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Determination of antimony in gunshot residues (GSR) by electrothermal atomic absorption spectrometry

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Simple and fast analytical procedure for antimony determination in gunshot residues by electrothermal atomic absorption spectrometry (ETAAS) is described. The sampling method of swab was tested by using adhesive tapes and both cotton rod and bandaged cotton moistened with boric acid. The optimal instrumental parameters for ETAAS measurements are defined: the maximum loss free pretreatment temperature found was 700ºC and the optimum atomization temperature was 1800ºC. Experiments performed with various modifiers (Pd, Ni, ascorbic acid, boric acid) showed that 5% (m/v) of boric acid is the most suitable modifier for Sb ensuring interference free ETAAS measurements. Linear analytical curve is ranging from 5 $\mu g \cdot L^{-1}$ to 40 $\mu g \cdot L^{-1}$ ($R^2 = 0.9998$, n = 3). Limit of detection (LOD) and limit of quantification (LOQ) calculated under optimum conditions are 0.4 $\mu g \cdot L^{-1}$ and 1.3 $\mu g \cdot L^{-1}$, respectively. The degree of interferences from matrix elements like Na, K, Ca, Fe, Pb, Ba, Ag, Cl, SO_4 and PO_4 was investigated and evaluated. Recoveries in the range 70–88% were achieved.

Key words: Antimony, ET-AAS, Zeeman correction, interference, gunshot residues.

INTRODUCTION

The gunshot residues (GSR) are essential samples in the forensic science for the identification of suspected persons. A small part of GSR is smeared on an index finger, back of the thumb and on palm of the person, who has fired the gun. Determination of GSR substances gives some information about the person who fired or touched the gun and about the firing distance [1, 2]. GSR substances could include lead styphnate as an explosive initiator, barium in nitrate form in small-arms and antimony sulphide fuel in primers, calcium silicide, zinc, zirconium, magnesium, titanium, trace amount of chloride, iron, potassium, sodium, phosphorus and also some organic compounds such as nitroglycerin, 2,4-dinitrotoluene and others. [3–5]. The quantities of these elements are affected by some factors such as type of weapon, burning process of powder, firing time and distance, personal hygiene, environmental conditions.

The GSR detection methods are based on analysis of the chemical residues, produced from discharge of cartridge. Several techniques have been used to determine the GSR; each one has advantages and disadvantages as usual. Sampling of GSR is very important to get accurate and reliable results. It is mentioned in the literature that level of GSR components is very low even after three hours of firing [6]. It is also well known that the amount of GSR on the hands could be cleaned out by some activities such as washing/rubbing/wiping of the hands, placing the hands in pockets, characteristics of perspiring of the person, etc. Therefore, sample collection must be done in a fast and proper way on the crime scene. Nowadays GSR samples are collected by "swab" technique via washing of hands by some acidic solutions or wiping some materials like cotton moistened with diluted acid, EDTA [2, 5, 7]. In the literature adhesive film was used principally for lifting organic compounds of GSR from a firer's hand [5] and lifting the particles via adhesive surface called as "tape lifting" technique [2]. Typically, this sampling could be used for all components determination in GSR. Conventional flame atomic absorption (FAAS) has sufficient sensitivity for the detection of Pb encountered in hand samples but it was inadequate for barium and antimony [4]. ICP-AES is a rapid technique with capabilities for multi-elemental analysis, which is relatively free from interference; however, it lacks the sensitivity required for accurate Sb determination on GSR swab extracts. Inductively coupled plasma mass spectrometry has benefits for GSR analyses due to its accuracy, multi-element capability and low detection limits for swab sampling 0.5 ng of Sb, 0.2 ng of Ba and 1.4 ng of Pb [8]. Few reports have been made on this technique because of relatively high cost of analysis. In recent years a scanning electron microscope (SEM) and its combinations such as

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energy dispersive X-ray analysis (SEM/EDX) was found able to acquire information about the distribution of elements in gunshot residue. The main disadvantage of SEM techniques is its high time and manpower consumption [2]. Nowadays anodic stripping voltammetry is also used for determination of GSR, but the determination of barium has insufficient detection limit. Electrothermal atomic absorption is preferable technique for Sb determination in GSR [9, 10]. It permits measurement of Sb at 10 ng level [11, 12]. The combination of ET-AAS and SEM techniques are mostly used by forensic laboratories [3, 5, 7, 8, 13].

In the present work, we optimize the instrumental parameters for Sb determination by ETAAS. The most appropriate pretreatment and atomization temperatures are defined in the presence of boric acid (BA) as matrix modifier. The degree of matrix interferences due to sodium, potassium, calcium, iron, lead, barium, silver, chloride, sulphate, phosphate and others on the Sb absorbance signal was investigated. Sampling and sample preparation procedures are also optimized; the most suitable acidic mixture is recommended. The adhesive tape and both cotton rod and bandaged cotton moistened with boric acid were used as a sampling from hands.

EXPERIMENTAL

Instrumentation

Varian GTA 120 model AA280Z (with Zeeman background corrector) electrothermal atomic absorption spectrometer was used for analysis. The absorbance values were measured with an antimony hollow cathode lamp, which was operated at 217.6 nm with a bandpass width of 0.5 nm at 10 mA current. Pyrolytically coated tubes were used as atomizers. Sample injections volumes of 20 μL were used. Mechanic shaker GFL-3015 ORG and magnetic stirrers with heating IKA-MS 2 VORTEX and ARE were employed for sample preparation. Yavuz 16 compact model of Turkish gun was used for real sampling.

Reagents

Ortho-phosphoric acid (85%, p.a. Merck), hydrochloric acid (37%, p.a. Merck), sulphuric acid (95–98%, p.a. Merck), nitric acid (65%, p.a. Merck), boric acid (BA) (p.a. Merck), ascorbic acid (AA) (p.a. Merck), sodium nitrate, potassium nitrate (p.a. Merck / Fluka), stock standard solutions of Ag, Ca, Ba, Sb, Pb and Fe 1000 $mg \cdot L^{-1}$ (Merck, BDH Lab. and SCP SCIENCE) were used. Doubly distilled water (J. T. Baker) was used throughout all experiments. Working Sb standard solutions were prepared by appropriate dilution of stock standard solution with 8% of HNO_3. Solutions of 1% (w/v) AA and 5% (w/v) BA were used as matrix modifier solutions. Calibration curve was prepared with 5, 10, 20, 30 and 40 $ng \cdot mL^{-1}$ antimony standards. The effect of different acids and acid mixtures (H_2O_2, HNO_3-H_2O_2 and HNO_3-H_2O_2-HCl) was investigated within the acid concentration range from 2 to 10%. A synthetic model solution was prepared containing from 1 to 400 $\mu g \cdot mL^{-1}$ of Ag, Ba, Pb, Fe, Na, K, Ca, as nitrate salts and SO_4, PO_4 and Cl in acid form to simulate the sampling problems of swab on the venue.

Sampling and sample preparation

The collection of samples from gun shots is typically performed by swabbing technique on the spot of event by police officers, so that sampling must be done easily, fast and accurately. It is well known that the efficiency of sampling is affected by interferences coming from the field of firing conditions and time, type of weapon, human activities of firing person (sweat, saliva *etc*.), personal hygiene and biometrics [5, 9, 13]. Sampling is important for both to get accurate, repeatable results and not to damage the hands of suspected person. In early times, nitric acid solution was used as a GSR's collector [2]. Sampling in the field for GSR generally is taken by adhesive tape. Collected GSRs migrated to bulk solution by acid or acid mixtures. On the other hand, sampling could be done with moistened cotton material. In early works, nitric acid was used for collecting of GSRs from hands although it is well known that nitric acid has corrosive effect on the skin. Because of this reason, less corrosive and injurious solutions and materials are examined such as EDTA and adhesive tape [2, 5, 7]. In this work 5% of BA solution is tested as a moistening solution of cotton. It is also known that median lethal dose (LD_{50}) of BA for mammals are given rating 2.66 $mg \cdot kg^{-1}$ bodies mass. BA is poisonous if taken internally and inhaled [14, 15]. BA is functional and harmless for intact skin. It has also some antibacterial and antiseptic usages [16, 17]. So that swabbing with cotton moistened by BA could be used for sample collection of GSR directly from hands.

Shootings were made by using a Yavuz 16 Compact model of Turkish gun. Samples were collected from palm and backsides of both right and left hands of the person who made the shootings via lifting the residues particles on 5 × 5 cm adhesive tapes kept into polyethylene tubes in field. Collected samples were prepared by adding of 4 ml of 8% HNO_3 and the solution was stirred in mechanical shaker at 50 rpm for 30 minutes. The final solution

was analyzed by ET-AAS under optimum working conditions. On the other hand, swabbing procedure also applied with cotton rods (plastic handled cotton tipped) and bandaged cotton moistened with 1 mL of 5% of BA. Then bulk solution of them was prepared analogously to this with adhesive tape. In our work we mentioned that 5 mL of 8% nitric acid and 30 minutes shaking ensures recoveries of about 90% for the determination of Sb.

RESULTS AND DISCUSSION

Optimization of the ETAAS

Furnace temperature program. The optimal furnace temperature program was defined through the pretreatment and atomization curves prepared with 10 ng·mL^{-1} of Sb standard and summarized in Table 1. Calibration plot obtained under optimal instrumental conditions was calculated by linear regression to fit the equation A = 0.0026[Sb] – 0.0012 and R^2 = 0.9998. Limit of detection (LOD) (3σ) and limit of quantification (LOQ) (10σ) were calculated according to IUPAC rules to be 0.4 μg·L^{-1} and 1.3 μg·L^{-1} in respectively.

Effect of acid and acid mixture in the absence of matrix modifier. The effect of different acid/acid mixtures on the antimony absorbance signal was examined. The results obtained are depicted in Table 2. It is well known that HNO_3 and H_2O_2 have oxidative effect, which will be helpful for the formation of Sb oxides on the tube surface before the atomization step. In general, in the presence of HCl acid negative effect on the Sb absorbance signal could be expected due to the volatile compounds formed with chloride ions. In this way parts of the element could be partially lost before the atomization step. However, experiments performed showed that on the contrary the interference effect observed in the presence of HCl as well as gaseous compounds (Sb, $SbCl_5$, SbH_3, Sb_2, Sb_4 and SbS) and condensed compounds (Sb, $SbCl_3$, SbOCl, SbO_2, Sb_2O_3, Sb_2O_5 and Sb_2S_3) formed was insignificant [18–20]. It could also be explained by entrance of chlorides into the graphite lattice at high temperatures [19, 20]. Because of this reason, there were not big differences in the data obtained in the presence of HNO_3, HCl and H_2O_2. It is also known that acids have both extracting and modifying effect in the heating procedure [8, 13, 18].

*Effect of modifier***.** It is well known that matrix modifier is used for thermal stabilization and for elimination of chemical interferences coming from the matrix. In the literature, Dash *et al*. [21] used boric acid as a modifier for the determination of trace amount of indium in high purity antimony by ET-AAS and they obtained satisfactory results. Therefore, in our work we used for the first time BA as a matrix modifier for the determination of antimony by ETAAS. Synthetic matrix solutions were spiked with Sb and analyzed in the presence of 2% and 5% of BA, 1% of AA, 10 μg Pd and Ni solutions as matrix modifiers. Recoveries obtained are presented in Table 3. When AA was used as a matrix modifier, it had no advantage and did not eliminate matrix interferences. In this study, we observed that 5% boric acid used as a matrix modifier has good recovery value compared with AA, Pd and Ni.

Table 1. Optimal temperature program for Sb with modifier.

Step	Temperature, ºC	Time, s	Gas flow, L·min^{-1}
1	95	5.0	0.1
2	120	25.0	0.3
3	700	30.0	0.3
4	1800	4.0	0.0
5	2300	3.0	0.3
6	40	20.9	0.3

Table 3. Recoveries for Sb in the presence of different matrix modifiers (n = 3).

Matrix modifier	maximum loss free pretreatment temperature, ºC	Optimal atomization temperature, ºC	Recovery in presence of a GSR, %
5% BA	700	1800	80–88
2% BA	700	1800	65–70
1% AA	700	1800	35–40
10 μg Pd	1500	2100	25–40
10 μg Ni	1100	2000	28–45

Table 2. Effect of acid/acid mixture on the Sb atomic absorbance signal as recovery (%).

%	Recovery (compared with 10 ng·mL^{-1} of Sb atomic absorbance signal), %					
	HNO_3	HCl	H_2O_2	HNO_3 + HCl	HNO_3 + H_2O_2	HNO_3 + H_2O_2 + HCl
2	80 ± 7	105 ± 2	86 ± 4	105 ± 3	102 ± 3	93 ± 8
4	84 ± 2	102 ± 5	99 ± 3	104 ± 5	107 ± 1	96 ± 3
6	97 ± 1	99 ± 3	103 ± 4	95 ± 3	107 ± 2	95 ± 4
8	100 ± 3	98 ± 3	104 ± 2	105 ± 2	106 ± 4	102 ± 5
10	101± 5	93 ± 4	111 ± 7	104 ± 2	110 ± 6	99 ± 6

Spectral interference effect could be expected in the presence of more than 1 $g \cdot L^{-1}$ of Pb, Cu and Ni because of their close alternative wavelength coincidence [13]. The interference effect of some metals and inorganic ions such as Na^+, Cl^-, PO_4^{3-} and K^+, which comes from the human perspiration and Pb, Ba, Ag, Fe, Ca and SO_4, which may be contained in the structure of gun and bullet material and the environment on the absorbance signal of Sb was also investigated. Model solutions in the range of 1–400 $mg \cdot L^{-1}$ were prepared and spiked with 10 $ng \cdot L^{-1}$ Sb. The interference effect was evaluated through the recoveries obtained. As it is seen from the results in Table 4 the presences of Cl, PO_4, Ca and Na have no serious effect on the Sb absorbance signal because of Zeeman's background correction. The absorbance signal for Sb decreased upon increasing of Ag, Ba, Pb, Fe, K and SO_4 concentration in the solution. Decreasing of recovery in the range of 61-81 % in the presence of Ag could be explained with amalgam formation [22].

Application of procedure

After every shooting with Yavuz Model of Turkish gun, sampling was performed with adhesive tapes, both cotton rods and bandaged cotton moistened with 5% of BA, according to the sampling procedure given in sampling part. Shooting and sampling were repeated three times for every procedure and also the hands were washed after each shot. Results for Sb from real sampling were obtained according to optimal instrumental conditions defined and summarized in Table 5 as concentration in the solution and distribution of amount on the palm and backside in $mg \cdot cm^{-2}$. Recovery tests were conducted for real sampling by putting on the hands' surface 10–20 $ng \cdot mL^{-1}$ of antimony standard. Recoveries achieved by using adhesive type and moistened cotton (both rod and bandaged) are found in the range of 95–122% and 95–140%, respectively. It could be concluded from recoveries that the swabbing procedure with cotton soaked in 5% BA ensures accurate and reliable results.

It is very difficult to compare and confirm results, obtained in this study with other works in the literature because of differences in gun type, bullet or cartridges, sampling procedure, *etc*. [23]. Another difficulty of such kind of studies is to find certified reference material. In spite of these difficulties, we tried to compare our results with the data for 9 mm parabellum type cartridges (such like our cartridges) with swabbing 2% of EDTA. A swabbing nearly resembles the technique used in this work. Results of Sb swabbing with EDTA are at the average range 3.19–60.70 with 2.30–13.3 standard deviations by ICP-MS technique [24]. Results of this work, seen in Table 5, are comparable with the result of Sarkis *et al*. [24]. It could be said that proposing sampling solution and bandaged cotton give also good results.

Table 4. Interference effects on the Sb atomic absorbance signal as recovery (%) without matrix modifier.

$mg \cdot L^{-1}$	Ag	Ba	Pb	Fe	Na	K	Ca	SO_4	PO_4	Cl
1	88 ± 3	109 ± 4	88 ± 2	96 ± 2	-	-	101 ± 2	-	96 ± 2	-
3	-	-	-	-	84 ± 2	73 ± 3	110 ± 7	81 ± 1	-	-
5	-	-	-	-	81 ± 3	71 ± 2	102 ± 5	76 ± 3	95 ± 2	-
10	76 ± 4	89 ± 2	86 ± 3	80 ± 1	-	-	-	-	95 ± 3	92 ± 1
15	-	-	-	-	83 ± 2	69 ± 4	114 ± 2	79 ± 2	95 ± 3	-
20	-	-	-	-	84 ± 1	68 ± 1	107 ± 2	75 ± 1	-	-
50	68 ± 2	57 ± 4	79 ± 4	65 ± 3		66 ± 2	103 ± 2	69 ± 3	-	91 ± 2
100	66 ± 3	33 ± 5	78 ± 4	61 ± 4		63 ± 4	92 ± 3	46 ± 6	-	89 ± 3
200	-	21 ± 3	71 ± 2	53 ± 8					-	89 ± 4
400									-	86 ± 3

Table 5. Results on antimony content in gunshot residues (n = 3).

	Adhesive band, mean ± s.d		Cotton rod, mean ± s.d		Bandaged cotton, mean ± s.d	
	$ng \cdot mL^{-1}$	$ng \cdot cm^{-2}$	$ng \cdot mL^{-1}$	$ng \cdot cm^{-2}$	$ng \cdot mL^{-1}$	$ng \cdot cm^{-2}$
Left hand						
palm	34.1 ± 0.3	5.5 ± 0.1	20.6 ± 1.4	3.3 ± 0.2	36.6 ± 0.4	5.9 ± 0.2
backside	32.4 ± 0.8	5.2 ± 0.2	19.9 ± 0.4	3.2 ± 0.1	30.5 ± 0.9	4.9 ± 0.2
Right hand						
palm	26.5 ± 0.6	4.3 ± 0.1	20.2 ± 4.1	3.2 ± 0.7	31.4 ± 1.2	5.1 ± 0.2
backside	34.1 ± 1.2	5.4 ± 0.2	20.4 ± 0.9	3.3 ± 0.2	37.5 ± 0.7	6.0 ± 0.2

CONCLUSION

It is known that antimony is an uncommon element and it's a kind of diagnostics of gunshot firing. For this reason concentrations of Sb on the hands are very low, ET-AAS technique can be used very sensitively for its detection. The performed study showed that swabbing with bandaged cotton moistened by 5% of BA could be successfully applied as routine sampling procedure for Sb determination in gunshot residues. BA is an efficient modifier for ETAAS measurement of Sb in this solution. However, improving studies are still necessary such as sole usage of standard bandaged cotton to increase the efficiency, accuracy and to decrease the necessity of skilled personnel for swab sampling.

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ОПРЕДЕЛЯНЕ НА АНТИМОН В БАРУТНИ ОСТАТЪЦИ ЧРЕЗ ЕЛЕКТРОТЕРМИЧНА АТОМНО-АБСОРБЦИОННА СПЕКТРОМЕТРИЯ

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(Резюме)

Описана е лесна и бърза аналитична процедура за определяне на антимон в барутни остатъци чрез електротермична атомно-абсорбционна спектрометрия (ETAAS). Тестван е метод на пробовземане с използване на адхезивни ленти, памучни тампони и превързочен памук намокрени с борна киселина. Определени са оптималните инструментални параметри за измерване с ETAAS: максимална температура за нагряване без загуби 700ºC и оптимална температура на атомизация 1800ºC. Експерименти с различни модификатори (Pd, Ni, аскорбинова киселина, борна киселина) показаха, че 5% (m/v) борна киселина е най-подходящ модификатор за Sb осигуряващ свободно от пречене измерване с ETAAS. Аналитичната крива е линейна в областта от 5 $\mu g \cdot L^{-1}$ до 40 $\mu g \cdot L^{-1}$ ($R^2 = 0.9998$, n = 3). Границата на откриване (LOD) и границата на определяне (LOQ) изчислени при оптималните условия са съответно 0.4 $\mu g \cdot L^{-1}$ и 1.3 $\mu g \cdot L^{-1}$. Изследвана и определена е степента на пречене от матрични елементи като Na, K, Ca, Fe, Pb, Ba, Ag, Cl, SO_4 и PO_4. Получени са аналитични добиви в границите на 70–88%.