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New Method for the Collection and Analysis of Gunshot Residues as Forensic Evidence

The detection of firearm discharge residues is of great importance in various criminal investigations involving the use of a firearm. One of the procedures introduced in the early 1930s was the "diphenylamine-sulfuric acid dermal nitrate test" on paraffin casts for the presence of nitrites and nitrates from gunpowder discharge residues. However, the limitations of these procedures were pointed out in 1935 and later in 1940 by the Federal Bureau of Investigation [1,2]. In spite of the known limitations of this procedure, the use of diphenylamine tests to detect gunpowder residues continued because of the lack of other suitable test procedures to satisfy this need in criminal investigations. In 1959, Harrison and Gilroy [3] demonstrated the presence of barium (Ba), antimony (Sb), and lead (Pb) in the firearm discharge residues and devised qualitative chemical tests to identify the presence of these elements, thus offering a unique new method to detect gunshot residues. Because of the limitations in the sensitivity of the colorimetric reactions used to detect Ba, Sb, and Pb, there was no widespread adoption of this method to replace the classical "diphenylamine test." The continued use of this test to identify gunshot residues is of great concern and this concern was eloquently expressed by practicing forensic chemists Cowan and Purdon [4]. Because of the rapid increase in new products for consumers, numerous materials around a person's environment can develop a positive reaction to the diphenylamine tests. This fact is now generally recognized, although the use of the diphenylamine test has not been altogether abandoned.

The applications of activation analysis to forensic investigation began in earnest in the late 1950s and several well-known applications were reported [5,6] at that time. In an extensive investigation of the applications of neutron activation analysis to forensic investigations, scientists at the General Atomics Division of General Dynamics Corp. (now Gulf Radiation Techcology of Gulf Oil Corp.) explored the possible uses of neutron activation analysis to the detection of gunshot residues through trace element analysis [7]. The high sensitivity of neutron activation analysis to the detection of barium, antimony, and copper (Cu) and its poor sensitivity to the detection of lead were the

reasons for choosing Ba, Sb, and Cu instead of Ba, Sb, and Pb, as originally suggested by Harrison and Gilroy [3]. Since that time, the applications of neutron activation analysis for the detection of firearm discharge residues have been gaining acceptance both in the forensic laboratories and in the courts. A decade of efforts by General Atomic's group produced considerable volumes of information on the various aspects of the applications of neutron activation analysis for the detection of gunpowder residues [8,9]. In addition to this major contribution, there were contributions to this field by other laboratories during the 1960's [10-12] and several new contributions were reported recently [13,14].

The present investigations were directed at developing a new method to collect gunshot residues from human body surfaces for forensic neutron activation analysis and to explore the possibilities of using additional trace elements from gunshot residues to distinguish the presence of gunshot residues from environmental contaminations. A simple and unique sampling technique called "film lift" was developed, and the analysis of copper and gold (Au) in addition to barium and antimony is suggested to assist in the interpretation of data from evidence analysis. A simple procedure is suggested to separate and quantitate copper and gold contents of film lifts in addition to barium and antimony.

Review of Current Practices of Evidence Collection and Analysis

A variety of materials and procedures is currently employed for the collection of firearm discharge residues to be identified through the detection and quantitation of unique trace element constituents. Harrison and Gilroy [3] employed cotton cloth moistened with 0.1 N HCl to extract firearm discharge residues from human body surfaces. The General Atomics group [7] reported the use of filter papers soaked with 1 percent HNO_3 or paraffin oil to extract gunshot residues from the hands of persons during test firings, although the use of nitric acid was preferred over the use of paraffin oil. In later years, after having attempted numerous other collection techniques, the General Atomics group preferred the use of high purity paraffin. The paraffin used in the collection of gunshot residues for neutron activation analysis must be of exceptionally high purity, and this is readily available in the U.S. and Canada through selective buying. However, in Australia, where such high purity paraffin is not readily available, cotton balls soaked in a mixture of hydrochloric acid and acetone have been employed [15] to swab the hands of suspects or victims.

The search for new materials to extract gunshot residues has been rather extensive, primarily because of the cumbersome nature of the paraffin cast method and the necessity of taking numerous precautions [16] to avoid contaminating the paraffin casts. One of the widely used procedures today is the use of dilute-nitric-acid-soaked cotton swabs [17]. Another suggestion [18] for extracting gunshot residues for the analysis of lead and copper by atomic absorption, and barium and antimony by neutron activation analysis, involves the use of dilute nitric acid or hydrochloric acid contained in plastic bags to rinse the hands of persons suspected of having discharged a firearm. Other alternatives to paraffin casts and cellulose fibers soaked in acids include attempts to deposit film-forming materials on the surface of hands and removing the crust that is formed. Coleman [19] reported the use of collodion by Scott et al for extracting gunshot residues from human body surfaces for the development of autoradiographic patterns. Recently, Albu-Yaron and Amiel [20] suggested the use of a spray containing 4 percent cellulose acetate and the subsequent analysis of only antimony. The main drawback of these film-forming preparations has been their nonsuitability for neutron activation analysis because of the impurities such as Ba, Pb, Sb, and Cu present in them. In addition, both collodion and cellulose acetate spray tend to block the pores on a person's

skin and they seldon form films that are removable from all the surfaces of the hand covered by the coating. A spray technique also suffers from the disadvantage of blowing off the residues from the surface, as well as washing off the residues when an excess spray solution is applied inadvertently. Considering all of the advantages and disadvantages, the paraffin cast method, despite all of its inconvenience in sample collection, is still one of the most satisfactory of all the methods mentioned above for the collection of gunshot residues for neutron activation analysis.

The analytical procedures used in the detection and quantitation of barium and antimony from gunshot residues collected involved neutron activation followed by chemical separation of barium and antimony. Because of the dissimilarity in the chemistry of barium and antimony, two-stage separations of barium and antimony are generally employed. One of the analytical schemes, when followed carefully, provides extremely reliable results and was reported by Schlesinger et al [16]. An alternative scheme combining the advantages of atomic absorption and neutron activation analysis was reported by Krishnan et al [18]. More recently, Rudzitis et al [14] suggested the possible use of ^{133}Ba and ^{124}Sb as tracers to determine the chemical yield of antimony and barium separations using a mixture of sodium sulfate and thioacetamide in acid medium. The method proposed by Albu-Yaron and Amiel [20] to determine the presence of gunshot residues through the analysis of a single element, antimony, would be highly undesirable considering the mushrooming increase in consumer products such as hair sprays, grease, and fabric finishes containing trace levels of antimony.

Film-Lift Techniques

While the method of collecting gunshot residues using high purity paraffin is generally considered as the most acceptable medium for neutron activation analysis, the desirability of employing an alternative procedure, simple enough to be used by field investigators, is accepted by most people familiar with present practices. The concept of extracting the residues on a crust or film that is readily removable from human body surfaces is again preferable to washing, swabbing, spraying, or vacuuming. Because of the rigid requirements of neutron activation analysis, it is desirable to have a matrix composed of elements whose neutron absorption cross sections are poor and those that do not produce significant amounts of long-lived radioisotopes. With these requirements, various natural and synthetic materials qualify as candidates. However, further requirements would include that the matrix be free from those trace elements being examined to detect gunshot residues. This latter requirement eliminates most of the natural fibers and plant products and almost all of the synthetic polymers containing traces of antimony or barium. Although polymers seem ideal, there are a number of these polymers containing Sb as a catalyst residue and a considerable number of them contain excessive amounts of chlorine (Cl) in the matrix, which makes the irradiated materials highly radioactive. A further important requirement of the matrix to be used for collecting gunshot residues for neutron activation analysis is that it should form a removable film capable of efficiently collecting residues from human body surfaces without causing irritation or injury to the person.

In exploring the possible applications of commercially available preparations, we have examined numerous materials, both natural and synthetic. The materials that were examined as possible candidates include products bearing trade names such as Spray Bandage®, Heddy Facial Mask®, Camag Laquer®, Quelspray®, Invisible Glove®, Krylon Acrylic Spray®, White Glue®, Casein Glue ®, and Kleerkote®, in addition to solutions of various commercially available polymers in volatile solvents. None of these

preparations was found to be a satisfactory substitute for taking hand casts using molten paraffin.

Preparation of Film-Lift Formulation

"Film-lift" is the name given to a formulation developed by one of the authors which is found to be a highly desirable matrix for the collection of gunshot residues for neutron activation analysis.

The three basic constituents of this preparation are highly purified cellulose acetate, acetone, and a plasticizer. Since most of the commercially available cellulose acetate contains varying amounts of Ba, Sb, Pb, Cu, and Au, an initial screening of various batches of cellulose acetate is necessary. Most of the cellulose acetate containing very low levels of Sb, Pb, Cu, and Au still shows significant levels of Ba. Therefore, the cellulose acetate is washed first with a dilute solution of acetic acid followed by deionized water. It is further washed with analytical-grade ethanol followed by diethyl ether. The cellulose acetate is then air-dried and preserved in clean containers. This washing procedure is capable of removing almost all the barium and considerably diminishing levels of other trace elements such as aluminum (Al), lead, chlorine, antimony, bromine (Br), sodium (Na), vanadium (V), etc, normally found in cellulose acetate.

The principal solvent used in the preparation is high purity acetone. Ordinary acetone (reagent grade) contains undesirable levels of copper, zinc (Zn), gold, etc and this can be considerably reduced by careful redistillation. However, spectrograde acetone available from some suppliers is quite satisfactory for direct use without purifications.

During this investigation, a number of plasticizers have been tested as a component of the film-lift preparation. The acceptable qualities of a suitable plasticizer for this preparation are: (1) the plasticizer must have acceptable minimum of trace element composition to be part of the film matrix, (2) the plasticizer should not cause any skin irritation and should not readily volitalize, and (3) the plasticizer should not coagulate or precipitate the components of the film-lift formulation during preparation or extended periods of storage. Several plasticizers were found to have acceptable qualities and they included several vegetable oils and commercially available plasticizers such as dibutyl phthalate, di-2-ethyl hexyl phthalate, dimethyl phthalate, triethyl citrate, and triacetin. Although most of these plasticizers and several others qualify for forming readily removable film, a few of them have been found to cause skin irritation on some people. One of the materials that was found to have no undesirable effects on any of the subjects tested during this study was specially purified coconut oil, and the film-lift solution prepared using this plasticizer has all other acceptable qualities as well. Most of the other plasticizers mentioned above have also been used after careful examination of their trace element constituents.

The purpose of adding a plasticizer to the solution of cellulose acetate in a volatile solvent is to make the film that is formed easily removable from the surface. However, the desired function of the film-lift is to extract and accumulate almost all the residues from the surface. Therefore, the amount of plasticizer added must be carefully controlled to prevent sacrificing one property of the film for another. The preparations containing 10 to 15 percent cellulose acetate with 80 to 90 percent acetone and 1.5 to 3.0 percent plasticizer (by weight) have all the acceptable characteristics to make film-lift an ideal matrix for the collection of gunshot residues from human body surfaces for forensic neutron activation analysis. Although the preparation of film-lift requires careful examination of the properties of the components, this preparation can be made from materials obtained through selective buying without too many purification stages. Furthermore, large quantities of this preparation can be made at one time and proper blank determination can be made for batches of each preparation.
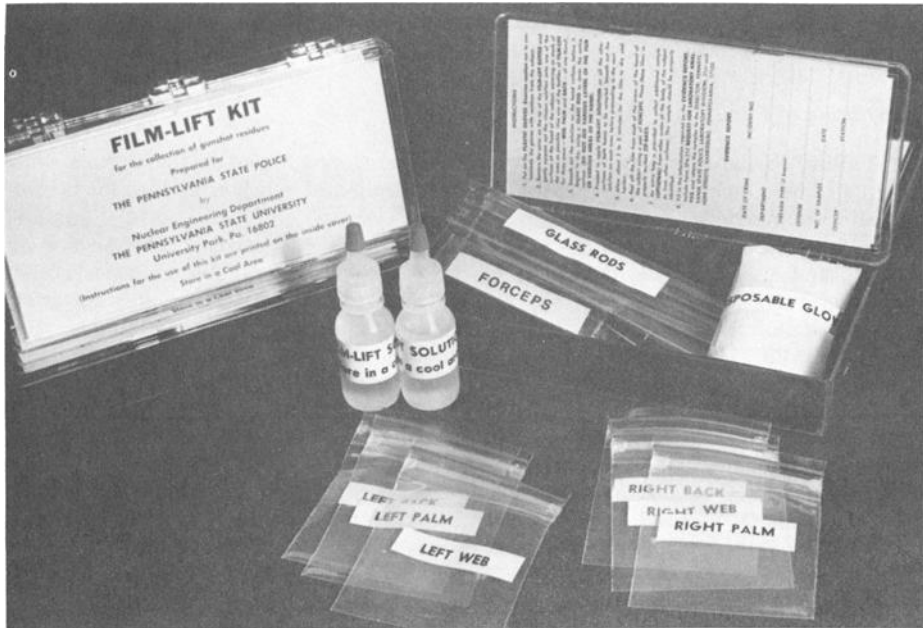
FIG. 1—*Kit used in the collection of gunshot residues.*

The application of film-lift material to collect residues from human body surfaces is simple and the film formed is readily removable. In addition, this matrix lends itself readily to further analysis of trace elements for detecting firearm discharge residues. The preparation is a homogeneous solution with the viscosity of ordinary honey or molasses, which lends itself to convenient application. Film-lift is spread on human body surfaces by squeezing out the solution from the nozzle of an all-polyethylene container and is smoothed out quickly by a glass rod or a polyethylene spatula to cover all the surface from which residue extraction is desired. The material dries to a hard film in three to four minutes and can be readily peeled off. The methods of application and removal of film lifts are illustrated in Figs. 1-3.

Neutron Activation Analysis of Firearm Discharge Residues

The high sensitivity of neutron activation analysis has been responsible for its becoming an accepted method to detect gunpowder residues through the analysis of traces of barium and antimony. Although the most desirable practice would be to perform nondestructive analysis, possibly using a high resolution detector system, this procedure cannot be recommended or practiced because of the interferences from various materials from human body surfaces that could be included during the process of collecting samples. Although the film-lift matrix is relatively "clean" from the point of view of gamma-ray spectrometric measurements of activated samples, nondestructive neutron activation analyses cannot be suggested for the analyses of all evidence samples because there are considerable amounts of other materials extracted from human body surfaces that cause significant interference problems.

The procedures suggested here for the isolation and analysis of barium, antimony, copper, and gold are designed to isolate the radionuclides of these elements from other
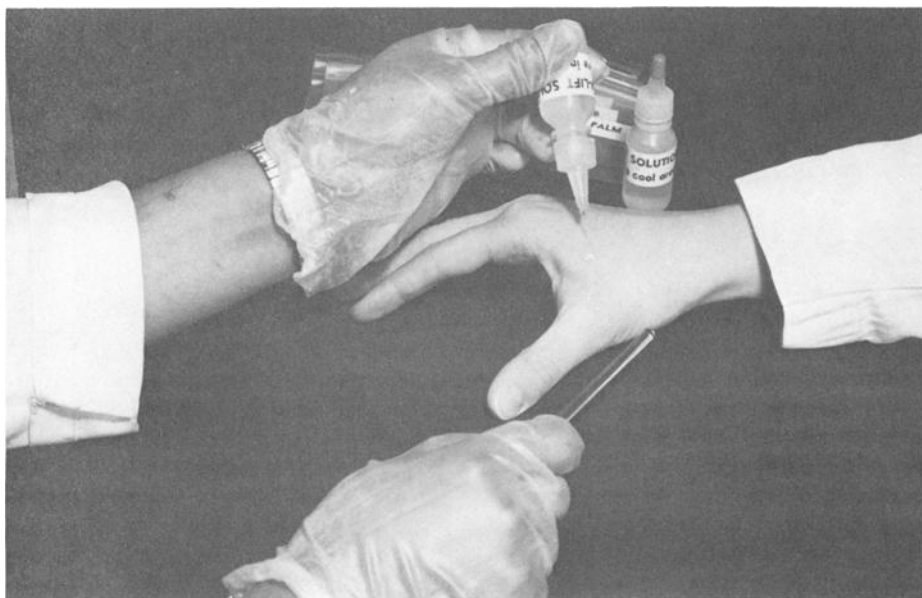
FIG. 2—*Application of film-lift on the web of a hand.*

interfering activities to a level at which they can be readily identified and reliably quanti-
tated. The films prepared from film-lift can be readily decomposed after neutron activa-
tion by a mixture of hydrochloric and nitric acids. In particular, samples exposed to
reactor fluxes of high energy gamma radiation, neutrons, and electrons are much easier
to digest than raw films. This is because of the structural damage and preliminary
degradations caused by the exposure to radiation.

The film samples suspected of containing the firearm discharge residues are weighed
and encapsulated in clean polyethylene bags and labelled appropriately prior to neutron
irradiation. The samples, along with analytical standards of the various elements to be
quantitated (Ba, Sb, Cu, and Au) are irradiated at a thermal neutron flux of 10^{13}
neutrons $cm^{-2} s^{-1}$ for 15 to 30 min. These irradiated samples are processed to isolate Ba,
Sb, Cu, and Au from other materials after a decay period of about 30 min.

Several chemical separation schemes have been suggested in the literature for the
isolation of barium and antimony [7,12,14,18]. The procedures suggested here have
adapted some of the best principles of the above separation schemes and include
additional steps to work with samples taken with film lifts and to quantitate the levels of
copper and gold in addition to barium and antimony.

The neutron-activated film samples are transferred to 50-ml centrifuge tubes
containing a mixture of nonradioactive carriers (10 mg Ba, 10 mg Sb, 5 mg Cu, and 100
μg Au in 5 ml of solution). The carrier mixture is prepared to have an acid concentration
of about 4 M HCl. After adding an additional millilitre of concentrated HNO_3, the
mixture is warmed in a water bath until the film samples degrade completely. Generally,
a film sample weighing 300 to 500 mg decomposes readily within 10 min. If undecom-
posed residues of film remain, they may be removed by centrifuging or filtration using
glass wool.

FIG. 3—Removal of the crusty film.

To the homogeneous digest of the film-lift sample, about 1.5 ml of 1:1 H_2SO_4 is added and the mixture is diluted to about 10 ml with deionized water. After allowing the precipitates to coagulate, the $BaSO_4$ precipitated is separated by centrifugation. The barium sulfate precipitate is washed with a wash solution containing holdback carriers Na^+, Cl^-, and PO_4^{-3} ions in a 2 M HCl solution. This precipitate is subsequently washed with deionized water followed by ethyl alcohol, and collected on a tared filter paper (Gelman GA-3 47-mm-diameter, 1.2-μm paper). These filter papers are folded when moist and placed in counting vials for gamma-ray spectrometric measurements. After counting, the samples are dried in a 60°C oven, cooled, and reweighed to determine the percent of recovery of barium from each sample.

The acidity of the supernatant from the separation of barium is adjusted to 1 to 2 M by careful addition of enough NH_4OH to neutralize the excess acid. This solution is warmed and hydrogen sulfide gas is passed through the solution to precipitate Cu, Sb, and Au, along with other sulfides. The H_2S treatment is repeated to complete the precipitation and coagulation of the sulfides. These sulfides separated by centrifuging are washed with warm dilute (1:20 by volume) hydrochloric acid. To each of the centrifuge tubes containing the sulfide precipitate is added two or three pellets (about 0.5 g) of NaOH and 3 ml of deionized water. The contents are mixed well and heated to boiling with continuous agitation of the contents of the centrifuge tube. The mixture is diluted with 2 to 3 ml of water and allowed to stand in a water bath at about 60°C. About 10 drops (0.5 ml) of 30-percent hydrogen peroxide are carefully added, avoiding violent bubbling, to assist the precipitation of gold from the sodium hydroxide solution and to separate copper as an insoluble oxide. The mixture is centrifuged and the supernatant containing antimony in solution is saved for the isolation of antimony. The treatment with NaOH and H_2O_2 may be repeated to extract residual amounts of antimony from

copper. The precipitates containing copper and gold are washed with an excess of warm water followed by ethyl alcohol. These precipitates are also collected on filter membranes (GA-3 type) and mounted in counting vials for gamma-ray spectrometry. After determining the ^{64}Cu and ^{198}Au radioactivities, these precipitates are left aside for a week to allow all the ^{64}Cu and most of the ^{198}Au radioactivities to decay out. These filter papers containing Cu and Au are reirradiated for about 10 min at a thermal neutron flux of 10^{11} neutrons cm^{-2} s^{-1} to determine the recoveries of copper and gold from each sample.

The sodium hydroxide extract containing antimony is scavenged with a drop of copper nitrate solution containing about 0.5 mg of copper. If a distinctly visible black precipitate is not observed, the precipitation is assisted by the addition of a drop of dilute ammonium polysulfide. The mixture is warmed to coagulate the copper precipitate and is filtered using a coarse filter paper. The filtrate at room temperature is mixed with 1 ml of 30-percent H_2O_2 solution and the mixture is warmed in a water bath to oxidize all the sulfide residues. The solution is then made distinctly acidic by adding about 6 to 8 ml of concentrated hydrochloric acid. This mixture is again warmed with a few additional drops of H_2O_2 to remove the final traces of H_2S, if any. After the effervescence has subsided completely, about 2 ml of chromous chloride solution (Fisher SO-C-169) is added to each of the centrifuge tubes containing the warm solution of antimony. This mixture is kept warm for 2 to 3 h to allow the complete precipitation of antimony as elemental antimony. The antimony precipitated is separated by centrifuging and washing with warm deionized water followed by ethyl alcohol. The precipitates are collected on tared filter membranes for chemical yield determination using the procedures employed for barium sulfate. The samples containing antimony are used to measure the ^{122}Sb radioactivities by gamma-ray spectrometry.

All the samples analyzed were counted using a large (10 by 10-cm) NaI(Tl) detector containing a well 4.5 cm deep. This detector, in association with a pulse height analyzer, was used to detect and quantitate the radioactivities efficiently. Because of the high radiochemical purity of the separated fractions, the use of a highly efficient detector system would be the ideal choice. In determining the recoveries of copper and gold by reirradiation, a high resolution Ge(Li) detector coupled to a 4096 channel pulse height analyzer was employed. This system could in principle be used to detect and measure the radiations from the various fractions isolated from gunshot residues, although in the processing of large numbers of samples the long counting time required by Ge(Li) detector systems would be a disadvantage, especially when several samples of ^{139}Ba with 83-min half-life need to be counted.

The radioactivities measured from barium (83.2-min ^{139}Ba), antimony (2.8-day ^{122}Sb), copper (12.8-h ^{64}Cu), and gold (2.693-day ^{198}Au) fractions of the gunpowder residues are compared with aliquots of the standards irradiated with the samples to quantitate the amounts of Ba, Sb, Cu, and Au present in the various fractions. These results are further corrected for the chemical yields of Ba, Sb, Cu, and Au to calculate the actual amounts of these trace elements that were originally present in the film sample being analyzed.

Results

The chemical separation procedures described here are capable of isolating barium, antimony, and copper from each other with extremely high radiochemical purity. The copper fraction, however, contains the gold separated. This, however, does not cause any problem in the determination of copper and gold using the NaI(Tl) crystal detector system for gamma-ray spectrometry. Generally, the chemical yields of barium separation

are in the range from 85 to 95 percent, while the yields of antimony are about 50 to 70 percent. The isolation of copper and gold using the procedures described here yields about 70 to 90 percent of these elements, although there is no one-to-one correspondence between the copper and gold recoveries. These yield determinations have been verified by using ^{133}Ba, ^{125}Sb, ^{64}Cu, and ^{198}Au tracers, confirming the reliability of the gravimetric methods for Ba and Sb and the reirradiation technique to determine recoveries of Cu and Au. Indeed, all the yield determinations can be made using this reirradiation technique, although the gravimetric procedures for Ba and Sb are relatively simple.

The other experimental results presented here include trace element composition data on a variety of materials used in the collection of gunshot residues for activation analysis, as well as data to compare the relative efficiency of residue collection by the film-lift technique. In addition, the results of the analyses of Ba, Sb, Cu, and Au in the film lifts collected after several test firings have been summarized. All the test-firing samples were collected from the web, palm, and back (three separate samples) of each of the firing hands and these samples were independently analyzed to determine the distribution of these trace elements in the various regions of the firing hand.

In examining the trace element levels of various materials useful for the collection of gunshot residues, emphasis was placed on examining the levels of Ba, Sb, Cu, and Au. These elements were determined by neutron activation followed by the chemical isolation procedures described above. The results of these analyses are presented in Table 1. These data represent the average of at least six independent analyses of these various materials. Although there have been large variations between aliquots of a few of the samples reported here, the average values in Table 1 are generally representative of most of the samples analyzed. In addition to determining these four elements, aliquots of

TABLE 1—Analyses of various materials used as matrices for collecting firearm discharge residues.

| | Concentrations of Elements, 10^{-9} g/g of Matrix | | | |
Materials Analyzed	Ba	Sb	Cu	Au
Paraffin (Fisher P-28)	180	140	4800	80
Paraffin (A. H. Thomas C-568-W51)	30	10	2100	42
Whatmann No. 1 filter paper	70	5	1220	18
Whatmann No. 541 filter paper	30	10	190	20
Cotton balls (Johnson & Johnson 6105BB)	130	5	270	180
Cotton gauze (Johnson & Johnson 8515)	190	60	1130	230
Cellulose acetate (Manufacturing Chemists/B Batch 20)	210	3	5300	190
Cellulose acetate (Manufacturing Chemists/B Batch 25)	270	10	3090	112
Cellulose acetate (Manufacturing Chemists/B 25 purified as described)	10	7	120	ND[a]
Cellulose acetate (Eastman Kodak Batch A2X)	54	4	58	ND
Film-lift blank when dry	50	20	320	ND
Collodion (J. T. Baker 9202—Lot 41.001)	820	180	3500	220
Cotton from swabs (Sirchie Kit-A)	120	250	260	ND
Cotton from swabs (Sirchie Kit-B)	320	100	570	28

[a] Not detectable.

some of these materials were irradiated and nondestructively analyzed to determine some of the short-lived radioisotopes produced. Using a gamma-ray spectrometry system involving a 40-cm^3 Ge(Li) detector and a 4096 channel pulse height analyzer, the various

TABLE 2—*Trace element composition of some of the materials used for collecting firearm discharge residues.*

Materials	Element/Matrix, µg/g						
	Na	Cl	Br	Mn	Ca	Al	V
Cotton balls (Johnson & Johnson)	116	140	0.78	0.42	20	22	0.05
Cotton gauze (Johnson & Johnson)	162	75	0.45	0.28	19	16	0.03
Cotton swab (Sirchie)	131	78	1.02	0.24	12	15	0.33
Cellulose acetate (Manufacturing Chemists/B 25)	6	142	6.11	0.23	63	2	ND[a]
Cellulose acetate (Manufacturing Chemists/B 25 purified as described)	2	75	2.61	ND	3	ND	ND
Film-lift blank	2	64	1.91	ND	3	ND	ND

[a] Not detectable.

constituents reported in Table 2 were quantitatively measured. It is worth noting from the results presented in Tables 1 and 2 that the purification procedures employed to clean the cellulose acetate matrix result in considerable decrease in the levels of Ba, Sb, Cu, and Au, in addition to several of the other trace elements. During the examination of several batches of cellulose acetate from various suppliers, a batch of cellulose acetate (Eastman Kodak Batch A2X) received was found to be extremely pure from the standpoint of making film-lift preparations. Other batches of cellulose acetate received prior to or since this have not been of the same high quality.

The efficiency of film-lift techniques for collecting gunpowder residues from human body surfaces is compared with paraffin-cast techniques by contrasting the amounts of barium and antimony contents of gunshot residues collected using these two different techniques. The results of these analyses are presented in Table 3. These results show that the film-lift techniques are generally as efficient as paraffin-cast techniques for collecting firearm discharge residues. In addition, in a few instances after removing the film lifts, paraffin casts were taken from the same areas of the hand. These paraffin casts did not show any detectable levels of Ba or Sb.

During the past two years, while developing the film-lift technique and these chemical separation procedures, several test firings were conducted to evaluate the potentials of these procedures. Since establishing the merits of these techniques, several test firings were performed using a variety of firearms and ammunitions. These results are summarized in Table 4. All these tests were conducted in indoor test facilities and, therefore, represent more or less ideal conditions. A close examination of the data shows that there are recognizable differences in the levels of these four trace elements on various regions of the firing hand that were monitored. However, in examining the values of barium, antimony, copper, or gold independently, it reveals that a significant proportion of the data does not follow a normal distribution and that there is considerable variation in the ratios of any two of the four elements that are being examined. In making these qualitative observations, it should be emphasized that these data are very limited for comparison with any extensive statistical analyses reported by other investigators [12,16].

This investigation has not yet undertaken a systematic survey of hand-blank values for copper and gold on the basis of occupational and environmental exposures. However, the

TABLE 3—Comparison of the Ba and Sb contents of paraffin casts and film lifts taken from firing hands after single firing using a .22 caliber, H&R Model 900 revolver, with long rifle, Western T2LR, Canadian-Imperial Ltd. ammunition.

Sampling Technique	No. of Samples	Areas of Firing Hand	Barium Content, 10^{-9} g			Antimony Content, 10^{-9} g		
			Range	Average	Median	Range	Average	Median
Paraffin cast	21	web	120–610	260	170	10–130	50	50
Paraffin cast	21	palm	40–620	240	110	10–140	60	40
Paraffin cast	21	back	20–450	170	80	10–30	20	20
Film lift	30	web	70–520	270	260	20–70	40	50
Film lift	30	palm	60–410	240	180	10–40	30	30
Film lift	30	back	60–210	130	170	10–70	20	30

TABLE 4—Summary of the analysis of Ba, Sb, Cu, and Au from single test firings.

Concentrations of Elements in the Film Lifts Taken from Various Regions of the Firing Hand, 10^{-9} g

Firearm Type and Ammunition	Test Firings	Elements Analyzed	Web			Palm			Back		
			Range	Average	Median	Range	Average	Median	Range	Average	Median
Revolver, cal. 0.22, H & R Model 900	29	Ba	70-870	365	300	40-1440	252	170	30-3520	288	140
		Sb	10-600	93	60	10-580	77	40	10-200	26	20
Ammunition: Long Rifle, Western T22LR		Cu	920-2680	2070	2120	480-2340	2080	1550	600-1540	850	630
		Au	12-156	56	90	8-97	40	68	24-190	80	75
Revolver, cal. 0.38, Colt Officers Model	14	Ba	240-1260	587	490	180-1030	362	300	140-590	248	230
		Sb	110-690	310	250	50-520	186	160	70-170	125	120
Ammunition: 0.38 Special Remington Arms		Cu	260-2360	1336	1050	320-3480	1430	1020	310-1130	790	670
		Au	16-90	42	30	24-160	89	60	10-90	20	24
Pistol, cal. 0.22, S & W Model 41	12	Ba	200-910	540	550	20-960	352	200	30-480	233	200
		Sb	50-360	228	200	30-430	288	270	10-310	163	120
Ammunition: Long Rifle, Remington-Peters		Cu	1260-3930	2780	2080	1510-3250	2530	2430	650-2300	1300	1230
		Au	54-320	170	190	72-410	107	140	16-490	140	90
Pistol, cal. 0.45, Remington-Rand Model 1911-A	12	Ba	1550-5560	3900	4240	520-1200	778	540	530-2000	1330	1470
		Sb	510-1580	913	630	350-570	467	460	260-650	405	290
Ammunition: 0.45 auto, Remington Arms		Cu	1050-2560	1700	1330	1070-3940	2040	1320	710-990	870	850
		Au	25-164	82	98	30-160	67	85	10-120	32	48
Pistol, cal. 0.32, Savage Arms Co. Model 1917	9	Ba	600-2030	1487	1560	380-1980	1263	1430	270-1430	610	360
		Sb	370-1040	780	930	210-1070	826	590	200-540	333	260
Ammunition: 0.32 Auto, Winchester-Western		Cu	1210-2990	2840	2690	930-1480	1465	1450	1070-1777	1620	1470
		Au	16-90	45	48	25-180	80	75	10-48	22	25

hand-blank samples collected from 14 different persons working at the reactor facility at Pennsylvania State University showed an average of 1085 ng of copper (median 820) and 20 ng of gold (median 32). This group included laboratory workers and secretarial staff, as well as students. All these hand-blank samples were taken from both the hands of the individuals (web and palm inclusive) at the end of a normal working day before washing their hands. The average hand-blank value for barium was 61 ng (median 50) and for antimony the average and median were 36 and 30 ng, respectively. The limited hand blanks we have analyzed, and some film lifts taken from the nonfiring hands of participants in the test firings, show significant differences between hand blanks and firing hands of a person who has recently discharged a gun. Therefore, it seems that the most desirable analyses for the interpretation of actual evidences from a criminal investigation would be samples from the various regions of both the hands, in addition to examining residues available from other parts of the body or garments or those remaining in a discharged firearm or an empty cartridge.

Discussion

Ever since the pioneering work of Harrison and Gilroy [3], considerable experience has been gained in the identification of firearm discharge residues using pyrolyzed trace metals from the ammunition. The analysts who employed neutron activation analysis to detect gunshot residues have always emphasized [7,8,9,12] the importance of the methods of evidence collection, the preservation of samples, and the procedures employed in the analysis. It is also well recognized that in the analysis of forensic evidence, the interpretation of the results is at least as important as the analysis itself. The desirabilities and advantages of proper sampling and analyses may be further illustrated by considering an ideal case involving a victim believed to have committed suicide by discharging a firearm, while the circumstances surrounding the incident are open to suspicion of possible homicide. If film lifts are taken from both hands of the victim, it would help to identify the firing hand or the complete absence of gunpowder residues under ideal conditions. However, ideal conditions rarely exist in actual cases involving criminal acts. Therefore, if film lifts were taken separately from various regions of both hands of the victim (web, palm, and back), along with the analysis of proper blanks, they could enable the analyst to interpret his findings in a meaningful manner, although this suggestion would involve the analysis of at least seven samples instead of two. The experience gained during this investigation supports the desirability of multiple sampling of various regions of each hand, instead of taking one sample from each of the hands. In cases involving rifles and other large firearms, it would be desirable to collect a sample from the cheek of the person suspected of having discharged the rifle, in addition to six samples from two hands. The best approach to collecting suitable samples would be educating the field investigators in the principles and limitations of the analysis and in using their best judgment to collect necessary samples from which useful evidence could result.

The neutron activation analysis procedures presently practiced are primarily directed at determining the barium and antimony contents of samples collected and, through careful analysis of blanks, determining the possible presence of gunshot residues. However, small caliber ammunition is sold in the market that does not contain barium or antimony in the primer. The emissions from discharging these ammunitions would not contain barium, although there would be traces of antimony from the volatilization of the lead bullet [13]. Not only in these limited cases, but in all analyses involving the use of unique trace elements to detect gunshot residues, the job of interpretation becomes

less burdensome if more elements characteristic of the gunshot residues are identified. While lead and copper are more abundant in our environment than barium, antimony, and gold, it would be desirable to determine as many of these elements as possible from film lifts. Through careful comparison of samples from various regions of the hand, one might be able to arrive at a better interpretation of the facts surrounding the incident. Many investigators are nowadays looking for the presence of lead as one of the additional elements to identify gunshot residues using X-ray fluoresence or the atomic absorption technique [18,21], although the environmental concentrations of lead in the United States are extremely high, a result of the discharge of more than 400 tons of lead into the atmosphere per day through gasoline consumption alone [22].

The choice of copper and gold as additional elements to be analyzed to determine the presence of gunshot residues is primarily due to the ease of analysis of these elements by neutron activation and their universal presence in all varieties of firearm discharge residues. Although copper is found in abundance in our surroundings, the environmental levels of copper as a constituent of particulate matter are much less than those of lead in the urban environment [23]. Gold, on the other hand, is a rare element and this could readily qualify as an additional element in the neutron activation analysis of gunshot residues. In all the test firings reported here, there have been recognizable differences in the levels of Ba, Sb, Cu, and Au from various regions of the firing hand, and much sharper differences between the hand blanks and the film lifts taken from the firing hands of persons who have recently discharged a gun.

The processes involved in the emission of barium, antimony, copper, and gold during the discharge of a firearm and its deposition on human body surfaces are controlled by numerous factors. These involve the pyrolytic volatilization of these elements from the various regions of an ammunition, namely the primer, the bullet, the primer cup, the bullet casing, and the coatings on the ammunition. Other major factors that influence the emission and deposition of gunshot residues include those dependent upon the firearm, the person discharging the firearm, and various environmental conditions. While it is possible to list numerous factors under these subtitles, it would be adequate for the present discussion to recognize that there exists an extremely large number of possible variations in the trace element concentrations in the firearm discharge residues deposited on human body surfaces and extracted for neutron activation analysis. These variations are fewer for the depositions on the firing hand and further restrictions can be imposed if the firearm and the ammunition employed are identified.

The elements Ba, Sb, Cu, and Au are found in trace levels in the film lifts taken from human body surfaces exposed to various environments. Therefore, the identification of firearm discharge residues through the analysis of trace elements has to be examined in the light of known levels of Ba, Sb, Cu, and Au found on hand blanks. Extensive investigations conducted by the General Atomic group [16] on the hand-blank levels of Ba and Sb on various occupational groups have demonstrated that several occupational exposures can result in hand-blank values that could make the interpretation of data rather difficult. Again, the changing patterns of consumer goods and the addition of new products for human consumption make the environmental exposure factors very significant. This necessitates the periodic reexamination of hand-blank values collected on various occupational groups. However, from the practical standpoint, a forensic analyst must design his sample collection in such a way that he will have representative hand blanks to compare for each of the evidence samples he analyzes. The most useful sampling, therefore, would be samples from various regions of both the firing and nonfiring hands of the suspects or the victims.

The findings of this investigation clearly demonstrate the usefulness of film-lift as a medium to collect gunshot residues for neutron activation analysis. The method of

employing multielement analysis, combined with sampling of various regions of both the hands of a person suspected of having discharged a firearm, would be of great assistance to the least ambiguous interpretation of the data. The suggestions made here of sampling at least six regions of the hands and analyzing four elements are directed toward this goal. The use of film-lift procedures in sample collection should considerably reduce the task of the field investigator and the forensic analyst, while the additional sampling and analyses suggested here would be of great value in developing the data into useful forensic evidence.

Summary

A unique formulation of pure reconstituted cellulose (called "film-lift") applied on surfaces to form readily removable film is employed for the collection of firearm discharge residues on human body surfaces for forensic neutron activation analysis. The analyses of traces of barium, antimony, copper, and gold are employed for the detection of gunshot residues.

The preparation and use of "film-lift" and the details of the radiochemical separation procedures employed for the isolation and analysis of Ba, Sb, Cu, and Au in gunshot residues are discussed. The results include data on the trace element compositions of various materials used in collecting gunshot residues, test results comparing the relative efficiency of sample collection using "film-lift," and the results of several test firings from which samples were collected and analyzed using the procedures described here. The simplicity of the film-lift technique for collection of gunshot residues from human body surfaces and the desirability of multielement analyses for the positive identification of gunshot residues are discussed.

Acknowledgments

References

[1] "The Dermal Nitrate Test," *Law Enforcement Bulletin,* Vol. 4, No. 10, 1935.
[2] "Further Observations on the Diphenylamine Test for Gun-Powder Residues," *Law Enforcement Bulletin,* Vol. 9, No. 6, 1940.
[3] Harrison, H. C. and Gilroy, R., "Firearm Discharge Residues," *Journal of Forensic Sciences,* JFSCA, Vol. 4, 1959, pp. 184-199.
[4] Cowan, M. E. and Purdon, P. L., "A Study of Paraffin Test," *Journal of Forensic Sciences,* JFSCA, Vol. 12, 1967, pp. 19-35.
[5] Kerr, M. F., "Application of Neutron Activation to Forensic Science," *Royal Canadian Mounted Police Gazette,* Vol. 21, No. 9, 1959.
[6] Forshufvud, S., Smith, H., and Wassen, W., "Arsenic Content of Napoleon I's Hair Probably taken Immediately after his Death," *Nature,* Vol. 192, 1961, pp. 103-105.
[7] Ruch, R. R., Guinn, V. P., and Pinker, R. H., "Detection of Gunpowder Residues by Neutron Activation Analysis," *Nuclear Science and Engineering,* Vol. 20, 1964, pp. 381-385.
[8] Guinn, V. P., Hackleman, R. P., Lukens, H. R. and Schlesinger, H. L., "Applications of Neutron Activation Analysis in Scientific Crime Investigation," USAEC Report GA-9882, U.S. Atomic Energy Commission, National Science and Technology Information Service, U.S. Department of Commerce, Springfield, Va., 1970.

[9] Lukens, H. R. and Schlesinger, H. L., "Applications of Neutron Activation Analysis in Scientific Crime Investigations," USAEC Report GA-10276, U.S. Atomic Energy Commission, National Science and Technology Information Service, U.S. Department of Commerce, Springfield, Va., 1970.

[10] Krishnan, S. S., "Firing Distance Determination by Neutron Activation Analysis," *Journal of Forensic Sciences*, JFSCA, Vol. 12, 1967, pp. 471-483.

[11] Krishnan, S. S., "Identification of Bullet Holes by Neutron Activation Analysis and Autoradiography," *Journal of Forensic Sciences*, JFSCA, Vol. 13, 1968, pp. 519-527.

[12] Pillay, K. K. S., Thomas, C. C., Jr., Hart, D. M., Didising, D., and Thomas, R. C., "Applications of Rare Earth Tracers to Gunpowder Residues," *Nuclear Applications and Technology*, Vol. 8, 1970, pp. 73-78.

[13] Renfro, W. B. and Jester, W. A., "Collection and Analysis of Airborne Gunshot Residues," Paper 7, *Proceedings*, Second International Conference on Forensic Activation Analysis, Western Regional Hospital Board, Glasgow, 1972.

[14] Rudzitis, E., Kopina, M., and Wahlgren, M., "Optimization of Firearm Residue Detection by Neutron Activation Analysis," *Journal of Forensic Sciences*, JFSCA, Vol. 18, 1973, 93-100.

[15] Goulding, J. A., "Forensic Activation Analysis—the Australian Scene," Paper 15, *Proceedings*, Second International Conference on Forensic Activation Analysis, Western Regional Hospital Board, Glasgow, 1972.

[16] Schlesinger, H. L., Lukens, H. R., Quinn, V. P., Hackleman, R. P., and Korts, R. F., "Special Report on Gunshot Residues Measured by Neutron Activation Analysis," USAEC Report GA-9829, U.S. Atomic Energy Commission, National Science and Technology Information Service, U.S. Department of Commerce, Springfield, Va., 1970.

[17] Hoffman, C. M., "A Simplified Method of Collecting Gunshot Residue for Examination by Neutron Activation Analysis," Publication 731 (1-71), Alcohol and Tobacco Tax Division of U.S. Treasury Department, Washington, D.C., 1968.

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

[19] Coleman, R. F., "The Applications of Neutron Activation Analysis to Forensic Science," *Journal of the Forensic Science Society*, Vol. 6, 1966, pp. 19-27.

[20] Albu-Yaron, A. and Amiel, "Instrumental Neutron Activation Analysis of Gunpowder Residues," *Journal of Radioanalytical Chemistry*, Vol. 11, 1972, pp. 123-132.

[21] Gage, S. J. and Whitworth, J. B., "Nuclear Analysis Applications in Cooperative Texas Forensic Investigation Program," Paper 30, *Proceedings*, Second International Conference on Forensic Activation Analysis, Western Regional Hospital Board, Glasgow, 1972.

[22] Muniak, S. E., "Long-Term Monitoring of Surface Atmospheric Lead at Argonne," USAEC Report ANL-7860, Part III, U.S. Atomic Energy Commission, National Science and Technology Information Service, U.S. Department of Commerce, Springfield, Va., 1971.

[23] Pillay, K. K. S. and Thomas, C. C., Jr., "Determination of the Trace Element Levels in Atmospheric Pollutants by Neutron Activation Analysis," *Journal of Radioanalytical Chemistry*, Vol. 7, 1971, pp. 108-118.

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