and a towel with blood spillage was placed on the chest. The left arm was adducted along the ipsilateral side, and a brown leather holster was lying on the left hand. The legs were spread and crossed along the footrest.

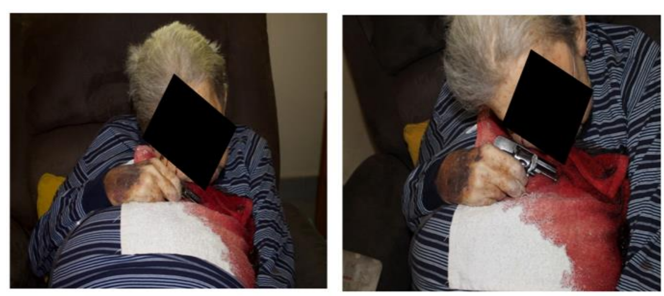

Figure 1. Location where the revolver was found.

The weapon was identified as a Belgian-made revolver, dating from before the year 1920, inner hammer, folding trigger, with 5-chamber drum and right-handed direction of rotation.

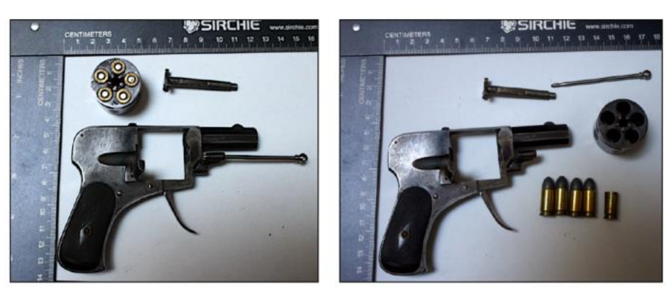

Figure 2. Weapon found during the inspection.

Upon opening the drum, one 7.65-caliber exploded shell casing lined with the barrel was found, while the other 4 chambers were loaded with 7.65-caliber cartridges, semi-rimmed and branded G.F.L. (Giulio Fiocchi Lecco).

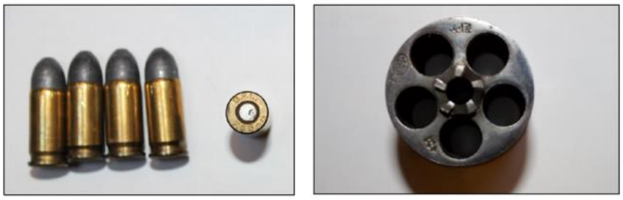

Figure 3. On the left, the observed cartridges found in the drum of the revolver, and on the right, the drum of the weapon.

The weapon wielded by the victim was identified as a 7.65-caliber revolver containing four intact cartridges and one exploded shell, all G.F.L. (Giulio Fiocchi Lecco) brand 7.65-caliber, semi-rimmed. Upon external examination, at the right temporal region, there was a continuous skin lesion, irregularly shaped, with introflexed and frayed margins, with exposure of the underlying soft tissues of blackish color, measuring about 2.6 x 1.8 cm, with a major oblique axis, directed from top to bottom and antero-posteriorly. The lesion also appeared to be surrounded by ecchymotic excoriated rim, reddish-brown in color, more represented at the posterior-inferior pole, indicating the typical features of an entrance hole.

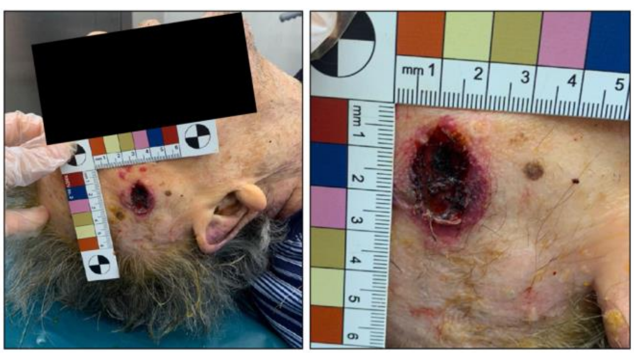

Figure 4. Entry hole in right temporal region.

Having found no lesion referable to an exit wound, and given the weak impact of the caliber used, the bullet was lodged inside the victim's skull, more precisely at the left temporal region, where, during external examination, it was possible to observe a slight deformation of the anatomical profile.

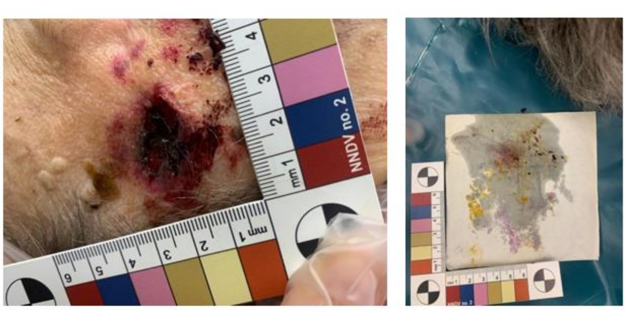

Figure 5. Right shows the positivity of the Sodium Rhodizonate Test performed on the entrance wound of the right temporal region (left photo).

4. Discussion

The Sodium Rhodizonate Test performed on the skin margins of the entry wound (right temporal region) was positive, confirming a shot fired in close contact.

With regards to the firing distance, it should be noted that the data by which this factor is determined (although with some approximation) are represented by the characteristics of the weapon used (length of the barrel, condition of the barrel, etc.) and the observation for any residue of the firing cycle on the skin bordering the entrance wounds, or if any clothing is present.

In our case, inspection and chemical examination using the sodium rhodizonate method was performed on the contour of the entrance wound in the right temporal region, revealing the presence of residues from the firing. In this regard, we recall that in shots at short distances and in any case within 40-50 cm, residues resulting from the combustion of the firing charge are deposited on the contour of the entrance wounds in the form of smoke or tattooing, depending on whether it is the action of smoke or unburned powder granules. Nevertheless, according to the data available in our case study (shape of the entrance hole and deposits of gunshot residue), it can be said that the shot was fired in close contact.

The circumstantial data strongly indicated the hypothesis of a suicide and the judge demanded a rapid and sure response. The location of the entry wound (right temporal region), the direction of the medium (bottom-up, latero-medially, and antero-posteriorly), and the distance of firing (close contact shot), as well as the number of shots fired (only one) are typical elements of death by suicide [22]. In fact, it should be considered that the attuned site (right temporal region) was self-inflicted and is among those typically chosen for suicidal purposes [23], as it is placed at the level of vital primary organic structures (encephalon). In fact, the suicidal person prefers regions that guarantee a safe and rapid death: lateral regions of the head and precordium predominantly with short-barreled weapons, submentorial region and oral cavity with shotguns.

In addition, the location of the entry wound, also given the type of weapon used, is compatible with a self-inflicted wound [24 - 25].

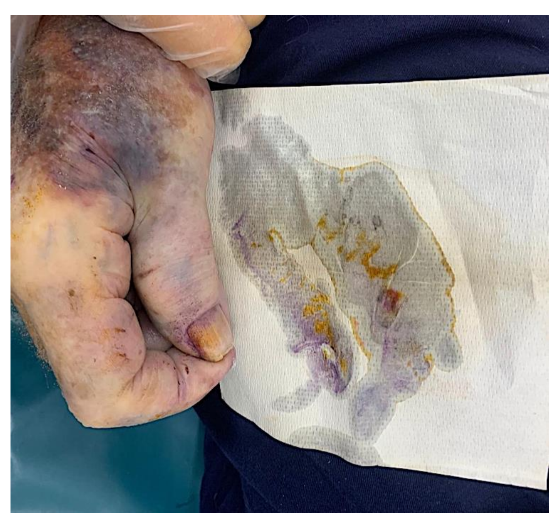

Figure 6. Positivity of the Sodium Rhodizonate Test performed on the suicide's right hand (hand with which he held the weapon).

Therefore, it can be confirmed that the elements at our disposal allowed the examined case to be easily framed among typical suicidal events [26]. To further confirm the suicide hypothesis, the Sodium Rhodizonate Test performed on the entry wound and the hand that held the weapon was positive.

In addition, the Rhodizonate Test was performed on both hands of the victim. The Test was positive for the right hand, specifically in all the areas of the hand placed in close proximity at the time of firing with the "vents" of the gunshot gas between the drum and the barrel: the dorsal-lateral surface of the 1st and 2nd rays of the right hand gave strongly positive results, as visible from Figure 7.

The left hand would have tested negative since the shot had not been fired from that hand.

As a result of what has been said, in this case report the GSRs should also have been ejected from the space between the drum and the barrel, given the fact that a drum weapon was used. Therefore, the anatomical areas that were most exposed and therefore most polluted by the residue of the firing, accounting for the grasping position of the weapon, were the dorsal region and second rays of the hand holding the weapon.

Therefore, using the Sodium Rhodizonate Test reaction, it was possible to state that this was a suicide and to exclude the homicidal hypothesis.

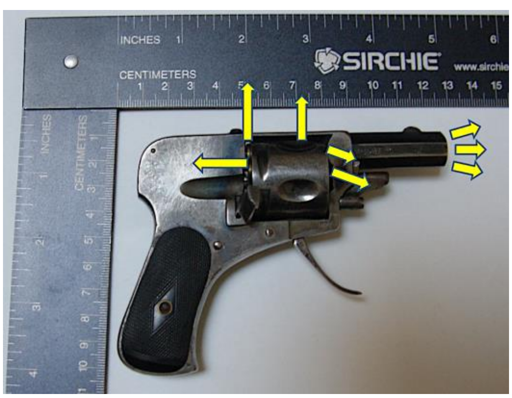

Figure 7. Parts of the weapon from which the gases of firing escape.

5. Conclusions

Often the medical examiner is called upon to answer questions by the Judges, as to whether a criminal act is homicidal in nature [27 - 31]. This is especially true, but not only, in cases where the death was caused by firearms. The case illustrated by the authors shows how when the weapon used is a revolver or an open-carriage pistol, positivity to the Sodium Rhodizonate Test on the dorsal region of the first two fingers and in the interdigital region of the hand holding the weapon can be a valuable aid in directing forensic pathologists toward a reconstruction of the event as suicidal in nature.

Moreover, one of the advantages of the morphological approach based on chromatic (also called chromogenic) reactions lies in the visual effect that the images have in court. An image that is immediately representative of the test performed, in fact, is easily appreciated even by those who are not experts in the subject, and it is the task of the Consultant and/or Expert, as a technician, to provide the Magistrate with useful tools that are easy to understand.

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