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Copper and Nickel Detection on Gunshot Targets by Dithiooxamide Test

ABSTRACT: Identification of a hole or mark as one produced by a bullet and characterization of the type of bullet are often important in reconstruction of shooting incidents. Dithiooxamide is used for the visual detection of copper and nickel deposited on a bullet hole periphery by the passage of a jacketed bullet through target material. The discrimination of jacketed and non-jacketed ammunition can be made on the basis of target analysis alone. This technique may be used in conjunction with the Modified Griess Test and the sodium rhodizonate test for detection of bullet holes and muzzle-to-target distance determinations. The test for copper and nickel can also be used at a crime scene to determine the type of bullet producing a mark in a variety of target materials.

KEYWORDS: criminalistics, ballistics, gunshot residues, bullet holes, spot tests, metal identification, dithiooxamide

In investigation of criminal activities it may be necessary, either in the field or in associated laboratory examination of evidence, to determine whether a hole or mark in an object was produced by a bullet. It may also be of value in many instances to determine the type of metal on the outer surface of the bullet. Presently, most laboratories analyze gunshot targets using the Modified Griess Test (MGT), a qualitative visual detection of nitrite residues, and the sodium rhodizonate test (SRT), a similar test for detection of lead residues. While both tests are useful for verifying the presence of a bullet hole or mark, neither is capable of a positive identification of the type of bullet involved.

Steinberg et al. [1] reported use of dithiooxamide (DTO, also known as rubeanic acid) in a field test kit to determine the presence of copper in bullet hole peripheries (BHP). They recommend their test in conjunction with a test for lead residues to detect bullet holes or marks and to distinguish between jacketed and unjacketed bullets. DTO forms colored precipitates with copper (dark green), nickel (pink or blue), and cobalt (brown) [2]. In our experience, the DTO test when used as recommended by Steinberg et al. does not allow for examination of the target using the MGT for nitrite residues. Steinberg et al. also do not discuss any results concerning nickel detection using DTO. In this paper, we report the results of our research using a modified DTO procedure for the detection of copper and

nickel traces on BHPs. We sought an optimized method which yields satisfactory results for both copper and nickel without interfering with or requiring substantial modification of existing tests for lead and nitrite residues. Our procedure, like that of Steinberg et al., is amenable to field as well as laboratory application.

Experimental Methods

Reagent Sensitivity Tests

A study was made to determine the optimum concentration of DTO (Baker Analyzed Reagent grade) to use for observing copper complexes on white cotton cloth. Solutions containing from 0.01 to 10 μg of Cu(II) in 200 μL were spotted on a cloth and allowed to air-dry. A series of the spots were treated with 95% ethanol solutions of DTO applied using a spray atomizer, and the resulting spots of copper-DTO complex were viewed under white light to determine the sensitivity of the test at selected DTO concentration levels. The results of this study, as shown in Table 1, indicate the detection limit for observation of the dark green copper-DTO complex decreases as the concentration of DTO is decreased from 1 to 0.2% and remains relatively constant at about 0.1 μg of copper at lower DTO levels. The improvement in detection at lower DTO levels results primarily from the lower intensity of the orange DTO background color on the white cloth. The spots formed by evaporation of the copper solutions used in this study were about 1 cm in diameter, so the lower limit of detection of the test is about 0.13 μg/cm. The same color density in a 1-mm-diameter spot, about the size one would expect from dissolution or transfer of a copper particle resulting from treatment of a gunshot target, requires 1 ng of copper. In comparison, a-10-μm-diameter sphere of copper (similar to the size of particles produced during a gunshot) has a mass of about 5 ng. Clearly, if efficient transfer of copper particles can be made to a viewing medium, DTO has enough sensitivity for use in visualizing copper in gunshot residues. We similarly studied cuproin and benzoin oxime, two other reagents used in copper detection, and found detection limits of 1 and 5 μg, respectively.

DTO also forms pink or blue complexes with nickel, another component of many bullet jackets. A sensitivity test for nickel using DTO yields results which are similar to those for copper. The sensitivity of the eye to viewing DTO-nickel complexes is less than the copper complexes, resulting in a nickel detection limit of about 1 μg in a 1-cm circle. Effective visualization of nickel-DTO complexes depends more upon the DTO level than with copper, because of the difficulty of viewing pink colors against the orange DTO background. A con-

TABLE 1—*Sensitivity test results for dithiooxamide reaction with Cu(II) on white cotton cloth. Signs indicate positive or negative visibility of copper-DTO complex. Copper solutions were spotted on cloth by application of 200-μL droplets.*

Percent DTO	Micrograms of Copper									
	10	5	1	0.5	0.1	0.05	0.01	0.005	0.001	0
1	+	+	+	+	−	−	−	−	−	−
0.5	+	+	+	+	+	−	−	−	−	−
0.1	+	+	+	+	+	+	−	−	−	−
0.05	+	+	+	+	+	+	−	−	−	−
0.01	+	+	+	+	+	−	−	−	−	−
0.005	+	+	+	+	−	−	−	−	−	−

Detection limit $\simeq$ 0.05-μg copper in a 1-cm-diameter spot on cloth.

centration of 0.1% DTO in 95% ethanol was selected as the optimum level for all further studies since this level of DTO results in the greatest contrast between nickel and copper complex colors and background.

Selection of Metal Transferring Medium

In developing a test for use with gunshot targets, consideration was given both to development of patterns directly on targets and transfer of the metal particles to a second medium for color development. Using targets produced by bullets forming good deposits of copper and nickel on BHPs, we found that direct development of metal-DTO complex colors on targets is not feasible for several reasons. No procedure could be found allowing development and effective visualization of the DTO complexes of copper and nickel directly on a target to which the MGT and the SRT had previously been applied. Difficulty in observing complex colors on dark or colored targets and the similarity in color of copper-DTO complexes and lead and carbonaceous deposits also hampers pattern development directly on targets. To alleviate these difficulties, a method was sought by which metals could be transferred to another medium for pattern development without interfering with MGT and SRT results.

Several concentrations of hydrochloric acid and ammonium hydroxide were compared for use in transferring copper and nickel. A pattern of copper solution spots similar to those described in the sensitivity tests above were made on sheets of aluminum foil. The copper was transferred to sheets of paper by moistening the paper with hydrochloric acid in concentrations ranging from 1 to 10% or ammonium hydroxide from 5 to 30%, placing the paper over the aluminum foil, and pressing lightly with a warm iron. The color patterns were developed using 0.1% DTO applied to the paper. Tests with several types of paper indicated that the best results were obtained using Whatman No. 1 chromatography paper. There was very little effect of transferring medium selection on sensitivity obtained. With ammonium hydroxide, sensitivity increased slightly with increasing concentration. The increase in sensitivity is offset somewhat by the disagreeable nature of concentrated ammonia solutions in field situations. The hydrochloric acid solutions all gave slightly less sensitivity than the ammonium hydroxide solutions for transferred copper. Hydrochloric acid, however, dissolved nickel much better than ammonium hydroxide, resulting in better transfer of that metal. Using a 10% ammonium hydroxide solution, the sensitivity of the test for copper was identical to that shown in Table 1, that is, there was no significant loss of sensitivity by inserting a transfer step into a pattern development procedure. These results were verified using metals deposited on cloth targets by the passage of jacketed bullets.

Another requirement of the transfer medium is that it not interfere with results for MGT and SRT evaluation. Both ammonium hydroxide and hydrochloric acid were used in combination with the MGT and SRT procedures in several different sequences using targets produced from 9-mm copper-jacketed ammunition. In all procedures we tested, the use of hydrochloric acid caused difficulties with the DTO test as a result of the presence of large amounts of lead transferred from the target to the color development paper along with the copper. Ammonium hydroxide was more useful as a transferring medium for targets containing many lead deposits because lead does not form soluble ammonia complexes. The MGT uses 15% acetic acid as a transferring medium for nitrite residues. The acetic acid also transfers some copper, nickel, and lead, reducing the sensitivity of subsequent tests of a target for any of these metals slightly. The SRT determination for lead results in deep purple or pink colors on the target, or when done by transfer, requires removal of copper and nickel along with the lead. As a result, no procedure could be found in which the DTO procedure could be used successfully following both the MGT and SRT procedures. It was found that the best results were obtained by performing the three tests in the following order: (1) MGT by transfer of the nitrites; (2) DTO by transfer of the copper, nickel, and some lead; and (3)

SRT either directly on the target if it is light colored or by transfer if the target is dark. The procedure adopted for all further studies, hereafter referred to as the DTO test, is shown in Table 2.

Results of Tests using Cloth Targets

The effectiveness of the DTO test for determining bullet jacket composition was evaluated using targets made by firing bullets through 22- by 22-cm squares of white cotton cloth on an indoor firing range. Target cloths were supported during firing by mounting them on cardboard range targets. Ammunition types and muzzle-to-target distances were varied with each test and will be discussed along with the results that follow.

The first test was to determine the accuracy and reproducibility of the DTO procedure for identification of selected full- and semi-jacketed gilding metal (copper alloyed with 5 or 10% zinc bullets), full-jacketed silver-tipped (nickel brass bullets), and unjacketed lead bullets. Targets were produced by firing .38-caliber and 9-mm bullets at a muzzle-to-target distance of 30 cm (12 in.). Each ammunition type was used to generate from 10 to 24 targets. Weapons were cleaned before firing the first bullet of each jacket composition.

The DTO test was performed on each target following application of the MGT by the procedure shown in Table 2. DTO test results for these targets, shown in Table 3, indicate two types of metal deposits were found on the targets. A colored ring on the BHP indicative of the bullet jacket material is present on all targets. In addition, small fragments of bullet jacket metal were observed on all targets at distances out to the edges of the target cloth.

In Table 3, we have described the BHP deposits as being either full or broken depending upon whether the metal-DTO complex color forms a full circle or not. The terms dark and light are used to describe our perception of the intensity of the metal-DTO complex color development. When evaluating targets where bullet surface composition is previously un-

TABLE 2—*Dithiooxamide test procedure for visualization of bullet jacket metals.*

REAGENTS AND MATERIALS NEEDED

1. Freshly prepared 0.1% (w/v) dithiooxamide in 95% ethanol (DTO).
2. 10% ammonium hydroxide.
3. Whatman No. 1 chromatography paper sufficient to cover target area.
4. Disposable laboratory gloves.
5. Pressing iron.
6. Plastic photo developing tray or nonmetallic spray dispenser for DTO.

PROCEDURE

1. Complete Modified Greiss Test [*3*] for nitrite residues.
2. Place target face up on a clean flat surface.
3. Cover target with a sheet of chromatography paper presaturated with ammonium hydroxide solution.
4. Press firmly with gloved hand to ensure good contact between bullet hole periphery and paper and then with hot iron for a few seconds until almost dry.
5. Develop residue pattern by dipping paper into tray containing DTO or by spraying DTO onto paper.
6. Pattern develops immediately; green for copper, blue-pink for nickel, and occasionally yellow for lead.
7. Visibility of pattern improves slightly upon drying and lead residues change from yellow to brick red.
8. Photograph pattern as required for documentation.
9. Use target for sodium rhodizonate test [*4*] for lead residues.

TABLE 3—*Results of dithiooxamide test on targets shot at 30-cm muzzle-to-target distance. Figures refer to number of positive test results of color indicated for each ammunition type. Dark and light describe relative intensity of colors developed in test. Full, broken, many, and few describes degree of completeness of ring on BHP and frequency of occurrence of metal fragments outside BHP.*

No. of Targets Tested	Ammunition	Color	Metal Ring at BHP				Metal Fragments Outside BHP			
			Full	Broken	Dark	Light	Many	Few	Dark	Light
18	Military round, Cu jacketed 9-mm parabellum	olive green	18	none	17	1	9	9	14	4
12	CCI Cu semijacket HP .38 special +P	olive green	none	12	7	5	none	12	8	4
14	Federal Cu semijacket HP .38 special +P	olive green	none	14	2	12	none	14	1	13
10	Remington Peters Cu semijacket HP .38 special +P	olive green	none	10	8	2	1	9	8	2
24	Winchester Western silver tipped 9-mm parabellum	pink/ blue	13	11	21	3	19	5	22	2
12	Winchester Western Nonjacketed .38 special +P	yellow	10	2	6	6	9	3	4	8

known, we have found it most effective to use only the BHP deposits and to ignore the metal fragments outside the BHP except in special circumstances to be discussed below. As shown in Table 3, identifiable rings characteristic of the jacketing metal are produced under the conditions of test-firing for all of the bullets tested. In this test, all of the fully jacketed copper ammunition produced full-circle BHP deposits, while the semi-jacketed hollow point ammunition consistently produced broken circle deposits. In addition, all of the unjacketed bullets produced targets yielding yellow turning to brick red deposits characteristic of lead-DTO complexes. In further studies using a wider range of test conditions, these results did not hold generally as will be discussed below. The colors produced by copper-jacketed, silver-tipped, and unjacketed bullets were uniquely identifiable and clearly distinguishable in all instances in this test.

DTO colors indicative of small fragments of bullet jacket metal were observed outside of the immediate vicinity of the bullet hole on all targets in this study. The frequency of observation of these particles is described in Table 3 as either many or few, with the division between these terms being ten particles per target. The metal fragments occur out to the edges of the target cloth or up to at least 15 cm from the bullet hole. Before this study, we had not expected to see metal fragments outside the BHP, so we examined them further. Several fragments were obtained by direct examination of the target cloths and by lifting them with tape from a target which had not been treated with DTO. Fragment composition and morphology were studied using a scanning electron microscope with X-ray emission spectrometer. Using X-ray emission, fragments were identified which matched the brass composition of the bullet jacket. These fragments have a morphology characteristic of sheared metal with some evidence of melting occurring along the edges. This shape is consistent with fragment formation by abrasion of the jacket metal from the surface of the bullet during passage through the gun barrel. No evidence could be found of particles originating from gas phase reactions such as those commonly observed in formation of typical gunshot primer residue deposits. The number and distribution of metal fragments outside the BHP was not consistent from shot to shot, so their presence is not as reliable as BHP deposits for making a determination of jacket metal on a target when the bullet type is unknown.

The second study was to evaluate the DTO test with a wider range of ammunition types than used previously and targets made at muzzle-to-target distances of 7.5 and 15 cm (3 and 6 in.). At these closer distances, targets are covered with much carbonaceous and vaporous lead deposits. Such a test was selected to determine whether the presence of these deposits interferes with the effectiveness of the DTO test for jacket metals. The results of DTO test application to targets using 16 different ammunition types at each of 2 shooting distances are shown in Table 4. As indicated, the presence of copper was correctly detected in the majority of the jacketed and coated (lubaloy) ammunition (20 out of 24 bullets). The targets on which copper was not detected were those made using the .357-caliber metal point and .38-caliber silver-tipped ammunition. Nickel was correctly identified as being present in only 3 of the 6 targets where silver-tipped bullets were used. In general, the DTO complex colors were darker, and determinations were easier to make for the 9-mm ammunition than for the other 2 calibers. Note that in no instances were either of the jacket metals detected for ammunition which did not contain them. That is, no "false positives" were obtained for unjacketed lead or Nyclad bullets. In general, the presence of large amounts of dark-colored deposits on the targets did not visually interfere with DTO test results because they were not efficiently transferred to the color development paper.

The third test was designed to find the maximum muzzle-to-target distance at which BHP metal deposits discernible by our DTO test procedure are made. Targets were generated by firing 9-mm copper fully jacketed ammunition (Remington) at muzzle-to-target distances of 0.15 to 15 m (6 in. to 50 ft). The DTO test results for these targets are shown in Table 5. As shown, positive test results were obtained at all shooting distances studied. Apparently, this occurs because jacket metal is transferred to the target by abrasion as a result of friction

TABLE 4—*Results of bullet metal determinations using DTO test for targets at short firing distances.*[a]

Bullet Type	Metals Known to be Present	Test Results at Firing Distance of: 7.5 cm (3 in.)	15 cm (6 in.)
9-mm S&W jacketed semiwadcutter	Cu	+ +Cu	+ +Cu
R-P jacketed hollow point	Cu	+ +Cu	+ +Cu
Federal jacketed hollow point	Cu	+ +Cu	+ +Cu
R-P metal point	Cu	+Cu	+Cu
W-W silvertip	Ni,Cu	+Cu	+Cu,+Ni
S&W nyclad	—	—	—
.357 magnum R-P jacketed hollow point	Cu	+ +Cu	+Cu
W-W superlubaloy	Cu	+Cu	+ +Cu
R-P metal point	Cu	—	—
R-P semiwadcutter	Cu	—	—
W-W silvertip	Ni,Cu	+ +Cu,+Ni	+ +Cu
S&W nyclad	—	—	—
.38 special R-P full jacket	Cu	+ +Cu	+Cu
W-W lubaloy	Cu	+Cu	+Cu
W-W silvertip	Ni,Cu	—	+Ni
Federal nyclad	—	—	—
R-P lead	—	—	—

[a] + + indicates strong, positive response for metal indicated, either very dark pattern or full ring.
+ indicates weaker but still positive response, either a light pattern or partial ring.
— indicates no response for either Cu or Ni.

TABLE 5—*DTO test results for targets using Remington Peters 9-mm fully jacketed Luger ammunition as a function of muzzle to target distance.*

Firing Distance, m	Ring on BHP Present	Intensity	Metal Fragments Outside BHP Frequency
0.15	yes	dark	many
0.3	yes	dark	many
0.6	yes	dark	few
1.5	yes	dark	few
3	yes	dark	few
4.5	yes	light	few
6	yes	dark	few
9	yes	light	few
15	yes	dark	few

during passage of the bullet through the target material. This phenomenon should occur whenever bullet speed is maintained above the threshold required to abrade the jacket material. A maximum distance for use of the DTO test was not determined in these studies, since it is longer than the distances at which targets could be obtained in our indoor range. However, measurements of copper in material removed from the immediate vicinity of bullet holes by Ravreby [5] and Jauhari et al. [6] indicate that the amount of copper deposited at firing distances of 100 m or more is about the same as at short distances. This would be expected since abrasion of the bullet appears to be the process causing the deposit of jacket metal on the BHP. We expect, therefore, that positive DTO test results should be obtained

on targets obtained at firing distances of several hundred metres when high-powered ammunition is used.

Metal fragments were found outside the BHP on all targets used in our distance tests. The distances used in this study are clearly longer than the distance over which fragments generated within the gun barrel could travel. Apparently, metal fragments can either be generated from the surface of the bullet or carried along with the bullet and dislodged upon bullet-target impact. In these studies, the targets were not firmly supported and could swing backward slightly upon impact.

The fourth study was to determine the effects of sequentially firing a series of jacketed bullets and then an unjacketed bullet from a weapon and looking for the presence of a "false positive" test on the target from the unjacketed bullets. Results of these tests indicate that in no instances was a jacket metal ring formed on the BHP using a nonjacketed bullet. The reverse of this test, firing a series of unjacketed bullets until the gun barrel was fouled with lead deposits and then firing a jacketed bullet into a target and performing the DTO test yielded in some instances a "false negative" result. That is, a jacketed bullet fired from a lead-fouled weapon can produce a bullet hole which gives a negative test for copper and nickel residues. Generally, we found this to occur only after a gun barrel was heavily coated with lead and carbonaceous deposits. Second and subsequent jacketed bullets from a dirty weapon generally yield positive test results for the jacketing metal, the metal deposits becoming more clearly identifiable with each succeeding bullet.

The last test to be discussed was a study to determine the effects of blood on DTO test results. For this test, targets were made at a muzzle-to-target distance of 60 cm (2 ft) using several types of ammunition which give good metal deposit patterns; however, before performing the DTO test, blood was poured on the targets in the vicinity of the BHP. DTO test results for these targets are shown in Table 6. The results show that the presence of large quantities of blood reduces the effectiveness of the DTO test. This occurs because the blood inhibits transfer of the metal deposits to the color development paper. The targets for which positive results were obtained are those on which the blood splatter did not completely cover the BHP. On all targets used in this study, metal fragments outside the BHP were observable in areas not covered with blood. When evaluating bloody targets of unknown ammunition type, the metal fragments outside the BHP can be used to determine bullet jacket composition when no BHP deposits can be observed. In no instances did blood chemically interfere with the DTO color development. The transfer procedure used did not result in noticeable quantities of blood transferred to the color development paper.

TABLE 6—*DTO test results for blood-splattered targets. Figures are number of targets yielding positive test results within each category.*

No. of Targets Tested	Ammunition	BHP Ring Deposits				Fragments Outside BHP			
		Full	Broken	Dark	Light	Many	Few	Dark	Light
10	Frontier Cu jacket hollow point .38 sp +P	0	1	0	1	0	10	6	4
6	Remington Peters Cu jacketed 9-mm Luger	0	6	4	2	6	0	3	3
6	Federal Cu jacket hollow point .38 sp +P	0	2	0	2	1	5	3	3

Conclusions

The DTO test, when used as described, produces reliable identification of metal composition of the outer surface of the bullet used to produce a hole in a target material. Occasionally, jacketed bullets cannot be distinguished from unjacketed bullets, but no false positives were observed for either copper- or nickel-clad bullets. Sources of nickel and copper other than from a bullet surface can be identified by the orientation of metal deposits around the BHP. No chemical interferences with the test procedure have been observed; however, blood and other materials that physically inhibit transfer of metal fragments cause negative results to be obtained when fragments are covered. The DTO test, as described, can either be used as a stand-alone test for bullet jacket metals or in a sequence with the MGT for nitrite residues and SRT for lead residues without affecting the reliability of either of these tests. The DTO test results are reliable at all shooting distances longer than those at which either gun barrel flash or heavy particle deposits destroy or cover the bullet wipe. In this paper, we have only discussed the results using cloth targets, but we have found similar results using wood and linoleum targets. Steinberg et al. [1] also have obtained good results using a variety of target materials. Another advantage of the DTO test, as described, is its applicability to field use. All reagents, dispensers, and paper fit easily into a briefcase-sized kit, which can be used at crime scenes or other field situations.

References

[1] Steinberg, M., Leist, Y., and Tassa, M., "A New Field Kit for Bullet Hole Identification," *Journal of Forensic Sciences*, Vol. 29, No. 1, Jan. 1984, pp. 169–176.
[2] Feigl, F. and Anger, V., *Spot Tests in Inorganic Analysis*, Elsevier Publishing Company, Amsterdam-New York, 1972, pp. 213–215 and 329–331.
[3] Dillon, J. H., "The Modified Griess Test, a Chemically Specific Chromophoric Test for Nitrite Compounds in Gunshot Residues," FBI Laboratory, Forensic Science Research and Training Center, Quantico, VA (available from the author).
[4] Dillon, J. H., "The Sodium Rhodizonate Test, a Chemically Specific Chromophoric Test for Lead in Gunshot Residues," FBI Laboratory, Forensic Science Research and Training Center, Quantico, VA (available from the author).
[5] Ravreby, M., "Analysis of Long-Range Bullet Entrance Holes by Atomic Absorption Spectrophotometry and Scanning Electron Microscopy," *Journal of Forensic Sciences*, Vol. 27, No. 1, Jan. 1982, pp. 92–112.
[6] Jauhari, M., Singh, T., and Chatterji, S. M., "Characterization of Firearm Discharge Residue of Ammunition of Indian Origin by Neutron Activation Analysis," *Forensic Science International*, Vol. 22, No. 2, July 1983, pp. 117–121.

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