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Measurement of airborne gunshot particles in a ballistics laboratory by sector field inductively coupled plasma mass spectrometry

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ABSTRACT

The present study aimed determines lead (Pb), antimony (Sb) and barium (Ba) as the major elements present in GSR in the environmental air of the Ballistics Laboratory of the São Paulo Criminalistics Institute (I.C.-S.P.), São Paulo, SP, Brazil. Micro environmental monitors (mini samplers) were located at selected places. The $PM_{2.5}$ fraction of this airborne was collected in, previously weighted filters, and analyzed by sector field inductively coupled plasma mass spectrometer (SF-HR-ICP-MS). The higher values of the airborne lead, antimony and barium, were found at the firing range (lead (Pb): 58.9 $\mu g/m^3$; barium (Ba): 6.9 $\mu g/m^3$; antimony (Sb): 7.3 $\mu g/m^3$). The mean value of the airborne in this room during 6 monitored days was Pb: 23.1 $\mu g/m^3$; Ba: 2.2 $\mu g/m^3$; Sb: 1.5 $\mu g/m^3$. In the water tank room, the air did not show levels above the limits of concern. In general the airborne lead changed from day to day, but the barium and antimony remained constant. Despite of that, the obtained values suggest that the workers may be exposed to airborne lead concentration that can result in an unhealthy environment and could increase the risk of chronic intoxication.

1. Introduction

The gases, vapors, and particulate matter formed by the discharge of ammunition in a firearm are collectively known as firearm discharge residue (FDR) or gunshot residue (GSR). The theory of GSR particles origin says that most GSR leaves the firearm after the discharge in the form of gas. The gas gradually condenses and individual particles sediment around the shooting firearm. The metallic components involved, namely, lead (Pb) and antimony (Sb), originate from the bullet, barium (Ba) and Sb may originate from the primer ignition. There are some others metals from the case alloys like cooper (Cu) and zinc (Zn) and aluminum (Al), but they are widely used in many others applications and are not considered typical for GSR residues. In fact, the Sb is considered the best indicator to the GSR particles presence, because of the low abundance in environment [1]. Exposures to airborne and settled lead, antimony and barium dust at firing ranges put Firearm Examiners and others employees at risk for lead and others metals poisoning [2]. Air monitoring indicates if Firearm Examiners are or not usually exposed above the safety level. The Federal OSHA General Industry Lead Standard (29 CFR 1910.1025) establishes specific airborne lead exposure levels for employees working in areas where airborne lead is present. The standard creates two levels of exposure. The action level for airborne lead exposure is 30 micrograms per cubic meter ($\mu g/m^3$) of air as an 8-h time-weighted average (TWA). The PEL (permissible exposure limit) of 50 $\mu g/m^3$ of air averaged over an 8-h day.

Lead exposure is determined through air sampling that measures the concentration of lead in the air (the number of micrograms of lead present in a cubic meter of air). The Brazilian legislation limit of exposure for lead (Pb) in a workplace is 100.0 $\mu g/m^3$/40 h/week and when this legislation fail to produce an occupational limit for a given element or compound, it advices to follow the ACGIH® (American Conference of Governmental Industrial Hygienists) [3]. Recently the American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a threshold limit value (TLV) for lead of 50 $\mu g/m^3$ [4].

These elements lead (Pb), antimony (Sb), and barium (Ba) must be considered as atmospheric particulate matter generated from firearm discharge, and is a matter of concern when it comes to the workers occupational health. In these environments the particulate matter is usually formed by GSR particles that are hollow or porous particles, which will have different sedimentation time [5]. Because the fine particulate matter ($PM_{2.5}$) remain suspended in

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the workplace atmosphere, inhalation is the major path of contamination.

Particulate matter at firing ranges has variable compositions, but lead (Pb), antimony (Sb), and barium (Ba) are elements of concern because of their toxicity, especially in the case of Pb. Lead exposure occurs mainly through inhalation of lead fumes or ingestion (e.g., eating or drinking with contaminated hands). If not detected early, people with high lead blood levels can suffer from high blood pressure, memory and concentration problems, digestive problems, shakiness, muscle and joint pain, irritability and difficulties during pregnancy. Besides, once deposited in the clothes, shoes or even in the body of the occupationally exposed workers, it can also be transported out of the workplace contaminating places and unprotect people. You can also carry lead from the range to your family on your clothes, shoes, and body. Lead carried in this way is known to as "take-home lead." Take-home lead affects mainly children by causing damage to the brain and nervous system, slowed growth, behavior and learning problems, hearing problems, and headaches.

Particles with an aerodynamic diameter of less than 10 μm (PM_{10}) are inhalable and, therefore, constitute the fraction of particles relevant for the assessment of health effects [6]. Some of studies have implied that the fine mass ($PM_{2.5}$) component of PM_{10} is more likely to be associated with the observed health effects than the coarse fraction [7].

Determination of metallic species in indoor PM is usually carried out through atomic spectrometric methods involving techniques such as FAAS (flame atomic absorption spectrometry), ICP-OES (inductively coupled plasma optical emission spectroscopy), ICP-MS (inductively coupled plasma mass spectrometry) and ETA-AS (electro thermal atomic absorption spectrometry) [8–11].

2. Materials and methods

The study was conducted between 15 and 25 October 2010. The evaluated facility the Laboratory of Ballistics at the Criminalistics Institute in the municipality of São Paulo, São Paulo State, Brazil. The room of the fire arms range and the tank were monitored because in these points the arms are fired. The ballistics expert's room, where the personnel spend most of time were monitored too. The exposure assessment was performed on 6 non-consecutive days; the atmosphere air was collected for 8 h, corresponding to 100% of the working day. The exhaustion air system was running on while the experiments were performed (same regime like in ordinary working days). The number of fired rounds in each ambient (fire arms range and the tank) day was noted.

2.1. Sampling

The samples were collected in the Firearm Examiner's office, the water tank room and the firearms testing room at the Ballistics Laboratory in the Sao Paulo Criminalistics Institute. The number of fired rounds was noted. One round consisted of three shoots as routinely for testing purposes. Were tested different types of arms, mainly .38, .32, .22, and 9 mm.

All the inlet probes were located at 1.8 m height, away from air disturbances, windows and walls; the flow rate was adjusted before and after each sampling with a bubble flow meter.

2.2. Pumps and filters

The mini sampler containing an Harvard Impactor with polycarbonate filters were used for this purpose. Pre-calibrated constant flow Harvard Impactors with operating at 1.8 L min^{-1} air pumps. Using silicone tubes, the pumps were connected to filter holders containing the polycarbonate filters with diameter of 37 mm and pore size of 0.8 μm.

2.3. Sample preparation

All the polycarbonate filters were weighed in the Laboratory of Analyzes of Atmospheric Processes (LAPAt), at the Institute of Astronomy, Geophysics and Atmospheric Science of USP, using a Mettler MT5 micro-balance (Mettler-Toledo, Greifensee, Switzerland) with 1 mg reading. Weighing was conducted in the same temperature and humidity conditioned room: 20 °C, 40% humidity.

After sampling the filters were weighted again and placed in cartridges until analysis. The sample digestion was made based on the OSHA Method 1006 [11]: The exposed filters and the blanks were transferred to clean beakers together with 3.0 mL concentrate, sub boiling HNO_3 (Merck, Germany), 1.0 mL 30% H_2O_2 (Merck, Germany) and covered with a watch glass. The reagent blanks were started at this step. The samples were heated on 140 °C hotplate until volume was reduced to 0.5 mL. The watch glass and the beaker were rinsed with deionized water (of resistivity 18 MΩ cm). Afterwards, extract sample solutions were diluted to 10 mL with deionized water (of resistivity 18 MΩ cm) and aspirated directly into a sector field inductively coupled plasma mass spectrometer (SF-HR-ICP-MS) (ELEMENT 1, Finnigan MAT, Bremen, Germany) for the determination of Sb, Ba and Pb.

2.4. Analytical instrumentation

The sector field inductively coupled plasma mass spectrometer (SF-HR-ICP-MS), a technique with many advantages, large dynamic linear range, multi-elemental analysis capability and very low detection limits.

To determine total analytic concentrations responses of the following isotopes were measured: 121Sb, 138Ba and 208Pb. Table 1 shows the main operating conditions. A Meinhard concentric nebulizer was used for simple introduction to a quartz torch, with peristaltic pumping, and 5.0 μg L^{-1} of 115In and 209Bi solution was used as an internal standard.

2.5. Reference solutions

All reference solutions were prepared in deionized distillated water from a Milli-Q-Plus system (Millipore®, USA). Working standard solutions of 1.6, 3.2, 4.8, 6.4, 16, 32 and 80 μg L^{-1} of Pb, Ba

Table 1
SF-HR-ICP-MS main operation conditions.

Cool gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.10 L min^{-1}
Sample gas	0.97 L min^{-1}
RF power	1250 W
Runs/passes	5/4
Wash time	40 s
Take up time	30 s
Sampling cone nickel	1.0 mm orifice
Skimmer cone nickel	0.8 mm orifice
Flow rate	1.0 L min^{-1}
Samples per peak	20
Integration window	80
Sample time	0.0100 s
Segment duration	0.240 s
Mass window	120
Search window	150
Scan type	Escan
Detection mode	Both
Spray chamber	Scott type (PE-Sciex)

Table 2
The confidence parameters based on the calibration curves.

	Sd	LOD (ng/L)	LOQ (ng/L)	LDM (ng/m^3)	LQM (ng/m^3)
Sb	0.00022	2.09	6.97	1.81	6.03
Ba	0.00144	4.28	14.28	3.7	12.34
Pb	0.00076	3.53	11.77	3.05	10.17

and 0.35, 0.7, 1.05, 1.4, 3.5, 7.0, 17.5 μg L^{-1} of Sb in 2% nitric acid were prepared by dilution of original 1000 mg L^{-1} SPEX standards (NJ, USA).

3. Results and discussion

This study investigated the occupational exposure of personnel in the Laboratory of Ballistics were large amounts of GSR are produced.

Detection and quantification limits for SF-HR-ICP were computed, respectively, with the expressions: LDM = 3Sd/m and LQM = 10Sd/m, where Sd is the standard deviation of the blank (n = 5) and m is the slope of the calibration curve. LOD (limit of detection) and LOQ (limit of quantification) in samples were computed from LDM (method limit detection) and LQM (method limit quantification), based on the sampled volume of 0.864 m^3 day^{-1}, which correspond to 100% of a 8 h (480 min) working day using the sampling flow rate of 1.8 L min^{-1}.

The confidence parameters were based on the LDM and LQM values obtained in solution by the SF-HR-ICP-MS from the calibration curves are shown in Table 2.

In the present case, the air in the analyzed facilities did not exceed the TLV-TWA (threshold limit value-time weighted average) requirements defined by ACGIH® for Sb and Ba elements. On the other hand, in 1 day, the Pb concentrations mean level surpassed the limit defined by the American Conference but, did not exceed the Brazilian occupational limit of 100.0 μg/m^3 of Pb air concentration in the workplace. However, the obtained values suggest that the workers may be exposed to airborne lead concentration that can result in an unhealthy environment and could increase the risk of chronic intoxication.

3.1. Sampling

Table 3 shows the mean metals concentration and the standard deviation. These three elements (Pb, Ba and Sb) were sampled for 6 non-consecutive days.

The concentration variability in the collected days is directly related to the number of shoots made each day by the experts. As expected, the fired rounds were strongly correlated with the observed amounts of lead, antimony and barium. It is clear shown that in the firing range the levels appears so high in 20 October, and the levels go up again in 22 October. In the case of the water tank, in 20 October the airborne levels increase, but they are lower than in the firing range, apparently because of the lower number of fired rounds. In the office, the levels show up much lower. Perhaps the airborne lead levels are below the national and international limits, with the exception of an increase in 20 October, the mean value for the airborne lead looks higher than the safety limits. These results are shown in graphics in Figs. 1 and 2.

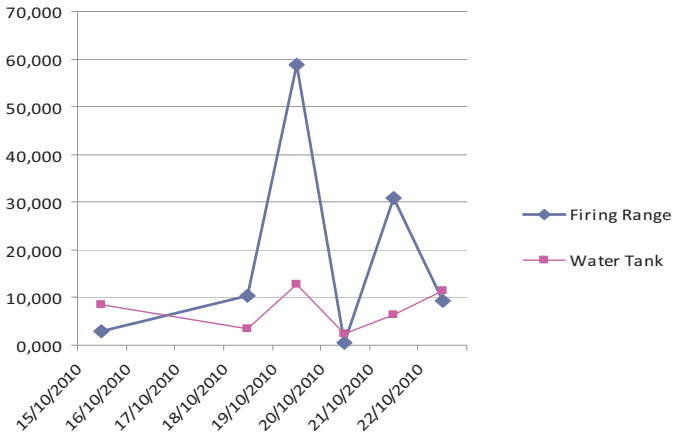

Fig. 1. Changes in the airborne lead from GSR in the monitored facilities firing range and water tank (Y axis units: μg/m^3).

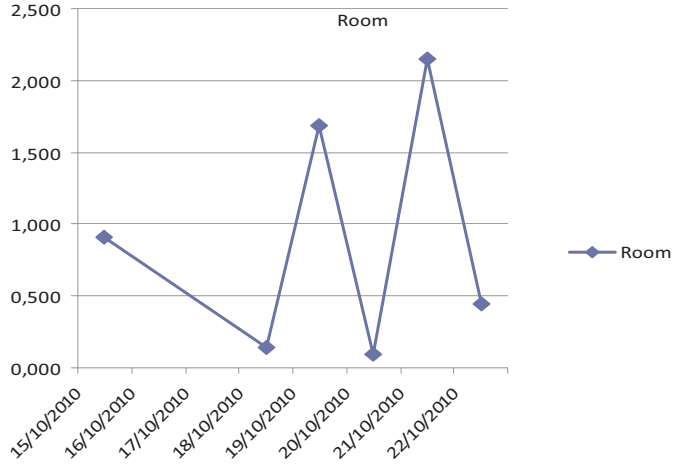

Fig. 2. The airborne lead in the experts room, note the low levels in this case (Y axis units: μg/m^3).

The blanks of two non-exposed filters were measured:

Blank 1: Pb 7.7 ng/m^3, Ba 22.9 ng/m^3, Sb 0.9 ng/m^3.
Blank 2: Pb 0.2 ng/m^3, Ba 16.0 ng/m^3, Sb 0.8 ng/m^3.

Table 3
The mean metal concentration in air, the standard deviation and the number of fired rounds.

Date	Firing ranges (μg/m^3)			Fired rounds	Water tank (μg/m^3)			Fired rounds	Experts office (μg/m^3)		
	Pb	Ba	Sb		Pb	Ba	Sb		Pb	Ba	Sb
15/10/2010	2.959	0.166	0.015	2	8.455	0.845	0.389	6	0.907	0.111	0.039
18/10/2010	10.331	1.413	0.454	16	3.519	0.549	0.144	2	0.14	0.037	0.003
20/10/2010	58.928	6.914	7.257	62	12.762	0.887	0.278	7	1.688	0.178	0.057
21/10/2010	0.441	0.061	0.009	1	2.375	0.226	0.038	3	0.091	0.044	0.002
22/10/2010	30.808	3.934	1.598	39	6.292	0.63	0.238	5	2.146	0.263	0.076
25/10/2010	9.326	0.15	0.159	12	11.444	0.539	0.226	8	0.441	0.051	0.009
Mean	23.101	2.188	1.506		6.869	0.547	0.198		0.773	0.098	0.027
Sd	23.385	2.549	2.604		4.146	0.28	0.122		0.848	0.093	0.031

From these results we can underestimate the contamination from the filters material.

The baseline control from Sao Paulo's air was sampled 5 km away from the laboratory, in the campus of the Sao Paulo's University (USP), using the same methodology. The airborne contaminants (Pb, Ba and Sb) were measured:

Baseline control: Pb 33.6 ng/m^3, Ba 44.0 ng/m^3, Sb 1.2 ng/m^3.

We regard that lead content increase meanwhile the barium and antimony remains almost like in the blanks, perhaps because of the presence of lead in the air pollution.

Regarding the metals Sb and Ba, the variations in observed concentrations for different days and places are correlated to the Pb concentrations. This is expected from the general composition of the GSR when mainly lead ammunition is used and the antimony and barium are in much lower concentration in the produced residues from the primer.

Based on these results and regarding the United States Code of Federal Regulations, 29 CFR 1910.1000, Subpart Z, (d)(i)(i), that indicates that the cumulative exposure E for an 8-h work shift shall be computed as follows:

$$E = \frac{C_a T_a + C_b T_b \ldots C_n T_n}{8}$$

where E, the equivalent exposure for the work shift; C, the concentration during any period of time ($a \ldots n$), where the concentration remains constant; T, the duration in hours of the exposure at concentration C.

Substituting the mean airborne lead concentration in the office, were the experts spend most of time (6 h), 1 h in the firing range and 1 h in the water tank. The equation results in the following:

$$E = \frac{1\,\text{mg/m}^3 \times 6 + 23\,\mu\text{g/m}^3 \times 1 + 7\,\mu\text{g/m}^3 \times 1}{8} = 4\,\mu\text{g/m}^3$$

In order to calculate the predicted total exposure, lets to assume a 20 L min^{-1} respiration rate and a lead concentration of 1 μg/m^3 during 6 h (360 min), a person would be exposed to 7.2 μg lead in 6 h in the experts' office; 27.6 μg lead in 1 h in the firing range and 8.4 μg lead during 60 min at the water tank room.

4. Conclusion

This study indicates that levels of air pollutants from GSR might be high, mainly the lead component, near the OSHA limits, in the firing range. In the water tank the levels are lower, but still concern about the cumulative exposure, especially to those experts that might be considered susceptible to lead intoxication. However, the airborne particle from GSR in the experts office, were they spend the most of time, shows a better situation, with lower levels of airborne lead.

The airborne antimony and barium levels resulted much lower than the limits for occupational exposure.

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References

[1] S.W. James, Chemical Analysis of Firearms, Ammunition, and Gunshot Residue, International Forensic Science and Investigation Series, Taylor & Francis Group, LLC, CRC Press, 2008.
[2] S.E. Valway, J.W. Martyny, J.R. Miller, M. Cook, E.J. Mangione, Lead absorption in indoor firing range users, Am. J. Public Health 79 (1989) 1029–1032.
[3] BRASIL, Ministério do Trabalho NR 15 Atividades e Operacoes Insalubres, 1977.
[4] American Conference of Governmental Industrial Hygienists (ACGIH), TLVs®, Cincinnati, ACGIH, 2008 (Standard).
[5] A.J. Schwoeble, D.L. Exline, Forensic Gunshot Residue Analysis, CRC Press, 2000.
[6] J. Spengler, R. Wilson, Emissions dispersion and concentration of particles, in: R. Wilson, J.D. Spengler (Eds.), Particles in Our Air: Concentrations and Health Effects, Harvard University Press, Cambridge, 1997, p. 4162.
[7] D.W. Dockery, C.A. Pope, X. Xu, et al., Mortality risk of air pollution: a prospective cohort study, N. Engl. J. Med. 329 (1993) 1753–1759.
[8] M. Kiilunen, Occupational exposure to chromium and nickel in Finland and its estimation by biological monitoring, in: Biomonitoring Laboratory, Institute of Occupational Health, Helsinki, 1994, pp. 215–257.
[9] National Institute for Occupational Safety (NIOSH), Health and Safety Guide for Foundries, NIOSH, USA, 1976, pp. 9–14 (Standard).
[10] World Health Organization – International Program on Chemical Safety (WHO/IPCS), Inorganic Lead Environmental Heath Criteria 165, IPCS, Geneva, 1995, pp. 32–78 (Standard).
[11] Occupational Safety and Health Administration (OSHA), Available from http://www.osha.gov/dts/sltc/methods/mdt/mdt1006/1006.pdf.