Simple and Sensitive Method for Sampling, Extraction and Determination of Lead Barium and Antimony in Gunshot Residue Samples

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Received: 11 May 2023; Revised: 31 October 2023; Accepted: 3 November 2023; Available online: 16 November 2023

Abstract

The determination of elements typically found in gunshot residues (GSRs) such as Lead (Pb), Barium (Ba) and Antimony (Sb) plays an important role in the forensic investigation of firearm-related events. The present work developed a simple and highly sensitive method for sampling, extraction and determination of those elements by Graphite Furnace Atomic Absorption Spectrometry (GFAAS). The factors that might influence the efficiency of the sampling and extraction were investigated. The studied results showed that 100 µL of 5% HNO_3 was sufficient for a single cotton swabbing. The extraction of Pb Ba and Sb was performed by using 1% HNO_3 for 30 min at room temperature. The figures of merit from the proposed method in aqueous solution and optimum conditions presented a highly sensitive of 1.31, 3.70 and 0.42 µg L^{-1} limit of detection and high accuracy of 99.48±3.02%, 99.42±6.15% and 97.21±3.90% of recovery for the determination of Pb, Ba and Sb in GSRs, respectively. The proposed method was applied for the forensic study. Under optimal sampling and extraction conditions, the GSR samples on the back of the hands of the shooter after shooting at various times were determined by GFAAS. Friedman and t-test statistical results showed that the amounts of all elements significantly decreased over time after firing and different cleaning conditions at a 95% confidence level. It was found that Pb, Ba and Sb from the hands after washing with tap water had been observed up to 3 hr after shooting. The developed sampling and extraction methods are beneficial and help to identify the criminals.

Keywords: Sampling, Extraction, GSRs, GFAAS and Firing time

Introduction

Firearms are used in many crimes and investigators must be able to provide clear evidence to support prosecution in court. The evidence that is employed to identify criminals and offenders must be accurate, precise and reliable (Polnparkh, Chimpalee, & Hintao, 2012). Results from the verification process are accepted as relevant accompanying evidence in the justice process, ensuring fair judgment. The determination of chemical compounds in gunshot residues is a very crucial step in the forensic investigation. As it is very important evidence, a great deal of weight is placed on it by the justices overseeing a trial. The main chemical compounds present in residues from an explosion, gunshot or fired primer, are characteristically the elements lead (Pb), barium (Ba) and antimony (Sb) (Polnparkh et al., 2012; Mingchanid & Kulnides, 2017). However, the residue could remain on the palm or the clothes of the shooter, allowing investigators to identify the shooter by determination of those three main elements of a primer residue sample collected from the palm or the clothes of a suspect. The results of the analysis of the sample are essential evidence for the Prosecution that can be used in the judicial process.

Various chemical methods provide accurate and precise results. For example, atomic absorption spectrometry (AAS) is a technique that converts an atom into a free atom before measuring (Turillazzi et al., 2003; Romolo & Margot, 2001; Yanez et al., 2012). The correlated methods of this technique are Flame Atomic Absorption

Spectrometry (FAAS) (Romolo, & Margot, 2001; Yanez et al., 2012) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS) (Turillazzi et al., 2003; Romolo & Margot, 2001; Yanez et al., 2012) which uses electrical energy to converts elements into free atoms. Another technique is Atomic Emission Spectrometry (AES) which activates elemental atoms and emits light with specific wavelengths. The quantity of any element present in a sample can be calculated based on the light intensity (Turillazzi et al., 2003; Romolo & Margot, 2001; Yanez et al., 2012; Tarifa & Almirall, 2015; Vanini et al., 2015; Vanini et al., 2015). A third technique is Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) which uses plasma for activation of the element to emit a specific light wavelength (Mingchanid & Kulnides, 2017; Turillazzi et al., 2003; Romolo & Margot, 2001; Yanez et al., 2012; Tarifa & Almirall, 2015; Vanini et al., 2015; Vanini et al., 2015; Nantasitangkool et al., 2020). Other methods are available that can be applied to analyze elements in gunpowder residues, such as the Neutron Activation Analysis (NAA) (Turillazzi et al., 2003) method, and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Mingchanid & Kulnides, 2017; Turillazzi et al., 2003; Romolo & Margot, 2001; Feeney et al., 2021; Phermpornsagul, Arepornrat, Palkawong Na Ayuthaya, & Khaenamkaew, 2020; Li, 2021). X-ray fluorescence spectroscopy (XRF) (Turillazzi et al., 2003) is another quantitative analytical technique. Anodic Stripping Voltammetry (ASV) and Anodic Stripping Differential Pulse Voltammetry (ASDPV) involve electrochemical techniques (Salles, Naozuka, & Bertotti, 2012; O′ Mahony, Windmiller, Samek, Bandodkar, & Wang, 2012). Additionally, morphological analysis techniques are widely used, such as Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) (Mingchanid & Kulnides, 2017; Romolo et al., 2013; Polovkova, Simonic, & Szegenyi, 2015; Brozek-Mucha, 2014) as well as Raman Spectroscopy (Lopez-Lopez, Delgado, & Garcia-Ruiz, 2013).

Limitations of the quantitative analysis of Lead, Barium, and Antimony in primer residue samples are always related to the insufficient sensitivity of analytical methods when a sample is collected well after the weapon has been fired, or the hands and clothes of the perpetrator have been thoroughly cleaned (Mingchanid & Kulnides, 2017). The remaining residues have very little content of the essential elements, making them difficult to detect. Thus, the study of methods used and extant conditions when collecting samples and extracting the desired elements is important to ensure effective sampling and extraction methods and increase the sensitivity of the analysis. Therefore, this research focused on the study of sampling and extracting conditions that create a friendly environment that provides the highest sensitivity, convenience, and flexibility for further analysis of the elements of interest. The optimal conditions for the design of a process for collecting residue samples from the hands of the shooter at various times after firing, and after both hand washing and non-hand washing have taken place, were investigated. The collected samples were analyzed by the GFAAS technique which is widely applied in the Evidence Center of the Royal Thai Police. The GFAAS technique is considered to be a highly sensitive technique that lends itself to automatic analysis.

Methods and Materials

Reagents and chemicals

All reagents were of analytical grade and used without further purification. 1,000 mg L^{-1} of Stock standard solution of Lead (Pb) and Barium (Ba) were purchased from LOBAL Chemie, India, and Antimony (Sb) was purchased from CARLO ERBA, France. All standard solutions were prepared with diluted 1% (w/v) nitric acid (HNO_3) from RCL-Labscan, Thailand, in high-purity deionized water (DI water, 10^8 Ω).

Apparatus

For the investigation of Pb Ba and Sb in GSRs, a .38-inch SMITH&WESSON, model 36 revolver with semi-jacket hollow point bullets (Winchester) was used. The amount of each target element was determined by using a graphite furnace atomic absorption spectrophotometer (GFAAS, SpectrAA 220Z Varian, Australia) and Agilent Standard Graphite Tubes with Partition (Agilent technologies, Germany). Gunshot residues were collected by using cotton brushes (Ambulance Brand, Thailand). An ultrasonic cleaning bath (Transsonic Digitals, Elma, Germany) and dry block heater (JSR, JSBL-01T, Korea) were used for the extraction study.

Calibration curve construction

To quantitatively analyse the Pb, Ba and Sb in the GSRs, calibration curves of these elements were constructed by diluting 1,000 mg L^{-1} of stock solutions to an intermediate concentration of 10.00 mg L^{-1} by using 1% (w/v) HNO_3 as the solvent. The initial (bulk) concentrations 50.00, 100.00 and 100.00 µg L^{-1} for Pb, Ba, and Sb were prepared by diluting the intermediate concentration with 1% (w/v) HNO_3 and employed to prepare appropriate concentrations for calibration curve construction. The working range concentrations used for the determination of Pb were 5.00 – 40.00 µg L^{-1}, L^{-1}, 10.00 – 80.00 µg L^{-1} for the Ba and 5.00 – 80.00 µg $L^{-1}$for the Sb. The summary of calibration curve construction conditions is shown in Table 1. The standard solutions at various concentrations were injected in triplicate and atomized in the graphite tube. The statistical mean ($\bar{x}$) of the absorbance were plotted against the concentrations and a standard deviation (SD) was applied as error bars on the curves.

Table 1 Condition used for calibration curve construction

Condition	Target elements		
	Pb	Ba	Sb
Absorption wavelength (nm)	283.3	553.6	217.6
Ashing temperature (^{O}C)	400	1,000	700
Atomization temperature (^{O}C)	2,100	2,600	2,000
Atomization time (s)	68.0	69.3	67.7
Injection volume (µL)	15	15	15
Chemical modifier	-	-	-
Bulk concentration (µg L^{-1})	50.00	100.00	100.00
Working range (µg L^{-1})	5.00 – 40.00	10.00 – 80.00	5.00 – 80.00

The study of parameters affecting Sampling and Extraction efficiency

GSR samples on the backs of the hands of the shooter were collected by swabbing with a cotton brush with an appropriate solvent volume after firing the revolver 170 times using the semi-jacket hollow point bullets. The same procedure was applied for blank solution preparation, by swabbing the backs of the hands of the shooter with a cotton brush with the same solvent volume, before firing the revolver. Various sampling parameters such as solvent type, solvent volume, swab replicates number and stored temperature were investigated over ranges of these parameters. The results are illustrated in **Table 2**. The selected optimum condition for the sampling procedure was evaluated by measuring the amount of the target elements found. These are also shown in **Table 2**.

The extraction efficiency of the target elements was studied using the optimum sampling condition. Extraction parameters such as extraction time, extractant volume, extraction temperature and nitric acid (HNO_3) content were studied. The extraction parameters and the optimum conditions identified are shown in Table 2.

Validation study

To validate the proposed method, 30 calibration curves were constructed both intraday and inter-day. The sensitivity or detection limit of the elements was represented in terms of the slope, whereas the precision was evaluated from the relative standard deviation (%RSD) of the slope. The Limit of Detection (LOD = 3SD of Blank/Slope) and Limit of Quantification (LOQ = 10SD of Blank/Slope) were computed and reported from the intercepts identified (defined as the blank signal, n=30). The amount of Pb, Ba and Sb in the same set of 5 GSR samples with (Added standard sample) and without (Sample) of 50.00 µg L^{-1} of Pb, Ba and Sb were determined by using the proposed method. The percentage of recovery (%R) was then calculated using Equation 1.

$$\%\mathrm{R} = \left[\frac{(\text{Added standard sample})-(\text{Sample})}{(\text{Added standard})}\right] \times 100 \qquad (1)$$

Table 2 The selected condition for sampling and extracting of GSRs

Sampling parameters	The studied range	The selected condition
Sampling solvent type	0 - 5% (w/v) HNO_3	5% (w/v) HNO_3
Sampling solvent volume	100 - 200 µL	100 µL
Swab replicates No.	1 - 3	1
Stored temperature	4 $^{\circ}$C and RT (30 $^{\circ}$C)	4 $^{\circ}$C
Extraction parameters	The studied range	The optimum condition
Extraction time	5.0 - 0.12 hr.	5.0 hr.
Extraction volume	0.2 - 10.0 mL	2.0 mL
Extraction temperature	30 - 60 $^{\circ}$C	0.30 $^{\circ}$C
% (w/v) HNO_3	0 -7 %	0 - 1 %

Application of the proposed method for the determination of Pb, Ba and Sb in GSRs at various firing times and cleaning conditions

The proposed methods of sampling and extraction were applied to study the determination of Pb, Ba and Sn in GSR tests at various firing times of 0, 3, 6 and 9 hr. Two of the hand cleaning conditions, "not washing hands" and "washing hands" before collecting GSR from the shooter after firing were also studied. For the first cleaning condition, without washing hands after firing, GSR on the backs of the hands of the shooter was collected by swabbing with a cotton brush. The optimum conditions for sampling and extraction procedures were applied. For the second condition, after firing the revolver at various firing times, the hands were washed with 0.5 L of tap water before collecting the GSRs on the backs of the hands by using the same method.

Results and Discussion

The analytical performance of the calibration curve

This work was on the development of sampling and extracting methods for determining Pb Ba and Sb in GSR. To validate the proposed method, several calibration curves were constructed for determining the target elements in the GSR samples, with 30 calibration curves being chosen for statistical analysis of both intraday and inter-day precision. The high-sensitivity curves were obtained which provided sufficient data for the determination of these target elements in GSR. These curves were also applied to study the parameters that affected sampling and extraction efficiency as described in the Materials and Methods Section. The analytical performance of the calibration curves is summarized in Table 3.

Table 3 Analytical performance obtained from 30 replicates calibration curve construction

Performance	Target elements		
	Pb	Ba	Sb
Slope ($\bar{X} \pm SD$)	$0.0022 \pm 1.2 \times 10^{-4}$	$0.0030 \pm 2.4 \times 10^{-4}$	$0.0020 \pm 1.9 \times 10^{-4}$
Intercept ($\bar{X} \pm SD$)	$0.0143 \pm 9.6 \times 10^{-4}$	$0.0119 \pm 3.7 \times 10^{-3}$	$0.0097 \pm 2.8 \times 10^{-4}$
LOD (μg L^{-1})	1.31	3.70	0.42
LOQ (μg L^{-1})	4.36	12.33	1.40
Inter-day slope (%RSD, n=30)	5.60	8.00	9.50
Intra-day slope (%RSD, n=5)	5.05	5.85	5.20

An investigation of Sampling and Extraction efficiency

The results of the study on the various parameters that affect the sampling and extraction efficiency are illustrated in Figure 1 and 2, respectively. The selected optimum condition for sampling and extraction was chosen by considering the amount of Pb, Ba and Sb found in the extracted GSR samples. DI water (0 % HNO_3) and 1-5 % HNO_3 were used as solvents in the sampling procedure. Since an acidic medium was favorable for target elements in the aqueous solution, 1-5 % of HNO_3 improved the sampling efficiency over that shown using DI water (see Figure 1A). With the relatively high amount of the target elements found, an increase in acid content provided a good sampling performance. According to the result, 5% HNO_3 was selected as the optimum condition for the solvent type. The effect of sampling solvent volume is shown in Figure 1B. An increase in the volume of the solvent from 100 μL to 200 μL results in a decrease in the amount of the target elements found commensurate with the increase in the dilution factor. Because of the relatively high amount of the target elements found, 100 μL was considered to be the appropriate volume and it also provided better results in sensitivity and precision. Figure 1C illustrates the effect of the number of replicates for swabbing the GSR on the backs of the hands. The result gave no significant efficiency between 1-3 replication times. This showed that 1 swab was sufficient to cover the main sampling area. The amounts of all target elements found at different storing temperatures are shown in Figure 1D. It was found that the storage temperatures that were tested did not affect the amount of Ba found but slightly affected the amount of Sn found. However, the amount of Pb found strongly depended on the storage temperature. At 4°C, the amount of Pb found was greater than that observed at 30°C. Therefore the choice of storing temperature was 4°C due to the storage stability of Pb at low temperature.

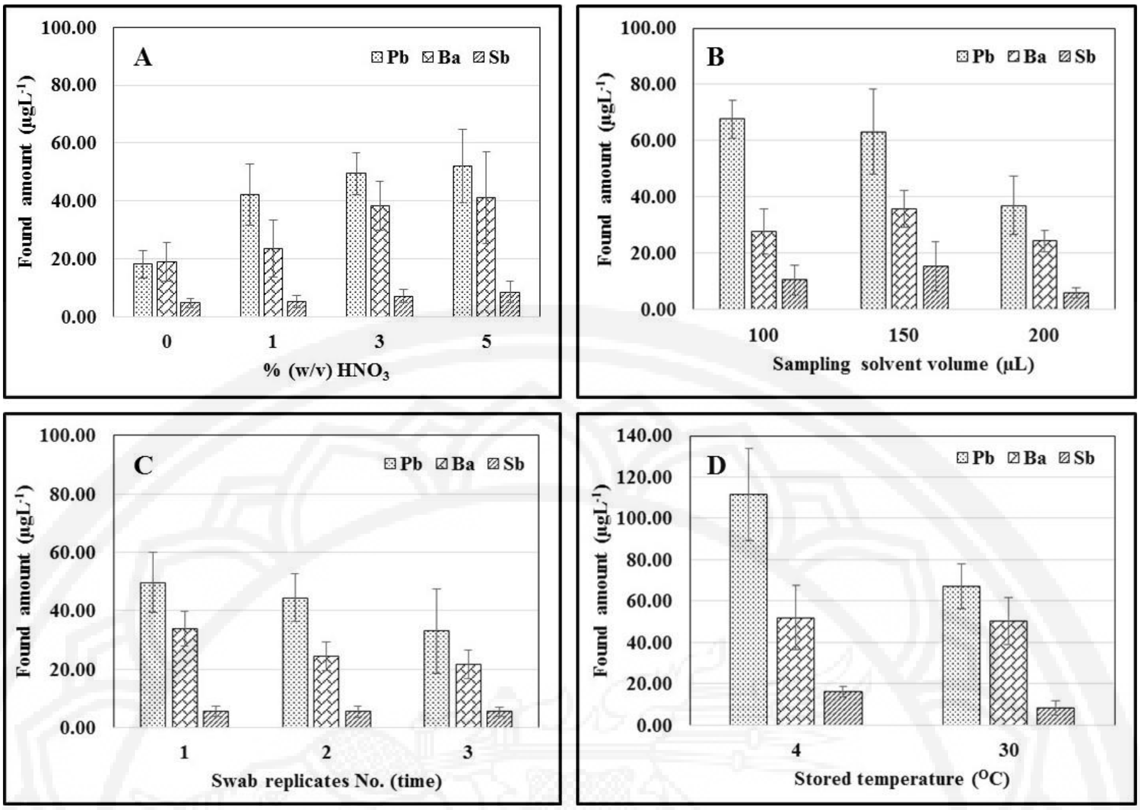

Figure 1 Effect of sampling parameters (n=5) **(A)** solvent type **(B)** solvent volume **(C)** swab replicates number and **(D)** stored temperature

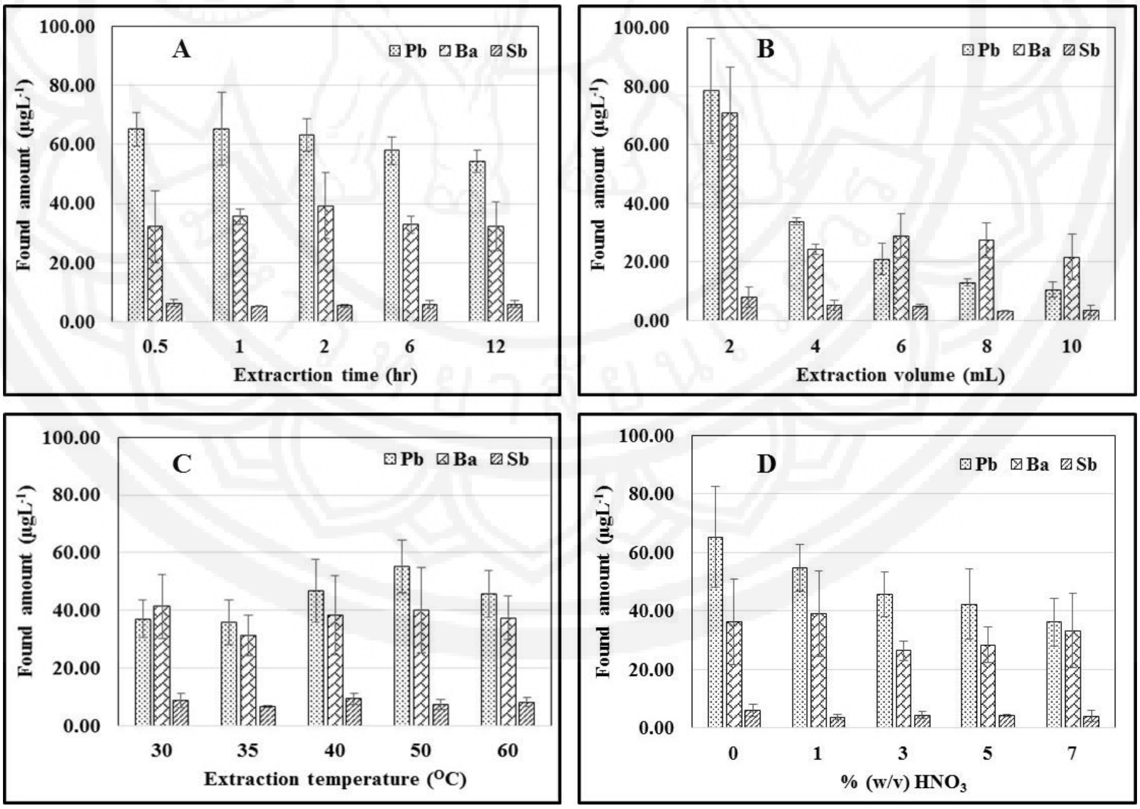

Figure 2 Effect of extracting parameters (n=3) **(A)** extraction time **(B)** solvent extraction volume **(C)** extraction temperature and **(D)** acid content (extracting solvent)

The effect of extraction time is shown in Figure 2A. There were no significant changes in the amount of the target elements found at the various extraction times of 0.5, 1, 2, 6, and 12 hr, hence 30 min was chosen for the optimum condition for the extraction time. When compared with Thailand's forensic protocol (Mingchanid & Kulnides, 2017), the proposed method provided a shorter extraction time for determining the target elements. The largest sensitivity of the method with the least dilution factor of extraction volume, the extraction efficiency, is shown in Figure 2 B. The largest amount of the target elements found were obtained from a 2.0 mL extraction volume. Figure 2C shows the results of the effect of temperature on extraction efficiency. There were no significant differences in the amount of all target elements found when increasing the temperature over the range of 30°C – 60°C. It is therefore convenient to perform the extraction at room temperature (30°C).

For the study of the effect of extracting solvent, DI water (0 % HNO_3) and 1, 3, 5 and 7% HNO_3 were investigated. From Figure 2D, it can be seen that the performance of extracting efficiency of DI water compared to 1% HNO_3 was approximately the same. In the sampling procedure with 5% HNO_3, the acidic solution remained in the swab cotton, therefore the range of 0-1% HNO_3 was chosen as the extracting solvent. The selected sampling and extracting conditions are summarized in Table 2.

Validation and Application of the proposed method

To validate the proposed method, 5 GSR samples were collected immediately after firing and extracted for 0.5 hr using 2 mL 1% HNO_3 at room temperature (30 ^{O}C). Consequently, 50.00 μg L^{-1} of Pb, Ba and Sb were added into extracted sample solutions and then quantified by using GFAAS and computing from the calibration curves, as shown in Table 2. The results are presented in Table 4. The acceptable recovery percentages of recoveries were in the range of 91.20 – 98.24% for Pb, 91.74 – 104.44% for BA and 93.44 – 102.32% for Sb. It was confirmed that the proposed method was highly accurate and reliable.

Table 4 The recovery studies of added standard 50.00 μg L^{-1} into extracted GSRs solution (n=5)

No.	Pb found (μg L^{-1})			Ba found (μg L^{-1})			Sb found (μg L^{-1})		
	Sample	Added sample	%R	Sample	Added sample	%R	Sample	Added sample	%R
1	26.15	75.27	98.24	40.60	92.40	103.60	7.57	55.89	96.64
2	41.91	88.64	93.46	119.10	171.32	104.44	8.04	59.20	102.32
3	34.31	79.91	91.20	42.50	89.37	93.74	5.73	52.45	93.44
4	39.84	88.61	97.54	47.63	93.50	91.74	5.38	55.37	99.98
5	37.72	86.21	96.98	45.30	97.10	103.60	8.86	55.69	93.66
$\overline{X}$±SD			99.48±3.02			99.42±6.15			97.21±3.90

In the hand cleaning study, a t-test was applied to compare between washing the hands and without washing the hands conditions. A significantly different amount of the target elements were retrieved at a 95% confidence level (t-value < t-critical). To demonstrate the capability of the proposed method, the GSR samples were collected at various durations of time under the two conditions of not washing the hands and washing the hands, with 0.5 L tap water, immediately after firing. The results are shown in Table 5. A Friedman test showed that the amounts of all elements significantly decreased with longer post-firing times at a 95% confidence level. The amounts of all elements decreased with increasing post-firing time. Pb and Ba were detected within a period of 9 hr whereas Sb was not detected after 3 hr after firing. The amount of these elements was significantly affected by cleaning conditions. The t-test was applied for a comparison between washing vs not washing conditions. This showed significantly different amounts of all target elements at a 95% confidence level (p-value < 0.05). The results also showed that the found amount of all target elements with washing condition were decreased as compared to without washing condition.

From these findings, the proposed method provided many advantages including being low cost, simple to administer and a shorter time to achieve a result as compared to results reported in previous reports (see Table 6). Extraction of target metals was simply done by a low-cost 1% HNO_3 extracting solvent with a short period (30 min) for extraction at room temperature. With this method, the commonly available and used method of Graphite Furnace Atomic Absorption Spectrometry was successfully applied for the analysis of Pb, Ba and Sb in GSR in forensic work.

Table 5 The found amount of Pb, Ba and Sb in GSRs obtained from different firing times and cleaning conditions (n=5)

Firing time (hr.)	Found Pb amount ($\mu g\ L^{-1}$) ($\bar{X}$±SD)		Found Ba amount ($\mu g\ L^{-1}$) ($\bar{X}$±SD)		Found Sb amount ($\mu g\ L^{-1}$) ($\bar{X}$±SD)	
	Not washing hand	Washing hand	Not washing hand	Washing hand	Not washing hand	Washing hand
0	52.26±9.79	35.58±10.71	197.76±25.55	79.00±13.48	8.79±2.55	2.18±0.56
3	35.93±7.04	21.69±3.02	88.64±14.98	72.60±13.78	3.93±0.49	1.59±0.37
6	27.58±10.25	17.18±8.22	68.28±15.90	62.44±7.71	ND	ND
9	25.52±9.03	14.80±3.93	63.76±11.59	47.78±8.47	ND	ND

Not washing hands = do not wash hands before collecting GSRs

Washing hands = wash hands with 0.5 L tab water before collecting GSRs

ND = Not detection (Lower than the Limit of detection, LOD)

Table 6 Forensic studies using the determination of Pb, Ba and Sb in GSRs

Technique	Sampling	Extraction	Forensic study	Ref.
ICP-AES	A cotton swab with 4-5 drops of 5% HNO_3 per swab	5% HNO_3 24 hr. at RT	Firing time and occupation	Mingchanid & Kulnides, 2017
ICP-AES	1 cm^2 pig's skin cut	Conc. HNO_3 pressure 20 bar 1 hr. at 100 ^{o}C	Firing distance and ammunition	Turillazzi et al., 2003
ICP-AES	A cotton swab soaked in 2% EDTA	10% HNO_3 ultrasonic 1 hr. at 100 ^{o}C	Firing distance of firearms and number of shots	Vanini et al., 2015
ICP-AES	A cotton swab soaked in 2% EDTA	10% HNO_3 ultrasonic 20 min at 100 ^{o}C	-	Vanini et al., 2015
SWV/GFAAS	A cotton swab soaked in 2% EDTA	10% HNO_3 ultrasonic 2 hr. at 60 ^{o}C	Firearms and ammunition	Salles et al., 2012
ICP-MS	A cotton swab soaked in 2% EDTA	10% HNO_3 ultrasonic 30 min at 80 ^{o}C	Different collection areas and incident bullet hole	Li, 2021
GFAAS	A cotton swab with 100 µL 5% HNO_3 per swab	1% HNO_3 30 min at RT	Firing time and cleaning condition	This work

RT = Room temperature

ICP-AES = Inductively Coupled Plasma Atomic Emission Spectrometry

SWV = Square Wave Voltammetry

GFAAS = Graphite Furnace Atomic Absorption Spectrometry

ICP-MS = Inductively Coupled Plasma Mass Spectrometry

Conclusion and Suggestions

This report presents a simple and low-cost procedure for sampling, extraction and determination of the target elements (Pb, Ba and Sb) in GSRs. The cotton swab technique was applied to collect GSR samples by using exactly 100 µL of 5% HNO_3 per swab. The extraction procedure was simply operated by 1% HNO_3 with 30 min extraction time at room temperature. The proposed method was successfully applied for the determination of target elements using the GFAAS technique which is commonly used in the Police Forensic Science Center, the Royal Thai Police. The detection of these target elements in GSRs within 3 hr after firing is useful information for finding criminals. In addition, the work presented here suggests that the proposed method provides a simple and convenient method which beneficial for the determination of Pb, Ba and Sb.

Acknowledgements

This research was funded by the National Research Council of Thailand (NRCT) with targeted research for the financial year of 2016 for public security and good governance issues. Instrument and apparatus used in the experiment and sampling were supported by the Science Center, Faculty of Science and Technology, Nakhon Ratchasima Rajabhat University (NRRU) and Police Forensic Science Center 3 (PFSC 3), the Royal Thai Police, Nakhon Ratchasima, Thailand. Thanks to Mr. Roy I. Morien of the Naresuan University Graduate School for his editing of the grammar, syntax and general English expression in this manuscript.

References

Brozek-Mucha, Z. (2014). On the prevalence of gunshot residue in selected populations - An empirical study performed with SEM-EDX analysis. *Forensic Science International*, *237*, 46-52.

Feeney, W., Menking-Hoggatt, K., Vander Pyl, C., E. Ott, C. E., Bell, S., Arroyo, L., & Trejos, T. (2021). Detection of organic and inorganic gunshot residues from hands using complexing agents and LC-MS/MS. *Analytical Methods*, *13*, 3024-3029. https://doi.org/10.1039/d1ay00778e

Li, X. (2021). Measurement of gunshot residues with inductively coupled plasma mass spectrometry from a 9 mm × 25 mm police revolver and 7.62 mm × 25 mm type 64 pistol. *Microchemical Journal*, *160*, 1-6. https://doi.org/10.1016/j.microc.2020.105678

Lopez-Lopez, M., Delgado, J. J., & Garcia-Ruiz, C. (2013). Analysis of macroscopic gunshot residues by Raman spectroscopy to assess the weapon memory effect. *Forensic Science International*, *231*, 1-5.

Mingchanid, P., & Kulnides, N. (2017). Study on Persistence of Gunshort Residue After Shooting From 9 mm Pistol on Back of Hands and Palms with Different Persistent Duration and Bullet Types. *KKU Research Journal (Graduate Studies)KKU Res (GS)*, *17*, 8-18.

Nantasitangkool, P., Kittirakshakula, N, Watcharayotinkul, W., Prongmanee, W., Lamdab, U., Sukhkhawuttigit, S., Muenkla H., Ratnarathorn N., Kumpoo R., Sihabunmak N. & Samransamruadkit, Z. (2020). Interlaboratory Comparison of Gunshot Residue Analysis. 17th IMEKO TC 10 and EUROLAB Virtual Conference "*Global Trends in Testing, Diagnostics & Inspection for 2030*": *Proceedings of an online international conference on 20-22 October 2020*, (pp. 156-161). Dubrovnik, Croatia: International Measurement Confederation (IMEKO).

O' Mahony, A. M., Windmiller, J. R., Samek, I. A., Bandodkar, A. J., & Wang, J. (2012). "Swipe and Scan": Integration of sampling and analysis of gunshot metal residues at screen-printed electrodes. *Electrochemistry Communications*, *23*, 52-55.

Phermpornsagul, Y., Arepornrat, S., Palkawong Na Ayuthaya, W., & Khaenamkaew, P. (2020). A Comparative Study of SEM-EDX and ICP-MS Detection Based on Gunshot Residue Originated from AK-47 and M16 Rifles. *American Journal of Applied Sciences*, *17*, 69-82. https://doi.org/10.3844/ajassp.2020.69.82

Polnparkh, U., Chimpalee, N., & Hintao, K. (2012). Comparison of Particles of Occupation Origins Residues and Lead-free Gunshot Residues. *KKU Research Journal (Graduate Studies)*, *KKU Res (GS)*, *12*, 34-45.

Polovkova, J., Simonic, M., & Szegenyi I. (2015). Study of gunshot residues from Sintox® ammunition containing marking substances. *Egyptian Journal of Forensic Sciences*, *5* (Issue 4), 174-179.

Romolo, F. S., & Margot, P. (2001). Identification of gunshot residue: a critical review. *Forensic Science International*, *119*, 195-211.

Romolo, F. S., Christopher, M. E., Donghi, M., Ripani, L., Jeynes, C., Webb, R. P., ...Ward N. I., Kirkby K. J. & Bailey, M. J. (2013). Integrated Ion Beam Analysis (IBA) in Gunshot Residue (GSR) characterization. *Forensic Science International*, *231*, 219-228.

Salles, M. O., Naozuka, J., & Bertotti, M. (2012). A forensic study: Lead determination in gunshot residues. *Microchemical Journal*, *101*, 49-53.

Tarifa, A., & Almirall, J. R. (2015). Fast detection and characterization of organic and inorganic gunshot residues on the hands of suspects by CMV-GC-MS and LIBS. *Science and Justice*, *55*, 168-175.

Turillazzi, E., Paolo Di Peri, G., Nieddu, A., Bello, S., Monaci, F., Neri, M., ...Pomara C., Rabozzi R., Riezzo I. & Fineschi, V. (2003). Analytical and quantitative concentration of gunshot residues (Pb, Sb, Ba) to estimate entrance hole and shooting-distance using confocal laser microscopy and inductively coupled plasma atomic emission spectrometer analysis: An experimental study. *Forensic Science International*, *231*, 142-149.

Vanini, G., Destefani, C. A., Merlo, B. B., Carneiro, M. T. W. D., Filgueiras, P. R., Poppi, R. J. & Romao W. (2015). Forensic ballistics by inductively coupled plasma-optical emission spectroscopy: Quantification of gunshot residues and prediction of the number of shots using different firearms. *Microchemical Journal*, *118*, 19-25.

Vanini, G., Souza, M. O., Carneiro, M. T. W. D., Filgueiras, P. R., Bruns, R. E., & Romao, W. (2015). Multivariate optimisation of ICP OES instrumental parameters for Pb/Ba/Sb measurement in gunshot residues. *Microchemical Journal, 120*, 58-63.

Yanez, J., Farías, M. P., Zuniga, V., Soto, C., Contreras, D., Pereira, E., …Mansilla H. D., Saavedra R., Castillo R. & Saez, P. (2012). Differentiation of two main ammunition brands in Chile by Regularized Discriminant Analysis (RDA) of metals in gunshot residues. *Microchemical Journal, 101*, 43-48.