Efficiency of Determination of Elemental Composition of Metals and their Topography in Objects of Biological Origin Using Spectrometers

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Abstract

Bodily injuries, caused by firearms and special non-lethal means, which are provided for law enforcement agencies and special services and they are available to the civilian population as well (pistols for firing ammunition equipped with elastic bullets, stun guns, etc.,) and the consequences of torture using various methods and the traumatic factors that caused by them have to get expert objective assessment. Among other laboratory studies, it is important to determine the characteristics of the composition of chemical elements in objects of biological and non-biological origin by performing X-ray fluorescence spectral analysis using modern spectrometers. The object: to determine the characteristics of the elemental composition of metals and their topography in injuries caused by gunshots and stun gun by conducting X-ray fluorescence spectral analysis using spectrometers "ElvaX CEP-01" and "M4 TORNADO". Conclusions: the use of spectrometers increases the accuracy and objectivity of expert examinations of injuries caused by firearms and electric shock device as they have a wide range of chemical elements detection in the composition of the products of the shot and the electro tag from sodium to uranium. Using X-ray fluorescence spectral analysis, it is possible not only to detect metals in the layers of soot on injuries, but also to conduct a targeted "microscopic" study of their topography for partial group identification of firearms and the installation of electrode metal, which acted as a contact body conductor. X-ray fluorescence spectral analysis is a non-destructive research method.

Key words: *gunshot wound, electric trauma, X-ray fluorescence spectral analysis.*

Introduction

Terrorism, local wars and internal conflicts, in which law enforcement officers act as one of the parties, are becoming more and more serious problems for all countries of the world. [4, 11, 16] This leads to a wide range of damages caused by the action of weapons on the standard equipment of certain law enforcement agencies, including an action of so-called "non-lethal weapons", such as means of shock and trauma, equipped with elastic bullets, electric shock devices and more. Situations of excessive use of force and torture, in which firearms and electrical devices can act as a traumatic factor have a special significance in these conditions. [2, 15]

Therefore, due to consistently significant number of injuries caused by firearms, special non-lethal means, which are provided for law enforcement agencies and special services and they are used in torture and they are available for locals, it is important to make assessment of the damage of objects of biological origin objectively with the use of highly efficient laboratory equipment, in particular, modern spectrometers.

Many countries around the world use highly sensitive spectrometers based on the use of physicochemical methods of analysis to determine the factors that accompany a shot from a firearm or the consequences of an electric shock device: atomic absorption

spectrophotometry (AAS), mass spectrometry with bound plasma (ICP-MS), atomic emission spectrometry (AES) or neutron activation analysis (NAA). In many cases, the instruments are equipped with scanning electron microscopy in combination with X-ray fluorescence microanalysis (SEM-EDX).

As practice shows, among many factors that characterize the features of gunshot wounds, detection of metals from bullets, shell casings, barrels of firearms formed during firing, and components of powder charge combustion, which are defined as "factors accompanying the shot" or "shot products " are provided sifficiently complete information. [3, 12, 14, 17]

It is essential to use the methods of elemental analysis and evaluation of the electrotag, which can act as an additional method of research that confirms the mechanism of damage, and even to some extent it indicates the electrode material that caused the damage. [7, 8, 13, 18]

Detection of chemical elements of metals in the composition of the shot products, electric tags and their identification is performed in the forensic laboratory by a set of methods and techniques known since the twentieth century. These are X-ray fluorescence analysis [4, 10], spark mass spectrometry, atomic absorption analysis, neutron activation analysis, flame emission photometry, emission spectrographic method, infrared spectrometry, etc. [1, 4, 5, 19, 21, 22,] The methods are highly sensitive and can detect almost the full range of chemical elements. One of their significant disadvantages is the preparation of the sample, which is accompanied by the inevitable destruction and loss of the object of study.

It should be noted that X-ray spectral analysis is a fairly effective and non-destructive method of studying metals from the fragments of explosive devices, bullets, shell casings, barrels of firearms in the composition of the products of the shot and electric tags. [9] Its essence is the X-ray irradiation of the object of study and the detection of the spectral composition of secondary radiation, which reflects the quantitative and qualitative indicators of the chemical elements of the object that is under a study.

However, conducting X-ray fluorescence spectral analysis using modern spectrometers is insufficient way to get information about the qualitative and quantitative composition of metal elements and their topography in objects of biological origin, formed as a result of gunshots and electric shock devices.

The object of this paper: to determine the characteristics of the elemental composition of metals and their topography in injuries caused by gunshots and electric shock devices by conducting X-ray fluorescence spectral analysis using spectrometers "ElvaX CEP-01" and "M4 TORNADO".

Materials and Methods

The archival material of the Department of Forensic Medicine of the Kyiv City Clinical Bureau of Forensic Medical Examination was used in the work number 15 "Expert Conclusions" on bodily injuries from shots fired from short-barreled weapons (pistols) and 12 "Expert Conclusions" regarding electric shock devices in cases of domestic and industrial electric injuries with a known contact electrode.

The material of the study in cases of gunshot wounds were 25 pieces of skin and 5 fragments of skull bones removed from the areas of gunshot wounds in people who have died being shot with 9 mm bullets from pistols. The distance of the shot ranged from 30-50 cm.

The study of chemical elements, formed in objects of biological origin due to the gunshot wounds, was performed by X-ray fluorescence spectral elemental analysis on a spectrometer "M4 TORNADO" company Bruker (Germany) using a package of standard analytical techniques.

Pieces of skin and fragments of skull bones with perforated fractures, which were removed from the areas of gunshot wounds in people who being killed by 9mm bullets from pistols, were placed in the working chamber of the spectrometer, where a vacuum pump created a pressure of 20 mbar. Using autofocus, the samples were translated into the focal plane. In the video images of skin flaps and fragments of skull bones with wounds, the scan plane was set, and the horizontal scan lines consisted of 600 points. As a result, the spectra of P, S, K, Ca, Fe, Cu, Zn and Pb. were obtained from the scanning plane of the wound area. Subsequently, the detected elements were mapped in the areas of wounds and perforated

fractures on fragments of skull bones. Photo illustrations were made using a personal computer with a Pentium-4 processor, followed by production of prints.

The materials of the study in cases of electric shock devices were 12 flaps of skin with electrogamps, selected from fatal cases of electric shock devices with known contact electrodes through which the transmission of electrical energy to the human body starts to occur. All 12 cases were selected, among others, taking into account the "material of the contact electrodes", due to which there was an electric shock (a typical metal wire with a predominance of copper in the chemical composition). The study of chemical elements, formed in objects of biological origin due to damage by electric shock device, was performed by X-ray fluorescence spectral elemental analysis on a spectrometer "ElvaX CEP-01" (country of manufacture is Ukraine). Before the study, flaps of skin with electrogamps were exposed to low temperature in the freezer (-20°C) in order to preserve. After thawing at room temperature and calibration of the spectrometer, skin flaps were placed in the working chamber of the spectrometer. As a result, the spectra of t Fe, Cu, and Ni were obtained from the damage sites. The analysis of the obtained data was performed using the integrated RStudio system. Analysis of variance was used to determine differences in the concentration of elements. The boundaries of the differences were determined using the Tukey's criterion. The distribution of residues was checked for normality using the Shapiro-Wilk test. The standard methods of variation statistics were used in the work.

Results and Discussion

In the study of skin flaps and fragments of skull bones removed from the areas of gunshot wounds in people who were killed by shots fired from 9 mm pistols at close range, the obtained maps of the distribution of elements showed an increased content of iron, copper, zinc and lead, which topographically in maximum concentrations were located at the edges of the wound of the skin (Fig. 1) and the entrance of the skull (Fig. 2) and around them in the form of irregularly shaped belt.

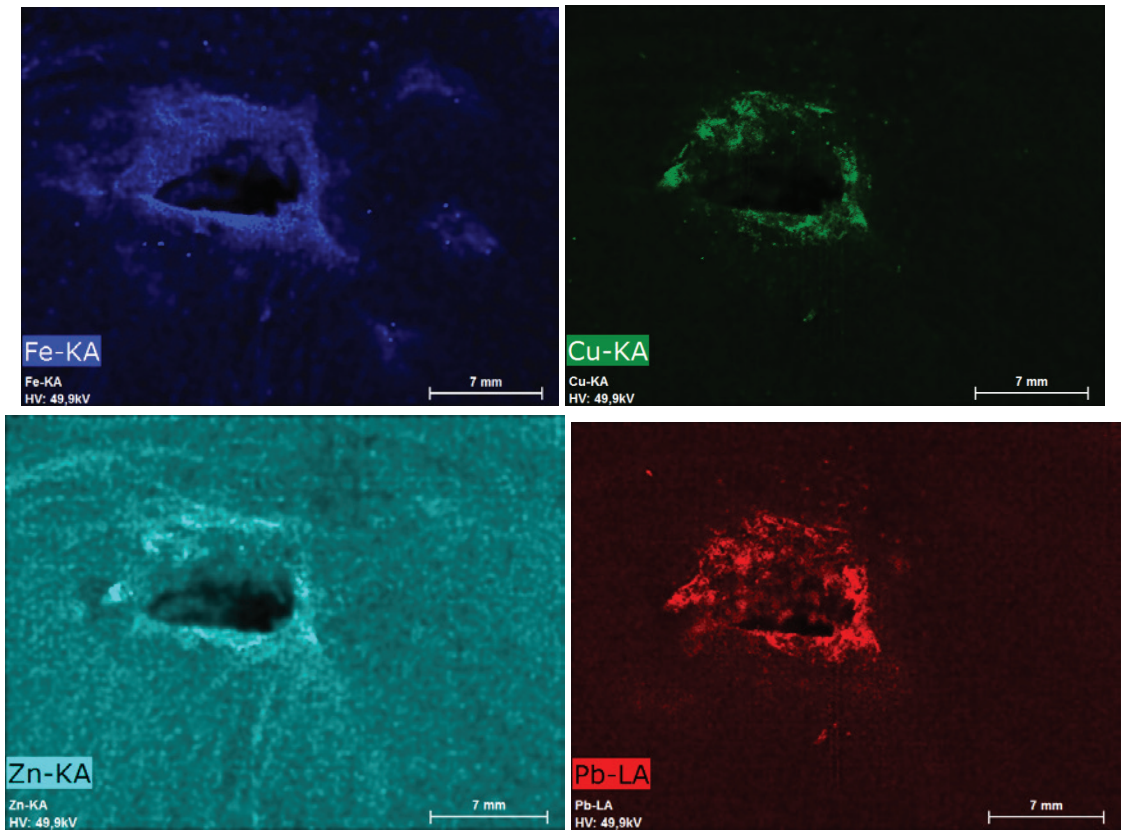

Fig. 1. Maps of distribution of iron (Fe), copper (Cu), zinc (Zn) and lead (Pb) on the edges of the wound on a piece of skin in the area of a gunshot wound due to a 9 mm bullet.

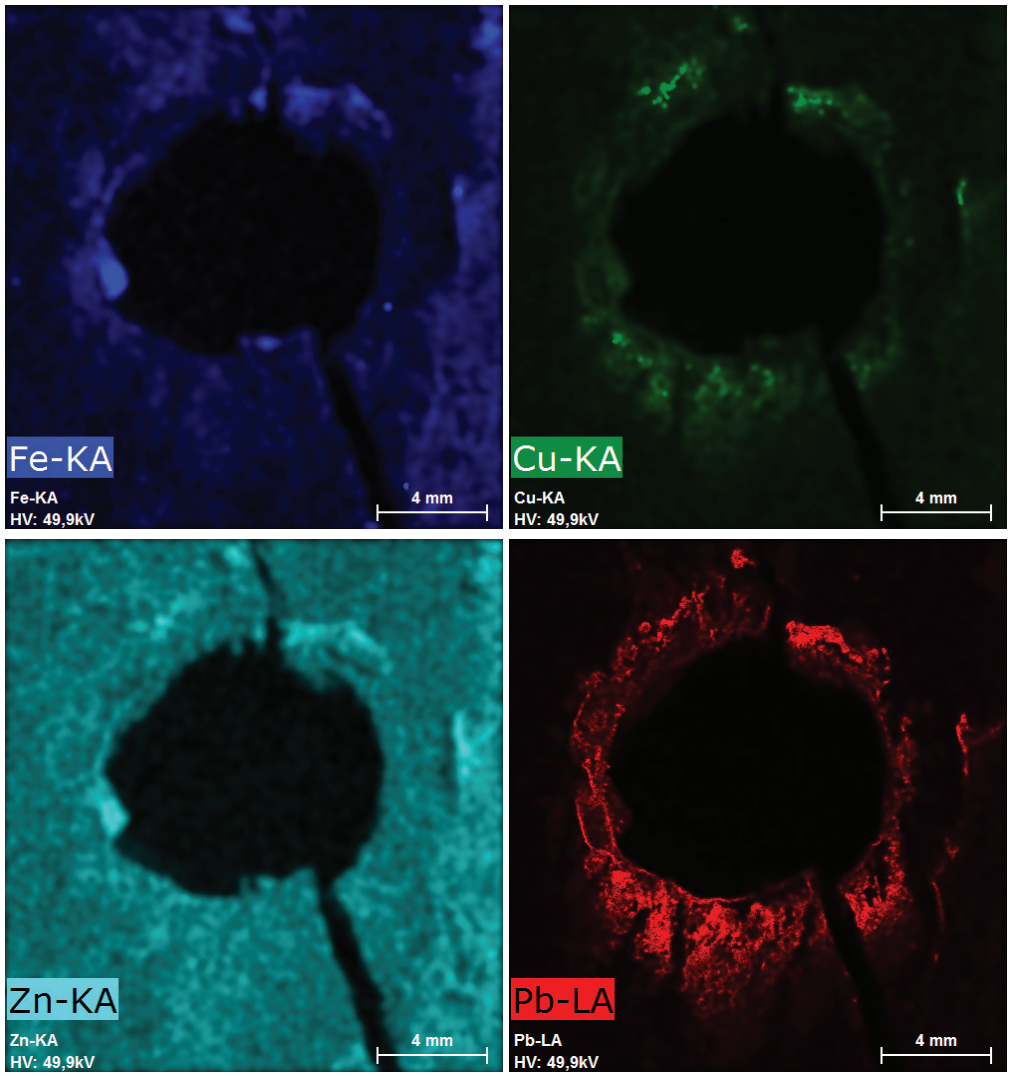

Fig. 2. Distribution maps of iron (Fe), copper (Cu), zinc (Zn) and lead (Pb) along the edges of the wound on a fragment of the skull bone in the area of the perforated fracture after a shot with a 9 mm bullet.

Subsequently, the detected elements in the wound area were mapped on skin flaps, for this purpose, a scan area was set on the object under study. On the received maps of elements distribution, the increased content of iron which in the maximum concentrations is located on edges of elements of damage on skin flaps was noted.

Thus, when applying X-ray fluorescence spectral analysis on the surface of the scan area on skin flaps in the areas of the entrance gunshot wound and on fragments of skull bones in the areas of perforated fracture was revealed elevated levels of iron, copper, zinc and lead, which were unevenly distributed at maximum concentrations on edges of wounds and perforated fractures in the form of irregularly shaped belt.

Detection and targeted "microscopic" study of the topography of chemical elements of iron (Fe), copper (Cu), zinc (Zn) and lead (Pb) in the layers of soot at the edges of the entrance gunshot wounds and in areas of perforated skull fractures caused by shots of 9 mm bullets, allowed not only to detect metals on injuries, but also to conduct a partial group identification of firearms, therefore, identify the weapon itself.

Among the twelve flaps of skin examined in the case of electric trauma, in six cases the electrotags had the appearance of an area of exfoliated dry epidermis of gray color. In two more cases, similar lesions with a slightly greenish tinge were identified. The crater-like form of damage was observed in three cases, and in one observation the damage had the appearance

of a superficial elongated abrasion. In the study of the elemental composition of metals on flaps of leather with electrodes caused by electric current through electrodes with a predominance of copper in their composition, using a spectrometer "ElvaX CEP-01", the following distribution of trace elements in the area of damage in percentage (Table 1).

Table 1. Distribution of the elemental composition of metals on 12 pieces of leather with electrical tags (%)

Skin flaps	Metals		
	Iron (Fe)	Nickel (Ni)	Cooper (Cu)
№1	5.558	8.889	85.553
№2	3.883	8.703	87.414
№3	7.513	9.482	83.005
№4	5.418	7.697	86.885
№5	4.458	6.224	89.318
№6	5.998	8.997	85.005
№7	5.913	9.079	85.008
№8	5.009	10.769	84.222
№9	6.885	7.615	85.500
№10	5.040	8.294	86.666
№11	5.813	9.189	84.998
№12	5.875	9.009	85.116

Distribution of the elemental composition of metals on 12 pieces of leather with electrical tags (%).

After statistical processing of the obtained data, a normal distribution of values with p.value 0.5417 was established, with a significant predominance in the elemental metal composition of the areas of electrical labels of copper content, the average value of which was 85.72417% with a standard measurement uncertainty of 0.474046.

Our own experience has shown that X-ray fluorescence spectrometers "M4 TORNADO" by Bruker (Germany) and "ElvaX CEP-01" (Ukraine) are successfuly used recently in Ukraine. They are used to determine the qualitative and quantitative composition of metal elements and their topography in objects of biological origin, formed as a result of shots from firearms and the action of electric shock devices. This opened new opportunities for laboratory diagnosis of gunshot wounds, weapons and ammunition, as well as damages investigations caused by electric shock devices. The results obtained by us make one deepen and supplement the previously known scientific and practical research. [3, 9, 12, 14, 17]

When using X-ray fluorescence spectral analysis in cases of electric shock device applying, opens up opportunities not only to confirm the effect of electric shocker on the body, but also determine the conformity of the metal composition in the area of damage to the metal composition of the electrode, which may be important in establishing circumstances and conditions of injury. Thus, in our study, the constancy and conformity of the metal elemental composition in the areas of electric shock damage to the contact electrode metal was confirmed. [6, 20]

Conclusions

The use of spectrometers increases the accuracy and objectivity of expert examinations of injuries caused by firearms and electric shock devices, as they have a wide range of detection of chemical elements in the composition of the products of the shot and the electric tags from sodium to uranium. Using X-ray fluorescence spectral analysis, it is possible not only to detect metals in the layers of soot on injuries, but also to conduct a targeted "microscopic" study of their topography for partial group identification of firearms and the installation of metal electrode, which acted as a body conductor. X-ray fluorescence spectral analysis is a non-destructive research method, as it does not involve the preparation and study of a control sample.

Ethical Clearance: Ethical clearance was obtained from the 'Ethics Committee' of the Institution prior to the start of the study.

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