FREQUENCY OF OCCURRENCE OF CERTAIN CHEMICAL CLASSES OF GSR FROM VARIOUS AMMUNITION TYPES

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ABSTRACT: The subject of the presented study were thirteen samples of primer residues originating from six types of ammunition, collected from shooters' hands immediately after shooting. The entire area of adhesive tabs with the secured material was examined with the use of SEM-EDX method in the automatic manner. Frequencies of occurrence of particles assigned to various chemical classes were calculated for each of the shooting experiment performed. In order to find out what kind of mutual relationships would reveal samples of gunshot residues collected from various types of ammunition as well as from the same type of ammunition cluster analysis was applied. The performed cluster analysis showed a promising tendency of grouping ammunitions according to their types. Moreover, it was checked that a sample of GSR from Makarov 9 mm ammunition, with some chemical classes weakly represented, may be correctly classified into the appropriate group of samples of GSR originating from this ammunition.

KEY WORDS: Gunshot residues (GSR); SEM-EDX automatic search; Frequency of occurrence of primer residues; Multivariate statistical methods; Cluster analysis.

Problems of Forensic Sciences, vol. XLVI, 2001, 281–287 Received 7 November 2000; accepted 15 September 2001

INTRODUCTION

Physical and chemical investigations of firearm discharge residues are performed for a number of purposes:

- identification of gunshot wounds/damages (establishing the entrance and the exit),
- estimation of shooting distance,
- distribution of GSR at a crime scene,
- estimation of the time since discharge of a firearm,
- establishing, whether a person has fired a gun, etc.

Fulfilling these tasks is always very helpful for reconstruction of an investigated crime. However, new challenges for GSR examiners arise, as with a growing frequency the administration of justice asks about the type of ammunition, and so the firearm, used in cases when the only evidence accessible for examinations are GSR. Thus, to the above list one more task should be added, i.e. the identification of an ammunition from GSR detected.

One of the attempts to solve this problem is consideration of the qualitative difference in the elemental composition of particles, i.e. searching for "signature elements" (R. Keeley – London Metropolitan Laboratory, The Forensic Science Service; private information). Another approach is a systematic study of GSR originating from various ammunition types and using statistical and chemometric methods for evaluation of the analytical data, presented by Niewoehner [4] and Brożek-Mucha [1, 3]. These works, performed for single examples of guns and ammunitions so far, revealed the possibility of group identification of the studied ammunition types. Moreover, it was found that primer residues collected within a number of experiments performed for the same ammunition, i.e. Makarov 9 mm, occur with similar frequencies within the appropriate chemical classes, and so the results are repeatable [2].

The aim of the presented work was to find out what kind of relations would reveal samples of gunshot residues collected from various types of ammunition (with a number of repetitions carried out for selected ammunitions). For the evaluation of possible differences and/or similarities of the analytical data, expressed as frequencies of occurrence of certain chemical classes in the entire population of the GSR detected in a sample, cluster analysis was applied.

EXPERIMENTAL

The subject of the presented study was 13 samples of primer residues originating from 6 types of pistol ammunition, collected from shooters' hands immediately after shooting three times (Table I).

Pistol	Ammunition	Number of experiments	Notation	
Browning 1900 Browning 7.65 mm		3	В	
Browning 1906	Browning 6.35 mm	1	b	
Beretta	Luger 9 mm	3	L	
P-64 & P-83	Makarov 9 mm	4	М	
Margolin	sporting 5.6 mm	1	s	
TT-33	7.62 mm	1	Т	

TABLE I. THE LIST OF PISTOLS AND THE APPROPRIATE AMMUNITION USED TO OBTAIN GUNSHOT RESIDUES

The whole area of adhesive tabs with the secured material was examined with the use of scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX) method in the automatic manner in the same conditions, presented in Table II. The obtained results were manually checked and corrected.

TABLE II. THE EQUIPMENT AND THE ANALYTICAL CONDITIONS OF THE MEASUREMENTS

Scanning electron microscope	JSM-5800, Jeol, Japan		
EDX Spectrometer	Link ISIS 300, Oxford Instruments Ltd.		
Automatic Search	GunShot, Oxford Instruments Ltd.		
Magnification	200 x		
Accelerating voltage	20 kV		
Working distance	10 mm		
Acquisition time for single particle	5 s		
Size of the scanned frame:			
height	514 mm		
width	658 mm		
area	0.338 mm^2		

RESULTS AND DISCUSSION

Primer residues containing a combination of lead, antimony and barium were taken into account. The number of particles representing these chemical classes was counted for each sample. Examples of obtained in such a manner results are presented in Table III. As the total numbers of particles observed for various samples were different, frequencies of occurrence of particles assigned to particular chemical classes were calculated according to the following formula:

$$f_i = \frac{N_i}{\sum_{i=1}^n N_i},$$
^{1}

where: N_i – number of particles of *i*-th chemical class; *n* – number of chemical classes of particles.

In order to compare the data sets obtained for particular samples, each of them was taken as a point in a multidimensional space where the co-ordinates were frequencies of occurrence of 7 chemical classes of particles. Thus, a measure of the differences between two sets of data, e.g. sample A and B can be the distance defined in the following manner:

$$d_{AB} = \sum_{i=1}^{n} W_i \left| f_{A_i} - f_{B_i} \right|,$$
⁽²⁾

where:

$$W_{i} = \frac{\left| r_{A_{i}} - r_{B_{i}} \right| + 1}{\left(\sum_{i=1}^{n} \left| r_{A_{i}} - r_{B_{i}} \right| \right) + n};$$

$$\{3\}$$

 r_{A_i} – a rank of -th chemical class in sample A; r_{A_i} – a rank of i-th chemical class in sample B.

	Ammunition				
Chemical classes of GSR	B1	L2	M4		
PbSbBa	222	136	4		
SbBa	22	11	2		
PbSb	108	89	43		
PbBa	2813	25	1		
Pb	733	260	11		
Sb	336	1164	1196		
Ba	914	19	0		
Total	5148	1704	1257		

TABLE III. SELECTED EXAMPLES OF THE RESULTS OF GSR SEARCH

For evaluation the distances among the studied samples cluster analysis was performed. As the clustering method, further neighbourhood was applied. Results of the cluster analysis are presented in Figure 1. One can observe in the dendrogram that four clusters are present. One of the clusters contains all of the studied samples of GSR obtained with Browning 1900 pistol and Browning 7.65 mm ammunition (B1, B2, B3) and solely them. The largest distance observed within this homogenous cluster was assumed as a formal border above which samples belong to separate clusters. Another cluster was created by all of the examined samples of GSR obtained with P-64 and P-83 pistols and Makarov 9 mm ammunition and one sample obtained with Beretta pistol and Luger 9 mm ammunition. Both remaining Luger samples are placed in a cluster together with the sample obtained with TT-33 pistol and the appropriate ammunition cal. 7.62 mm. The last cluster consists of two samples originating from Browning 1906, Browning 6.35 mm and Margolin, 5.6 mm, thus from ammunition of the smallest calibre. The performed cluster analysis showed a promising tendency of grouping ammunitions according to their types. Thus, it was worthwhile to check how this approach works in the case of an "unknown" sample – X. For this purpose a sample was chosen that was an evidence in a real case examined in the Institute of Forensic Research, Cracow (Table IV). This sample resembled these routinely studied materials, i.e. with not all chemical classes represented, usually with the unique particles absent. The results of the cluster analysis performed for all the experimental data, together with these of sample X, are presented in Figure 2. One can observe that this sample is placed within Makarov 9 mm cluster. Indeed that was a sample originating from the use of P-64 and Makarov 9 mm ammunition. In Table IV the numbers of particles of the considered chemical classes together with the appropriate frequencies of occurrence and ranks are listed for both, sample X and the most similar to it sample M3 for comparison. Although in X sample some of the considered chemical classes were weakly represented, it was correctly classified into the group of data obtained for other samples of GSR originating from Makarov 9 mm ammunition.

	Ammunition					
Chemical classes of GSR	Х			M3		
	N_i	f_i	r_i	N_i	f_i	r_i
PbSbBa	-	0.00	5.5	52	0.02	4
SbBa	-	0.00	5.5	2	0.00	7
PbSb	7	0.05	3	263	0.10	2
PbBa	-	0.00	5.5	5	0.00	6
Pb	21	0.15	2	213	0.08	3
Sb	111	0.80	1	2059	0.79	1

TABLE IV. DATA FOR SAMPLE X IN COMPARISON TO SAMPLE M3



Fig. 1. Results of the cluster analysis for the experimental data.



Fig. 2. Results of the cluster analysis for the data including these from the experiments performed and from sample X.

Ba	-	0.00	5.5	8	0.00	5

CONCLUSIONS

Frequencies of occurrence of primer residues of various chemical classes are easy to obtain from the analytical results of GSR search and can provide an additional feature characterising an ammunition.

The performed cluster analysis utilising this features showed a promising tendency of grouping ammunitions according to their types. Thus, it can contribute to at lest a group identification of an ammunition in cases when the only accessible for investigations evidence are gunshot residues collected at a crime scene.

In order to elaborate a reliable ammunition classification scheme however, an extensive checking of the repeatability of the analytical results for each considered ammunition is required. Also, additional information might be necessary to be included for a more precise differentiation, e.g., from inspection into the internal structure of primer residues by means of the focused ion beam spectrometry [5] or on the chemical composition of other types of residues (originating from the projectile, case and propellant).

Acknowledgement:

The authors are grateful to senior commissar Krzysztof Snopkowski from the Forensic Research Department, the Regional Headquarters of the Police, Cracow for help in performing the experiment in shooting pool.

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