Prasanta Sen,[1] *Ph.D.; Nokuleswar Panigrahi,*[1] *M.S.; M. S. Rao,*[2] *M.S.; K. M. Varier,*[3] *Ph.D.; Sudhir Sen,*[3] *Ph.D.; and G. K. Mehta,*[3] *Ph.D.*

Application of Proton-Induced X-Ray Emission Technique to Gunshot Residue Analyses

REFERENCE: Sen, P., Panigrahi, N., Rao, M. S., Varier, K. M., Sen, S., and Mehta, G. K., **"Application of Proton-Induced X-Ray Emission Technique to Gunshot Residue Analyses,"** *Journal of Forensic Sciences,* JFSCA, Vol. 27, No. 2, April 1982, pp. 330–339.

ABSTRACT: The proton-induced X-ray emission (PIXE) technique was applied to the identification and analysis of gunshot residues. Studies were made of the type of bullet and bullet hole identification, firearm discharge element profiles, the effect of various target backings, and hand swabbings. The discussion of the results reviews the sensitivity of the PIXE technique, its nondestructive nature, and its role in determining the distance from the gun to the victim and identifying the type of bullet used and whether a wound was made by a bullet or not. The high sensitivity of the PIXE technique, which is able to analyze samples as small as 0.1 to 1 ng, and its usefulness for detecting a variety of elements should make it particularly useful in firearms residue investigations.

KEYWORDS: criminalistics, gunshot residues, radiography

The small size of gunshot residue samples and the need for preservation of physical evidence for possible later use put restrictions on the scientific techniques available to evaluate their significance. For precisely this reason destructive analytical techniques such as wet chemistry, atomic absorption, or emission spectroscopy might not be very convenient for characterizing the presence of certain specific elements present in small quantities as traces. The above-mentioned techniques, in contrast to the technique described here, proton-induced X-ray emission (PIXE), lack the required sensitivity and involve time-consuming exercises for a complete multielement analysis of a few samples. The multielement analytical technique known as neutron activation analysis (NAA) has its own limitations [*1*]. Radiochemical separation may be necessary for the NAA technique and may require several days to complete. Moreover, it is insensitive to the presence of lead, an important element in gunshot residue studies. Multielement analysis employing X-ray fluorescence could be quite useful. Identification of gunshot residues on the hands by a scanning electron microscope

A portion of this work was presented in the *Proceedings of Nuclear Physics and Solid State Physics Symposium,* Bombay, 28–31 Dec. 1978, organized by the Department of Atomic Energy, Government of India. Received for publication 5 Aug. 1981; accepted for publication 23 Oct. 1981.

[1]Assistant professor and doctoral fellow, respectively, Institute of Physics, Bhubaneswar-751007, India. Dr. Sen is currently with the Saha Institute of Nuclear Physics, Calcutta, India, and Mr. Panigraphi is with the department of Physics, Case Western Reserve University, Cleveland, OH.

[2]Scientific officer, District Forensic Science Laboratory, Sambalpur-768001, India.

[3]Postdoctoral fellow, assistant professor, and professor, respectively, Department of Physics, Indian Institute of Technology, Kanpur-208016, India.

equipped with energy dispersive X-ray analysis capabilities has been described in detail by Wolten et al [2].

The work of Wolten et al [2] thoroughly documents the state of the art so far as studies of hand swabs are concerned. However, it does not say anything about gunshot residue profile studies for estimating the firing distance, which will be discussed below for the present investigation. Moreover, the X-ray cross section for electrons is about the same in the 10 to 100 keV range as for MeV protons. The background, which is dominated by direct bremsstrahlung produced by the beam, is much greater, however, because of the smaller mass of the electron. This gives an increased background compared with proton excitation, between three and four orders of magnitude higher. Hence, the limit of detection is rather higher, as has been pointed out by Johansson and Johansson [3].

The present paper gives results obtained by the PIXE technique on firearms identification and related problems. The discussion includes the sensitivity of the technique, its nondestructive nature, and its role in determining the distance from the gun to the victim and identifying the type of bullet used and whether a wound was made by a bullet or not. Some recent articles on firing distance are given as references [4–10]. To the best of our knowledge, this is the first time that the PIXE technique has been applied extensively to study the firearms residue problem in forensic science. Several review articles [11–13] and the references therein summarize the theoretical aspects of the PIXE technique.

Materials and Methods

A proton beam accelerated by the 2-MV Van de Graaff accelerator at the Indian Institute of Technology in Kanpur was momentum-analyzed, focused by quadrupole magnets, and allowed to pass through a system of collimators and was incident on a target at the center of a specially designed scattering chamber. The X-rays emitted from the target were detected by a Si(Li) photon detector and analyzed in a multichannel analyzer. Some of the features of the experimental setup are described further below. The experimental arrangement may be broadly divided into three parts: target preparation, the scattering chamber and beam collimators, and the X-ray detector system and its accessory electronics.

Target Preparation

The preparation of suitable targets is of prime importance in PIXE analysis. For the firearm discharge studies, the targets were prepared under laboratory conditions by firing different types of bullets onto a pair of Whatman filter papers, as shown in Fig. 1. The firing distances used were 15, 25, 38, 76, 127, and 250 cm. The back filter paper blocked possible contamination by recoil from the backing material onto the front filter paper. All the firings except three were performed with cotton wool as the backing material for the filter paper target. In the remaining three cases, the backing materials used were aluminum, glass, and goat meat.

The targets were placed inside the scattering chamber facing the proton beam at 45°, as shown in Fig. 2. Five specimens could be mounted at a time inside the target chamber, permitting tests to be run one after another on all five specimens without breaking the scattering chamber vacuum.

Scattering Chamber and Beam Collimation

The scattering chamber, which was made of aluminum, was cylindrical and coupled with a Si(Li) detector as shown in Fig. 2. The chamber had viewing ports, a multiple target holder, a Faraday cup with electron suppressor, and graphite collimators for the Si(Li) detector. An externally operated filter wheel containing Mylar® filters of different thicknesses

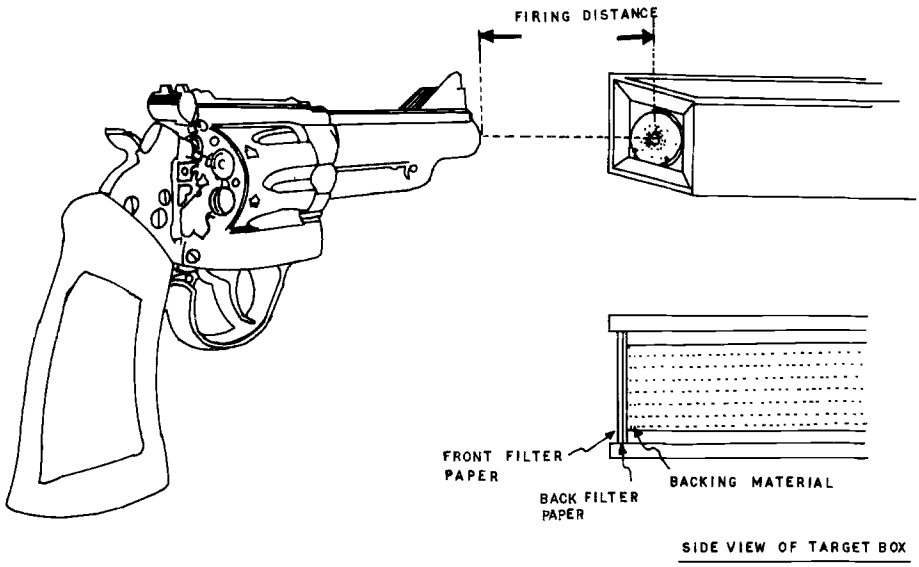

FIG. 1—*Preparation of the targets.*

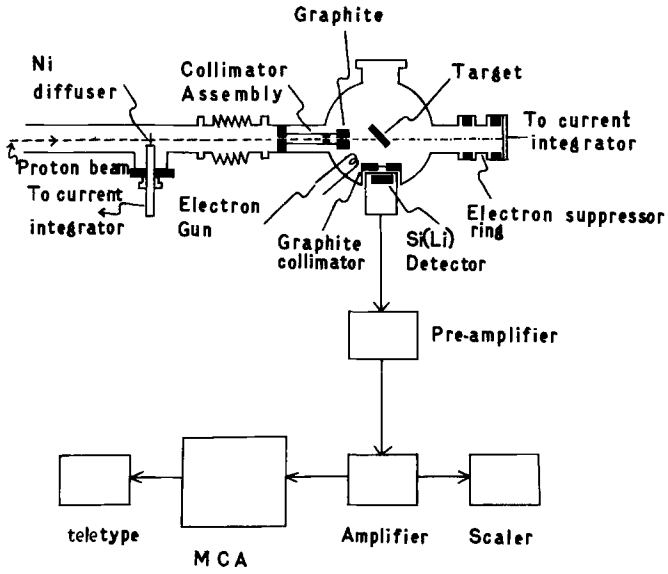

FIG. 2—*Scattering chamber, showing the target placement and the detector assembly.*

and located in front of the graphite collimator was used to absorb low energy X-rays whenever necessary for controlling the count rate. An electron gun facing the target was used to neutralize the positive charge build-up encountered in nonconducting and thick targets. The use of the electron gun considerably reduced the background coming from bremsstrahlung radiation in the PIXE spectrum.

In order to obtain a homogeneous beam, protons were allowed to pass through a 0.4-μm-

thick nickel diffuser foil. The size of the diffused beam spot on the target was limited by a set of collimators. In firearm discharge element profile studies, one of the collimators was restricted to a small hole, 1.00 mm in diameter, to define precisely the position of the proton beam spot on the target. The charge collected on the nickel foil served as a monitor of the proton flux on the target. The validity of charge normalization by monitoring the diffuser foil charge for the thick target was checked by using thin targets.

Detector Systems

A high-resolution ORTEC Si(Li) X-ray detector having a resolution (full width at half maximum intensity) of 170 eV at 6.3 keV was used in the present investigation. The detector was placed at 90° to the incident beam. This arrangement allowed the detector to be moved very close to the target so that a larger solid angle could be used. The pulses from the cooled-FET (field effect transistor) preamplifier were fed into a research amplifier (ORTEC 450) and then to a multichannel analyzer and a scalar. The count rate at the detector was kept less than 1000 cps to avoid any deterioration in the system resolution resulting from pile-up effects. The count rate was also controlled with the help of a filter wheel containing four replaceable Mylar X-ray filters of varying thicknesses that could be placed between the target and the detector. The particular Mylar filter was selected according to the known X-rays of the target in use. The multichannel analyzer was calibrated from the known X-ray energies emitted by standard nuclear sources like ^{57}Co and ^{241}Am to determine the energies of the observed X-ray peaks. Further details of the complete experimental setup are given elsewhere [*14-16*].

Results and Discussion

The results have been grouped as follows: (1) investigations of the type of bullet used and bullet hole identification, (2) firearm discharge element profile studies for determining firing distance, (3) the effect of various backing materials on the pattern caused by the bullet, and (4) residue studies of hand swabbings.

Type of Bullet and Hole Identification

Figure 3 represents one typical PIXE spectrum taken by irradiating the contact ring (bullet hole entrance) with the proton beam. This clearly shows the presence of the major firearm discharge elements, namely barium, tin, and lead. The expected L line X-ray peaks of antimony from firearm discharge are masked by the large K line X-ray peaks of calcium originating from the filter paper. The other small peaks in the spectrum result from impurities in the bullet materials. For bullet holes from a copper-jacketed bullet, the spectrum shows strong copper peaks, which were not observed in the case of an unjacketed bullet. This demonstrates that just by irradiating the contact ring with the proton beam, one can readily determine whether the bullet was copper-jacketed or not. Two kinds of cartridges were used for the present investigation and the firearm used was a .38 caliber Webly & Scott revolver No. 2213. The nature and pattern are similar for the PIXE spectra obtained using copper-jacketed Kirkee Factory (KF) .38 revolver cartridges, as is the case with the PIXE spectra obtained by firing unjacketed KyNOC® .38 Smith & Wesson cartridges. It is hoped that the distinctive nature of the PIXE spectra obtained from the contact ring might be sufficient to determine whether a wound was made by a bullet or not.

Firearm Discharge Element Profile Studies

Spectra were taken for gunshot residue samples 2, 4, and 6 mm away from the contact ring. Such spectra were also taken along the four radial directions (north, south, east, and

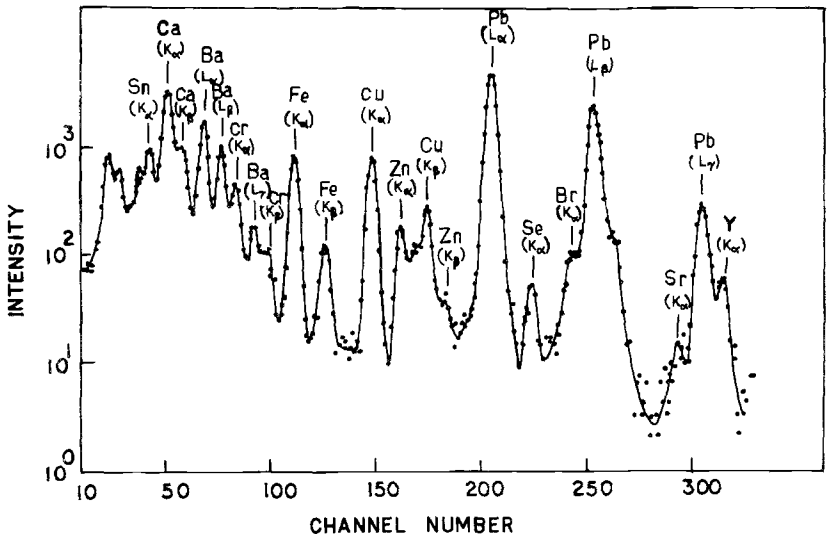

FIG. 3—*Typical PIXE spectrum of the contact ring (bullet hole entrance) of an unjacketed bullet. The energy calibration is 1 channel = 43.5 eV.*

west) by cutting four strips of filter paper along these directions and subsequently irradiating them. After the PIXE run they were reassembled; Fig. 4 illustrates the nondestructive nature of the PIXE technique. The spots represent the points where the proton beam hit the target while recording PIXE spectra.

From each PIXE spectrum the intensities of the firearm discharge elements barium, copper, iron, and lead were calculated and normalized to the respective proton beam charges. Figure 5 shows the radial distribution of the intensities of the various elements for a firing distance of 15 cm. Such data were also plotted for firing distances of 25, 38, and 76 cm (these plots are not shown). For longer firing distances no profile studies could be made as the intensities decreased sharply. The radius of the contact ring was also taken into account in these plots so that the distances plotted on the x axis measured the same as the distance from the center of the contact ring. The intensity of the peak decreased with the radial distance, but the firearm discharge elements could be detected even for radial distances of 40 mm for some firing distances. The profiles also showed a systematic decrease in the intensity of the peaks of the respective elements with increases in firing distance. For the cases of the firing distances of 127 and 250 cm no profile could be obtained because of the sharp decrease of intensity away from the center of the hole. However, the contact rings still indicated the presence of the firearm discharge elements. Element profiles were also plotted so as to show a direct comparison among the intensities at different firing distances. Figure 6 gives such a plot for lead for four firing distances, 15, 25, 38, and 76 cm. From comparisons with firearm discharge element profiles corresponding to known firing distances obtained by firing known sets of bullets it might be possible in an actual case to identify the type of the bullet used and to make a tentative assignment of the firing distance.

Targets with Various Backings

The placement of the two filter papers (Fig. 1) and variations in the backing material had a marked effect on the back filter paper [*17*]. To check this, a glass plate, an aluminum plate, and goat meat were used as backings. For the firearm discharge element profile

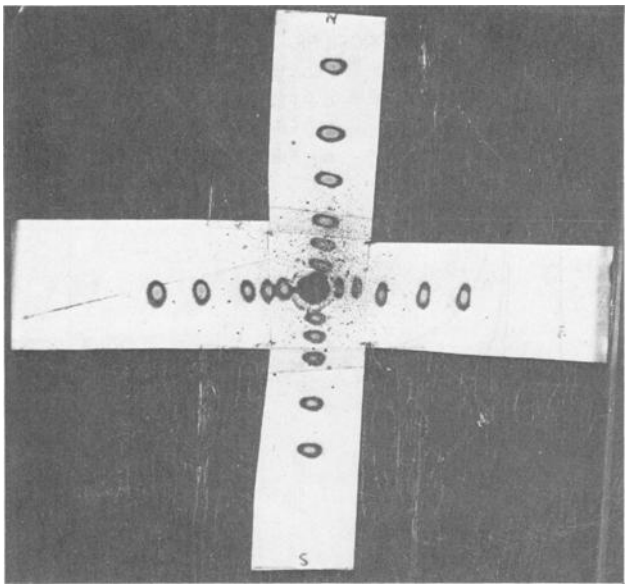

FIG. 4—*Assembled proton-irradiated target strips used in the study of the variation of the profile along the four directions for a copper-jacketed bullet fired at 15 cm.*

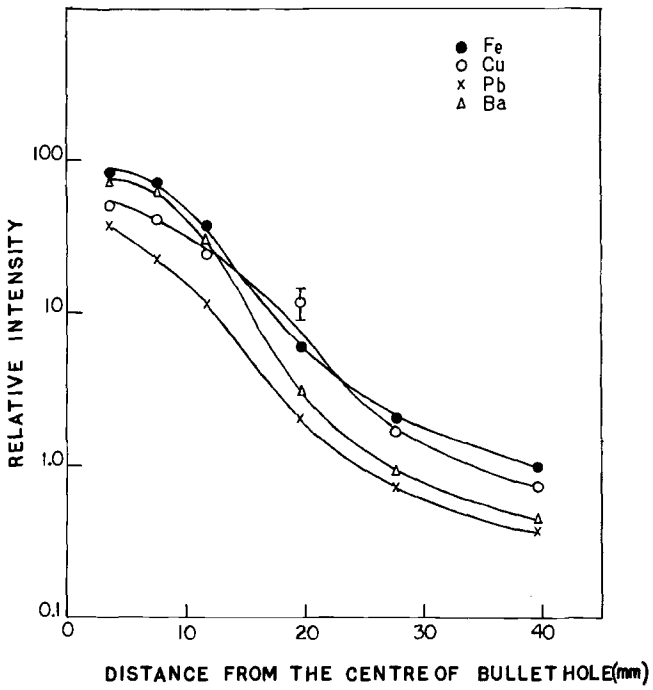

FIG. 5—*Radial distribution of the intensities of the firearm discharge elements for firing distance of 15 cm. Representative error bars are shown.*

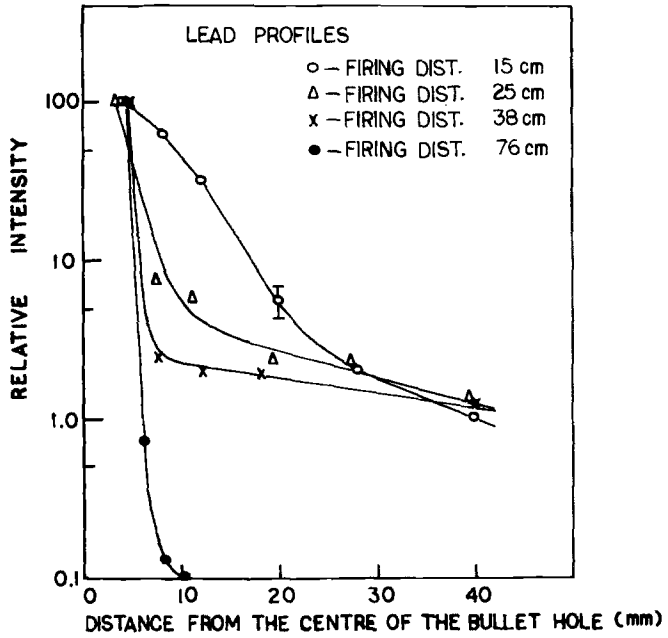

FIG. 6—*Radial distribution of the intensity of lead for various firing distances—15, 25, 38, and 76 cm. Representative error bars are shown.*

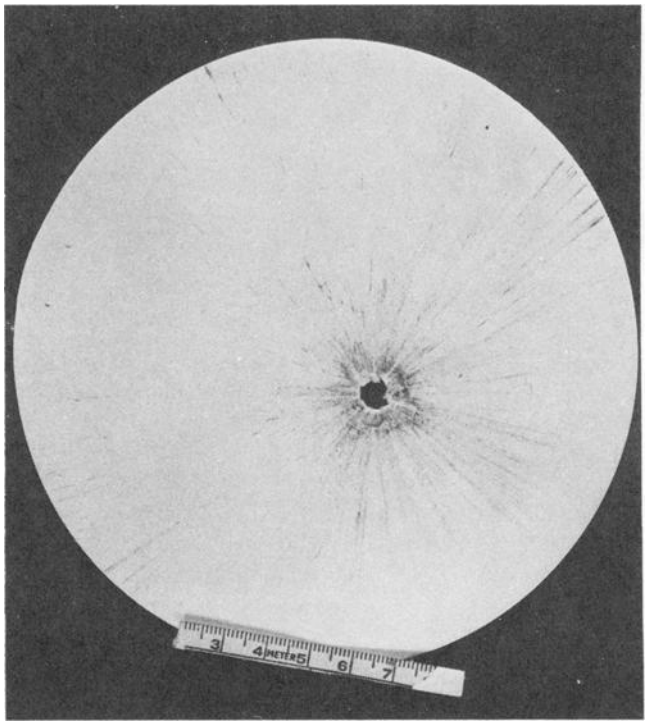

FIG. 7—*Photograph of the side of the back filter paper that was in contact with the glass backing (firing distance of 180 cm).*

studies cotton wool was generally used as the backing material; there was no visible effect on the face of the back filter paper touching the cotton wool. Similar results were observed with the aluminum and meat backings, although the PIXE spectra at the contact rings showed traces of lead and some other associated elements. Glass, however, gave very different results. Figure 7 shows a photograph of the side of the back filter paper that was in contact with the glass backing. Figure 8 presents two PIXE spectra taken at the contact ring and 4 mm away from the contact ring, along one of the black streaks shown in Fig. 7. It clearly shows the dominance of lead over other firearm discharge elements. The PIXE spectra from the back filter papers used with aluminum and goat meat backings did not show any significant presence of the gunshot residue elements.

Swabbing

Swabbings from the back of the hand, if taken early from suspects, can be valuable to a forensic science investigator, assuming that the suspect has not cleaned off his hands by washing or rubbing. By subjecting the swabs to PIXE studies it might be possible to detect the presence of the firearm discharge elements on the back of the hand. Keeping this in

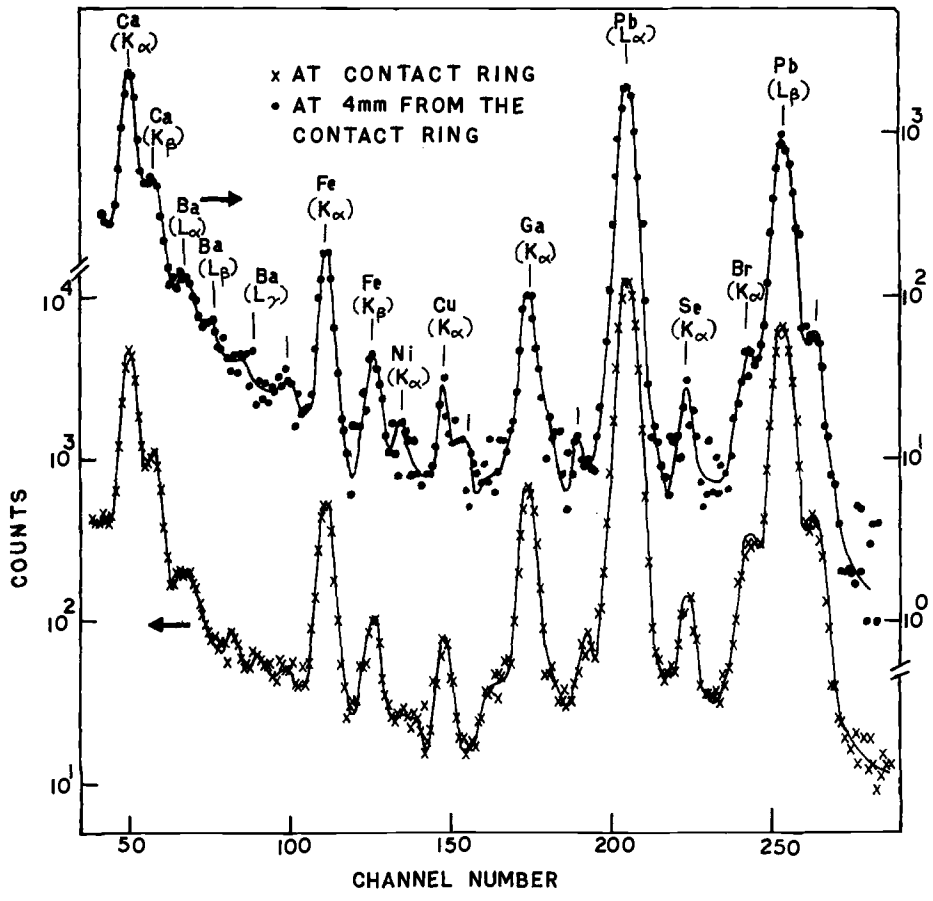

FIG. 8—*The PIXE spectrum taken at the contact ring and at a point 4 mm distant from the contact ring along a black streak from Fig. 7. The energy calibration is 1 channel = 43.5 eV. The arrows indicate the relevant scales for the two spectra.*

mind various swabbings of firearm discharges on the back of the hand were taken on Whatman filter papers moistened with dilute acetic acid. These filter papers were subjected to PIXE studies. Figure 9 represents one such typical PIXE spectrum. The PIXE spectrum taken from the hand swabbing clearly showed the presence of the firearm discharge elements copper, lead, iron, tin, and barium.

Summary and Conclusions

The PIXE technique has been applied to study the firearms residue problem in forensic science. Studies of firearm discharge element profiles around the bullet hole entrance have indicated that the firing distance could be estimated by the PIXE technique. This technique can also be used to identify the type of bullet and the cause of a wound—that is, whether it was made by a bullet or not. Spectra from hand swabs show that the sensitivity of the PIXE technique can help to screen out suspects who have not handled a gun.

The high sensitivity of the PIXE technique, which is able to analyze samples as small as 0.1 to 1 ng, and its usefulness for detecting a variety of elements, should make it particularly valuable in firearms residue investigations.

Acknowledgments

The authors thank the technical staff of the Van de Graaff Laboratory at the Indian Institute of Technology for their cooperation during the running of the tests. Discussions with and encouragement from Professor T. Pradhan, director of the Institute of Physics in Bhubaneswar, Mr. B. K. Ray, former police inspector general in Orissa, and Mr. S. S. Mahapatra, assistant director of the State Forensic Science Laboratory in Orissa, are appreciated. This

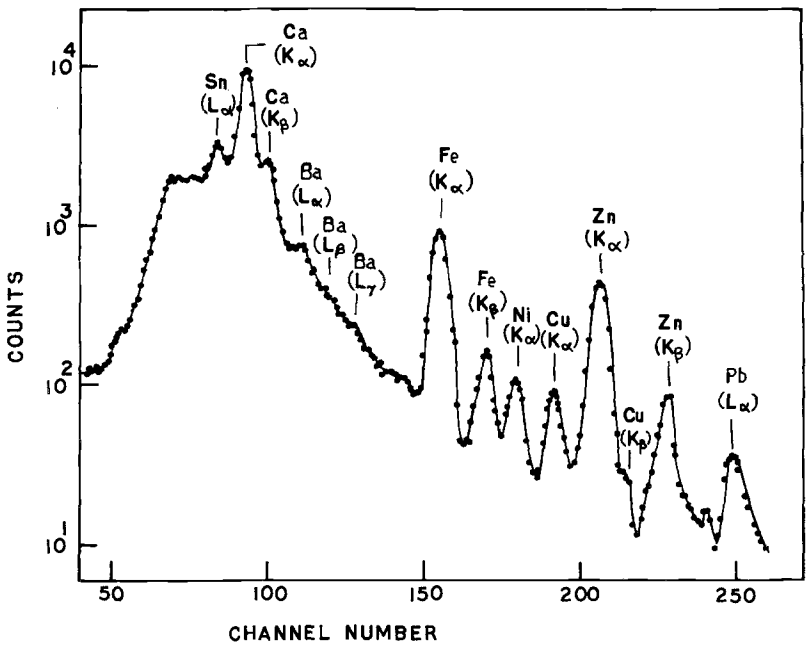

FIG. 9—*Typical PIXE spectrum of a hand swab taken after firing. Then energy calibration is 1 channel = 43.8 eV.*

work was partially supported by a research grant from the Department of Science and Technology, Government of India.

References

[1] Cooper, J. A., *Industrial Research,* Vol. 19, 1977, pp. 22-26.

[2] Wolten, G. M., Nesbitt, R. S. Calloway, A. R., Loper, G. L., and Jones, P. F., "Particle Analysis for the Detection of Gunshot Residue. I: Scanning Electron Microscopy/Energy Dispersive X-Ray Characterization of Hand Deposits from Firing," *Journal of Forensic Sciences,* Vol. 24, No. 2, April 1979, pp. 409-422.

[3] Johansson, S. A. E. and Johansson, T. B., "Analytical Application of Particle-Induced X-Ray Emission," *Nuclear Instruments and Methods,* Vol. 137, No. 3, Sept. 1976, pp. 473-516.

[4] Burger, H. and Neuninger, H., "Determination of Firing Distance by X-Ray Fluorescence and Emission Spectrographic Techniques," *Archiv für Kriminologie,* Vol. 146, 1970, pp. 11-16.

[5] Barnes, F. C. and Helson, R. A., "An Empirical Study of Gunpowder Residue Patterns," *Journal of Forensic Sciences,* Vol. 19, No. 3, July 1974, pp. 448-462.

[6] Krishnan, S. S., "Firing Distance Determination by Atomic Absorption Spectrophotometry," *Journal of Forensic Sciences,* Vol. 19, No. 2, April 1974, pp. 351-356.

[7] Menke, H., Leszcynski, C., and Weber, M., "Determination of Gunshot Residues by Neutron Activation Analysis," *Journal of Radioanalytical Chemistry,* Vol. 15, No. 1, Sept. 1973, pp. 27-32.

[8] Guinn, V. P., "Application of Nuclear Science in Crime Investigation," *Annual Review of Nuclear Science,* Vol. 24, 1974, pp. 561-591.

[9] Schmitz, J., "Experience with the Method of Autoradiography for Firing Distance Determination," *Journal of Radioanalytical Chemistry,* Vol. 15, No. 1, Sept. 1973, pp. 219-228.

[10] Schontag, A. and Suchenwith, F., "A Method for the Determination of Short Range (0.5- to 5-cm) Firing Distance," *Archiv für Kriminologie,* Vol. 146, 1970, pp. 62-68.

[11] Garcia, J. D., "Inner-Shell Ionization by Proton Impact," *Physical Review Annual,* Vol. 1, No. 2, Feb. 1970, pp. 280-285.

[12] Hansteen, J. M. and Mosebekk, O. P., "Atomic Coulomb Excitation by Heavy Charged Particles," *Nuclear Physica Acta,* Vol. 201, No. 3, Feb. 1973, pp. 541-560.

[13] Meyrhof, W. E. and Taulbjerg, K., "K-Shell Ionization in Heavy-Ion Collisions," *Annual Review of Nuclear Science,* Vol. 27, 1977, pp. 279-332.

[14] Sen, S., Varier, K. M., Mehta, G. K., Rao, M. S., Sen, P., and Panigrahi, N., "Application of the Proton-Induced X-Ray Emission (PIXE) Technique to the Study of Problems in Forensic Science," *Nuclear Instruments and Methods,* Vol. 181, No. 1-3, March 1981, pp. 519-521.

[15] Sen, P., Mahapatra, D. P., Panigrahi, N., Rao, M. S., Varier, K. M., Mehta, G. K., and Sen, S., "Studies of Forensic-Related Trace Elemental Problems by the Particle-Induced X-Ray Emission (PIXE) Method," *Proceedings of the Nuclear Physics and Solid State Physics Symposium,* Vol. 21B, Department of Atomic Energy, Government of India, Bombay, 1978, p. 301.

[16] Sen, S., Mehta, G. K., Varier, K. M., Sinha, A. K., Jha, K. M. L., and Masood, K., "Trace Element Analysis by Proton-Induced X-Ray Emission," Technical Report VDG/15/79, Indian Institute of Technology, Kanpur, India, 1979.

[17] Messler, H. R. and Armstrong, W. R., "Bullet Residue as Distinguished from Powder Pattern," *Journal of Forensic Sciences,* Vol. 23, No. 4, Oct. 1978, pp. 687-692.

Address requests for reprints or additional information to
P. Sen, Ph.D.
Saha Institute of Nuclear Physics
92, Acharya Prafulla Ch. Road
Calcutta—700 009, India