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The Application of Oxygen Plasma Ashing to Gunshot Residue Analysis

In the analysis of hand samples for barium and antimony levels indicative of gunshot residue, severe problems are encountered with swabs contaminated by blood, dirt, or grease. These problems originate from two main sources: decreased effectiveness of sample leaching and high instrumental backgrounds. When the flameless atomic absorption spectroscopy (FAAS) method developed in our laboratory [*1*] is used, the choice of sample collection materials is restricted to those that can be easily separated from the elements of interest. In our approach, a sample such as a cotton swab is leached with dilute nitric acid to extract any residues present. Surface contamination may make the swab impervious to solvent penetration and, therefore, inefficient leaching occurs. Contaminants such as blood, dirt, or grease on the sample can coat any primer residue particles present and prevent their dissolution in the acid, resulting in the amount of the elements of interest being lower in the solution than expected. The measured level of these elements will thus be lower than that actually present in the sample. Increasing the contact time between solvent and sample, or rigorous agitation to improve solvent attack, usually results in enhancement of the background response during the atomization phase of the AA analysis with no improvement in analytical results. This enhanced background, especially notable at the 217.6- and 217.9-nm (2176- and 2179-Å) lines used for antimony detection, may be attributed to light scattering by organic materials not completely destroyed during the drying and ashing cycle of the AA determination. Destruction of the matrix by ashing of the samples prior to analysis significantly decreases the analytical background and eliminates leaching difficulties.

Sample pre-ashing does, however, increase sample handling and lengthen analysis time, and it could result in the loss of volatile elements. Despite these limitations, sample ashing appears to be the most promising alternative for use with contaminated samples and other samples on lift materials such as tape and film that are not effectively handled by direct leaching. Three approaches available for sample ashing are wet ashing, dry ashing, and ashing in a low pressure oxygen plasma. Wet and dry ashing are both widely applied in the atomic absorption analysis of biological materials. Studies have shown the two methods to be generally equivalent [*2–4*]. Special techniques such as the use of microwave excitation [*5*] have been developed for wet ashing, and the method has been adapted to the digestion of gunshot residue samples collected on cotton swabs [*6*][2] or plastic film lifts [*7*]. One procedure for wet ashing of swabs recommends a mixture of nitric and perchloric acids [*8*]. When this method was tested in our laboratory, effective destruction of the cotton matrix was obtained but serious problems were encountered during analysis. The sample

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solution was placed on the atomizer and the drying and ashing cycles were initiated. Copious quantities of smoke from the decomposition of perchlorates were produced during drying and ashing on the tantalum strip. The smoke was difficult to clear from the atomizer chamber prior to sample atomization and posed a sufficiently serious problem so that wet ashing was abandoned. Dry ashing of samples collected on tape, film, and cotton swabs had previously been tested in our laboratory [*9*]. While effective, this approach did not appear applicable to relatively large numbers of samples and had not been studied with samples contaminated with materials other than blood.

The use of an electrically excited oxygen plasma for low temperature ashing of biological materials has been reported by several investigators. Gleit and Holland [*10*] described the construction and operation of such a plasma ashing system and evaluated it for the ashing of blood samples containing volatile inorganic compounds. Later investigators have applied the technique to drug characterization [*11*], to the detection of arsenic in lung tissue [*12*], and to coal, beef liver, and leaf materials which were then analyzed for trace elements by neutron activation analysis [*13*]. We had earlier reported a limited study in which simulated gunshot residue swabs containing known amounts of barium and antimony and contaminated by blood were ashed in a plasma furnace and analyzed by FAAS [*1*]. Excellent recovery of both elements had been obtained in this initial work. The present study was designed to evaluate the use of plasma furnace ashing as a precursor to the FAAS analysis of a variety of gunshot residue collection materials, both clean and contaminated with blood, grease, dirt, and other substances.

Method

The instrument used is a commercially available Series 1000 plasma system manufactured by International Plasma Corp. It consists of two individual sample chambers (or reactors), a radio frequency (RF) generator, and a vacuum pump. The vacuum pump is fitted with a trap, and special oil is used to prevent degradation of the pump oil. The instrument is shown in Fig. 1. In operation, samples in porcelain spot plates, dishes, or crucibles are placed in the cylindrical chambers, as shown in Fig. 2. The chambers are sealed and evacuated to a pressure of about 133 Pa (0.1 torr). Oxygen is introduced slowly and excited by RF energy. The excited oxygen attacks any oxidizable materials, such as cellulose or plastic, converting them to gases which are continuously removed from the chamber by the vacuum pump. No external heating is applied and oxidation occurs at a temperature dictated by the power setting on the instrument, usually about 150 °C. Samples are left in the chamber until ashing is complete.

Tape and contaminated samples require somewhat longer times for complete oxidation compared to clean cotton swabs; however, film lifts ash readily. For convenience, samples are normally ashed overnight and analyzed the following morning.

Experimentation

To evaluate the recovery of barium and antimony, clean plastic shaft cotton swabs containing a known concentration of each element were prepared. Contaminated swabs were simulated by adding either blood, dirt from a table top in the laboratory, or grease to swabs containing known barium and antimony levels. Tape and film lifts were also examined because they are occasionally encountered in our laboratory and, with the high lifting efficiency of tape, they may become more common.

Spot plates containing a variety of sample types are shown in Fig. 3. The same samples after ashing are shown in Fig. 4.

Following oxidation, the ash is taken up in 1 ml of 1*M* nitric acid. A smaller volume of acid may be used if sample concentration is desired. Analyses for barium and antimony

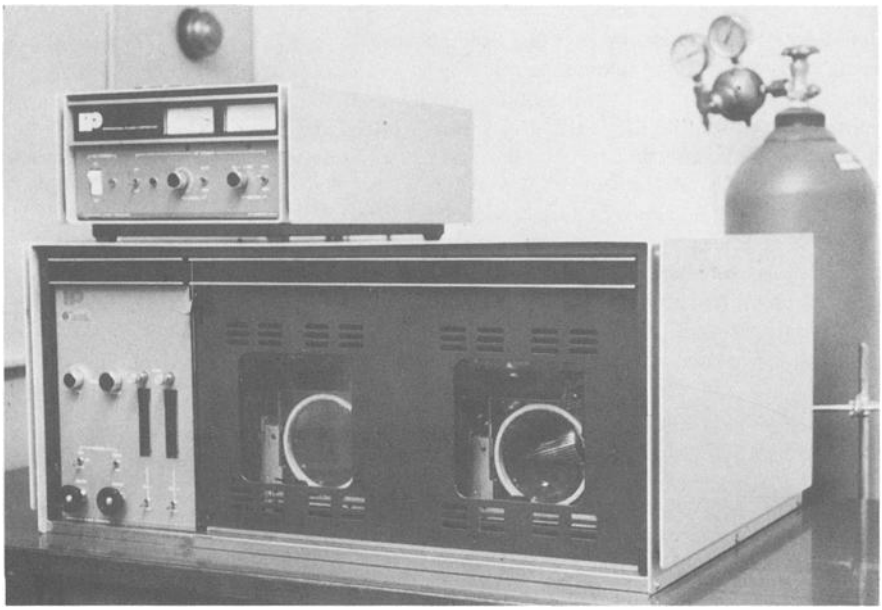

FIG. 1—*Instrument used for oxygen plasma ashing.*

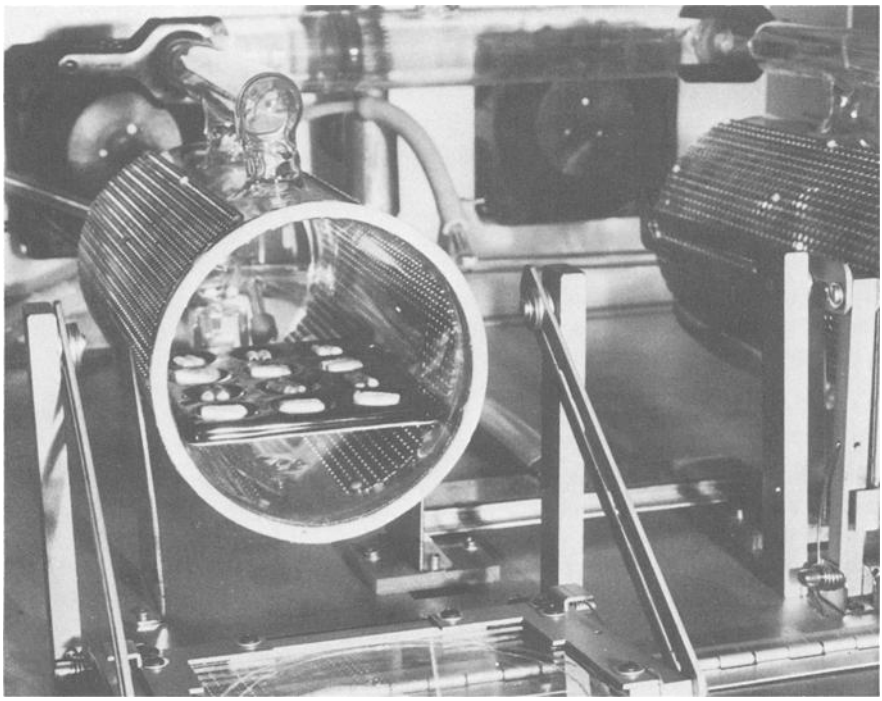

FIG. 2—*Cylindrical chambers (or reactors) for samples.*

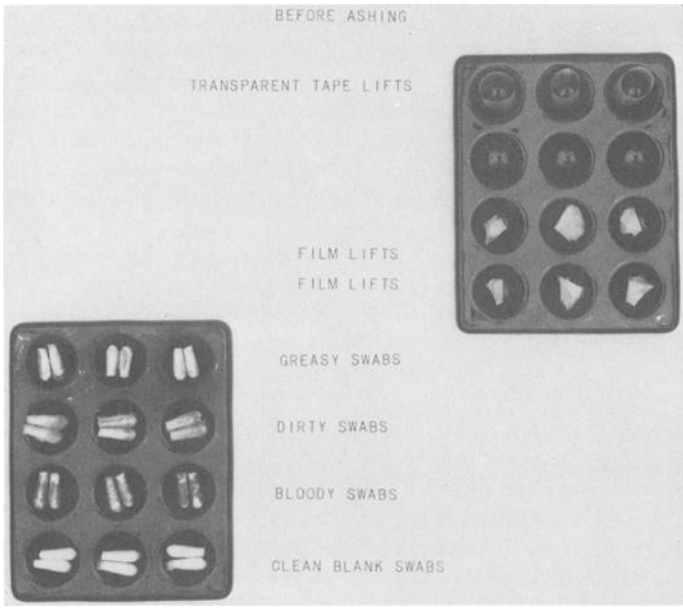

FIG. 3—*Spot plates before ashing.*

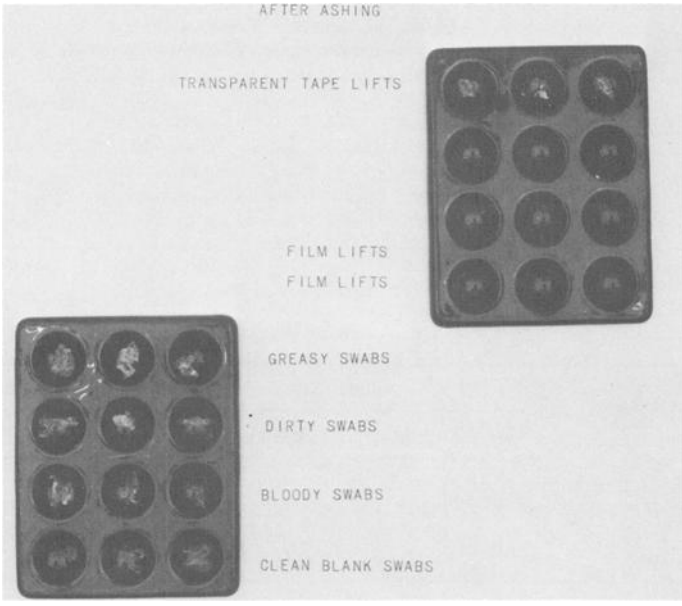

FIG. 4—*Spot plates after ashing.*

are conducted by using our normal method [*1*] on a Jarrell-Ash Model 810 AA spectrophotometer equipped with a tantalum strip atomizer.

Table 1 shows the results of ashing 24 samples each of clean or control cotton swabs, film lifts, and transparent tape. Barium levels were quite low for both swabs and film lifts and virtually nondetectable with tape. Antimony levels were low in each of the materials tested. Recovery of known additions of barium and antimony is shown in Table 2. In all instances

recovery was satisfactory and was generally within the expected precision of the analysis. The results of analyses of nonspiked contaminated swabs are shown in Table 3. It may be noted that some barium was detected in the greasy swabs and in the dirty swabs. The barium in the greasy swabs may be attributable to the use of barium soaps in commercial greases, but the source in the dirty swab is unclear. It is known, however, that low levels of barium are relatively common in the environment. Studies routinely show approximately 0.1 μg on the hands of one who has not recently handled or discharged a firearm. In none of the blank, contaminated samples was significant antimony detected. Table 4 contains the results of 24 tests each conducted with bloody, dirty, and greasy swabs. For comparison, the results on similar samples not ashed but leached with nitric acid are shown. In each instance the results are considerably lower with the leached samples, indicating ineffective leaching. In addition, the leached samples had more scatter in individual analytical results, in part because of the difficulty in making accurate quantitative measurements in the presence of high instrumental backgrounds.

To demonstrate the application of the plasma ashing technique to actual hand samples, Table 5 shows values for ashed samples from a limited number of actual firings. Each test was made by firing two shots from a 9.5-mm (.38 caliber) revolver with Remington-Peters roundnose ammunition. After each test we used three different collection media to collect samples from the firing hand; the samples were then ashed and analyzed. While it appears that transparent tape is superior to the other two collection media used, the small number of tests precludes any firm conclusion on this point.

In addition to the materials tested in this study, we have also successfully applied plasma ashing to gunshot residue samples collected on paraffin and cotton cloth. Each of those,

TABLE 1—*Barium and antimony in collection materials.*

Material	Samples Analyzed, *n*	Average Barium, μg	Average Antimony, μg
Cotton swabs	24	0.05	<0.01
Film lifts	24	0.05	<0.01
Transparent tape	24	<0.01	<0.01

TABLE 2—*Barium and antimony recovery from uncontaminated materials. These values represent the average recoveries from the analysis of 24 samples of each type of material.*

	Added, μg		Recovered, μg	
Material	Barium	Antimony	Barium	Antimony
Cotton swabs	0.40	0.20	0.39	0.19
Cotton swabs	0.50	0.30	0.47	0.27
Film lifts	0.50	0.30	0.50	0.25
Transparent tape	0.50	0.30	0.49	0.29

TABLE 3—*Blank, contaminated swabs.*

Type of Contamination	Samples Analyzed, *n*	Average Barium, μg	Average Antimony, μg
Bloody swabs	24	0.06	<0.01
Greasy swabs	24	0.21	<0.01
Dirty swabs	24	0.12	<0.01

TABLE 4—*Comparison of recoveries by plasma ashing and acid leaching.*

Process	Contaminant		
	Blood	Dirt	Grease
Barium added, μg	0.50	0.50	0.50
Antimony added, μg	0.30	0.30	0.30
Plasma ashing			
Barium recovered, %	96	92	98
Antimony recovered, %	93	90	86
Acid leaching			
Barium recovered, %	66	54	56
Antimony recovered, %	63	73	60

TABLE 5—*Actual firings. These data represent six samples taken from the back of the firing hand.*

Lift Material	Average Barium, μg	Average Antimony, μg
Cotton swab	0.55	0.22
Film lifts	0.69	0.17
Transparent tape	0.78	0.25

when ashed, gave little background even though the cloth samples had been previously tested with sodium rhodizonate for the presence of lead. The colorimetric reagent did not interfere with either ashing or analysis.

Discussion

Pre-ashing of gunshot residue samples in a low pressure oxygen plasma is an attractive alternative to either wet or drying ashing. Sample handling is minimal, and excellent recoveries are obtained with known samples. When contaminated samples are examined, destruction of the sample matrix eliminates recovery problems related to inefficient leaching. In addition, the reduction in instrumental background from light scattering by matrix materials improves analytical precision. Plasma ashing is useful with cotton swabs and other types of collection materials such as tape, film lifts, and paraffin that are not easily handled by direct leaching. The oxygen plasma ashing technique, with its ability to handle a range of sample types and samples contaminated with foreign materials, significantly broadens the ability of the laboratory to examine samples for the presence of materials indicative of firearms discharge residue.

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