J Forensic Sci, Oct. 1974, Vol. 19, No. 4

*S. S. Krishnan,*[1] *Ph.D.*

# Detection of Gunshot Residue on the Hands by Neutron Activation and Atomic Absorption Analysis

Neutron activation analysis (NAA) for antimony and barium has been described as the most effective technique for the detection of gunshot residues on the hands of a suspect [*1,2*]. The method, however, is not used routinely for a number of reasons. Among the reasons are the complex nature of the statistical treatment of the data and the difficulty experienced by individual laboratories of collecting the voluminous background data required for these calculations. One of the important aspects of the technique is that the sample has to be collected with extreme care so that the contamination is minimal. Because the amounts of the elements analyzed are at microgram levels, specially designed procedures and training are required to be able to collect the samples without contamination. The existing techniques, such as paraffin lift and cotton swabbing, are found to be unsatisfactory in this respect. By taking repeated samples from hands by these procedures, it was found that three or four collections are required for complete removal of the trace elements. Thus, a single collection by these methods is not quantitative, and therefore, any subsequent calculation would be in error.

Neutron activation analysis is not effective in detecting lead, which is one of the important constituents of leakage residues. Hence, a method such as atomic absorption spectrometry (AAS) must be used in addition to NAA for this analysis. Preliminary experiments had shown that AAS is not a suitable technique for antimony and barium analysis in this application. With flame atomization, the amounts actually encountered in some samples are below the detection limits. When a heated graphite atomizer is used, the detection limits are adequate but the precision is poor. Further research efforts are, therefore, necessary before AAS can be used routinely for all three elements. Thus, the results reported by Green and Sauve [*3*] and Renshaw et al [*4*] could not be reproduced or confirmed by our attempts using the limited details given.

## Experimental

### *Neutron Activation Analysis*

The irradiation is done in a nuclear reactor yielding a thermal neutron flux of approximately $10^{13}$ neutrons $s^{-1}$ $cm^{-2}$. The radioactivity is measured with a 3 by 3-in. (76.2 by 76.2-mm) sodium iodide scintillation detector connected to a 400 channel analyzer.

Received for publication 15 Nov. 1973; revised manuscript received 7 Feb. 1974; accepted for publication 11 Feb. 1974.

[1] Chemistry Section, The Centre of Forensic Sciences, Toronto, Ontario, Canada.

*Atomic Absorption Spectrophotometry*

The measurements are made using a Perkin-Elmer 303 instrument with a Perkin-Elmer Hollow Cathode lamp and a three-slot Boling burner. The lead is determined by a standard procedure [5].

*Reagents and Chemicals*

The reagents and chemicals used were of "Analar" grade. Double-distilled and deionized water was used.

*Sample Collection*

The method of sample collection in this work is based on washing the hand with 1 *M* nitric acid. The kit supplied for this purpose consists of a plastic bottle containing 50 ml of 1 *M* nitric acid and an acid-cleaned plastic bag. The acid from the bottle is carefully poured into the bag without touching its inside. The suspect's hand is inserted into the bag, shaken for 10 to 15 seconds to wet all parts of the hand, and removed. The acid is poured back into the bottle and sent to the laboratory for analysis. It is found that a single wash as described above completely removes the entire residue from the hand. Further, because the procedure takes only a few seconds and during that time only the outsides of the bags are handled, the problem of contamination is minimal. The liquid is concentrated by freeze-drying, since it was observed that antimony is retained by the container walls if heated. If freeze-drying equipment is not available, it may be possible to extract the metals in an organic medium which can then be evaporated at room temperature. The analysis was done by the procedure shown in Fig. 1.

## Results and Discussion

*Amounts of Trace Elements Deposited*

In order to decide whether or not a person has fired a gun, six factors are considered. These are the absolute amounts of lead, antimony, and barium and the ratios of each of these amounts on one hand compared with the other. The data obtained are summarized in Tables 1 and 2.

The amounts of lead, antimony, and barium, as well as the ratios, were found to be higher on hands that have fired a gun than on normal hands. There is, however, quite a spread in the values with some overlap between the normal blank values and those obtained after firing. Thus, it seems that the concept of establishing a deposit on the hand after a firing is meaningful, although 100 percent success cannot be expected on account of this overlap of data.

## Treatment of Data

Having obtained analytical data for hand washes of normal hands and those that have fired a weapon, it is necessary to develop some criteria for establishing with some certainty whether or not a gun has been fired. All the variables involved in the study are not completely known, and the few known are of a random nature. Thus, the treatment of data has to be of a statistical nature. Schlesinger et al [2] have reported a procedure based on the bivariate normal statistical model. However, their procedure is difficult to apply directly to this or other worker's data for several reasons. First of all, it would be necessary to collect a voluminous amount of background data, particularly on occupational levels. Further, their method utilizes antimony and barium values only and

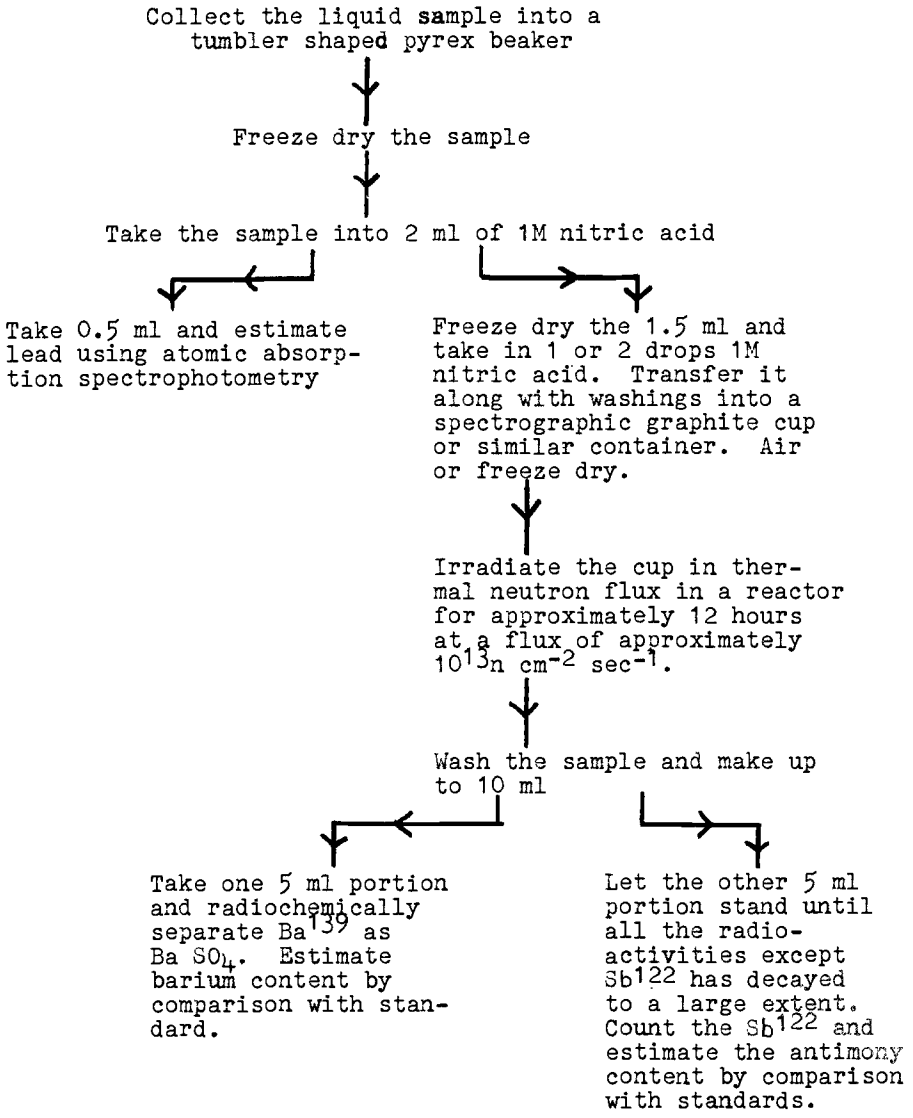


FIG. 1—*Analytical procedure.*

no account is taken of the amounts of lead or the ratios of concentration on one hand to concentration on the other. It is difficult to simplify sufficiently their statistical procedure for use in actual criminal case investigation and to be able to point out the relevance and peculiarity, if any, of the sample in a particular criminal case. Thus, the high ratios of amounts on one hand to amounts on the other are perhaps more valuable evidence at face value in a criminal case than to be able to state in a general manner that the absolute levels found are statistically significant. The statistical calculations are difficult for a jury to understand.

In this work, an alternative method of treatment of data has been developed with the above difficulties in mind. The three absolute concentration values and the three ratios

TABLE 1—*Range of amounts of trace elements found on normal hands.*

| Element | Subjects[a] | Range of Amounts | | Most Frequent Value | |
|---|---|---|---|---|---|
| | | Amount on Either Hand, μg | Amount on Right Hand/ Amount on Left Hand | Amount on Either Hand, μg | Amount on Right Hand/ Amount on Left Hand |
| Lead | 30 | <5 to 95 | 0.8/2.2 | 5 to 10 | 1.0/1.4 |
| Antimony | 23 | <0.003 to 0.94 | 0.6/2.8 | <0.02 | 0.6/1.0 |
| Barium | 12 | 0.07 to 0.27 | 0.8/1.5 | <0.2 | 0.8/1.0 |

[a] Occupation: forensic science laboratory workers.

TABLE 2—*Range of amounts of trace elements found after shooting on hands not cleaned prior to shooting: weapon—.38 revolver, ammunition—Dominion.*

| Element | Shots Fired[a] | Range of Amounts | | | Most Frequent Value | | |
|---|---|---|---|---|---|---|---|
| | | Firing Hand, μg | Nonfiring Hand, μg | Firing Hand/ Nonfiring Hand | Firing Hand, μg | Nonfiring Hand, μg | Firing Hand/ Nonfiring Hand |
| Lead | 30 | 13-326 | <10-110 | 1.0/12.4 | 35-85 | 10-40 | 1.5/2.0 |
| Antimony | 19 | 0.35-5.9 | <0.05-0.5 | 1.0/7.0 | 0.1-0.3 | <0.2 | 1.5/3.5 |
| Barium | 20 | 0.19-1.4 | 0.05-0.45 | 0.4/5.5 | 0.25-0.3 | 0.05-0.15 | 1.5/2.5 |

[a] Occupation of subjects: forensic science laboratory workers.

are all important, but not necessarily of equal value. By reference to the frequency distribution curve and particularly to the most probable values, statistical weights were attached to the different absolute amounts and the ratios. These were added to obtain a combined weight called the point count total for a particular analysis. Approximately a dozen combinations of these weights were tried, and the set of weights which gave the best differentiation of the point count index between a normal pair of hands and one involved in shooting is given in Table 3. A representative sample of the point count for normal hands and for those involved in a single firing is given in Tables 4 and 5. It is seen that a total point count higher than 5 indicates the presence of gunshot residue. By this method, a maximum success rate of 85 to 90 percent has been realized. In the remaining cases, no differentiation can be made. There are probably many reasons for this, and among them are high occupational background values or a lack of leakage residues on a particular firing.

In calculating the point count, no assumption is made as to which is the firing hand. It can be seen that if the wrong assumption is made, the point count is low, indicating that the assumption is invalid or insignificant. The results are valid when either the right or the left hand is used for firing.

### Firing Versus Handling A Gun

It has been reported [6] that firing a gun leaves residues on the back of the hand, while merely handling a recently fired weapon leaves the residue on the palm. The

TABLE 3—*Points given for various levels of trace element contents on the hand: weapon—.38 revolver, ammunition—Dominion.*

| Element | Amount, μg | Amount on Firing Hand/ Amount on Other Hand | Points |
|---|---|---|---|
| Lead | ≥85 | | 2 |
| | ≥35 | | 1 |
| | <35 | | 0 |
| | | ≥2 | 4 |
| | | ≥1.5 | 3 |
| | | <1.5 | 0 |
| Antimony | ≥0.3 | | 2 |
| | ≥0.1 | | 1 |
| | <0.1 | | 0 |
| | | ≥3.5 | 4 |
| | | ≥1.5 | 3 |
| | | <1.5 | 0 |
| Barium | ≥0.3 | | 2 |
| | ≥0.25 | | 1 |
| | <0.25 | | 0 |
| | | ≥2.5 | 4 |
| | | ≥1.5 | 3 |
| | | <1.5 | 0 |

TABLE 4—*Point count for normal hand blanks.*

| | Lead | | Antimony | | Barium | | |
|---|---|---|---|---|---|---|---|
| Subject | Amount | Ratio[a] | Amount | Ratio[a] | Amount | Ratio[a] | Total |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0 | 4 | 0 | 0 | 0 | 0 | 4 |
| 3 | 0 | 0 | 0 | 3 | 0 | 0 | 3 |
| 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 6 | 0 | 0 | 3 | 0 | 0 | 0 | 3 |
| 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11 | 0 | 0 | 0 | 3 | 0 | 0 | 3 |
| 12 | 0 | 0 | 1 | 3 | 0 | 0 | 4 |
| 13 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 14 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 15 | 0 | 0 | 1 | 3 | 0 | 0 | 4 |
| 16 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 17 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 18 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 19 | 0 | 0 | 1 | 3 | 0 | 0 | 4 |
| 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 21 | 0 | 0 | 1 | 0 | 0 | 0 | 1 |
| 22 | 0 | 0 | 2 | 3 | 0 | 0 | 5 |
| 23 | 2 | 0 | 1 | 0 | 0 | 0 | 3 |

[a] Amount on firing hand/amount on the other hand.

TABLE 5—*Point count for shots fired without prior cleaning (one shot fired with a .38 revolver and Dominion ammunition).*

| | Lead | | Antimony | | Barium | | |
|---|---|---|---|---|---|---|---|
| Subject | Amount | Ratio[a] | Amount | Ratio[a] | Amount | Ratio[a] | Total |
| 1 | 1 | 4 | 1 | 3 | 0 | 3 | 12 |
| 2 | 2 | 4 | 1 | 0 | 0 | 0 | 7 |
| 3 | 2 | 3 | 0 | 3 | 0 | 0 | 8 |
| 4 | 1 | 0 | 1 | 0 | 0 | 0 | 2 |
| 5 | 2 | 4 | 2 | 4 | 2 | 0 | 14 |
| 6 | 2 | 3 | 1 | 3 | 0 | 3 | 12 |
| 7 | 3 | 4 | 2 | 4 | 0 | 3 | 16 |
| 8 | 1 | 4 | 1 | 3 | 0 | 3 | 12 |
| 9 | 1 | 4 | 0 | 3 | 1 | 4 | 13 |
| 10 | 2 | 0 | 1 | 0 | 0 | 0 | 3 |
| 11 | 1 | 3 | 2 | 0 | 0 | 0 | 6 |
| 12 | 1 | 3 | 0 | 0 | 2 | 4 | 10 |
| 13 | 1 | 4 | 2 | 3 | 2 | 3 | 15 |
| 14 | 1 | 3 | 2 | 0 | 2 | 0 | 8 |
| 15 | 2 | 0 | 2 | 3 | 2 | 0 | 9 |
| 16 | 2 | 4 | 2 | 0 | 2 | 3 | 13 |
| 17 | 1 | 4 | 2 | 3 | 1 | 0 | 11 |
| 18 | 1 | 4 | 2 | 3 | 1 | 0 | 11 |
| 19 | 1 | 4 | 2 | 0 | 0 | 0 | 7 |
| 20 | 1 | 0 | 2 | 0 | 0 | 0 | 3 |

[a] Amount on firing hand/amount on the other hand.

experiments conducted in this work indicated that, while this may be generally true, the results are not consistent in all cases. The technique used in this work collects the samples from all areas of the hands together and, hence, it cannot determine the relative amounts on the palms and backs of the hands. However, an interesting result is that in the case of an actual firing, the point count on the firing hand is greater than 5, while for the other hand it is usually below 5. If the gun has merely been handled in a random manner, but not fired, the residues are usually left on both hands. In these instances, the point count for both hands is above 5.

### Other Guns

Preliminary experiments have been done to study the amount of residues deposited from guns other than .38 caliber revolvers. These include .22 caliber revolvers, pistols, and shotguns. Compared to the amounts of residue from .38 caliber revolvers, the .22 caliber revolver, the .22 caliber semiautomatic rifle, and the .22 caliber Cooey single-shot rifle deposit less residues. The .45 caliber semiautomatic pistol yields considerably more residues, while the .22 caliber semiautomatic pistol deposits comparable amounts. The .308 caliber semiautomatic rifle yields comparable amounts. Further work and more data are necessary to establish the method for use with other weapons.

### Trace Elements from Other Sources

Firearm discharge residues are present at a shooting scene and on the fired weapon and spent cartridges. They are easily transferred by contact and, therefore, it is possible that touching the hands of a person who has recently fired a weapon, handling a fired

weapon, removing a fired cartridge, and similar acts could leave residues on a person's hand, although he himself has not fired a weapon. However, it is found that these acts usually contaminate both hands, thereby giving point counts of greater than 5 for each hand.

### Effect of Time Lapsed Between Shooting and Sample Collection

The length of time during which the residues remain on the hands after the shooting is an important factor. This obviously depends on what is done to the hands during the interval. If the residue is easily and quickly removed in normal hand usage, the value of the technique for application to cases in which the subject is examined some hours after the incident is limited. If the residue is relatively difficult to remove in the course of normal hand activity for several days, a different problem exists. A suspect could claim that the residue found on his hand is a result of firing several days previous to the incident. The results of experiments to study this possibility show that the residue can remain for up to 17 h during normal activity, but can be quickly removed by vigorous scrubbing with soap and water. This is an encouraging and useful result.

### Blind Tests

An attempt was made to test the criteria and hypothesis developed above in simulated situations similar to those encountered in actual criminal cases. Test shots were fired by some members of a group and not by others. The samples were taken immediately after the firing in order to simulate suicide situations. In other similar tests, the samples were taken two hours later to simulate holdup situations. The actual identities of the individuals who had fired the guns were not known to the analyst and their identities were revealed only after the final reports were made. The results are given in Tables 6 and 7. These results indicate that the concept of the method developed for deducing that an individual has recently fired a gun is meaningful. Correct deductions were arrived at in seven out of ten firings. No false positives were obtained; that is, in no case was a firing indicated by the analysis when it had not, in fact, occurred.

In order to test the method completely, gunshot residue collection kits were given to police officers. They conducted blind tests similar to the above series using mainly laboratory workers, collected the samples themselves, and sent them to the laboratory for analysis. The results of the analysis are given in Table 8. The results were excellent

TABLE 6—*Results of blind tests to simulate suicide situations: weapon—.38 revolver, ammunition—Dominion. Samples taken immediately after shooting.*

| Subject[a] | Point Count | | Report Turned In | Actual incident |
|---|---|---|---|---|
| | Right Hand | Left Hand | | |
| 1 | 5 | 5 | no evidence of gunshot residue | fired one shot with right hand |
| 2 | 8 | 7 | evidence of residue | fired with both hands |
| 3 | 3 | 3 | no evidence of residue | fired one shot with right hand |
| 4 | 4 | 3 | no evidence of residue | did not fire |
| 5 | 9 | 0 | evidence of residue on right hand | fired one shot with right hand |

[a] Laboratory workers.

TABLE 7—*Results of blind tests to simulate holdup situations: weapon—.38 revolver, ammunition—Dominion. Samples taken 2 h after the shooting.*

| Subject[a] | Point Count Right Hand | Left Hand | Report Turned In | Actual Incident |
|---|---|---|---|---|
| 1 | 1 | 4 | no evidence of gunshot residue | fired one shot with right hand |
| 2 | 6 | 1 | evidence of residue on right hand | fired one shot with right hand |
| 3 | 3 | 0 | no evidence of residue | did not fire |
| 4 | 3 | 4 | no evidence of residue | did not fire |
| 5 | 6 | 1 | evidence of residue on right hand | fired one shot with right hand |

[a] Laboratory workers.

TABLE 8—*Blind tests conducted by police officers: weapon—.38 revolver, ammunition: Dominion. Samples taken immediately after shooting.*

| Subject[a] | Point Count Right Hand | Left Hand | Report Turned In | Actual Incident |
|---|---|---|---|---|
| 1 | 13 | 0 | evidence of residue on right hand | fired one shot with right hand |
| 2 | 0 | 0 | no evidence of residue | did not fire or handle gun |
| 3 | 10 | 5 | evidence of residue on right hand | fired one shot by right hand and removed spent cartridge |
| 4 | 5 | 1 | slight evidence of residue on right hand | fired using both hands |
| 5 | 10 | 2 | evidence of residue on right hand | fired one shot with right hand |
| 6 | 3 | 11 | evidence of residue on left hand | fired with right hand and removed cartridges |
| 7 | 6 | 12 | evidence of residue on both hands | handled and removed cartridges from fired weapon, did not fire |
| 8 | 13 | 0 | evidence of residue on right hand | fired one shot with right hand |
| 9 | 10 | 0 | evidence of residue on right hand | did not fire or handle gun |
| 10 | 11 | 0 | evidence of residue on right hand | fired one shot with right hand |

[a] Laboratory workers except for Subjects 3 and 9, who are police officers.

except for Subject 9. The results for Subject 9 appear to be a false positive, the only such one in all the tests conducted. Discussions have revealed that the subject is a police officer and regularly carries a gun. Therefore, it appears that the method may not always be applicable to people such as police officers who may frequently handle or fire guns.

When the technique gives a point count greater than 5 for one hand and lower than 5

for the other, then it is clearly indicative that the subject has fired a gun. In instances where the point counts for both hands are greater than 5, other possibilities such as contamination, firing with both hands, partial washing of the hands, and several others exist and these must be carefully considered.

It has been reported that the trace elements discussed in this work arise from the primer composition. Although this may well be true, no conclusive experimental evidence exists that these elements originate in their entirety from the primer. In our opinion, it is possible that certain amounts of the trace elements arise from other parts of the ammunition as well. The presence of leakage residues is decided by several factors, among these the ammunition composition and the type of gun. Thus, when encountered with a case involving, for example, a .22 caliber revolver with ammunition having no antimony or barium in the primer, it would still be necessary to perform test firings in order to decide that leakage residues would not be emanated from the gun and ammunition.

## Summary

A practical and effective method of detecting firearm discharge residues on hands is reported. This involves the quantitative determination of lead by atomic absorption spectrophotometry and antimony and barium by neutron activation analysis. A procedure is developed in which a criterion is established for distinguishing between hands that have fired a weapon and those that may not have fired one. This is based on the absolute amounts of the trace elements and the ratios of these on one hand to the other. Collection of voluminous background data is not required. The method has been successfully tested in twenty simulated case situations and is ready to be presented in court.

*Acknowledgments*

The author wishes to acknowledge the excellent cooperation and help of the director, D. M. Lucas, Mr. E. G. Clair, Mr. R. C. Nichol, and the members of the Firearms and Chemistry Sections of the Centre of Forensic Sciences.

## References

[1] Krishnan, S. S., "Rapid Detection of Firearm Discharge Residues by Atomic Absorption and Neutron Activation Analysis," *Journal of Forensic Sciences*, JFSCA, Vol. 16, 1971, pp. 144-151.

[2] Schlesinger, H. L., Lukens, H. R., Guinn, V. P., Hackleman, R. P., and Korts, R. F., "Special Report on Gunshot Residues Measured by Neutron Activation Analysis," Gulf General Atomic Inc. Report No. GA-9829, 1970.

[3] Green, A. L. and Sauve, J. P., "The Analysis of Gunshot Residue by Atomic Absorption Spectrophotometry," *Atomic Absorption Newsletter*, Vol. 11, 1972, pp. 93-95.

[4] Renshaw, G. D., Pounds, C. A., and Pearson, E. F., "The Quantitative Estimation of Lead, Antimony and Barium in Gunshot Residues by Non-Flame Atomic Absorption Spectrophotometry," *Atomic Absorption Newsletter*, Vol. 12, 1973, pp. 55-56.

[5] Gillespie, K. A. and Krishnan, S. S., "Analysis of Lead Shot—A Comparison of Analysis Using Atomic Absorption Spectrophotometry and Neutron Activation Analysis," *Canadian Society of Forensic Science Journal*, Vol. 2, 1969, pp. 95-103.

[6] Guinn, V. P., private communication, 1972.

The Centre of Forensic Sciences
8 Jarvis St.
Toronto, Ontario, Canada
M5E 1M8