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Analysis of gunshot residues as trace in nasal mucus by GFAAS

Marina Aliste [a,*], Luis Guillermo Chávez [b]

[a] Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, Murcia E-30100, Spain
[b] Policía de Investigaciones de Chile (PDI), Laboratorio de Criminalística Regional La Serena, Chile

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ABSTRACT

When a gun is fired, the majority of gunshot residues are deposited on the shooter's hands. But these residues disappear through contact with surfaces or washing. Therefore, the maximum time frame to find GSR on a suspect's hands is 8 h. The mucus, inside of a nostril, forms a surface layer where they are trapped foreign particles. In this way, mucus inside of a gunshot suspect's nostrils could act like an adhesive medium to stick on it gaseous particles from a gunshot. In this study, the presence of GSR in nasal mucus and its residence time is examined. A new procedure for the sampling of possible gunshot residue accumulated in the nasal mucus is designed. Samples are taken with cotton swabs moistened with a solution of EDTA and, after an acid digestion, are analysed by graphite furnace atomic absorption spectrometry. In addition, samples of hands are taken for comparison purposes. GSR recovery has been successful. The concentration of GSR in nasal mucus is found to be lower than on the hands, but with a longer residence time. Thus, it is possible to expand the sampling time of a suspect also, as nasal mucus cannot be contaminated by handling weapons.

1. Introduction

When a gun is fired, a number of particles and gases are discharged and deposited or condensed on all surfaces near the weapon. According to Schwoeble and Exline, 2000 [1], most Gunshot Residues from weapons, hereinafter GSR, leave the gun in gaseous form after firing. Gradually the gas condenses and individual particles settle near the gun, for example on the shooter's hands. The lifetime and morphology of these particles depends on the weapon used and the ammunition calibre, under normal shooting conditions [1]. These particles can disappear from the hands after contact with other surfaces or liquids. It is impossible to determine a general GSR particle settling time curve after discharge. But the results of the experiments conducted by Fojtášek and Kmječ, 2005 [2] confirmed the assumption that the particles remain in the air for a certain period of time after shooting.

There are numerous GSR sample types that, depending on their origin, are more or less disadvantageous. Originally, suction was used for collecting GSR on clothing. Tape lifting is most frequently method used to collect inorganic residues on skin surfaces [3], such as the hands. To a lesser extent, it can also be used to collect samples from hair [4], clothing [5] and other origins [6,7]. However, there is a limited time frame in which to collect GSR on hands as sweat secretion and hand washing remove GSR [8]. Furthermore, others transfer evidence types are gunshot residues such as glass fragments and fibres. They support an inference of contact between specific source following any contact with a receiving surface. The acceptable time limit between shot and sampling varies depending on the country and the police institution, being 4 to 6 h an acceptable time limit [9]. In the police institution that carried out this study, Policía de Investigaciones de Chile, hereinafter PDI, forensic experts have considered 6 to 8 h such as time limit, depending on the analytical technique. That is 6 h to scanning electron microscopy with energy dispersive X-ray analyser, hereinafter SEM/EDX, and 8 h to graphite furnace atomic absorption spectrometry, hereinafter GFAAS; according to official protocols. When a criminal act occurs, time is crucial. So, to extend the sampling hours of GSR would be of great help to police investigations. It is hoped that sampling nasal mucus to detect GSR would extend the time frame in which testing could be done.

In 1995, Schwartz [10] studied the presence of GSR particles adhering to the nasal mucus with a .38 calibre revolver by SEM/EDX. The samples were collected by the blow out of a nose. Schwartz found GSR present up to 48 hours after shooting. But this technique was not used effectively because the sampling was too invasive, causing discomfort and occasional nosebleeds. Also, the subject had to be over a period of 12-48 hours without blowing his nose, an unrealistic situation. In addition, Schwartz used only a .38

* Corresponding author.
E-mail address: marina.aliste@um.es (M. Aliste).

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calibre revolver for his study, but as every weapon has a different structure and system, his results cannot be extrapolated to all types of weapons. This study was carried out by SEM/EDX, which has become the chosen technique for GSR analysis. However, the origin of the samples used must be evaluated to determine the preparation and analysis conditions of samples. Usually the non-conductive samples can be imaged by SEM with variable pressure mode or treating them so that they are conductive, for example, with a coating of carbon/gold [11,12]. In his analysis, Schwartz carried out a rather laborious multi-step sample treatment: (1) submerge the sample with distilled water (200 mL) at 50–60 °C, (2) filter the mucus and water onto a 47 mm diameter MCE membrane filter (0.3 μm pore size), (3) place it into a 30 mL Vycor™ crucible which has been heated in a muffle furnace at 550 °C, (4) heat up the sample to white ash during 2–5 h, depending on the mucus quantity and moisture percentage, (5) cool the crucible, filled with distilled water, and place it in an ultrasonic bath, (6) filter the contents of the crucible onto a 25 mm diameter PC membrane filter (0.8 μm pore size) with vacuum filtration, and rinse with distilled water until 100-125 mL, (7) wet PC filters are dried inside a covered petri dish and (8) it can be prepared for SEM/EDX analysis. In contrast, the analysis method proposed here by GFAAS, is minimally affected by the conditions of the sample.

The recent developments in methods of analysis in investigations of GSR are studied by Zeichner [13]. Nowadays, equipment of SEM/EDX offers a GSR automatic search. This search system is easier than a manual search, but may spend many hours of analysis per sample. The most conventional bulk method is atomic absorption spectrometry (AAS) [14]. During recent years other techniques have been developed for the analysis of GSR; such as micro-X-ray fluorescence (μXRF) [15,16] and inductively coupled plasma mass spectrometry (ICP/MS) [17]. In addition, focused ion beam (FIB) [18], Raman microscopy [19] and time-of-flight secondary-ion mass spectrometry (TOF-SIMS) [20]; which to date are in research phase. All these techniques have qualities and limitations. Methods based in bulk analysis techniques have not the specificity required for GSR detection. Results just show that the elements Sb, Pb and Ba are present on a surface, but they could come from anywhere or anything: plumbing materials, battery plates, solder, glass, paint, cotton and polyester blend fibres or paper [21,22]. Distribution of Sb and Ba on the hands of 269 non-shooters was studied by Havekost et al. They found high levels of Sb and Ba on the hands of auto mechanic, electrician and construction works [23]. Particle analysis is carried out by SEM/EDX, giving morphologic and analytic information of single particles with the higher specificity in GSR. Moreover, SEM/EDX is a non-destructive technique. GFAAS has a limited selectivity for GSR if it is compared with SEM/EDX [3]. Anyway, GFAAS may be best suited to this analysis for several reasons: (1) availability, ease of operation and automation, (2) susceptibility to all GSR elements, and (3) sensitivity and specificity [24]. Likewise, the development of electro thermal atomizers (carbon rod, tantalum, and graphite tube furnace) has made GFAAS most attractive for forensic laboratories [25].

Taking Schwartz's idea [10], a sampling technique for nasal mucus should be designed that is much less invasive, simple, quick and inexpensive. Furthermore, in order for it to have good application, it must be effective in getting GSR data with weapons with different calibres and different types of ammunition, also a sampling at various post-firing times in subjects with diverse occupations; such as police officers, auto mechanics, secretaries, teachers, welders, petrol pump attendants and others. In order to give the greatest possible reality to this study, subjects could do their normal lives regardless of work, sport, disease, personal hygiene and so forth. Thus, police institutions could have a second opportunity in the event that a suspect has washed his hands or more than 6 hours has passed since the shooting.

This paper proposes the design of a new procedure for the sampling of possible gunshot residue stored in nasal mucus, through sample analysis by GFAAS. It also seeks to establish a comparison of GSR results obtained in nasal mucus with GSR results obtained from hands; in order to complement both sampling procedures. Finally, the variation of the GSR concentration stored in the nasal mucus with time is studied.

2. Experimental

2.1. Instrumentation

For instrumental analysis, an atomic absorption spectrometry Thermo® (Cambridge, United Kingdom) was used with graphite furnace model GF95 with extended lifetime cuvette (ELC), model M6, with Zeeman correction system and auto-sampler model FS95. It was equipped with Sb, Pb and Ba hollow cathode lamps (Thermo Scientific). The analytical parameters and operating conditions are shown in Tables 1 and 2 respectively.

2.2. Standard solutions and reagents

Standard solutions of 1000 mg/L of Sb, Pb and Ba for AAS, which were acquired by Merck® (Darmstadt, Germany), were used. Distilled water was produced with a UV/UF ultrapure water system Easy Pure II, Barnstead®. The multi-elemental standard working solution 0.08 mg/L Sb, 0.40 mg/L and 0.08 mg Pb/L Ba in 10% HNO_3 (v/v) was prepared by dilution of the various standard solutions of 1000 mg/L of Sb, Pb and Ba. Nitric acid HNO_3 (65% purity, Merck®) were of analytical grade. Ethylendiaminetetraacetic acid solution, hereinafter EDTA, 2% (m/v) was prepared from reagent Merck® and 99% purity was obtained.

2.3. Sample generation and collection

GSR samples were generated in the ballistic shot room in the Laboratorio de Criminalística Regional La Serena (Chile), PDI. 10 samples were taken from the nostrils of the subject, following the sampling protocol described below, immediately after shooting

Table 1
Instrumental parameters for Sb, Pb and Ba analysis.

	Sb	Pb	Ba
Wavelength, nm	217.6	283.3	553.6
Lamp current, %	90	90	100
Slit, nm	0.2	0.5	0.2
Dispensed simple volume, μL	20.0	20.0	20.0
Standard, mg/L	0.08	0.4	0.08
Detection limit of the instrument [26], μg/L	0.4	0.11	0.5

Table 2
Furnace program conditions for Sb, Pb, and Ba analysis.

	Step	Temperature, °C	Hold time, s	Ramp, °C/s	Gas flow, L/min
Sb	1	150	30	10	0.2
	2	800	15	150	0.2
	3	2300	3	0	Turn off
	4	2900	3	0	0.2
Pb	1	150	30	10	0.2
	2	500	15	150	0.2
	3	2300	3	0	Turn off
	4	2900	3	0	0.2
Ba	1	140	30	10	0.2
	2	1600	15	150	0.2
	3	2750	3	0	Turn off
	4	2900	3	0	0.2