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A new method to reduce false positives due to antimony in detection of gunshot residues

Çağdaş Aksoy [a,*], Taner Bora [b], Nilgün Şenocak [c], Fırat Aydın [d]

[a] Diyarbakir Police Forensic Laboratory, 21070 Diyarbakir, Turkey
[b] Ankara Police Forensic Laboratory, 06830 Ankara, Turkey
[c] Police Academy, Forensic Science Institute, 06834 Ankara, Turkey
[d] Dicle University, Science Faculty, 21010 Diyarbakir, Turkey

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ABSTRACT

False positives due to the presence of antimony in vehicle seat fabrics are a problem in gunshot residue (GSR) analysis, in particular, when graphite furnace atomic absorption spectrometry (GFAAS) is employed. In this study, we sought to determine the reason for the prevalence of false positive results and to propose a new approach for the analysis of GSR on vehicle seats. GFAAS was used to examine adhesive tape swabs collected from 100 seats of 50 different automobiles. Characterization of seat fabrics was carried out by using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy with energy dispersive X-ray (SEM/EDX) spectroscopy. The results of FTIR analysis indicated that all seat covers containing antimony were composed of polyester. Experimental results obtained by SEM/EDX analysis revealed that the fabrics in these seat covers contained evenly distributed antimony within the structure of polyester fibers. This study shows that the type of seat fabric should be determined by FTIR spectroscopy before elemental GSR analysis. In this way, most of the false positives caused by polyester fibers in GSR analysis can be prevented.

1. Introduction

Trace evidence detection from firearms is commonly used to determine whether a person fired a gun. Trace evidence usually is not detectable by the naked eye. Gunshot residue (GSR) is one of the most common and most extensively scrutinized sources of trace evidence examined in violent crime investigations [1]. GSR is composed of a variety of materials that include burned and unburned propellants and primers, chemical elements in the bullet and cartridge case, and residue from the barrel of the firearm itself [2]. The explosion of a cartridge produces a heterogeneous mixture of particles that are characteristic of GSR containing different chemicals. Many of these particles contain substances found in the primer mixture that combine with metals from the cartridge case and barrel [3].

In 2010, the American Society of Testing and Materials (ASTM) stated that particles that are "characteristic of GSR" must contain Pb, Ba, and Sb, and possibly one or more of the following elements: Al, Si, P, S (trace), Cl, K, Ca, Fe (trace), Ni, Cu, Zn, Zr, and Sn [4].

There are numerous environmental sources of Pb, Ba, and Sb that potentially can lead to false positives [5,6]. Sb, which is the focus of this study, is found in several alloys, pyrotechnics, and polymers and is used as a fire retardant in cotton and polyester blend fibers [5,7]. However, a mix of lead styphnate, barium nitrate, and antimony sulfide is specific to primer cap components [1]. These particles, which are characteristic of GSR, are determined by elemental analysis methods and imaging systems [8].

The adhesive tape method, which is widely used as a GSR sampling method in Turkey, provides an easy, rapid, and reliable way to collect GSR from surfaces [9–12]. Because of the low persistence of GSR on hands, sampling of a suspect's clothing is needed in some cases. The persistence of GSR on clothes is reported to be greater than that on the hands or face [13]. Vehicle seat covers also provide a useful area for collection of GSR. Vehicles may be involved in shooting incidents in a number of ways. The most common are: shots are fired from a vehicle, shots are fired inside a vehicle, shots are fired adjacent to or over a vehicle and a vehicle is used by the shooter to leave the scene of the crime. Miscellaneous surface types can be sampled to establish whether a person with

* Corresponding author. Tel.: +90 507 6871030.
E-mail address: cagdas.aksoy@egm.gov.tr (Ç. Aksoy).

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GSR on them may have contacted a surface; or whether damage was caused by a bullet or shot [14]. Vehicle swabs gain importance when hand swab results are negative or a hand swab could not be obtained from the crime scene. The area from which GSR is collected in a vehicle is greater than that on the hands or face. Moreover, problems associated with human activities, such as wiping of hands on various materials and washing of hands with water, and secretion of sweat are avoided on vehicle surfaces. The limited period of time to collect GSR is also another disadvantage of hand swabs. Despite having advantages over hand and face swabs, vehicle swabs have a greater risk of contamination and have no direct link with suspects. Collecting swabs from fabrics using tape lifts also may create problems due to collection of GSR along with fibers and other debris [5,15].

SEM/EDX has become the technique of choice for GSR analysis. However, the origin of the samples used in examinations should be evaluated to determine the sample preparation and conditions of analysis. Despite the fact that analyses of cloth and fabric surfaces using SEM/EDX usually require a carbon/gold coating, which increases the sample preparation time [16], the total analysis time is shorter, because fewer electronic charges are observed during the automatic run. Also, non-conducting specimens may be imaged uncoated using environmental SEM or a low-voltage mode of SEM operation [17].

In contrast, the analysis method using GFAAS is minimally affected by sample conditions. Thus, determination of the GSR elements, Sb, Pb, and Ba by GFAAS is a simple, rapid, and inexpensive means for analyzing clothes and goods. However, GSR analysis with GFAAS does not take into account the morphology of individual particles, therefore, the possibility of false positive results is much greater. Identification of sample sources is crucial to prevention of false positives.

The main goals of the present study are to investigate the presence of antimony on vehicle seats and to analyze the efficiency of the swabbing method for vehicle seats. For these reasons, we have determined Sb content of different types of vehicle seats commonly swabbed by crime scene investigators in Turkey. Raw materials of the seat covers were studied by infrared spectroscopy. Sb was selected for the study owing to its tendency to generate lower false positives and its lower risk of contamination in real cases in comparison with Pb and Ba [8].

2. Experimental

2.1. Instrumentation

A PerkinElmer® AAnalyst™ 600 atomic absorption spectrometer, equipped with a Zeeman background corrector, a graphite furnace with THGA™ pyrolytically coated graphite tubes, and a PerkinElmer AS-800 autosampler, were used (PerkinElmer, Inc., Shelton, CT, USA). The operating conditions and analytical parameters, optimized as before [8], are listed in Table 1.

Table 1
Instrumental operating conditions for antimony analysis.

Lamp: Perkin Elmer Lumina Sb
Wavelength: 217.6 nm
Slit: 0.5 nm
Dispensed sample volume: 20 μl

Step	Temperature (°C)	Ramp time (s)	Hold time (s)
1	110	1	20
2	130	15	20
3	1000	10	15
4	2100	0	5
5	2450	1	3

Total program time: 90 s.

A Thermo® Nicolet Model 6700 FTIR (USA) with a diamond ATR (attenuated total reflection) kit (Smart Orbit, USA) was used to identify the raw materials of the fabrics.

Imaging and other elemental analyses were carried out with a Jeol Jsm Model 6400 SEM (Jeol Co., USA) with EDX (Inca from Oxford Instruments, United Kingdom). The operating conditions were as follows: voltage, 15.0 kV; working distance, 39 mm; takeoff angle, 35 D; and elapsed lifetime, 100 s.

2.2. Standard solutions and reagents

A standard Sb solution containing 1000 mg L^{-1} for AAS was purchased from E. Merck (Darmstadt, Germany). Distilled water was produced with an NS-104 system (Nüve Co., Turkey). Working standard solutions of 5, 10, 20, 30, and 40 μg L^{-1} Sb in 1% nitric acid were prepared by dilution of the 1000 mg L^{-1} Sb standard. Nitric acid (65%, Merck) was of analytical purity.

2.3. Sample collection

Medical fabric adhesive tape (Seyitler Kimya Co., Turkey) was used for sampling, because of its good recovery [8]. The tape was cut into 5 cm × 5 cm pieces to simulate samples normally submitted by crime scene investigators. Cylindrical polystyrene sample boxes of 2.5 cm bottom diameter and 4 cm height (LP Italiana Spa, Italy) were used to place swab samples.

One hundred adhesive tape swabs were collected from 50 different vehicles (two swabs from each vehicle) of 10 different companies (five vehicles from each company) representing more than 80% of total automobile sales in Turkey. Sampled vehicles, which were vacuum-cleaned, were selected randomly from three different regions of Turkey; Ankara, Antalya, and Diyarbakir. The vehicles were swabbed and checked with SEM/EDX to confirm the absence of GSR persistence.

A 9-mm Beretta FS92 pistol (Italy) and MKE 9 mm × 19 mm parabellum cartridges (Turkey) were used to simulate firing within the vehicle. The fabric samples taken for FTIR and SEM/EDX analyses had a surface area of 1 cm^2 and were placed in antimony-free paper envelopes.

2.4. Sample preparation

Quantitative determination of Sb was carried out by using GFAAS, which is the analytical method used for GSR detection in Turkish Police Forensic Laboratories [8]. Prior to GFAAS analysis, samples, which were placed in boxes, were shaken for 45 min with 4 mL 8% nitric acid (v/v).

Fabric samples were analyzed directly by ATR-FTIR to determine the raw material used. Swabs from the surface of vehicle seats were taken one day after firing.

3. Results and discussion

Confidence parameters were based on the relative standard deviation (%RSD), limit of detection (LOD), and limit of quantitation (LOQ) values obtained by GFAAS from the calibration curves shown in Table 2.

In the five samples numbered 7 (left-right), 26 (left-right), and 30 (left), the mean antimony concentrations were 93.6, 143.7, 71.4, 137.4, and 65.6 μg L^{-1}, respectively. These samples were diluted by a factor of four before analyze. The mean antimony concentration of 23 samples from 12 different vehicles were exceeded 5.0 μg L^{-1}, which was found to be the lower limit of quantification (LOQ) determined by our statistical analysis. Therefore, concentrations over 5.0 μg L^{-1} were assumed to be sufficient to cause false positives. All positive results are listed in Table 3.