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Firearms Discharge Residue Sample Collection Techniques

Several tests have been employed by law enforcement agencies to demonstrate that an individual has handled or discharged a firearm. With the paraffin test being of doubtful reliability [*1*] and the sodium rhodizonate spot test lacking sensitivity [*2*], the most commonly used test for firearms discharge residue is the measurement of barium and antimony (Ba and Sb), principally from the primer composition, deposited on the hands during weapon handling or discharge. However, this test is of limited effectiveness, even under optimal conditions. One study [*3*] has reported a 15% failure to indicate the presence of residue in a series of test firings. Factors responsible for this inefficiency include variable residue deposition, residue retention, and effectiveness of sample collection. Our study examines several sample collection materials to define a system which will combine high lifting efficiency for gunshot residue components with convenience of use in the field. Until recently, hand lift samples were examined for these two elements primarily by neutron activation analysis (NAA) [*4–6*]. While NAA affords excellent sensitivity for Ba and Sb, it suffers from long analysis time, high cost, and limited availability of neutron sources. The inherent simplicity and high sensitivity of flameless atomic absorption spectrometry (FAAS) have prompted several investigators to utilize this technique to determine trace quantities of Ba and Sb (and occasionally copper and lead) present in gunshot residues [*7–9*].

A number of collection materials have been used for removal of residues from the hands of one suspected of having recently discharged a firearm. The cotton swab sample collection technique developed in our laboratory [*10*] is currently the most commonly employed method for the collection of samples in actual case investigation situations. Despite its wide application, the efficiency of the cotton swab system is unknown. It has been reported [*11*] that it is less effective than the "paraffin glove" used previously, or an acid spray of the hands followed by swabbing with cotton balls. Filter paper moistened with nitric acid has also been utilized [*12*]. Other methods proposed include lifting the gunshot residue with films made from solutions of film-forming polymers [*13,14*] and rinsing the hands with a dilute acid solution either directly [*15*] or in a plastic bag [*16*]. Operationally, several of these proposed sampling procedures pose problems, either in the field or in the laboratory. Paraffin hand lifts are especially cumbersome, both for on-the-scene use by the investigator and in the laboratory. The major advantages of paraffin are its extremely low background levels of Ba and Sb and the ability to examine the lift microscopically for visible residue. When large portions of cotton are used either in the form of balls or gauze, difficulty is

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encountered in effective leaching with small volumes of solution. Therefore, larger volumes may require preconcentration or chemical separations to obtain adequate sensitivity for analysis. Either of these is undesirable when large numbers of samples are involved. Similar difficulties are encountered with rinsing of the hands, since the relatively large volumes of solution obtained will require either time-consuming concentration prior to analysis, or chemical separations which afford opportunity for both contamination and loss of part of the element of interest. When extraction of Ba is used for sample concentration, serious losses may occur [*17*].

Of the various collection systems currently in use, only cotton swabs and film-lifting procedures appeared to combine ease of use in the field with suitability for rapid laboratory examination by FAAS. However, one additional material, transparent adhesive tape, also appeared suitable for routine use. This material is readily available, inexpensive, convenient to use, and amenable to reproducible sample collection. An added advantage of tape as a collection material is that the sample can be examined microscopically for particles of partially burned gunpowder or bullet lead fragments, as is often done with paraffin lifts. When detected, these provide a much more definitive identification of weapon discharge than measurement of Ba and Sb levels. For evaluation purposes, three candidate materials—cotton swabs on plastic shafts, high purity cellulose acetate in acetone ("Film Lift," prepared by Pennsylvania State University), and Scotch® Brand transparent adhesive tape—were selected. The material desired was one which would have low background levels of both Ba and Sb and good lifting efficiency for recovery of gunshot residues from the hands, and which would be convenient for use in the field as well as for rapid processing in the laboratory.

Experimental

Instrumentation and Equipment

A Jarrell-Ash Model 810 dual-channel double-beam atomic absorption spectrophotometer, equipped with a tantalum strip atomizer, was used for Ba and Sb determinations. Instrument-operating parameters, preparation of analytical curves, and sample-handling procedures have been previously described [*9*]. Plastic containers free of Ba and Sb were used throughout for sample and solution storage to avoid possible contamination, particularly Ba when glass containers are used [*18*]. Glazed ceramic crucibles were used for convenience for ashing Film Lift and adhesive tape samples, although platinum may be preferable. Blanks showed no Ba or Sb pickup from ceramic crucibles. A four-hour ashing period in a muffle furnace at 375°C was used in this work, but previous experience with cotton swabs ashed in a plasma furnace indicates that this technique would also be satisfactory.

Results

Recovery Studies Using Transparent Tape

Background levels of Ba and Sb in the tape were determined using samples of ¾-in. tape (approximately 3 in. long) taken from each of three rolls of tape. Samples were ashed for 4 h at 375°C. The ash residue was taken up in 1 ml of 1*M* HNO_3 and transferred to a plastic vial. A 10-μl aliquot of this solution was analyzed for both elements. Less than 0.02 μg of Sb and 0.05 μg of Ba were detected in each sample. These results indicate that the tape is of sufficient purity for use as a gunshot residue collection medium and that no significant cross-contamination of either element from nearby crucibles occurs during ashing.

To evaluate the potential loss of Ba or Sb or both during ashing, three separate

tests were made with tape samples containing known additions. Each sample was prepared by treating a portion of tape with 10 μl of 1*M* HNO_3 containing 1 μg each of Ba and Sb. The tape was air-dried, ashed as described, and examined for Ba and Sb levels. In each test, complete recovery of both elements was obtained, indicating no loss during ashing at 375°C.

Tape collection efficiency for Ba and Sb on the hands was tested on eight subjects. A 10-μl aliquot of 1*M* HNO_3 containing 1 μg of each element was placed on the back of the hand (the area covered approximately 2.5 cm in diameter) and dried with warm air from a hand drier. Tape was pressed onto the sample area several times. The tape was ashed and examined as described. Essentially complete recoveries of Ba and Sb were obtainable from each subject.

Recovery studies using tape as a collection medium in actual firings were conducted using a .38 caliber revolver. Each of ten subjects fired a single shot with the weapon held in the right hand. Samples were collected immediately from the thumb web area of the hand. The tape was pressed onto the skin, rubbed on the back to insure good surface contact, and then peeled off. The collected tape was folded with the adhesive inside and stored in a plastic bottle. The collected samples were ashed and analyzed for Ba and Sb. Results are shown in Table 1. In nine of the ten cases, positive indications of firearm discharge residue (greater than 0.2 μg Sb and 0.3 μg Ba) were obtained. Average values for Ba and Sb collected from the hands of the ten shooters were 1.2 μg and 0.62 μg, respectively.

TABLE 1—*Scotch® Brand tape lift.*

	Antimony, μg		Barium, μg	
Subject	First Collection	Second Collection	First Collection	Second Collection
1	0.50	0.03	1.5	0.10
2	0.60	0.03	1.2	0.15
3	0.65	0.03	0.80	0.05
4	1.1	0.02	1.5	0.05
5	0.42	0.02	0.80	0.05
6	0.65	0.02	1.4	0.15
7	0.42	0.02	0.70	0.10
8	1.2	0.02	1.1	0.01
9	0.50	0.02	2.0	0.15
10	0.17	0.03	1.1	0.05
Avg	0.62	0.02	1.2	0.09

Lifting efficiency for the tapes was measured by applying a second portion of tape to the hands of the test subjects immediately upon removal of the first tape lift. Results of these lifts are also shown in Table 1. No positive indications of weapon discharge residue were obtained in any of the subjects in the second sampling. Average values obtained were 0.09 μg of Ba and 0.02 μg of Sb. Since these values are equivalent to expected background levels, the data indicates essentially complete lifting of gunshot residues from the hands with a single tape application.

Recovery Studies Using Plastic Film Lift

Barium and antimony background levels were determined on three samples of dried film. Each sample (approximately 1 g) was ashed and examined for both elements by FAAS. Levels obtained were less than 0.01 μg of Ba per sample and less than 0.02 μg of Sb.

Possible Sb and Ba losses during ashing were studied. A portion of dried Film Lift material (about 1 g) was treated with 10 μl of HNO_3 solution containing 1 μg each of Ba and Sb. The film was dried, ashed, and analyzed. Complete recovery for each added element was obtained on three separate tests.

Recovery of known amounts of Ba and Sb on the hands was measured using eight subjects. A portion of the back of the hand was treated with a solution containing 1 μg of each element as discussed with tape lifts. After the samples on the hands had been dried, a thin film of the plastic solution was spread over the test area and allowed to dry for five minutes. The dry film was peeled from the hand using tweezers. Some difficulty was encountered with this step, since the fragile film tended to tear into small fragments. The film samples were ashed and analyzed. Of the 1 μg of Ba and Sb deposited, only about 50% was recovered with a single application of the Film Lift preparation.

Film Lift was used to sample the hands of ten subjects, immediately following the firing of one shot from the same .38 caliber revolver. Results for the first application of the film lift are shown in Table 2. Five of the ten subjects showed Ba and Sb levels in excess of our criteria. Average Ba recovered was 0.61 μg and Sb was 0.23 μg. A second application of the film-forming polymer applied immediately upon removal of the first film gave no positive indications of gunshot residue. Results are shown in Table 2. Average values for the second sampling were 0.19 μg of Ba and 0.05 μg of Sb.

TABLE 2—*Cellulose acetate in acetone lift.*

	Antimony, μg		Barium, μg	
Subject	First Collection	Second Collection	First Collection	Second Collection
1	0.32	0.02	0.60	0.15
2	0.04	0.03	0.30	0.15
3	0.32	0.03	0.75	0.15
4	0.04	0.05	0.15	0.15
5	0.38	0.07	1.1	0.30
6	0.50	0.13	1.4	0.35
7	0.04	0.08	0.20	0.15
8	0.44	0.04	1.1	0.15
9	0.15	0.03	0.25	0.20
10	0.10	0.02	0.25	0.20
Avg	0.23	0.05	0.61	0.19

Recovery Studies Using Cotton Swabs

We have previously reported results of the examination of cotton swabs on plastic shafts. Background levels are less than 0.02 μg of Sb and 0.05 μg of Ba. Complete recoveries of microgram quantities of Ba and Sb were found from spiked swabs both by ashing and by direct leaching in 1*M* HNO_3 [*9*]. Recovery of added Ba and Sb from the hands of eight subjects was studied in this work. Hands were spiked with 1 μg of each element as previously described. Two swabs were used for sample collection; the first swab was used to moisten the skin and the second swab was used to dry the skin. This procedure represents a variation of the swab procedure used routinely in our method of sample collection, where two swabs, both moistened with HNO_3, are used simultaneously to swab the hand test area. Following sample collection, the moist and dry swab were combined and analyzed for Ba and Sb levels. Complete recoveries of each of the added elements were obtained.

Recoveries from actual firings, using ten subjects, were conducted. The hands were tested as described above. Results are shown in Table 3. Positive indications of firearm discharge residue were obtained in eight of the ten cases tested, with average values of 0.88 μg of Ba and 0.39 μg of Sb. These results are in general agreement with values previously reported by our laboratory in tests of 40 subjects, collected using the two-swab simultaneous method (0.95 μg of Ba and 0.47 μg of Sb). In that work, frequency of positive indication of gun firing was about 84% [3]. In this study a second sampling of the hands with cotton swabs gave positive indications for seven of the ten subjects, and average values of 0.49 μg of Ba and 0.23 μg of Sb. This indicates relatively poor lifting efficiency for the swab technique with actual firing residues. It is notable that results in the second collection gave values for the two initial failures considerably lower than the first swabbing (see Table 3). This supports the contention that in these two firings low levels of residue were deposited or that residue was not retained on the surface of the firing hand. The latter point is of interest, as it has been observed both in our own laboratory and by others that certain individuals give high incidences of inconclusive results, even in known firings.

TABLE 3—*Cotton swab lift.*

	Antimony, μg		Barium, μg	
Subject	First Collection	Second Collection	First Collection	Second Collection
1	0.43	0.32	0.80	0.50
2	0.55	0.30	0.60	0.50
3	0.40	0.30	0.70	0.40
4	0.50	0.25	0.70	0.40
5	0.14	0.07	1.0	0.30
6	0.14	0.10	0.30	0.25
7	0.50	0.20	1.2	0.60
8	0.25	0.30	1.0	0.65
9	0.40	0.15	1.0	0.40
10	0.55	0.30	1.5	0.90
Avg	0.39	0.23	0.88	0.49

Discussion and Conclusions

Table 4 shows a comparison of the three methods studied using the actual firing test data. The data indicate the tape collection method to be the most efficient with a single application. This method gives the highest average levels of Ba and Sb. For positive indication of weapon discharge the cotton swab technique is nearly as efficient as the tape lift, but in this study the average Ba and Sb levels obtained with a single lift were considerably lower. By combining the values of the two tests with cotton swabs, results comparable to those obtained with tape are obtained. The plastic Film Lift method gives the fewest indications of firing, being much lower than either tape or cotton swabs. In addition, lower values for Ba and Sb are obtained with a single lift, and no significant improvement occurs when a second lift is employed. The plastic film method is cumbersome to use since it is difficult to remove the film, particularly from an area of the hand containing hair. When tape was employed, visible particles were observed in about 50% of the samples collected. In future work these particles will be examined microscopically to determine if partially burned smokeless powder and bullet fragments can be identified. Should particle examination be successful, this would provide a routine basis for examination of lifts for firearms discharge residue prior to destructive

TABLE 4—*Comparison of lift techniques for antimony and barium.*

Lift Technique	Average Antimony, μg			Average Barium, μg		
	First Collection	Second Collection	Total	First Collection	Second Collection	Total
Scotch® Brand Tape	0.62	0.02	0.64	1.2	0.09	1.29
Cellulose Acetate Dissolved in Acetone	0.23	0.05	0.28	0.61	0.19	0.80
Cotton Swabs Wetted in 1*M* HNO_3	0.39	0.23	0.62	0.88	0.49	1.37

elemental analysis by FAAS. The work conducted to date indicates that transparent plastic tape can be a useful material for the field collection of evidence of recent firearms discharge.

Summary

Critical comparisons of Ba and Sb in firearms discharge residue were made on samples collected by three independent collection techniques. Collection materials studied were transparent adhesive tape, (Scotch® Brand), a solution of cellulose acetate in acetone ("Film Lift"), and plastic-shafted cotton swabs wetted with dilute nitric acid. Flameless atomic absorption analyses were performed with a Jarrell-Ash Model 810 instrument equipped with a tantalum strip atomizer. Tape and cotton swabs gave comparable positive indications of residue, with frequencies of 90 and 80%, respectively. The plastic Film Lift gave fewer positives, with a frequency of 50%. With the transparent tape lift, gunshot residue particles are discernible, making nondestructive microscopic identification possible prior to destructive elemental analysis.

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