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Determination of Firing Distance. Lead Analysis on the Target by Atomic Absorption Spectroscopy (AAS)*

ABSTRACT: This paper reports a method for the determination of the firing distance. Atomic absorption spectroscopy (AAS) was used to determine the lead (Pb) pattern around bullet holes produced by shots on test targets from the gun. Test shots were made with a Colt 38 Special at 5, 10, 20, 25, 30, 35, 40, 45, 50, 60, 80, and 100 cm target distance. The target was created with sheets of Whatman no. 1 paper on a polystyrene support. The target was subdivided into three carefully cut out rings (1, 2, and 3; with external diameters of 1.4 cm; 5 cm; 10.2 cm, respectively). Each sample was analyzed with graphite furnace AAS. Lead values analysis performed for each ring yielded a linear relation between the firing distance (cm) and the logarithm of lead amounts ($\mu g/cm^2$) in definite target areas (areas 2 + 3): [$\ln dPb_{2+3} = a_0 + a_1 l$]; where dPb_{2+3} = lead $\mu g/cm^2$ of area 2 + 3; a_0 and a_1 are experimentally calculated; l = distance in cm.

KEYWORDS: forensic sciences, firing distance, lead residues analysis, gunshot residues pattern, atomic absorption spectroscopy

Identification of gunpowder residues has a great importance in the resolution of forensic science problems and especially in legal medicine, for shooting distance determination.

The gunshot range is routinely estimated by visually comparing the casework powder residue pattern on the garments or on the skin of the victim with the patterns obtained from a series of test firings at known distances, using the same gun and ammunition (1). A more reliable and accurate method is based on the analytical determination of the amount of material ejected from the bore of the weapon around the entrance hole of the bullet, which includes burned and unburned powder grains, carbonaceous particles, bullet jacket debris, shavings, and dirt.

A color reaction for the identification of incompletely burned residues (2), or various analytical methods (Atomic Absorption, Neutron Activation Analysis, Polarographic Techniques) for the determination of nitrites, copper, lead, or antimony around the hole, have been used (3–6).

The chosen element concentration is usually determined in two "rings" around the hole. The internal ring ("ring of dirt") does not depend on the firing distance, according to some authors (7), and in our experience is related only in the case of short distances, up to 20–25 cm (5). The internal ring is usually used for the identification of the entrance hole of the bullet, as it contains dirt, primer residues, and lead and jacket metals (copper and iron) deposited or wiped from the projectile; moreover, the concentration of elements in the internal ring can be altered by blood soaking (8).

In the outer ring, the concentrations of characteristic elements (nitrites, lead, antimony, copper) ejected from the gun are determined and compared with the ones obtained in a series of firing tests vs. distances, under the same experimental conditions. Usually, the higher the elemental concentration, the shorter the firing distance, in accordance with a calibration curve, which is characteristic for each gun and ammunition brand.

Powder residue patterns will vary significantly, not only as a result of a different barrel length, caliber, or other characteristics of different weapons (9), but also with changes in primer, powder type and lot, and propellant loading. All of these parameters generally vary for different brands, because not all manufacturers use the same composition or the same raw materials in ammunition of the same caliber and bullet weight, and even the same brand can be subject to changes in composition at different dates of manufacture.

The precision and accuracy of firing distance determination in casework is, in our experience, strongly dependent on the experimental accuracy in obtaining the calibration curve and on an accurate consideration of all the variables involved, i.e., differences in powder composition, possible overlapping of two or more powder patterns in multiple shots, differences in firing angles, folded or woven garments.

In a previous study, we showed the metallic gunpowder residues distribution on the target at different distances after their visualization by a specific colorimetric reaction (5). We also showed both the relationships between the residue amounts and the firing distance, and the distribution of the residues on the target in three concentric circles around the entrance hole; the diameter of the rings depends on the weapon type, propellant, and distance.

In the present paper, we present a method for the evaluation of the firing distance involving lead analysis on the target by atomic absorption spectroscopy (AAS). Among the metallic elements on the target, lead was chosen because it is always present in modern primer, unlike antimony that is absent in some cartridges for caliber 0.22" weapons.

Materials and Methods

Test shots were made with a Colt 38 Special at 5, 10, 20, 25, 30, 35, 40, 45, 50, 60, 80, and 100 cm target distance, two for each

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distance. The target was created with sheets of Whatman no. 1 paper on a polystyrene support.

On the basis of the results obtained in a previous work, the target was subdivided into three carefully cut out rings (1, 2 and 3; with external diameters of 1.4 cm; 5 cm; 10.2 cm, respectively) (Fig. 1).

The first ring on the target, 1.4 cm diameter, includes the entrance hole, and bullet wiping rim. As shown in preliminary test shots made at various distances, with both jacket bullets and lead bullets, this rim is invariably present and for greater distances (beyond 20–25 cm), is independent of the distance. The second ring (or circular crown), having an internal diameter of 1.4 cm and an external diameter of 5 cm, includes much of the first smoke halo. The third ring, with an internal diameter of 5 cm and an external diameter of 10.2 cm, contains the rest of the firearm discharge residue. These rings were cut out from each of the test shot targets.

All the fabric squares were placed in 10 mL glass vials, added with 5 mL hydrochloric acid 0.1 N and put in an oven at 45°C for 1–2 h, to dissolve lead, soluble at examined concentrations. Aliquots of 25 μL of each extraction liquid were analyzed, after appropriate dilution depending on lead amount, by atomic absorption spectroscopy (mod. 460 with an HGA-76 graphite furnace, equipped with a recorder, Perkin-Elmer, Monza, Italy). The wavelength used was 283.3 nm, spectral, bandpass 0.5 nm). The graphite furnace heating program was: drying 130°C (15°C/s for 40 s); pyrolysis 1000°C for 30 s (100°C/s); autozero 1000°C (for 6 s); atomization 1800°C (3000°C/s for 5 s); cleanout 2600°C (3000°C/s for 4 s).

Results

The total amounts of lead (mean of two shots) found in the three rings, in μg, present in the three rings and their combinations, according to the firing distance (cm), are reported in Table 1.

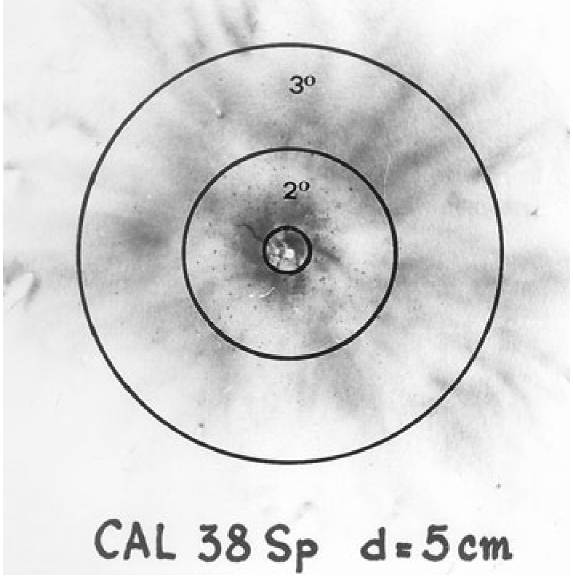

FIG. 1—*A target sample obtained by firing at 5 cm distance with a two-inch barrel Colt 38 Special pistol and lead bullet Fiocchi cartridges. Firing smoke is distributed around the entrance hole in three main areas: the wiping rim, the first visible smoke ring, the second visible smoke ring. The target was subdivided into three carefully cut out rings (1, 2, and 3; with external diameters of 1.4 cm; 5 cm; 10.2 cm, respectively).*

Our aim was to obtain a linear relationship between distance and measured Pb values:

$$y = a_0 + a_1 x$$

where y is the Pb concentration and x is the firing distance. Firing distances were calculated with linear relation obtained, after determination of Pb amounts in well-located zones of target.

Pb amounts (μg) were determined in three rings indicated with 1, 2, and 3. Rings values and their combinations (1 + 2, 1 + 3, 2 + 3, 1 + 2 + 3) are reported in Table 1. Pb densities were calculated in μg/cm^2 from Table 1 values and from respective rings area. Results are reported in Table 2.

In view of the fact that the further the firing distance (within the first 20–25 cm) the less the amounts of lead present, and that this difference grows gradually less beyond 25 cm distance, it can be hypothesized that the relationship between the amounts of lead and the distance is of semi-logarithmic type. Therefore, the natural logarithms of both the total amounts of lead and of their densities were determined.

The data obtained by simple calculation and therefore not showed, were inserted in the linear equation ($y = a_0 + a_1x$), where a_0 and a_1 were calculated with the minimum squares method according to Spiegel (10).

Calculation of correlation coefficients (r), enabling verification of the linearity of y according to variations of x and the relative standard error (S_{yx}), yielding the dispersion of the points outside the linear curve, with the minimum squares method, was then made according to Spiegel (10).

TABLE 1—*Total amounts of lead in μg, present in the three rings and their combinations, according to the firing distance (cm).*

Rings	1	2	3	1 + 2	1 + 3	2 + 3	1 + 2 + 3
Distance							
5	2840	5820	3290	8660	6130	9110	12,000
10	393	2640	839	3030	1230	3480	3870
20	182	2060	1030	2240	1210	3090	3270
25	92.5	1190	888	1280	981	2080	2170
30	38.8	624	2630	663	2670	3250	3290
35	37.6	196	1470	234	1510	1670	1700
40	68.7	78.6	1040	147	1110	1120	1190
45	63.9	30.8	649	94.7	713	680	744
50	41.6	15.1	609	56.7	651	624	666
60	60.0	10.0	146	70.0	206	156	216
80	56.2	5.60	14.6	61.8	70.8	20.2	76.4
100	25.5	4.10	4.10	28.2	29.6	6.80	32.3

TABLE 2—*Density of the lead (μg/cm^2) present in the three rings and their combinations, according to the firing distance (cm).*

Rings	1	2	3	1 + 2	1 + 3	2 + 3	1 + 2 + 3
Distance							
5	916	161	26.5	220	48.2	56.8	73.1
10	127	73.0	6.80	77.2	9.70	21.7	23.7
20	58.7	56.9	8.30	57.0	9.50	19.3	20.0
25	29.8	32.9	7.20	32.6	7.70	13.0	13.3
30	12.5	17.2	21.2	16.9	21.0	20.3	20.2
35	12.1	5.40	11.8	5.90	11.9	10.4	10.4
40	22.2	2.20	8.40	3.70	8.70	7.00	7.30
45	20.6	0.90	5.20	2.40	5.60	4.20	4.60
50	13.4	0.40	4.90	1.40	5.10	3.90	4.10
60	19.4	0.30	1.20	1.80	1.60	1.00	1.30
80	18.1	0.20	0.10	1.60	0.60	0.10	0.50
100	8.20	0.10	0.00	0.70	0.20	0.00	0.20

Lead concentrations measured on target rings was reported in various ways [weight (μg); density (μg/cm^2); natural logarithm of weight (ln μg); natural logarithm of density (ln μg/cm^2)], in order to find the best linear regression of "shooting distance versus lead concentration."

In Table 3 are reported a_0, a_1, r, and S_{yx} values in various ways expressing lead concentrations.

The choice of the curve best describing the linear progress of the amounts of lead at the different distances x was made as follows:

(1) The linear regressions y, x, showing a significant correlation, i.e., at least >0.9 were firstly selected.
(2) Among the regression satisfying the conditions in point (I) S_{yx} value is much low as low is the measured dispersion.

Table 3 shows that r and S_{yx} best values are those of linear regression obtained for "y = ln μg/cm^2 Pb_{2+3}" for ring 2 + 3. Indicating as "d^{Pb}_{2+3}" the lead amounts in μg/cm^2 of ring 2 + 3 and as x the firing distances from the target, the linear ratio is

$$\ln d^{Pb}_{2+3} = a_0 + a_1 x \tag{1}$$

where the values of a_0 and a_1 are reported in Table 3.

The graph in Fig. 2 shows the curve described by Eq. (1), in which the value $2S_{yx}$ is taken as the dispersion value, corresponding to approximately 95% of the points sampled (11).

With a simple graphic elaboration it is possible to identify the interval (x'–x') which gives an error measure in shooting distance evaluation, knowing lead amounts like y = ln d(Pb) [μg/cm^2].

In Table 3, various values of ln d(Pb) [μg/cm^2], calculated in well-located zones of target, underlines correspondent errors of shooting distance determination. The smaller measured error (S_{yx}) regards the ring 2 + 3; for this ring, S_{yx} value is the smaller in table (S_{yx} = 0.19).

Therefore, it can be seen, albeit simply as a trend due to the small sample, that the interval is small enough to be able to clearly distinguish distances from the target exceeding 15 cm.

The use of density instead of mass does not change the linearity as shown by the same values of r for the two measurements. Nevertheless, the use of density offers advantage over mass if is not possible to use complete rings but only partial rings.

Figure 3 shows the three curves that relate the value "ln" of the density of the rings 1, 2, and 3 to the firing distance.

The graph shows that the curve of the natural logarithms for the lead density with the firing distance is most linear at the following distances:

(1) For the first ring there is on the target a swifter lead concentration change between 5 and 35 cm.
(2) For the second ring there is on the target a swifter lead concentration change between 25 and 50 cm;
(3) For the third ring there is on the target a swifter lead concentration change between 40 and 100 cm.

These findings are evident for the values of r, a_1, and S_{yx} for indicated segments reported in Table 4.

To use second ring data for distances between 25 and 50 cm is a valid system of calculation of the firing distance as the natural logarithm of the density of lead "ln μg/cm^2"; in this experiment, the interval x'–x' indicates that the 95% confidence limit for calculated firing distances between 25 and 50 cm is only 3 cm.

TABLE 3—*For different rings and their combinations are reported the intercept (a_0), the slope (a_1), the correlation coefficients (r), and the relative standard error (S_{yx}), relatively to the total amounts of lead "μg Pb," the density "μg/cm^2 Pb," the natural logarithm of the amounts of lead, and the natural logarithm of the density.*

Elaborated values	Rings	Intercept a_0	Slope a_1	r	S_{yx}
μg Pb	1	739	−12.5	−0.44	722
	2	2498	−41.9	−0.66	1480
	3	2170	−27.1	−0.67	735
	1 + 2	3240	−54.0	−0.61	2210
	1 + 3	2910	−39.6	−0.65	2580
	2 + 3	4665	−69.0	−0.74	1970
	1 + 2 + 3	5411	−81.7	−0.69	2710
μg/cm^2 Pb	1	238	−4.03	−0.44	249
	2	69.0	−1.15	−0.66	40.9
	3	17.5	−0.22	−0.67	5.97
	1 + 2	82.4	−1.38	−0.61	56.2
	1 + 3	22.8	−0.31	−0.65	10.9
	2 + 3	29.1	−0.43	−0.74	12.3
	1 + 2 + 3	33.1	−0.50	−0.69	16.6
ln μg Pb	1	5.57	−0.03	−0.64	1.49
	2	8.65	−0.10	−0.93	1.52
	3	9.05	−0.07	−0.89	0.07
	1 + 2	8.16	−0.06	−0.88	1.22
	1 + 3	8.71	−0.05	−0.92	0.79
	2 + 3	9.83	−0.08	−0.97	0.52
	1 + 2 + 3	10.2	−0.08	−0.95	0.88
ln μg/cm^2 Pb	1	4.44	−0.03	−0.64	1.38
	2	5.06	−0.10	−0.93	0.80
	3	4.23	−0.07	−0.89	0.68
	1 + 2	4.49	−0.06	−0.88	1.01
	1 + 3	3.86	−0.05	−0.92	0.29
	2 + 3	4.76	−0.08	−0.97	0.19
	1 + 2 + 3	4.02	−0.08	−0.95	0.55

Lead concentrations ln μg/cm^2 Pb are related with shooting distance to evaluate the best linear regression.

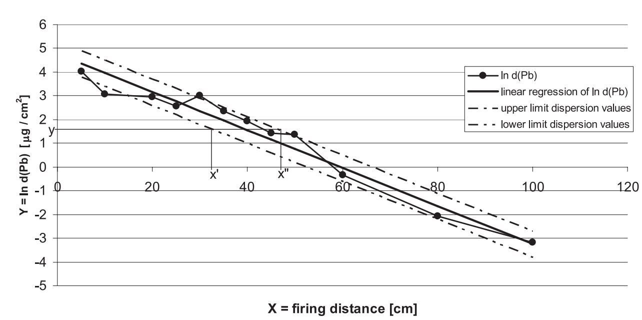

FIG. 2—*Curve described by the equation "ln d^{Pb}_{2+3} = a_0 + $a_1 l$" with a dispersion equal to $2S_{yx}$.*

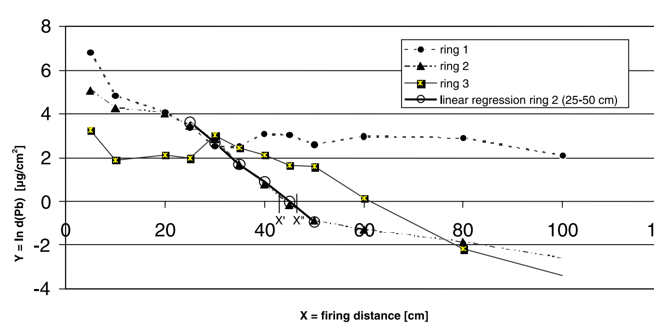

FIG. 3—*Curve "ln" of the density of lead in the three rings according to the firing distance. The best curve is obtained for the second ring, for distances between 25 and 50 cm and for this curve the confidence interval is (x′–x′) for y = 0.*

TABLE 4—*Values of* a_0, a_1, r *and* S_{yx} *of the ratios "ln* $d^{Pb} = a_0 + a_1 l$" *calculated for the three rings.*

Elaborated Values	Rings	Firing Distances (cm)	Intercept a_0	Slope a_1	r	S_{yx}
ln μg/cm² Pb	1	5–35	6.85	−0.13	−0.96	0.54
	2	25–50	8.10	−0.18	−0.99	0.05
	3	40–100	6.10	−0.97	−0.97	0.28

Values of "ln μg/cm² Pb" are easily obtained from values reported in Table 2.

Conclusions

Determination of the lead concentration on the target by atomic absorption spectroscopy (AAS) is a valid method for estimating short firing distances, up to 100 cm. Together with the usual macro and microscopic assessments of the bullet residues and the color reaction test (Rhodizonate test), we employed AAS to solve forensic cases posing greater difficulties.

The results we obtained show a linear relation between the firing distance and the lead amounts in well-defined areas of the target. This is particularly true if the densities are calculated (total amounts on the target) rather than the absolute lead amounts.

This paper shows the shooting example with short firearm (Colt 38), perpendicular to the experimental substrate target (Whatman filter paper).

The operations to be performed in practice to make a correct determination of the firing distance are therefore:

(1) To examine the weapon and cartridges used in the case, or at least an analogous weapon and cartridges;
(2) To perform correct sampling of the material present in the three rings (having, if possible, an external diameter of 1.4 cm, 5 cm, and 10.2 cm, respectively) or at least in the second and third rings, excluding the first, wiping rim. For very close distances, < 35 cm, serving to distinguish suicide from homicide, if this is not possible it may be sufficient to examine only the first ring;
(3) In case of a not perpendicular fire, to split up rings into sectors (at least four). To determine the angle of incidence determination on the target doing trial fires at various distances;
(4) Preferably on a similar target (e.g., clothes), to make a series of reference test shots at different distances to see which yields the nearest pattern, and perform the relative sampling procedures;
(5) To extract the metal (lead in the present case) in the rings on the real target and test targets, and also extract a similar sample from a target that has certainly not been hit by gunshot, as negative control; in case of stained targets (e.g., bloodstains), are requested hardest extractions (e.g., with hard acids — nitric and perchloric acid mixture — microwave oven destruction)
(6) To perform quantitative analyses searching for the metal (lead).
(7) With known internal and external diameters of the rings, to calculate the respective areas of the rings and then, for each sample, the density of the metal per cm^2.
(8) To determine the firing distance by applying the equation [$\ln dPb_{2+3} = a_0 + a_1 l$], with

dPb_{2+3} = lead μg/cm² of area 2 + 3, l = distance in cm, a_0 and a_1 are experimentally calculated:

$$a_0 = \frac{(\Sigma y)(\Sigma x^2) - (\Sigma x)(\Sigma xy)}{N\Sigma x^2 - (\Sigma x)^2} \quad a_1 = \frac{N\Sigma xy - (\Sigma y)(\Sigma y)}{N\Sigma x^2 - (\Sigma x)^2}$$

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