

Analysis of Gunshot Primer Residue Collection Swabs by Inductively Coupled Plasma-Mass Spectrometry*

REFERENCE: Koons RD. Analysis of gunshot primer residue collection swabs by inductively coupled plasma-mass spectrometry. *J Forensic Sci* 1998;43(4):748–754.

ABSTRACT: The concentrations of antimony, barium, and lead in gunshot residue collection swab extract solutions were determined using inductively coupled plasma-mass spectrometry. Analytical advantages of inductively coupled plasma-mass spectrometry are a lack of interferences by swab extract constituents, low detection limits, wide linear dynamic ranges, short analysis times, and good precision and accuracy. This procedure is applicable to both hand blank and shooter-associated levels of antimony, barium, and lead in gunshot residue swab extracts.

KEYWORDS: forensic science, criminalistics, gunshot residue, barium, antimony, lead, inductively coupled plasma-mass spectrometry

Determination of the amounts of antimony (Sb), barium (Ba), and lead (Pb) in hand swabs from suspects in firearms discharge cases has been used for gunshot primer residue (GSR) detection since the late 1960s. Several analytical methods have been used successfully for this analysis. Radiochemical neutron activation analysis (NAA) was the initial method reported for quantitative determination of Sb and Ba in GSR collection swabs (1) and a modified version of this procedure remained the predominant analytical method in the FBI Laboratory for about 20 years. Graphite furnace atomic absorption spectrophotometry (GFAAS) found acceptance in many crime laboratories because of its relatively low cost, ease of use, wide availability, and the added capability of determining Pb (2,3). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) has more recently been used by a few laboratories, particularly for determination of Ba (4) in conjunction with GFAAS determination of Sb and Pb. These techniques are not without their drawbacks, however. NAA is not widely used because most laboratories lack access to a high-flux neutron source. GFAAS methods are relatively time consuming and are subject to some interferences resulting from the presence of high concentrations of nonanalyte constituents. ICP-AES is a rapid, multi-element technique that is relatively free of matrix interferences, but commercial instruments lack the sensitivity required for accurate determination of Sb at relevant levels. A relatively new analytical

technique, inductively coupled plasma-mass spectrometry (ICP-MS), offers both the required sensitivity for all elements used in GSR detection and the rapidity to handle large caseloads on a timely basis.

The use of ICP-MS instruments has increased steadily since their commercial introduction in 1982. Most commercial ICP-MS instruments are equipped with quadrupole mass analyzers having roughly unit mass number resolution, allowing rapid full mass scanning and multi-element analysis. Additional analytical benefits of ICP-MS are low detection limits, wide linear dynamic ranges, relative freedom from interferences particularly for elements above mass 80, and good precision and accuracy if proper precautions are taken. Several papers have appeared in the scientific literature comparing the analytical merits of ICP-MS with both NAA and ICP-AES (5,6). ICP-MS is now a widely accepted method for trace and ultra-trace analysis of a variety of liquid, gaseous, and solid samples in environmental, industrial, nuclear, medical, and other diverse applications (7). The acceptability of ICP-MS methods has been recognized in several judicial and regulatory arenas. For example, the U.S. Environmental Protection Agency (EPA) accepts ICP-MS measurements for determination of trace elements in water and wastes (8). There are currently several hundred ICP-MS instruments in operation in industrial, government, and university laboratories throughout the world. However, despite their acceptance in other disciplines, few forensic laboratories have adopted the ICP-MS technique to date. A few applications of ICP-MS in forensic examinations have been reported, particularly in the areas of toxicology and characterization of glass, minerals, and metals (6,9–13). This paper reports the use of ICP-MS for analysis of GSR swab extracts.

Experimental Details

Details concerning cleaning of glassware and storage containers, and spiking and extraction procedures, have been given previously (2). Discussion here is limited to a summary of and changes to those procedures.

Spiking Procedure

Samples for recovery studies were prepared by pipetting spiking solutions containing Sb, Ba, and Pb in 5% (v/v) nitric acid (HNO₃) onto pairs of cotton tipped swabs (Johnson & Johnson, New Brunswick, NJ). Single-element standard solutions containing 10,000 µg/mL of Ba and Sb (National Institute of Standards and Technology, Gaithersburg, MD) and 1000 µg/mL of Pb (Aldrich, Milwaukee, WI), high purity HNO₃ (Fisher Scientific, Pittsburgh, PA), and deionized water of 18 MΩ quality were used in this study. A stock standard solution containing 50.0 µg/mL Ba and Pb and 10.0

¹ Research Chemist, Forensic Science Research Unit, FBI Laboratory, FBI Academy, Quantico, VA.

* This is Publication No. 97-13 of the Laboratory Division of the Federal Bureau of Investigation (FBI). Names of commercial manufacturers are provided for information only, and inclusion does not imply endorsement by the FBI.

Received 26 Sept. 1997; and in revised form 17 Nov. 1997; accepted 19 Nov. 1997.

$\mu\text{g/mL}$ Sb in 5% HNO_3 was made by dilution of the single-element standards and used throughout this study. Spiking solutions were made daily by appropriate dilution of the stock standard solution in 5% HNO_3 . To construct standard response curves, 12 spike levels ranging from 0 to 10 μg Ba and Pb and 0 to 2 μg Sb were made by pipetting aliquots of the spiking or stock solution onto pairs of swabs. A 5% HNO_3 solution was also added to each swab pair to bring the total volume of solution added to 200 μL . The two swabs of each pair were then placed in 15 mL polypropylene screw-top tubes. In some studies, two sets of standards were prepared for analysis, one by pipetting the spiking solutions into empty extraction tubes and the other by pipetting the spiking solutions onto pairs of swabs. The samples were dried by placing the tubes with caps removed in an 80°C oven overnight before further handling.

Extraction Procedure

The extraction procedure used in this study is a modification of the procedure described previously (2). The procedure consists of cutting the two swab tips from their plastic shafts, placing them in a 15 mL polypropylene screw-top tube, and adding 10.00 mL of a 10% (v/v) HNO_3 solution containing 50 $\mu\text{g/L}$ each of indium (In) and bismuth (Bi) as internal standards. The tube contents are then mixed, heated for 2 h at 80°C, remixed, and the extract separated from the swab material by centrifugation. The extract solution is then transferred by pipetting to another tube for analysis.

Instrumental Operating Parameters

An Elan 6000 ICP-MS (Perkin Elmer/Sciex, Norwalk, CT) was used in these studies for measurement of Sb, Ba, and Pb concentrations in the GSR swab extract solutions. Samples were introduced into the quartz torch using a peristaltic pump, crossflow nebulizer and Scott design Ryton spray chamber. The spray chamber drain was pumped using a second channel on the same peristaltic pump as was used for sample introduction. Instrumental operating conditions and mass spectrometer data acquisition settings are summarized in Table 1.

TABLE 1—ICP-MS operating conditions and acquisition parameters.

OPERATING CONDITIONS	
RF Power:	forward: 1100 W reflected: <5 W
Gas flow rates:	plasma: 15.0 L·min ⁻¹ nebulizer: 0.98 L·min ⁻¹ auxiliary: 2 L·min ⁻¹ (optimized)
Sample uptake rate:	0.5 mL·min ⁻¹
Nebulizer:	gem tip, crossflow
Spray chamber:	Ryton, double-pass (Scott type)
Working distance:	10 mm from top of load coil (nominal)
Sampling cone:	nickel, 0.045 in. (1.14 mm) orifice
Skimmer cone:	nickel, 0.035 in. (0.89 mm) orifice
Lens voltages:	optimized daily
DATA ACQUISITION PARAMETERS	
Sweeps/reading:	50
Readings/replicate:	1
Number of replicates:	6
Points across peak:	1
Resolution:	normal (1.0 amu)
Scanning mode:	peak hop
Dwell time per mass:	20 ms
Replicate time:	1000 ms
Detector mode:	dual
Auto lens:	on
Monitored ions:	m/z 115, 121, 123, 137, 138, 206, 207, 208, 209

Results and Discussion

Mass Spectra

A bar graph representation of a mass spectrum of the regions containing the Sb, Ba, and Pb isotopes is shown in Fig. 1. The data shown were obtained from a swab extract solution containing 0.005 $\mu\text{g/mL}$ Sb and 0.025 $\mu\text{g/mL}$ Ba and Pb as well as the 0.050 $\mu\text{g/mL}$ In and Bi internal standards. The spectra are characterized by low ion count rates (typically about 30 s⁻¹) for isotopes not present in the samples (m/z 125, 126, 203, and 205) and high count rates (greater than 20,000 s⁻¹) for at least two isotopes of each element of interest. Antimony has two isotopes with masses of 121 and 123 with natural abundances of 57.25 and 42.75, respectively. The only elemental spectral overlap is a minor abundance (0.87%) isotope of tellurium at mass 123, for which correction is readily made. Tin, a minor constituent in the extract solution used here, has isotopes at masses 112, 114, 116, 117, 118, 119, 120, 122, and 124, but they do not affect Sb determination at the levels of tin normally present in GSR swab extracts. No significant polyatomic species occur at masses 121 or 123. Barium has seven naturally occurring isotopes, with the two most abundant at masses 137 and 138 having 11.32 and 71.66% abundances, respectively. The only elemental spectral interferences are the minor isotopes of lanthanum (0.089% abundance) and cerium (0.250% abundance) at mass 138, for which corrections based on more abundant isotopes for these elements are readily made. No significant polyatomic species have been found in GSR solutions which overlap the 137 or 138 isotopes of barium. Most of the ion counts shown in Fig. 1 in the mass range of 128 to 136 are from isotopes of xenon, a contaminant in the argon gas. These isotopes cause no interferences with the major Ba isotopes at masses 137 and 138. Lead has four naturally occurring isotopes at masses 204, 206, 207, and 208. Lead isotopes may vary in abundance depending upon the source of the lead. To minimize errors caused by differences in isotopic distribution, the sum of the intensities for the three isotopes at masses 206, 207, and 208 was used as recommended by the EPA for environmental samples (8). There are no analytically significant interferences with these three lead isotopes from any other elements or polyatomic species.

In this study, the isotopes, ¹²¹Sb, ¹³⁸Ba, and ²⁰⁶⁺²⁰⁷⁺²⁰⁸Pb were used for determination of total element concentrations of Sb, Ba, and Pb. In casework application, a total scan of the full mass range for each sample can also be made using the rapid semiquantitative capability of ICP-MS. Comparison of the isotopic ratios for an element in the sample extract to the ratios in a standard solution can be used to indicate the presence or absence of interfering species and simple, appropriate corrections can be made. In this study, quantitation of element concentrations was made using ¹¹⁵In and ²⁰⁹Bi as internal standards by monitoring the intensity ratios of m/z 121/115 for Sb, 138/115 for Ba, and (206 + 207 + 208)/209 for Pb.

Analytical Responses

The analytical responses for Sb, Ba, and Pb both as ion intensities and ion ratios in non-swab standard solutions and swab standard extracts are shown in Fig. 2. For all three elements, both the ion intensities and the ion ratios to the internal standards (In and Bi) exhibit excellent linear responses over the concentration ranges encountered in the determination of the presence of GSR. The mass of each element in micrograms per swab pair can be obtained from the solution concentration data shown in Fig. 2 by dividing

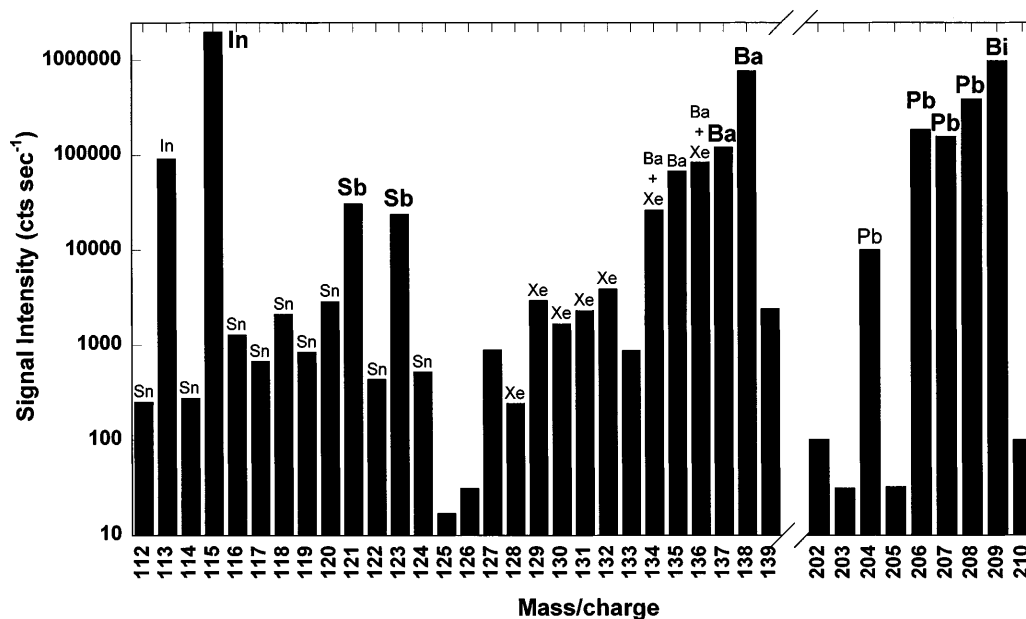


FIG. 1—Mass spectrum of extract solution containing 0.005 $\mu\text{g/mL}$ of Sb and 0.025 $\mu\text{g/mL}$ of Ba and Pb.

the values on the x-axes by 100. The linearity and near identity of standard curves for non-swab and swab mounted standards indicates that no uncorrected matrix effects due to swab constituents are present and the recovery of all three elements by this extraction procedure is nearly complete.

The sensitivities, measured as $\text{s}^{-1} \text{ppm}^{-1}$ (cts/s-ppm) for isotopes shown in Fig. 1 are 8.0×10^6 for ^{121}Sb , 3.8×10^6 for ^{138}Ba , and 3.6×10^7 for $^{206+207+208}\text{Pb}$. Consequently, for Sb, the most difficult element in the GSR analytical scheme, a typical GSR extract solution containing 0.005 $\mu\text{g/mL}$, yields a ^{121}Sb count rate of $40,000 \text{ s}^{-1}$ compared with a count rate of about 30 s^{-1} for a solution containing no Sb. Such a count rate is readily measured with good precision.

The linear ranges for the three elements extend from the lower quantitation limits to the maximum detectable signal, about $40,000,000 \text{ s}^{-1}$. In situations where determination of higher levels of analytes are required, dilution provides a simple method of making the measurements. For quantitative determinations, dilution of the sample extracts is best made using the extracting solution to keep the In, Bi, and HNO_3 concentrations constant.

Nonspectral Interferences

Although mass spectral interferences are unimportant in the determination of Sb, Ba, and Pb in GSR swab extract solutions, general signal depression or enhancement effects may occur in some samples. Changes in ion count rates (matrix effects) may be caused by high concentrations of non-analyte constituents, such as easily ionized elements or by differences in ionic strength or acid concentrations between samples and standards. Similarly, shifts in measured ion intensities (drift) may result from changes in instrumental parameters, such as a gradual clogging of the cones during analysis of samples containing high dissolved solids. An effective method for minimizing a variety of matrix and drift effects in ICP-MS is to measure the ratios of analyte ion intensities to internal standards for quantitation of elemental concentrations (14). General requirements for an element or isotope to be useful as an internal standard are that it must have a mass which is free from spectral interferences, be as

close to the analyte isotope masses as possible, behave in a similar manner to the analyte elements in terms of chemical and ionization processes, and must not be present in significant amounts in the samples to be analyzed. For determination of Sb, Ba, and Pb in GSR extract solutions, the ^{115}In and ^{209}Bi isotopes meet these requirements for use as internal standards.

In order to evaluate the effectiveness of internal standards for correcting the effects of nonspecific interferences in GSR extract analysis, two experiments were performed. In the first, over a 1.5 h period while the ICP-MS was being used to analyze a series of GSR swab extract solutions, a single solution was repeatedly analyzed by interjecting it following every sixth sample. The results of this study are shown in Fig. 3. The intensities of the isotopes of Sb, Ba, and Pb shown in Fig. 3a display a slight upward drift over the 1.5 h time period. This slow drift in signal is some variety of instrumental drift. The ratios of analyte intensities for these same measurements to the internal standard intensities are shown in Fig. 3b. The ratios display less variation with time than do the uncorrected analyte intensities. The repeatability of measurements both with and without internal standard correction shown in Fig. 3 is quite good. In instances where signal drift is more severe, such as when a nebulizer becomes partially clogged, the internal standard corrected values display much improved stability compared to the individual analyte ion signals.

Another well-documented form of nonspecific interference in ICP-MS is signal suppression caused by high concentrations of easily ionizable elements (14). In GSR swab extract solutions, the predominant element of this sort is sodium (Na), both because it is present in bleached swabs and because it is a major constituent of human perspiration. To test the effects of Na concentrations on the analytical results, standards containing 0.020 $\mu\text{g/mL}$ Sb, 0.100 $\mu\text{g/mL}$ Ba, and 0.100 $\mu\text{g/mL}$ Pb and varying amounts of Na (as the chloride) over the range observed in GSR collection swab extracts were analyzed. The analytical responses for these solutions are shown as a function of Na concentration in Fig. 4. The intensities for the Sb, Ba, and Pb ions fluctuate significantly and decrease generally with increasing Na content (Fig. 4a). Again, the ion intensity ratios shown in Fig. 4b are largely unaffected by Na

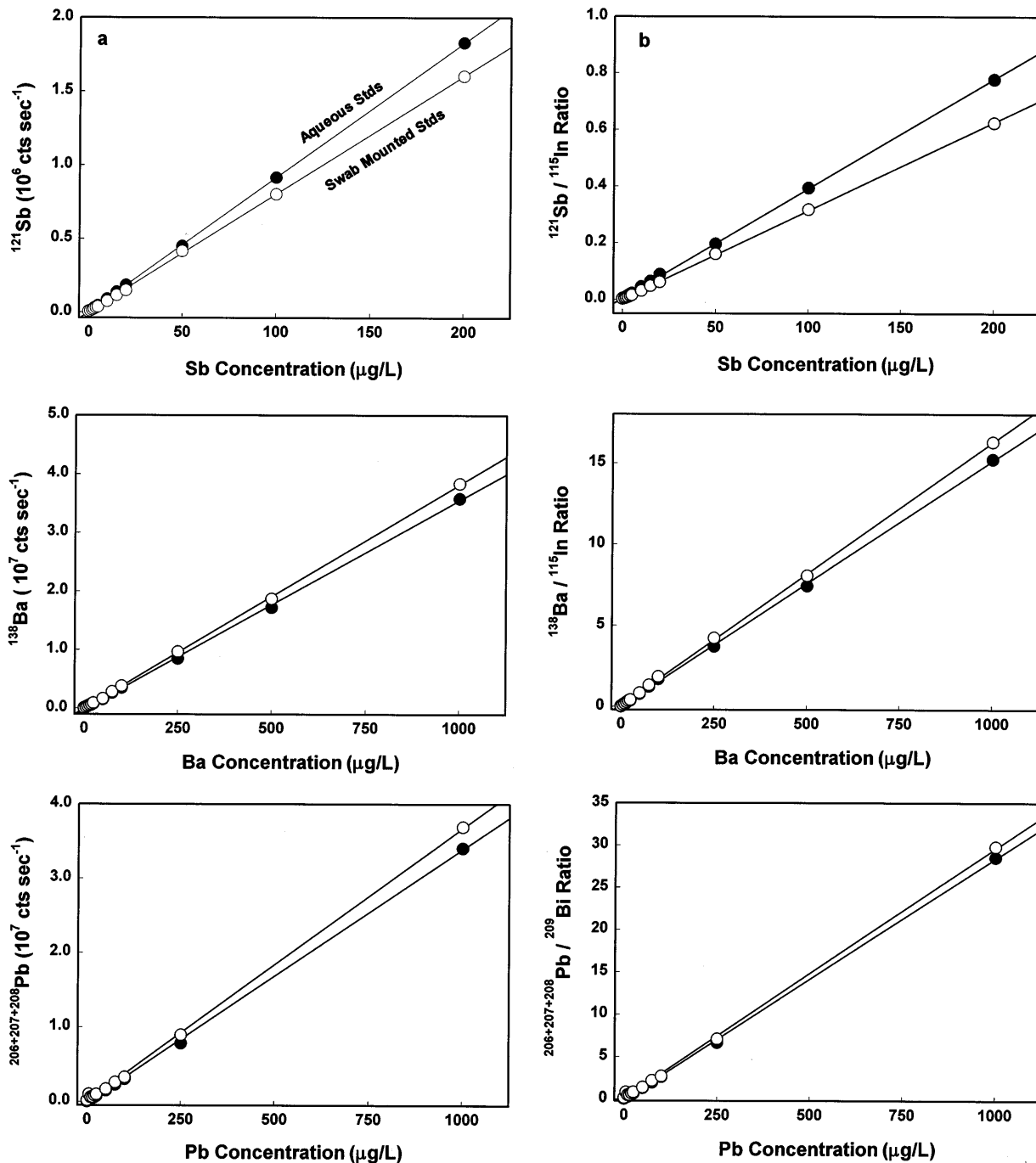


FIG. 2—Standard response curves for Sb, Ba, and Pb in two matrices (● aqueous standards, ○ swab-mounted standards): (a) ion intensities, (b) ion intensity ratios to internal standards.

concentrations in the range studied and the use of internal standards corrects well for the changing instrument sensitivities.

As a result of these studies and because of the unknown nature of the constituents which may be present in case samples, it is recommended that internal standards always be used for GSR determinations using ICP-MS. In this study, the internal standards were included in the extracting solution. Alternatively, they could be added to the solutions following extraction. Since recovery of both In and Bi is complete using the extraction procedure as in this study, both methods of adding the internal standards yield the same results. The procedure of including the In and Bi in the

extracting solution is procedurally easier in that it eliminates a later spiking step and automated data handling makes calculation of results straightforward.

Precision

The precision of ICP-MS results for GSR extracts can be estimated from the scatter of the individual data points about the regression estimates in Fig. 2. Since the analytical responses were measured using extractions of swabs containing the standards, the scatter shown represents the combined uncertainties inherent in the

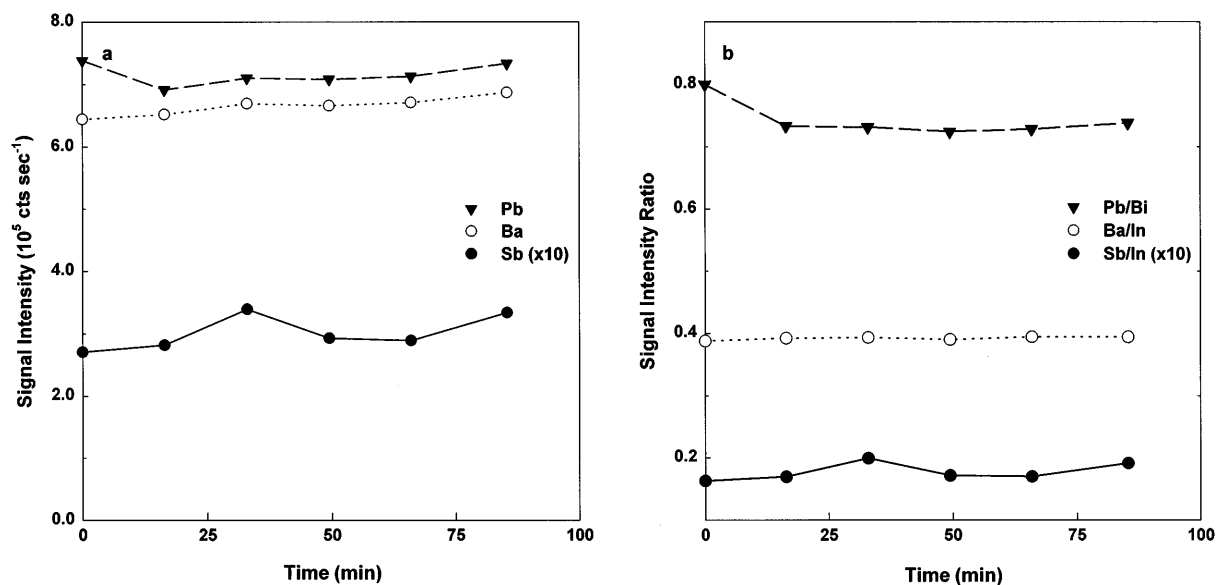


FIG. 3—Signal intensity as a function of time for Sb, Ba, and Pb in a swab extract solution: (a) ion intensities, (b) ion intensity ratios to internal standards.

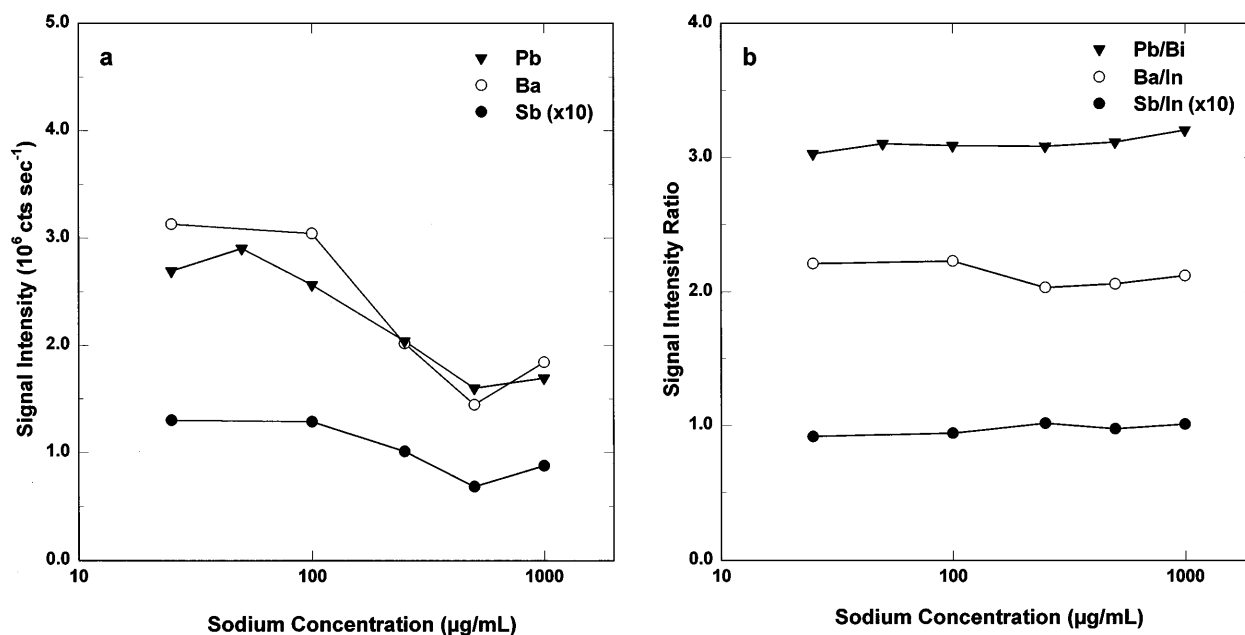


FIG. 4—Effects of increasing sodium concentrations on Sb, Ba, and Pb signals in a swab extract solution: (a) ion intensities, (b) ion intensity ratios to internal standards.

spiking procedure, the extraction procedure and the instrumental measurement. It is readily apparent from the very small deviations of individual data points about the response curves shown in Fig. 2 that the overall precision is excellent. The differences between the results estimated by the statistical fit of the data to first-order regression equations and the measured responses expressed in units of mass are 0.12 ng for Sb, 27 ng for Ba, and 40 ng for Pb for the standard containing 0.15 μg of Sb and 0.75 μg each of Ba and Pb. Another means of estimating the method precision is to make repeated measurements of a mid-range standard solution. Typically, the precision measured in this manner is better than 5% relative standard deviation for all three elements. The precision of

this method is well within the requirements for interpretation of GSR swab extracts.

Detection Limits

Detection limits were determined by making repeated measurements of a control swab (spiked with 5% HNO_3 only) extract solution to determine the standard deviation of the blank. The 3σ detection limit, obtained by multiplying the standard deviation of the blank by three and dividing by the sensitivity (slope of the standard response curve), is 0.000052, 0.000020, and 0.00014 $\mu\text{g/mL}$ for Sb, Ba, and Pb, respectively. For a 10 mL extraction

TABLE 2—Detection limits of ICP-MS (this study), ICP-AES (unpublished results, FBI Laboratory), and GFAAS (2) methods of determination of element concentrations in GSR swab extract solutions. Results are in µg/L.

	ICP-MS	ICP-AES	GFAAS
Antimony	0.05	2	0.5
Barium	0.02	0.04	5
Lead	0.1	2	1

volume, this corresponds to mass detection limits of 0.5 ng of Sb, 0.2 ng of Ba, and 1.4 ng of Pb per swab pair. These values are all well below the 40 to 500 ng levels generally associated with the presence of GSR (15) and are also below the levels of these elements in most hand blank (nonshooter) samples (16). The ICP-MS detection limits are compared with representative detection limits for GFAAS and ICP-AES methods in Table 2. As shown, the detection limits obtained using ICP-MS are superior to those using the other methods, particularly for Sb and Pb. The detection limits for both Ba and Pb calculated in this study are adversely affected by the fact that the control swab extracts contain detectable amounts of these elements. Tests of individual components of the extraction procedure show the sources of the Ba and Pb to be the nitric acid and the cotton swabs. In fact, determination of Ba and Pb concentrations in control swab extracts is straightforward by ICP-MS. Instrumental detection limits determined by repeated measurements of high purity 10% HNO₃ solutions are in the sub-ng range for Ba and Pb, as is widely reported in the ICP-MS literature (e.g., see Ref 14). However, use of very high purity reagents and specially cleaned swabs is not required for GSR interpretation, because the blank values are considerably lower than levels of interest of the target elements.

Accuracy

To verify the accuracy of results obtained by the ICP-MS procedure, two swab samples obtained from test shooters were analyzed by both ICP-MS and GFAAS/ICP-AES procedures. For these studies, a 5 mL extraction was used for the GFAAS/ICP-AES measurements and the extracts were further diluted twofold and internal standards added for the ICP-MS measurements. The procedures used for GFAAS and ICP-AES measurements were those routinely used for evidentiary samples in the FBI Laboratory. The results of this comparative study, shown in Table 3, indicate good agreement between the results obtained by ICP-MS and the traditional methods for all three elements.

Washout Time

A problem sometimes noted with analytical methods with high sensitivity, such as ICP-MS, is carryover during analysis of a sample with a low analyte concentration immediately following one with a high concentration. To test the significance of this effect in GSR analysis, a washout study was conducted. Extract solutions from a control swab, high level swab-mounted standard, and a control swab were aspirated sequentially into the ICP-MS. The ion intensities were continuously monitored at approximately 500 ms intervals and the results are shown in Fig. 5. As indicated, all three elements are removed to background levels in about one minute. The noisy signal at each solution change results from an air bubble entering the plasma torch between solutions. If the sample pump rate is speeded up briefly during a rinse-out cycle, the ICP-MS

TABLE 3—Comparison of results of analysis of GSR swabs by ICP-MS and GFAAS/ICP-AES. All results are in µg/swab pair.

Single shot, right-handed, Δt = 0, copper-plated bullet, .38 Sp Winchester ammunition .38 Sp S + W Model 10-6						
	Sb ICPMS	Sb GFAAS	Ba ICPMS	Ba ICPES	Pb ICPMS	Pb ICPES
Right back	0.036	0.04	0.060	0.060	0.55	0.55
Right palm	0.069	0.08	0.099	0.098	0.87	0.95
Left back	0.004	0.017	0.013	0.011	0.13	0.15
Left palm	0.006	0.010	0.026	0.025	0.19	0.17
Control	0.000	0.007	0.002	0.000	0.001	0.00

Single shot, right handed, Δt = 0, semijacketed bullet (base jacketed), .38 Sp R-P ammunition .38 Sp S+W Model 10-6						
	Sb ICPMS	Sb GFAAS	Ba ICPMS	Ba ICPES	Pb ICPMS	Pb ICPES
Right back	0.017	0.02	0.042	0.040	0.31	0.31
Right palm	0.092	0.10	0.130	0.131	0.26	0.27
Left back	0.002	<0.005	0.009	0.006	0.050	0.05
Left palm	0.004	0.011	0.016	0.013	0.099	0.09
Control	0.000	0.00	0.004	0.000	0.018	0.00

method can readily accommodate determination of multiple element concentrations in swab extract solutions at a rate of approximately 2 min per sample.

Recovery Efficiency

A difficulty often noted in extraction of GSR swabs is the incomplete recovery of Sb (2). The recovery efficiency of Sb in this study can be determined by comparison of the slopes of the two Sb/In curves in Fig. 2. The deviation of the two slopes indicates approximately an 81% recovery of the Sb spikes using the extraction procedure of this study. This result agrees well with observations made over the past 10 years, indicating that Sb recovery is typically 75 to 80% using the 2 mL extraction volume commonly used for GFAAS determination (2). The recoveries of Ba and Pb are complete, as indicated by the agreement of swab-mounted and aqueous standards shown in Fig. 2b.

Conclusions

ICP-MS provides the analytical capability for determination of the concentrations of Sb, Ba, and Pb in GSR swab extract solutions with the accuracy and precision required for bulk GSR detection. The analytical detection limits are superior to those which can be obtained by GFAAS or ICP-AES and the analysis time is much shorter than that of GFAAS. An advantage of MS detection is that several isotopes for each element can be used to monitor and correct for spectral interferences. Monitoring of isotope ratios indicates that no spectral interferences have occurred in any samples examined to date. Use of internal standards and the ability to use large dilutions when analytes are present at positive GSR levels make nonspecific interference problems (matrix effects) negligible.

Although not part of this study, there are two additional potential advantages of using an ICP-MS method for GSR detection and characterization. First, the ICP-MS procedure allows the determination of the levels of additional elements which may be associated with handling of a weapon or ammunition component, or elements which may be present in specific ammunitions, such as strontium in some nontoxic primers, cobalt in Nyclad™ bullets, or copper,

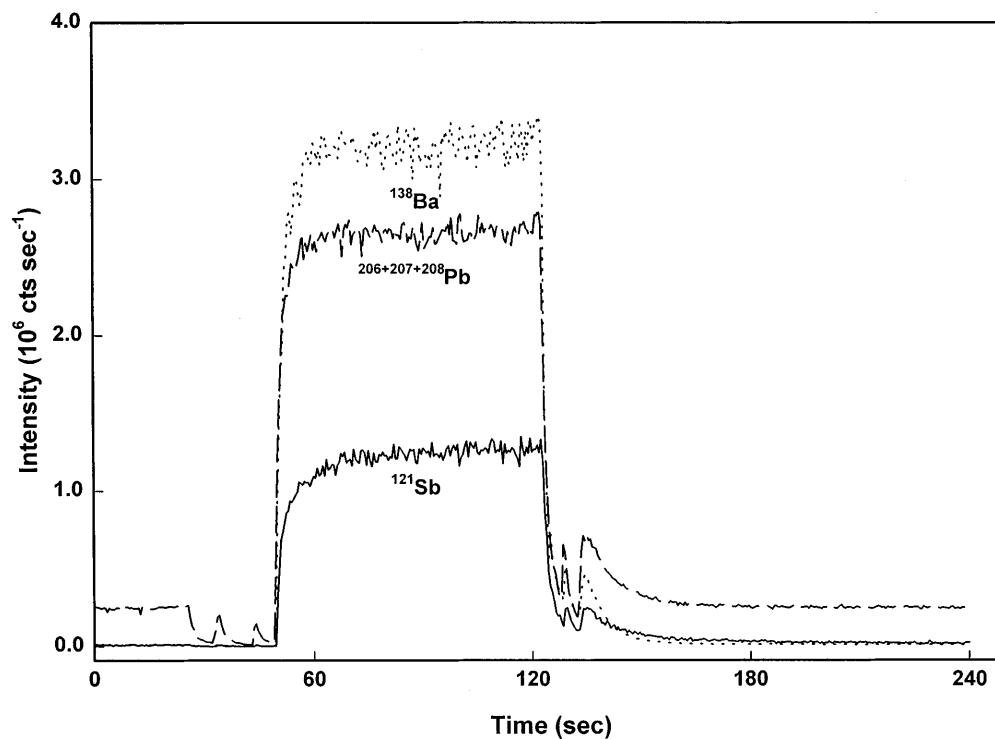


FIG. 5—Signal intensity for Sb, Ba, and Pb as a function of time for successive introduction of a control solution, a high-level standard, and a control solution.

nickel, or zinc in jacketed bullets. Second, the use of MS detection also allows the possibility of some sourcing of primer-derived Pb by isotope distributions (13). The extent to which these applications are of use in criminal investigations is the subject of current investigations in this laboratory.

Acknowledgments

I would like to acknowledge Donald G. Havekost for his helpful discussions and encouragement during the course of this project, Stephanie Lenzenweger for her assistance in method development, calibration and operation of the ICP-MS instrument, and JoAnn Buscaglia and an anonymous reviewer for their suggestions during preparation of this paper.

References

- Schlesinger HL, Lukens HR, Guinn VP, Hackleman RP, Korts RF. 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.
- Koons RD, Havekost DG, Peters CA. Analysis of gunshot primer residue collection swabs using flameless atomic absorption spectrophotometry: a reexamination of extraction and instrument procedures. *J Forensic Sci* 1987;32:846–65.
- Renshaw GD, Pounds CA, Pearson EF. The quantitative estimation of lead, antimony, and barium in gunshot residues by non-flame atomic absorption spectrophotometry. *Atomic Abs Newsl* 1973;12: 55–6.
- Koons RD, Havekost DG, Peters CA. Determination of barium in gunshot residue collection swabs using inductively coupled plasma-atomic emission spectrometry. *J Forensic Sci* 1988;33:35–41.
- Moens L, Dams R. NAA and ICP-MS: A comparison between two methods for trace and ultra-trace element analysis. *J Radioanal Nucl Chem* 1995;192:29–38.
- Koons RD. ICP atomic spectrometry in the forensic laboratory. *Spectroscopy* 1993;8:16–21.
- Taylor HE, Garbarino JR. Analytical applications of inductively coupled plasma-mass spectrometry. In: Montaser A, Golightly DW, editors. *Inductively coupled plasmas in analytical atomic spectrometry*. New York: VCH Publishers, 1992:651–76.
- U.S. Environmental Protection Agency. EPA Method 200.8, Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry, Ver 4.3, Aug. 1990.
- Watling RJ, Herbert HK, Delev D, Abell ID. Gold fingerprinting by laser ablation inductively coupled plasma mass spectrometry. *Spectrochim. Acta, Part B* 1994;49:205.
- Zurhaar A, Mullings L. Characterisation of forensic glass samples using inductively coupled plasma mass spectrometry. *J Anal Atomic Spectr* 1990;5:611–7.
- Parouchais T, Warner IM, Palmer LT, Kobus H. The analysis of small glass fragments using inductively coupled plasma mass spectrometry. *J Forensic Sci* 1996;41:351–60.
- Lyon TDB, Fell GS, McKay K, Scott RD. Accuracy of multi-element analysis of human tissue obtained at autopsy using inductively coupled plasma mass spectrometry. *J Anal Atomic Spectr* 1991;6: 559–64.
- Hinners TA, Heithmar EM, Spittler TM, Henshaw JM. Inductively coupled plasma mass spectrometric determination of lead isotopes. *Anal Chem* 1987;59:2658–62.
- Horlick G, Shao Y. Inductively coupled plasma-mass spectrometry for elemental analysis. In: Montaser A, Golightly DW, editors. *Inductively coupled plasmas in analytical atomic spectrometry*. New York: VCH Publishers, 1992:551–612.
- Singer RL, Davis D, Houck MM. A survey of gunshot residue analysis methods. *J Forensic Sci* 1996;41:195–8.
- Havekost DG, Peters CA, Koons RD. Barium and antimony distributions on the hands of nonshooters. *J Forensic Sci* 1990;35: 1096–114.

Additional information and reprint requests:
Robert D. Koons, Ph.D.
Forensic Science Research Unit
FBI Academy
Quantico, VA 22135