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

Determination of Barium in Gunshot Residue Collection Swabs Using Inductively Coupled Plasma-Atomic Emission Spectrometry

REFERENCE: Koons, R. D., Havekost, D. G., and Peters, C. A., **"Determination of Barium in Gunshot Residue Collection Swabs Using Inductively Coupled Plasma-Atomic Emission Spectrometry,"** *Journal of Forensic Sciences*, JFSCA, Vol. 33, No. 1, Jan. 1988, pp. 35–41.

ABSTRACT: Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was compared with atomic absorption spectrophotometry (AAS) for barium determination in gunshot residue (GSR) collection swabs. Lack of interferences by common swab extract constituents, a wide linear dynamic range, and good precision and accuracy of ICP-AES make it superior to AAS for barium determination in GSR swab extracts.

KEYWORDS: forensic science, ballistics, gunshot residues, atomic absorption spectrophotometry, firearms discharge, barium determination, inductively coupled plasma-atomic emission spectrometry

Determination of the amounts of antimony (Sb), barium (Ba), and sometimes lead (Pb) present on cotton-tipped swabs after swabbing a suspected shooter's hands is commonly used as an indicator of the presence of gunshot primer residues (GSR). Recently, we reported a procedure which provides accurate, reproducible measurements of Sb, Ba, and Pb present on clean, spiked swabs by extraction and analysis using graphite furnace atomic absorption spectrophotometry (AAS) [*1*]. A potential source of error which was identified in that study is enhancement of Ba atomic absorbance by nonanalyte constituents in extract solutions. This error is minimized by comparison of GSR swabs with standards prepared by placing known amounts of Ba on clean cotton-tipped swabs for extraction and AAS analysis. Evidential GSR swabs, however, may contain a variety of contaminants such as dirt, grease, perspiration, or blood which will not be present in swab mounted standards. Inability to match the standard and sample nonanalyte concentrations can result in enhancement of Ba absorbance in the samples and positive errors in reported Ba concentrations.

In this paper, we report the results of application of inductively coupled plasma-atomic emission spectrometry (ICP-AES) to the measurement of Ba concentrations in swab extract solutions. There have been several reported applications in which ICP-AES has been shown

This is Publication No. 87-5 of the Laboratory Division of the Federal Bureau of Investigation. Names of commercial manufacturers are provided for identification only, and inclusion does not imply endorsement by the Federal Bureau of Investigation. Received for publication 28 March 1987; accepted for publication 20 May 1987.

[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.

to offer improved accuracy and precision compared with AAS for determination of Ba in complex solutions [2–4]. ICP-AES offers the advantages over AAS of wider linear dynamic ranges, relative freedom from chemical interferences, better sensitivity for many elements, including Ba, and greater precision than graphite furnace AAS methods. Although ICP-AES is widely used, it is only recently that its application to forensic science analyses has been reported [5–7].

Experimental Details

Details concerning cleaning of glassware and storage containers, and spiking, extraction, and AAS analysis procedures have been described previously [1]. Discussion here is limited to a summary of, and changes to, those procedures.

Spiking Procedure

Swabs for recovery studies were prepared by pipetting 200 μL of spiking solutions containing Ba in 5% nitric acid (HNO_3) on pairs of swabs. The spike levels used were 0, 0.05, and 0.25 μg of Ba. Contaminants were added following analyte spikes by pipetting 50 μL of perspiration or a 20% aqueous solution of hand lotion (Vaseline Intensive Care) to each pair of swabs. The two swabs of each pair were then rubbed together to distribute the contaminant and placed in 12- by 75-mm polystyrene snap-top tubes. The samples were dried by placing the tubes with caps removed in an 80°C oven overnight before further handling. Triplicate samples were made at each analyte spike level for each of the contaminants. Two sets of standards were prepared, one by pipetting the spiking solutions into empty extraction tubes and the other by pipetting the spiking solutions onto pairs of swabs to which no contaminants were added.

Extraction Procedure

The extraction procedure consists of removing the swab material from the plastic shaft, placing it in a plastic snap-top tube, adding 2.00 mL of 10% HNO_3, mixing, heating for 2 h at 80°C, remixing, and separating the extract from the swab material before AAS analysis. In this study, Ba AAS measurements were made after a twofold dilution of the extract solutions, rather than the larger dilutions suggested previously [1]. This procedural change was made because, in this study, the 1.00-μg Ba spikes used previously were omitted and further dilution was not needed to reduce extract concentrations into the linear working ranges of the AAS method. The swab mounted standards were treated in an identical manner to the samples so that relative recovery percentages could be calculated as previously suggested [1]. The set of standards without swab material was diluted to 2.00 mL with 10% HNO_3 and used to calculate absolute recovery percentages from contaminated swabs and swab mounted standards.

AAS Description

Operating conditions for the AAS, graphite furnace, autosampler, and data station used for Ba atomic absorbance measurements have been described previously [1]. These conditions included atomization of Ba from the wall of a pyrolytic carbon tube using maximum power heating. The 553.6-nm atom line was used for absorbance measurements with peak areas recorded using the fast electronics of the data station.

ICP-AES Description

The Plasma II ICP-AES (Perkin Elmer) used in these studies consists of a 27.12-MHz rf induced argon plasma source operated at a forward power of 1 kW and a 1-m Ebert scanning monochromator used for measurement of the Ba emission intensity at the 455.4-nm ion line. Sample was introduced into the torch using the peristaltic pump, cross-flow nebulizer, and spray chamber provided by the manufacturer. Pertinent operating conditions are listed in Table 1. The same sample and standard solutions used for AAS analysis were aspirated directly into the ICP-AES for Ba determination without further dilution.

Results and Discussion

It has been demonstrated that the absorbance of Ba at the 553.6-nm atom line is enhanced by constituents leached from clean cotton swabs [*1*]. The principal element leached from swabs is sodium at about 60 μg/swab. The intensities of the Ba atomic absorbance for a series of solutions containing 0.100 μg/mL of Ba and various amounts of Na are shown as the curve labelled AAS in Fig. 1. The solutions used for these measurements contained 10% HNO_3 by volume in addition to the Ba and Na indicated to make them similar to GSR swab extract solutions. As shown, the barium response is fairly constant at low Na levels and increases sharply with increasing Na concentration up to a few hundred μg/mL where the rate of increase diminishes. The sodium nitrate used for preparing the solutions contained no measurable Ba, so the observed response must be one of enhancement of the Ba absorbance, rather than an uncorrected blank effect. Thus, for accurate AAS determination of Ba concentrations in GSR swabs, the standards used must approximately match the evidential swab extracts not only in Ba concentration, but also in Na concentration. The procedure of placing standards on clean swabs for extraction provides a good match of standard and sample Na concentrations only when the evidential swabs are not highly contaminated or otherwise different from the standards.

Since other elements besides Na may be present in swab extract solutions, we determined the Ba response in the presence of 500 μg/mL of a variety of contaminants. The method we selected for evaluating the effects of contaminants on Ba atomic absorbance is to ratio the slope of the Ba standard response curve in the presence of the contaminant to that obtained

TABLE 1—*Analytical conditions for ICP-AES determination of Ba in GSR swab extract solutions.*

Condition	Value
Incident plasma power	1000 W
Reflected power	<5 W
Plasma gas flow	15 L/min
Auxiliary gas flow	1.0 L/min
Nebulizer gas flow	1.0 L/min
Viewing height	15 mm above rf coil
Monochromator	B—1800 lines/mm
Signal compensation	off
Photomultiplier tube voltage	600 V
Emission peak wavelength	455.40 nm
Survey window	0.100 nm
Peak window	0.050 nm
Background correction	off
Integration time	100 ms
Sample uptake rate	1.0 mL/min

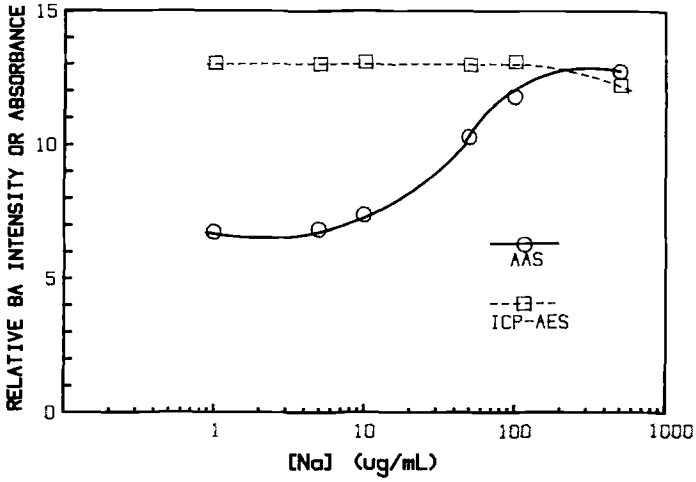

FIG. 1—*Effects of sodium on observed barium AAS and ICP-AES responses. All solutions contain 0.100 μg/mL Ba: vertical scales are arbitrary units.*

in 10% HNO_3. The relative slopes of Ba responses within the linear working range of the AAS instrument for solutions containing 500 μg/mL of various contaminants are given in Table 2. In our previous studies, the optimum atomization temperature for Ba determination was found to be 2700°C. The distribution of Ba atoms in the graphite furnace between ionic and atomic ground states is temperature dependent, and it has been demonstrated [8] that lower atomization temperatures diminish enhancement effects resulting from ionization of Ba by favoring the lower energy atomic ground state. For comparison, the Ba responses at an atomization temperature of 2500°C, the lowest temperature giving reproducible absorbance peak areas, are also listed in Table 2.

TABLE 2—*Effects of interferants on barium response. Results are ratios of the slope of the barium response in the presence of 500 μg/mL of interferant to slope of the barium response without interferant present.*

Interferant	AAS at 2700°C	AAS at 2500°C	ICP-AES
Pb^{2+}	0.97	1.05	0.93
Cu^{2+}	0.99	1.00	0.95
Zn^{2+}	1.00	1.06	0.99
Sb^{4+}	1.01	0.82	0.87
PO_4^{3-}	1.01	1.04	1.01
glucose	1.03	1.00	0.99
Cl^-	1.07	1.00	0.96
CH_3COO^-	1.08	1.00	1.03
Ni^{2+}	1.22	1.06	1.01
Fe^{3+}	1.25	1.00	1.07
Al^{3+}	1.61	1.68	0.97
Na^+	1.66	1.68	0.96
Ca^{2+}	1.78	2.27	0.87
K^+	1.87	1.50	0.89
Cr^{3+} (+K)	2.05	1.47	1.02

At the 500-μg/mL level, several of the elements listed cause a significant enhancement of the Ba absorbance response at both atomization temperatures as evidenced by response ratios greater than 1.0. Enhancement is most pronounced for Fe, Al, and easily ionized elements such as K, Ca, and Na. The large enhancement for dichromate ion reflects the use of the potassium salt to make the solution. Use of lower atomization temperatures does not significantly lessen the degree of enhancement of the Ba absorbance signal.

For comparison with AAS, we reanalyzed the solutions used for construction of Fig. 1 and Table 2 using ICP-AES. The Ba atomic emission responses are largely unaffected by changes in Na concentrations, as indicated by the relatively constant ICP-AES response shown in Fig. 1. Only at Na concentrations higher than a few hundred μg/mL is there a depression in the emission intensity. This results from both cooling of the plasma and diminished transport rates of the high-salt solutions to the ICP torch. The relative slopes for ICP-AES emission measurements of Ba standard solutions in the presence of the contaminants studied are shown in the last column of Table 2. In contrast to the AAS results, all of the potential interferants listed, even at the high levels of 500 μg/mL used in this study, have no significant enhancing effect on Ba emission responses. In fact, slight depression of the emission signal is observed for several elements, probably resulting from diminished transport rates through the nebulizer and spray chamber. Clearly, ICP-AES offers superior performance to AAS for Ba determination from the standpoint of interference effects. An additional advantage of ICP-AES is that the sensitivity for Ba is so great that in instances where high concentrations of contaminants occur, dilution of samples can be used to diminish signal depression effects without loss of analytical precision.

In a further comparison of ICP-AES and AAS for determination of Ba concentrations in more realistic swab extract solutions, we extracted and analyzed swabs containing known amounts of Ba and either perspiration or hand lotion. The levels of analytes used in this study (0, 0.05, and 0.25 μg) are at about the level normally encountered in the nonshooting population and the levels of contaminants are quite high. This represents a "worst case" analysis, which is useful for comparing analytical techniques. The results of AAS and ICP-AES measurements of extract solutions from these contaminated swabs are shown in Table 3. The two parts of this table are calculated using two different sets of standards. In the top half of Table 3, the results are calculated using Ba standards which do not contain swab constituents. Thus, these results reflect the effects of both recovery efficiency and signal

TABLE 3—*Recovery efficiency for extraction of Ba from contaminated swabs determined by AAS and ICP-AES. Results are expressed as micrograms of Ba for the blank level spikes and percent of Ba recovered (after correction for the blank) and standard deviation of three replicates for the 0.05- and 0.25-μg-level spikes.*

Swab Contaminant	AAS Results at Ba Level of			ICP-AES Results at Ba Level of		
	0.00, μg	0.05, %	0.25, %	0.00, μg	0.05, %	0.2, %
Results calculated using acid solution standards:						
perspiration	n.d.[a]	114	159	0.010	96.9	99.5
		±15	±5	±0.001	±1.5	±0.6
hand lotion	0.007	118	144	0.007	95	93.8
	±0.003	±12	±7	±0.002	±7	±0.4
Results calculated using swab mounted standards:						
perspiration	n.d.	83	118.0	0.005	101.7	104.7
		±11	±1.7	±0.001	±1.6	±0.6
hand lotion	n.d.	96	109	n.d.	107	99.6
		±9	±5		±7	±0.4

[a]Not detected.

enhancement or depression caused by nonanalyte constituents. In the bottom half of Table 3, the results are calculated using standards placed on clean swabs and carried through the extraction procedure. These results are those which are obtained using our previously suggested procedure [*1*] and represent recoveries of the added Ba from the sample swabs relative to those from uncontaminated swabs plus any effects resulting from mismatch of standard and sample matrices arising from contaminants in the samples. All results are expressed as recovery percentage of the known element addition with one standard deviation based on the triplicate analyses except for the blank levels which are expressed in micrograms of the element. Recovery percentages have been corrected for the contaminant blank where appropriate. The same solutions were used for both the AAS and ICP-AES measurements.

The AAS results are given in the first three data columns of Table 3. There is significant enhancement of the Ba absorbance measurements in the samples and results calculated using aqueous standards are higher than 100%. For the swabs containing 0.25 μg of Ba, the apparent recoveries are 159 and 144% in the presence of perspiration and hand lotion, respectively. Use of swab mounted standards reduces the magnitude of positive errors to acceptable levels for most of the contaminants and Ba levels studied. Results calculated using swab mounted standards indicate recoveries are complete within the total uncertainty of the measurements. Precision using AAS is relatively poor with a mean relative standard deviation for all samples of 7% (11% at the 0.05-μg level and 3% at the 0.25-μg level).

Results of Ba determination by ICP-AES for the same solutions used for AAS measurements are given in the three columns on the right side of Table 3. All results shown are between 95 and 105%, indicating that complete recovery of Ba is achieved in the presence of both contaminants. Results calculated using swab mounted standards are not significantly improved over those using acid solution standards, indicating that interfering effects of nonanalyte constituents are not as severe with ICP-AES as with AAS. For every sample, results by ICP-AES are closer to 100% than those by AAS for that sample. The precision of ICP-AES results is much better than AAS results for the same solutions, with the mean relative standard deviation for all samples being 2.3% (4.2% at the 0.05-μg level and 0.5% at the 0.25-μg level).

Conclusions

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) offers superior precision and accuracy compared to AAS for determination of Ba in GSR swab extract solutions. Enhancement of Ba absorbance in AAS in the presence of nonanalyte extract constituents can cause positive errors on the order of 150% or more. Effects of nonanalyte concentrations on the Ba emission levels in ICP-AES are generally insignificant at levels encountered in GSR swab extract solutions. Accurate ICP-AES determination of Ba concentrations can be made using standards having nonanalyte concentrations several orders of magnitude different from samples.

Figures of merit for AAS and ICP-AES indicate the advantages of ICP-AES for determination of Ba in GSR swab extract solutions. Detection limits for Ba, defined as three times the baseline noise levels, are 0.002 μg/mL for AAS and 0.0008 μg/mL for ICP-AES for a 10% HNO_3 solution. The upper linear range for AAS is 0.1 μg/mL, and for ICP-AES the response is linear to higher than 50 μg/mL, a level rarely observed in actual GSR swab extracts. Practical working ranges for the best results are 0.005 to 0.1 μg/mL for AAS and 0.002 to 10 μg/mL for ICP-AES. The wide linear dynamic range of ICP-AES practically eliminates the need for dilution when analyzing GSR extracts. Because of the low detection limits, however, dilution may be used to lessen the few matrix interferences when they are present. Short-term precision, indicated by the relative standard deviations of multiple measurements of the same solution having a barium concentration of 0.05 μg/mL is 5 to 10% by AAS and less than 1% by ICP-AES. In addition, AAS precision is strongly dependent upon

furnace alignment and graphite tube condition, factors which can change dramatically from day to day. Realistically, one can expect precision of about 2% relative standard deviation for real GSR samples which contain Ba concentrations within the working range of the ICP-AES.

As a result of this work and our previous studies, we believe that the best method for obtaining accurate analysis of GSR swab extract solutions is to use swab mounted standards to afford approximate match of nonanalyte concentrations with the sample extracts and determine Sb and Pb concentrations using AAS and Ba concentrations using ICP-AES. The wide linear dynamic range of ICP-AES for Ba will allow measurements of Ba concentrations using the same solutions as used for Sb or Pb by AAS. It has been suggested [9] that highly contaminated swabs are best analyzed using a complete dissolution procedure. While this approach may be useful for obtaining complete recovery of elements from the swabs, note that complete dissolution of a contaminated swab results in a solution with higher concentrations of nonanalytes than does an extraction procedure. Enhancement of AAS Ba measurements will thus be more severe for completely digested samples than extracts. In these instances, Ba determination by ICP-AES becomes even more advantageous compared with AAS than when analyzing extract solutions.

References

[1] 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*, Vol. 32, No. 4, July 1987, pp. 846–855.

[2] Dahlquist, R. L. and Knoll, J. W., "Inductively Coupled Plasma-Atomic Emission Spectrometry: Analysis of Biological Materials and Soils for Major, Trace, and Ultra-trace Elements," *Applied Spectroscopy*, Vol. 32, No. 1, Jan.–Feb. 1978, pp. 1–29.

[3] Thompson, M. and Walsh, J. N., *A Handbook of Inductively Coupled Plasma Spectrometry*, Methuen, Inc., New York, 1983.

[4] Morrison, G. H., "Elemental Trace Analysis of Biological Materials," *Critical Reviews of Analytical Chemistry*, Vol. 8, 1979, pp. 287–320.

[5] Locke, J., "The Application of Plasma Source Atomic Emission Spectroscopy in Forensic Science," *Analytica Chimica Acta*, Vol. 113, No. 1, Jan. 1980, pp. 3–12.

[6] Catterick, T. and Hickman, D. A., "The Quantitative Analysis of Glass by Inductively Coupled Plasma-Atomic Emission Spectrometry: a Five Element Survey," *Forensic Science International*, Vol. 17, No. 3, May–June 1981, pp. 253–263.

[7] Carpenter, R. C. and Till, C., "Analysis of Small Samples of Brasses by ICP-OES and their Classification by Two Pattern-recognition Techniques," *Analyst*, Vol. 109, No. 7, July 1984, pp. 881–884.

[8] 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.

[9] 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, Ph.D.
Forensic Science Research, FBI Lab
FSRTC, FBI Academy
Quantico, VA 22135