ANALYSIS OF GUNSHOT RESIDUES BY LA-ICP-MS

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ABSTRACT

The aim of this work was detection and elementary analysis of gunshot residues from hands of shooter by means of LA-ICP-MS method. Gunshot residues belong to the group of microtrace. Gunshot residues are solid metal and non-metal particles. These particles are submicroscopic size. These calibres were investigated: 22 LR S&B; 7,65 Br. S&B; 9 mm Luger S&B; 45 AUTO S&B. Gunshot residues were determined on the basis of combination of characteristic elements (Pb, Ba, Sb or Sn). Correlation matrix and Spearman correlation were used for statistical evaluation. Statistical evaluation was executed with program R. Significant non-homogeneousness of analyzed particles were observed. The composition of particles originating from the same cartridge is very variable what is caused by high temperature and pressure at shot. Hence the sorting of GSR to their originate cartridge is not possible.

Key words: gunshot residues, LA-ICP-MS

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INTRODUCTION

Gunshot residues (GSR) belong to the category of forensic microtrace. Microtraces were applied in forensic branch in recent years. New sensitive methods were found out for trace element analysis. GSR are often sought trace in criminal cases, where the firearm was used. Primary importance of GSR was only for distance shooting. Nowadays they are used to identify the person, who was in contact with a weapon (Planka B. *et. al*. 2010).

GSR produced by burning primer composition and powder charge (Straus J. *et. al.* 2004); (Mazánek M. *et. al*. 2000), (Dalby O. *et. al.* 2010). In the vicinity GSR come in the gas form cloud that after firing rapidly condenses (Kišová P. e*t. al*. 2011). This cloud is composed of CO_2, CO, NO_X, water vapor, partially burned and unburned particles of gunpowder and primer composition (Dalby O. *et. al.* 2010), (Heard B. J. 2008), (Haag L. C. 2006). These solid particles are called GSR (Heard B. J. 2008), (Haag L. C. 2006), (Hueske E. E. 2006). Condensation causes scattering of particles in the vicinity, so GSR can be found out not only on the hands of the shooter, but also to clothes and neighbourhood shooting (Mazánek M. *et. al*. 2000), (Dalby O. *et. al.* 2010), (Tripmple M. 2011).

Ensuring GSR is done in several ways. GSR are secured from the hand of the shooter. This sampling is performed using special disc with carbon adhesive layer. GSR are always taken from several location: the upper side of the forefinger and thumb and the basic joint of the thumb and forefinger (Mazánek M. *et. al*. 2000).

Determination GSR is performed by their morphology (spherical shape) and the chemical composition (Dalby O. *et. al.* 2010), (Heard B. J. 2008), (Wallace J. S. 2008). The characteristic elements (Pb, Sb and Ba) are important for chemical composition (Planka B. *et. al*. 2010), (Kišová P. e*t. al*. 2011). These characteristic elements consist of a fixed combination, according to the particles are identified as GSR. The combination of characteristic chemical elements of GSR, where are characteristics for GSR (Planka B. *et. al*. 2010):

1. Pb, Sb, Sn nebo Pb, Sb nebo Sn, Pb nebo Ba, Pb
2. Sn, Ba nebo Sb, Ba
3. Sb, Hg nebo Sn, Hg

Scanning electron microscopy with an energy-dispersive X-ray analyzer (SEM-EDX) is the most widely used method for the detection of GSR (Heard B. J. 2008). SEM can detect GSR by their morphology (Dalby O. *et. al.* 2010), (Schwoeble A. J. *et. al.* 2000) and their elemental composition. Elemental composition of GSR is given by characteristic elements (Pb, Ba and Sb). The advantage of this method is the direct analysis of specific discs (Haag L. C. 2006). Method SEM does not destroy the sample as in the case of other methods (Heard B. J. 2008). The disadvantage of this method is the higher limit of detection. This disadvantage led to the research of new methods for the analysis of GSR. A method LA-ICP-MS can be applied in forensic science for analysis of microtrace. The advantages of LA-ICP-MS are high sensitivity and bulk analysis with low detection limits.

Due to the sensitivity of LA-ICP-MS, we wanted to test whether it would be possible GSR not only identify, but assign individual identified GSR to the calibre, from which it originates.

MATERIAL AND METHODS

The laser ablation UP213 (New Wave Research, Inc., ESI, Fremont, CA, USA) and ICP-MS instrument Agilent 7500CE (Agilent Technologies, Santa Clara, CA, USA) with a dynamic reaction cell were used for analysis. Operating conditions of LA-ICP-MS are mentioned in the Tab.1 and 2.

Tab.1 Operating parameters of Nd:YAG laser ablation system

Wavelength	213 nm
Pulse width	4.2 ns
Repetition rate	10 Hz
Fluence	7 J·cm^{-2}
Ablation mode	single spots
Laser spot diameter	25 μm
Ablation cell volume	33 cm^{3}

Tab. 2 q-ICP-MS operating parameters

Carrier gas flow rate (He)	1.0 l min^{-1}
Plasma gas flow rate (Ar)	15.0 l min^{-1}
Auxiliary gas flow rate (Ar)	1.0 l min^{-1}
Carrier gas flow rate (Ar)	0.6 l min^{-1}
Collision gas (He)	2 ml min^{-1}
RF power	1500 W

Gunshot residues samples were get from shooter´s hand by using special LT-Sezam disks. Each disk consists of stick-on tape in a plastic container. Gunshot residues inside spent cartridges were mechanically removed and used as standard. GSR of four different caliber were analyzed (22 Long Rifle S&B, 9 mm Luger S&B, 45 AUTO S&B, 7,65 Browning S&B). All measurements were performed at the same operating conditions. These isotopes were measured: ^{27}Al, ^{28}Si, ^{39}K, ^{43}Ca, ^{47}Ti, ^{55}Mn, ^{56}Fe, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{88}Sr, ^{90}Zr, ^{118}Sn, ^{121}Sb, ^{137}Ba, ^{157}Gd, ^{202}Hg and ^{208}Pb. Sn, Sb, Ba and Pb are typical isotopes of GSR. 110 single spots of standard and 110 single spots of samples were chosen for GSR determination.

The data, obtained by LA-ICP-MS system, was processed by normalization method based on a total sum signals of isotopes (Latkoczy Ch. *et.al.* 2005). Data processing was performed by R statistical software. Elements correlation was searched. It was necessary to apply "centred logratio transformation" (Reimann C. *et. al.* 2008). This transformation breaks the closeness of the data, which arises by normalization of the total amount. The transformed data was evaluated by Spearman correlation. The correlation matrix was created for chosen elements. Positive and negative correlations are observed. The analyzed GSR samples were very non-homogeneous. The distribution of data was lognormal. No suitable statistical test was found out.

RESULT AND DISCUSSION

GSR coming from the cartridge of calibre .45 AUTO served as a standard for the characteristic elements. Elements Pb, Ba, Sb and Sn were determined as the characteristic elements for calibre .45 AUTO. In these particles were determined also other elements: Cu, Zn, Fe, K, Si, Al. The elements Zn and Cu comes from cartridge and Fe come from the gun. GSR form calibre .45 AUTO secured at the shooter´s hand were determined on the same combination of characteristic elements as the previously analyzed cartridge (Pb, Ba, Sb and Sn). GSR from shooter´s hand included these other elements: Cu, Zn, Zr, K, Si and Al.

If the matrix elements coming from the GSR from the cartridge are compared we can see large correlation between elements Ba and Sb, Pb and Sb, Sn and Cu (Fig 1A). Large negative

correlation is seen between Sb and Sn. Sample is a very non-homogeneous. This information is result of correlation matrix. In the correlation matrix (Fig. 1B), formed from elements of GSR from the shooter´s hand, we can see positive correlation between Ba and Sb. The correlation of these elements is the greatest. We can see other correlation between Pb and Ba; Zn and Cu. Positive correlation is observed in characteristic elements, which means that is GSR. The elements Cu and Zn come from cartridge. Positive correlation between these elements is visible.

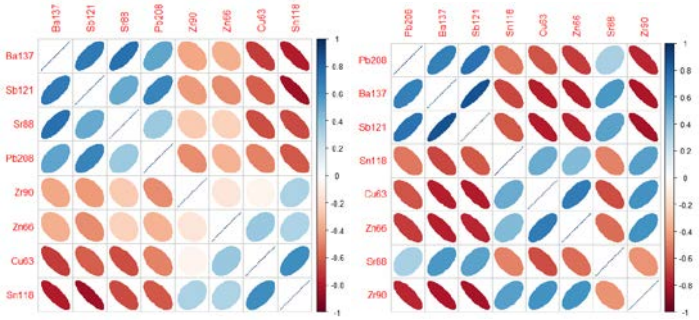

Fig. 1 A: GSR correlation matrix of chosen elements - cartridge caliber 45 AUTO; B: GSR correlation matrix of chosen elements – shooter's hand caliber 45 AUTO)

CONCLUSIONS

The gunshot residual of different caliber (22 Long Rifle S&B, 9 mm Luger S&B, 45 AUTO S&B, 7,65 Browning S&B) were analyzed by means of LA-ICP-MS. The samples of GSR were obtained from shooter's hand by using special LT-Sezam disks. Gunshot residues inside spent cartridges were used as standard. First of all, it was important to find out the characteristic combination of elements Pb, Ba, Sb and Sn for each caliber. The elemental combination of Pb, Ba, Sb and Sn was determined in the sample of caliber 45 AUTO S&B. This combination contains all characteristic elements for GSR. This combination of characteristic elements was applied for GSR detection of shooter's hand.

Considering that GSR samples are very inhomogeneous, it was impossible to do a outlying data test of percentage contents of elements. It was also the main reason why only qualitative analysis of characteristic elements was applied for GSR identification. To sum up, only the particles contained some characteristic elements combination were considered as gunshot residual. LA-ICP-MS was used for identification of GSR. Although the sensitivity of this method is high it has not found out the suitable resolution how to match each GSR to corresponding caliber. Some elements which are necessary for GSR identification weren't detect due to above mentioned inhomogeneity.

LA-ICP-MS can be applied for elemental analyses of GSR. It is possible to detect characteristic elements due to its high sensitivity. The biggest problem of this analysis is caused of samples inhomogeneity. SEM analysis can be much suitable because SEM enables recognize the morphology of the particles. Knowledge of this information greatly facilitates their detection.

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