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A few remarks about the use of Griess reagent in firearm examinations

Summary

The purpose of this article is, inter alia, to determine whether it is possible to define the time that has elapsed since the last shot from a firearm, based on chemical tests of the post-firing residue remaining in the interior of the gun barrel after combustion of gunpowder and firing the primer mass, using Griess reagent. The article also presents the firearm examination findings related to the use of Griess reagent, including the risk of falsification of the results due to previous use of red fluorescent dye in dactyloscopic firearm examinations.

Key words: residue, post-firing residue, Griess reagent

Introduction

Tests of post-firing residue are carried out by experts in the field of firearms and ballistics as part of the so-called chemical ballistics, and include analyses of residue taken from the barrel interior, cartridge chamber and other surfaces of firearms. The collected residue is tested with the use of Griess reagent. This reagent is a solution of sulphanilic acid and α-naphthylamine in acetic acid. It is used in colorimetric analysis of nitrites, in the presence of which it forms the azo dye that stains the solution pink or – at higher concentrations of nitrites – red. The tests are carried out to determine the presence of nitrate ions (III) (nitrites) in the extracted residue; they are one of the components of the post-firing soot. A positive result of the test with the use of Griess reagent manifested by a reddish color of the residue aqueous extract or dry residue indicates that a shot was fired from the particular firearm. The result of the test does not allow to deduce the time of the last shot from the tested firearm. However, experts in the field of firearms and ballistics research are often asked, especially in the courtroom, to determine at least an approximate time of firing the last shot. In view of the above, an attempt was made to determine, on the basis of chemical tests with Griess reagent, the maximum time that has elapsed since the last shot and, in particular, to check whether with time – and if so, after what time – Griess reagent would not stain the residue taken from the gun barrel.

Research methodology

The research was carried out in the Department of Weapons Research and Ballistics of the Forensic Laboratory of the Voivodeship Police Headquarters in Wroclaw from October 23rd 2013 to January 3rd 2020. Two types of Griess reagents were used, i.e.: a POCH-TEST PIR-S Kit (in the first stage of research), which required making an aqueous extract of the residue and heating it to boiling point, and a single-component Chempur Griess reagent (in the second stage of research), which was applied directly to the residue on a swab. The incentive for the experiments were previous positive results of the analysis of residues taken from the barrel interiors of various evidence firearms. It was noticed that the collected residue reacted intensively upon contact with the applied reagent after: 1 month and 23 days (Skorpion ver. 61 machine gun cal. 7.65 mm made in Czechoslovakia), 2 months (Glock 30 pistol cal. .45 ACP made in Austria), 2 months and 12 days (P-64 pistol cal. 9 mm made in Poland), 2 months and 13 days (Bock CZ Mod. 4CPL rifle cal. 12 made in Czech Republic), 3 months and 7 days (Margo MCMK pistol cal. 5.6 mm made in Russia), 4 months and 23 days (IŻ-58MA shotgun cal. 12 made in USSR), 8 months and 14 days (Merkel SUHL shotgun cal. 12 made in GDR), counting from the day of firearm seizure (Table 1). In the periods of time given above, no shots were fired from any of the firearms, but there was neither knowledge of when the last shot was fired (prior to the seizure by the Police), nor what kind of ammunition was used (except in two cases of suicidal shots). Apart from these exceptions, the periods given determined the minimum time that has elapsed since the last shot was fired from the particular firearm. The tests involved shooting off one or more cartridges from the firearm units from the laboratory Reference Firearms Collection, followed by the analysis of the residue taken from the barrel interior using Griess reagent, at various time intervals. Each time before the

cartridge was shot, control test was carried out (the so-called blank control) by collecting the residue from the barrel interior with a clean swab. The blank sample taken was treated with a single-component Griess reagent, and the expected outcome was a negative result, i.e. no staining observed. The results are presented in Table 2. Out of ten tests involving seven short and long firearms of different systems, models and calibers, ten positive results were obtained with different degrees of staining of the tested residue, from dark red to hardly visible pink (Fig. 1–3). Fifteen cartridges were fired, including: eight rimfire cartridges cal. 5.6 mm (.22 Short, .22 Long Rifle), five pistol cartridges cal. 6.35 mm × 15.5 SR Browning and 2 pistol cartridges cal. 9 × 18 mm Makarov from different manufacturers and production periods. Positive results were obtained with Griess reagent after: 1 day, 7 days, 15 days, 17 days, 1 month, 2 months, 3 months and 6 years. The longest period (6 years) has passed since firing from Astra pistol (cal. 5.6 mm, made in Spain) five rimfire cartridges cal. 5.6 mm, including three .22 Short cartridges, made in Finland (Lapua), and two .22 Long Rifle cartridges made in Poland (Nitron Erg) and UK (Eley) on November 5, 2013 – until November 5, 2019 when the residue extracted with a swab from the barrel interior was examined using a single-component Griess reagent. As a result of the chemical reaction, the residue displayed pronounced staining (Fig. 4). During the testing period, the pistol under examination was located in a closed metal cabinet at room temperature and humidity. This period corresponded to the time frame of the experiment conducted. In another test, the authors noticed a very weak staining reaction, almost imperceptible, as a result of the action of a single-component Griess reagent on a clear dark residue collected from the barrel of the Dreyse pistol cal. 6.35 mm made in Gemany, from which a single cartridge cal. 6.35 mm Broning made in Czechoslovakia with nickel-plated brass shell (ref. "SBP") was fired. This test was performed one month after the shot was fired (Fig. 3). As the barrel interior of the tested gun had traces of cleaned corrosion cavities, further attempts were made to shoot the same ammunition using another gun with intact barrel (Phoenix Arms pistol model Raven cal. 6.35 mm made in USA). As a result of four tests of the pistol's barrel residue, carried out 1 day, 1 week, more than 2 weeks and 1 month after the shot with the use of a single-component Griess reagent, more pronounced staining reactions were obtained, yet still weak in comparison with the color saturation of the other residues tested. It was also found that the lapse of time after the shot does not reduce the intensity of staining, but on the contrary, the residue collected after one month yielded the most pronounced staining (Table 2).

During the tests, the risk of contamination with red dye, used to contrast dactyloscopic traces revealed by the cyanoacrylate method, was encountered. Such risk may be related to evidentiary firearms that are subject

Tab. 1. Chemical tests of residues taken from the barrel interior of the evidence firearms treated with Griess reagent.

Item #	Firearm	Date of firearm seizure	Date of test	Time frame	Test results
1	Skorpion vz. 61 machine gun cal. 7.65 mm made in Czechoslovakia	23.09.2013	15.11.2013	1 month and 23 days	positive
2	Glock P30 pistol cal. 11.43 mm (.45 ACP) made in Austria	23.10.2014 suicide – 1 shot after firing several .45 ACP S&B FMJ cartridges	23.12.2014	2 months	positive
3	P-64 pistol cal. 9 mm made in Poland	23.09.2013	05.12.2013	2 months and 12 days	– "Red Basic" color – positive Griess result
4	Bock CZ Mod. 4CPL rifle cal. 12 made in Czech Republic	26.09.2013	10.12.2013	2 months and 13 days	positive
5	Margo MCMK pistol cal. 5.6 mm made in Russia	31.03.2017, 8:00 AM suicide – 1 shot with .22 Long Rifle S&B "HV" cartridge	08.07.2017	3 months and 7 days	positive
6	IŻ-58MA shotgun cal. 12 made in USSR	13.06.2013	05.11.2013	4 months and 23 days	positive
7	Merkel SUHL shotgun cal. 12 made in GDR	14.03.2013	28.11.2013	8 months and 14 days	positive

Tab. 2. Tests of residues collected from the barrel interiors of the firearms from the Reference Firearms Collection of the Forensic Laboratory, Voivodeship Police Headquarters in Wrocław, treated with Griess reagent.

Item #	Firearm	Ammunition	Date of shot	Date of test	Time frame	Result
1	Homemade pistol cal. 5.6 mm	.22 Long Rifle Nitron "SPORT-75" cartridge – 1 shot	23.10.2013	07.11.2013	15 days	positive
2	Brno-2 carabine cal. 5.6 mm made in Czechoslovakia	.22 Long Rifle Nitron "SPORT-75" cartridge – 1 shot	05.10.2019	05.11.2019	1 month	positive
3	Dreyse pistol cal. 6.35 mm made in Germany	6.35 mm Browning "SBP FMJ" cartridge – 1 shot	05.10.2019	05.11.2019	1 month	positive – very weak
4	Margolin pistol cal. 5.6 mm made in USSR	.22 Long Rifle Nitron "S&B-75" cartridge – 1 shot	03.10.2019	03.12.2019	2 months	positive
5	P-64 pistol cal. 9 mm made in Poland	9 × 18 mm Makarow "21 85" cartridges – 2 shots	30.09.2019	30.12.2019	3 months	positive
6	Astra pistol cal. 5.6 made in Spain	.22 Short Lapua – 3 pcs. and .22 Long Rifle – 2 pcs. Nitron/Eley cartridges – total: 5 shots	05.11.2013	05.11.2019	**6 years**	positive
7	Phoenix Arms Mod. Raven pistol cal. 6.35 mm made in USA	6.35 mm Browning "SBP FMJ" – 1 shot	07.11.2019	08.11.2019	1 day	positive – weak (slightly pink)
8	Phoenix Arms Mod. Raven pistol cal. 6.35 mm made in USA	6.35 mm Browning "SBP FMJ" – 1 shot	08.11.2019	15.11.2019	1 week	positive – weak (locally slightly pink)
9	Phoenix Arms Mod. Raven pistol cal. 6.35 mm made in USA	6.35 mm Browning "SBP FMJ" – 1 shot	15.11.2019	02.12.2019	17 days	positive – weak (slightly pink)
10	Phoenix Arms Mod. Raven pistol cal. 6.35 mm made in USA	6.35 mm Browning "SBP FMJ" – 1 shot	03.12.2019	03.01.2020	1 month	positive – pronounced

to both dactyloscopic and ballistic examination as part of a comprehensive forensic opinion or separate examinations conducted on the same pieces of evidence. Dactyloscopic tests are performed prior to the ballistic tests and therefore attention was paid to the fluorescent dye – Basic Red used in them. It was found that this dye covered the evidentiary P-64 pistol (the case mentioned in Table 1, item 3) and penetrated deep into its parts and into the barrel interior, as a result of which, a clearly visible grayish residue collected from the barrel interior was already contaminated with red dactyloscopic dye. After adding distilled water into the tube containing the residue, the solution turned pale reddish violet (Fig. 5). The addition of Griess reagent to the solution only caused the change of its color (Fig. 6). Distinguishing between these colors can be problematic and may lead to false conclusions. The expert may not be sure whether the red staining of the residue or its solution was a reaction to the Griess reagent used or whether it resulted from the contact of the residue (spatula used) with a red dye contrasting the dactyloscopic traces.

In addition to the main course of the above mentioned research, an attempt was made to determine whether Griess reagent gives staining reaction also with the residues of the primer mass firing, including the residues left after firing cartridges that do not contain gunpowder. To this end, a single rimfire Flobert cartridge cal. 6 mm made in Czech Republic ("Sellier & Bellot 6 mm ME Flobert Court") was fired, which does not contain gunpowder, but only primer mass, which serves as both the initiating and propelling material for the bullet. The shot was fired from a Bersa Model 23 semi-automatic pistol cal. 5.6 mm made in Argentina, after previous testing of the barrel interior (blank control). After 1 hour, a black residue was collected from the barrel interior with a spatula and covered with a single-component Griess reagent with which it reacted very intensively, yielding

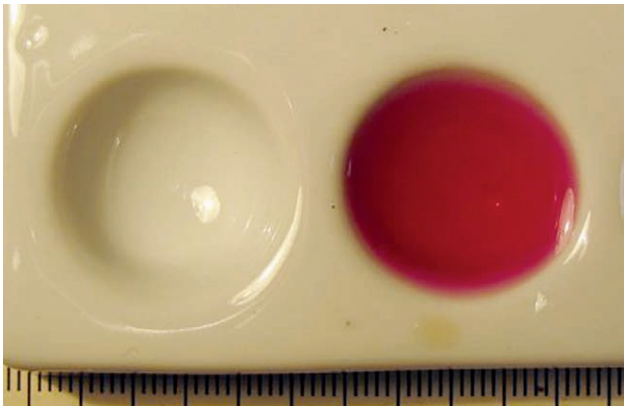

Fig. 1. Intensive staining reaction with residue collected from the barrel interior of a Merkel Suhl cal. 12 shotgun, made in GDR, after 8 months and 14 days (POCH-TEST PIR-S Kit).

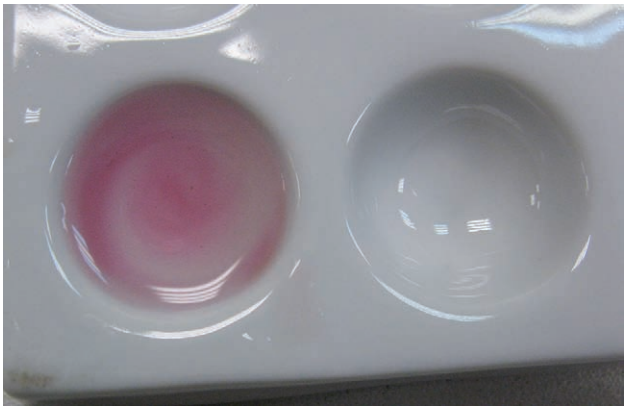

Fig. 2. Staining reaction with residue collected from the barrel interior of a Glock 30 pistol cal. 11.43 (.45 ACP) made in Austria, after 2 months (POCH-TEST PIR-S Kit).

Fig. 3. Very weak staining reaction of a single-component Griess reagent with the residue collected from the barrel interior of a Dreyse pistol cal. 6.35 mm made in Germany, after 1 month from shooting a 6.35 mm × 15.5 SR Browning cartridge made in Czechoslovakia ("SBP" with nickel-plated shell).

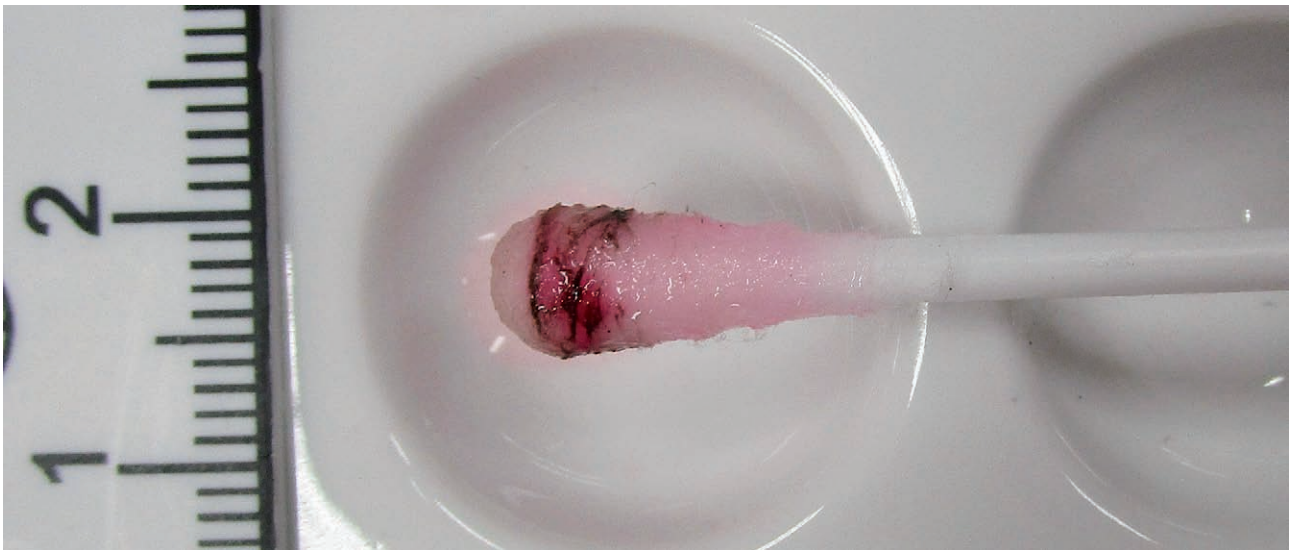

Fig. 4. Strong staining reaction of a single-component Griess reagent with the residue collected from the barrel interior of an Astra pistol cal. 5.6 mm made in Spain, after 6 years from shooting.

Fig. 5. Staining of aqueous barrel residue solution with dactyloscopic dye – Basic Red.

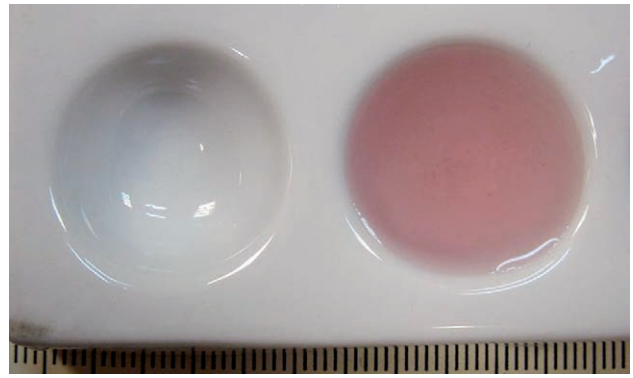

Fig. 6. Staining of the same solution additionally with Griess reagent.

red-purple stain. Next, the residue build-up inside the gun barrel after firing the primers was examined. The primers were located in the bottoms of the shells of the disintegrated cartridges that were inserted into the cartridge chambers of the proper caliber firearm. Before the tests, the barrel interiors were routinely cleaned subjected to blank controls. The tests with a single-component Griess reagent were performed within about ten minutes after firing the primer. All the tests conducted yielded positive results as shown in Table 3. Subsequently, the residues of gunpowder combustion (gunpowder originating from disintegrated cartridges) were tested with a single-component Griess reagent. Gunpowder samples (weight between 0.26 g and 1 g) were ignited by means of an external fire source (gas lighter) on the surface of the glass plate, after prior testing of the surface with a blank control. The remaining residue was collected with a standard spatula. As previously, all the tests conducted yielded positive results. The types of gunpowder tested are shown in Table 4.

Tab. 3. Tests of barrel residues remaining after firing the primer with Griess reagent.

Item #	Type of cartridge	Type of firearm	Result
1.	pistol cartridge primer cal. 9 × 18 mm Makarow from 1993, made in Poland (“21 93”)	P-83 pistol	positive – very weak local reddening
2.	pistol cartridge primer cal. 7.65 mm × 17SR Browning, made in Austria (“HP 7,65”)	Manurhin/Walther model PPK pistol	positive – intensive red-purple
3.	rifle cartridge primer cal. .30-06 Springfield, made in Czech Republic (“S&B .30-06 SPRG.”)	TIKKA M695 rifle	positive
4.	hunting rifle cartridge primer cal. 12, made in Poland (“12 PAWAM 12 PIONKI”)	IŻ-58M shotgun	positive – intensive red-purple

Tab. 4. Tests of gunpowder combustion residues with Griess reagent.

Item #	Type of gunpowder	Type of cartridge	Result
1.	smokeless lamellar powder “SOKÓŁ” made in Poland	12/70 PAWAM PIONKI	positive – weak reddening
2.	smokeless cylindrical multitubular powder	9 × 18 mm Makarow (“21 93”)	positive
3.	smokeless spherical powder (grains flattened on both sides)	.300 Winchester Magnum (“Winchester Power Point”)	positive
4.	black powder (smoke powder) Vesuvit LC made in Czech Republic	–	positive

Conclusions

1. The positive reaction of Griess reagent with the residue extracted e.g. from the barrel interior of the tested firearm does not give grounds to conclude about the time that has elapsed since the last shot was fired. It can be one day or several years. The longest period of time that has passed from the shot to the examination of the barrel residue with Griess reagent was 6 years – the test gave a positive result in the form of a pronounced red color of the residue.
2. The intensity of the staining reaction involving Griess reagent and the residue extracted e.g. from the barrel interior of the tested firearm also does not give grounds to conclude about the time that has elapsed since the last shot was fired; a strong saturation with red color does not prove that the time was short or, more specifically, shorter than in the case of a weaker saturation.
3. After the shot, the staining reaction with the clearly visible residue extracted from the barrel interior of the firearm can be so weak as to be almost imperceptible against the background of the dark-colored residue. This may depend on the type of cartridge used or the condition of the firearm's barrel interior. In the tests conducted, such a case occurred after firing the pistol cartridge cal. 6,35 mm × 15,5 SR Browning made in Czechoslovakia from a Dreyse pistol cal. 6.35 mm, made in Germany (barrel interior with corrosive changes).
4. During dactyloscopic examination of firearms, the Basic Red fluorescent red dye used for contrasting fingerprint traces revealed by the cyanoacrylate method should be avoided. This dye may be a source of contamination and cause false results in subsequent tests of the barrel residue with Griess reagent. Therefore, it is suggested that when dactyloscopic traces are revealed by the cyanoacrylate method on the surface of a firearm, a contrasting dye of a different color should be used, e.g. Basic Yellow 40.

Source of Figures and Tables: author

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