Robert D. Koons,[1] *Ph.D.; Donald G. Havekost,*[2] *M.S.; and Charles A. Peters,*[2] *B.S.*

Analysis of Gunshot Primer Residue Collection Swabs Using Flameless Atomic Absorption Spectrophotometry: A Reexamination of Extraction and Instrument Procedures

REFERENCE: Koons, R. D., Havekost, D. G., and Peters, C. A., **"Analysis of Gunshot Primer Residue Collection Swabs Using Flameless Atomic Absorption Spectrophotometry: A Reexamination of Extraction and Instrument Procedures,"** *Journal of Forensic Sciences,* JFSCA, Vol. 32, No. 4, July 1987, pp. 846-865.

ABSTRACT: Methods of extraction of gunshot residue (GSR) swabs for determination of antimony (Sb), barium (Ba), and lead (Pb) by flameless atomic absorption spectrophotometry (AAS) have been studied. Optimum extraction parameters were determined using recovery studies of Sb, Ba, and Pb added to swabs at amounts representative of actual GSR and handblank levels. Two difficulties with most extraction-AAS procedures are incomplete extraction of Sb and incorrect Ba results arising from improper matching of sample and standard matrices before AAS determinations. Utilization of standards made by spiking analyte elements on swabs and extraction along with samples by an efficient procedure minimizes errors in Sb, Ba, and Pb determination.

KEYWORDS: criminalistics, gunshot residues, ballistics, spectroscopic analysis, shooter identification, firearms discharge, antimony determination, barium determination, lead determination, flameless atomic absorption spectrophotometry

When a firearm is discharged, an assortment of vaporous and particulate materials are expelled in the area around the firearm. These products of firearm discharge, collectively referred to as gunshot residue (GSR), may be deposited on the hands of the person holding the firearm when it discharged. Collection of GSR from a suspected shooter's hands and quantitative analysis for antimony (Sb), barium (Ba), and sometimes lead (Pb), major elemental components of most cartridge primer mixtures, provide data commonly used to associate the suspect with the recent discharge of a firearm or handling of a contaminated firearm or ammunition component.

Several procedures have been advocated for the collection of GSR from the hands for quantitative elemental analysis. The procedure most commonly used in the United States involves swabbing the suspected shooter's hands using pairs of plastic shafted cotton tipped swabs moistened with 5% nitric acid solution. As a result of publications in the 1970s [*1,2*] and GSR seminars held at the FBI Academy in 1982 and 1984, there is general agreement among investigative jurisdictions in the United States as to the number of swabs used and areas of the hands swabbed. Consistent materials and collection procedures are a necessity if

Received for publication 22 Sept. 1986; accepted for publication 25 Nov. 1986.

[1]Research chemist, Forensic Science Research Unit, FBI Laboratory, FBI Academy, Quantico, VA.

[2]Special agent and chemist, respectively, Gunshot Residue and Metals Analysis Unit, FBI Laboratory, Washington, DC.

interlaboratory handblank and test-firing data bases are to be used in the interpretation of GSR results.

Gunshot residue swabs are analyzed for Sb, Ba, and sometimes Pb using one or more of several analytical methods depending upon the capabilities of the forensic science laboratory. The most common methods of analysis of GSR swabs are neutron activation analysis (NAA) and atomic absorption spectrophotometry (AAS). NAA first received widespread acceptance [*3*] and was used to obtain the bases which are still used for the interpretation of data obtained by other methods. Primarily because of cost considerations and the lack of adequate nuclear facilities to conduct NAA, most forensic science laboratories currently analyzing GSR samples do so using AAS. A published, favorable comparison of NAA and AAS without direct accuracy measurements of either method contributed to the ready acceptance of AAS [*4*].

Earliest attempts to use AAS to analyze GSR samples involved flame atomization and were generally unsuccessful because of unacceptable sensitivity for the analyte elements [*5*]. The first flameless AAS procedures used to analyze GSR samples were introduced in the early 1970s [*6–9*]. Problems were encountered regarding the determination of barium using a carbon rod atomizer, reportedly as a result of carbide formation [*6*]. A tantalum strip atomizer and tantalum lining of graphite tubes were reported to overcome these problems [*6,7*]. The AAS technique then became widely accepted. However, since its initial acceptance, there have been several noteworthy developments including changes in analytical instrumentation, swab composition, and swab extraction procedures. Principal among these changes was the introduction of carbon furnace atomizers of the hollow tube design which are currently used by virtually all forensic science laboratories doing GSR analysis. More recently, fast digital electronic integration of absorbance-time profiles and higher purity carbon furnaces have been introduced by instrument manufacturers. Concurrent with these changes, participants of the 1982 and 1984 GSR seminars reported difficulties in extraction and measurement of both Sb and Ba in GSR swabs. Published procedures do not adequately resolve these difficulties, so analysts in forensic science laboratories throughout the United States have developed individual procedures of cotton swab extraction and analysis.

This paper reports the results of our investigation of several factors that can affect the efficiency of removal of Sb, Ba, and Pb from swabs of the type used in most GSR collection kits and of the AAS procedures used to analyze the resulting extract solutions. For these studies, we used swabs to which known amounts of Sb, Ba, and Pb were added in solution form and recovery percentages of these elements were determined. In the analysis of GSR samples, inaccurate results can arise because of either incomplete extraction of the analyte from the swabs or errors in determination of element concentrations in the extract solution, or both. A general analytical procedure was sought which would meet the following four requirements:

1. Result in essentially complete recoveries of Sb, Ba, and Pb from swabs.
2. Provide accurate measurement of Sb, Ba, and Pb in the extract solution.
3. Have adequate sensitivity for Sb, Ba, and Pb in the ranges of concentrations found on the hands of shooters and nonshooters.
4. Be amenable to batch analysis to handle the sample load of the typical forensic science laboratory employing AAS for GSR analysis.

Experimental Details

Materials

The plastic shafted swabs used in our studies (Johnson & Johnson) are similar to those found in most commercially available GSR sampling kits. According to the manufacturer, the swabs are composed of 75% cotton and 25% rayon.

Polystyrene and polypropylene 15- by 75-mm tubes with polyethylene snap tops (Falcon) were used interchangeably for swab extraction. No differences in their behavior were detected. Preleaching of these tubes with acid for contaminant removal was determined to be unnecessary.

All analytical glassware was cleaned by leaching with 5% nitric acid solution for two weeks before initial use. All reagent and standard solutions were transferred to prewashed polyethylene or Teflon® bottles for storage immediately following their preparation.

Standard Ba, Sb, and Pb solutions were prepared by dilution of 1000-μg/mL stock solutions (Fisher Scientific and Aldrich Chemical). All dilutions were made using deionized water of 18 MΩ quality and ultrapure nitric acid (Baker "Ultrex").

Spiking Procedure for Recovery Studies

For comparison of the recovery efficiency for Sb, Ba, and Pb from GSR swabs as a function of extraction parameters, three levels of each element were studied. The levels of Sb, Ba, and Pb selected represent the ranges in amounts of these elements typically observed in swabs taken from the hands of shooters and the general nonshooting population.

A working standard solution containing 10 μg/mL of Sb, 50 μg/mL of Ba, and 50 μg/mL of Pb in 5% nitric acid (HNO_3) was prepared by dilution of 1000-μg/mL stock standard solutions. Four solutions were used for spiking known amounts of each element on pairs of swabs. BLANK, LOW, MID, and HIGH spiking solutions were made by dilution of the working standard solution in 5% HNO_3 to give the element concentrations shown in Table 1.

For each value of the altered extraction parameter under study, a set of sixteen tubes was prepared, as follows. Twelve of the tubes contained samples made up in triplicate at each of the four spike levels. Each sample was prepared by pipetting 200 μL of the appropriate spiking solution onto a pair of swabs and placing these swabs in a plastic snap-top tube. The remaining four tubes contained standards prepared by pipetting 200 μL of each of the four spiking solutions into tubes to which no swabs had been added. During the extraction and analysis procedure, the standards and samples within a set were treated identically. This procedure of having a set containing standards and samples for each value of the extraction parameter under study allows exact matrix matches of samples and standards for each analysis, as will be discussed in the basic extraction procedure to follow. The amounts of elements added to the spiked swabs for our studies were 0.05 μg of Ba and Pb and 0.01 μg of Sb on LOW, 0.25 μg of Ba and Pb and 0.05 μg of Sb on MID, and 1.0 μg of Ba and Pb and 0.2 μg of Sb on HIGH level spiked samples. Recoveries of these elements are expressed in terms of either micrograms of element or percent of the amount of element added.

For most values of extraction parameters, complete recovery of added elements from the standard tubes was achieved. Comparison between standard absorption response curves within each experiment indicated those few cases where incomplete recoveries of spiked elements in the standards occurred (example, when extraction acid concentrations were less than 1%). In these instances, recovery percentages for elements in samples were calculated using the best similar set of standards.

TABLE 1—*Composition of spiking solutions used to make element addition to swabs for recovery studies. All spiking solutions are 5% HNO_3.*

Spike Level	Sb, μg/mL	Ba, μg/mL	Pb, μg/mL
BLANK	0	0	0
LOW	0.050	0.250	0.250
MID	0.250	1.25	1.25
HIGH	1.00	5.00	5.00

Basic Swab Extraction and Analysis Procedure

The following procedure was used as the basic procedure by which to compare the effects of altering extraction parameters on subsequent recovery of Sb, Ba, and Pb spikes from GSR swabs. In each experiment, one extraction parameter was selected and altered under controlled conditions to determine its effect on element recovery efficiency. For each value of the altered parameter under study, 1 set of 16 tubes containing samples and standards prepared as stated in the spiking procedure was analyzed, except for the altered parameter, as follows:

1. Uncapped tubes containing the spiked swabs and standards were placed in an 80°C oven overnight or as needed to obtain dryness.
2. Into each tube, 2.00 mL were pipetted of 10% (v/v) HNO_3, the caps were replaced in the tightly closed position, and the tubes vortex mixed for approximately 30 s or until swabs were dispersed. Caps were loosened slightly and tubes placed in an 80°C oven for 2 h.
3. Tubes were removed from oven, caps snapped on tightly, and tubes vortex mixed again for approximately 30 s. Tubes were allowed to cool to room temperature and centrifuged for approximately 5 min to pack swab material firmly below supernate.
4. Supernate solution was removed from BLANK, LOW, and MID level samples and standards by pipet, taking care not to remove swab material, and transferred to a second set of tubes. HIGH level samples and standards were diluted fivefold by pipetting a precise amount of extract supernate and four times that amount of 10% HNO_3 into the vials.
5. Concentrations of Sb in sample solutions were determined by AAS without further dilution by transferring a portion of the extract solutions to a set of autosampler cups and analysis of samples and standards.
6. Before determination of Ba and Pb, all samples and standards were diluted twofold to bring the concentrations into the linear response range of the AAS instrument and to match the matrices of samples and standards. To effect this dilution, a third set of tubes was prepared in correspondence to the LOW, MID, and HIGH level samples and standards. Sample and standard solutions from the tubes used for Sb analysis were pipetted into the third set of sample tubes and either 10% HNO_3 or the BLANK solution was added to each tube to make a twofold dilution of both the analyte concentrations and the concentrations of all nonanalyte constituents in the original BLANK extract.
7. Ba and then Pb concentrations in these samples were determined using AAS. The concentrations of all nonanalyte constituents from both extracting solution and swabs were present at the same levels in all sample and standard solutions. There were no BLANK level solutions to be analyzed for Ba and Pb using this procedure since they had been added to all standards as part of the matrix matching operation.

Instrument Operating Parameters

The atomic absorption spectrophotometer used in our studies is a Model 5000 with HGA 500 controlled temperature furnace, AS-40 autosampler, and 3600 data station (Perkin-Elmer). Optimization of instrumental operating parameters for the determination of Sb, Ba, and Pb in GSR swab extract solutions is not as straightforward as with many other elements and matrices. These three elements exhibit wide ranges of chemical, physical, and spectral properties. As a result, instrument operating parameters were carefully selected to insure reliable AAS results. These parameters are shown in Table 2. In the following discussion some details are given of the considerations used in selecting these parameters.

Antimony—We considered atomization of Sb both directly from the wall of the graphite tube and using the stabilized temperature platform furnace insert (STPF). The sensitivity using the 217.6-nm Sb atom line is greater and detection limits are lower with the STPF than with wall atomization. Since amounts of Sb expected in GSR swab extracts are close to the detection limits of the AAS method, the lower detection limits of STPF make it the method

TABLE 2—*AAS instrument and graphite furnace operating parameters for determination of Sb, Ba, and Pb in 10% HNO_3 extracts of GSR collection swabs.*

	Sb	Ba	Pb
Wavelength, nm	217.6	553.6	283.3
Slit width, mm	0.2	0.14	0.7
Light source	EDL	HCL	EDL
Background correction source	D_2	W	D_2
Furnace configuration	STPF	Pyro	STPF
Injection volume, μL	20	20	20
Purge gas	Ar	Ar	Ar
	PROGRAM		
Step 1 (Dry)			
temp(°C)/ramp(s)/hold(s)	200/5/25	140/5/25	200/5/25
internal gas flow (mL/min)	300	300	300
Step 2 (Char)			
temp(°C)/ramp(s)/hold(s)	1000/15/15	1600/15/15	500/15/15
internal gas flow (mL/min)	300	300	300
Step 3 (Atomize)			
temp(°C)/ramp(s)/hold(s)	2700/0/5	2700/0/6	2300/0/5
internal gas flow (mL/min)	0	300	0
Step 4 (Burnoff)			
temp(°C)/ramp(s)/hold(s)	2700/0/2		2700/1/1
internal gas flow (mL/min)	300		300

of choice. Selection of optimum temperature programming with the STPF is more difficult than with wall atomization, however.

The absorbance-time profiles of Sb in solutions containing swab extract constituents and 10% HNO_3 solutions of Sb standard are shown in Fig. 1. The profiles shown in Fig. 1 are typical, that is, standards generally result in doublet peaks and swab extract solutions have sharper singlet profiles. In experiments with a variety of matrices, we have observed that highly ionic media tend to improve the shape of the Sb absorbance-time profile to the single peak. Mechanisms for the production of absorbance-time profiles similar to that shown in Fig. 1 for both Sb and Pb on several furnace platform configurations have been reported [*10,11*]. It is apparent from these studies and ours that the mechanisms for interferences during STPF atomization of Sb are at present poorly understood. Fortunately, however, the integrated absorbance-time profile (peak area) for a given mass of Sb is independent of its shape.

A fast-response recorder, such as the one used in our studies, or the peak area mode of the AAS instrument provide accurate integrated absorbance measurements of both Sb profiles of the types shown in Fig. 1. If a chart recorder or similar slow response device is used to record absorbance or if the peak height mode of the AAS instrument is used, then samples will result in positive errors relative to standards. In the development of a procedure for GSR extraction and Sb determination, use of such a recording device may hide low recovery efficiencies by high apparent absorbance measurements. These two effects cannot be used to cancel each other, because the shape of the Sb absorbance-time profile is dependent upon the sample matrix, a factor which cannot be completely controlled when analyzing GSR swabs. The changes in absorbance-time profile behavior with different sample matrices are more pronounced using STPF atomization than with furnace tube wall atomization, but they are present to some degree in both configurations.

The addition of nickel to the sample before atomization is reported to improve Sb determinations using the STPF by permitting a substantial increase in charring temperature without loss of volatile Sb species [*12*]. For GSR extract solutions, the addition of nickel produced no significant improvement in Sb absorbance measurements. In our studies, a charring temper-

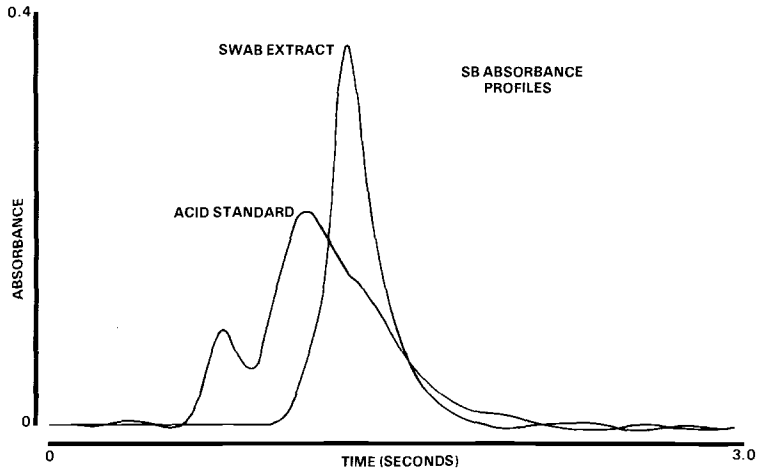

FIG. 1—*Absorbance versus time behavior of antimony. Each curve represents atomization of 20 μL of solution containing 0.5 ng of Sb. Curve labelled acid standard is absorbance of Sb in 10% HNO_3 and curve labelled swab extract is Sb extracted from a cotton swab using 10% HNO_3.*

ature of 1000°C removed potential interfering species without loss of Sb. However, for extracts of GSR swabs which contain large amounts of grease or dirt, it may be necessary to add a matrix modifier and increase charring temperatures.

The useful linear range for Sb absorbance measurements using the parameters shown in Table 2 is 0.01 to 1.0 ng of Sb in the 20-μL sample injection or a solution concentration of 0.0005 to 0.05 μg/mL of Sb.

Barium—Barium is difficult to determine accurately by AAS at the levels found in GSR swab extracts. It is critical that the furnace and both source and background light paths be carefully aligned to make accurate background corrections at the relatively high noise levels occurring in the 553.6-nm wavelength region. Our AAS instrument uses a tungsten background source lamp since a deuterium-arc lamp does not provide enough intensity at 553.6 nm to balance the hollow cathode lamp intensity. Pyrolytically coated graphite tubes (PE part 091504) were used for our studies. The useful lifetime of these tubes when injecting 10% HNO_3 solutions under the conditions of Table 2 is about 150 injections. This is a significant improvement over uncoated furnace tubes or furnaces of older manufacture dates.

Some discussion has appeared in the literature concerning the difficulties in making Ba absorbance measurements because of carbide formation, chemical interferences, and intense emission levels characteristic of the wavelength region of Ba atomic absorption [*13-15*]. In our studies, the most significant difficulty associated with the determination of Ba in GSR swab extract solutions is enhancement of the absorbance signal at the Ba I line resulting from the presence of constituents leached from the swabs. Absorbance measurements of two series of Ba standard solutions made up in 10% HNO_3 and in a 10% HNO_3 extract of unspiked GSR swabs are shown in Fig. 2. The greater slope of the Ba response curve in the presence of swab blank components compared to that of nitric acid alone indicates an interference which is similar in effect to ionization interferences common to flame AAS methods. Sodium (Na) is the predominant element leached from swabs. Extraction of swabs of the variety used in our studies removes about 125 μg of Na per swab. Therefore, a 2-mL extraction of a pair of swabs results in a solution concentration of approximately 125 μg/mL of Na. We have found that about the same 20% enhancement in Ba absorbance as shown in Fig. 2 for swab extract solutions, occurs when 125 μg/mL of Na is added to Ba standard solutions in nitric acid. This effect is in general agreement with results reported in

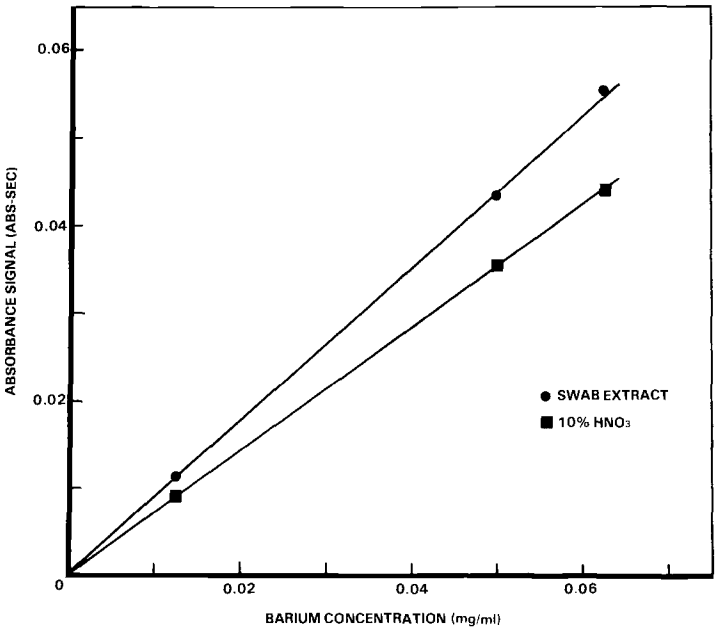

FIG. 2—*Effect of presence nonanalyte cotton swab extract constituents on the atomic absorbance of barium. Lines represent responses for standard barium solutions in 10% HNO_3 and in a 10% HNO_3 extract of cotton swabs.*

the literature [*16*]. Errors of the type shown in Fig. 2 are particularly critical for GSR swab analysis because they result in higher reported levels of Ba than are actually removed from the swabs.

There are several methods that can be used to minimize the effects of absorbance enhancement arising from the presence of nonanalyte constituents in swab extracts. These include dilution of samples, the method of standard additions, addition of swab constituents to standards (matrix matching), addition of an easily ionized element to both samples and standards to diminish the effects of swab constituents, and removal of the interfering ions by some separation procedure. All of these methods require additional steps in the GSR analytical procedure. In our basic extraction and analysis procedure and the recommended procedure for analysis of actual GSR swabs (Appendix), steps are included to match the matrix of samples and standards, thereby reducing the effects of nonanalyte constituents on measured Ba concentrations.

The useful linear range for Ba absorbance measurements using the parameters shown in Table 2 is 0.1 to 2.0 ng of Ba in a 20-μL injection or a solution concentration of 0.005 to 0.1 μg/mL of Ba.

Lead—The instrument parameters used for the determination of Pb are shown in Table 2. Optimization of instrumental parameters for Pb determination using the 283.3-nm line and STPF atomization are straightforward. In our studies, we did not detect any advantage in using matrix modification methods mentioned in the literature [*17*]. The lack of a matrix modifier, however, does not allow use of charring temperatures above 500°C or loss of some Pb occurs. Therefore, in actual GSR cases involving dirty swabs, it may become necessary to add a matrix modifier and raise charring temperatures. The levels of Pb tested in our recovery studies and typically found on GSR swabs are close to the upper limit of the linear range using the instrument parameters shown in Table 2. As a result, procedures including further

dilution of samples and the addition of a matrix modifier can easily be implemented. The loss of lead as volatile chlorides as reported in other studies [*18*] was not found to be a problem in GSR extract solution analysis because the excess of nitric acid present causes loss of all chloride as HCl at low temperatures. The principal difficulty associated with Pb analysis is laboratory contamination. This will become particularly critical in the forensic science laboratory conducting GSR analyses in close proximity to the firearms examination or test-firing areas.

The useful linear range for Pb absorbance measurements using the parameters shown in Table 2 is 0.02 to 1.6 ng in a 20-μL injection volume, or a solution concentration of 0.001 to 0.08 μg/mL of Pb.

Results and Discussion

The effects of varying several extraction parameters on recoveries of Sb, Ba, and Pb from GSR-type swabs were evaluated in this study. In each experiment, the basic extraction procedure was used as a reference point by which to compare the effects of altering extraction variables. The basic procedure was devised using extraction parameters determined in preliminary studies in which a wide range of extraction procedures were tested. In each experiment, one of the extraction parameters was varied under controlled conditions and all the others were held constant at the values described in the basic extraction procedure. One of the values selected for the parameter under study was that stated in the basic extraction procedure. By having one set of samples in each experiment extracted and analyzed under the same set of conditions, daily experimental biases were apparent when they occurred. Discussion of the results of experiments to study each extraction parameter follow.

Method of Drying Spiked Swabs Before Extraction

GSR swabs, as received by the laboratory, may contain various amounts of the solution used in swabbing the suspect's hand. To determine accurately the quantity of elements on the swabs by an AAS procedure which measures solution concentrations, the analyst must either know this solution volume or dry the swabs before analysis. To illustrate, the 200 μL of solution which is typically contained by a pair of swabs immediately after swabbing a hand will contribute a relative error of 10% in measured element levels when using a 2-mL extraction volume. The evaporation loss of 200 μL of MID level spiking solution from pairs of swabs stored at room temperature (20°C) for a period of up to three weeks is shown in Fig. 3. The upper curve in the figure represents the loss of solution from swabs stored in snap-top tubes with the cap placed in the loosely closed position. The lower curve represents the loss for swabs which were placed in tubes with the caps tightly closed. As demonstrated by Fig. 3, unless the amount of solution originally retained by the swabs after use and the conditions of storage are known, there is no reliable way to predict the solution volume following swab extraction. Therefore, quantitative determination of element concentrations in actual GSR swabs requires drying the swabs before analysis.

In our preliminary studies, we found evidence that the extraction efficiency of Sb from cotton swabs depended upon the manner in which the spiking solution was dried on the swabs before extraction. In those studies, the recovery of Sb was better for swabs which were dried quickly than for those dried more slowly at a lower temperature. To investigate the effects of the method of drying spiked swabs before extraction, we compared recoveries from spiked swabs dried at 55°C in tubes with the caps in the loosely closed position for three days, swabs dried at 80°C in uncapped tubes for 20 h, and swabs which were not dried after spiking. Extraction and analysis of the three sets of samples was carried out using the basic extraction procedure. The recoveries of Sb, Ba, and Pb in this experiment are shown in Table 3. The data for the undried swabs are corrected for solution volume by using undried

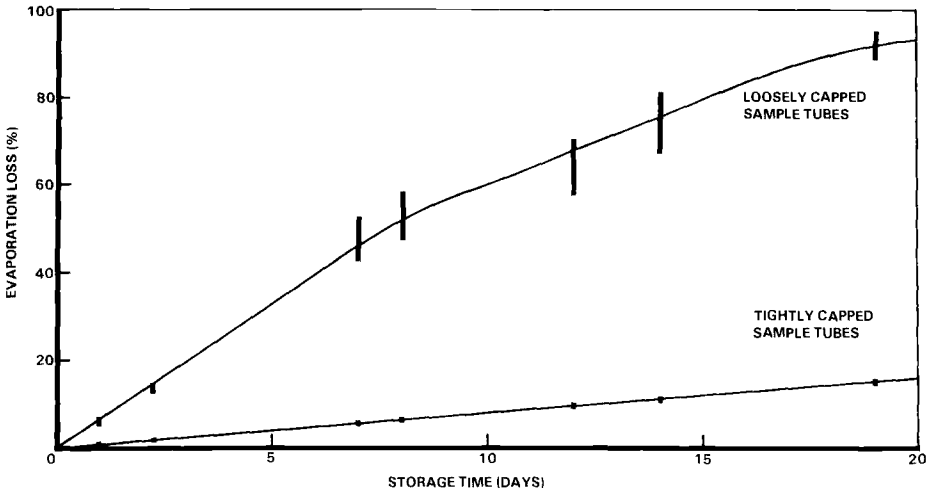

FIG. 3—*Rate of loss of solution from spiked swabs during storage at 20°C. Swabs were spiked with 200 μL of MID level spiking solution and amount of solution remaining determined by weight. Bar lengths indicate ranges of loss for five brands of swabs.*

TABLE 3—*Results of study of effects of method of drying spiked swabs on recoveries of Sb, Ba, and Pb. Results shown are mean ± standard deviation of percent recovery of triplicate samples.*

		Recovery Percentage		
Element	Level	Undried	Dried at 55°C	Dried at 80°C
Sb	LOW	88 ± 19	54.7 ± 1.2	55.0 ± 1.8
	MID	84.9 ± 0.4	55.0 ± 0.5	61.3 ± 1.3
	HIGH	97.9 ± 0.6	61 ± 2	68.2 ± 0.9
Ba	LOW	99 ± 7	106 ± 7	98 ± 5
	MID	111 ± 6	103.3 ± 1.8	95.3 ± 0.3
	HIGH	123 ± 5	102.4 ± 1.7	103 ± 3
Pb	LOW	99 ± 4	102 ± 7	97 ± 2
	MID	99.9 ± 0.8	106 ± 9	100 ± 4
	HIGH	106 ± 2	101.5 ± 0.7	102 ± 3

standards for calculation of analyte masses. As shown in Table 3, the only procedure by which nearly complete recovery of Sb is obtained is the one in which the swabs were not dried after spiking solution was added. The recovery of Sb from the swabs dried rapidly at 80°C is slightly higher than the recovery from the swabs dried more slowly at the lower temperature. There is no significant difference in recovery of Ba and Pb from swabs dried under any of the conditions used in this experiment.

Method of Placing Swabs in Extraction Tube

Recovery efficiencies of Sb, Ba, and Pb from swabs were studied as a function of the manner in which the cotton portion of the swabs were introduced into the extraction tube. The two methods considered were complete removal of the swabs from the shafts using a scalpel

and snipping each shaft at the base of the swab, leaving a small piece of shaft inside the swab. This study was undertaken because, in our experience, swabs which are cut off with a short piece of the shaft remaining do not get as wet under some extraction conditions, and extraction is consequently less efficient than when swabs are removed completely from the shaft. For this study, we cut the swabs off of the shafts before spiking them as stated in the spiking procedure to eliminate incomplete transfer of solution during swab handling as a variable in these studies. The Sb, Ba, and Pb recoveries using these two methods of swab introduction into extraction tubes are shown in Table 4. As shown, Sb, Ba, and Pb recoveries are not affected by the method of handling the swabs. Note that recovery efficiency for spike elements using the basic extraction procedure is greater than by the several other procedures we tested in prior studies. Also, the lower yielding procedures showed improvement when swabs were removed from the shafts as compared to being snipped off with a piece of shaft remaining.

Effect of Composition of Extractant

In the third series of experiments, we compared the use of nitric, hydrochloric, acetic, and citric acids for extraction of Ba, Sb, and Pb from spiked swabs. Of these four extractants, only nitric acid is suitable for routine analysis of GSR swabs. Hydrochloric acid is not a suitable matrix for electrothermal AAS because of the formation of volatile chlorides of lead and, possibly, antimony. Acetic acid causes severe absorbance signal depression of Sb. The loss in sensitivity for Sb in an acetic acid matrix makes this extract unsuitable for determination of Sb at the levels expected in GSR extracts. Citric acid is a relatively good extractant for all three elements of concern, probably as a result of the stability of both Sb and Ba citrate complexes. However, smoke formation from citrate during the atomization cycle in the graphite furnace makes it difficult to determine accurately the absorbance signals for Sb and Pb, since for these two elements charring temperatures must be kept below the temperature required to remove all citrate. Of the reagents tested, only nitric acid meets the requirements of relatively high extraction efficiency for all three elements and routine measurement of absorbances of the resulting solutions using AAS. One disadvantage of nitric acid solutions is that repeated injection of nitric acid into graphite furnace tubes decreases their useful lifetime somewhat. The problems of furnace tube deterioration are much less with the newer furnace tubes than with those of older manufacture. In this study, all further data were acquired using nitric acid solutions for extraction.

TABLE 4—*Results of comparison of recovery efficiencies for swabs removed completely from plastic shafts and swabs cut off by snipping shaft with a short piece retained inside swab. Results shown are mean recovery percentages ± one standard deviation for three replicates.*

Element	Level	Recovery Percentage	
		Without Shaft	With Shaft
Sb	LOW	53 ± 2	54.1 ± 1.4
	MID	60.1 ± 1.4	58 ± 2
	HIGH	67 ± 7	64.2 ± 1.6
Ba	LOW	106 ± 8	99 ± 7
	MID	101 ± 2	103 ± 4
	HIGH	104 ± 2	101 ± 3
Pb	LOW	95 ± 2	94 ± 11
	MID	88.8 ± 1.2	84 ± 3
	HIGH	101.5 ± 1.5	99.1 ± 1.0

Effect of Nitric Acid Concentration in Extract

The effect of the concentration of nitric acid on the recovery of Sb, Ba, and Pb from spiked swabs was evaluated using nitric acid extract concentrations from 0.1 to 20% (v/v). The results of this experiment are shown in Fig. 4. In the figure, the percent recovery of each element is shown as a function of the concentration of nitric acid in the extracting solution. The bar lengths represent the range of results for triplicate extractions at each of three levels of an element, or a total of nine individual measurements. As shown in Fig. 4, recovery of Sb increases throughout the nitric acid concentration range studied. However, the rate of increase diminishes and recovery of Sb becomes nearly constant above 10% HNO_3. The results for both Ba and Pb indicate a rapid increase in recovery with increasing acid concentration up to about 1% HNO_3 and a constant nearly 100% recovery at higher acid concentrations. The results for Ba using 20% HNO_3 have greater uncertainty than results obtained using other conditions because of high noise levels resulting from deterioration of the graphite furnace when injecting 20% HNO_3. A practical upper limit to nitric acid concentration dictated by lifetime of the graphite furnace tubes and reproducibility of Ba absorbance measurements is about 10%.

Effect of Extraction Time

The effect of time during which the extraction tube is placed in the oven at a temperature of 80°C was evaluated over the range of 15 min to 16 h. The results of this experiment are shown in Fig. 5. Each result shown in Fig. 5 is the average recovery percentage of the three spike levels for the element indicated (nine samples) at each extraction time. For extraction times of less than about 1 h, the extract solution does not reach 80°C. This results in the

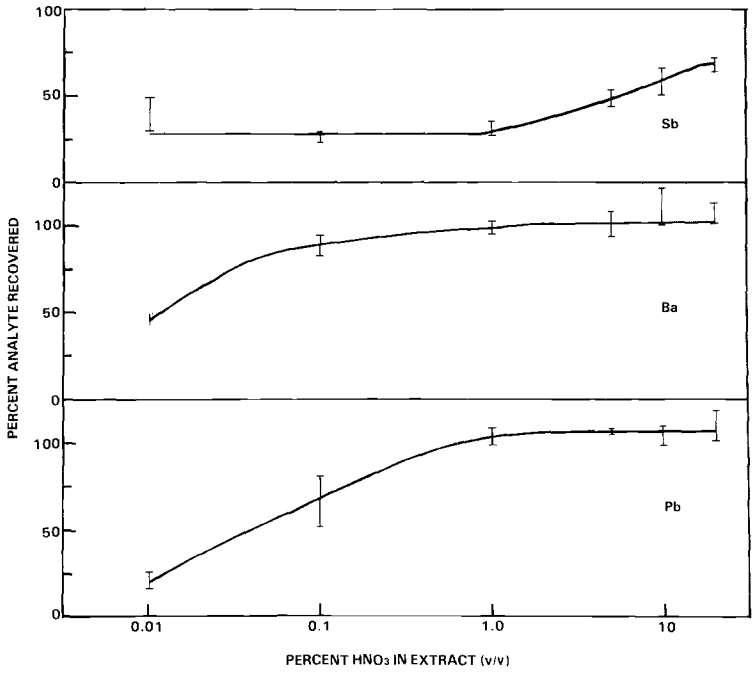

FIG. 4—*Effects of concentration of HNO_3 on recoveries of Sb, Ba, and Pb. Length of bars indicates range of recoveries for three spiking levels of each element.*

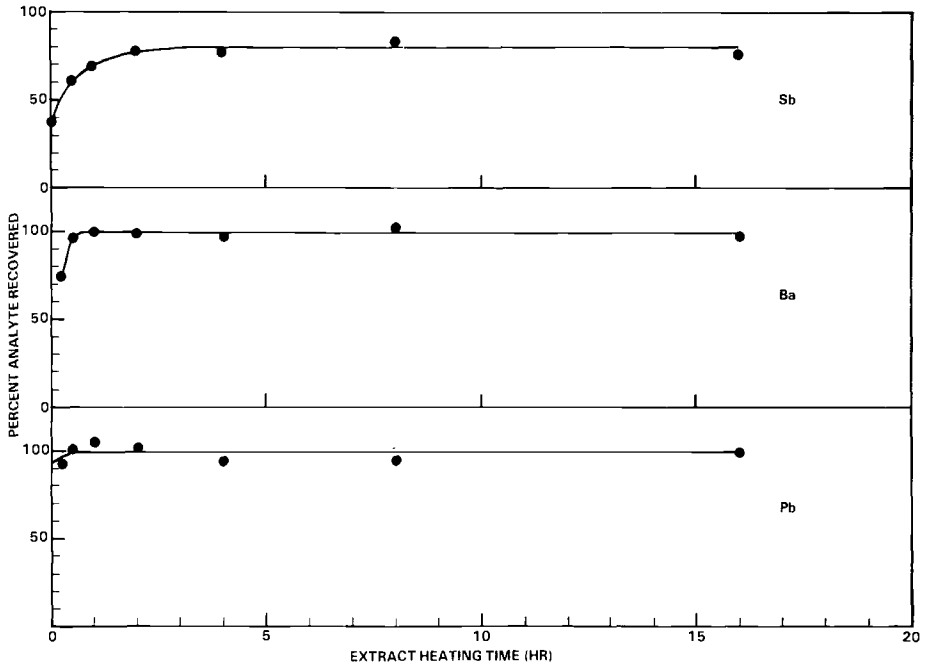

FIG. 5—*Effect of extraction time on recoveries of Sb, Ba, and Pb. Points represent mean recovery of triplicate measurements at each of three spiking levels.*

relatively low recoveries of Pb and Ba at short extraction times. The extraction efficiency of Sb improves for times up through about 2 h and then remains constant for longer extraction times. The data for an extraction time of 16 h were corrected for a loss in solution volume of 25%. The sample-to-sample error in applying a volume correction factor and the difficulties associated with measurements of the more concentrated solutions resulting from prolonged oven treatment result in greater uncertainties associated with these recoveries. At 8 h, the volume loss was less than 1%, so a correction was not applied to the data for this time. Eight hours represents the upper time limit beyond which correction factors must be applied.

Effect of Extraction Temperature

Extraction of spiked swabs was conducted at three temperatures, namely room temperature (27°C), 60°C, and 80°C. The results of this experiment are shown in Fig. 6. In this figure, the recovery efficiency for each element is plotted against the temperature of the extraction. The points shown in Fig. 6 are connected for ease of comparison although an explicit functional relationship between variables is not implied. As shown, the recovery efficiency for Sb increases as the extraction temperature is raised throughout the range studied. An upper limit on extraction temperature is set by the polystyrene extraction tubes, which begin to soften at temperatures above about 80°C.

Effect of Analyte Element Mass

In each of the experiments in our studies, three spiking levels of Sb, Ba, and Pb were used. The effect of analyte mass on recovery can be studied using the results of any of the experiments previously discussed. For ease of display, results have been presented thus far as aver-

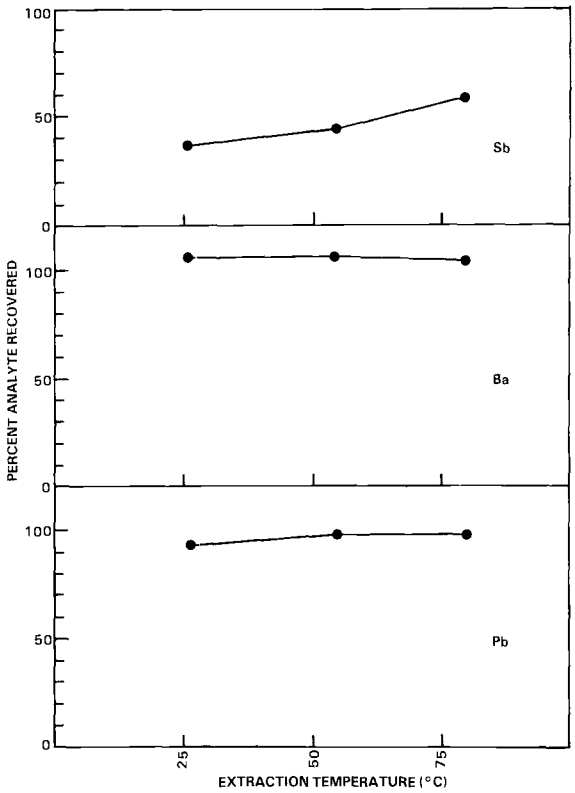

FIG. 6—*Effect of extraction temperature on recoveries of Sb, Ba, and Pb. Each point represents mean of triplicate measurements at each of three spiking levels.*

age recovery for LOW, MID, and HIGH level spikes for each element after correcting for blank levels. Comparison of the individual spike level results of all experiments consistently indicates that the amount of Ba and Pb added to the swabs has no effect on subsequent recovery efficiencies for these elements. There is, however, an effect of Sb level on its recovery efficiency. To demonstrate this, the portion of Fig. 4 showing the effect of nitric acid concentration on recovery efficiency for Sb is redisplayed as Fig. 7 with the mean values for each spike level shown rather than the overall mean. As shown in Fig. 7, for all extraction conditions, the recovery percentage of Sb improves as the analyte mass is increased. This result was observed in all experiments where Sb recoveries were higher than about 15% of the amount added.

The observation that the recovery efficiency for Sb from GSR-type swabs increases as the amount of Sb on the swab increases suggests the existence of at least two mechanisms by which Sb is retained by the swabs. In the first, a number of Sb ions are bound to swabs so that they are not removed by the extracting acid. The number of sites per swab available for this binding mechanism is nearly constant from swab to swab, so the relative amount of Sb which is strongly bound is greater the less the total Sb applied to the swab. To account for the mass balance of Sb in our studies, there must also be an additional bonding mechanism of Sb with the cotton such that the Sb is released by ion exchange or solubility of a solid phase in the extracting acid. Regardless of the mechanism of Sb retention by swabs, it is apparent from our data that extraction methods which result in good recovery of Sb at high spike levels may not do so at lower levels. Previous procedures reported for GSR swab extraction

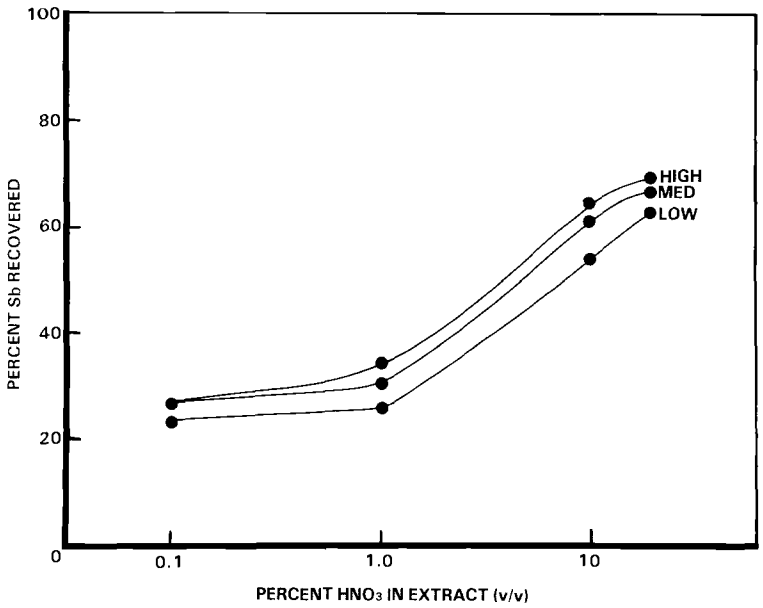

FIG. 7—*Effect of mass of Sb on swab on subsequent recovery. Each point represents results of extraction and analysis of triplicate samples at the spiking level indicated.*

and analysis were evaluated using 1 μg or more of Sb [*6*]. This level is 5 times greater than our highest spiking level and higher than generally observed on GSR swabs taken from the hands of known shooters. From the results shown in Fig. 7, it can be estimated by extrapolation that even relatively poor extraction procedures will give 95% recovery of Sb for 1-μg spike levels. It is important that recovery studies be performed at the levels of Sb, Ba, and Pb which are expected in real GSR swabs.

Conclusions and Recommendations

This study was undertaken to investigate extraction and AAS analysis parameters and their effects on measured recovery efficiencies of Sb, Ba, and Pb from swabs of the type used for GSR collection. As a result of these studies, the principal difficulties associated with extraction of GSR swabs and determination of Sb, Ba, and Pb in the resulting extract solutions have been defined and improvements in methodology can be suggested to diminish the significance of the identified problems. Our goals were to develop a procedure providing consistent high recoveries of Sb, Ba, and Pb at realistic GSR levels in a solution amenable to accurate AAS analysis at sample loads of a typical forensic science laboratory. The procedure that we suggest as best meeting these goals is given in the Appendix.

The major problem in the extraction process is incomplete removal of Sb from the cotton swabs. The selection of conditions for method of drying swabs, introduction of swabs into the extraction tube, composition and concentration of the extractant, extraction time and temperature, and analyte mass all affect the recovery efficiency for Sb from spiked swabs. An acceptable extraction procedure for GSR swabs should provide maximum recovery of Sb at a high level of reproducibility. In our studies, Sb recoveries greater than about 70% of the amount added could not be obtained consistently. The extraction procedure given in the Appendix consistently produces 60 to 70% recovery of Sb at realistic GSR levels. Recovery of added Ba and Pb is nearly complete for many choices of extraction variables, so optimization

made for Sb results in complete recoveries of the other two elements. Note that one could theoretically use a procedure yielding much lower Sb recovery, say 20%, if it were known to be reproducible and correction in interpretation of results could be made. We do not recommend this approach because reproducibility of extraction is poorer at lower levels of recovery than at higher levels, and the relative analytical uncertainty increases as the AAS detection limit is approached.

The second area where errors in GSR swab analysis can arise is in the AAS analysis of extract solutions. Two problems which have been identified are variable absorbance-time profiles of Sb and enhancement of Ba absorbance caused by the presence of various matrix constituents. The variability of Sb absorbance peak shapes is not significant when absorbance peak areas are carefully monitored by the rapid response recording systems available on most newer AAS instruments. The barium enhancement problem was eliminated in our recovery studies using clean spiked swabs by matching of the samples and standards with regard to every constituent except the elements of interest. This was accomplished by adding the extract from the unspiked swabs (BLANK level solutions) to each standard solution as detailed in the basic extraction and analysis procedure. However, the basic procedure must be modified somewhat for the analysis of actual GSR swabs. In this case, it is not possible to match the matrices of standards to the samples, since the composition of the sample swabs varies tremendously from one sample to another and no true swab blank containing all of the contaminants present on hand swabs exists. In our suggested GSR swab extraction procedure detailed in the Appendix, standards are mounted on swabs so that their extracts contain swab constituents. Both dilution and matrix modification can readily be applied to GSR swabs containing high levels of contaminants with only slight modifications of this procedure.

Based on results of recovery tests discussed previously, the procedure detailed in the Appendix is proposed for use in determination of Sb, Ba, and Pb concentrations in actual GSR swabs. This procedure is similar to the basic extraction procedure with modification of the method of handling the standards to diminish the effects of swab constituents on Ba absorbance signals and to handle the wide range of compositions which may be encountered in analyzing GSR swabs. The key to the proposed extraction and analysis method is the use of standards made by spiking standard solutions on cotton swabs and extracting them by the same method as used for the samples. This procedure offers the dual advantages of automatically correcting sample Sb concentrations for incomplete extraction and approximating the extract solution matrix composition as needed to diminish the effects of barium absorbance enhancement.

The recommended extraction and analysis procedure offers several advantages over other procedures which we have tested. The parameters selected for extraction are chosen to provide the maximum reproducible recovery of Sb, thereby improving the reliability of standard recoveries as being representative of sample recoveries. The proposed procedure also offers the advantages of allowing for the addition of matrix modifiers and ionization suppressants and dilution of concentrated samples without reworking the entire procedure.

There are two potential drawbacks to the proposed procedure arising from violations of inherent assumptions. First, the spiking of standards on swabs matching the samples in composition is done so that recovery of Sb will be similar for samples and standards. Similar recoveries of samples and standards will be difficult to achieve when either the sample swabs cannot be matched by the laboratory performing the analysis or the samples are so greatly soiled that extraction of the GSR is physically inhibited. The first of these drawbacks, lack of a match to swab compositions, should not present a problem to the forensic science laboratory that has control over the swabs sent in by its contributors. In addition, it is our experience that Sb recoveries do not vary much among plastic shafted, cotton tipped swabs from different manufacturers. The case of heavily soiled swabs which prevent effective extraction of GSR constituents has always presented a problem when using extraction-AAS techniques.

It has been suggested that heavily soiled swabs should be ashed and dissolved rather than extracted for AAS analysis [*19*]. Using the procedure given in the Appendix minimizes the effects of physical inhibition of extraction of swabs because the swabs fall apart during extraction, resulting in good recoveries even in the presence of soil. Further studies comparing ashing and extraction techniques for analysis of swabs contaminated with a variety of substances are ongoing in our laboratory and will be published separately.

The second potential drawback to the proposed procedure lies in the assumption that extracting the standards from swabs will generate solutions of the same composition regarding nonanalyte constituents as the sample solutions. This is needed to diminish the effects of enhancement of Ba absorbance signals. Again, the presence of high amounts of contamination on sample GSR swabs will cause a mismatching of the sample and standard extract solution matrices. When this occurs, there are several methods of overcoming the enhancement. Samples can be analyzed by the method of standard addition, which will eliminate the effects of absorbance enhancement. Another method of diminishing the effects of enhancement resulting from contamination is the addition of large amounts of an easily ionized element to both samples and standards. For example, addition of Na (as nitrate) to a concentration of 500 μg/mL in both sample and standard extracts will reduce the effects of Na and other hand swab constituents to negligible levels. This is readily accomplished in the proposed procedure by making a 1 : 1 dilution of all samples and standards with a 1000-μg/mL Na solution before determination of Ba. In those cases where Ba concentrations are high enough in the samples, dilution of the sample will reduce the Ba concentrations into the range of the standards and diminish the enhancing effects of other constituents by lowering their concentrations. A third method which can be used to diminish or eliminate the effects of enhancement of Ba absorbance signals is to use atomic emission for Ba analysis. The most practical means of making this measurement is with the use of inductively coupled plasma-atomic emission spectrometry (ICP-AES). Further studies in our laboratory comparing ICP-AES and AAS for Ba determination are ongoing and results will be presented elsewhere.

Acknowledgments

We gratefully acknowledge John W. Kilty for his encouragement and helpful discussions during the course of our investigations. We also would like to acknowledge Rena A. Merrill for her assistance during the preliminary stages of our studies and Rodger A. Asbury, Robert C. Halberstam, Ernest R. Peele, and John P. Riley for reading the manuscript and making many helpful suggestions.

APPENDIX

Analysis of Gunshot Residue Swabs for Antimony, Barium, and Lead Using Flameless Atomic Absorption Spectrophotometry

This method describes the determination of antimony, barium, and lead in cotton applicator swabs which have been applied to the hands of suspected shooters. It can also be used to determine the lower levels of these elements in cotton applicator swabs which have been applied to the hands of nonshooters.

Equipment

Atomic absorption spectrometer with flameless atomizer, background correction, autosampler, chart recorder, and data recorder
Gravity convection oven
Vortex mixer
Table top centrifuge
Assorted volumetric flasks
Assorted glass pipets
Assorted micropipets
Test tube racks
Assorted plastic storage bottles

Expendable Supplies

12- by 75-mm (5-mL) polypropylene tubes with snap caps
Micropipet tips
Plastic beakers
Autosampler cups
Disposable scalpels
Pyrolytic graphite furnace tubes and platform inserts

Expendable Chemicals

Ultrapure concentrated nitric acid (Baker "Ultrex" or equivalent)
Certified barium, antimony, and lead standard solutions
Deionized water
Argon gas

Reagents

5% (v/v) Nitric Acid Solution—Dilute 50 mL of ultrapure concentrated nitric acid to 1000 mL with deionized water. Store in a clean dedicated plastic bottle.

10% (v/v) Nitric Acid Solution—Dilute 100 mL of ultrapure concentrated nitric acid to 1000 mL with deionized water. Store in a clean dedicated plastic bottle.

Standards

Stock Standard Solution—Pipet 25 mL of 1000-μg/mL barium standard, 25 mL of 1000-μg/mL lead standard, and 5 mL of 1000-μg/mL antimony standard into a 500-mL volumetric flask. Dilute to mark using 5% nitric acid solution. Thoroughly mix and transfer this solution to a 500-mL plastic bottle for storage. Label and date bottle. This solution, which contains 50-μg/mL barium, 50-μg/mL lead, and 10-μg/mL antimony, has a shelf life of several months if care is taken to maintain its integrity.

Working Standard Solution—Pipet 10 mL of stock standard solution into a dedicated 100-mL volumetric flask and dilute to mark with 5% nitric acid solution. Thoroughly mix and transfer the solution to a 100-mL Teflon® bottle for short-term storage. Label and date this bottle. This solution, which contains 5-μg/mL barium, 5-μg/mL lead, and 1-μg/mL antimony, has a short shelf life and should be prepared fresh daily.

Analytical Standard Preparation

Prelabel seven 12- by 75-mm (5-mL) polypropylene snap-top tubes to be used for standards. Using a clean surgical scalpel, remove two cotton tips from applicator swabs, and place into each standard tube. Micropipet the following volumes of standard working solution into the seven tubes:

S0	S1	S2	S3	S4	S5	S6
0 mL	0.050 mL	0.100 mL	0.150 mL	0.200 mL	0.500 mL	1.000 mL

Sample Preparation

Using a clean surgical scalpel, remove the cotton from the plastic shafts of each sample and place into prelabelled tubes like those used for the analytical standards. Since sample swabs will have varying volumes of liquid associated with them, it is essential that they be dried in a contamination-free environment before further processing. The analytical standards must be similarly dried. This can be accomplished by placing open sample and standard tubes in an 80°C oven overnight, or as needed to remove moisture.

Sample and Standard Digestion

Pipet 2.00 mL of 10% nitric acid solution into each sample and standard tube. Tightly cap each tube and vortex mix each for approximately 30 s. Loosen the caps from all tubes and place tubes in an 80°C oven for 2 h.

Remove all tubes from the oven at the conclusion of the extraction period, reseal caps on the tubes, and again vortex mix each for approximately 30 s or until the cotton is dispersed. Centrifuge all tubes for approximately 5 min to pack the swab fibers into the bottoms of the tubes.

Before analysis for antimony, barium, and lead, samples and standards generally must be diluted to bring analyte concentrations into the working range of the atomic absorption instrument. The magnitude of these dilutions will be dependent upon the particular instrument used. The following dilutions have been determined to be most appropriate for the atomic absorption spectrophotometer used in the FBI Laboratory (Perkin Elmer Model 5000).

Sample and Standard Dilutions

For Antimony Determination—Prepare a second set of 5-mL polypropylene tubes in a one-to-one correspondence with the first set. Micropipet 0.500 mL of extract solution from each sample and standard into their corresponding tubes followed by the addition of 0.500 mL of deionized water. For some instruments, it may be advantageous to substitute a matrix modifier solution for the deionized water. Mix each solution thoroughly and transfer to disposable autosampler cups for immediate analysis.

For Barium and Lead Determinations—Prepare a third set of 5-mL polypropylene tubes in a one-to-one correspondence with the first set. Micropipet 0.200 mL of extract solution from each primary sample and standard into their corresponding tubes followed by the addition of 2.00 mL of deionized water. Mix each solution thoroughly and transfer 1 mL of each to disposable autosampler cups for immediate analysis.

Analyses

Make antimony, barium, and lead absorbance measurements on sample and standard solutions using the optimum operating parameters for the particular instrument being used. All absorbance values should be determined using peak areas. The use of peak heights or output directly from the spectrometer can lead to incorrect absorbance measurements, particularly for antimony.

Determination of Micrograms of Antimony, Barium, and Lead in Hand Swabs and Control Swabs

The standards described in this procedure correspond to 0, 0.25, 0.50, 0.75, 1.0, 2.5, and 5.0 μg of barium and lead and 0, 0.05, 0.10, 0.15, 0.20, 0.50, and 1.0 μg of antimony. Sample analyte weights in micrograms may be directly interpolated from the instrument standard response curves or from manual standard working curves provided all dilutions of standards and samples are made equally.

References

[1] Goleb, J. A. and Midkiff, C. R., Jr., "Firearms Discharge Residue Sample Collection Techniques," *Journal of Forensic Sciences,* Vol. 20, No. 4, Oct. 1975, pp. 701-707.

[2] Kilty, J. W., "Activity After Shooting and Its Effect on the Retention of Primer Residue," *Journal of Forensic Sciences,* Vol. 20, No. 2, April 1975, pp. 219-230.

[3] 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," U.S. Atomic Energy Commission Report GA 9829, National Science and Technology Information Service, U.S. Department of Commerce, Springfield, VA, 1970.

[4] Kinard, W. D. and Lundy, D. R., "A Comparison of Neutron Activation Analysis and Atomic Absorption Spectroscopy on Gunshot Residue," in *Forensic Science,* G. Davies, Ed., American Chemical Society Symposium Series, No. 13, 1975, pp. 97-107.

[5] Green, A. L. and Sauve, J. P., "The Analysis of Gunshot Residue by Atomic Absorption Spectrophotometry," *Atomic Absorption Newsletter,* Vol. 11, No. 5, 1972, pp. 93-95.

[6] Goleb, J. A. and Midkiff, C. R., Jr., "The Determination of Barium and Antimony in Gunshot Residue by Flameless Atomic Absorption Spectroscopy Using a Tantalum Strip Atomizer," *Applied Spectroscopy,* Vol. 29, No. 1, Jan.-Feb. 1975, pp. 44-48.

[7] Renshaw, G. D., "The Determination of Barium by Flameless Atomic Absorption Spectrophotometry using a Modified Graphite Tube Atomizer," *Atomic Absorption Newsletter,* Vol. 12, No. 6, Nov.-Dec. 1973, pp. 158-160.

[8] 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, No. 2, March-April 1973, pp. 55-56.

[9] Cone, R. D., "Detection of Barium, Antimony, and Lead in Gunshot Residue by Flameless Atomic Absorption Spectrophotometry," *Police Weapons Center Bulletin,* Vol. 6, Dec. 1973, pp. 4-6.

[10] Welz, B., Akman, S., and Schlemmer, G., "Investigations of Interferences in Graphite Furnace Atomic-Absorption Spectrometry Using a Dual Cavity Platform. Part 1. Influence of Nickel Chloride on the Determination of Antimony," *Analyst,* Vol. 110, No. 5, May 1985, pp. 459-465.

[11] Hunt, D. T. E. and Winnard, D. A., "Appraisal of Selected Techniques for the Determination of Lead and Cadmium in Waters by Graphite Furnace Atomic Absorption Spectrometry," *Analyst,* Vol. 111, No. 7, July 1986, pp. 785-789.

[12] Constantini, S., Giordano, R., Rizzica, M., and Benedetti, F., "Applicability of Anodic-stripping Voltammetry and Graphite Furnace Atomic-Absorption Spectrometry to the Determination of Antimony in Biological Matrices: A Comparative Study," *Analyst,* Vol. 110, No. 11, Nov. 1985, pp. 1355-1359.

[13] Roe, K. K. and Froelich, P. N., "Determination of Barium in Seawater by Direct Injection Graphite Furnace Atomic Absorption Spectrometry," *Analytical Chemistry,* Vol. 56, No. 14, Dec. 1984, pp. 2724-2726.

[14] Styris, D. L., "Atomization Mechanisms for Barium in Furnace Atomic Absorption Spectrometry," *Analytical Chemistry,* Vol. 56, No. 7, June 1984, pp. 1070-1076.

[15] Rollemberg, M. C. E. and Curtius, A. J., "Flameless Atomic Absorption Determination of Barium in Natural Waters Using the Technique of Standard Additions," *Mikrochimica Acta,* Vol. 2, No. 5-6, May 1982, pp. 441-447.

[16] Sturgeon, R. E. and Berman, S. S., "Analyte Ionization in Graphite Furnace Atomic Absorption Spectrometry," *Analytical Chemistry,* Vol. 53, No. 4, April 1981, pp. 632–639.
[17] Slavin, W., Carnrick, G. R., Manning, D. C., and Pruszkowska, E., "Recent Experiences with the Stabilized Temperature Platform Furnace and Zeeman Background Correction," *Atomic Spectroscopy,* Vol. 4, No. 3, May-June 1983, pp. 69–86.
[18] Slavin, W., Carnrick, G. R., and Manning, D. C., "Chloride Interferences in Graphite Furnace Atomic Absorption Spectrometry," *Analytical Chemistry,* Vol. 56, No. 2, Feb. 1984, pp. 163–168.
[19] Kinard, W. D. and Midkiff, C. R., Jr., "The Application of Oxygen Plasma Ashing to Gunshot Residue Analysis," *Journal of Forensic Sciences,* Vol. 23, No. 2, April 1978, pp. 368–374.

Address requests for reprints or additional information to
Robert D. Koons
Forensic Science Research Unit
FBI Laboratory
FBI Academy
Quantico, VA 22135