

TECHNICAL NOTE

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Analysis of Gunshot Primer Residue Collection Swabs Using Flameless Atomic Absorption Spectrophotometry and Inductively Coupled Plasma-Atomic Emission Spectrometry: Effects of a Modified Extraction Procedure and Storage of Standards

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ABSTRACT: Two modifications to a previously reported extraction procedure for determination of antimony, barium, and lead in gunshot primer residue swab extract solutions have been studied. Removal of cotton tips from swabs by cutting their shafts results in extraction efficiencies for all elements that compare favorably with those obtained by complete removal of the cotton from the swab shaft. Swab-mounted standards can be made and stored in a dry condition for periods of at least four months before use without adverse effects on analytical results. Long-term relative precision estimates for the combined extraction and analysis are approximately 5% for all three elements.

KEYWORDS: criminalistics, gunshot residues, spectroscopic analysis, shooter identification, firearms discharge, antimony determination, barium determination, lead determination, flameless atomic absorption spectrophotometry, inductively coupled plasma-atomic emission spectrometry

Procedures for accurate determination of barium (Ba), antimony (Sb), and lead (Pb) concentrations on cotton-tipped swabs used for gunshot primer residue (GSR) collection have recently been reported [1,2]. The key to these procedures is the use of swab-mounted stan-

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dards to correct results for incomplete extraction of Sb and to normalize sample and standard matrices before determination of Sb, Pb, and Ba using flameless atomic absorption spectrophotometry (FAAS) or Ba using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Also important is the use of an extraction procedure which yields nearly complete, reproducible recoveries of all three elements. These extraction and analysis procedures have been presented in training sessions to analysts in a number of laboratories as reference procedures to be used for comparison of other extraction and analytical protocols. Following two years' experience in the use of the reference procedures in routine case applications, two suggested changes have been made.

The first suggested modification is preparation of many sets of standard swabs at one time by pipetting standard solutions onto a number of swabs and drying them. These dried swab-mounted standards could then be stored and used for case samples received over a period of weeks to months, saving the time required to make new standard solutions and spiked swabs with each set of samples to be analyzed.

The second suggested modification to the reference procedure is to cut the swab shafts at the juncture with the cotton tip, rather than remove the cotton tip from the shaft. This modification minimizes sample handling and associated contamination and decreases the time required for sample preparation. This procedure has previously been shown to have no effect on element recovery efficiencies, provided the remainder of the extraction procedure is followed [1]. In this study, we have used the modified procedure to evaluate the effects of preparing spiked standard swabs and storing them for periods of up to four months before analysis. The results of these experiments give a good measure of the precision and accuracy which can be obtained using this modified sample extraction procedure.

Materials and Methods

For this study, spiking solutions containing known amounts of Sb, Ba, and Pb were pipetted onto swabs and into empty sample extraction tubes. These swab-mounted and liquid samples were then dried, stored, and analyzed along with freshly prepared samples. Two levels of each element, plus controls, were used. The low-level samples contained 0.02 μg of Sb and 0.1 μg of Ba and Pb, and the high-level samples contained 0.2 μg of Sb and 1.0 μg of Ba and Pb. A large number of samples containing spiking solutions both on swabs and in empty tubes were prepared at one time and dried for this study. The spiking solutions were saved in polyethylene bottles and used to prepare fresh standards for each set of analyses. For each aging time to be studied, four sets of samples were used. They included stored and freshly made swab-mounted standards, and stored and fresh standards which contained no swab material (aqueous standards). All samples and standards were dried immediately after preparation. Use of two sets of standards in this manner allowed the fourfold objective of determining integrity of spiking solutions over the aging time period, absolute recoveries of elements from swabs, effects of aging on recoveries relative to freshly prepared swab-mounted standards, and long-term precision of the results.

Details of the extraction and analysis procedures used (with the exception that all swabs were cut off with a short piece of shaft remaining, rather than cut completely off the shaft) have previously been reported [1]. The extract solution consisted of 2 mL of 10% nitric acid with heating to 80°C for 2 h. Sb and Pb were determined using FAAS, and Ba was determined using ICP-AES. Dilutions before analysis were twofold for control and low-level spikes and tenfold for high-level spikes. Within each analytical set, all samples and corresponding standards were treated identically once extraction was begun.

Results and Discussion

The first comparison in this study is between aqueous standards made by pipetting standard spiking solution into empty tubes, drying, and storing for up to 120 days, and freshly

made aqueous standards. On each analysis date, aged aqueous standard response curves were indistinguishable from the freshly prepared standards for each element. These results indicate that spiking solutions stored in polyethylene bottles are stable for periods of at least 120 days. These results are important in this study because they indicate that freshly made spiked swabs can be compared with aged spiked swabs with the assurance that the masses of the elements added to each swab are the same. It was also observed that the atomic absorbances for Sb and Pb in a given aqueous standard remained essentially constant over a 4-month period despite possible changes in furnace alignment, graphite tube and furnace condition, and other variables during this period. The characteristic mass, defined as the mass of analyte giving a signal of 0.0044 A-s [3], was 28 for Sb and 20 for Pb, using the conditions of this study. For routine use, these characteristic masses provide a useful means of checking instrument operating conditions and standard preparation.

The second comparison in this study is between the analytical responses of the aged sample extracts and those of freshly prepared swab-mounted standards to calculate relative recovery efficiencies as suggested in the reference procedure. The recovery efficiencies for Sb, Ba, and Pb spikes from swab-mounted standards as a function of their age are given in Table 1. These results indicate that the calculated recoveries of all three elements are complete at all aging times studied. The long-term precision of the combined extraction and analysis methods have been calculated by averaging all results for each element. The mean recoveries relative to swab-mounted standards and standard deviations for Sb, Ba, and Pb are 97 ± 4 , 100 ± 3 , and $100 \pm 6\%$, respectively.

The third comparison in this study is between the aqueous and the swab-mounted samples to calculate the absolute recoveries of elements from the swabs. The absolute recoveries are between 63 and 75% for Sb, greater than 95% for Ba, and between 70 and 100% for Pb. Factors causing the variability in recovery of Sb and Pb from day to day appear to affect both aged and fresh swab-mounted standards equally, as evidenced by the good precision shown in Table 1. The absolute recoveries of all three elements are about the same as those obtained when swabs were completely removed from their shafts before extraction and analysis [1]. These results are not surprising, considering that during extraction the cotton swabs become completely separated from their shafts for almost all samples. Therefore, modifying the procedure to snip the shafts with a clean pair of scissors, rather than cutting the swabs completely off their shafts, does not reduce element recoveries and does have the advantages of decreasing sample handling and preparation time.

TABLE 1—Recovery of elements from cotton-tipped swabs at two spiking levels of Sb, Ba, and Pb. Results are percent recovery for swabs stored for number of days indicated relative to freshly prepared swabs.

Age, days	Antimony (by FAAS)		Barium (by ICP-AES)		Lead (by FAAS)	
	(0.02 μg)	(0.2 μg)	(0.1 μg)	(1.0 μg)	(0.1 μg)	(1.0 μg)
3	95	98	102	100	99	100
7	97	101	100	99	101	99
15	94	96	93	99	81	101
22	102	93	100	102	98	99
30	94	103	99	102	108	100
45	88	98	99	98	105	103
59	98	99	95	104	100	105
92	95	104	98	105	93	103
120	100	94	99	99	102	97
Mean		97		100		100
Standard deviation		4		3		6

Conclusions

As a result of these studies, the two modifications to the reference procedures for GSR swab examination are warranted. The modified procedure yields results which are comparable to the slightly more cumbersome reference procedures. Our recommendation for GSR swab examination is to use swab-mounted standards (up to four months old), extraction using the modified procedure, and analysis of extract solutions for Sb and Pb by FAAS and Ba by ICP-AES. It is also important to emphasize that long-term storage of swab-mounted standards must be in a dry state and under conditions which do not cause contamination or loss of sample.

References

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